Human health and oil and gas development: An assessment of chemical usage in oil and gas activities in the Los Angeles Basin and the City of Los Angeles

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List of Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
ACToR	U.S. EPA, Aggregated Computational Toxicology Resource Database
ATSDR	U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry
BOD	Biological oxygen demand
CASRN	Chemical Abstracts Service registry numbers
CCST	California Council on Science and Technology
City of LA	City of Los Angeles
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
DOGGR	California Division of Oil, Gas, and Geothermal Resources
ECHA	European Chemicals Agency
EPISuite™	U.S. EPA Estimation Programs Interface Suite
EU	European Union
FCR	finding, conclusion, and recommendation
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
HEAST	U.S. EPA, Health Effects Assessment Summary Tables
HHBP	U.S. EPA, Human Health Benchmarks for Pesticides
HSDB	Hazardous Substance Data Bank
IARC	International Agency for Research on Cancer
IPCS	World Health Organization, International Programme on Chemical Safety
IRIS	U.S. EPA Integrated Risk Information System
IUCLID	European Chemicals Agency, International Uniform Chemical Information Database
K_H	Henry's constant
K_{oc}	Organic carbon-water partition coefficients
K_{ow}	Octanol-water partition coefficients
LC_{50}	Lethal concentration to 50% of a study population
MRL	Minimal risk level
NIOSH	National Institute for Occupational Safety and Health
OECD	United Nations Organisation for Economic Co-operation and Development
OEHHA	California Office of Environmental Health and Hazard Assessment
OSHA	Occupational Safety and Health Administration
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PAH	Polycyclic aromatic hydrocarbons
PBT/vPvB	Persistent, bioaccumulative, and toxic/very persistent and very bioaccumulative
PEL	Permissible exposure limits
pK_a	Acid dissociation constant
POM	Polycyclic organic matter
PPRTV	U.S. EPA, Provisional Peer-Reviewed Toxicity Values
RAHC	Reasonably anticipated to be a human carcinogen
REACH	Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals
NIOSH REL	Recommended exposure limit set by NIOSH

REL	Reference exposure level
RfC	Reference concentration
RfD	Reference dose
RfV	Reference value
SB 4	Senate Bill 4
SCAQMD	South Coast Air Quality Management District
SVHC	Substances of Very High Concern
TAC	Toxic Air Contaminants
$ThCO_2$	Theoretical carbon dioxide
ThOD	Theoretical oxygen demand
TLV	Threshold limit values
TOXNET	National Library of Medicine, Toxicology Data Network
UR	Unit risk
URE	Unit risk estimates
VOC	Volatile organic compound

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About PSE Healthy Energy

Physicians, Scientists, and Engineers for Healthy Energy (PSE) is a multidisciplinary, non-profit research institute that studies the way energy production and use impact public health and the environment. We share our work and translate complex science for all audiences. Our headquarters is located in Oakland, California.

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1.0. Executive Summary

An April 2017 motion from City of Los Angeles council member Wesson directed the Petroleum Administrator to work with the Los Angeles County Department of Public Health and other agencies to assess the health effects of oil and gas production in the City of Los Angeles. Physicians, Scientists and Engineers for Healthy Energy (PSE) was retained by the Office of Petroleum and Natural Gas Administration and Safety in the City of Los Angeles to conduct an assessment of chemical use in upstream oil and gas development in the Los Angeles Basin and the City of Los Angeles in particular.

The South Coast Air Quality Management District (SCAQMD) manages air quality for Los Angeles and Orange Counties, and parts of Riverside and San Bernardino Counties. The SCAQMD requires oil and gas operators within its jurisdiction to disclose chemical use during multiple types of oil and gas development events in their wells. In this study, we analyzed the chemical and event dataset maintained by the SCAQMD with respect to inhalation hazards. Event data was analyzed spatially and temporally. Individual chemicals were identified, characterized using public databases, and assessed for potential inhalation hazards.

Our analysis of chemical use in upstream oil and gas operations in the City of Los Angeles and the SCAQMD more generally resulted in six findings, conclusions and research and policy recommendations (FCR):

FCR 1: Chemicals of concern are used in upstream oil and gas operations in the City of Los Angeles and in the SCAQMD more generally.

Findings: The identity of 324 chemicals used in the SCAQMD were verified, of which 140 were used in events taking place in the City of Los Angeles. Biodegradability data was generally more available with 74% of relevant chemicals being classified according to OECD biodegradability standards. 40 chemicals were identified on air pollution screening lists and 23 chemicals were identified as known or possible carcinogens. When screened against lists of biodegradability, air pollutant and carcinogenic screening lists, a total of 56 chemicals of concern were identified as used in the SCAQMD, of which 36 were used in the City of Los Angeles.

Conclusion: Chemicals of concern pose a risk to nearby residents if environmental and exposure pathways are present (e.g. inhalation). Although some chemicals are clearly of greater concern than others (e.g. highly toxic chemicals used in large quantities that are also air pollutants), chemicals of concern are not explicitly ranked. Additional information regarding environmental profiles, acute and chronic toxicity is needed before a more thorough assessment of risk can be completed. There are no regulations in place to limit the use of chemicals of concern in upstream oil and gas development operations.

Recommendation: Given the findings of toxicological hazard, engineering controls, increased environmental monitoring, and increased minimum surface setbacks between these operations and sensitive receptors should be considered. Furthermore, agencies with jurisdiction may consider the implementation of green chemistry principals to all oil and gas operations to limit risk by reducing the use of hazardous and poorly understood chemicals and replacing hazardous chemicals with less hazardous chemicals.

FCR 2: Events taking place outside the City of Los Angeles may still negatively impact residents within the city.

Finding: A total of 1,688 oil and gas events were reported from the period of 2013-2018, with 131 events occurring within the City of LA. Although the majority of oil and gas events reported in the SCAQMD took place outside of the City of LA, specifically in the City of Long Beach, they are located relatively close to City of LA boundaries and there is nothing to prevent more events from occurring within the city. Chemicals used in oil and gas events within the City of LA did not significantly differ from chemicals used outside of the city in terms of type, frequency of use, and median masses used.

Conclusion: The close proximity of oil and gas events occurring outside the City of LA to communities that lie within the city suggest that negative impacts associated with emissions of TACs and other chemicals from events (particularly in Inglewood and Long Beach) could be transported via air pathways into the City of LA. Furthermore, our analysis of chemical usage across oil fields, event types, and city boundaries revealed significant overlap in chemicals used, regardless of location or oil field, suggesting potential air pollution and inhalation hazards from events outside the City of LA would be similar to those within the city.

Recommendation: Agencies with jurisdiction should consider implementing a uniform and effective plan to reduce exposure to potential inhalation hazards associated with chemical use in oil and gas operations. Operations outside the City of LA should be monitored and subjected to the same regulations as those within the City of LA to prevent negative impacts from airborne hazards migrating across city or jurisdictional boundaries.

FCR 3: Major data gaps regarding chemical identities, properties, and data reliability need to be addressed before a full chemical risk assessment can be completed.

Finding: Major data gaps exist regarding the identities of chemicals and associated environmental and toxicological profiles. A total of 327 chemicals reported in the SCAQMD dataset could not be definitively identified by CASRN and were labeled trade secret chemicals. 79% and 77% of chemicals identified by CASRN did not have available acute inhalation toxicity data or chronic inhalation toxicity data, respectively. Furthermore, chemical information that is submitted by operators includes errors, such as incorrect CASRNs, obvious misspellings, and inconsistent data entries. The SCAQMD dataset is maintained as separate event and chemical reporting datasets, which themselves are further divided into the periods before and after September 4th, 2015.

Conclusions: The lack of strict quality control over operator submitted data and the disjointed nature of the SCAQMD dataset hinders analysis of the dataset. Furthermore, major data gaps regarding chemical identities, physical and chemical properties, toxicity, and environmental fate and transport prevent further characterization of chemical hazards and risk. Assessing chemicals for toxicity, biodegradability, and hazard is a vital first step; however, more data is needed before a risk analysis can be completed.

Recommendations: SCAQMD should verify and validate all submitted chemical and mass usage information. Mass, density, concentration, and volume data should be required for all chemical disclosures, including trade secret chemicals, to ensure mass usage data is adequate and verifiable. Data reported to SCAQMD should be compared to and verified against other datasets, including those which are only reported to regulators and not publicly available. SCAQMD should maintain their data as one integrated dataset that combines both event and chemical reporting data from all time periods. SCAQMD should adopt approaches to chemical use reporting similar to SB 4 (Pavley, 2013) but also require operators to disclose all trade secret chemicals for all events associated with oil and gas operations in general and not only for hydraulic fracturing and well stimulation. SCAQMD should continue to work with chemical suppliers to come up with solutions to protecting trade secrets while at the same time encouraging disclosure, such as is exercised under AB 1328 (Limón, 2017). Comprehensive environmental and toxicological profiles should be developed for all oil and gas chemicals that are missing key data such as chronic and acute toxicity and biodegradability and ideally agencies with jurisdiction could consider phasing out the use of chemicals for which toxicological and environmental profiles have not been developed.

FCR 4: Setback distances and other controls may reduce health impacts of events taking place near sensitive receptors.

Finding: Of the 1,688 events where chemical use was reported in the SCAQMD, 597 events (106 in the City of LA) were located within 1,500 feet of sensitive receptors such as residences, preschools, K-12 schools, hospitals, and other health care facilities. Of all 131 events reported in the City of LA, 81 events (62%) were within 600 feet of the sensitive receptor.

Conclusion: These events have the potential to negatively impact surrounding populations and should be prioritized for engineering controls and monitoring. The City of Los Angeles currently only has a 200-foot setback requirement for upstream oil and gas development operations which has multiple conditions which can circumnavigate this requirement.

Recommendation: Agencies with jurisdiction should consider the implementation of a larger minimum surface setback between oil and gas development and sensitive receptors to reduce the risk of exposure to chemicals of concern. A minimum surface setback distance should also be accompanied by increased emission control and environmental monitoring appropriate to reported chemical use should be implemented, in particular at locations in close proximity to sensitive receptors.

FCR 5: SCAQMD reporting follows the overall statewide trend of declining well drilling and completion.

Finding: The number of events reported by the SCAQMD has significantly decreased since 2014. This trend is consistent with statewide oil and gas production and with the number of wells drilled and completed statewide over the same period (DOGGR, 2018a).

Conclusion: Overall, California has seen a steady decline in oil and gas production since the mid 1980's. It has been suggested anecdotally that SCAQMD Rule 1148.2 under-reports oil and gas events in its jurisdiction; however, this cannot be determined without a thorough comparison of SCAQMD event submissions and DOGGR records.

Recommendation: A detailed comparison of SCAQMD and DOGGR records is suggested to determine if oil and gas events are accurately reported in the 1148.2 database.

FCR 6: The majority of events reported by SCAQMD are conventional oil and gas operations and data suggests this trend will continue.

Finding: Maintenance acidizing, gravel packing, and well drilling account for approximately 83% of reported events that involve the use of chemicals in the SCAQMD. In contrast, well stimulation activities such as hydraulic fracturing, matrix acidizing, and acid fracturing play a minimal role in oil and gas development, accounting for approximately 1% of all events. The distribution of events by activity type has remained relatively consistent throughout the study period.

Conclusion: Despite the decrease in reported events since 2014, the distribution of events by activity type remained relatively consistent, suggesting that maintenance acidizing, gravel packing and well drilling will continue to be the dominant oil and gas activities in the SCAQMD and the City of Los Angeles. An examination of the underlying petroleum geology of the Los Angeles Basin revealed the similarity between the oil producing reservoirs in the region. If new oil fields are developed in the basin, development practices are not expected to significantly differ from past development (CCST et al., 2015b).

Recommendation: Future studies should focus on chemical hazards in routine and conventional oil and gas operations in the SCAQMD. Full disclosure of chemical identities in a manner similar to SB 4 is required for a more thorough understanding of chemical use in oil and gas operations in the City of LA and the Los Angeles Basin.

2.0. Introduction

2.1. Purpose of this Report

An April 2017 motion from Councilman Wesson directed the Petroleum Administrator to work with the Los Angeles County Department of Public Health and other agencies to assess the health effects of oil and gas production in the City of Los Angeles. As such, in this assessment we conduct a chemical hazard assessment on chemical use reported as used in oil and gas development operations within the City of Los Angeles and the South Coast Air Quality Management District in general.

2.2. Background

Los Angeles is a global megacity where intensive oil development occurs in close proximity to large urban populations. In 2017, 19.8 million barrels of oil and 9.6 billion cubic feet of gas were produced from 3,359 active wells in Los Angeles county, making it the second largest county in the state in terms of oil and gas production (DOGGR, 2018a, 2018b). Of the roughly 10 million people living in Los Angeles county, approximately 4 million live within the City of Los Angeles (City of LA), which has an estimated 850 active wells (Shamasunder et al., 2018; U.S. Census Bureau, 2017). This co-occurrence of dense oil and gas activities and human populations poses potential human health hazards that are less present in areas of lower population density.

This chemical assessment focuses on inhalation hazards associated with chemical use in *upstream* oil and gas development in the City of LA and surrounding areas. Upstream activities include the transport of equipment and materials to and from the well pad; well drilling, mixing, handling, and injection of oil and gas chemicals; and management of recovered fluids/produced water, drill cuttings, and other waste products (Adgate et al., 2014; Johnston et al., 2019; NRC, 2014; Shonkoff et al., 2014). Sources of air pollutants include products of incomplete combustion and chemicals emitted directly and indirectly from surface and subsurface equipment including, but not limited to, wells, pumps, generators, compressors, pneumatic devices, storage and separator tanks, surface impoundments, solid and liquid waste handling and from venting and flaring of gases. Air pollutant emissions from upstream oil and gas development can include toxic air contaminants (TACs), criteria pollutants, and reactive organic gases which are associated with the formation of tropospheric ozone (i.e., smog). Air pollutant emissions associated with oil and gas development are the primary focus of this assessment because of the current context of decision making in the City of LA. The Los Angeles City Council desires a synthesis of available information that is directly relevant to human health and oil and gas development in the City of LA. In particular, there is a need to understand the relationship between exposure to health damaging air pollutant constituents directly or indirectly emitted from upstream oil and gas development. Exposure to pollutants via inhalation is the most relevant environmental and exposure pathway in the Los Angeles Basin and as such we focused exclusively on inhalation hazards in this chemical assessment.

Statewide data concerning chemical usage in routine oil and gas operations in California is limited; the South Coast Air Quality Management District (SCAQMD) maintains the only known database which makes this information publicly available for the South Coast region, including the City of LA, and the greater Los Angeles county and Orange county. Although this study focuses on the City of LA, due to the nature of air emissions, oil and gas operations outside the City of LA can potentially pose a health hazard to residents living within the city.

In this report, we describe and analyze chemical usage for all oil and gas activities reported by the SCAQMD in order to address the following issues:

- What is the geographical and temporal distribution of oil and gas events reported by the SCAQMD?
- What chemicals are being used for oil and gas production in the SCAQMD?
- What are the chemical, physical, biological, and toxicological properties of these chemicals?
- What are potential chemicals of concern in terms of inhalation exposure?

The objective of this report is to provide an assessment and hazard ranking of chemicals used in oil and gas operations within the SCAQMD with respect to human health.

Within the context of this chemical assessment, event and chemical usage data was downloaded from the SCAQMD. The temporal and geographic distribution of oil and gas events within the SCAQMD was analyzed. Individual chemicals were identified and characterized for physical/chemical properties and for biological and toxicological properties including: acute inhalation mammalian toxicity, inhalation slope factors, inhalation reference doses and concentrations, and biodegradability. Frequency of chemical use and mass data were combined with chemical toxicity data to rank chemicals based on hazard. Hazard rankings, along with relevant data concerning carcinogenicity and air pollutants, were used to identify potential chemicals of concern.

Methods and analyses in this report build off the work of previous studies done on the SCAQMD dataset by Abdullah et al. (2017) and Stringfellow et al. (2017b), and broader studies of assessing chemical hazards in oil and gas activities in the entirety of California done by Stringfellow et al. (2017a, 2014) and the California Council on Science and Technology (CCST) (2015a, 2015b, 2014). An analysis of available literature relevant to human health and oil and gas development with respect to the Los Angeles Basin is provided in a separate report.

3.0. Methods

3.1. Data Sources

Chemical usage data for oil and gas operation in Southern California were obtained from the SCAQMD. SCAQMD is the air pollution control agency that covers Orange County and the urban portions of Los Angeles, San Bernardino, and Riverside counties (SCAQMD, 2018a). Pursuant to

Rule 1148.2, onshore oil and gas well operators and their chemical suppliers are required to submit data on chemical usage for events including well drilling, well completion, well rework, and well stimulation within the SCAQMD (SCAQMD, 2015). Operators must submit notification of well drilling, completion, or rework between 10 and 2 days prior to starting (SCAQMD, 2015). Rule 1148.2 went into effect on June 4, 2013 and was amended on September 4th, 2015 to require new, more detailed, oil and gas chemical reporting forms. These datasets are publicly available online on the SCAQMD oil and gas well electronic notification and reporting portal (SCAQMD, 2018b).

SCAQMD chemical and event data from June 4, 2013 to August 31, 2018 were downloaded on August 31, 2018. Chemical reporting data (e.g. chemical names, masses, etc.) and event notification data (e.g. event type, start date, latitude, longitude) were in separate datasets. Chemical reporting and event notification datasets were downloaded and merged together using event IDs, thus creating one dataset that combined operation start dates, well latitude and longitude, and chemical usage data. Data reported before and after September 4th, 2015 were in a slightly different format due to the change in reporting rules. Data from these two periods were initially managed separately and were later merged together into a single dataset for further analysis.

Other oil and gas chemical data, such as chemicals disclosed to the City of LA Fire Department via the California EPA and California Certified Unified Program Agencies are only available to regulators and are not publicly available. As a result, these datasets were not analyzed but are provided in an appendix.

3.2. Data Quality Assurance/Quality Control

This report follows data quality control and validation methods used in multiple studies of oil and gas chemical datasets by CCST (2015b, 2014), Stringfellow et al. (2017b, 2017a, 2015), Shonkoff et al. (2016) and Camarillo et al. (2016).

Well drilling, well completion, well rework activities were reported to SCAQMD using event IDs. In cases where a revision was made to a previously submitted event, the new event ID and associated data were included in the dataset; the old event ID and associated data were excluded. Cancelled events and notifications of event cancellations (which were assigned separate event IDs) were excluded from the dataset. Events were classified according to specific activity (e.g. maintenance acidizing, matrix acidizing, hydraulic fracturing, well drilling, etc.) using activity data from both the chemical reporting and event notification datasets. The SCAQMD notes that event notification submissions prior to April 2014 did not differentiate between maintenance acidizing and matrix acidizing, and were all reported as "acidizing" (SCAQMD, 2014). For submissions from this time period, data from the chemical reporting dataset that specified the type of acidizing event was prioritized when available.

Individual chemicals were identified using Chemical Abstracts Service Registration Number (CASRN). CASRN is a unique chemical identifier consisting of three groups of numbers, separated by two dashes (e.g. 7732-18-5), where the last digit is a verification digit used to determine if a CASRN is valid or not. CASRNs were formatted, validated, and chemical names were standardized.

Chemicals that were listed with invalid CASRNs were individually evaluated, and if possible, identified. If a CASRN was listed with leading zeros, missing or added digits, one or two wrong digits, or swapped digits AND if the provided chemical named matched another chemical with a similar (but correct) CASRN, the chemical could be identified with high certainty. Examples are provided in Table 1. In some cases, chemicals listed with a generic name and an invalid CASRN that were not similar to other existing chemicals in the database could not be identified and no further analysis was done on these chemicals. A complete list of chemicals reported with invalid CASRNs and their corrected CASRNs is available in Appendix A, Table A.1

Table 1. Examples of chemicals with invalid CASRNs that could be identified.

Standardized Name	Correct CASRN	Original Reported Name	Original Invalid CASRNs
Alcohols, C12-15 ethoxylated	68131-39-5	Ethoxylated alcohol C12-15	683131-39-5
Bentonite	1302-78-9	Bentonite	1305-78-9
Isotridecanol, ethoxylated	9043-30-5	Isotridecanol, ethoxylated	9403-30-5
Pine oil	8002-09-3	Terpene hydrocarbon	80020-90-3 8002-09-0

Chemicals that were listed without CASRN could not be definitively identified. Changes to the names of these chemicals were limited to fixing obvious spelling errors (e.g. aicd to acid), adding or removing dashes for consistency, and changing capitalization. Trade secret chemical names that suggested chemical mixtures (e.g. amine salts vs amine salt, fatty acids vs fatty acid) were maintained as separate entries. Without additional information, chemical usage patterns were evaluated (e.g., well drilling, well rework) but no further chemical characterization could be done on these chemicals.

Individual chemical masses (in lbs) were typically reported for each event. If chemical mass usage was not reported, mass was calculated using density (lbs/gal), volume (gal), and maximum concentration of the additive (%). For events where multiple instances of the same chemical were reported, the chemical masses were summed. For example, if water was reported as a base fluid, it might also be listed as an individual component in other chemical mixtures used in the event. This approach was used by Stringfellow et al. (2017b) in a previous study of chemical mass usage in the SCAQMD.

3.3. Mapping of Oil and Gas Events

Latitude and longitude data for individual events were mapped using ArcGIS and used to determine locations of events and corresponding chemical usage relative to city, county, and oil field boundaries, as well as temporally. City and county boundaries were obtained from the County of Los Angeles GIS Data Portal (Los Angeles County Enterprise GIS, 2017). Oil and gas field boundaries were obtained from the California Department of Conservation, Division of Oil, Gas, and Geothermal Resources GIS Mapping website (DOGGR, 2018c).

3.4. Characterization of Chemicals

Physical, chemical, biological, and toxicological data for all chemicals identified by CASRN were obtained from various national and international online databases. These databases are listed in Table **3** 3.

3.4.1. Characterization of Physical and Chemical Properties

Physical and chemical data can help further chemical understanding with respect to exposure pathways and potential hazards. Physical and chemical data gathered included: chemical formula, molecular weight, density, acid dissociation constants (pK_a), melting and boiling point, log octanol-water partition coefficients (log K_{ow}), log organic carbon-water partition coefficients (log K_{oc}), water solubility, vapor pressure, and Henry's constant (K_H). When experimental data could not be found, computational estimates from the U.S. EPA Estimation Programs Interface Suite (EPISuite™) KOWWIN™, MPBPWIN™, HENRYWIN™, and KOCWIN™ modules were used (U.S. EPA 2012). These modules are used to estimate log K_{ow}, melting/boiling points, Henry's constant, and log K_{oc}, respectively. EPISuite™ is a screening-level tool and should not be used if reliable experimental results are available (U.S. EPA, 2012).

3.4.2. Characterization of Acute Inhalation Toxicity

Acute inhalation toxicity data was collected for common mammalian test species, including *Rattus norvegicus* (rat) and *Mus musculus* (mice). Acute toxicity represents short-term effects of a single or continuous exposure over a short period (typically hours). Acute toxicity results were rated according to United Nations Globally Harmonized System (GHS) of Classification and Labelling of Chemicals (United Nations, 2017). GHS categories range from 1-4 for acute inhalation toxicity (Table 2). In GHS classifications, lower numbered categories indicate higher toxicity, with GHS 1 being the most toxic. GHS categorization utilizes 4-hour LC_{50} values (lethal concentration to 50% of a study population) for acute inhalation mammalian toxicity. When multiple values for acute toxicity were available, the most conservative (i.e. most toxic) value was used to determine GHS category. When acute toxicity values exceeded the maximum GHS category, the chemicals were labeled as ">GHS 4" for acute inhalation toxicity. Chemicals that exceeded the GHS scale were considered non-toxic for the purposes of hazard evaluation.

Table 2. GHS categories for acute inhalation toxicity.

GHS Category	Acute Inhalation Toxicity		
	LC_{50} Gases (ppm/4hr)	LC_{50} Vapors (mg/L/4hr)	LC_{50} Dusts and mists (mg/L/4hr)
1	≤ 100	≤ 0.5	≤ 0.05
2	$100<x\leq 500$	$0.5<x\leq 2$	$0.05<x\leq 0.5$
3	$500<x\leq 2500$	$2<x\leq 10$	$0.5<x\leq 1.0$
4	$2500<x\leq 20000$	$10<x\leq 20$	$1.0<x\leq 5$

Due to the general lack of acute inhalation data, and because this report focuses on air pollution and inhalation hazards, an attempt was made to categorize all available acute inhalation data that did not meet GHS 4-hour testing standards. In instances where acute inhalation LC_{50} values fell within the range for GHS category 1, but the time frame was shorter than 4 hours, it could be safely assumed to fall into GHS Category 1. For example, a reported LC_{50} value of 0.25 mg/L/30min for vapor does not meet the standard 4-hour test time frame, however, it is inherently more toxic than a GHS Category 1 LC_{50} value of 0.25 mg/L/4hr value due to its shorter time frame. In some instances, inhalation toxicity was listed as a range (e.g. >4 mg/L/4hr). These instances were categorized was based on the “floor level” value, therefore providing a very conservative estimate of inhalation toxicity. For example, an inhalation toxicity range of >4 mg/L/4hr for a vapor would be assigned a GHS value of 3 based on 4 mg/L/4hr. Floor level values should be interpreted with caution.

Chemicals with no chronic toxicity data, or with toxicity data that were not compatible with time-periods for GHS categorization standards or “floor level” estimates for acute inhalation toxicity were labeled as “inadequate data.”

3.4.3. Characterization of Chronic Inhalation Toxicity

Chronic toxicity values generally represent an upper limit of inhalation exposure over a lifetime period where there is unlikely to be appreciable risk of deleterious effects to a human population. Chronic toxicity studies span the course of years or a lifetime. Chronic chemical toxicity values were categorized from multiple databases including U.S. EPA Integrated Risk Information System (IRIS), U.S. EPA Provisional Peer-Reviewed Toxicity Values (PPRTV), U.S. Department of Health Agency for Toxic Substances and Disease Registry (ATSDR), California Office of Environmental Health Hazard Assessment (OEHHA), and U.S. EPA Health Effects Assessment Summary Tables (HEAST). Chronic toxicity sources were sorted into three tiers, where chronic toxicity values from higher tiered sources were given priority over values from lower tiers. If multiple toxicity values were available from sources within the same tier, the most conservative value was chosen.

- Tier 1: OEHHA
- Tier 2: IRIS, PPRTV, ATSDR, HEAST
- Tier 3: Occupational exposure limits

Noncancer chronic inhalation toxicity values were reported as chronic reference exposure levels (RELs), chronic reference concentrations (RfCs), and chronic minimal risk levels (MRLs) from various toxicity databases. For carcinogenic compounds, inhalation unit risk (UR) and unit risk estimate (URE) values were reported in databases. These toxicity values are defined as follows:

> Reference exposure level (REL): concentrations for which adverse non-cancer health effects are not anticipated over a specified exposure period (μg/m^3)
>
> Reference concentrations (RfC): estimate of continuous inhalation exposure of a substance in humans without significant risk of negative effects during a lifetime (mg/m^3)
>
> Minimal risk levels (MRL): estimate of daily exposure to a substance without appreciable risk of adverse non-cancer health effects over a specified exposure period (ppm)
>
> Unit risk (UR) factors: estimate of increased cancer risk from inhalation exposure over a lifetime (μg/m^3)$^{-1}$

In order to form a consistent scale for comparison of chemical toxicity values across multiple databases, RELs, RfCs, MRLs, and UR factors were converted to a standardized inhalation reference value (RfV) with units in mg/m^3. Conversion of chronic toxicity values followed the approach used by Shonkoff et al (2015). MRLs were converted from to mg/m^3 by multiplying ppm by the molecular weight of the chemical and dividing by 24.45 L air per mole at 25°C. Unit risk factors were converted to mg/m^3 using an acceptable cancer risk of 1 in 100,000 over an average human lifetime of 70 years.

If no chronic inhalation information was available from Tier 1 or Tier 2 databases, occupational exposure limits were used to compare chemicals. Sources for occupational exposure limits include the National Institute for Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA), and the American Conference of Governmental Industrial Hygienists (ACGIH). These occupational limits include permissible exposure limits (PEL), threshold limit values (TLV), and recommended exposure limits (NIOSH REL) (NIOSH, 2016, 2007). These limits are defined as:

> NIOSH Recommended exposure limits (NIOSH REL): recommended guideline for upper exposure limits to hazardous substances, set by NIOSH, that would be protective of employee health over a working lifetime (mg/m^3 or ppm, time weighted average)
>
> OSHA Permissible exposure limits (PEL): legal limit for worker exposure to a substance set by OSHA (mg/m^3 or ppm, time weighted average)

ACGIH Threshold limit values (TLV): limit to which a worker can be exposed to daily without adverse effects, or "workday concentration," set by ACGIH (mg/m^3 or ppm, time weighted average)

Occupational exposure limits are reported as time weighted averages for healthy adults for an 8-hour workday over the course of a working lifetime of 45 years, and as such, are not appropriate for direct comparison with chronic inhalation screening values. Occupational exposure limits were converted to a standardized occupational reference value (RfV) (mg/m^3) following the approach used by Shonkoff et al (2015). Occupational exposure values were converted to an equivalent 24-hour exposure level and then an uncertainty factor of 30 was applied to account for sensitive subpopulations, such as children. It must be noted that occupational exposure limits are not developed for protection of the general public and are inappropriate for community-based decision making.

3.4.4. Characterization of Biodegradability

Biodegradability data was categorized according to United Nations Organisation for Economic Co-operation and Development (OECD) criteria for biodegradability (OECD, 1981, 1992a, 1992b, 2009). The OECD specifies two major tests for biodegradability: Test No. 301: Ready Biodegradability and Test No. 302: Inherent Biodegradability. A chemical is classified as readily biodegradable if meets two requirements: (1) demonstrates a biodegradation greater than 60% theoretical oxygen demand (ThOD) removal, 60% theoretical carbon dioxide ($ThCO_2$) removal, or 70% dissolved organic carbon (DOC) removal, under aerobic conditions, in 28 days, and (2) the 60%/70% level is reached within 10 days of reaching the 10% mark ("10-day window" criterion) using unacclimated bacteria. For structurally similar compounds that are provided by chemical suppliers as mixtures and cannot be reasonably separated, such as hydrocarbons or surfactants, the 10-day window criterion is not applied to account for sequential biodegradation of individual compounds.

A chemical classified as inherently biodegradable had demonstrated biodegradation above 20% of theoretical as measured by biological oxygen demand (BOD), DOC removal, or chemical oxygen demand (COD). Inherent biodegradability is generally a separate test from ready biodegradability, however, when readily biodegradability tests are slightly below the 60%/70% mark, or when they fail the 10-day window criterion, they can be considered inherently biodegradable.

There is no OECD test for non-biodegradability, so chemicals that failed readily biodegradability tests were categorized as "not readily biodegradable." In the absence of experimental biodegradability data, computational estimates from the U.S. EPA EPISuite™ BIOWINN™ module were used (U.S. EPA, 2012).

Table 3. Databases and other sources used to characterize physical, chemical, and toxicological properties of chemicals (X indicates this category of chemical information was obtained from the database).

Database Name	**Physical/Chemical Properties**	**Acute Toxicity**	**Chronic Toxicity**	**Biodegradation**
American Chemical Society SciFinder Database	X			
World Health Organization, International Programme on Chemical Safety (IPCS) Database	X	X		X
National Library of Medicine, Toxicology Data Network (TOXNET) Hazardous Substance Data Bank (HSDB) and ChemIDplus	X	X		X
Syracuse Research Corporation (SRC), Physical Properties Database (PHYSPROP)	X			
European Chemicals Agency, International Uniform Chemical Information Database (IUCLID)	X	X		X
National Institute of Technology and Evaluation, Chemical Risk Information Platform (NITE-CHRIP), Japan.	X			X
European Chemicals Agency – Information on Chemicals Website	X	X		X
U.S. EPA, Aggregated Computational Toxicology Resource Database (ACToR)	X	X		X
U.S. EPA, Integrated Risk Information System (IRIS)			X	
U.S. EPA, Human Health Benchmarks for Pesticides (HHBP)			X	
U.S. EPA, Provisional Peer Reviewed Toxicity Values (PPRTV)			X	
U.S. EPA, Health Effects Assessment Summary Tables (HEAST)			X	
California Office of Environmental Health and Hazard Assessment (OEHHA)			X	
U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR) Priority List of Hazardous Substances			X	
U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health (NIOSH), Pocket Guide to Chemical Hazards			X	

3.4.5. Characterization of Carcinogenicity, Air Pollutants, and Other Hazards

All chemicals with valid CASRNs were screened using lists of known carcinogens, hazardous air pollutants, and other priority action lists for potential hazards from government agencies (see Table 4).

Table 4. Screening lists and databases used to identify potentially hazardous chemicals.

Screening Type	Screening List
Carcinogenicity	California EPA Chemicals Known to the State to Cause Cancer or Reproductive Toxicity (Proposition 65 List)
	National Toxicity Program Report on Carcinogens 14^{th} Ed.
	International Agency for Research on Cancer Monographs
Air Pollution	U.S. EPA Clean Air Act Hazardous Air Pollutants
	California Air Resources Board Air Toxics "Hot Spots" Program - Substances for Which Emissions Must Be Quantified
	California EPA Toxic Air Contaminant (TAC) Identification List
General Hazard	EU REACH Substances of Very High Concern (SVHC) Authorization List
	EU REACH Substances of Very High Concern (SVHC) Candidate List
	EU REACH Restricted List
	OSPAR List of Substances of Possible Concern

4.0. Results and Discussion

4.1. Distribution and Type of Events

A total 1,688 events were reported in the SCAQMD dataset from June 2013 to August 2018. Events include well drilling, well completion, or rework of an onshore oil or gas well. A brief description of these terms as defined by SCAQMD are provided below (SCAQMD, 2015).

> Well drilling: digging or boring into the earth to develop, extract, or produce oil or gas. Does not include remediation or clean-up efforts.
>
> Well completion: production, stimulation, or treatment activities, that establish flow paths for hydrocarbons between the reservoir and the surface, in order to prepare a well for production
>
> Rework: any operation involving deepening, re-drilling, stimulation, or treatment activity of an existing well.

Well completion and rework events can be further categorized according to activity type including: acidizing, maintenance acidizing, acid fracturing, matrix acidizing, gravel packing, and hydraulic fracturing. A brief description of these activities are provided below (CCST et al., 2015b; SCAQMD, 2015).

- **Acidizing:** use of acid to clean out scale, damage, or other debris in the wellbore/formation, or to react with the soluble substances in the formation, thereby enhancing permeability and well production
- **Matrix acidizing**: use of low-pressure acid injection into a formation to dissolve solids and sediments, thereby enhancing permeability and well production
- **Maintenance acidizing:** use of acid to clean out scale, damage, or other debris in the wellbore or reservoir formation
- **Acid fracturing:** stimulating a formation by pressurized injection of acidic fluid to fracture the formation and etch walls of fractures, thereby enhancing permeability and well production
- **Gravel packing:** use of water and additives to place sand and gravel near the wellbore to limit entry of formation sand and particles into the wellbore
- **Hydraulic fracturing:** stimulating a formation by pressurized injection of hydraulic fracturing fluid (typically carrier fluid, chemical additives, and a proppant) to fracture the formation, thereby enhancing permeability and well production

Events were mapped using latitude and longitude (Figure 1). 131 events occurred within the boundaries of the City of LA and 1,437 events occurred in the rest of Los Angeles county (not counting the City of LA). The majority of all events reported occurred in Long Beach, which borders the City of LA. 120 events took place in Orange County, with the majority occurring near Huntington Beach.

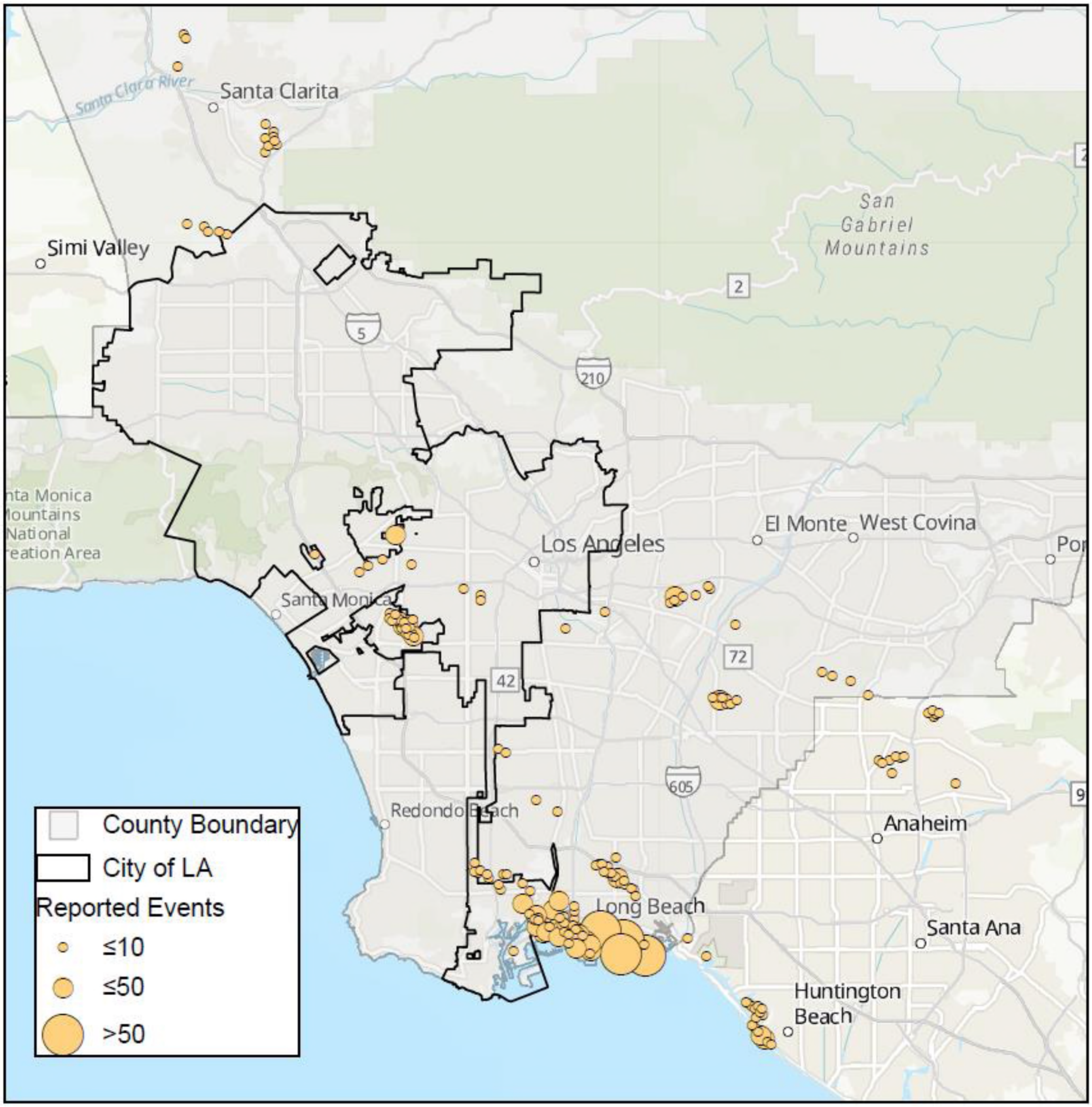

Figure 1. Events reported in the SCAQMD database from 2013 to 2018. Events within a 100-meter range of each other were combined and assigned weighted symbols.

Table 5. Number of events within 1,500 feet of a sensitive receptor in the SCAQMD.

Distance to Sensitive Receptor (ft)	All SCAQMD Events	City of LA Events
0-300	115	47
301-600	253	34
601-900	132	5
901-1200	49	13
1201-1500	48	7
Total	**597**	**106**

Table 6. Number of events with chemical data according to event type in all of SCAQMD and the City of LA from 2013-2018. The first value is the number of events in SCAQMD, the value in parenthesis is the number of events in the City of LA.

Event Type	2013	2014	2015	2016	2017	2018	Total
Acidizing	195 (22)	44 (2)	0 (0)	0 (0)	0 (0)	0 (0)	239 (24)
Gravel packing	40 (2)	93 (8)	29 (0)	2 (0)	28 (0)	20 (4)	212 (14)
Matrix acidizing	0 (0)	7 (0)	1 (0)	1 (1)	0 (0)	0 (0)	9 (1)
Hydraulic fracturing	13 (0)	0 (0)	1 (0)	0 (0)	0 (0)	0 (0)	14 (0)
Well drilling	57 (9)	108 (18)	27 (1)	0 (0)	1 (0)	1 (0)	194 (28)
Well drilling and gravel packing	38 (1)	62 (2)	7 (0)	5 (0)	10 (0)	16 (0)	138 (3)
Well drilling, gravel packing, and maintenance acidizing	0 (0)	0 (0)	0 (0)	0 (0)	5 (0)	6 (0)	11 (0)
Maintenance acidizing	13 (2)	242 (16)	196 (17)	148 (10)	148 (10)	90 (3)	837 (58)
Maintenance acidizing and gravel packing	0 (0)	2 (1)	0 (0)	0 (0)	0 (0)	0 (0)	2 (1)
Well completion and rework (type unspecified)	6 (0)	23 (1)	3 (1)	0 (0)	0 (0)	0 (0)	32 (2)
Total City of LA Events	36	48	19	11	10	7	131 (7.5%)
Total Non-City of LA Events	326	533	245	145	182	126	1557 (92.5%)
Total All SCAQMD Events	362	581	264	156	192	133	1688

Operators are required to notify SCAQMD if an event occurs within 1,500 feet of a sensitive receptor such as a residence, school, hospital, or other health care facility (SCAQMD, 2015). A total of 597 (35%) events in the SCAQMD were located near sensitive receptors, of which 368 were within 600 feet of the receptor (Table 5). 106 of 131 (81%) events in the City of LA were located near a sensitive receptor. 81 of the 131 events were within 600 feet of the receptor. California has no minimum setback requirement for oil and gas development. Other cities, such as

Dallas, have setback distances as far as 1500-feet (City of Dallas, 2013) and it is unclear if similar ordinances in the City of LA would be feasible without significantly impacting oil and gas development, given the population density of the Los Angeles Basin.

A temporal analysis of the SCAQMD dataset reveals that the majority (71.5%) of reported events took place from 2013-2015, with a sharp drop-off after 2014 (Table 6). This trend is consistent with statewide trends in well drilling and completion operations reported by DOGGR for the entirety of California from 2013-2017 and with the overall decrease in state oil and gas production from the same period (Table 7; DOGGR, 2018a). An investigation into underreporting on part of SCAQMD would involve a detailed comparison of submissions to both DOGGR and SCAQMD and is beyond the scope of this report.

Table 7. Well drilling and completion activity reported by DOGGR from 2013-2017 (DOGGR, 2018a).

	2013	2014	2015	2016	2017
Wells Drilled	2723	3249	1016	759	996
Wells Completed	3037	3647	1346	1111	1108
State Oil Production (million barrels)	199.7	205.4	201.7	186.7	174.0
State Net Gas Production (billion cubic feet)	216.7	186.9	182.8	157.3	162.7

Maintenance acidizing, gravel packing, and well drilling, were the most commonly reported events types in the SCAQMD. Prior to April 2014, submissions to SCAQMD were not required to differentiate between maintenance acidizing and matrix acidizing, instead grouping them both under the "acidizing" label (SCAQMD, 2014). After 2014, no additional acidizing events were reported and maintenance acidizing became the most commonly reported type of event. Hydraulic fracturing and matrix acidizing events were the least common, accounting for 1% of all reported events. Hydraulic fracturing events were only reported in the Brea-Olinda and Wilmington oil fields, none of which took place in the City of LA. No acid fracturing events were reported. Events that occurred in the City of LA did not account for a disproportionate fraction of events for any activity type.

The number of events by activity type may differ slightly from previous studies due to different study periods, exclusion of canceled events, updates to previously submitted events, and attempts to categorize "acidizing" events prior to April 2014. Events were reported for 24 unique facilities within the City of LA (Table 8). The median number of events reported per facility ID was two; however, three facilities accounted for 57% of the 131 total events reported in the City of LA. These facilities were Warren E&P, Inc (facility ID: 144681; Wilmington oil field), Tidelands Oil Production Co/Pier A West (facility ID: 149881; Wilmington oil field), and Plains Exploration & Production Company (facility ID: 133989; Salt lake oil field)[1]. Facility ID was not specified for 4 events within the City of LA.

[1] This facility is now associated with Sentinel Peak Resources; current facility ID: 184301.

Table 8. Number of events within the City of LA according to facility ID and event type.

Facility ID	Acidizing	Gravel packing	Maintenance acidizing	Well drilling	Matrix acidizing	Maintenance acidizing & gravel packing	Gravel packing & well drilling	Well completion & rework (unspecified)	Total
Unspecified	3	1	0	0	0	0	0	0	4
3061	1	0	1	0	0	0	0	0	2
10245	0	0	0	2	0	0	0	0	2
13627	0	0	1	0	0	0	0	0	1
82513	3	0	2	2	0	0	0	0	7
98158	1	0	2	0	1	0	0	0	4
101222	1	1	3	0	0	0	0	0	5
133987	1	0	0	0	0	0	0	0	1
133988	4	0	2	0	0	0	0	0	6
133989	5	0	9	0	0	0	0	1	15
144664	2	0	2	0	0	0	0	0	4
144681	0	8	13	19	0	0	1	0	41
144797	0	0	4	0	0	0	0	0	4
149027	0	0	1	0	0	0	0	0	1
149881	3	3	9	2	0	0	2	0	19
149883	0	1	0	0	0	0	0	0	1
165309	0	0	2	0	0	0	0	0	2
171042	0	0	1	0	0	0	0	0	1
171043	0	0	0	0	0	1	0	0	1
171050	0	0	1	0	0	0	0	0	1
175159	0	0	0	1	0	0	0	0	1
175164	0	0	2	0	0	0	0	0	2
175165	0	0	2	0	0	0	0	0	2
184298	0	0	1	0	0	0	0	0	1
800128	0	0	0	2	0	0	0	1	3
Total	**24**	**14**	**58**	**28**	**1**	**1**	**3**	**2**	**131**

4.2. Chemicals Identified in SCAQMD Dataset

Chemicals in the SCAQMD dataset were reported as either 1) trade name products (chemical mixtures without CASRN), 2) chemicals with CASRN, or 3) trade secret chemicals. In part to standardize with California Senate Bill 4 (SB 4) reporting requirements regarding well stimulation activities, and in part to help encourage disclosure, SCAQMD updated Rule 1148.2 in 2015 to unlink trade name products (chemical mixtures without CASRN) from their individual chemical components with CASRN (SCAQMD, 2015b). Although the individual chemical compositions of trade name products cannot be determined, other than what was disclosed prior to the updated Rule 1148.2 going into effect or inferring from similar mass usages with chemicals with CASRN, the total sum of their components is reported and disclosed as chemicals with CASRN.

459 trade name products were disclosed, consisting of 378 individual chemicals with CASRN. 54 of these chemicals with CASRN were reported with incorrect CASRNs. Of these 54 chemicals, 51 could be positively identified based on the similarities of their CASRN and chemical names to other chemicals in the dataset. Entries for three chemicals, alkylaryl sulfonate (CASRN: 68484-27-0), xanthan gum (CASRN: 59370-00-0), and d-limonene (CASRN: 254504-00-1) had invalid CASRNs and could not be identified with confidence. Alkylaryl sulfonate was reported 24 times throughout the dataset and was not similar in name or CASRN to any other known chemical. Xanthan gum (CASRN: 59370-00-0), and d-limonene (CASRN: 254504-00-1) were both reported once in the dataset, and although other entries for d-limonene and xanthan gum appear in the SCAQMD dataset with the correct CASRNs, the incorrect CASRNs provided were not similar enough to the correct CASRNs to identify them with confidence. These three chemicals were grouped with trade secret chemicals for the purposes of this study.

A total of 327 trade secret chemicals identified by name only were reported in the SCAQMD dataset. Trade secret chemicals could not be definitively identified or characterized for hazard analysis. The 459 identified trade name products do not have CASRN, and their composition is not always disclosed in a manner which is linked to individual chemicals with CASRN. However, because the total sum of their components is reported and disclosed as chemicals with CASRN, they are neither counted as trade secret chemicals nor are they counted for the total chemical count in the SCAQMD dataset. Complete lists of trade secret chemicals and disclosed trade name products are provided in Appendix A, Tables A.3 and A.4, respectively.

In total, 651 chemicals were identified in the SCAQMD dataset. A total of 324 chemicals (approximately 50%) with unique, valid CASRNs were identified for further chemical analysis and 327 chemicals were identified as trade secrets. A previous study of the SCAQMD dataset by Stringfellow et al. (2017b) identified a total of 548 chemicals (249 chemicals with unique, valid CASRN) for the period prior to September 2, 2015. A complete list of chemicals with unique, valid CASRNs is provided in Appendix A, Table A.2.

Other oil and gas chemical data, such as chemicals disclosed to the City of LA Fire Department via the California EPA and California Certified Unified Program Agencies are only available to regulators and are not publicly available. These data were not analyzed in this report; however, future studies comparing these data to reporting in the SCAQMD dataset would be prudent.

4.3. Comparison of Chemical Usage by Geographic Area and Event Type

The SCAQMD dataset includes events occurring in 26 oil fields in southern California. In the City of Los Angeles, 131 oil and gas events were reported across 7 oil fields: Torrance, Wilmington, Las Cienegas, Cheviot Hills, Beverly Hills, Salt Lake, and Aliso Canyon (Figure 2).

The Wilmington oil field accounted for most of the events within the City of LA with 70 events (53%) and most of the events in the entire SCAQMD dataset at 1,174 (69%) (Table 9). Although most of the events in the Wilmington oil field take place outside of the City of Los Angeles, they occur in close proximity to the city borders. The oil field with the second highest number of events is the Inglewood oil field with 145 events. While the Inglewood oil field is not within the city limits, it is completely surrounded by the City of LA. Emissions from oil and gas operations in these areas, while not technically in the City of LA, may still impact residents living within the city due to their close proximity.

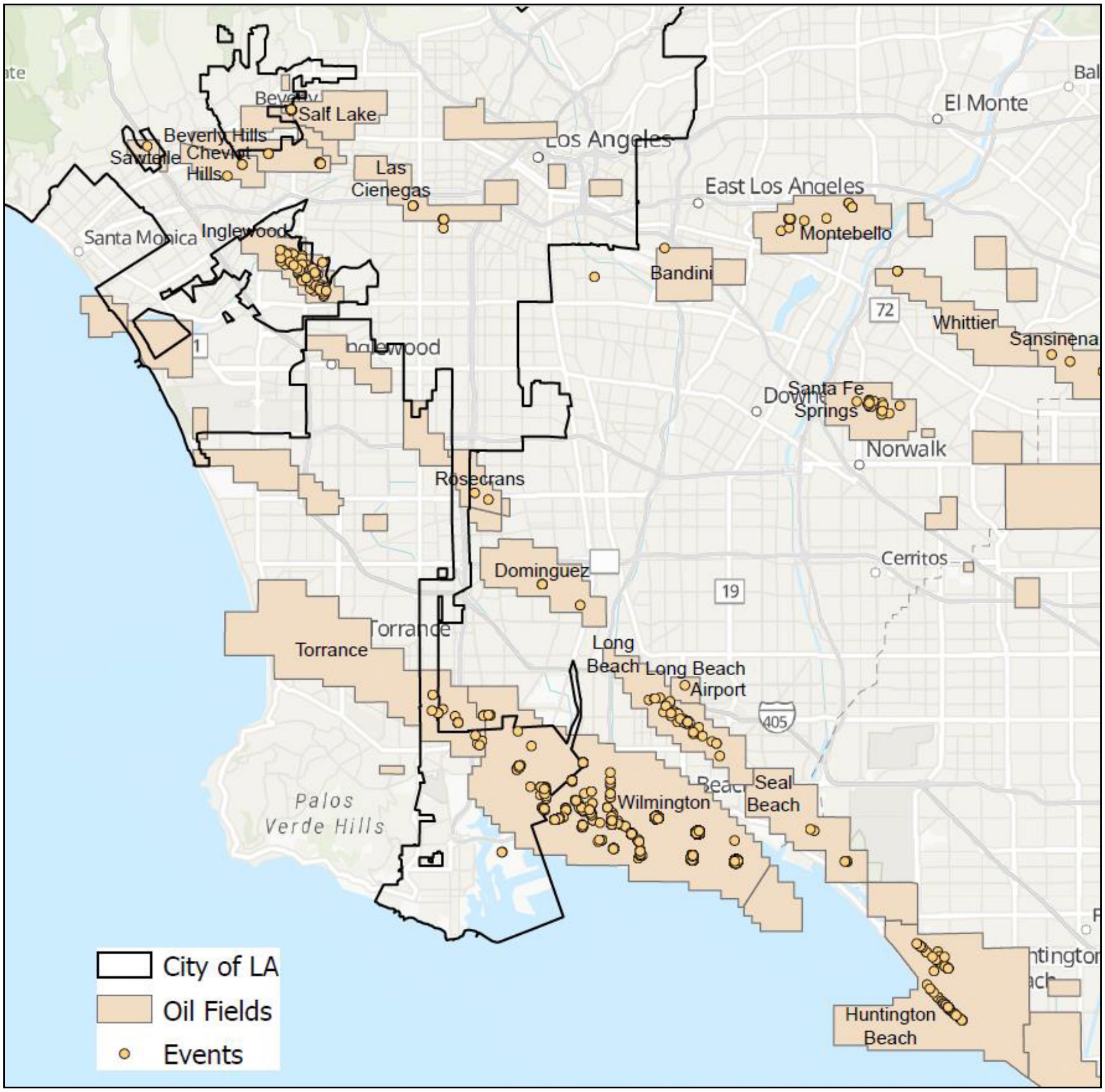

Figure 2. Events reported in the SCAQMD database from 2013 to 2018 by oil field.

Table 9. Total events and chemicals reported by oil field.

Oil Field	Total Events[1]	Events within the City of LA[2]	Chemicals with CASRN Reported (Entire Oil Field)	County
Wilmington	1174	70	181	LA
Salt Lake	20	20	46	LA
Beverly Hills	12	12	41	LA
Las Cienegas	11[3]	11	50	LA
Torrance	20	11	22	LA
Aliso Canyon	9	3	34	LA
Cheviot Hills	3	3	17	LA
Inglewood	145	0	50	LA
Huntington Beach	81	0	53	Orange
Long Beach	51	0	54	LA
Santa Fe Springs	39	0	59	LA
Montebello	26	0	84	LA
Placerita	22	0	15	LA
Coyote, East	16[4]	0	18	Orange
Brea Olinda	15	0	74	LA/Orange
Wayside Canyon	9	0	15	LA
Seal Beach	6	0	39	LA/Orange
Dominguez	5	0	47	LA
Sansinena	5	0	22	LA
Whittier	3	0	22	LA
Rosecrans	2	0	15	LA
Honor Rancho	2	0	18	LA
Richfield	2	0	8	Orange
Long Beach Airport	1	0	17	LA
Sawtelle	1	0	14	LA
Bandini	1	0	20	LA

1. 7 events occurred offshore and were not categorized according to oil field
2. 1 event in the City of LA occurred on Terminal Island, outside of oil field GIS boundaries
3. Contains 1 event that was outside the borders of the oil field by less than 2000 feet, that was not close to any other oil field
4. Contains 2 events that were outside the borders of the oil field by less than 2000 feet, that were not close to any other oil field

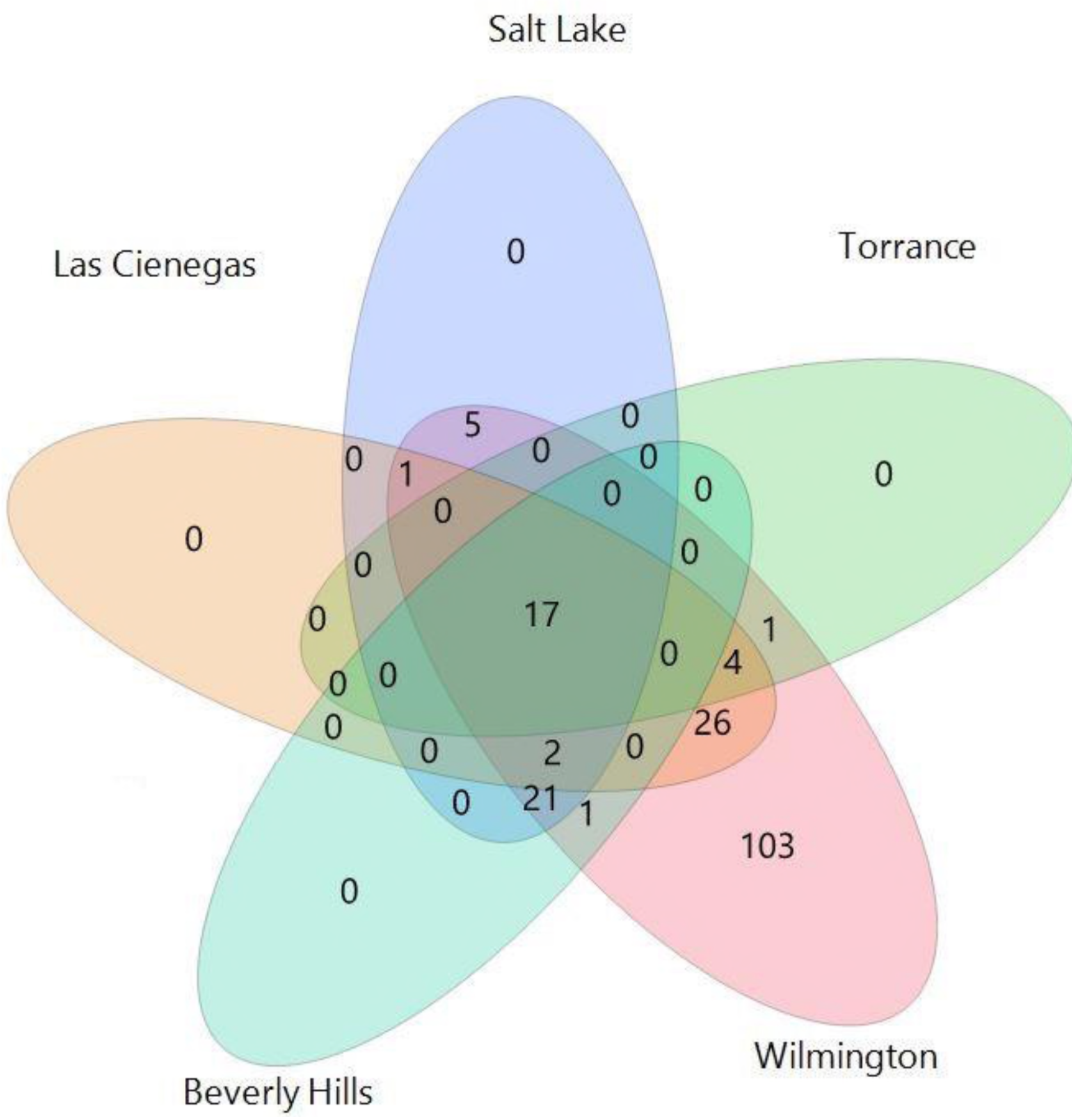

Figure 3. Comparison of chemical use between five oil fields with the greatest number of events in the City of Los Angeles. This comparison is done using total chemicals reported with CASRN in the entire oil field.

A comparison of the chemicals used in the five oil fields with the greatest number of events in the City of Los Angeles reveals that chemical usage between oil fields is similar (Figure 3). 17 chemicals were reported as used in all five oil fields. Although 103 of the reported chemicals used were unique to the Wilmington oil field, no chemicals reported were unique to any other oil field.

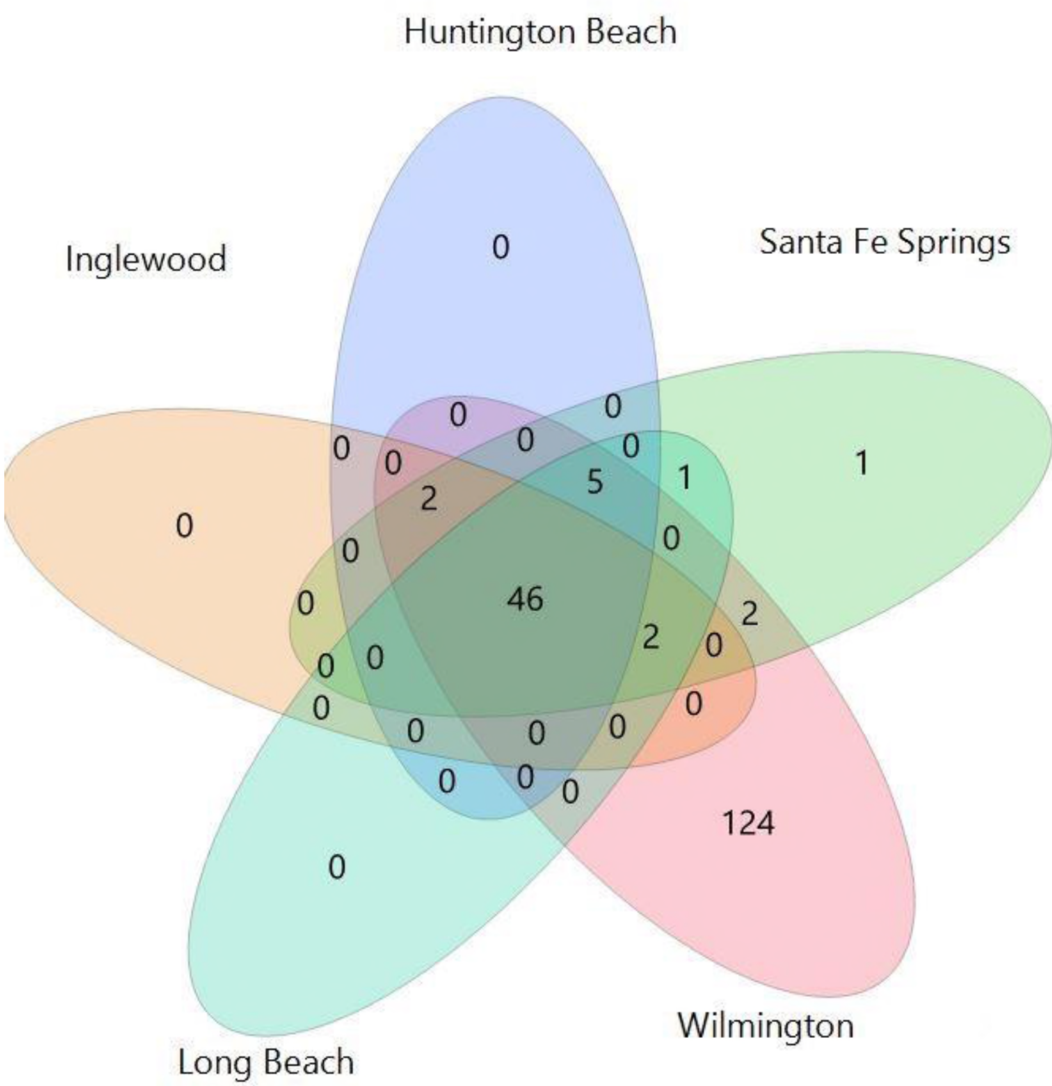

Figure 4. Comparison of chemical use between five oil fields with the greatest number of events in the SCAQMD dataset. This comparison is done using total chemicals reported with CASRN in the entire oil field.

A comparison of the chemicals used in the five oil fields with the greatest number of events in the entirety of the SCAQMD reveals that chemical usage between oil fields is more similar than it is different (Figure 4). 46 chemicals are common to all five oil fields. Similar to the analysis of chemicals used in the City of LA oil fields, only the Wilmington oil field has a significant number of chemicals unique to its oil and gas operations. This is possibly due to the sheer number of events taking place in the Wilmington oil field compared to other oil fields in the SCAQMD. Another possible explanation may be the inclusion of the THUMS Islands, which are artificial islands built off the coast of Long Beach to exploit the Wilmington oil field.

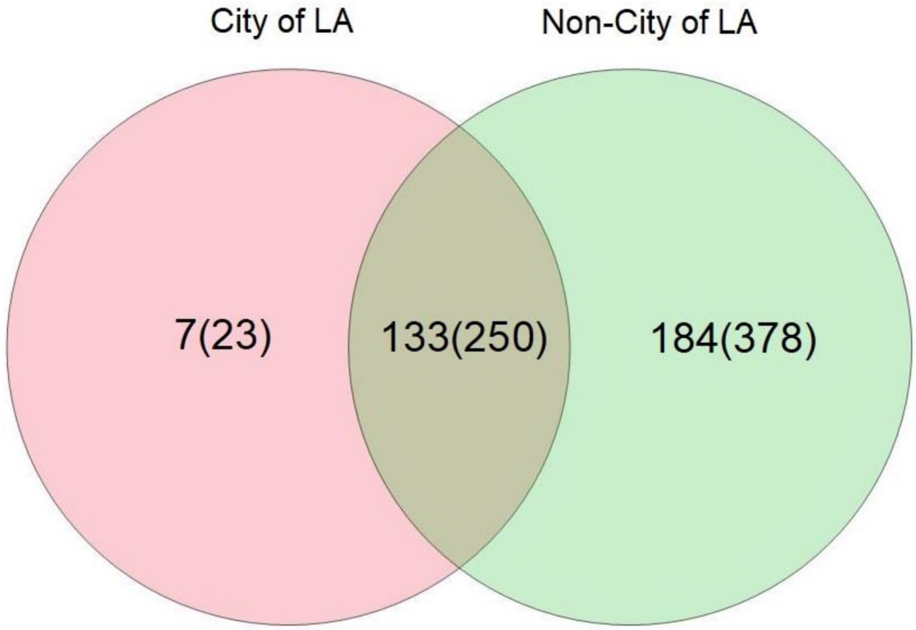

Figure 5. Chemicals used in City of LA and Non-City of LA events. The first number represents chemicals with CASRN and the number in parentheses represents the total number of chemicals (CASRN and trade secret).

A total of 273 chemicals (140 with CASRN) were identified in all the events taking place in the City of Los Angeles. When compared to the entire SCAQMD dataset, only 23 chemicals (7 with CASRN) are unique to City of Los Angeles events, with 250 being used in both City of LA and Non-City of LA events (Figure 5). This further shows that there is major overlap between events occurring within the City of Los Angeles and events occurring in the rest of Los Angeles County and Orange County in terms of the variety of chemicals used.

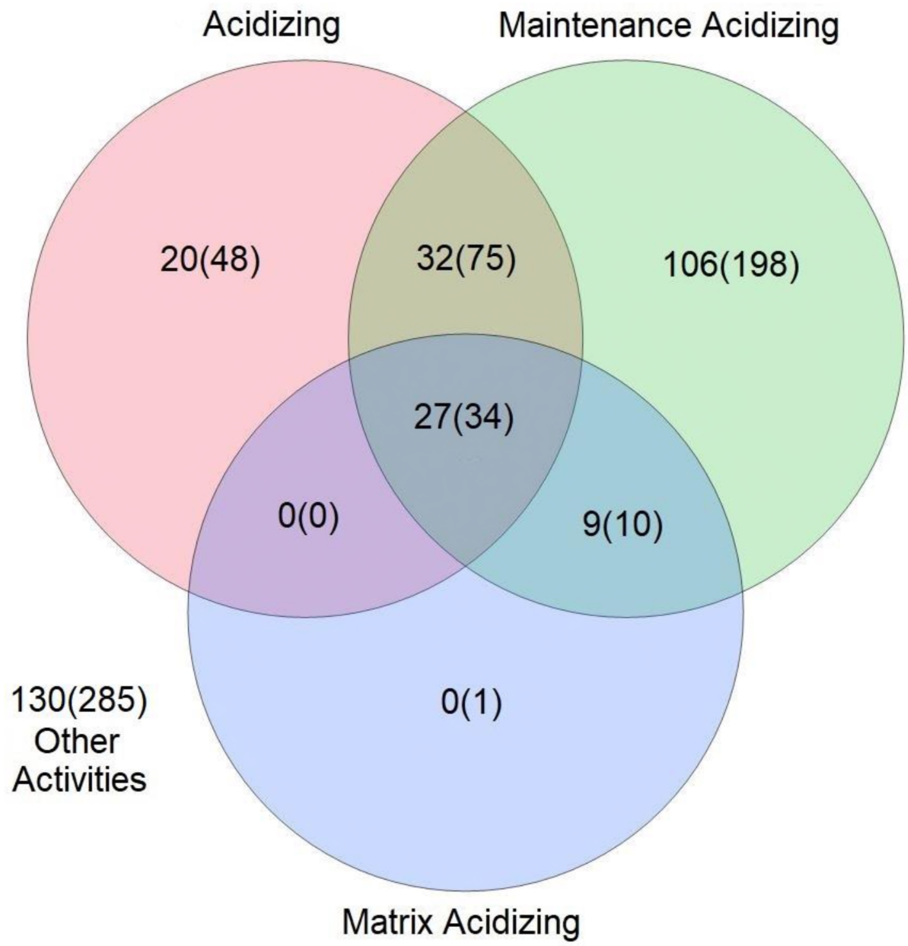

Figure 6. Chemical usage in acidizing, maintenance acidizing, and matrix acidizing events. The first number represents chemicals with CASRN and the number in parentheses represents the total number of chemicals (CASRN and trade secret).

Chemical usage for different acidizing events is presented in Figure 6. There is significant overlap in chemical usage between all acidizing events, making it difficult to determine with certainty if events labeled "acidizing" from 2013-2014 were maintenance acidizing or matrix acidizing events. An earlier analysis by Stringfellow et al. (2017b) reached a similar conclusion. Maintenance acidizing accounts for almost half of all reported events in the SCAQMD and the large number of chemicals unique to maintenance acidizing is expected (198 chemicals, 106 with CASRN). Almost half of all chemicals were not identifiable by CASRN for both acidizing (78 of 157) and maintenance acidizing (143 of 317). No chemicals identifiable by CASRN were unique to matrix acidizing events.

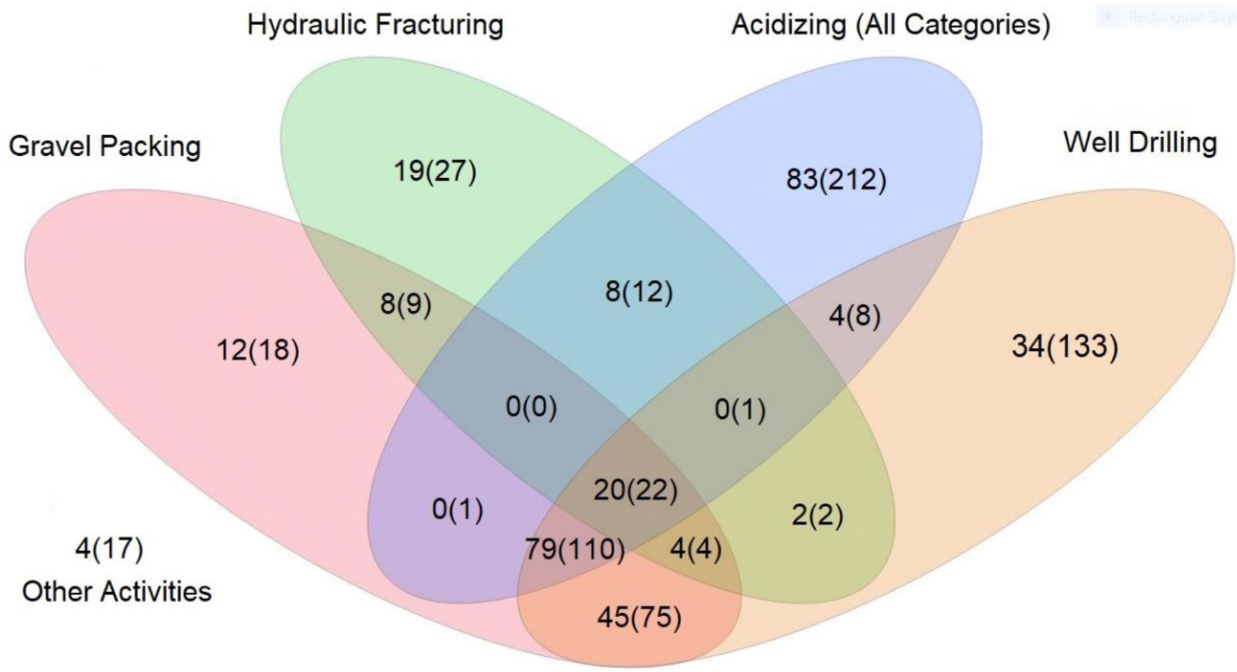

Figure 7. Chemical use in gravel packing, hydraulic fracturing, acidizing, and well drilling events. Acidizing includes all events reported as matrix acidizing, acidizing, and maintenance acidizing. The first number represents chemicals with CASRN and the number in parentheses represents the total number of chemicals (CASRN and trade secret).

Chemical usage for all event types is presented in Figure 7. Although 212 and 133 chemicals are unique to acidizing and well drilling, respectively, there is significant overlap in chemical usage between all event types. Of the 239 chemicals used in gravel packing, 211 are also used in well drilling, which is consistent with the fact that well drilling and gravel packing activities are commonly reported for the same event. Overall, the greatest number of chemicals with CASRN and trade secret chemicals without CASRN are used in acidizing (specifically maintenance acidizing) and well drilling operations. Seventeen chemicals were unique to unspecified well completion and rework events.

4.3. Median Mass and Frequency of Chemical Usage

The top 40 most frequently reported chemicals with CASRN and their median masses per event for both the entire SCAQMD dataset and just events occurring in the City of Los Angeles are provided in Table 10 and Table 11, respectively. Comparing the frequency and median masses of chemicals used in the City of Los Angeles and the entirety of the SCAQMD reveals that the most commonly used chemicals and the median masses at which they are used are similar; 31 of the top 40 most commonly reported chemicals in the City of Los Angeles were also in the top 40 for the entire SCAQMD dataset.

Frequently used chemicals include strong acids, minerals, carboxylic acids, solvents, petroleum products, and salts (Table 10). Strong acids such as hydrofluoric acid and hydrochloric acid are routinely used in high masses for acidizing and well-maintenance operations (Stringfellow et al., 2017b). Solvents, petroleum products, and salts are commonly used when blending commercial chemical formulations (Stringfellow et al., 2017b). Carboxylic acids, such as erythorbic acid and citric acid, can be utilized for a variety of functions including as corrosion inhibitors and to control scaling (Stringfellow et al., 2017b). Mineral additives including silica, Portland cement, and bentonite are frequently used in high masses for operations such as gravel packing, sealing wells, and cementing well casings (Stringfellow et al., 2017b). Water is a principal component of well drilling, completion, and rework fluids, as well as many pre-formulated chemical mixtures, and is accounted for in this analysis.

The three most common forms of crystalline silica (quartz, cristobalite, and tridymite) were used in 548 events in the SCAQMD. Crystalline silica is commonly used in hydraulic fracturing as a proppant; however, hydraulic fracturing is relatively rare in the SCAQMD with only 14 reported events. Crystalline silica was predominantly used in well drilling operations (158 events) as a cement additive, in gravel packing (211 events) as a component of gravel, or any combination of the two (149 events). Crystalline silica compounds are rarely used in maintenance acidizing events (4 events). Of the three forms of crystalline silica, quartz (CASRN: 14808-60-7) was used in all 548 events. Cristobalite and tridymite were only used in conjunction with quartz.

A previous study done by Stringfellow et al. (2017b) compared chemical usage in the SCAQMD dataset to chemical usage in oil fields in other areas of the world, specifically off-shore oil operations in the North Sea and the Gulf of Mexico. Although this study was limited to SCAQMD events prior to September 2, 2015, the results suggest that many of the SCAQMD chemicals are not unique to operations in the SCAQMD. SCAQMD chemicals, or functionally similar compounds, are routinely used for well cleaning and to control scaling and microbial growth in the oil and gas industry worldwide suggesting that engineering controls, monitoring methods, and other mitigation techniques used in other parts of the world may be relevant for operations in the SCAQMD.

Table 10. Forty most commonly reported chemicals with CASRN and their median use in entire SCAQMD dataset (sorted by times reported).

Chemical Name	CASRN	Times Reported	Median Mass (lbs)	Total Mass (lbs)	Chemical Name	CASRN	Times Reported	Median Mass (lbs)	Total Mass (lbs)
Water	7732-18-5	1651	107,089	489,961,351	Hydrotreated Light Petroleum Distillate	64742-47-8	417	64	809,410
Methanol	67-56-1	1319	75	301,432	Cumene	98-82-8	376	64	24,062
Sodium chloride	7647-14-5	1184	266	13,389,499	Bentonite	1302-78-9	312	1,438	2,033,032
Citric acid	77-92-9	1108	300	770,049	Portland cement	65997-15-1	306	63,732	23,173,711
Hydrochloric acid	7647-01-0	1050	14,501	24,283,348	Phosphogypsum	13397-24-5	305	56,024	6,831,484,103
Ammonium chloride	12125-02-9	926	1,333	6,025,517	Xanthan gum	11138-66-2	304	800	299,547
Formaldehyde	50-00-0	924	74	86,426	Magnesium oxide	1309-48-4	303	44,764	14,563,529
Propargyl alcohol	107-19-7	920	74	84,823	Calcium oxide	1305-78-8	301	52,226	15,849,469
Hydrofluoric acid	7664-39-3	835	10,575	11,487,931	Alcohols, C14-C15, ethoxylated	68951-67-7	295	16	6,563
Thiourea, polymer with formaldehyde and 1-phenylethanone	68527-49-1	705	60	47,879	Barium sulfate	7727-43-7	294	44,820	19,833,022
Citrus terpenes	94266-47-4	683	147	325,908	Disodium metasilicate	6834-92-0	294	823	262,377
Erythorbic acid	89-65-6	683	25	24,234	Glyoxal	107-22-2	286	675	225,407
Hydrocarbons, terpene processing by-products	68956-56-9	675	147	164,230	Glutaraldehyde	111-30-8	285	144	98,650
Heavy aromatic naphtha	64742-94-5	645	64	95,989	Fatty acids, tall-oil	61790-12-3	285	16	6,169
Naphthalene	91-20-3	617	72	106,363	Acetic acid ethenyl ester, polymer with ethenol	25213-24-5	284	145	58,623
Crystalline silica (quartz)	14808-60-7	547	42,300	54,311,959	Sodium bicarbonate	144-55-8	283	875	337,045

Chemical Name	CASRN	Times Reported	Median Mass (lbs)	Total Mass (lbs)		Chemical Name	CASRN	Times Reported	Median Mass (lbs)	Total Mass (lbs)
Xylenes	1330-20-7	544	84	1,009,029		Sodium carboxymethylcellulose	9004-32-4	280	2,150	720,581
Ethylbenzene	100-41-4	533	80	368,621		Propylene glycol	57-55-6	280	28	8,630
Potassium chloride	7447-40-7	532	23,691	54,279,997		Alkenes, C>10 a-	64743-02-8	280	3	2,444
2-Butoxyethanol	111-76-2	461	141	222,028		Limestone	1317-65-3	279	57,246	15,165,589

Table 11. Forty most commonly reported chemicals with CASRN and median use in City of LA events (sorted by times reported).

Chemical Name	CASRN	Times Reported	Median Mass (lbs)	Total Mass (lbs)		Chemical Name	CASRN	Times Reported	Median Mass (lbs)	Total Mass (lbs)
Water	7732-18-5	119	76,164	30,286,693		Non-crystalline silica (impurity)	7631-86-9	29	9,345	519,534
Methanol	67-56-1	98	111	27,593		Erythorbic acid	89-65-6	28	43	1,830
Hydrochloric acid	7647-01-0	72	17,640	2,458,354		Calcium oxide	1305-78-8	28	12,200	820,206
Citric acid	77-92-9	66	242	31,729		Aluminum oxide	1344-28-1	28	5,735	208,482
Ammonium chloride	12125-02-9	65	1,500	893,747		Iron oxide	1309-37-1	28	5,402	182,269
Propargyl alcohol	107-19-7	59	74	7,922		Bentonite	1302-78-9	27	2,475	224,504
Sodium chloride	7647-14-5	54	3,632	866,393		Hydrotreated Light Petroleum Distillate	64742-47-8	26	277	186,111
Hydrofluoric acid	7664-39-3	54	13,755	1,183,501		Phosphogypsum	13397-24-5	26	62,162	1,625,938
Heavy aromatic naphtha	64742-94-5	54	84	19,361		Xanthan gum	11138-66-2	26	1,025	29,826
2-Butoxyethanol	111-76-2	54	353	35,994		Disodium metasilicate	6834-92-0	26	118	28,838
Formaldehyde	50-00-0	45	74	7,700		Sodium bicarbonate	144-55-8	26	925	35,400
Crystalline silica (quartz)	14808-60-7	44	19,350	2,838,928		Acetic acid	64-19-7	26	613	23,624

Chemical Name	CASRN	Times Reported	Median Mass (lbs)	Total Mass (lbs)		Chemical Name	CASRN	Times Reported	Median Mass (lbs)	Total Mass (lbs)
Xylenes	1330-20-7	35	708	80,875		Thiourea, polymer with formaldehyde and 1-phenylethanone	68527-49-1	25	74	2,388
Ethylbenzene	100-41-4	35	282	53,621		Portland cement	65997-15-1	25	70,674	1,769,380
Potassium chloride	7447-40-7	34	25,179	4,038,271		Magnesium oxide	1309-48-4	25	20,086	661,558
Naphthalene	91-20-3	32	68	12,907		Glutaraldehyde	111-30-8	25	188	7,969
Pine oil	8002-09-3	31	63	5,488		Acetic acid ethenyl ester, polymer with ethenol	25213-24-5	25	370	9,918
Ethyl octynol	5877-42-9	31	63	5,478		Sodium carboxymethylcellulose	9004-32-4	25	2,200	62,700
Isoquinoline	119-65-3	30	75	5,163		Carbon	7440-44-0	25	3,696	132,867
Quinaldine	91-63-4	30	75	5,475		Citrus terpenes	94266-47-4	24	213	6,407

4.4. Chemical Properties

4.4.1. Acute Inhalation Toxicity

Acute toxicity data for standard mammalian species (rat and mouse) was the most commonly available toxicity data. Acute toxicity tests represent short-term cases of extreme chemical exposure, where the outcome is measured (in this case) by death of the test animal. Acute toxicity data is generally considered less useful for assessing health outcomes than chronic toxicity data, however, it is still useful for comparing chemicals to one another and identifying chemicals that are clearly hazardous (Shonkoff et al., 2015).

Toxicity values are typically reported for pure compounds. In practice, most chemical additives are mixed on site or pre-mixed chemical formulations are provided by suppliers for use in oil and gas operations. Standard toxicity tests do not account for chemical interactions and synergistic effects of complex mixtures used in oil and gas operations. Assessing chemical mixtures is beyond the scope of this analysis.

Acute mammalian inhalation toxicity data classifiable according to GHS category were available for 50 (15%) chemicals reported with valid CASRNs (Figure 8). Fourteen of these chemicals are classified as GHS category 1 or 2. An additional 18 chemicals were classified according to estimated "floor level" GH values (Figure 9). Floor level estimated GHS values represent a conservative estimate of inhalation GHS and need to be interpreted with caution. When "floor level" GHS values were taken into consideration, a total of 68 (21%) chemicals were characterized for acute inhalation toxicity (Figure 10) with a total of 20 chemicals classified as GHS category 1 or 2. Of the 68 chemicals with acute inhalation toxicity data, 37 chemicals (8 classified as GHS category 1 or 2) were used in events taking place in the City of Los Angeles. Despite efforts to categorize all available data, significant data gaps remain as 79% of all chemicals could not be categorized according to acute inhalation toxicity. A complete list of all chemicals with acute inhalation toxicity data and their associated GHS categories can be found in Appendix A, Table A.5.

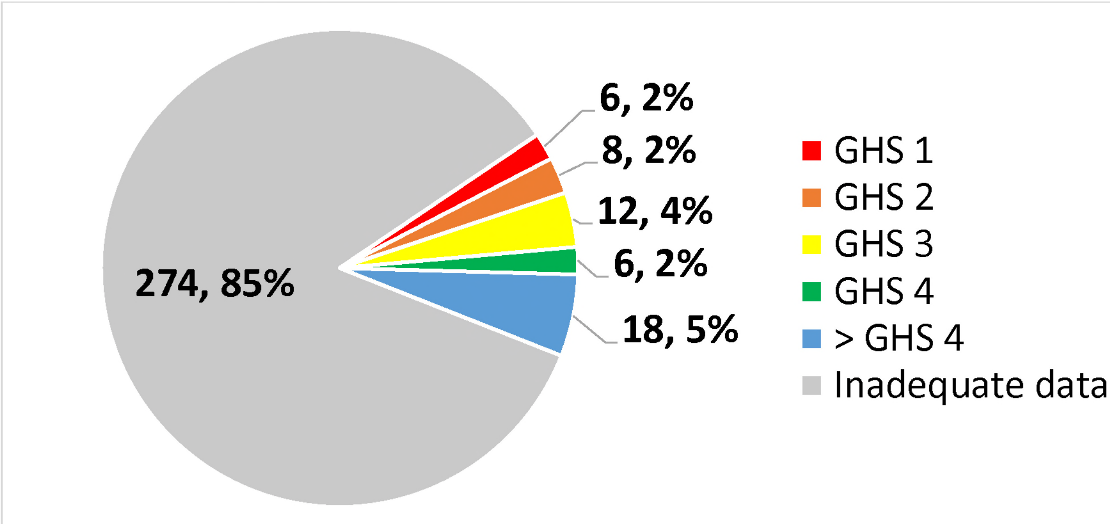

Figure 8. Availability of acute mammalian inhalation toxicity data according to GHS category for entire SCAQMD dataset.

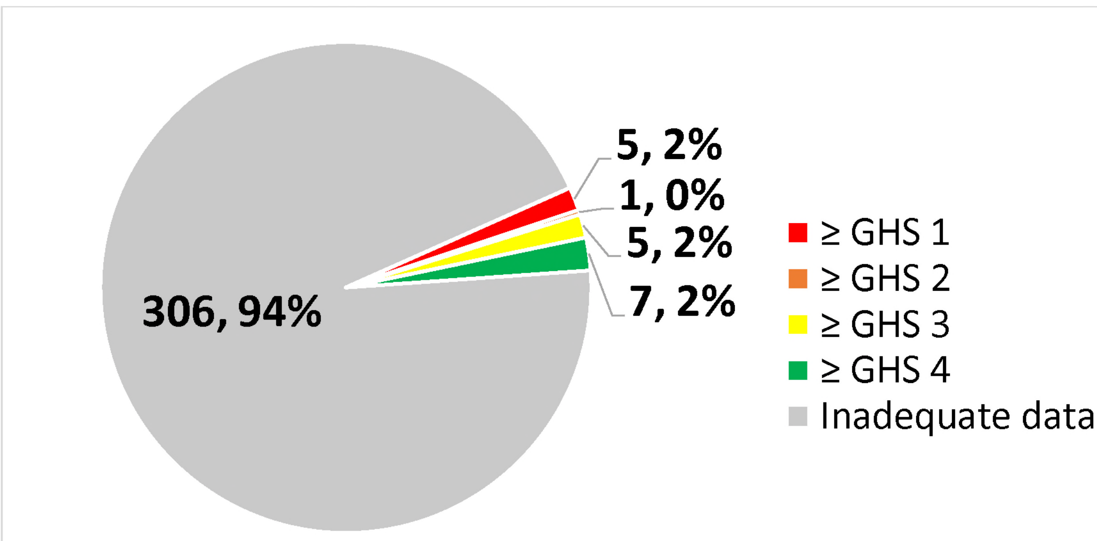

Figure 9. Acute mammalian inhalation toxicity data estimated from toxicity ranges according to GHS category for entire SCAQMD dataset. This is based off of the "floor level" analysis done using toxicity values listed as a range and provides a very conservative estimate of inhalation GHS.

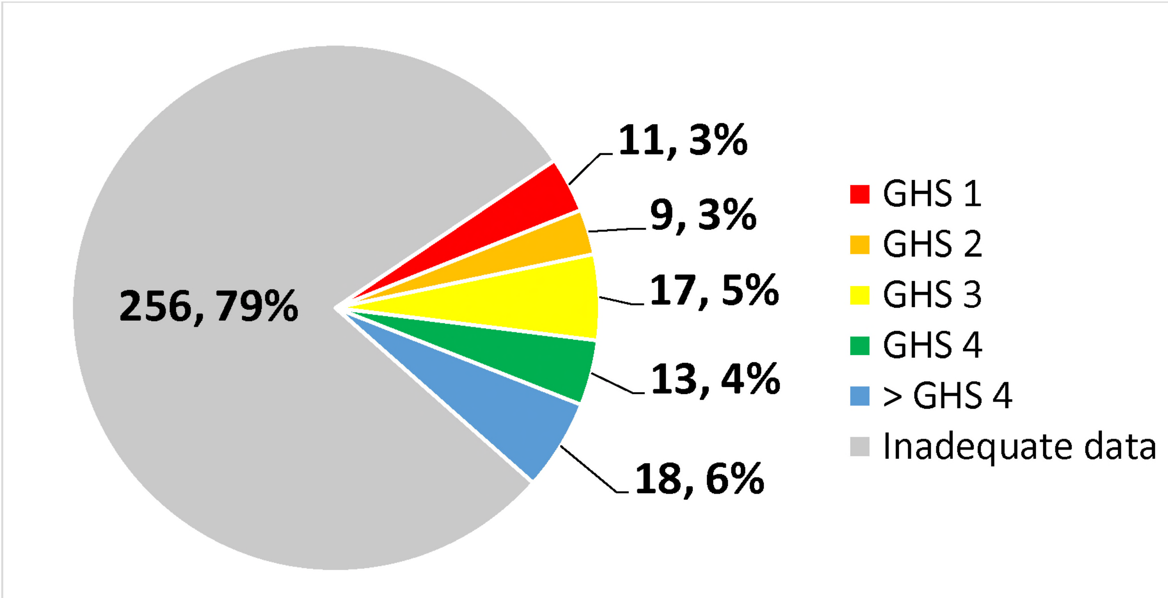

Figure 10. Combined acute mammalian inhalation toxicity data and estimated "floor level" analysis from toxicity ranges according to GHS category for entire SCAQMD dataset. This combines Figure 8 and Figure 9.

4.4.2. Chronic Inhalation Toxicity

Chronic toxicity data, while generally less available than acute toxicity data, is important to determine health outcomes associated with repeated exposure. Common endpoints for chronic toxicity studies include increased frequency of cancer and tumors, and adverse reproductive, developmental, neurological, respiratory, and lifespan changes. Most chronic toxicity data is collected using animal studies; however, a few chemicals have human-based chronic data often as a result of accidents, occupational exposure, or unregulated release of chemicals. In isolation, it seems that the availability of chronic toxicity is similar to acute toxicity for the SCAQMD dataset; however, this study does not consider acute and chronic *oral* toxicity, whereby the availability of acute toxicity data then becomes significantly greater than chronic toxicity.

Similar to evaluations of acute toxicity, chronic toxicity values are typically reported for pure compounds. Standard toxicity tests do not account for chemical interactions in complex mixtures used in oil and gas operations. Assessing chemical mixtures is beyond the scope of this analysis.

Chronic inhalation toxicity data (e.g. RfC, MRL, REL, and UR) were available for 37 (11%) chemicals reported with valid CASRNs in the SCAQMD dataset. An additional 39 chemicals had available occupational exposure limits from OSHA, NIOSH, or ACGIH. Despite efforts to categorize all available data, significant data gaps remain as 77% of all chemicals could not be categorized according to chronic inhalation toxicity (Figure 11). Complete lists of chronic inhalation reference concentrations and occupational exposure values can be found in Appendix A, Tables A.6 and A.7, respectively.

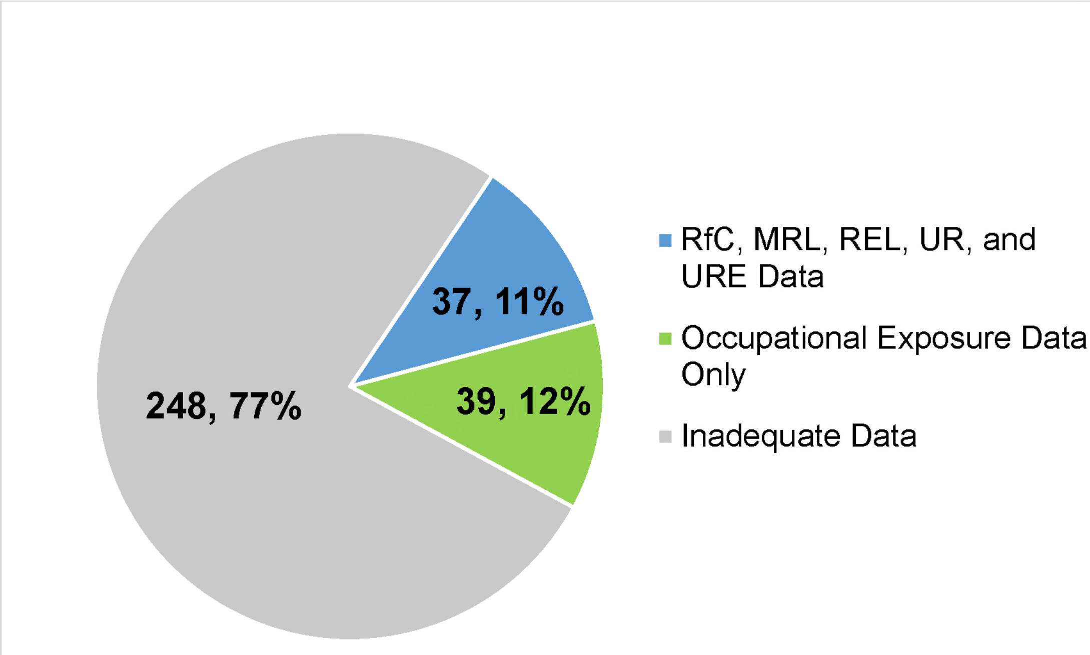

Figure 11. Availability of chronic inhalation toxicity data for entire SCAQMD dataset.

4.4.3. Biodegradability

A key factor in evaluating the risk of chemical exposure is how persistent a chemical is in the environment. Biodegradation is a major mechanism for environmental attenuation. Chemicals that are readily biodegradable typically do not persist for long periods of time in the environment. Chemicals that are resistant to biodegradation are more likely to accumulate in the environment and are more likely to be subject to exposure pathway (e.g. inhalation) transport mechanisms. Biodegradable chemicals are expected to have reduced risk of chemical exposure for pathways that occur over the course of days or months; however, the impact of biodegradation is expected to be negligible for exposure pathways that take place over the course of seconds to minutes.

Similar to acute and chronic toxicity, biodegradability is typically reported for pure compounds. Although standard testing does account for simple mixtures of similar compounds that are inseparable, such as hydrocarbon distillates, it does not account for chemical interactions (e.g. bacterial inhibition) in complex mixtures used in oil and gas operations. Assessing chemical mixtures is beyond the scope of this analysis.

Experimental biodegradation data was found for 40% of chemicals identified by CASRN, with another 14% of chemicals being characterized using EPISuite™ computational software. Approximately 70% of all chemicals with biodegradation data were found to be readily or inherently biodegradable. Only 19% of chemicals had inadequate data to categorize them according to OECD standards. A total of 51 (16%) chemicals were classified as not readily biodegradable (Figure 12). Biodegradability is not relevant for inorganic chemicals. A complete list of chemicals classified as not readily biodegradable according to OECD standards can be found in Appendix A, Table A. 8.

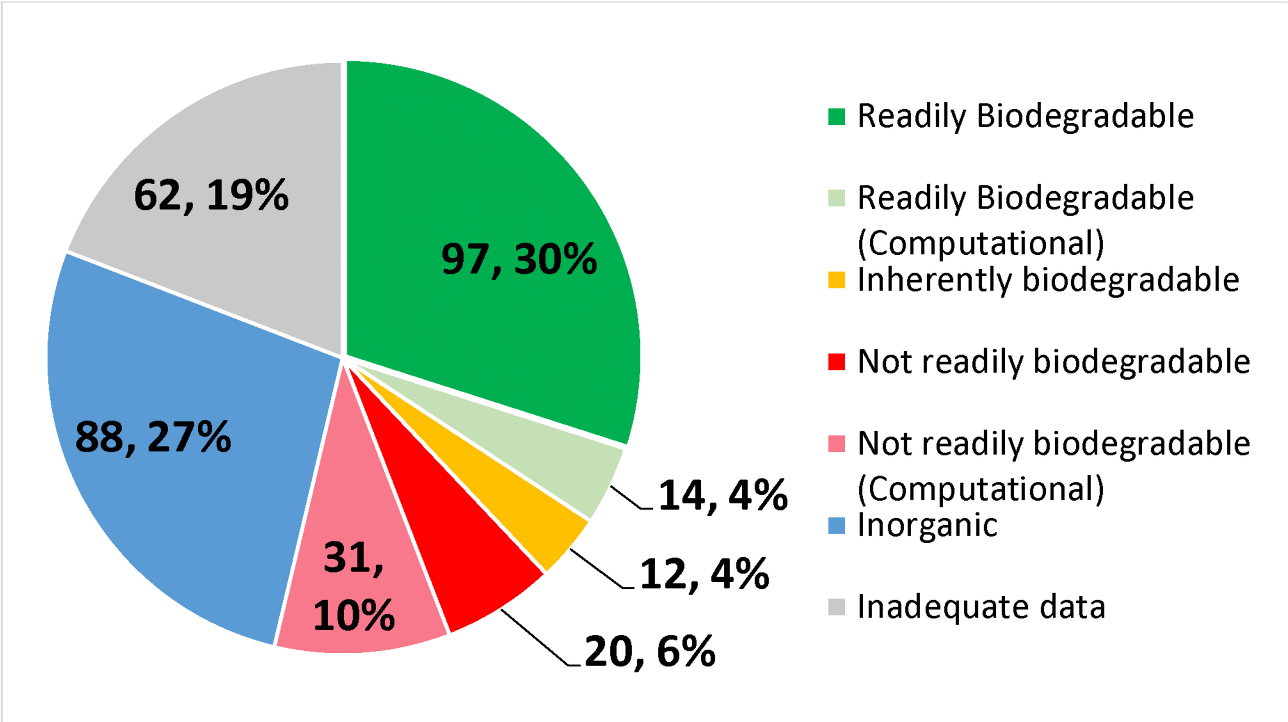

Figure 12. Available biodegradability data according to OECD standards for entire SCAQMD dataset.

4.4.4. Carcinogenicity

Various factors can contribute to the increased risk of cancer in humans, including exposure to carcinogenic chemicals, either synthetic and naturally occurring. It has long been assumed that there is no safe level of exposure to carcinogens; however, recent studies suggests some carcinogens exhibit a nonlinear response and carcinogenesis is not anticipated below certain levels of exposure (Whittaker et al., 2016). Nevertheless, most carcinogens have no known safe exposure level and risk management based on this notion is recommended (Whittaker et al., 2016).

Chemicals were screened for carcinogenicity using the International Agency for Research on Cancer (IARC) Monographs on the Evaluation of Carcinogenic Risks to Humans, the U.S. Department of Health and Human Services National Toxicity Program 14th Report on Carcinogens, and California's Proposition 65 List (California Environmental Protection Agency, 2018; International Agency for Research on Cancer (IARC), 2018; U.S. Department of Health and Human Services, 2016).

Chemicals on the Proposition 65 List are either listed as causing cancer or reproductive toxicity (California Environmental Protection Agency, 2018). The National Toxicity Program 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). The IARC system categorizes chemicals into 5 groups (International Agency for Research on Cancer (IARC), 2018):

Group 1: Carcinogenic to humans

Group 2A: Probably carcinogenic to humans

Group 2B: Possibly carcinogenic to humans

Group 3: Not classifiable as to its carcinogenicity to humans

Group 4: Probably not carcinogenic to humans

In this study, only chemicals in IARC Group 1, 2A, and 2B are considered carcinogenic.

Overall, 23 (6%) chemicals with CASRN were identified on cancer screening lists, of which 14 were used in the City of LA. A total of 18 chemicals were classified by IARC as Group 1, 2A, or 2B and 17 additional chemicals were classified as Group 3 but are not listed in Table 12. 19 chemicals were on California's Prop 65 list, with 4 being listed for reproductive toxicity. One chemical, crystalline silica (tridymite) (CASRN: 15468-32-3), was classified as a known carcinogen by the National Toxicity Program and was on the Prop 65 list but was not classified by the IARC. The IARC only classified the quartz and cristobalite forms of crystalline silica; tridymite, while mentioned in monographs, was not given an IARC group classification (International Agency for Research on Cancer (IARC), 2012).

Table 12. Chemicals recognized as carcinogenic or possibly carcinogenic by IARC, CA Prop 65, and National Toxicity Program for the entire SCAQMD dataset.

Chemical Name	CASRN	Used in City of LA	IARC Group[1]	National Toxicity Program	Prop 65 List
Ethylene oxide	75-21-8		1	Known	X
Crystalline silica (cristobalite)	14464-46-1	X	1	Known	X
Crystalline silica (quartz)	14808-60-7	X	1	Known	X
Ethanol	64-17-5	X	1	Known	X
Hydrochloric acid	7647-01-0	X	1[1]		
Sulfuric acid	7664-93-9	X	1[1]	Known	X
Formaldehyde	50-00-0	X	1	Known	X
Benzene	71-43-2		1	Known	X
Magnesium nitrate	10377-60-3		2A[2]		
Acrylamide	79-06-1		2A	RAHC	X
Methyl isobutyl ketone	108-10-1		2B		X
Diethanolamine	111-42-2		2B		X
Naphthalene	91-20-3	X	2B	RAHC	X
Ethylbenzene	100-41-4	X	2B		X
Cumene	98-82-8	X	2B	RAHC	X
Gilsonite	12002-43-6		2B		
Nitrilotriacetic acid	139-13-9	X	2B	RAHC	X
Bis(isopropyl)naphthalene	38640-62-9		2B		
Ethylene glycol	107-21-1	X			X[3]
Methanol	67-56-1	X			X[3]
Crystalline silica (tridymite)	15468-32-3	X		Known[4]	X[4]
Lithium carbonate	554-13-2				X[3]
Toluene	108-88-3	X	3		X[3]

1. Listed as acid mist, strong inorganic
2. Listed as nitrate or nitrite under conditions that result in endogenous nitrosation
3. Listed for developmental toxicity
4. Listed as silica, crystalline (airborne particles of respirable size)

4.4.4. Air Pollutants

Air pollutants pose a health risk to both oil and gas workers and residents living nearby active well sites. Chemicals were screened for air pollutants using the Clean Air Act List of Hazardous Air Pollutants, California Air Resources Board Hot Spots Program, and California Air Resources Board Toxic Air Contaminants (TAC) lists (42 C.F.R. §7412, 1990; California Air Resources Board, 2010, 2007).

The Clean Air Act identifies 170 individual chemicals and 17 major chemical categories as hazardous air pollutants. These chemical categories include fine mineral fibers, glycol ethers, polycyclic organic matter (POM), cyanide compounds, and various metal compounds. Polycyclic organic matter (POM) is broad category defined as any organic compound that contains more than one benzene ring and has a boiling point greater than 100°C (42 C.F.R. §7412, 1990), and includes polycyclic aromatic hydrocarbons (PAHs). POM is generally emitted through fuel combustion processes or the direct volatilization of compounds (U.S. EPA, 1998). Glycol ethers is another broad category that consists of mono- and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol with the general formula $R\text{-}(OCH_2CH_2)_n\text{-}OR'$, where (65 FR 47342, 2000):

n = 1, 2, or 3

R = alkyl C7 or less; or phenyl or alkyl substituted phenyl;

R' = H or alkyl C7 or less; or OR' consisting of carboxylic acid ester, sulfate, phosphate, nitrate, or sulfonate

The California Air Resources Board defines toxic air contaminants (TACs) as any air pollutant that may pose a potential hazard to human health or cause an increase in serious illness or mortality. TACs includes all hazardous air pollutants and are divided into categories including (California Air Resources Board, 2010):

Category 1: Substances identified as Toxic Air Contaminants, known to be emitted in California, with a full set of health values

Category 2a: Substances identified as Toxic Air Contaminants, known to be emitted in California, with one or more health values under development

Category 2b: Substances NOT identified as Toxic Air Contaminants, known to be emitted in California, with one or more health values under development

Category 3: Substances known to be emitted in California and are NOMINATED for development of health values or additional health values.

Category 4a: Substance identified as Toxic Air Contaminants, known to be emitted in California and are to be evaluated for entry into Category 3.

Category 4b: Substance NOT identified as Toxic Air Contaminants, known to be emitted in California and are to be evaluated for entry into Category

Category 5: Substance identified as Toxic Air Contaminants, and NOT KNOWN TO BE EMITTED from stationary source facilities in California

Overall, 40 (12%) chemicals were identified on air pollution screening lists, of which 24 were used in the City of LA (Table 13). A total of 22 chemicals were identified as Clean Air Act hazardous air pollutants, half of which were reported as used in the City of Los Angeles. Thirty-eight chemicals were identified on the TAC list, however, 12 fell under categories 2b or 4b and, while not classified as toxic air contaminants, are under review or have health values under development. Three chemicals meet the criteria for POM; however, EPISuite™ was used to estimate boiling point data for two of them. Two additional chemicals may possibly be considered POM due to their chemical structures; however, boiling point data was unavailable for further classification. These chemicals include naphthalenesulfonate-formaldehyde condensate, sodium salt (CASRN: 9008-63-3) and sodium polynaphthalenesulfonate (CASRN: 9084-06-4).

Table 13. Chemicals identified as toxic air contaminants by the U.S. EPA Clean Air Act and California Air Resources Board for the entire SCAQMD dataset.

Chemical Name	CASRN	Used in City of LA	Clean Air Act Hazardous Air Pollutant	California Air Resources Board Hot Spots Program	California Air Resources Board TAC Category
Ethylene oxide	75-21-8		X	X	2a
2-Butoxyethanol	111-76-2	X	[1]	X	2a
Diethanolamine	111-42-2		X	X	2a
Ethylene glycol	107-21-1	X	X	X	2a
Hydrochloric acid	7647-01-0	X	X	X	2a
Hydrofluoric acid	7664-39-3	X	X	X	2a
Methanol	67-56-1	X	X	X	2a
Naphthalene	91-20-3	X	X	X	2a
Ethylbenzene	100-41-4	X	X	X	2a
Toluene	108-88-3	X	X	X	2a
Xylenes	1330-20-7	X	X	X	2a
Formaldehyde	50-00-0	X	X	X	2a
Acrylamide	79-06-1		X	X	2a
Benzene	71-43-2		X	X	2a
Diisopropylnaphthalenesulfonic acid	28757-00-8		X[2]	X[2]	2a[2]
Bis(isopropyl)naphthalene	38640-62-9		X[3]	X[3]	2a[3]
Naphthalenesulfonic acid, bis(1-methylethyl)-, compd. with cyclohexanamine (1:1)	68425-61-6		X[3]	X[3]	2a[3]
Diethylene glycol mono-n-butyl ether	112-34-5		X[4]	X[4]	2a[4]
2,2''-oxydiethanol (impurity)	111-46-6		X[4]	X[4]	2a[4]
Glutaraldehyde	111-30-8	X		X	2b
Isopropanol	67-63-0	X		X	2b
Sodium hydroxide	1310-73-2	X		X	2b
Sulfuric acid	7664-93-9	X		X	2b

Chemical Name	**CASRN**	**Used in City of LA**	**Clean Air Act Hazardous Air Pollutant**	**California Air Resources Board Hot Spots Program**	**California Air Resources Board TAC Category**
Phosphoric acid	7664-38-2	X		X	2b
Non-crystalline silica (impurity)	7631-86-9	X			3
Methyl isobutyl ketone	108-10-1		X	X	4a
Cumene	98-82-8	X	X	X	4a
Acetophenone	98-86-2		X	X	4a
1,2,4-Trimethylbenzene	95-63-6	X		X	4b
Ammonium sulfate	7783-20-2	X		X	4b
Peracetic acid	79-21-0			X	4b
n-Butyl alcohol	71-36-3			X	4b
Aluminum oxide	1344-28-1	X		X	4b
Nitrilotriacetic acid	139-13-9	X		X	4b
Aluminum	7429-90-5	X		X	4b
Quinoline	91-22-5	X	X		5
1-Methoxy-2-propanol	107-98-2	X		X	
Tributyl phosphate	126-73-8			X	
Cyclohexanol	108-93-0			X	
Trimethylbenzenes	25551-13-7			X	

1. 2-butoxyethanol was removed from the list of hazardous air pollutants in November, 2004
2. Listed as polycyclic organic matter (POM)
3. Listed as polycyclic organic matter (POM), boiling point estimated using U.S. EPA EPISuite™ MPBPWIN™ module
4. Listed as glycol ethers

4.4.5. Other Priority Lists

Chemicals were screened using other priority lists including the European Union (EU) Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Substances of Very High Concern (SVHC) Candidate List, Authorization List, Restricted Substances List, and the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) Priority Action Chemical List, Substances of Possible Concern List, and the Norway and UK National Lists of Candidates for Substitution.

Overall, 6 chemicals (~2%) were identified on the OSPAR Substance of Possible Concern List and the EU REACH SVHC Candidate List (Table 14). Only one of these chemicals was used in events in the City of Los Angeles. Chemicals are typically placed on the SVHC list if they are classified as persistent, bioaccumulative, and toxic, or very persistent and very bioaccumulative (PBT/vPvB), or if they are identified as a carcinogen, reproductive mutagen, or endocrine disruptor (European Chemicals Agency, 2015). Chemicals are selected for OSPARs Substances of Possible Concern list for reasons similar to those of the EU SVHC list. None of the chemicals identified by CASRN appeared on the EU REACH SVHC Authorization List, Restricted Substances List, or the OSPAR Priority Action Chemical List or the Norway and UK National Lists of Candidates for Substitution.

Table 14. Chemicals identified on national and international priority lists for the entire SCAQMD dataset.

Chemical Name	CASRN	OSPAR Substance of Possible Concern	EU Candidate List of Substances of Very High Concern Candidate List	Used in City of LA
Poly(oxy-1,2-ethandiyl), a-(nonylphenyl)-w-hydroxy-	9016-45-9	X		X
Bis(isopropyl)naphthalene	38640-62-9	X		
Boric acid	10043-35-3		X	
Sodium tetraborate decahydrate	1303-96-4		X	
Boron sodium oxide	1330-43-4		X	
Acrylamide	79-06-1		X	

4.5. Estimated Hazard Metric

To aid in organizing and ranking the chemicals by potential hazard, we used an estimated hazard metric (EHM) was used. The estimated hazard metric (EHM) was developed by CCST in their Independent Scientific Assessment of Well Stimulation in California to rank chemicals used in well stimulation operations in terms of potential impacts on human health (Shonkoff et al., 2015). The EHM is a semi-quantitative value, where higher values indicate higher concern, and takes into account “frequency of use, mass or mass fraction used per treatment, and acute and/or chronic health hazard criteria” (Shonkoff et al., 2015) according to the following equation:

$$EHM = (\textit{frequency of use}) \times (\textit{mass or mass fraction used})/(\textit{toxicity criterion}) \qquad \text{Eq. 1}$$

This allows for chemicals with moderate or low toxicity to be ranked higher than highly toxic chemicals if they are used with enough frequency and in high enough concentrations.

Frequency of use was determined by the total number of events the chemical was reported as being used in. Mass or mass fraction used was calculated using the median mass reported for each chemical across all events. Both frequency of use and median mass data were used as surrogates for potential release and subsequent exposure (Shonkoff et al., 2015).

For acute inhalation toxicity, the toxicity criterion was calculated using GHS categories. LC_{50} values for acute inhalation toxicity cannot be directly used due to the differences in scale between vapors, dusts, and gasses (see Table 2). Instead, GHS categories are used to first normalize the differences in toxicity based on exposure. However, because GHS categories are not linear in nature, GHS categories 1, 2, 3, and 4 were then assigned the mid-point exposure toxicity criteria of 0.25, 1.25, 6, and 15 mg/L, respectively, to more accurately reflect the relative hazard posed. Vapors, dusts, and gases were assigned the same mid-point exposure toxicity criteria to make the results directly comparable to another. Chemicals categorized as ">GHS 4" were considered non-toxic and were not evaluated according to EHM. The most conservative (i.e. lowest) toxicity values were used for acute inhalation EHM calculations.

For chronic inhalation toxicity, standard non-cancer reference concentrations (RfC, REL, MRL) and inhalation unit risk (UR) and unit risk estimates (UREs) were all standardized to mg/m^3 and this inhalation reference value (RfV) was used as the toxicity criterion. When no other chronic inhalation data were available, occupational exposure limits (PEL, TLV, and NIOSH REL) were standardized to an occupational reference value and used to calculate EHM.

Estimated hazard metric was calculated for all chemicals with acute and chronic inhalation data for both the entire SCAQMD dataset and for the subset of events that occurred in the City of Los Angeles. EHM values for chronic inhalation ranged from the order of magnitude of 10^9 to 10^{-1} for the entire SCAQMD dataset, and from 10^8 to 10^{-1} for the subset of events that occurred in the City of LA. EHM values for acute inhalation ranged from order of magnitude of 10^5 to 10^{-4} for the entire SCAQMD dataset, and from 10^4 to 10^{-3} for the subset of events that occurred in the City of LA.. Chemicals with higher relative EHM values are associated with higher concern (Shonkoff et al., 2015). Although EHM values were higher for the chronic inhalation route, they cannot and should not be directly compared to one another due to the differences in calculating the toxicity criteria. Complete lists of EHM values for both chronic and acute inhalation for the subset of events that occurred in the City of LA can be found in Table 15 and Table 16 respectively. EHM calculations for the entire SCAQMD dataset can be found in Appendix A, Tables A.9 and A.10.

The chemicals with the highest EHM values for both chronic and acute inhalation include hydrofluoric acids, hydrochloric acid, naphthalene, glutaraldehyde, and various silica-based compounds. Hydrochloric and hydrofluoric acid rank high using EHM due to the predominance of maintenance acidizing events in the SCAQMD dataset, as they were used in 1,030 and 835 events (72 and 54 events within the City of LA), respectively. Glutaraldehyde is a commonly used biocide in the oil and gas industry to control bacterial growth and prevent fouling, and although it was only used in 285 events (25 events within the City of LA), it has one of the lowest (i.e. most toxic) chronic inhalation reference value of all chemicals in the SCAQMD dataset. EHM rankings for chemicals used in City of LA events are overall very similar to rankings for the entire SCAQMD dataset.

A significant number of chemicals with high chronic inhalation EHM are minerals and other inorganic compounds that are used in extremely high masses as cement additives, components of gravel packing, or for other uses in a variety of activities. While not particularly toxic, these compounds are expected to pose an inhalation hazard primarily due to airborne particles and respirable dust.

Out of the 41 unique chemicals that make up the top 25 EHM values for both chronic and acute inhalation toxicity for the entire SCAQMD dataset, only 7 are used in a single type of event (Table 17 and Table 18). It is far more common for a chemical to be used in 4 or 5 different event types. This can be accounted for by the fact that frequency of use plays a key role in EHM calculations, and chemicals that are used in multiple types of events are used more frequently and are subsequently given higher EHMs.

Table 15. Estimated hazard metric for chronic inhalation toxicity for chemicals used in events within the City of LA.

Chemical Name	CASRN	Frequency of use (wells)	Median Mass Used (lbs)	RfV (mg/m^3)	EHM
Crystalline silica (quartz)	14808-60-7	44	19350.00	3.00E-03	2.84E+08
Hydrochloric acid	7647-01-0	72	17639.73	9.00E-03	1.41E+08
Glutaraldehyde	111-30-8	25	187.85	8.00E-05	5.87E+07
Hydrofluoric acid	7664-39-3	54	13755.00	1.40E-02	5.31E+07
Portland cement	65997-15-1	25	70674.00	5.95E-02	2.97E+07
Phosphogypsum	13397-24-5	26	62162.20	5.95E-02	2.72E+07
Limestone	1317-65-3	24	61372.60	5.95E-02	2.48E+07
Formic acid	64-18-6	1	5040.00	3.00E-04	1.68E+07
Calcium oxide	1305-78-8	28	12200.00	2.38E-02	1.44E+07
Mica	12001-26-2	6	48200.00	3.57E-02	8.10E+06
Naphthalene	91-20-3	32	68.00	2.94E-04	7.40E+06
Barite	7727-43-7	15	23000.00	5.95E-02	5.80E+06
Magnesium oxide	1309-48-4	25	20086.00	1.19E-01	4.22E+06
Non-crystalline silica (impurity)	7631-86-9	29	9345.00	7.14E-02	3.80E+06
Aluminum oxide	1344-28-1	28	5735.00	5.95E-02	2.70E+06
Iron oxide	1309-37-1	28	5402.00	5.95E-02	2.54E+06
Ethylbenzene	100-41-4	35	282.10	4.00E-03	2.47E+06
Formaldehyde	50-00-0	45	74.00	1.66E-03	2.01E+06

Chemical Name	CASRN	Frequency of use (wells)	Median Mass Used (lbs)	RfV (mg/m^3)	EHM
Crystalline silica (cristobalite)	14464-46-1	4	1057.50	3.00E-03	1.41E+06
Nitrilotriacetic acid	139-13-9	12	690.00	6.66E-03	1.24E+06
Ammonium chloride	12125-02-9	65	1500.00	1.19E-01	8.19E+05
Crystalline silica (tridymite)	15468-32-3	9	168.00	3.00E-03	5.04E+05
Phosphoric acid	7664-38-2	7	294.00	7.00E-03	2.94E+05
2-Butoxyethanol	111-76-2	54	352.73	8.20E-02	2.32E+05
Propargyl alcohol	107-19-7	59	74.00	2.38E-02	1.83E+05
Potassium hydroxide	1310-58-3	1	1800.00	2.38E-02	7.56E+04
Cellulose, microcrystalline	9004-34-6	5	850.00	5.95E-02	7.14E+04
1,2,4-Trimethylbenzene	95-63-6	5	676.50	6.00E-02	5.64E+04
Acetic acid	64-19-7	26	613.25	2.98E-01	5.36E+04
Aluminum	7429-90-5	5	39.00	5.00E-03	3.90E+04
Xylenes	1330-20-7	35	707.90	7.00E-01	3.54E+04
1,3,5-Trimethylbenzene	108-67-8	3	159.10	6.00E-02	7.96E+03
Solvent naphtha, petroleum, light arom.	64742-95-6	6	130.70	1.00E-01	7.84E+03
Sodium hydroxide	1310-73-2	3	53.00	2.38E-02	6.68E+03
1,2,3-Trimethylbenzene	526-73-8	3	65.30	6.00E-02	3.27E+03
Methanol	67-56-1	98	110.55	4.00E+00	2.71E+03
Toluene	108-88-3	20	35.63	3.00E-01	2.38E+03
Sulfuric acid	7664-93-9	1	2.00	1.00E-03	2.00E+03
Cumene	98-82-8	12	64.00	4.00E-01	1.92E+03
Ethylene glycol	107-21-1	1	25.00	4.00E-01	6.25E+01
Calcium sulfate	7778-18-9	1	2.50	5.95E-02	4.20E+01
Acetone	67-64-1	3	22.00	3.08E+01	2.14E+00
Ethanol	64-17-5	4	8.32	2.26E+01	1.47E+00
Isopropanol	67-63-0	4	2.25	7.00E+00	1.28E+00
1-Methoxy-2-propanol	107-98-2	4	1.66	7.00E+00	9.51E-01

Table 16. Estimated hazard metric for acute inhalation toxicity for chemicals used in events within the City of LA.

Chemical Name	CASRN	Frequency of use (wells)	Median Mass Used (lbs)	Acute Toxicity Criteria	EHM
Hydrofluoric acid	7664-39-3	54	13755.00	25	2.97E+04
Hydrochloric acid	7647-01-0	72	17639.73	200	6.35E+03
Potassium chloride	7447-40-7	34	25179.00	200	4.28E+03
Glutaraldehyde	111-30-8	25	187.85	2.5	1.88E+03
Naphthalene	91-20-3	32	68.00	2.5	8.70E+02
Phosphoric acid	7664-38-2	7	294.00	2.5	8.23E+02
Non-crystalline silica (impurity)	7631-86-9	29	9345.00	1150	2.36E+02
Formaldehyde	50-00-0	45	74.00	25	1.33E+02
Glyoxal	107-22-2	24	1025.00	200	1.23E+02
Glycolic acid	79-14-1	3	98.00	2.5	1.18E+02
2-Butoxyethanol	111-76-2	54	352.73	200	9.52E+01
Hydrotreated Light Petroleum Distillate	64742-47-8	26	277.00	200	3.60E+01
Formic acid	64-18-6	1	5040.00	200	2.52E+01
Propargyl alcohol	107-19-7	59	74.00	200	2.18E+01
Xylenes	1330-20-7	35	707.90	1150	2.15E+01
2-Ethylhexan-1-ol	104-76-7	4	84.50	25	1.35E+01
Sodium carbonate	497-19-8	23	600.00	1150	1.20E+01
Ethylbenzene	100-41-4	35	282.10	1150	8.59E+00
1,2,4-Trimethylbenzene	95-63-6	5	676.50	1150	2.94E+00
Solvent naphtha, petroleum, light arom.	64742-95-6	6	130.70	1150	6.82E-01
Cumene	98-82-8	12	64.00	1150	6.68E-01
Triethylene glycol	112-27-6	1	18.52	200	9.26E-02
Sulfuric acid	7664-93-9	1	2.00	25	8.00E-02
1-Methoxy-2-propanol	107-98-2	4	1.66	1150	5.79E-03

Table 17. Chemicals with the highest estimated hazard metric for chronic inhalation toxicity within the entire SCAQMD dataset and the factors that contributed most to their rankings (from high EHM to low).

Chemical Name	CASRN	Frequency of use	Median mass usage	Chronic Inhalation Screening Value	Rankings for only events in the City of LA	Event Type(s) Reported as Used in
Crystalline silica (quartz)[1]	14808-60-7	X	X		1	Hydraulic fracturing, gravel packing, maintenance acidizing, acidizing, well drilling, well completion & rework
Hydrochloric acid	7647-01-0	X	X		2	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing, well completion & rework
Calcium oxide	1305-78-8		X	[3]	9	Gravel packing, maintenance acidizing, well drilling
Hydrofluoric acid	7664-39-3	X	X		4	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing, well completion & rework
Glutaraldehyde	111-30-8			X	3	Hydraulic fracturing, gravel packing, maintenance acidizing, well drilling, well completion & rework
Portland cement	65997-15-1		X	[4]	5	Gravel packing, maintenance acidizing, well drilling, well completion & rework
Phosphogypsum	13397-24-5		X	[4]	6	Gravel packing, maintenance acidizing, well drilling, well completion & rework
Mica	12001-26-2		X	[3]	10	Gravel packing, maintenance acidizing, well drilling, well completion & rework
Limestone	1317-65-3		X	[4]	7	Gravel packing, maintenance acidizing, well drilling, well completion & rework
Barite	7727-43-7		X	[4]	12	Gravel packing, maintenance acidizing, well drilling, well completion & rework
Naphthalene	91-20-3	X		X	11	Gravel packing, maintenance acidizing, acidizing, well drilling
Magnesium oxide	1309-48-4		X	[3]	13	Gravel packing, maintenance acidizing, well drilling, well completion & rework
Formaldehyde	50-00-0	X		X	18	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing, well completion & rework
Mullite[2]	1302-93-8		X			Gravel packing, well drilling
Boron sodium oxide	1330-43-4		X	[3]		Hydraulic fracturing, well drilling

Chemical Name	CASRN	Frequency of use	Median mass usage	Chronic Inhalation Screening Value	Rankings for only events in the City of LA	Event Type(s) Reported as Used in
Aluminum oxide	1344-28-1		X	[4]	15	Gravel packing, maintenance acidizing, well drilling, well completion & rework
Iron oxide	1309-37-1		X	[4]	16	Gravel packing, maintenance acidizing, well drilling, well completion & rework
Ethylbenzene	100-41-4	X		X	17	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing
Ammonium chloride	12125-02-9	X	X	[3]	21	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing, well completion & rework
Formic acid	64-18-6			X	8	Maintenance acidizing, acidizing,
Tetrasodium pyrophosphate	7722-88-5		X	[3]		Gravel packing, well drilling
Propargyl alcohol	107-19-7	X		[3]	25	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing, well completion & rework
Phosphoric acid	7664-38-2		X	X	23	Gravel packing, maintenance acidizing, well drilling, well completion & rework
Cellulose, microcrystalline	9004-34-6		X	[4]	27	Gravel packing, maintenance acidizing, well drilling
Nitrilotriacetic acid	139-13-9		X	X	20	Maintenance acidizing, acidizing, well completion & rework
2-Butoxyethanol	111-76-2	X			24	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing, well completion & rework

1. To reduce redundancy, all other forms of silica that fell in the top 25 for EHM were excluded. These forms included Crystalline silica (cristobalite) CASRN: 14464-46-1 (ranked 14^{th} [19^{th} for City of LA]), Non-crystalline silica (impurity) CASRN:7631-86-9 (ranked 16^{th} [14^{th} for City of LA].
2. Crystalline silica (quartz) (CASRN: 14808-60-7) was used as reference chemical for chronic inhalation hazard screening
3. Chronic inhalation screening value calculated using occupational exposure limits
4. Chronic inhalation screening value calculated using occupational exposure limits (as respirable dust)

Table 18. Chemicals with the highest estimated hazard metric for acute inhalation toxicity within the entire SCAQMD dataset and the factors that contributed most to their rankings (from high EHM to low).

Chemical Name	CASRN	Frequency of use	Median mass usage	Acute Inhalation Screening Value	Rankings for only events in the City of LA	Event Type(s) Reported as Used in
Hydrofluoric acid	7664-39-3	X	X	X	1	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing, well completion & rework
Hydrochloric acid	7647-01-0	X	X		2	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing, well completion & rework
Potassium chloride	7447-40-7	X	X		3	Gravel packing, maintenance acidizing, acidizing, well drilling, well completion & rework
Petroleum distillates	64741-44-2		X			Well drilling
Naphthalene	91-20-3	X		X[1]	5	Gravel packing, maintenance acidizing, acidizing, well drilling
Glutaraldehyde	111-30-8	X		X	4	Hydraulic fracturing, gravel packing, maintenance acidizing, well drilling, well completion & rework
Phosphoric acid	7664-38-2		X	X	6	Gravel packing, maintenance acidizing, well drilling, well completion & rework
Formaldehyde	50-00-0	X			8	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing, well completion & rework
Non-crystalline silica (impurity)	7631-86-9		X	[1]	7	Hydraulic fracturing, gravel packing, maintenance acidizing, acidizing, well drilling, well completion & rework
Glyoxal	107-22-2	X	X		9	Hydraulic fracturing, gravel packing, maintenance acidizing, well drilling
Boric acid	10043-35-3			X[1]		Hydraulic fracturing, gravel packing, well drilling

Chemical Name	CASRN	Frequency of use	Median mass usage	Acute Inhalation Screening Value	Rankings for only events in the City of LA	Event Type(s) Reported as Used in
Paraffinic petroleum distillate, hydrotreated light	64742-55-8		X			Hydraulic fracturing
Propargyl alcohol	107-19-7	X			14	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing, well completion & rework
2-Butoxyethanol	111-76-2	X			11	Gravel packing, maintenance acidizing, acidizing, well drilling, matrix acidizing, well completion & rework
Thioglycolic acid	68-11-1			X		Acidizing
Boron sodium oxide	1330-43-4		X	[1]		Hydraulic fracturing, well drilling
2-Ethylhexan-1-ol	104-76-7			X[1]	16	Maintenance acidizing, acidizing, well drilling, well completion & rework
Sodium carbonate	497-19-8		X	[1]	17	Gravel packing, maintenance acidizing, acidizing, well drilling, well completion & rework
Hydrotreated light petroleum distillate	64742-47-8	X		[1]	12	Hydraulic fracturing, gravel packing, maintenance acidizing, acidizing, well drilling, well completion & rework
Hexylene glycol	107-41-5		X	X		Well completion & rework
Glycolic acid	79-14-1			X	10	Maintenance acidizing
2,2 Dibromo-3-nitrilopropionamide	10222-01-2			X		Hydraulic fracturing, gravel packing
Lithium hydroxide	1310-65-2		X			Well drilling
Mullite	1302-93-8		X	[1]		Gravel packing, well drilling
Peracetic acid	79-21-0			X		Maintenance acidizing

1. Acute inhalation screening value calculated using "floor level" toxicity estimate

4.5.1. Potential Chemicals of Concern

Potential chemicals of concern were identified using EHM and various screening list. In this study, the major criteria for being considered a chemical of concern is being ranked in the top 10 for acute or chronic inhalation EHM, being a known toxic air contaminant, OR being a known carcinogen.

Additional information concerning volatility and biodegradability is provided to assist with evaluating risk. As discussed previously, readily biodegradable chemicals are expected to rapidly degrade when released in the environment, reducing the risk of human exposure. Volatile chemicals, as determined by vapor pressure or boiling point, are expected to readily evaporate (or sublimate) and have a higher risk of inhalation exposure. The definition of a volatile chemical varies between regulatory and governmental agencies (Brandt et al., 2015). The U.S. EPA defines volatile organic compounds (VOCs) as organic chemicals that have vapor pressure greater than 1 Torr (~1mm Hg) at 25°C and 760 mm Hg (U.S. EPA, 1999). The European Union defines VOCs as having a boiling point of less than or equal to 250°C under standard atmospheric conditions (European Union, 2004). Chemicals that met either one of these requirements were classified as volatile.

56 potential chemicals of concern are listed in Table 19, of which 36 were used in events in the City of LA. Chemicals that are identified as hazardous air pollutants, carcinogens, and volatile compounds are of high concern, with those meeting several of these requirements being of the highest concern. However, many chemicals that meet these standards are also readily biodegradable and as a result have a reduced risk of human exposure. Only 4 chemicals in Table 16 were classified as not readily biodegradable and 1 chemical had inadequate biodegradability data; the remaining 51 chemicals are considered biodegradable or inorganic.

As previously mentioned, inorganic minerals and oxides used extensively in well drilling and gravel packing are of particular concern due to their high median mass usage and frequency of use. The mixing, handling, and use of these chemicals can release respirable particulates that (in the case of silica compounds) are known to cause cancer.

Based on available data concerning inhalation toxicity, occupational exposure limits, air pollutant screening lists, and volatility, a total of 72 chemicals used in the City of LA were identified as having the potential for travel by air and subsequent inhalation exposure (Table 20). Chemicals that were considered volatile according to U.S. EPA or EU standards, that were on any air pollution screening lists, or that had any available inhalation toxicity data (acute, chronic, sub-chronic, occupational, etc.) were included in Table 20. This is a conservative estimate due to data gaps regarding chemical volatility and the particle sizes of chemicals used. It is important to note that depending on operational and atmospheric conditions (e.g. well blow-out, high wind speeds, height of release, particle size, etc), almost any chemical has the potential to travel by air and present an inhalation exposure risk.

Table 19. Potential chemicals of concern based on EHM and available air pollutant and carcinogenicity data. This list currently contains the top 10 for Acute and Chronic EHM rankings, along with most air pollutants and carcinogens within the entire SCAQMD dataset. Listed in alphabetical order starting with chemicals used in the City of LA.

Chemical Name	CASRN	Acute Inhalation EHM Rank	Chronic Inhalation EHM Rank	Known Air Pollutant	Known or Probable Carcinogen	Volatile Compound	Biodegradability	Used in City of LA
1,2,4-Trimethylbenzene	95-63-6	36	41	X[1]		X	Readily biodegradable	X
1-Methoxy-2-propanol	107-98-2	43	72	X[1]		X	Readily biodegradable	X
2-Butoxyethanol	111-76-2	14	29	X[1]		X	Readily Biodegradable	X
Aluminum	7429-90-5		30	X[1]			Inorganic	X
Aluminum oxide	1344-28-1		18	X[1]			Inorganic	X
Ammonium sulfate	7783-20-2			X[1]			Inorganic	X
Barite	7727-43-7		10				Inorganic	X
Calcium oxide	1305-78-8		3				Inorganic	X
Crystalline silica (cristobalite)	14464-46-1		14		X		Inorganic	X
Crystalline silica (quartz)	14808-60-7		1		X		Inorganic	X
Crystalline silica (tridymite)	15468-32-3		27		X		Inorganic	X
Cumene	98-82-8	30	43	X	X	X	Readily Biodegradable	X
Ethanol	64-17-5		69		X	X	Readily Biodegradable	X
Ethylbenzene	100-41-4	28	20	X	X	X	Readily Biodegradable	X
Ethylene glycol	107-21-1		53	X	X[2]	X	Readily Biodegradable	X
Formaldehyde	50-00-0	8	13	X	X	X	Readily biodegradable	X

Chemical Name	CASRN	Acute Inhalation EHM Rank	Chronic Inhalation EHM Rank	Known Air Pollutant	Known or Probable Carcinogen	Volatile Compound	Biodegradability	Used in City of LA
Glutaraldehyde	111-30-8	6	5	X[1]		X	Readily Biodegradable	X
Glyoxal	107-22-2	10				X	Readily Biodegradable	X
Hydrochloric acid	7647-01-0	2	2	X	X	X	Inorganic	X
Hydrofluoric acid	7664-39-3	1	4	X		X	Inorganic	X
Isopropanol	67-63-0		70	X[1]		X	Readily Biodegradable	X
Limestone	1317-65-3		9				Inorganic	X
Methanol	67-56-1		49	X	X[2]	X	Readily Biodegradable	X
Mica	12001-26-2		8				Inorganic	X
Naphthalene	91-20-3	5[3]	11	X	X	X	Inherently biodegradable	X
Nitrilotriacetic acid	139-13-9		28	X[1]	X		Readily biodegradable	X
Non-crystalline silica (impurity)	7631-86-9	9[3]	16	X			Inorganic	X
Phosphogypsum	13397-24-5		7				Inorganic	X
Phosphoric acid	7664-38-2	7[3]	25	X[1]			Inorganic	X
Portland cement	65997-15-1		6				Inorganic	X
Potassium chloride	7447-40-7	3					Inorganic	X
Quinoline	91-22-5			X		X	Not readily biodegradable	X
Sodium hydroxide	1310-73-2		37	X[1]			Inorganic	X
Sulfuric acid	7664-93-9	39	46	X[1]	X		Inorganic	X

Chemical Name	CASRN	Acute Inhalation EHM Rank	Chronic Inhalation EHM Rank	Known Air Pollutant	Known or Probable Carcinogen	Volatile Compound	Biodegradability	Used in City of LA
Toluene	108-88-3		52	X	X[2]	X	Readily Biodegradable	X
Xylenes	1330-20-7	27	42	X		X	Readily Biodegradable	X
2,2"-oxydiethanol (impurity)	111-46-6			X		X	Readily Biodegradable	
Acetophenone	98-86-2			X		X	Readily biodegradable	
Acrylamide	79-06-1	50[3]	38	X	X	X	Readily Biodegradable	
Benzene	71-43-2		45	X	X	X	Readily biodegradable	
Bis(isopropyl)naphthalene	38640-62-9			X	X		Not readily biodegradable	
Cyclohexanol	108-93-0	49[3]	76	X[1]		X	Readily biodegradable	
Diethanolamine	111-42-2		68	X	X		Readily biodegradable	
Diethylene glycol mono-n-butyl ether	112-34-5		36	X		X	Readily biodegradable	
Diisopropylnaphthalenesulfonic acid	28757-00-8			X			Not readily biodegradable	
Ethylene oxide	75-21-8	40	35	X	X	X	Readily biodegradable	
Gilsonite	12002-43-6				X		Inadequate data	
Lithium carbonate	554-13-2	33			X[2]		Inorganic	
Magnesium nitrate	10377-60-3				X		Inorganic	

Chemical Name	CASRN	Acute Inhalation EHM Rank	Chronic Inhalation EHM Rank	Known Air Pollutant	Known or Probable Carcinogen	Volatile Compound	Biodegradability	Used in City of LA
Methyl isobutyl ketone	108-10-1	48	75	X	X	X	Readily Biodegradable	
Naphthalenesulfonic acid, bis(1-methylethyl)-, compd. with cyclohexanamine (1:1)	68425-61-6			X			Not readily biodegradable	
n-Butyl alcohol	71-36-3	46	71	X[1]		X	Readily biodegradable	
Peracetic acid	79-21-0	25		X[1]		X	Readily Biodegradable	
Petroleum distillates	64741-44-2	4				X	Readily Biodegradable	
Tributyl phosphate	126-73-8		58	X[1]			Readily biodegradable	
Trimethylbenzenes	25551-13-7			X[1]		X	Not readily biodegradable	

1. Not identified as Clean Air Act Hazardous Air Pollutants, but on California Air Resources Board TAC and Hot Spots Lists
2. On Prop 65 List for developmental toxicity
3. Acute inhalation EHM calculated using "floor level" toxicity estimate

Table 20. Chemicals used in the City of LA identified as having the potential for travel by air and subsequent inhalation exposure.

Chemical Name	CASRN		Chemical Name	CASRN
1,2,3-Trimethylbenzene	526-73-8		Hydrochloric acid	7647-01-0
1,2,4-Trimethylbenzene	95-63-6		Hydrofluoric acid	7664-39-3
1,3,5-Trimethylbenzene	108-67-8		Hydrotreated Light Petroleum Distillate	64742-47-8
1-Methoxy-2-propanol	107-98-2		Iron oxide	1309-37-1
2-Butoxyethanol	111-76-2		Isopropanol	67-63-0
2-Ethylhexan-1-ol	104-76-7		Isoquinoline	119-65-3
Acetic acid	64-19-7		Isotridecanol, ethoxylated	9043-30-5
Acetone	67-64-1		Limestone	1317-65-3
Alkenes, C>10 a-	64743-02-8		Limonene	138-86-3
Aluminum	7429-90-5		Magnesium oxide	1309-48-4
Aluminum oxide	1344-28-1		Methanol	67-56-1
Ammonium chloride	12125-02-9		Mica	12001-26-2
Ammonium sulfate	7783-20-2		Naphthalene	91-20-3
Barium sulfate	7727-43-7		Nitrilotriacetic acid	139-13-9
Calcium oxide	1305-78-8		Non-crystalline silica (impurity)	7631-86-9
Calcium sulfate	7778-18-9		Octamethylcyclotetrasiloxane	556-67-2
Carbon	7440-44-0		Orange terpenes	68647-72-3
Cellulose, microcrystalline	9004-34-6		Phosphogypsum	13397-24-5
Citrus terpenes	94266-47-4		Phosphoric acid	7664-38-2
Crystalline silica (cristobalite)	14464-46-1		Pine oil	8002-09-3
Crystalline silica (quartz)	14808-60-7		Poly(oxy-1,2-ethandiyl), a-(nonylphenyl)-w-hydroxy-	9016-45-9
Crystalline silica (tridymite)	15468-32-3		Portland cement	65997-15-1
Cumene	98-82-8		Potassium chloride	7447-40-7
Cyclohexasiloxane, 2,2,4,4,6,6,8,8,10,10,12,12-dodecamethyl-	540-97-6		Potassium hydroxide	1310-58-3
Cyclopentasiloxane, 2,2,4,4,6,6,8,8,10,10-decamethyl-	541-02-6		Propargyl alcohol	107-19-7
Dimethyl siloxanes and silicones	63148-62-9		Propylene glycol	57-55-6
Ethanol	64-17-5		Quinaldine	91-63-4
Ethyl octynol	5877-42-9		Quinoline	91-22-5
Ethylbenzene	100-41-4		Sodium carboxymethylcellulose	9004-32-4
Ethylene glycol	107-21-1		Sodium chloride	7647-14-5
Formaldehyde	50-00-0		Sodium hydroxide	1310-73-2
Formic acid	64-18-6		Sodium sulfate	7757-82-6
Glutaraldehyde	111-30-8		Solvent naphtha, petroleum, light arom.	64742-95-6
Glycolic acid	79-14-1		Sulfuric acid	7664-93-9
Glyoxal	107-22-2		Toluene	108-88-3
Heavy aromatic naphtha	64742-94-5		Xylenes	1330-20-7

5.0. Findings, Conclusions, and Recommendations

FCR 1: chemicals of concern are used in upstream oil and gas operations in the City of Los Angeles and in the SCAQMD more generally

Findings: The identity of 324 chemicals used in the SCAQMD were verified, of which 140 were used in events taking place in the City of Los Angeles. Biodegradability data was generally more available with 74% of relevant chemicals being classified according to OECD biodegradability standards. 40 chemicals were identified on air pollution screening lists and 23 chemicals were identified as known or possible carcinogens. When screened against lists of biodegradability, air pollutant and carcinogenic screening lists, a total of 56 chemicals of concern were identified as used in the SCAQMD, of which 36 were used in the City of Los Angeles.

Conclusion: Chemicals of concern pose a risk to nearby residents if environmental and exposure pathways are present (e.g. inhalation). Although some chemicals are clearly of greater concern than others (e.g. highly toxic chemicals used in large quantities that are also air pollutants), chemicals of concern are not explicitly ranked. Additional information regarding environmental profiles, acute and chronic toxicity is needed before a more thorough assessment of risk can be completed. There are no regulations in place to limit the use of chemicals of concern in upstream oil and gas development operations.

Recommendation: Given the findings of toxicological hazard, engineering controls, increased environmental monitoring, and increased minimum surface setbacks between these operations and sensitive receptors should be considered. Furthermore, agencies with jurisdiction may consider the implementation of green chemistry principals to all oil and gas operations to limit risk by reducing the use of hazardous and poorly understood chemicals and replacing hazardous chemicals with less hazardous chemicals.

FCR 2: Events taking place outside the City of Los Angeles may still negatively impact residents within the city

Finding: A total of 1,688 oil and gas events were reported from the period of 2013-2018, with 131 events occurring within the City of LA. Although the majority of oil and gas events reported in the SCAQMD took place outside of the City of LA, specifically in the City of Long Beach, they are located relatively close to City of LA boundaries and there is nothing to prevent more events from occurring within the city. Chemicals used in oil and gas events within the City of LA did not significantly differ from chemicals used outside of the city in terms of type, frequency of use, and median masses used.

Conclusion: The close proximity of oil and gas events occurring outside the City of LA to communities that lie within the city suggest that negative impacts associated with emissions of

TACs and other chemicals from events (particularly in Inglewood and Long Beach) could be transported via air pathways into the City of LA. Furthermore, our analysis of chemical usage across oil fields, event types, and city boundaries revealed significant overlap in chemicals used, regardless of location or oil field, suggesting potential air pollution and inhalation hazards from events outside the City of LA would be similar to those within the city.

Recommendation: Agencies with jurisdiction should consider implementing a uniform and effective plan to reduce exposure to potential inhalation hazards associated with chemical use in oil and gas operations. Operations outside the City of LA should be monitored and subjected to the same regulations as those within the City of LA to prevent negative impacts from airborne hazards migrating across city or jurisdictional boundaries.

FCR 3: Major data gaps regarding chemical identities, properties, and data reliability need to be addressed before a full chemical risk assessment can be completed

Finding: Major data gaps exist regarding the identities of chemicals and associated environmental and toxicological profiles. A total of 327 chemicals reported in the SCAQMD dataset could not be definitively identified by CASRN and were labeled trade secret chemicals. 79% and 77% of chemicals identified by CASRN did not have available acute inhalation toxicity data or chronic inhalation toxicity data, respectively. Furthermore, chemical information that is submitted by operators includes errors, such as incorrect CASRNs, obvious misspellings, and inconsistent data entries. The SCAQMD dataset is maintained as separate event and chemical reporting datasets, which themselves are further divided into the periods before and after September 4th, 2015.

Conclusions: The lack of strict quality control over operator submitted data and the disjointed nature of the SCAQMD dataset hinders analysis of the dataset. Furthermore, major data gaps regarding chemical identities, physical and chemical properties, toxicity, and environmental fate and transport prevent further characterization of chemical hazards and risk. Assessing chemicals for toxicity, biodegradability, and hazard is a vital first step; however, more data is needed before a risk analysis can be completed.

Recommendations: SCAQMD should verify and validate all submitted chemical and mass usage information. Mass, density, concentration, and volume data should be required for all chemical disclosures, including trade secret chemicals, to ensure mass usage data is adequate and verifiable. Data reported to SCAQMD should be compared to and verified against other datasets, including those which are only reported to regulators and not publicly available. SCAQMD should maintain their data as one integrated dataset that combines both event and chemical reporting data from all time periods. SCAQMD should adopt approaches to chemical use reporting similar to SB 4 (Pavley, 2013) but also require operators to disclose all trade secret chemicals for all events associated with oil and gas operations in general and not only for hydraulic fracturing and well stimulation. SCAQMD should continue to work with chemical suppliers to come up with solutions to protecting trade secrets while at the same time encouraging disclosure, such as is exercised under AB 1328 (Limón, 2017). Comprehensive environmental and toxicological profiles should be developed for all oil and gas chemicals that are missing key data such as chronic and acute toxicity and biodegradability and ideally agencies with jurisdiction could consider phasing out the use of chemicals for which toxicological and environmental profiles have not been developed.

FCR 4: Setback distances and other controls may reduce health impacts of events taking place near sensitive receptors

Finding: Of the 1,688 events where chemical use was reported in the SCAQMD, 597 events (106 in the City of LA) were located within 1,500 feet of sensitive receptors such as residences, preschools, K-12 schools, hospitals, and other health care facilities. Of all 131 events reported in the City of LA, 81 events (62%) were within 600 feet of the sensitive receptor.

Conclusion: These events have the potential to negatively impact surrounding populations and should be prioritized for engineering controls and monitoring. The City of Los Angeles currently only has a 200-foot setback requirement for upstream oil and gas development operations which has multiple conditions which can circumnavigate this requirement.

Recommendation: Agencies with jurisdiction should consider the implementation of a larger minimum surface setback between oil and gas development and sensitive receptors to reduce the risk of exposure to chemicals of concern. A minimum surface setback distance should also be accompanied by increased emission control and environmental monitoring appropriate to reported chemical use should be implemented, in particular at locations in close proximity to sensitive receptors.

FCR 5: SCAQMD reporting follows the overall statewide trend of declining well drilling and completion.

Finding: The number of events reported by the SCAQMD has significantly decreased since 2014. This trend is consistent with statewide oil and gas production and with the number of wells drilled and completed statewide over the same period (DOGGR, 2018a).

Conclusion: Overall, California has seen a steady decline in oil and gas production since the mid 1980's. It has been suggested anecdotally that SCAQMD Rule 1148.2 under-reports oil and gas events in its jurisdiction; however, this cannot be determined without a thorough comparison of SCAQMD event submissions and DOGGR records.

Recommendation: A detailed comparison of SCAQMD and DOGGR records is suggested to determine if oil and gas events are accurately reported in the 1148.2 database.

FCR 6: The majority of events reported by SCAQMD are conventional oil and gas operations and data suggests this trend will continue

Finding: Maintenance acidizing, gravel packing, and well drilling account for approximately 83% of reported events that involve the use of chemicals in the SCAQMD. In contrast, well stimulation activities such as hydraulic fracturing, matrix acidizing, and acid fracturing play a minimal role in oil and gas development, accounting for approximately 1% of all events. The distribution of events by activity type has remained relatively consistent throughout the study period.

Conclusion: Despite the decrease in reported events since 2014, the distribution of events by activity type remained relatively consistent, suggesting that maintenance acidizing, gravel packing and well drilling will continue to be the dominant oil and gas activities in the SCAQMD and the City of Los Angeles. An examination of the underlying petroleum geology of the Los Angeles Basin revealed the similarity between the oil producing reservoirs in the region. If new oil fields are developed in the basin, development practices are not expected to significantly differ from past development (CCST et al., 2015b).

Recommendation: Future studies should focus on chemical hazards in routine and conventional oil and gas operations in the SCAQMD. Full disclosure of chemical identities in a manner similar to SB 4 is required for a more thorough understanding of chemical use in oil and gas operations in the City of LA and the Los Angeles Basin.

6.0. References

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