Analysis of Refinery Chemical Emissions and Health Effects

March 2019

Office of Environmental Health Hazard Assessment

California Environmental Protection Agency

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PREFACE

The Office of Environmental Health Hazard Assessment (OEHHA) has collaborated with the California Air Resources Board (CARB) and the Interagency Refinery Task Force to develop information on chemicals emitted from refineries and their health effects. This information can support CARB and other groups in developing plans for air monitoring in the vicinity of refineries in California. In the event of a refinery emergency, knowledge of health guidance values and emissions of chemicals can also help emergency responders characterize potential health effects that may occur following a chemical release.

In August 2012, there was a serious fire at the Chevron Refinery in Richmond, CA. During that event, an estimated 15,000 people from the nearby community sought care at local emergency departments and clinics. Follow-up investigations of the incident revealed a number of refinery safety issues. In July 2013, CARB released a report entitled “Air Monitoring for Accidental Refinery Releases: Assessment of Capabilities and Potential Improvements Project Plan.” This report laid out a stepwise plan to improve California’s refinery air monitoring and emergency response system.

In February 2014, Governor Brown issued a report titled “Improving Public and Worker Safety at Oil Refineries,” which echoed the importance of monitoring air quality near refineries and resulted in the establishment of the Interagency Refinery Task Force coordinated by the California Environmental Protection Agency (CalEPA). In public meetings following the release of the governor’s report, community members asked if a complete list of chemicals that could be released from refineries existed, and if those chemicals had been prioritized for monitoring to ensure that monitoring systems would be tailored—insofar as feasible—to measure the most important chemicals.

As a result of these questions from the public, OEHHA compiled the information in this report. The report presents as comprehensive a list of chemicals as possible using existing data sources, and then prioritizes the chemicals according to their emissions and toxicity. This report does not attempt to estimate exposure or risk in communities.

OEHHA released a draft of this report in September 2017, while CARB concurrently released a draft report titled *Refinery Emergency Air Monitoring Assessment Report. Objective 2: Evaluation of Air Monitoring Capabilities, Gaps and Potential Enhancements.* OEHHA, CARB, and CalEPA participated in a series of workshops throughout California in 2018 to receive feedback on the reports. During the workshops, OEHHA did not receive any comments on its report that necessitated any changes or additions. The final OEHHA report is now being released. This report offers a useful compendium of information to assist local air districts and communities as they make decisions about air monitoring, emergency response, and other efforts related to refinery chemicals and public health.

EXECUTIVE SUMMARY

Introduction

The Office of Environmental Health Hazard Assessment (OEHHA), in collaboration with the California Air Resources Board (CARB) and the California Environmental Protection Agency's (CalEPA) Interagency Refinery Task Force, has developed information on chemicals emitted from refineries, and their health effects. This information may assist CARB, local air districts, and communities in developing plans for air monitoring at refineries in California. In the event of a refinery emergency, this information may also help emergency responders characterize the potential health effects that may occur following a chemical release.

OEHHA has compiled a list of 188 chemicals that have been reported to be emitted from California refineries. This list can assist the CARB in identifying candidate chemicals for potential air monitoring near refineries.

OEHHA created this list of chemicals based on:

- Data on routine releases of toxic air contaminants from California refineries reported to CARB during the years 2009-2012 and 2014.
- Data on routine and non-routine emissions from California refineries reported to the US Environmental Protection Agency (US EPA) as part of a data call-in in 2010.
- Publicly available data in government reports, internet databases, and peer-reviewed journal articles.

The presence of a chemical on this list does not necessarily mean it is released from all refineries, at all times, or in significant quantities. Nor does it indicate the chemical's degree of toxicity.

For these reasons, OEHHA took steps to screen the list of 188 chemicals, based on exposure and toxicity potential.

Comparisons between high routine emissions of chemicals and health guidance values or emergency exposure levels that measure the toxicity of those chemicals may help determine which chemicals are appropriate for air monitoring, and may ultimately help protect communities surrounding these refineries by limiting exposures to those chemicals. To that end, OEHHA has performed some preliminary analyses of the compiled data. Measures of toxicity of individual chemicals included OEHHA's Reference Exposure Levels (RELs), Cancer Potency Factors (CPFs) and Unit Risk Values, No Significant Risk Levels and Maximum Allowable Dose Levels for chemicals on California's Proposition 65 list, and the US Environmental Protection Agency's (US EPA) Reference Concentrations (RfCs). In addition, OEHHA looked at US EPA's Acute Emergency Exposure Guidelines (AEGLs) and the National Institute for Occupational Safety and Health's (NIOSH) Immediately Dangerous to Life and Health (IDLH) values.

These health guidance values and toxicity designations were compared to routine and non-routine (including accidental) emissions from refineries, chemicals involved in previous incidents, and chemicals with involvement in the most refinery equipment or processes. Finally, US EPA toxicity-weighting factors were used in conjunction with routine emissions data to calculate toxicity-weighted emissions scores. The report also provides health and safety information for select candidate chemicals known to be emitted in high quantities from refineries in California, with the understanding that potential health effects are dependent on the extent and duration of exposure.

Toxicity: Health Guidance Values and Toxicity Designations for the General Population

OEHHA and other agencies develop health guidance values for cancer and noncancer endpoints, to guide regulatory agencies like CARB in taking actions that protect the general public from the effects of possible toxic chemical exposures. In general, the health guidance value for an airborne pollutant is the air concentration of the chemical that is not likely to cause adverse health outcomes in humans, including sensitive subgroups, for the specified exposure duration.

After compiling the list of chemicals emitted from California refineries, OEHHA determined which chemicals had health guidance values. Specific types of health guidance values included in our analysis are described below. Any one chemical may have multiple types of health guidance values.

OEHHA determines Reference Exposure Levels (RELs) for airborne chemicals as required by California's Air Toxics 'Hot Spots' Program. The REL assessments identify human systems (e.g. the respiratory system) or organs that could be affected by the noncancer effects of the chemicals. These RELs can cover three types of exposure durations: acute (for infrequent 1-hour exposure), 8-hour (for repeated 8-hour exposures), and chronic (for continuous long-term exposure). OEHHA determined which refinery chemicals from the list of 188 had each of these RELs. OEHHA found that 67 chemicals have at least one REL and some of these have more than one REL. Forty chemicals have an acute REL, 10 have an 8-hour REL, and 62 have a chronic REL. OEHHA found that there are RELs for all the listed chemicals with combined releases of greater than 10,000 pounds per year across all refineries in California.

US EPA also establishes noncancer health guidance values referred to as Reference Concentrations (RfCs) for air contaminants. US EPA RfCs are developed using a different risk assessment methodology, and therefore may be different from OEHHA's RELs. OEHHA identified 48 chemicals found in refinery emissions with RfC values, of which nine do not have RELs. Overall, 109 of the 188 chemicals reported to be released from California refineries were determined to have at least one REL or RfC.

OEHHA develops Cancer Potency Factors (CPF) and Unit Risk Factors (URF) for the Air Toxics 'Hot Spots' program to address the carcinogenic effects of chemicals. These values are applied to measured or modeled airborne chemical concentrations to estimate the cancer risks to an exposed population. Of the 188 refinery chemicals on the list, OEHHA identified 70 chemicals that have CPFs, and 57 that have URFs.

For each chemical in the refinery chemical list, OEHHA noted whether it was also on the Proposition 65 list for cancer or reproductive toxicity. Of the 188 chemicals on the list, 54 are listed under Proposition 65 as carcinogens with No Significant Risk Levels, 21 are listed for developmental effects, and 13 are listed for effects on the male or female reproductive system with a Maximum Allowable Dose Level.

Overall, 46 of the listed chemicals have none of the types of health guidance values described here; however, the absence of health guidance values does not necessarily mean that the chemicals are not hazardous.

Refinery accidents, if they occur, may release high concentrations of chemicals into the air. Therefore, in accident scenarios where high concentrations of chemicals are measured or estimated in the air, it can be appropriate to reference *emergency exposure levels*. These levels are designed to evaluate risks during emergencies related to emergency-response worker exposure. They are *not* applicable in evaluating exposures for the general public or sensitive populations such as children and the elderly.

Emergency exposure levels can help emergency responders evaluate the immediate dangers from such chemical releases. OEHHA identified which chemicals from the list have emergency exposure levels using Acute Exposure Guideline Levels (AEGL) and Immediately Dangerous to Life and Health (IDLH) values. AEGLs are developed by US EPA, and IDLH values are developed by the National Institute for Occupational Safety and Health. Of the 188 chemicals on the list, 94 chemicals have at least one of these two emergency exposure levels. The absence of emergency exposure levels does not necessarily mean that these chemicals are not hazardous.

Most Highly Emitted Chemicals and Other Supporting Information

OEHHA investigated publicly available data on California's refinery incident history and the process units or equipment associated with such incidents. For the years 2001-2012, OEHHA found reports on 127 incidents. Flares were the most common category/source of incidents that resulted in emissions to outdoor air. The term "smoke" (from explosion, fire, or flares) was associated with the highest number of incidents (63) reported during that period. The most frequently cited chemicals are included on the candidate list for air monitoring provided below: benzene, 1,3-butadiene, hydrogen fluoride, hydrogen sulfide, particulate matter (PM), sulfur dioxide, sulfuric acid, toluene, and hydrocarbons (not otherwise specified).

All California refineries active during the year 2010 were required to measure air emissions from each of their process or emission points for a certain amount of time, and to submit this data to US EPA. OEHHA used these emissions inventories to identify the most commonly occurring processes along with their associated chemical emissions. A total of 20 processes were examined and chemicals involved in the most processes or equipment were considered for the candidate chemical list. The candidate chemicals released in the majority of processes were benzene, naphthalene, and toluene.

OEHHA collected information on routine and non-routine emissions from California refineries. One source of data on routine emissions came from the Assembly Bill 2588 Air Toxics 'Hot Spots' Program reported in the California Emission Inventory Development and Reporting System database (CEIDARS) for 2009-2012 and 2014.

The ten most frequently reported routine toxic air contaminant emissions from California refineries from 2009-2012 (starting with the highest) were:

- ammonia
- formaldehyde
- methanol
- sulfuric acid
- hydrogen sulfide
- toluene
- xylene
- benzene
- hexane
- hydrogen chloride

The average routine emissions for all chemicals reported in CEIDARS for California refineries for 2009-2012 in pounds per year are compiled in this report.

OEHHA also used additional data for routine and non-routine emissions of all pollutants (not just TACs) that California refineries reported to the US EPA for the year 2010 only. Using these data, OEHHA determined the most frequently emitted chemicals (starting with the highest) were:

- sulfur dioxide
- carbon monoxide
- nitrogen oxides
- PM_{10} and $PM_{2.5}$
- butane
- nitrogen dioxide
- propylene
- hexane

OEHHA totaled the amount of routine and non-routine emissions for all chemicals reported in this data set in the report.

Conclusions

Of the 188 chemicals identified as emitted from California refineries, the chemicals listed below are the top candidates for air monitoring, based on their toxicity, average levels of emissions from refineries statewide, and involvement in multiple refinery processes and incidences. OEHHA also derived a “toxicity-weighted” emissions score for each chemical for which emissions data were available for all refineries across California. OEHHA calculated the toxicity-weighted emissions scores using emissions data (pounds emitted per year) obtained from the Air Toxics ‘Hot Spots’ Emissions Inventory database (CEIDARS) for 2014, and a toxicity weight derived from US EPA’s Inhalation Toxicity Scores for individual chemicals. The candidate chemicals that had high calculated toxicity-weighted emissions are noted in the candidate list below with an asterisk (in alphabetical order).

These candidates for air monitoring were not further ranked or prioritized.

- acetaldehyde*
- ammonia*
- benzene*
- 1,3-butadiene*
- cadmium*
- diethanolamine*
- formaldehyde*
- hydrogen fluoride
- hydrogen sulfide*
- manganese*
- naphthalene*
- nickel*
- nitrogen oxide
- polycyclic aromatic hydrocarbons (PAH)*
- particulate matter (PM)
- sulfur dioxide
- sulfuric acid
- toluene

An important consideration for air monitoring at individual refineries is that the candidate chemicals will differ based on location as well as year. Some top-candidate chemicals are only released in small amounts from individual refineries.

Finally, the release of these chemicals from refineries does not necessarily mean that local communities face substantial exposures or significant health risks. However, it does increase their likelihood of exposure. Air monitoring of these chemicals may inform decisions that could reduce exposure.

I. INTRODUCTION

This report may assist the California Air Resources Board (CARB) in making decisions for the air monitoring of communities near refineries, and assist local air districts in selecting the most appropriate monitoring methods and tools when responding to future emergency releases. This report may inform statewide guidance and recommendations being developed by CARB and the California Air Pollution Control Officers Association (CAPCOA) as part of their joint effort to improve air monitoring near California's refineries.

CARB and CAPCOA initiated a statewide assessment of emergency air monitoring capabilities at California oil refineries in an effort to improve employee and public safety. CARB is collaborating with other members of the California Environmental Protection Agency's (CalEPA) Interagency Refinery Task Force (IRTF) to develop findings, recommendations, and proposed implementation measures for improving emergency air monitoring at refineries.

As part of this interagency collaboration, the Interagency Refinery Task Force asked the Office of Environmental Health Hazard Assessment (OEHHA) to assess the potential health effects of chemicals commonly emitted from California refineries and to provide specific regulatory and advisory health values for these chemicals. To this end, OEHHA first compiled an initial list of chemicals emitted from California refineries based on data for Toxic Air Contaminants (TACs)[1] reported in the California Emission Inventory Development and Reporting System (CEIDARS) database for all California refineries active from 2009 to 2012. Further data on California refinery chemicals, not limited to TACs, were provided by internet databases, publicly available data, government reports, and peer-reviewed journal articles. Upon completion of the refinery chemicals list, OEHHA researched chemical-specific information regarding health effects and advisory health standards. Information on chemical health effects was obtained from the OEHHA Reference Exposure Level (REL) web page, the US Environmental Protection Agency (US EPA) Integrated Risk Information System (IRIS) web page, and the Agency for Toxic Substances and Disease Registry (ATSDR) Toxic Substances Portal. Additional sources include the web pages for the National Institutes of Health (NIH) Hazardous Substances Data Bank (HSDB) and Toxicology Data Network (TOXNET), the Centers for Disease Control and Prevention (CDC) Emergency Preparedness and Response web page, the NIOSH Pocket Guide to Chemical Hazards, and the National Oceanic and Atmospheric Administration's (NOAA) Computer-Aided Management of Emergency Operations (CAMEO) Chemicals.

[1] "Toxic air contaminants" are defined in California law as air pollutants which may cause or contribute to an increase in mortality or in serious illness, or which may pose a present or potential hazard to human health (Health and Safety Code section 39655)
URL to current list: https://www.arb.ca.gov/toxics/quickref.htm#TAC

II. LIST OF CHEMICALS EMITTED FROM CALIFORNIA REFINERIES

To create an initial list of chemicals that have been reported as emitted from California oil refineries, OEHHA obtained a list of TACs reported in the CEIDARS database from CARB for all California refineries active at any point during 2009 to 2012. These emissions data were reported in accordance with the Air Toxics Hot Spots Information and Assessment Act (AB 2588) and served as the foundation of OEHHA's list of refinery-emitted chemicals. Chemicals other than TACs were added to the list based on California refinery emissions data provided by US EPA. To identify other chemicals not included in the CEIDARS or US EPA datasets, OEHHA also performed a literature search and compiled information on refinery air monitoring and incidents in California. This search resulted in additional sources such as peer-reviewed journal articles, government reports such as Bay Area Air Quality Management District (BAAQMD) incident reports, and online databases such as the US Chemical Safety Board (CSB) Industrial Chemical Incident Screening Database and the list of major accidents at refineries reported by Contra Costa Health Services (CCHS). After the later release of CEIDARs data for 2014, OEHHA also examined and analyzed this dataset

The name and Chemical Abstracts Service Registry Number (CAS RN) of each chemical included in the initial list of California refinery chemicals are shown in Table 1 below. Some chemicals on this list are routinely emitted from refineries, others may be emitted only during incidents, and others may rarely be emitted.

Table 1. List of Chemicals Emitted from California Refineries

Chemical	CAS RN	Source[1]	Chemical	CAS RN	Source
Acenaphthene	83329	[1]	Carbon monoxide	630080	[2]
Acenaphthylene	208968	[1]	Carbon tetrachloride	56235	[1]
Acetaldehyde	75070	[1]	Carbonyl sulfide	463581	[2]
Acetone	67641	[2]	Chlorine	7782505	[1]
Acetylene	74862	[2]	Chlorobenzene	108907	[2]
Acrolein	107028	[1]	Chlorodifluoromethane	75456	[2]
Aluminum	7429905	[1]	Chloroform	67663	[1]
Ammonia	7664417	[1]	2-Chloronaphthalene	91587	[2]
Aniline	62533	[2]	Chromium	7440473	[2]
Anthracene	120127	[1]	Chromium (hexavalent & compounds)	18540299	[1]
Antimony	7440360	[2]	Chromium III (& compounds)	16065831	[2]
Arsenic	7440382	[2]	Chrysene	218019	[2]
Asbestos	1332214	[1]	Cobalt	7440484	[2]
Barium	7440393	[2]	Copper	7440508	[1]
Benz[a]anthracene	56553	[1]	Cresols (mixtures of)	1319773	[2]
Benzene	71432	[1]	m-Cresol	108394	[2]
Benzo[b]fluoranthene	205992	[1]	o-Cresol	95487	[2]
Benzo[j]fluoranthene	205823	[1]	p-Cresol	106445	[2]
Benzo[k]fluoranthene	207089	[1]	Cumene	98828	[2]
Benzo[g,h,i]perylene	191242	[1]	Cyclohexane	110827	[2]
Benzo[a]pyrene	50328	[1]	Cyclopentadiene	542927	[2]
Benzo[e]pyrene	192972	[1]	Cyclopentane	287923	[2]
Beryllium	7440417	[1]	Dibenz[a,h]anthracene	53703	[1]
Biphenyl	92524	[2]	Dibenzo-p-dioxins (chlorinated)	—	[1]
1,2-Butadiene	590192	[2]	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	35822469	[2]
1,3-Butadiene	106990	[2]	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	39227286	[2]
Butane	106978	[2]	1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	57653857	[2]
1-Butene	106989	[2]	1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	19408743	[2]
2-Butene	107017	[2]	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	3268879	[1]
Cadmium	7440439	[1]	1,2,3,7,8-Pentachlorodibenzo-p-dioxin	40321764	[2]

[1] Sources: 1 Air Resources Board; 2 US EPA, 2012a; US EPA, 2012b; 3 Chemical Safety Board (CSB)

Chemical	CAS RN	Source[1]	Chemical	CAS RN	Source
Carbon disulfide	75150	[2]	2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746016	[2]
Dibenzofuran	132649	[2]	Ethylene glycol monoethyl ether acetate	111159	[2]
Dibenzofurans (chlorinated)	1080	[1]	Fluoranthene	206440	[2]
1,2,3,4,6,7,8-Heptachlorodibenzofuran	67562394	[2]	Fluorene	86737	[2]
1,2,3,4,7,8,9-Heptachlorodibenzofuran	55673897	[2]	Formaldehyde	50000	[1]
1,2,3,4,7,8-Hexachlorodibenzofuran	70648269	[2]	Glutaraldehyde	111308	[2]
1,2,3,6,7,8-Hexachlorodibenzofuran	57117449	[2]	Glycol ethers (& acetates)	1115	[1]
1,2,3,7,8,9-Hexachlorodibenzofuran	72918219	[2]	Heptane	142825	[2]
2,3,4,6,7,8-Hexachlorodibenzofuran	60851345	[2]	Hexachloroethane	67721	[2]
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	39001020	[2]	Hexane	110543	[2]
1,2,3,7,8-Pentachlorodibenzofuran	57117416	[2]	Hydrogen	1333740	[3]
2,3,4,7,8-Pentachlorodibenzofuran	57117314	[2]	Hydrogen chloride	7647010	[1]
2,3,7,8-Tetrachlorodibenzofuran	51207319	[2]	Hydrogen cyanide	74908	[2]
Dibutyl phthalate	84742	[2]	Hydrogen fluoride	7664393	[1]
1,4-Dichlorobenzene	106467	[2]	Hydrogen sulfide	7783064	[1]
1,1-Dichloroethane	75343	[2]	Indeno[1,2,3-c,d]pyrene	193395	[2]
1,1-Dichloroethylene	75354	[2]	Isobutane	75285	[3]
1,2-Dichloropropane	78875	[1]	Isobutene	115117	[2]
1,3-Dichloropropene	542756	[1]	Isopentane	78784	[2]
Diesel engine exhaust	9901	[1]	Isoprene	78795	[2]
Diethanolamine	111422	[2]	Isopropanol	67630	[1]
Diethyl phthalate	84662	[2]	Lead	7439921	[2]
Di(2-ethylhexyl)phthalate	117817	[2]	Manganese	7439965	[2]
1,1-Dimethylallene	598254	[2]	Mercury	7439976	[2]
7,12-Dimethylbenz[a]anthracene	57976	[1]	Methane	74828	[2]
1,4-Dioxane	123911	[1]	Methanol	67561	[1]
Ethane	74840	[2]	Methyl bromide	74839	[2]
Ethyl chloride	75003	[2]	Methyl chloride	74873	[2]
Ethylbenzene	100414	[2]	Methyl chloroform	71556	[1]
Ethylene	74851	[1]	Methyl ethyl ketone	78933	[2]
Ethylene dibromide	106934	[2]	Methyl isobutyl ketone	108101	[2]
Ethylene dichloride	107062	[2]	Methyl tert-butyl ether	1634044	[2]
Ethylene glycol monoethyl ether	110805	[2]	3-Methylcholanthrene	56495	[2]

Chemical	CAS RN	Source[1]	Chemical	CAS RN	Source
Methylcyclohexane	108872	[2]	Propane	74986	[2]
Methylene chloride	75092	[2]	Propylene	115071	[2]
2-Methylnaphthalene	91576	[1]	Propylene glycol monomethyl ether	107982	[2]
Molybdenum	7439987	[2]	Propylene glycol monomethyl ether acetate	108656	[2]
Naphthalene	91203	[2]	Propylene glycol mono-t-butyl ether	57018527	[2]
Nickel	7440020	[2]	Propylene oxide	75569	[2]
Nitrogen dioxide	10102440	[2]	Pyrene	129000	[2]
Nitrogen oxides	—	[2]	Selenium (& compounds)	7782492	[1]
Nitrous oxide	10024972	[1]	Selenium sulfide	7488564	[2]
Octane	111659	[2]	Styrene	100425	[2]
PAHs, total, w/ individ. components reported	1150	[1]	Sulfur dioxide	7446095	[2]
PAHs, total, w/o individ. components reported	1151	[1]	Sulfur monoxide	13827322	[3]
1,2-Pentadiene	591957	[2]	Sulfur trioxide	744619	[3]
cis-1,3-Pentadiene	1574410	[2]	Sulfuric acid	766439	[1]
trans-1,3-Pentadiene	2004708	[2]	1,1,2,2-Tetrachloroethane	79345	[1]
1,4-Pentadiene	591935	[2]	Toluene	108883	[2]
2,3-Pentadiene	591968	[2]	1,1,2-Trichloroethane	79005	[1]
Pentane	109660	[2]	Trichloroethylene	79016	[2]
Perchloroethylene	127184	[2]	Trichlorofluoromethane	75694	[2]
Perylene	198550	[2]	1,1,2-Trichloro-1,2,2-trifluoroethane	76131	[2]
Phenanthrene	85018	[2]	Triethylamine	121448	[2]
Phenol	108952	[2]	Trimethylbenzene	25551137	[2]
Phosphoric acid	7664382	[1]	1,2,4-Trimethylbenzene	95636	[1]
Phosphorus	7723140	[1]	2,2,4-Trimethylpentane	540841	[2]
PM (condensable)	—	[2]	Vanadium	7440622	[1]
PM_{10}	—	[2]	Vinyl chloride	75014	[2]
PM_{10} (filterable)	—	[2]	Xylenes (mixed)	1330207	[2]
$PM_{2.5}$	—	[2]	m-Xylene	108383	[2]
$PM_{2.5}$ (filterable)	—	[2]	o-Xylene	95476	[2]
Polychlorinated biphenyls	1336363	[2]	p-Xylene	106423	[2]
Propadiene	463490	[2]	Zinc	7440666	[1]

~~[1] Air Resources Board; [2] US EPA, 2012a; US EPA, 2012b; [3] Chemical Safety Board (CSB)~~

III. HEALTH GUIDANCE AND EMERGENCY EXPOSURE VALUES

A. OEHHA and US EPA Health Guidance Values

The release of chemicals from refineries may potentially result in exposure to workers, bystanders (persons proximate to the refinery), and nearby communities. In the event of a refinery emergency, health guidance values can help responders characterize potential health effects that may result following a chemical release. OEHHA determines Reference Exposure Levels (RELs) associated with physiological systems that are could be affected (for example, respiratory system) for the noncancer effects of airborne chemicals as part of the Air Toxics Hot Spots program. US EPA also establishes noncancer health guidance values referred to as Reference Concentrations (RfCs) for air contaminants. It can be reasonably anticipated that no adverse health effects will occur in exposed populations, including sensitive subpopulations for exposures to concentrations at or below the OEHHA RELs, including the acute REL for short-term exposures (one-hour), the eight-hour REL for repeated eight-hour exposures, and the chronic REL for continuous long-term exposures. The US EPA RfCs are similar to OEHHA's chronic RELs for long-term exposures, but are developed using a different risk assessment methodology than OEHHA employs and therefore may be different.

Cancer Potency Factors (CPF), also referred to as Cancer Slope Factors (CSF), and unit risk values are calculated for chemicals known to be carcinogenic. These values are developed under several OEHHA's programs: the Air Toxics Hot Spots Program; Public Health Goals (PHG) for drinking water; Toxic Air Contaminant Program; and Proposition 65. In addition, CPFs are obtained from US EPA's Integrated Risk Information System (IRIS). These factors are used in combination with measured or modeled airborne concentrations to estimate lifetime cancer risks to an exposed population.

The health guidance values shown in Table 2 below have been developed to protect the general public from the cancer and noncancer endpoints that may result from toxic chemical exposures.

Table 2. OEHHA and US EPA Health Guidance Values and Descriptions

Guidance Value[1]	Source	Description
Reference Exposure Level (**REL**) (µg/m^3 inhalation, µg/kg-day oral)	OEHHA	Airborne concentration level at or below which no adverse health effects are anticipated for a specified exposure duration. OEHHA has acute RELs for an exposure lasting one hour[2], eight-hour RELs for long-term, repeated (up to daily) exposures of eight hours, and chronic RELs for continuous exposures lasting ≥12% of a lifetime. A few RELs are based on an oral exposure.
Reference Concentration (**RfC**) (mg/m^3)	US EPA (IRIS)	Estimate of continuous inhalation exposure to the human population (including sensitive subgroups) lasting ≥12% of an individual's lifetime that is likely to be without an appreciable risk of deleterious effects during a lifetime.
Cancer Slope Factor (**CSF**) (mg/kg-day)$^{-1}$	OEHHA (Air Toxics Hot Spots, TAC, Proposition 65), US EPA (IRIS)	Upper 95% confidence limit of the slope of the extrapolated dose-response curve; this is equivalent to the probability of developing cancer from continuous lifetime exposure to a substance (in units of milligram per kilogram of body weight per day).
Unit Risk (µg/m^3)$^{-1}$	OEHHA (Air Toxics Hot Spots, TAC, Proposition 65), US EPA (IRIS)	Upper 95% confidence limit of the slope of the extrapolated dose-response curve; this is equivalent to the probability of developing cancer from continuous lifetime exposure to a substance (in units of microgram per cubic meter of air).

[1] micrograms per meter cubed, micrograms per kilogram-day
[2] A few acute RELs are for slightly longer durations – see OEHHA (2008).

This section does not include all potential health guidance values. Regional Screening Levels (RSLs), for instance, are developed by US EPA and can be used to determine chemical-specific concentrations for contaminants found in air, drinking water, and soil that warrant hazardous waste site cleanup. Additionally, OEHHA develops California Human Health Screening Levels (CHHSLs) to enable property owners and government officials to determine the degree of effort that may be required to remediate contaminated soil. CHHSLs include Soil-Screening Numbers for nonvolatile chemicals based on total exposure to contaminated soil (inhalation, ingestion, and dermal absorption), and Soil-Gas Screening Numbers for volatile chemicals below buildings constructed with and without engineered fill below sub-slab gravel. For further information on RSLs and CHHSLs, see the US EPA regional screening levels web page or the OEHHA soil and soil gas risk assessment web page (URLs in References section).

Table 3 lists the refinery-emitted chemicals from Table 1 that have one or more of the health guidance values described above, or that are included on the Proposition 65 list of carcinogens and reproductive or developmental toxicants.

Table 3. Health Guidance Values for Chemicals Emitted from California Refineries

Chemical	US EPA RfC[1] (µg/m^3)	OEHHA Inhalation REL[2] (µg/m^3)		OEHHA Oral REL[2] (µg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (µg/m^3)$^{-1}$
Acetaldehyde	—	A	470	—	Eyes; respiratory system (sensory irritation)	C	0.01[a]	2.7x10^{-6}
	—	8	300	—	Respiratory system	—	—	—
	9	C	140	—	Respiratory system	—	—	—
Acrolein	—	A	2.5	—	Eyes, respiratory system (sensory irritation)	—	—	—
	—	8	0.7	—	Respiratory system	—	—	—
	0.02	C	0.35	—	Respiratory system	—	—	—
Ammonia	—	A	3,200	—	Respiratory system; eyes	—	—	—
	100	C	200	—	Respiratory system	—	—	—
Aniline	1	—	—	—	—	C	5.7x10^{-3} [b]	1.6x10^{-6}
Arsenic	—	A	0.2	—	Development; cardiovascular system; nervous system	C	12[a]	3.0x10^{-3}
	—	8	0.015	—	Development; cardiovascular system; nervous system; respiratory system; skin	—	1.5[b] (oral)	—
	—	C	0.015	3.5x10^{-3}	Inhalation and Oral: Development; cardiovascular system; nervous system; respiratory system; skin	—	—	—
Asbestos	—	—	—	—	—	C	220[a]	0.063

[1] US EPA Inhalation Reference Concentrations (RfC). http://www2.epa.gov/iris.
[2] OEHHA acute, eight-hour, and chronic Reference Exposure Levels (REL) with corresponding hazard index target organs. https://oehha.ca.gov/air/general-info/oehha-acute-8-hour-and-chronic-reference-exposure-level-rel-summary
[3] Proposition 65 status, Chemicals denoted with a *C* are classified as carcinogens; those with a *D* are classified as developmental toxicants; those with R_m, R_f, or $R_{m/f}$ are reproductive toxicants in males, females or both.
[4] OEHHA Cancer Potency Factors (CPF), also known as Cancer Slope Factors (CSF) and Unit Risk Factors, from *Appendix A* (updated 2011) of the *Technical Support Document for Cancer Potency Factors*. http://oehha.ca.gov/media/downloads/crnr/appendixa.pdf. Sources of values: (a) Toxic Air Contaminant (TAC); (b) Integrated Risk Information System (IRIS); (c) Proposition 65; (d) Public Health Goal (PHG) document.

Chemical	US EPA RfC[1] (µg/m^3)	OEHHA Inhalation REL[2] (µg/m^3)		OEHHA Oral REL[2] (µg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (µg/m^3)$^{-1}$
Benz[a]anthracene	—	—	—	—	—	C	0.39[a]	1.1x10^{-4}
	—	—	—	—	—	—	1.2 (oral)	—
Benzene	—	A	27	—	Development; immune system; hematologic system	C	0.1[a]	2.9x10^{-5}
	—	8	3	—	Hematologic system	D, R_m	—	—
	30	C	3	—	Hematologic system	—	—	—
Benzo[a]pyrene	—	—	—	—	—	C	3.9[a]	1.1x10^{-3}
	—	—	—	—	—	—	12 (oral)	—
Benzo[b]fluoranthene	—	—	—	—	—	C	0.39[a]	1.1x10^{-4}
	—	—	—	—	—	—	1.2 (oral)	—
Benzo[j]fluoranthene	—	—	—	—	—	C	0.39[a]	1.1x10^{-4}
	—	—	—	—	—	—	1.2 (oral)	—
Benzo[k]fluoranthene	—	—	—	—	—	C	0.39[a]	1.1x10^{-4}
	—	—	—	—	—	—	1.2 (oral)	—
Beryllium	0.02	C	7.0x10^{-3}	2	Inhalation: Respiratory system, immune system; Oral: Alimentary system (gastrointestinal tract)	C	8.4[b]	2.4x10^{-3}
1,3-Butadiene	—	A	660	—	Development	C	0.6[a]	1.7x10^{-4}
	—	8	9	—	Reproductive system	D, $R_{m/f}$	—	—
	2	C	2	—	Reproductive system	—	—	—
Cadmium	—	C	0.02	0.5	Inhalation: Kidney, respiratory system; Oral: Kidney	C	15[a]	4.2x10^{-3}
	—	—	—	—	—	D, R_m	—	—
Carbon disulfide	—	A	6,200	—	Reproductive/development; nervous system	D, $R_{m/f}$	—	—
	700	C	800	—	Nervous system; reproductive system	—	—	—
Carbon monoxide	—	A	2.3x10^{4}	—	Cardiovascular system	D	—	—
Carbon tetrachloride	—	A	1,900	—	Alimentary system (liver); reproductive/development; nervous system	C	0.15[a]	4.2x10^{-5}
	100	C	40	—	Alimentary and nervous systems; development	—	—	—

Chemical	US EPA RfC[1] (µg/m^3)	OEHHA Inhalation REL[2] (µg/m^3)		OEHHA Oral REL[2] (µg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (µg/m^3)$^{-1}$
Carbonyl sulfide		A	660		Nervous system	—	—	—
		8	10		Nervous system	—	—	—
		C	10		Nervous system	—	—	—
Chlorine	—	A	210	—	Respiratory system; eyes	—	—	—
	—	C	0.2	—	Respiratory system	—	—	—
Chlorobenzene	—	C	1,000	—	Alimentary system (liver); kidney; reproductive system	—	—	—
Chlorodifluoromethane	$5.0x10^{4}$	—	—	—	—	—	—	—
Chloroform	—	A	150	—	Reproductive/development; respiratory system; nervous system	C	0.019[a]	$5.3x10^{-6}$
	—	C	300	—	Alimentary system; kidney; development	D	—	—
Chromium (hexavalent)& compounds)	$8.0x10^{-3}$ (aerosols)	C	0.2	20	Inhalation: Respiratory system; Oral: Hematologic system	C	510[a]	0.15
	0.1 (particulates)	—	—	—	—	D, $R_{m/f}$	0.42[c] (oral)	—
Chrysene	—	—	—	—	—	C	0.039[a]	$1.1x10^{-5}$
	—	—	—	—	—	—	0.12 (oral)	—
Cobalt	—	—	—	—	—	C	—	—
Copper	—	A	100	—	Respiratory system	—	—	—
Cresols (mixtures of)	—	C	600	—	Nervous system	—	—	—
Cumene	400	—	—	—	—	C	—	—
Cyclohexane	6,000	—	—	—	—	—	—	—
Dibenz[a,h]anthracene	—	—	—	—	—	C	4.1[c]	$1.2x10^{-3}$
Dibenzo-p-dioxins[5] (chlorinated)	—	C	$4.0x10^{-5}$	$1.0x10^{-5}$	Inhalation and Oral: Alimentary (liver), reproductive, endocrine, respiratory, hematologic systems; development	C	—	—
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin[5]	—	—	—	—	—	—	1,300[a]	0.38
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin[5]	—	—	—	—	—	—	$1.3x10^{4}$ [a]	3.8

Chemical	US EPA RfC[1] (µg/m^3)	OEHHA Inhalation REL[2] (µg/m^3)		OEHHA Oral REL[2] (µg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (µg/m^3)$^{-1}$
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin[5]	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin[5]	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
1,2,3,7,8-Pentachlorodibenzo-p-dioxin[5]	—	—	—	—	—	—	1.3x10^{5} [a]	38
2,3,7,8-Tetrachlorodibenzo-p-dioxin[5]	—	C	4.0x10^{-5}	1.0x10^{-5}	Inhalation and Oral: Alimentary (liver), reproductive, endocrine, respiratory, hematologic systems; development	C	1.3x10^{5} [a]	38
1,2,3,4,6,7,8-Heptachlorodibenzofuran	—	—	—	—	—	—	1,300[a]	0.38
1,2,3,4,7,8,9-Heptachlorodibenzofuran	—	—	—	—	—	—	1,300[a]	0.38
1,2,3,4,7,8-Hexachlorodibenzofuran	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
1,2,3,6,7,8-Hexachlorodibenzofuran	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
1,2,3,7,8,9-Hexachlorodibenzofuran	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
2,3,4,6,7,8-Hexachlorodibenzofuran	—	—	—	—	—	—	1.3x10^{4} [a]	3.8
1,2,3,7,8-Pentachlorodibenzofuran	—	—	—	—	—	—	6,500[a]	1.9
2,3,4,7,8-Pentachlorodibenzofuran	—	—	—	—	—	—	6.5x10^{4} [a]	19
2,3,7,8-Tetrachlorodibenzofuran	—	—	—	—	—	C	1.3x10^{4} [a]	3.8

[5] Polychlorinated biphenyls individual congeners evaluated using toxic equivalent factor (TEF) methodology, relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin. No specific value

Chemical	US EPA RfC[1] (µg/m³)	OEHHA Inhalation REL[2] (µg/m³)		OEHHA Oral REL[2] (µg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] $(mg/kg\text{-}day)^{-1}$	Unit Risk Factor[4] $(µg/m^3)^{-1}$
1,4-Dichlorobenzene	800	C	800	—	Nervous and respiratory; alimentary system (liver); kidney	C	0.04[c]	$1.1x10^{-5}$
1,1-Dichloroethane	—	—	—	—	—	C	$5.7x10^{-3}$[c]	$1.6x10^{-6}$
1,1-Dichloroethylene	200	C	70	—	Alimentary system (liver)	—	—	—
1,2-Dichloropropane	4	—	—	—	—	C	—	—
1,3-Dichloropropene	20	—	—	—	—	C	—	—
Mercury	—	A	0.6	—	Nervous system; development	D		
	—	8	0.06	—	Nervous system; development; kidney	—	—	—
	0.3	C	0.03	0.16	Inhalation & Oral: Nervous system; development; kidney	—	—	—
Methanol	—	A	$2.8x10^4$	—	Nervous system	D	—	—
	$2.0x10^4$	C	4,000	—	Development	—	—	—
Methyl bromide	—	A	3,900	—	Nervous system; respiratory system; reproductive/ development	D	—	—
	5	C	5	—	Respiratory system; nervous system; development	—	—	—
Methyl chloride	90	—	—	—	—	D, R_m	—	—
Methyl chloroform	—	A	$6.8x10^4$	—	Nervous system	—	—	—
	5,000	C	1,000	—	Nervous system	—	—	—
Methyl ethyl ketone	5,000	A	$1.3x10^4$	—	Respiratory system; eyes	—	—	—
Methyl isobutyl ketone	3,000	—	—	—	—	C	—	—
	—	—	—	—	—	D	—	—
Methyl tert-butyl ether	3,000	C	8,000	—	Kidney; eyes; alimentary system (liver)	—	$1.8x10^{-3}$[a]	$2.6x10^{-7}$
3-Methylcholanthrene	—	—	—	—	—	C	22[c]	$6.3x10^{-3}$
Methylene chloride	—	A	$1.4x10^4$	—	Cardiovascular system; nervous system	C	$3.5x10^{-3}$[a]	$1.0x10^{-6}$
	600	C	400	—	Cardiovascular system; nervous system	—	—	—
Naphthalene	3	C	9	—	Respiratory system	C	0.12[a]	$3.4x10^{-5}$

Chemical	US EPA RfC[1] (µg/m³)	OEHHA Inhalation REL[2] (µg/m³)		OEHHA Oral REL[2] (µg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] $(mg/kg\text{-}day)^{-1}$	Unit Risk Factor[4] $(µg/m^3)^{-1}$
Nickel	—	A	0.2	—	Immune system	C	0.91[a]	$2.6x10^{-4}$
	—	8	0.06	—	Respiratory, immune systems	—	—	—
	—	C	0.014	11	Inhalation: Respiratory system; hematologic system; Oral: Development	—	—	—
Nitrogen dioxide	—	A	470	—	Respiratory system	—	—	—
Nitrous oxide	—	—	—	—	—	D, R_f	—	—
Perchloroethylene	—	A	$2.0x10^4$	—	Nervous system; respiratory system; eyes	C	0.21[a]	$5.9x10^{-6}$
	40	C	35	—	Kidney; alimentary system (liver)	—	0.051[c] (oral)	—
Phenol	—	A	5,800	—	Respiratory system; eyes	—	—	—
	—	C	200	—	Alimentary system; cardiovascular system; kidney; nervous system	—	—	—
Phosphoric acid	10	C	7	—	Respiratory system	—	—	—
Polychlorinated biphenyls	—	C[5]	—	—	Inhalation and Oral: Alimentary (liver), reproductive, endocrine, respiratory, hematologic systems; development	C	2[b]	$5.7x10^{-4}$
	—	—	—	—	—	D	—	—
Propylene	—	C	3,000	—	Respiratory system	—	—	—
Propylene glycol monomethyl ether	2,000	C	7,000	—	Alimentary system (liver)	—	—	—
Propylene glycol mono-t-butyl ether	—	—	—	—	—	C	—	—
Propylene oxide	—	A	3,100	—	Respiratory system; eyes; reproductive/development	C	0.013[b]	$3.7x10^{-6}$
	30	C	30	—	Respiratory system	—	0.24 (oral)	—
Selenium (& compounds)	—	C	20	5	Inhalation and Oral: Alimentary system (liver); cardiovascular system; nervous system	—	—	—

Chemical	US EPA RfC[1] (µg/m^3)	OEHHA Inhalation REL[2] (µg/m^3)		OEHHA Oral REL[2] (µg/kg-day)	Hazard Index Target Organs[2]	Proposition 65[3]	Cancer Slope Factor[4] (mg/kg-day)$^{-1}$	Unit Risk Factor[4] (µg/m^3)$^{-1}$
Selenium sulfide	—	C	20	5	Inhalation and Oral: Alimentary system (liver); cardiovascular system; nervous system	C	—	—
Styrene	—	A	2.1×10^{4}	—	Respiratory system; eyes; reproductive/development	—	—	—
	1,000	C	900	—	Nervous system	—	—	—
Sulfur dioxide	—	A	660	—	Respiratory system	D	—	—
Sulfuric acid	—	A	120	—	Respiratory system	C (mist)	—	—
	—	C	1	—	Respiratory system	—	—	—
1,1,2,2-Tetrachloroethane	—	—	—	—	—	C	0.2[b]	5.8×10^{-5}
Toluene	—	A	3.7×10^{4}	—	Respiratory, nervous systems; eyes; reproductive/development	D	—	—
	5,000	C	300	—	Nervous system; respiratory system; development	—	—	—
1,1,2-Trichloroethane	—	—	—	—	—	C	0.057[b]	1.6×10^{-5}
Trichloroethylene	2	C	600	—	Nervous system; eyes	C	7.0×10^{-3} [a]	2.0×10^{-6}
	—	—	—	—	—	D, R_m	0.015[c] (oral)	—
Triethylamine	—	A	2,800	—	Nervous system; eyes	—	—	—
	7	C	200	—	Eyes	—	—	—
Vinyl chloride	100	A	1.8×10^{5}	—	Nervous system; respiratory system; eyes	C	0.27[a]	7.8×10^{-5}
Xylenes (mixed and m-xylene, o-xylene, and p-xylene isomers)	—	A	2.2×10^{4}	—	Nervous and respiratory systems; eyes	—	—	—
	100	C	700	—	Nervous and respiratory systems; eyes	—	—	—

For information on the development of Reference Exposure Levels, see OEHHA (2008), and to access the complete list of existing OEHHA RELs, see OEHHA's Acute, 8-hour and Chronic Reference Exposure Level (REL) Summary. For US EPA RfCs, see the US EPA IRIS website. Additional information regarding chemical-specific cancer studies and the development of CSFs can be found in OEHHA (2009) and on OEHHA's Proposition 65 web page. The International Agency for Research on Cancer (IARC) Monographs on Evaluation of Carcinogenic Risks to Humans provides information on studies related to carcinogenicity in animals and humans. These Monographs can be accessed on the IARC web page (URLs in References section).

B. US EPA and NIOSH Emergency Exposure Levels

Refinery accidents are unpredictable and may release high concentrations of chemicals into the air. Emergency exposure levels can help emergency responders evaluate the immediate dangers from such chemical releases. While health guidance values can be used to anticipate the health risks associated with exposure to low chemical concentrations, emergency exposure levels may be applied in scenarios in which high concentrations of chemicals are measured or estimated in the air. For this reason, OEHHA has compiled information on the emergency exposure levels for chemicals in Table 1 including: US EPA's Acute Exposure Guideline Levels (AEGL), and the National Institute for Occupational Safety and Health's (NIOSH) Immediately Dangerous to Life and Health (IDLH) values In addition, OEHHA notes which chemicals have Lower Explosive Limits (LEL).

AEGLs and IDLHs are used to protect workers and emergency responders. Based on the severity of toxic effects resulting from exposure, chemicals can have up to three AEGLs and an IDLH. AEGLs are used to make informed decisions on shelter-in-place orders or emergency evacuations. The US EPA Office of Pollution Prevention and Toxics' (OPPT) National Advisory Committee for the Development of Acute Exposure Guideline Levels for Hazardous Substances (NAC/AEGL Committee) and NIOSH, respectively develop AEGLs and IDLHs for chemical exposures.

LELs and Upper Explosive Limits (UEL) establish a range of concentrations in which a flash will occur or a flame will travel if flammable vapor or gas in air is ignited. Thus, LELs are calculated for flammable chemicals and may be used as guidelines to avoid accidental chemical explosions.

AEGLs are established for varying durations of exposure. The 10-minute AEGLs listed can be used in acute exposure scenarios such as those which may occur in a refinery emergency. There are additional emergency exposure levels which are also used to plan for and respond to uncontrolled chemical releases. Chemicals can have up to three AEGLs, Emergency Response Planning Guidelines (ERPG), Temporary Emergency Exposure Limits (TEEL), and Protective Action Criteria (PAC) depending on the severity of toxic effects resulting from inhalation exposure. The American Industrial Hygiene Association (AIHA) Emergency Response Planning Committee develops

ERPGs to assist emergency responders in evaluating the potential spread and airborne concentration in the event of a release, particularly for chemicals that have high potential for uncontrolled releases and those that may pose hazards due to their volatility and toxicity. Because AEGLs and ERPGs exist only for a limited number of chemicals, the US Department of Energy Subcommittee on Consequence Assessment and Protective Actions (SCAPA) also develops Temporary Emergency Exposure Levels (TEELs), which serve as temporary limits for chemicals until AEGLs or ERPGs are developed. TEELs are used in similar situations as one-hour AEGLs and ERPGs. TEELs estimate the concentrations at which most people will begin to experience health effects from exposure in air. In combination, AEGLs, ERPGs, and TEELs are referred to as PACs. During an emergency, these criteria may be used to assess the severity of the event and its health consequences, identify potential outcomes, and determine what protective actions should be taken.

Further information about the development, application, and current list of ERPGs can be found on the AIHA web page. For additional information on the PAC dataset and TEEL development, visit the SCAPA PAC/TEEL web page.

The definitions of AEGLs, IDLHs, and LELs are shown in Table 4 below.

Table 4. US EPA and NIOSH Emergency Exposure Levels and Descriptions

Exposure Level	Source	Description
Acute Exposure Guideline Level (**AEGL**) (mg/m^3)	US EPA (NAC/AEGL Committee)	1: Airborne concentration above which the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects after an exposure duration of 10 minutes, 30 minutes, 1 hour, 4 hours, or 8 hours. Effects are not disabling and are transient and reversible upon cessation of exposure. 2: Airborne concentration above which the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or impaired ability to escape after an exposure duration of 10 minutes, 30 minutes, 1 hour, 4 hours, or 8 hours.
Immediately Dangerous to Life and Health (**IDLH**) (mg/m^3)	NIOSH	Airborne concentration likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment as a consequence of a 30-minute exposure.

Table 5 displays the chemicals from OEHHA's list of refinery chemical emissions (Table 1) that have 10-minute AEGLs, IDLHs, or LELs.

Table 5. Emergency Exposure Levels for Chemicals Emitted from California Refineries

Chemical	AEGL-1[1] (µg/m³)	AEGL-2[1] (µg/m³)	IDLH[2] (µg/m³)	LEL[3] (%)
Acenaphthene	—	—	—	0.6
Acetaldehyde	8.11×10^4	6.13×10^5	3.60×10^6	4
Acetone	4.75×10^5	2.21×10^7	5.95×10^6	2.5
Acetylene	—	—	—	2.5
Acrolein	69	1,009	4,580	2.8
Ammonia	2.09×10^4	1.53×10^5	2.09×10^5	15
Aniline	1.83×10^5	2.74×10^5	3.81×10^5	1.3
Anthracene	—	—	—	0.6
Antimony	—	—	5.00×10^4	—
Arsenic	—	—	5,000	—
Barium	—	—	5.00×10^4	—
Benzene	4.15×10^5	6.39×10^6	1.60×10^6	1.2
Beryllium	—	—	4,000	—
Biphenyl	—	7.57×10^4	1.00×10^5	0.6 (232˚F)
1,3-Butadiene	1.48×10^6	1.48×10^7	4.43×10^6	2
Butane	2.38×10^7	5.71×10^7	—	1.6
1-Butene	—	—	—	1.6
Cadmium	130	1,400	9,000	—
Carbon disulfide	5.30×10^4	6.23×10^5	1.56×10^6	1.3
Carbon monoxide	—	4.81×10^5	1.37×10^6	12.5
Carbon tetrachloride	—	1.70×10^5	1.26×10^6	—
Carbonyl sulfide	—	1.70×10^5	—	—
Chlorine	1,450	8,120	2.90×10^4	—
Chlorobenzene	4.60×10^4	1.98×10^6	4.60×10^6	1.3
Chloroform	—	5.86×10^5	2.44×10^6	—
Chromium (hexavalent & compounds)	—	—	2.50×10^5	—
Chromium III	—	—	2.50×10^4	—
Cobalt	—	—	2.00×10^4	—
Copper	—	—	1.00×10^5	—
m-Cresol	—	—	1.11×10^6	1.1 (300˚F)
o-Cresol	—	—	1.11×10^6	1.4 (300˚F)
p-Cresol	—	—	1.11×10^6	1.1 (300˚F)
Cumene	2.46×10^5	2.70×10^6	4.42×10^6	0.9

[1] US EPA 10-minute Acute Exposure Guideline Levels (AEGL) from OPPT.
[2] NIOSH Immediately Dangerous to Life and Health (IDLH) values.
[3] Lower Explosive Limits (LEL) for flammable chemicals, expressed as percent in air from NIOSH.

Chemical	AEGL-1[1] (µg/m^3)	AEGL-2[1] (µg/m^3)	IDLH[2] (µg/m^3)	LEL[3] (%)
Cyclohexane	—	—	4.47×10^6	1.3
Cyclopentadiene	—	—	2.03×10^6	—
Cyclopentane	—	—	—	1.1
Dibutyl phthalate	—	—	4.00×10^6	0.5
1,4-Dichlorobenzene	—	—	9.02×10^5	2.5
1,1-Dichloroethane	—	—	1.22×10^7	5.4
1,1-Dichloroethylene	—	—	—	6.5
1,2-Dichloropropane	—	—	1.85×10^6	3.4
1,3-Dichloropropene	—	—	—	5.3
Diethanolamine	—	—	—	1.6
Diethyl phthalate	—	—	—	0.7 (368˚F)
Di(2-ethylhexyl)phthalate	—	—	5.00×10^6	0.3 (473˚F)
1,4-Dioxane	6.13×10^4	2.09×10^6	1.80×10^6	2
Ethane	—	—	—	2.9
Ethyl chloride	—	—	1.00×10^7	3.8
Ethylbenzene	1.43×10^5	1.26×10^7	3.47×10^6	0.8
Ethylene	—	—	—	2.75
Ethylene dibromide	4.00×10^5	5.61×10^5	7.68×10^5	—
Ethylene dichloride	—	—	2.02×10^5	6.2
Ethylene glycol monoethyl ether	—	—	1.85×10^6	1.8
Ethylene glycol monoethyl ether acetate	—	—	2.71×10^6	1.7
Formaldehyde	1,105	1.72×10^4	2.46×10^4	7
Heptane	—	—	3.07×10^6	1.05
Hexachloroethane	—	—	2.90×10^6	—
Hexane	—	1.41×10^7	3.88×10^6	1.1
Hydrogen	—	—	—	4
Hydrogen chloride	2,687	1.49×10^5	7.46×10^4	—
Hydrogen cyanide	2,761	1.88×10^4	5.52×10^4	5.6
Hydrogen fluoride	818	7.77×10^4	2.45×10^4	—
Hydrogen sulfide	1,045	5.71×10^4	1.39×10^5	4
Isobutane	—	—	—	1.6
Isopropanol	—	—	4.92×10^6	2
Lead	—	—	1.00×10^5	—
Manganese	—	—	5.00×10^5	—
Mercury	—	3,100	1.00×10^4	—
Methane	—	—	—	5
Methanol	8.78×10^5	1.44×10^7	7.86×10^6	6
Methyl bromide	—	3.65×10^6	9.73×10^5	10

Chemical	AEGL-1[1] (µg/m³)	AEGL-2[1] (µg/m³)	IDLH[2] (µg/m³)	LEL[3] (%)
Methyl chloride	—	2.27×10^6	4.13×10^6	8.1
Methyl chloroform	1.25×10^6	5.08×10^6	3.82×10^6	7.5
Methyl ethyl ketone	5.90×10^5	1.45×10^7	8.85×10^6	1.8
Methyl isobutyl ketone	—	—	2.05×10^6	1.4
Methyl tert-butyl ether	1.80×10^5	5.05×10^6	—	—
Methylcyclohexane	—	—	4.82×10^6	1.2
Methylene chloride	1.01×10^6	5.91×10^6	7.99×10^6	13
Molybdenum	—	—	5.00×10^6	—
Naphthalene	—	—	1.31×10^6	0.9
Nickel	—	—	1.00×10^4	—
Nitrogen dioxide	941	3.76×10^4	3.76×10^4	—
Octane	—	—	4.67×10^6	1
Pentane	—	—	4.43×10^6	1.5
Perchloroethylene	2.37×10^5	1.56×10^6	1.02×10^6	—
Phenol	7.31×10^4	1.12×10^5	9.62×10^5	1.8
Phosphoric acid	—	—	1.00×10^6	—
Phosphorus	—	—	5,000	—
Propane	—	—	3.79×10^6	2.1
Propylene	—	—	—	2
Propylene glycol monomethyl ether	—	—	—	1.6
Propylene oxide	1.73×10^5	1.06×10^6	9.50×10^5	2.3
Selenium (& compounds)	—	—	1,000	—
Styrene	8.52×10^4	9.80×10^5	2.98×10^6	0.9
Sulfur dioxide	524	1,965	2.62×10^5	—
Sulfur trioxide	200	8,700	—	—
Sulfuric acid	200	8,700	1.50×10^4	—
1,1,2,2-Tetrachloroethane	—	—	6.87×10^5	—
Toluene	2.52×10^5	5.28×10^6	1.88×10^6	1.1
1,1,2-Trichloroethane	—	—	5.46×10^5	6
Trichloroethylene	1.40×10^6	5.16×10^6	5.37×10^6	12.5
1,1,2-Trichloro-1,2,2-trifluoroethane	—	—	1.53×10^7	—
Triethylamine	—	—	8.28×10^5	1.2
1,2,4-Trimethylbenzene	8.85×10^5	2.26×10^6	—	0.9
Vanadium (fume or dust)	—	—	3.50×10^4	—
Vinyl chloride	1.16×10^6	7.17×10^6	—	3.6
Xylenes (mixed)	5.64×10^5	1.09×10^7	—	—
m-Xylene	—	—	3.91×10^6	1.1
o-Xylene	—	—	3.91×10^6	0.9
p-Xylene	—	—	3.97×10^6	1.1

To learn more about the AEGLs, IDLHs, and LELs described in this section, visit the US EPA AEGL web page or the NIOSH Pocket Guide to Chemical Hazards web page (URLs in References section).

IV. HEALTH EFFECTS OF SELECT CALIFORNIA REFINERY CHEMICALS

This section provides further information for select California refinery chemicals on various health and safety risks to exposed populations. These include noncancer health effects, carcinogenic effects, and effects on development or reproduction. Appendix A provides an expanded description of the acute and chronic health effects for a number of refinery chemicals. The chemicals described below are only a few of many chemicals that may have adverse effects on human health. OEHHA selected these chemicals based on their high emissions, low health guidance values, emissions from multiple processes and equipment, involvement in incident history, or level of toxicity-weighted emissions.

Table 6 presents health effects for select California refinery chemicals including information on the physical/chemical properties, acute health effects, and chronic health effects of each chemical. These effects are dependent on level and duration of exposure. Web sources for the health summaries are also included below.

Table 6. Health Effects of Select California Refinery Chemicals

Chemical	Health Effects
Acetaldehyde	Physical/Chemical Properties: Colorless liquid with distinct, pungent odor. Flammable. Acute Health Effects: bronchoconstriction; irritation of the eye, upper respiratory tract, nose, throat, and lung; decreased pulmonary function Chronic Health Effects: degeneration, inflammation, and hyperplasia of nasal airways; in animals: changes in nasal mucosa, respiratory distress, growth retardation, early mortality
Ammonia	Physical/Chemical Properties: Colorless gas with pungent and irritating odor. Corrosive at high concentrations. Slight fire hazard. Acute Health Effects: irritation of the eyes, nose, throat, and skin; corrosive injury to the skin and mucus membranes of the eyes, lungs, and gastrointestinal tract; eye redness and lacrimation; cough, choking sensation; dyspnea; death from pulmonary edema Chronic Health Effects: decreased pulmonary function; irritation of the eyes, skin, and respiratory tract; chronic cough; asthma; lung fibrosis; chronic irritation of the eye membranes and skin
Arsenic	Physical/Chemical Properties: Grey metallic solid with no characteristic taste or smell. Noncombustible in large amounts, but a slight fire hazard if dust is exposed to flame. Acute Health Effects: decreased fetal weight (mice); respiratory tract irritation, cough, dyspnea, chest pain, sore throat, dermatitis, laryngitis, mild bronchitis, conjunctivitis, death if ingested
	Chronic Health Effects: impairment of intellectual function and neurobehavioral development; malaise; peripheral sensorimotor neuropathy; anemia; jaundice; gastrointestinal discomfort; darkened skin with warts on the palms, soles, and torso; irritation of the throat and respiratory tract; perforation of the nasal septum
Benzene	Physical/Chemical Properties: Colorless liquid with a petroleum-like smell. Highly flammable.
	Acute Health Effects: developmental damage in blood cells (mice); irritation of the eyes, nose, and throat; central nervous system depression; drowsiness; dizziness; rapid heart rate; headache; tremor; confusion; unconsciousness; death from respiratory failure
	Chronic Health Effects: increases and decreases in blood cell count, aplastic anemia, excessive bleeding, damage to the immune system

Chemical	Health Effects
Benzo[a]pyrene	Physical/Chemical Properties: Pale yellow solid with a faint aromatic odor. Nonflammable.
	Acute Health Effects: irritation and burning sensation of the eyes and skin
1,3-Butadiene	Physical/Chemical Properties: Colorless gas with a mild gasoline-like odor. Highly flammable.
	Acute Health Effects: decreased male fetal weight (mice); irritation of the eyes, nose, throat, and lungs; blurred vision; nausea; paresthesia; dryness of the mouth, throat, and nose; fatigue; headache; vertigo; hypotension; unconsciousness; central nervous system depression
	Chronic Health Effects: ovarian atrophy (mice); exacerbation of asthmatic symptoms, increased incidence of respiratory tract infections, cardiovascular diseases, effects on the blood and female reproductive organs
Dibenzofurans (PCDF), Dibenzo-p-dioxins (PCDD)	Physical/Chemical Properties: Colorless crystals. Nonflammable.
	Acute Health Effects: chloracne, gastrointestinal upsets, increased levels of serum enzymes and triglycerides, numbness of the extremities
	Chronic Health Effects: increased mortality; decreased weight gain; changes in the liver, lungs, and lymphoid and vascular tissues (rats)
Diethanolamine	Physical/Chemical Properties: Colorless powder or liquid with ammonia-like odor. Combustible.
	Acute Health Effects: cough, nausea, headache, lacrimation, sneezing, smothering sensation, eye and skin burns, corneal necrosis
	Chronic Health Effects: asthmatic airway obstruction

Chemical	Health Effects
Ethylbenzene	Physical/Chemical Properties: Colorless liquid with a gasoline-like odor. Highly flammable.
	Acute Health Effects: chest constriction, irritation of the eyes and throat, dizziness, vertigo; in animals: eye irritation, central nervous system toxicity, effects on the liver and kidney, pulmonary effects
	Chronic Health Effects: cellular alterations and necrosis in the liver, nephrotoxicity, pituitary gland hyperplasia (mice, rats); developmental toxicity (rats, rabbits); other effects in animals: effects on the blood, irreversible damage to the inner ear and hearing
Formaldehyde	Physical/Chemical Properties: Colorless gas with distinct, pungent odor. Flammable.
	Acute Health Effects: mild and moderate eye irritation, headache, rhinitis, dyspnea, lacrimation, mucous membrane irritation, burning, difficulty breathing, bronchitis, pulmonary edema, pneumonia
	Chronic Health Effects: nasal obstruction and discomfort, lower airway discomfort, allergic sensitization, cough, running nose, lacrimation, cellular changes in airway membranes, decreased lung function, headache, depression, mood changes, insomnia, attention deficit, impairment of dexterity and memory
Hydrogen Fluoride	Physical/Chemical Properties: Colorless fuming liquid or gas with a strong, pungent odor. Emits highly irritating and poisonous fumes that are corrosive to metals and body tissues when heated. Nonflammable.
	Acute Health Effects: eye, nose, and throat irritation; lacrimation; sore throat; cough; chest tightness; wheezing; pulmonary edema
	Chronic Health Effects: dental fluorosis; congestion and irritation of the nose, throat, and bronchi; liver and kidney damage

Chemical	Health Effects
Hydrogen Sulfide	Physical/Chemical Properties: Colorless gas with a pungent rotten egg odor. Corrosive and highly flammable.
	Acute Health Effects: headache; nausea; irritation of the skin, eyes, mucus membranes, and respiratory tract; conjunctivitis with ocular pain, lacrimation, and photophobia; death from respiratory arrest
	Chronic Health Effects: nasal inflammation (mice); low blood pressure, headache, nausea, loss of appetite, weight loss, ataxia, eye membrane inflammation, chronic cough
Manganese	Physical/Chemical Properties: Silver solid. Combustible.
	Acute Health Effects: impaired function, nonspecific pulmonary edema, brain damage
	Chronic Health Effects: impaired visual reaction time, hand-eye coordination, and hand steadiness; manganism; changes in neurobehavioral and cognitive abilities; increased incidence of cough, bronchitis, and dyspnea during exercise; increased susceptibility to infectious lung disease
Naphthalene	Physical/Chemical Properties: Volatile white crystalline volatile solid. Flammable in the presence of an ignition source.
	Acute Health Effects: headache, nausea, vomiting, diarrhea, malaise, confusion, anemia, jaundice, convulsions, neurological damage in infants, hemolytic anemia, liver damage, coma
	Chronic Health Effects: nasal inflammation, olfactory epithelia metaplasia, respiratory epithelial hyperplasia (mice); hemolytic anemia, cataracts, retinal hemorrhage; in animals: chronic inflammation of the lung, chronic nasal inflammation, hyperplasia of nasal respiratory epithelium, metaplasia of the olfactory epithelium

Chemical	Health Effects
Nitrogen Oxides (Nitrogen Dioxide)	Physical/Chemical Properties: Yellow-brown liquid or reddish brown gas with a strong odor. Corrosive. Noncombustible, but will accelerate burning of combustible materials.
	Acute Health Effects: increased airway reactivity in asthmatics, cough, fatigue, nausea, choking, headache, abdominal pain, strained breathing, anxiety, mental confusion, lethargy, loss of consciousness, pneumonitis, bronchitis, death from pulmonary edema and inflammatory changes
	Chronic Health Effects: permanent and obstructive lung disease, increased risk of respiratory infections in children
Particulate Matter (PM10, PM2.5)	Physical/Chemical Properties: Mixture of liquid droplets and solids such as dust, dirt, soot, and smoke. Nonflammable.
	Acute Health Effects: irritation of the eyes, nose, and throat; reduced lung function; asthma attacks; irregular heartbeat; cough; wheezing; increased risk of heart attack, stroke, cardiac arrest, and/or congestive heart failure; premature death
	Chronic Health Effects: increased incidence of heart and lung problems
Sulfur Dioxide	Physical/Chemical Properties: Colorless, irritating gas with a choking or suffocating odor. Nonflammable.
	Acute Health Effects: impairment of airway function; irritation of the eyes, mucous membrane, skin, and respiratory tract; airway obstruction from reflex laryngeal spasm and edema, bronchospasm, pneumonitis, pulmonary edema; death
	Chronic Health Effects: altered sense of smell, increased susceptibility to respiratory infections, symptoms of chronic bronchitis, accelerated decline in pulmonary function

Chemical	Health Effects
Sulfuric Acid	Physical/Chemical Properties: Colorless, oily liquid. Corrosive to metals and all body tissues. Noncombustible, but may be explosive or incompatible with other substances.
	Acute Health Effects: small changes in airway function, dental erosion, respiratory tract irritation, bronchoconstriction, altered lung function
	Chronic Health Effects: hyperplasia of bronchial cells in lungs (monkeys); decreased lung function, tracheobronchitis, stomatitis, conjunctivitis, gastritis
Toluene	Physical/Chemical Properties: Clear, volatile liquid with an aromatic odor. Flammable.
	Acute Health Effects: irritation of the eyes, skin, and respiratory tract; impaired reaction time; headache; dizziness; feeling of intoxication; fatigue; sleepiness; nausea; central nervous system depression; ataxia; euphoria; hallucinations; tremors; seizures; coma; death
	Chronic Health Effects: decreased brain weight and altered dopamine receptor binding (rats); nausea, fatigue, eye and upper respiratory tract irritation, dizziness, headache, difficulty with sleep, disorders of the optic nerve, central nervous system depression, permanent neuropsychiatric effects, muscle disorders, cardiovascular effects, renal tube damage, death
Xylene	Physical/Chemical Properties: Colorless, volatile liquid with an aromatic odor. Flammable.
	Acute Health Effects: irritation of the eyes, skin, and respiratory tract; headache; decreased muscle coordination; dizziness; confusion; lung function, liver, and memory impairment; delayed response to visual stimuli; stomach discomfort; ventricular arrhythmias; acute pulmonary edema; death
	Chronic Health Effects: eye irritation; sore throat; floating sensation; lack of appetite; headache; fatigue; dizziness; tremors; loss of coordination; anxiety; impairment of short-term memory; inability to concentrate; cardiovascular, renal, and gastrointestinal effects; permanent neuropsychiatric manifestations; chronic toxic encephalopathy

Health effects described should not be considered a complete profile of the toxicity of the listed chemicals. For more information about the health effects of specific chemicals, see the OEHHA REL web page, the US EPA IRIS web page, or the Agency for Toxic Substances and Disease Registry (ATSDR) Toxic Substances Portal. Additional information can be obtained from sources such as the web pages for the National Institutes of Health (NIH) Hazardous Substances Data Bank (HSDB) and Toxicology Data Network (TOXNET), the Centers for Disease Control and Prevention (CDC) Emergency Preparedness and Response web page, the NIOSH Pocket Guide to Chemical Hazards, or the National Oceanic and Atmospheric Administration's (NOAA) Computer-Aided Management of Emergency Operations (CAMEO) Chemicals.

V. MOST HIGHLY EMITTED CHEMICALS AND OTHER SUPPORTING INFORMATION

High emissions increase a person's risk of exposure. Refinery incident history, common processes, chemical emission rates, and knowledge of health guidance values and emergency exposure levels can help to judge whether air monitoring is needed and guide decisions that may reduce adverse health effects caused by chemical exposures. Refinery incident history and knowledge of common refinery processes can provide responders with information about which processes have had non-routine emissions in the past, and chemicals that may be released in the event of a refinery emergency. Chemical emissions can be useful in assessing the acute and chronic health effects that are anticipated based on the degree of chemical exposure. OEHHA has collected further information on these factors and summarized the findings below.

A. California Refinery Incident History

Refinery incidents are unanticipated conditions at facilities that allow chemicals to be released into the ambient air. These events can include situations in which chemical emissions exceed typical emissions in an accidental release, normal controls are bypassed, or the effectiveness of the normal controls is reduced. During refinery emergencies, large amounts of chemical-rich emissions may be carried to populated areas and cause exposure to a number of compounds. The extent of exposure depends on factors such as the quantity released, chemical properties, and meteorological conditions. In addition to these factors, understanding the chemicals present in a release, the amount emitted, the acute and chronic health effects of exposure, and the air monitoring capabilities for chemicals can help responders characterize the risk associated with a refinery incident or emergency event. Furthermore, members of nearby communities may experience cumulative exposure from multiple events over time and may be more susceptible to pollution-related health problems.

To compile data on recent refinery incidents in California, OEHHA performed searches using the Google search engine. Searches on individual web pages included: CalEPA IRTF, the Chemical Safety Board (CSB), the Bay Area Air Quality Management District's (BAAQMD), various other California Air Quality Management District (AQMD) and Air Pollution Control District (APCD) web pages, and the Contra Costa Health Services web page. OEHHA performed these searches between August and December of 2015.

Based on this research, sulfur dioxide, hydrogen sulfide, and hydrocarbons were the most commonly reported chemicals emitted during refinery incidents. In many instances, adverse health effects were reported following the release of sulfur compounds. Symptoms were consistent with those associated with acute sulfur dioxide and/or hydrogen sulfide exposure: nausea; dizziness; irritation of the eyes, nose, throat, and skin; and unconsciousness.

OEHHA also looked for information on the process units, emission points, and equipment linked to refinery incidents since knowledge of individual refinery processes involved in incidents can provide information on which chemicals are likely to be released into the air. Of the process units, emission points, and equipment identified, flares were the most common sources involved in incidents resulting in emissions to outdoor air. Flares are used at refineries for the combustion and disposal of combustible gases and hydrocarbons to prevent release directly into the atmosphere. Flare events can be planned or unplanned, and usually occur due to emergency relief, overpressure, process upsets, startups, shutdowns, power outages, and other operational safety reasons. Certain chemicals such as sulfur dioxide, hydrogen sulfide, and carbon monoxide are commonly associated with such events. Because they involve the release of smoke, flaring events also result in the release of particulate matter.

Other process units, emission points, and equipment associated with emissions commonly identified in the literature include heaters, storage tanks, cokers, sulfur recovery units, boilers, gas compressors, fluid catalytic cracking units (FCCU), and crude units. Table 7 below displays the process units, emission points, and equipment reported to be associated with refinery incidents based on data for 2001-2012 for California.

Table 7. Process Units, Emission Points, and Equipment Reported to be Associated with California Refinery Incidents[3]

Ammonia recovery unit	FCCU[4]	Oxidizer
Boiler	Flares	Sonic meter system
Cogeneration unit	Gas compressor	Storage tank
Coker	Heater/furnace	Sulfur recovery unit
Cooling unit	Hydrogen plant	Vacuum distillation unit
Crude unit	Hydrotreater	Vapor recovery unit
Diesel unit	Jet fuel unit	

[3] Process units reported to be associated with refinery incidents are listed in alphabetical order based on California data for 2001-2012 reported by Chemical Safety Board, Bay Area Air Quality Management District, and Contra Costa Health Services web pages. Note that the process units listed above may not constitute all equipment or processes involved in refinery incidents in the state.
[4] Fluid catalytic cracking unit (FCCU)

Findings discussed in this section refer to the frequency of refinery incidents with identified chemical releases in California from 2001-2012. They are based on limited data and do not represent all of the refinery incidents during this period. The majority of incidents included in this search was self-reported by personnel from California refineries and community residents and were not the result of air monitoring efforts. The occurrence of refinery incidents varies from refinery to refinery and may reflect site-specific equipment failure and equipment maintenance and upkeep.

B. California Refinery Process Units, Emission Points, and Equipment

To expand OEHHA's list of refinery chemical emissions, chemicals associated with specific refinery areas, equipment, or processes were identified using data provided by US EPA (2012a, 2012b). In response to a request from US EPA, all refineries active during the year 2010 were asked to measure air emissions from each process, emission point, or piece of equipment for a specified period and submit the data to that agency. This request resulted in a list of chemicals routinely emitted and measured for each process unit, emission point, or equipment. OEHHA used these emissions inventories to identify the most commonly occurring processes and their associated chemical emissions.

Appendix B displays a list of chemical emissions associated with each process unit or emission point based on these 2010 California data. The process data and chemicals shown in Appendix B are those most commonly found based on OEHHA's research and do not represent a complete list of all refinery processes or chemicals emitted from each process.

Table 8 shows a sample of process units and release types (fugitive and point emissions) selected based on comparison of data obtained from California refineries active during the year 2010.

Table 8. California Refinery Process Units, Emission Points, and Equipment Sorted by Release Type

Fugitive Emissions	Point Emissions	Fugitive and Point Emissions
Hydrogen plant	Boiler	Alkylation unit
Product loading	Flare	Cogeneration unit
Wastewater treatment	Heater	Coker
	Hydrotreater	Cooling tower
	Sulfur recovery unit	Crude unit
	Thermal oxidizer	Fluid catalytic cracking unit
	Vent	Hydrocracker
		Incinerator
		Stack
		Storage tank

C. Chemical Analysis Categories for Air Monitoring

Upon completion of OEHHA's compilation of California refinery chemicals (Table 1), chemicals were sorted by CARB (Appendix C) into chemical analysis categories based upon air monitoring capabilities and methodology for collecting air samples. This classification scheme allowed for the consideration of emissions, health effects, and health guidance values of chemicals that require similar procedures for air monitoring. Table 9 is an overview of the chemical analysis categories provided by CARB.

Table 9. Chemical Analysis Categories for Air Monitoring

Acid	Metal
Aldehyde	Microscopy (for asbestos)
Dioxin/Dibenzofuran	Mass/Particulate Matter (PM)
Extractable	Polycyclic Aromatic Hydrocarbons (PAH)
Gas	Volatile Organic Compounds (VOC)
Glycol	

D. Most Highly Emitted Routine Emissions of Toxic Air Contaminants from California Refineries

Since high emissions increase a person's risk of exposure, consideration of chemical emission rates can help CARB make judgements about air monitoring. Routine emissions data from California refineries for 2009-2012 were obtained from the CEIDARS database facility search tool. The emissions data were submitted to CARB under the AB 2588 Air Toxics Hot Spots Program requirements and reflect TAC releases that occurred during routine facility operations. The Hot Spots program requires facilities to report emission inventory updates every four years. Therefore, not all facilities update emission inventories in the same year. As a result, some chemicals may not be reported each year. Based on this quadrennial method of updating emission inventories in the Hot Spots Program, the information that the CEIDARS database provides on the TACs emitted from refineries may underestimate total routine emissions across refineries in any given year.

US EPA's Toxics Release Inventory (TRI) Program is an additional resource for learning about toxic chemical releases into the air, as well as into land and water. The TRI Program requires certain industrial facilities in the US to report annual release data in accordance to the Emergency Planning and Community Right-to-Know Act (EPCRA). The TRI database contains data by facility and by year. The focus of this report is the potential health effects of chemicals emitted from refineries. This is not an assessment of the potential health effects of all emissions. However, OEHHA found it useful to understand the relative routine and non-routine emissions to compare with the health effects of those chemicals to assist CARB in prioritizing chemicals for air monitoring.

Appendix D provides the complete list of average routine TAC emissions obtained from CEIDARS from 2009-2012. A four-year average was calculated for each chemical. The 10 pollutants routinely released from refineries in California in the greatest quantities per year based on 2009-2012 data are displayed in Table 10.

In evaluating the emissions, the toxic potency of the chemical emitted can also be taken into account. Summing emissions of a chemical for all California refineries and weighting it by a value related to its toxic potency results in a "toxicity-weighted" emissions score. The toxicity-weighted emissions score was calculated using emissions data (pounds emitted per year) obtained from the Air Toxics "Hot Spots' Emissions Inventory" (2014) multiplied by a toxicity-weight derived from US EPA's Inhalation Toxicity Scores for individual chemicals. (https://www.epa.gov/rsei/rsei-toxicity-data-and-calculations).

In terms of toxicity, by applying toxicity weights to the total pounds released, the top toxicity-weighted releases, starting with the highest are: formaldehyde, nickel, arsenic, cadmium, and benzene followed by polycyclic aromatic hydrocarbons (PAHs) (total), hexavalent chromium, benzo(a)pyrene, phenanthrene, beryllium, ammonia, 1,3-butadiene, naphthalene, hydrogen sulfide, acetaldehyde, manganese, and diethanolamine. However, it should be noted that the amount released of hexavalent chromium, arsenic, and beryllium are minimal, all less than 100 lbs annually. Appendix H provides more information on TAC emissions for the 2014 CEIDARs data and the toxicity-weighted emissions scores.

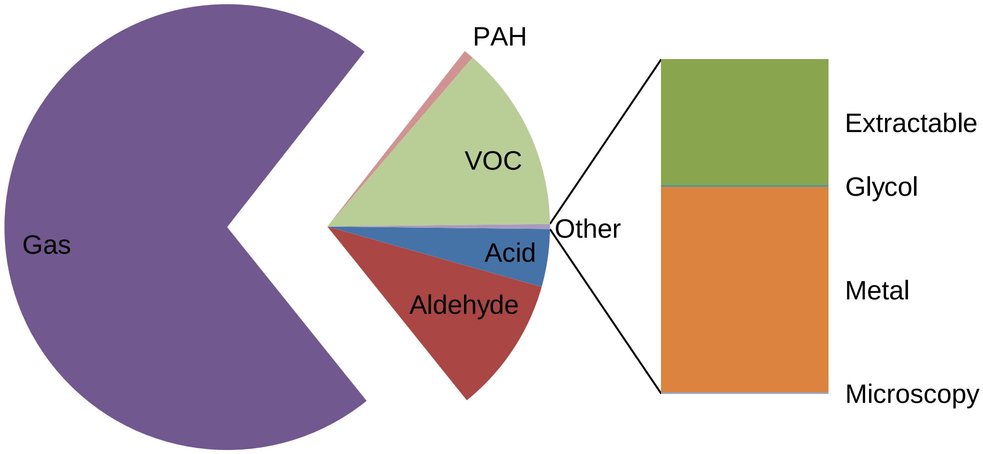
Table 10. Toxic Air Contaminants with the Ten Highest Routine Emissions from California Refineries

Chemical	Emissions (lb/year)[5]
Ammonia	2,085,824
Formaldehyde	288,412
Methanol	122,611
Sulfuric acid	104,573
Hydrogen sulfide	103,385
Toluene	87,945
Xylenes	79,177
Benzene	43,308
Hexane	39,646
Hydrogen chloride	21,450

[5] Average annual routine TAC emissions from 28 California refineries based on data from the Air Resources Board CEIDARS database for 2009-2012.

Routine TAC emissions from California refineries during 2009-2012 were examined based on the chemical analysis categories provided by CARB. Gases made up the majority of the routine TAC emissions. The VOC, aldehyde, and acid categories also had notable amounts. Figure 1 below displays the relative occurrence of CARB's chemical analysis categories for air monitoring (Table 9) among the routine TAC emissions from the refineries during this period.

Figure 1. Relative Occurrence of Chemical Analysis Categories in Routine Toxic Air Contaminant Emissions from California Refineries



E. Routine and Non-routine Chemical Emissions by California Refineries

OEHHA compiled data on routine and non-routine chemical emissions, not limited to TACs, from the California refineries active during 2010 using data provided by US EPA (2012a, 2012b). Routine emissions represent chemical releases that occur during normal facility operations, while non-routine releases reflect emissions during any non-routine refinery operation. Non-routine operations include startups, shutdowns, and malfunction operations such as refinery-wide power loss, maintenance, and flaring events.

The refinery emissions shown in this section were measured or calculated at various process units, emission points, and equipment and reported by refineries to US EPA; however, these data were limited to a single reporting year of 2010, and therefore may not be representative of all non-routine emissions from California refineries. Appendix E includes the complete list of routine and non-routine emissions data reported by California refineries for 2010. In some instances, non-routine emissions exceeded routine emissions during this period. The 10 pollutants routinely released from refineries in California in the greatest quantities in 2010 based on data from US EPA are displayed in Table 11 below.

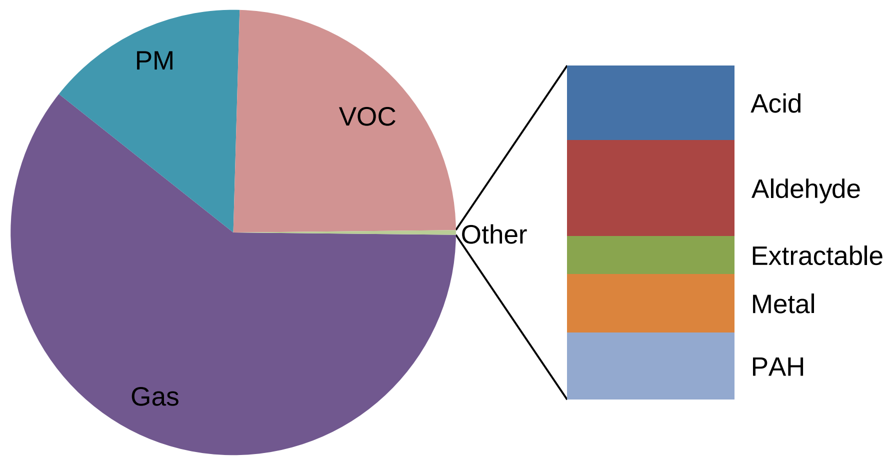
Table 11: Ten Highest Routine Chemical Emissions by California Refineries[1]

Chemical	Emissions (lb)
Sulfur dioxide	21,158,748
Carbon monoxide	16,972,733
Nitrogen oxides	16,415,674
Volatile organic compounds (VOC)	13,562,963
PM_{10}	6,617,952
Butane	5,881,551
PM_{10} (filterable)	2,805,076
$PM_{2.5}$	2,004,663
Nitrogen dioxide	1,971,085
PM (condensable)	1,677,433

[1] Annual routine chemical emissions from California refineries based on data for 2010 (US EPA, 2012a; US EPA, 2012b).

Routine emissions from California refineries were composed primarily of chemicals in the gas, VOCs, and particulate matter categories. Although data for routine emissions is limited to 2010, OEHHA included this dataset because it provides information about the chemicals other than TACs that are present in refinery emissions. Figure 2 shows the relative occurrence of CARB's categories for air monitoring (Table 9) found in routine refinery emissions during 2010.

Figure 2. Relative Occurrence of Chemical Analysis Categories in Routine Toxic Air Contaminant Emissions from California Refineries[1]



[1] PM is Particulate Matter and includes PM10 and PM2.5. The chemical analysis category is also referred to as "mass".

Table 12 displays the ten highest non-routine chemical emissions from refineries in California in the greatest quantities in 2010 based on data from US EPA.

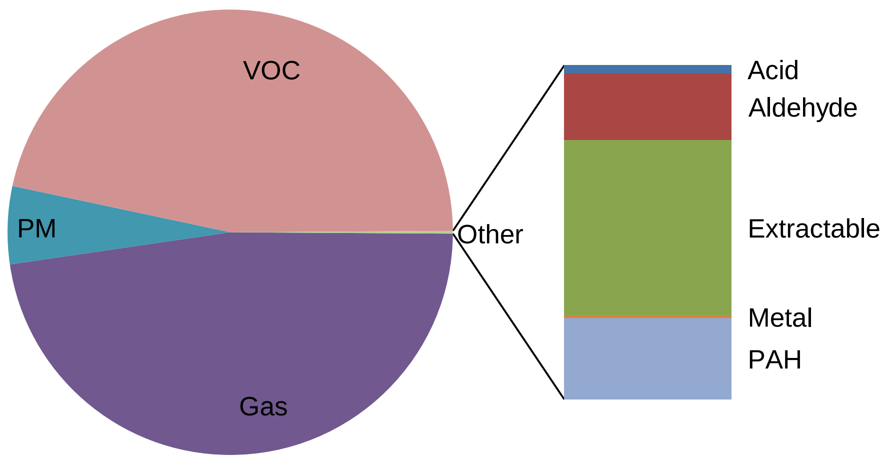
Table 12. Ten Highest Non-routine Chemical Emissions by California Refineries[1]

Chemical	**Emissions (lb)**
Volatile organic compounds (VOC)	1,123,158
Sulfur dioxide	553,834
Carbon monoxide	418,331
Nitrogen oxides	223,792
PM_{10}	89,572
$PM_{2.5}$	26,306
PM_{10} (filterable)	22,802
Nitrogen dioxide	12,397
Propylene	7,799
Hexane	7,625

[1] Annual non-routine emissions from California refineries based on data for 2010 (US EPA, 2012a; US EPA, 2012b).

While these emissions appeared to have a similar profile of chemical analysis categories to that of routine emissions, non-routine emissions from California refineries were composed of a greater fraction of VOC releases than releases of gases and particulate matter. The relative occurrence of CARB's chemical analysis categories for air monitoring (Table 9) found in non-routine refinery emissions during 2010 are shown in Figure 3 below.

Figure 3. Relative Occurrence of Chemical Analysis Categories in Non-routine Chemical Emissions by California Refineries



F. Refinery Emissions in the US and Fuel-Burning Experiments

Because refineries are only required to report emissions of regulated chemicals, knowledge of unregulated chemicals also released can provide information on chemical speciation or characteristics that can ultimately be used by officials for air monitoring or risk assessment purposes. To this end, OEHHA conducted a literature search in peer-reviewed journal articles to find additional chemicals associated with refinery emissions in the US. Appendix F lists the chemicals and CAS RNs found in literature describing refinery air monitoring in the US or controlled burning experiments during 1979-2007.

VI. CONCLUSIONS

OEHHA has compiled a list of chemicals emitted from petroleum refineries in California. This list identifies possible acute and chronic health effects resulting from exposure to these chemicals, including cancer and effects on development or reproduction. OEHHA has compiled a list of health guidance values and emergency exposure levels for refinery chemicals that can be referenced during or after emergencies to evaluate the potential for health risks associated with unanticipated chemical releases into the air. Health effects were summarized for a selection of chemicals based on the availability of health guidance values and emergency exposure levels, the quantities emitted in routine and non-routine emissions, and the frequency of occurrence of these chemical emissions in refinery processes and emissions. The refinery chemicals were sorted by chemical analysis categories based on current air monitoring capabilities.

The list of California refinery chemicals, processes, and routine and non-routine emissions included in this report represent data obtained from sources that represent different periods and durations of time in different levels of detail. The data does not encompass all of the refinery chemicals, processes, and emissions points occurring in California. OEHHA has compiled this information to assist CARB and local air districts in making decisions and recommendations for air monitoring of chemicals in communities near refineries, especially during emergencies.

The top candidates for air monitoring based on amounts of emission and toxicity considerations include acetaldehyde, ammonia, benzene, 1,3-butadiene, cadmium, diethanolamine, formaldehyde, hydrogen sulfide, manganese, naphthalene, nickel, PAHs, PM, sulfur dioxide, sulfuric acid, and toluene. The release of these chemicals from refineries does not necessarily mean that local communities face a significant health risk or substantial exposures, but it does increase the likelihood of exposure for nearby communities. Air monitoring of these chemicals may inform decisions that could reduce exposure.

The top toxicity-weighted releases, starting with the highest, are: formaldehyde, nickel, arsenic, cadmium, and benzene followed by polycyclic aromatic hydrocarbons (PAHs) (total), hexavalent chromium, the individual PAHs benzo(a)pyrene and phenanthrene, beryllium, ammonia, 1,3-butadiene, naphthalene, hydrogen sulfide, acetaldehyde, manganese, and diethanolamine. However, it should be noted that the total amount released of hexavalent chromium, arsenic, and beryllium from all California refineries is minimal, less than 100 lbs annually, so these would be unlikely candidates for air monitoring. This data was obtained from CEIDARS for 2014.

The top candidates for air monitoring are not ranked or prioritized further, as this report identifies the top candidates based on their average emissions across all California refineries. An important consideration for air monitoring at individual refineries is that the candidate chemicals will differ based on location as well as year. Some top-candidate chemicals are only released in small amounts from individual refineries.

REFERENCES

Abdo KM, Grumbein S, Chou BJ and Herbert R (2001). Toxicity and carcinogenicity study in F344 rats following 2 years of whole-body exposure to naphthalene vapors. Inhal Toxicol 13: 931-950.

Agency for Toxic Substances and Disease Registry (ATSDR). *Toxic Substances Portal. Substances A-Z*. Centers for Disease Control and Prevention. http://www.atsdr.cdc.gov/substances/indexAZ.asp. Last updated March 3, 2011. Accessed September 3, 2015.

American Industrial Hygiene Association (AIHA). *Emergency Response Planning Guidelines*. https://www.aiha.org/get-involved/AIHAGuidelineFoundation/EmergencyResponsePlanningGuidelines/Pages/default.aspx. Accessed March 15, 2016.

Arisawa K, Takeda H and Mikasa H (2005). Background exposure to PCDDs/PCDFs/PCBs and its potential health effects: A review of epidemiologic studies. J Med Invest 52: 10-21.

ATSDR. (2000). *Medical Management Guidelines (MMGs) for Acute Chemical Exposures*. In: Managing Hazardous Materials Incidents. Vol. 3. Agency for Toxic Substances and Disease Registry, Centers for Disease Control and Prevention. http://www.atsdr.cdc.gov/MHMI/mhmi_v1_2_3.pdf. Accessed January 13, 2016.

Bay Area Air Quality Management District (BAAQMD). *Incidents and Advisories*. http://www.baaqmd.gov/about-air-quality/incidents-and-advisories. Last updated June 9, 2015. Accessed September 3, 2015.

Booher LE and Janke B (1997). Air Emissions from Petroleum Hydrocarbon Fires During Controlled Burning. Am Ind Hyg Assoc J 58: 359-365.

Bord N, Cretier G, Rocca JL, Bailly C and Souchez JP (2004). Determination of diethanolamine or N-methyldiethanolamine in high ammonium concentration matrices by capillary electrophoresis with indirect UV detection: Application to the analysis of refinery process waters. Anal Bioanal Chem 380: 325-332.

California Air Resources Board (CARB). *California Emission Inventory Development and Reporting System*. California Environmental Protection Agency. http://www.arb.ca.gov/app/emsinv/emssumcat.php. Last updated June 9, 2014. Accessed September 3, 2015.

CARB and CAPCOA. (2015). *Refinery Emergency Air Monitoring Assessment Report. Objective 1: Delineation of Existing Capabilities*. Air Resources Board, California Environmental Protection Agency. California Air Pollution Control Officers Association Air Monitoring Committee. http://www.arb.ca.gov/fuels/carefinery/crseam/crseam.htm. Accessed August 28, 2015.

CARB and OEHHA. (2002). *Chapter 7: Health Effects of Particulate Matter*. In: Public Hearing to Consider Amendments to the Ambient Air Quality Standards for Particulate Matter and Sulfates. Air Resources Board and Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. http://www.arb.ca.gov/carbis/research/aaqs/std-rs/pm-final/ch7-9.pdf. Last updated May 16, 2005. Accessed December 21, 2015.

Catoggio JA, Succar SD and Roca AE (1989). Polynuclear aromatic hydrocarbon content of particulate matter suspended in the atmosphere of La Plata, Argentina. Sci Total Environ 79: 43-58.

California Environmental Protection Agency (CalEPA). *Interagency Refinery Task Force*. http://www.calepa.ca.gov/Refinery/. Accessed March 15, 2016.

Centers for Disease Control and Prevention (CDC). *Emergency Preparedness and Response: Chemical Agents*. http://emergency.cdc.gov/agent/agentlistchem.asp. Last updated April 8, 2013. Accessed September 3, 2015.

Chemical Safety Board (CSB). (2013). *Industrial Chemical Incident Screening Database*. United States Chemical Safety and Hazard Investigation Board.

CSB. *US Chemical Safety Board*. United States Chemical Safety and Hazard Investigation Board. http://www.csb.gov/. Accessed September 3, 2015.

Contra Costa Health Services (CCHS). *Major Accidents at Chemical/Refinery Plants*. http://cchealth.org/hazmat/accident-history.php. Accessed September 3, 2015.

Fingas MF, Lambert P, Li K, Wang Z, Ackerman F, Whiticar S and Goldthorp M (2001). Studies of Emissions from Oil Fires. Int Oil Spill Conf 2001(1): 539-544.

IARC. *Monographs and Supplements Available Online.* International Agency for Research on Cancer, World Health Organization. http://monographs.iarc.fr/ENG/Monographs/PDFs/index.php. Accessed September 3, 2015.

Kulkarni P, Chellam S and Fraser MP (2007). Tracking Petroleum Refinery Emission Events Using Lanthanum and Lanthanides as Environmental Markers for $PM_{2.5}$. Environ Sci Technol 41: 6748-6754.

Lewis RC, Gaffney SH, Le MH, Unice KM and Parstenbach DJ (2012). Airborne concentrations of metals and total dust during solid catalyst loading and unloading operations at a petroleum refinery. Int J Hyg Environ Health 215: 514-521.

Lucas R (2002). *Petroleum Refinery Source Characterization and Emission Model for Residual Risk Assessment*. Office of Air Quality Planning and Standards, United States

Environmental Protection Agency. http://www3.epa.gov/ttnchie1/efpac/protocol/refinery_RR_model_documentation_Final.pdf. Accessed January 13, 2016.

National Institutes of Health (NIH). *Hazardous Substances Data Bank (HSDB).* United States National Library of Medicine. http://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm. Accessed March 15, 2016.

National Institute for Occupational Safety and Health (NIOSH). C*hemical Listing and Documentation of Revised IDLH Values (as of 3/1/95).* Centers for Disease Control and Prevention. http://www.cdc.gov/niosh/idlh/intridl4.html. Last updated December 4, 2014. Accessed September 3, 2015.

Nelson TP (2013). An Examination of Historical Air Pollutant Emissions from US Petroleum Refineries. Environ Progr Sustain Energy 32(2): 425-432.

NIH. *Toxicology Literature Online (TOXLINE)*. National Institutes of Health, United States National Library of Medicine. http://toxnet.nlm.nih.gov/newtoxnet/toxline.htm. Accessed March 15, 2016.

NIOSH. *Occupational Safety and Health Guideline for Ammonia*. National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention. http://www.cdc.gov/niosh/topics/ammonia/. Last updated February 4, 2014. Accessed September 2, 2015.

NIOSH. *NIOSH Pocket Guide to Chemical Hazards*. National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention. http://www.cdc.gov/niosh/npg/. Last updated February 13, 2015. Accessed September 3, 2015.

NOAA. *CAMEO Chemicals. Database of Hazardous Materials*. National Oceanic and Atmospheric Administration, United States Department of Commerce. http://cameochemicals.noaa.gov/. Accessed September 9, 2015.

NOAA. *Immediately Dangerous to Life and Health Limits (IDLHs)*. National Oceanic and Atmospheric Administration, United States Department of Commerce. http://response.restoration.noaa.gov/idlhs. Last updated September 18, 2015. Accessed September 21, 2015.

OEHHA. (2008). *Technical Support Document for the Derivation of Noncancer Reference Exposure Levels*. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. http://oehha.ca.gov/media/downloads/crnr/noncancertsdfinal.pdf.

OEHHA. (2009). *Technical Support Document for Cancer Potency Factors: Methodologies for derivation, listing of available values, and adjustments to allow for* *early life stage exposures*. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. http://oehha.ca.gov/media/downloads/crnr/tsdcancerpotency.pdf.

OEHHA. *Appendix A. Hot Spots Unit Risk and Cancer Potency Values*. In: Technical Support Document for Cancer Potency Factors: Methodologies for derivation, listing of available values, and adjustments to allow for early life stage exposures. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. http://oehha.ca.gov/media/downloads/crnr/appendixa.pdf. Accessed January 13, 2016.

OEHHA. *Appendix B. Chemical-specific summaries of the information used to derive unit risk and cancer potency values*. In: Technical Support Document for Cancer Potency Factors: Methodologies for derivation, listing of available values, and adjustments to allow for early life stage exposures. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. http://oehha.ca.gov/media/downloads/crnr/appendixb.pdf. Accessed January 13, 2016.

OEHHA. *OEHHA Acute, 8-hour and Chronic Reference Exposure Level (REL) Summary*. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. http://oehha.ca.gov/air/general-info/oehha-acute-8-hour-and-chronic-reference-exposure-level-rel-summary. Accessed September 3, 2015.

OEHHA. *Chemicals Known to the State to Cause Cancer or Reproductive Toxicity*. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. http://oehha.ca.gov/media/downloads/proposition-65//p65single04222016.pdf. Accessed September 3, 2015.

OEHHA. *California Human Health Screening Levels (CHHSLs)*. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. http://oehha.ca.gov/risk-assessment/california-human-health-screening-levels-chhsls. Accessed March 15, 2016.

OEHHA. *About Proposition 65*. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. http://oehha.ca.gov/proposition-65/about-proposition-65. Accessed March 15, 2016.

OPPT. *Acute Exposure Guideline Levels (AEGLs).* Office of Pollution Prevention and Toxics, United States Environmental Protection Agency. http://www.epa.gov/oppt/aegl/pubs/chemlist.htm. Last updated June 15, 2015. Accessed September 3, 2015.

SCAPA. *Protective Action Criteria for Chemicals - Including AEGLs, ERPGs, & TEELs*. Subcommittee on Consequence Assessment and Protective Actions, United States Department of Energy. http://orise.orau.gov/emi/scapa/chem-pacs-teels/. Accessed March 15, 2016.

SCAQMD. *Special Monitoring and Emissions Studies*. South Coast Air Quality Management District. http://www.aqmd.gov/home/library/air-quality-data-studies/special-monitoring. Accessed September 4, 2015.

Sexton K and Westberg H (1979). Ambient Air Measurements of Petroleum Refinery Emissions. J Air Poll Control Assoc 29(11): 1149-1152.

Shaw SD, Berger ML, Harris JH, Yun SH, Wu Q, Liao C, Blum A, Stefani A and Kannan K (2013). Persistent organic pollutants including polychlorinated and polybrominated dibenzo- p-dioxins and dibenzofurans in firefighters from Northern California. Chemosphere 91: 1386-1394.

Skrtic L (2006). Hydrogen Sulfide, Oil and Gas, and People's Health. University of California, Berkeley. http://www.bouldercounty.org/doc/landuse/hydrogensulfidestudy.pdf. Accessed January 13, 2016.

Stigter JB, de Haan HPM, Guicherit R, Dekkers CPA and Daane ML (2000). Determination of cadmium, zinc, copper, chromium and arsenic in crude oil cargoes. Environ Pollut 107: 451-464.

Strosher MT (2000). Characterization of Emissions from Diffusion Flare Systems. J Air & Waste Manage Assoc 50: 1723-1733.

Thompson TS, Clement RE, Thornton N and Luyt J (1990). Formation and Emission of PCDDs/PCDFs in the Petroleum Refining Industry. Chemosphere 20: 1525-1532.

US EPA. (2012a). *Petroleum Refinery ICR Responses*. *DVD 1 of 6: Facilities AK5A0040 – CA5A0260*. United States Environmental Protection Agency.

US EPA. (2012b). *Petroleum Refinery ICR Responses*. *DVD 2 of 6: Facilities CA5A0270 – LA3C0580*. United States Environmental Protection Agency.

US EPA. *Integrated Risk Information System (IRIS).* United States Environmental Protection Agency. http://www.epa.gov/iris/. Last updated March 15, 2016. Accessed October 6, 2015.

US EPA. *Acute Exposure Guideline Levels for Airborne Chemicals*. United States Environmental Protection Agency. https://www.epa.gov/aegl. Last updated October 5, 2015. Accessed October 6, 2015.

US EPA. *TTN*Web - *Technology Transfer Network*. United States Environmental Protection Agency. https://www3.epa.gov/ttn/. Last updated September 10, 2015. Accessed October 6, 2015.

US EPA. *Regional Screening Levels (RSLs) - Generic Tables (November 2015)*. United States Environmental Protection Agency. https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-november-2015. Last updated March 7, 2016. Accessed March 15, 2016.

US EPA. *Toxics Release Inventory (TRI) Program*. United States Environmental Protection Agency. https://www.epa.gov/toxics-release-inventory-tri-program. Last updated April 19, 2016. Accessed April 28, 2016.

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APPENDIX A: SUPPLEMENTARY INFORMATION ON HEALTH EFFECTS OF SELECT REFINERY CHEMICALS

Appendix A provides further information on select California refinery chemicals based on various factors that may pose health and safety risks to exposed populations, such as noncancer health effects, carcinogenic effects, effects on development or reproduction, and flammability. OEHHA selected these specific chemicals for inclusion here based on their high emissions, low health guidance values, emissions from multiple processes and equipment, involvement in incident history, or based on their toxicity-weighted emissions.

The health summaries included in Appendix A expand upon the basic acute and chronic health effects of the refinery-associated chemicals in California shown in Table 6, but should not be considered a complete list of health effects of the chemicals. The health and exposure summaries described in this section are derived primarily from the OEHHA web page for REL documents, the US EPA IRIS and Technology Transfer Network web pages, the ATSDR Medical Management Guidelines for Acute Chemical Exposures, or the NIOSH Pocket Guide to Chemical Hazards. Additional information on chemical toxicity profiles can be obtained from sources such as the web pages for NIH's Hazardous Substances Database (HSDB) and Toxicology Data Network (TOXNET), CDC's Emergency Preparedness and Response, or CAMEO Chemicals (URLs in References section).

Information regarding CPFs and the Proposition 65 status of carcinogens and developmental or reproductive toxicants was obtained from publically available OEHHA documents. To learn more about chemical-specific cancer studies, the development of CSFs, and Proposition 65 status, see OEHHA (2009) and visit the OEHHA air toxics and Proposition 65 web pages, or the IARC web page (URLs in References section).

Descriptions of California refinery incidents occurring in 2001-2012 were derived from data provided by CSB, BAAQMD, and CCHS. In addition, California refinery process and air emissions data were provided by US EPA (2012a, 2012b) and CARB unless otherwise noted.

The following chemicals are discussed in Appendix A:

i. Acetaldehyde
ii. Ammonia
iii. Arsenic
iv. Benzo[a]pyrene
v. Benzene, Toluene, Ethylbenzene, and Xylene (BTEX)
vi. 1,3-Butadiene
vii. Dibenzofurans/Dibenzo-p-dioxins
viii. Diethanolamine
ix. Formaldehyde
x. Hydrogen Fluoride

xi. Hydrogen Sulfide
xii. Manganese
xiii. Naphthalene
xiv. Nitrogen Oxides
xv. Particulate Matter (PM_{10} and $PM_{2.5}$)
xvi. Sulfur Dioxide
xvii. Sulfuric Acid

i. Acetaldehyde

At room temperature, acetaldehyde is a colorless liquid with a distinct, pungent odor detectable even at low concentrations. Acetaldehyde is found in air in the vapor, water vapor, and particulate phases. It is flammable with an LEL of 4%, and combustion may generate carbon monoxide. Emissions of acetaldehyde into the environment commonly occur during combustion processes, making inhalation the primary route of exposure.

Acetaldehyde has been detected in both ambient air emissions and at several refinery process units such as boilers, cokers, crude units, FCCUs, heaters, and incinerators (Lucas, 2002). Vapors of acetaldehyde are heavier than air and can cause asphyxiation in low-lying, enclosed, or poorly ventilated areas. In addition, it has been shown that this respiratory irritant has a more severe impact on infants and children.

In acute and chronic inhalation studies, the respiratory system has been the hazard index target tissue for acetaldehyde. Acute exposure to acetaldehyde has been linked to eye redness and swelling, sensory (eye, nose, throat) irritation, and bronchoconstriction in asthmatics. Asthmatics are more sensitive to the adverse effects of acetaldehyde and may be more likely to show symptoms such as shortness of breath, bronchoconstriction, wheezing, and decreased pulmonary function. Because children are more likely to be diagnosed with asthma than adults and their asthma episodes can be more severe, they are particularly vulnerable to the effects of acetaldehyde exposure. In a study conducted on adult human volunteers, asthmatics exhibited bronchoconstriction after inhalation of 142 mg/m^3 acetaldehyde for two to four minutes. In a supporting study, eye irritation, followed by upper respiratory tract, nose, throat, and lung irritation, was observed following whole-body exposure to 45 mg/m^3 for 15 minutes. At high concentrations, the temporary onset of transient conjunctivitis (inflammation or infection of the eye) was also noted. The OEHHA acute REL for acetaldehyde was determined to be 470 $\mu g/m^3$ after time and dose adjustments and consideration of uncertainties in these studies.
Inflammation and injury to the respiratory tract occurs following prolonged exposure to acetaldehyde. In animals, acetaldehyde exposure targets the nasal cavity and has been shown to lead to effects such as changes in the nasal mucosa, respiratory distress, growth retardation, and early mortality in rats. OEHHA used an inhalation study on rats exposed to various concentrations of acetaldehyde as the basis for the OEHHA chronic REL. The degenerative, inflammatory, and hyperplastic (increased cell proliferation) effects on the nasal airways observed in this study at 270 mg/m^3 were

used as the point of departure to derive the OEHHA chronic REL and US EPA RfC for acetaldehyde of 140 µg/m^3 and 9 µg/m^3, respectively.

Acetaldehyde is a carcinogenic TAC with CPFs derived by OEHHA based on the nasal tumors observed in rats following exposure. In hamsters, laryngeal tumors have also been reported. Acetaldehyde has a CSF of 1.0×10^{-2} (mg/kg-day)$^{-1}$ and a unit risk value of 2.7×10^{-6} (µg/m^3)$^{-1}$. In addition, this chemical has been shown to cause developmental and teratogenic effects in rats and mice and may have a role in the manifestation of fetal alcohol syndrome. It has also been shown to cross the placenta in animals.

ii. Ammonia

At room temperature, ammonia is a colorless gas that is typically found in air in the form of water vapor or particulates. Ammonia is corrosive at high concentrations. Although the odor of ammonia is pungent and irritating, it provides precautionary warning of its presence in most cases. However, after prolonged exposure to this chemical, it is more difficult to detect due to olfactory fatigue or adaptation. Ammonia has been categorized as a slight fire hazard by the National Fire Protection Association (LEL = 15%), but this hazard is increased in the presence of oil or other combustible materials. The majority of exposures occur by way of inhalation, and accidental releases of ammonia can form toxic, dense vapor clouds that travel downwind and put nearby residents at risk.

In California refineries, ammonia emissions have been detected at several process units. Major emissions are primarily from the FCCU process. Ammonia is the most commonly released routine facility emission of all the chemicals examined in this report. In addition, two nonfire incidents during 2001-2012 have been reported in the CSB Chemical Incident Screening Database. Ammonia is listed as the worst-case-scenario toxic release in the Risk Management Plans (RMP) of multiple California refineries evaluated in the 2015 Refinery Emergency Air Monitoring Assessment Report prepared by CARB OER and CAPCOA (CARB and CAPCOA, 2015). It is also listed in the RMPs of many refineries as an alternative release scenario, indicating that it is considered to be more likely than the worst-case-scenario.

Acute inhalation of ammonia may lead to corrosive injury to the skin and mucus membranes of the eyes, lungs, and gastrointestinal tract. Exposure to very high concentrations may result in eye redness and lacrimation (tearing), nose and throat irritation, cough, choking sensation, dyspnea (labored breathing or shortness of breath), lung damage, or death. Fatalities from ammonia exposure are most commonly caused by pulmonary edema (fluid accumulation in the lung). People with asthma and other respiratory conditions such as cardiopulmonary disease or with no tolerance developed from recent exposure may be more sensitive to the toxic effects of ammonia. In addition, blood ammonia levels are increased by chronic high dose aspirin therapy and therapy with valproic acid. Several studies, including one in which human volunteers were exposed to ammonia for 10 minutes, have demonstrated effects of exposure such as the urge to cough and irritation of the eyes, nose, and throat beginning at concentrations around 36 mg/m^3. These critical effects were used as the point of departure for the ammonia OEHHA acute REL of 3.2 mg/m^3.

Chronic exposure to ammonia may impact pulmonary function tests or lead to subjective symptomatology in workers. Chronic cough, asthma, lung fibrosis, and chronic irritation of the eye membranes and skin have also been reported. The most sensitive endpoints of chronic ammonia exposure are decreased pulmonary function, and eye, skin, and respiratory irritation, which were reported in an occupational inhalation study at a concentration of 6.5 mg/m^3. After time and dose adjustments and consideration of uncertainties, a chronic OEHHA REL of 200 µg/m^3 and US EPA RfC of 100 µg/m^3 for ammonia have been developed.

iii. Arsenic

In its elemental form, arsenic is a grey metallic solid with no characteristic taste or smell. Inorganic arsenic compounds are respiratory irritants and may vary in relative toxicity. Arsenic exists in air in the particulate phase. Contact with acid or acid vapors produces arsine, the most dangerous form of arsenic. While ingestion is the most important route of exposure for arsenic trioxide, exposure to other arsenic compounds sufficient to cause toxicity may be more likely to occur via inhalation.

Arsenic likely originates as an impurity in crude oil (Stigter et al., 2000), and it has been detected at many of the process units such as boilers, crude units, heaters, storage tanks, cokers, FCCUs, and incinerators. Arsenic has also been detected in routine and non-routine refinery emissions.

Acute exposure to arsenic has been associated with severe irritation of the mucus membranes of the respiratory tract and symptoms of cough, dyspnea (labored breathing or shortness of breath), and chest pain. Breathing high levels of arsenic may lead to a sore throat and lung irritation. Ingestion may result in symptoms characteristic of severe gastritis or gastroenteritis (inflammation, irritation, or erosion of the stomach) and even death due to severe inflammation of the mucus membranes and increased capillary permeability. Signs of acute arsenic poisoning include dermatitis, nasal mucosal irritation, laryngitis, mild bronchitis, and conjunctivitis (inflammation or infection of the eye). In an inhalation study of pregnant mice, decreased fetal weight was reported at concentrations starting at 0.2 mg/m^3. After time and dose adjustments and consideration of uncertainties, OEHHA derived an acute REL for arsenic of 0.2 µg/m^3.

Chronic exposure to arsenic has been associated with symptoms such as malaise (general feeling of discomfort), peripheral sensorimotor neuropathy (nerve damage), anemia, jaundice, and gastrointestinal discomfort. Prolonged exposure to arsenic also targets the lungs and skin and can cause darkened skin and the appearance of small “corns” or “warts” on the palms, soles, and torso. Conjunctivitis (inflammation or infection of the eye), irritation of the throat and respiratory tract, and perforation of the nasal septum have also been reported. Additionally, literature suggests that arsenic exposure during childhood may impart greater toxicity than adult exposure. In a study conducted on 10-year-old children exposed to 0.23 $\mu g/m^3$ of arsenic by drinking water, the impairment of intellectual function and neurobehavioral development was observed. After time and dose adjustments and consideration of uncertainties, OEHHA developed a chronic inhalation REL of 0.015 $\mu g/m^3$ and a chronic oral REL of 0.035 µg/kg-day.

Arsenic is listed by IARC as a known human carcinogen of the lung, urinary bladder, and skin. Some studies have also observed carcinogenesis in several other organs. Arsenic is on the Proposition 65 list for both cancer and developmental toxicity. Arsenic has an inhalation and oral CSF of 12 $(mg/kg\text{-}day)^{-1}$ and 1.5 $(mg/kg\text{-}day)^{-1}$, respectively, based on the incidence of lung tumors in workers occupationally exposed via inhalation and the incidence of skin cancer in individuals exposed via drinking water. The unit risk for arsenic is 0.003 $(\mu g/m^3)^{-1}$. Arsenic ions originating from arsenic trioxide have been shown to cross the placenta and can also be excreted in breast milk. In animals exposed to arsenic compounds, embryonic lethality, fetal malformations, decreased fetal weight, delayed bone maturation, skeletal malformations, and increased risk of chromosome aberrations in liver cells have been reported. A decrease in spermatozoa motility has also been observed following exposure.

iv. Benzo[a]pyrene

In pure form, benzo[a]pyrene is a pale yellow solid with a faint aromatic odor. Most benzo[a]pyrene in air is bound to particulates and is formed as a by-product of incomplete combustion from sources like volcanoes, automobile exhaust, cigarette smoke, and burning coal. Although it is considered to be nonflammable, benzo[a]pyrene emits acrid smoke and toxic carbon monoxide and carbon dioxide fumes or vapors when it is heated to decomposition. Due to its consistent association with the presence of smoke, benzo[a]pyrene may serve as an air monitoring surrogate for other polycyclic aromatic hydrocarbons (PAH) and smoke itself in addition to particulate matter in the event of a refinery emergency.

The general population is exposed to benzo[a]pyrene primarily by breathing air containing PAHs attached to particles and by consumption of PAHs in food. Once in the environment, PAHs are of concern due to their ability to travel long distances in the air, persist in the environment for extended periods of time, and bioaccumulate up the food chain. Benzo[a]pyrene has been detected in routine refinery emissions and around many areas of petroleum refineries such as separators, boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents.

Benzo[a]pyrene generally occurs in conjunction with other PAHs, therefore most available information on its relevant health effects is in reference to the chemical as part of a mixture containing benzo[a]pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, dibenz[a,h]anthracene, and other carcinogenic or potentially carcinogenic compounds. Acute exposure can cause irritation and a burning sensation of the eyes and skin.

Benzo[a]pyrene is currently classified as a known carcinogen by OEHHA and US EPA, and has additionally been classified as a human carcinogen by IARC, based on the increased incidence of tumors observed in animals on the skin, in lymphoid and hematopoietic tissues, and in various organs such as the lung, forestomach, liver, oesophagus, and tongue. Benzo[a]pyrene has an inhalation CSF of 3.9 $(mg/kg\text{-}day)^{-1}$ based on the occurrence of respiratory tract tumors in male hamsters exposed via inhalation and an oral CSF of 12 $(mg/kg\text{-}day)^{-1}$ based on the occurrence of gastric tumors in male and female mice exposed via diet. The unit risk for benzo[a]pyrene is 0.0011 $(\mu g/m^3)^{-1}$.

Benzo[a]pyrene has also been shown to cause reproductive effects in humans such as decreased sperm quality and fertility in males. In animals, decrements in sperm quality, changes in testicular histology, and hormone alterations in males and decreased fertility and ovotoxic effects in females have been reported. In addition, adverse effects on fetal survival, postnatal growth, and development have been associated with human exposure during gestation. Changes in fetal survival, pup weight, blood pressure, fertility, reproductive organ weight and histology, and neurological function have also been observed in animals exposed during gestation and/or early life.

v. Benzene, Toluene, Ethylbenzene, and Xylene (BTEX)

Benzene, toluene, ethylene, and xylene, collectively called BTEX, are volatile and well-absorbed chemicals that are found in petroleum products such as gasoline, jet fuels, and kerosene. BTEX chemicals often occur simultaneously at hazardous waste sites and emissions of each have been widely detected in similar areas within California refineries. BTEX is both an environmental and health concern because it can contaminate all media (air, water, and soil) and cause neurological impairment with exposure.

Benzene

Benzene is an aromatic hydrocarbon emitted into the air during the production and combustion of diesel and petroleum fuels. It is highly volatile and primarily found in the vapor phase. At room temperature, benzene is a colorless and highly flammable liquid (LEL = 1.2%) with a petroleum-like smell. Benzene vapor is heavier than air and can cause asphyxiation in enclosed, poorly ventilated, or low-lying areas. Benzene is of concern because it is emitted from numerous routine refinery operations (sulfuric acid loading, separators, boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents) and is commonly found in refinery emissions.

In humans, acute inhalation of benzene may lead to eye, nose, and throat irritation, and central nervous system depression. Acute hazard index targets include developmental effects and potential damage to the immune and hematologic systems. Drowsiness, dizziness, rapid heart rate, headaches, tremors, confusion, and unconsciousness may result from breathing high levels of benzene. Acute exposure can also increase cardiac sensitivity to epinephrine-induced arrhythmias. Brief exposure to very high levels in air can lead to death through respiratory failure. People with existing hematologic disorders and cellular anemias or heart conditions may be at increased risk for bone marrow toxicity and cardiac arrhythmias, respectively. In addition, intake of epinephrine and ethanol has been shown to increase the cardiac toxicity of benzene in humans and the bone marrow toxicity of benzene in mice, respectively. In mice, acute benzene exposure has been shown to cause developmental damage in the blood cells of fetal and neonatal mice. This is the basis of OEHHA's acute benzene REL of 27 $\mu g/m^3$.

The hematologic system is the main hazard index target for chronic benzene exposure. Long-term or repeated benzene exposure may cause noncancer detrimental health effects, including decreases in blood cell count, as well as leukemia. Chronic exposure to benzene can also lead to aplastic anemia, excessive bleeding, and damage to the immune system. Metabolic breakdown products of benzene have been shown to cause chromosomal changes that are consistent with those occurring in cases of hematopoietic cancer. Both the OEHHA chronic REL (3 $\mu g/m^3$) and the US EPA RfC (30 $\mu g/m^3$) for benzene are derived from human occupational inhalation studies finding decreased blood cells counts in workers exposed to an average concentration of 0.61 mg/m^3 for durations lasting 1 to 21 years.

Any benzene exposure is a concern regardless of exposure length. Benzene is currently listed under Proposition 65 as a carcinogen, a developmental toxicant, and a male reproductive toxicant. It has also been classified as a known human carcinogen of the hematopoietic system, primarily leukemia, by IARC. At benzene exposures between 0.13 – 0.45 $\mu g/m^3$, US EPA estimates that 1 in 1,000,000 individuals will be at risk of benzene-induced cancer. Children are at particular risk to the carcinogenic effects of benzene due to the high level of cell growth and turnover in their developing systems. Based on both animal and human data, the benzene CSF is 0.1 $(mg/kg\text{-}day)^{-1}$. The unit risk for benzene is 2.9×10^{-5} $(\mu g/m^3)^{-1}$.

Benzene has been shown to cross the placenta and, in animals exposed to benzene via inhalation, developmental effects such as low birth weight, bone marrow toxicity, and delayed bone formation have been observed. At very high levels of exposure, benzene has also been associated with adverse effects on the reproductive organs of animals.

Ethylbenzene

Ethylbenzene is a colorless, highly flammable liquid (LEL = 0.8%) with an odor similar to that of gasoline. Ethylbenzene vapor is formed in air during the combustion of oil, gas, and coal, and breaks down within a few days by reaction with sunlight. The general population is exposed to ethylbenzene by breathing air, especially in cities with multiple factories or busy highways. Residential drinking water wells near landfills, waste sites, or leaking underground storage tanks can also lead to high levels of exposure. Because it occurs naturally in oil, ethylbenzene vapors can additionally be released into the environment during the production, transport, and refining of petroleum. Ethylbenzene emissions have been detected at many refinery process units including: separators, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents, and in routine and non-routine refinery emissions.

Acute exposure to ethylbenzene can cause chest constriction, irritation of the eyes and throat, and neurological effects such as dizziness and vertigo in humans. In animals acutely exposed to ethylbenzene by inhalation, eye irritation, central nervous system toxicity, effects on the liver and kidney, and pulmonary effects have been observed.

Studies on long-term occupational exposure to ethylbenzene have provided limited information regarding its effects on the blood, likely due to the presence of other chemicals such as xylenes in the same environment. In animals chronically exposed to ethylbenzene, effects on the blood, liver, and kidneys have been reported. Irreversible damage to the inner ear and hearing has also been noted. Based on the adverse effects on the liver (cellular alterations and necrosis), kidney (nephrotoxicity), and pituitary gland (hyperplasia) appearing in mice and rats discontinuously exposed to 1.1 $\mu g/m^3$ ethylbenzene via inhalation, OEHHA developed a chronic REL of 2 mg/m^3. A US EPA RfC for ethylbenzene of 1 mg/m^3 has also been established due to the developmental toxicity observed in rats and rabbits following chronic exposure.

Because inhalation exposure has been associated with an increase in tumors of the kidney in rats and of the lung and liver in mice, ethylbenzene was classified by IARC in 2010 as a possible human carcinogen. In 2004, it was also listed as a carcinogen by OEHHA under Proposition 65. The inhalation and oral CSFs for ethylbenzene are 8.7×10^{-3} $(mg/kg\text{-}day)^{-1}$ and 1.1×10^{-2} $(mg/kg\text{-}day)^{-1}$, respectively, and are based on the incidence of kidney cancer in male rats. Ethylbenzene also has a unit risk value of 2.5×10^{-6} $(\mu g/m^3)^{-1}$.

Toluene

Toluene is a clear, volatile liquid with an aromatic odor that generally serves as an adequate warning of acutely toxic concentrations. It can be ignited under almost all ambient temperature conditions (LEL = 1.1%). While toluene may give rise to toxic effects by inhalation, ingestion, or dermal contact, the general population is primarily exposed to toluene by way of inhalation. Because its vapors are heavier than air, caution should be taken to avoid possible asphyxiation in enclosed, poorly ventilated, or low-lying areas. Toluene is a natural constituent in crude oil and is produced in large quantities by distillation during petroleum refining, serving as a sentinel chemical for benzene exposure. As with the rest of the BTEX chemicals, toluene vapors have been widely detected at various refinery emission points (sulfuric acid loading, separators, boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents) and in outdoor refinery emissions.

Both acute and chronic exposures to toluene are a serious concern because they target the nervous system. Symptoms such as fatigue, sleepiness, headaches, nausea, and irritation of the eyes, skin, and respiratory tract may be experienced in people acutely exposed to low or moderate levels in air. Central nervous system depression, ataxia (lack of muscle control during voluntary movements), euphoria, hallucinations, tremors, seizures, coma, and death may occur at higher levels of exposure. Some people with liver, neurological, or heart disease may be at increased risk for adverse effects resulting from exposure. Concurrent use of salicylates, alcohol, or over-the-counter bronchial dilators containing epinephrine may also increase an individual’s susceptibility to toluene. A human acute inhalation study demonstrated eye and nose irritation, impaired reaction time, headache, dizziness, and a feeling of intoxication. This study of toluene exposure was used in OEHHA’s development of the acute REL (37 mg/m^3).

Most studies regarding the effects of chronic toluene exposure involve deliberate sniffing of toluene-containing solvents or workplace exposures and have reported a range of neurotoxic effects such as brain damage and decreased performance on psychometric tests. Prolonged exposure has also been associated with nausea, fatigue, eye and upper respiratory tract irritation, sore throat, dizziness, headache, and difficulty with sleep. In cases of occupational exposure, disorders of the optic nerve and neurobehavioral effects such as loss of coordination, memory loss, and loss of appetite have been reported. Chronic toluene abuse can lead to symptoms indicative of central nervous system depression including: drowsiness, ataxia (lack of muscle control during voluntary movements), tremors, cerebral atrophy (loss of neurons), involuntary eye movements, and impairment of speech, hearing, and vision. Permanent neuropsychiatric effects, muscle disorders, cardiovascular effects, renal tube damage, and sudden death can also occur. OEHHA derived the chronic REL (300 $\mu g/m^3$) for toluene based on an inhalation study on rats that began showing neurotoxic effects (decreased brain weight and altered dopamine receptor binding) at a concentration of 300 $\mu g/m^3$ following exposure to an average of 26.3 mg/m^3. Neurological effects in occupationally-exposed workers were also observed in multiple studies, serving as the basis for the US EPA inhalation RfC of 5 mg/m^3.

Toluene is listed under Proposition 65 as a developmental toxicant and has been shown to cross the placenta and be excreted in breast milk. Children whose mothers were toluene abusers during pregnancy were born with small heads and have head, face, and limb abnormalities, attention deficits, hyperactivity, and developmental delay with language impairment. Preterm delivery, perinatal death, and growth retardation have also been reported.

Xylene

Xylene exists in three forms (m-xylene, o-xylene, and p-xylene) that are commonly combined to form what is known as mixed or technical xylene. An entry for each constituent of technical xylene, as well as the mixture itself, is included in Table 1. For the purposes of this section, the term “xylene” will refer to technical xylene, which is richest in m-xylene and usually also contains ethylbenzene and traces of toluene.

Xylene is a colorless, volatile, flammable liquid (LEL = 1.1%) with an aromatic odor. In air, xylene exists as vapor and may be an explosion hazard. Combustion of this chemical will produce irritating gases that are corrosive and/or toxic. Xylene can be found in drinking water, but because it easily evaporates into the air, exposure typically occurs via inhalation. Exposure to high concentrations of xylene vapors can result in asphyxiation in low-lying or poorly ventilated areas. Xylenes occur naturally in petroleum and coal and are additionally used as solvents and gasoline additives in the petroleum industry. Data from US EPA show that xylene vapors have been detected in refinery emissions and around separation, conversion, product handling, and auxiliary processes carried out in refineries.

Both short-term and long-term exposure to high levels of xylene may cause eye, skin, and respiratory tract irritation, but the central nervous system is the primary target of such encounters. Headaches, decreased muscle coordination, dizziness, confusion, and altered sense of balance may be experienced following acute exposure. Short-term exposure to elevated levels in air have also been associated with symptoms such as strained breathing, lung function impairment, delayed response to visual stimuli, impaired memory, stomach discomfort, ventricular arrhythmias, acute pulmonary edema (fluid accumulation in the lung), and hepatic impairment. Very high levels may be fatal. In addition, studies have shown that xylene may increase the rate of metabolism of other chemicals; however, the presence of other solvents inhibits the breakdown of xylene itself and may thus lead to increased toxicity. OEHHA used acute exposure studies demonstrating eye, nose, and throat irritation in humans exposed to xylene to develop the acute REL of 22 mg/m^3.

Chronic exposure to xylene in occupational settings has led to neurological effects such as headache, fatigue, dizziness, tremors, loss of coordination, anxiety, impairment of short-term memory, and inability to concentrate. Cardiovascular effects (labored breathing, impairment of pulmonary function, heart palpitations, chest pain, and abnormal electrocardiogram) and effects on the gastrointestinal system (nausea, vomiting, and gastric discomfort) have also been associated with prolonged exposure. Some studies also report effects on the kidneys. Xylene exposure from solvent abuse has also been shown to lead to permanent neuropsychiatric manifestations, which can progress to become chronic toxic encephalopathy (malfunction or degradation of brain function). In workers occupationally exposed to xylene, eye irritation, sore throat, floating sensation, and lack of appetite were observed at a concentration of 61.6 ng/m^3 and used as the basis for the OEHHA chronic REL of 700 µg/m^3. A US EPA RfC of

100 µg/m^3 was also established for this chemical based on the impaired motor coordination seen in rats following subchronic inhalation exposure.

Xylene has been reported to cross the placenta in humans and high doses may be fetotoxic in animals. Animal inhalation studies have shown developmental effects such as skeletal variations in fetuses, delayed bone formation, fetal resorptions, decreased body weight, and decreased motor performance during adolescence. Maternal toxicity has also been observed. The isomers with the greatest fetotoxicity and maternal toxicity are p-xylene and m-xylene, respectively.

vi. 1,3-Butadiene

1,3-Butadiene is a colorless gas with a mild gasoline-like odor that is usually an adequate warning to protect individuals against acutely hazardous levels. Although this gas is noncorrosive, it is highly flammable (LEL = 2%) and forms explosive peroxides upon prolonged exposure to air. The primary route of exposure to 1,3-butadiene is inhalation. While motor vehicle exhaust contributes to ambient levels of 1,3-butadiene, exposure to higher levels of the chemical primarily occurs in occupational settings since it is produced through the processing of petroleum, and used in making other products. 1,3-Butadiene is heavier than air and at high concentrations can cause asphyxiation in enclosed, poorly ventilated, or low-lying areas.

In refineries 1,3-butadiene emissions have been detected in many different areas: sulfuric acid loading, separators, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, and wastewater treatment. Boilers, internal combustion engines, and turbines may be additional sources of release. 1,3-Butadiene has been detected in routine and non-routine refinery emissions and has been identified in a refinery fire incident linked to the coking unit.

At low concentrations, acute inhalation of 1,3-butadiene vapors may be irritating to the eyes, nose, throat, and lungs. OEHHA reports that blurred vision, nausea, paresthesia (tingling or pricking sensation), and mouth, throat, and nose dryness are the initial signs of acute exposure to high concentrations, and may be followed by fatigue, headache, vertigo, hypotension, decreased heart rate, and unconsciousness. At very high concentrations, central nervous system depression can occur. A whole-body inhalation study of pregnant mice leading to decreased male fetal weight was the basis of the OEHHA acute REL (660 µg/m^3) for 1,3-butadiene chemical because it addressed the most sensitive endpoint of 1,3-butadiene exposure, developmental effects.

Chronic exposure to 1,3-butadiene, in the presence of other pollutants, has been found to exacerbate symptoms of asthma and increase incidence of respiratory tract infections. While long-term exposure to the gas has been linked to cardiovascular diseases and effects on the blood, female reproductive organs are considered the critical target of chronic exposure for noncancer effects. In addition, animal studies have shown that chronic exposure to 1,3-butadiene can lead to bone marrow depression and DNA repair deficiencies. The chronic OEHHA REL and US EPA RfC of 2 µg/m^3 are the same for 1,3-butadiene and were derived based on the increased occurrence of ovarian atrophy (degeneration of cells) observed during an inhalation study conducted on mice exposed daily for 6 hours, 5 days per week, for a duration of 9 to 24 months.

1,3-Butadiene is a carcinogen and a male and female developmental toxicant under Proposition 65. It has also been classified as a human carcinogen by IARC based on evidence that it causes cancer of the hematolymphatic organs. The CSF and unit risk for 1,3-butadiene are 0.6 (mg/kg-day)$^{-1}$ and 1.7x10^{-4} (µg/m^3)$^{-1}$, respectively, and were derived by OEHHA based on the incidence of lung tumors reported in inhalation studies of female mice. Although information regarding the developmental or reproductive effects of 1,3-butadiene is limited, animal studies have reported developmental effects such as skeletal malformations and decreased fetal weights, and reproductive effects such as damage to the ovaries and testes following inhalation exposure.

vii. Dibenzo-p-dioxins/Dibenzofurans

Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) make up a group of 210 closely related halogenated aromatic compounds collectively referred to as “dioxins.” In pure form, many dioxins are colorless crystals. Polyhalogenated compounds like dioxins are one of eight major categories of polycyclic organic matter, a broad class of compounds that is present in the atmosphere. Dioxins released into the air are deposited on land or water, where they persist for long periods of time and can build up in the fatty tissues of animals that ingest it (bioaccumulation). In refineries, dioxins are formed during catalyst regeneration and during the combustion of organic materials in the presence of chlorine and have been detected at process units such as heaters, incinerators, and wastewater (Thompson et al., 1990; Shaw et al., 2013).

Dioxins are a major concern due to the wide range of severe health effects induced by chronic exposure to low doses. In humans, exposure to dioxins has been shown to lead to the development of a skin condition resembling severe acne (chloracne), gastrointestinal upset, increased levels of serum enzymes and triglycerides, and numbness of the extremities. Although the toxic responses observed in animals treated with various members of this group are generally similar, those chlorinated at the 2, 3, 7, and 8 positions are particularly toxic. 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) is considered the most potent congener of the dioxin family and is thus the most widely studied of the group. The most sensitive targets of chronic dioxin exposure include the alimentary system (liver), reproductive system, development, endocrine system (pineal, pituitary, thyroid, parathyroid, and adrenal glands, pancreas, ovaries, testes, hypothalamus, and gastrointestinal tract), respiratory system, and hematopoietic system (bone marrow, spleen, tonsils, and lymph nodes). In a study on rats continuously exposed to TCDD for two years via diet, effects such as increased mortality, decreased weight gain, and changes in the liver, lungs, and lymphoid and vascular tissues were noted at a dose of 0.001 µg/kg/day, which served as the point of departure for the chronic REL for dioxins ($4x10^{-5}$ µg/m^3). Because of the ability of dioxins to bioaccumulate, a chronic oral REL of $1x10^{-5}$ µg/kg-day has also been developed. There is no acute REL or RfC for this group of chemicals. US EPA developed a Reference Dose (RfD) for 2,3,7,8-tetrachlorodibenzo-p-dioxin of $7x10^{-10}$ mg/kg-d based on decreased sperm count in men exposed as boys and decreased thyroid stimulating hormone (TSH) in neonates.

Both PCDDs and PCDFs are carcinogenic TACs with CPFs derived by OEHHA based on the occurrence of liver tumors in male mice after exposure. Dioxin-related cancer mortality following an accidental release of TCDD from a 1,2,3-trichloropropane-producing plant in Seveso, Italy included conditions such as digestive cancer, stomach cancer, lymphatic and hemopoietic cancer, multiple myeloma, rectal cancer, leukemia, ovarian cancer, and thyroid cancer. TCDD has a CSF and a unit risk value of $1.3x10^5$ (mg/kg-day)$^{-1}$ and 38 (µg/m^3)$^{-1}$, respectively. PCDDs and PCDFs have been classified as carcinogens by OEHHA under Proposition 65 and by US EPA. PCDDs including TCDD have also been classified as multi-site carcinogens in animals by IARC. Immunotoxicity, particularly from perinatal exposure, and developmental toxicity are key endpoints of concern for infants and children. In addition, dioxins have been shown to cross the placenta and can be transferred from mother to infant during breastfeeding. Effects on thyroid development and infant neurodevelopment and an increased risk of diabetes and endometriosis from dietary intake have also been reported (Arisawa et al., 2005).

viii. Diethanolamine

Diethanolamine is a hydrocarbon found in air in the water vapor and particulate phases. It is a colorless powder or liquid in pure form and has an odor resembling that of ammonia. Diethanolamine produces acrid vapors when heated that are slightly heavier than air. It has been classified as a slight fire hazard by the National Fire Protection Association, but must be preheated prior to ignition. In petroleum refineries, diethanolamine is used in desulfurization processes and may contaminate wastewater (Bord et al., 2004). This chemical has been detected at multiple refinery process units included in this report (crude units, storage tanks, cokers, and wastewater treatment) and may also be found in amine scrubbers used for natural gas purification (Nelson, 2013).

In humans, acute inhalation exposure to diethanolamine may cause nose and throat irritation. Coughing, nausea, headache, and a smothering sensation may result from breathing its vapors. Other effects of acute exposure may include eye burns, corneal necrosis (death of corneal cells), skin burns, lacrimation (tearing), and sneezing.

Currently, there is inadequate information on the chronic effects of diethanolamine in humans. The respiratory and cardiovascular systems are the targets for chronic exposure. In one occupational case report, the handling of diethanolamine-containing cutting fluid caused asthmatic airway obstruction. Diethanolamine may exacerbate asthma; thus, children may be more vulnerable to its irritant effects. The chronic REL of 3 µg/m^3 was derived based on an inhalation study in rats that showed chronic inflammation and abnormal cellular changes (squamous hyperplasia, metaplasia) of the larynx at a concentration of 15 mg/m^3. Diethanolamine has been shown to cause liver tumors in rats by IARC and has been classified as a carcinogen by OEHHA under Proposition 65.

ix. Formaldehyde

At room temperature, formaldehyde is a colorless gas with a distinct, pungent odor detectable even at low concentrations. Formaldehyde is found in air in the vapor, water vapor, and particulate phases. Formaldehyde is flammable with an LEL of 7%, and its combustion may generate carbon monoxide. Emissions of this chemical into the environment commonly occurs during combustion processes; thus, inhalation is the primary route of exposure. Formaldehyde has been detected in both ambient air emissions and at several refinery process units such as boilers, cokers, crude units, FCCUs, heaters, and incinerators (Lucas, 2002). Vapors of formaldehyde are heavier than air and high concentrations can cause asphyxiation in low-lying, enclosed, or poorly ventilated areas. In addition, this respiratory irritant may have a more severe impact on infants and children.

Acute exposure to low concentrations of formaldehyde can result in eye irritation, headache, rhinitis (irritation or inflammation of mucous membrane in the nose), and dyspnea (labored breathing or shortness of breath). Some people may be more sensitive to the effects of formaldehyde exposure and experience exacerbation of asthma and dermatitis at low doses. Higher doses may cause lacrimation (tearing), severe mucous membrane irritation, burning, difficulty breathing, and effects on the lower respiratory system such as bronchitis, pulmonary edema (fluid accumulation in the lung), or pneumonia. Asthmatics and individuals previously sensitized to formaldehyde may be more vulnerable to the adverse respiratory effects resulting from exposure. Because studies have shown that asthma is more common and may be more severe in children than adults, formaldehyde exposure is also a concern for infants and children. An acute REL was derived for formaldehyde based on a study in which non-asthmatic, nonsmoking individuals were exposed to the chemical for three hours and began experiencing mild and moderate eye irritation at an airborne concentration of 0.9 mg/m^3. The OEHHA acute REL is 55 µg/m^3 after adjustments for dose, time, and uncertainties.

Long-term exposure to formaldehyde primarily targets the respiratory system and may lead to allergic sensitization, respiratory symptoms such as coughing and wheezing, nasal symptoms such as running nose and crusting, lacrimation (tearing), cellular changes in airway membranes, and decreased lung function. Effects on the nervous system such as headaches, depression, mood changes, insomnia, attention deficit, and dexterity and memory impairment have also been reported. OEHHA used an occupational study in which workers experienced nasal obstruction and discomfort and lower airway discomfort at an average concentration of 0.09 mg/m^3 to derive the chronic REL of 9 µg/m^3 for formaldehyde.

Formaldehyde is a carcinogenic TAC with CPFs derived by OEHHA based on the incidence of nasal tumors in male and female rats and male mice resulting from exposure. In humans, formaldehyde exposure has additionally been associated with cancers of the upper respiratory tract, specifically buccal cancer, pharyngeal cancer, and nasopharyngeal cancer. Formaldehyde has also been associated with an elevated risk of leukemia and sinonasal cancer. The CSF for formaldehyde is 2.1x10^{-2} (mg/kg-day)$^{-1}$ and the unit risk value is 6.0x10^{-6} (µg/m^3)$^{-1}$. Formaldehyde has been classified as a carcinogen by OEHHA, US EPA, and IARC.

x. Hydrogen Fluoride

Hydrogen fluoride is a colorless fuming liquid or gas with a strong, pungent odor. Dissolution in water forms corrosive hydrofluoric acid, a systemic poison. Although it will not burn under typical fire conditions, this acid emits highly irritating and poisonous vapors that are corrosive to metals and body tissues when heated. Because it is corrosive to metals, hydrogen fluoride may yield hydrogen and may thus indirectly create a fire hazard. Hydrogen fluoride in air is normally found in the water vapor and particulate phases. The general population may be exposed to hydrogen fluoride in the ambient environment from industrial process emissions and coal combustion. In refineries, this chemical is used as a catalyst during alkylation or cracking and has been detected in refinery emissions and around crude units and cokers.

Short-term inhalation of hydrogen fluoride can lead to severe respiratory damage (irritation and fluid accumulation in the lung), lacrimation (tearing), sore throat, cough, chest tightness, and wheezing. Due to the ability of the fluoride ion to penetrate tissues, some health effects may be delayed for one to two days after exposure. Breathing high levels of the gas or in combination with dermal exposure may be fatal due to pulmonary edema (fluid accumulation in the lung) and bronchial pneumonia. People with cardiopulmonary disease may be particularly vulnerable to lower airway irritation at high concentrations. The most sensitive endpoint for short-term inhalation exposure to hydrogen fluoride is eye, nose, and throat irritation, which was observed in an inhalation study of healthy, male volunteers after one hour of exposure to concentrations of 0.2-0.6 mg/m^3. After time and dose adjustments and consideration of uncertainties, OEHHA established an acute REL of 240 µg/m^3 to protect individuals from these effects.

Long-term exposure to low levels of hydrogen fluoride has been linked to congestion and irritation of the nose, throat, and bronchi. Liver and kidney damage has also been noted. Exposure to higher levels has been associated with increased bone density (skeletal fluorosis). This was observed in a study on fertilizer plant workers chronically exposed to an average of 0.14 mg/m^3 hydrogen fluoride. In this study, OEHHA determined the point of departure for increased bone density to be 1.13 mg/m^3, which served as the basis of the chronic REL of 14 µg/m^3. Because fluorides may contaminate food and drinking water, OEHHA has also developed a chronic oral REL for hydrogen fluoride, based on the dental fluorosis observed in the inhabitants of several US cities exposed via drinking water. A point of departure of 0.82 mg/m^3 at which the incidence of moderate to severe dental fluorosis was considered to be rare among the population was used to calculate the chronic oral REL of 40 µg/kg-day. Dental fluorosis has additionally been noted in children after maternal exposure to high levels during pregnancy.

xi. Hydrogen Sulfide

Found in air in the water vapor and particulate phases, hydrogen sulfide is a corrosive gas with a pungent rotten egg odor. For this chemical, odor is not a reliable indicator of its presence due to the olfactory fatigue that occurs at both high concentrations and continuous low concentrations. Hydrogen sulfide is highly flammable (LEL = 4%) and may produce an explosion at levels above 4.5% in air. When heated, highly toxic sulfur oxide fumes or vapors are emitted. Hydrogen sulfide is slightly heavier than air and may be present at higher levels in enclosed, poorly ventilated, and low-lying areas. Because it is released naturally as a product of decaying organic matter, hydrogen sulfide is a natural component and the predominant impurity of crude oil and natural gas (Skrtic, 2006).

In oil refineries, hydrogen sulfide is formed during the removal of sulfur compounds from petroleum products and has been detected at various process units such as boilers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, and incinerators. Hydrogen sulfide is one of the most routinely emitted refinery pollutants included in this report and its distinct smell made it one of the most frequently mentioned chemicals in refinery incident reports during 2001-2012. As with ammonia, it appears in many refineries' RMPs as the worst-case-scenario toxic release and alternate release scenario (CARB and CAPCOA, 2015).

Hydrogen sulfide is very toxic by inhalation. Because exposure to this chemical affects most organ systems, hydrogen sulfide is considered to be a broad spectrum toxicant and may pose a significant health risk to those exposed. Acute exposure to hydrogen sulfide targets the central nervous system and leads to symptoms such as headache, nausea, and irritation of the skin, eyes, mucus membranes, and respiratory tract. Acute exposure to higher levels of hydrogen sulfide can cause conjunctivitis (inflammation or infection of the eye) with ocular pain, lacrimation (tearing), and photophobia. Concentrations in air high enough to exceed the body's detoxification threshold lead to cellular respiratory poisoning and asphyxiation (Skrtic, 2006). Death due to hydrogen sulfide exposure is typically caused by respiratory arrest. In addition, ethanol has been shown to decrease the average time-to-unconsciousness in mice exposed to the gas and may thus potentiate its effects.

The most sensitive endpoints for acute hydrogen sulfide exposure are headache and nausea in human volunteers, which were reported at levels below the odor threshold after exposure to doses ranging from 16.8 to 96.6 µg/m^3. After time and dose adjustments and consideration of uncertainties, an acute REL of 42 µg/m^3 was developed by OEHHA.

Chronic effects of hydrogen sulfide include: low blood pressure, headache, nausea, loss of appetite, weight loss, ataxia (lack of muscle control during voluntary movements), eye membrane inflammation, and chronic cough. In mice, prolonged exposure to hydrogen sulfide targets the respiratory system and causes nasal inflammation (chronic REL = 10 µg/m^3). The inhalation RfC of 2 µg/m^3 was derived based on a study showing olfactory loss and nasal lesions in rats following subchronic exposure to 42.5 mg/m^3 of the chemical. Individuals living in close proximity to oil refineries may be at risk of chronic exposure to hydrogen sulfide. Hydrogen sulfide is not listed as a carcinogen under Proposition 65, but the literature indicates that this chemical may be a reproductive toxicant that increases risk of spontaneous abortion.

xii. Manganese

Naturally-occurring manganese compounds are often associated with organic materials or metals. The general public is exposed to manganese through inhalation, particularly in areas where it is used in manufacturing and through consumption of food and water. Manganese is of concern because of the amount of routine refinery emissions and the many process units with which it is associated (boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, and incinerators). Manganese may be ignited by friction, heat, sparks, or flames. It may also react violently or explosively with water, and dusts or vapors may yield explosive mixtures in air.

Both short-term and long-term inhalation exposures to manganese have the potential to cause adverse health effects and appear to target the nervous system. While small amounts of manganese are beneficial to human health, exposure to higher levels may cause brain damage. Acute manganese exposure may lead to impaired function and nonspecific pulmonary edema (fluid accumulation in the lung).

Chronic manganese exposure may lead to more serious health effects, including “manganism” neurotoxicity. The symptoms of “manganism” appear similar to those of Parkinson’s disease, with affected individuals suffering from dystonia (involuntary muscle contractions), altered gait, generalized rigidity, and fine tremor. Some individuals may also suffer from psychiatric disturbances. Lower levels of prolonged manganese exposure can lead to changes in neurobehavioral and cognitive abilities such as slower visual reaction time, poorer hand steadiness, and impaired hand-eye coordination in both adults and children. Chronic exposure may also cause respiratory effects such as increased incidence of cough, bronchitis, dyspnea (labored breathing or shortness of breath) during exercise, and increased susceptibility to infectious lung disease. Manganese exposure in early life may affect behavioral and intellectual capabilities. The manganese OEHHA chronic REL of 0.09 µg/m^3 was derived based on the impaired human neurobehavioral functioning (impaired visual reaction time, hand-eye coordination, and hand steadiness) reported in a study of battery plant workers occupationally exposed to 0.04 to 4.43 mg manganese/m^3 per year via inhalation of respirable dust. US EPA's RfC for manganese is 0.05 µg/m^3, and is similarly based on impairment of neurobehavioral functioning seen in individuals occupationally exposed to manganese.

Animal studies have shown decreased dopamine in the striatum and poorer performance on behavioral tests in rats orally exposed to manganese. Decreased activity levels and average pup weights have been noted in mice exposed via inhalation. High levels of exposure may also lead to accumulation of the metal in brain regions such as the striatum and the midbrain.

xiii. Naphthalene

Naphthalene is a volatile white crystalline solid that exists in air in the form of vapor or adsorbed to particulates. It is released into the atmosphere from coal and oil combustion and from the use of mothballs. The primary route of human exposure to naphthalene is inhalation. Naphthalene emissions have been detected at several refinery process units (separators, boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents) and naphthalene has been detected in both routine and non-routine emissions. Naphthalene is of particular concern due to its flammability in the presence of an ignition source (LEL = 0.9%). Fire may yield irritating or toxic gases, and powders, dusts, and shavings may be explosive.

People who are acutely exposed to naphthalene may experience headache, nausea, vomiting, diarrhea, malaise (general feeling of discomfort), confusion, anemia, jaundice, convulsions, and coma. Short-term exposure has also been associated with neurological damage in infants, hemolytic anemia, and liver damage.

Prolonged exposure to large amounts of naphthalene may damage or destroy red blood cells, leading to hemolytic anemia, and has been reported to cause cataracts and retinal hemorrhage in humans. In mice chronically exposed to naphthalene via inhalation, chronic inflammation of the lung, chronic nasal inflammation, hyperplasia of nasal respiratory epithelium, and metaplasia of the olfactory epithelium has been noted. The OEHHA chronic REL of 9 µg/m^3 for naphthalene was derived (after time and dose adjustments and consideration of uncertainties) on the noncancer respiratory effects observed in mice chronically exposed to a concentration of 52.6 ng/m^3 including: nasal inflammation, olfactory epithelia metaplasia, and respiratory epithelial hyperplasia (Abdo et al., 2001). Such symptoms are indicative of the carcinogenic potential of naphthalene. An RfC of 3,000 µg/m^3 has also been developed by US EPA based on this study.

Naphthalene is listed as a carcinogen on the Proposition 65 list and has been classified as a possible human carcinogen by IARC based on the nasal tumors seen in rats and the lung tumors seen in female mice exposed by inhalation. Naphthalene has a CSF of 0.12 $(mg/kg\text{-}day)^{-1}$, which is based on data for incidence of nasal tumors, specifically nasal respiratory epithelial adenoma and nasal olfactory epithelial neuroblastoma, in male rats. In mice, inhalation exposure to naphthalene has also been shown to increase the incidence of lung tumors. The unit risk for naphthalene is 3.4×10^{-5} $(\mu g/m^3)^{-1}$.

Because their bodies have not fully developed detoxification mechanisms, newborns and infants are thought to be especially vulnerable to the effects to naphthalene exposure. In infants born to mothers who were exposed by inhalation and ingestion during pregnancy, hemolytic anemia has been reported. Oral exposure in mice has also been shown to cause maternal toxicity (increased mortality and decreased weight gain) and fetotoxicity.

xiv. Nitrogen Oxides (NOx)

Nitrogen oxides (NOx) represent a group of highly reactive gasses including nitric oxide, nitrogen dioxide, nitrogen trioxide, nitrogen tetroxide, and nitrogen pentoxide that are released into the air from combustion sources. Because nitrogen dioxide is considered to be one of the most toxicologically significant of the nitrogen oxides and is used by both the US EPA and CalEPA as the indicator for the group, it will be the focus of this subsection. Nitrogen dioxide is a yellow-brown liquid at room temperature that takes the form of a reddish brown gas at temperatures above $70^{o}F$. It is a corrosive gas with a strong odor that generally provides adequate warning of acute exposure to high levels. Although it is nonflammable, nitrogen dioxide will accelerate the burning of combustible materials and may react violently with cyclohexane, fluorine, formaldehyde and alcohol, nitrobenzene, petroleum, and toluene. In the environment, nitrogen dioxide can form nitric acid, a major constituent of acid rain, and contributes to the formation of ozone and fine particle pollution. Gaseous nitrogen dioxide is also heavier than air and at high concentrations can lead to asphyxiation in poorly ventilated, enclosed, or low-lying areas.

NOx has been detected in non-routine refinery emissions and around many refinery process units such as boilers, crude units, heaters, storage tanks, cokers, FCCUs, incinerators, and flares. It has also been associated with multiple fire incidents reported during 2001-2012.

Coughing, fatigue, nausea, choking, headache, abdominal pain, and strained breathing may be experienced immediately following acute exposure to nitrogen dioxide. Short-term exposure to nitrogen dioxide may also have delayed health effects such as pulmonary edema (fluid accumulation in the lung) with anxiety, mental confusion, lethargy, loss of consciousness, pneumonitis (inflammation of lung tissue), and bronchitis. Exposure to high concentrations of nitrogen dioxide may lead to pulmonary edema (fluid accumulation in the lung) and delayed inflammatory changes, which can be life-threatening. Burns, spasms, swelling of tissues in the throat, and upper airway obstruction may also occur. In addition to children and the elderly, individuals with asthma and other preexisting pulmonary diseases, especially RADS, may be more sensitive to the toxic effects of nitrogen dioxide. OEHHA developed an acute REL of 470 µg/m^3 for nitrogen dioxide based on the increased airway reactivity observed in asthmatics following a one-hour exposure at this concentration. Since that time, the CARB has promulgated a one-hour AAQS of 340 µg/m^3 based on OEHHA's health-based recommendation.

Chronic exposure to nitrogen oxides can cause permanent and obstructive lung disease from bronchiolar damage. Increased risk of respiratory infections in children has also been associated with long-term exposure. While NOx has not been classified as carcinogens or developmental or reproductive toxicants under Proposition 65, they have mutagenic, clastogenic (inducing disruption or breakage of chromosomes), and fetotoxic effects in rats. In one study exposing pregnant rats to nitrogen dioxide, an increased occurrence of intrauterine deaths, stillbirths, developmental abnormalities, and low birth weights was observed.

xv. Particulate Matter (PM_{10} and $PM_{2.5}$)

Particulate matter (PM) is a mixture of liquid droplets and solids such as dust, dirt, soot, and smoke in the air. These particles exist in a large variety of shapes, sizes, and chemical compositions. In addition to the well-characterized health effects of PM, particle pollution reduces visibility and damages welfare such as crops and buildings. Two size categories of PM are regulated at the state and federal levels. Respirable particles (PM_{10}) are those with a mass mean aerodynamic diameter of 10 micrometers or less, and pose a health concern due to their ability to pass through the nose and throat and into the deeper portions of the respiratory system. Fine particles ($PM_{2.5}$) are those with a diameter of 2.5 micrometers or smaller and are considered to be a significant health risk due to their ability to travel into deep areas of the lungs and smaller ultrafine particles (generally less than 100 nanometers) may even enter the bloodstream.

The composition of PM largely depends on particle size and origin. Fine particles commonly contain ionic species (e.g. sulfate, nitrate, and ammonium), acid (e.g., hydrogen ion, H+), organic and elemental carbon, and trace elements (e.g. aluminum, silicon, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, nickel, copper, zinc, selenium, bromine, arsenic, cadmium, and lead). $PM_{2.5}$ can also contain larger amounts of PAHs such as naphthalene, chrysene, phenanthrene, and anthracene than PM_{10} (Catoggio et al., 1989).

Particulates have been detected at many emissions points in petroleum refineries (abrasive blasting, asbestos abatement, boilers, cooling towers, crude units, heaters, cokers, FCCUs, incinerators, and flares) and in non-routine emissions outdoors. Because of the ubiquitous nature of particulates in smoke, all fire events reported in the 2001-2012 data also involved the unintentional release of particulate matter.

Short-term exposure to $PM_{2.5}$ has been linked to increased hospitalizations and emergency room visits for heart and lung-related illnesses and premature death. Inhalation of fine particles can be harmful to the heart and blood vessels, and may increase risk of heart attack, stroke, cardiac arrest, and/or congestive heart failure. Other symptoms of exposure include eye, nose, and throat irritation, reduced lung function, asthma attacks, irregular heartbeat, and increased respiratory symptoms such as coughing, wheezing, and shortness of breath.

Chronic exposure to fine particle pollution also leads to increased incidence of heart and lung problems, and some studies further suggest its possible association with cancer and reproductive and developmental toxicity. Population-based epidemiological studies have found associations between ambient particulate pollution and lung cancer. While healthy individuals may experience temporary symptoms, the elderly, children, people with heart or lung conditions, and people exposed to unusually high levels of pollution are considered to be more susceptible to the adverse health effects of particulate matter exposure. Pregnant women, newborns, and individuals with certain health conditions such as obesity and diabetes may also be at increased risk. For further information on the health effects of PM, see CARB and OEHHA (2002).

xvi. Sulfur Dioxide

At room temperature, the criteria air pollutant sulfur dioxide is a colorless, irritating gas with a choking or suffocating odor that generally provides adequate warning of exposure at high levels of exposure. Found in the vapor and particulate phases, sulfur dioxide in the atmosphere is formed both endogenously from volcanic eruptions and marine and terrestrial biogenic emissions and exogenously from the combustion of coal and oil. It may be converted to sulfuric acid, sulfur trioxide, and sulfates in air, and its dissolution in water can yield corrosive sulfurous acid. Gaseous sulfur dioxide will not burn under typical fire conditions. Exposure to sulfur dioxide occurs mainly via inhalation. Sulfur dioxide is heavier than air and asphyxiation may result from exposure to high concentrations in poorly ventilated, enclosed, or low-lying areas.

Sulfur dioxide and its vapors have been detected at various refinery emission points including boilers, crude units, heaters, cokers, FCCUs, and incinerators. Sulfur dioxide has been detected in non-routine refinery emissions and was noted in incident reports more frequently than any other chemical included in this report, often during or after flaring events.

Acute inhalation exposure to sulfur dioxide has been associated with eye, mucous membrane, skin, and respiratory tract irritation. Symptoms of respiratory irritation include sneezing, sore throat, wheezing, shortness of breath, chest tightness, and a feeling of suffocation. Breathing very high levels can be life-threatening. Airway obstruction from reflex laryngeal spasm and edema, bronchospasm, pneumonitis (inflammation of lung tissue), and pulmonary edema (fluid accumulation in the lung) after exposure has been reported. Asthmatics, especially when exercising or when in cold, dry air, and some individuals that are atopic (predisposed toward developing certain allergic hypersensitivity reactions) or have RADS are more sensitive to the irritant properties of sulfur dioxide. Since the occurrence of asthma is most common in African Americans, children ages 8-11 years, and people living in cities, African American children in urban areas are also expected to have increased vulnerability to this chemical. Further, adverse effects on pulmonary function may be more severe in asthmatics and those with cardiopulmonary disease dually exposed to sulfur dioxide and other irritants such as sulfuric acid, nitrogen dioxide, and ozone. OEHHA used multiple inhalation studies of healthy, asthmatic, and atopic (predisposed toward developing certain allergic hypersensitivity reactions) volunteers for the derivation of the acute REL for sulfur dioxide (660 $\mu g/m^3$). This value is identical to the California AAQS for one-hour exposure. The most sensitive endpoint observed at this concentration was impairment of airway function, particularly in asthmatics.

Chronic exposure to sulfur dioxide may lead to an altered sense of smell, increased susceptibility to respiratory infections, symptoms of chronic bronchitis, and accelerated decline in pulmonary function. The California AAQS for 24-hour averaging is 0.04 ppm (105 $\mu g/m^3$) for sulfur dioxide. In 2011, sulfur dioxide was added to the Proposition 65 list as a developmental toxicant based on studies showing increased incidence of preterm birth and indicators of fetal growth retardation such as low birth weight. Evidence that air pollution containing sulfur dioxide induces DNA damage in human sperm has also been reported.

xvii. Sulfuric Acid

Sulfuric acid is a colorless, oily liquid that exists in air in water vapor and particulates. It is corrosive to metals and organic materials and emits toxic sulfur trioxide-containing fumes or vapors when heated. While it will not burn under typical fire conditions, sulfuric acid in high concentrations is explosive or incompatible with a variety of substances including organic materials, chlorates, carbides, fulminates, water, and powdered metals. The general population is exposed to this chemical by breathing ambient air where oil, gas, or coal is burned. In petroleum refineries, sulfuric acid is used as a catalyst during alkylation and in various treatment processes (Lewis, 2012). This chemical has also been detected in large amounts in refinery air emissions and reported in multiple fire and non-fire incidents.

Both acute and chronic exposures to sulfuric acid target the respiratory system. Breathing sulfuric acid mists for short periods of time in occupational settings has been associated with dental erosion and respiratory tract irritation, which leads to bronchoconstriction and altered lung function. Multiple exposures to other pollutants also common to industrial areas may increase the irritant effects of sulfuric acid, particularly for individuals with asthma. In addition, animal studies suggest that the young may be more sensitive to adverse effects than adults. The most sensitive endpoint of acute exposure was observed in a human study that showed small changes in airway function, particularly in asthmatics, following a 16-minute exposure to 450 µg/m^3 of sulfuric acid. After time and dose adjustments and consideration of uncertainties, an OEHHA acute REL of 120 µg/m^3 was established.

Long-term exposure to sulfuric acid has been associated with decreased lung function. Chronic exposure may also lead to tracheobronchitis (inflammation of the windpipe and bronchioles), stomatitis (inflamed or sore mouth), conjunctivitis (inflammation or infection of the eye), and gastritis (inflammation, irritation, or erosion of the stomach). The chronic REL for sulfuric acid was derived from a continuous inhalation study that led to abnormal changes in bronchial cells in the lungs of monkeys (increased cell reproduction and organ/tissue enlargement) at a concentration of 380 µg/m^3. OEHHA determined the chronic REL for sulfuric acid to be 1 µg/m^3.

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APPENDIX B: CALIFORNIA REFINERY PROCESS UNITS AND EMISSION POINTS WITH ASSOCIATED CHEMICAL EMISSIONS

In response to a request by US EPA, all refineries active during 2010 measured air emissions from each process and emission point for a specified time period and submitted the data to US EPA. This request resulted in a list of chemicals measured to be routinely emitted in each process, and OEHHA used these emissions inventories to identify the most commonly occurring processes in California refineries (Table 8) and their reported chemical emissions. Since some refinery processes are associated with a particular chemical profile, such information can be used to help anticipate the types of chemicals that may be released during a refinery accident and characterize the potential health effects of chemical exposure. Thus, consideration of common processes and characteristic emissions, in addition to knowledge of health guidance values and emergency exposure levels, can be used to help CARB make judgements about air monitoring.

Appendix B displays a list of chemical emissions associated with each process based on California data for 2010. The processes and chemicals shown in Appendix B reflect a sample of those most commonly found in our research based on California data for 2010 provided by US EPA but are not intended to be a complete list of all refinery processes or chemicals emitted from each process.

Table B1. California Refinery Process Units and Emissions Points Associated with Chemical Emissions

Chemical [2]	Process[1]: Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
Acenaphthene	X	X	X	X	X			X	X	X	X	X	X	X	X
Acenaphthylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Acetaldehyde	X	X	X	X	X	X	X	X	X	X			X	X	X
Acetylene				X			X	X	X					X	
Acrolein		X	X	X	X	X	X	X	X				X	X	
Ammonia	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Analine	X	X	X	X	X	X	X	X	X	X		X	X	X	
Anthracene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Antimony		X	X	X	X	X	X	X	X	X			X	X	
Arsenic		X	X	X	X	X	X	X	X	X	X		X	X	
Barium		X	X	X	X	X	X	X	X	X			X	X	
Benz[a]anthracene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzo[b]fluoranthene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzo[k]fluoranthene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzo[g,h,i]perylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzo[a]pyrene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Benzo[e]pyrene	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Beryllium		X	X	X	X	X	X	X	X	X	X		X	X	
Biphenyl	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
1,2-Butadiene				X	X		X	X	X					X	

[1] Abbreviations for the fluid catalytic cracking unit (FCCU), the sulfur recovery unit (SRU), and wastewater treatment (WWT) have been used.
[2] Chemical emissions detected at California refinery process units and emission points in 2010 (US EPA, 2012a; US EPA, 2012b).

Chemical [2]	Process[1]														
	Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
1,3-Butadiene	X		X	X	X	X	X	X	X	X	X	X		X	X
Butane	X		X	X	X	X	X	X	X	X		X	X	X	X
1-Butene	X		X	X			X	X	X	X		X		X	
2-Butene	X		X	X			X		X	X		X		X	
Cadmium		X	X	X	X	X	X	X	X	X	X		X	X	
Carbon disulfide	X		X	X	X	X	X		X	X	X	X	X	X	X
Carbon monoxide		X	X	X	X	X	X	X	X		X		X	X	
Carbonyl sulfide	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Chlorine					X					X			X	X	
Chloroform	X		X		X	X				X		X	X	X	X
Chloromethane	X			X		X				X		X	X		
2-Chloronaphthalene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Chromium (hexavalent)		X	X	X	X	X	X	X	X		X		X	X	
Chromium (total)		X	X	X	X	X	X	X	X	X	X		X	X	
Chrysene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Cobalt		X	X	X	X	X	X	X	X	X			X	X	
Copper		X	X	X	X	X	X	X	X	X	X		X	X	
Cresols (total)	X		X	X	X	X	X	X	X	X	X	X	X	X	X
m-Cresol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
o-Cresol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
p-Cresol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Cumene	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Cyclohexane	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Cyclopentadiene				X			X	X	X					X	
Cyclopentane				X			X		X					X	

Chemical [2]	Process[1]														
	Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
Dibenz[a,h]anthracene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin														X	
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin														X	
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin														X	
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin														X	
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin														X	
1,2,3,7,8-Pentachlorodibenzo-p-dioxin														X	
2,3,7,8-Tetrachlorodibenzo-p-dioxin			X						X				X	X	
Dibenzofuran(s)	X		X	X	X	X			X	X		X		X	
1,2,3,4,6,7,8-Heptachlorodibenzofuran														X	
1,2,3,4,7,8,9-Heptachlorodibenzofuran														X	
1,2,3,6,7,8-Hexachlorodibenzofuran														X	
1,2,3,7,8,9-Hexachlorodibenzofuran														X	
2,3,4,6,7,8-Hexachlorodibenzofuran														X	
1,2,3,4,6,7,8,9-Octachlorodibenzofuran														X	
1,2,3,7,8-Pentachlorodibenzofuran			X											X	
2,3,4,7,8-Pentachlorodibenzofuran														X	
2,3,7,8-Tetrachlorodibenzofuran					X									X	
Dibutyl phthalate														X	
1,4-Dichlorobenzene	X		X		X			X	X	X		X	X		X
1,1-Dichloroethane													X		
Di(2-ethylhexyl)phthalate								X						X	

Chemical [2]	Process[1]: Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
1,1-Dichloroethylene											X		X	X	
1,2-Dichloropropane													X		
1,3-Dichloropropene													X		
Diethanolamine	X		X	X	X	X				X	X	X	X	X	X
Diethyl phthalate														X	
7,12-Dimethylbenz[a]anthracene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Ethane	X		X	X			X	X	X	X		X	X	X	
Ethylbenzene	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Ethylene	X		X	X	X	X	X	X	X	X		X		X	X
Ethylene dibromide	X		X							X		X	X		
Ethylene dichloride	X		X							X	X	X	X		X
Fluoranthene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Fluorene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Formaldehyde		X	X	X	X	X	X	X	X	X			X	X	
Heptane (& isomers)				X			X		X					X	
Hexachloroethane													X		
Hexane	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Hydrogen chloride				X	X	X	X	X	X		X		X	X	
Hydrogen cyanide (& compounds)	X		X	X	X	X	X	X	X				X	X	
Hydrogen fluoride	X			X		X				X		X			X
Hydrogen sulfide	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Indeno[1,2,3-cd]pyrene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Isobutane	X		X					X		X		X		X	
Isobutene	X		X	X			X	X	X	X		X		X	X
Isopentane			X	X			X		X					X	

Chemical [2]	Process[1]: Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
Isoprene				X			X		X					X	
Lead		X	X	X	X	X	X	X	X	X	X		X	X	X
Manganese		X	X	X	X	X	X	X	X	X	X		X	X	
Mercury		X	X	X	X	X	X	X	X	X	X		X	X	
Methanol	X		X		X	X		X	X	X	X	X	X	X	X
Methyl bromide													X		
3-Methyl-1,2-butadiene				X			X							X	
Methyl ethyl ketone	X		X	X	X	X	X	X	X	X	X	X		X	X
Methyl isobutyl ketone	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Methyl tert-butyl ether	X		X	X	X	X	X	X	X	X	X	X	X	X	X
3-Methylchloranthrene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Methylcylcohexane				X			X		X					X	
2-Methylnaphthalene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Molybdenum			X	X		X	X	X	X	X			X		
Naphthalene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Nickel		X	X	X	X	X	X	X	X	X	X		X	X	
Nitrogen dioxide		X	X	X	X		X	X	X				X	X	
Nitrogen oxides		X	X	X	X	X	X	X	X		X	X	X	X	
Octane (& isomers)				X			X		X	X				X	
1,2-Pentadiene				X			X		X					X	
cis-1,3-Pentadiene				X			X		X					X	
trans-1,3-Pentadiene				X			X		X					X	
1,4-Pentadiene				X			X		X					X	
2,3-Pentadiene				X			X		X					X	
Pentane	X		X	X		X	X	X	X			X	X	X	X

Chemical [2]	Process[1]: Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
Perchloroethylene			X		X					X			X	X	X
Perylene	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Phenanthrene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Phenol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Phosphorus			X	X			X	X	X				X		
PM (condensable)		X	X	X	X	X	X	X	X	X			X	X	
PM_{10}		X	X	X	X	X	X	X	X	X			X	X	
PM_{10} (filterable)		X	X	X	X	X	X		X	X			X	X	
$PM_{2.5}$		X	X	X	X	X	X	X	X	X			X	X	
$PM_{2.5}$ (filterable)		X	X	X	X	X	X		X	X			X	X	
Polychlorinated biphenyls		X	X		X				X				X	X	
Propadiene				X			X	X	X					X	
Propane	X		X	X		X	X	X	X	X		X	X	X	
Propylene	X	X	X	X	X	X	X	X	X	X		X	X	X	X
Pyrene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Selenium		X	X	X	X	X	X	X	X	X	X		X	X	
Styrene	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Sulfur dioxide		X	X	X	X	X	X	X	X	X		X	X	X	
1,1,2,2-Tetrachloroethane													X	X	
Tetrachloroethylene				X	X	X								X	
Toluene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
1,1,2-Trichloroethane	X									X		X		X	X
Trichloroethylene	X											X	X	X	
Triethylamine	X		X	X		X				X	X	X	X	X	X
Trimethylbenzene(s)	X		X	X	X	X	X	X	X	X	X	X	X	X	X

	Process[1]														
Chemical [2]	Alkylation Unit (Fugitive and Point)	Boiler (Point)	Cogeneration Unit (Fugitive and Point)	Coker (Fugitive and Point)	Cooling Tower (Fugitive and Point)	Crude Unit (Fugitive and Point)	FCCU (Fugitive and Point)	Flare (Point)	Heater (Point)	Product Loading (Fugitive and Point)	Storage Tank (Fugitive and Point)	SRU (Fugitive and Point)	Thermal Oxidizer (Point)	Vent (Point)	WWT (Fugitive)
2,2,4-Trimethylpentane	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Vanadium		X	X	X	X	X	X	X	X	X			X	X	
Vinyl chloride												X		X	
Volatile organic compounds	X		X	X	X	X	X	X	X	X	X	X	X	X	X
Xylenes (total)	X		X	X	X	X	X	X	X	X	X	X	X	X	X
m-Xylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
o-Xylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
p-Xylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Zinc			X	X	X	X	X	X	X	X	X		X	X	

APPENDIX C: CALIFORNIA REFINERY CHEMICALS SORTED BY CHEMICAL ANALYSIS CATEGORY

OEHHA used a classification scheme provided by CARB by assigning specific chemical analysis categories, shown in Table 9, to chemicals included in OEHHA's list of California refinery chemicals (Table 1). The classification of chemicals by air monitoring capability allowed for the consideration of emissions, health effects, and health guidance values of chemicals with similar properties. Appendix C displays the chemicals included in each chemical analysis category. The analysis categories and chemicals within them are sorted in alphabetical order.

Table C1. California Refinery Chemicals Sorted by Chemical Analysis Category

Chemical Analysis Category	Chemical
Acid	Hydrogen chloride
Acid	Hydrogen cyanide
Acid	Hydrogen fluoride
Acid	Phosphoric acid
Acid	Sulfuric acid
Aldehyde	Acetaldehyde
Aldehyde	Formaldehyde
Aldehyde	Glutaraldehyde
Dioxins, Dibenzofurans	Dibenzo-p-dioxins (chlorinated)
Dioxins, Dibenzofurans	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	1,2,3,7,8-Pentachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	2,3,7,8-Tetrachlorodibenzo-p-dioxin
Dioxins, Dibenzofurans	Dibenzofurans (chlorinated)
Dioxins, Dibenzofurans	1,2,3,4,6,7,8-Heptachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,4,7,8,9-Heptachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,4,7,8-Hexachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,6,7,8-Hexachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,7,8,9-Hexachlorodibenzofuran
Dioxins, Dibenzofurans	2,3,4,6,7,8-Hexachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,4,6,7,8,9-Octachlorodibenzofuran
Dioxins, Dibenzofurans	1,2,3,7,8-Pentachlorodibenzofuran
Dioxins, Dibenzofurans	2,3,7,8-Tetrachlorodibenzofuran
Extractable	Phenol
Extractable Aromatic	Biphenyl

Chemical Analysis Category	Chemical
Extractable Aromatic	Cresols (mixtures of)
Extractable Aromatic	Dibutyl phthalate
Extractable Aromatic	Di(2-ethylhexyl)phthalate
Extractable Hetero Aromatic	Aniline
Extractable Hetero Aromatic	Polychlorinated biphenyls
Extractable Hetero Hydrocarbon	Diethanolamine
Gas	Ammonia
Gas	Methane
Gas	Nitrous oxide
Gas	Propylene oxide
Gas, CEM	Nitrogen oxides
Gas, CEM	Sulfur dioxide
Gas, Colorimetric, CEM	Carbonyl sulfide
Gas, Colorimetric, CEM	Chlorine
Gas, Colorimetric, CEM	Hydrogen sulfide
Gas, Colorimetric, VOC, CEM	Carbon monoxide
Glycol	Ethylene glycol monoethyl ether
Glycol	Propylene glycol monomethyl ether
Glycol Acid	Ethylene glycol monoethyl ether acetate
Glycol Acid	Propylene glycol monomethyl ether acetate
Glycol Ether	Propylene glycol mono-t-butyl ether
Glycol, Glycol Acid	Glycol ethers (& acetates)
Mass	PM_{10}
Mass	$PM_{2.5}$
Metal	Aluminum
Metal	Antimony
Metal	Arsenic
Metal	Barium
Metal	Beryllium
Metal	Cadmium
Metal	Chromium III
Metal	Chromium (hexavalent & compounds)
Metal	Cobalt
Metal	Copper
Metal	Lead
Metal	Manganese
Metal	Mercury
Metal	Nickel
Metal	Particulate divalent mercury

Chemical Analysis Category	Chemical
Metal	Selenium (& compounds)
Metal	Selenium sulfide
Metal	Vanadium (fume or dust)
Metal	Zinc
Metal Spectrophotometric	Elemental gaseous mercury
Metal Spectrophotometric	Gaseous divalent mercury
Metal, Acid	Phosphorus
Microscopy	Asbestos
PAH	Acenaphthene
PAH	Acenaphthylene
PAH	Anthracene
PAH	Benz[a]anthracene
PAH	Benzo[b]fluoranthene
PAH	Benzo[j]fluoranthene
PAH	Benzo[k]fluoranthene
PAH	Benzo[g,h,i]perylene
PAH	Benzo[a]pyrene
PAH	Benzo[e]pyrene
PAH	2-Chloronaphthalene
PAH	Chrysene
PAH	Dibenz[a,h]anthracene
PAH	7,12-Dimethylbenz[a]anthracene
PAH	Fluoranthene
PAH	Fluorene
PAH	Indeno[1,2,3-c,d]pyrene
PAH	3-Methylcholanthrene
PAH	2-Methylnaphthalene
PAH	Naphthalene
PAH	PAHs, total, w/ individ. components reported
PAH	PAHs, total, w/o individ. components reported
PAH	Perylene
PAH	Phenanthrene
PAH	Pyrene
VOC Canister	Acetylene
VOC Canister	Acrolein
VOC Canister	1,3-Butadiene
VOC Canister	Butane
VOC Canister	1-Butene
VOC Canister	2-Butene

Chemical Analysis Category	Chemical
VOC Canister	Carbon disulfide
VOC Canister	Chlorodifluoromethane
VOC Canister	Ethylene
VOC Canister	Isopropanol
VOC Canister	Methyl bromide
VOC Canister	Methyl chloride
VOC Canister	Methylene chloride
VOC Canister	cis-1,3-Pentadiene
VOC Canister	Propylene
VOC Canister	Trichlorofluoromethane
VOC Canister	1,1,2-Trichloro-1,2,2-trifluoroethane
VOC Canister	Vinyl chloride
VOC Canister, Sorbent	Benzene
VOC Canister, Sorbent	Carbon tetrachloride
VOC Canister, Sorbent	Chlorobenzene
VOC Canister, Sorbent	Chloroform
VOC Canister, Sorbent	Cumene
VOC Canister, Sorbent	Cyclohexane
VOC Canister, Sorbent	Cyclopentadiene
VOC Canister, Sorbent	Cyclopentane
VOC Canister, Sorbent	1,4-Dichlorobenzene
VOC Canister, Sorbent	1,2-Dichloropropane
VOC Canister, Sorbent	1,3-Dichloropropene
VOC Canister, Sorbent	Ethylbenzene
VOC Canister, Sorbent	Ethylene dibromide
VOC Canister, Sorbent	Ethylene dichloride
VOC Canister, Sorbent	Hexane
VOC Canister, Sorbent	Methyl chloroform
VOC Canister, Sorbent	Methyl ethyl ketone
VOC Canister, Sorbent	Methyl isobutyl ketone
VOC Canister, Sorbent	Methyl tert-butyl ether
VOC Canister, Sorbent	Perchloroethylene
VOC Canister, Sorbent	Propylene dichloride
VOC Canister, Sorbent	Styrene
VOC Canister, Sorbent	1,1,2,2-Tetrachloroethane
VOC Canister, Sorbent	Toluene
VOC Canister, Sorbent	1,1,2-Trichloroethane
VOC Canister, Sorbent	Trichloroethylene
VOC Canister, Sorbent	1,2,4-Trimethylbenzene
VOC Canister, Sorbent	2,2,4-Trimethylpentane

Chemical Analysis Category	Chemical
VOC Canister, Sorbent	Xylenes (mixed)
VOC Canister, Sorbent	m-Xylene
VOC Canister, Sorbent	o-Xylene
VOC Canister, Sorbent	p-Xylene
VOC Sorbent	Methanol

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APPENDIX D: ROUTINE TOXIC AIR CONTAMINANT EMISSIONS FROM CALIFORNIA REFINERIES

OEHHA obtained a list of TACs reported in the California Emission Inventory Development and Reporting System (CEIDARS) database for all California refineries active during 2009-2012. The emissions data obtained from CEIDARS were submitted to CalEPA in accordance with the AB 2588 Air Toxics Hot Spots Program requirements, and reflect TAC releases that occurred during routine facility operations. The Hot Spots program requires facilities to report emission inventory updates every four years. Therefore, not all facilities update emission inventories in the same year. As a result, some chemicals may not be reported each year. Based on this quadrennial method of updating emission inventories in the Hot Spots Program, the information that the CEIDARS database provides on the TACs emitted from refineries are likely underestimates of total routine emissions across refineries in any given year.

Appendix D is an expanded version of Table 10 and displays the average annual routine TAC emissions for California refineries during 2009-2012 based on data provided by CARB. Emissions data are reported in pounds per year and listed in descending order.

Table D1. Average Annual Routine Toxic Air Contaminant Emissions for California Refineries

Chemical	Routine Emissions (lb/year)[1]
Ammonia	2,085,824
Formaldehyde	288,412
Methanol	122,611
Sulfuric acid	104,573
Hydrogen sulfide	103,385
Toluene	87,945
Xylenes (mixed)	79,177
Benzene	43,308
Hexane	39,646
Hydrochloric acid	21,450
Naphthalene	17,836
Acetaldehyde	16,136
Carbonyl sulfide	15,111
Ethyl benzene	11,960
1,2,4-Trimethylbenzene	9,815
Propylene	6,022
Diethanolamine	3,511

[1] Average annual routine Toxic Air Contaminant (TAC) emissions for California refineries during 2009-2012, listed in descending order.

Chemical	Routine Emissions (lb/year)[1]
Hydrogen fluoride	3,463
1,3-Butadiene	3,156
Acrolein	2,804
Perchloroethylene	2,742
PAHs, total, w/o individ. components reported	2,666
o-Xylene	2,662
Manganese	2,587
Chloroform	2,048
Nickel	1,720
Copper	1,145
m-Xylene	1,000
Selenium	826
Phenanthrene	817
Methane	790
Benzo[a]pyrene	735
Methyl chloroform	720
p-Xylene	677
Chlorodifluoromethane	621
Phenol	598
Lead	431
Mercury	415
Cadmium	283
Phosphorus	275
Styrene	249
Chlorine	228
Glutaraldehyde	168
Fluorene	156
Arsenic	145
Diesel engine exhaust	123
Methyl ethyl ketone	111
PAHs, total, w/ individ. components reported	103
Trichloroethylene	86
Methyl tert-butyl ether	74
1,1,2-Trichloro-1,2,2-trifluoroethane	65
Glycol ethers (& acetates)	50
Asbestos	45
Isopropanol	45
Trichlorofluoromethane	36
Nitrous oxide	31

Chemical	Routine Emissions (lb/year)[1]
Chromium (hexavalent & compounds)	24
Beryllium	23
Methylene chloride	21
Chrysene	14
Propylene oxide	13
Cresols (mixtures of)	11
Phosphoric acid	10
Ethylene dichloride	7
Ethylene dibromide	6
Propylene glycol monomethyl ether	3
Fluoranthene	3
Pyrene	3
Vanadium (fume or dust)	2
Indeno[1,2,3-cd]pyrene	2
Methyl isobutyl ketone	2
Acenaphthylene	2
Benzo[b]fluoranthene	2
Anthracene	1
2-Methyl naphthalene	1
Benz[a]anthracene	1
Carbon tetrachloride	1
Carbon disulfide	1
Benzo[k]fluoranthene	1
Acenaphthene	1
Zinc	1
Benzo[e]pyrene	0.4
Vinyl chloride	0.3
1,1,2,2-Tetrachloroethane	0.3
Dibenz[a,h]anthracene	0.2
1,1,2-Trichloroethane	0.2
1,2-Dichloropropane	0.2
1,3-Dichloropropene	0.2
Benzo[g,h,i]perylene	0.2
Methyl chloride	0.1
Aluminum	0.1
Propylene glycol monomethyl ether acetate	0.06
Perylene	0.03
7,12-Dimethylbenz[a]anthracene	0.01
Benzo[j]fluoranthene	0.006

Chemical	Routine Emissions (lb/year)[1]
Chlorobenzene	0.005
1,4-Dioxane	0.004
Dibenzofurans (chlorinated)	0.002
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	$9x10^{-6}$

APPENDIX E: NON-ROUTINE AND ROUTINE EMISSIONS

OEHHA has compiled data on routine and non-routine emissions, not limited to TACs, from the California refineries active during 2010 using data provided by US EPA (Tables 11 and 12). While routine emissions represent chemical releases that occur during normal facility operations, non-routine releases reflect emissions during any non-routine refinery operation, including startups, shutdowns, and malfunction operations such as refinery-wide power loss, maintenance, and flaring events.

The refinery emissions shown in Appendix E were measured or calculated at various processes and emission points and self-reported by refineries to US EPA; however, these data were limited to 2010, and therefore may not be representative of all chemical emissions based on reporting requirements.

Table E1. Annual Routine and Non-routine Chemical Emissions by California Refineries

Chemical	Routine Emissions (lb)[1]	Non-routine Emissions (lb)[1]
Acenaphthene	855	0.03
Acenaphthylene	129	0.02
Acetaldehyde	14,613	60
Acrolein	85,112	22
Ammonia	1,457,960	1,735
Aniline	462	—
Anthracene	959	1
Antimony	348	0.5
Arsenic	129	0.2
Barium	1,248	4
Benz[a]anthracene	242	0.02
Benzene	91,584	6,755
Benzo[b]fluoranthene	118	0.02
Benzo[k]fluoranthene	78	0.01
Benzo[g,h,i]perylene	146	0.002
Benzo[a]pyrene	225	0.04
Benzo[e]pyrene	41	—
Beryllium	62	0.09
Biphenyl	22,021	681
1,2-Butadiene	16	—
1,3-Butadiene	7,781	5,374

[1] Routine and non-routine emissions as reported by California refineries for 2010, listed in alphabetical order (US EPA, 2012a; US EPA, 2012b).

Chemical	Routine Emissions (lb)[1]	Non-routine Emissions (lb)[1]
Butane	5,881,551	4,446
1-Butene	179	155
2-Butene	165	—
Cadmium	5,781	1
Carbon disulfide	21,240	27
Carbon monoxide	16,972,733	418,331
Carbonyl sulfide	68,329	90
Chlorine	3,040	—
Chloroform	690	0.02
2-Chloronaphthalene	3	—
Chromium	1,291	2
Chromium (hexavalent & compounds)	226	0.2
Chrysene	285	0.01
Cobalt	167	0.07
Copper	1,062	1
Cresols (mixtures of)	3,265	417
m-Cresol	351	1
o-Cresol	364	—
p-Cresol	364	—
Cumene	21,988	237
Cyclohexane	22,567	204
Cyclopentadiene	—	3,190
Cyclopentane	23	—
Dibenz[a,h]anthracene	134	0.001
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	0.03	—
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	$6x10^{-6}$	—
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	$8x10^{-6}$	—
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	$8x10^{-6}$	—
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	0.001	—
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	$5x10^{-6}$	—
2,3,7,8-Tetrachlorodibenzo-p-dioxin	$5x10^{-4}$	—
Dibenzofuran	0.03	—
1,2,3,4,6,7,8-Heptachlorodibenzofuran	$7x10^{-4}$	—
1,2,3,4,7,8,9-Heptachlorodibenzofuran	$1x10^{-5}$	—
1,2,3,4,7,8-Hexachlorodibenzofuran	$2x10^{-4}$	—

Chemical	Routine Emissions (lb)[1]	Non-routine Emissions (lb)[1]
1,2,3,6,7,8-Hexachlorodibenzofuran	0.04	—
1,2,3,7,8,9-Hexachlorodibenzofuran	$5x10^{-6}$	—
2,3,4,6,7,8-Hexachlorodibenzofuran	$2x10^{-4}$	—
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	$3x10^{-4}$	—
1,2,3,7,8-Pentachlorodibenzofuran	$2x10^{-5}$	—
2,3,4,7,8-Pentachlorodibenzofuran	0.02	—
2,3,7,8-Tetrachlorodibenzofuran	$5x10^{-5}$	—
Dibutyl phthalate	0.03	—
1,4-Dichlorobenzene	129	0.03
1,1-Dichloroethane	2	—
1,2-Dichloropropane	2	—
1,3-Dichloropropene	2	—
Diethanolamine	3,496	321
Diethyl phthalate	0.3	—
Di(2-ethylhexyl)phthalate	5	—
7,12-Dimethylbenz[a]anthracene	8	0.01
Ethane	502,829	3,029
Ethyl chloride	0.2	—
Ethylbenzene	75,917	1,317
Ethylene	15,450	2,184
Ethylene dibromide	5	—
Ethylene dichloride	3	—
Fluoranthene	181	0.02
Fluorene	1,228	0.2
Formaldehyde	78,370	923
Heptane	243	—
Hexane	809,803	7,625
Hydrogen chloride	37,893	121
Hydrogen cyanide	34,445	3
Hydrogen fluoride	62	—
Hydrogen sulfide	79,310	2,981
Indeno[1,2,3-c,d]pyrene	124	0.05
Isobutane	794	2,437
Isobutene	168	167
Isopentane	803	—
Lead	1,084	1
Manganese	3,238	0.4

Chemical	Routine Emissions (lb)[1]	Non-routine Emissions (lb)[1]
Mercury	519	0.2
Methanol	308,640	0.02
Methyl bromide	51	—
Methyl chloride	1	—
Methyl ethyl ketone	157	—
Methyl isobutyl ketone	123	—
Methyl tert-butyl ether	23,558	1,980
3-Methylcholanthrene	3	0.002
Methylcyclohexane	111	—
2-Methylnaphthalene	23,387	0.02
Molybdenum	6,629	1
Naphthalene	33,216	1,192
Nickel	3,509	2
Nitrogen dioxide	1,971,085	12,397
Nitrogen oxides	16,415,674	223,792
Octane	35	—
Pentane	433,457	2,457
Perchloroethylene	1,354	$4x10^{-6}$
Perylene	41	—
Phenanthrene	2,979	3
Phenol	6,509	1,171
Phosphorus	602	0.1
PM (condensable)	1,677,433	3,855
PM_{10} (filterable)	2,805,076	22,802
PM_{10} (primary)	6,617,951	89,572
$PM_{2.5}$ (filterable)	1,088,791	1,303
$PM_{2.5}$ (primary)	2,004,663	26,306
Polychlorinated biphenyls	0.1	—
Propadiene	—	0.1
Propane	332,004	5,012
Propylene	71,931	7,799
Pyrene	465	0.01
Selenium (& compounds)	1,583	1
Styrene	58,849	1
Sulfur dioxide	21,158,748	553,834
1,1,2,2-Tetrachloroethane	$6x10^{-5}$	—
Toluene	273,000	4,530
1,1,2-Trichloroethane	2	—

Chemical	Routine Emissions (lb)[1]	Non-routine Emissions (lb)[1]
Triethylamine	111	—
Trimethylbenzene	31,177	21
2,2,4-Trimethylpentane	501,931	84
Vanadium (fume or dust)	8,455	2
Volatile organic compounds	13,562,963	1,123,158
Xylenes (mixed)	274,547	4,700
m-Xylene	1,209	—
o-Xylene	1,096	—
p-Xylene	1,151	—
Zinc	20,726	26

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APPENDIX F: REFINERY EMISSIONS IN THE US AND FUEL-BURNING EXPERIMENTS

Based on research in peer-reviewed journal articles, OEHHA has provided a list of additional chemicals measured in US refinery emissions or oil-burning experiments during 1979-2007. Because refineries are only required to report emissions of regulated chemicals, knowledge of unregulated chemicals also released can provide information on chemical speciation or characteristics that may ultimately be used by officials for air monitoring or risk assessment purposes. The chemicals found in the literature describing controlled burning experiments or refinery air monitoring in the US are listed in Appendix F.

Table F1. Additional Chemicals Found in the Literature on Refinery Emissions in the US and Fuel-Burning Experiments

Chemical	CAS RN	Source
Benzaldehyde	100527	[2]
Benzo[a]fluorine	238846	[3]
Benzo[b]fluorine	30777196	[2]
Benzo[b]thiophene	55712602	[3]
Benzo[def]fluorine	203645	[3]
Benzoic acid	65850	[3]
2-Benzylnaphthalene	613592	[3]
Biphenylene	259790	[3]
Butyraldehyde	123728	[4]
Cerium	7440451	[5]
cis-1,3-Dimethyl cyclohexane	638040	[3]
Crotonaldehyde	123739	[2]
Cymene	99876	[3]
Decane	124185	[2]
1,3-Diethyl-5-methylbenzene	2050240	[3]
Diethylbenzene	25340174	[3]
2,2-Dimethyl-1-hexene	6975924	[3]
2,5-Dimethylbenzaldehyde	93027	[2]
1,2-Dimethylcyclopentane	2452995	[3]
4,4'-Dimethyldiphenylmethane	4957146	[3]
2,3-Dimethylfluorene	4612639	[3]
3,4-Dimethylheptane	922281	[3]
1,2-Dimethylindane	17057828	[3]
1,4-Dimethylnaphthalene	571584	[3]
1,5-Dimethylnaphthalene	571619	[3]
1,7-Dimethylnaphthalene	575371	[3]
2,3-Dimethylnaphthalene	581408	[3]
2,6-Dimethylnaphthalene	1123564	[4]
4,5-Dimethylnonane	17302237	[3]
2,6-Dimethyloctane	2051301	[3]

Chemical	CAS RN	Source
3,3-Dimethylpentane	562492	[3]
2,3-Dimethylphenanthrene	3674655	[3]
2,5-Dimethylphenanthrene	3674666	[3]
3,6-Dimethylphenanthrene	1576676	[3]
2,5-Dimethylphenol	95874	[3]
3,4-Dimethylphenol	95658	[3]
3,5-Dimethylphenol	108689	[3]
1,1-Dimethylpropylbenzene	2049958	[3]
1,2-Diphenoxybenzene	3379371	[3]
1,4-Diphenoxybenzene	3061367	[3]
2,5-Diphenyl-1,4-benzoquinone	844519	[3]
Diphenylbutadiyne	886668	[3]
Dodecane	112403	[2]
Dysprosium	7429916	[5]
1-Ethenyl-2-methylbenzene	611154	[3]
1-Ethenyl-3-methylenecyclopentene	61142072	[3]
1-Ethyl-2,3-dimethylbenzene	933982	[3]
1-Ethyl-2-methylbenzene	611143	[3]
2-Ethyl-1,1’-biphenyl	1812517	[3]
2-Ethyl-4-methylphenol	3855263	[3]
Ethylcyclohexane	1678917	[3]
3-Ethylhexane	619998	[3]
2-Ethylnaphthalene	939275	[3]
2-Ethylphenol	90006	[3]
1-Ethylpropylbenzene	1196583	[3]
m-Ethyltoluene	620144	[3]
o-Ethyltoluene	611143	[3]
p-Ethyltoluene	622968	[3]
Ethynylbenzene	536743	[3]
Europium	7440531	[5]
Gadolinium	744542	[5]
Hexadecane	544763	[2]
Hexanal	66251	[2]
Iron	7439896	[6]
1-Isobutyl-3-methylcyclopentane	29053041	[3]
Isohexane	107835	[1]
Isopentane	78784	[2]
Isovaleraldehyde	590863	[2]
Lanthanum	7439910	[5]
1-Methyl-2-[2-phenylethenylbenzene]	74685420	[3]
1-Methyl-2-[3-methylphenyl-methylbenzene]	21895136	[3]

Chemical	CAS RN	Source
1-Methyl-3-[4-methylphenyl-methylbenzene]	21895169	[3]
1-Methyl-3-[2-phenylethenylbenzene]	14064483	[3]
1-Methyl-2-phenylmethylbenzene	713360	[3]
1-Methyl-4-phenylmethylbenzene	620837	[3]
1-Methyl-2-propylbenzene	1074175	[3]
3-Methyl-1,1’-biphenyl	643936	[3]
3-Methyl-2-butenylbenzene	4489843	[3]
2-Methylanthracene	613127	[3]
4-Methylbenzaldehyde	104870	[3]
3-Methyldecane	13151343	[3]
9-Methylenefluorene	4425825	[3]
9-Methylene-fluorene	4425825	[3]
1-Methylethenyl-1,1’-biphenyl	—	[3]
1-Methylfluorene	730376	[2]
1-Methylfluorene	1730376	[3]
2-Methylfluorene	1430973	[3]
5-Methylhexan-5-olide	2610959	[3]
3-Methylhexane	589344	[3]
1-Methylnaphthalene	90120	[4]
3-Methylnonane	5911046	[3]
2-Methylpentane	107835	[3]
3-Methylpentane	96140	[1]
1-Methylphenanthrene	832699	[4]
2-Methylphenanthrene	2531842	[3]
3-Methylphenanthrene	832713	[3]
2-Methylpropylcyclohexane	1678984	[3]
2-Methylpyrene	3442782	[3]
Naphtho[2,1-b]furan	232951	[3]
Neodymium	7440008	[5]
Nonane	111842	[2]
Pentamethylbenzene	700129	[3]
Propyne	74997	[2]
3-Penten-1-yne	2206237	[3]
1-Pentene	109671	[1]
Platinum	7440064	[6]
Praseodymium	7440100	[5]
Propionaldehyde	123386	[2]
Propylbenzene	103651	[3]
Samarium	7440199	[5]
Silicon	7440213	[6]
Silver	7440224	[6]

Chemical	CAS RN	Source
Tetradecane	629594	[2]
1,2,3,4-Tetramethylbenzene	488233	[3]
1,2,3,5-Tetramethylbenzene	527537	[3]
1,2,4,5-Tetramethylbenzene	95932	[3]
p-Tolualdehyde	104870	[2]
1,3,5-Trimethylbenzene	108678	[3]
1,2,4-Trimethylcyclohexane	2234755	[3]
1,3,5-Trimethylcyclohexane	1839630	[3]
1,4,5-Trimethylnaphthalene	2131411	[3]
1,4,6-Trimethylnaphthalene	2131422	[3]
2,3,5-Trimethylnaphthalene	2245387	[4]
2,3,5-Trimethylphenanthrene	3674735	[3]
Triphenylene	217594	[3]
Undecane	1120214	[2]
Valeraldehyde	110623	[2]

[1] Sexton and Westberg, 1979.
[2] Booher and Janke, 1997.
[3] Strosher, 2000.
[4] Fingas et al., 2001.
[5] Kulkarni et al., 2007.
[6] Lewis et al., 2012.

APPENDIX G: DATA ANALYSIS OF REFINERY CHEMICALS ACROSS CATEGORIES

Comparisons between high routine emissions and health guidance values or emergency exposure levels may help determine chemicals for air monitoring and may help protect the community surrounding these refineries by limiting exposure. To that end, OEHHA has performed some preliminary analysis of the compiled data to offer comparisons between various categories of information and to note which chemicals are most common in the comparisons. Table G-1 uses information already in the report to make these assessments.

The analysis in Table G-1 compares chemicals with health guidance values with chemicals that have high routine emissions. The footnotes to the table explain each comparison in detail.

Table G1. Comparison of Chemicals with High Routine Emissions and Other Health Guidance Values

High Routine Emissions and OEHHA Noncancer REL[1]	High Routine Emissions and US EPA RfC[2]	High Routine Emissions and OEHHA Proposition 65 (D or R)[3]	High Routine Emissions and OEHHA Proposition 65 (C)[4]	High Routine Emissions and OEHHA CPF[5]	High Routine Emissions and Noncancer and Cancer Effects[6]	High Routine Emissions and Emergency Exposure Levels[7]	Incident History[8]	High Routine Emissions and Processes[9]
Ammonia (A, C)	Ammonia					Ammonia		Ammonia
Benzene (A,8,C)	Benzene	Benzene (D, Rm)	Benzene	Benzene	Benzene	Benzene		Benzene
						Butane		
Carbon Monoxide (A)		Carbon Monoxide (D)				Carbon Monoxide		
Formaldehyde (A,8,C)			Formaldehyde	Formaldehyde	Formaldehyde	Formaldehyde		Formaldehyde
Hexane (C)						Hexane		Hexane
							Hydrocarbons	
Hydrogen Chloride (A,C)	Hydrogen Chloride					Hydrogen Chloride		
Hydrogen Sulfide (A,C)	Hydrogen Sulfide					Hydrogen Sulfide	Hydrogen Sulfide	Hydrogen Sulfide
Methanol (A,C)	Methanol	Methanol (D)				Methanol		
Nitrogen Dioxide (A)	Nitrogen Dioxide					Nitrogen Dioxide		
Sulfur Dioxide (A)	Sulfur Dioxide	Sulfur Dioxide (D)				Sulfur Dioxide	Sulfur Dioxide	
Sulfuric Acid (A,C)	Sulfuric Acid		Sulfuric Acid		Sulfuric Acid	Sulfuric Acid		
Toluene (A,C)	Toluene	Toluene (D)				Toluene		Toluene
Xylenes (mixed) (A,C)	Xylenes (mixed)					Xylenes (mixed)		Xylenes (mixed)

[1] Have Acute (A), 8-hour (8), or Chronic (C) OEHHA noncancer RELs (Table 3) and high routine emissions (Table 10, 11)
[2] Have US EPA RfC (Table 3) and high routine emissions (Table 10, 11)
[3] Have Proposition 65 status for Reproductive (R) or Developmental (D) harm (Table 3) and high routine emissions (Table 10, 11)
[4] Have Proposition 65 status as Carcinogenic (C) (Table 3) and high routine emissions (Table 10, 11)
[5] Have OEHHA CPF (Table 3) and high routine emissions (Table 10, 11)
[6] Have OEHHA RELs and/or US EPA RfCs and Proposition 65 status as carcinogenic and/or CPFs (Table 3) and high routine emissions (Table 10, 11)
[7] Have US EPA AEGL 1 or AEGL 2, NIOSH IDLH, or LEL (Table 5) and high routine emissions (Table 10, 11)
[8] Involved in incidents mentioned in Section V-4: California Refinery Incident History
[9] Involved in the most processes (15 of 15 total processes) (Table D-1)

To complement Table G-1, OEHHA expanded on the analysis in column 1 of Table I-1 comparing chemicals with high routine emissions to specific values of OEHHA noncancer RELs for acute, 8-hour, and chronic exposure in Table 1-2.

Table G2. OEHHA REL Values for Chemicals with High Routine Emissions

Chemical	Acute (μg/m^3)	8-Hour (μg/m^3)	Chronic (μg/m^3)
Ammonia	3,200		200
Benzene	27	3	3
Carbon Monoxide	2.3×10^4		
Formaldehyde	55	9	9
Hexane			7×10^3
Hydrogen Chloride	2,100		9
Hydrogen Sulfide	42		10
Methanol	2.8×10^4		4,000
Nitrogen Dioxide	470		
Sulfur Dioxide	660		
Sulfuric Acid	120		1
Toluene	3.7×10^4		300

In Table G3, OEHHA prioritized chemicals by chemical analysis category based on presence in all the tables in the report. In addition to total number of categories, some chemicals were prioritized based on considerations of toxicity, volatility, and highest or lowest values in particular categories (highest routine or non-routine emissions or lowest RELs/RfCs). The top chemicals for each chemical analysis category are noted.

Table G3. Chemicals Sorted by Chemical Analysis Category

Chemical Analysis Category	Avg Routine emissions	Non-routine 2010	REL	RfC	Prop 65	Processes	Incident History 2001-12	AEGLs	IDLH	TOTAL
ACIDS										
Sulfuric acid	X		X				X	X	X	**5**
Hydrogen fluoride		X	X				X	X	X	**5**
Hydrogen Cyanide		X	X	X	X	X				**5**
ALDEHYDES										
Acetaldehyde*	X		X	X	X	X		X	X	**7**
Formaldehyde*	X		X		X	X		X	X	**6**
DIOXINS, DIBENZOFURANS										
Dibenzofurans (chlorinated) {PCDFs}	X		X		X	X				**4**
Tetrachlorodibenzo-p-Dioxin (2,3,7,8) **			X		X	X				**3**
Hexachlorodibenzofuran (1,2,3,7,8,9)			X		X					**2**
Hexachlorodibenzofuran (2,3,4,6,7,8)			X		X					**2**
EXTRACTABLES (PHENOLS, AROMATICS, HYDROCARBONS)										
Phenol	X	X	X			X		X		**5**
Aniline				X	X			X	X	**4**
Cresols (mixtures of) {Cresylic acid}		X	X						X	**3**
GASES										

Chemical Analysis Category	Avg Routine emissions	Non-routine 2010	REL	RfC	Prop 65	Processes	Incident History 2001-12	AEGLs	IDLH	TOTAL
Hydrogen sulfide {H2S}			X	X			X	X	X	**5**
Chlorine	X		X					X	X	**4**
Carbon monoxide		X	X		X	X				**4**
Propylene oxide			X	X	X					**3**
Sulfur dioxide		X	X		X		X			**3**
Ammonia {NH3}	X		X			X				**3**
Carbonyl sulfide	X	X	X							
GLYCOLS										
Propylene glycol monomethyl ether	X		X	X						**3**
ethylene glycol monoethyl ether			X	X	X					**3**
Glycol ethers (and their acetates)	X		X							**2**
MASS										
Diesel engine exhaust, particulate matter (Diesel PM)	X		X	X	X					**4**
PM10						X				**1**
PM2.5						X				**1**
METALS										
Cadmium			X		X	X		X		**4**
Beryllium			X	X	X	X				**4**
Manganese	X		X	X		X				**4**
Arsenic			X		X	X			X	**4**
Mercury					X	X		X		**3**
Lead			X		X	X				**3**

Chemical Analysis Category	Avg Routine emissions	Non-routine 2010	REL	RfC	Prop 65	Processes	Incident History 2001-12	AEGLs	IDLH	TOTAL
PAH										
Naphthalene	X	X	X	X	X	X			X	**7**
Anthracene		X				X				**2**
Benz[a]Anthracene					X	X				**2**
Benzo[a]pyrene					X	X				**2**
Benzo[k]fluoranthene					X	X				**2**
Dibenz[a,h]anthracene					X	X				**2**
PAHs, total, w/o individ. components reported [Treated as B(a)P for HRA]	X				X					**2**
VOC CANISTER										
Butadiene (1,3) **	X		X		X	X	X			**5**
Methyl Bromide			X	X	X			X	X	**5**
Acrolein			X	X				X	X	**4**
Carbon disulfide			X		X	X		X		**4**
Propylene	X	X	X			X				**4**
Methylene chloride {Dichloromethane} **			X		X					**2**
Vinyl chloride			X		X					**2**
VOC CANISTER, SORBENT										
Benzene	X		X		X	X	X			**5**
Styrene			X		X			X		**3**
Carbon tetrachloride **	X		X		X					**3**
Ethylene dichloride {EDC}			X		X				X	**3**
Hexane (listed as n-Hexane in CA refinery)		X	X			X				**3**
Ethyl benzene **			X		X	X				**3**
Toluene			X			X	X			**3**
Xylenes (mixed)			X		X	X				**3**
Chlorobenzene			X					X		**2**

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APPENDIX H: TOXICITY WEIGHTED TOTALS FOR CHEMICALS RELEASED FROM CALIFORNIA REFINERIES

OEHHA reviewed recent data from CEIDARs on Toxic Air Contaminants (TACs) routinely released from California refineries in 2014. OEHHA used the average annual routine TAC emissions for California refineries during 2014 to derive a "toxicity-weighted" emission score for each chemical across all refineries in California for which emissions data were available. The toxicity-weighted emissions score was calculated using emissions data (pounds emitted per year) obtained from the Air Toxics "Hot Spots' Emissions Inventory and a toxicity-weight derived from US EPA's Inhalation Toxicity Scores for individual chemicals. For more information on toxicity weights see: https://www.epa.gov/rsei/rsei-toxicity-data-and-calculations.

Chemicals listed in Table H1 have the highest calculated overall toxicity-weighted pounds emitted. Table H1 shows the sum of emissions by chemical for all California refineries included in this analysis. The calculated toxicity-weighted pounds emitted for each chemical across all California refineries are the product of total pounds released and their corresponding chemical specific toxicity-weights.

Table 1. Toxicity Weighted Totals for Chemicals Released From California Refineries (2014)

Chemical	Total lbs. released[1]	Toxicity weights[2]	Toxicity-weighted lbs. released[3]
Formaldehyde	91682	46,000	4,217,368,613
Nickel	1338	930,000	1,244,140,036
Arsenic	65	17,000,000	1,101,338,814
Cadmium	155	6,400,000	992,557,509
Benzene	20313	28,000	568,775,348
PAHs	711	710,000	504,822,625
Hexavalent chromium	10	43,000,000	426,073,431
Benzo[a]pyrene	500	710,000	355,219,396
Phenanthrene	280	710,000	198,694,330
Beryllium	12	8,600,000	106,826,366
Ammonia	2,517,005	35	88,095,180
1,3-Butadiene	740	110,000	81,404,664
Naphthalene	6,313	12,000	75,756,270
Hydrogen Sulfide	12,321	1,800	22,178,439
Acetaldehyde	1,392	7,900	10,997,059
Manganese	474	12,000	5,691,981
Diethanolamine	1,778	1,200	2,133,390

[1] Total amount of chemical released across California refineries
[2] Proportional numerical weight given to each chemical based on chronic adverse health outcomes
[3] Total chemical release multiplied by the toxicity weight

APPENDIX I: LIST OF ABBREVIATIONS

AAQS	Ambient Air Quality Standards
AEGL	Acute Exposure Guideline Levels
AIHA	American Industrial Hygiene Association
APCD	Air Pollution Control District
AQMD	Air Quality Management District
ATSDR	Agency for Toxic Substances and Disease Registry
BAAQMD	Bay Area Air Quality Management District
BTEX	Benzene, toluene, ethylene, and xylene
CAD	Coronary Artery Disease
CalEPA	California Environmental Protection Agency
CAMEO	Computer-Aided Management of Emergency Operations
CAPCOA	California Air Pollution Control Officers Association
CARB	California Air Resources Board
CAS RN	Chemical Abstracts Service Registry Number
CCHS	Contra Costa Health Services
CDC	Centers for Disease Control and Prevention
CEIDARS	California Emission Inventory Development and Reporting System
CHHSL	California Human Health Screening Level
COPD	Chronic Obstructive Pulmonary Disease
CPF	Cancer Potency Factor
CSB	Chemical Safety Board
CSF	Cancer Slope Factor
EPCRA	Emergency Planning and Community Right-to-Know Act
ERPG	Emergency Response Planning Guidelines
FCCU	Fluid Catalytic Cracking Unit
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
ICR	Information Collection Request
IDLH	Immediately Dangerous to Life and Health
IRIS	Integrated Risk Information System
IRTF	Interagency Refinery Task Force
LEL	Lower Explosive Limit
NAAQS	National Ambient Air Quality Standard
NAC/AEGL	National Advisory Committee for the Development of Acute Exposure Guideline Levels for Hazardous Substances
NIH	National Institutes of Health
NIOSH	National Institute for Occupational Safety and Health
NOAA	National Oceanic and Atmospheric Administration
NOx	Nitrogen oxides
OEHHA	Office of Environmental Health Hazard Assessment
OER	Office of Emergency Response
OPPT	Office of Pollution Prevention and Toxics
PAC	Protective Action Criteria
PAH	Polycyclic Aromatic Hydrocarbon

PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
PHG	Public Health Goal
PM	Particulate matter
PM_{10}	Particulate matter ≤10 μm in diameter
$PM_{2.5}$	Particulate matter ≤2.5 μm in diameter
RADS	Reactive Airway Dysfunction Syndrome
REL	Reference Exposure Level
RfC	Reference Concentration
RfD	Reference Dose
RMP	Risk Management Plan
RSL	Regional Screening Level
SCAPA	Subcommittee on Consequence Assessment and Protective Actions
SCAQMD	South Coast Air Quality Management District
SRU	Sulfur Recovery Unit
TAC	Toxic Air Contaminant
TCDD	2,3,7,8-Tetrachlorodibenzo-p-dioxin
TEEL	Temporary Emergency Exposure Limit
TOXNET	Toxicology Data Network
TRI	Toxics Release Inventory
TSH	Thyroid stimulating hormone
US EPA	United States Environmental Protection Agency
UEL	Upper Explosive Limit
VOC	Volatile Organic Compound
WWT	Wastewater treatment