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Analysis of Air Monitoring Data Collected During Oil Field Well Stimulation Treatments in California: Implications for Human Health

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Abstract

This report evaluates ambient air pollutant concentrations measured during hydraulic fracturing (HyF) and subsequent cleanout activities conducted as part of well stimulation treatments (WST) in California from a public health perspective. As part of this air monitoring study, measurements were also made at reference locations, including locations on the oil field but away from WST activities (background) and off-field (ambient) locations away from oil fields. The air monitoring data suggest that cancer risks and noncancer health risks associated with acute and chronic exposures are largely driven by benzene concentrations observed at off-field (ambient) locations. The proximity of off-field (ambient) locations to oil field activities and the similarities observed between off-field and on-field air quality suggest off-field (ambient) reference sites may be more reflective of oil field air quality than regional air quality. It is recommended that specific locations known to represent regional air quality be selected for ambient monitoring locations. Based on this study, it is recommended that the approach to air quality monitoring should be modified to more adequately capture and characterize the influence of episodic emissions from oil and gas development on air quality; shorter and longer-term air sampling durations at each site would enable more robust evaluations of acute and chronic exposures. Additionally, WST activities are relatively short-lived and only represent a limited set of activities involved in oil and gas development that warrant further investigations into potential air quality impacts. As such, adequate characterization of oil field air quality should include a focus on the multiple and varied processes that enable the production, separation and processing of hydrocarbons in the upstream oil and gas environment.

Executive Summary

Background

The objective of this report is to evaluate air pollutant concentration measurements collected during well stimulation treatments (WST), well cleanout operations and reference sites within oil fields (background) and outside of oil fields (ambient) in California from a public health perspective. In this report, detected analytes are screened for health-relevance and carcinogenicity, and cancer and noncancer risks are evaluated using detected air pollutant concentrations and health guidance values. This report is a companion report to a descriptive and comparative analysis of the same air quality monitoring data (Stringfellow and Camarillo, 2020).

Methods

As part of a joint program of the California Air Resources Board (CARB) and the California Geologic Management Division (CalGEM)¹, oil field operators hired contractors to conduct air monitoring following protocols described in “Air Sampling and Analysis Plan for Well Stimulation Treatment Operations” (California Air Resources Board, 2018; Appendix A). Under this plan, air quality was measured at eight locations in a 300- to 500-foot perimeter around wells as they were being stimulated and then an additional set of samples were collected around the perimeter of the well as they were being cleaned out after stimulation. In addition to collecting monitoring data at locations around the perimeter of the well, the CARB monitoring protocol specified the collection of “background” and “ambient” air quality measurements. Background samples were collected at locations intended to represent air quality on the oil field (“on-field”), but in areas away from WST activities. Ambient samples are intended to represent air quality away from an active oil and gas operation (“off-field”) (California Air Resources Board, 2018; Appendix A). Air monitoring was conducted in five oil fields (North and South Belridge, Buena Vista Nose, Elk Hills, and Lost Hills) between December 2016 and December 2018. Each sample event included a minimum of eight hours of continuous sampling, resulting in 8-hour time-weighted average (8-hr TWA) air samples.

Detected compounds were screened for public health relevance using authoritative lists for state, federal, and international health agencies. State and federal noncancer health guidance values for acute and chronic exposures were used to evaluate the potential for adverse noncancer health effects during individual and multi-pollutant exposures. Cancer risk was also assessed considering individual and multi-pollutant continuous exposures over a lifetime. Both cancer risks and noncancer health risks were evaluated across all sites and by site type (i.e., ambient, background, hydraulic fracturing, and cleanout).

Results

Of the 64 detected compounds, 38 (59%) are health-relevant state- or federally-designated air pollutants and 22 (34%) are known or suspected human carcinogens. Given the observed mean (8-hr TWA) concentrations of these detected compounds, cumulative lifetime excess cancer risks exceeded the U.S. EPA de minimis benchmark of 1 in a million at each site type (i.e., ambient, background, hydraulic fracturing, and cleanout), with the highest cumulative lifetime excess cancer risk observed at ambient (“off-field”) locations. Benzene – a naturally occurring constituent in petroleum that is co-emitted during oil and gas development and also associated with combustion and use of fossil fuels – accounted for 85% of the total cancer risk observed at ambient

¹ Formerly the Division of Oil, Gas and Geothermal Resources (DOGGR).

sites. Benzene also accounted for elevated acute and chronic hazard quotients ($HQ > 1$) and elevated acute and chronic hazard indices ($HI > 1$) at ambient sites, indicating potential for noncancer adverse health effects associated with exposures to benzene. As noted in the companion study to this report (Appendix E in Stringfellow and Camarillo, 2020), benzene concentrations observed at ambient sites were statistically significantly higher than background, HyF, and cleanout sites and no statistically significant differences in benzene concentrations were observed between background, HyF and cleanout sites. While ambient sites were intended to be “control” sites to compare air pollutant concentrations to “on-field” sites, our report agrees with Stringfellow and Camarillo (2020) that sampling at sites that were selected for ambient monitoring may not be representative of air quality that is independent of oil and gas development operations given their proximity to oil field activities. All chemical-specific acute HQs and target organ system-specific acute HIs for background, HyF, and cleanout site types were less than 1, suggesting that acute exposures associated with the detected air pollutants may not be associated with adverse health effects. Similarly, all chemical-specific chronic HQs and target organ system-specific chronic HIs (calculated using mean 8-hr TWA concentrations) for background, HyF, and cleanout site types were also less than 1, also suggesting that chronic exposures associated with detected air pollutants may not be associated with adverse health effects. However, given that simultaneous exposure to multiple chemicals or to multiple chemicals in close temporal succession may be additive, antagonistic (less than additive) or synergistic (greater than additive), HI less than 1 may not confirm the absence of risk for adverse health effects.

Conclusion

In this study, cancer risks and noncancer health risks associated with acute and chronic exposures are largely driven by benzene concentrations observed at ambient (“off-field”) sites. As noted in the companion study to this report (Stringfellow and Camarillo, 2020), ambient monitoring locations due to their proximity to oil field activities may be more reflective of oil field air quality than regional air quality. Given that air sampling data were not collected over a shorter duration (e.g., 1 hour), maximum (8-hr TWA) concentrations were used to assess acute noncancer health risks, which may underestimate acute exposure. Additionally, given that air sampling data collected over a longer duration (i.e., more 8 hours) were not available, cancer and chronic noncancer risks were calculated using mean (8-hr TWA) concentrations, which may overestimate chronic exposure over the long-term. Based on the results of this study and the companion report (Stringfellow and Camarillo, 2020), it is recommended that specific locations known to represent ambient air quality – outside of the influence of oil and gas development operations – be selected for ambient monitoring locations.

This evaluation resulted in multiple recommendations related to the air sampling efforts that provided data for this public health assessment. First, the approach to air quality monitoring should be modified to more adequately capture and characterize the influence of episodic emissions from oil and gas development on air quality. Additional shorter and longer-term air sampling durations at each site would enable more robust evaluations of acute and chronic exposures. Second, WST activities are relatively short-lived and only represent a limited set of activities involved in oil and gas development that warrant further investigations into potential air quality impacts. As such, adequate characterization of oil field air quality should include a focus on the multiple and varied processes that enable the production, separation and processing of hydrocarbons in the upstream oil and gas environment. Third, reporting of monitoring results should be standardized in an electronic format to facilitate future evaluations of similar air monitoring datasets.

Introduction & Background

Well stimulation treatments (WST) are a class of oil and gas development methods used to increase the permeability of tight geological formations to facilitate the production of hydrocarbons. There are three main types of WST as defined by Senate Bill 4 (SB 4) (Pavley, 2013): (1) hydraulic fracturing; (2) matrix acidizing; and (3) acid fracturing. Hydraulic fracturing is the most commonly reported WST in the State of California and involves the injection of water, chemicals and sand or other proppants down an oil and gas well at a pressure high enough to fracture or otherwise increase the permeability of the target geological formation (Long et al., 2015a). This releases tightly held oil and gas that is then, upon release of pressure, able to flow up a well and be collected at the wellhead. Alternatively, matrix acidizing involves the injection of strong acids, usually hydrofluoric and hydrochloric acid, into a well to dissolve the target formation, thus enabling oil and gas to flow up the well to be collected at the surface. Finally, acid fracturing is a combination of both hydraulic fracturing and matrix acidizing in that it injects acids down a well at pressures that exceed the fracture gradient.

As of 2015, approximately 20% of the oil and gas produced in the State of California was enabled by the application of hydraulic fracturing with only small other contributions from matrix acidizing and nearly no contribution from acid fracturing (Long et al., 2015a). The vast majority of oil and gas development in the State of California is enabled by enhanced oil recovery techniques including but not limited to water flooding and steam injection.

Hydraulic fracturing and well stimulation have generated significant public and policymaker concern regarding hazards, risks and impacts of these operations on topics including air quality, water quality, induced seismicity and public health. These concerns prompted the California legislature to pass Senate Bill 4 (SB 4) (Pavley, 2013).

Senate Bill 4 (SB 4) was signed into law on September 20, 2013 by Governor Brown, and required the development of more stringent regulations for well stimulation treatment (WST) operations in California including hydraulic fracturing, acid fracturing, and matrix acidizing. Additionally, SB 4 required an independent scientific study on the geological, engineering, air, water, climate and public health dimensions of WST and their application within oil and gas development to help to inform policy. The California Council on Science and Technology (CCST) convened scientific experts and completed the independent scientific review of well stimulation (Long et al., 2015a; Long et al., 2015b), which also contained two public health assessment chapters (Shonkoff et al., 2015a and Shonkoff et al., 2015b). The CCST report concluded that WST and oil and gas development more broadly are sources of health-damaging air pollutant emissions in California and that these emissions could be concentrated near oil and gas production wells. The CCST report also recommended additional research be conducted to better understand air pollutant emissions from oil and gas development as a function of distance (Long et al., 2015a; Long et al., 2015b).

As part of SB 4 implementation efforts, the California Air Resources Board (CARB) entered into a formal agreement with California Geologic Energy Management Division (CalGEM)² to review WST permit application materials and to provide comments and recommendations to CalGEM during its application review process. In some cases, CARB's comments included recommendations for CalGEM to require air sampling and analysis as a permit condition. CARB

² Formerly the Division of Oil, Gas and Geothermal Resources (DOGGR).

requested the permit condition for certain operations based on oil field, operator, proximity to sensitive receptors, and well stimulation fluid composition. CalGEM has implemented CARB recommendations and oil field operators have conducted air monitoring and submitted air monitoring reports to CARB.

As part of the review of these air monitoring reports, CARB contracted Physicians, Scientists, and Engineers for Healthy Energy (PSE) to evaluate WST air sampling results and identify, to the extent possible, potential public health concerns of air pollutant concentrations measured during WST and well cleanout events. Air pollutant measurements collected during oil field activities (including WST) that occurred between December 2016 and December 2018 were organized, described, and analyzed by PSE and Stringfellow & Associates (S&A) researchers. Results of the descriptive statistical analysis of the WST air monitoring data are available in Stringfellow and Camarillo (2020). The objective of this report is to evaluate air pollutant concentration measurements collected by oil field operators during well stimulation treatments (WST), well cleanout operations and reference sites within and outside of oil fields in California from a public health perspective. Air pollutant measurements were collected and reported by oil and gas companies and submitted to the California Air Resources Board (CARB) pursuant to requirements outlined in the “Air Sampling and Analysis Plan for Well Stimulation Treatment Operations” (CARB, 2018; Appendix A).

Methods

Air monitoring data collection and reporting

WST air sampling was conducted by oil field operators following protocols described in CARB's “Air Sampling and Analysis Plan for Well Stimulation Treatment Operations” guidelines (CARB, 2018; Appendix A).

As part of this study, CARB provided PSE researchers with several WST air sampling and analysis reports (Monitoring Reports), written by consultants (Consultants) for the oil field operators and owners (Producers). In most cases, the Monitoring Reports include tables and figures of analytical and weather station results. Some reports included appendices containing copies of laboratory reports and other detailed sources of information. The Monitoring Reports were provided in PDF or similar format. Data and analytical results were not consistently provided independently (electronically) of the reports and the data used in this study were extracted from report files by either CARB staff or S&A, as described below.

Monitoring Reports were prepared by four different consultants working for five oil and gas producers (Appendix B, Table B-1). Data were collected from WST on five fields (North and South Belridge, Buena Vista Nose, Elk Hills, and Lost Hills). Air quality analytical results were reported from five contract laboratories (ALS Salt Lake City; ALS Simi Valley; BC Laboratories; Eurofins; and TestAmerica) and from portable air monitoring equipment used on location by the Consultants.

Air quality sampling took place during WST and well-cleanout operations as well as at off-field “ambient” reference locations and on-field “background” locations. In most cases, industry consultants relied on nearby weather stations to provide wind data for the sample sites, but where these were not available they set up and recorded data from temporary weather stations. Sampling was conducted continuously over 8 hours, resulting in 8-hr time-weighted average (8-hr TWA)

concentrations.³ Approved sampling media included vacuum canisters (e.g., Summa), sorbent tubes with multiple sorbent materials, DNPH cartridges (2,4-dinitrophenylhydrazine), PUF/XAD cartridges (polyurethane foam/adsorbent ion exchange resin), XAD-7 tubes, silica gel tubes, tedlar bags and charcoal tubes (CARB, 2018; Appendix A). Additional description of the structure of the air quality monitoring data is provided in Stringfellow and Camarillo (2020).

Data compilation by CARB

CARB staff extracted chemical analytical data from the Monitoring Reports and entered the data manually into Microsoft Excel spreadsheets. All data above the limit of detection (LOD), including measurements that were below the reporting limit (RL), were extracted from the Monitoring Reports. Different laboratories were used to analyze air samples, and in some cases, it appears that not all analytes included in the CARB sampling plan were evaluated for in certain samples (Stringfellow and Camarillo, 2020). Results from duplicate samples were included in the compiled data provided by CARB (CARB Excel File).

Data cleaning and compilation

The methods and approach to data cleaning and compilation in support of the descriptive statistical analysis of the air monitoring data is detailed in Stringfellow and Camarillo (2020). Briefly, the analytical results from the CARB Excel file were aggregated and formatted for JMP statistical analysis software by S&A researchers. The analytical data were aggregated by well using API well number and all extraneous columns and rows were deleted. Data were stripped of all formulas and values were imported into JMP as calculated by CARB. Results from duplicate samples were included in the compiled data and were included as independent samples for most analyses in alignment with data presented in Stringfellow and Camarillo (2020). Data imported into JMP from the CARB Excel File were coded to include spatial information, temporal information, meteorological measurements, and other variables using the monitoring reports and the CARB Excel file.

PSE reviewed initial data provided by S&A to identify anomalies and inconsistencies. S&A and PSE reviewed identified areas for further evaluation, consulted the monitoring reports and staff from CARB and the Office of Environmental Health Hazard Assessment (OEHHA), and re-evaluated data as necessary.

Public health assessment of detected compounds

The analyses in this report focus on chemical compounds detected in at least one sample using data provided in Microsoft Excel format by S&A. Chemical Abstract Service Registry Number (CASRN) is a unique identifier for chemicals that can be used to identify corresponding chemical and physical properties and toxicity information. CASRN and molecular weight were verified and assigned to all compounds detected in at least one sample using the United States Environmental Protection Agency (U.S. EPA) Substance Registry Services (U.S. EPA, 2019a).

³ Recommended sampling procedures, sampling media and sample duration by location (i.e. ambient, background, WST, or cleanout) are included in CARB's "Air Sampling and Analysis Plan for Well Stimulation Treatment Operations" (CARB, 2018; Appendix A). Site-specific sample location information is included in individual Monitoring Reports.

Measurements for five atmospheric gases (carbon dioxide, hydrogen, methane, nitrogen, and oxygen) were reported in parts per million (ppm) and/or percent volume (%v/v). Concentrations for atmospheric gases were converted to %v/v (1% = 10,000 ppm). Measurements for the remaining detected compounds were reported in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$), milligrams per cubic meter (mg/m^3), and parts per billion (ppb). To create a standard measurement of comparison, all measurements were converted to $\mu\text{g}/\text{m}^3$. Measurements presented in mg/m^3 were multiplied by 1,000 to convert to $\mu\text{g}/\text{m}^3$. Measurements presented in ppb were multiplied by the chemical-specific molecular weight divided by molar volume (24.45 L air per mole at 25°C) to convert to $\mu\text{g}/\text{m}^3$.

For analytes included in EPA Method TO-11A, measurements were provided in more than one concentration unit in the CARB Excel File, resulting in duplicative measurements when data were aggregated using JMP statistical software. Duplicate measurements for EPA Method TO-11A analytes were identified and removed from further analysis.

Monitoring was conducted in association with four types of activities or conditions: 1) samples collected in the absence of any oil field activities (ambient samples); 2) samples collected on oil fields, but in areas away from hydraulic fracturing (HyF) and other WST activities (background samples); 3) samples collected during hydraulic fracturing and acid stimulation activities (WST samples); and 4) samples collected during well-cleanout activities that follow WST (cleanout samples). Sampling during the single acid treatment was only conducted during a three-hour period on the first day. As acid fracturing is typically a three-day process, these acid treatment measurements are not representative and were excluded from further analysis. All WST are HyF treatment and are herein referred to as such. Results are presented by the four activity conditions (i.e. activities; ambient, background, HyF, and cleanout) in this report, in alignment with the companion study evaluating the underlying air quality data (Stringfellow and Camarillo, 2020). Mean, median, 95th percentile, and maximum ambient air concentrations (8-hr TWA) were calculated for all detected compounds across all sites and by activity type.

Detection limit information was not extracted from the individual Monitoring Reports, and therefore chemical- and method-specific detection limits were not readily available to support additional sensitivity analyses (e.g., supplementing non-detections with the detection limit or half of the detection limit; U.S. EPA, 2017). As such, calculations presented throughout this report include non-detections as zero values (i.e., $0.0 \mu\text{g}/\text{m}^3$), potentially underestimating the true health risks associated with these observed pollutant concentrations.

Detected compounds were screened for public health relevance using authoritative lists for state, federal, and international health agencies. Noncancer health guidance values and cancer risk estimates were identified for each detected compound, if available. Screening lists and toxicological data used in this report are summarized in Table 1 and are discussed in detail below.

Table 1. Databases and other sources used to characterize chemical-specific toxicological properties or health guidance values. (X indicates this category of chemical information was obtained from the source).

Screening List / Toxicological Data Source	Air Pollution	Carcinogenicity	Cancer Risk	Acute Toxicity	Chronic Toxicity
California EPA Toxic Air Contaminant (TAC) Identification List	X				
U.S. EPA Clean Air Act Hazardous Air Pollutants (HAP)	X				
California Air Resources Board Air Toxics “Hot Spots” Program - Substances for Which Emissions Must Be Quantified (AB 2588)	X				
California EPA Chemicals Known to the State to Cause Cancer or Reproductive Toxicity (Proposition 65 List)		X			
National Toxicity Program (NTP) Report on Carcinogens 14 th Ed.		X			
International Agency for Research on Cancer (IARC) Monographs		X			
California Office of Environmental Health and Hazard Assessment (OEHHA)			X	X	X
U.S. EPA Provisional Peer-Reviewed Toxicity Values				X	X
U.S. EPA, Integrated Risk Information System (IRIS)				X	X
U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR) Priority List of Hazardous Substances				X	X

Air pollution

Analytical methods employed in this air monitoring effort quantified concentrations of atmospheric gases (e.g., hydrogen, nitrogen, oxygen) and known air pollutants with health relevance. Health-relevant air pollutants were identified using the authoritative lists described below:

- **California Environmental Protection Agency (CalEPA) Toxic Air Contaminants (TAC):** Air pollutants that may cause or contribute to an increase in mortality or in serious illness, or that may pose a present or future hazard to human health (CARB, 2010).
- **U.S. EPA Clean Air Act Hazardous Air Pollutants (HAP):** Includes 170 individual chemicals and 17 major chemical categories (e.g., fine mineral fibers, glycol ethers), which are known or suspected to cause cancer or other serious health effects, such as reproductive effects of birth defects, or adverse environmental effects (42 C.F.R. §7412, 1990).
- **Assembly Bill 2588 (AB 2588) Hot Spots Program:** The California Air Toxics “Hot Spots” Information and Assessment Act (AB 2588) of 1987 requires the California Air Resources Board (CARB) to compile and maintain a list of “substances for which emissions must be

quantified”. Chemicals on this list may pose a threat to public health when present in the air and emissions of such substances must be reported (CARB, 2007).

Carcinogenicity

Various environmental factors can contribute to the increased risk of cancer in humans, including exposure to carcinogenic chemicals, either synthetic or naturally occurring. Many carcinogens have no known safe exposure level and risk management based on this notion is recommended (Whittaker et al., 2016). However, our analysis in this report relies on authoritative cancer risk estimates which are nearly always above zero. Detected compounds were screened for carcinogenicity using the following authoritative lists:

- **California Environmental Protection Agency (CalEPA) Proposition 65 List:** Chemicals on the CalEPA Proposition 65 List are known to cause cancer or birth defects or reproductive harm (CalEPA, 2019). Chemicals known to cause cancer were identified.
- **International Agency for Research on Cancer (IARC) Monographs on the Evaluation of Carcinogenic Risks to Humans:** IARC categorizes chemicals into 5 groups (IARC, 2019); in this report, only chemicals in IARC Groups 1 (carcinogenic to humans), 2A (probably carcinogenic to humans) and 2B (possibly carcinogenic to humans) are considered to be carcinogenic.
- **U.S. Department of Health and Human Services National Toxicity Program (NTP) 14th Report on Carcinogens:** The NTP categorizes chemicals as either known human carcinogens or reasonably anticipated to be a human carcinogen (RAHC) (U.S. Department of Health and Human Services, 2016).

Cancer risk

Lifetime inhalation cancer risk is calculated by multiplying the average daily inhalation dose (mg/kg-day) by the cancer potency factor (mg/kg-day)⁻¹. Given sampling data collected over longer duration (i.e., more than 8 hours) were not available, mean concentrations (8-hr TWA) measured across all sites and by activity type (i.e., ambient, background, HyF, cleanout) were used to estimate dose. Dose was calculated using mean age-specific daily breathing rate normalized to body weight per OEHHA guidance (OEHHA, 2015; Equation 5.4.1.1).

Cancer potency factors generally represent the 95% upper confidence limit on the modeled dose-response slope at the low dose range (OEHHA, 2015). The cancer slope factor (mg/kg/day)⁻¹ assumes continuous lifetime exposure to a substance (OEHHA, 2015). OEHHA inhalation slope factors (mg/kg/day)⁻¹ were compiled for each detected compound (OEHHA, 2020). Lifetime cancer risk (70-year exposure) and “chances per million” (i.e., chance of developing cancer per million individuals exposed) were calculated across all sites and by activity type using age-specific exposure variates per OEHHA guidance (Equation 8.2.4., OEHHA, 2015).

Noncancer health risk

Inhalation noncancer health guidance values and associated target organ systems were compiled for each compound to assess acute and chronic noncancer health risk. The source of health guidance values and their corresponding descriptions are included below:

- **Office of Environmental Health Hazard Assessment (OEHHA) Reference exposure level (REL):** Concentrations for which adverse noncancer health effects are not anticipated over a specified exposure period ($\mu\text{g}/\text{m}^3$), even in sensitive populations such as pregnant women and children (OEHHA, 2008).
- **Agency for Toxic Substances and Disease Registry (ATSDR) Minimal risk levels (MRL):** estimate of daily exposure to a substance without appreciable risk of adverse noncancer health effects over a specified exposure period (ppm) (ATSDR, 2018).
- **U.S. EPA Reference concentration (RfC):** An estimate of continuous inhalation exposure of a substance in humans without significant risk of negative effects during a lifetime (mg/m^3) (U.S. EPA, 2019b).
- **U.S. EPA Provisional Peer-Reviewed Toxicity Value (PPRTV):** An estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious health effects during a lifetime (mg/m^3) (U.S. EPA, 2019c).

To form a consistent scale for comparison of chemical toxicity values across multiple databases, health guidance values were converted to a standardized value in units of $\mu\text{g}/\text{m}^3$. OEHHA RELs, U.S. EPA RfCs and U.S. EPA PPRTVs reported in mg/m^3 were multiplied by 1,000 to convert to $\mu\text{g}/\text{m}^3$. ATSDR MRLs reported in ppm were first multiplied by 1,000; then multiplied by chemical-specific molecular weight; and then divided by molar volume (24.45 L air per mole at 25°C) to convert to $\mu\text{g}/\text{m}^3$.

Assessing acute and chronic exposures

This monitoring effort included 8-hour continuous sampling resulting in 8-hour time-weighted-average (8-hr TWA) ambient air concentrations. Given measurements with finer temporal resolution (i.e., collected over less than 8 hours) were not available, the maximum (8-hr TWA) concentration of each compound measured across all sites and by activity type (i.e., ambient, background, HyF, cleanout) was used to evaluate acute exposure. OEHHA acute RELs were used to assess acute exposures. If an OEHHA acute REL was not available, the following acute health guidance values were used (in order of preference): ATSDR acute REL, U.S. EPA subchronic RfC, U.S. EPA subchronic PPRTV. Different sources of acute health guidance values were included in this assessment to gather a comprehensive list of compounds with available health guidance values. However, it is important to note that acute and subchronic health guidance values provided by different state and federal agencies are often based on different exposure durations, which presents a limitation in this assessment. For example, OEHHA acute RELs are relevant to assess acute 1 hour exposures, while ATSDR acute MRLs are relevant to assess acute exposures of 1 to 14 days.

Given sampling data over longer duration (i.e., more than 8 hours) were not available, mean (8-hr TWA) concentrations of each compound measured across all sites and by activity type were used to assess chronic exposures. Chronic exposure was also evaluated using the median and 95th percentile of measured concentrations by activity type to provide additional context. The most conservative (lowest) chronic health guidance value was selected among the following: OEHHA chronic REL, U.S. EPA chronic RfC, and ATSDR chronic MRL.

Calculating hazard quotient (HQ) and hazard index (HI)

A hazard quotient (HQ) is the ratio between the estimated or observed exposure concentration and a health guidance value for a given chemical. Acute HQs were calculated for each compound by using the maximum (8-hr TWA) concentration measured across all sites and by activity type. Chronic HQs were calculated for each compound using the mean (8-hr TWA) concentration calculated across all sites and by activity type.

Exposures at or below the health guidance value (i.e., HQs of 1 or less) are not likely to be associated with adverse health effects. However, as exposures increase above the health guidance value (i.e., HQs are greater than 1), the potential for adverse effects increases. To consider exposure from multiple air pollutants, acute and chronic hazard indices (HI) were calculated by summing HQs for individual compounds that are anticipated to affect the same target organ system based on acute or chronic exposure duration. Target organ systems include the respiratory system, hematologic system, alimentary system, endocrine system, development, reproductive system, nervous system, cardiovascular system, skin, eyes, and general toxicity (OEHHA, 2015).

Similar to HQ, an HI value less than or equal to 1 indicates that the known exposure is not likely to result in adverse noncancer health effects. Calculating HI assumes an additive effect of cumulative exposure to multiple chemicals; however, effects from simultaneous exposure to multiple chemicals or to multiple chemicals in close temporal succession may be additive, antagonistic (less than additive) or synergistic (greater than additive) (U.S. EPA, 1986). Therefore, a HI value lower than 1, may not necessarily confirm the absence of risk for adverse health effects.

Comparison of air quality measurements to occupational health guidance values

The 8-hour sampling is most relevant for assessing occupational exposures among workers during a typical work day. While general population exposures were the primary consideration in this public health assessment it is worth putting these air pollution data into an occupational health context as well. To do this, mean, median, 95th percentile, and maximum (8-hr TWA) concentrations of the air pollutants observed in this dataset were compared to the California Division of Occupational Safety and Health (Cal/OSHA) permissible exposure limits (PELs). PELs reflect the maximum permitted 8-hr TWA concentration of an airborne contaminant (8 CCR §5155, n.d.; OSHA, 2019) and are nearly always higher than health guidance values for community exposure (e.g., OEHHA RELs). Additionally, it is important to note that occupational health guidance values, such as PELs, are not necessarily based on protecting sensitive populations, and also include additional considerations such as technical and economic feasibility.

Chemical additives used during well stimulation events

Chemicals are used regularly in both well stimulation fluids and during routine activities (routine maintenance, wellbore cleanouts, well reworks, etc.) and some of these chemicals are volatile compounds and health-relevant air pollutants (Shonkoff et al., 2019; Stringfellow et al., 2017). Using sampling dates and well identifier (API) provided by CARB, chemical disclosure data were extracted from the Well Stimulation Disclosure dataset (CalGEM, 2019) for chemical additives used at relevant oil wells during the time periods of interest. Chemical additives with available CASRN were compared to compounds that were monitored for and compounds that were detected in at least one sample.

Results

Of 166 monitored compounds (Appendix B, Table B-2), 64 (39%) were detected at least once during the sampling effort (Table 2). Detected compounds (N=64) are shown by frequency of detection across all samples (i.e. all activity types) in Table 3. Of the 64 detected compounds, five (8%) were atmospheric gases (carbon dioxide, hydrogen, methane, oxygen, and nitrogen). Oxygen was the only compound detected in all samples collected. Eight compounds were detected in only one sample. Of these eight compounds, five were detected during HyF (1,1-Dichloroethane; 1,1-Dichloroethene; Dibromochloromethane; Ethane; Styrene) and three were detected during cleanout (1,1,2,2-Tetrachloroethane; 1,1,2-Trichloroethane; Bis(2-Ethylhexyl)phthalate). Summary of results for detected compounds by activity type (i.e. ambient, background, HyF, cleanout) are shown in Appendix B, Table B-3 and Table B-4.

Table 2. Analytes detected in at least one sample collected as part of the SB 4 well stimulation treatment monitoring program (N=64). Also provided in Stringfellow and Camarillo (2020).

Analyte	CASRN	Analyte	CASRN
1,1-Dichloroethane	75-34-3	Chloroform	67-66-3
1,1-Dichloroethene	75-35-4	Chloromethane	74-87-3
1,1,1-Trichloroethane	71-55-6	Cyclohexane	110-82-7
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	Dibromochloromethane	124-48-1
1,1,2-Trichloroethane	79-00-5	Dichlorodifluoromethane	75-71-8
1,1,2,2-Tetrachloroethane	79-34-5	Ethane	74-84-0
1,2-Dichloro-1,1,2,2-Tetrafluoroethane	76-14-2	Ethanol	64-17-5
1,2-Dichloroethane	107-06-2	Ethylbenzene	100-41-4
1,2,4-Trichlorobenzene	120-82-1	Formaldehyde	50-00-0
1,2,4-Trimethylbenzene	95-63-6	Heptane	142-82-5
1,3-Butadiene	106-99-0	Hexaldehyde	66-25-1
1,3,5-Trimethylbenzene	108-67-8	Hexane	110-54-3
1,4-Dichlorobenzene	106-46-7	Hydrogen	1333-74-0
2-Butanone	78-93-3	I-Butane	75-28-5
2-Hexanone	591-78-6	m,p-Xylene	1330-20-7
2-Methylnaphthalene	91-57-6	Methane	74-82-8
2,2,4-Trimethylpentane	540-84-1	Methylene Chloride	75-09-2
2,5-Dimethyl Benzaldehyde	5779-94-2	Naphthalene	91-20-3
4-Ethyltoluene	622-96-8	Nitrogen	7727-37-9
4-Methyl-2-Pentanone	108-10-1	Nonane	111-84-2
Acetaldehyde	75-07-0	o-Tolualdehyde	529-20-4
Acetone	67-64-1	o-Xylene	1330-20-7
Benzaldehyde	100-52-7	Octane	111-65-9
Benzene	71-43-2	Oxygen	7782-44-7
Bis(2-Ethylhexyl)phthalate	117-81-7	Pentane	109-66-0
Butane	106-97-8	Propionaldehyde	123-38-6
Butyraldehyde	123-72-8	Styrene	100-42-5
C-1,2-Dichloroethene	156-59-2	Tetrachloroethene	127-18-4
Carbon Dioxide	124-38-9	Tetraethylene Glycol	112-60-7
Carbon Disulfide	75-15-0	Toluene	108-88-3
Carbon Tetrachloride	56-23-5	Trichloroethene	79-01-6
Chloroethane	75-00-3	Trichlorofluoromethane	75-69-4

Table 3. Summary of results for all detected analytes, showing percent detected when analyzed (% Det.); mean, median and maximum concentration (conc., $\mu\text{g}/\text{m}^3$; 8-hr time-weighted average)¹; the 95th percentile, indicating that 95% of the measurements were at or below this value. Sorted by frequency of detection. Calculations presented include non-detections as zero values (i.e., 0.0 $\mu\text{g}/\text{m}^3$). Adapted from Stringfellow and Camarillo (2020).

Analyte ($\mu\text{g}/\text{m}^3$) ¹	CASRN	% Det.	Mean Conc.	Median Conc.	95% Value	Max Conc.
Oxygen (%v)	7782-44-7	100.0	18.121	19.000	22.000	32.000
Butane	106-97-8	96.6	20.377	9.033	65.608	1354.945
Formaldehyde	50-00-0	95.4	2.819	2.475	6.300	8.090
Nitrogen (%v)	7727-37-9	95.2	73.138	77.000	79.000	85.000
Methane (%v)	74-82-8	93.4	0.000	0.000	0.001	0.009
Ethanol	64-17-5	82.1	6.141	5.464	13.604	170.000
I-Butane	75-28-5	80.0	6.003	2.800	18.589	451.648
Acetone	67-64-1	67.0	2.297	1.725	6.907	17.000
Dichlorodifluoromethane	75-71-8	62.5	1.493	2.028	2.819	3.214
Acetaldehyde	75-07-0	61.5	1.804	1.370	5.800	16.000
Pentane	109-66-0	50.4	5.661	2.361	16.761	560.675
Cyclohexane	110-82-7	39.2	1.542	0.000	6.884	55.074
Hexane	110-54-3	35.9	38.444	0.000	362.344	951.681
Toluene	108-88-3	33.1	1.049	0.000	3.995	31.279
Chloromethane	74-87-3	31.8	0.504	0.000	1.996	3.717
Propionaldehyde	123-38-6	28.7	0.111	0.000	0.549	1.710
2-Butanone	78-93-3	25.4	1.297	0.000	4.560	103.225
Benzene	71-43-2	23.5	0.988	0.000	1.732	188.486
Heptane	142-82-5	20.0	0.704	0.000	4.344	20.491
Carbon Dioxide (%v)	124-38-9	19.0	0.009	0.000	0.045	0.410
m,p-Xylene	1330-20-7	18.4	0.400	0.000	1.572	13.894
o-Xylene	1330-20-7	16.8	0.116	0.000	0.368	4.777
Ethylbenzene	100-41-4	16.3	0.102	0.000	0.298	5.645
Trichlorofluoromethane	75-69-4	15.2	0.168	0.000	1.180	2.500
Hexaldehyde	66-25-1	15.0	0.218	0.000	2.491	5.070
Carbon Tetrachloride	56-23-5	14.9	0.059	0.000	0.409	0.447
Methylene Chloride	75-09-2	13.8	0.460	0.000	1.281	65.000
Benzaldehyde	100-52-7	13.5	0.100	0.000	0.529	3.840
4-Ethyltoluene	622-96-8	10.7	0.107	0.000	0.426	4.916
1,2,4-Trimethylbenzene	95-63-6	10.5	0.076	0.000	0.370	6.882
Naphthalene	91-20-3	10.3	0.026	0.000	0.056	5.085
1,2-Dichloro-1,1,2,2-Tetrafluoroethane	76-14-2	9.8	0.010	0.000	0.100	0.120
1,2-Dichloroethane	107-06-2	9.8	0.005	0.000	0.052	0.066
Chloroform	67-66-3	9.8	0.014	0.000	0.092	0.780

Analyte ($\mu\text{g}/\text{m}^3$) ¹	CASRN	% Det.	Mean Conc.	Median Conc.	95% Value	Max Conc.
Tetrachloroethene	127-18-4	9.6	0.392	0.000	0.091	88.171
Carbon Disulfide	75-15-0	9.1	0.921	0.000	4.733	168.162
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	7.0	0.034	0.000	0.446	0.950
Octane	111-65-9	6.8	0.272	0.000	2.392	8.800
1,4-Dichlorobenzene	106-46-7	6.5	0.001	0.000	0.018	0.045
Trichloroethene	79-01-6	5.8	0.179	0.000	0.019	50.004
2,5-Dimethyl Benzaldehyde	5779-94-2	4.3	0.021	0.000	0.000	0.630
Butyraldehyde	123-72-8	4.3	0.027	0.000	0.000	1.750
o-Tolualdehyde	529-20-4	4.3	0.012	0.000	0.000	0.485
1,3,5-Trimethylbenzene	108-67-8	2.8	0.022	0.000	0.000	3.638
4-Methyl-2-Pentanone	108-10-1	2.8	0.319	0.000	0.000	94.220
2-Methylnaphthalene	91-57-6	2.2	0.016	0.000	0.000	1.600
Chloroethane	75-00-3	1.9	0.001	0.000	0.000	0.100
2-Hexanone	591-78-6	1.4	0.020	0.000	0.000	2.253
Tetraethylene Glycol	112-60-7	1.4	2.097	0.000	0.000	260.000
1,1,1-Trichloroethane	71-55-6	1.2	0.000	0.000	0.000	0.049
1,3-Butadiene	106-99-0	1.2	0.003	0.000	0.000	0.575
C-1,2-Dichloroethene	156-59-2	1.2	0.008	0.000	0.000	2.220
Hydrogen (%v)	1333-74-0	1.1	0.000	0.000	0.000	0.036
Nonane	111-84-2	1.0	0.107	0.000	0.000	14.157
Bis(2-Ethylhexyl)phthalate	117-81-7	0.9	0.068	0.000	0.000	7.200
2,2,4-Trimethylpentane	540-84-1	0.7	0.023	0.000	0.000	3.738
1,2,4-Trichlorobenzene	120-82-1	0.5	0.017	0.000	0.000	6.679
1,1-Dichloroethane	75-34-3	0.2	0.000	0.000	0.000	0.012
1,1,2,2-Tetrachloroethane	79-34-5	0.2	0.000	0.000	0.000	0.080
Dibromochloromethane	124-48-1	0.2	0.008	0.000	0.000	3.493
Styrene	100-42-5	0.2	0.005	0.000	0.000	2.172
1,1-Dichloroethene	75-35-4	0.2	0.000	0.000	0.000	0.069
1,1,2-Trichloroethane	79-00-5	0.2	0.006	0.000	0.000	2.510
Ethane	74-84-0	0.2	0.000	0.000	0.000	6518.240

¹ Measurements of atmospheric gases (carbon dioxide, hydrogen, methane, nitrogen, and oxygen) are shown in %v/v.

Screening detected compounds – air pollution and carcinogenicity

One-third (n=22) of the detected compounds (n=64) are recognized as known or potential human carcinogens by state, federal, or international agencies (Table 4). Thirty-eight compounds (59% of those detected) were identified as air pollutants, of which 31 are designated as hazardous air pollutants (HAPs) under the Clean Air Act; 32 are designated toxic air contaminants (TACs); and 38 are considered under the Air Toxics Hot Spots Program (AB 2588) (Table 4). Formaldehyde was the most frequently detected carcinogen and air pollutant (95.4%). Ethanol, the second most frequently detected compound (82.1%), is noted as carcinogenic to humans (Group 1) by IARC, and OEHHA Prop 65 but via an oral rather than inhalation exposure pathway (i.e., ethanol in alcoholic beverages).

Table 4. Detected compounds identified as carcinogens and/or air pollutants. Sorted by frequency of detection.

Analyte ¹	CASRN	% Det.	Carcinogenicity				Air pollution			
			IARC	NTP	Prop 65	Carcinogen	HAP	TAC	AB 2588	Air pollutant
Formaldehyde	50-00-0	95.4	1	Known	X	X	X	X	X	X
Ethanol	64-17-5	82.1	1 ²	-	X ²	X	-	-	-	-
Dichlorodifluoromethane	75-71-8	62.5	-	-	-	-	-	-	X	X
Acetaldehyde	75-07-0	61.5	2B	RAHC	X	X	X	X	X	X
Cyclohexane	110-82-7	39.2	-	-	-	-	-	-	X	X
Hexane	110-54-3	35.9	-	-	-	-	X	X	X	X
Toluene	108-88-3	33.1	- ³	-	-	-	X	X	X	X
Chloromethane	74-87-3	31.8	- ³	-	-	-	X	X	X	X
Propionaldehyde	123-38-6	28.7	-	-	-	-	X	X	X	X
2-Butanone	78-93-3	25.4	-	-	-	-	- ⁶	X	X	X
Benzene	71-43-2	23.5	1	Known	X	X	X	X	X	X
m,p-Xylene	1330-20-7	18.4	- ³	-	-	-	X	X	X	X
o-Xylene	1330-20-7	18.4	- ³	-	-	-	X	X	X	X
Ethylbenzene	100-41-4	16.3	2B	-	X	X	X	X	X	X
Trichlorofluoromethane	75-69-4	15.2	-	-	-	-	-	-	X	X
Carbon Tetrachloride	56-23-5	14.9	2B	RAHC	X	X	X	X	X	X
Methylene Chloride	75-09-2	13.8	2A	RAHC	X	X	X	X	X	X
1,2,4-Trimethylbenzene	95-63-6	10.5	-	-	-	-	-	-	X	X
Naphthalene	91-20-3	10.3	2B	RAHC	X	X	X	X	X	X
1,2-Dichloroethane	107-06-2	9.8	2B	RAHC	X	X	X	X	X	X
Chloroform	67-66-3	9.8	2B	RAHC	X	X	X	X	X	X
Tetrachloroethene	127-18-4	9.6	2A	RAHC	X	X	X	X	X	X
Carbon Disulfide	75-15-0	9.1	-	-	-	-	X	X	X	X
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	7	-	-	-	-	-	-	X	X
1,4-Dichlorobenzene	106-46-7	6.5	2B	RAHC	X	X	X	X	X	X

Analyte ¹	CASRN	% Det.	Carcinogenicity				Air pollution			
			IARC	NTP	Prop 65	Carcinogen	HAP	TAC	AB 2588	Air pollutant
Trichloroethene	79-01-6	5.8	1	Known	X	X	X	X	X	X
4-Methyl-2-Pentanone	108-10-1	2.8	2B	-	X	X	X	X	X	X
2-Methylnaphthalene	91-57-6	2.2	-	-	-	-	-	-	X	X
Chloroethane	75-00-3	1.9	- ³	-	X	X	X	X	X	X
1,1,1-Trichloroethane	71-55-6	1.2	- ³	-	-	-	X	X	X	X
1,3-Butadiene	106-99-0	1.2	1	Known	X	X	X	X	X	X
Bis(2-Ethylhexyl)phthalate	117-81-7	0.9	2B	RAHC	X	X	X	X	X	X
2,2,4-Trimethylpentane	540-84-1	0.7	-	-	-	-	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	0.5	-	-	- ⁴	-	X	X	X	X
1,1-Dichloroethane	75-34-3	0.2	-	-	X	X	X	X	X	X
1,1-Dichloroethene	75-35-4	0.2	2B	-	X	X	X	X	X	X
1,1,2-Trichloroethane	79-00-5	0.2	- ³	-	X	X	X	X	X	X
1,1,2,2-Tetrachloroethane	79-34-5	0.2	2B	-	X	X	X	X	X	X
Dibromochloromethane	124-48-1	0.2	- ³	-	- ⁵	-	-	-	-	-
Styrene	100-42-5	0.2	2A	RAHC	X	X	X	X	X	X
COUNT (N=64)	-		19	14	21	22	31	32	38	38

¹ Detected compounds not included in Table 4 include five atmospheric gases [carbon dioxide (124-38-9); hydrogen (1333-74-0); methane (74-82-8); nitrogen (7727-37-9); oxygen (7782-44-7)] and 19 additional compounds [1,2-dichloro-1,1,2,2-tetrafluoroethane (76-14-2); 1,3,5-trimethylbenzene (108-67-8); 2-hexanone (591-78-6); 2,5-dimethyl benzaldehyde (5779-94-2); 4-ethyltoluene (622-96-8); acetone (67-64-1); benzaldehyde (100-52-7); butane (106-97-8); butyraldehyde (123-72-8); C-1,2-dichloroethene (156-59-2); ethane (74-84-0); heptane (142-82-5); hexaldehyde (66-25-1); i-butane (75-28-5); nonane (111-84-2); o-tolualdehyde (529-20-4); octane (111-65-9); pentane (109-66-0); tetraethylene glycol (112-60-7).

² Ethanol listed by IARC and OEHHA Prop 65 in alcoholic beverages, oral exposure pathway.

³ IARC Group 3, not considered carcinogen.

⁴ Prop 65 Carcinogen – Considered, but not listed.

⁵ Prop 65 Carcinogen – Formerly listed.

⁶ HAP formerly listed under the Clean Air Act.

Cancer risk

Of the 22 detected carcinogens, 15 had OEHHA cancer slope factors for inhalation (mg/kg/day)⁻¹ (Table 5). Formaldehyde was the most frequently detected carcinogen (detected in 95% of all samples), followed by acetaldehyde (detected in 62% of the samples) and benzene (detected in 24% of the samples). Bis(2-Ethylhexyl)phthalate and 1,1,2,2-Tetrachloroethane were each detected in only one sample, during well cleanout. Additionally, 1,1-Dichloroethane was only detected in one sample, during HyF.

Cancer risks are expressed based on continuous exposure over 70 years (OEHHA, 2015). Lifetime cancer risks exceeded the U.S. EPA de minimis benchmark of 1 in a million at each site type, with the highest cumulative lifetime excess cancer risk observed at ambient (off-field) locations (Table 6). Benzene – a naturally occurring constituent in petroleum that is co-emitted during oil and gas development and also associated with combustion and use of fossil fuels – accounted for 85% of the total cancer risk observed at ambient locations and 19-27% of total cancer risk observed at other site types. Of note, the mean benzene concentration calculated at ambient sites and used to calculate lifetime cancer risk was largely driven by two air samples collected at the same time at the same well (i.e., one sample and one duplicate sample) that indicated benzene concentrations of 188 µg/m³ (59 ppb) and 115 µg/m³ (36 ppb).

Meanwhile, formaldehyde – also associated with the combustion of fossil fuels – accounted for 45% of total cancer risk observed at background sites; 47-48% of total cancer risk at HyF and cleanout sites; and 5% of total cancer risk at ambient sites (Table 6). It should be noted that air quality at ambient sites likely reflect atmospheric pollutant enhancements attributable to oil field activities and not a control (Stringfellow and Camarillo, 2020).

Table 5. Carcinogens with available OEHHA inhalation slope factors (mg/kg/day)⁻¹ ; percent detected when analyzed (% Det.); and mean (8-hr TWA) concentrations (µg/m³) across all sites and by activity type.¹ Sorted in alphabetical order. Calculations presented include non-detections as zero values (i.e., 0.0 µg/m³).

Analyte (CASRN)	Inhalation Slope Factor (mg/kg-day) ⁻¹	All Sites		Ambient		Background		HyF		Cleanout	
		% Det.	Mean Conc. (µg/m ³)	% Det.	Mean Conc. (µg/m ³)	% Det.	Mean Conc. (µg/m ³)	% Det.	Mean Conc. (µg/m ³)	% Det.	Mean Conc. (µg/m ³)
1,1-Dichloroethane (75-34-3)	5.70E-03	0.2	2.80E-05	0.0	-	0.0	-	0.5	6.35E-05	0.0	-
1,1,2,2-Tetrachloroethane (79-34-5)	2.00E-01	0.2	1.86E-04	0.0	-	0.0	-	0.0	-	0.6	4.44E-04
1,2-Dichloroethane (107-06-2)	7.20E-02	9.8	5.16E-03	7.7	3.69E-03	11.8	6.82E-03	9.5	5.00E-03	10.0	5.22E-03
1,3-Butadiene (106-99-0)	6.00E-01	1.2	2.79E-03	0.0	-	0.0	-	1.6	4.79E-03	1.1	1.61E-03
Acetaldehyde (75-07-0)	1.00E-02	61.5	1.80E+00	76.9	2.39E+00	61.1	2.08E+00	66.5	1.96E+00	56.4	1.51E+00
Benzene (71-43-2)	1.00E-01	23.5	9.88E-01	26.9	1.18E+01	29.4	3.94E-01	23.8	2.79E-01	21.7	2.79E-01
Bis(2-Ethylhexyl)phthalate (117-81-7)	8.40E-03	0.9	6.79E-02	0.0	-	0.0	-	0.0	-	2.2	1.60E-01
Carbon Tetrachloride (56-23-5)	1.50E-01	14.9	5.88E-02	15.4	6.28E-02	17.6	6.93E-02	14.3	5.65E-02	15.0	5.88E-02
Chloroform (67-66-3)	1.90E-02	9.8	1.44E-02	7.7	6.81E-03	11.8	9.35E-03	9.5	1.16E-02	10.0	1.94E-02
Ethylbenzene (100-41-4)	8.70E-03	16.3	1.02E-01	15.4	2.29E-01	17.6	1.30E-01	14.8	7.82E-02	17.8	1.04E-01
Formaldehyde (50-00-0)	2.10E-02	95.4	2.82E+00	100.0	3.45E+00	100.0	3.23E+00	100.0	3.12E+00	92.7	2.34E+00
Methylene Chloride (75-09-2)	3.50E-03	13.8	4.60E-01	15.4	8.23E-01	17.6	5.06E-01	14.3	7.10E-01	12.2	1.37E-01
Naphthalene (91-20-3)	1.20E-01	10.3	2.61E-02	7.7	8.85E-03	11.8	2.19E-02	10.1	4.75E-02	10.6	6.89E-03
Tetrachloroethene (127-18-4)	2.10E-02	9.6	3.92E-01	19.2	4.35E+00	14.7	1.94E-01	11.1	2.51E-01	5.6	5.94E-03
Trichloroethene (79-01-6)	7.00E-03	5.8	1.79E-01	3.8	8.85E-04	11.8	3.41E-03	7.4	3.62E-01	3.3	4.57E-02

¹ The following seven carcinogens lacked OEHHA inhalation slope factors: 1,1-dichloroethene, 1,1,2-trichloroethane, 1,4-dichlorobenzene, 4-methyl-2-pentanone, chloroethane, ethanol and styrene.

Table 6. Inhalation lifetime (70-year) cancer risk calculated by compound across all sites and by activity type. Lifetime excess cancer risk > EPA de minimis risk level of 1 in a million is shown in *bold italics*. “Chances per million” represent chances of developing cancer per million individuals exposed. Sorted in alphabetical order. Calculations presented include non-detections as zero values (i.e., 0.0 µg/m³).

Analyte (CASRN)	All Sites		Ambient		Background		HyF		Cleanout	
	Cancer risk ¹	Chances per million ²	Cancer risk ¹	Chances per million ²	Cancer risk ¹	Chances per million ²	Cancer risk ¹	Chances per million ²	Cancer risk ¹	Chances per million ²
1,1-Dichloroethane (75-34-3)	7.13E-11	0	0.00E+00	- ³	0.00E+00	-	1.62E-10	0	0.00E+00	-
1,1,2,2-Tetrachloroethane (79-34-5)	1.67E-08	0	0.00E+00	-	0.00E+00	-	0.00E+00	-	3.98E-08	0
1,2-Dichloroethane (107-06-2)	1.66E-07	0	1.19E-07	0	2.20E-07	0	1.61E-07	0	1.68E-07	0
1,3-Butadiene (106-99-0)	7.48E-07	1	0.00E+00	-	0.00E+00	-	1.29E-06	1	4.33E-07	0
Acetaldehyde (75-07-0)	8.07E-06	8	1.07E-05	11	9.32E-06	9	8.75E-06	9	6.76E-06	7
Benzene (71-43-2)	4.42E-05	44	5.29E-04	529	1.76E-05	18	1.25E-05	12	1.25E-05	12
Bis(2-Ethylhexyl)phthalate (117-81-7)	2.55E-07	0	0.00E+00	-	0.00E+00	-	0.00E+00	-	6.01E-07	1
Carbon Tetrachloride (56-23-5)	3.95E-06	4	4.21E-06	4	4.65E-06	5	3.79E-06	4	3.95E-06	4
Chloroform (67-66-3)	1.22E-07	0	5.79E-08	0	7.95E-08	0	9.87E-08	0	1.65E-07	0
Ethylbenzene (100-41-4)	3.99E-07	0	8.90E-07	1	5.06E-07	1	3.04E-07	0	4.06E-07	0
Formaldehyde (50-00-0)	2.65E-05	26	3.24E-05	32	3.03E-05	30	2.93E-05	29	2.20E-05	22
Methylene Chloride (75-09-2)	7.20E-07	1	1.29E-06	1	7.93E-07	1	1.11E-06	1	2.14E-07	0
Naphthalene (91-20-3)	1.40E-06	1	4.75E-07	0	1.17E-06	1	2.55E-06	3	3.70E-07	0
Tetrachloroethene (127-18-4)	3.69E-06	4	4.09E-05	41	1.83E-06	2	2.36E-06	2	5.58E-08	0
Trichloroethene (79-01-6)	5.61E-07	1	2.77E-09	0	1.07E-08	0	1.13E-06	1	1.43E-07	0
TOTAL	9.08E-05	90	6.20E-04	619	6.65E-05	67	6.34E-05	62	4.78E-05	46

¹ Dose calculated using mean (8-hr TWA) concentration measured across all sites and by activity type and mean age-specific breathing rate normalized to body weight (Eq. 5.4.1.1 in OEHHA, 2015). Cancer risk calculated using age-specific exposure variates for all age groups relevant to assessing 70-year cancer risk (Equation 8.2.4 A in OEHHA, 2015).

² Cancer risk multiplied by 10⁶ and then rounded to represent “chances per million” or chances of developing cancer per million individuals exposed.

³ ‘-’ = Compound not detected.

Noncancer health risk

Of the 64 compounds detected in at least one sample, 34 (53%) had inhalation noncancer acute health guidance values and 31 (48%) had inhalation noncancer chronic health guidance values. Compiled inhalation noncancer health guidance values for both acute and chronic exposures were available for 40 (59%) of the detected compounds and are shown in Appendix B, Table B-5.

Acute

Chemical-specific acute health guidance values and maximum concentrations ($\mu\text{g}/\text{m}^3$, 8-hr TWA) measured across all samples and by activity type are shown in Table 7. Acute HQs by compound across all sites and by activity type are shown in Table 8. Acute HIs calculated by target organ system and by activity type are shown in Table 9.

The maximum (8-hr TWA) benzene concentration observed across ambient site locations contributed to an acute hazard quotient (HQ) greater than one ($\text{HQ}=6.98$) and acute hazard indices (HI) greater than one for the hematologic, immune, and respiratory system ($\text{HI}= 6.98, 6.98, 7.01$, respectively). This result indicates potential for noncancer health risks associated with acute benzene exposure at ambient sites. All chemical-specific acute HQs for background, HyF, and cleanout site types were less than 1, indicating that acute exposures associated with the detected air pollutants are not likely to be associated with adverse health effects. Additionally, all target organ system-specific acute HIs calculated for background, HyF and cleanout site types also did not exceed one. However, given that simultaneous exposure to multiple chemicals or to multiple chemicals in close temporal succession may be additive, antagonistic (less than additive) or synergistic (greater than additive), HI less than 1 may not confirm the absence of risk for adverse health effects (U.S. EPA, 1986).

Table 7. Chemical-specific acute health guidance values and maximum (8-hr TWA) concentration ($\mu\text{g}/\text{m}^3$) measured across all sites and by activity type. Sorted in alphabetical order. Calculations presented include non-detections as zero values (i.e., $0.0 \mu\text{g}/\text{m}^3$).

Analyte (CASRN)	All Sites		Ambient		Background		HyF		Cleanout		Guidance Value (Acute) ($\mu\text{g}/\text{m}^3$)	Source	Target Organ System
	% Det.	Max Conc.	% Det.	Max Conc.	% Det.	Max Conc.	% Det.	Max Conc.	% Det.	Max Conc.			
1,1,1-Trichloroethane (71-55-6)	1.2	4.90E-02	0.0	-	0.0	-	2.6	4.90E-02	0.0	-	6.80E+04	OEHHA	Nervous system
1,1,2-Trichloro-1,2,2-Trifluoroethane (76-13-1)	7.0	9.50E-01	7.7	5.00E-01	5.9	4.90E-01	6.3	9.50E-01	7.8	5.20E-01	5.00E+04	PPRTV (Subchronic)	Alimentary tract, respiratory system
1,1,2-Trichloroethane (79-00-5)	0.2	2.51E+00	0.0	-	0.0	-	0.0	-	0.6	2.51E+00	1.57E+02	ATSDR MRL	Respiratory system
1,2-Dichloroethane (107-06-2)	9.8	6.60E-02	7.7	4.90E-02	11.8	5.90E-02	9.5	6.60E-02	10.0	6.60E-02	7.00E+01	PPRTV (Subchronic)	Nervous system
1,2,4-Trichlorobenzene (120-82-1)	0.5	6.68E+00	0.0	-	0.0	-	0.0	-	1.1	6.68E+00	2.00E+01	PPRTV (Subchronic)	Alimentary tract
1,2,4-Trimethylbenzene (95-63-6)	10.5	6.88E+00	7.7	6.88E+00	11.8	6.20E-01	9.0	5.80E-01	12.2	6.88E+00	2.00E+02	IRIS (Subchronic)	Nervous system
1,3-Butadiene (106-99-0)	1.2	5.75E-01	0.0	-	0.0	-	1.6	5.75E-01	1.1	1.60E-01	6.60E+02	OEHHA	Developmental
1,3,5-Trimethylbenzene (108-67-8)	2.8	3.64E+00	3.8	3.64E+00	11.8	3.00E-01	1.1	2.40E-01	2.8	3.49E+00	2.00E+02	IRIS (Subchronic)	Nervous system
1,4-Dichlorobenzene (106-46-7)	6.5	4.52E-02	3.8	1.64E-02	11.8	2.67E-02	5.8	2.77E-02	6.7	4.52E-02	1.24E+04	ATSDR	Respiratory system
2-Butanone (78-93-3)	25.4	1.03E+02	34.6	2.71E+01	50.0	1.03E+02	28.0	1.15E+01	16.7	4.13E+01	1.30E+04	OEHHA	Eyes, respiratory system
Acetaldehyde (75-07-0)	61.5	1.60E+01	76.9	5.90E+00	61.1	1.60E+01	66.5	1.37E+01	56.4	1.35E+01	4.70E+02	OEHHA	Eyes, respiratory system
Acetone (67-64-1)	67.0	1.70E+01	79.2	1.41E+01	68.8	5.72E+00	82.6	1.70E+01	55.9	8.98E+00	6.18E+04	ATSDR	Nervous system

Analyte (CASRN)	All Sites		Ambient		Background		HyF		Cleanout		Guidance Value (Acute) (µg/m³)	Source	Target Organ System
	% Det.	Max Conc.	% Det.	Max Conc.	% Det.	Max Conc.	% Det.	Max Conc.	% Det.	Max Conc.			
Benzene (71-43-2)	23.5	1.88E+02	26.9	1.88E+02	29.4	2.17E+00	23.8	4.15E+00	21.7	4.47E+00	2.70E+01	OEHHA	Hematological, immune system, developmental
Carbon Disulfide (75-15-0)	9.1	1.68E+02	7.7	1.68E+02	17.6	8.10E+00	12.2	9.34E+00	4.4	2.34E+01	6.20E+03	OEHHA	Nervous system, reproductive, developmental
Carbon Tetrachloride (56-23-5)	14.9	4.47E-01	15.4	4.40E-01	17.6	4.40E-01	14.3	4.47E-01	15.0	4.47E-01	1.90E+03	OEHHA	Nervous system, alimentary tract, reproductive, developmental, physiological response to odors
Chloroethane (75-00-3)	1.9	1.00E-01	0.0	-	0.0	-	4.2	1.00E-01	0.0	-	3.96E+04	ATSDR	Developmental
Chloroform (67-66-3)	9.8	7.80E-01	7.7	9.30E-02	11.8	8.40E-02	9.5	4.40E-01	10.0	7.80E-01	1.50E+02	OEHHA	Nervous system, reproductive, developmental, respiratory system
Chloromethane (74-87-3)	31.8	3.72E+00	34.6	2.27E+00	23.5	1.98E+00	34.9	3.72E+00	29.6	2.89E+00	1.03E+03	ATSDR	Nervous system
Cyclohexane (110-82-7)	39.2	5.51E+01	15.4	1.17E+00	47.1	7.57E+00	34.4	5.51E+01	46.1	1.82E+01	1.80E+04	PPRTV (Subchronic)	Developmental
Dichlorodifluoromethane (75-71-8)	62.5	3.21E+00	57.7	3.07E+00	67.6	2.82E+00	59.3	3.21E+00	65.6	3.07E+00	1.00E+03	PPRTV (Subchronic)	General toxicity
Ethylbenzene (100-41-4)	16.3	5.65E+00	15.4	5.65E+00	17.6	1.10E+00	14.8	5.21E+00	17.8	4.78E+00	2.17E+04	ATSDR	Nervous system
Formaldehyde (50-00-0)	95.4	8.09E+00	100.0	6.40E+00	100.0	6.70E+00	100.0	8.09E+00	92.7	7.12E+00	5.50E+01	OEHHA	Eyes
Heptane (142-82-5)	20.0	2.05E+01	15.4	1.39E+00	23.5	5.74E+00	19.0	2.05E+01	21.1	1.39E+01	4.00E+03	PPRTV (Subchronic)	General toxicity
Hexane (110-54-3)	35.9	9.52E+02	23.1	2.93E+02	29.4	2.11E+02	36.5	6.34E+02	38.3	9.52E+02	2.00E+03	PPRTV (Subchronic)	Nervous system
m,p-Xylene (1330-20-7)	18.4	1.39E+01	19.2	1.30E+01	17.6	3.90E+00	16.9	1.39E+01	20.0	1.17E+01	2.20E+04	OEHHA	Nervous system, respiratory system, eyes

Analyte (CASRN)	All Sites		Ambient		Background		HyF		Cleanout		Guidance Value (Acute) (µg/m ³)	Source	Target Organ System
	% Det.	Max Conc.	% Det.	Max Conc.	% Det.	Max Conc.	% Det.	Max Conc.	% Det.	Max Conc.			
Methylene Chloride (75-09-2)	13.8	6.50E+01	15.4	1.53E+01	17.6	1.35E+01	14.3	6.50E+01	12.2	5.56E+00	1.40E+04	OEHHA	Cardiovascular, nervous system
Nonane (111-84-2)	1.0	1.42E+01	15.4	1.42E+01	0.0	-	0.0	-	0.0	-	2.00E+02	PPRTV (Subchronic)	General toxicity
o-Xylene (1330-20-7)	16.8	4.78E+00	15.4	4.78E+00	17.6	1.20E+00	15.3	3.95E+00	18.3	3.43E+00	2.20E+04	OEHHA	Nervous system, respiratory system, eyes
Pentane (109-66-0)	50.4	5.61E+02	27.3	6.49E+00	71.4	2.54E+01	48.1	5.61E+02	52.3	2.57E+01	1.00E+04	PPRTV (Subchronic)	Nervous system
Styrene (100-42-5)	0.2	2.17E+00	0.0	-	0.0	-	0.5	2.17E+00	0.0	-	2.10E+04	OEHHA	Eyes, reproductive, developmental, respiratory system
Tetrachloroethene (127-18-4)	9.6	8.82E+01	19.2	8.82E+01	14.7	6.17E+00	11.1	2.10E+01	5.6	2.85E-01	2.00E+04	OEHHA	Nervous system, respiratory system, eyes
Toluene (108-88-3)	33.1	3.13E+01	34.6	1.09E+01	26.5	4.52E+00	30.7	3.13E+01	36.7	1.58E+01	3.70E+04	PPRTV (Subchronic)	Nervous system, eyes, reproductive, developmental, respiratory system
Trichlorofluoromethane (75-69-4)	15.2	2.50E+00	15.4	1.24E+00	17.6	1.24E+00	14.8	2.50E+00	15.0	1.29E+00	1.00E+03	PPRTV (Subchronic)	Nervous system

Table 8. Acute HQs calculated by compound across all sites and by activity type.¹ HQ > 0.1 and < 1 are shown in *italics*. HQ >1 are shown in *bold italics***. Sorted in alphabetical order. Calculations presented include non-detections as zero values (i.e., 0.0 µg/m³).**

Analyte (CASRN)	ACUTE HQ				
	All Sites	Ambient	Background	HyF	Cleanout
1,1,1-Trichloroethane (71-55-6)	7.21E-07	- ²	-	7.21E-07	-
1,1,2-Trichloro-1,2,2-Trifluoroethane (76-13-1)	1.90E-05	1.00E-05	9.80E-06	1.90E-05	1.04E-05
1,1,2-Trichloroethane (79-00-5)	1.60E-02	-	-	-	1.60E-02
1,2-Dichloroethane (107-06-2)	9.43E-04	7.00E-04	8.43E-04	9.43E-04	9.43E-04
1,2,4-Trichlorobenzene (120-82-1)	<i>3.34E-01</i>	-	-	-	<i>3.34E-01</i>
1,2,4-Trimethylbenzene (95-63-6)	3.44E-02	3.44E-02	3.10E-03	2.90E-03	3.44E-02
1,3-Butadiene (106-99-0)	8.72E-04	-	-	8.72E-04	2.42E-04
1,3,5-Trimethylbenzene (108-67-8)	1.82E-02	1.82E-02	1.50E-03	1.20E-03	1.75E-02
1,4-Dichlorobenzene (106-46-7)	3.66E-06	1.33E-06	2.16E-06	2.25E-06	3.66E-06
2-Butanone (78-93-3)	7.94E-03	2.09E-03	7.94E-03	8.85E-04	3.18E-03
Acetaldehyde (75-07-0)	3.40E-02	1.26E-02	3.40E-02	2.91E-02	2.87E-02
Acetone (67-64-1)	2.75E-04	2.28E-04	9.26E-05	2.75E-04	1.45E-04
Benzene (71-43-2)	<i>6.98E+00</i>	<i>6.98E+00</i>	8.05E-02	<i>1.54E-01</i>	<i>1.66E-01</i>
Carbon Disulfide (75-15-0)	2.71E-02	2.71E-02	1.31E-03	1.51E-03	3.77E-03
Carbon Tetrachloride (56-23-5)	2.35E-04	2.32E-04	2.32E-04	2.35E-04	2.35E-04
Chloroethane (75-00-3)	2.53E-06	-	-	2.53E-06	-
Chloroform (67-66-3)	5.20E-03	6.20E-04	5.60E-04	2.93E-03	5.20E-03
Chloromethane (74-87-3)	3.60E-03	2.20E-03	1.92E-03	3.60E-03	2.80E-03
Cyclohexane (110-82-7)	3.06E-03	6.50E-05	4.21E-04	3.06E-03	1.01E-03
Dichlorodifluoromethane (75-71-8)	3.21E-03	3.07E-03	2.82E-03	3.21E-03	3.07E-03
Ethylbenzene (100-41-4)	2.60E-04	2.60E-04	5.07E-05	2.40E-04	2.20E-04
Formaldehyde (50-00-0)	<i>1.47E-01</i>	<i>1.16E-01</i>	<i>1.22E-01</i>	<i>1.47E-01</i>	<i>1.29E-01</i>
Heptane (142-82-5)	5.12E-03	3.48E-04	1.43E-03	5.12E-03	3.48E-03
Hexane (110-54-3)	<i>4.76E-01</i>	<i>1.46E-01</i>	<i>1.06E-01</i>	<i>3.17E-01</i>	<i>4.76E-01</i>
m,p-Xylene (1330-20-7)	6.32E-04	5.92E-04	1.77E-04	6.32E-04	5.33E-04

Analyte (CASRN)	ACUTE HQ				
	All Sites	Ambient	Background	HyF	Cleanout
Methylene Chloride (75-09-2)	4.64E-03	1.09E-03	9.68E-04	4.64E-03	3.97E-04
Nonane (111-84-2)	7.08E-02	7.08E-02	-	-	-
o-Xylene (1330-20-7)	2.17E-04	2.17E-04	5.45E-05	1.80E-04	1.56E-04
Pentane (109-66-0)	5.61E-02	6.49E-04	2.54E-03	5.61E-02	2.57E-03
Styrene (100-42-5)	1.03E-04	-	-	1.03E-04	-
Tetrachloroethene (127-18-4)	4.41E-03	4.41E-03	3.09E-04	1.05E-03	1.42E-05
Toluene (108-88-3)	8.45E-04	2.95E-04	1.22E-04	8.45E-04	4.28E-04
Trichlorofluoromethane (75-69-4)	2.50E-03	1.24E-03	1.24E-03	2.50E-03	1.29E-03

¹ Acute HQ calculated using acute health guidance values and maximum (8-hr TWA) concentration measured across all sites and by activity type presented in Table 7.

² '-' = Compound not detected.

Table 9. Acute HI presented by target organ system across all sites and by activity type. HI >1 shown in *bold italics*. Calculations presented include non-detections as zero values (i.e., 0.0 µg/m³).

	Hematologic system ¹	Cardiovascular system ²	Nervous system ³	Eyes ⁴	Alimentary tract ⁵	Immune system ⁶	Reproductive ⁷	Development ⁸	Respiratory system ⁹	Skin ¹⁰	Physiological response to odors ¹¹	Endocrine system ¹²	General Toxicity ¹³
All Sites	<i>6.98E+00</i>	4.64E-03	6.35E-01	1.95E-01	3.34E-01	<i>6.98E+00</i>	3.35E-02	<i>7.02E+00</i>	6.94E-02	-	2.35E-04	-	7.91E-02
Ambient	<i>6.98E+00</i>	1.09E-03	2.39E-01	1.37E-01	2.42E-04	<i>6.98E+00</i>	2.83E-02	<i>7.01E+00</i>	2.08E-02	-	2.32E-04	-	3.41E-03
Background	8.05E-02	9.68E-04	1.21E-01	1.64E-01	2.42E-04	8.05E-02	2.22E-03	8.31E-02	4.32E-02	-	2.32E-04	-	4.25E-03
HyF	1.54E-01	4.64E-03	3.97E-01	1.80E-01	2.54E-04	1.54E-01	5.62E-03	1.63E-01	3.58E-02	-	2.35E-04	-	8.34E-03
Cleanout	1.66E-01	3.97E-04	5.46E-01	1.62E-01	3.34E-01	1.66E-01	9.63E-03	1.77E-01	5.42E-02	-	2.35E-04	-	6.55E-03

¹ HQ for benzene (71-43-2).

² HQ for methylene chloride (75-09-2).

³ Sum of HQs for 1,1,1-trichloroethane (71-55-6); 1,2-dichloroethane (107-06-2); 1,2,4-trimethylbenzene (95-63-6); 1,3,5-trimethylbenzene (108-67-8); acetone (67-64-1); carbon disulfide (75-15-0); carbon tetrachloride (56-23-5); chloroform (67-66-3); chloromethane (74-87-3); ethylbenzene (100-41-4); hexane (110-54-3); m,p-xylene (1330-20-7); methylene chloride (75-09-2); o-xylene (1330-20-7); pentane (109-66-0); tetrachloroethene (127-18-4); toluene (108-88-3); and trichlorofluoromethane (75-69-4).

⁴ Sum of HQs for 2-butanone (78-93-3); acetaldehyde (75-07-0); formaldehyde (50-00-0); m,p-xylene (1330-20-7); o-xylene (1330-20-7); styrene (100-42-5); tetrachloroethene (127-18-4); and toluene (108-88-3).

⁵ Sum of HQs for 1,1,2-trichloro-1,2,2-trifluoroethane (76-13-1); 1,2,4-trichlorobenzene (120-82-1); and carbon tetrachloride (56-23-5).

⁶ HQ for benzene (71-43-2).

⁷ Sum of HQs for carbon disulfide (75-15-0); carbon tetrachloride (56-23-5); chloroform (67-66-3); styrene (100-42-5); and toluene (108-88-3).

⁸ Sum of HQs for 1,3-butadiene (106-99-0); benzene (71-43-2); carbon disulfide (75-15-0); carbon tetrachloride (56-23-5); chloroethane (75-00-3); chloroform (67-66-3); cyclohexane (110-82-7); styrene (100-42-5); toluene (108-88-3).

⁹ Sum of HQs for 1,1,2-trichloro-1,2,2-trifluoroethane (76-13-1); 1,1,2-trichloroethane (79-00-5); 1,4-dichlorobenzene (106-46-7); 2-butanone (78-93-3); acetaldehyde (75-07-0); chloroform (67-66-3); m,p-xylene (1330-20-7); o-xylene (1330-20-7); styrene (100-42-5); tetrachloroethene (127-18-4); and toluene (108-88-3).

¹⁰ Skin: no relevant acute exposures for this target organ system.

¹¹ HQ for carbon tetrachloride (56-23-5).

¹² Endocrine system: no relevant acute exposures for this target organ system.

¹³ Sum of HQs for dichlorodifluoromethane (75-71-8); heptane (142-82-5); and nonane (111-84-2).

Chronic

Chemical-specific chronic health guidance values and mean concentrations ($\mu\text{g}/\text{m}^3$, 8-hr TWA) measured across all samples and by activity type are shown in Table 10. Chronic HQs by compound across all sites and by activity type are shown in Table 11. Chronic HIs calculated using mean, median, and 95th percentile (8-hr TWA) concentrations by target organ system and by activity type are shown in Table 12.

Similar to the evaluation of noncancer health effects associated with acute exposures, the mean (8-hr TWA) benzene concentration calculated across ambient site locations accounted for a chronic HQ greater than one ($\text{HQ}=3.94$) and chronic HI greater than one ($\text{HI}=3.94$) for the hematologic system (Table 11 & Table 12). This result indicates the potential for noncancer health risks associated with chronic benzene exposure at ambient sites. Of note, the mean benzene concentration calculated at ambient sites and used to calculate chronic noncancer health risk was largely driven by two air samples collected at the same time at the same well (i.e., one sample and one duplicate sample) that indicated benzene concentrations of $188 \mu\text{g}/\text{m}^3$ (59 ppb) and $115 \mu\text{g}/\text{m}^3$ (36 ppb).

All chemical-specific chronic HQs (calculated using mean 8-hr TWA concentrations) for background, HyF and cleanout site types were less than 1, suggesting that chronic exposure associated with the detected air pollutants at these sites may not result in adverse noncancer health effects. Additionally, all target organ system-specific chronic HIs calculated for background, HyF and cleanout site types also did not exceed one. However, given that simultaneous exposure to multiple chemicals or to multiple chemicals in close temporal succession may be additive, antagonistic (less than additive) or synergistic (greater than additive), HI less than 1 may not confirm the absence of risk for adverse health effects (U.S. EPA, 1986).

To provide additional context, chronic HQs and HIs were also calculated using median and 95th percentile (8-hr TWA) concentrations. Chronic HQs calculated using median and 95th percentile (8-hr TWA) concentrations are shown in Appendix B, Table B-6 and Table B-7, respectively. Chronic HQs calculated using median (8-hr TWA) concentrations were less than 1 for all detected compounds (Table B-6); chronic HIs calculated using median (8-hr TWA) concentrations were also less than 1 for all target organ systems (Table 12). Chronic HQs calculated using 95th percentile (8-hr TWA) concentrations were less than 1 for all detected compounds, except for benzene ($\text{HQ}=28.9$; Table B-7). Chronic HIs calculated using 95th percentile (8-hr TWA) concentrations were greater than 1 for the hematologic system, nervous system, and respiratory system (Table 12; see footnotes 1,3 and 9 for compounds that contribute to target organ specific-HIs that exceed 1).

Table 10. Chemical-specific chronic health guidance values and mean (8-hr TWA) concentration ($\mu\text{g}/\text{m}^3$) measured across all sites and by activity type. Sorted in alphabetical order. Calculations presented include non-detections as zero values (i.e., $0.0 \mu\text{g}/\text{m}^3$).

Analyte (CASRN)	All Sites		Ambient		Background		HyF		Cleanout		Guidance Value (Chronic) ($\mu\text{g}/\text{m}^3$)	Source	Target Organ System
	% Det.	Mean Conc.	% Det.	Mean Conc.	% Det.	Mean Conc.	% Det.	Mean Conc.	% Det.	Mean Conc.			
1,1-Dichloroethene (75-35-4)	0.2	1.55E-04	0.0	-	0.0	-	0.5	3.65E-04	0.0	-	1.00E+00	ATSDR	Respiratory system, alimentary tract
1,1,1-Trichloroethane (71-55-6)	1.2	3.64E-04	0.0	-	0.0	-	2.6	8.25E-04	0.0	-	1.00E+03	OEHHA	Nervous system
1,2-Dichloroethane (107-06-2)	9.8	5.16E-03	7.7	3.69E-03	11.8	6.82E-03	9.5	5.00E-03	10.0	5.22E-03	4.00E+02	OEHHA	Alimentary tract
1,2,4-Trimethylbenzene (95-63-6)	10.5	7.63E-02	7.7	2.74E-01	11.8	7.00E-02	9.0	2.74E-02	12.2	1.00E-01	6.00E+01	EPA IRIS (Chronic)	Nervous system
1,3-Butadiene (106-99-0)	1.2	2.79E-03	0.0	-	0.0	-	1.6	4.79E-03	1.1	1.61E-03	2.00E+00	OEHHA	Reproductive
1,3,5-Trimethylbenzene (108-67-8)	2.8	2.20E-02	3.8	1.40E-01	11.8	2.94E-02	1.1	2.38E-03	2.8	2.42E-02	6.00E+01	EPA IRIS (Chronic)	Nervous system
1,4-Dichlorobenzene (106-46-7)	6.5	1.47E-03	3.8	6.32E-04	11.8	3.02E-03	5.8	1.27E-03	6.7	1.51E-03	6.18E+01	OEHHA	Nervous system, alimentary tract, respiratory system
2-Butanone (78-93-3)	25.4	1.30E+00	34.6	2.55E+00	50.0	4.86E+00	28.0	1.06E+00	16.7	6.91E-01	5.00E+03	EPA IRIS (Chronic)	Developmental
2-Hexanone (591-78-6)	1.4	2.04E-02	7.7	1.45E-01	0.0	-	2.1	2.64E-02	0.0	-	3.00E+01	EPA IRIS (Chronic)	Nervous system
4-Methyl-2-Pentanone (108-10-1)	2.8	3.19E-01	3.8	1.73E-01	0.0	-	3.7	1.06E-01	2.2	6.24E-01	3.00E+03	EPA IRIS (Chronic)	Developmental
Acetaldehyde (75-07-0)	61.5	1.80E+00	76.9	2.39E+00	61.1	2.08E+00	66.5	1.96E+00	56.4	1.51E+00	9.00E+00	EPA IRIS (Chronic)	Nervous system, respiratory system
Acetone (67-64-1)	67.0	2.30E+00	79.2	3.35E+00	68.8	2.40E+00	82.6	2.70E+00	55.9	1.72E+00	3.09E+04	ATSDR	Nervous system
Benzene (71-43-2)	23.5	9.88E-01	26.9	1.18E+01	29.4	3.94E-01	23.8	2.79E-01	21.7	2.79E-01	3.00E+00	OEHHA	Hematological system
Carbon Disulfide (75-15-0)	9.1	9.21E-01	7.7	6.85E+00	17.6	1.30E+00	12.2	5.54E-01	4.4	3.79E-01	7.00E+02	EPA IRIS (Chronic)	Nervous system, reproductive
Carbon Tetrachloride (56-23-5)	14.9	5.88E-02	15.4	6.28E-02	17.6	6.93E-02	14.3	5.65E-02	15.0	5.88E-02	4.00E+01	OEHHA	Nervous system, alimentary tract, developmental

Analyte (CASRN)	All Sites		Ambient		Background		HyF		Cleanout		Guidance Value (Chronic) (µg/m ³)	Source	Target Organ System
	% Det.	Mean Conc.	% Det.	Mean Conc.	% Det.	Mean Conc.	% Det.	Mean Conc.	% Det.	Mean Conc.			
Chloroethane (75-00-3)	1.9	1.45E-03	0.0	-	0.0	-	4.2	3.26E-03	0.0	-	1.00E+04	EPA IRIS (Chronic)	Developmental
Chloroform (67-66-3)	9.8	1.44E-02	7.7	6.81E-03	11.8	9.35E-03	9.5	1.16E-02	10.0	1.94E-02	9.77E+01	ATSDR	Alimentary tract, developmental
Chloromethane (74-87-3)	31.8	5.04E-01	34.6	5.78E-01	23.5	3.30E-01	34.9	5.79E-01	29.6	4.48E-01	9.00E+01	EPA IRIS (Chronic)	Nervous system
Cyclohexane (110-82-7)	39.2	1.54E+00	15.4	1.27E-01	47.1	1.09E+00	34.4	1.54E+00	46.1	1.83E+00	6.00E+03	EPA IRIS (Chronic)	Developmental
Ethylbenzene (100-41-4)	16.3	1.02E-01	15.4	2.29E-01	17.6	1.30E-01	14.8	7.82E-02	17.8	1.04E-01	2.61E+02	ATSDR	Alimentary tract, developmental, endocrine system
Formaldehyde (50-00-0)	95.4	2.82E+00	100.0	3.45E+00	100.0	3.23E+00	100.0	3.12E+00	92.7	2.34E+00	9.00E+00	OEHHA	Respiratory system
Hexane (110-54-3)	35.9	3.84E+01	23.1	1.95E+01	29.4	1.37E+01	36.5	2.77E+01	38.3	5.72E+01	7.00E+02	EPA IRIS (Chronic)	Nervous system
m,p-Xylene (1330-20-7)	18.4	4.00E-01	19.2	9.45E-01	17.6	4.74E-01	16.9	2.60E-01	20.0	4.54E-01	1.00E+02	EPA IRIS (Chronic)	Nervous system
Methylene Chloride (75-09-2)	13.8	4.60E-01	15.4	8.23E-01	17.6	5.06E-01	14.3	7.10E-01	12.2	1.37E-01	4.00E+02	OEHHA	Cardiovascular system, nervous system
Naphthalene (91-20-3)	10.3	2.61E-02	7.7	8.85E-03	11.8	2.19E-02	10.1	4.75E-02	10.6	6.89E-03	3.00E+00	EPA IRIS (Chronic)	Nervous system, respiratory system
o-Xylene (1330-20-7)	16.8	1.16E-01	15.4	3.25E-01	17.6	1.50E-01	15.3	7.08E-02	18.3	1.26E-01	1.00E+02	EPA IRIS (Chronic)	Nervous system
Propionaldehyde (123-38-6)	28.7	1.11E-01	42.3	2.03E-01	44.4	1.75E-01	32.4	1.46E-01	19.0	5.07E-02	8.00E+00	EPA IRIS (Chronic)	Nervous system, respiratory system
Styrene (100-42-5)	0.2	5.06E-03	0.0	-	0.0	-	0.5	1.15E-02	0.0	-	8.52E+02	ATSDR	Nervous system
Tetrachloroethene (127-18-4)	9.6	3.92E-01	19.2	4.35E+00	14.7	1.94E-01	11.1	2.51E-01	5.6	5.94E-03	3.50E+01	OEHHA	Alimentary tract
Toluene (108-88-3)	33.1	1.05E+00	34.6	9.60E-01	26.5	7.38E-01	30.7	1.11E+00	36.7	1.06E+00	3.00E+02	OEHHA	Nervous system, developmental, respiratory system
Trichloroethene (79-01-6)	5.8	1.79E-01	3.8	8.85E-04	11.8	3.41E-03	7.4	3.62E-01	3.3	4.57E-02	2.00E+00	EPA IRIS (Chronic)	Immune system, developmental

Table 11. Chronic HQs calculated by compound across all sites and by activity type.¹ HQ > 0.1 and < 1.0 are shown in *italics*. HQ >1 are shown in *bold italics***. Sorted in alphabetical order. Calculations presented include non-detections as zero values (i.e., 0.0 µg/m³).**

Analyte (CASRN)	CHRONIC HQ				
	All Sites	Ambient	Background	HyF	Cleanout
1,1-Dichloroethene (75-35-4)	1.55E-04	- ²	-	3.65E-04	-
1,1,1-Trichloroethane (71-55-6)	3.64E-07	-	-	8.25E-07	-
1,2-Dichloroethane (107-06-2)	1.29E-05	9.23E-06	1.71E-05	1.25E-05	1.30E-05
1,2,4-Trimethylbenzene (95-63-6)	1.27E-03	4.56E-03	1.17E-03	4.56E-04	1.67E-03
1,3-Butadiene (106-99-0)	1.39E-03	-	-	2.39E-03	8.06E-04
1,3,5-Trimethylbenzene (108-67-8)	3.67E-04	2.33E-03	4.90E-04	3.97E-05	4.04E-04
1,4-Dichlorobenzene (106-46-7)	2.38E-05	1.02E-05	4.89E-05	2.05E-05	2.44E-05
2-Butanone (78-93-3)	2.59E-04	5.11E-04	9.73E-04	2.12E-04	1.38E-04
2-Hexanone (591-78-6)	6.80E-04	4.83E-03	-	8.80E-04	-
4-Methyl-2-Pentanone (108-10-1)	1.06E-04	5.78E-05	-	3.52E-05	2.08E-04
Acetaldehyde (75-07-0)	<i>2.00E-01</i>	<i>2.66E-01</i>	<i>2.31E-01</i>	<i>2.17E-01</i>	<i>1.68E-01</i>
Acetone (67-64-1)	7.44E-05	1.09E-04	7.78E-05	8.74E-05	5.56E-05
Benzene (71-43-2)	<i>3.29E-01</i>	<i>3.94E+00</i>	<i>1.31E-01</i>	9.31E-02	9.31E-02
Carbon Disulfide (75-15-0)	1.32E-03	9.78E-03	1.86E-03	7.92E-04	5.41E-04
Carbon Tetrachloride (56-23-5)	1.47E-03	1.57E-03	1.73E-03	1.41E-03	1.47E-03
Chloroethane (75-00-3)	1.45E-07	-	-	3.26E-07	-
Chloroform (67-66-3)	1.47E-04	6.97E-05	9.58E-05	1.19E-04	1.98E-04
Chloromethane (74-87-3)	5.60E-03	6.42E-03	3.67E-03	6.44E-03	4.97E-03
Cyclohexane (110-82-7)	2.57E-04	2.11E-05	1.82E-04	2.57E-04	3.05E-04
Ethylbenzene (100-41-4)	3.93E-04	8.78E-04	4.99E-04	3.00E-04	4.00E-04
Formaldehyde (50-00-0)	<i>3.13E-01</i>	<i>3.84E-01</i>	<i>3.59E-01</i>	<i>3.47E-01</i>	<i>2.60E-01</i>
Hexane (110-54-3)	5.49E-02	2.79E-02	1.95E-02	3.95E-02	8.17E-02
m,p-Xylene (1330-20-7)	4.00E-03	9.45E-03	4.74E-03	2.60E-03	4.54E-03
Methylene Chloride (75-09-2)	1.15E-03	2.06E-03	1.27E-03	1.77E-03	3.42E-04
Naphthalene (91-20-3)	8.70E-03	2.95E-03	7.29E-03	1.58E-02	2.30E-03
o-Xylene (1330-20-7)	1.16E-03	3.25E-03	1.50E-03	7.08E-04	1.26E-03
Propionaldehyde (123-38-6)	1.39E-02	2.54E-02	2.19E-02	1.82E-02	6.34E-03
Styrene (100-42-5)	5.94E-06	-	-	1.35E-05	-
Tetrachloroethene (127-18-4)	1.12E-02	<i>1.24E-01</i>	5.56E-03	7.17E-03	1.70E-04
Toluene (108-88-3)	3.50E-03	3.20E-03	2.46E-03	3.69E-03	3.53E-03
Trichloroethene (79-01-6)	8.95E-02	4.42E-04	1.71E-03	<i>1.81E-01</i>	2.29E-02

¹ Chronic HQ calculated using chronic health guidance values and mean (8-hr TWA) concentration measured across all sites and by activity type presented in Table 10.

² '-' = Compound not detected.

Table 12. Chronic HI presented by target organ system across all sites and by activity type. HI >1 shown in *bold italics*. Calculations presented include non-detections as zero values (i.e., 0.0 µg/m³).

		Hematologic system ¹	Cardiovascular system ²	Nervous system ³	Eyes ⁴	Alimentary tract ⁵	Immune system ⁶	Reproductive ⁷	Development ⁸	Respiratory system ⁹	Skin ¹⁰	Physiological response to odors ¹¹	Endocrine system ¹²	General Toxicity ¹³
Mean	All Sites ¹	3.29E-01	1.15E-03	2.99E-01	-	1.34E-02	8.95E-02	2.71E-03	9.57E-02	5.40E-01	-	-	3.93E-04	0.00E+00
	Ambient ²	3.94E+00	1.15E-03	3.70E-01	-	1.27E-01	4.42E-04	9.78E-03	6.75E-03	6.81E-01	-	-	8.78E-04	0.00E+00
	Background ³	1.31E-01	1.15E-03	2.99E-01	-	7.95E-03	1.71E-03	1.86E-03	7.65E-03	6.22E-01	-	-	4.99E-04	0.00E+00
	HyF ⁴	9.31E-02	1.15E-03	3.10E-01	-	9.40E-03	1.81E-01	3.19E-03	1.87E-01	6.02E-01	-	-	3.00E-04	0.00E+00
	Cleanout ⁵	9.31E-02	1.15E-03	2.77E-01	-	2.28E-03	2.29E-02	1.35E-03	2.91E-02	4.40E-01	-	-	4.00E-04	0.00E+00
Median	All Sites	0.00E+00	0.00E+00	1.52E-01	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.27E-01	-	-	0.00E+00	0.00E+00
	Ambient	0.00E+00	0.00E+00	1.65E-01	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.99E-01	-	-	0.00E+00	0.00E+00
	Background	0.00E+00	0.00E+00	1.31E-01	-	0.00E+00	0.00E+00	0.00E+00	2.80E-04	4.49E-01	-	-	0.00E+00	0.00E+00
	HyF	0.00E+00	0.00E+00	1.79E-01	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.03E-01	-	-	0.00E+00	0.00E+00
	Cleanout	0.00E+00	0.00E+00	9.49E-02	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.09E-01	-	-	0.00E+00	0.00E+00
95th percentile	All Sites	5.77E-01	3.20E-03	1.33E+00	-	1.54E-02	9.30E-03	6.76E-03	3.70E-02	1.45E+00	-	-	1.15E-03	0.00E+00
	Ambient	2.89E+01	9.27E-03	1.18E+00	-	2.83E-01	0.00E+00	1.06E-02	2.55E-02	1.44E+00	-	-	5.25E-04	0.00E+00
	Background	6.30E-01	2.58E-03	9.64E-01	-	2.03E-02	1.30E-02	1.16E-02	4.19E-02	1.47E+00	-	-	3.67E-03	0.00E+00
	HyF	5.43E-01	6.63E-03	1.11E+00	-	1.48E-02	1.25E-02	7.56E-03	4.15E-02	1.44E+00	-	-	9.42E-04	0.00E+00
	Cleanout	5.24E-01	1.38E-03	1.53E+00	-	1.34E-02	0.00E+00	0.00E+00	2.64E-02	1.38E+00	-	-	1.18E-03	0.00E+00

¹ HQ for benzene (71-43-2).

² HQ for methylene chloride (75-09-2).

³ Sum of HQs for 1,1,1-trichloroethane (71-55-6); 1,2,4-trimethylbenzene (95-63-6); 1,3,5-trimethylbenzene (108-67-8); 1,4-dichlorobenzene (106-46-7); 2-hexanone (591-78-6); acetaldehyde (75-07-0); acetone (67-64-1); carbon disulfide (75-15-0); carbon tetrachloride (56-23-5); chloromethane (74-87-3); hexane

(110-54-3); m,p-xylene (1330-20-7); methylene chloride (75-09-2); naphthalene (91-20-3); o-xylene (1330-20-7); propionaldehyde (123-38-6); styrene (100-42-5); and toluene (108-88-3).

⁴ Eyes: no relevant chronic exposures for this target organ system.

⁵ Sum of HQs for 1,1-dichloroethene (75-35-4); 1,2-dichloroethane (107-06-2); 1,4-dichlorobenzene (106-46-7); carbon tetrachloride (56-23-5); chloroform (67-66-3); ethylbenzene (100-41-4); and tetrachloroethene (127-18-4).

⁶ HQ for trichloroethene (79-01-6).

⁷ Sum of HQs for 1,3-butadiene (106-99-0); carbon disulfide (75-15-0); and chloroethane (75-00-3).

⁸ Sum of HQs for 2-butanone (78-93-3); 4-methyl-2-pentanone (108-10-1); carbon tetrachloride (56-23-5); chloroform (67-66-3); cyclohexane (110-82-7); ethylbenzene (100-41-4); toluene (108-88-3); and trichloroethene (79-01-6).

⁹ Sum of HQs for 1,1-dichloroethene (75-35-4); 1,4-dichlorobenzene (106-46-7); acetaldehyde (75-07-0); formaldehyde (50-00-0); naphthalene (91-20-3); propionaldehyde (123-38-6); and toluene (108-88-3).

¹⁰ Skin: no relevant chronic exposures for this target organ system.

¹¹ Physiological response to odors: no relevant chronic exposures for this target organ system.

¹² HQ for ethylbenzene (100-41-4).

¹³ General Toxicity: no relevant chronic exposures for this target organ system

Comparison of air quality measurements to occupational health guidance values

The 8-hour sampling is most relevant for assessing occupational exposures among workers during a typical work day. While general population exposures were the primary consideration in this public health assessment it is worth putting these air pollution data into an occupational health context as well. To do this, mean, median, 95th percentile, and maximum (8-hr TWA) concentrations of the air pollutants observed in this dataset were compared to the California Division of Occupational Safety and Health (Cal/OSHA) permissible exposure limits (PELs) (see Appendix B, Table B-8). PELs reflect the maximum permitted 8-hr TWA concentration of an airborne contaminant (8 CCR §5155, n.d.; OSHA, 2019) and are nearly always higher than health guidance values for community exposure (e.g., OEHHA RELs). Additionally, it is important to note that occupational health guidance values, such as PELs, are not based on protecting sensitive populations, and also include additional considerations such as technical and economic feasibility. Thirty-eight compounds had available Cal/OSHA PELs. Chemical-specific mean, median, 95th percentile and maximum (8-hr TWA) concentrations across all sites did not exceed Cal/OSHA PELs (Appendix B, Table B-8).

Chemical additives used during well stimulation treatments

Chemical additives with available CASRN and used in stimulation fluid formulations at wells during air monitoring activities are shown in Table 13. Overall, seventy-seven chemical additives with available CASRN were used during well stimulation events where air monitoring was conducted. Of these chemicals reported during well stimulation, five chemical additives were monitored in this study: benzoic acid (65-85-0); ethanol (64-17-5); ethylene glycol (107-21-1); methanol (67-56-1); and propylene glycol (57-55-6). Only one chemical additive, ethanol, was detected during air quality monitoring. Notably, ethanol was detected at each event type (ambient, background, well stimulation, and cleanout), with the highest mean and median concentrations reported at ambient site locations. Well stimulation yielded the highest ethanol concentration observed (170 µg/m³) (Table 14). While ethanol is noted as a carcinogen via oral exposure (i.e. alcohol), inhalation of ethanol can result in respiratory irritation, headache, fatigue, and drowsiness (IARC, 2018; PubChem, 2020). Ethanol is emitted from multiple sources, and not only well stimulation fluids; therefore, source attribution is uncertain. Ethanol and the other four nondetected chemical additives lacked acute and chronic noncancer health guidance values and cancer slope factors for the inhalation pathway. Silica, while not a volatile compound monitored during this study, is chemical additive reported as used at these well pads during the sampling period and is a known respiratory irritant and carcinogen.

Table 13. Chemical constituents, with Chemical Abstracts Service Registry Number (CASRN), used in stimulation fluid formulations for the following wells where air sampling was completed: 029-27186, 030-53804, 030-54057, 030-55084, 030-55090, 030-55091, 030-55914, 030-60081, 030-60471, 030-60841, 030-60844, 030-62169, 030-62399, 030-62704, 030-63043, 030-63120, 030-63550. Fluid formulation records were located for 17 of the wells using data obtained from the California Geologic Energy Management Division (CalGEM) on June 14, 2019. Sorted by number of stimulations. Adapted from Stringfellow and Camarillo (2020).

Chemical constituents	CASRN	Number of stimulations
Sodium chloride	7647-14-5	25
Water	7732-18-5	25
2,2 Dibromo-3-nitrilopropionamide	10222-01-2	24
2-Monobromo-3-nitrilopropionamide	1113-55-9	24
Crystalline silica, quartz	14808-60-7	24
Guar gum	9000-30-0	24
Sodium hydroxide	1310-73-2	24
Hemicellulase enzyme	9012-54-8	21
Lactose	63-42-3	21
Monoethanolamine borate	26038-87-9	21
Sodium persulfate	7775-27-1	21
Sodium sulfate	7757-82-6	21
Ammonium chloride	12125-02-9	19
Polydimethyl diallyl ammonium chloride	26062-79-3	18
Sodium bisulfite	7631-90-5	12
Laryl dimethyl hydroxysulfobetaine	13197-76-7	10
Sodium polyacrylate	9003-04-7	9
Methanol ¹	67-56-1	7
Ethanol ^{1,2}	64-17-5	6
Glutaraldehyde	111-30-8	6
Hexamethylenetetramine	100-97-0	6
Phenol / formaldehyde resin	9003-35-4	6
Phosphoric acid	7664-38-2	6
Potassium chloride	7447-40-7	6
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl chlorides	68424-85-1	6
Castor oil, ethoxylated	61791-12-6	4
Isopropanol	67-63-0	4
Sorbitan, monohexadecanoate, poly(oxy-1,2-ethanediy) derivs.	9005-66-7	4
Terpenes and Terpenoids, sweet orange-oil	68647-72-3	4
4-Methyl-1,3-dioxolan-2-one	108-32-7	3
Acrylic acid, butyl ester, polymer with ethenylbenzene and 2-propenamide	25037-33-6	3
Alcohols, C10-16, ethoxylated propoxylated	69227-22-1	3

Chemical constituents	CASRN	Number of stimulations
Alcohols, C6-12, ethoxylated propoxylated	68937-66-6	3
Aluminum oxide	1344-28-1	3
Aluminum silicate	1302-76-7	3
Ammonium acetate	631-61-8	3
Arsenic	7440-38-2	3
Chlorous acid, sodium salt	7758-19-2	3
Colbalt acetate	71-48-7	3
Hydrotreated light petroleum distillate	64742-47-8	3
Isotridecyl alcohol ethoxylates	9043-30-5	3
Potassium hydroxide	1310-58-3	3
Potassium metaborate	13709-94-9	3
Propylene glycol ¹	57-55-6	3
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl, salts with bentonite	68953-58-2	3
Sodium polyacrylate	9003-4-7	3
Sorbitan, monododecanoate, poly(oxy-1,2-ethanediyl) dervis	26266-58-0	3
Ulexite	1319-33-1	3
Poly lactide resin	9051-89-2	2
1-Eicosene	567040	1
1-Hexadecene	629-73-2	1
1-Octadecene	112-88-9	1
1-Tetradecene	1120-36-1	1
2-Ethyl hexanol	104-76-7	1
Acetic acid	64-19-7	1
Alcohols, C14-C15, ethoxylated	68951-67-7	1
Alkenes, C >10 alpha-	64743-02-8	1
Amines, hydrogenated tallow alkyl, acetates	61790-59-8	1
Ammonium fluoride	12125-01-8	1
Benzoic acid ¹	65-85-0	1
Citric acid	77-92-9	1
Copper dichloride	7447-39-4	1
Dodecylbenzene sulfonic acid	27176-87-0	1
Ethoxylated hexanol	68439-45-2	1
Ethylene glycol ¹	107-21-1	1
Ethylene glycol monobutyl ether	111-76-2	1
Ethylene oxide	75-21-8	1
Hydrochloric acid	7647-01-0	1
Hydroxylamine hydrochloride	1304222	1
Mixture of dimer and trimer fatty acids of indefinite composition derived from tall oil	61790-12-3	1

Chemical constituents	CASRN	Number of stimulations
Poly(oxy-1,2-ethandiyl), a-(nonylphenyl)-w-hydroxy-	9016-45-9	1
Poly(oxy-1,2-ethanediyl), alpha-hexyl-omega-hydroxy	31726-34-8	1
Propargyl alcohol	107-19-7	1
Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	68527-49-1	1
Silica, amorphous - fumed	7631-86-9	1
Sodium carbonate	497-19-8	1
Tricalcium phosphate	7758-87-4	1

¹ Compound monitored for during air sampling.

² Compound detected during air sampling.

Table 14. Summary of results for ethanol across all sites and by site type, showing percent detected when analyzed (% Det.); mean, median and maximum concentration (conc., $\mu\text{g}/\text{m}^3$; 8-hr time-weighted average)¹; the 95th percentile, indicating that 95% of the measurements were at or below this value. Calculations presented include non-detections as zero values (i.e., $0.0 \mu\text{g}/\text{m}^3$).

	% Det.	Mean Conc.	Median Conc.	95% Value	Max Conc.
All Sites	82.1	6.141	5.464	13.604	170.000
Ambient	73.1	7.862	7.469	22.140	22.611
Background	88.2	6.280	6.406	10.135	22.611
HyF	87.3	6.958	5.841	12.511	170.000
Cleanout	76.7	5.008	4.145	13.218	22.611

Discussion

The following section includes discussion of the general approaches to field sampling that produced the underlying air quality data used in this report, as well as additional commentary on the evaluation of air pollutant concentrations associated with upstream oil and gas systems to determine potential public health risks.

Reference sites that represent ambient “off-field” air quality

As noted in the companion study Stringfellow and Camarillo (2020), sites chosen to represent ambient (“off-field”) air quality likely are not representative of air quality that is independent of influence from oil and gas development operations, including but not limited to WST, given their proximity to oil field activities. This fundamentally limits the ability to reliably determine differences between measured air quality concentrations and associated potential health risks both between ambient (“off-field”) and background (“on-field”) sites and between ambient sites and HyF and cleanout sites.

Limitations of constraining air quality assessment to hydraulic fracturing and well stimulation

The fundamental question put forth by this data collection program was, *are hydraulic fracturing, well stimulation and wellbore cleanout activities associated with impaired air quality?* While this is a reasonable question, it is worth stating that well stimulation – which in California is predominantly composed of hydraulic fracturing – is only a small part of the O&G development process. Hydraulic fracturing only lasts on the order of hours to days compared with other oil and gas development activities that can last on the order of years to decades (e.g., hydrocarbon production, oil-water separation, oil flashing, condensate collection and storage, hydrocarbon processing, etc.) and there are questions as to whether hydraulic fracturing is a high-emitting activity relative to these other activities (Long et al., 2015c). Notably, the most in-depth independent scientific study of well stimulation in the State of California undertaken by the California Council on Science and Technology (CCST) pursuant to SB 4 arrived at the following overarching conclusion:

“Conclusion 3.3. The majority of impacts associated with hydraulic fracturing are caused by the indirect impacts of oil and gas production enabled by the hydraulic fracturing. Impacts caused by additional oil and gas development enabled by well stimulation (i.e. indirect impacts) account for the majority of environmental impacts associated with hydraulic fracturing. A corollary of this conclusion is that all oil and gas development causes similar impacts whether the oil is produced with well stimulation or not. As hydraulic fracturing enables only 20-25% of production in California, only about 20-25% of any given indirect impact is likely attributable to hydraulically fractured reservoirs” (Long et al., 2015c).

Study designs that appropriately assess air quality implications of oil and gas development – and subsets of activities associated with it such as hydraulic fracturing and wellbore cleanouts – benefit greatly from access to wellpad-level oil and gas development activity information. This is due to the fact that there is reasonable scientific certainty that emissions of air pollutants from upstream O&G development are episodic and are not always associated with the same type of infrastructure or process (Allen et al. 2014; Brown et al. 2015; Colborn et al., 2014). As such, without this pad-level activity information, researchers are more likely to miss these episodic emission events due to both timing and geographic dimensions of air quality monitoring (Garcia-Gonzales et al., 2019).

Chemical additive use in oil and gas development and air quality monitoring

A proportion of chemicals reported as used during hydraulic fracturing and other processes in California and nationally are well known to be air pollutants due to their volatility or other attributes (Shonkoff et al., 2019). Hydraulic fracturing fluids have received the majority of public attention for the use of chemicals and resulted in significant statewide scrutiny and associated regulatory reform in chemical disclosure in the State of California (e.g., SB 4). However, multiple studies (Danforth et al., 2019; GWPC, 2019; Stringfellow et al., 2017; Shonkoff et al., 2016; Shonkoff et al., *In Press*) and chemical disclosures databases (SCAQMD, 2020; CVRWQCB, 2018) have concluded that chemical use in oil and gas development is widespread and not restricted to well stimulation. To inform air quality monitoring plans, it is important to incorporate information as to which chemical additives are also air pollutants.

Additionally, the deployment of matrix acidizing and associated chemical use under SB 4 requires that the oil and gas operator report information on these activities (Pavley, 2013). If the intent to

increase the permeability of the geological formation is stated, the use of hydrochloric and hydrofluoric acid along with other chemical use is required to be publicly disclosed. However, there is currently no statewide chemical disclosure mechanism for acidizing a well if the intent is routine maintenance and wellbore cleanouts (Stringfellow et al., 2017). Virtually all wells, surface and subsurface infrastructure are acidized and treated with other chemicals for routine maintenance (Long et al., 2015a; Stringfellow et al., 2017). It is prudent to gain access to this type of chemical use information to facilitate a fundamental understanding of the chemicals of interest when developing an air quality monitoring program that is appropriately calibrated to the oil field operations in question.

Consideration of criteria air pollutants associated with oil and gas development

The air quality monitoring activities discussed in this report collected data on many chemical constituents, however they did not collect data on particulate matter and – with the exception of carbon monoxide – other criteria air pollutants. While this study never intended to collect data on these air pollutants, future air quality monitoring at oil fields should consider including them. Some studies in California have found that emissions of PM_{2.5} may constitute higher portions of the health risk burden from the inhalation exposure pathway than a number of the air toxics (STI, 2015). The integration of black carbon (BC) monitoring may also be helpful for understanding the contribution of the oil field to particulate matter pollution compared to other offsite sources; the short atmospheric lifetime and primary emission nature of BC offers opportunities to assess the spatial distribution of primary PM emitted from nearby oil field sources compared to secondary sources of PM that form in the atmosphere from more geographically distal sources (Caubel et al., 2019).

Sampling durations relevant to assessing acute and chronic health risks

Requirements and recommendations for air sampling for this monitoring effort led to 8-hour continuous sampling, resulting in measurements that reflect the average air concentration of a given compound over an 8-hour period. As noted above, emissions of health-damaging air pollutants can be episodically elevated, resulting in degraded air quality in proximity to and downwind from oil and gas development (Allen et al. 2014; Brown et al. 2015; Colborn et al., 2014). Acute (e.g., one hour) exposures and associated health risks are more likely to be influenced by short-term and intermittent spikes in emissions. Given that air sampling in this program evaluated average concentrations measured continuously over an 8-hour timeframe, acute exposures and related acute health risks are difficult to assess.

Additionally, WST and cleanout operations occur intermittently. Evaluations of chronic (e.g., one year or multi-year) exposure would likely consider durations when WST activities occur and when WST activities do not occur. The 8-hr TWA air samples do not allow for appropriate assessment of chronic exposures from WST activities.

An array of sampling durations, including shorter term (i.e., 1 hour), 8-hour, and longer-term (i.e., >24 hour) continuous air sampling at each site would provide more appropriate air concentrations to compare to respective acute, 8-hr, and chronic health guidance values to assess potential air quality impacts associated with WST and cleanout activities and inform health risk assessments.

Non-detections treated as air concentrations of 0.0 µg/m³

Data sets that include large numbers of “less than detection limit” values are sometimes referred to as left-censored data. In other words, measurements in samples that are above the level of detection have a known distribution of concentration values, but the distribution of concentration values below the level of detection is unknown. There are a number of possible approaches to analyzing censored data, including substituting non-detect data with a value of zero (0) or a concentration equal to the detection limit, or some fraction of the detection limit (Helsel and Gilliom, 1986; Kayhanian et al., 2002).

While some air quality assessments have used zeros to stand in for non-detects (Sokal and Rohlf, 1995; Hollander and Wolfe, 1999; Kayhanian et al., 2002; Zar, 2010), this may bias estimates of health risks towards the null by making the a priori assumption that if a chemical is found to be below the detection limit, it is not present in the air. While analytical detection limits used in this project were required to be at or below conservative health guidance values (<1 µg/m³) (CARB, 2018; Appendix A), multiple air pollutants in an air mixture below health guidance values can, collectively, exceed a hazard quotient (HQ) of 1 and pose a human health risk.

Detection limit information was not extracted from the individual Monitoring Reports, and therefore chemical- and method-specific detection limits were not readily available to support additional sensitivity analyses (e.g., supplementing non-detections with the detection limit or half of the detection limit; U.S. EPA, 2017). As such, all calculations performed in this analysis considered non-detections to represent 0.0 µg/m³, potentially underestimating the true health risks associated with these observed pollutant concentrations.

Conclusions

The objective of this report is to evaluate air pollutant concentration measurements collected during well stimulation treatments (WST), well cleanout operations and reference sites within oil fields (background) and outside of oil fields (ambient) in California from a public health perspective. Detected compounds were screened for public health relevance using authoritative lists for state, federal, and international health agencies. State and federal noncancer health guidance values for acute and chronic exposures were used to evaluate the potential for adverse noncancer health effects during individual and multi-pollutant exposures. Cancer risk was also assessed considering individual and multi-pollutant continuous exposures over a lifetime. Both cancer risks and noncancer health risks were evaluated across all sites and by site type (i.e., ambient, background, hydraulic fracturing, and cleanout).

Of the 64 detected compounds, 38 (59%) are health-relevant state- or federally-designated air pollutants and 22 (34%) are known or suspected human carcinogens. Given the observed mean (8-hr TWA) concentrations of these detected compounds, cumulative lifetime excess cancer risks exceeded the U.S. EPA de minimis benchmark of 1 in a million at each site type (i.e., ambient, background, hydraulic fracturing, and cleanout), with the highest cumulative lifetime excess cancer risk observed at ambient (off-field) locations. Benzene – a naturally occurring constituent in petroleum that is co-emitted during oil and gas development and also associated with combustion and use of fossil fuels – accounted for 85% of the total cancer risk observed at ambient sites. Benzene also accounted for elevated acute and chronic hazard quotients (HQ>1) and elevated acute and chronic hazard indices (HI>1) at ambient sites, indicating potential for noncancer adverse health effects associated with exposures to benzene. As noted in the companion study to

this report (Appendix E in Stringfellow and Camarillo, 2020), benzene concentrations observed at ambient sites were statistically significantly different from background, HyF, and cleanout sites and no statistically significant differences in benzene concentrations were observed between background, HyF and cleanout sites. Also noted in Stringfellow and Camarillo (2020), sampling at sites that were selected for ambient monitoring may not be representative of air quality that is independent of oil and gas development operations given their proximity to oil field activities.

All chemical-specific acute HQs and target organ system-specific acute HIs for background, HyF, and cleanout site types were less than 1, suggesting that acute exposures associated with the detected air pollutants may not be associated with adverse health effects. Furthermore, all chemical-specific chronic HQs and target organ system-specific chronic HIs (calculated using mean 8-hr TWA concentrations) for background, HyF, and cleanout site types were also less than 1, suggesting that the chronic exposures associated with detected air pollutants may not be associated with adverse health effects. However, given that simultaneous exposure to multiple chemicals or to multiple chemicals in close temporal succession may be additive, antagonistic (less than additive) or synergistic (greater than additive), HI less than 1 may not confirm the absence of risk for adverse health effects.

Based on the results of this study, cancer risks and noncancer health risks associated with acute and chronic exposures are largely driven by benzene concentrations observed at ambient (“off-field”) sites. However, as noted in the companion study to this report that further examines the underlying air quality data, ambient monitoring locations due to their proximity to oil field activities may be more reflective of oil field air quality than regional air quality (Stringfellow and Camarillo, 2020). Given that air sampling data were not collected over a shorter duration (e.g., 1 hour), maximum (8-hr TWA) concentrations were used to assess acute noncancer health risks, which may underestimate acute exposure. Given that air sampling data collected over a longer duration (i.e., more 8 hours) were not available, cancer and chronic noncancer risks were calculated using mean (8-hr TWA) concentrations, which may overestimate chronic exposure over the long-term.

Recommendations

The following recommendations for future air quality sampling in upstream oil and gas systems in the context of public health emerged from this assessment. Additional recommendations presented in Stringfellow and Camarillo (2020) and relevant to the underlying air monitoring data used in this report are also included below.

Expand focus of air quality monitoring beyond hydraulic fracturing and well stimulation.

Hydraulic fracturing and well stimulation are temporally short activities compared with other oil and gas development processes. Well stimulation is only one of many processes that enable oil and gas development and it is not clear whether hydraulic fracturing and well stimulation are more elevated emission events compared with other oil and gas development processes, such as well drilling, well cleanout, routine well maintenance, produced water handling and disposal, etc. As such, to assess the air quality and potential public health risks and impacts of oil and gas development that is enabled by hydraulic fracturing and well stimulation it would be better to monitor and collect data on the full suite of oil and gas development processes present on a well pad or in an oil field that is dependent on well stimulation to continue or expand production. Future

air pollution monitoring and analysis efforts focused on well stimulation-enabled oil and gas development should consider siting air pollution monitoring equipment in ways that can observe air pollution emissions and resultant atmospheric concentrations from the full suite of activities and equipment types deployed to support the collection, processing and transport of hydrocarbons.

Conduct QA/QC on limits of detection (LOD) and monitoring approaches used compared to lowest (most conservative) health guidance values. The Air Sampling Plan states: “Detection limits for laboratory analysis are required to be less than one microgram per cubic meter ($\mu\text{g}/\text{m}^3$) for most analyses to assess any potential health hazards” (CARB, 2018). While a thorough examination to verify that appropriate limits of detection (below health guidance values) were met by analytical laboratories would be ideal, an independent QA/QC verification was beyond the scope of this report due to resource and time constraints. Future research that relies on this current or expanded dataset and future sampling and reporting activities should ensure that LODs and Reporting Limits (RLs) are extracted from the datasets and reports and provided in electronic format. Additionally, future sampling and reporting activities should ensure that LODs are equal to or lower than the most conservative health guidance values.

Monitoring should be sensitive to and informed by oil field activities and timing of emissions. Air pollutant emissions from oil and gas development activities are often episodic and non-continuous. This air pollution emission variability complicates the task of collecting representative air quality measurements within and near oil field operations and short-term, grab sampling approaches often produce data that are difficult to interpret. To ensure adequate characterization of air pollution concentrations in these settings, air monitoring should ideally be continuous and informed by detailed oil field operation information. Time-integrated monitoring such as with sorbent tubes also may fail to capture episodic spikes in emissions. For certain sources of health-damaging air pollutants that are routinely co-emitted with methane (e.g., wellhead leaks, gas processing infrastructure, etc.) continuous methane monitoring paired with trigger samples should be considered for deployment. In this approach, when methane concentrations reach above the regional average, a grab sample is “triggered” which can then be speciated in a laboratory to identify the composition of pollutants in the air during those times. An array of sampling durations, including shorter term (i.e., 1 hour), 8-hour, and longer-term (i.e., >24 hour) continuous air sampling at each site would provide more appropriate air pollution measurements to compare to respective acute, 8-hr, and chronic health guidance values to assess potential air quality impacts associated with WST and cleanout activities and inform health risk assessments.

Integrate chemicals used in well stimulation and other oil field activities that are air pollutants into the list of air pollutants to be monitored. Oil and gas operators use chemicals during well stimulation and routine activities such as drilling, maintenance, well cleanouts and other oil and gas development activities. As noted in this report, a proportion of these chemicals are known air pollutants and could, without proper containment, be emitted to the atmosphere. In order to ensure that relevant sources of air pollutants are included, chemical use reporting pursuant to SB 4 and other relevant datasets should be reviewed and volatile and semi-volatile compounds should be included in monitoring efforts.

Integrate source testing of circulation tanks during cleanouts

While ambient monitoring is important to inform health management efforts and regulatory decisionmaking, health risk assessment would be greatly informed by the more direct testing of circulation tanks during cleanout operations. This source testing may be important given that circulation tanks are often at least partially open during this process, providing opportunities for health damaging air pollutants to be emitted to the atmosphere. Data collected from such efforts would enable more informed risk assessments of the cleanout process.

Additional recommendations also presented in Stringfellow and Camarillo (2020)

As noted above, the following recommendations – while not specifically addressed with data analysis in this report – also appear in the companion report (Stringfellow and Camarillo, 2020) that focused on statistical analysis of the air pollution samples evaluated. The following recommendations are relevant to robust data collection efforts that could help to facilitate strong environmental public health analysis.

Ambient reference monitoring sites should be specified. CARB has established criteria for selection of locations for ambient monitoring. However, each operator selected their final ambient monitoring locations independently and in some cases ambient sites in proximity to oil field or oil field associated activities. CARB should consider identifying one or more specific locations where operators should collect ambient samples. This location should be an area with public access or with arranged access for consultants to conduct sampling. Locations such as parks, state owned property, or a specific public access area away from major traffic (i.e. open field or lot, remote intersection in farming area) should be considered for ambient sampling locations. Having more samples collected from a single site chosen to represent ambient conditions would increase the value of the reference data by ensuring the data truly represent ambient conditions.

More data should be collected at ambient and background reference monitoring sites. More data should be collected at reference sites with the objective of achieving more equal sample population size (N) as measurements made during WST activities. Equal sample sizes will enhance the certainty of statistical comparisons. For on-field (background) samples, information on proximity to on-field activities other than WST, such as drilling and oil-water separation facilities, should be noted. For both ambient and background monitoring, a specific effort should be made to collect more reference data for comparison with WST activities. Other sources of ambient air quality information, such as data collected by local air districts, could also be useful for increasing the sample size for reference data.

Reporting of monitoring analytical data should be standardized. Standardization should include requirements for electronic reporting of analytical data. Extraction of data from PDF files is both time consuming and inherently prone to error. Electronic data will reduce error and streamline oversight. Monitoring reports should include appendix of the laboratory reports containing the analytical data.

Reporting of wind and other weather data should be standardized. Standardization should include requirements for electronic reporting of weather station data. Direct comparison among different companies was particularly challenging when they used different formats for wind rose,

different units, different data collection time range and frequencies. As possible, the contractor should clearly designate the predominant wind direction and assign upwind and downwind designations to monitoring samples.

Report formats and section headers should be standardized. Different consultants used different reporting formats and report sections, so there was little consistence between consultants concerning what information was reported and where in the report specific information (e.g. weather data, geographic information) could be found. Standardization of report section headers, having requirements for types of data to be included, and specifying the reporting units would assist CARB and CalGEM staff in determining if appropriate monitoring was conducted and if all reporting of primary and ancillary information was complete.

Reports should use API number and limit the number of wells included in one report. In many cases, the on-field well name was used on the report cover and in tables and figures, but the API number of the well was not and it was difficult to establish which wells were included in which reports. The number of WST included per report varied and in some cases it was difficult to relate information in the reports to the data (which was reported by API number). Requiring the use of API numbers in the report and limiting the maximum number of WST in one report should be considered. Having only one well or one WST per report is recommended.

References

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Glossary of Terms, Abbreviations, and Symbols

API	American Petroleum Institute
ATSDR	Agency for Toxic Substances and Disease Registry
CalEPA	California Environmental Protection Agency
CalGEM	California Geologic Energy Management Division
CARB	California Air Resources Board
CASRN	Chemical Abstract Service Registry Number
CCST	California Council on Science and Technology
DOGGR	Division of Oil, Gas and Geothermal Resources
HAP	Hazardous air pollutant
HQ	Hazard quotient
HI	Hazard index or indices
HyF	Hydraulic fracturing
IARC	International Agency for Research on Cancer
IRIS	Integrated Risk Information System
JMP	Statistical software from SAS Institute Inc. (Cary, NC)
LOD	Limit of detection
m ³	cubic meter
MRL	Minimum risk level
mg	milligram
N	Sample size
NTP	National Toxicology Program
OEHHA	Office of Environmental Health Hazard Assessment
ppb	part per billion
ppm	part per million
PPRTV	Provisional Peer-Reviewed Toxicity Value
PSE	Physicians, Scientists, and Engineers for Healthy Energy
REL	Reference Exposure Level
RfC	Reference concentration
RL	Reporting limit
S&A	Stringfellow & Associates
SB 4	Senate Bill 4
TAC	Toxic air contaminant
TWA	Time-weighted average
US EPA	United States Environmental Protection Agency
WST	Well stimulation treatment
µg	microgram

Appendix A - B