

GASOLINE-RELATED AIR POLLUTANTS IN CALIFORNIA

TRENDS IN EXPOSURE AND HEALTH RISK 1996 TO 2014

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List of Selected Acronyms and Definitions

List of Acronyms

CAAQS	California Ambient Air Quality Standard
CalEnviroScreen	California Communities Environmental Health Screening Tool
CalEPA	California Environmental Protection Agency
CARB	California Air Resources Board
CASRN	Chemical Abstracts Services Registry Number
cREL	Chronic reference exposure level
MATES III	Multiple Air Toxics Exposure Study III (monitoring and evaluation study conducted in the South Coast Air Basin)
MTBE	Methyl <i>t</i> -butyl ether
NAAQS	National Ambient Air Quality Standards
NATTS	National Air Toxics Trends Stations
NMOC	Non-methane organic compound
OEHHA	Office of Environmental Health Hazard Assessment
PAH	Polycyclic aromatic hydrocarbon
PAMS	Photochemical Assessment Monitoring Stations
PEF	Potency equivalency factor
PM ₁₀	Particulate matter with diameter less than 10 microns
PM _{2.5}	Particulate matter with diameter less than 2.5 microns
ppbC	Parts per billion on a carbon basis
ppmC	Parts per million on a carbon basis
ppbV	Parts per billion by volume
RfC	Reference concentration
ROG	Reactive organic gases
SC	South Coast Air Basin
SCOS	Southern California Ozone Study
SCAQMD	South Coast Air Quality Management District
SD	San Diego Air Basin
SFB	San Francisco Bay Area Air Basin
SJV	San Joaquin Valley Air Basin
SLAMS	State and Local Air Monitoring Stations
SOA	Secondary organic aerosol
SV	Sacramento Valley Air Basin
SWRCB	State Water Resources Control Board
TAC	Toxic Air Contaminant
TOG	Total organic gases
US EPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds

Glossary of Selected Terms (as used in this report)

Cancer risk	Estimated excess risk of cancer in a population assuming a lifetime exposure to a specific ambient air concentration of a chemical. A cancer risk of 5 in 1 million, which can also be expressed as 5×10^{-6} (the format used in this report), means that 5 excess cancer cases are estimated for a population of 1 million people exposed for life to the chemical at that concentration.
Gasoline-attributable fraction	Fraction of a chemical's emissions from gasoline-related sources, out of the total emissions from all sources
Hazard quotient	Ratio of the gasoline-attributable ambient air concentration to a health benchmark for non-cancer health effects (such as a chronic Reference Exposure Level). A hazard quotient above one indicates a potential health concern.
Population-weighted annual average ambient air concentration	Annual average ambient air concentration calculated for an air basin, using annual average concentrations in each census tract and weighting by census tract population over air basin population
Gasoline-attributable population-weighted annual average ambient air concentration (also referred to in this report as "gasoline-attributable concentration")	Product of the gasoline-attributable fraction multiplied by the population-weighted annual average ambient air concentration

Preface

The Office of Environmental Health Hazard Assessment (OEHHA), along with other boards and departments in the California Environmental Protection Agency (CalEPA), helps evaluate human health and environmental risks associated with the use of gasoline and other fuels.

OEHHA's activities in this area include:

- Characterization of potential health concerns associated with the hundreds of components in the current gasoline formulation.
- Evaluation of new fuel components for their potential to cause adverse impacts on human and environmental health, prior to their widespread introduction into the fuel supply.
- Investigation of the impacts of traffic-related air pollution on human health, particularly in sensitive individuals such as children.

This report describes OEHHA's evaluation of trends in exposure and health risk for gasoline-related pollutants in California over the period 1996 to 2014. We applied screening approaches to broadly assess average exposures to gasoline-related pollutants and associated health risks for the general public in five major air basins and statewide. We carried out the analysis by using existing emissions and ambient air-monitoring data, basic exposure modeling methods, and well-established screening risk assessment approaches. Evaluating peak exposures and exposures in heavily impacted areas, such as those near major roadways, was beyond the scope of the current project. CalEPA efforts that are focusing on assessing cumulative exposures to air pollutants at the community scale include the new Community Air Protection Program established under AB 617 (C. Garcia, Chapter 136, Statutes of 2017).

The primary purpose of the current analysis is to establish a baseline "report card" for gasoline-related exposures and associated health risks, which can be used in later evaluations of new fuel formulations. We also flag potential concerns for further evaluation, and recommend follow-up research to help fill identified data gaps.

Executive Summary

Motor vehicles have long been recognized as a major source of air pollution, particularly in urban areas with high population density. Gasoline-related air pollutants, as defined in this report, arise from the following processes:

- Evaporation of liquid gasoline
- Emission of exhaust from gasoline-powered engines
- Formation of atmospheric transformation products

Many chemicals emitted from gasoline-related sources, which include on- and off-road vehicles and gasoline-powered equipment, are known to be potentially harmful to human health.

This report describes OEHHA's evaluation of trends in exposure and health risk for gasoline-related pollutants in California from 1996 to 2014. We used available emissions and ambient air monitoring data to estimate average exposures across air basins and statewide, and conducted a screening-level health risk assessment for selected gasoline-related air pollutants. The specific aims of the project were to:

- Develop a comprehensive list of gasoline-related air pollutants, including those that are directly emitted or formed in the atmosphere
- Identify gasoline-related pollutants of concern in terms of widespread exposure and/or toxicity
- For gasoline-related pollutants selected based on exposure potential and/or toxicity and with adequate data:
 - Estimate average exposures for the general population, based on ambient air monitoring data in five air basins and statewide
 - Estimate the proportion of the ambient air concentrations attributable to gasoline use
 - Conduct a screening-level cancer and non-cancer risk assessment
- Examine time trends in exposure and health risk for gasoline-related pollutants

The assessment was conducted using data from 1996 to 2014¹, which spans the time before and after the removal of methyl *t*-butyl ether (MTBE) from gasoline. Beginning in 1996, MTBE was used as an oxygenate to improve the combustion efficiency of gasoline and reduce smog-forming and toxic emissions. After significant environmental concerns were identified, MTBE was voluntarily phased out between 2000 and 2003, and was banned from California gasoline beginning in 2004. Ethanol replaced MTBE as the oxygenate of choice in 2004. By evaluating the period 1996 to 2014 in this report, we were able to track the changing chemical exposures

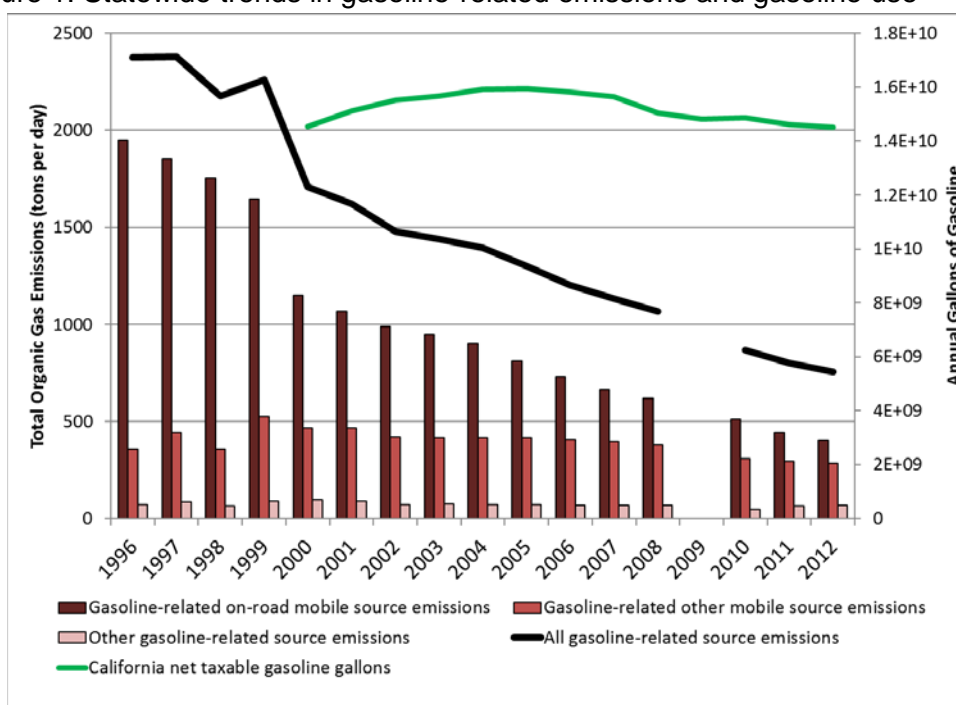
¹ Not all chemicals had ambient air monitoring data available for every year, and this is noted where relevant. We used data from the California Air Resources Board (CARB) Emission Inventory for the source apportionment; these data were available through 2012.

and potential health concerns associated with the changing gasoline formulation. The results of our analysis can be used as a baseline against which future changes in gasoline formulations, and associated exposures and health concerns, can be tracked. Major findings are highlighted below.

Emissions from Gasoline-Related Sources

- Estimated emissions of total organic gases² from gasoline-related sources have declined by nearly 70% statewide since 1996 (see Figure 1). This significant reduction is attributable primarily to the decline in on-road mobile source emissions, which occurred even while gasoline sales remained steady and California’s population continued to grow.

Figure 1. Statewide trends in gasoline-related emissions and gasoline use



Data from CARB Emission Inventory and State Board of Equalization. Mobile source emissions estimates not available for 2009.

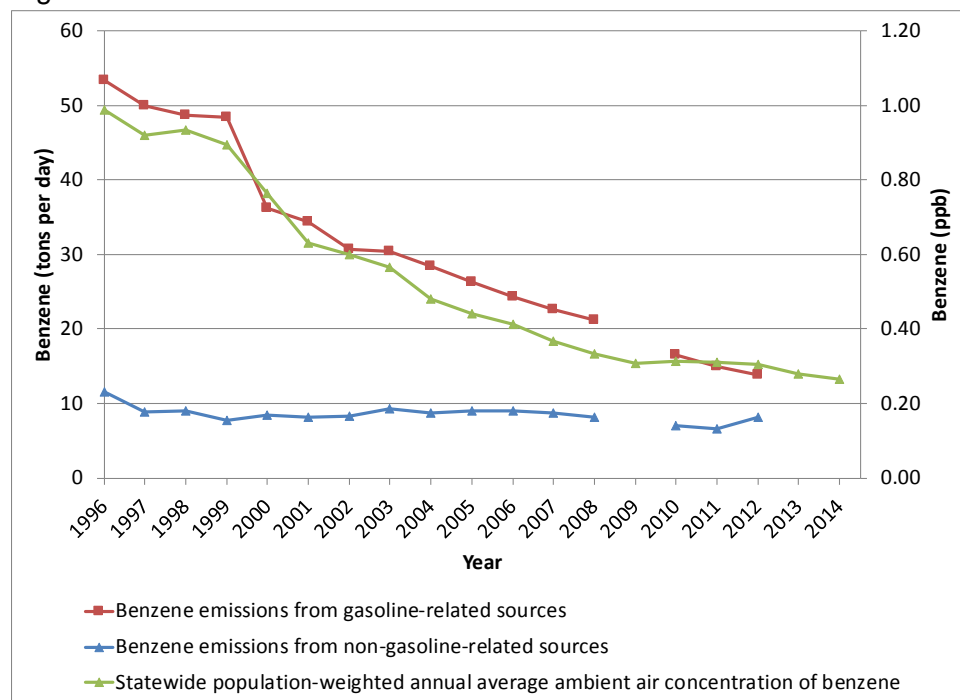
- By 2012, emissions from on-road motor vehicles had decreased so substantially that they were approaching levels similar to emissions from other gasoline-related mobile sources, which include lawn and garden equipment, recreational boats and off-road vehicles. Less apparent in Figure 1 is the decline in emissions from these other mobile sources, dropping almost in half since 1999.

²“Total organic gases” (TOG) include gaseous and lower volatility organic compounds emitted to the atmosphere. TOG excludes carbon monoxide, carbon dioxide and some other carbon compounds (for more details, see http://www.arb.ca.gov/ei/speciate/factsheets_model_ei_speciation_tog_8_00.pdf).

Gasoline-Related VOCs

- There are over 350 volatile organic compounds (VOCs) emitted from gasoline-related sources. Ninety-five of the top 100 VOCs emitted from these sources had lower primary emissions in 2012 compared to 1996, with reductions of between 20 and 90%. Ethanol was the only VOC with substantially increased gasoline-related emissions, which were 17-fold higher in 2012 compared to 1996. This increase was expected because ethanol replaced methyl t-butyl ether (MTBE) as a fuel oxygenate.
- The most highly emitted gasoline-related VOCs with known toxicity concerns were (in order of highest to lowest primary emissions): toluene, *m*-xylene, propylene, benzene, *n*-hexane, formaldehyde, ethylbenzene, isobutene, 1,2,4-trimethylbenzene, and 1,3-butadiene. After accounting for secondary atmospheric formation, two additional gasoline-related VOCs with toxicity concerns - acetaldehyde and propionaldehyde - were found to be emitted at comparably high levels.
- Emissions of gasoline-related VOCs identified as having the most significant health concerns have been steadily declining in California. Figure 2 plots the data for benzene, illustrating the substantial reductions in gasoline-related emissions and population-weighted ambient air concentrations since 1996. Figure 2 also shows that benzene emissions from non-gasoline-related sources were relatively constant over the same time period, and lower than gasoline-related emissions.

Figure 2. Trends in statewide benzene emissions and ambient air concentrations



Emission Inventory data available through 2012; mobile source data not available for 2009.

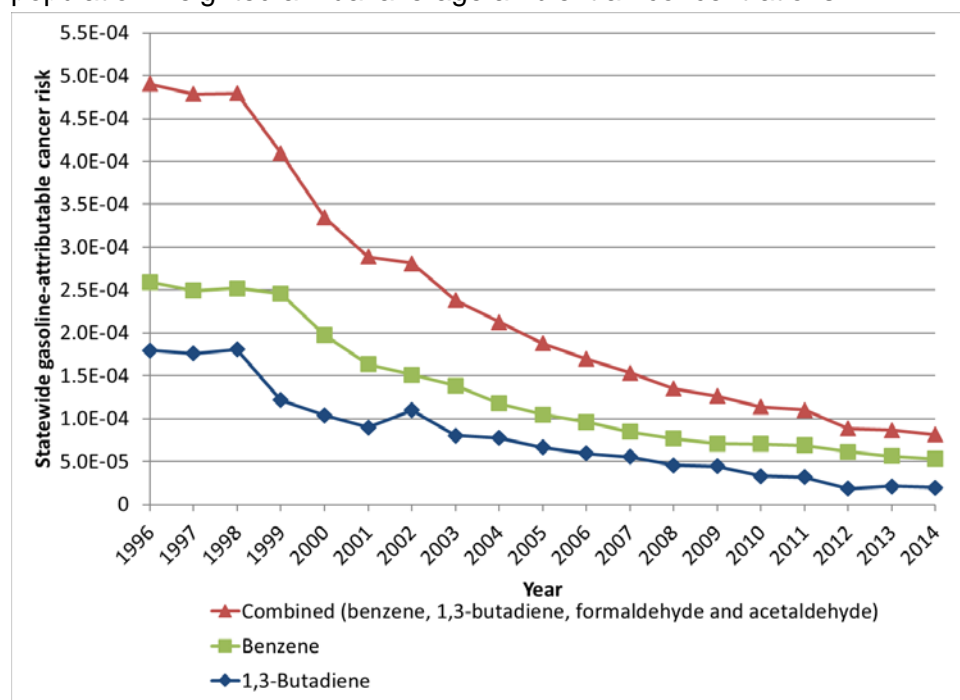
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- VOCs emitted from gasoline-related sources can react with other chemicals in the atmosphere to produce a range of potentially toxic transformation products, including carbonyls (e.g., many types of aldehydes, including aromatic aldehydes), dicarbonyls (e.g., diacetyl), peroxy nitrates (e.g., PAN), and phenols. With the notable exceptions of formaldehyde, acetaldehyde and acrolein, gasoline-related atmospheric transformation products that we identified are generally not routinely monitored in ambient air.

Screening Assessment of Cancer and Noncancer Risks

- The combined statewide annual average gasoline-attributable exposures to acetaldehyde, benzene, 1,3-butadiene and formaldehyde were estimated to result in about 500 excess cancer cases in 1 million exposed people in 1996, dropping to 80 excess cancer cases in 1 million in 2014. The statewide gasoline-attributable cancer risk³ for exposures to benzene or 1,3-butadiene each still exceeded 1 in 1 million in 2014 (about 50 and 20 excess cancer cases in 1 million, respectively). Figure 3 plots the combined gasoline-attributable cancer risk for these four carcinogens and for benzene and 1,3-butadiene individually. The screening calculations in this report account for early-in-life sensitivity to carcinogens.

Figure 3. Statewide cancer risks for selected VOCs based on gasoline-attributable population-weighted annual average ambient air concentrations



- Polycyclic aromatic hydrocarbons (PAHs) can be found in gasoline and are also formed during combustion. Naphthalene was the most abundant gasoline-related PAH identified in

³ See the glossary (on page v) for a definition of cancer risk and how to interpret these values.

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ambient air in the South Coast Air Basin. Gasoline-attributable exposures to naphthalene in the South Coast Air Basin in 1996 were estimated to result in approximately 50 excess cancer cases in 1 million exposed people, dropping by an order of magnitude to about 5 excess cancer cases in 1 million in 2014.

- The combined cancer risks based on 2014 data from two sites in the South Coast Air Basin for other gasoline-related PAHs, including benzo(a)pyrene and six additional particle-bound PAHs, were estimated to be at least an order of magnitude lower than the cancer risks associated with naphthalene exposure (i.e., less than 1 excess cancer case in 1 million exposed people).
- Gasoline-attributable hazard quotients⁴ for non-cancer health effects, including chronic respiratory toxicity and neurotoxicity, were generally below one (indicating a lack of health concern) for annual average exposures in the South Coast Air Basin and across the state. This was the case over the entire study period (1996 to 2014) for all of the toxicants we were able to evaluate, except acrolein (discussed in the next bullet) and benzene. For benzene, the hazard quotient for hematologic effects was slightly elevated at 1.1 in 1996, dropping to 0.21 by 2014.
- Hazard quotients for respiratory toxicity were elevated for gasoline-related exposures to acrolein, based on 2014 data from the South Coast Air Basin and statewide. There are some known technical issues with measuring acrolein in ambient air, so this respiratory risk estimate is uncertain. However, our finding is consistent with previous studies that have flagged ambient concentrations of acrolein as a concern for respiratory toxicity (Morello-Frosch *et al.*, 2000; Woodruff *et al.*, 2007).
- We could not assess the cancer and non-cancer risks for a number of gasoline-related VOCs that we flagged as having toxicity concerns, such as benzaldehyde, malonaldehyde, and peroxyacetyl nitrate [PAN], due to insufficient ambient air data and/or lack of health reference levels.

PM_{2.5} and Nitrogen Dioxide Exposures

- Fine particulate matter (PM_{2.5}) is directly emitted from a range of primary sources (e.g., vehicle tailpipes), and also formed via highly complex secondary atmospheric reactions. OEHHA roughly approximated gasoline-attributable fractions for PM_{2.5} based on available primary emissions data and proxies for secondary PM_{2.5} components, a method that had substantial uncertainties. The estimated gasoline-attributable fractions were higher for the South Coast Air Basin compared to those for the San Francisco Bay Area, San Joaquin Valley and Sacramento Valley Air Basins, and generally decreased with time across the state.

⁴ See the glossary (on page v) for a definition of hazard quotient and how to interpret these values.

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- Ambient air concentrations of PM_{2.5} dropped by about 50% statewide from 1999 to 2013. The estimated fractions of PM_{2.5} attributable to gasoline-related sources dropped over this same period, and varied by geographic region. Gasoline-related sources contributed most significantly to PM_{2.5} in the South Coast Air Basin, with an estimated gasoline-attributable fraction of about 20% in 2012 (the date of the most recent Emission Inventory available at the time this report was written), compared to only about 10% for the San Joaquin Valley Air Basin in the same year. However, the method used to estimate these fractions has a number of limitations, and does not fully capture spatial and seasonal variability in the components of PM_{2.5}. Gasoline-related PM_{2.5} remains a potential health concern, particularly in urban areas with heavy traffic. Continued research on the contribution of gasoline sources to PM_{2.5} exposures and associated health impacts in California is warranted.
- Ambient air concentrations of nitrogen dioxide have dropped significantly since 1996, as has the fraction of nitrogen dioxide from gasoline-attributable sources. In the South Coast Air Basin in 1996, the population-weighted annual average ambient air concentration of nitrogen dioxide exceeded the annual average California Ambient Air Quality Standard (CAAQS) of 0.03 ppm, with an estimated 47% of emissions coming from gasoline-related sources (based on primary emissions of nitrogen oxides). By 2013, the population-weighted ambient air concentration in the South Coast Air Basin dropped below the CAAQS, with the fraction from gasoline-related sources dropping to 29% by 2012.

Recommended Future Research

While this report documents substantial declines in air pollution from gasoline-related sources, it also shows that an ongoing commitment to air quality improvements is essential in California. Below we describe follow-up research that would help fill some data gaps identified in this report, advance our understanding of the overall impact of gasoline-related pollution, and inform future risk reduction measures.

Better understanding of the universe of gasoline-related air pollutants and associated health risks: New analytical methods that can more broadly screen for chemicals in the ambient air (so-called “non-targeted analyses”) could be carried out to more fully elucidate the universe of gasoline-related VOCs and their associated atmospheric transformation products. Such research could help identify new chemicals of concern, and focus resources for monitoring and health risk assessment on the most abundant gasoline-related VOCs. Additionally, a number of chemicals with high emissions were not evaluated in the screening assessment in this report because they did not have adequate toxicity information, such as Reference Exposure Levels or cancer potency values. Novel toxicity “read-across” approaches that rely on structure-activity analyses and non-conventional toxicology data sets could potentially be applied to help evaluate the toxicity of gasoline-related chemicals that have not been well studied.

Closer examination of neighborhoods and communities for gasoline-related impacts: We applied screening methods to estimate average exposure and health risk for broad regions of the state,

and this approach does not examine the higher levels of gasoline-related air pollution in neighborhoods near highways and other heavily trafficked roads. We recommend further work to quantify the potentially much higher exposures in these locations, by building on previous California projects that have mapped air pollution and health effects in heavily impacted communities. For example, gasoline-related air pollution could be studied in communities identified by OEHHA's California Communities Environmental Health Screening Tool (CalEnviroScreen) as already burdened by a disproportionate share of environmental pollution, and faced with socioeconomic and health challenges. One way to do this would be to design a targeted biomonitoring study to measure indicators for gasoline-related chemicals in the blood and urine of people living in areas heavily impacted by vehicle traffic. Pending resources, we could potentially extend our current biomonitoring study of diesel emissions in San Francisco Bay Area communities by measuring stable urinary metabolites or DNA or protein adducts in blood of selected VOCs linked to gasoline use. This potential research could aid in the understanding of cumulative exposure to air pollutants in impacted communities and complement CARB's newly launched Community Air Protection Program, established under AB 617 (C. Garcia, Chapter 136, Statutes of 2017).

Expanded monitoring of gasoline-related atmospheric transformation products: Atmospheric transformation products are less widely monitored in ambient air in general, with a few important exceptions (e.g., acetaldehyde and formaldehyde). A short-term pilot study to monitor additional transformation products of concern, such as PAN, could be carried out to examine current ambient air levels and help determine if long-term monitoring would be warranted. Acrolein is also recommended for further monitoring based on our screening results that showed elevated exposures associated with respiratory health risks. CARB recently acquired several new analyzers to measure ambient air levels of selected VOCs, including acrolein. After testing and evaluating these devices, CARB plans to use them to measure VOCs of concern in communities impacted by air pollution. We also recommend research on chemicals in blood or urine that are reliable indicators of exposure to acrolein and related compounds.

Further research on gasoline-related contributions to particulate matter: Exposures to particulate matter remain a significant health concern. CARB is already sponsoring research in this area, including a study on the association between ultrafine particle exposures and premature death. Additional research is recommended to better characterize the contributions of gasoline-related sources to ambient particulate matter, particularly the ultrafine and secondary components.

Analysis of health effects associated with exposure to gasoline-related criteria air pollutants: Epidemiological studies in California indicate that elevated PM_{2.5} and nitrogen dioxide concentrations are associated with increased mortality and other health effects. A quantitative assessment of health impacts associated with exposure to gasoline-related criteria air pollutants was beyond the scope of this report, and would be worth pursuing in a future project.

California's continued dependence on gasoline-fueled transportation means the State will need to maintain its efforts to address public health issues associated with vehicle-related air pollution. CARB has already established a broad mobile source strategy, which includes

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initiatives to promote zero-emission technologies and further tightening of emission standards for small off-road engines, such as those used in lawn and garden equipment. California's strong commitment to innovative scientific research and ongoing regulatory efforts will build on the impressive reductions in toxicants already achieved and help ensure clean air for future generations of Californians.

Introduction

Emissions from cars have declined over the past 30 years due to improved vehicle emission controls and cleaner burning gasoline. In spite of these improvements, traffic-related air pollution remains a public health problem. A large number of studies, including some funded by OEHHA and CARB, have linked exposure to traffic and traffic-related air pollution to negative health outcomes in California. Children in the San Francisco Bay Area that lived in close proximity to major roadways had double the odds of current asthma compared to children who lived further away (Kim et al., 2008) while children in Southern California that lived or studied in areas with more traffic had an increased risk of new-onset asthma (McConnell et al., 2010). Decreased lung function in Northern California adults with asthma was associated with traffic exposure (Balmes et al., 2009). The California Children's Health Study found that exposures to traffic-related pollutants are associated with increased asthma prevalence, new-onset asthma, risk of bronchitis and wheezing, deficits of lung function growth, and airway inflammation (Chen et al., 2015). Delfino et al. (2016) found emergency room visits / hospital admissions for asthma increased as traffic-related air pollution increased and that the relationship was stronger in neighborhoods with heavy traffic density. Wilhelm et al. (2011) reported that prenatal exposures to elevated levels of traffic-related air pollutants, such as benzene, naphthalene and PM_{2.5}, were associated with increased risk of pre-term birth in a study in Southern California. Results from a study in the San Joaquin Valley suggested that prenatal exposure to traffic-related pollutants adversely affected the birth weight of full-term babies (Padula et al., 2012). Coker et al. (2016) investigated the relationship between term low birth weight and concentrations of traffic-related air pollutants (nitrogen dioxide, nitrogen oxide, and PM_{2.5}) in Southern California by creating clusters of census blocks with similar levels of air pollution. They found that the clusters with the highest risk of term low birth weight had the shortest maternal distance to highways. The population of California is increasing and more vehicles will be on the road. The public health impact of motor vehicle use will continue to be an important factor in setting state air pollution policies and in community and use planning, such as siting of schools and hospitals away from heavily trafficked roadways (CARB, 2005).

California has invested enormous effort and resources to meet ambient air quality standards, and identify and implement strategies to reduce air pollutant exposures (see for example, CARB, 2016; 2017). This includes ongoing regulation of vehicle emissions and fuel composition. The composition of California's gasoline is subject to both federal and state regulations. The California Clean Air Act of 1988 mandated that standards for vehicle emissions and fuel formulations in the state be equivalent to or more stringent than those required under federal law. Regulations promulgated by the California Air Resources Board (CARB) allow flexibility in the precise composition of gasoline, and refiners may choose their preferred fuel formulas as long as they meet specified standards. For a brief history of the changes in the California gasoline formulation since the 1990s, including the phase-out of MTBE and the addition of ethanol as the replacement oxygenate, see Appendix A.

Introduction

In view of the changing fuel formulations together with anticipated changes in vehicle technologies and fleet composition, the California Legislature recognized the need to track potential health impacts attributable to the use of gasoline in the state. With other boards and departments in CalEPA, the Office of Environmental Health Hazard Assessment (OEHHA) works to proactively evaluate the human and environmental health impacts of motor vehicle fuels, with particular attention to children's health. The ultimate goal of CalEPA's proactive research is to allow state regulators to take timely action to mitigate or avert predicted adverse impacts and avoid a repetition of the 1990s experience with MTBE, a fuel additive widely used in that decade to reduce vehicle emissions that was banned after it was found to be a pervasive groundwater contaminant. OEHHA has undertaken a number of activities to fulfill our particular responsibilities for conducting fuels research, including preparing the current report to evaluate trends in exposures and health risks associated with gasoline-related pollution in California. See Appendix B for a listing of additional related OEHHA research activities.

Other state and regional agencies have carried out exposure and health evaluations of gasoline-related air pollutants in California. For example, CARB regularly issues an Almanac of Emissions and Air Quality⁵ that summarizes data on emissions and ambient air concentrations for monitored air pollutants, including some gasoline-related chemicals (CARB, 2013). The 2009 Almanac included estimates of the fraction of total emissions that came from gasoline mobile sources for selected Toxic Air Contaminants (TACs) and also reported estimates of statewide cancer risks for carcinogenic TACs. The 2013 version of the Almanac included estimates of aggregate volatile organic compound (VOC) emissions from gasoline-related motor vehicles. Propper et al. (2015) analyzed trends in selected TAC emissions and ambient air concentrations and discussed the impact that regulations, such as cleaner fuels and vehicle regulations, have had on these trends. The South Coast Air Quality Management District (SCAQMD) conducted a series of studies known as the Multiple Air Toxics Exposure Studies⁶ (MATES), which included a number of gasoline-related chemicals of concern (SCAQMD, 2008; 2015). The MATES reports summarized emissions and ambient air concentrations of selected air pollutants in the South Coast Air Basin, and provided associated cancer risk estimates.

In the current report, we applied screening approaches to broadly assess average exposures to and health risks associated with gasoline-related pollutants for the general public across five air basins and statewide. The purpose of this analysis is to establish a baseline understanding of the impacts of gasoline use, track trends in exposure to gasoline-related pollutants and associated health risks over time, and identify priorities for future research. Some of the key elements of this work include the following:

- Compilation of a comprehensive list of gasoline-related VOCs ranked by emissions.
- Identification of other gasoline-related chemicals of concern, including criteria air pollutants, particulate PAHs, and atmospheric transformation products.

⁵ <http://www.arb.ca.gov/aqd/almanac/almanac.htm>

⁶ <http://www.aqmd.gov/home/library/air-quality-data-studies/health-studies>

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- Estimation of the fraction of emissions attributable to gasoline-related sources, on a statewide basis and at the air basin level, for pollutants with adequate data.
- Calculation of gasoline-attributable population-weighted annual average ambient air concentrations (also referred to as “gasoline-related concentrations”) for chemicals of potential health concern that had adequate air monitoring data.
- Evaluation of potential cancer and non-cancer risks associated with exposures to gasoline-related chemicals in California.
- Tracking of time trends in exposures to gasoline-related pollutants and associated health risks in California over the period 1996 to 2014.

This report is organized as follows:

I. Gasoline-Related Sources of Air Pollution (p. 13)

This section compares emissions for major categories of pollutants (e.g., VOCs, criteria air pollutants) from gasoline and non-gasoline-related sources.

II. Hazard Identification for Gasoline-Related Chemicals (p. 20)

This section identifies compounds emitted by gasoline-related sources that have toxicological concerns associated primarily with chronic exposures (e.g., cancer and chronic respiratory toxicity). We conducted the hazard identification on the following categories of gasoline-related chemicals: VOCs, criteria air pollutants, PAHs, and atmospheric transformation products. Section II describes the results of our hazard evaluation and provides a complete list of those chemicals with sufficient data available for a detailed exposure analysis and screening-level risk assessment.

III. Exposure Assessment for Gasoline-Related Chemicals (p. 42)

This section provides an overview of the methods and results from our exposure assessment for a subset of gasoline-related compounds, selected based on results from our hazard identification and data availability. We focused on annual average exposures and did not evaluate short-term or peak exposures. Exposure assessment results discussed in this section include:

- Fractions of emissions attributable to gasoline-related sources for selected compounds.
- Population-weighted annual average ambient air concentrations for selected gasoline-related compounds in California based on data from 1996 to 2014.
- Gasoline-attributable population-weighted annual average ambient air concentrations of selected compounds (i.e., the product of the above two factors; also referred to as the “gasoline-attributable concentration”).

Complete exposure assessment methods and results are described in the Chemical Profiles and Appendices D and E.

IV. Screening Cancer and Non-Cancer Risk Assessment (p. 65)

This section presents an overview of our methods and results from the screening-level assessment of cancer risks and non-cancer hazard quotients based on annual average exposures for selected gasoline-related chemicals with sufficient data (i.e., available health reference values and adequate data to generate a gasoline-attributable concentration). Complete details on the risk assessment methods and results are provided in the Chemical Profiles and Appendix G.

V. Challenges and Limitations (p. 76)

Here we discuss some key challenges and limitations we encountered while conducting our analysis of trends in exposure and risk for gasoline-related chemicals.

VI. Highlights of Key Findings (p. 79)

This section summarizes the main results of the report, compares this report to other related reports and suggests future research that would advance our understanding of gasoline-related pollution.

VIII. Chemical Profiles (p. 85)

This section contains the results of the source apportionment, exposure analysis, and screening risk assessment for each gasoline-related chemical we were able to evaluate in detail.

I. Gasoline-Related Sources of Air Pollution

Gasoline-related air pollutants arise from a number of processes, including evaporation of liquid gasoline, emission of gasoline combustion products, and formation of atmospheric transformation products. The pollutants can be volatile, semi-volatile or particle-bound. Some of the pollutants are emitted directly from the source (primary emissions) while others are formed in secondary atmospheric reactions. This report addresses three major categories of gasoline-related chemicals of potential concern:

- Volatile organic compounds (VOCs), which are directly emitted and/or formed through secondary atmospheric reactions
- Polycyclic aromatic hydrocarbons (PAHs)
- Criteria air pollutants

This section illustrates the relative importance of emission sources, based on analyses of data from the CARB Emission Inventories for 1996 through 2012. The Emission Inventory is described in the box below.

Description of the CARB Emission Inventory

- Catalogs air pollution sources in California, with estimated tonnage of primary emissions from each source. Emissions resulting from secondary atmospheric reactions are not addressed.
- Includes tonnage of total organic gases (TOG), reactive organic gases (ROG), carbon monoxide, nitrogen oxides, sulfur oxides and particulate matter from each air pollution source.
 - Total organic gases (TOG) include VOCs and lower volatility organic compounds emitted to the atmosphere. TOG excludes carbon monoxide, carbon dioxide and some other carbon compounds (for more details, see: http://www.arb.ca.gov/ei/speciate/factsheets_model_ei_speciation_tog_8_00.pdf).
 - Reactive organic gases (ROG) are defined as TOG minus "exempt" VOCs, which have been determined to have negligible photochemical reactivity. Exempt VOCs include methane, ethane, and chlorofluorocarbons (CFCs) (complete list available at: http://www.arb.ca.gov/ei/speciate/voc_rog_dfn_1_09.pdf).
- Tabulates a range of air pollution sources, including mobile sources (e.g., cars), stationary sources (e.g., power plants), area-wide sources (e.g., fireplaces and farming activities) and natural sources (e.g., plants, trees and wildfires).
- Splits out gasoline and non-gasoline-related sources of pollution.
- Links each source to a "speciation profile." The speciation profile provides estimates of the chemical composition of the primary emissions from each source. The profile includes the identity of the constituent chemicals and the estimated percentages of the source TOG attributable to each constituent.

For more details on CARB's methods for constructing the Emission Inventory, visit this link:

<http://www.arb.ca.gov/ei/documentation.htm>

Comparison of Gasoline-Related Emissions to Other Sources

Figure 4 shows the 2012 percentages of total primary⁷ emissions for various types of pollutants from gasoline-related, non-gasoline-related and natural sources, including the following: primary reactive organic gases (ROG), total organic gases (TOG), carbon monoxide (CO), nitrogen oxides (NO_x), sulfur oxides (SO_x), particulate matter up to 2.5 μm (PM_{2.5}), and particulate matter up to 10 μm (PM₁₀).

Figure 5 displays the total tonnages emitted instead of percentages. See the box above for a description of ROG and TOG.

Figures 4 and 5 capture only primary emissions, because secondary atmospheric formation of pollutants is not accounted for in the Emission Inventory. This could particularly impact the interpretation of the PM_{2.5} data displayed in these figures, as a large proportion is known to be formed through secondary reactions (see the Chemical Profile on particulate matter in Section VIII for more details on this complex issue).

⁷ Primary emissions are chemicals directly emitted from a source as opposed to secondary reaction products which are formed through atmospheric reactions.

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Gasoline-Related Sources of Air Pollution

Figure 4. Estimated 2012 percentages of statewide primary⁸ emissions for organic gases and selected criteria air pollutants from gasoline- and non-gasoline-related sources (data from CARB Emission Inventory).

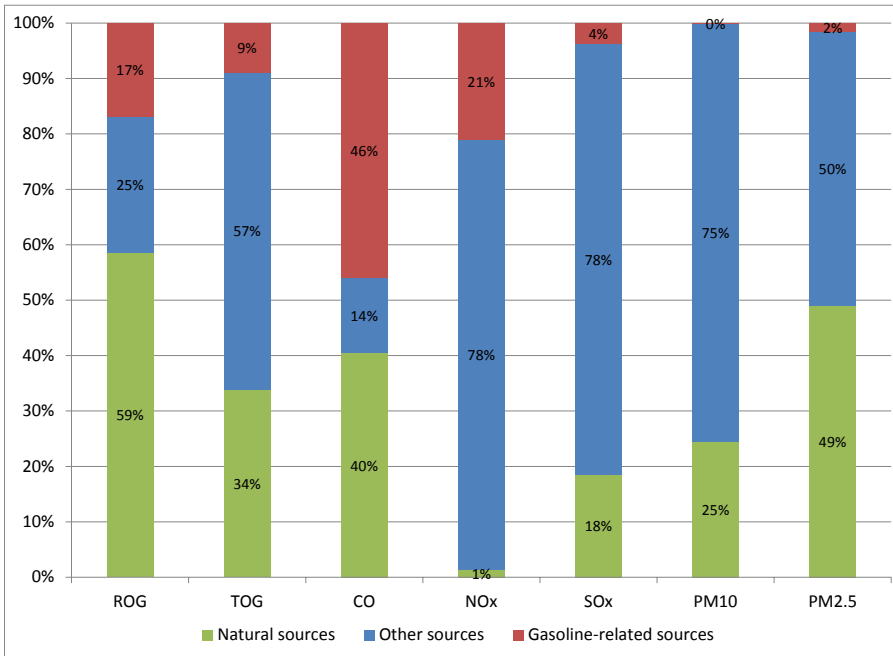
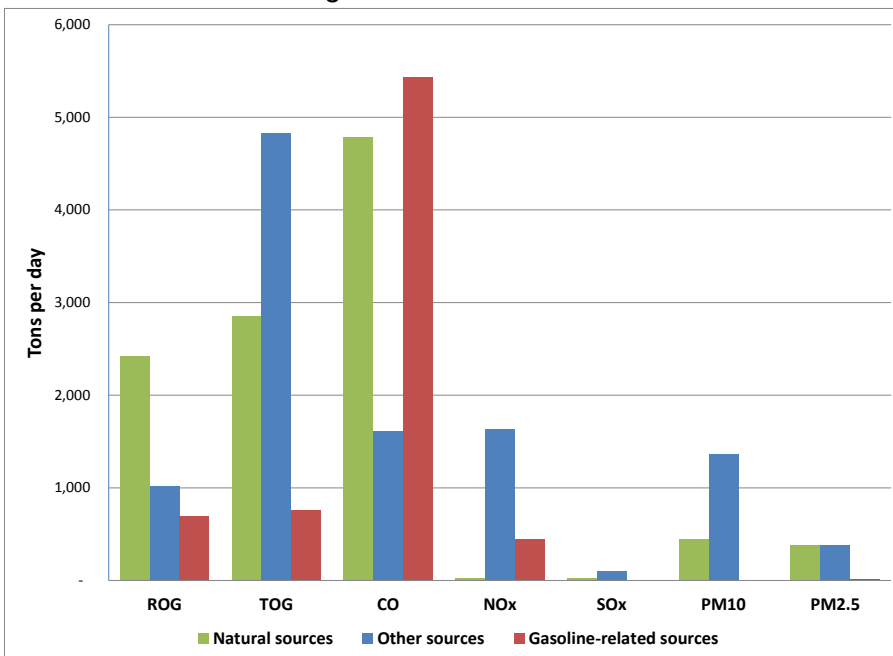


Figure 5. Estimated 2012 statewide primary⁸ emission tonnage from gasoline-related sources and other sources (data from CARB Emission Inventory).

Note: Vertical axis is a log scale.



⁸ Figures 4 and 5 do not account for secondary formation of pollutants.

Emissions of Total Organic Gases (TOG): Characteristics and Trends

Figures 6, 7 and 8 display estimated TOG emissions from primary sources over time, using data from CARB's Emission Inventory. TOG includes VOCs and lower volatility organic compounds emitted to the atmosphere (see the description of TOG in the box on p. 13).

Figure 6 illustrates the trends in TOG emissions from gasoline-related and other sources from 1996 through 2012. There was a steady reduction in estimated TOG from gasoline-related sources after 1999 through 2012, with a total drop of more than 55%. Over the same period, the estimated TOG emissions from non-gasoline-related anthropogenic sources were more constant, with an increase apparent after 2010.

Figure 6. Time course of estimated daily primary TOG emissions from gasoline-related and non-gasoline-related sources (data from CARB Emission Inventory; mobile source data not available for 2009).

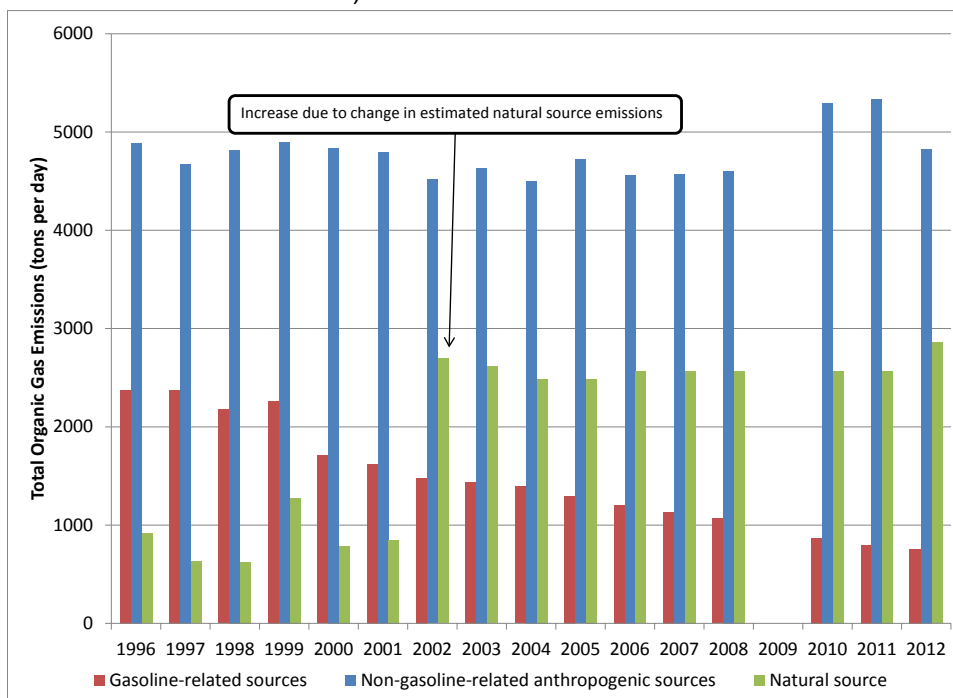
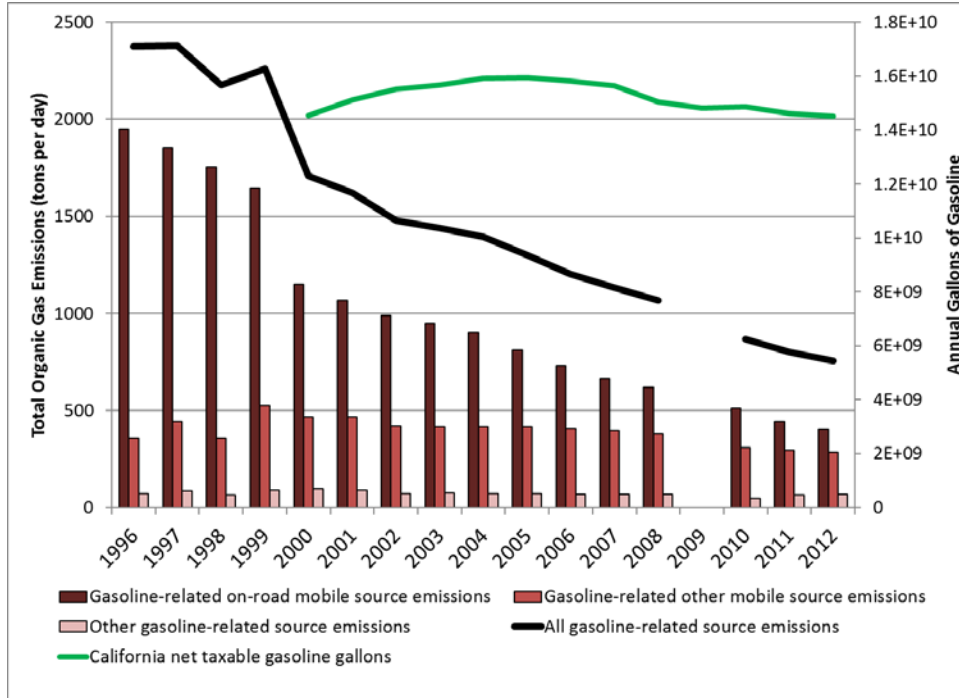


Figure 7 shows the trend in TOG emissions from gasoline-related sources from 1996 to 2012 in more detail, with the major sub-categories of on-road mobile vehicles, other mobile sources, and other sources (primarily petroleum storage and delivery) split out. The box below Figure 7 provides examples of sources included in each of these major sub-categories. The substantial reduction over time in gasoline-related TOG emissions illustrated in Figure 6 and 7 is attributable primarily to declines in on-road mobile source emissions, linked to the introduction of cleaner burning fuel and fleet turnover. These reductions are even more impressive given that gasoline sales were roughly the same in

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2000 and 2012 (also shown in Figure 7) and motor vehicle registrations declined by less than 5% between 2001 and 2012.⁹

Figure 7. Trends in gasoline-related TOG emissions and gasoline sales



Note: Data from CARB Emission Inventory and State Board of Equalization.

Example sources for Figure 6 sub-categories	2012 Emissions (tons per day)
Gasoline-related on-road mobile sources	
Passenger vehicles	151
Light duty trucks	110
Heavy duty work trucks	99
Motorcycles	39
Other vehicles, including motorhomes and buses	5
Gasoline-related other mobile sources	
Recreational boats	113
Off-road equipment including lawn and garden	112
Off-road recreational vehicles including motorcycles and ATVs	37
Agricultural equipment and fuel storage	22
Other gasoline-related sources	
Petroleum production and distribution	66

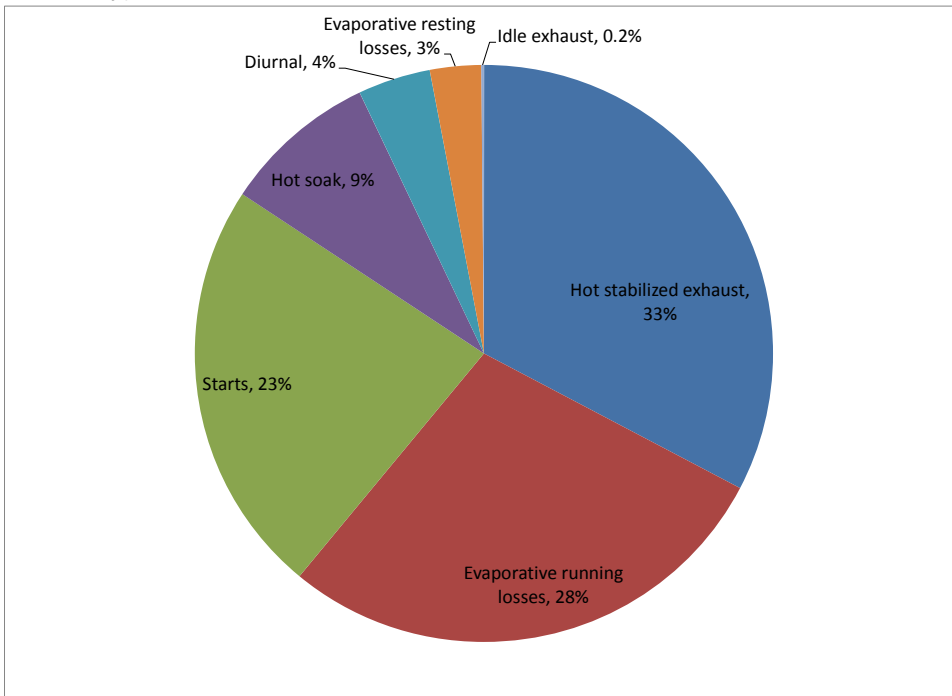
⁹ The total number of registered private and commercial vehicles in California was about 30 million in 2001 and 29 million in 2012. (see https://www.rita.dot.gov/bts/publications/state_transportation_statistics).

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By 2012, emissions from on-road mobile sources had decreased so substantially that they were approaching levels similar to emissions from other gasoline-related mobile sources, which include lawn and garden equipment, recreational boats and off-road vehicles. Less apparent in Figure 7 is the decline in emissions from these other mobile sources, dropping almost in half since 1999.

Figure 8 shows how parts of the driving cycle contributed to TOG emissions from gasoline-related on-road vehicles. About 55% of the TOG emissions came out of the tailpipe, which includes emissions when the car starts, while the car is driving (known as “hot stabilized exhaust”), and while the car is idling. The remaining 45% of TOG came from evaporation of gasoline from various processes, including evaporative losses while the car is running, during the first hour after engine shutdown (known as “hot soak emissions”) and from daytime heating of the fuel delivery systems in the vehicle (known as “diurnal emissions”).

Figure 8. Estimated fraction of TOG emissions from different parts of the driving cycle¹⁰ for gasoline-related on-road motor vehicles in 2012 (data from CARB Emission Inventory).



¹⁰ “Resting loss” emissions occur during periods of constant or decreasing temperature. “Start” emissions occur in the first few minutes of engine operation. “Hot soak” emissions occur during the first hour after engine shutdown. “Diurnal” emissions occur during daytime heating of fuel delivery systems (Scott et al., 1999).

Emissions of Criteria Air Pollutants and PAHs from Gasoline-related Sources

Primary emissions of the criteria air pollutants carbon monoxide, nitrogen oxides (or NO_x) and sulfur oxides from gasoline-related sources declined by 74%, 72% and 60%, respectively, between 1996 and 2012. Estimated primary emissions of PM_{2.5} from gasoline-related sources ranged from 19 to 26 tons per day during 1996 through 2008, decreasing to 12 to 13 tons per day for the period of 2010 to 2012. Almost all of this reduction was associated with lower estimated emissions of PM_{2.5} from on-road mobile sources starting in 2010. Gasoline-related PM_{2.5} primary emissions are relatively low compared to emissions from other sources (see Figure 4).

The volatile PAHs naphthalene, 1-methylnaphthalene and 2-methylnaphthalene are included in the Emission Inventory. In 2012, 33% of estimated statewide emissions of naphthalene came from gasoline-related sources; the comparable percentages for 1- and 2-methylnaphthalene were 99% and 21% respectively.

A large number of semi-volatile and particle bound PAHs have been detected in gasoline-vehicle exhaust as well (Schauer et al., 2002; Zielinska et al., 2004; Riddle et al., 2007). These types of PAHs are not captured in the Emission Inventory, so we examined other options for quantifying the relative contribution of gasoline-related emissions compared to other sources. We were not able to find a reliable method to estimate the gasoline-attributable fraction, so applied a conservative fraction of 1 in the screening risk assessment. Appendix H provides a list of gasoline-related PAHs and other polycyclic organic compounds identified by these studies. Additional discussion of PAHs can be found in the Chemical Profiles section of this report.

II. Hazard Identification for Gasoline-Related Chemicals

Gasoline-related mixtures include liquid fuel, gasoline vapors, and engine exhaust. OEHHA convened two workshops on possible approaches for evaluating human health effects from exposure to these complex mixtures (OEHHA, 2000). We also reviewed available toxicology literature on gasoline exhaust emissions (see for example, McDonald et al., 2007; International Agency for Research on Cancer [IARC], 2014; Mauderly et al., 2014). IARC (2014) concluded that gasoline engine exhaust is possibly carcinogenic to humans (Group 2B). Mauderly et al. (2014) studied the non-cancer health effects in rodents exposed to gasoline exhaust, reporting lung cytotoxicity, suppressed oxidant production by alveolar macrophages, and induced oxidant stress and pro-atherosclerotic responses in aorta. However, these findings are not directly applicable for evaluating the particular gasoline formulation used in California. Further, and more broadly, assessing exposure to and risks from complex mixtures is an ongoing area of research and poses many unresolved scientific challenges (see for example, Carlin et al., 2013; Dominici et al., 2010; OEHHA, 2000). Therefore, the remainder of the report focuses on evaluating individual gasoline-related chemicals of concern.

This section describes how gasoline-related chemicals were evaluated for potential health concerns and selected for further assessment. Categories examined were VOCs, PAHs, criteria air pollutants, and atmospheric transformation products.

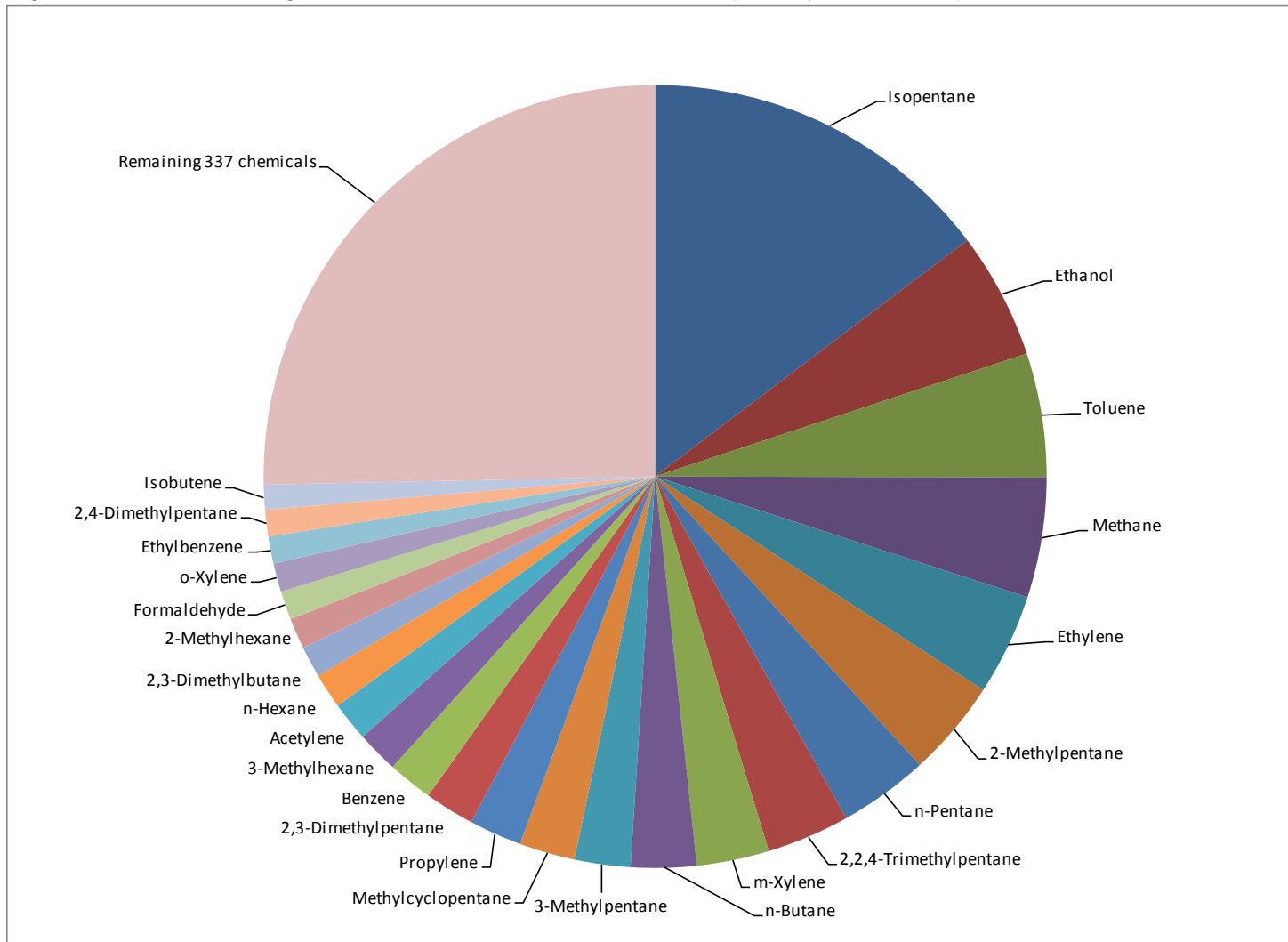
Hazard Identification Results for Gasoline-Related VOCs

The first step in evaluating potential hazards of gasoline-related VOCs was to construct a list of these chemicals. CARB advised OEHHA that gasoline-related air pollution sources have the materials description code 1100 in the Emission Inventory. We used this code to identify gasoline-related sources in the Inventory and the VOCs emitted by these sources. We then ranked the gasoline-related VOCs by primary emissions for the years 1996 and 2012 (see Appendix E for more details on the methods). Appendix C provides the complete list of gasoline-related VOCs and ranks for 1996 and 2012. Ranking by emissions was one way to prioritize the chemicals by exposure potential, an important factor in identifying VOCs for in-depth hazard research.

Figure 9 illustrates the breakdown of gasoline-related primary VOC emissions into component chemicals for 2012. The top 25 most emitted VOCs in 2012 are listed in Table 1; the rank in 1996 is provided for comparison. These top 25 VOCs made up 74% of the primary emission tonnage from gasoline-related sources.

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Figure 9. Breakdown of gasoline-related VOCs based on 2012 primary emissions (data from CARB Emission Inventory).



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Table 1. Top 25 Gasoline-related VOCs ranked by 2012 primary emissions from gasoline-related sources (data from CARB Emission Inventory; 1996 emissions rank included for comparison)

Chemical Name	CASRN	2012 Emissions Rank	1996 Emissions Rank¹¹
Isopentane	78-78-4	1	1
Ethanol	64-17-5	2	89
Toluene	108-88-3	3	4
Methane	74-82-8	4	2
Ethylene	74-85-1	5	5
2-Methylpentane	107-83-5	6	8
<i>n</i> -Pentane	109-66-0	7	7
2,2,4-Trimethylpentane	540-84-1	8	16
<i>m</i> -Xylene	108-38-3	9	9
<i>n</i> -Butane	106-97-8	10	6
3-Methylpentane	96-14-0	11	15
Methylcyclopentane	96-37-7	12	12
Propylene	115-07-1	13	10
2,3-Dimethylpentane	565-59-3	14	20
Benzene	71-43-2	15	13
3-Methylhexane	589-34-4	16	26
Acetylene	74-86-2	17	14
<i>n</i> -Hexane	110-54-3	18	17
2,3-Dimethylbutane	79-29-8	19	22
2-Methylhexane	591-76-4	20	58
Formaldehyde	50-00-0	21	18
<i>o</i> -Xylene	95-47-6	22	21
Ethylbenzene	100-41-4	23	23
2,4-Dimethylpentane	108-08-7	24	35
Isobutene	115-11-7	25	11

¹¹ MTBE was rank 362 in 2012 (down from rank 3 in 1996); it therefore does not appear in Table 1, which tabulates only the top 25 gasoline-related VOCs in 2012.

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Hazard Identification for Gasoline-Related Chemicals

We screened the complete list of gasoline-related VOCs (see Appendix C) for chemicals with toxicity concerns. We focused primarily on identifying toxicants with chronic health effects, particularly carcinogens and chronic respiratory toxicants. Chronic effects are amenable to screening-level risk assessment based on annual average exposures. We also identified known reproductive and developmental toxicants and searched for information on other toxicological endpoints, such as neurotoxicity. We did not address potential additional health effects from short-term peak exposures, other types of chemical hazards like explosivity and flammability, or potential for climate change impacts (such as from methane emissions).

Carcinogens were identified based on the following sources:

- Proposition 65 list of chemicals known to the state to cause cancer: <http://oehha.ca.gov/proposition-65/proposition-65-list>
- TACs identified as carcinogenic: <http://oehha.ca.gov/air/toxic-air-contaminants>
- International Agency for Research on Cancer (IARC), 1, 2A or 2B carcinogens: <http://monographs.iarc.fr/ENG/Classification/>
- National Toxicology Program Technical Reports: <https://ntp.niehs.nih.gov/results/pubs/longterm/reports/longterm/index.html>

We used the following sources to identify gasoline-related VOCs with non-cancer health effects, including chronic respiratory toxicity, neurotoxicity, and reproductive and/or developmental toxicity:

- OEHHA chronic Reference Exposure Level (cREL) documents: <https://oehha.ca.gov/air/general-info/oehha-acute-8-hour-and-chronic-reference-exposure-level-rel-summary>
- Proposition 65 listed chemicals known to the state to cause reproductive toxicity (including male and female reproductive toxicity and developmental toxicity): <http://oehha.ca.gov/proposition-65/proposition-65-list>
- US EPA Integrated Risk Information System (IRIS): <http://www.epa.gov/IRIS/>

Table 2 lists gasoline-related VOCs that we identified as having known or suspected toxicological concerns based on the above secondary sources and a high-level literature review. Table 2 also notes whether adequate ambient air data were available. All VOCs identified as having toxicity concerns that also had at least some ambient air data were retained for exposure analysis and screening risk assessment. Ethanol was also retained for further evaluation, as requested by CARB because of its wide use as a fuel oxygenate. However, OEHHA (1999) found that toxicity concerns are not likely to be significant for ethanol at expected ambient air levels.

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Table 2. Gasoline-related VOCs of potential health concern

A check mark (✓) indicates that the chemical is a known carcinogen or chronic respiratory toxicant (see page 24 for explanation). For suspected carcinogens or chronic respiratory toxicants, supporting information is provided in a footnote. Selected toxicity concerns other than carcinogenicity and respiratory toxicity are also noted.

Gasoline-related VOC	Emissions rank		Carcinogen	Chronic respiratory toxicant	Selected other toxicity concerns	Ambient air monitoring data available
	1996	2012				
Acetaldehyde	45	47	✓	✓		✓
Acrolein	86	94		✓		✓
Benzaldehyde	59	62	Suspected carcinogenicity ¹	Suspected respiratory toxicity ²		Limited data
Benzene	13	15	✓		Proposition 65 developmental and male reproductive toxicant Other target organs/systems ³ : Hematologic	✓
1,3-Butadiene	38	45	✓		Proposition 65 developmental, female and male reproductive toxicant	✓
<i>n</i> -Butanal (butyraldehyde)	139	161		Suspected respiratory toxicity ⁴		Limited data

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Gasoline-related VOC	Emissions rank		Carcinogen	Chronic respiratory toxicant	Selected other toxicity concerns	Ambient air monitoring data available
	1996	2012				
2-Butenal (crotonaldehyde)	114	128		Suspected respiratory toxicity ⁴		Limited data
Cumene (isopropylbenzene)	133	140	✓		US EPA (1997) developed reference concentration; targets of toxicity include: endocrine and urinary systems	Limited data
Ethylbenzene	23	23	✓		Other target organs/systems: Alimentary; reproductive/development; endocrine; kidney	✓
Formaldehyde	18	21	✓	✓		✓
Hexaldehyde	143	177		Suspected respiratory toxicity ⁴		Limited data
<i>n</i> -Hexane	17	18			Other target organs/systems: Nervous	✓
Isobutene (isobutylene)	11	25		Suspected respiratory toxicity ⁵		✓

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Gasoline-related VOC	Emissions rank		Carcinogen	Chronic respiratory toxicant	Selected other toxicity concerns	Ambient air monitoring data available
	1996	2012				
Isoprene	79	91	✓			Limited data
Methanol	34	75			Proposition 65 developmental toxicant	No data
3-Methylbutanal (isovaleraldehyde)	125	149		Suspected respiratory toxicity ⁴		Minimal data ⁶
Methyl <i>t</i> -butyl ether (MTBE)	3	362	✓		Other target organs/systems: alimentary; eye; kidney	✓
Naphthalene ⁷	107	95	✓	✓		Limited data
Propionaldehyde	111	124		Suspected respiratory toxicity ⁴		Limited data
Propylene	10	13		✓		✓
Styrene	85	93	✓		Other target organs/systems: nervous	✓
<i>m</i> -Tolualdehyde	57	63		Suspected respiratory toxicity ⁴		No data

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Gasoline-related VOC	Emissions rank		Carcinogen	Chronic respiratory toxicant	Selected other toxicity concerns	Ambient air monitoring data available
	1996	2012				
Toluene	4	3		✓	<p>Proposition 65 developmental and female reproductive toxicant</p> <p>Other target organs/systems: nervous</p>	✓
1,2,3-Trimethylbenzene	69	71			<p>US EPA (2016b) developed reference concentrations based on decreased pain sensitivity; targets of toxicity include nervous, respiratory, and hematologic systems</p>	✓
1,2,4-Trimethylbenzene	25	27				✓
1,3,5-Trimethylbenzene	44	46				✓

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Gasoline-related VOC	Emissions rank		Carcinogen	Chronic respiratory toxicant	Selected other toxicity concerns	Ambient air monitoring data available
	1996	2012				
<i>m</i> -Xylene	9	9		✓	Other target organs/systems: eye; nervous	✓
<i>o</i> -Xylene	21	22				✓
<i>p</i> -Xylene	146	54				✓

Table 2 footnotes

1. NTP (1990) found some evidence of carcinogenicity in male and female mice.
2. Subchronic study identified goblet cell metaplasia in the nasal septum of rats (Laham et al., 1991).
3. “Other target organs/systems” are those identified by OEHHA (2015) as toxicity targets for the cRELs. Note that the respiratory system as a target is captured in the “chronic respiratory toxicant” column.
4. Based on comparison to known respiratory toxicants.
5. Draft health protective concentration based on respiratory toxicity (OEHHA, 1999).
6. Isovaleraldehyde had 3-hour measurements from one monitoring site, which were not sufficient data for the exposure analysis.
7. Naphthalene is also discussed in the section on PAHs below (p. 30).

Hazard Identification Results for Gasoline-Related PAHs

Polycyclic aromatic hydrocarbons (PAHs) are present in gasoline and can be formed when gasoline is burned. PAHs can be volatile, semi-volatile or particle-bound. Gas-phase PAHs can react further to form atmospheric transformation products such as nitro-PAHs (OEHHA, 2006). Polycyclic organic matter, which includes PAHs, is identified as a TAC in California. Many PAHs are known carcinogens. PAH exposures may also contribute to asthma, bronchitis, and other respiratory problems, may affect the developing fetus, and may reduce fertility.

The main sources used to identify gasoline-related PAHs were: four automobile exhaust speciation studies (Schauer et al., 2002; Zielinska et al., 2004; Riddle et al., 2007); the Department of Energy National Renewable Energy Laboratory's (DOE NREL) Gasoline/Diesel PM Split Study¹²; and CARB's Emission Inventory (which includes data for the volatile PAHs naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene). In addition, we reviewed speciation profiles of gasoline vehicles in the US Environmental Protection Agency's (US EPA) database of speciation profiles¹³ (hereafter referred to as US EPA's Speciate database).

We also consulted the following references:

- Fraser et al. (1998a), who collected ambient air samples from a tunnel in Los Angeles in 1993 and determined emission rates for many PAHs.
- Miguel et al. (1998), who collected ambient air samples of particle-bound PAHs from a tunnel in the San Francisco Bay Area in summer 1996. One bore of the tunnel had diesel truck traffic and light duty traffic while another bore had primarily light duty traffic. They compared the concentrations of ten particle-bound PAHs in the two bores.
- Marr et al. (1999), who collected gasoline and diesel fuel samples in 1997. They measured the amount of 16 PAHs in the fuel samples and found that naphthalene made up 97% of those PAHs. They also measured ambient air concentrations of 10 PAHs in a tunnel in the San Francisco Bay Area.

We reviewed availability of ambient air data and health reference levels (typically cancer potency factors) for the PAHs, nitro-PAHs, oxo-PAHs (e.g., ketones and quinones derived from PAHs) and selected other polycyclic matter (e.g., methylbiphenyls) identified in the speciation studies and databases noted above (see Appendix H).

Table 3 lists the PAHs that were retained for exposure analysis and screening-level risk assessment. Cancer potency equivalency factors were available for the gasoline-related PAHs

¹² See for example, Lough et al. 2007 and Fujita et al. 2007. A summary of the Gasoline/Diesel PM Split Study is available at <http://www.arb.ca.gov/research/seminars/doe/doe.htm>. Archived results from Gasoline/Diesel PM Split Study are available at http://web.archive.org/web/20121010113724/http://www.nrel.gov/vehiclesandfuels/nfti/feat_split_study.html.

¹³ <https://www.epa.gov/air-emissions-modeling/speciate-version-45-through-32>

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benzo[j]fluoranthene, 5-methylchrysene and 1-nitropyrene, but these lacked ambient air monitoring data and could not be assessed further.

Table 3. Gasoline-related PAHs retained for further analysis

CASRN	Chemical name
56-55-3	Benz[a]anthracene ^{1,4}
50-32-8	Benzo[a]pyrene ^{1,4}
205-99-2	Benzo[b]fluoranthene ^{1,4}
207-08-9	Benzo[k]fluoranthene ^{1,4}
218-01-9	Chrysene ^{1,4}
53-70-3	Dibenz[ah]anthracene ^{1,4}
193-39-5	Indeno[1,2,3-cd]pyrene ^{1,4}
91-20-3	Naphthalene ^{1,2,3,4,5}
90-12-0	1-Methylnaphthalene ³
91-57-6	2-Methylnaphthalene ³

1. Potency or potency equivalency factor available (OEHHA, 2015)
2. Chronic Reference Exposure Level (cREL) available (OEHHA, 2015)
3. Gasoline-attributable fraction calculated
4. Ambient air data available
5. Also discussed in the section above on gasoline-related VOCs

The following gasoline-related PAHs are frequently detected in the South Coast Air Basin, but were not retained for further analysis because no health reference values are available: acenaphthene, acenaphthylene, anthracene, fluoranthene, fluorene, phenanthrene and pyrene.

Hazard Identification Results for Gasoline-Related Criteria Air Pollutants

California has established ambient air quality standards for six criteria air pollutants (carbon monoxide, nitrogen dioxide, sulfur dioxide, ozone, lead and particulate matter). The current standards are available on-line here: <https://www.arb.ca.gov/research/aags/caaqs/caaqs.htm>. Related reports by CARB and OEHHA can be accessed from the same link.

All criteria air pollutants have been associated with current and/or historical gasoline use. Lead has been banned from gasoline¹⁴ and was not considered further. The focus of our hazard identification for the remaining criteria air pollutants was on health effects from chronic exposures.

Criteria air pollutants are well known to be associated with a range of health effects, as described in detail in reports by CARB and OEHHA (see for example, CARB and OEHHA, 2002, 2005, 2007; CARB, 2008, 2010), and US EPA (see for example, US EPA, 2009, 2010, 2013, 2016a). In the San Joaquin Valley, prenatal and early life exposures to carbon monoxide, nitrogen dioxide and PM₁₀ were associated with decreased pulmonary function in subgroups of asthmatic children (Mortimer et al., 2008). Basu et al. (2017) found that ambient PM_{2.5} was associated with increased risk of preterm delivery in California. Ammonium, nitrate and bromine in PM_{2.5}, which are constituents linked to traffic and biomass combustion, showed the strongest association. Ritz et al. (2006) found that elevated average outdoor concentrations of nitrogen dioxide in the South Coast Air Basin were associated with increased risk of infant death from all causes and SIDS while elevated particulate matter concentrations were associated with increased risk of infant death from all causes and respiratory causes. A study of New Jersey birth records from 1998 through 2004 found that elevated average ambient air levels of nitrogen dioxide, sulfur dioxide and carbon monoxide increased the odds of stillbirth (Faiz et al., 2012). In a study of nine California counties, elevated PM_{2.5} levels were associated with increased mortality in California (Ostro et al., 2006). Jerrett et al. (2013) reported that nitrogen dioxide concentrations were associated with all-cause mortality, and mortality from cardiovascular disease, ischemic heart disease, stroke, and lung cancer. Based on a metanalysis, Faustini et al. (2014) concluded that there was evidence for an independent effect of nitrogen dioxide on mortality that may be as great as that of PM_{2.5}. Ostro et al. (2015) reported significant positive associations between ischemic heart disease mortality and specific sources and types of species of fine and ultrafine particles in a cohort of California teachers. Green et al. (2016) found that prior year exposures to PM_{2.5} and ozone in California were associated with adverse cardiovascular outcomes in women.

The health effects from peak exposures to criteria air pollutants are also important and well documented (some relevant reports include CARB and OEHHA, 2005; US EPA, 2010; 2013). For example, researchers have found increased hospital visits due to asthma attacks and

¹⁴ Lead is still allowed in some specialty aircraft fuels (<https://www.scientificamerican.com/article/lead-in-aviation-fuel/>).

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cardiovascular complications like heart attacks during peak criteria air pollutant episodes (see Dominici et al., 2006 and Ostro et al., 2006, which relate short-term increases in PM_{2.5} levels to increases in hospitalizations and mortality). Evaluating potential health concerns from peak exposures to criteria air pollutants was beyond the scope of the current assessment.

Chronic exposure to ozone can affect lung function (see for example, Tager et al., 2005). CAAQS for ozone are available for exposures averaged over 1 hour and daily exposures averaged over 8 hours. Ozone is not directly emitted, but rather is an atmospheric product of NO_x and many hydrocarbon precursors. Modeling of ozone attributable to gasoline emissions is a complex undertaking and was beyond the scope of this report.

Measurements of sulfur dioxide in California are generally well below ambient air standards, in part because the current gasoline formulation is low in sulfur. Thus, sulfur dioxide was not addressed in the current assessment.

The criteria air pollutant carbon monoxide is emitted from gasoline-powered engines and poses health concerns. It is regulated in California under 1-hour and 8-hour standards. An annual average standard is not set, so this pollutant was not amenable to the type of assessment conducted in the current report.

We retained the gasoline-related criteria air pollutants PM and nitrogen dioxide for assessment. Table 4 summarizes selected health effects and lists the CAAQS for PM and nitrogen dioxide.

For PM_{2.5}, the CAAQS of 12 µg/m³ (annual average) was derived based on studies showing that higher levels of ambient particulate matter are linked to increased mortality. Because PM_{2.5} is a greater health concern than PM₁₀, as reflected in the relative annual average standards, we evaluated PM_{2.5} in more detail in this report.

The CAAQS for nitrogen dioxide of 0.030 ppm (annual average) is based on protecting lung development and preventing exacerbation of existing diseases in compromised individuals such as those with asthma and heart disease.

Refer to the Chemical Profiles on particulate matter and nitrogen dioxide for additional information.

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Table 4. Criteria air pollutants addressed in this assessment

Criteria air pollutant	Selected health effects	California Ambient Air Quality Standards			
		1 hour	8 hour	24 hour	Annual arithmetic mean
Nitrogen dioxide ¹	Respiratory effects: irritation, bronchitis, aggravation of asthma, decreased lung function in patients with lung disease	0.18 ppm	--	--	0.030 ppm
Particulate matter ² (PM _{2.5} , PM ₁₀)	Respiratory effects: irritation, decreased lung function, aggravation of asthma, chronic bronchitis. Cardiovascular effects: irregular heartbeat, nonfatal heart attacks. Premature death in people with heart or lung disease.	--	--	PM ₁₀ : 50 µg/m ³	PM _{2.5} : 12 µg/m ³ PM ₁₀ : 20 µg/m ³

Table notes:

1. The CAAQS for nitrogen dioxide was reviewed in 2007 (CARB and OEHHA, 2007).
2. CARB and OEHHA (2002) summarized the health effects of PM_{2.5} as part of a review of the CAAQS. More recently, CARB (2008, 2010) estimated premature deaths associated with exposure to PM_{2.5}.

Hazard Identification Results for Atmospheric Transformation Products of Gasoline-Related Chemicals

This section reviews atmospheric transformation products of gasoline-related chemicals, briefly summarizes earlier research sponsored by OEHHA, and describes the additional analyses we were able to conduct on selected chemicals of concern.

Summary of Previous Research on Atmospheric Chemistry for Gasoline-Related Compounds

Drs. Roger Atkinson and Janet Arey of the University of California Riverside (UCR) reviewed and summarized the atmospheric chemistry of the 25 most highly emitted gasoline-related VOCs (excluding methane) in 1998 and several less highly emitted compounds of toxicological concern (OEHHA, 2006). Some gasoline-related chemicals that are formed only via atmospheric transformation (such as PAN, furan, and phenol), and selected gasoline-related PAHs (such as naphthalene), were also included in their review.

As described in OEHHA (2006), categories of atmospheric transformation products related to gasoline emissions include:

- Carbonyls, such as formaldehyde, acetaldehyde and acetone
- Dicarbonyls, such as diacetyl, glyoxal and 3-hexene-2,5-dione
- Hydroxycarbonyls, such as 4-hydroxypentanal
- Hydroperoxides, such as ethyl hydroperoxide
- Organic nitrates, including alkyl nitrates and hydroxynitrates, such as pentyl nitrate and 2-hydroxy-1-propyl nitrate
- Peroxynitrates (including peroxyacyl nitrates, [RC(O)OONO₂] and peroxyalkyl nitrates [ROONO₂]), such as peroxyacetyl nitrate (PAN)
- Phenolic compounds, such as phenol, cresols and nitrophenols
- Ozone
- Nitrogen oxides
- Secondary organic aerosol (SOA)

As a follow up to the 2006 report, OEHHA entered into an Interagency Agreement with UCR from 2006 to 2008 to determine the presence and concentration in ambient air of selected atmospheric transformation products of gasoline-related emissions. The focus of this study was to measure in ambient air atmospheric products of potential concern, such as carbonyls, that were known or predicted to form from gasoline-related VOCs. Some of the chemicals measured in this study had never before been detected in ambient air. This work was published in Arey et al. (2009) and Obermeyer et al. (2009) (for more details see Appendix F).

OEHHA sponsored research by Dr. Judith Charles' group at UC Davis to measure acrolein and other carbonyls identified as potential toxicity concerns in ambient air in the San Francisco Bay

Section II Hazard Identification for Gasoline-Related Chemicals

Area. The results of the study were published in Destailats et al. (2002). Three ambient air samples were collected at the toll plaza of the San Francisco-Oakland Bay Bridge, two in the evening rush hour and one in the morning rush hour. Thirty-six carbonyls were identified in the samples, including 14 saturated aliphatic carbonyls, six unsaturated carbonyls, four aromatic carbonyls, six dicarbonyls, and six hydroxyl carbonyls. The authors highlighted their identification of malonaldehyde as the first report of this chemical in ambient air. Malonaldehyde (sodium salt) was listed as known to the state to cause cancer under Proposition 65 in 2011. Destailats et al. also quantified the ambient air concentrations of acrolein, methacrolein, crotonaldehyde, *p*-tolualdehyde, methylglyoxal, benzaldehyde, hydroxyacetone, and glycolaldehyde. They found that levels of acrolein measured during rush hour exceeded the cREL of 0.06 µg/m³ in effect at that time.¹⁵ See the Chemical Profile for acrolein for a further discussion of these results.

OEHHA also funded the development of formation potentials for selected transformation products by Dr. William Carter of UCR (Carter, 2001; see Appendix E for details).

Further Evaluation of Atmospheric Transformation Products in the Current Report

Table 5 lists gasoline-related atmospheric transformation products reviewed in the current assessment. The Table notes potential toxicity concerns, possible VOC precursors (*i.e.*, parent compounds), and whether we retained the transformation products for further evaluation.

We estimated gasoline-attributable ambient air concentrations for the few atmospheric transformation products that are also found in primary emissions and have adequate ambient air monitoring data (*i.e.*, acetaldehyde, acrolein, and formaldehyde). We also carried out that analysis for benzaldehyde, which had limited ambient air monitoring data.

For transformation products that had available formation potentials from Carter (2001) but inadequate ambient air monitoring data, OEHHA estimated only gasoline-attributable fractions (determined by applying formation potentials to the Emission Inventory; see the list below and Appendix E for more details).

The atmospheric transformation products retained for exposure assessment and the specific types of calculations carried out for each one are summarized below.

Gasoline-attributable ambient air concentrations were estimated for:

- Acetaldehyde
- Acrolein
- Aromatic aldehydes, as represented by benzaldehyde, which had limited ambient air monitoring data.
- Formaldehyde

¹⁵ The current cREL for acrolein is 0.35 µg/m³; see the Chemical Profile for more information.

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Gasoline-attributable fractions were estimated for:

- Alkyl nitrates
- *n*-Butanal (butyraldehyde) and propionaldehyde, as selected higher aldehydes
- Cresols
- Nitrophenols and similar aromatic nitro compounds
- PAN and PAN analogues
- Peroxybenzoyl nitrate and other aromatic PAN analogues

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Table 5. Selected atmospheric transformation products of potential concern

Selected atmospheric transformation products of potential concern	Selected toxicity concerns ¹	Possible VOC precursors (OEHHA, 2006; Carter, 2001)	Retained for further analysis ²
<i>Simple aldehydes</i>			
Acetaldehyde ^{3,4,5}	Carcinogenicity, respiratory toxicity	Isopentane, ethanol, propylene, 2,3,4-trimethylpentane	✓
Formaldehyde ^{3,4,5}	Carcinogenicity, respiratory toxicity	Acetaldehyde, acrolein, 1,3-butadiene isobutene, MTBE, PAN, propylene, styrene	✓
<i>Higher aldehydes⁵</i>			
<i>n</i> -Butanal (butyraldehyde) ³	Respiratory toxicity	<i>n</i> -Butane	✓
Hexanal (hexaldehyde) ³		1-Octene ⁷	✓
2-Methylpropanal (isobutyraldehyde) ³		2-Methylpropane (isobutane)	
Propionaldehyde (propanal) ⁶		2-Methylpentane, <i>n</i> -pentane	✓
<i>Unsaturated aldehydes</i>			
Acrolein (propenal) ^{3,4,5}	Respiratory toxicity	1,3-Butadiene	✓
Crotonaldehyde (2-butenal) ³	Respiratory toxicity		
<i>Aromatic aldehydes⁵</i>			
Benzaldehyde ³	Respiratory toxicity	Toluene, ethylbenzene	✓
<i>o</i> -Tolualdehyde ³	Respiratory toxicity, neurotoxicity	<i>o</i> -Xylene	
<i>m</i> -Tolualdehyde ³		<i>m</i> -Xylene	
<i>p</i> -Tolualdehyde ³		<i>p</i> -Xylene	
<i>1,2-Dicarbonyls</i>			
Diacetyl ³	Chemical in butter flavor, associated with bronchiolitis obliterans	<i>o</i> -Xylene, trimethylbenzenes	

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Hazard Identification for Gasoline-Related Chemicals

Selected atmospheric transformation products of potential concern	Selected toxicity concerns ¹	Possible VOC precursors (OEHHA, 2006; Carter, 2001)	Retained for further analysis ²
Glyoxal ³	Mutagenicity	Aromatics, such as benzaldehyde toluene, trimethylbenzenes and xylenes. Other VOCs, such as acetylene (17 th most highly emitted in 2012) and acrolein	
Methylglyoxal ³	Mutagenicity, neurotoxicity potential cardiovascular injury; mitochondrial dysfunction	Aromatics, such as toluene, trimethylbenzenes and xylenes	
Ethylglyoxal ³	Genotoxicity	Ethylbenzene, ethyltoluenes	
<i>Unsaturated 1,4-dicarbonyls</i>			
2-Butenedial ²	Carbonyl structure poses toxicity concerns	Toluene, ethylbenzene, <i>o</i> -xylene, <i>o</i> -ethyltoluene	
3-Hexene-2,5-dione ²		<i>p</i> -Xylene, 1,2,4-trimethylbenzene	
<i>Other dicarbonyls</i>			
Malonaldehyde ³	Mutagenicity, carcinogenicity	Acrolein, <i>n</i> -butane	
3-Oxo-butanal ³	Carbonyl structure poses toxicity concerns	<i>n</i> -Pentane	
1,4-Butanedial ³	Respiratory toxicity	<i>n</i> -Butane	
<i>Phenols</i>			
Cresols (<i>o</i> -, <i>m</i> -, <i>p</i> -) ²	Neurotoxicants, possible carcinogens	Toluene	✓
Phenol	Respiratory toxicity	Benzene	
<i>Heterocyclic aromatics</i>			
Furan	Carcinogen	1,3-Butadiene	
<i>Nitrates</i>			
Alkyl nitrates ²	Respiratory irritation, possible central nervous system effects	Alkanes, alkenes and other compounds	✓

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Hazard Identification for Gasoline-Related Chemicals

Selected atmospheric transformation products of potential concern	Selected toxicity concerns ¹	Possible VOC precursors (OEHHA, 2006; Carter, 2001)	Retained for further analysis ²
Peroxyacetyl nitrate (PAN) and PAN analogues ²	Respiratory toxicity	PAN: Acetaldehyde, methyl-substituted alkenes, methylbenzenes Higher saturated PAN analogues: Alkyl-substituted alkenes, alkylbenzenes Unsaturated PAN analogues: Acrolein, methacrolein, 1,3-butadiene, crotonaldehyde, isoprene	✓
Peroxybenzoyl nitrate and aromatic PAN analogues ²	Eye irritation, evidence of mutagenicity, respiratory toxicity	Benzaldehyde and other aromatic aldehydes	✓
<i>Nitroaromatics²</i>			✓
Nitrophenols	Methemoglobinemia, some evidence of mutagenicity	Benzaldehyde, phenol	✓
3-Nitrotoluene	Methemoglobinemia	Toluene	
<i>Selected products of PAHs</i>			
2-Formylcinnamaldehyde	Carbonyl structure poses toxicity concerns	Naphthalene	
Naphthols (1- and 2-)	Respiratory toxicity	Naphthalene	
Quinones, such as 1,4-Naphthoquinone	Electrophilic, redox-agents capable of modifying DNA and proteins	Naphthalene and other PAHs	
<i>Nitro-PAHs</i>			
1-Nitronaphthalene	Respiratory toxicity, mutagenicity	Naphthalene	
2-Nitronaphthalene	Mutagenicity	Naphthalene	
3-Nitrobiphenyl	Structurally related to 4-nitrobiphenyl, a Proposition 65 carcinogen	Biphenyl	

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Hazard Identification for Gasoline-Related Chemicals

Table 5 notes:

1. Based on secondary sources and a limited literature review, as well as consideration of structural features potentially associated with toxicity concerns.
2. Gasoline-attributable fraction developed and, if possible, ambient air concentration reported.
3. Detected in ambient air in Riverside by UCR and/or in SF Bay Area by Destailats et al. (2002). Findings from UCR studies were published in Arey et al., 2009 and Obermeyer et al., 2009.
4. Regularly monitored by CARB in ambient air in California.
5. Formation potential developed (Carter, 2001).
6. Limited data from CARB.
7. Koppmann (2008), p. 304.

III. Exposure Assessment for Gasoline-Related Chemicals

We conducted an exposure assessment for selected gasoline-related chemicals, which involved the following elements:

- Source apportionment to determine the gasoline-attributable fraction of emissions and compare emissions from gasoline and non-gasoline-related sources.
- Estimation of population-weighted annual average ambient air concentrations
- Estimation of the gasoline-attributable portion of the population-weighted ambient air concentrations. This is the product of the gasoline-attributable fraction and the population-weighted ambient air concentration for a particular chemical. It is also referred to in this report as the “gasoline-attributable concentration.”

In this section, we tabulate the chemicals retained for assessment, provide an overview of the methods applied, and briefly describe the results. For complete details on exposure assessment methods and results, refer to Appendices D and E, and the Chemical Profiles.

Some chemicals have partial results due to data limitations, which are noted in this section of the report and described in more detail in the Chemical Profiles.

Chemical Retained for Exposure Assessment

Table 6 lists the chemicals retained for exposure assessment and whether the chemical is found in primary emissions, formed in secondary reactions, or both. Table 6 also lists the air basins for which population-weighted annual average ambient air concentrations could be calculated.

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Exposure Assessment for Gasoline-Related Chemicals

Table 6. Gasoline-related chemicals retained for exposure assessment

Gasoline-related chemical	Type of emissions used to estimate gasoline-attributable fractions	Locations for which population-weighted annual average ambient air concentrations were calculated	Comments
<i>VOCs that are directly emitted</i>			
Benzene	Primary	SC, SD, SF, SJV, SV ¹ , State	
1,3-Butadiene	Primary	SC, SD, SF, SJV, SV, State	
Cumene	Primary	SC	
Ethanol	Primary	SF (2012-2015)	
Ethylbenzene	Primary	SC	
<i>n</i> -Hexane	Primary	SC	
Isobutene	Primary	SC	
Isoprene	Primary	None	Annual averages available from selected sites in SC
Methanol	Primary	None	
MTBE	Primary	SC, SD, SF, SJV, SV, State	Ambient air monitoring data were available for 1996 to 2004 due to the phase-out of MTBE; data from 2003 and 2004 included many non-detects
Propylene	Primary	SC	
Styrene	Primary	SC	
Toluene	Primary	SC, SD, SF, SJV, SV, State	
Trimethylbenzenes ²	Primary	SC	
Xylenes ³	Primary	SC, SD, SF, SJV, SV, State	

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Gasoline-related chemical	Type of emissions used to estimate gasoline-attributable fractions	Locations for which population-weighted annual average ambient air concentrations were calculated	Comments
<i>VOCs that are both directly emitted and formed through secondary atmospheric reactions</i>			
Acetaldehyde	Primary + secondary	SC, SD, SF, SJV, SV, State	
Acrolein	Primary + secondary	SC, SD, SF, SJV, SV, State	
Benzaldehyde	Primary + secondary (for aromatic aldehydes as a group)	SC	Ambient air data from DRI (Zielinska et al., 1999) Additional measurements for comparison from Fresno, Kern and Sacramento Counties (US EPA Air Data)
Butyraldehyde	Primary + secondary (for higher aldehydes as a group)	None	Ambient air measurements from Fresno, Kern and Sacramento Counties (US EPA Air Data)
Formaldehyde	Primary + secondary	SC, SD, SF, SJV, SV, State	
Hexaldehyde	Primary + secondary (for higher aldehydes as a group)	None	Ambient air measurements from Sacramento County (US EPA Air Data)
Propionaldehyde	Primary + secondary (for higher aldehydes as a group)	None	Ambient air measurements from Fresno, Kern and Sacramento Counties (US EPA Air Data)

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 Exposure Assessment for Gasoline-Related Chemicals

Gasoline-related chemical	Type of emissions used to estimate gasoline-attributable fractions	Locations for which population-weighted annual average ambient air concentrations were calculated	Comments
<i>VOCs formed mostly through secondary atmospheric reactions</i>			
Cresols	Primary + secondary	None	Cresols were measured in ambient air in a Los Angeles tunnel study (Fraser et al., 1998a).
Nitrophenols and aromatic nitro-compounds	Primary + secondary	None	
Alkyl nitrates	Secondary	None	
Peroxy nitrates ⁴	Secondary	None	PAN measured during Southern California Ozone Study (SCOS)
<i>Criteria air pollutants</i>			
Nitrogen dioxide	Primary ⁵	SC, SD, SF, SJV, SV, State	
Particulate matter	Primary and estimate of secondary ⁶	SC, SD, SF, SJV, SV, State	

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Gasoline-related chemical	Type of emissions used to estimate gasoline-attributable fractions	Locations for which population-weighted annual average ambient air concentrations were calculated	Comments
PAHs			
<i>Volatile PAHs included in Emission Inventory</i>			
Naphthalene	Primary	SC ⁷	Ambient air data from DRI (Zielinska et al., 1999) and US EPA NATTS Additional measurements from other studies included for comparison (see Chemical Profile for details)
1-Methylnaphthalene	Primary	None	No ambient air data available
2-Methylnaphthalene			
<i>Other PAHs</i>			
Benzo[a]pyrene	Not calculated because these PAHs are not in the Emission Inventory ⁸	SC (1996-2004) ⁹	Additional ambient air data from other studies also included (see Chemical Profile for details)
Benzo[b]fluoranthene			
Benzo[k]fluoranthene			
Dibenz[ah]anthracene			
Indeno[1,2,3-cd]pyrene			

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Gasoline-related chemical	Type of emissions used to estimate gasoline-attributable fractions	Locations for which population-weighted annual average ambient air concentrations were calculated	Comments
<u>Other PAHs (continued)</u>			
Acenaphthene	Not calculated because these PAHs are not in the Emission Inventory ⁸	None	Ambient air monitoring data from US EPA (NATTS) and some short-term studies.
Acenaphthylene			
Anthracene			
Benzo[a]anthracene			
Benzo[e]pyrene			
Benzo[ghi]perylene			
Chrysene			
Coronene			
Cyclopenta[cd]pyrene			
Fluoranthene			
Fluorene			
Fluorenone			
Perylene			
Phenanthrene			
Pyrene			
Retene			

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Exposure Assessment for Gasoline-Related Chemicals

Table 6 notes

1. South Coast, San Diego, San Francisco Bay Area, San Joaquin Valley and Sacramento Valley Air Basins.
2. 1,2,3-Trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene are analyzed separately.
3. Separate gasoline-attributable fractions were calculated for *m*-xylene, *p*-xylene and *o*-xylene. Ambient air concentrations were calculated for *m*- and *p*-xylene together (because these are reported together in ambient air measurements) and *o*-xylene separately.
4. Peroxyacetyl nitrate (PAN), PAN analogues, peroxybenzoyl nitrate, and other aromatic PAN analogues.
5. Based on NO_x.
6. Separate estimates for PM_{2.5} and PM₁₀. It is known that significant fractions of ambient particulate matter form through secondary atmospheric reactions. Estimates of the contribution of gasoline-related sources to total PM_{2.5} (primary and secondary) were made using various approaches described in the Chemical Profile.
7. Two models of naphthalene ambient air concentrations were developed. The first model was based on 1996 data collected by DRI (published in Zielinska et al., 1999). The second model was based on data collected by US EPA NATTS from 2007 to 2014. Estimated values were compared to many other studies of naphthalene.
8. Although speciation profiles were available in the US EPA Speciate database, it was not possible to calculate gasoline-attributable fractions for PAHs (other than naphthalene) due to uncertainty in linking CARB Emission Inventory emission tonnage to US EPA speciation profiles. For these PAHs, the gasoline-attributable fractions were assumed to be 1 in the screening risk assessment.
9. Population-weighted average concentrations of PAHs in the South Coast Air Basin were based on California Toxic Monitoring Network dataset. CARB stopped analyzing PAHs identified as TACs in February 2005. There were a large number of non-detects in the data (see Chemical Profiles for details).

Exposure Assessment Methods

Methods for Calculating Gasoline-Attributable Fractions

This section gives a brief overview of the methods used to estimate the gasoline-attributable fractions in the five most populated air basins (South Coast, San Diego, San Francisco Bay Area, San Joaquin Valley and Sacramento) and statewide from 1996 to 2012. Detailed descriptions of the methods are in Appendix E; later in the main report, we go over limitations of the methods.

The gasoline-attributable fractions were estimated as the fraction of the chemical's total emissions that came from gasoline-related sources. Estimates of the gasoline-attributable fractions were calculated as follows:

$$\text{Gasoline-attributable fraction} = \frac{\text{tons of chemical from gasoline-related sources}}{\text{tons of chemical from all sources}}$$

The CARB Emission Inventory was used to calculate the tons of each chemical released directly from all pollution sources and gasoline-related sources. Gasoline-related sources were identified as sources having Emission Inventory material code 1100.

For some chemicals like acetaldehyde, acrolein and formaldehyde, substantial portions of their ambient air concentration were formed through secondary atmospheric reactions. Carter (2001) modeled these secondary reactions and provided factors, called direct formation potentials, that were used in conjunction with the CARB Emission Inventory to estimate the tons of the chemicals formed through these secondary reactions. Direct formation potentials were calculated for: formaldehyde, acetaldehyde, aromatic aldehydes (like benzaldehyde), higher aldehydes (like propionaldehyde), acrolein, cresols, nitrophenols and aromatic nitro-compounds, alkyl nitrates, peroxyacetyl nitrate, higher saturated acyl peroxy nitrates, aromatic peroxy nitrates (like peroxybenzoyl nitrate) and unsaturated PAN analogues (such as that formed from methacrolein). See Appendix E for more details.

If the chemical had a significant portion of its ambient air concentration produced through secondary atmospheric reactions, then the gasoline-attributable fraction was calculated as:

$$\text{Gasoline-attributable fraction} = \frac{\text{tons of chemical from gasoline-related sources and secondary reactions}}{\text{tons of chemical from all sources and secondary reactions}}$$

If the chemical was formed solely through secondary atmospheric reactions, then the gasoline-attributable fraction was calculated as:

$$\text{Gasoline-attributable fraction} = \frac{\text{tons of chemical from gasoline-related secondary reactions}}{\text{tons of chemical from all secondary reactions}}$$

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Exposure Assessment for Gasoline-Related Chemicals

We used data from the Emission Inventory to estimate the contribution of gasoline-related sources to *primary* PM_{2.5}. To examine the contribution of gasoline-related sources to secondary PM_{2.5}, we applied gasoline-attributable fractions for NO_x, SO_x, and ROG, as proxies for ammonium nitrate, ammonium sulfate, and SOA, respectively. More details on the approach we applied to approximate gasoline-attributable fractions for total PM_{2.5} are provided in the Chemical Profile.

The Emission Inventory includes emission estimates for volatile PAHs (i.e., naphthalene, and 1- and 2-methylnaphthalene), but not for particle-bound PAHs (e.g., benzo[a]pyrene). We reviewed published studies on PAH source apportionment (see for example, Ravindra et al., 2008), but did not locate sufficient data to estimate gasoline-related fractions for PAHs not included in the Emission Inventory. Therefore, we made the very conservative assumption that 100% of these PAHs came from gasoline-related sources (i.e., a gasoline-attributable fraction of 1) when calculating health risks.

Emission Inventory estimates were available for the years 1996 to 2012. Mobile source emissions were not available for 2009 so gasoline-attributable fractions were not calculated for this year. Natural source emission estimates were available for 1996 to 2008 and 2012. The 2008 natural source emission estimates were applied to 2010 and 2011.

Methods for Calculating Population-Weighted Annual Average Ambient Air Concentrations for Selected Chemicals

This section provides an overview of our approach for estimating population-weighted average concentrations. For complete details, see Appendix D.

The three steps for estimating population-weighted average concentration of a chemical in an air basin were:

- Estimate the annual average concentration of a chemical at as many monitoring sites as possible within the air basin.
- Estimate the annual average at each census tract in the air basin by interpolating the annual averages from nearby monitoring sites.
- Create a population-weighted average of the census tract annual average concentrations that gives more weight to the concentrations in locations where more people live.

CARB compiles data on ambient air concentrations of many chemicals at monitoring sites throughout the State of California. The extent of monitoring sites and frequency of measurements depend on the program for which the measurements were taken. The different programs include, for example, monitoring TACs (California Toxic Monitoring Network); VOCs that contribute to ozone formation (Photochemical Assessment Monitoring Stations [PAMS]); and criteria air pollutants (State and Local Air Monitoring Stations [SLAMS]). Appendix D describes the various data files that were used in this study. Other sources of ambient air data included the US EPA's AirData website, from which data on various PAHs, ethanol, and some aldehydes were obtained. Additional measurements of PAHs were extracted from published articles.

We estimated population-weighted annual averages based on measured ambient air concentrations, supplemented with modeled ambient air values using carbon monoxide as a surrogate to account for spatial and temporal variation (CARB, OEHHA and SWRCB, 1999; Parrish et al., 2002; Von Schneidmesser et al., 2010). More sophisticated modeling approaches are being developed (see for example, US EPA's Hazardous Air Pollutant Exposure Model¹⁶), but applying these more complex estimation methods was beyond the scope of this report. The California Toxic Monitoring Network has only a few monitoring sites in some air basins, so using modeled values in addition to measured data produced more robust population-weighted annual averages. The table below illustrates this point for benzene in 2014.

¹⁶ See <https://www.epa.gov/fera/human-exposure-modeling-hazardous-air-pollutant-exposure-model-hapem>.

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Analysis approach	Percentage of basin population included in the population-weighted annual average of benzene in 2014				
	SC ¹⁷	SD	SFB	SJV	SV
Measured data only	77%	65%	67%	22%	54%
Measured data supplemented with modeled values	99%	98%	93%	60%	71%

PAMS collected 24-hour average data at some monitoring sites in selected years only. Thus, using only the measured data often led to averages that changed dramatically from year to year because of missing data. By supplementing with modeled values, variability due to missing data was reduced. The results for individual chemicals are provided in the Chemical Profiles section, with plots showing the range of the measured data and the population-weighted averages based on measured data and modeled values.

For isoprene, propionaldehyde, butyraldehyde, and a number of PAHs, it was not possible to calculate population-weighted annual average ambient air concentrations due to insufficient data. In these cases, annual averages were calculated for individual monitoring sites.

The percentage of non-detects was reviewed for the gasoline-related pollutants prior to modeling and calculating population-weighted annual averages (see Appendix D). In cases with a significant percentage of non-detects, a sensitivity analysis was conducted by changing the value substituted for non-detects from half the level of detection (LOD) to the LOD and recalculating the model and population-weighted annual averages. These results are provided where relevant in the Chemical Profiles (starting on page 85).

Methods for Obtaining Gasoline-Attributable Ambient Air Concentrations

The gasoline-attributable population-weighted annual average ambient air concentration (referred to as the “gasoline-attributable concentration”) is the ambient concentration of a chemical estimated to come from gasoline-related sources. This was calculated simply by multiplying the population-weighted average ambient air concentration of a chemical by the gasoline-attributable fraction for that chemical.

¹⁷ South Coast (SC), San Diego (SD), San Francisco Bay Area (SFB), San Joaquin Valley (SJV) and Sacramento Valley Air Basins (SV)

Exposure Assessment Results

This section provides an overview of results from the exposure assessment for gasoline-related VOCs (including some volatile PAHs) and criteria air pollutants. The Chemical Profiles provide detailed exposure assessment results for the full set of gasoline-related chemicals we were able to evaluate (see list in Table 6).

Exposure Assessment Results – VOCs

General Trends in Ambient Air Concentrations - VOCs

This section provides a brief description of general trends in overall population-weighted annual average ambient air concentrations for selected gasoline-related VOCs statewide and in the South Coast Air Basin. The population-weighted averages are based on measured ambient air concentrations and include some modeled values. Unlike the gasoline-attributable concentrations discussed below, these values reflect both gasoline and non-gasoline-related sources.

To examine statewide trends, we had adequate data to estimate average concentrations only for gasoline-related VOCs that are identified as TACs, because TACs are measured in a more extensive monitoring network compared to other VOCs. Between 1996 and 2014, declines in the statewide population-weighted annual average ambient air concentrations of benzene, 1,3-butadiene, *m*- and *p*-xylene, *o*-xylene and toluene were substantial, ranging between 68% and 81%. The declines for acetaldehyde and formaldehyde were 37% and 28%, respectively during the same time period. Because the annual averages for acetaldehyde and formaldehyde were highly variable, a five-year moving average was also calculated. The declines based on the five-year moving averages were somewhat lower, at 24% and 20% for acetaldehyde and formaldehyde, respectively, between 1996 and 2014.

We were able to assess additional VOCs in the South Coast Air Basin, which has a more extensive monitoring system. Table 7 shows the percentage declines (as ranges) in population-weighted annual average ambient air concentrations observed in the South Coast Air Basin. For more detailed results on these and other gasoline-related VOCs, see the Chemical Profiles.

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Table 7. Summary of changes in population-weighted annual average ambient air concentrations of gasoline-related VOCs in the South Coast Air Basin between 1996 and 2014 (unless otherwise noted). Chemicals are grouped by ranges noted in the first column.

Percentage decline in population-weighted ambient air concentration	Chemicals
30-39%	Formaldehyde ^c
40-49%	Acetaldehyde ^c
50-59%	--
60-69%	Benzaldehyde ^a , isobutene ^a
70 -79%	Benzene, <i>n</i> -hexane ^b , propylene ^b , styrene ^b , <i>m</i> - and <i>p</i> -xylene, <i>o</i> -xylene
80-89%	1,3-Butadiene, cumene ^b , ethylbenzene ^b , toluene, 1,3,5-trimethylbenzene ^b
90-99%	Naphthalene ^a , 1,2,3-trimethylbenzene ^b , 1,2,4-trimethylbenzene ^b

- Benzaldehyde, isobutene, naphthalene concentrations were modeled for 1996 and 2014
- For chemicals monitored by PAMS network 2014 population-weighted annual averages were extrapolated from 1996-2011 data
- The population-weighted annual average ambient air concentrations of acetaldehyde and formaldehyde were highly variable. The percent decreases based on a five-year moving average were lower, at 35% and 27% for acetaldehyde and formaldehyde respectively.

Gasoline-Related Emissions - VOCs

Consistent with the observed trends in ambient air concentrations outlined above, gasoline-related sources emitted fewer tons of VOCs in 2012 compared to 1996. Figure 10 shows the dramatic decline in aggregate primary emissions from gasoline-related sources for the top 100 gasoline-related VOCs over this time period. Ninety-five of the top 100 had lower emissions in 2012 compared to 1996. For almost all of the VOCs retained for our detailed exposure analysis, the observed decline was between 60 and 80%. Reductions in emissions from on-road gasoline-powered mobile sources (cars and trucks) accounted for the bulk of the decline. The striking drops in emissions also occurred for the VOCs with the most significant health concerns, including benzene and 1,3-butadiene (see Figure 11 for the example of 1,3-butadiene).

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Figure 10. Trend in aggregate primary emissions for the top 100 gasoline-related VOCs

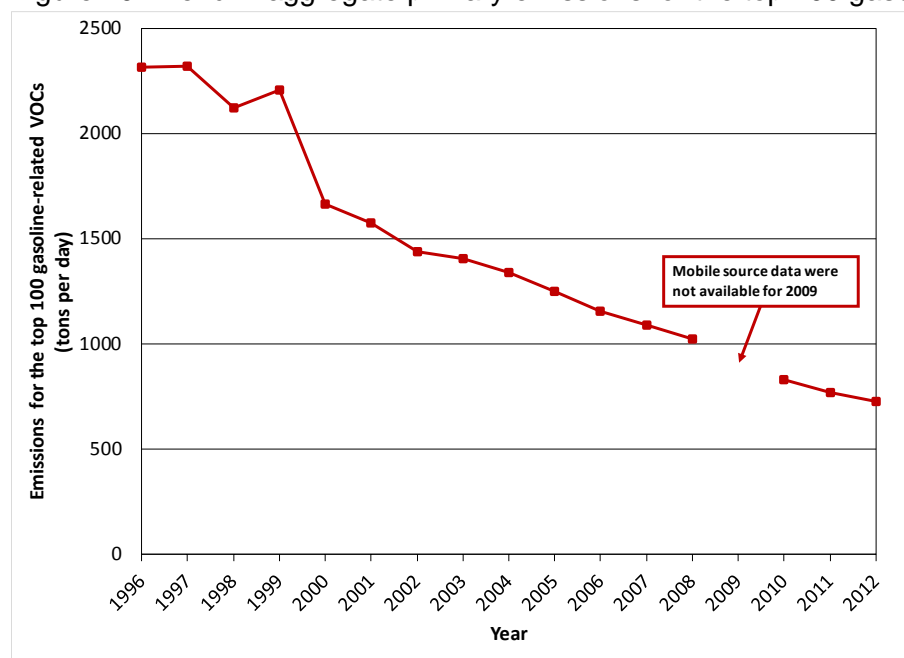
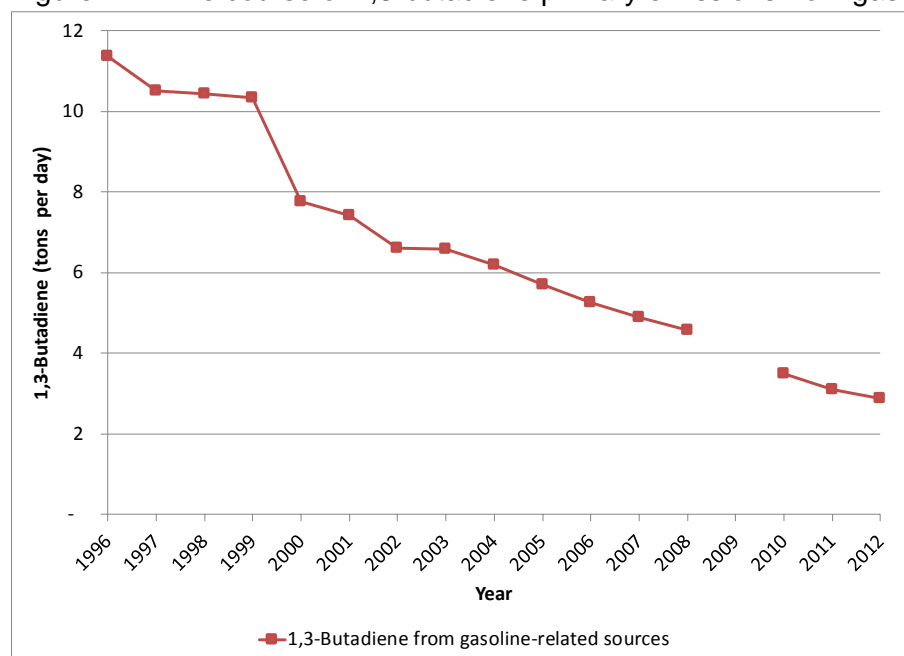


Figure 11. Time course of 1,3-butadiene primary emissions from gasoline-related sources



Note: Mobile source data were not available for 2009.

Of the top 100 most highly emitted gasoline-related VOCs, the five that showed increased emissions between 1996 and 2012 were (approximate increase noted in parenthetical): ethanol (17-fold), 2-methylhexane (1.5-fold), 2,3,3-trimethylpentane (4-fold), *p*-xylene (4-fold) and *trans*-1,2-dimethylcyclopentane (4-fold). The increased emissions of ethanol were expected due to its use as a replacement oxygenate for MTBE. The increases in emissions for the other four

Section III
Exposure Assessment for Gasoline-Related Chemicals

VOCs were associated with adjustments in Emission Inventory source profiles due to fuel formulation changes. Of these five VOCs, we evaluated ethanol and *p*-xylene in detail (see Hazard Identification section and Chemical Profiles for more information).

The VOCs we evaluated in detail in this report with the top 10 highest *primary* emissions from gasoline-related sources in 2012 were (in order of highest to lowest emissions): ethanol, toluene, *m*-xylene, propylene, benzene, *n*-hexane, formaldehyde, *o*-xylene, ethylbenzene, and isobutene. When we accounted for both primary emissions and secondary formation (from atmospheric reactions) in 2012, the top 10 most highly emitted gasoline-related chemicals that we were able to evaluate in detail were (in order of highest to lowest emissions): PAN, ethanol, formaldehyde, toluene, alkyl nitrates¹⁸, acetaldehyde, higher PAN analogues, *m*-xylene, propylene, and benzene (see Table 8 below).

Table 8. Top 10 chemicals evaluated in detail in this report that were emitted and/or formed from gasoline-related sources. Chemicals are sorted by descending total emissions.

Chemical	2012 Primary emissions rank	2012 Emissions from gasoline-related sources (tons per day)		
		Primary emissions	Secondary formation	Total
PAN	--	-	46.7	46.7
Ethanol	2	39.0	-	39.0
Formaldehyde	21	8.8	30.1	38.9
Toluene	3	38.3	-	38.3
Alkyl nitrates	--	-	36.1	36.1
Acetaldehyde	47	2.8	31.6	34.4
Higher PAN analogues	--	-	24.3	24.3
<i>m</i> -Xylene	9	22.3	-	22.3
Propylene	13	16.2	-	16.2
Benzene	15	13.9	-	13.9

Naphthalene and 1- and 2-methylnaphthalene are the only PAHs included in the Emission Inventory, because they are also VOCs. Gasoline-related emissions of naphthalene decreased by 57% between 1996 and 2012 to 0.6 tons per day in 2012. In contrast, gasoline-related emissions of 1- and 2-methylnaphthalene increased five-fold during this same period. However, 2012 emissions of 1- and 2-methylnaphthalene were still low at 0.1 and 0.2 tons per day and ranks of 206 and 167, respectively.

¹⁸ The category “alkyl nitrates” is used primarily to represent the nitrate formation products that result when higher molecular weight peroxy radicals react with nitrogen oxide (Carter, 2001). These products include hydroxynitrates and other oxygen-containing nitrates.

Gasoline-Attributable Fractions and Concentrations - VOCs

Gasoline-attributable fractions were generated based on the Emission Inventory, and applied to the population-weighted annual average ambient air concentrations to generate gasoline-attributable concentrations. This calculation required having adequate ambient air monitoring data as well as emissions estimates, so it was carried out only for a subset of gasoline-related VOCs.

Table 9 below lists ranges of statewide gasoline-attributable fractions and the VOCs that fall into those ranges. For some VOCs, the gasoline-attributable fractions take into account both primary emissions and secondary atmospheric reactions.

Table 9. Summary of selected statewide gasoline-attributable fractions for VOCs based on 2012 Emission Inventory. VOCs are grouped by the ranges noted in the first column, and listed in order of highest to lowest fractions.

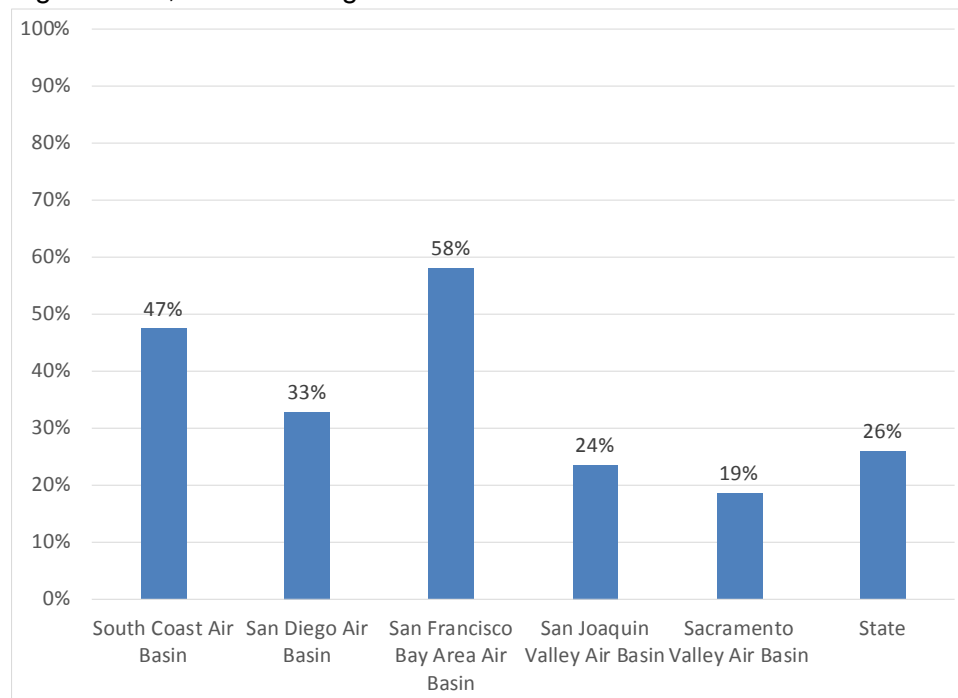
Ranges of statewide gasoline-attributable fraction	VOCs based on primary emissions only	VOCs for which secondary formation was included
90-100%	1-Methylnaphthalene	--
80-89%	Isobutene, 1,3,5-trimethylbenzene,	--
70-79%	Ethylbenzene, 1,2,4-trimethylbenzene, <i>m</i> -xylene	--
60-69%	1,2,3-Trimethylbenzene, benzene	Benzaldehyde and other aromatic aldehydes, cresols
50-59%	<i>n</i> -Hexane, <i>o</i> -xylene	Nitrophenols and aromatic nitrates
40-49%	Toluene, cumene	Peroxybenzoyl nitrate and other aromatic acyl peroxy nitrates
30-39%	Naphthalene	--
20-29%	<i>p</i> -Xylene, 1,3-butadiene, ethanol, propylene, 2-methylnaphthalene	Acrolein
10-19%	Styrene	Higher PAN analogues, acetaldehyde, PAN, alkyl nitrates, formaldehyde, higher aldehydes
0-9%	Methanol, isoprene	Unsaturated PAN analogues

Gasoline-attributable fractions varied by geographical region. Figure 12 provides the example of 1,3-butadiene based on 2012 data. The gasoline-attributable fractions for 1,3-butadiene were higher in the South Coast Air Basin than in the San Joaquin Valley Air Basin, because of differences between these two basins in estimated emissions from gasoline-related sources (like mobile sources) and non-gasoline-related sources (like agricultural burning and wildfires).

Section III Exposure Assessment for Gasoline-Related Chemicals

Gasoline-attributable fractions were also higher for chemicals in the South Coast Air Basin than statewide (illustrated for 1,3-butadiene in Figure 12). The chemicals with the largest differences between the South Coast Air Basin and statewide gasoline-attributable fractions included many that had substantial contributions from secondary emissions (acrolein, higher PAN analogues, alkyl nitrates, PAN, acetaldehyde, formaldehyde, and higher aldehydes) and a few others that were largely in primary emissions (propylene, naphthalene, 1,3-butadiene and benzene).

Figure 12. 1,3-Butadiene gasoline-attributable fractions in 2012



There were some notable changes in gasoline-attributable fractions immediately after 2003, when MTBE was banned. Most of the differences in gasoline-attributable fractions from 2003 to 2004 could be linked to changes made by CARB to source profiles¹⁹, which were adjusted to reflect the changes in California gasoline that occurred in 2004. With the MTBE phase-out, its gasoline-attributable fraction dropped from almost 100% in 2003 to near 0% in 2004. Over the same period, statewide gasoline-attributable fractions for ethanol increased from 2% to 39%, as expected with its increased use as an oxygenate. Other chemicals with marked increases in statewide gasoline-attributable fractions between 2003 to 2004 included *p*-xylene, 1-methylnaphthalene and 2-methylnaphthalene. For *p*-xylene, the fraction increased from 6% in 2003 to 37% in 2004 (see Chemical Profiles for details). These increases were associated with adjustments to gasoline-related source profiles due to fuel formulation changes. The statewide gasoline-attributable fractions increased less dramatically (by about 6 to 7%) from 2003 to 2004 for a number of other chemicals, including naphthalene, toluene and *o*-xylene.

¹⁹ Source profiles are part of the CARB Emission Inventory and are described on p. 13.

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Exposure Assessment for Gasoline-Related Chemicals

Styrene, isobutene, methanol and *n*-hexane gasoline-attributable fractions declined by up to 7% between 2003 and 2004. However, a general decline in gasoline-attributable fractions over a longer time period was also observed for these and other chemicals, so these particular reductions from 2003 to 2004 may not be traceable only to the fuel formulation change.

Gasoline-attributable fractions of criteria air pollutants also declined between 1996 and 2012. Statewide gasoline-attributable fractions of NO_x declined from 39% (1996) to 21% (2012) due to reduced estimated emissions from gasoline-related on-road mobile sources and increased estimated emissions from non-gasoline-related on-road and other mobile sources. Gasoline-attributable fractions for NO_x in the South Coast and San Diego Air Basins were somewhat higher compared to the statewide value in both 1996 and 2012 (by about 10%).

In the South Coast Air Basin, for which the most data were available, the gasoline-attributable ambient air concentrations declined by 50 to 90% between 1996 and 2014 for the VOCs we could assess in detail. Table 10 summarizes changes in the 2012 South Coast Air Basin gasoline-attributable concentrations for these VOCs.

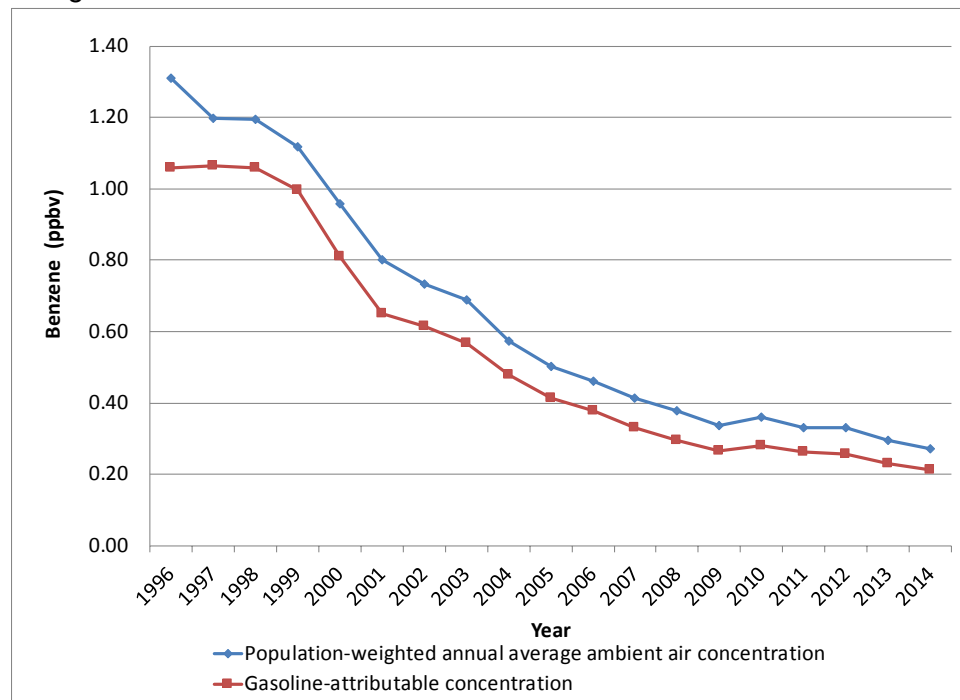
Table 10. Percent decrease in gasoline-attributable concentrations of VOCs between 1996 and 2014 for the South Coast Air Basin

Percent decrease	VOCs
90-100	1,2,4-Trimethylbenzene, 1,3-butadiene, styrene
80-90	Ethylbenzene, toluene, propylene, 1,3,5-trimethylbenzene 1,2,3-trimethylbenzene
70-80	Isobutene, <i>n</i> -hexane, <i>m</i> - and <i>p</i> -xylene, <i>o</i> -xylene, cumene, benzene
60-70	Acetaldehyde, formaldehyde

Figure 13 illustrates the decline over time for benzene, and also shows that gasoline-related emissions are the dominant source (>75%) of this toxicant in the South Coast Air Basin. Other VOCs with emissions similarly dominated by gasoline-related sources include isobutene, ethylbenzene and trimethylbenzenes. These air pollutants also showed a significant drop in ambient air in the South Coast region over this time period (see individual Chemical Profiles for details).

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Exposure Assessment for Gasoline-Related Chemicals

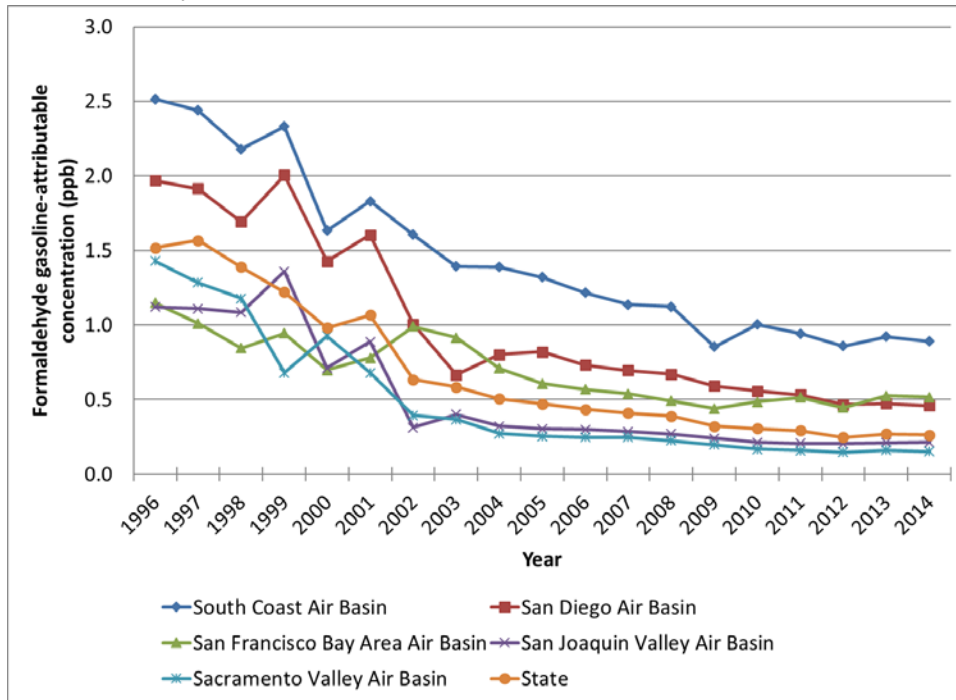
Figure 13. South Coast Air Basin population-weighted annual average ambient air concentration and gasoline-attributable concentration for benzene



A comparison of gasoline-attributable concentrations across air basins was possible only for VOCs identified as TACs because they had sufficient ambient air monitoring. The highest gasoline-attributable concentrations of TACs were observed in the South Coast Air Basin in 1996. The gasoline-attributable concentrations generally declined over time across all of the basins and the differences between air basins became less pronounced. However, the 2014 acetaldehyde and formaldehyde gasoline-attributable concentrations in the South Coast Air Basin were still considerably higher than in other air basins and statewide (see Figure 14 for the example of formaldehyde).

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Figure 14. Gasoline-attributable population-weighted annual average ambient air concentrations for formaldehyde



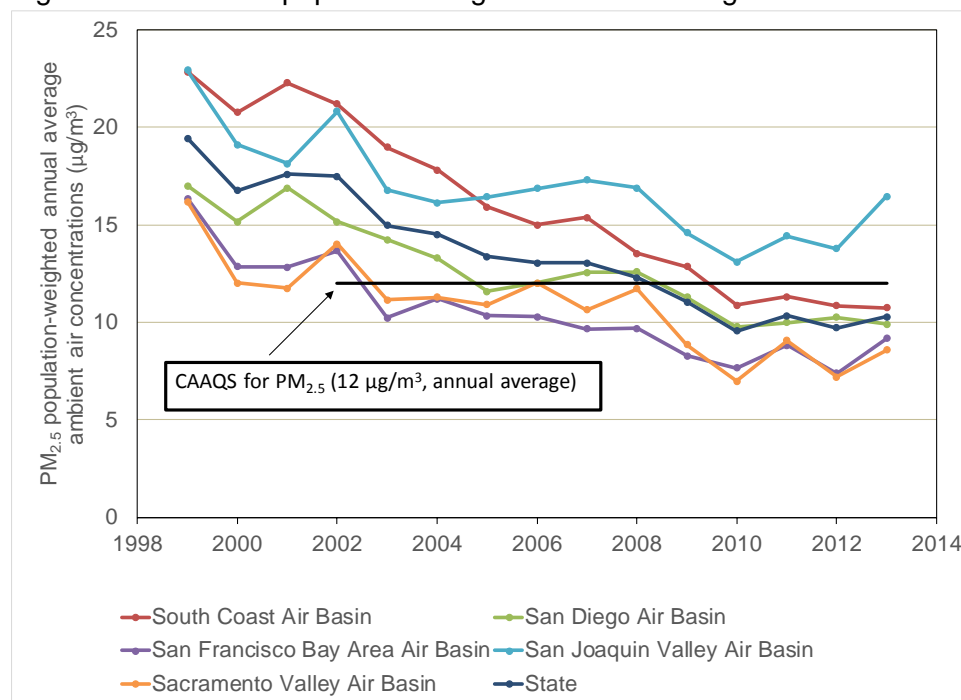
Exposure Assessment Results – Criteria Air Pollutants

General Trends in Ambient Air Concentrations – Criteria Air Pollutants

We assessed two gasoline-related criteria air pollutants: PM_{2.5} and nitrogen dioxide.

Figure 15 shows the overall population-weighted annual average ambient air concentrations of PM_{2.5}, which reflect emissions from both gasoline-related and non-gasoline sources. The Figure covers 1999 to 2013, which are the years for which PM_{2.5} monitoring data were available. Over this time period, annual average concentrations of all-source PM_{2.5} declined by 47% statewide and by 53% in the South Coast Air Basin. By 2013, all basins except the San Joaquin Valley Air Basin had population-weighted annual average ambient air concentrations for PM_{2.5} below the current CAAQS of 12 µg/m³ (annual average, adopted in 2002). The major sources of 2012 emissions of primary PM_{2.5} in the San Joaquin Valley were wildfires (35%) and miscellaneous sources (44%; including farming operations [14%] and fugitive windblown dust [8%]).

Figure 15. Trends in population-weighted annual average ambient air concentrations for PM_{2.5}

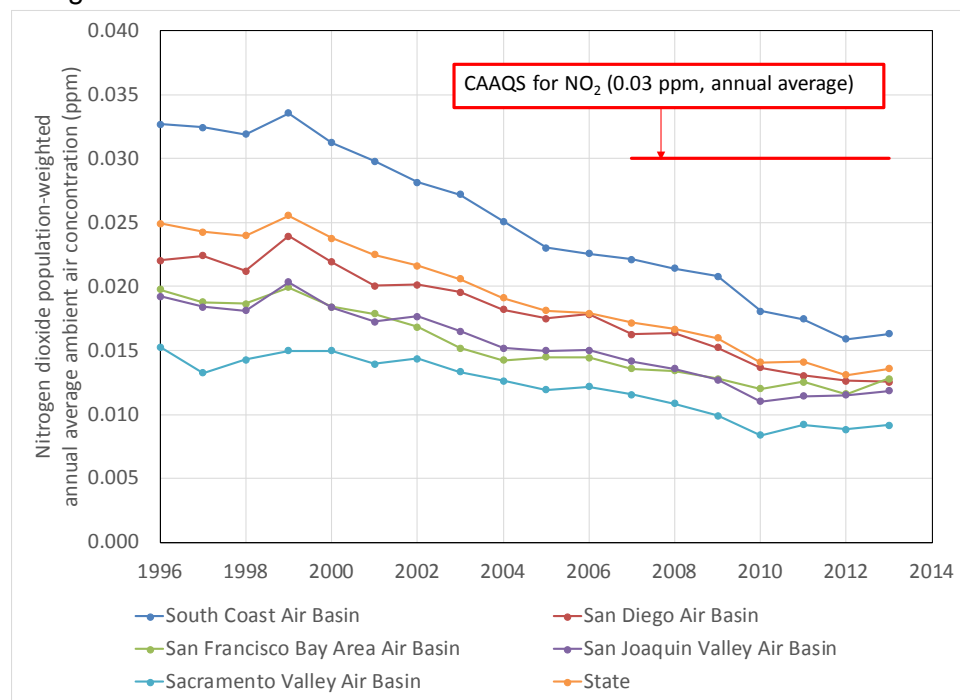


Note: The CAAQS of 12 µg/m³ shown in Figure 15 became effective in 2002.

Figure 16 shows the trends in the overall population-weighted annual average ambient air concentrations of nitrogen dioxide, which reflect emissions from both gasoline-related and non-gasoline sources. In the South Coast Air Basin and statewide, concentrations of nitrogen dioxide declined by 50% and 46%, respectively, between 1996 and 2013 (the most recent year with data).

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Exposure Assessment for Gasoline-Related Chemicals

Figure 16. Trends in population-weighted annual average ambient air concentrations for nitrogen dioxide



Gasoline-Attributable Emissions, Fractions and Concentrations – Criteria Air Pollutants

PM_{2.5}

For PM_{2.5}, the Emission Inventory includes information on *primary* emissions of PM_{2.5}. Primary PM_{2.5} emissions from gasoline-related sources decreased in the South Coast Air Basin and statewide by 45% and 37%, respectively, from 1996 to 2012.

We used Emission Inventory data to calculate gasoline-attributable fractions for *primary* PM_{2.5}. To estimate these fractions for secondary PM_{2.5}, we used the fractions for NO_x, SO_x, and ROG as proxies for ammonium nitrate, ammonium sulfate, and SOA, respectively (see the Chemical Profile for details on the method and a discussion of the substantial uncertainties with this approach). The estimated gasoline-attributable fractions for the South Coast Air Basin declined from about 30% in 1996 to about 20% in 2012. Other air basins had lower gasoline-attributable fractions compared to the South Coast, and these also declined over the same time period.

Population-weighted ambient air concentrations of PM_{2.5} dropped by 53%, 42%, 44%, 28%, 47% and 47% in the South Coast, San Diego, San Francisco Bay Area, San Joaquin Valley and Sacramento Valley Air Basins and statewide, respectively, over the period 1999 to 2013. Gasoline-attributable concentrations of PM_{2.5} declined even more substantially, reflective of the declines in gasoline-attributable fractions described above. For example, the estimated South Coast Air Basin gasoline-attributable concentrations declined by about 70% during this period.

Nitrogen Dioxide

Consistent with the observed trend in ambient air concentrations of nitrogen dioxide (see Figure 16 above), the estimated statewide emissions of NO_x from gasoline-related sources decreased dramatically, by 72% between 1996 and 2012. Similar declines in emissions of NO_x from gasoline-related sources over the same time period were observed in the five air basins studied: South Coast (77%), San Diego (74%), San Francisco Bay Area (65%), San Joaquin (76%), and Sacramento Valley (70%).

Based on the Emission Inventory data for NO_x , we generated gasoline-attributable fractions and examined the results over time and by region (for complete results see the Chemical Profile). In the South Coast Air Basin, the fraction attributable to gasoline-related sources declined from 47% to 29% between 1996 and 2012. During the same time period, the statewide gasoline-attributable fractions for NO_x declined from 39% to 21%.

The gasoline-attributable fraction for NO_x was applied to population-weighted concentrations for *nitrogen dioxide*. As expected, the resulting gasoline-attributable concentrations for nitrogen dioxide decreased substantially from 1996 to 2013, mirroring the trends in emissions and measured air concentrations. In the South Coast Air Basin and statewide, the gasoline-attributable nitrogen dioxide concentration declined by about 70% over this time period.

IV. Screening Cancer and Non-Cancer Risk Assessment

A screening cancer and non-cancer risk assessment was carried out for selected gasoline-related chemicals. Chemicals were retained for risk assessment based on availability of an exposure measure (i.e., gasoline-attributable concentration; see page 52 in the Exposure Assessment Section) and a health reference value (e.g., cancer potency value or chronic reference exposure level).

The following pages contain a summary of the results of the screening cancer and non-cancer risk assessment. There were four main results:

- Estimated cancer risks for selected gasoline-related VOCs
- Estimated cancer risks for selected gasoline-related PAHs
- Estimated non-cancer hazard quotients for selected gasoline-related VOCs

Screening Risk Assessment Methods

A brief description of methods used in the screening risk assessment is provided below. Additional details are provided in Appendix G.

Methods for Estimating Cancer Risks for Gasoline-Related VOCs

Cancer risks were estimated for the South Coast Air Basin and statewide for gasoline-related VOCs (including the volatile PAH naphthalene) that were known carcinogens and had available potency values. The reason for selecting the South Coast Air Basin to highlight is that ambient air monitoring data were available for more chemicals in this basin compared to other air basins. In addition, the South Coast Air Basin is known to have more gasoline-related mobile sources, so the health risk results would represent a worst-case scenario.

Cancer risks were estimated based on gasoline-attributable population-weighted annual average ambient air concentrations. The calculation also took into account early-in-life sensitivity using a method developed by OEHHA. This method incorporates age sensitivity factors and 95th percentiles of age-specific breathing rates. For further details and an example calculation, see Appendix G.

Methods for Estimating Cancer Risks from Selected PAHs, Other than Naphthalene

Naphthalene is a volatile PAH that is included in the Emission Inventory, and cancer risks were assessed using the methods for VOCs as noted in the previous section. We identified additional PAHs that had available air monitoring data in California (see Chemical Profiles for details), as well as cancer potency values or potency equivalency factors, and retained these for screening risk assessment (see Table 3 on page 31). We used potency values developed by OEHHA (2015) for California's Air Toxics Hot Spots Program (for specific values, refer to Appendix G). It was not possible to calculate gasoline-attributable fractions for these PAHs, because they are

Section IV Screening Cancer and Non-Cancer Risk Assessment

not in the Emission Inventory, so cancer risks were conservatively calculated by assuming that 100% of the ambient air concentrations are attributable to gasoline-related sources.

The sources used for PAH ambient air data were:

- California Toxic Monitoring Network
- South Coast Air Basin ambient air study of PAHs (Eiguren-Fernandez et al., 2004)
- Multiple Air Toxics Exposure Study III (SCAQMD, 2008)
- National Air Toxics Trends Stations, available at the US EPA AQS Data Mart database website (<https://aqs.epa.gov/api>)

Many of these PAH data sets had a large number of non-detects. Non-detects were set equal to half the limit of detection prior to calculating the annual average. The ambient air concentrations of these PAHs were highest in the fall and winter with most of the non-detects occurring in the spring and summer months.

Methods for Estimating Non-Cancer Hazard Quotients for Selected Gasoline-Related VOCs

Non-cancer hazard quotients were calculated for gasoline-related chemicals with a chronic Reference Exposure Level (cREL) developed by OEHHA for the Air Toxics Hot Spots Program (OEHHA, 2015; <https://oehha.ca.gov/air/general-info/oehha-acute-8-hour-and-chronic-reference-exposure-level-rel-summary>). We carried out these calculations in the South Coast Air Basin, which has the most complete set of ambient air data on pollutants with cRELs (data available for all but methanol). Non-cancer hazard quotients were also calculated on a statewide basis for the few chemicals with adequate ambient air monitoring data across all air basins.

The hazard quotient for a chemical was calculated as follows:

$$\text{Gasoline-attributable hazard quotient} = (\text{Gasoline-attributable concentration of chemical})/(\text{cREL})$$

For each cREL, OEHHA identifies “hazard index target organs”. Hazard indices (i.e., sums of hazard quotients) were examined for the respiratory system and the nervous system.

Screening Risk Assessment Results

Cancer Risks for Selected Gasoline-Related VOCs

Gasoline-attributable cancer risks for the South Coast Air Basin are plotted over time in Figure 17 (benzene and 1,3-butadiene) and Figure 18 (acetaldehyde, ethylbenzene, formaldehyde, naphthalene, MTBE and styrene). The estimated combined cancer risks for these carcinogens²⁰ dropped by almost a factor of seven (from 9.4×10^{-4} in 1996 to 1.4×10^{-4} in 2014). This is equivalent to an estimated reduction of 797 cancer cases per 1 million people.

The statewide gasoline-attributable cancer risks are shown in Figure 19 (benzene and 1,3-butadiene) and Figure 20 (acetaldehyde, formaldehyde and MTBE). The set of carcinogenic VOCs evaluated statewide is smaller due to more limited availability of ambient air monitoring data. The statewide combined cancer risk²⁰ for acetaldehyde, benzene, 1,3-butadiene and formaldehyde dropped by about a factor of six (from 4.9×10^{-4} based on 1996 data to 8.2×10^{-5} based on 2014 data). Note that the combined 2014 estimated cancer risks for these four chemicals in the South Coast Air Basin was almost a factor of two higher (1.3×10^{-4}) compared to statewide.

For both the South Coast Basin and statewide, the majority of the drop in estimated cancer risk from 1996 to 2014 was driven by reductions in the ambient air concentrations of benzene and 1,3-butadiene. In 2014, these two carcinogens were still the major contributors to the estimated cancer risk for the South Coast Air Basin and statewide.

Though less apparent from Figure 17, the gasoline-attributable cancer risk of the other VOCs declined as well. In the South Coast Air Basin, the gasoline-attributable cancer risks of formaldehyde, acetaldehyde and ethylbenzene decreased by 65%, 63% and 81% between 1996 and 2014.

²⁰ MTBE was excluded from the calculation of combined cancer risks because ambient air monitoring data were not available in 2014.

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 Screening Cancer and Non-Cancer Risk Assessment

Figure 17. Cancer risks for benzene and 1,3-butadiene in the South Coast Air Basin based on gasoline-attributable population-weighted annual average ambient air concentrations

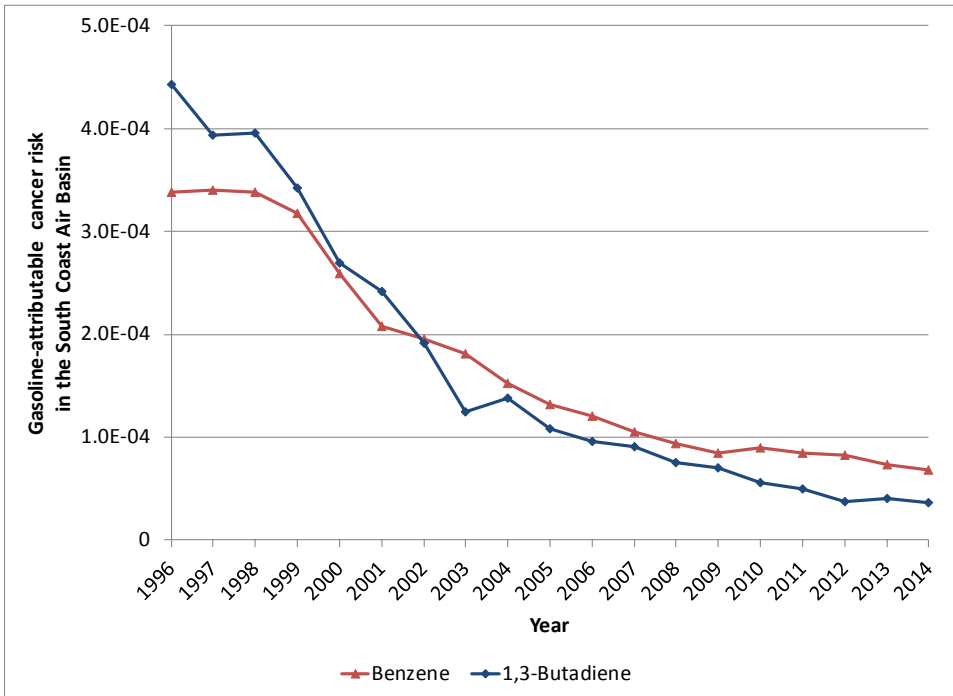
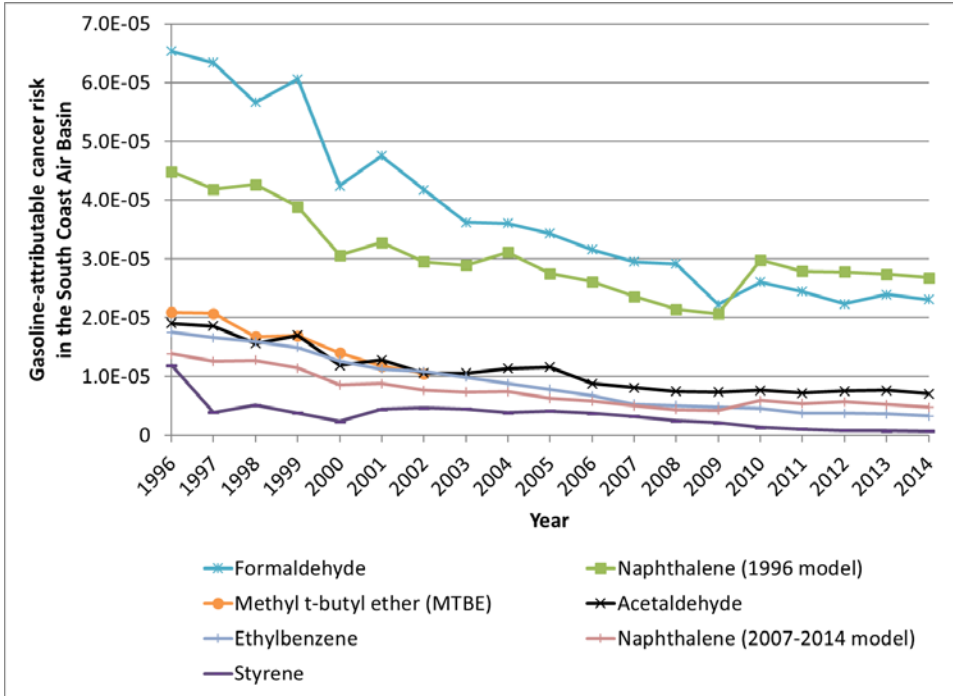


Figure 18. Cancer risks for other carcinogenic VOCs in the South Coast Air Basin based on gasoline-attributable population-weighted annual average ambient air concentrations



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Figure 19. Statewide cancer risks for benzene and 1,3-butadiene based on gasoline-attributable population-weighted annual average ambient air concentrations

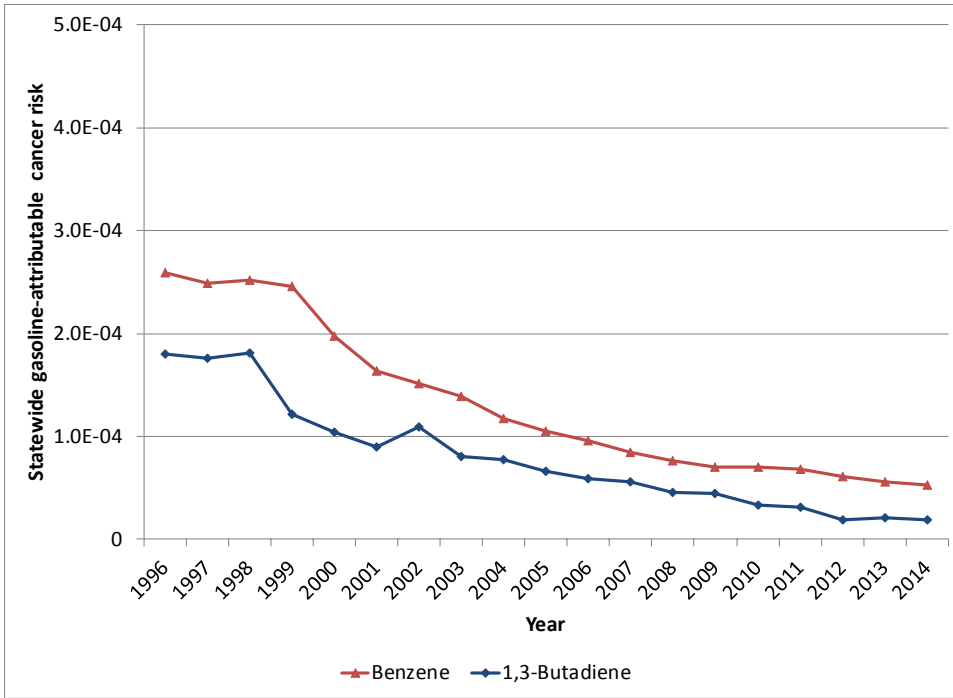
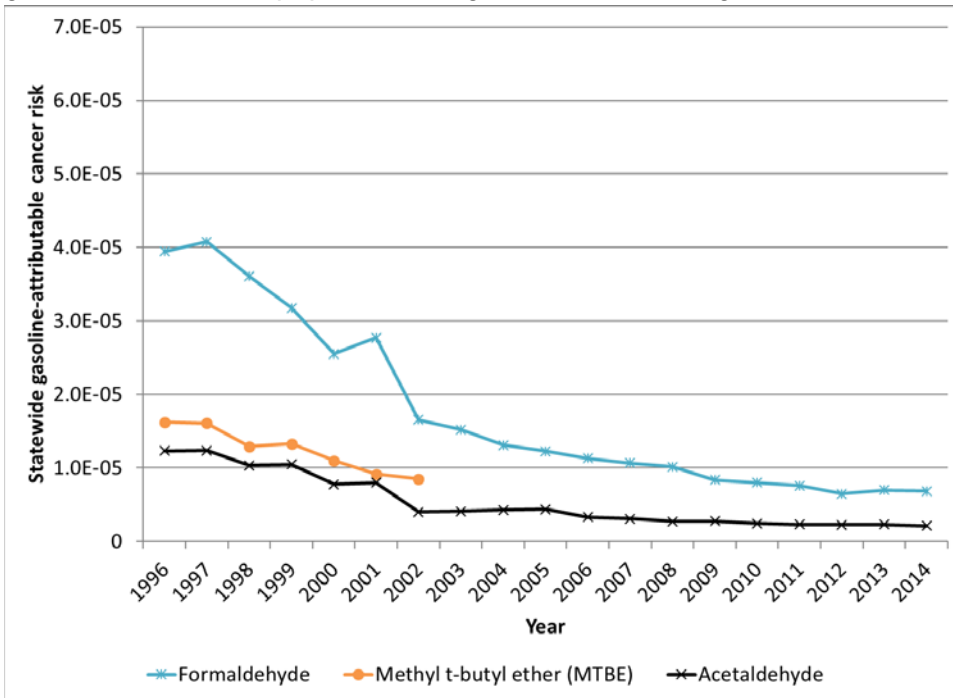


Figure 20. Statewide cancer risks for acetaldehyde, formaldehyde and MTBE based on gasoline-attributable population-weighted annual average ambient air concentrations



Cancer Risks for Selected Gasoline-Related PAHs (Other than Naphthalene)

The following gasoline-related PAHs had a cancer potency value or a potency equivalency factor and ambient air monitoring data:

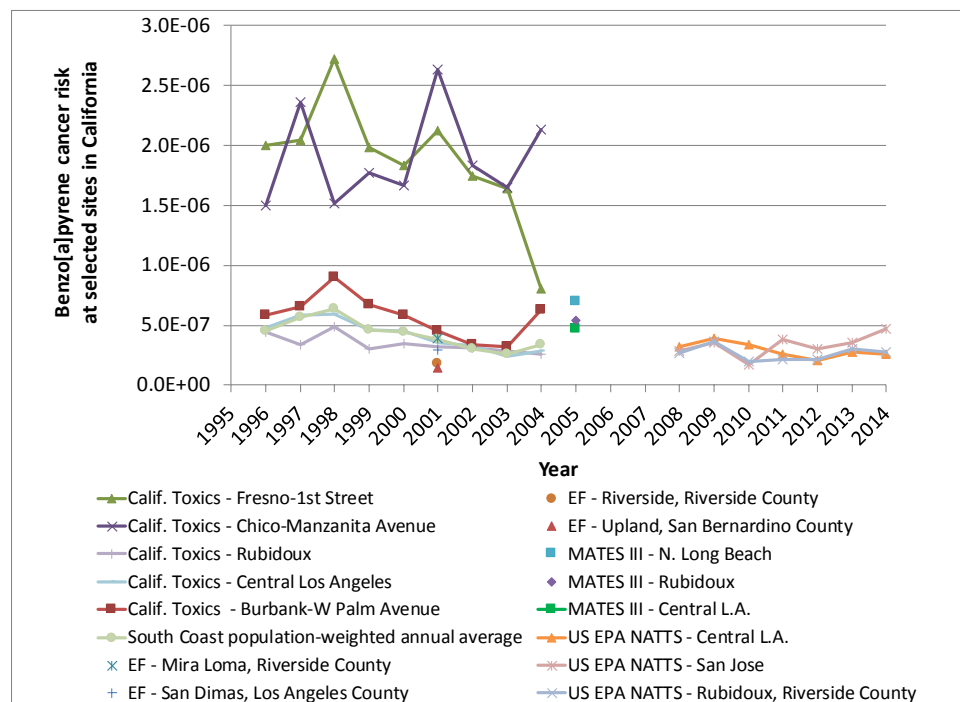
- Benz[a]anthracene
- Benzo[a]pyrene
- Benzo[b]fluoranthene
- Benzo[k]fluoranthene
- Chrysene
- Dibenz[ah]anthracene
- Indeno[1,2,3-cd]pyrene

We had insufficient data to determine gasoline-attributable fractions for these PAHs, which are not included in the Emission Inventory. Therefore, cancer risks were estimated based on the highly conservative assumption that 100% of the ambient air concentrations of these PAHs were from gasoline-related sources.

This section provides an overview of results from the screening cancer risk assessment for PAHs other than naphthalene; for more details, see the Chemical Profiles on PAHs. Figure 21 plots the cancer risks based on annual average concentrations of benzo[a]pyrene (BaP) calculated based on measurements at selected monitoring sites across California. The highest BaP cancer risks statewide were estimated for California Toxic Monitoring Network sites in Chico, Fresno, Burbank, and North Long Beach (the last site is not included in Figure 21). Two other sites in the California Toxic Monitoring Network, Rubidoux and Central Los Angeles, had measurements for a longer time period and so are also included in Figure 21. The California Toxic Monitoring Network stopped measuring BaP in early 2005. We used data from MATES III (SCAQMD, 2008) and US EPA NATTS (<https://aqg.epa.gov/api>) studies to extend the timeframe of BaP measurements for the Rubidoux and Central Los Angeles sites. Figure 21 also graphs BaP cancer risks estimated based on data from Eiguren-Fernandez et al. (2004) (abbreviated “EF” in Figure 21 below). Eiguren-Fernandez et al. measured ambient air PAHs at six sites in 2001 and 2002, including four near Los Angeles (San Dimas, Upland, Mira Loma and Riverside).

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Figure 21. Benzo[a]pyrene cancer risk based on annual average ambient air concentrations at selected sites



Benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[ah]anthracene and indeno[cd]pyrene were also monitored by the California Toxic Monitoring Network. Figure 22 shows the estimated cancer risks associated with exposure to these four PAHs and BaP based on measurements at 1st St. in Fresno, which was one of the two sites with the highest concentrations in the state (similar concentrations were found at Chico; data not shown). Figure 23 plots population-weighted cancer risks calculated for the South Coast Air Basin, which had PAH data for many more sites. For additional information, refer to the Chemical Profiles on PAHs.

We estimated combined cancer risks in 2014 for seven PAHs (the five listed above, plus benz[a]anthracene and chrysene) based on data from two sites in the South Coast Air Basin (North Main St. in Los Angeles and Rubidoux in Riverside) and assuming a gasoline-attributable fraction of 1. Combined cancer risks for these seven PAHs were 4.8×10^{-7} and 5.1×10^{-7} , respectively, or about an order of magnitude lower than the estimated gasoline-attributable population-weighted cancer risk for naphthalene in the South Coast Air Basin in 2014.

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 Screening Cancer and Non-Cancer Risk Assessment

Figure 22. Cancer risk for selected PAHs based on annual average ambient air concentrations at 1st St. Fresno²¹

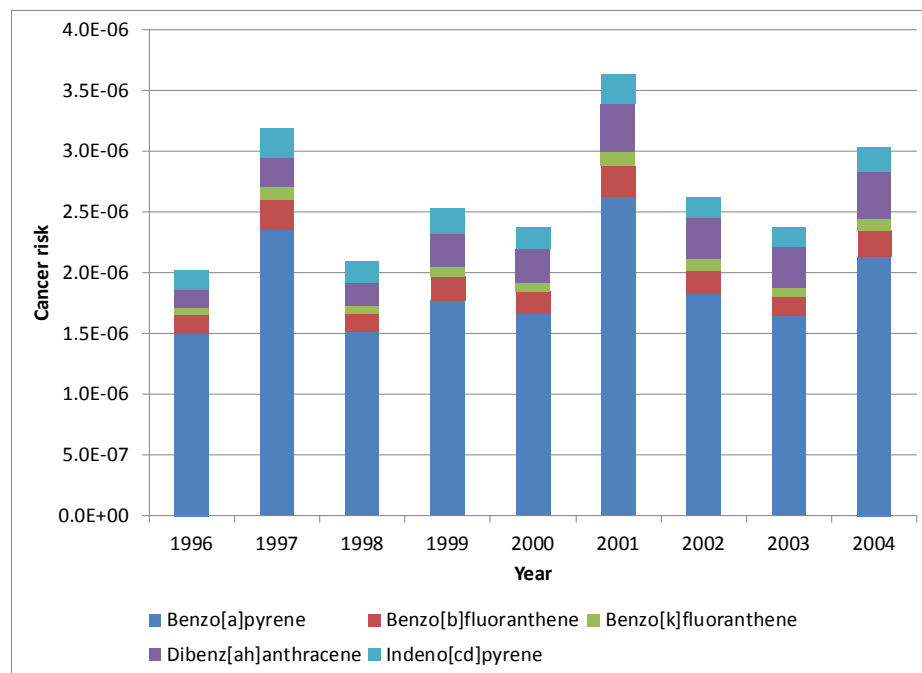
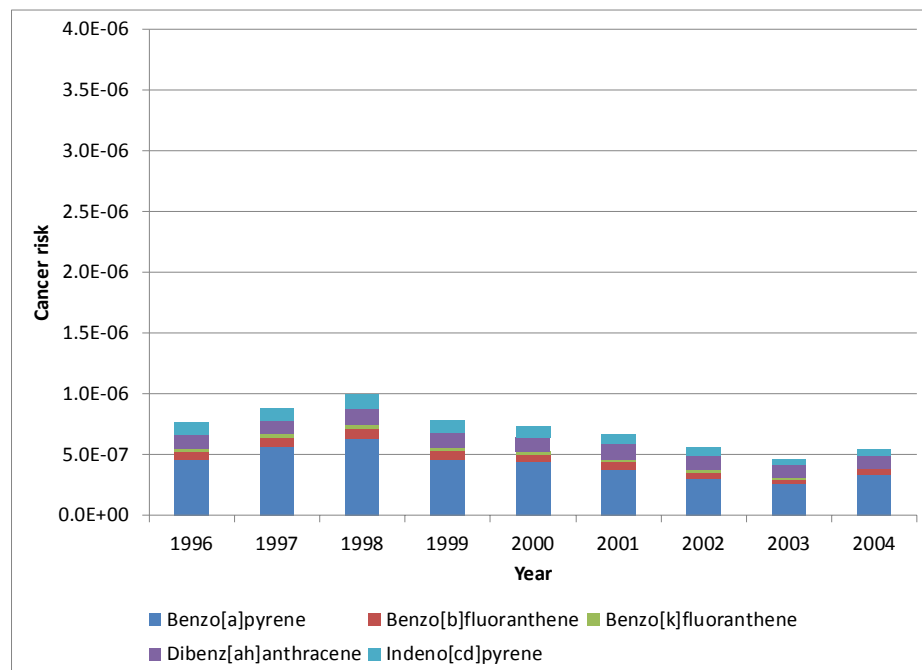


Figure 23. Cancer risk for selected PAHs based on population-weighted annual average ambient air concentrations in the South Coast Air Basin²¹



²¹ Figure design is based on MATES III report.

Non-Cancer Hazard Quotients for Selected Gasoline-Related VOCs

Gasoline-attributable hazard quotients were calculated for respiratory toxicants with health reference values and adequate ambient air monitoring data in the South Coast Air Basin (see Figure 24) and statewide. Statewide hazard quotients were all lower than the corresponding South Coast Air Basin values.

Acrolein and formaldehyde had the highest gasoline-attributable hazard quotients in the South Coast Air Basin in 2014 (3 and 0.1 respectively). The statewide gasoline-attributable hazard quotient for acrolein was also slightly elevated (1.2) in 2014. There are challenges in accurately measuring acrolein in ambient air, so more work is needed to evaluate the potential risks for respiratory toxicity (see the Chemical Profile for acrolein for details).

We identified other suspected respiratory toxicants, including a number of carbonyls (e.g., benzaldehyde, hexaldehyde, propionaldehyde and butyraldehyde), that could not be assessed because chronic reference exposure levels were not available and ambient air monitoring data were limited.

Figure 25 shows hazard quotients for nervous system toxicants, with available health reference values, calculated based on gasoline-attributable population-weighted annual average ambient air concentrations for the South Coast Air Basin. These gasoline-attributable hazard quotients are all well below one, as was the overall hazard index. However, this is not a comprehensive list of gasoline-related nervous system toxicants. For example, OEHHA set a chronic reference exposure level for cresol mixtures of 600 $\mu\text{g}/\text{m}^3$ based on adverse effects to the nervous system but ambient air data are not available for cresols. Statewide nervous system hazard quotients were also calculated for chemicals with adequate data (toluene and combined xylenes) and were all lower than the corresponding South Coast Air Basin values.

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Screening Cancer and Non-Cancer Risk Assessment

Figure 24. Gasoline-attributable hazard quotients for chronic respiratory toxicants based on estimated annual average exposures in the South Coast Air Basin (vertical axis is log-scale)

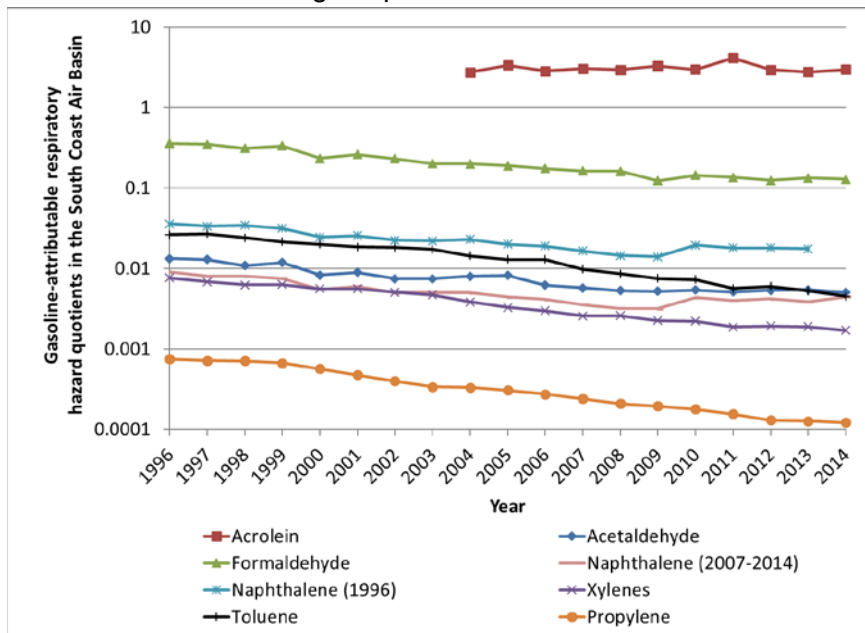
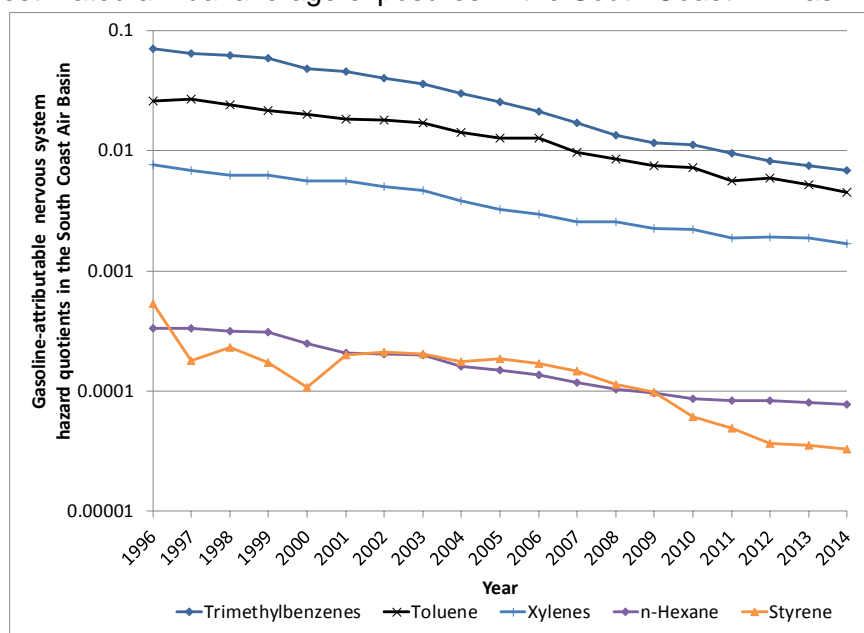


Figure 25. Gasoline-attributable hazard quotients for nervous system toxicants based on estimated annual average exposures in the South Coast Air Basin (vertical axis is log-scale)



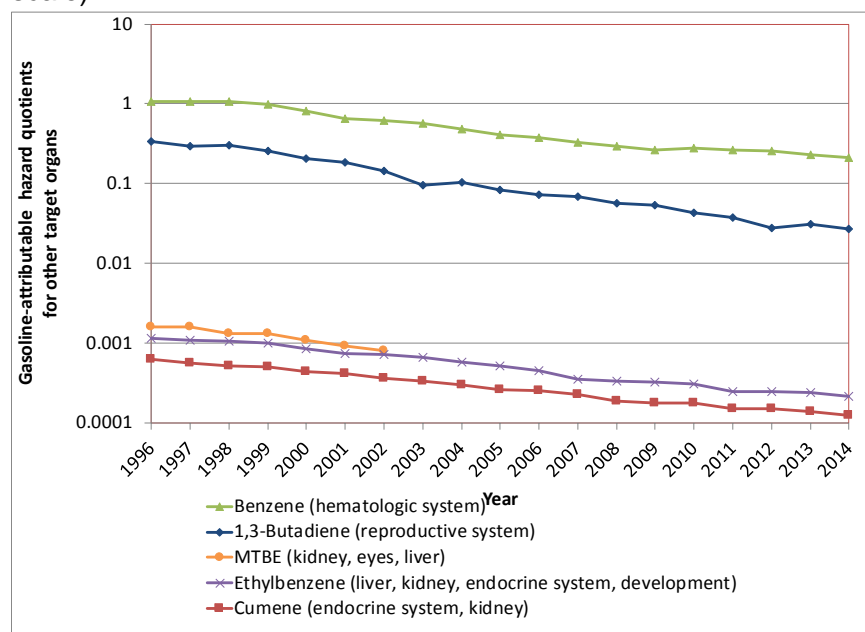
Notes on Figures 24 and 25

1. Acetaldehyde, acrolein and formaldehyde include primary emissions and secondary formation
2. Acrolein ambient air monitoring started in 2004.
3. Two models were developed for naphthalene air concentrations based on limited data from 1996 and 2007-2014.
4. Hazard quotients for trimethylbenzenes and xylenes were based on the sum of the ambient air concentrations for the individual isomers.

Section IV
 Screening Cancer and Non-Cancer Risk Assessment

We also reviewed available non-cancer health reference values for other endpoints. Figure 26 shows the hazard quotients for benzene, 1,3-butadiene, MTBE and ethylbenzene based on various non-cancer effects. The hazard quotient for hematologic effects of benzene was 1.1 in 1996; by 2014 it had dropped to 0.21. The hazard quotient for reproductive effects of 1,3-butadiene dropped by twelve-fold from 1996 to 2014. For MTBE, the hazard quotient in 1996 was well below 1, and by 2004, ambient air levels had mostly dropped below the limit of detection. Statewide hazard quotients for these other endpoints were calculated for chemicals with adequate data (benzene, 1,3-butadiene and MTBE) and were all lower than the corresponding South Coast Air Basin values.

Figure 26. Gasoline-attributable hazard quotients for target organs other than respiratory system based on estimated annual average exposures in the South Coast Air Basin (vertical axis is log-scale)



Note: MTBE ambient air data were no longer collected after 2004. In 2004, most measurements were below the limit of detection (0.3 ppb).

V. Challenges and Limitations

In this section, we describe some of the challenges and data limitations we encountered as we carried out the screening assessment described in this report.

Limitations in Hazard Identification

In carrying out hazard identification for gasoline-related pollutants, we focused primarily on VOCs (i.e., those present in liquid fuel, exhaust, and/or evaporative emissions, or as secondary transformation products). This approach was driven by data availability.

Gasoline-related particle phase pollutants are less well elucidated, so we examined gasoline-related PM (unspeciated) and a few individual particle-phase PAHs. Assessing other pollutants arising from processes associated with gasoline vehicle operation, such as releases of metals and other particulate matter from engine, tire and brake wear (Grigoratos 2015; Dahl et al., 2006), was beyond the scope of this report.

The hazard identification for gasoline-related atmospheric transformation products was limited in several ways. First, detailed atmospheric chemistry was examined for the top 25 most highly emitted gaseous pollutants, accounting for 77% of non-methane gasoline-related emissions in 1998, and a few other toxicologically important compounds. However, the universe of potential atmospheric transformation products associated with gasoline use is greater than described in this report. Second, in general, only first-generation products were identified, and second or third generation products were not characterized.

Our screening for toxicologically important compounds among the entire set of gasoline-related substances we identified was limited by gaps in toxicological data. For the most highly emitted gasoline-related VOCs in primary exhaust, toxicity concerns have been relatively well characterized, but this was not the case for other VOCs or atmospheric transformation products.

Limitations in the Calculation of Population-Weighted Annual Average Ambient Air Concentrations

For many of the chemicals studied, ambient air data were spatially or temporally limited. Often, data were collected at a few sites in each air basin and the data from a single monitoring site were available for most but not all of the years between 1996 and 2014. We supplemented measured ambient air levels with modeled concentrations, based on carbon monoxide levels at additional locations and for missing time points, where possible. This approach has significant uncertainty because it assumes a constant relationship between carbon monoxide and the air pollutant over time and space. There are more sophisticated modeling approaches being developed, which could be applied in future work assessing exposure to mobile source pollutants. For example, US EPA's Hazardous Air Pollutant Exposure Model (HAPEM) no

Section V Challenges and Limitations

longer uses carbon monoxide as a tracer. The updated and improved HAPEM applies ambient air concentration data, population data, and human activity pattern data to estimate inhalation exposure concentrations for various air toxics. It addresses exposures in microenvironments, and includes adjustments for proximity to major roadways.

We calculated annual average ambient air concentrations across entire air basins, and this approach does not address potentially highly elevated exposures in specific communities, such as those next to a major roadway. We also did not address intermittent peak excursions in exposures that can occur during poor air quality episodes or the elevated exposures drivers and passengers routinely experience while commuting (Ham et al., 2017).

Limitations in Evaluation of Gasoline-Attributable Emissions

We used CARB's Emission Inventory, which compiles data for over 3,000 sources, to study trends in gasoline-related emissions and to calculate gasoline-attributable fractions. A major limitation of this approach was that we calculated gasoline-attributable fractions on a basin-wide basis, and could not address the known issue of locally elevated impacts from gasoline-related sources.

Complete Emission Inventory data extracts were available for 1996-2008 and 2012. We used the available data to extrapolate to missing years (i.e., 2009, 2013, and 2014) and to fill in missing natural source emissions for 2010 and 2011. The Emission Inventory is updated periodically by CARB, and some of these changes had large impacts on the gasoline-attributable fractions. In particular, the approach for estimating natural source emissions was updated in 2002, which dramatically affected the calculated fractions.

For PAHs, we were able to determine gasoline-attributable fractions only for naphthalene and 1- and 2-methylnaphthalene, because these volatile compounds are included in the Emission Inventory. For particle phase PAHs, a highly conservative assumption that 100% of emissions were attributable to gasoline-related sources was applied for the screening risk assessment.

For PM_{2.5}, the approach we applied to estimate the gasoline-attributable fractions included a number of simplifying assumptions that introduced substantial uncertainties. First, we used proxies for the gasoline-attributable fractions of the main secondary PM_{2.5} components - NO_x as a proxy for ammonium nitrate, SO_x as a proxy for ammonium sulfate, and ROG as a proxy for SOA. However, the relationship between NO_x and nitrate is complex and likely does not follow a simple linear relationship. Further, the formation of SOA depends on a number of factors, such as the composition of VOCs emitted and atmospheric conditions. These complexities were not incorporated into the method for approximating PM_{2.5} gasoline-attributable fractions. For more details on the approach applied and additional limitations, see the Chemical Profile for PM_{2.5}.

Limitations in Evaluating Contributions from Secondary Atmospheric Formation from VOC Emissions

For a small subset of 12 VOCs, including acrolein, acetaldehyde, formaldehyde, aromatic aldehydes, higher aldehydes, and PAN, we estimated contributions from secondary atmospheric formation based on a report by Dr. William Carter (2001), which was commissioned by OEHHA. A number of simplifying assumptions were applied in the development of formation potentials. For example, the atmospheric reactions of many VOCs were approximated using those of better-studied model species. Assumptions were made about atmospheric conditions, which affected reaction yields. Some secondary reaction products such as aromatic aldehydes and higher aldehydes could only be modeled as groups.

A more sophisticated modeling system, US EPA's Community Multiscale Air Quality (CMAQ) Modeling System, could be considered for future work on secondary transformation products. US EPA (2017) describes CMAQ as bringing together "meteorological models, to represent atmospheric and weather activities, emission models to represent man-made and naturally-occurring contributions to the atmosphere, and an air chemistry-transport model to predict the atmospheric fate of air pollutants under varying conditions."

Limitations in Health Risk Calculations

We focused primarily on reviewing health effects associated with chronic exposures (e.g., cancer and chronic respiratory toxicity) to individual gasoline-related pollutants. We did not evaluate health effects associated with acute exposures, other types of chemical hazards like explosivity or flammability, or potential impacts on climate from gasoline-related emissions.

For a number of chemicals identified as a potential health hazard, health reference values were not available. For example, cumene is a known carcinogen but lacked a cancer potency value; aldehydes such as butyraldehyde and hexaldehyde were flagged as suspected respiratory toxicants but did not have established cREL values.

For the screening risk assessment calculations, we used point estimates for all parameters and did not examine distributions in exposure or potential interindividual differences in responses to toxic substances.

Our screening assessment evaluated potential health risks for individual gasoline-related air pollutants. We were not able to evaluate health risks associated with exposure to gasoline-related complex mixtures because of insufficient data and lack of an accepted methodology. It is well known that concurrent exposure to multiple pollutants can have a synergistic toxic effect (Mauderly and Samet, 2009; Carlin et al., 2013). Dominici et al. (2010) recommend a multipollutant approach to controlling air pollution, while acknowledging that this is a challenging task.

VI. Highlights of Key Findings

Emissions from Gasoline-Related Sources

Estimated emissions of TOG from gasoline-related sources have declined by nearly 70% statewide since 1996. This significant reduction is attributable primarily to the decline in on-road mobile source emissions, which occurred even while gasoline sales remained steady and California's population continued to grow. By 2012, emissions from on-road motor vehicles had decreased so substantially that they were approaching levels similar to emissions from other gasoline-related mobile sources, which include lawn and garden equipment, recreational boats and off-road vehicles. Emissions from these other mobile sources also declined over the same period, dropping almost in half since 1999. CARB (2016) has a broad strategy in place to seek additional reductions in mobile source emissions, which includes initiatives to promote zero-emission technologies and further tightening of standards for small-off road engines.

Gasoline-Related VOCs

We identified close to 300 VOCs in primary emissions from gasoline-related sources based on 1996 data. By 2012, this number increased to more than 350. Isopentane has consistently been the most highly emitted chemical from gasoline-related sources, but was not assessed in detail in this report because of low toxicity. Between 1996 and 2003, the second most highly emitted gasoline-related VOC was MTBE. In 2004, MTBE was phased out and MTBE emissions dropped to nearly zero. Ethanol replaced MTBE as the oxygenate of choice and became the fifth most highly emitted gasoline-related VOC in 2004. By 2012, ethanol was the second most highly emitted gasoline-related VOC. Methane, an important greenhouse gas, was the fourth most highly emitted VOC from gasoline-related sources in 2012. However, only about 1% of total methane emissions came from gasoline-related sources.

Among the top 25 most highly emitted VOCs from gasoline-related sources (primary emissions) in 1996 and 2012, toluene, *m*- and *o*-xylene, propylene, benzene, *n*-hexane, formaldehyde, ethylbenzene and isobutene were identified as having both health concerns and available health reference values. The primary emission tonnage of these highly emitted chemicals of particular concern declined by about 65 to 85% between 1996 and 2012.

The findings above are based on primary emissions only, drawn from the Emission Inventory data. When we accounted for secondary emissions, based on Carter's formation potentials (Carter, 2001; see Appendix E in the current report for more details), we identified acetaldehyde and propionaldehyde (a higher aldehyde) as additional highly emitted gasoline-related VOCs that we were able to evaluate in our screening health risk assessment. Total emissions (primary and secondary) of acetaldehyde and higher aldehydes declined by 65 and 67%, respectively, between 1996 and 2012.

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Highlights of Key Findings

Similar to the patterns we observed for estimated emissions, population-weighted ambient air concentrations for gasoline-related VOCs generally declined between 1996 and 2014. Based on data from the South Coast Air Basin, which has ambient air measurements on the largest number of chemicals and a more extensive monitoring network than other basins, concentrations of acetaldehyde and formaldehyde declined by 47% and 37%, respectively, when comparing 1996 and 2014. However, the annual average aldehyde concentrations were quite variable over this entire time period and a 5-year moving average in the South Coast Air Basin showed less dramatic declines (24% for acetaldehyde and 20% for formaldehyde). Concentrations for most other VOCs declined even more substantially (by between 67% for benzaldehyde to 92% for 1,2,4-trimethylbenzene). Acrolein was an exception, with ambient air concentrations fluctuating between 2004 and 2014 (the years with available data).

We compared our findings on VOCs in this report with the conclusions of the earlier assessment of ethanol as a replacement oxygenate for MTBE (CARB, OEHHA and SWRCB, 1999). In that 1999 report, acetaldehyde and PAN were predicted to be the major products of potential concern from combustion of ethanol-containing fuel. We found that gasoline-related emissions of acetaldehyde and PAN increased slightly between 2003 and 2004, but declined overall between 1996 and 2014. The longer-term decline of these VOCs reflected overall reductions in emissions from newer cars. We also found that the population-weighted annual average ambient air concentrations of acetaldehyde in the South Coast Air Basin and statewide declined by 47% and 37% between 1996 and 2014. PAN is not monitored in ambient air, so possible changes in concentrations over time cannot be assessed for this chemical.

Despite the overall observed declines in emissions and ambient air concentrations of gasoline-related VOCs that we document in this report, potential health concerns associated with some VOCs still remain:

- Estimated gasoline-attributable cancer cases for benzene and 1,3-butadiene still exceeded 1 in 1 million exposed individuals in 2014, at 53 and 19 cases, respectively. Estimated cancer cases per 1 million were even higher in the South Coast Air Basin in 2014: 68 for benzene and 36 for 1,3-butadiene. Continued efforts to reduce gasoline-related emissions of carcinogenic VOCs will be necessary as an ongoing investment in public health in California.
- The gasoline-attributable concentration of acrolein in the South Coast Air Basin exceeded the cREL based on respiratory toxicity by a factor of 3 in 2014, while the hazard quotient statewide was 1.2 (see discussion in the Chemical Profile). Further research is warranted on acrolein exposures in California and associated respiratory health risks.

Gasoline-Related PAHs

Based on available ambient air data, naphthalene was the dominant gasoline-related PAH with the highest measured concentrations over the time period assessed. Gasoline-related

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emissions of naphthalene decreased by 57% between 1996 and 2012, to 0.6 tons per day in 2012 (rank 95). The gasoline-attributable cancer risk for naphthalene in 2014 was 4.8×10^{-6} . This is about an order of magnitude higher than was estimated for other gasoline-related PAHs (see the Screening Risk Assessment Results section for more details). We based our evaluation of naphthalene on modeled concentrations developed from limited ambient air studies. Additional ambient air monitoring of naphthalene in areas impacted by gasoline-related pollution should be considered to better understand potential exposures and health risks.

Particulate Matter

Ambient air concentrations of PM_{2.5} substantially declined across the state from 1999 to 2013, with even greater drops predicted for gasoline-attributable concentrations. Gasoline-attributable fractions for PM_{2.5} were higher in the South Coast Air Basin than in other basins, and generally declined across the state over time. Gasoline-related sources remain an important source of urban PM_{2.5} and ultrafine particles, with particular concerns for communities heavily impacted by traffic (Zhu et al., 2002; Health Effects Institute, 2013). CARB is currently funding a study that is investigating potential associations between exposures to ultrafine particles and premature death (Kleeman, 2014). Additional research into the contribution of gasoline sources to ambient particulate matter and associated health risks in California is warranted.

Nitrogen Dioxide

Nitrogen dioxide concentrations fell by 46% from 1996 to 2013, but exposures to nitrogen dioxide remain a concern. A number of studies have shown a significant relationship between elevated nitrogen dioxide concentrations and adverse health outcomes such as term low birth weight and increased mortality rates in infants and adults in California. Future work to quantify the health impacts of gasoline-related nitrogen dioxide exposure in California is warranted.

Atmospheric Transformation Products

In general, we were very limited in our ability to assess exposure potential and health concerns for the majority of the gasoline-related atmospheric transformation products (see Table 5 for more details).

We developed a list of gasoline-related atmospheric transformation products of potential concern based on our previous report (OEHHA, 2006). We were able to estimate the extent of secondary formation for a subset of these by applying formation potentials developed by Carter (2001) to the Emission Inventory. Our analysis predicted that some of these atmospheric transformation products, including PAN and PAN analogues, alkyl nitrates, and a number of carbonyls, are among the most highly emitted (via secondary formation) gasoline-related chemicals.

VII. Recommended Future Research

This report documents substantial declines in air pollution from gasoline-related sources, but also shows that an ongoing commitment to air quality improvements is essential in California. The following areas of research would help fill some data gaps identified in this report, advance our understanding of the overall impact of gasoline-related pollution, and inform future risk reduction measures.

Better understanding of the universe of gasoline-related air pollutants and associated health risks:

New analytical methods that can more broadly screen for chemicals in the ambient air (so-called “non-targeted analyses”) could be carried out to more fully elucidate the universe of gasoline-related VOCs and their associated atmospheric transformation products. Such research could help identify new chemicals of concern, and focus resources for monitoring and health risk assessment on the most abundant gasoline-related VOCs. Additionally, a number of chemicals with high emissions were not evaluated in the screening assessment in this report because they did not have adequate toxicity information, such as Reference Exposure Levels or cancer potency values. Novel toxicity “read-across” approaches that rely on structure-activity analyses and non-conventional toxicology data sets could potentially be applied to help evaluate the toxicity of gasoline-related chemicals that have not been well studied.

Closer examination of neighborhoods and communities for gasoline-related impacts:

We applied screening methods to estimate average exposure and health risk for broad regions of the state, and this approach does not examine the higher levels of gasoline-related air pollution in neighborhoods near highways and other heavily trafficked roads. We recommend further work to quantify the exposures associated with gasoline-related sources in these locations, by building on previous projects that have mapped air pollution and health effects in heavily impacted communities (see for example, Ostro and Kim, 2004; Health Effects Institute, 2010; Delfino et al., 2015). Gasoline-related air pollution could be studied in communities identified by CalEnviroScreen as already burdened by a disproportionate share of environmental pollution, and faced with socioeconomic and health challenges (OEHHA, 2017; Cushing et al., 2015). One way to do this would be to design a targeted biomonitoring study of selected gasoline-related chemicals in areas heavily impacted by vehicle traffic. OEHHA is launching a collaborative study with UC Berkeley and the University of Washington of diesel exhaust exposures in the San Francisco Bay Area, using 1-nitropyrene as a biomarker (see, for example, Miller-Schulze et al., 2013). Pending adequate resources, we could potentially extend this study by measuring gasoline-related VOCs, using urinary metabolites or DNA or protein adducts in blood as biomarkers (Alwis et al., 2012; Rudel et al., 2014). For example, ethylbenzene and benzene both have relatively high gasoline-attributable fractions and could be considered for possible biomonitoring. Another approach would be to carry out a more detailed modeling approach of gasoline-related exposures in impacted communities, for example by

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using US EPA's HAPEM to account for time spent in microenvironments and adjust for proximity to busy roadways.

AB 617 (C. Garcia, Chapter 136, Statutes of 2017) is aimed at addressing high cumulative exposure to toxic air contaminants and criteria air pollutants in communities across California. CARB has established the Office of Community Air Protection to implement the new mandates under the law, which include developing a statewide strategy to reduce emissions impacting communities, deploying community level air monitoring, and engaging with communities to design and implement emission reduction plans. A targeted biomonitoring study of selected VOCs could aid in the understanding of cumulative air pollutant exposures in communities impacted by gasoline-related sources and other emissions, and complement the work being carried out by CARB under AB 617.

California's programs aimed at reducing greenhouse gas emissions include the implementation of the low carbon fuel standard, and the addition of more zero-emission vehicles to California's fleet. Analyzing the effects of these activities on gasoline-related pollutants would be worthwhile as one aspect of assessing changes in community exposures resulting from these programs.

Expanded monitoring of gasoline-related atmospheric transformation products:

Atmospheric transformation products are less widely monitored in ambient air in general, with a few important exceptions (e.g., acetaldehyde and formaldehyde). A short-term pilot study to monitor additional transformation products of concern, such as PAN, could be carried out to examine current ambient air levels and help determine if long-term monitoring would be warranted. Acrolein is recommended for more in-depth study based on our screening results that showed elevated exposures associated with respiratory health risks. CARB recently acquired several analyzers that employ gas chromatography, mass spectrometry, and Fourier Transform Infrared Reference spectroscopy to measure ambient air levels of selected VOCs, including acrolein. After testing and evaluation of the devices, CARB plans to use them to measure VOCs of concern in communities impacted by air pollution. We also recommend investigation of potential biomarkers for acrolein and related compounds that could be used to estimate human exposure directly (see for example, Li et al., 2004).

Further research on gasoline-related criteria air pollutant exposures and health impacts:

Studies in California have shown that elevated PM_{2.5} and nitrogen dioxide concentrations are linked to higher mortality and other health effects (Basu et al., 2017; Ostro et al., 2015; Jerrett et al., 2013; Lipsett et al., 2011; Mortimer et al., 2008; Ritz et al., 2006). Additional research on gasoline-related contributions to these pollutants is warranted. Further work could include refining the estimates of the gasoline-attributable fraction of ambient particulate concentrations, particularly the portion arising from secondary reactions in the atmosphere. Research on ultrafine particles (less than 0.1 μm in size) is also important, and new work is underway (see for example, Kleeman, 2014). Estimating mortality and other health impacts associated with gasoline-related PM_{2.5} and nitrogen dioxide exposures would be another useful extension of the

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current report. Such an analysis could build on existing reports by CARB and other agencies (see for example, CARB, 2010; European Environment Agency, 2017).

California's dependence on gasoline-fueled transportation means the state will need to maintain its efforts to address public health impacts from vehicle-related pollution. CARB (2016) has already adopted a broad mobile source strategy, which includes initiatives to promote zero-emission technologies for vehicles and other equipment. Additional gains are being sought through further tightening of evaporative emission and exhaust standards for small off-road engines, including those used in lawn and garden equipment. California's continued commitment to both scientific research and regulatory efforts will build on the already impressive reductions in pollutants demonstrated in this report, and help ensure clean air for future generations of Californians.

VIII. Chemical Profiles

The Chemical Profiles summarize results from the exposure assessment and screening risk assessment for the gasoline-related chemicals that we were able to review in detail (see the Hazard Identification Section for more information).

The exposure assessment results include:

- Gasoline-attributable fractions and other source apportionment information
- Population-weighted annual average concentrations
- Gasoline-attributable concentrations (product of the above two factors)
- Trends in chemical emissions from gasoline and non-gasoline sources

Screening risk assessment results include:

- Gasoline-attributable cancer risks for the South Coast Air Basin and statewide in 1996 and 2014
- Gasoline-attributable hazard quotients for the South Coast Air Basin and statewide in 1996 and 2014

The results presented for each chemical depended on data availability, so not all chemicals have the complete set of information outlined above.

Guide to Exposure Assessment Results for Gasoline-Related Chemicals

The following figures are presented in the Chemical Profiles, depending on data availability:

- Statewide annual emissions of the chemical from gasoline-related sources and non-gasoline-related sources between 1996 and 2012. These plots are based on estimated emissions from the CARB Emission Inventory; for some chemicals the plots also take into account estimated secondary atmospheric reaction tonnage. Mobile source emission data were not available for 2009, so there are gaps in the plots as a result.
- Gasoline-related and non-gasoline-related sources of chemicals. These plots are based on CARB's 2012 Emission Inventory (the latest year for which emission estimates were available). A guide to interpreting these plots is provided on the next few pages using acetaldehyde as an example.
- Gasoline-attributable fractions in the state and five air basins (South Coast, San Diego, San Francisco Bay Area, San Joaquin Valley and Sacramento Valley) between 1996 and 2012. As noted above, mobile source emission data were not available for 2009.
- Estimated population-weighted annual average ambient air concentrations and gasoline-attributable population-weighted annual average ambient air concentration (or "gasoline-attributable concentrations") of the chemical in the South Coast Air Basin between 1996 and 2014.

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- Comparison of estimated population-weighted annual average ambient air concentrations to available ambient air measurements in the South Coast Air Basin. This was a visual check on the robustness of modeled values included in the estimated averages.

The figures are reduced in size for space considerations. Readers can use the zoom feature in Adobe Reader to expand the figures.

Due to data limitations, some chemicals have only partial results. For example, it was not possible to calculate population-weighted values for isoprene, propionaldehyde, butyraldehyde and many PAHs. For these chemicals, summaries of available ambient air data are presented instead. Any limitations are noted in the introductory text in each Chemical Profile.

For more information on the exposure assessment methods see Appendix D and Appendix E.

Guide to Reading Emission Source Plots

This guide uses acetaldehyde as an example (the full Chemical Profile on acetaldehyde starts on p. 190).

The emission source plot for acetaldehyde is shown in Figure 113 on p. 192 and reproduced below. It shows the tons of acetaldehyde emitted from different sources. The plot is based on CARB's 2012 Emission Inventory.

- The vertical axis shows the tons of chemical emitted in the five most populated air basins: South Coast (SC), San Diego (SD), San Francisco Bay (SF), San Joaquin Valley (SJV) and Sacramento Valley (SV). The tonnage is broken into gasoline-related and non-gasoline-related sources; these are labeled as (G) and (NG) respectively on the plots.
- The tonnage is further broken down into seven emission categories from the Emission Inventory: cleaning and surface coatings, fuel combustion, industrial processes, miscellaneous processes, natural sources, on-road motor vehicles, other mobile sources, petroleum production, solvent evaporation, and waste disposal. These categories are described briefly in Table 11 below. Refer to CARB's website for a complete description of the Emission Inventory categories (<http://www.arb.ca.gov/ei/ei.htm>).
- The vertical axis label for acetaldehyde indicates that the tonnage is from primary emissions and secondary atmospheric reactions. Each plot has a similar label indicating if the emissions were primary, secondary, or both.
- The table immediately below each plot contains the tonnage values for the different emission categories. For acetaldehyde, gasoline-related on-road mobile sources contributed 5.58 tons per day in the South Coast Air Basin through primary emissions and secondary reactions in 2012.
- The bubble captions on the plot are example sources from the emission category. For example, for acetaldehyde, "biogenic sources" are example natural sources in the South

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Coast Air Basin. The sources highlighted in this way are significant contributors to emissions from the category but are not the only sources in the category.

Example plot: Acetaldehyde (also shown on p. 192 as Figure 113)

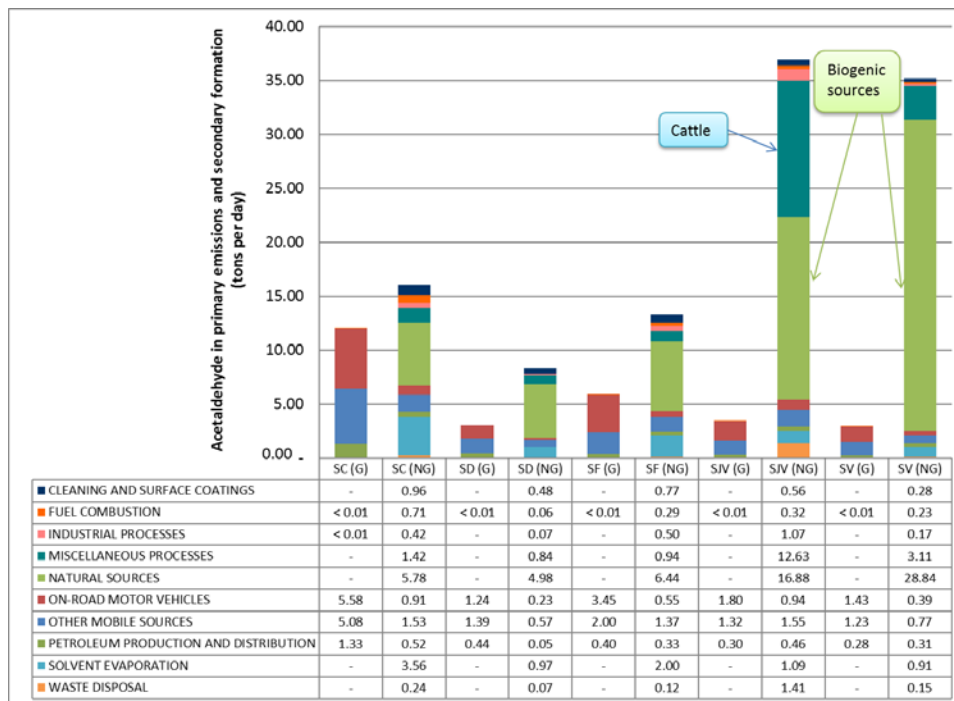


Table 11. Emissions categories

Emissions Category	Examples
Cleaning and surface coatings	<ul style="list-style-type: none"> • Dry cleaning • Emissions resulting from the use of solvents in degreasing operations in the manufacturing and maintenance industries • Coatings and related solvents (e.g., auto refinishing, plastic parts, industrial coatings, aircraft coatings) • Emissions from solvents contained in adhesives and sealants used for the following industries: construction, transportation and other
Fuel combustion	<ul style="list-style-type: none"> • Internal combustion engines, boilers and process heaters used in electricity generation, oil and gas production and manufacturing. • Other areas like commercial natural gas burning
Industrial processes	<ul style="list-style-type: none"> • Plastic production • Fiberglass production

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Emissions Category	Examples
Miscellaneous processes	<ul style="list-style-type: none"> • Livestock • Woodstoves • Forest management (burning) • Agricultural burning
Natural sources	<ul style="list-style-type: none"> • Biological and geological sources • Wildfires • Windblown dust • Biogenic emissions from plants and trees
On-road motor vehicles	<ul style="list-style-type: none"> • Passenger cars • Light, medium and heavy duty trucks • Buses • Motorcycles • Motorhomes
Other mobile sources	<ul style="list-style-type: none"> • Aircraft • Boats • Trains • Farm equipment • Lawn and garden equipment
Petroleum production and marketing	<ul style="list-style-type: none"> • Natural gas transmission losses • Fugitive emissions from valves and fittings during oil and gas production • Spills during vehicle refueling
Solvent evaporation	<ul style="list-style-type: none"> • Consumer products (a consumer product is any chemically formulated product used by household and institutional consumers, e.g., detergents, home and garden products, cosmetics, aerosol paints) • Architectural coatings like non-aerosol paint and paint thinner • Pesticides and fertilizers • Asphalt paving and roofing
Waste disposal	<ul style="list-style-type: none"> • Landfills • Composting • Sewage treatment

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Chemical Profiles: Gasoline-Related VOCs Based on Primary Emissions Only

This section reviews exposure assessment results for chemicals with ambient air concentrations primarily resulting from direct emissions. Source apportionment results are presented for all gasoline-related chemicals we assessed. Population-weighted gasoline-attributable ambient air concentrations could only be calculated for some chemicals. Emission Inventory estimates were not available for 2009, 2013 or 2014. Gasoline-attributable fractions for those years were taken from 2008, 2012 and 2012, respectively.

Benzene: Exposure and Screening Risk Assessment Results

Benzene is a carcinogen and had the 15th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Estimated emissions of benzene from gasoline-related sources declined between 1996 and 2012 (Figure 27). Statewide, in 2012, gasoline-related sources, including cars, trucks, motorcycles, off-road equipment and boats, were the dominant contributor to benzene emissions, accounting for 63% of the total. Examples of non-gasoline-related sources of benzene include waste disposal and other mobile sources like airplanes and construction equipment (Figure 28). Table 13 and Figure 29 show the gasoline-attributable fractions for benzene in the various air basins between 1996 and 2012. The gap in the graph is due to lack of mobile source data for 2009. The fractions are lower in the San Joaquin Valley Air Basin because benzene emissions from waste disposal (a non-gasoline-related source) made up a larger part of total benzene tonnage compared to other air basins.

The population-weighted annual average ambient air concentrations were based on measurements from the California Toxic Monitoring Network and were supplemented with modeled values to produce more robust estimates. The model was based on data²² from 1996-2014 (see Appendix D). The five most populated air basins (South Coast, San Diego, San Francisco Bay Area, San Joaquin Valley and Sacramento Valley Air Basins) had between two and six monitoring stations active annually between 1996 and 2014. The South Coast Air Basin had the most monitoring stations with five to six stations collecting data at any time.

Table 14 provides the population-weighted annual average ambient air concentrations for the South Coast, San Diego, San Francisco Bay Area, San Joaquin Valley and Sacramento Valley Air Basins and statewide. Figures 30 and 31 compare the population-weighted annual average ambient air concentrations of benzene in the South Coast Air Basin to actual ambient air measurements from the California Toxic Monitoring Network and PAMS monitoring network for sites within the basin.

²² CARB adjusted the benzene data from California Toxics Monitoring Network from 1996-1999 for consistency with an improved measurement technique used in later years (<ftp://ftp.arb.ca.gov/aqd/aqcdcd/web2011/BzButAdj.pdf>).

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Table 15 tabulates the gasoline-attributable population-weighted annual average ambient air concentrations (referred to as gasoline-attributable concentrations). Figure 32 shows that the gasoline-attributable concentrations of benzene declined by 80% between 1996 and 2014 in the South Coast Air Basin.

Cancer risks and non-cancer hazard quotients were calculated based on gasoline-attributable concentrations (see Appendix G for details). The gasoline-attributable cancer risk for annual average exposures to benzene in the South Coast Air Basin declined from 3.4×10^{-4} in 1996 to 6.8×10^{-5} in 2014, corresponding to a reduction of an estimated 271 cancer cases per 1 million people. In comparison, the statewide gasoline-attributable cancer risk for benzene declined from 2.6×10^{-4} in 1996 to 5.3×10^{-5} in 2014, or a reduction of about 200 cancer cases per 1 million people. The gasoline-attributable hazard quotient for benzene, based on hematologic toxicity, declined from 1.1 in 1996 to 0.21 in the South Coast Air Basin in 2014. The statewide gasoline-attributable hazard quotient declined from 0.81 in 1996 to 0.17 in 2014.

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Figure 27. Benzene emissions from gasoline-related and non-gasoline-related sources in California (data from CARB Emission Inventory)

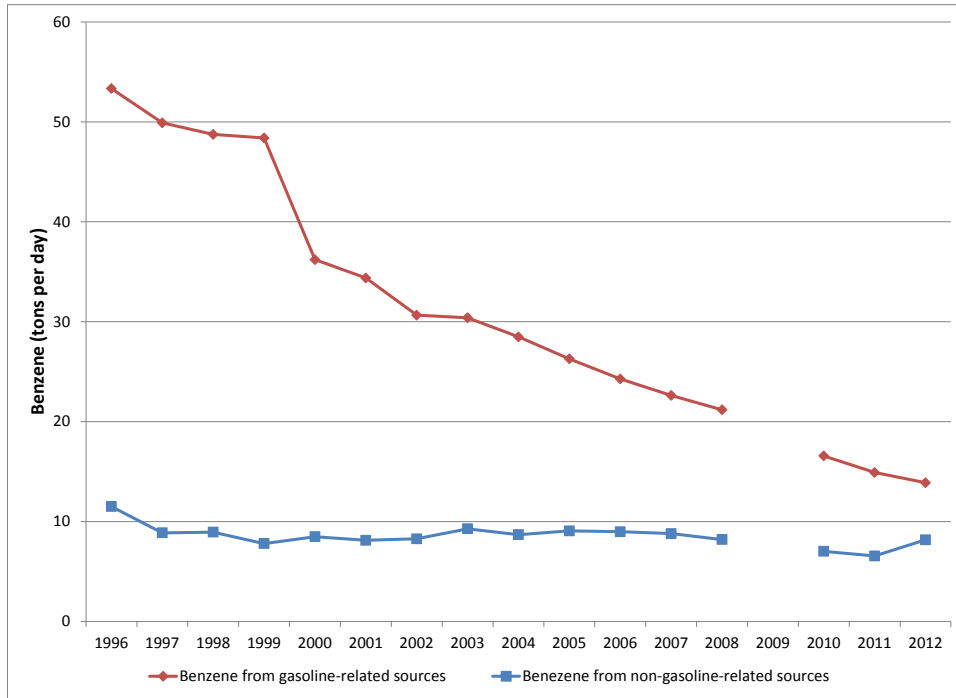
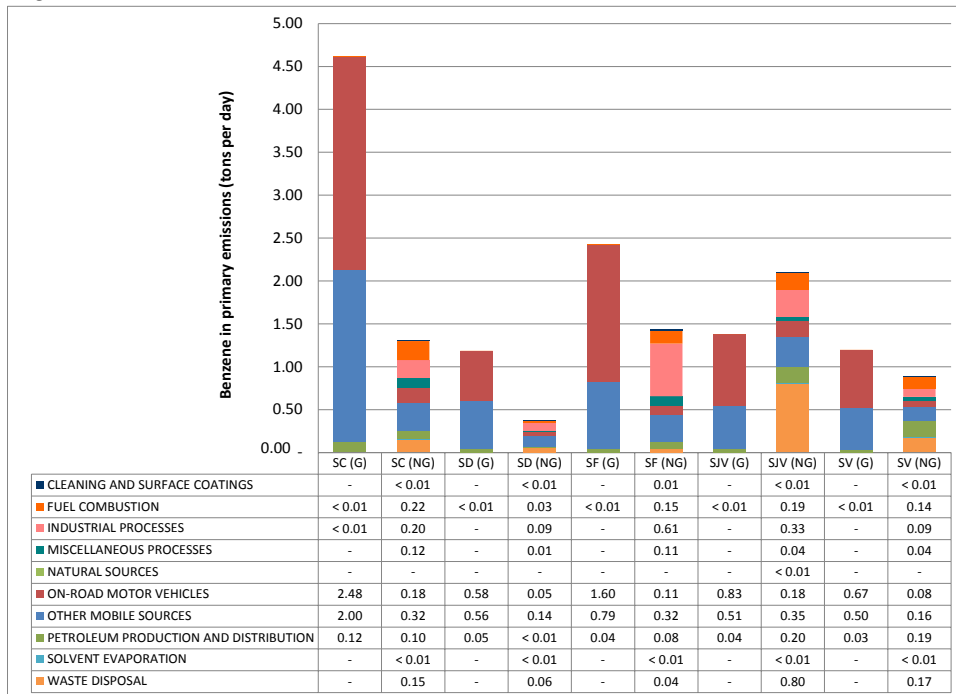


Figure 28. Emission sources of benzene in 2012



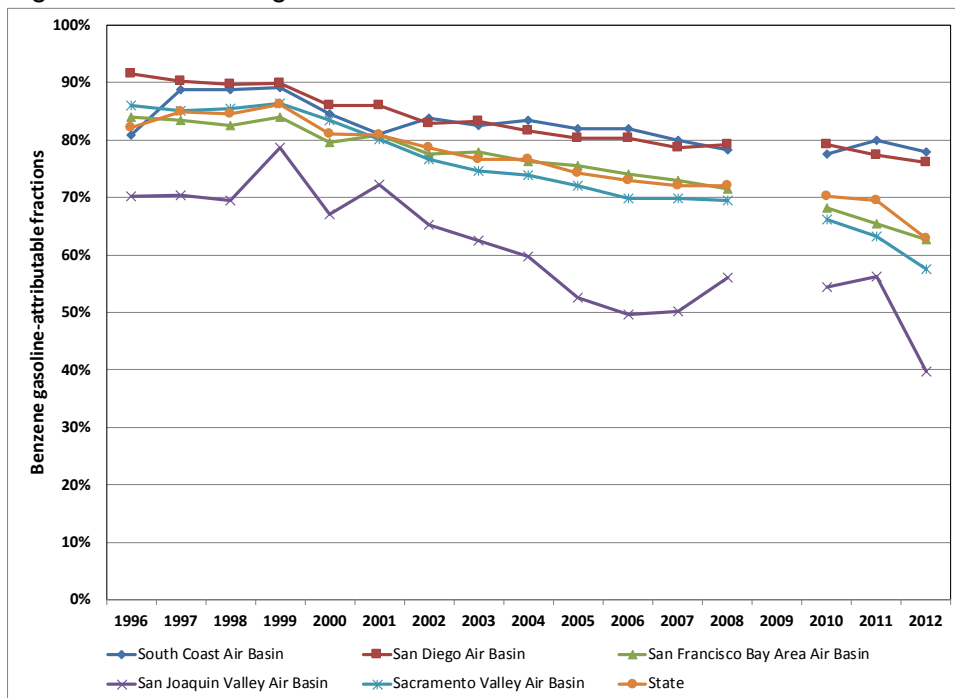
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Table 13. Benzene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	81%	92%	84%	70%	86%	82%
1997	89%	90%	83%	70%	85%	85%
1998	89%	90%	83%	70%	85%	84%
1999	89%	90%	84%	79%	86%	86%
2000	84%	86%	80%	67%	83%	81%
2001	81%	86%	81%	72%	80%	81%
2002	84%	83%	78%	65%	77%	79%
2003	83%	83%	78%	62%	75%	77%
2004	83%	82%	76%	60%	74%	77%
2005	82%	80%	76%	53%	72%	74%
2006	82%	80%	74%	50%	70%	73%
2007	80%	79%	73%	50%	70%	72%
2008	78%	79%	72%	56%	70%	72%
2009	--	--	--	--	--	--
2010	78%	79%	68%	54%	66%	70%
2011	80%	77%	65%	56%	63%	69%
2012	78%	76%	63%	40%	58%	63%

Note: Mobile source emissions were unavailable for 2009.

Figure 29. Benzene gasoline-attributable fractions



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Table 14. Benzene population-weighted annual average ambient air concentrations (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	1.3	0.89	0.77	0.65	0.60	0.99
1997	1.2	0.88	0.72	0.62	0.58	0.92
1998	1.2	0.87	0.78	0.70	0.58	0.94
1999	1.1	1.0	0.70	0.64	0.58	0.89
2000	0.96	0.83	0.61	0.60	0.47	0.76
2001	0.80	0.70	0.48	0.49	0.38	0.63
2002	0.73	0.67	0.48	0.49	0.45	0.60
2003	0.69	0.63	0.47	0.44	0.45	0.57
2004	0.57	0.55	0.41	0.36	0.39	0.48
2005	0.50	0.62	0.36	0.36	0.36	0.44
2006	0.46	0.54	0.34	0.36	0.37	0.41
2007	0.41	0.46	0.30	0.32	0.33	0.37
2008	0.38	0.43	0.25	0.29	0.34	0.33
2009	0.34	0.38	0.24	0.27	0.30	0.31
2010	0.36	0.38	0.25	0.25	0.27	0.31
2011	0.33	0.35	0.29	0.27	0.29	0.31
2012	0.33	0.35	0.28	0.27	0.27	0.31
2013	0.30	0.30	0.28	0.26	0.27	0.28
2014	0.27	0.28	0.25	0.26	0.22	0.26

Note: Non-detects were replaced by half the limit of detection.

Table 15. Benzene gasoline-attributable concentrations (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	1.1	0.81	0.65	0.45	0.51	0.81
1997	1.1	0.79	0.60	0.44	0.49	0.78
1998	1.1	0.78	0.64	0.49	0.49	0.79
1999	1.00	0.92	0.59	0.50	0.50	0.77
2000	0.81	0.71	0.49	0.40	0.40	0.62
2001	0.65	0.60	0.39	0.35	0.30	0.51
2002	0.61	0.56	0.38	0.32	0.35	0.47
2003	0.57	0.52	0.37	0.28	0.34	0.43
2004	0.48	0.45	0.31	0.22	0.29	0.37
2005	0.41	0.49	0.27	0.19	0.26	0.33
2006	0.38	0.43	0.25	0.18	0.26	0.30
2007	0.33	0.36	0.22	0.16	0.23	0.26
2008	0.29	0.34	0.18	0.16	0.23	0.24
2009	0.26	0.30	0.17	0.15	0.21	0.22
2010	0.28	0.30	0.17	0.13	0.18	0.22
2011	0.26	0.27	0.19	0.15	0.18	0.22
2012	0.26	0.27	0.17	0.11	0.16	0.19
2013	0.23	0.22	0.17	0.10	0.15	0.18
2014	0.21	0.21	0.16	0.10	0.13	0.17

Note: The 2009 gasoline-attributable concentrations were calculated with the 2008 gasoline-attributable fractions and the 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fractions.

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Figure 30. Population-weighted annual average ambient air concentration of benzene in the South Coast Air Basin compared to California Toxic Monitoring Network data²³

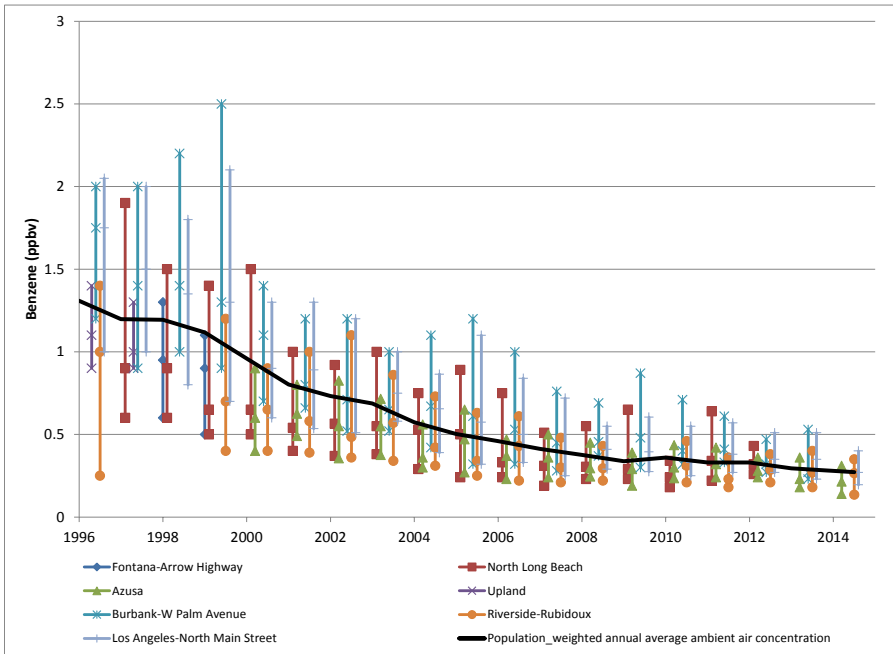
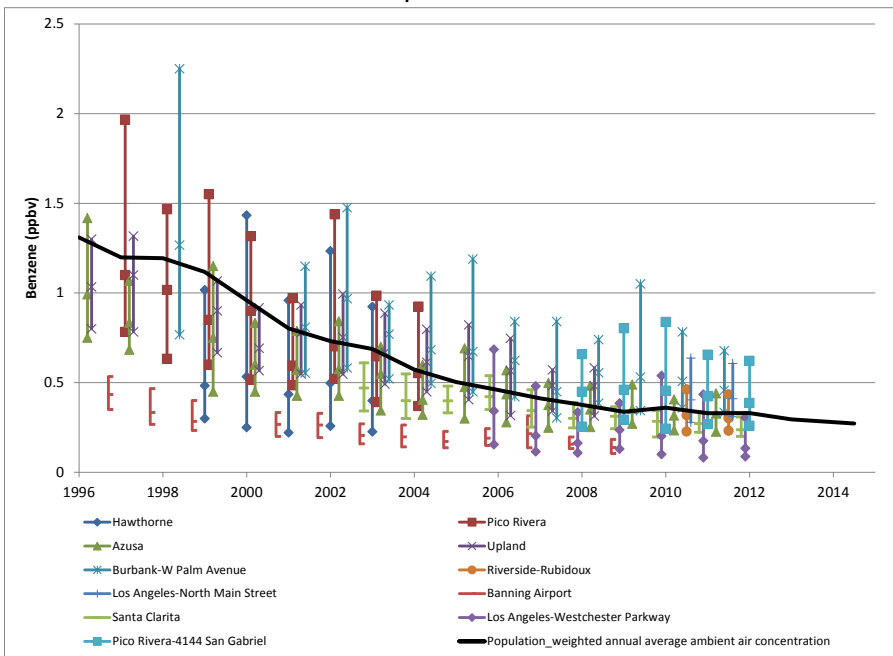


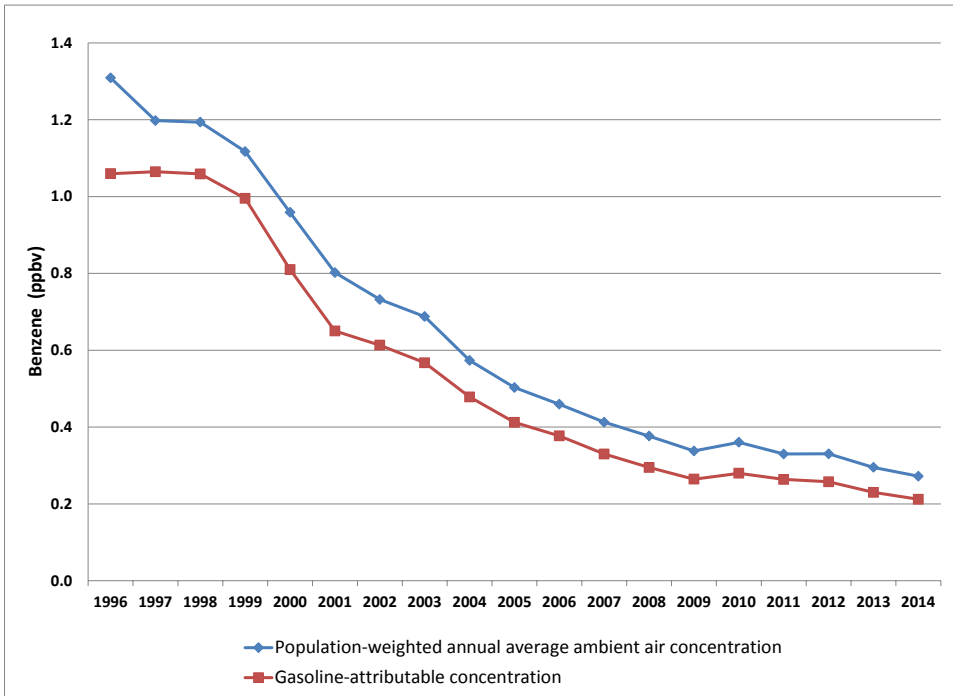
Figure 31. Population-weighted annual average ambient air concentration of benzene in the South Coast Air Basin compared to data from PAMS data²³



²³ The first quartile, median and third quartile are plotted for sites/years with ≥10 months of data.

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Figure 32. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of benzene



1,3-Butadiene: Exposure and Screening Risk Assessment Results

1,3-Butadiene is a carcinogen and had the 45th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Figure 33 shows that statewide emissions of 1,3-butadiene from gasoline-related sources declined between 1996 and 2012. Figure 34 shows the emission sources of 1,3-butadiene. Statewide, in 2012, 47% of 1,3-butadiene came from gasoline-related sources, including cars, trucks, motorcycles, off-road equipment and recreational boats. Aircraft and plastics manufacturing were non-gasoline-related sources of 1,3-butadiene. Table 16 and Figure 35 show the gasoline-attributable fractions of 1,3-butadiene. The gasoline-attributable fractions were higher in the South Coast, San Diego and San Francisco Bay Area Air Basins. In the San Joaquin Valley and Sacramento Valley Air Basins, wildfires and controlled burning (agricultural burning and forest management) contributed to 1,3-butadiene emissions and caused the gasoline-attributable fractions to be lower in these two basins.

In the Emission Inventory, estimated natural source emissions were allowed to vary more prior to 2002 than afterwards. Since natural sources, such as wildfires, were significant 1,3-butadiene sources, 1,3-butadiene emission tonnage fluctuated during these earlier years also and affected the gasoline-attributable fractions. In the San Francisco Bay Area Air Basin, the estimated emissions of 1,3-butadiene from natural sources dropped in 2002 and subsequent years, which caused the gasoline-attributable fractions to increase. Between 2004 and 2012, the gasoline-attributable fractions varied by air basin primarily because of differences in 1,3-butadiene emissions from natural sources.

The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from the California Toxic Monitoring Network and were supplemented with modeled values at additional locations. A detailed description of the model is in Appendix D. The model was based on data²⁴ from 1996-2014. By supplementing measured values with modeled values, we produced more robust estimates of population-weighted averages. The five most populated air basins (South Coast, San Diego, San Francisco Bay Area, San Joaquin Valley and Sacramento Valley Air Basins) had between two and six monitoring stations active annually between 1996 and 2014. The South Coast Air Basin had the most monitoring stations with five to six stations collecting data at any time.

Population-weighted averages were calculated for the South Coast, San Diego, San Francisco Bay Area, San Joaquin Valley and Sacramento Valley Air Basins and

²⁴ The 1,3-butadiene data from California Toxic Monitoring Network from 1996-1999 were adjusted by CARB to make earlier measurements consistent with an improved measurement technique that was used in later years (<ftp://ftp.arb.ca.gov/aqd/aqdc/d/web2011/BzButAdj.pdf>).

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statewide (see Table 17). Half the limit of detection was substituted for non-detects. Figure 36 compares the population-weighted annual average ambient air concentrations of 1,3-butadiene in the South Coast Air Basin to actual ambient air measurements from monitoring sites within the basin.

Table 18 tabulates the gasoline-attributable population-weighted annual average ambient air concentrations (referred to as gasoline-attributable concentrations) for all air basins. Figure 37 shows that the gasoline-attributable concentration of 1,3-butadiene in the South Coast Air Basin declined by 89% between 1996 and 2014.

The number of non-detects in the California Toxic Monitoring Network data increased from 11% in 2000 to 63% in 2014. The population-weighted average was calculated with half the limit of detection substituted for non-detects. For comparison, Table 19 contains population-weighted annual average concentrations of 1,3-butadiene calculated with the limit of detection substituted for non-detects. In 2014, the statewide population-weighted annual average was 25% higher (0.070 versus 0.056 ppbv) when the limit of detection was substituted for non-detects than when half the limit of detection was substituted. The discrepancy was lower in previous years.

Cancer risks and hazard quotients for non-cancer health effects were calculated based on gasoline-attributable ambient air concentrations (see Appendix G for details). The cancer risk for 1,3-butadiene in the South Coast Air Basin declined from 4.4×10^{-4} in 1996 to 3.6×10^{-5} in 2014, corresponding to a reduction of about 400 cancer cases per 1 million people. The statewide cancer risk for 1,3-butadiene declined from 1.8×10^{-4} in 1996 to 1.9×10^{-5} in 2014, or a reduction of 160 cancer cases per 1 million people. The gasoline-attributable hazard quotient for 1,3-butadiene, based on reproductive toxicity, declined from 0.33 in 1996 to 0.027 in the South Coast Air Basin in 2014. The statewide gasoline-attributable hazard quotient declined from 0.14 in 1996 to 0.015 in 2014.

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Figure 33. 1,3-Butadiene emissions from gasoline-related and non-gasoline-related sources in California (data from CARB Emission Inventory)

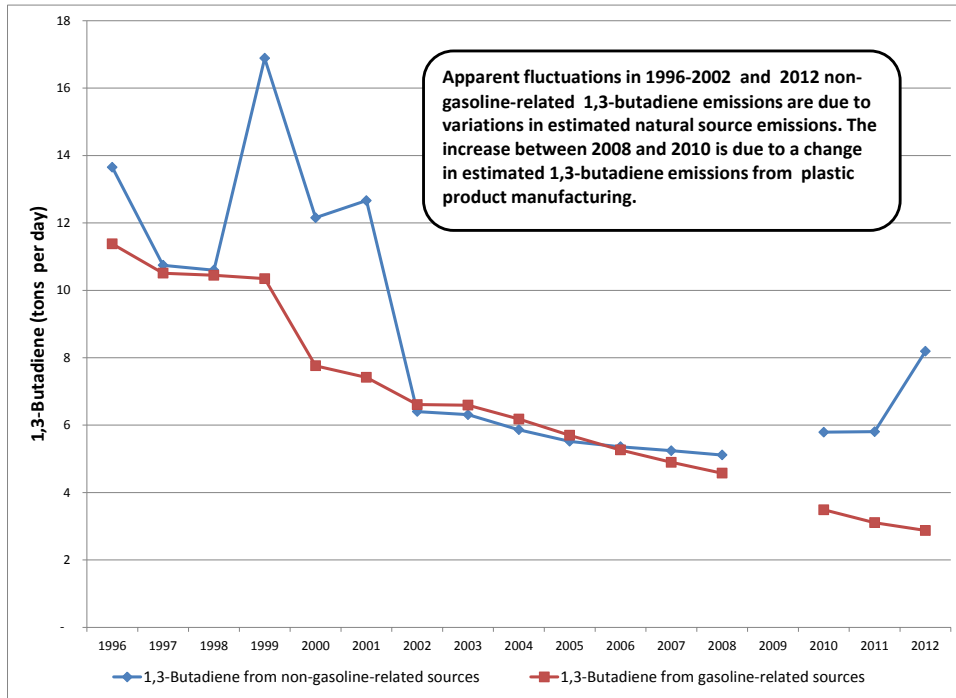
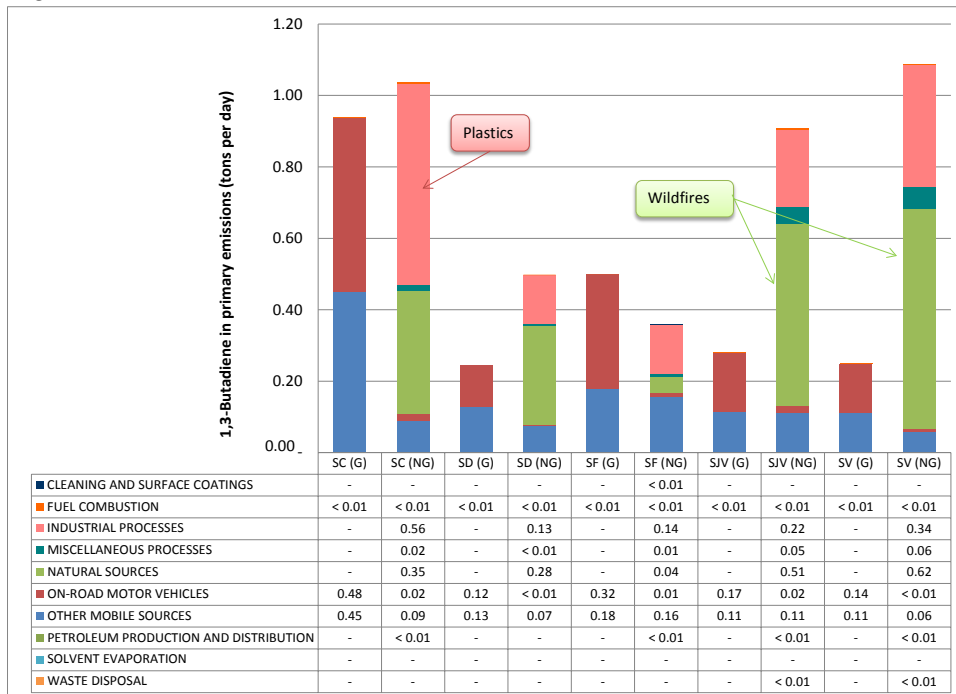


Figure 34. Emission sources of 1,3-butadiene in 2012



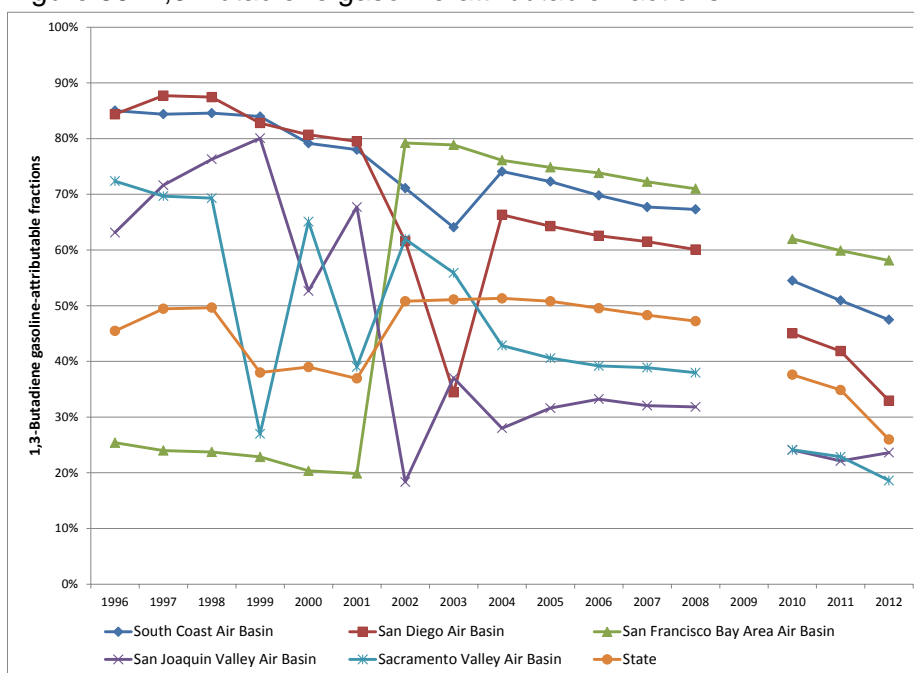
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Table 16. 1,3-Butadiene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	85%	84%	25%	63%	72%	45%
1997	84%	88%	24%	72%	70%	49%
1998	85%	87%	24%	76%	69%	50%
1999	84%	83%	23%	80%	27%	38%
2000	79%	81%	20%	53%	65%	39%
2001	78%	79%	20%	68%	39%	37%
2002	71%	62%	79%	18%	62%	51%
2003	64%	34%	79%	37%	56%	51%
2004	74%	66%	76%	28%	43%	51%
2005	72%	64%	75%	32%	41%	51%
2006	70%	63%	74%	33%	39%	50%
2007	68%	61%	72%	32%	39%	48%
2008	67%	60%	71%	32%	38%	47%
2009	--	--	--	--	--	--
2010	54%	45%	62%	24%	24%	38%
2011	51%	42%	60%	22%	23%	35%
2012	47%	33%	58%	24%	19%	26%

Note: Mobile source emissions were not available for 2009.

Figure 35. 1,3-Butadiene gasoline-attributable fractions



Note: Gasoline-attributable fractions fluctuate prior to 2002 because natural source emissions were estimated differently (see Figure 33).

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Table 17. Population-weighted annual average ambient air concentrations of 1,3-butadiene (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	0.39	0.27	0.24	0.20	0.18	0.30
1997	0.35	0.25	0.22	0.18	0.16	0.27
1998	0.35	0.25	0.23	0.21	0.17	0.28
1999	0.31	0.27	0.19	0.16	0.14	0.24
2000	0.26	0.22	0.16	0.15	0.12	0.20
2001	0.23	0.20	0.14	0.14	0.11	0.18
2002	0.20	0.18	0.13	0.13	0.12	0.16
2003	0.15	0.13	0.096	0.088	0.094	0.12
2004	0.14	0.13	0.096	0.079	0.087	0.11
2005	0.11	0.14	0.082	0.079	0.078	0.099
2006	0.10	0.12	0.072	0.073	0.078	0.090
2007	0.10	0.11	0.068	0.070	0.074	0.087
2008	0.085	0.097	0.052	0.059	0.071	0.073
2009	0.079	0.093	0.055	0.062	0.068	0.071
2010	0.078	0.082	0.054	0.047	0.054	0.067
2011	0.074	0.078	0.067	0.058	0.063	0.069
2012	0.059	0.066	0.048	0.044	0.046	0.054
2013	0.065	0.067	0.063	0.059	0.057	0.062
2014	0.057	0.059	0.054	0.057	0.045	0.056

Note: half the limit of detection substituted for non-detects

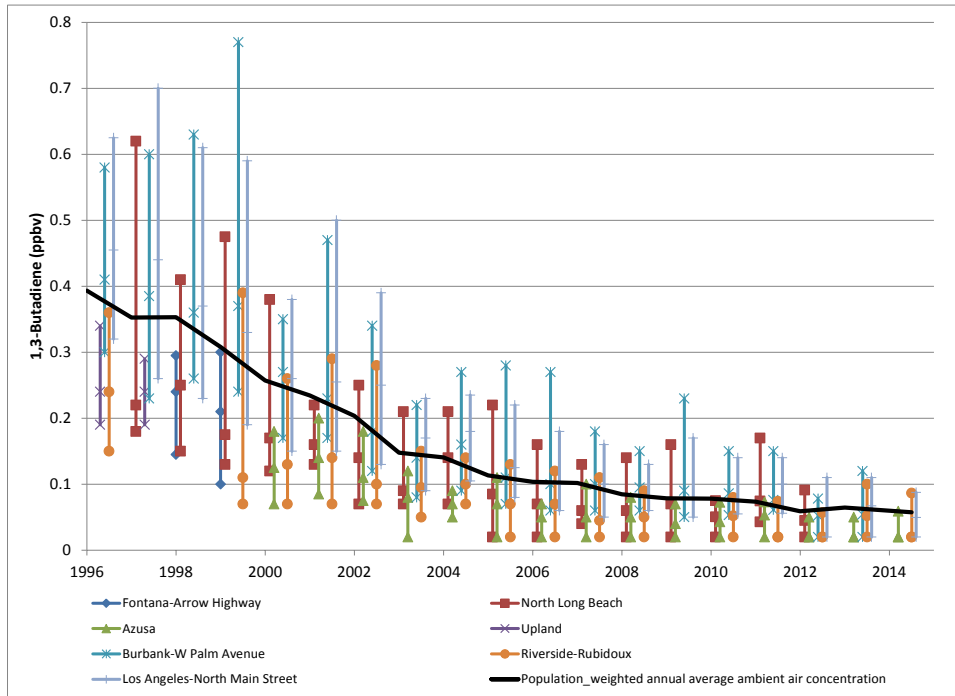
Table 18. Gasoline-attributable concentrations of 1,3-butadiene (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	0.33	0.23	0.061	0.13	0.13	0.14
1997	0.30	0.22	0.052	0.13	0.11	0.13
1998	0.30	0.22	0.055	0.16	0.12	0.14
1999	0.26	0.23	0.043	0.13	0.039	0.092
2000	0.20	0.17	0.033	0.080	0.077	0.078
2001	0.18	0.16	0.029	0.094	0.041	0.068
2002	0.14	0.11	0.10	0.024	0.072	0.083
2003	0.095	0.046	0.076	0.033	0.052	0.061
2004	0.10	0.087	0.073	0.022	0.038	0.059
2005	0.082	0.091	0.061	0.025	0.032	0.050
2006	0.072	0.076	0.053	0.024	0.030	0.045
2007	0.069	0.066	0.049	0.023	0.029	0.042
2008	0.057	0.058	0.037	0.019	0.027	0.034
2009	0.053	0.056	0.039	0.020	0.026	0.034
2010	0.043	0.037	0.033	0.011	0.013	0.025
2011	0.037	0.033	0.040	0.013	0.014	0.024
2012	0.028	0.022	0.028	0.010	0.0086	0.014
2013	0.031	0.022	0.037	0.014	0.0107	0.016
2014	0.027	0.020	0.031	0.013	0.0084	0.015

Note: The 2009 gasoline-attributable concentrations were calculated with the 2008 gasoline-attributable fractions and the 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fractions.

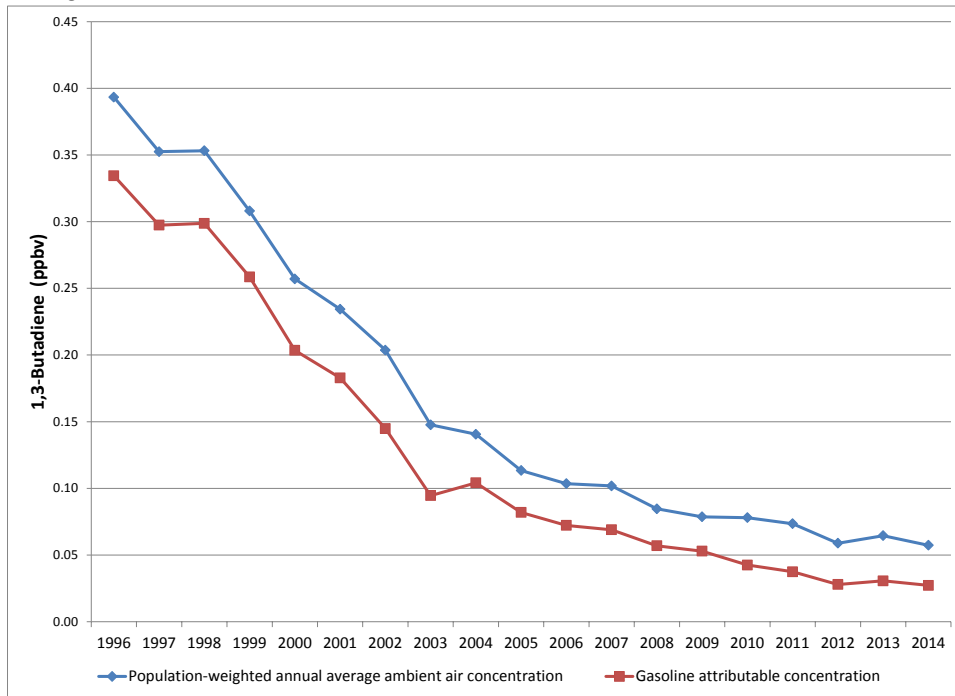
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Figure 36. Population-weighted annual average ambient air concentration of 1,3-butadiene in the South Coast Air Basin



Note: Vertical bars show the first quartile, median and third quartile of daily average concentrations for sites with ≥ 10 months of data.

Figure 37. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of 1,3-butadiene



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Table 19. Population-weighted average concentrations of 1,3-butadiene with limit of detection substituted for non-detects (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	0.39	0.27	0.24	0.20	0.18	0.30
1997	0.35	0.25	0.22	0.18	0.17	0.27
1998	0.35	0.25	0.23	0.21	0.17	0.27
1999	0.30	0.27	0.19	0.17	0.15	0.24
2000	0.26	0.22	0.16	0.16	0.12	0.20
2001	0.23	0.20	0.15	0.14	0.11	0.19
2002	0.21	0.18	0.13	0.14	0.12	0.17
2003	0.15	0.14	0.10	0.10	0.10	0.13
2004	0.15	0.14	0.11	0.088	0.10	0.12
2005	0.12	0.15	0.092	0.088	0.089	0.11
2006	0.11	0.13	0.082	0.083	0.088	0.10
2007	0.11	0.12	0.078	0.081	0.087	0.10
2008	0.094	0.11	0.064	0.070	0.083	0.083
2009	0.087	0.10	0.065	0.072	0.080	0.081
2010	0.087	0.093	0.064	0.058	0.066	0.077
2011	0.082	0.089	0.077	0.068	0.074	0.079
2012	0.072	0.080	0.063	0.059	0.062	0.068
2013	0.076	0.080	0.076	0.072	0.071	0.074
2014	0.071	0.074	0.068	0.072	0.060	0.070

Cumene: Exposure and Screening Risk Assessment Results

Cumene (isopropylbenzene) is a carcinogen and had the 140th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Estimated emissions of cumene have declined between 1996 and 2012 (see Figure 38). Figure 39 displays the breakdown of gasoline-related and non-gasoline-related sources for cumene in each air basin. Between 1996 and 2012, gasoline-attributable fractions ranged from 38% to 57% across the air basins. In 2012, a little less than half of ambient cumene came from gasoline-related sources statewide (see Table 20 and Figure 40).

Population-weighted annual average concentrations were calculated for the South Coast Air Basin. The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from PAMS and was supplemented with modeled values at additional locations (see Table 21). Figure 41 shows the population-weighted annual average concentration along with measured data from South Coast Air Basin monitoring sites. Figure 42 shows that the gasoline-attributable concentration of cumene declined by 80% between 1996 and 2014 in the South Coast Air Basin.

A cancer risk assessment was not carried out for cumene because a cancer potency value has not been developed. US EPA (2007) developed a chronic reference concentration (RfC) of 0.4 mg/m³ (80 ppb) for cumene, with the endocrine and urinary systems as targets for toxicity. Hazard quotients based on gasoline-attributable concentrations in the South Coast Air Basin were all well below 1, decreasing from 6.3x10⁻⁴ in 1996 to 1.3x10⁻⁴ in 2014. There were inadequate data to calculate a statewide hazard quotient for cumene.

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Figure 38. Cumene emissions from gasoline-related and non-gasoline-related sources in California (data from CARB Emission Inventory)

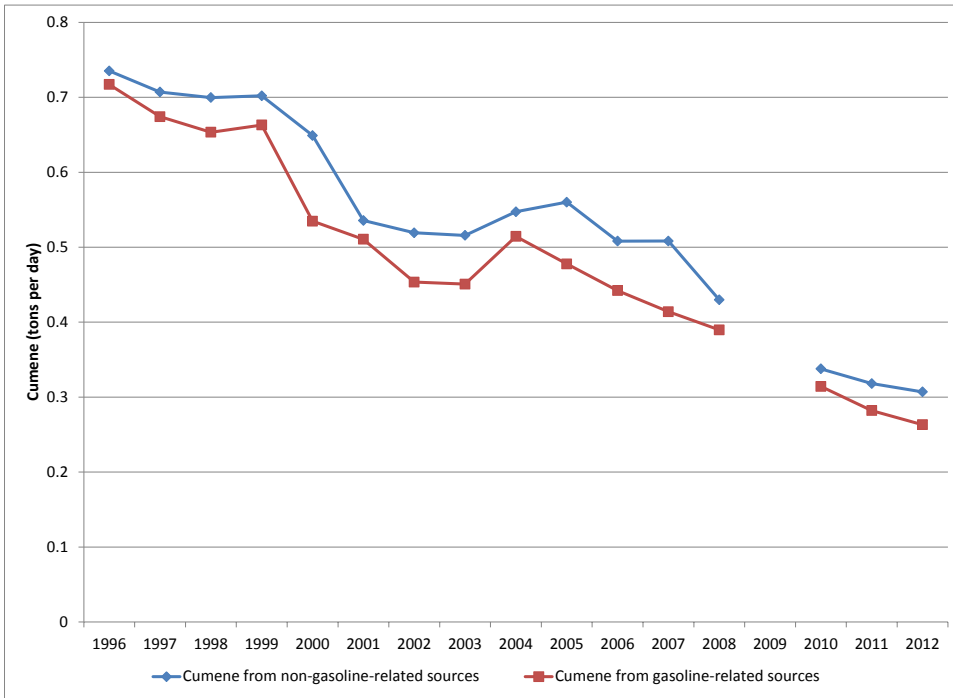
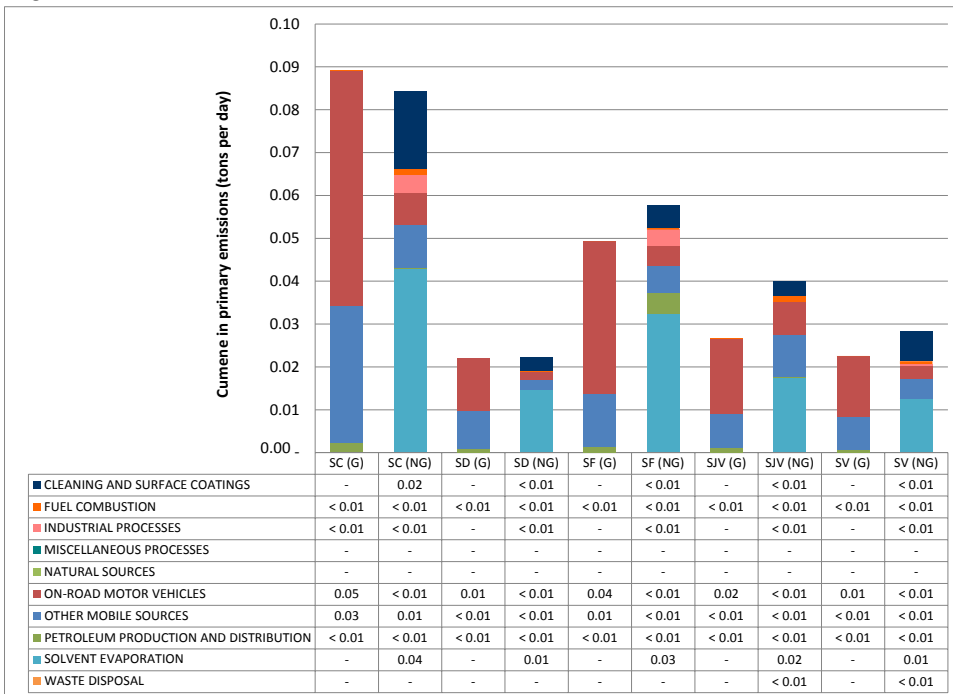


Figure 39. Emission sources of cumene in 2012



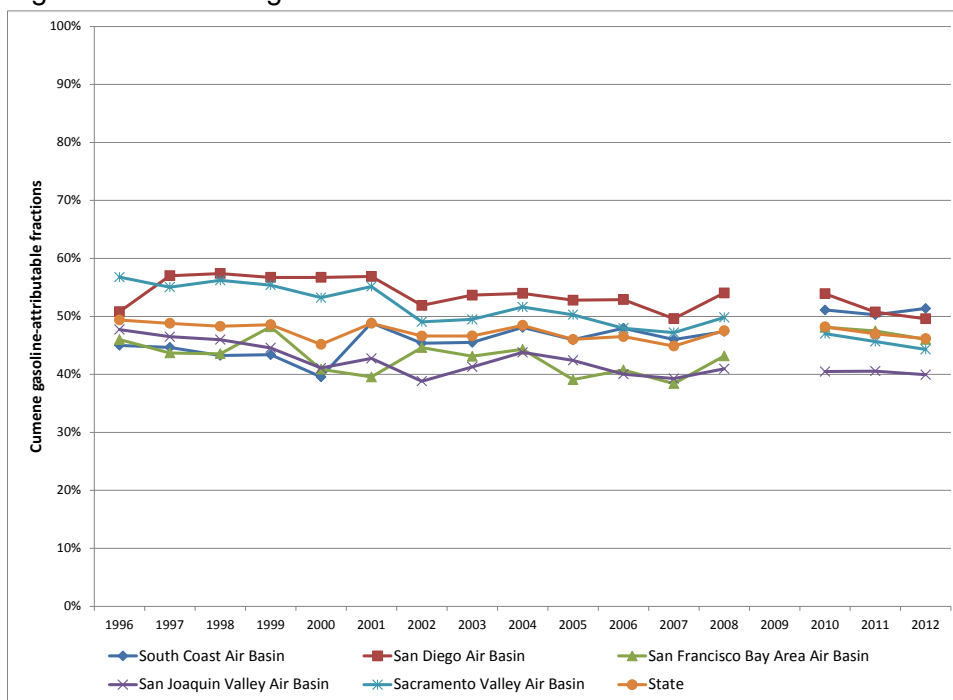
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Table 20. Cumene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	45%	51%	46%	48%	57%	49%
1997	45%	57%	44%	47%	55%	49%
1998	43%	57%	44%	46%	56%	48%
1999	43%	57%	48%	45%	55%	49%
2000	40%	57%	41%	41%	53%	45%
2001	49%	57%	40%	43%	55%	49%
2002	45%	52%	45%	39%	49%	47%
2003	46%	54%	43%	41%	49%	47%
2004	48%	54%	44%	44%	52%	48%
2005	46%	53%	39%	42%	50%	46%
2006	48%	53%	41%	40%	48%	47%
2007	46%	50%	38%	39%	47%	45%
2008	47%	54%	43%	41%	50%	48%
2009	--	--	--	--	--	--
2010	51%	54%	48%	40%	47%	48%
2011	50%	51%	47%	41%	46%	47%
2012	51%	50%	46%	40%	44%	46%

Note: Mobile source emissions were not available for 2009.

Figure 40. Cumene gasoline-attributable fractions



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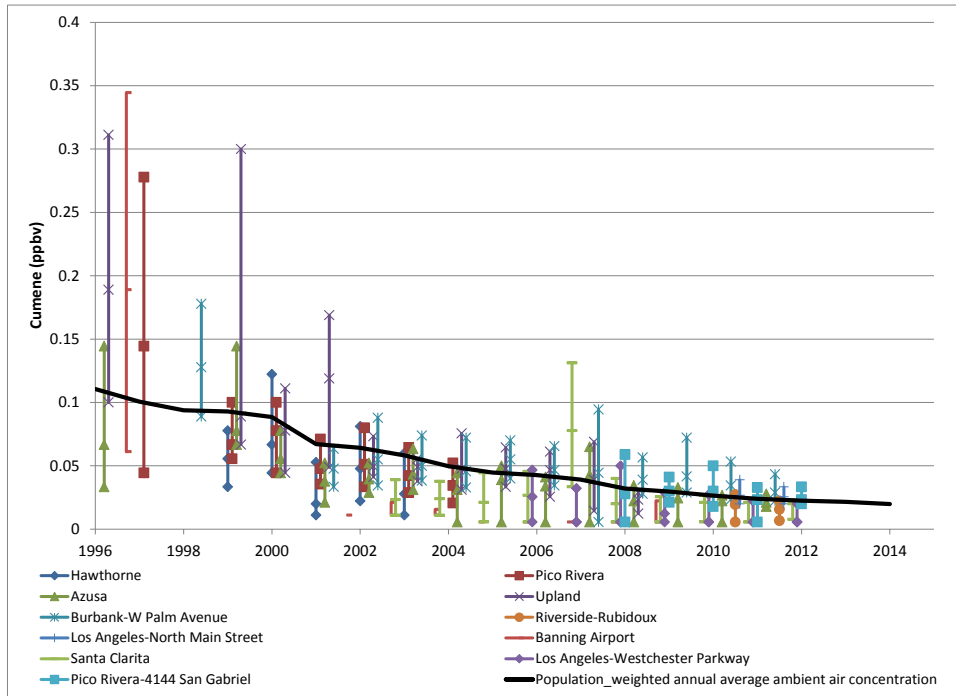
Table 21. Cumene results for the South Coast Air Basin

Year	Population-weighted average concentration of cumene (ppbv)	Gasoline-attributable fraction	Gasoline-attributable concentration (ppbv)
1996	0.11	45%	0.050
1997	0.10	45%	0.045
1998	0.094	43%	0.041
1999	0.093	43%	0.040
2000	0.088	40%	0.035
2001	0.067	49%	0.033
2002	0.064	45%	0.029
2003	0.058	46%	0.027
2004	0.050	48%	0.024
2005	0.045	46%	0.021
2006	0.043	48%	0.020
2007	0.039	46%	0.018
2008	0.032	47%	0.015
2009	0.030	47%	0.014
2010	0.027	51%	0.014
2011	0.024	50%	0.012
2012	0.023	51%	0.012
2013	0.022	51%	0.011
2014	0.020	51%	0.010

Note: The 2009 gasoline-attributable concentrations were calculated with the 2008 gasoline-attributable fractions. The 2012 - 2014 population-weighted averages were based completely on modeled values (see Figure 41). The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fractions.

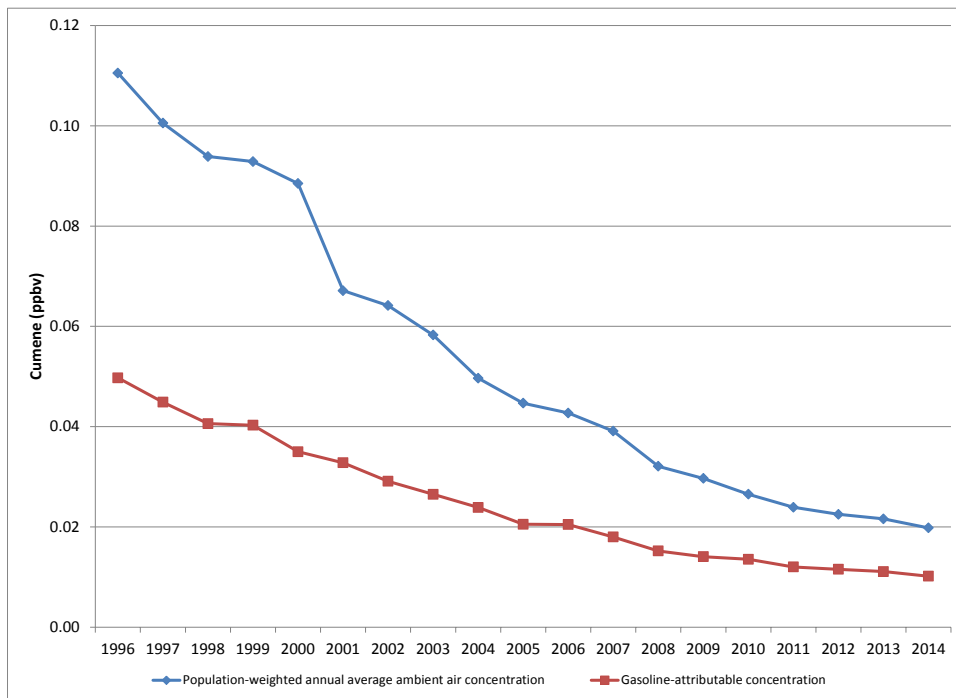
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Figure 41. Population-weighted annual average ambient air concentration of cumene in the South Coast Air Basin



Note: Vertical bars show the quartiles for sites with ≥ 10 months of data.

Figure 42. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of cumene



Ethanol: Exposure Assessment Results

Ethanol had the 2nd highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Gasoline-attributable fractions of ethanol increased in 2004 due to its use as a replacement for the oxygenate MTBE. In 2004, California gasoline contained about 5.7% added ethanol by volume but that percentage increased over time to the maximum allowed percentage of 10%. Figure 43 shows that the estimated statewide daily emissions of ethanol from gasoline-related sources increased from 3 tons in 2003 to 62 tons in 2004. Fifty-four percent of this increase came from on-road mobile sources, 36% came from other mobile sources, and 10% came from petroleum production and distribution. Figure 44 shows the components of the driving cycle of on-road mobile sources that contributed to the increase, with 35% coming from changes in emissions during engine starts and hot stabilized exhaust and the remaining 65% coming from changes in evaporative emissions.

In 2012, less ethanol was emitted from gasoline-related sources than from non-gasoline-related sources, such as livestock and consumer products (see Figure 45). Gasoline-attributable fractions are shown in Table 22 and Figure 46. The gasoline-attributable fraction for ethanol in the San Joaquin Valley Air Basin is substantially lower than in other basins because of the extensive emissions from livestock, consumer products and industrial processes (e.g., winemaking).

A number of studies have researched changes over time in pollutant emissions associated with the use of reformulated gasoline in California (see for example, Harley et al, 2006; Kirchstetter et al., 1999), including the impact of adding ethanol. In a study of seven vehicles, Karavalakis et al. (2011) found that NO_x emissions increased with increasing ethanol content in gasoline burned by older vehicles but was roughly constant in newer vehicles. These authors also found that acetaldehyde emissions increased with increasing ethanol content in two vehicles (one older and one newer), as predicted in the CARB, OEHHA and SWRCB (1999) study. Other VOC emissions either declined or remained roughly constant with increasing ethanol content.

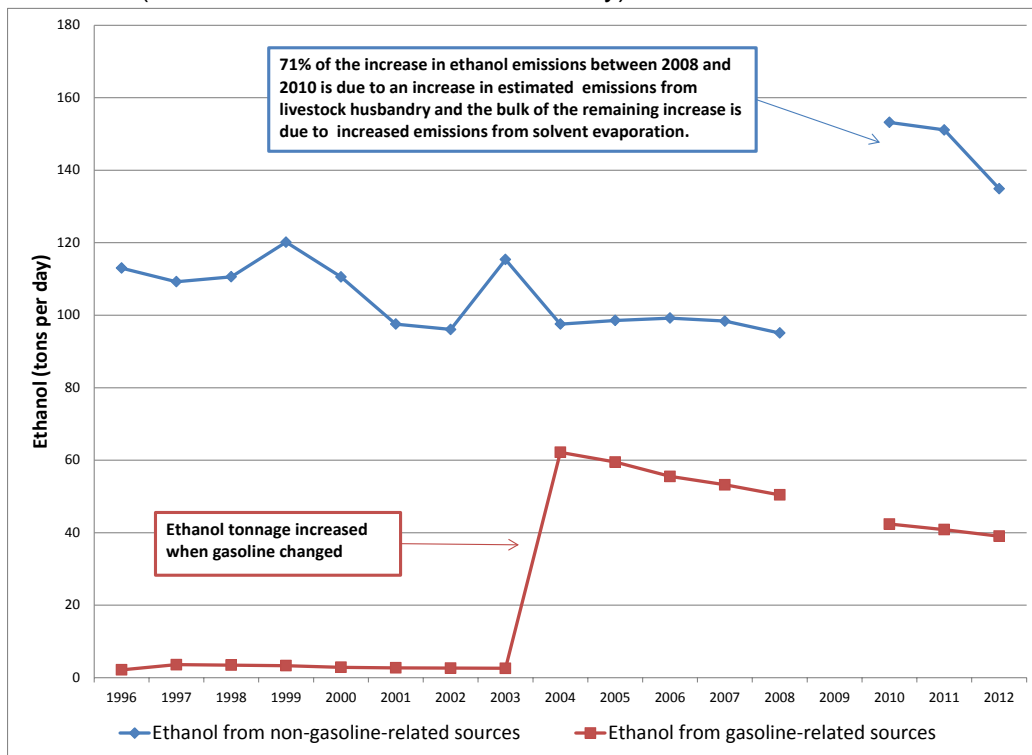
In the CARB, OEHHA and SWRCB (1999) study of the use of ethanol as an oxygenate in California gasoline, ambient air concentrations of ethanol under different fuel formulation scenarios were estimated for the South Coast Air Basin (see Table 4.8 on page 36 of volume 3 of that report). Based on the use of fuel, which was 10% by volume (3.5% oxygen by weight), the estimated maximum daily average air concentration was between 75 and 81 ppb and the estimated population-weighted annual average air concentration was 8.8 ppb.

We looked for ambient air measurements of ethanol to compare with the predictions made in the CARB, OEHHA and SWRCB (1999) study. The measurements that were available came from sites in the San Francisco Bay Area Air Basin from 2012 to 2015 (see Table 23). When these measurements were made, California gasoline was 10%

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ethanol as in the study model. The measured maximum concentrations rarely exceeded the maximums predicted in the study for the South Coast Air Basin. The maximum daily average ethanol concentrations exceeded the maximum estimate of 75 ppb at 5 of 18 sites in 2012, 2 of 19 sites in 2013, 1 of 21 sites in 2014 and 0 of 19 sites in 2015. The population-weighted annual averages could be compared to the annual average predicted in the model. The population-weighted annual average ambient air concentrations of ethanol for the San Francisco Bay Area Air Basin were 20, 9.0, 8.0 and 7.9 ppb in 2012 to 2015. When two sites with large outliers were excluded from the dataset for this air basin, the population-weighted annual average ambient air concentrations of ethanol were 16, 8.0, 7.0 and 7.0 ppb between 2012 and 2015. These values are in the same range as the projected value of 8.8 ppb for 2003 in the South Coast Air Basin.

Figure 43. Ethanol emissions from gasoline-related and non-gasoline-related sources in California (data from CARB Emission Inventory)



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Figure 44. Components of the driving cycle of gasoline-related on-road mobile sources that contributed to the increase in ethanol emissions between 2003 and 2004.²⁵

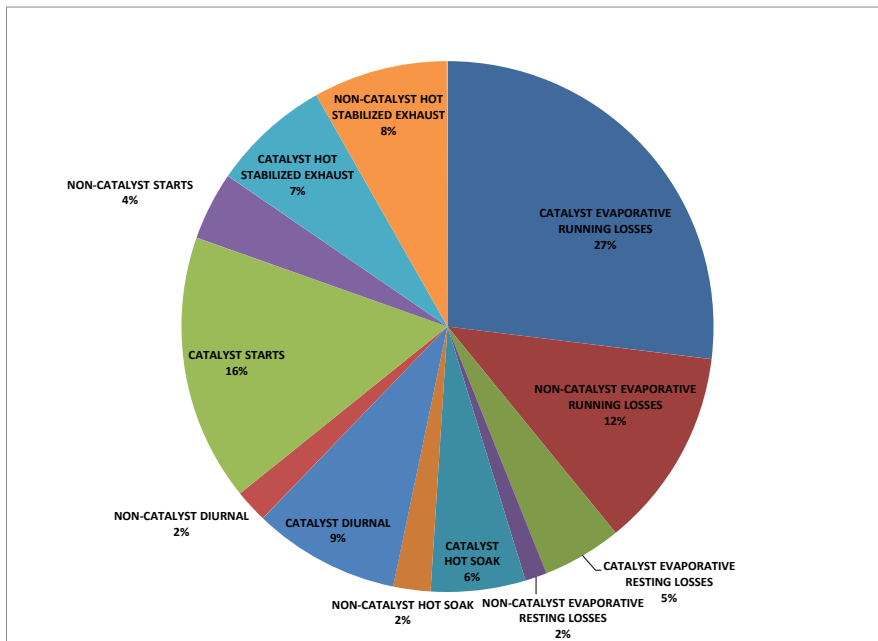
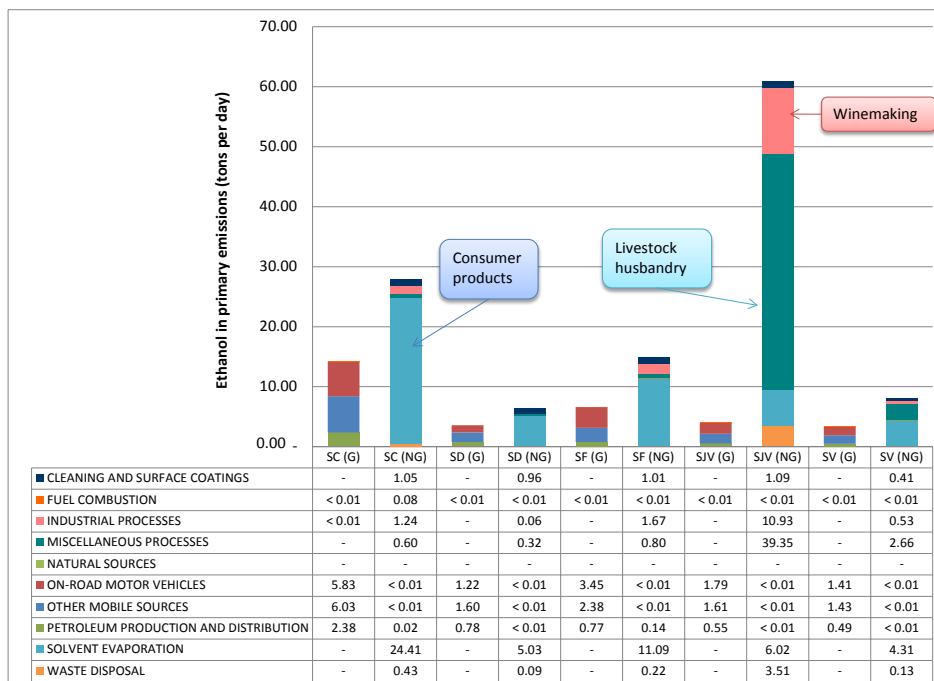


Figure 45. Emission sources of ethanol in 2012



²⁵ “Resting loss” emissions occur during periods of constant or decreasing temperature. “Start” emissions occur in the first few minutes of engine operation. “Hot soak” emissions occur during the first hour after engine shutdown. “Diurnal” emissions occur during daytime heating of fuel delivery systems (Scott et al., 1999).

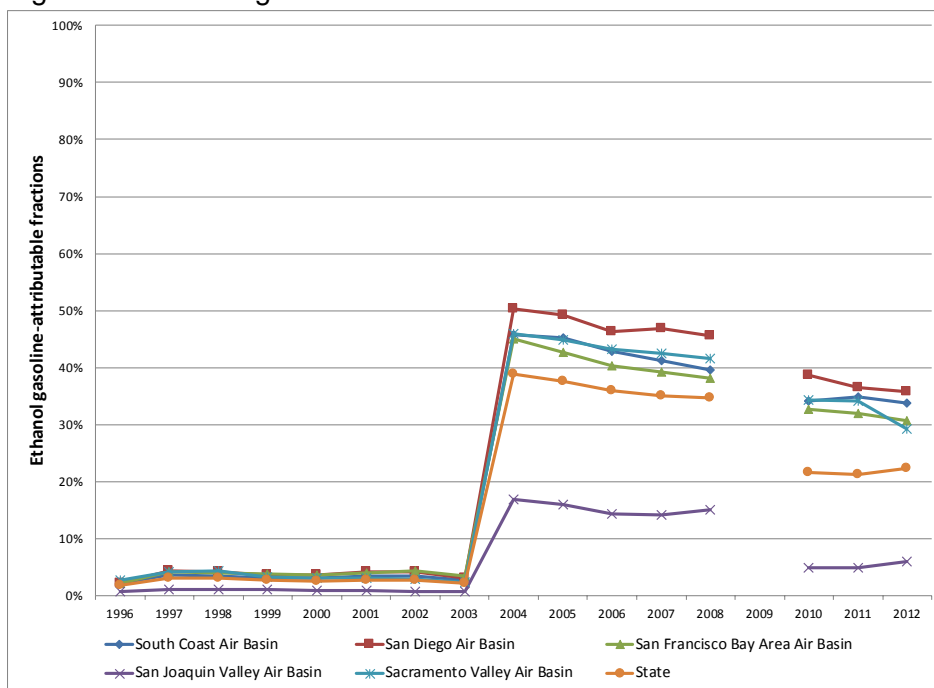
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Table 22. Ethanol gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	2%	2%	2%	1%	3%	2%
1997	4%	4%	4%	1%	4%	3%
1998	3%	4%	4%	1%	4%	3%
1999	3%	4%	4%	1%	3%	3%
2000	3%	4%	4%	1%	3%	3%
2001	4%	4%	4%	1%	3%	3%
2002	4%	4%	4%	1%	3%	3%
2003	3%	3%	3%	1%	2%	2%
2004	46%	50%	45%	17%	46%	39%
2005	45%	49%	43%	16%	45%	38%
2006	43%	46%	40%	14%	43%	36%
2007	41%	47%	39%	14%	43%	35%
2008	40%	46%	38%	15%	42%	35%
2009	--	--	--	--	--	--
2010	34%	39%	33%	5%	34%	22%
2011	35%	37%	32%	5%	34%	21%
2012	34%	36%	31%	6%	29%	22%

Note: Mobile source emissions were not available for 2009.

Figure 46. Ethanol gasoline-attributable fractions



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Table 23. Ethanol ambient air measurements from San Francisco Bay Area Air Basin (ppbv)

County Name	Site Name	Year	N	Mean	Standard deviation	Minimum	Frist quartile	Median	Third quartile	95 th percentile	Maximum
Alameda	Fremont-Chapel Way	2008	19	17.1	19.8	5.1	6.1	9.8	16.5	90.0	90.0
	Livermore-793 Rincon Avenue	2012	28	12.4	11.8	2.2	5.5	8.3	14.6	33.8	58.5
		2013	31	7.3	6.9	1.1	2.5	5.0	8.0	22.5	31.1
		2014	29	4.8	3.0	1.5	3.0	3.8	5.1	12.2	13.5
		2015	24	5.7	7.8	0.9	2.3	3.5	6.5	11.9	40.0
	Oakland-9925 International Blvd	2012	30	22.1	17.1	7.2	10.0	17.8	28.6	61.2	83.8
		2013	31	9.7	7.5	3.2	5.1	8.6	11.7	32.7	35.4
		2014	30	5.4	1.9	2.5	4.2	5.3	6.3	8.8	9.1
		2015	25	5.4	3.1	1.8	3.3	4.3	6.6	10.4	14.5
	Oakland-9925 International Blvd #11	2012	30	15.0	17.8	3.6	6.4	9.3	13.6	40.2	96.2
		2013	31	8.8	15.3	1.1	2.7	4.5	8.9	38.8	82.3
		2014	29	4.0	3.0	1.2	2.0	3.0	5.5	7.2	16.2
		2015	25	3.4	3.2	0.6	1.2	1.9	4.2	9.2	14.1
	Oakland-Laney College	2014	28	3.4	2.0	1.0	2.2	3.0	4.1	6.7	10.8
2015		25	3.1	2.0	0.9	1.7	2.4	5.0	6.2	7.9	
Contra Costa	Bethel Island Road	2012	30	10.0	6.8	3.9	5.3	7.6	11.3	22.1	35.2
		2013	22	4.0	3.0	1.4	1.8	3.4	4.6	9.4	14.1
		2014	29	3.3	2.2	1.1	1.9	2.4	3.9	7.9	9.4
		2015	25	4.2	3.4	0.7	1.6	3.0	5.5	11.6	12.6
	Concord-2975 Treat Blvd	2012	30	9.5	8.4	2.4	4.6	5.7	13.9	28.3	38.8
		2013	31	4.0	3.0	0.9	1.8	2.8	6.0	12.4	13.1
		2014	30	2.6	1.4	0.1	1.8	2.2	3.1	5.6	7.0
		2015	25	2.0	1.1	0.6	1.1	1.7	3.1	3.7	4.0
	Crockett-Kendall Avenue	2012	29	4.9	5.4	0.1	1.7	3.3	5.4	13.3	26.3
		2013	29	2.8	2.3	0.4	1.1	2.0	4.0	7.9	9.7
		2014	30	1.7	2.4	0.5	0.8	1.1	1.5	4.5	13.3
		2015	25	1.3	0.7	0.3	0.7	1.1	1.5	2.5	2.8
	Martinez-Jones Street	2012	30	8.6	8.3	2.9	4.4	6.3	9.8	36.1	39.2
		2013	30	4.2	3.2	0.8	1.8	3.1	5.5	11.4	14.1
		2014	29	2.7	1.4	1.1	1.6	2.4	3.2	5.8	6.5
		2015	25	2.2	1.4	0.6	1.0	1.7	3.7	4.2	4.9
	Richmond-7th Street	2012	29	9.9	7.0	3.6	5.2	7.9	12.0	18.0	38.7
		2013	30	5.9	5.0	0.9	2.3	4.1	7.7	18.1	19.1
		2014	30	2.5	1.5	0.7	1.7	2.2	2.8	5.3	6.8
		2015	24	2.1	1.7	0.3	0.8	1.4	3.1	5.1	7.3
San Pablo-Rumrill Blvd	2012	30	10.3	6.3	4.2	6.7	8.4	11.6	29.5	29.8	
San Pablo-Rumrill Blvd	2013	31	4.9	3.1	0.9	2.7	4.0	6.7	9.4	16.2	
	2014	30	3.3	1.5	1.4	2.3	2.8	3.6	6.7	7.6	
	2015	24	2.7	1.1	1.2	1.8	2.4	3.5	4.4	5.4	
Marin	Fort Cronkhite	2012	30	0.7	0.7	0.1	0.1	0.6	0.9	1.6	3.6
		2013	29	0.3	0.3	0.1	0.1	0.3	0.4	0.8	1.5
		2014	29	1.8	3.0	0.1	0.2	0.5	2.6	5.5	15.1
		2015	25	1.7	0.5	1.1	1.3	1.7	2.0	2.8	3.0
	San Rafael	2012	30	20.9	19.5	4.0	6.4	13.8	26.1	69.5	74.3
		2013	30	7.6	12.1	1.5	2.9	4.7	6.6	37.5	61.9
		2014	28	5.5	5.4	1.8	2.8	4.0	6.8	10.7	29.7
		2015	24	3.6	1.7	1.1	2.1	3.4	5.0	6.2	7.2

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County Name	Site Name	Year	N	Mean	Standard deviation	Minimum	Frist quartile	Median	Third quartile	95 th percentile	Maximum
Napa	Napa-Jefferson Avenue	2012	28	78.6	72.8	10.8	28.4	51.4	110.7	244.0	334.3
		2013	28	37.1	51.4	9.3	15.7	21.7	36.0	166.0	253.3
		2014	29	18.4	10.6	0.1	8.8	18.6	25.6	35.6	38.0
		2015	24	13.1	9.6	0.3	6.1	12.7	18.7	32.1	33.2
San Francisco	San Francisco-Arkansas Street	2012	30	26.8	42.4	7.2	10.2	13.9	19.4	90.9	227.4
		2013	33	10.5	11.1	2.6	3.7	7.2	12.7	36.4	57.7
		2014	34	8.0	6.4	2.0	3.8	5.9	9.5	25.4	26.0
		2015	27	6.5	4.9	1.6	3.2	5.2	7.2	16.6	22.8
San Mateo	Redwood City	2012	29	23.5	12.6	11.1	13.8	17.7	33.6	46.6	58.3
		2013	30	9.7	6.6	2.5	5.2	8.8	12.8	27.6	29.9
		2014	28	14.4	15.7	4.8	6.4	8.3	15.8	51.2	77.9
		2015	24	10.8	5.5	3.8	6.8	9.4	12.0	20.1	25.7
Santa Clara	Cupertino-Monte Vista Park	2012	61	11.4	7.0	2.7	6.4	10.0	14.9	23.9	37.7
		2013	59	4.0	2.6	1.0	2.4	3.6	5.0	10.0	17.1
	San Jose-Jackson Street	2008	59	27.3	14.0	0.3	18.7	25.9	31.8	58.0	69.2
		2009	52	15.9	13.4	4.5	8.6	11.9	16.9	51.1	70.6
		2010	61	11.6	4.3	4.0	8.2	11.1	14.3	18.2	22.7
		2011	60	12.3	5.7	3.7	8.1	11.7	16.1	22.9	25.9
		2012	59	27.1	17.2	3.3	15.8	22.6	35.4	53.3	115.1
		2013	60	12.0	10.8	2.3	5.9	9.3	15.1	23.8	61.6
		2014	60	11.6	6.9	1.1	6.2	9.8	15.1	26.5	32.7
	2015	50	15.1	5.7	7.0	10.2	13.4	18.4	26.8	28.8	
	San Jose-Knox Avenue	2014	13	5.6	2.8	2.8	3.6	5.2	6.6	12.4	12.4
		2015	23	4.1	2.7	1.0	2.3	3.5	5.8	9.5	11.8
Solano	Vallejo-304 Tuolumne Street	2012	30	8.7	12.5	1.6	3.4	5.0	8.5	23.5	69.6
		2013	28	5.6	5.6	0.9	1.2	4.1	8.2	14.2	25.4
		2014	28	3.4	2.7	0.9	1.7	2.3	4.3	7.8	12.7
		2015	25	2.3	1.5	0.6	1.1	1.7	3.2	4.9	5.9
Sonoma	Santa Rosa-5th Street	2012	28	5.9	4.4	2.0	3.1	4.7	7.2	13.0	23.4
		2013	28	5.5	4.5	0.9	2.6	4.2	6.9	14.9	19.6
	Sebastopol	2014	28	4.5	3.4	1.7	2.8	3.4	5.0	13.1	16.2
		2015	25	3.1	2.1	1.0	1.7	2.4	4.1	6.8	9.7

Note: Summary statistics for 2015 measurements were based on data from January to October.

Ethylbenzene: Exposure and Screening Risk Assessment Results

Ethylbenzene is a carcinogen and had the 23rd highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Figure 47 shows the decline of estimated ethylbenzene emissions from gasoline-related sources between 1996 and 2012.

Gasoline-related sources of ethylbenzene included light duty passenger cars and trucks (see Figure 48). Table 24 and Figure 49 show that the gasoline-attributable fractions for ethylbenzene remained close to 80% between 1996 and 2012. The apparent increases in gasoline-attributable fractions from the San Francisco Bay Area and statewide in 2002 were due to an adjustment by CARB of natural source emissions in the Emission Inventory. In particular, "non-agricultural biogenic sources", a component of "natural sources" was removed from San Francisco Bay Area Emission Inventory causing the ethylbenzene gasoline-attributable fractions to increase in 2002.

Population-weighted annual average concentrations were calculated for the South Coast Air Basin (see Table 25). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from PAMS and was supplemented with modeled values at additional locations to produce more robust estimates. Figure 50 shows the population-weighted annual average concentration along with the quartiles of measured data from South Coast Air Basin monitoring sites. Figure 51 shows that gasoline-attributable concentrations of ethylbenzene declined by 81% between 1996 and 2014.

Cancer risks were calculated based on gasoline-attributable ambient air concentrations (see Appendix G for details). The gasoline-attributable cancer risk for ethylbenzene in the South Coast Air Basin declined from 1.8×10^{-5} in 1996 to 3.3×10^{-6} in 2014, corresponding to a reduction of an estimated 14 cancer cases per 1 million people. There were inadequate data to calculate a statewide cancer risk for ethylbenzene.

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Figure 47. Ethylbenzene emissions from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

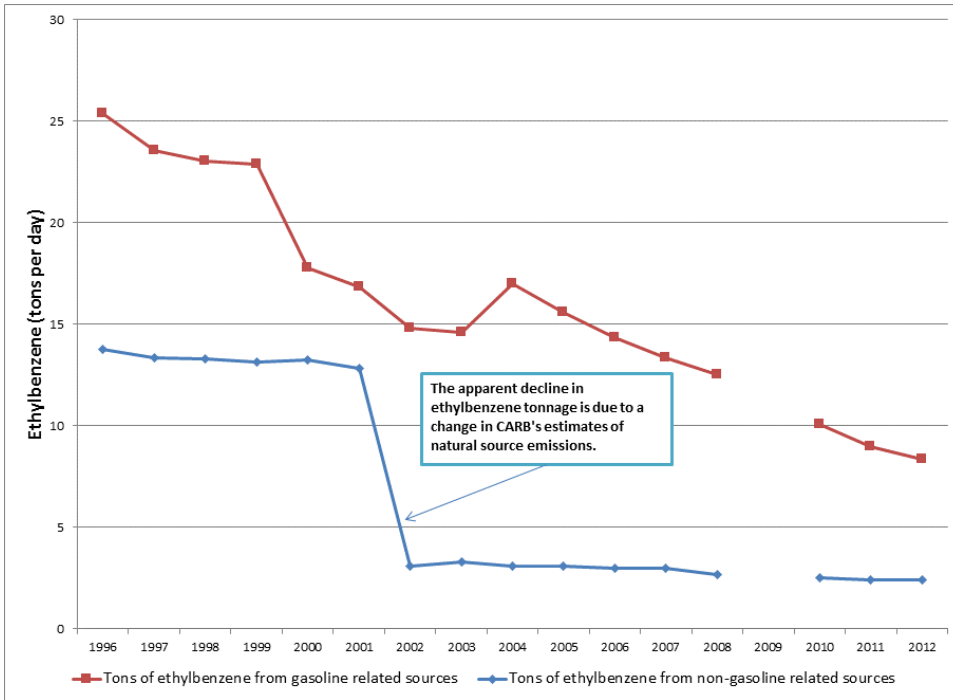
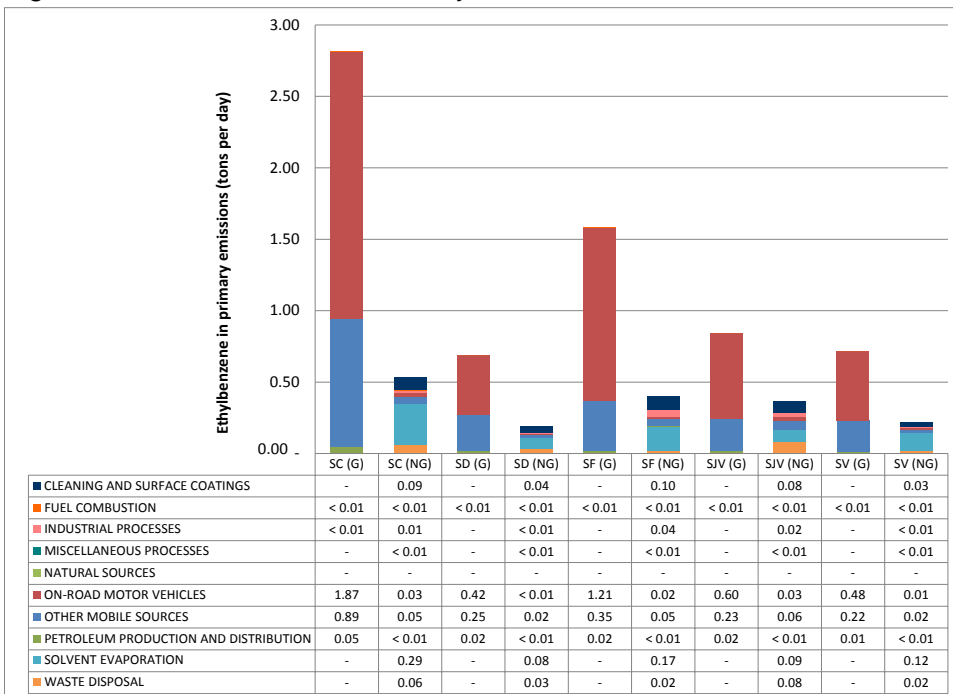


Figure 48. Emission sources of ethylbenzene in 2012



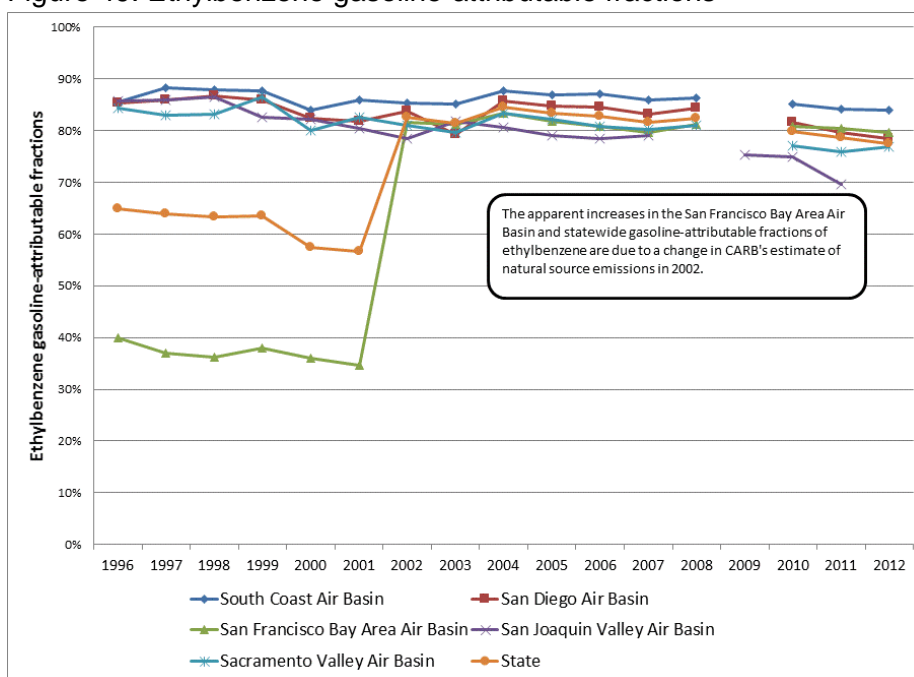
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Table 24. Ethylbenzene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	86%	85%	40%	86%	84%	65%
1997	88%	86%	37%	86%	83%	64%
1998	88%	87%	36%	86%	83%	63%
1999	88%	86%	38%	86%	87%	64%
2000	84%	82%	36%	82%	80%	57%
2001	86%	82%	35%	82%	83%	57%
2002	85%	84%	82%	80%	81%	83%
2003	85%	79%	81%	78%	80%	81%
2004	88%	86%	83%	82%	83%	85%
2005	87%	85%	82%	81%	82%	83%
2006	87%	85%	81%	79%	81%	83%
2007	86%	83%	80%	78%	80%	82%
2008	86%	84%	81%	79%	81%	82%
2009	--	--	--	--	--	--
2010	85%	82%	81%	75%	77%	80%
2011	84%	80%	80%	75%	76%	79%
2012	84%	78%	80%	70%	77%	78%

Note: Mobile source emissions were not available for 2009.

Figure 49. Ethylbenzene gasoline-attributable fractions



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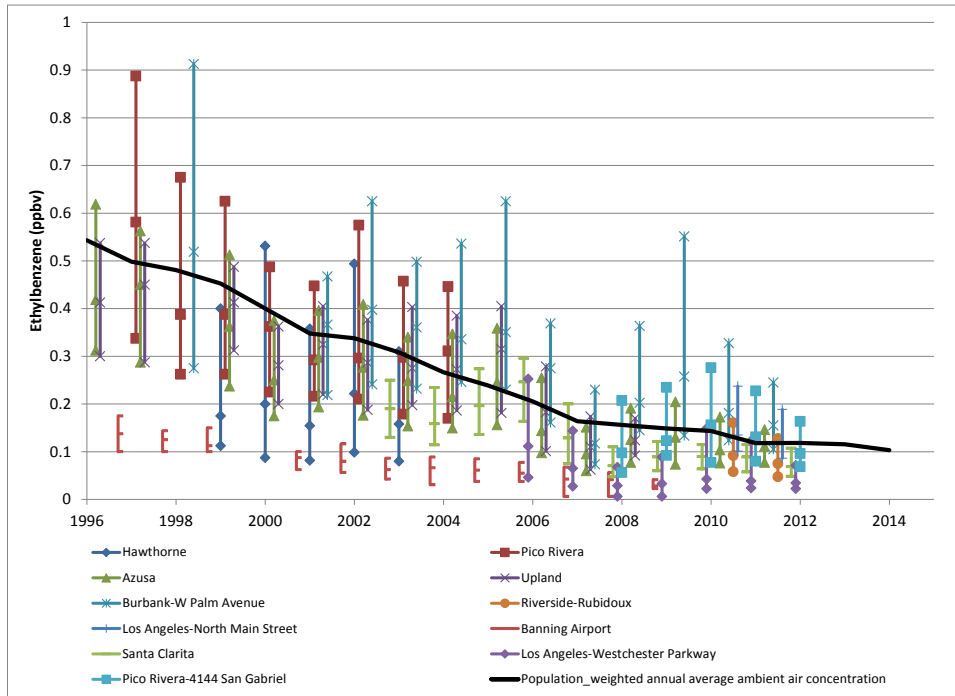
Table 25. Ethylbenzene results for the South Coast Air Basin

Year	Population-weighted annual average ambient air concentration of ethylbenzene (ppbv)	Gasoline-attributable fraction	Gasoline-attributable concentration (ppbv)
1996	0.54	86%	0.46
1997	0.50	88%	0.44
1998	0.48	88%	0.42
1999	0.45	88%	0.40
2000	0.40	84%	0.34
2001	0.35	86%	0.30
2002	0.34	85%	0.29
2003	0.31	85%	0.26
2004	0.27	88%	0.23
2005	0.24	87%	0.21
2006	0.21	87%	0.18
2007	0.16	86%	0.14
2008	0.16	86%	0.13
2009	0.15	86%	0.13
2010	0.14	85%	0.12
2011	0.12	84%	0.10
2012	0.12	84%	0.10
2013	0.12	84%	0.097
2014	0.10	84%	0.087

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2012 - 2014 population-weighted averages were based completely on modeled values (see Figure 50). The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

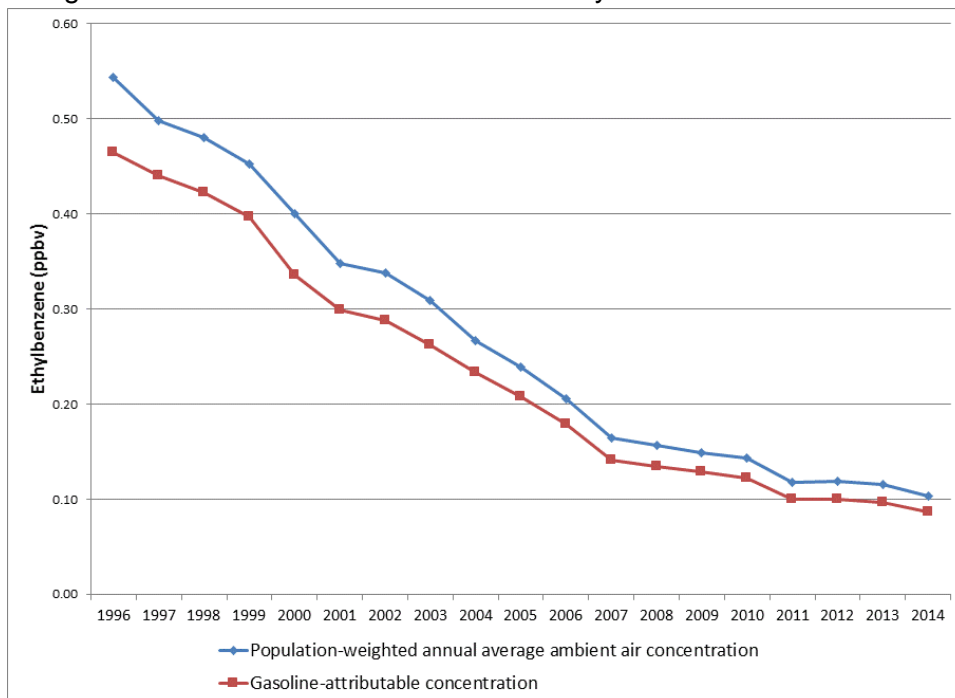
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Figure 50. Population-weighted annual average ambient air concentration of ethylbenzene in the South Coast Air Basin



Note: Vertical bars show the quartiles for sites with ≥ 10 months of data.

Figure 51. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of ethylbenzene



***n*-Hexane: Exposure and Screening Risk Assessment Results**

n-Hexane is a neurotoxicant and had the 18th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Figure 52 shows the decline in estimated gasoline-related *n*-hexane emissions in California between 1996 and 2012.

Figure 53 displays *n*-hexane emission sources. Table 26 and Figure 54 show *n*-hexane gasoline-attributable fractions. Statewide, in 2012, 63% of total *n*-hexane emissions came from gasoline-related sources. In the South Coast and San Diego Air Basins, about two-thirds of *n*-hexane emissions came from gasoline-related sources. In the San Francisco Bay Area, Sacramento Valley and San Joaquin Valley Air Basins roughly equal amounts of *n*-hexane were produced by gasoline and non-gasoline-related sources. There were many substantial non-gasoline-related sources of *n*-hexane, with examples including: consumer products (all air basins); fugitive losses from oil and gas production (San Joaquin Valley and Sacramento Valley Air Basins); plastic manufacturing (South Coast, San Diego, San Joaquin and Sacramento Air Basins); fiberglass manufacturing (South Coast and San Diego Air Basins); wastewater treatment during petroleum refining (San Francisco Bay Area Air Basin); and auto refinishing (San Francisco Bay Area Air Basin).

Population-weighted annual average ambient air concentrations were calculated for the South Coast Air Basin (see Table 27). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from PAMS and was supplemented with modeled values at additional locations. The reason for including modeled values was that some years lacked sufficient data, different years had data from different sites leading to inconsistent results, and adding modeled values produced a more robust estimate of the population-weighted average. Figure 55 shows the population-weighted annual average concentration along with a summary of measured data from South Coast Air Basin monitoring sites. Figure 56 shows that the gasoline-attributable ambient air concentrations of *n*-hexane in the South Coast Air Basin declined by 77% between 1996 and 2014.

Hazard quotients for non-cancer health effects were calculated based on gasoline-attributable concentrations (see Appendix G for details). The gasoline-attributable hazard quotient for *n*-hexane, based on neurotoxicity, declined from 3.3×10^{-4} in 1996 to 7.7×10^{-5} in 2014 in the South Coast Air Basin. There were inadequate data to calculate a statewide hazard quotient for *n*-hexane.

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Figure 52. *n*-Hexane emissions from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

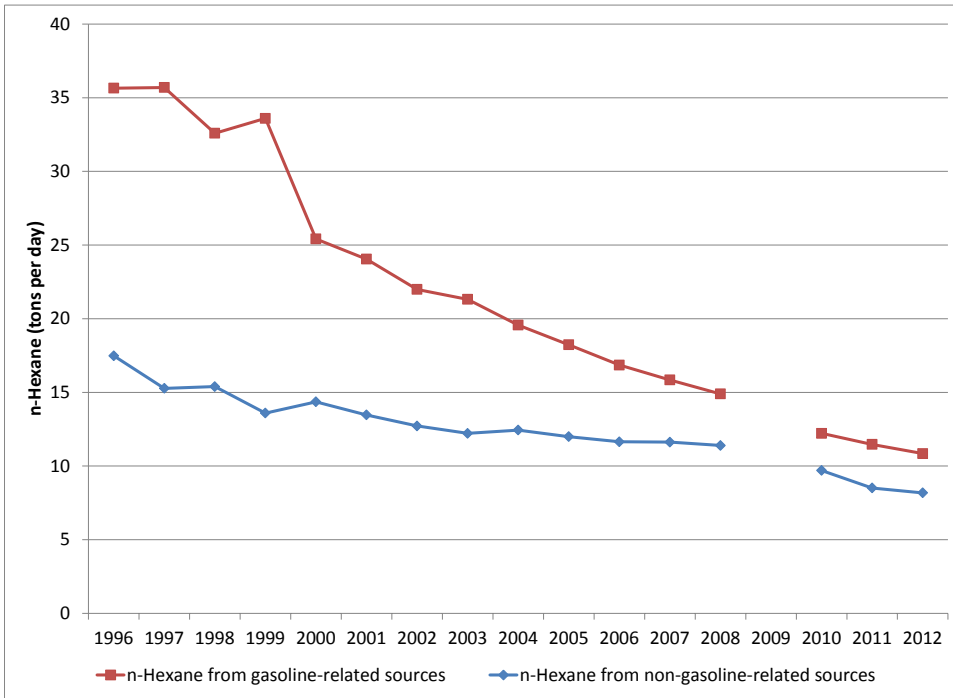
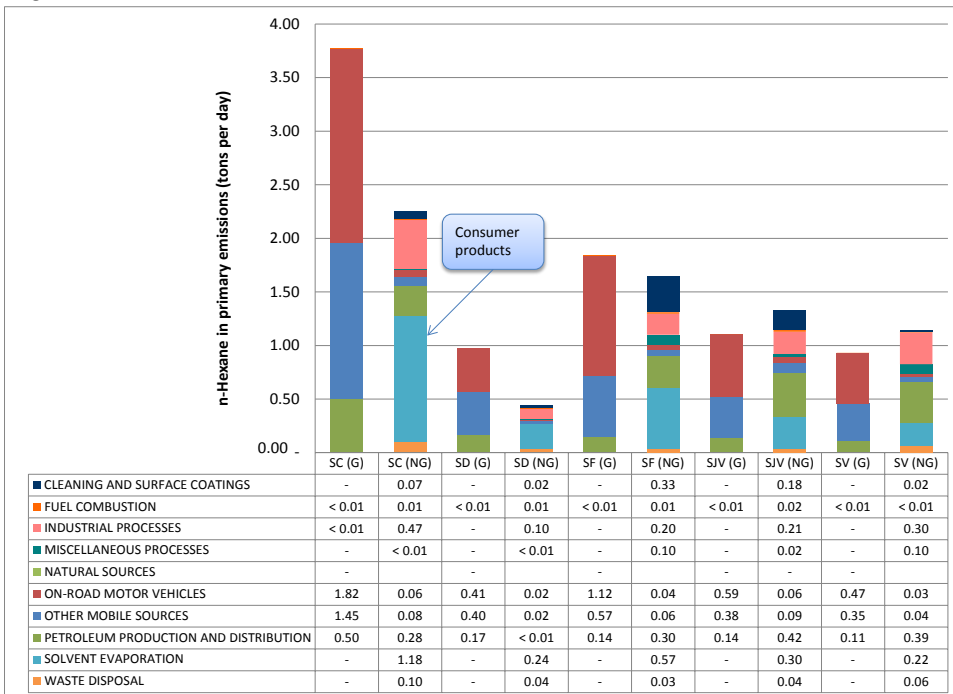


Figure 53. Emission sources of *n*-hexane in 2012



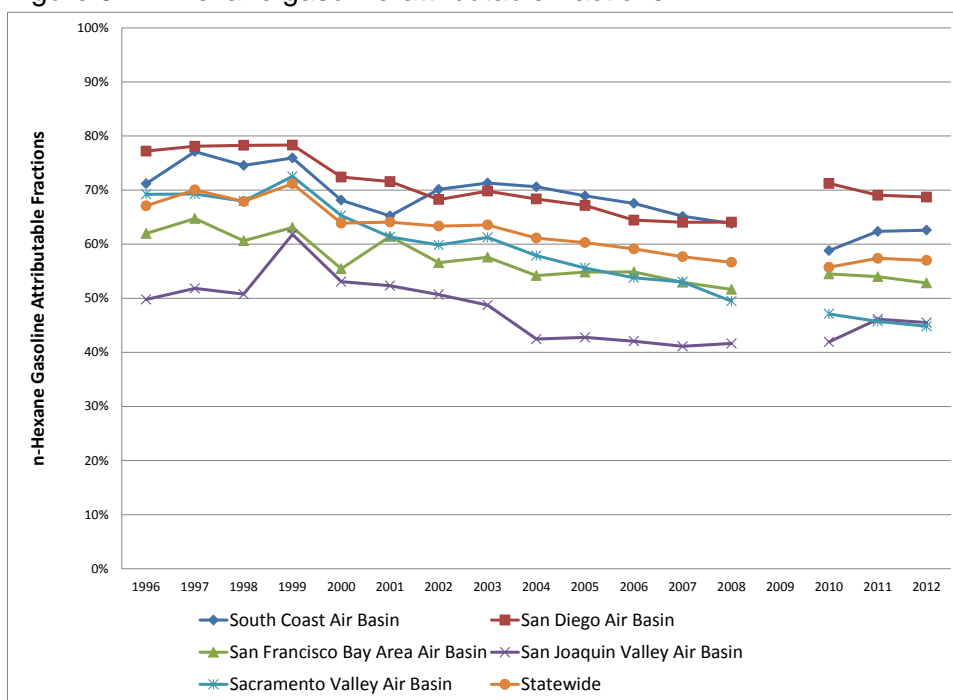
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Table 26. Gasoline-attributable fractions of *n*-hexane

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	71%	77%	62%	50%	69%	67%
1997	77%	78%	65%	52%	69%	70%
1998	75%	78%	61%	51%	68%	68%
1999	76%	78%	63%	62%	73%	71%
2000	68%	72%	55%	53%	65%	64%
2001	65%	72%	61%	52%	61%	64%
2002	70%	68%	57%	51%	60%	63%
2003	71%	70%	58%	49%	61%	64%
2004	71%	68%	54%	42%	58%	61%
2005	69%	67%	55%	43%	56%	60%
2006	68%	64%	55%	42%	54%	59%
2007	65%	64%	53%	41%	53%	58%
2008	64%	64%	52%	42%	49%	57%
2009	--	--	--	--	--	--
2010	59%	71%	55%	42%	47%	56%
2011	62%	69%	54%	46%	46%	57%
2012	63%	69%	53%	46%	45%	57%

Note: Mobile source emissions were not available for 2009.

Figure 54. *n*-Hexane gasoline-attributable fractions



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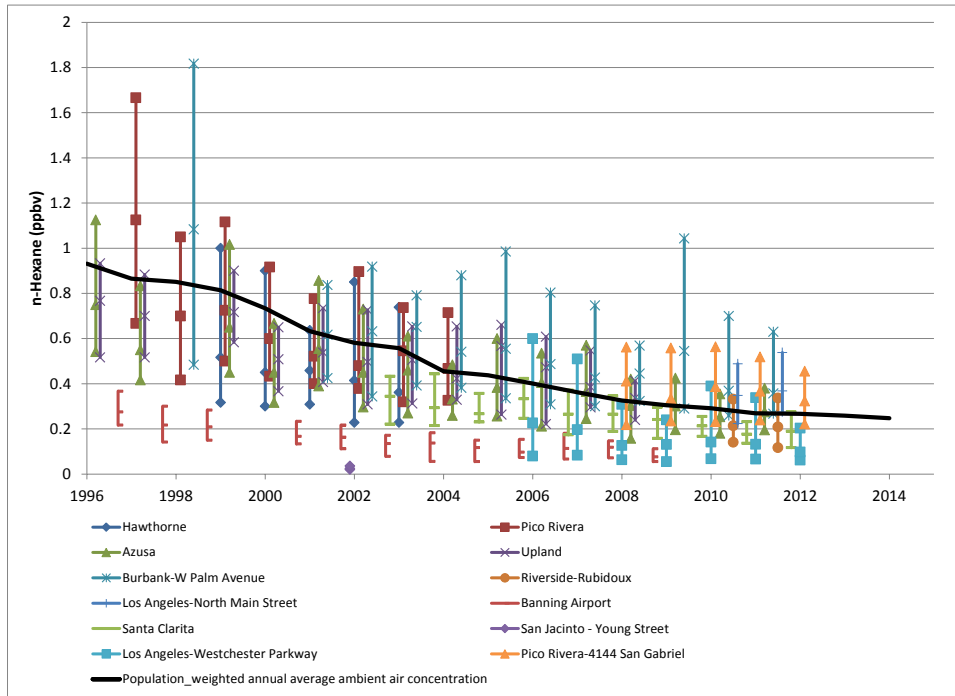
Table 27. *n*-Hexane results in the South Coast Air Basin

Year	Population-weighted annual average ambient air concentration of <i>n</i> -hexane (ppbv)	Gasoline-attributable fraction	Gasoline-attributable concentration (ppbv)
1996	0.93	71%	0.66
1997	0.87	77%	0.67
1998	0.85	75%	0.63
1999	0.81	76%	0.62
2000	0.73	68%	0.50
2001	0.63	65%	0.41
2002	0.58	70%	0.41
2003	0.56	71%	0.40
2004	0.46	71%	0.32
2005	0.44	69%	0.30
2006	0.40	68%	0.27
2007	0.36	65%	0.24
2008	0.33	64%	0.21
2009	0.31	64%	0.19
2010	0.29	59%	0.17
2011	0.27	62%	0.17
2012	0.27	63%	0.17
2013	0.26	63%	0.16
2014	0.25	63%	0.15

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2012 - 2014 population-weighted averages were based completely on modeled values (see Figure 55). The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction

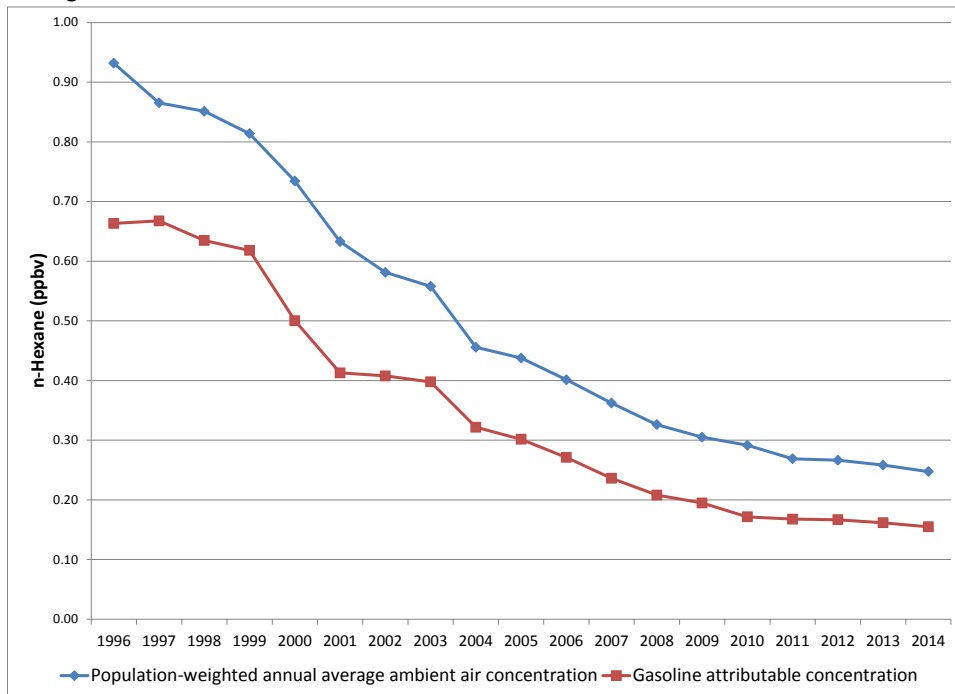
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Figure 55. Population-weighted annual average ambient air concentration of n-hexane in the South Coast Air Basin



Note: The vertical bars show the quartiles from South Coast Air Basin monitoring sites with 10 or more months of data.

Figure 56. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of n-hexane



Isobutene: Exposure and Screening Risk Assessment Results

Isobutene is a respiratory toxicant and had the 25th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Estimated annual emissions of isobutene from gasoline-related sources in California declined between 1996 and 2012. Figure 57 shows that the change in fuel blend that occurred between 2003 and 2004 resulted in a 50% decrease in isobutene emissions from gasoline-related sources. Isobutene is a byproduct of MTBE combustion (CARB, OEHHA and SWRCB, 1999). Emissions of isobutene declined by 86% between 1996 and 2012 due to the phaseout of MTBE and reduced emissions from newer vehicles. Plots of emission sources and gasoline-attributable fractions are in Figures 58 and 59. The gasoline-attributable fractions are also shown in Table 28. The plots show that isobutene is emitted primarily by gasoline-related sources. Statewide, in 2012, 86% of isobutene came from gasoline-related sources including cars, gasoline trucks, buses and motorcycles. Non-gasoline-related sources included construction, mining and farming equipment. Gasoline-attributable fractions dropped off in all basins between 2003 and 2004. A review of emissions from the South Coast Air Basin showed that one of the major sources of the change was the decline in isobutene from catalyst-stabilized exhaust.

Isobutene ambient air monitoring data were only available from summer months. A model was developed using data from PAMS in the South Coast Air Basin to estimate isobutene concentrations as described in Appendix D. The model was used to estimate isobutene concentrations in other seasons and years. The data came from 1996 to 2002 but the bulk of the measurements were from 2001 and 2002. Because of the need to use a model based primarily on 2001 and 2002 data, isobutene results for other years should be interpreted cautiously.

Table 29 contains the gasoline-attributable population-weighted annual average ambient air concentration (also referred to as gasoline-attributable concentration). Figure 60 graphs the gasoline-attributable ambient air concentrations of isobutene in the South Coast Air Basin, which declined by 68% between 1996 and 2014.

Figure 61 compares the estimated population-weighted annual average ambient air concentration of isobutene in the South Coast Air Basin to the first and third quartiles from monitoring sites in the South Coast and San Diego Air Basins. Figure 61 shows that the modeled values in the South Coast Air Basin were higher than the ambient air concentrations of isobutene in the San Diego Air Basin. Ambient air measurements from the South Coast Air Basin were not available from these later years (i.e., 2003 - 2014).

A draft health protective concentration of 1100 ppb was developed for isobutene by OEHHA (1999). The average concentration for isobutene in 2014 was over 1000-fold lower than this health protective concentration. There were inadequate data to calculate a statewide hazard quotient for isobutene.

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Figure 57. Isobutene emissions from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

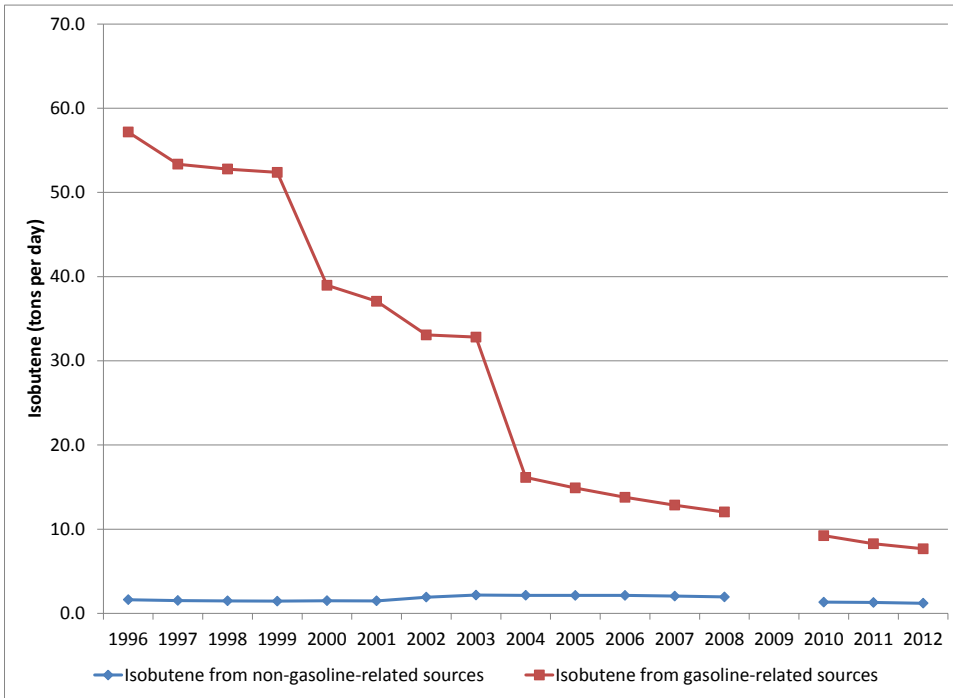
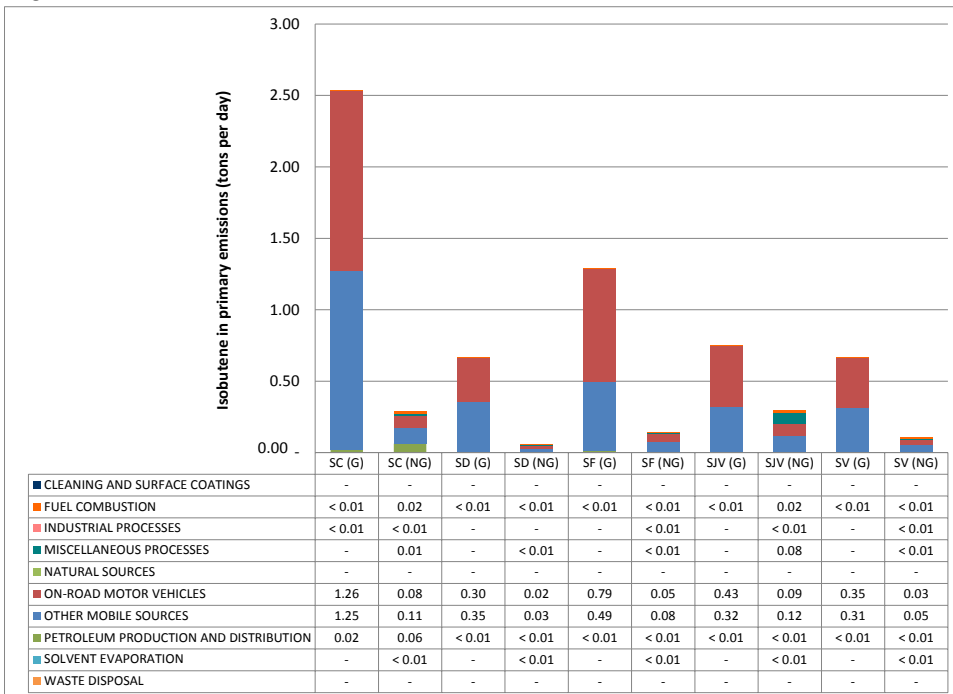


Figure 58. Emission sources of isobutene in 2012



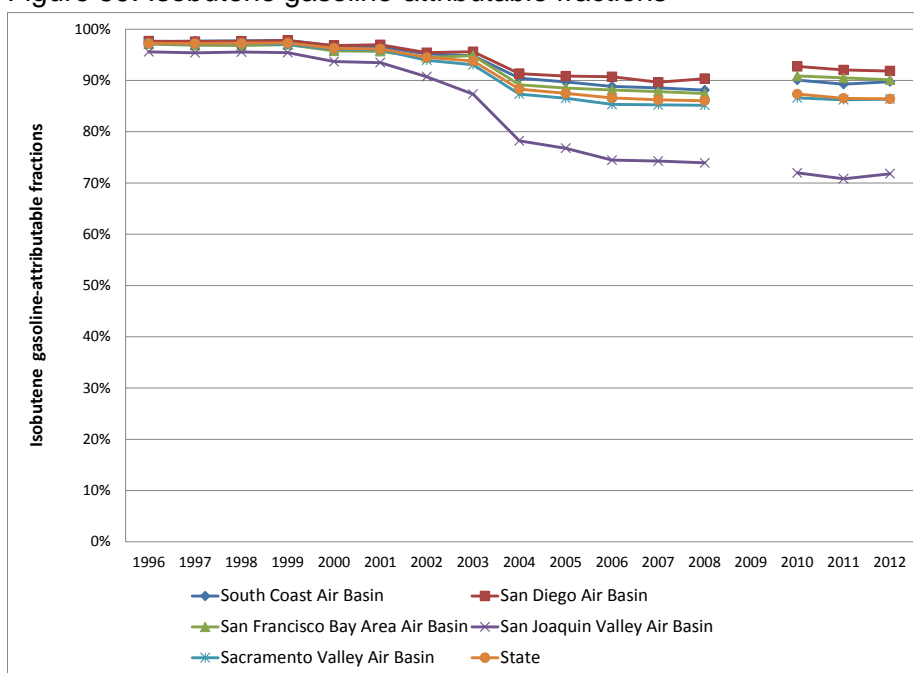
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Table 28. Isobutene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	98%	98%	97%	96%	97%	97%
1997	98%	98%	97%	95%	97%	97%
1998	98%	98%	97%	96%	97%	97%
1999	98%	98%	97%	95%	97%	97%
2000	97%	97%	96%	94%	96%	96%
2001	97%	97%	96%	93%	96%	96%
2002	95%	95%	94%	91%	94%	94%
2003	95%	96%	95%	87%	93%	94%
2004	90%	91%	89%	78%	87%	88%
2005	90%	91%	89%	77%	87%	87%
2006	89%	91%	88%	74%	85%	87%
2007	89%	90%	88%	74%	85%	86%
2008	88%	90%	87%	74%	85%	86%
2009	--	--	--	--	--	--
2010	90%	93%	91%	72%	87%	87%
2011	89%	92%	90%	71%	86%	87%
2012	90%	92%	90%	72%	86%	86%

Note: Mobile source emissions were not available for 2009.

Figure 59. Isobutene gasoline-attributable fractions



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Table 29. Isobutene results for the South Coast Air Basin

Year	Population-weighted average concentration of isobutene (ppbv)	Gasoline-attributable fraction	Gasoline-attributable concentration (ppb)
1996	0.96	98%	0.94
1997	0.87	98%	0.85
1998	0.86	98%	0.84
1999	0.82	98%	0.80
2000	0.72	97%	0.70
2001	0.65	97%	0.63
2002	0.60	95%	0.57
2003	0.58	95%	0.55
2004	0.50	90%	0.45
2005	0.44	90%	0.40
2006	0.42	89%	0.37
2007	0.38	89%	0.34
2008	0.34	88%	0.30
2009	0.32	88%	0.28
2010	0.32	90%	0.29
2011	0.30	89%	0.27
2012	0.31	90%	0.28
2013	0.30	90%	0.27
2014	0.30	90%	0.27

Note: The 2009 gasoline-attributable concentration was calculated with 2008 gasoline-attributable fraction. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction

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Figure 60. Modeled population-weighted isobutene ambient air concentration in the South Coast Air Basin

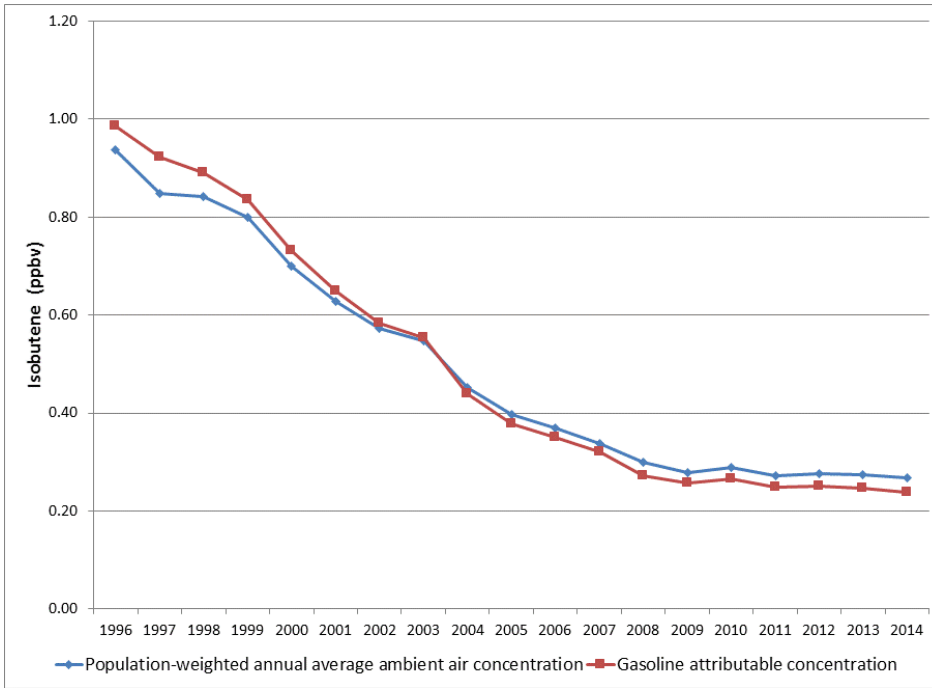
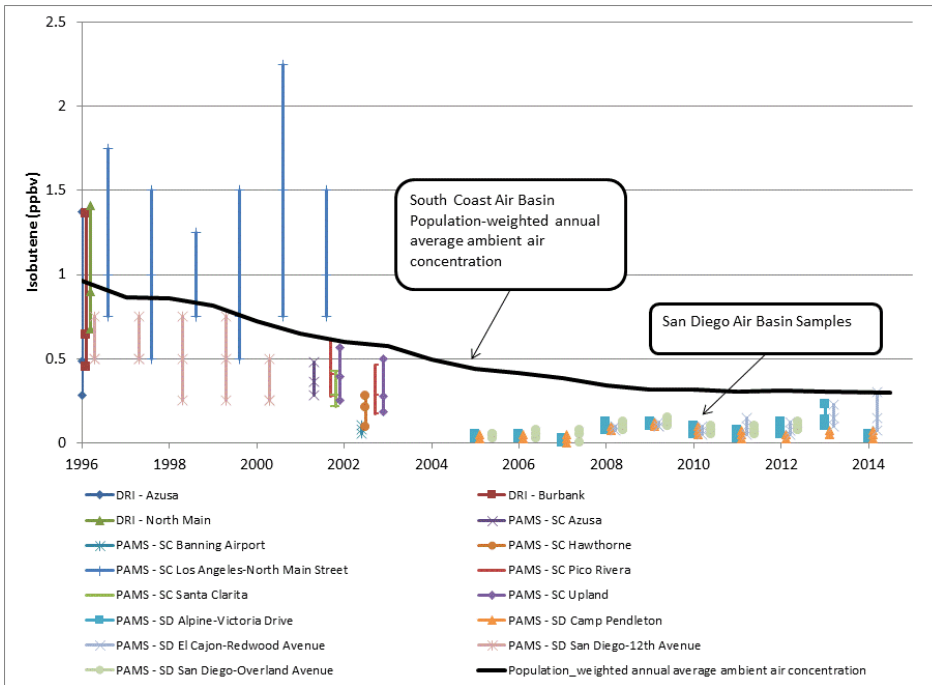


Figure 61. Population-weighted annual average ambient air concentration of isobutene in the South Coast Air Basin.



Note: The vertical bars show the quartiles of data from monitoring sites in the South Coast and San Diego Air Basins. The data were 3-hour samples collected by DRI during the summer months of 1995 and 1996 (Zielinska et al., 1999)

Isoprene: Exposure and Screening Risk Assessment Results

Isoprene is a carcinogen and had the 91st highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Figure 62 shows that isoprene came almost entirely from natural sources in 2012. The gasoline-attributable fractions of isoprene were close to zero in 2012.

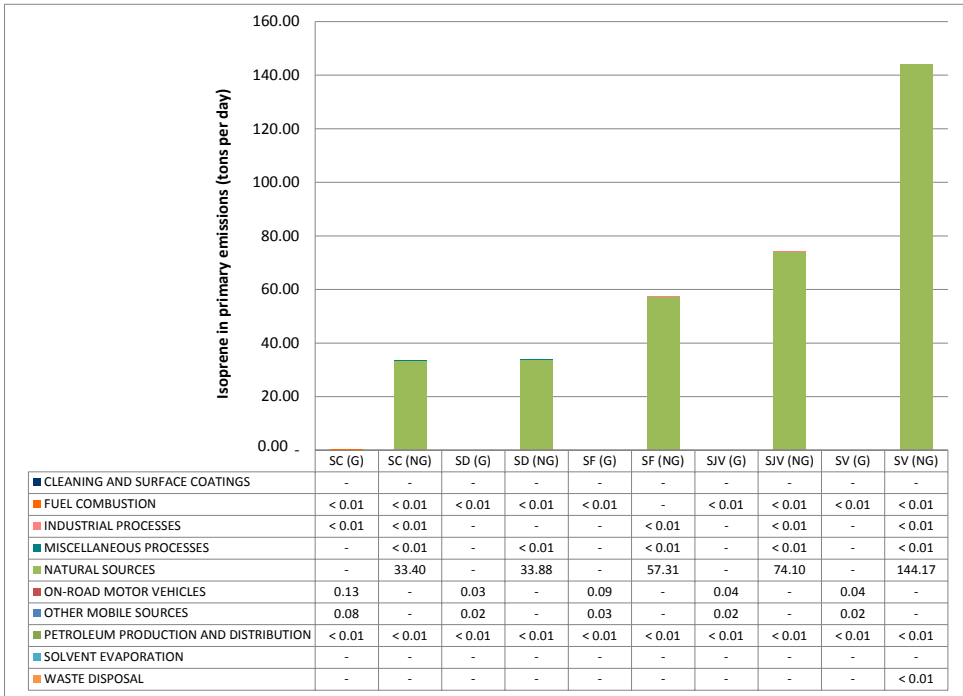
Isoprene ambient air concentrations were available from a few monitoring stations in the South Coast Air Basin. Tables 30 and 31 contain the annual average ambient air concentrations from these stations and the gasoline-attributable fractions of isoprene. The annual average concentrations of isoprene from these stations were roughly constant between 1996 and 2011. There were insufficient isoprene data to calculate population-weighted annual average ambient air concentrations.

In the South Coast Air Basin, the gasoline-attributable concentration of isoprene is 99%-100% between 1996 and 2001. Between 2002 and 2008, the gasoline-attributable fraction falls to 1%-2%. The reason for the decline is that the estimated tonnage of isoprene from natural sources increased in 2002 and onward. The same thing happened in San Diego, San Joaquin Valley and Sacramento Valley Air Basins. The San Francisco Bay Area Air Basin had biogenic sources included prior to 2002 and so did not see the large changes in isoprene tonnage.

Haney et al. (2015) derived a unit risk value for isoprene of 6.2×10^{-8} per ppb. The highest observed ambient air concentration for isoprene in 2011 was 0.25 ppb (Table 30). A rough estimate of the cancer risk associated with lifetime exposure to 0.25 ppb is 1.6×10^{-8} or about 2 additional cancer cases per 100 million people. Less than 1% of this risk is gasoline-related.

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Figure 62. Emission sources of isoprene in 2012



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Table 30. Annual average concentrations of isoprene (ppb) in South Coast Air Basin

Year	Azusa	Banning Airport	Burbank-W Palm Avenue	Hawthorne	Los Angeles-North Main Street	Los Angeles-Westchester Parkway	Pico Rivera	Pico Rivera-4144 San Gabriel	Riverside-Rubidoux	Santa Clarita	Upland
1996	0.16										0.38
1997											
1998											
1999							0.25				0.39
2000	0.23			0.21							
2001	0.16	0.06	0.24	0.12			0.21				0.37
2002	0.16		0.31	0.13						0.22	0.31
2003	0.36	0.11		0.13			0.22				0.40
2004	0.20	0.08	0.24				0.18			0.25	0.30
2005	0.15	0.08	0.23			0.10				0.25	0.30
2006	0.25	0.10				0.10				0.27	0.36
2007	0.27	0.09				0.09				0.25	0.34
2008	0.17	0.06	0.29			0.08		0.17		0.30	0.30
2009	0.13		0.24			0.05		0.14		0.28	
2010	0.11		0.18		0.11	0.05		0.12	0.15	0.24	
2011	0.16		0.21		0.12	0.05		0.15	0.15	0.25	

Note: monitoring sites in the South Coast Air Basin with 12 months of data

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Table 31. Isoprene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	>99%	>99%	1%	>99%	>99%	3%
1997	>99%	>99%	1%	>99%	>99%	3%
1998	>99%	>99%	1%	>99%	>99%	3%
1999	>99%	>99%	1%	>99%	>99%	3%
2000	99%	>99%	1%	99%	99%	2%
2001	99%	99%	1%	99%	99%	2%
2002	2%	<1%	1%	<1%	<1%	<1%
2003	2%	<1%	<1%	<1%	<1%	<1%
2004	1%	<1%	<1%	<1%	<1%	<1%
2005	1%	<1%	<1%	<1%	<1%	<1%
2006	1%	<1%	<1%	<1%	<1%	<1%
2007	1%	<1%	<1%	<1%	<1%	<1%
2008	1%	<1%	<1%	<1%	<1%	<1%
2009	--	--	--	--	--	--
2010	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%
2011	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%
2012	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%

Note: Gasoline-attributable fractions from 2001 and earlier in the South Coast, San Diego, San Joaquin Valley and Sacramento Valley did not include natural sources, and so are too large. The statewide estimates from 1996-2001 are inflated for the same reason. Mobile source emissions were unavailable for 2009.

Methanol: Exposure and Screening Risk Assessment Results

Methanol is a developmental toxicant and had the 75th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Figure 63 shows that in 2012 methanol came primarily from non-gasoline-related sources, with the main source being biogenic. Figures 64 and 65 show the emission sources and gasoline-attributable fractions of methanol. The gasoline-attributable fractions are also provided in Table 32. Gasoline-attributable fractions of methanol declined in 2002 due to a large increase in estimated emissions from natural sources, which was an adjustment made by CARB to the Emission Inventory. Estimated emissions of methanol from gasoline-related sources declined in 2004, but this was a small change relative to CARB's adjustment to natural source emissions.

Ambient air monitoring data were not available for methanol so population-weighted annual average ambient air concentrations and gasoline-attributable concentrations of the chemical could not be calculated. Methanol has a cREL of 4 mg/m³, based on developmental toxicity. A hazard quotient for methanol was not calculated due to lack of ambient air data.

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Figure 63. Emissions of methanol from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

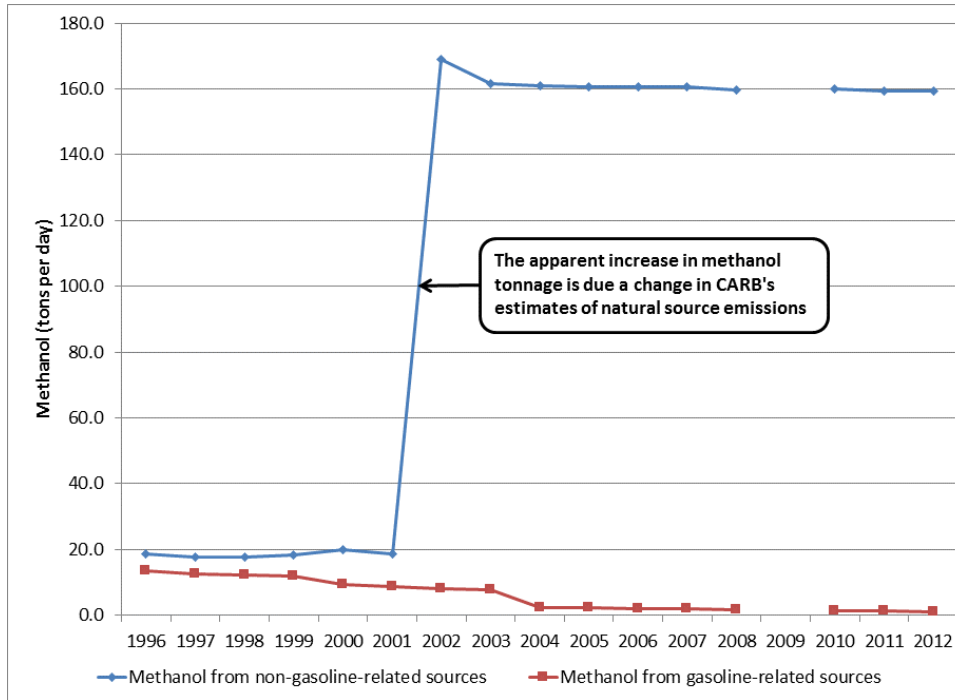
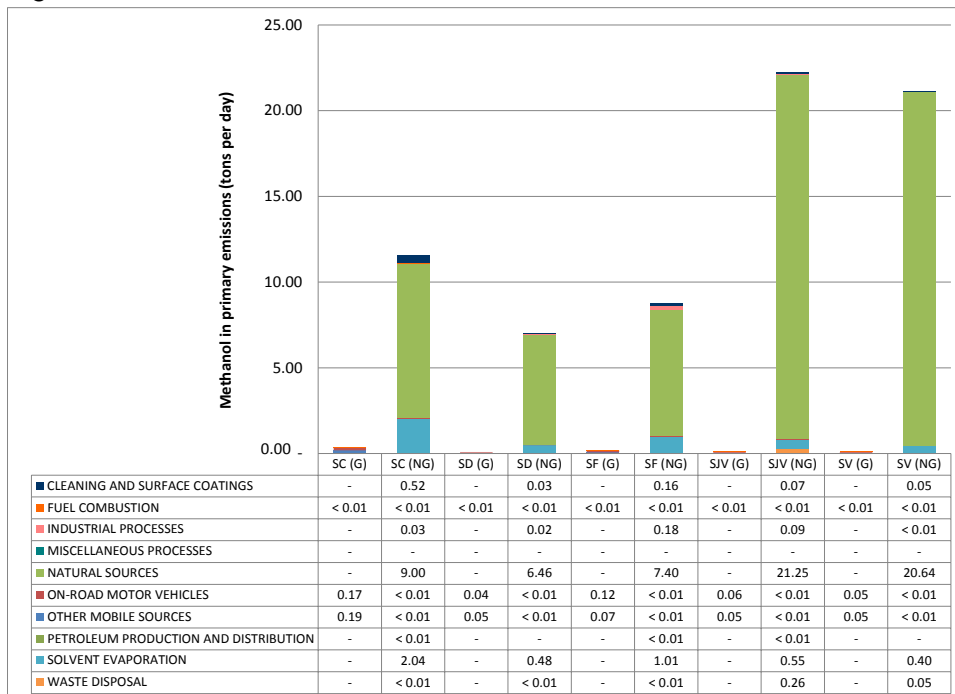


Figure 64. Emission sources of methanol in 2012



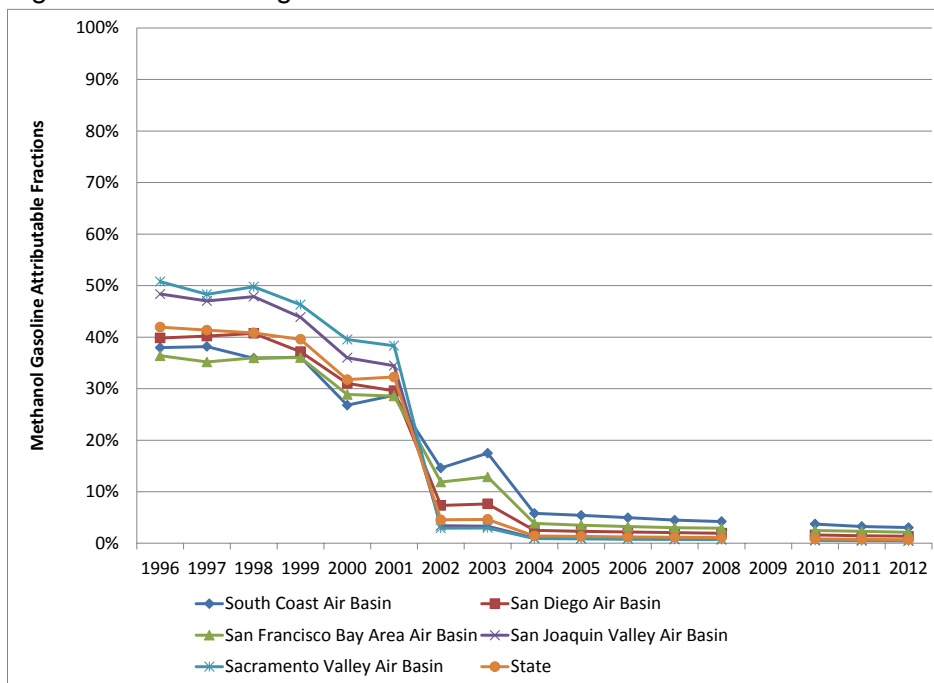
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Table 32. Methanol gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	38%	40%	36%	48%	51%	42%
1997	38%	40%	35%	47%	48%	41%
1998	36%	41%	36%	48%	50%	41%
1999	36%	37%	36%	44%	46%	40%
2000	27%	31%	29%	36%	40%	32%
2001	29%	30%	29%	34%	38%	32%
2002	15%	7%	12%	3%	3%	5%
2003	17%	8%	13%	3%	3%	5%
2004	6%	3%	4%	1%	1%	1%
2005	5%	2%	4%	1%	1%	1%
2006	5%	2%	3%	1%	1%	1%
2007	4%	2%	3%	1%	1%	1%
2008	4%	2%	3%	1%	1%	1%
2009	--	--	--	--	--	--
2010	4%	2%	2%	1%	1%	1%
2011	3%	1%	2%	1%	< 1%	1%
2012	3%	1%	2%	< 1%	< 1%	1%

Note: Mobile source emissions were unavailable for 2009.

Figure 65. Methanol gasoline-attributable fractions



Methyl *t*-Butyl Ether (MTBE): Exposure and Screening Risk Assessment Results

Between 1996 and 2003, almost all MTBE primary emissions in California came from gasoline-related sources. Due to the phase out of MTBE, the gasoline-attributable fractions of MTBE fell to zero in 2004 (see Table 34). The ambient air concentrations of MTBE also fell dramatically, as expected. In 2003, more than 50% of the ambient air measurements of MTBE were below the limit of detection; the percentage of non-detects rose to 97% in 2004.

Population-weighted annual average ambient air concentrations of MTBE were estimated for the South Coast, San Diego, San Francisco Bay Area, Sacramento Valley and San Joaquin Valley Air Basins and state for the years 1996 to 2002 (see Table 33). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from the California Toxic Monitoring Network and was supplemented with modeled values at additional locations to produce more robust estimates. Figure 66 shows the population-weighted annual average ambient air concentrations of MTBE in the South Coast Air Basin between 1996 and 2002 along with the quartiles of measured values from South Coast monitoring sites. In Figure 67, the gasoline-attributable concentration and ambient air concentration essentially overlap for all years shown (up to 2002), because the MTBE gasoline-attributable fraction was close to 100%. Tables 33 and 35 contain the population-weighted annual average ambient air concentration and gasoline-attributable concentrations of MTBE in the other air basins.

Cancer risks and non-cancer hazard quotients were calculated based on gasoline-attributable ambient air concentrations (see Appendix G for details). The gasoline-attributable cancer risk for MTBE in 1996 was 2.1×10^{-5} in the South Coast Air Basin and 1.6×10^{-5} statewide. The 1996 gasoline-attributable hazard quotient for MTBE, based on toxicity to the kidney, eyes and alimentary system, was only 0.0016 in the South Coast Air Basin and 0.0013 statewide. In 2004, when ambient air monitoring of MTBE ceased, nearly all of the measurements were below the detection limit, and similarly negligible MTBE exposures would be expected in 2014.

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Table 33. Population-weighted annual average concentration of MTBE (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	3.2	2.4	2.0	1.8	1.7	2.5
1997	3.2	2.4	1.9	1.8	1.6	2.5
1998	2.6	1.9	1.5	1.6	1.3	2.0
1999	2.6	2.3	1.5	1.5	1.3	2.1
2000	2.2	1.9	1.3	1.3	1.1	1.7
2001	1.8	1.6	1.0	1.1	0.87	1.4
2002	1.6	1.5	1.0	1.1	1.0	1.3

Note: Half the limit of detection substituted for non-detects

Table 34. Gasoline-attributable fractions of MTBE

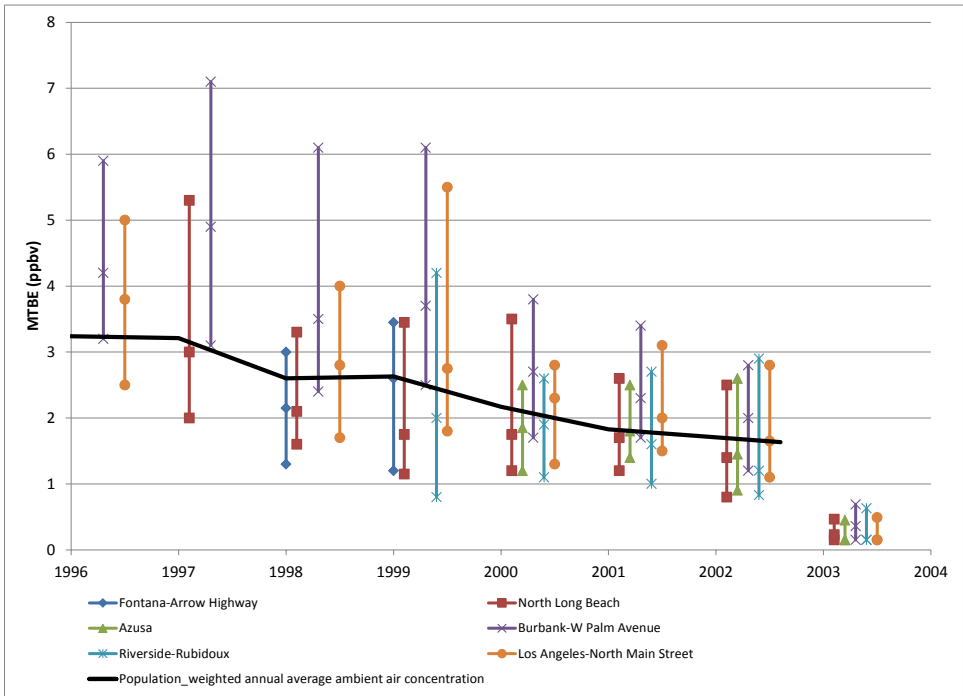
Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996-2003	>99%	>99%	>99%	>99%	>99%	>99%
2004-2008	0%	0%	0%	0%	0%	0%

Table 35. Gasoline-attributable concentrations of MTBE (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	3.2	2.4	2.0	1.8	1.7	2.5
1997	3.2	2.4	1.9	1.8	1.6	2.5
1998	2.6	1.9	1.5	1.5	1.3	2.0
1999	2.6	2.3	1.5	1.5	1.3	2.1
2000	2.2	1.9	1.3	1.3	1.1	1.7
2001	1.8	1.6	0.98	1.1	0.86	1.4
2002	1.6	1.5	0.97	1.1	0.98	1.3

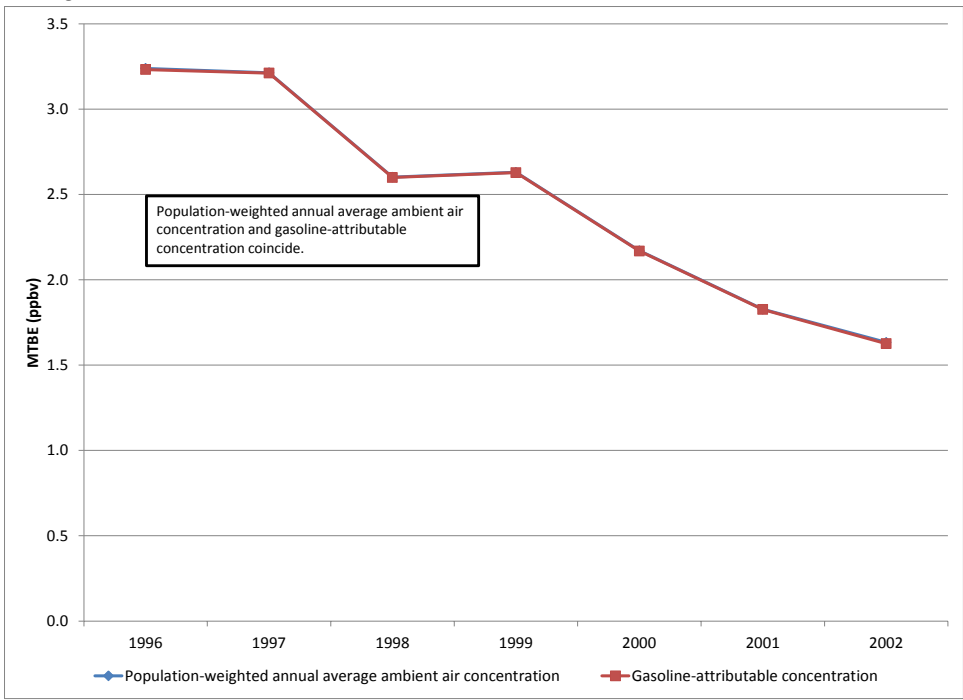
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Figure 66. Population-weighted annual average ambient air concentration of MTBE in the South Coast Air Basin



Note: The vertical bars show the quartiles of measurements at South Coast Air Basin monitoring sites with 10 or more months of data.

Figure 67. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of MTBE



Propylene: Exposure and Screening Risk Assessment Results

Propylene is a respiratory toxicant and had the 13th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. The estimated annual emissions of propylene from gasoline-related sources declined between 1996 and 2012 (see Figure 68). Figure 69 displays the emissions sources of propylene in 2012. Statewide, in 2012, 22% of propylene emissions came from gasoline-related sources. Some non-gasoline-related sources of propylene include wildfires (San Diego, San Joaquin Valley and Sacramento Valley Air Basins), agricultural burning (San Joaquin Valley and Sacramento Valley Air Basins), emissions from aircraft, emissions from construction and mining equipment, and emissions from petroleum refining and manufacturing industries.

Table 36 and Figure 70 show that the gasoline-attributable fractions varied by air basin, with lower percentages of propylene from gasoline-related sources in the San Joaquin and Sacramento Valley Air Basins. The fractions vary between 1996 and 2002 and between 2011 and 2012 for some basins due to fluctuations in the emissions estimates from natural sources (e.g., emissions from wildfires). Between 2003 and 2011, estimated emissions from natural source were roughly constant, leading to more stable gasoline-attributable fractions for propylene during those years.

Population-weighted annual average concentrations were calculated for the South Coast Air Basin (see Table 37). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from PAMS and was supplemented with modeled values at additional locations to produce more robust estimates. Figure 71 shows the population-weighted annual average along with the quartiles of measured data from South Coast Air Basin monitoring sites. Figure 72 shows that the gasoline-attributable ambient air concentration of propylene in the South Coast Air Basin declined by 84% between 1996 and 2014.

Hazard quotients for non-cancer health effects were calculated based on gasoline-attributable concentrations (see Appendix G for details). The gasoline-attributable hazard quotient for propylene, based on respiratory toxicity, declined from 7.5×10^{-4} in 1996 to 1.2×10^{-4} in 2014 in the South Coast Air Basin. There were inadequate data to calculate a statewide hazard quotient for propylene.

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Figure 68. Emissions of propylene from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

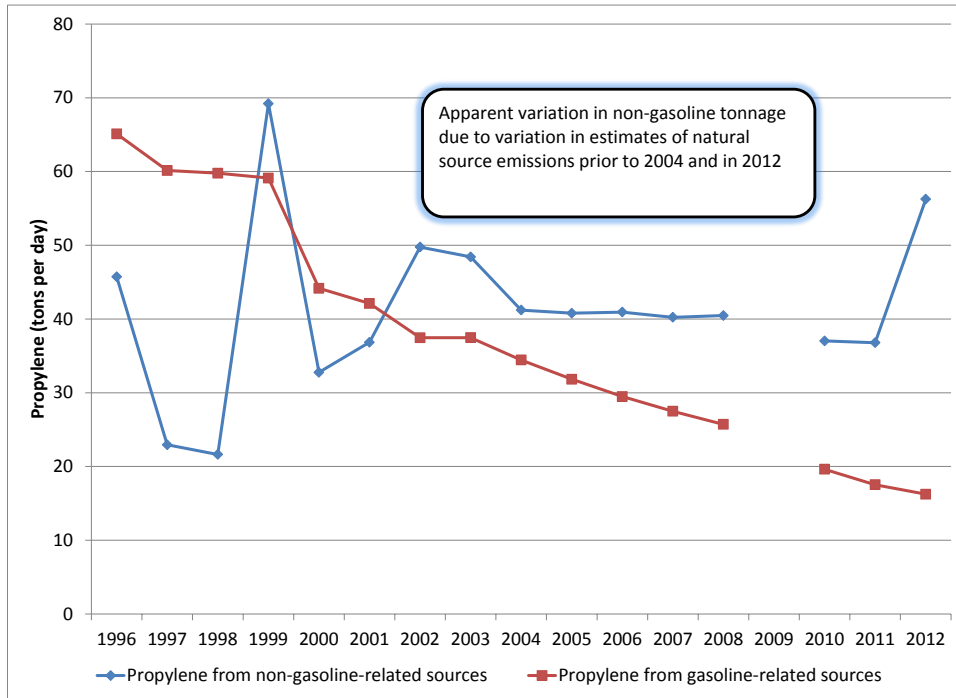
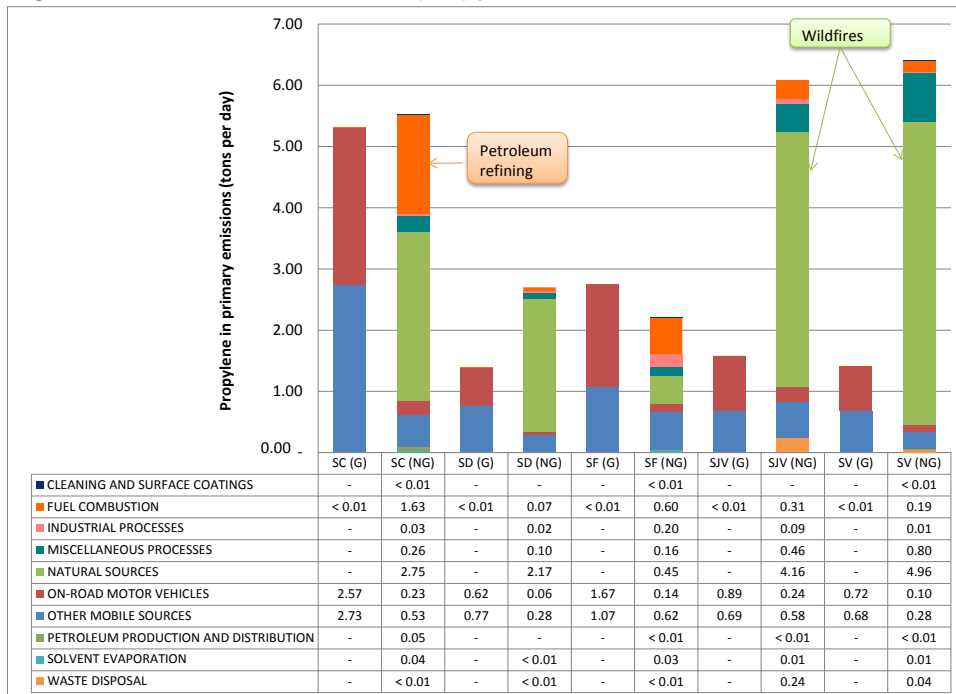


Figure 69. Emission sources of propylene in 2012



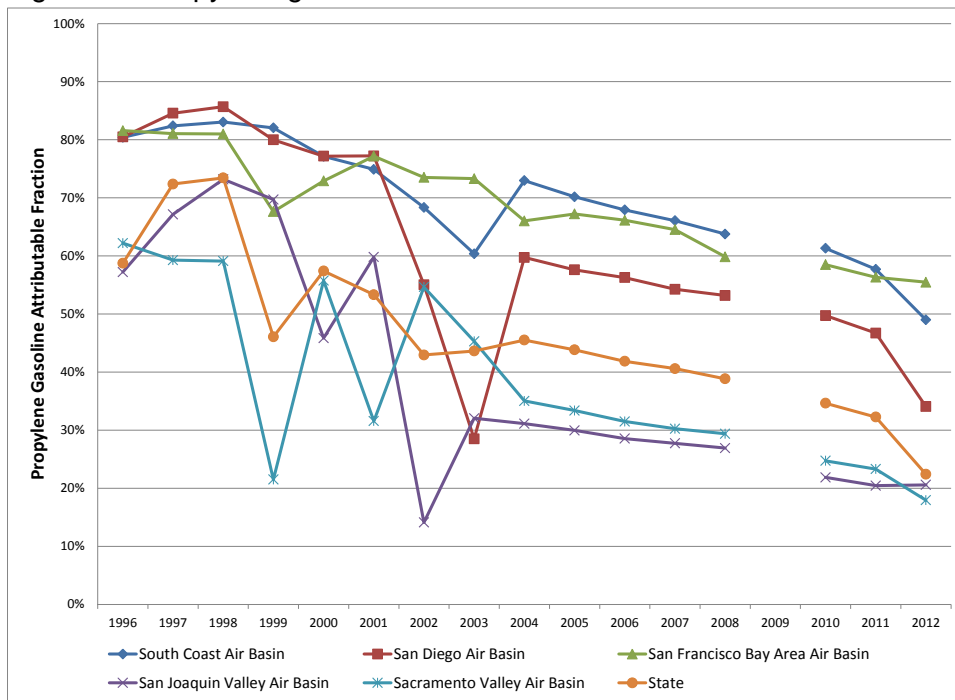
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Table 36. Gasoline-attributable fractions of propylene

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	80%	80%	82%	57%	62%	59%
1997	82%	85%	81%	67%	59%	72%
1998	83%	86%	81%	73%	59%	73%
1999	82%	80%	68%	70%	22%	46%
2000	77%	77%	73%	46%	56%	57%
2001	75%	77%	77%	60%	32%	53%
2002	68%	55%	74%	14%	55%	43%
2003	60%	29%	73%	32%	45%	44%
2004	73%	60%	66%	31%	35%	46%
2005	70%	58%	67%	30%	33%	44%
2006	68%	56%	66%	29%	32%	42%
2007	66%	54%	65%	28%	30%	41%
2008	64%	53%	60%	27%	29%	39%
2009	--	--	--	--	--	--
2010	61%	50%	59%	22%	25%	35%
2011	58%	47%	56%	20%	23%	32%
2012	49%	34%	55%	21%	18%	22%

Note: Mobile source emissions were unavailable for 2009.

Figure 70. Propylene gasoline-attributable fractions



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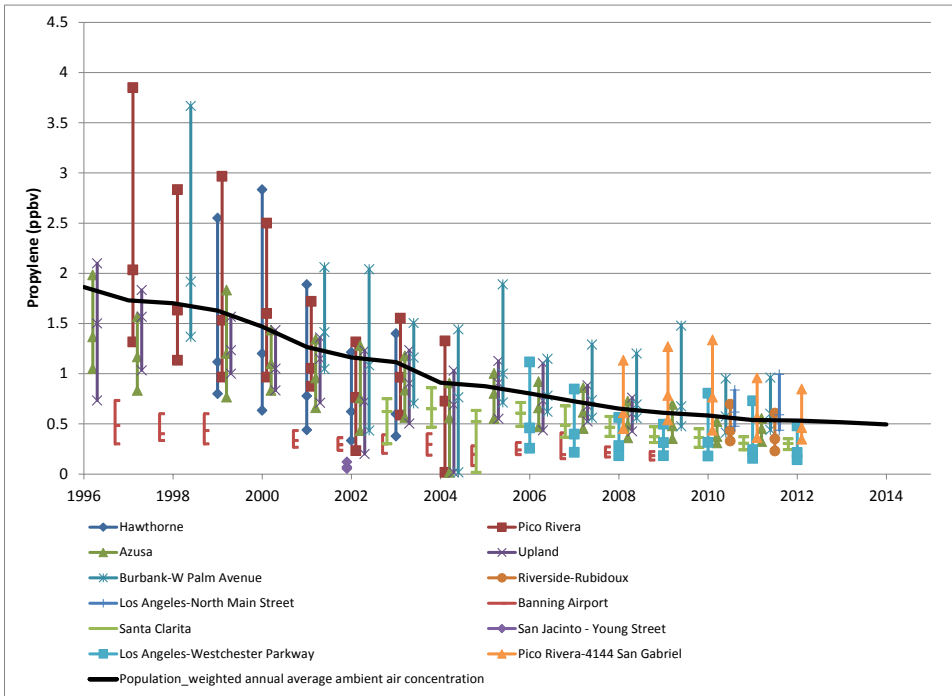
Table 37. Propylene results for the South Coast Air Basin

Year	Population-weighted average concentration of propylene (ppbv)	Gasoline-attributable fraction	Gasoline-attributable concentration (ppbv)
1996	1.9	80%	1.5
1997	1.7	82%	1.4
1998	1.7	83%	1.4
1999	1.6	82%	1.3
2000	1.5	77%	1.1
2001	1.3	75%	0.95
2002	1.2	68%	0.79
2003	1.1	60%	0.67
2004	0.91	73%	0.66
2005	0.88	70%	0.61
2006	0.80	68%	0.55
2007	0.72	66%	0.48
2008	0.65	64%	0.42
2009	0.61	64%	0.39
2010	0.58	61%	0.36
2011	0.54	58%	0.31
2012	0.53	49%	0.26
2013	0.52	49%	0.25
2014	0.49	49%	0.24

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2012-2014 population-weighted annual average ambient air concentrations were based completely on modeled values. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

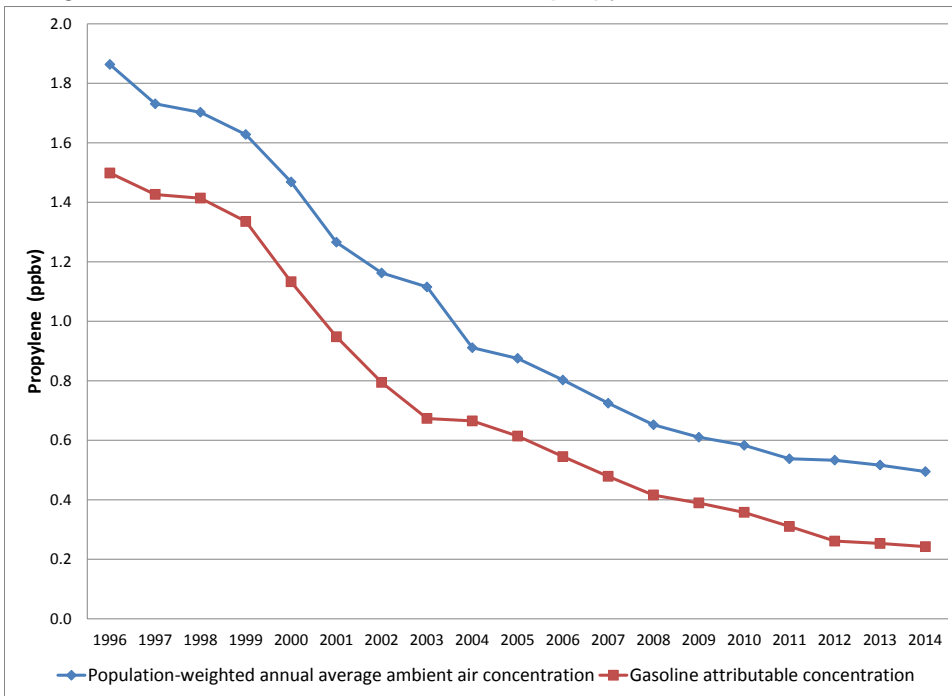
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Figure 71. Population-weighted annual average ambient air concentration of propylene in the South Coast Air Basin



Note: The vertical bars show the quartiles of measurements of propylene from South Coast Air Basin monitoring sites with 10 or more months of data.

Figure 72. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of propylene



Styrene: Exposure and Screening Risk Assessment Results

Styrene is a carcinogen and neurotoxicant and had the 93rd highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Figure 73 shows that the emissions of styrene from gasoline-related sources have declined between 1996 and 2012. Figure 74 shows the emission sources. Table 38 and Figure 75 show gasoline-attributable fractions of styrene. Statewide, in 2012, 12% of styrene emissions came from gasoline-related sources. The gasoline-attributable fractions varied by air basin. In the South Coast, San Francisco Bay Area and San Joaquin Valley Air Basins, more styrene emissions came from non-gasoline-related sources than from gasoline-related sources. Plastic and fiberglass manufacturing made up a large part of these non-gasoline emissions. In the San Joaquin Valley and Sacramento Valley Air Basins, the gasoline-attributable fractions of styrene varied dramatically over the years due to variation in emission estimates from fiberglass manufacturing.

Population-weighted annual average ambient air concentrations were calculated for the South Coast Air Basin (see Table 39). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from PAMS, included the years 1996-2011 and was supplemented with modeled values at additional locations to produce more robust estimates. Figure 76 shows the population-weighted annual average along with the quartiles of measured data from PAMS in the South Coast Air Basin. The data from the California Toxic Monitoring Network had a large percentage of non-detects and are shown in Figure 77 for comparison. Figure 78 shows that the gasoline-attributable ambient air concentration of propylene in the South Coast Air Basin declined by 94% between 1996 and 2014.

Cancer risks and non-cancer hazard quotients were calculated based on gasoline-attributable ambient air concentrations (see Appendix G for details). The gasoline-attributable cancer risk for styrene in the South Coast Air Basin declined from 1.2×10^{-5} in 1996 to 7.3×10^{-7} in 2014, corresponding to a reduction of an estimated 11 cancer cases per 1 million people. The gasoline-attributable hazard quotient for styrene, based on neurotoxicity, declined from 5.4×10^{-4} in 1996 to 3.3×10^{-5} in 2014 in the South Coast Air Basin. There were inadequate data to calculate a statewide cancer risk or non-cancer hazard quotient for styrene.

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Figure 73. Emissions of styrene from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

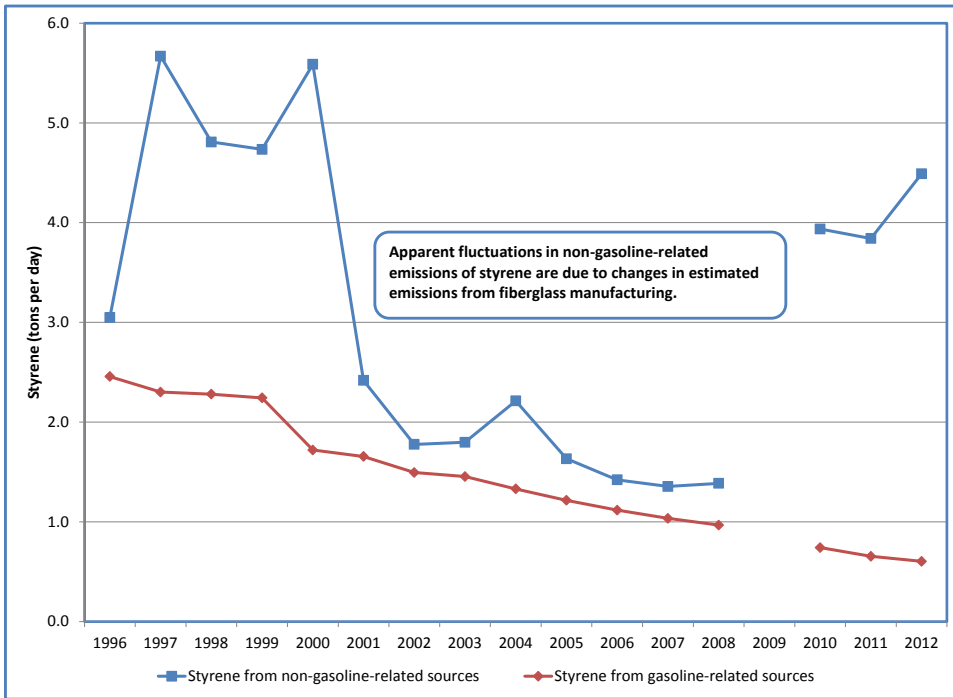
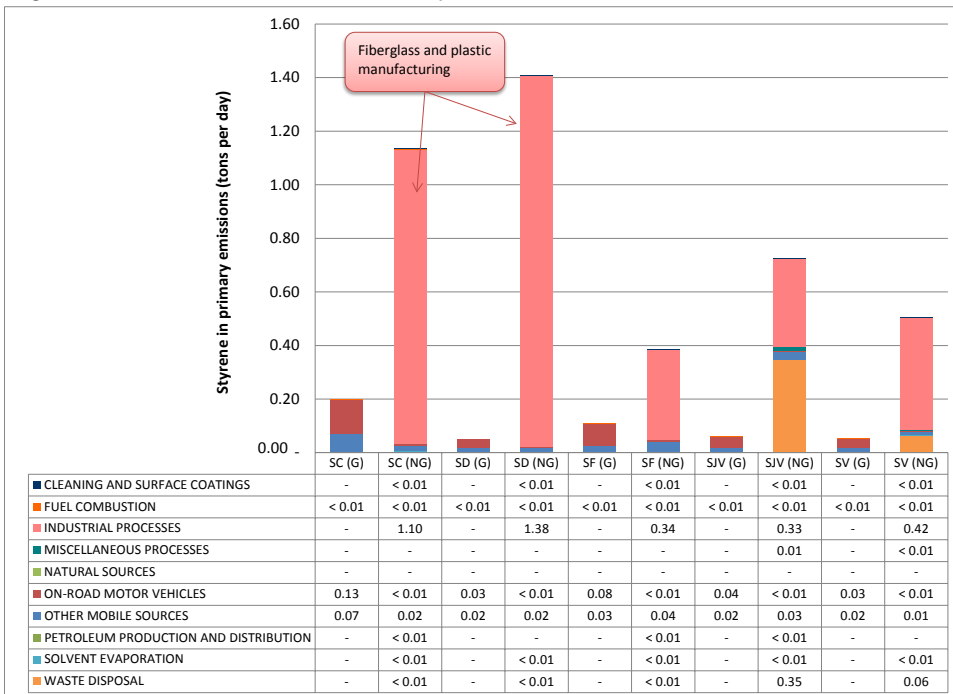


Figure 74. Emission sources of styrene in 2012



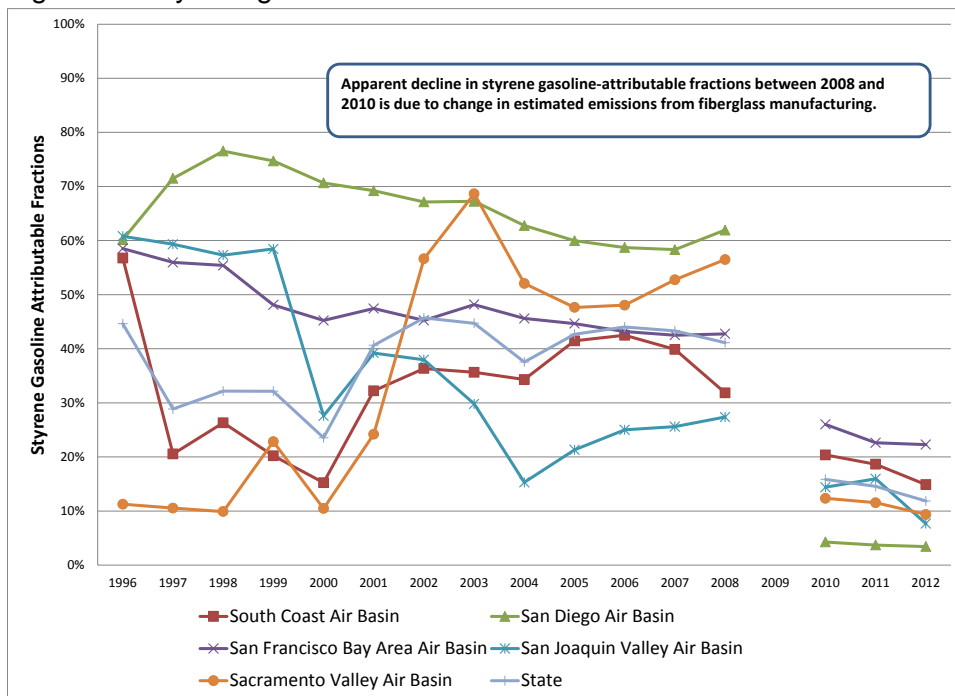
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Table 38. Styrene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	57%	60%	59%	61%	11%	45%
1997	21%	71%	56%	59%	11%	29%
1998	26%	77%	55%	57%	10%	32%
1999	20%	75%	48%	58%	23%	32%
2000	15%	71%	45%	28%	10%	24%
2001	32%	69%	47%	39%	24%	41%
2002	36%	67%	45%	38%	57%	46%
2003	36%	67%	48%	30%	69%	45%
2004	34%	63%	46%	15%	52%	38%
2005	41%	60%	45%	21%	48%	43%
2006	42%	59%	43%	25%	48%	44%
2007	40%	58%	43%	26%	53%	43%
2008	32%	62%	43%	27%	56%	41%
2009	--	--	--	--	--	--
2010	20%	4%	26%	14%	12%	16%
2011	19%	4%	23%	16%	12%	15%
2012	15%	3%	22%	8%	9%	12%

Note: Mobile source emissions were unavailable for 2009.

Figure 75. Styrene gasoline-attributable fractions



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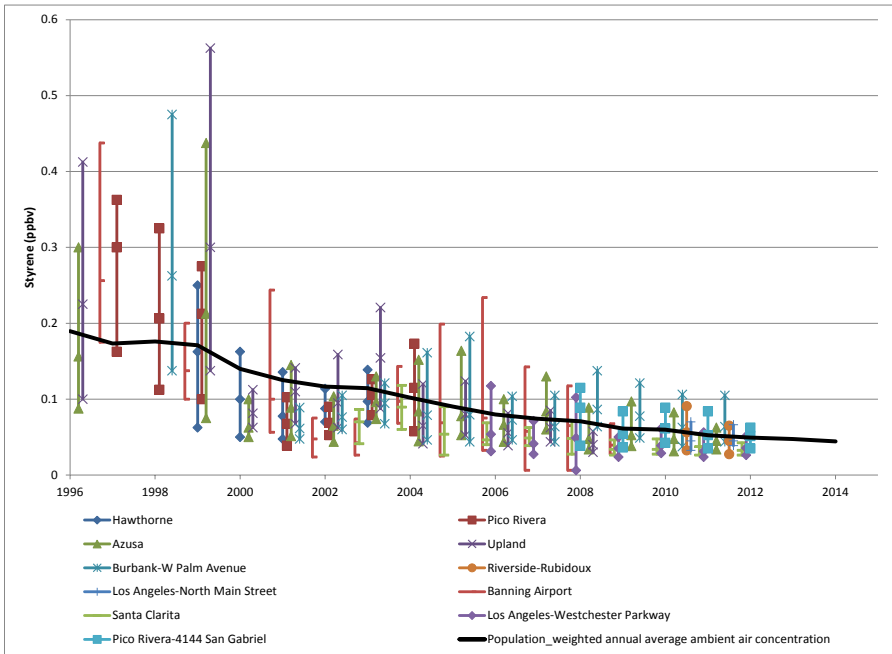
Table 39. Styrene exposure results for the South Coast Air Basin

Year	Population-weighted average concentration of styrene (ppbv)	Gasoline-attributable fractions	Gasoline-attributable concentration (ppbv)
1996	0.19	57%	0.11
1997	0.17	21%	0.036
1998	0.18	26%	0.046
1999	0.17	20%	0.035
2000	0.140	15%	0.021
2001	0.125	32%	0.040
2002	0.117	36%	0.042
2003	0.115	36%	0.041
2004	0.102	34%	0.035
2005	0.090	41%	0.037
2006	0.080	42%	0.034
2007	0.074	40%	0.030
2008	0.071	32%	0.023
2009	0.061	32%	0.020
2010	0.060	20%	0.012
2011	0.053	19%	0.010
2012	0.049	15%	0.0074
2013	0.047	15%	0.0071
2014	0.044	15%	0.0066

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2012 - 2014 population-weighted annual average ambient air concentrations were based completely on modeled values. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

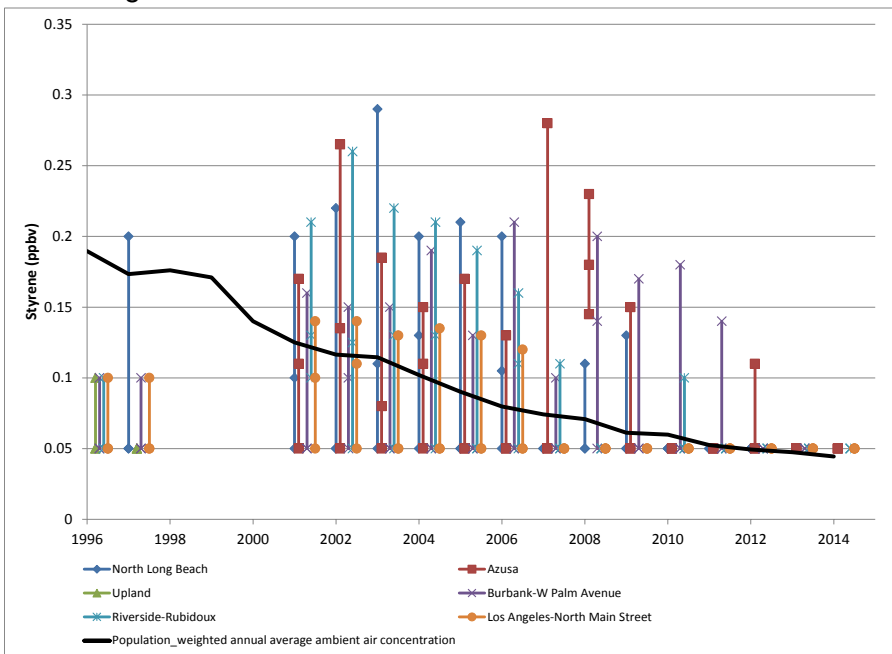
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Figure 76. Population-weighted annual average ambient air concentration of styrene in the South Coast Air Basin compared to styrene measurements from PAMS data



Note: The vertical bars show the quartiles of measurements from South Coast Air Basin monitoring sites with 10 or more months of data.

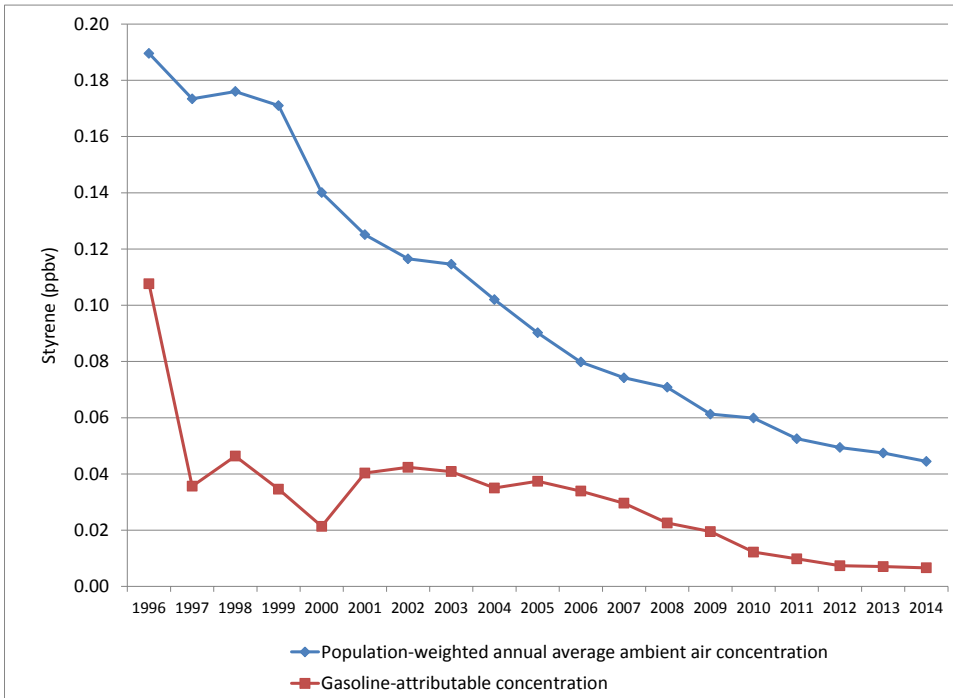
Figure 77. Population-weighted annual average ambient air concentration of styrene in the South Coast Air Basin compared to styrene measurements from the California Toxic Monitoring Network



Note: The vertical bars show the quartiles of measurements from South Coast Air Basin monitoring sites with 10 or more months of data.

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Figure 78. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of styrene



Toluene: Exposure and Screening Risk Assessment Results

Toluene is a respiratory toxicant, neurotoxicant, and developmental and reproductive toxicant. It had the third highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Figure 79 shows that emissions of toluene from gasoline-related sources declined between 1996 and 2012. Figure 80 shows the emission sources of toluene. Table 40 and Figure 81 show the gasoline-attributable fractions of toluene. Statewide, in 2012, 48% of toluene emissions came from gasoline-related sources. Non-gasoline-related sources of toluene included landfills, paints and consumer products.

Population-weighted annual average ambient air concentrations of toluene were estimated for the South Coast, San Diego, San Francisco Bay Area, Sacramento Valley and San Joaquin Valley Air Basins and statewide for the years 1996 to 2014 (see Table 41). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from the California Toxic Monitoring Network and was supplemented with modeled values at additional locations to produce more robust estimates. Figure 82 compares the population-weighted annual average ambient air concentrations of toluene in the South Coast Air Basin to actual ambient air measurements from monitoring sites within the basin.

Table 42 tabulates the gasoline-attributable population-weighted annual average ambient air concentrations (referred to as gasoline-attributable concentrations) for all air basins. Figure 83 shows that the gasoline-attributable concentrations of toluene declined by 80% between 1996 and 2014 in the South Coast Air Basin. The results for the other air basins are tabulated in Table 42.

Hazard quotients for non-cancer health effects were calculated based on gasoline-attributable concentrations (see Appendix G for details). The gasoline-attributable hazard quotient for toluene in the South Coast Air Basin declined from 0.026 in 1996 to 0.0045 in 2014. The statewide gasoline-attributable hazard quotient declined from 0.020 in 1996 to 0.0039 in 2014.

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Figure 79. Emissions of toluene from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

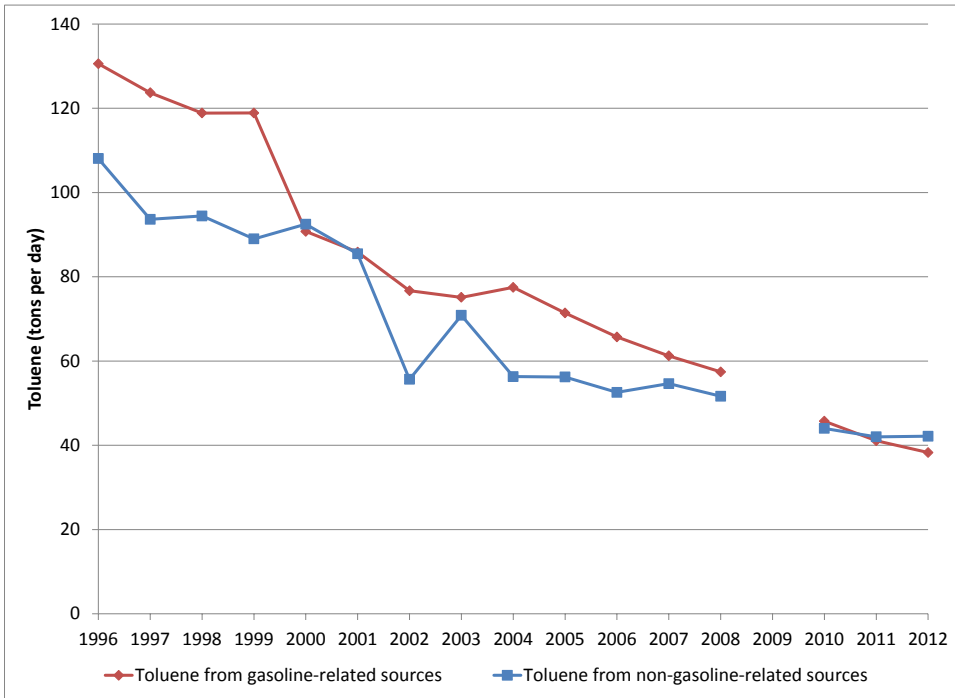
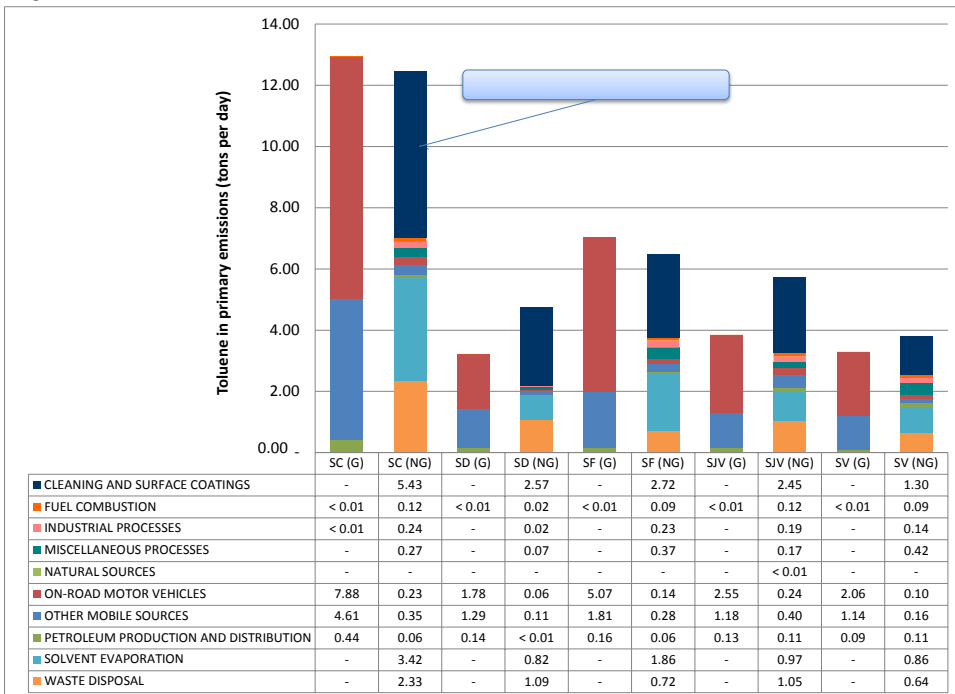


Figure 80. Emission sources of toluene in 2012



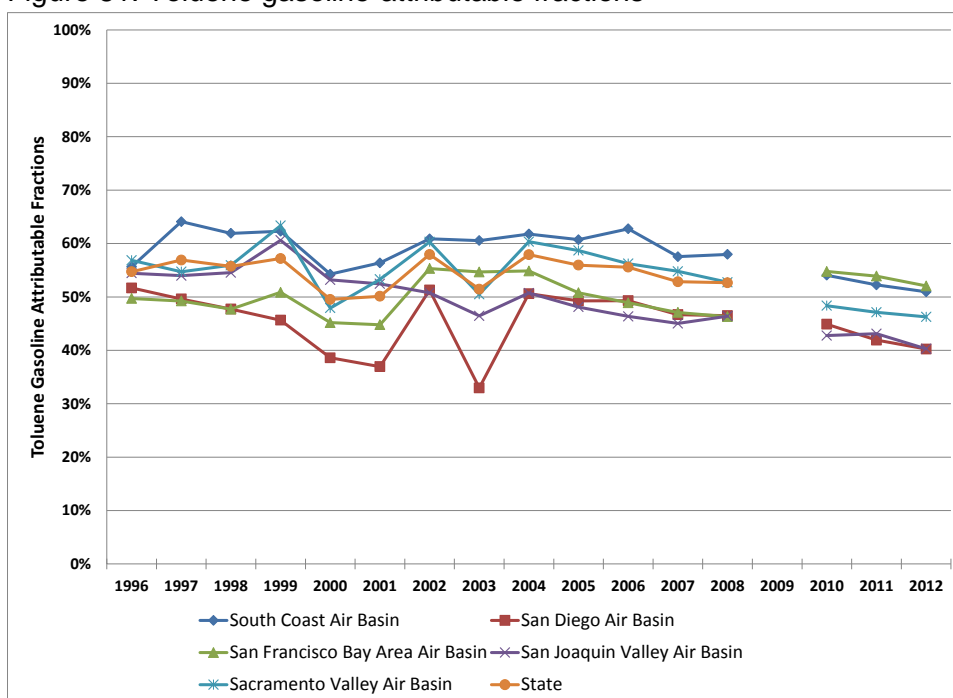
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Table 40. Toluene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	56%	52%	50%	54%	57%	55%
1997	64%	50%	49%	54%	55%	57%
1998	62%	48%	48%	55%	56%	56%
1999	62%	46%	51%	61%	63%	57%
2000	54%	39%	45%	53%	48%	50%
2001	56%	37%	45%	52%	53%	50%
2002	61%	51%	55%	51%	60%	58%
2003	61%	33%	55%	46%	50%	51%
2004	62%	51%	55%	51%	60%	58%
2005	61%	49%	51%	48%	59%	56%
2006	63%	49%	49%	46%	56%	56%
2007	58%	47%	47%	45%	55%	53%
2008	58%	46%	46%	46%	53%	53%
2009	--	--	--	--	--	--
2010	54%	45%	55%	43%	48%	51%
2011	52%	42%	54%	43%	47%	49%
2012	51%	40%	52%	40%	46%	48%

Note: Mobile source emissions were unavailable for 2009.

Figure 81. Toluene gasoline-attributable fractions



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Table 41. Population-weighted average concentration of toluene (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	3.3	2.3	2.0	1.6	1.5	2.5
1997	3.0	2.1	2.0	1.5	1.4	2.3
1998	2.7	2.0	1.7	1.5	1.2	2.1
1999	2.4	2.2	1.5	1.3	1.2	1.9
2000	2.6	2.1	1.6	1.5	1.2	2.0
2001	2.3	1.9	1.3	1.4	1.0	1.8
2002	2.1	1.9	1.4	1.4	1.3	1.7
2003	2.0	1.7	1.3	1.2	1.2	1.6
2004	1.6	1.5	1.2	0.98	1.3	1.4
2005	1.5	1.8	1.03	1.03	1.05	1.3
2006	1.4	1.5	0.91	0.98	0.98	1.2
2007	1.2	1.2	0.85	0.87	0.88	1.0
2008	1.0	1.2	0.64	0.74	0.81	0.89
2009	0.91	0.99	0.63	0.70	0.73	0.81
2010	0.94	1.0	0.66	0.64	0.64	0.82
2011	0.75	0.77	0.65	0.59	0.60	0.69
2012	0.82	0.81	0.61	0.61	0.59	0.72
2013	0.72	0.68	0.65	0.61	0.58	0.66
2014	0.62	0.58	0.52	0.55	0.44	0.57

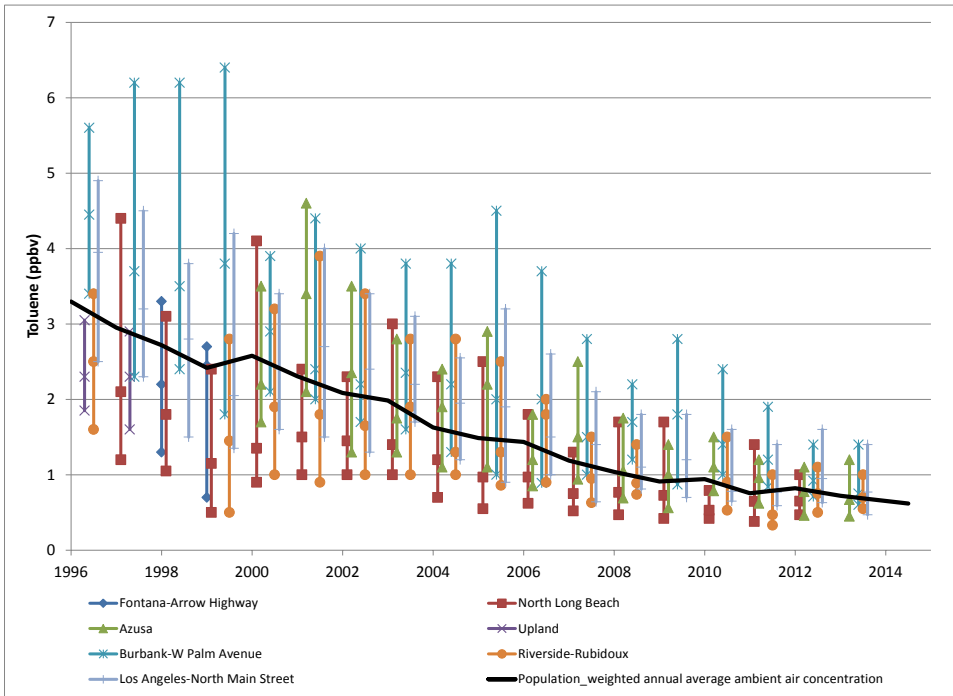
Table 42. Gasoline-attributable concentration of toluene (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	1.8	1.2	1.00	0.86	0.86	1.4
1997	1.9	1.0	0.96	0.82	0.75	1.3
1998	1.7	1.0	0.81	0.83	0.70	1.2
1999	1.5	1.0	0.79	0.78	0.74	1.1
2000	1.4	0.82	0.73	0.82	0.58	1.01
2001	1.3	0.70	0.59	0.71	0.56	0.90
2002	1.3	0.98	0.78	0.72	0.76	1.00
2003	1.2	0.57	0.74	0.57	0.61	0.83
2004	1.0	0.76	0.63	0.50	0.78	0.79
2005	0.90	0.89	0.52	0.49	0.61	0.72
2006	0.90	0.72	0.45	0.45	0.55	0.67
2007	0.68	0.57	0.40	0.39	0.48	0.54
2008	0.60	0.55	0.30	0.35	0.43	0.47
2009	0.53	0.46	0.29	0.33	0.39	0.42
2010	0.51	0.45	0.36	0.27	0.31	0.42
2011	0.39	0.32	0.35	0.26	0.28	0.34
2012	0.42	0.33	0.32	0.25	0.27	0.34
2013	0.37	0.27	0.34	0.25	0.27	0.32
2014	0.31	0.23	0.27	0.22	0.20	0.27

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

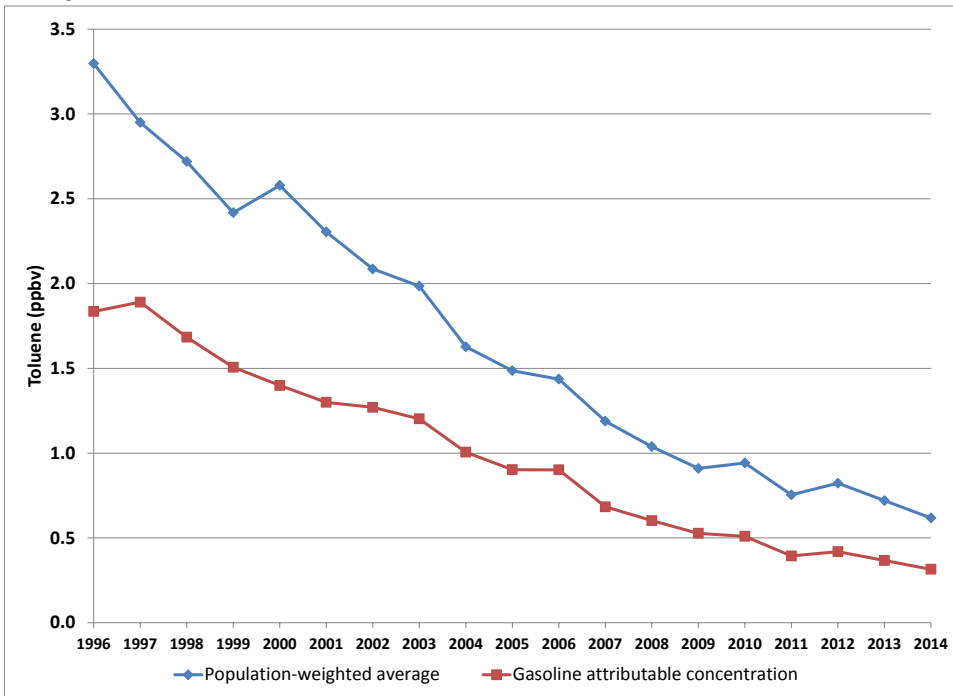
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Figure 82. Population-weighted annual average ambient air concentration of toluene in the South Coast Air Basin



Note: The vertical bars show the quartiles of 24-hour measurements from South Coast Air Basin monitoring sites.

Figure 83. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of toluene



Trimethylbenzenes: Exposure and Screening Risk Assessment Results

In this Chemical Profile, the exposure assessment results are presented for the individual trimethylbenzene isomers, and the screening risk assessment results for the group are presented after that.

1,2,3-Trimethylbenzene: Exposure Assessment Results

1,2,3-Trimethylbenzene had the 71st highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Figure 84 shows that the emissions of 1,2,3-trimethylbenzene from gasoline-related sources declined between 1996 and 2012. Figure 85 shows the emission sources of 1,2,3-trimethylbenzene. Table 43 and Figure 86 show the gasoline-attributable fractions of 1,2,3-trimethylbenzene. Statewide, in 2012, 64% of 1,2,3-trimethylbenzene emissions came from gasoline-related sources. Non-gasoline-related sources included consumer products, other mobile sources (like construction and mining equipment), and very heavy diesel trucks.

Population-weighted annual average ambient air concentrations of 1,2,3-trimethylbenzene were calculated for the South Coast Air Basin (see Table 44). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from PAMS and was supplemented with modeled values at additional locations to produce more robust estimates. Figure 87 shows the population-weighted average along with the quartiles of measured data from South Coast Air Basin monitoring. Figure 88 shows that the gasoline-attributable concentration of 1,2,3-trimethylbenzene declined by 90% in the South Coast Air Basin between 1996 and 2014.

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Figure 84. Emissions of 1,2,3-trimethylbenzene from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

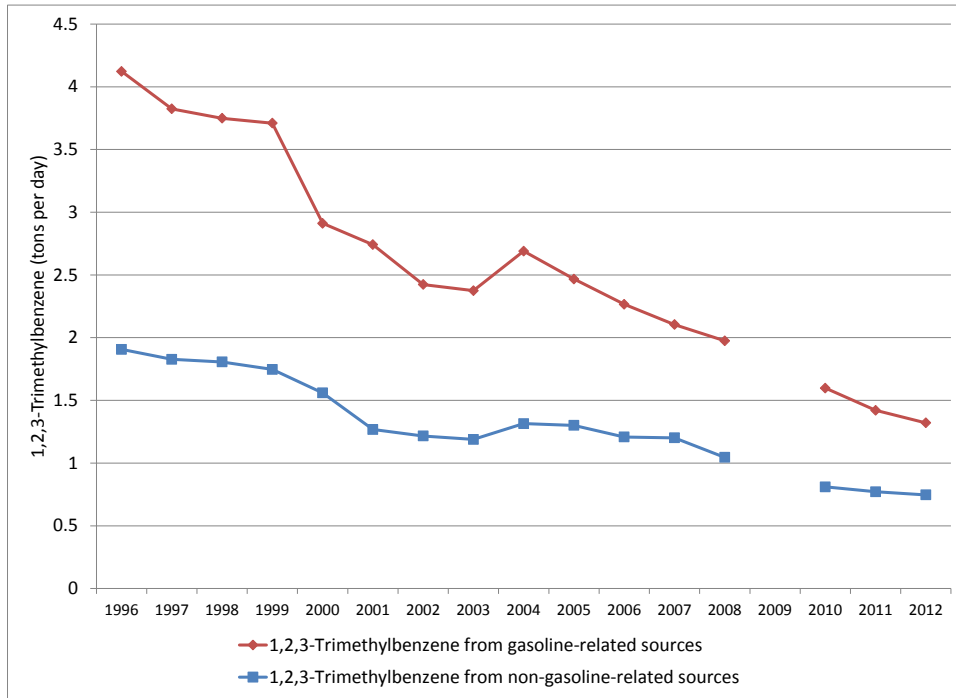
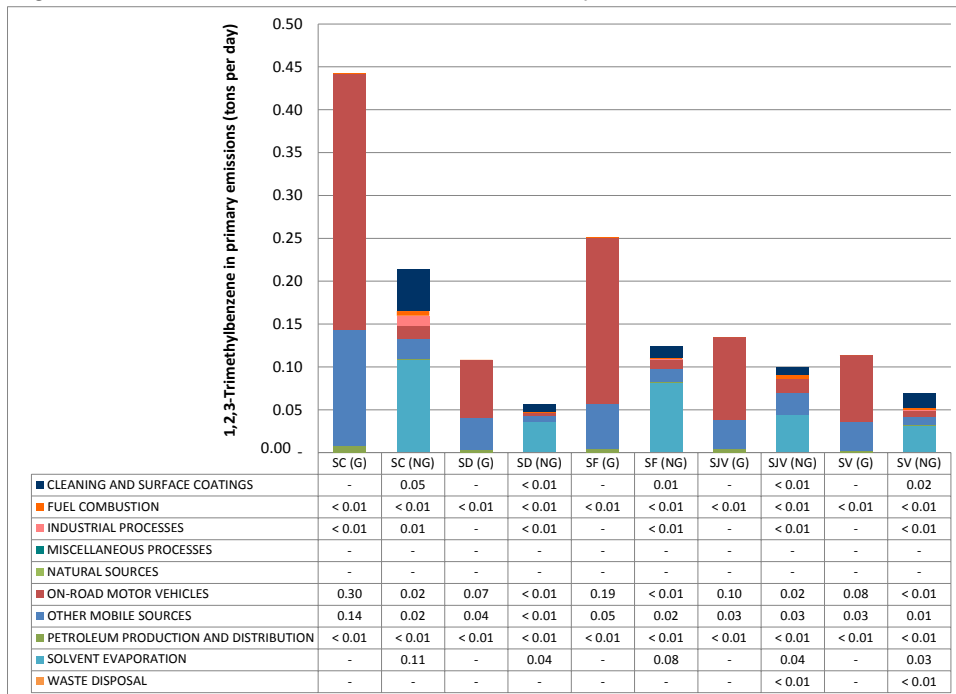


Figure 85. Emission sources of 1,2,3-trimethylbenzene in 2012



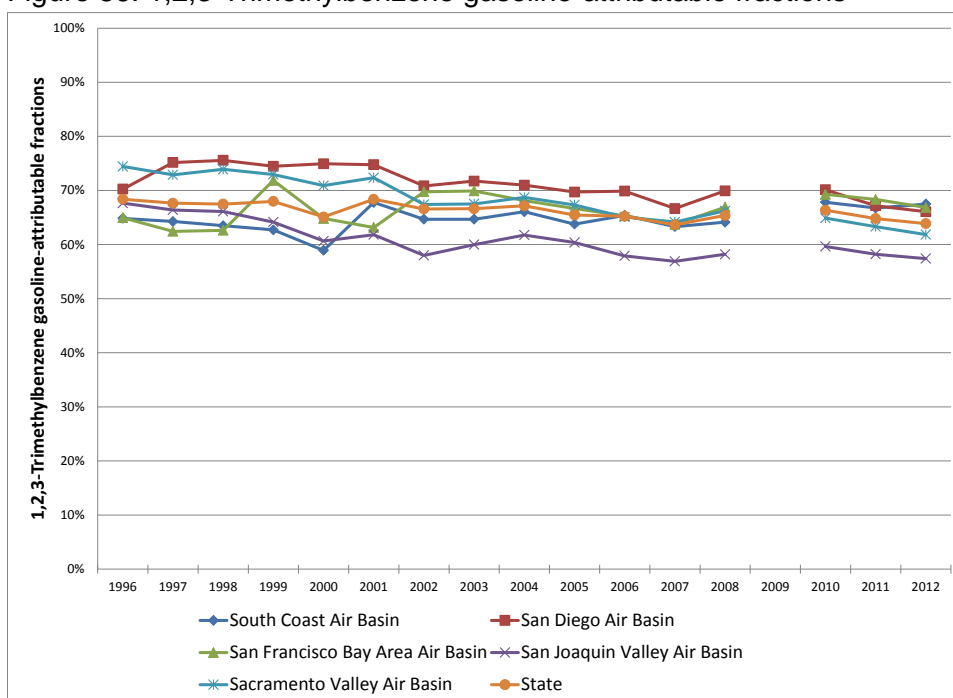
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Table 43. 1,2,3-Trimethylbenzene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	65%	70%	65%	68%	74%	68%
1997	64%	75%	62%	66%	73%	68%
1998	63%	76%	63%	66%	74%	67%
1999	63%	74%	72%	64%	73%	68%
2000	59%	75%	65%	61%	71%	65%
2001	68%	75%	63%	62%	72%	68%
2002	65%	71%	70%	58%	67%	67%
2003	65%	72%	70%	60%	68%	67%
2004	66%	71%	68%	62%	69%	67%
2005	64%	70%	67%	60%	67%	65%
2006	65%	70%	65%	58%	65%	65%
2007	63%	67%	64%	57%	64%	64%
2008	64%	70%	67%	58%	66%	65%
2009	--	--	--	--	--	--
2010	68%	70%	69%	60%	65%	66%
2011	67%	67%	68%	58%	63%	65%
2012	67%	66%	67%	57%	62%	64%

Note: Mobile source emissions were unavailable for 2009.

Figure 86. 1,2,3-Trimethylbenzene gasoline-attributable fractions



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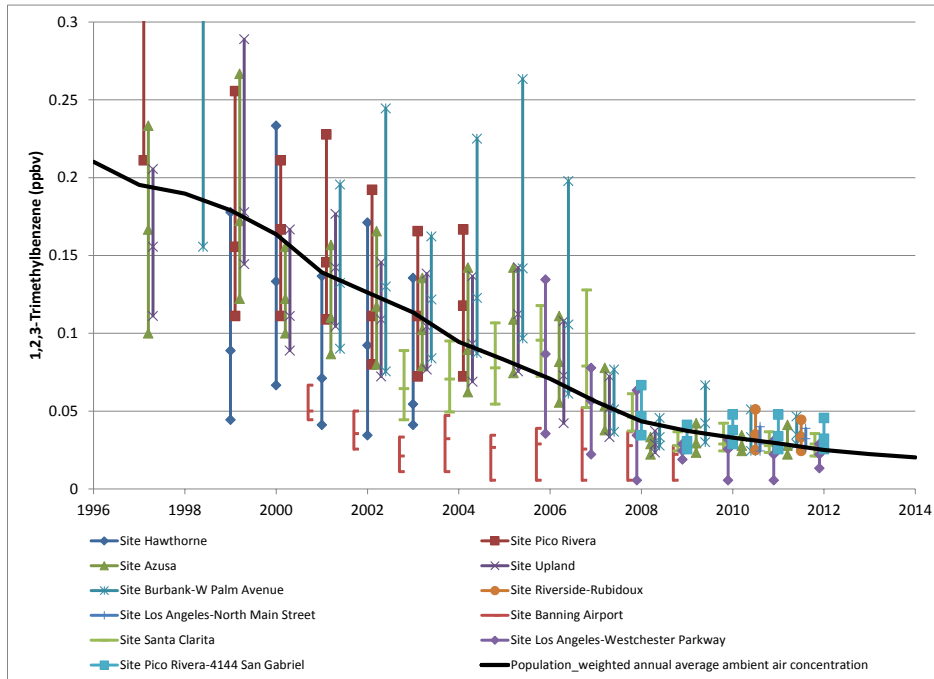
Table 44. 1,2,3-Trimethylbenzene results for South Coast Air Basin

Year	Population-weighted average concentration of 1,2,3-trimethylbenzene	Gasoline-attributable fraction	Gasoline-attributable concentration (ppbv)
1996	0.21	65%	0.14
1997	0.20	64%	0.13
1998	0.19	63%	0.12
1999	0.18	63%	0.11
2000	0.16	59%	0.096
2001	0.14	68%	0.094
2002	0.13	65%	0.082
2003	0.11	65%	0.073
2004	0.094	66%	0.062
2005	0.083	64%	0.053
2006	0.071	65%	0.046
2007	0.056	63%	0.036
2008	0.043	64%	0.028
2009	0.037	64%	0.024
2010	0.033	68%	0.022
2011	0.029	67%	0.020
2012	0.025	67%	0.017
2013	0.022	67%	0.015
2014	0.020	67%	0.014

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2012-2014 population-weighted annual average ambient air concentrations were based completely on modeled values. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

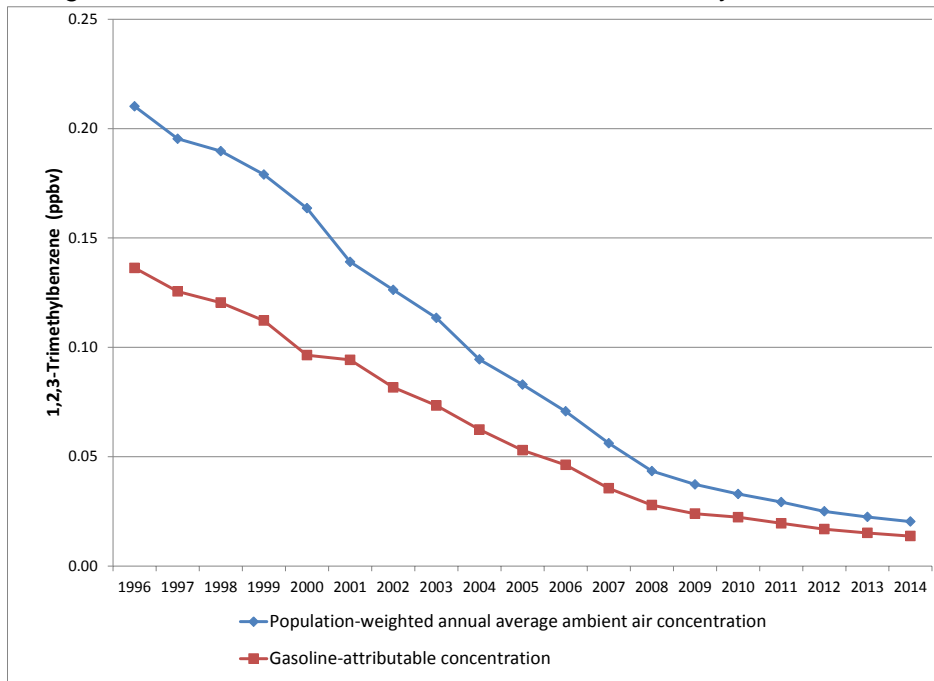
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Figure 87. Population-weighted annual average ambient air concentration of 1,2,3-trimethylbenzene in the South Coast Air Basin



Note: The vertical bars show the quartiles of measurements from South Coast Air Basin monitoring sites with 10 or more months of data. Note that the vertical axis was truncated to show the results more clearly.

Figure 88. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of 1,2,3-trimethylbenzene



1,2,4-Trimethylbenzene: Exposure Assessment Results

1,2,4-Trimethylbenzene had the 27th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. The statewide emissions of 1,2,4-trimethylbenzene from gasoline-related sources declined between 1996 and 2012 (see Figure 89). Figure 90 shows the emission sources of 1,2,4-trimethylbenzene. Table 45 and Figure 91 show the gasoline-attributable fractions of 1,2,4-trimethylbenzene.

Depending on the air basin, 71-81% of 1,2,4-trimethylbenzene came from gasoline-related sources in 2012. Non-gasoline-related sources of 1,2,4-trimethylbenzene included cold cleaning (a process used to remove grease from metal parts), heavy diesel trucks, construction and mining equipment and consumer products.

Population-weighted annual average ambient air concentrations were calculated for the South Coast Air Basin (see Table 46). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from PAMS and was supplemented with modeled values at additional locations to produce more robust estimates. Figure 92 shows the population-weighted average along with the quartiles of measured data from South Coast Air Basin monitoring sites. Figure 93 shows that the gasoline-attributable concentration of 1,2,4-trimethylbenzene declined by 92% in the South Coast Air Basin between 1996 and 2014.

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Figure 89. Emissions of 1,2,4-trimethylbenzene from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

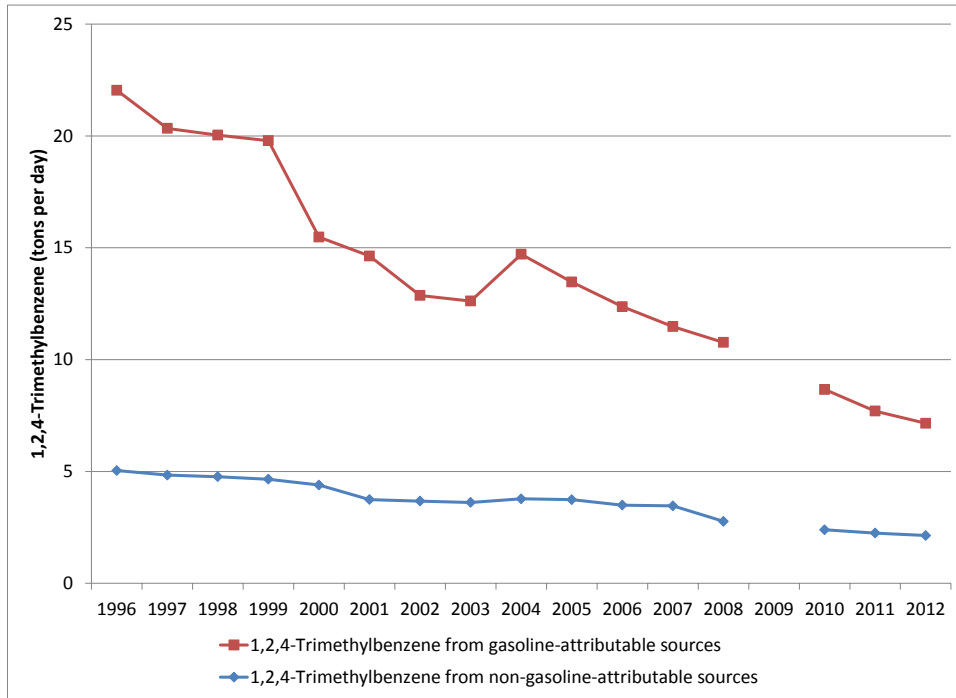
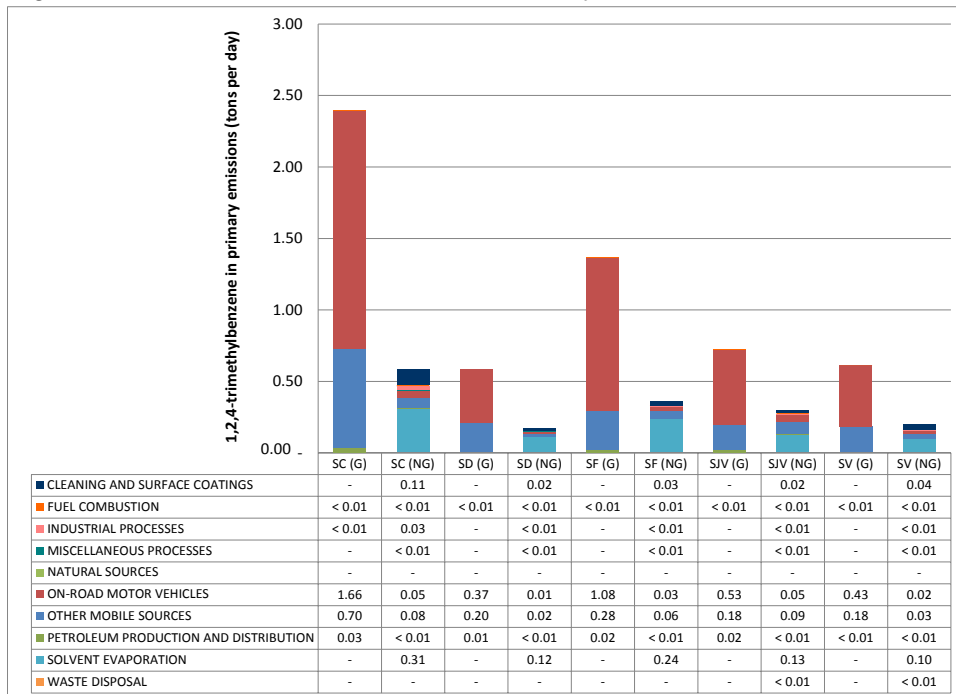


Figure 90. Emission sources of 1,2,4-trimethylbenzene in 2012



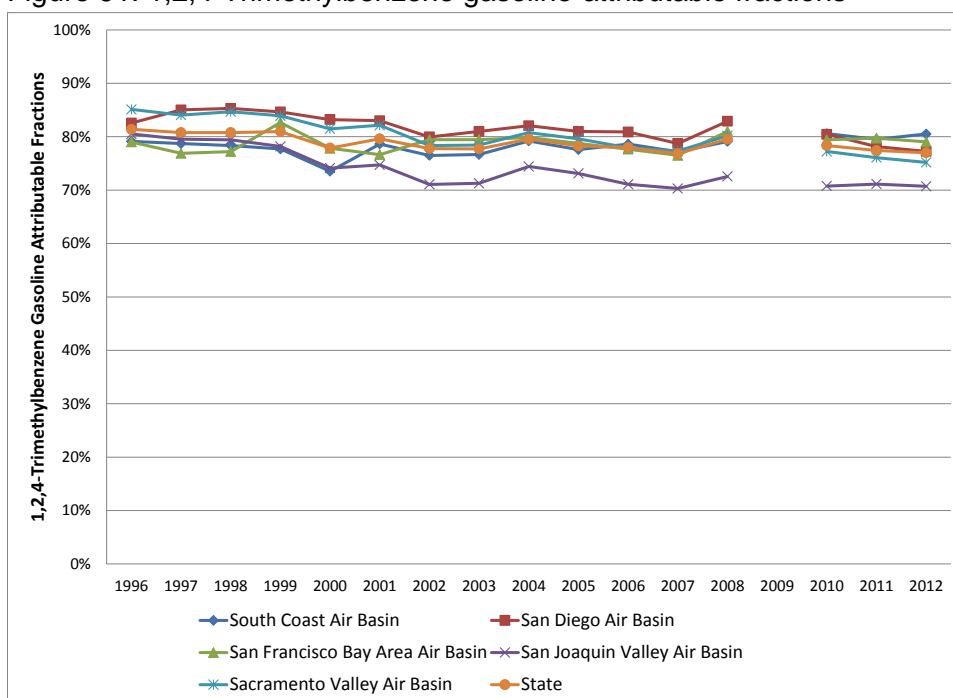
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Table 45. 1,2,4-Trimethylbenzene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	79%	83%	79%	81%	85%	81%
1997	79%	85%	77%	80%	84%	81%
1998	78%	85%	77%	79%	85%	81%
1999	78%	85%	83%	78%	84%	81%
2000	74%	83%	78%	74%	81%	78%
2001	79%	83%	77%	75%	82%	80%
2002	76%	80%	79%	71%	78%	78%
2003	77%	81%	79%	71%	78%	78%
2004	79%	82%	80%	74%	81%	80%
2005	78%	81%	79%	73%	80%	78%
2006	79%	81%	78%	71%	78%	78%
2007	77%	79%	77%	70%	77%	77%
2008	79%	83%	81%	73%	80%	80%
2009	--	--	--	--	--	--
2010	81%	80%	79%	71%	77%	78%
2011	80%	78%	80%	71%	76%	77%
2012	81%	77%	79%	71%	75%	77%

Note: Mobile source emissions were unavailable for 2009.

Figure 91. 1,2,4-Trimethylbenzene gasoline-attributable fractions



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Table 46. 1,2,4-Trimethylbenzene results for the South Coast Air Basin

Year	Population-weighted average concentration of 1,2,4-trimethylbenzene (ppbv)	Gasoline-attributable fraction	Gasoline-attributable concentration (ppbv)
1996	0.61	79%	0.48
1997	0.56	79%	0.44
1998	0.54	78%	0.43
1999	0.51	78%	0.40
2000	0.44	74%	0.32
2001	0.39	79%	0.31
2002	0.35	76%	0.27
2003	0.31	77%	0.24
2004	0.25	79%	0.20
2005	0.22	78%	0.17
2006	0.18	79%	0.14
2007	0.14	77%	0.11
2008	0.11	79%	0.087
2009	0.094	79%	0.074
2010	0.089	81%	0.072
2011	0.074	80%	0.059
2012	0.062	81%	0.050
2013	0.056	81%	0.045
2014	0.050	81%	0.041

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2012-2014 population-weighted annual average ambient air concentrations were based completely on modeled values. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

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Figure 92. Population-weighted annual average ambient air concentration of 1,2,4-trimethylbenzene in the South Coast Air Basin

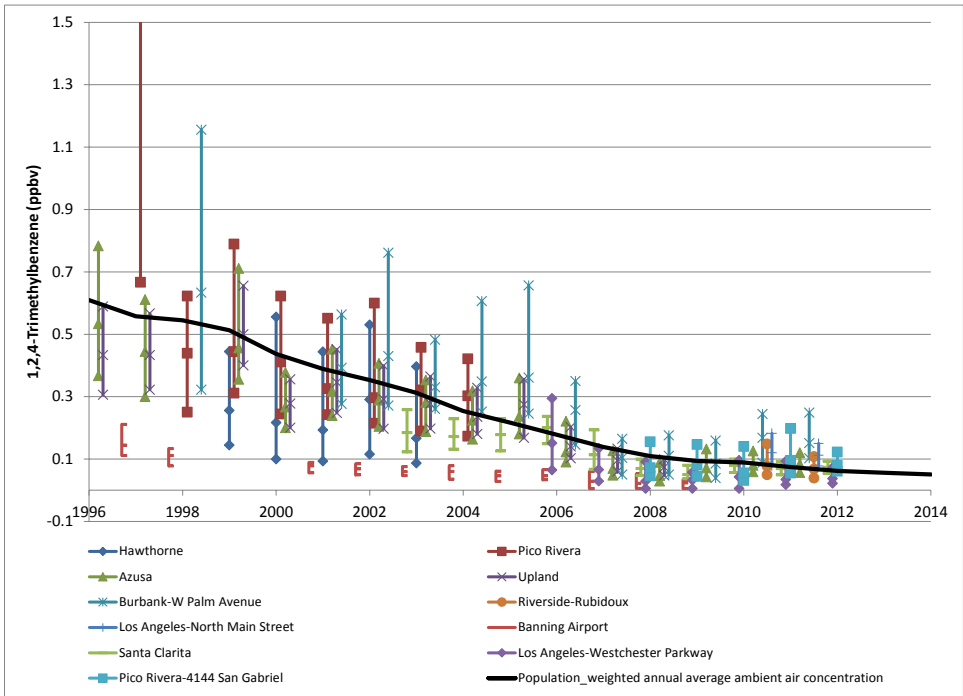
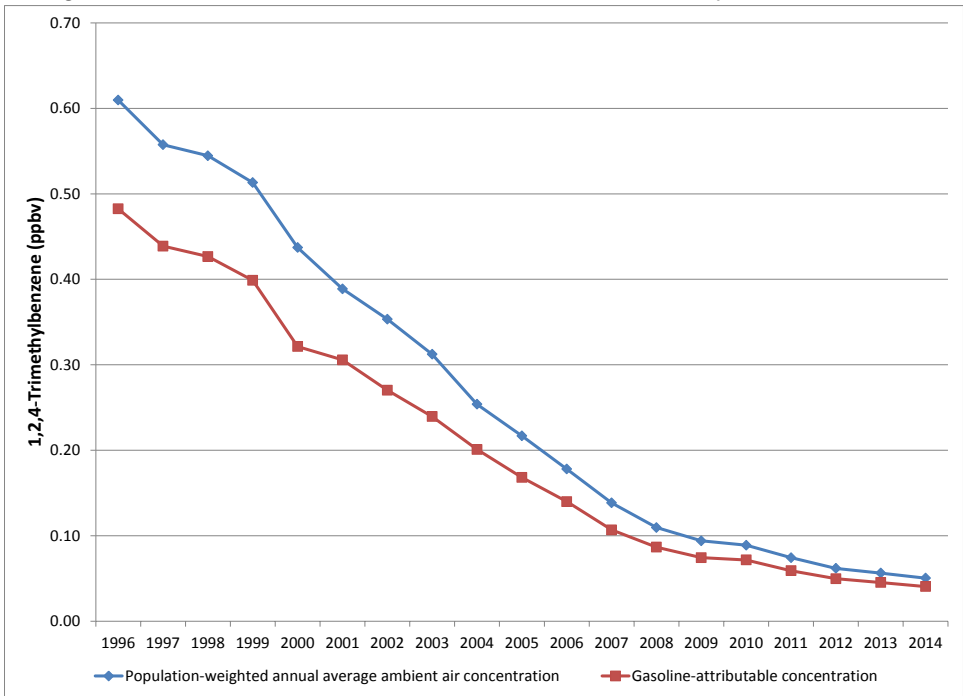


Figure 93. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of 1,2,4-trimethylbenzene



1,3,5-Trimethylbenzene: Exposure Assessment Results

1,3,5-Trimethylbenzene had the 46th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Statewide emissions of 1,3,5-trimethylbenzene from gasoline-related sources declined between 1996 and 2012 (see Figure 94). Figure 95 shows the emission sources of 1,3,5-trimethylbenzene. Table 47 and Figure 96 show gasoline-related sources of 1,3,5-trimethylbenzene. Depending on the air basin, 78-90% of 1,3,5-trimethylbenzene came from gasoline-related sources in 2012. Non-gasoline-related sources of 1,3,5-trimethylbenzene were primarily mobile sources such as very heavy diesel trucks, construction and mining equipment, farm equipment and aircraft. Gasoline-attributable fractions of 1,3,5-trimethylbenzene in the San Francisco Bay Area Air Basin increased in 2002 due to a change in estimated emissions from natural sources. This Emission Inventory adjustment also affected the statewide gasoline-attributable fraction.

Population-weighted annual average ambient air concentrations were calculated for the South Coast Air Basin (see Table 48). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from the PAMS and was supplemented with modeled values at additional locations to produce more robust estimates. Figure 97 shows the population-weighted average along with the quartiles of measurements from monitoring sites in the South Coast Air Basin.

Figure 98 shows that the gasoline-attributable concentration of 1,3,5-trimethylbenzene was 88% lower in 2014 than in 1996.

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Figure 94. Emissions of 1,3,5-trimethylbenzene from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

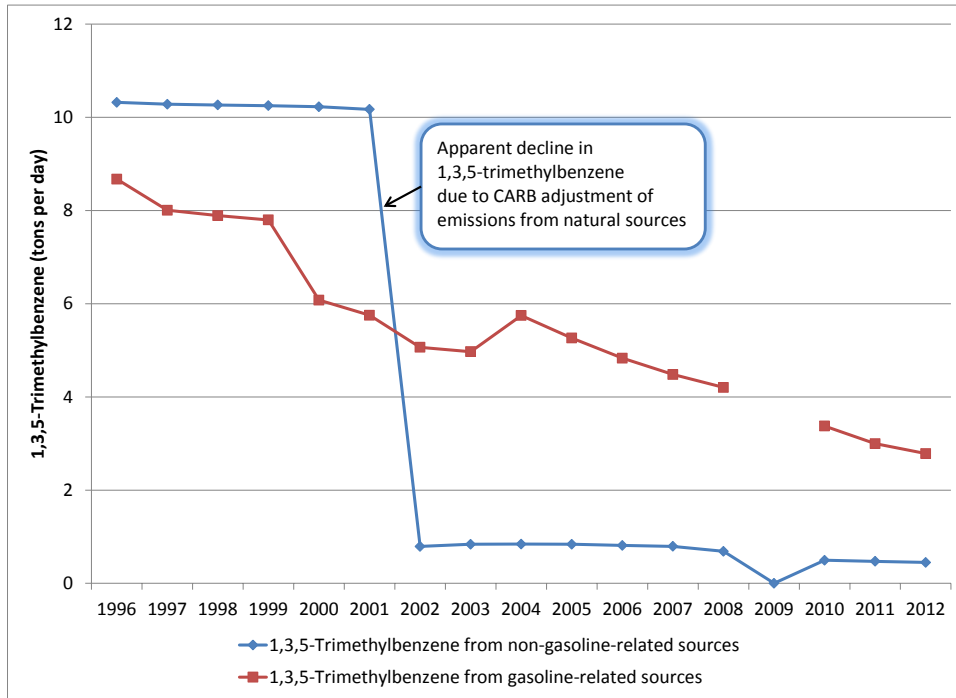
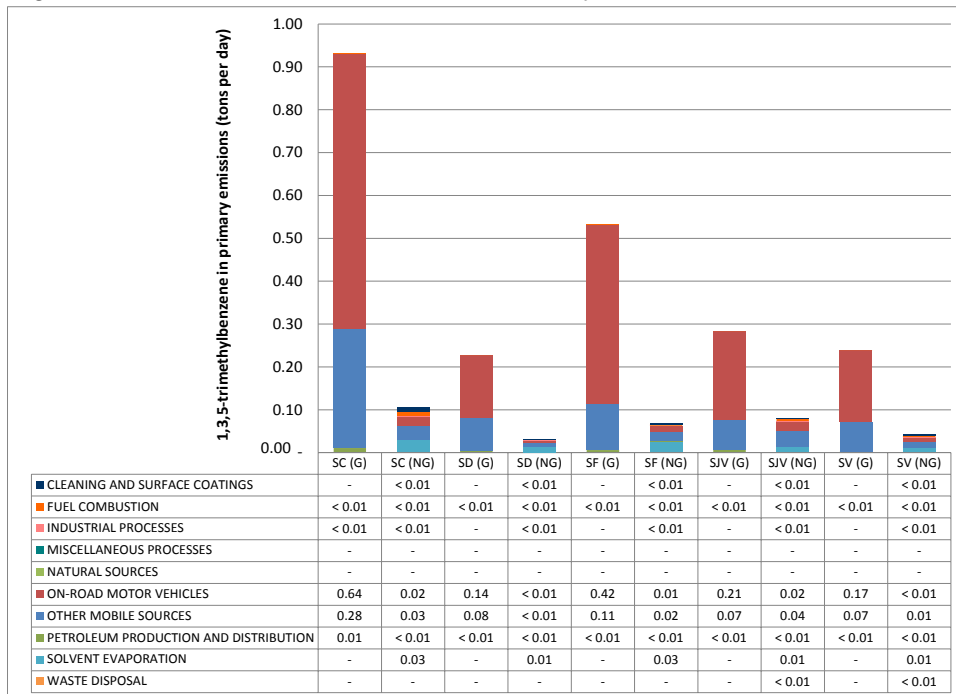


Figure 95. Emission sources of 1,3,5-trimethylbenzene in 2012



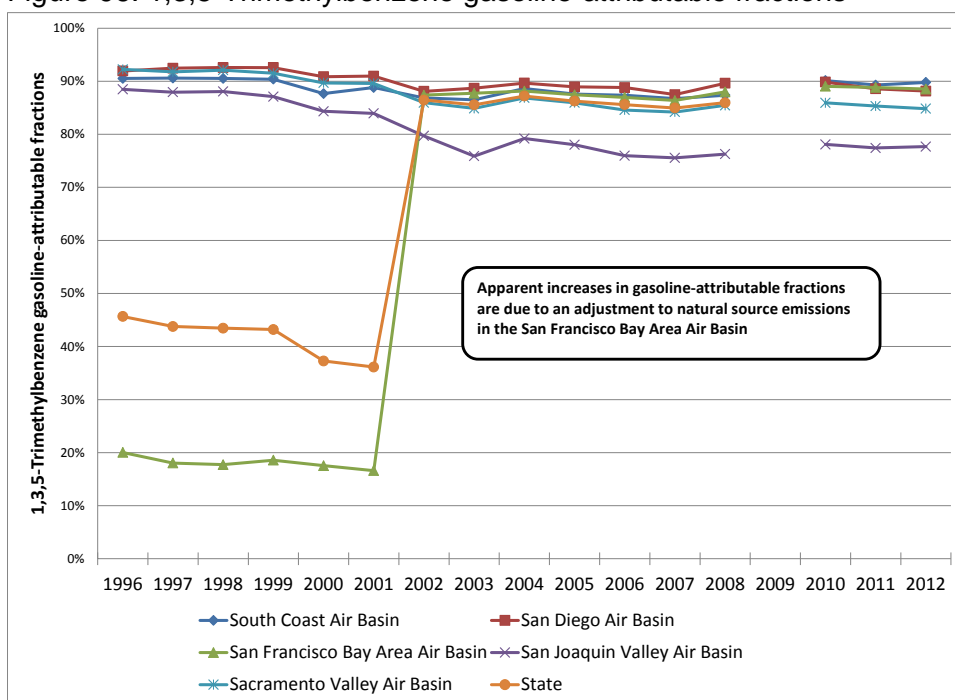
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Table 47. 1,3,5-Trimethylbenzene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	91%	92%	20%	88%	92%	46%
1997	91%	92%	18%	88%	92%	44%
1998	91%	93%	18%	88%	92%	43%
1999	90%	93%	19%	87%	92%	43%
2000	88%	91%	18%	84%	90%	37%
2001	89%	91%	17%	84%	90%	36%
2002	87%	88%	87%	80%	86%	86%
2003	87%	89%	88%	76%	85%	86%
2004	89%	90%	88%	79%	87%	87%
2005	88%	89%	87%	78%	86%	86%
2006	87%	89%	87%	76%	85%	86%
2007	87%	87%	86%	76%	84%	85%
2008	87%	90%	88%	76%	85%	86%
2009	--	--	--	--	--	--
2010	90%	90%	89%	78%	86%	87%
2011	89%	89%	89%	77%	85%	86%
2012	90%	88%	89%	78%	85%	86%

Note: Mobile source emissions were unavailable for 2009.

Figure 96. 1,3,5-Trimethylbenzene gasoline-attributable fractions



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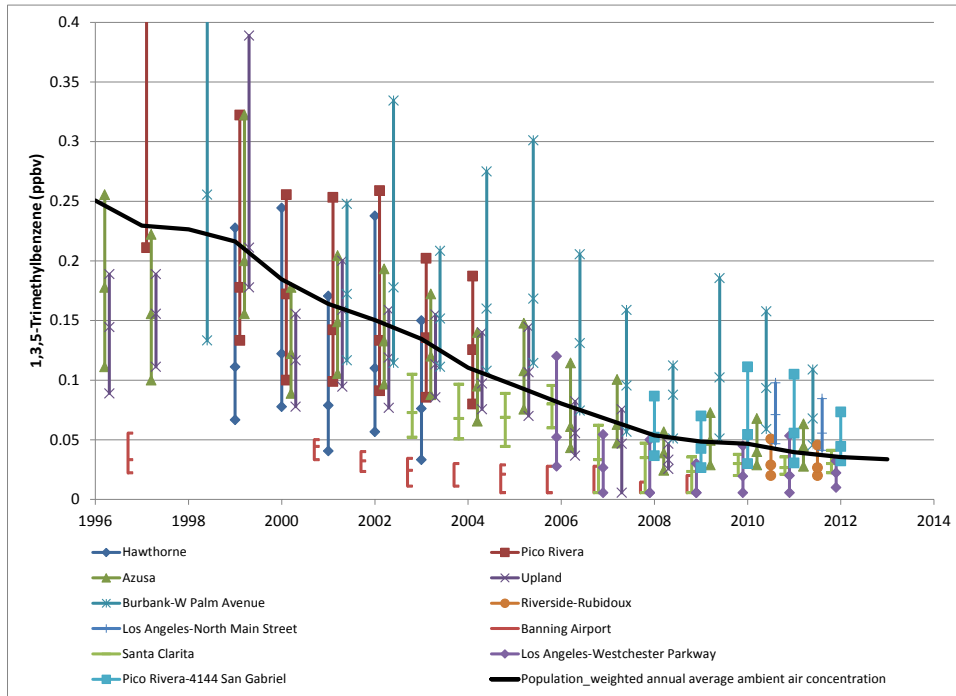
Table 48. 1,3,5-Trimethylbenzene results from the South Coast Air Basin

Year	Population-weighted average concentration of 1,3,5-trimethylbenzene (ppbv)	Gasoline-attributable fraction	Gasoline-attributable concentration (ppbv)
1996	0.25	91%	0.23
1997	0.23	91%	0.21
1998	0.23	91%	0.20
1999	0.22	90%	0.20
2000	0.18	88%	0.16
2001	0.16	89%	0.15
2002	0.15	87%	0.13
2003	0.13	87%	0.12
2004	0.11	89%	0.098
2005	0.096	88%	0.084
2006	0.080	87%	0.070
2007	0.067	87%	0.058
2008	0.054	87%	0.047
2009	0.048	87%	0.042
2010	0.047	90%	0.042
2011	0.040	89%	0.035
2012	0.036	90%	0.032
2013	0.034	90%	0.030
2014	0.031	90%	0.028

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2012-2014 population-weighted annual average ambient air concentrations were based completely on modeled values. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

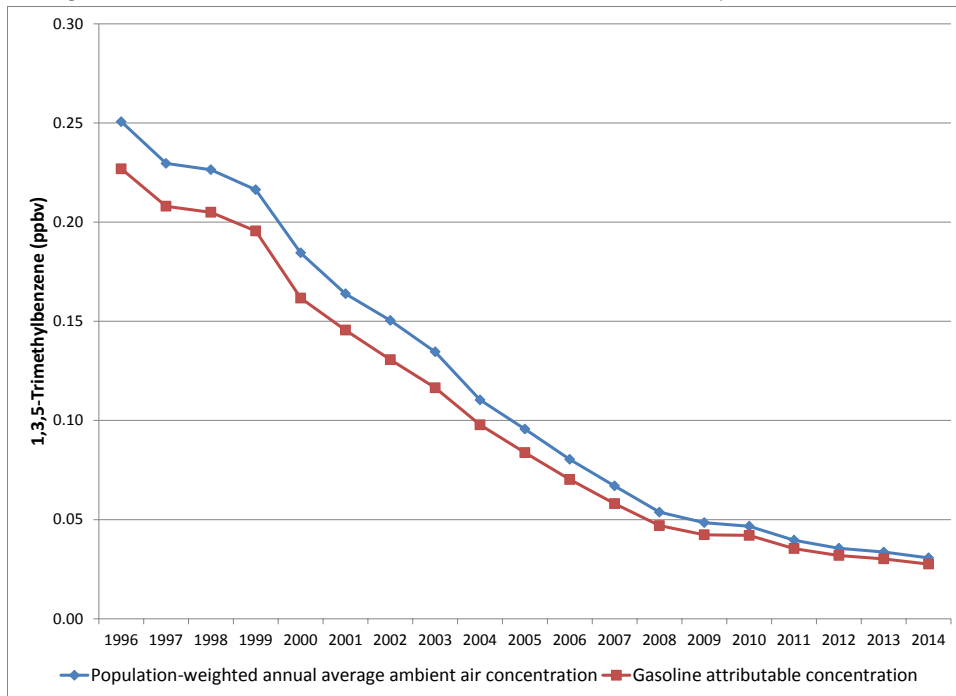
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Figure 97. Population-weighted annual average ambient air concentration of 1,3,5-trimethylbenzene in the South Coast Air Basin



Note: The vertical bars show the quartiles from monitoring sites in the South Coast Air Basin with 10 or more months of data.

Figure 98. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of 1,3,5-trimethylbenzene



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Trimethylbenzenes: Screening Risk Assessment Results

US EPA (2016b) developed an RfC of 6×10^{-2} mg/m³ (12 ppb) for trimethylbenzenes, based on decreased pain sensitivity (a neurological effect). Hazard quotients were calculated using the sum of the gasoline-attributable concentrations for the individual trimethylbenzene isomers in the South Coast Air Basin. The hazard quotients for total trimethylbenzenes were all well below 1, decreasing from 0.07 in 1996 to 0.007 in 2014. There were inadequate data to calculate a statewide hazard quotient for total trimethylbenzenes.

Xylenes: Exposure and Screening Risk Assessment Results

In this Chemical Profile, the exposure assessment results are presented for the xylene isomers (*m*-/*p*-, followed by *o*-), and the screening risk assessment results for the group are presented after that.

***m*- and *p*-Xylene: Exposure Assessment Results**

Ambient air monitoring data are reported for *m*-xylene and *p*-xylene together, and the exposure results are therefore presented in this section for the two isomers combined. *m*-Xylene and *p*-xylene are respiratory toxicants and neurotoxicants and had the 9th and 54th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Figure 99 shows that the statewide emissions of *m*-xylene from gasoline-related sources declined between 1996 and 2012. Figure 101 shows that the estimated statewide emissions of *p*-xylene from gasoline-related sources increased in 2004 and then decreased through 2012. The increase was primarily due to a new emission profile for light duty passenger vehicles that burn reformulated gasoline.

Figures 100 and 102 show the emission sources of *m*-xylene and *p*-xylene. Table 49, Figure 103, Table 50 and Figure 104 show the gasoline-attributable fractions of *m*-xylene and *p*-xylene. Statewide, in 2012, 76% of *m*-xylene came from gasoline-related sources. The remaining 21% came primarily from consumer products and surface coatings (like auto refinishing). The breakdown of *m*-xylene emissions by source category was similar for the five air basins considered. Statewide, in 2012, 29% of *p*-xylene came from gasoline-related sources. Non-gasoline sources of *p*-xylene included paint (e.g., auto refinishing) and consumer products. While it was possible to separate out *m*-xylene from *p*-xylene in the Emission Inventory, ambient air concentrations of *m*- and *p*-xylene were measured together. A combined *m*- and *p*-xylene gasoline-attributable fraction was calculated by combining the emission tonnage of the two chemicals from the Emission Inventory (Table 51). This combined fraction was used to determine the gasoline-attributable concentration of *m*- and *p*-xylene.

Population-weighted annual average ambient air concentrations of *m*- and *p*-xylene were estimated for the South Coast, San Diego, San Francisco Bay Area, Sacramento Valley and San Joaquin Valley Air Basins and statewide for the years 1996 to 2014 (see Table 52). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from the California Toxic Monitoring Network and was supplemented with modeled values at additional locations to produce more robust estimates. Figure 105 compares the population-weighted annual average ambient air concentrations of *m*- and *p*-xylene in the South Coast Air Basin to actual ambient air measurements from monitoring sites within the basin.

Table 53 tabulates the gasoline-attributable population-weighted annual average ambient air concentrations (referred to as gasoline-attributable concentrations) for all air

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basins. Figure 106 shows that the gasoline-attributable concentration of *m*- and *p*-xylene in the South Coast Air Basin declined by 78% between 1996 and 2012.

Table 54 contains population-weighted annual average ambient air concentrations calculated with the limit of detection substituted for non-detects; they are provided for comparison with Table 52.

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Figure 99. Emissions of *m*-xylene from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

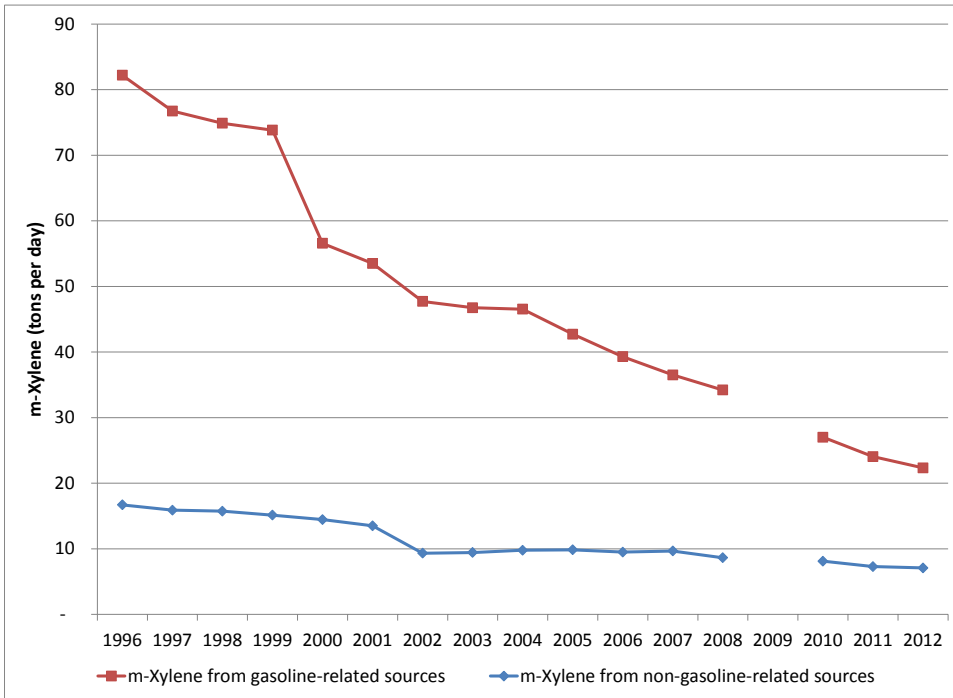
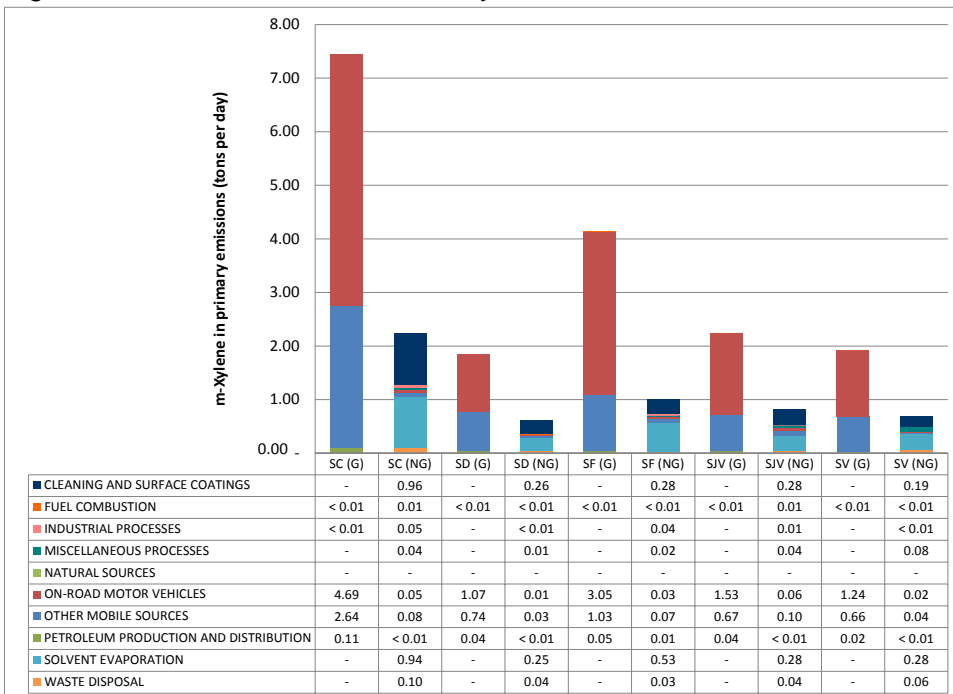


Figure 100. Emission sources of *m*-xylene in 2012



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Figure 101. Emissions of *p*-xylene from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

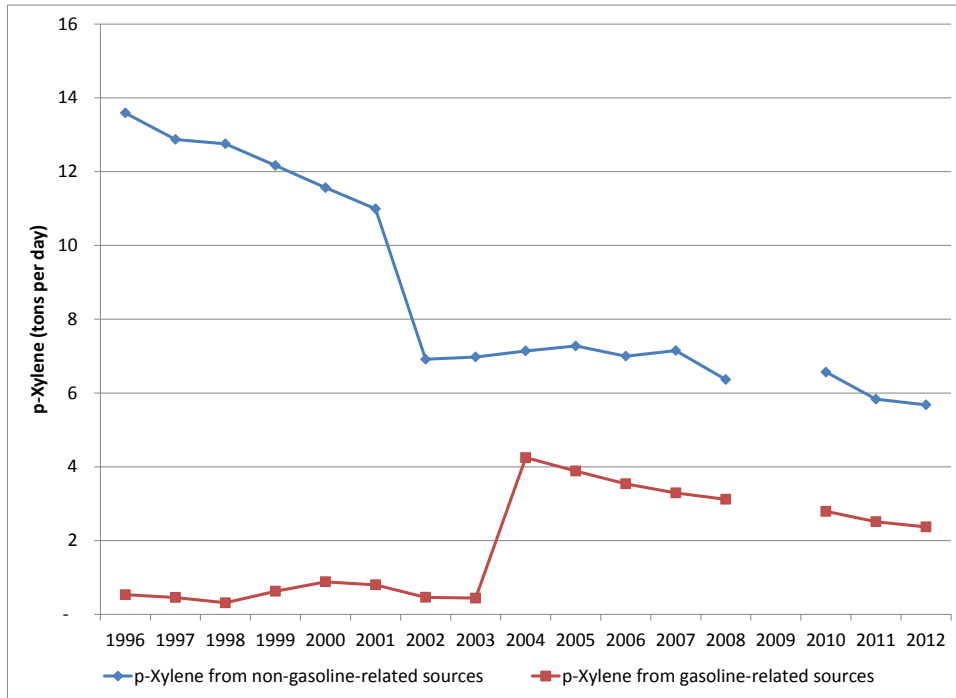
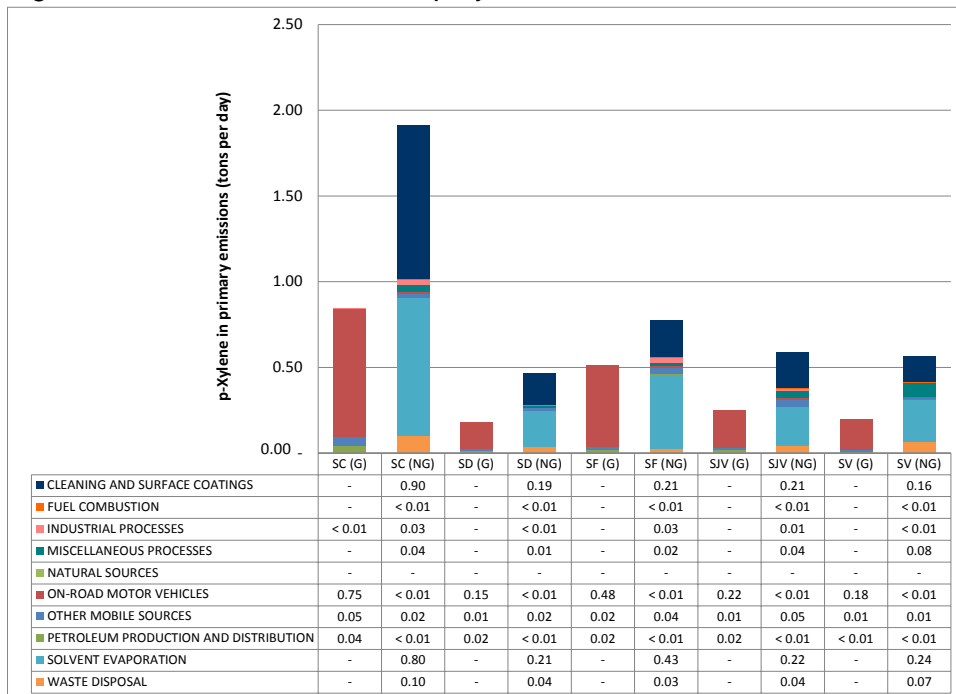


Figure 102. Emission sources of *p*-xylene in 2012



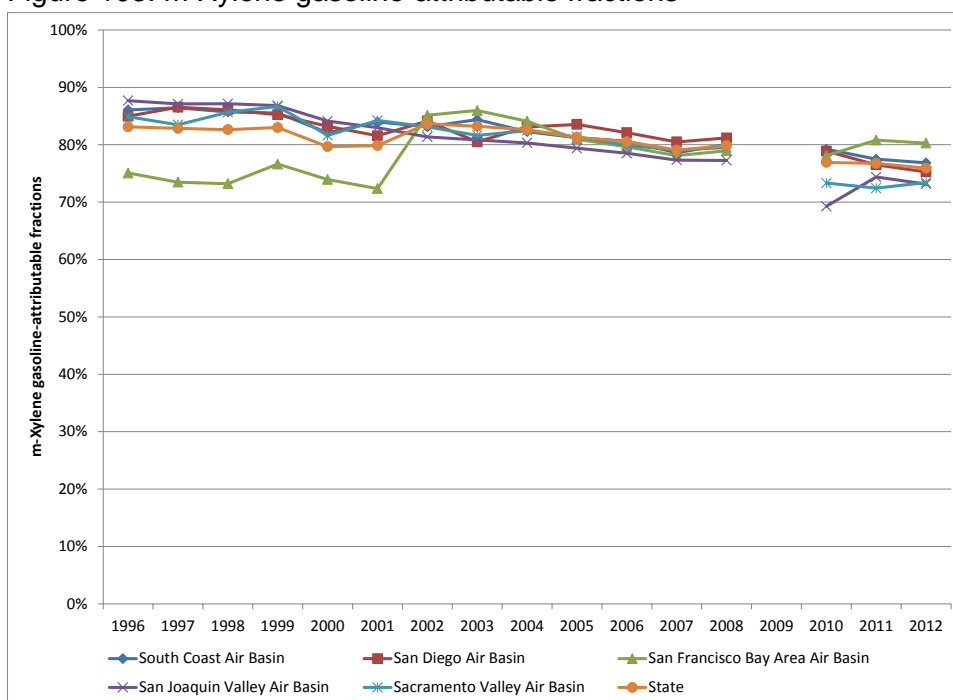
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Table 49. *m*-Xylene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	86%	85%	75%	88%	85%	83%
1997	86%	87%	73%	87%	83%	83%
1998	86%	86%	73%	87%	86%	83%
1999	86%	85%	77%	87%	87%	83%
2000	82%	83%	74%	84%	82%	80%
2001	84%	82%	72%	83%	84%	80%
2002	83%	84%	85%	81%	83%	84%
2003	84%	81%	86%	81%	82%	83%
2004	82%	83%	84%	80%	82%	83%
2005	81%	84%	81%	79%	81%	81%
2006	81%	82%	80%	79%	80%	81%
2007	79%	80%	78%	77%	79%	79%
2008	80%	81%	79%	77%	80%	80%
2009	--	--	--	--	--	--
2010	79%	79%	78%	69%	73%	77%
2011	77%	76%	81%	74%	72%	77%
2012	77%	75%	80%	73%	73%	76%

Note: Mobile source emissions were unavailable for 2009.

Figure 103. *m*-Xylene gasoline-attributable fractions



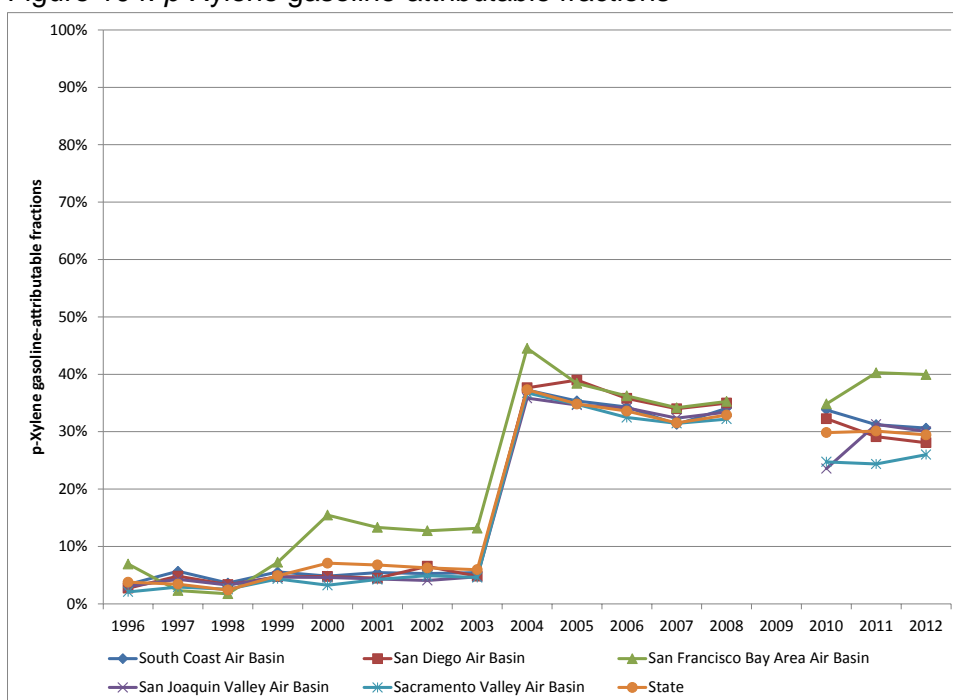
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Table 50. *p*-Xylene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	3%	3%	7%	3%	2%	4%
1997	6%	5%	2%	4%	3%	3%
1998	4%	3%	2%	3%	3%	2%
1999	6%	5%	7%	5%	4%	5%
2000	5%	5%	15%	5%	3%	7%
2001	5%	4%	13%	4%	4%	7%
2002	5%	7%	13%	4%	5%	6%
2003	5%	5%	13%	5%	5%	6%
2004	37%	38%	45%	36%	37%	37%
2005	35%	39%	38%	35%	35%	35%
2006	34%	36%	36%	34%	32%	34%
2007	31%	34%	34%	32%	31%	32%
2008	34%	35%	35%	33%	32%	33%
2009	--	--	--	--	--	--
2010	34%	32%	35%	24%	25%	30%
2011	31%	29%	40%	31%	24%	30%
2012	31%	28%	40%	30%	26%	29%

Note: Mobile source emissions were unavailable for 2009.

Figure 104. *p*-Xylene gasoline-attributable fractions



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Table 51. Gasoline-attributable fraction of *m*- and *p*-xylene

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	78%	76%	62%	81%	75%	73%
1997	79%	79%	60%	80%	73%	73%
1998	78%	78%	60%	80%	77%	73%
1999	78%	77%	64%	80%	79%	73%
2000	73%	74%	62%	76%	71%	69%
2001	75%	71%	60%	74%	75%	69%
2002	74%	76%	77%	72%	74%	75%
2003	76%	70%	78%	72%	72%	74%
2004	74%	76%	77%	73%	75%	75%
2005	73%	77%	73%	72%	73%	73%
2006	72%	74%	71%	71%	71%	72%
2007	70%	72%	69%	69%	70%	70%
2008	72%	73%	70%	69%	71%	71%
2009	--	--	--	--	--	--
2010	70%	70%	69%	58%	62%	67%
2011	67%	67%	73%	65%	61%	67%
2012	67%	65%	72%	64%	63%	66%

Note: Mobile source emissions were unavailable for 2009.

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Table 52. *m*- and *p*-Xylene population-weighted annual average concentrations (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	1.5	0.98	0.91	0.71	0.65	1.1
1997	1.4	0.94	0.80	0.61	0.60	1.0
1998	1.3	0.90	0.74	0.67	0.59	0.97
1999	1.3	1.1	0.77	0.66	0.62	0.99
2000	1.21	0.99	0.81	0.75	0.55	0.96
2001	1.2	0.95	0.74	0.71	0.50	0.92
2002	1.0	0.90	0.66	0.70	0.57	0.83
2003	0.92	0.80	0.67	0.61	0.56	0.76
2004	0.78	0.72	0.57	0.50	0.52	0.65
2005	0.69	0.80	0.50	0.49	0.47	0.60
2006	0.63	0.69	0.45	0.46	0.47	0.55
2007	0.57	0.59	0.43	0.43	0.42	0.50
2008	0.55	0.58	0.34	0.38	0.42	0.47
2009	0.48	0.52	0.35	0.37	0.39	0.43
2010	0.47	0.47	0.35	0.33	0.32	0.41
2011	0.43	0.43	0.39	0.35	0.34	0.40
2012	0.43	0.44	0.35	0.33	0.32	0.39
2013	0.43	0.40	0.41	0.36	0.35	0.40
2014	0.40	0.36	0.33	0.35	0.29	0.37

Note: half the limit of detection substituted for non-detects

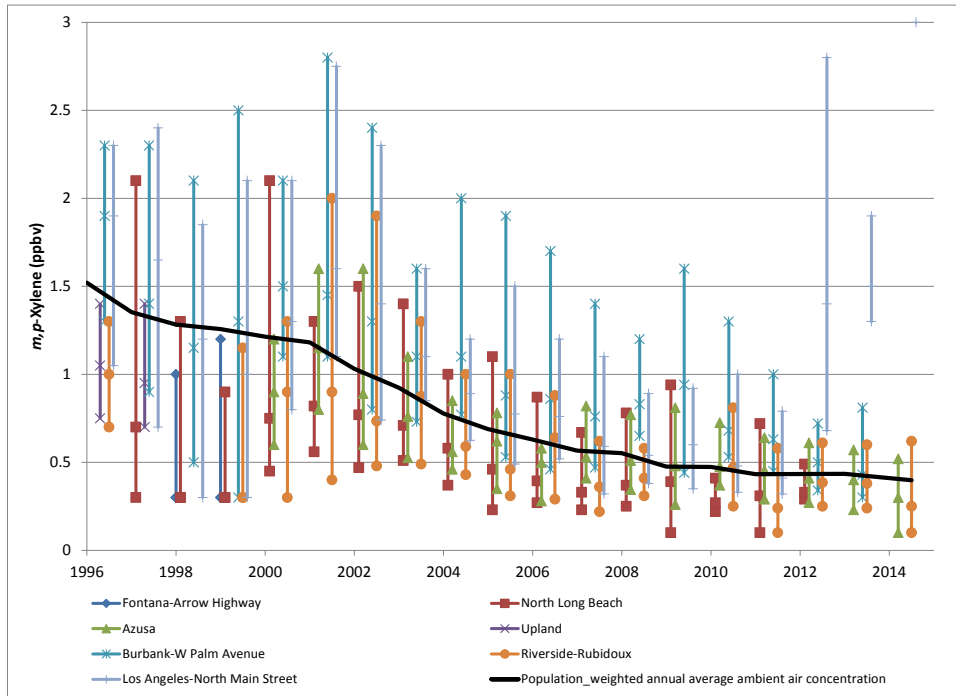
Table 53. Gasoline-attributable concentrations of *m*- and *p*-xylene

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	1.2	0.75	0.57	0.57	0.49	0.83
1997	1.1	0.74	0.48	0.49	0.44	0.74
1998	1.0	0.70	0.44	0.53	0.46	0.70
1999	0.97	0.84	0.50	0.53	0.49	0.72
2000	0.88	0.73	0.50	0.57	0.39	0.66
2001	0.89	0.68	0.45	0.53	0.38	0.64
2002	0.76	0.68	0.51	0.51	0.42	0.62
2003	0.70	0.56	0.53	0.44	0.40	0.57
2004	0.58	0.54	0.44	0.36	0.39	0.49
2005	0.50	0.61	0.36	0.35	0.35	0.44
2006	0.45	0.51	0.32	0.32	0.34	0.40
2007	0.39	0.43	0.30	0.30	0.30	0.35
2008	0.40	0.42	0.24	0.26	0.30	0.33
2009	0.34	0.38	0.24	0.26	0.28	0.30
2010	0.33	0.33	0.24	0.19	0.20	0.28
2011	0.29	0.29	0.28	0.23	0.21	0.27
2012	0.29	0.29	0.25	0.21	0.20	0.26
2013	0.29	0.26	0.29	0.23	0.22	0.26
2014	0.27	0.24	0.24	0.22	0.18	0.24

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

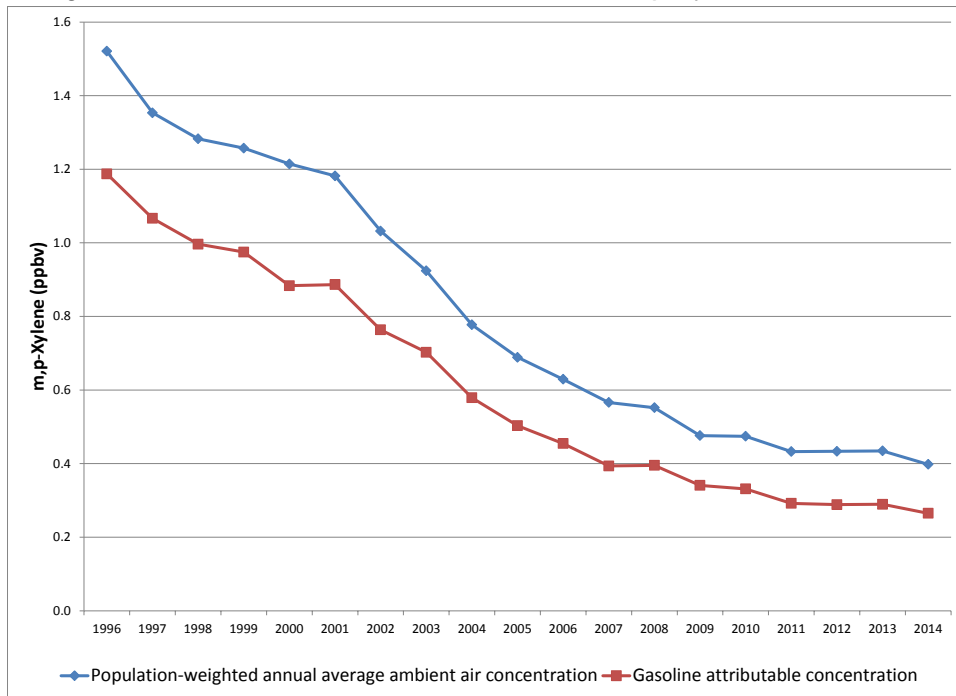
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Figure 105. Population-weighted annual average ambient air concentration of *m-* and *p*-xylene in the South Coast Air Basin



Note: The vertical bars show the quartiles of measurements from monitoring stations in the South Coast Air Basin with 10 or more months of data.

Figure 106. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of *m-* and *p*-xylene



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Table 54. *m*- and *p*-Xylene population-weighted annual average concentrations (ppbv) with limit of detection substituted for non-detects

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	1.5	0.98	0.91	0.71	0.65	1.1
1997	1.4	0.94	0.80	0.61	0.60	1.0
1998	1.3	0.90	0.74	0.67	0.59	0.97
1999	1.3	1.1	0.77	0.66	0.62	0.99
2000	1.2	0.99	0.81	0.75	0.55	0.96
2001	1.2	0.95	0.74	0.71	0.50	0.92
2002	1.0	0.90	0.66	0.70	0.57	0.83
2003	0.92	0.80	0.67	0.61	0.56	0.76
2004	0.78	0.72	0.57	0.50	0.52	0.65
2005	0.69	0.80	0.50	0.49	0.47	0.60
2006	0.63	0.69	0.45	0.46	0.47	0.55
2007	0.57	0.59	0.43	0.43	0.42	0.50
2008	0.55	0.58	0.34	0.38	0.42	0.47
2009	0.48	0.52	0.35	0.37	0.39	0.43
2010	0.47	0.47	0.35	0.33	0.32	0.41
2011	0.43	0.43	0.39	0.35	0.34	0.40
2012	0.43	0.44	0.35	0.33	0.32	0.39
2013	0.43	0.40	0.41	0.36	0.35	0.40
2014	0.40	0.36	0.33	0.35	0.29	0.37

o-Xylene: Exposure Assessment Results

o-Xylene is a respiratory toxicant and neurotoxicant and had the 22nd highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Figure 107 shows that the emissions of *o*-xylene from gasoline-related sources declined between 1996 and 2012. Figure 108 displays the emission sources of *o*-xylene. Table 55 and Figure 109 show the gasoline-attributable fractions of *o*-xylene. Statewide, in 2012, 52% of *o*-xylene came from gasoline-related sources. A significant non-gasoline-related source of *o*-xylene was paint (e.g., auto refinishing) and consumer products.

Population-weighted annual average ambient air concentrations of *o*-xylene were estimated for the South Coast, San Diego, San Francisco Bay Area, Sacramento Valley and San Joaquin Valley Air Basins and statewide for the years 1996 to 2014 (see Table 56). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from the California Toxic Monitoring Network and was supplemented with modeled values at additional locations to produce more robust estimates. Figure 110 compares the population-weighted annual average ambient air concentrations of *o*-xylene in the South Coast Air Basin to ambient air measurements from monitoring sites within the basin.

Table 57 tabulates the gasoline-attributable population-weighted annual average ambient air concentrations (referred to as gasoline-attributable concentrations) for all air basins. Figure 111 shows that the gasoline-attributable concentration of *o*-xylene in the South Coast Air Basin declined by 78% between 1996 and 2014. The results for the other air basins are tabulated in Table 57.

Table 58 contains population-weighted annual average ambient air concentrations calculated with the limit of detection substituted for non-detects; they are provided for comparison with Table 56.

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Figure 107. Emissions of *o*-xylene from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

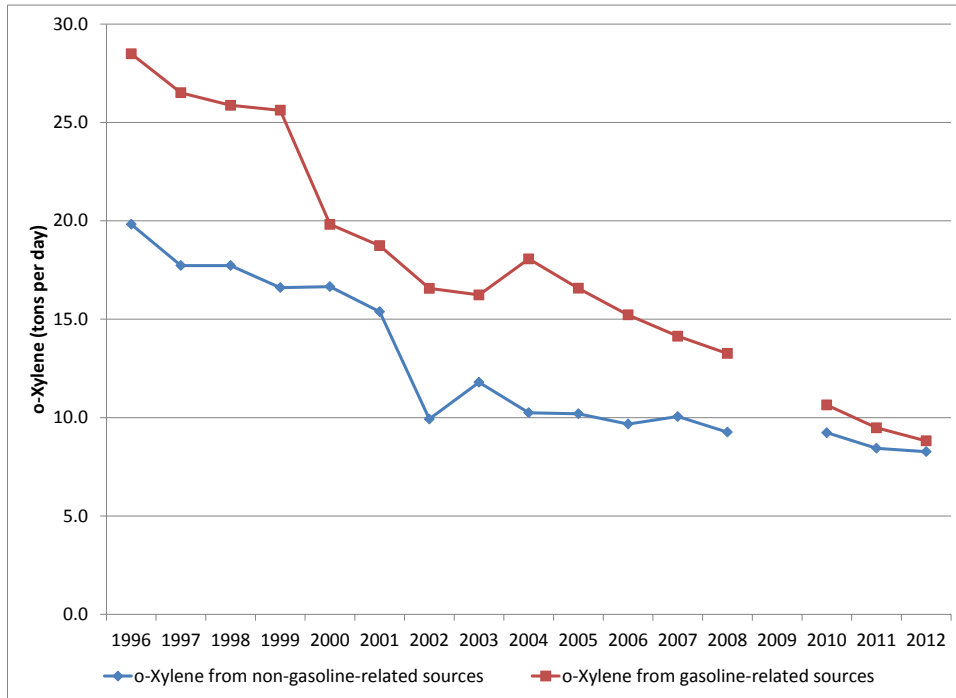
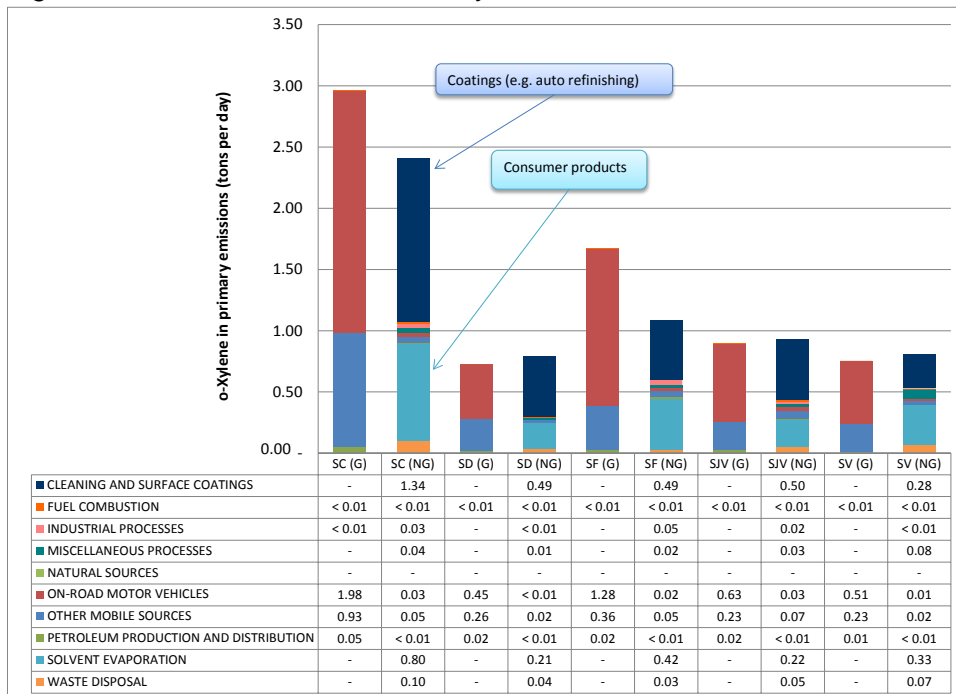


Figure 108. Emission sources of *o*-xylene in 2012



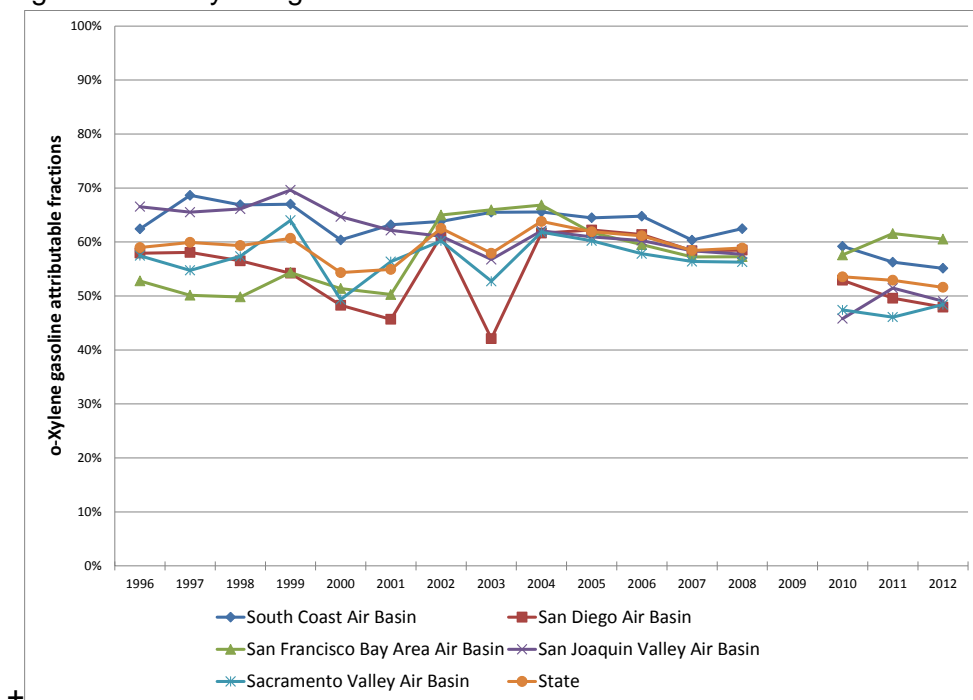
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Table 55. o-Xylene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	62%	58%	53%	67%	57%	59%
1997	69%	58%	50%	66%	55%	60%
1998	67%	57%	50%	66%	57%	59%
1999	67%	54%	54%	70%	64%	61%
2000	60%	48%	51%	65%	49%	54%
2001	63%	46%	50%	62%	56%	55%
2002	64%	61%	65%	61%	60%	63%
2003	66%	42%	66%	57%	53%	58%
2004	66%	62%	67%	62%	62%	64%
2005	64%	62%	62%	61%	60%	62%
2006	65%	61%	60%	60%	58%	61%
2007	60%	58%	57%	58%	56%	58%
2008	62%	58%	57%	58%	56%	59%
2009	--	--	--	--	--	--
2010	59%	53%	58%	46%	47%	54%
2011	56%	50%	62%	51%	46%	53%
2012	55%	48%	61%	49%	48%	52%

Note: Mobile source emissions were unavailable for 2009.

Figure 109. o-Xylene gasoline-attributable fractions



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Table 56. *o*-Xylene population-weighted average concentration

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	0.54	0.36	0.32	0.25	0.23	0.40
1997	0.44	0.30	0.26	0.19	0.18	0.33
1998	0.38	0.26	0.21	0.19	0.14	0.28
1999	0.43	0.38	0.26	0.22	0.19	0.33
2000	0.39	0.32	0.25	0.23	0.17	0.31
2001	0.37	0.31	0.23	0.21	0.16	0.29
2002	0.40	0.36	0.27	0.27	0.24	0.33
2003	0.35	0.31	0.25	0.23	0.22	0.29
2004	0.29	0.27	0.21	0.18	0.19	0.24
2005	0.23	0.27	0.16	0.16	0.16	0.20
2006	0.22	0.23	0.15	0.16	0.16	0.19
2007	0.20	0.20	0.15	0.15	0.15	0.17
2008	0.19	0.20	0.12	0.13	0.15	0.16
2009	0.18	0.19	0.13	0.14	0.15	0.16
2010	0.19	0.19	0.14	0.13	0.13	0.16
2011	0.15	0.15	0.13	0.12	0.12	0.14
2012	0.17	0.17	0.13	0.13	0.13	0.15
2013	0.16	0.14	0.15	0.13	0.13	0.15
2014	0.13	0.12	0.11	0.12	0.098	0.12

Note: There were a large number of non-detects; half the limit of detection was substituted.

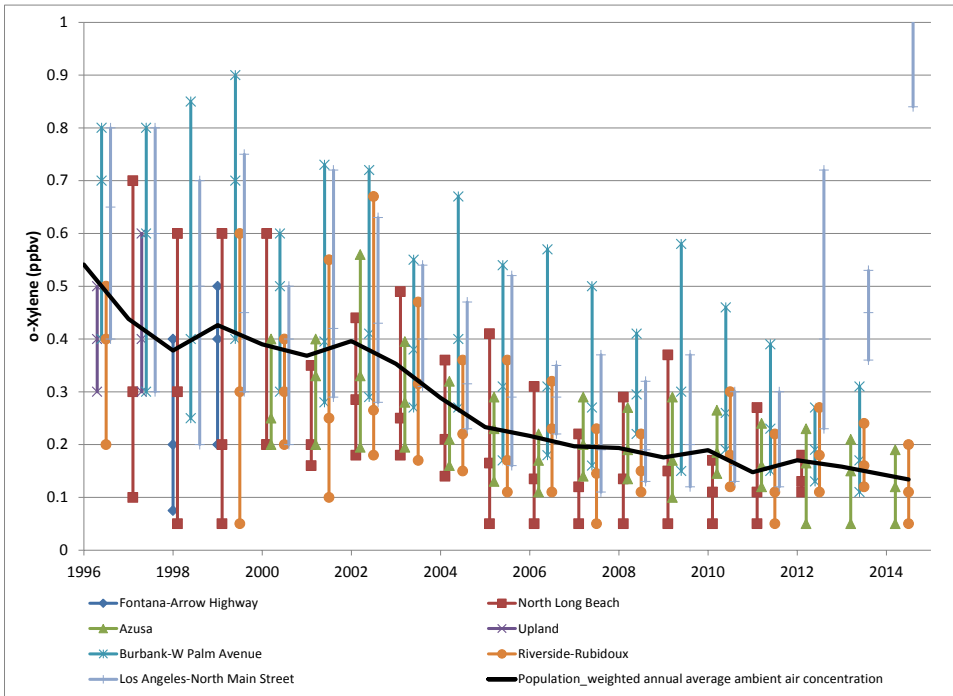
Table 57. Gasoline-attributable concentrations of *o*-xylene (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	0.34	0.21	0.17	0.17	0.13	0.24
1997	0.30	0.17	0.13	0.13	0.097	0.19
1998	0.25	0.14	0.11	0.13	0.082	0.17
1999	0.29	0.21	0.14	0.15	0.12	0.20
2000	0.24	0.16	0.13	0.15	0.086	0.17
2001	0.23	0.14	0.11	0.13	0.088	0.16
2002	0.25	0.22	0.17	0.16	0.14	0.20
2003	0.23	0.13	0.17	0.13	0.12	0.17
2004	0.19	0.17	0.14	0.11	0.12	0.15
2005	0.15	0.17	0.10	0.098	0.094	0.12
2006	0.14	0.14	0.090	0.094	0.093	0.11
2007	0.12	0.12	0.085	0.086	0.082	0.10
2008	0.12	0.12	0.067	0.077	0.085	0.096
2009	0.11	0.11	0.074	0.079	0.082	0.093
2010	0.11	0.10	0.079	0.058	0.063	0.088
2011	0.083	0.075	0.082	0.063	0.053	0.072
2012	0.094	0.083	0.081	0.063	0.063	0.079
2013	0.087	0.069	0.089	0.065	0.063	0.075
2014	0.074	0.060	0.069	0.058	0.047	0.064

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

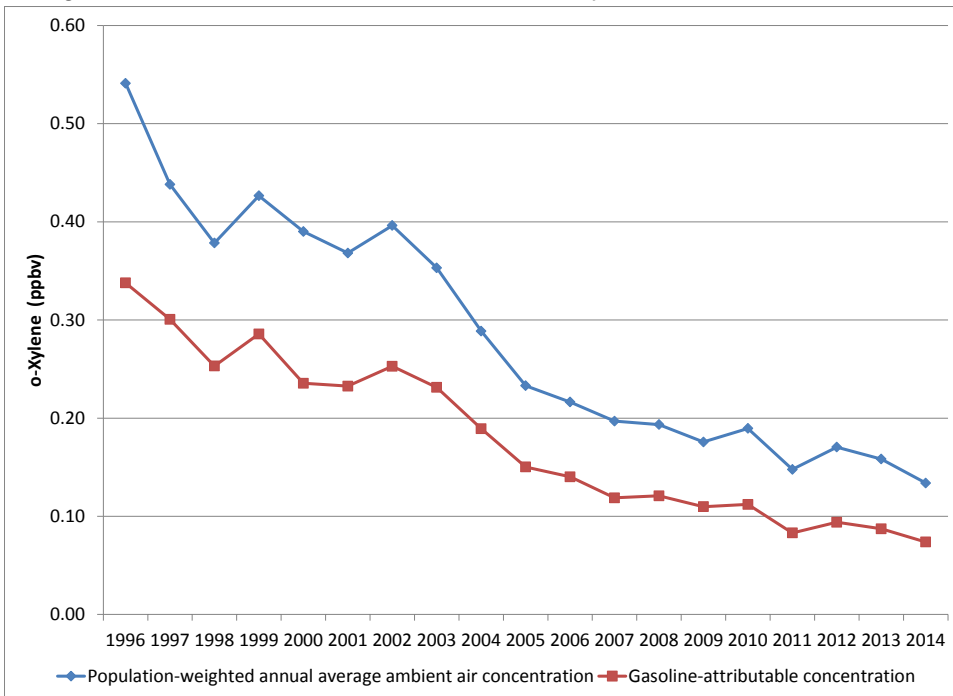
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Figure 110. Population-weighted annual average ambient air concentration of *o*-xylene in the South Coast Air Basin



Note: The vertical bars show the quartiles of the data from monitoring sites in the South Coast Air Basin with 10 or more months of data per year.

Figure 111. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of *o*-xylene



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Table 58. *o*-Xylene population-weighted average concentration with limit of detection substituted for non-detects (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	0.53	0.36	0.33	0.27	0.24	0.41
1997	0.45	0.32	0.28	0.22	0.21	0.35
1998	0.40	0.28	0.24	0.22	0.18	0.30
1999	0.44	0.40	0.29	0.25	0.22	0.35
2000	0.39	0.33	0.26	0.24	0.19	0.31
2001	0.37	0.32	0.24	0.23	0.18	0.30
2002	0.39	0.36	0.28	0.27	0.25	0.33
2003	0.36	0.32	0.26	0.24	0.23	0.30
2004	0.30	0.28	0.23	0.20	0.21	0.25
2005	0.25	0.29	0.19	0.18	0.18	0.22
2006	0.23	0.25	0.18	0.18	0.18	0.21
2007	0.22	0.23	0.18	0.17	0.18	0.20
2008	0.21	0.23	0.15	0.16	0.18	0.19
2009	0.20	0.22	0.16	0.16	0.17	0.18
2010	0.21	0.21	0.16	0.15	0.16	0.18
2011	0.17	0.18	0.16	0.15	0.15	0.16
2012	0.19	0.20	0.17	0.15	0.16	0.18
2013	0.18	0.17	0.17	0.16	0.16	0.17
2014	0.17	0.16	0.15	0.15	0.13	0.16

Xylenes: Screening Risk Assessment Results

Gasoline-attributable hazard quotients for non-cancer health effects were calculated from gasoline-attributable concentrations (see Appendix G for details) for total xylenes. Xylenes are respiratory toxicants and neurotoxicants. The combined South Coast Air Basin gasoline-attributable hazard quotient for xylenes declined from 0.0076 in 1996 to 0.0017 in 2014. The statewide gasoline-attributable hazard quotient declined from 0.0053 in 1996 to 0.0015 in 2014.

Chemical Profiles: Gasoline-related VOCs Based on Primary Emissions and Secondary Atmospheric Formation

The gasoline-related VOCs in this section are emitted from both primary sources and are also formed via secondary atmospheric reactions. The emission tonnage for these chemicals includes primary emissions from the Emission Inventory and estimated tonnage from secondary atmospheric reactions. The combined primary emissions and estimated tonnage from secondary formation were used to calculate the gasoline-attributable fractions for these gasoline-related VOCs.

Acetaldehyde: Exposure and Screening Risk Assessment Results

Acetaldehyde is a carcinogen and a respiratory toxicant and had the 47th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Acetaldehyde is also formed through secondary atmospheric reactions. Secondary reaction tonnage was calculated using formation potentials as described in Appendix E. An estimated 81% of total acetaldehyde tonnage was formed through secondary reactions statewide in 2012. Figure 112 shows that the statewide tons of acetaldehyde emitted from gasoline-related sources (primary and secondary combined) declined between 1996 and 2012. After the Emission Inventory update in 2002, the estimated acetaldehyde emissions from non-gasoline related sources remained roughly constant.

Figure 113 and Figure 114 show the sources and gasoline-attributable fractions of acetaldehyde based on primary emissions and secondary reactions. Statewide, in 2012, 18% of all acetaldehyde tonnage (primary emissions plus secondary formation) came from gasoline-related sources. Table 59 shows that gasoline-attributable fractions of acetaldehyde varied greatly by air basin. Non-gasoline-related sources included biogenic sources (all basins), livestock (San Joaquin Valley, Sacramento Valley and San Francisco Bay Area Air Basins), aircraft and construction and mining equipment. The large drop in gasoline-attributable fractions in 2002 and subsequent years was due to an update of natural sources in the Emission Inventory.

Population-weighted annual average ambient air concentrations of acetaldehyde were estimated for the South Coast, San Diego, San Francisco Bay Area, Sacramento Valley and San Joaquin Valley Air Basins and statewide for the years 1996 to 2014 (see Table 60). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from the California Toxic Monitoring Network and was supplemented with modeled values at additional locations to produce more robust estimates. Figure 115 compares the population-weighted annual average ambient air concentrations of acetaldehyde in the South Coast Air Basin to ambient air measurements from monitoring sites within the basin.

Table 61 tabulates the gasoline-attributable population-weighted annual average ambient air concentrations (referred to as gasoline-attributable concentrations) for all air basins. Figure 116 shows that the gasoline-attributable concentration in the South Coast Air Basin declined by 63% between 1996 and 2012.

Cancer risks and non-cancer hazard quotients were calculated based on gasoline-attributable ambient air concentrations (see Appendix G for details). The gasoline-attributable cancer risk for acetaldehyde in the South Coast Air Basin declined from 1.9×10^{-5} in 1996 to 7.1×10^{-6} in 2014, corresponding to an estimated reduction of 12 cancer cases per 1 million people. The statewide gasoline-attributable cancer risk for acetaldehyde declined from 1.2×10^{-5} in 1996 to 2.1×10^{-6} in 2014, or a reduction of about 10 cancer cases per 1 million people. The gasoline-attributable hazard quotient, based

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on respiratory toxicity, declined in the South Coast Air Basin from 0.013 in 1996 to 0.0050 in 2014. The statewide gasoline-attributable hazard quotient declined from 0.0086 in 1996 to 0.0020 in 2014.

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Figure 112. Emissions of acetaldehyde from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

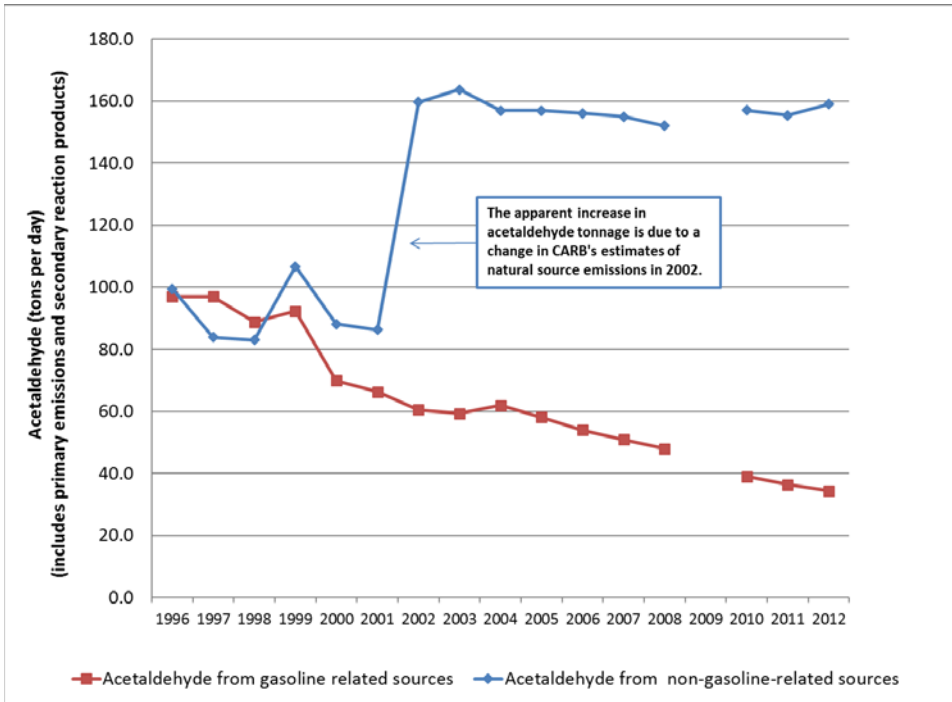
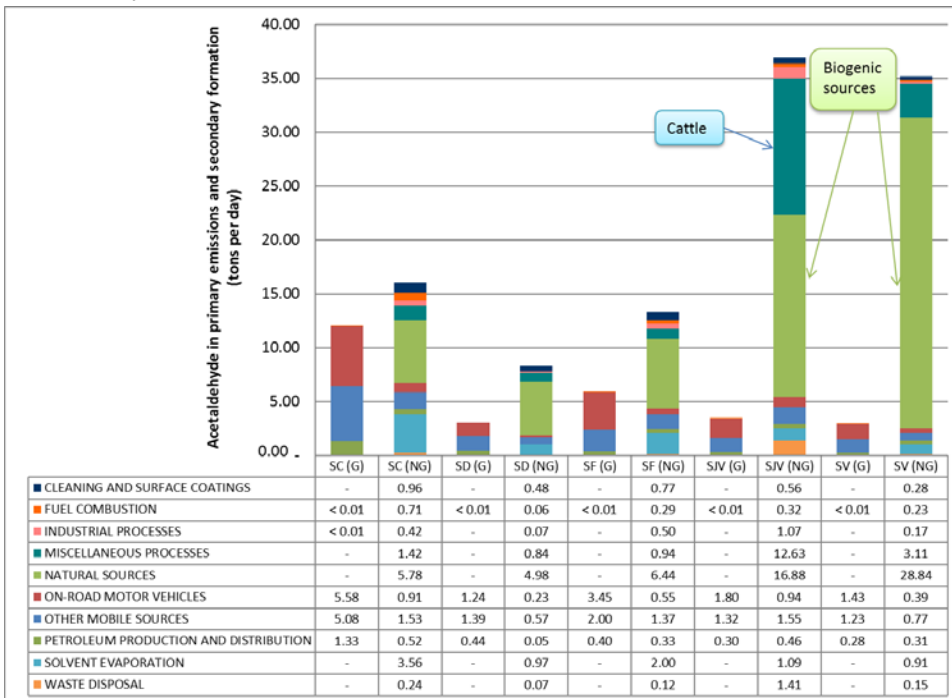


Figure 113. Primary emission sources and sources of secondary formation of acetaldehyde in 2012



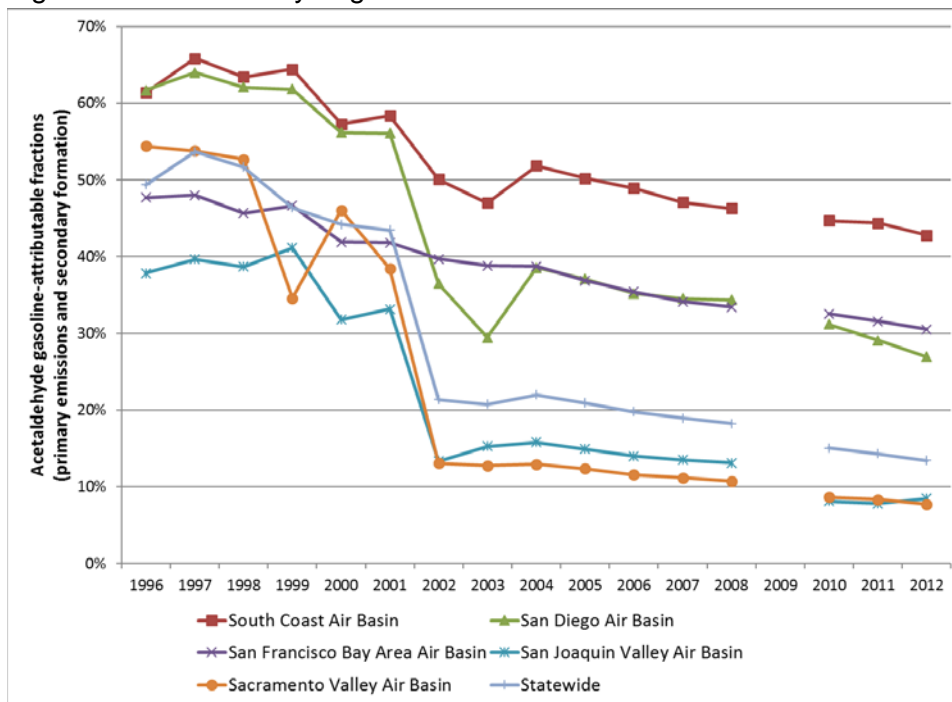
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Table 59. Acetaldehyde gasoline-attributable fractions based on primary emissions and secondary atmospheric reactions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	61%	62%	48%	38%	54%	49%
1997	66%	64%	48%	40%	54%	54%
1998	63%	62%	46%	39%	53%	52%
1999	64%	62%	47%	41%	35%	46%
2000	57%	56%	42%	32%	46%	44%
2001	58%	56%	42%	33%	38%	43%
2002	50%	36%	40%	13%	13%	21%
2003	47%	29%	39%	15%	13%	21%
2004	52%	39%	39%	16%	13%	22%
2005	50%	37%	37%	15%	12%	21%
2006	49%	35%	35%	14%	12%	20%
2007	47%	35%	34%	14%	11%	19%
2008	46%	34%	33%	13%	11%	18%
2009	--	--	--	--	--	--
2010	45%	31%	33%	8%	9%	15%
2011	44%	29%	32%	8%	8%	14%
2012	43%	27%	31%	8%	8%	13%

Note: Mobile source emissions unavailable in 2009.

Figure 114. Acetaldehyde gasoline-attributable fractions



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Table 60. Population-weighted annual average ambient air concentrations of acetaldehyde (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	1.7	1.3	1.1	1.2	1.0	1.4
1997	1.6	1.2	1.0	1.1	0.97	1.3
1998	1.4	1.1	0.83	1.0	0.86	1.1
1999	1.5	1.3	0.98	1.2	1.0	1.3
2000	1.2	1.0	0.78	0.91	0.74	0.97
2001	1.2	1.1	0.81	0.93	0.70	1.0
2002	1.2	1.1	0.85	1.0	0.93	1.0
2003	1.3	1.1	0.89	1.1	0.97	1.1
2004	1.2	1.1	0.90	1.0	0.98	1.1
2005	1.3	1.3	0.94	1.2	1.1	1.2
2006	1.0	1.1	0.75	1.1	0.91	0.93
2007	1.0	0.99	0.72	1.0	0.92	0.90
2008	0.90	0.94	0.64	0.90	0.86	0.83
2009	0.89	0.96	0.70	0.94	0.85	0.85
2010	1.0	0.95	0.76	1.0	0.84	0.90
2011	0.91	0.96	0.82	1.1	0.83	0.89
2012	1.0	1.0	0.81	1.0	0.87	0.94
2013	1.0	0.93	0.90	1.0	0.92	0.95
2014	0.92	0.85	0.81	0.98	0.79	0.88

Note: Half the limit of detection substituted for non-detects

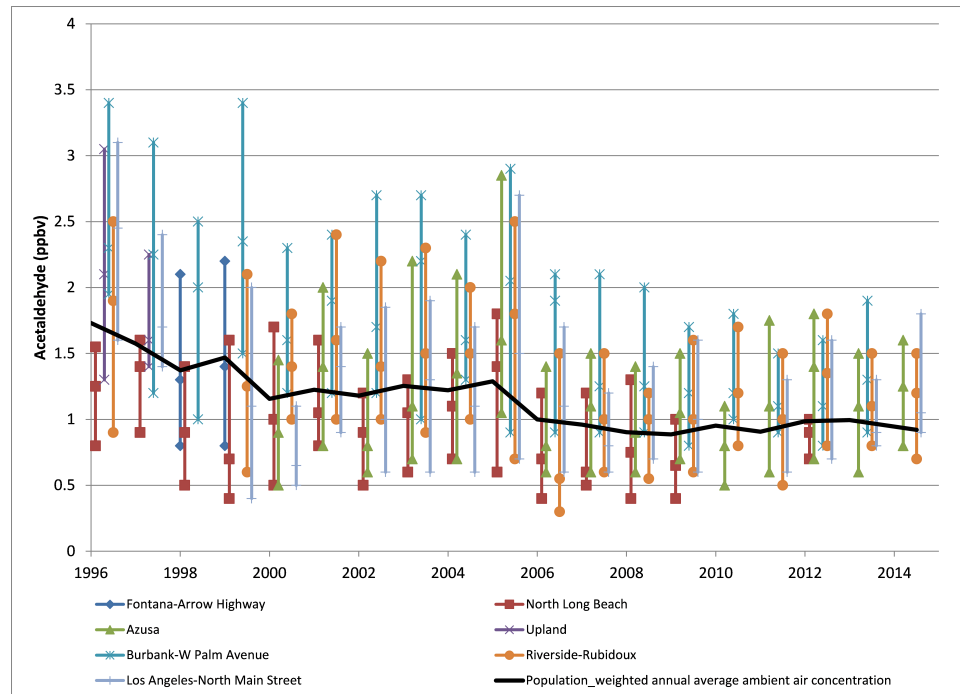
Table 61. Gasoline-attributable concentrations of acetaldehyde (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	1.1	0.8	0.51	0.44	0.56	0.69
1997	1	0.79	0.48	0.43	0.52	0.69
1998	0.87	0.67	0.38	0.39	0.45	0.58
1999	0.95	0.83	0.46	0.51	0.35	0.58
2000	0.66	0.58	0.33	0.29	0.34	0.43
2001	0.71	0.61	0.34	0.31	0.27	0.44
2002	0.59	0.41	0.34	0.14	0.12	0.22
2003	0.59	0.33	0.35	0.16	0.12	0.23
2004	0.63	0.44	0.35	0.16	0.13	0.24
2005	0.65	0.49	0.35	0.18	0.13	0.24
2006	0.49	0.37	0.27	0.15	0.11	0.18
2007	0.45	0.34	0.24	0.14	0.1	0.17
2008	0.42	0.32	0.22	0.12	0.093	0.15
2009	0.41	0.33	0.23	0.12	0.092	0.15
2010	0.43	0.3	0.25	0.085	0.073	0.14
2011	0.4	0.28	0.26	0.083	0.07	0.13
2012	0.42	0.27	0.25	0.089	0.067	0.13
2013	0.43	0.25	0.27	0.089	0.071	0.13
2014	0.39	0.23	0.25	0.083	0.061	0.12

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

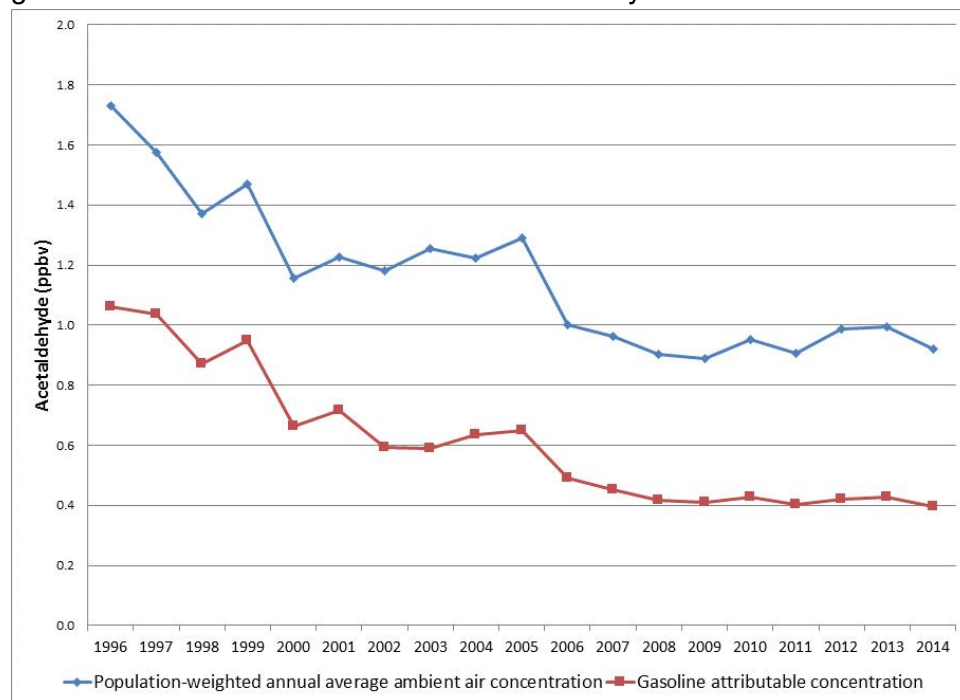
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Figure 115. Population-weighted annual average ambient air concentration of acetaldehyde in the South Coast Air Basin



Note: The vertical bars show the quartiles of acetaldehyde at South Coast Air Basin monitoring sites.

Figure 116. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of acetaldehyde



Acrolein: Exposure and Screening Risk Assessment Results

Acrolein is a respiratory toxicant and had the 94th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Acrolein is also formed through secondary atmospheric reactions, so the true emissions rank is likely higher.

1,3-Butadiene is the main precursor chemical for acrolein (OEHHA, 2006). Secondary reaction tonnage was calculated using formation potentials as described in Appendix E. Based on these calculations using 2012 data, 39% of total emissions of acrolein were formed through these secondary reactions statewide. Figure 117 shows that the statewide tons of acrolein emitted from gasoline-related sources (primary and secondary combined) declined between 1996 and 2012. Figure 117 also shows that acrolein emissions from non-gasoline related sources increased in 2012, which was attributable primarily to a higher estimate of emissions from waste disposal.

Figure 118 displays the emissions sources of acrolein. Table 62 and Figure 119 show the gasoline-attributable fractions of acrolein based on primary emissions and secondary formation. Statewide, in 2012, 28% of total emissions of acrolein came from gasoline-related sources including cars, light duty trucks, boats and off-road equipment. Non-gasoline-related sources included aircraft, agricultural pesticides, wildfires and industrial processes including plastics manufacturing. The apparent increase in the gasoline-attributable fractions in the San Francisco Bay Air Basin in 2002 and later was due to a reduction in estimated emissions from natural sources of acrolein precursor chemicals (i.e., the denominator decreased, so the gasoline-attributable fraction increased).

The California Toxic Monitoring Network began measuring ambient air concentrations of acrolein in 2004. Ambient air samples are collected in passivated stainless steel containers and then analyzed using gas chromatography mass spectrometry (GC/MS). The method is similar to that recommended by US EPA for analyzing ambient air concentrations of acrolein. US EPA studied the reliability of this method and found some potential issues.²⁶ First, acrolein concentrations can increase over time in containers that have been previously cleaned and stored. Second, the accuracy of acrolein gas standards used to calibrate GC/MS equipment varied by laboratory. CARB recently acquired several analyzers that employ gas chromatography, mass spectrometry, and Fourier Transform Infrared Reference spectroscopy to measure ambient air levels of selected VOCs, including acrolein. After testing and evaluating the devices, CARB plans to use them to measure VOCs of concern in communities impacted by air pollution.

A study funded by OEHHA and carried out by Dr. Judith Charles' group at UC Davis measured concentrations of acrolein and other carbonyls at the San Francisco-Oakland Bay Bridge Toll Plaza in 2001 using a new method for acrolein measurements

²⁶ <http://www3.epa.gov/ttnamti1/files/ambient/airtox/20101217acroleindataqualityeval.pdf>

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(Destailats et al., 2002). Destailats et al. collected three samples during one morning and two evening periods of rush hour traffic. Each sample was collected over four hours. The estimated mean acrolein concentrations were 0.100 $\mu\text{g}/\text{m}^3$ during the morning rush hour period, and 0.032 and 0.058 $\mu\text{g}/\text{m}^3$ for the two evening rush hour periods. They noted that the morning commute concentration exceeded the OEHHA cREL at that time of 0.06 $\mu\text{g}/\text{m}^3$ (the cREL was subsequently increased by OEHHA to 0.35 $\mu\text{g}/\text{m}^3$). However, Destailats et al. also noted that the acrolein concentrations they measured were lower than mean values predicted for Alameda County (0.154 $\mu\text{g}/\text{m}^3$) and San Francisco County (0.272 $\mu\text{g}/\text{m}^3$) by an earlier US EPA analysis based on 1996 data (Morello-Frosch et al. 2000). The means reported by Destailats et al. were also about an order of magnitude lower than the population-weighted annual average ambient air concentration of 1.15 $\mu\text{g}/\text{m}^3$ (reported as 0.5 ppb in Table 63 below) that we calculated for the San Francisco Bay Air Basin for 2004 (the earliest year for which data were available for our analysis).

More recently, Cahill (2014) measured concentrations of acrolein in remote, rural, and urban areas in California between September and October 2013. He reported a median below the method detection limit (MDL) in the remote areas. In the rural and urban areas, the median measurements were 0.068 and 0.165 $\mu\text{g}/\text{m}^3$ (0.030 and 0.080 ppb). These medians were about an order of magnitude lower than the population-weighted annual averages we estimated based on 2013 data across the state (see Table 63 below). He also compared his ambient outdoor acrolein measurements to those from previous studies and found a wide range of values that depended on location of measurement and method used to make the measurement.

Population-weighted annual average concentrations of acrolein were calculated for the years 2004 through 2014 using ambient air measurements of acrolein collected by the California Toxic Monitoring Network (see Table 63). Figure 120 compares the estimated population-weighted annual average concentrations to actual ambient air measurements in the South Coast Air Basin. During this time period, ambient air concentrations of acrolein increased, gasoline-attributable fractions fell and gasoline-attributable concentrations of acrolein remained roughly constant (see Table 64 and Figure 121).

Hazard quotients for non-cancer health effects were calculated based on gasoline-attributable ambient air concentrations (see Appendix G for details). Acrolein is a respiratory toxicant, with a gasoline-attributable hazard quotient of 3 in the South Coast Air Basin in 2014. The statewide gasoline-attributable hazard quotient was 1.2 in 2014. As noted above, there are some uncertainties about the methods used to measure acrolein ambient air concentrations, and there have been discrepancies in measured concentrations versus predicted means. However, acrolein has been consistently flagged as a potential respiratory health concern in ambient air by previous authors (Destailats et al., 2002; Woodruff et al., 2007; Logue et al., 2010), and our work supports that concern. Further research is warranted to better evaluate the respiratory health risks of acrolein in California. This could include work to refine sample collection

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and analytical methods for measuring acrolein in ambient air; and investigation of an appropriate biomarker for acrolein (see for example, Li et al., 2004) to more directly evaluate potential exposure in humans.

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Figure 117. Emissions of acrolein from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

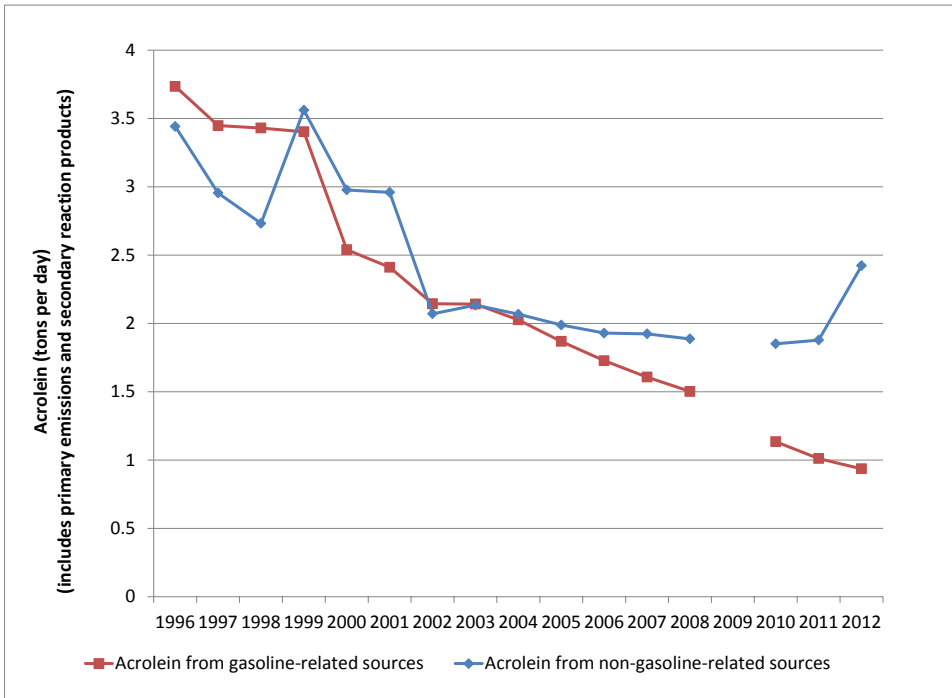
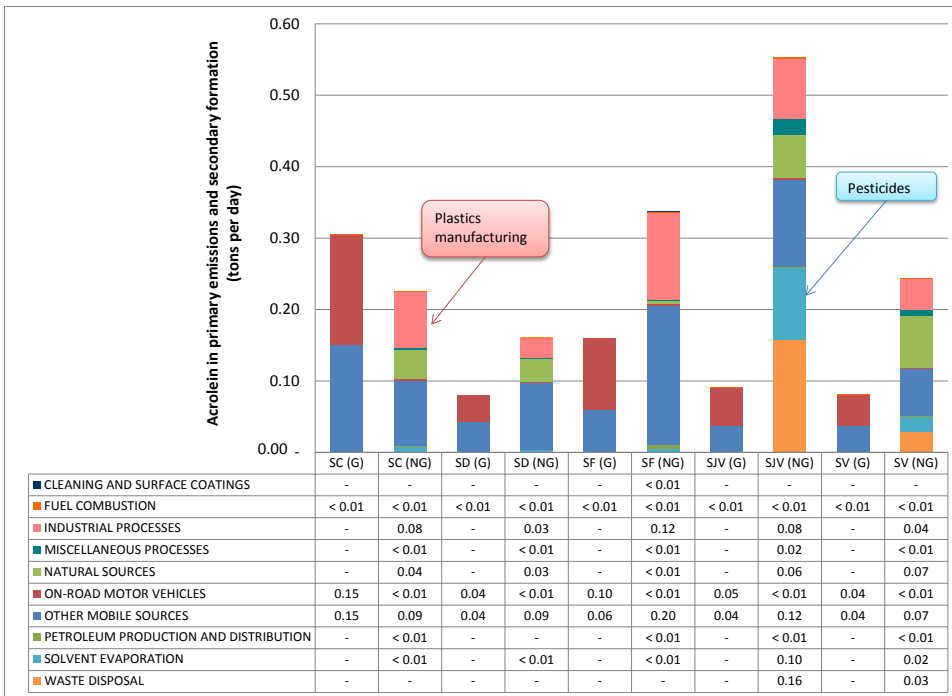


Figure 118. Primary emission sources and sources of secondary formation of acrolein in 2012



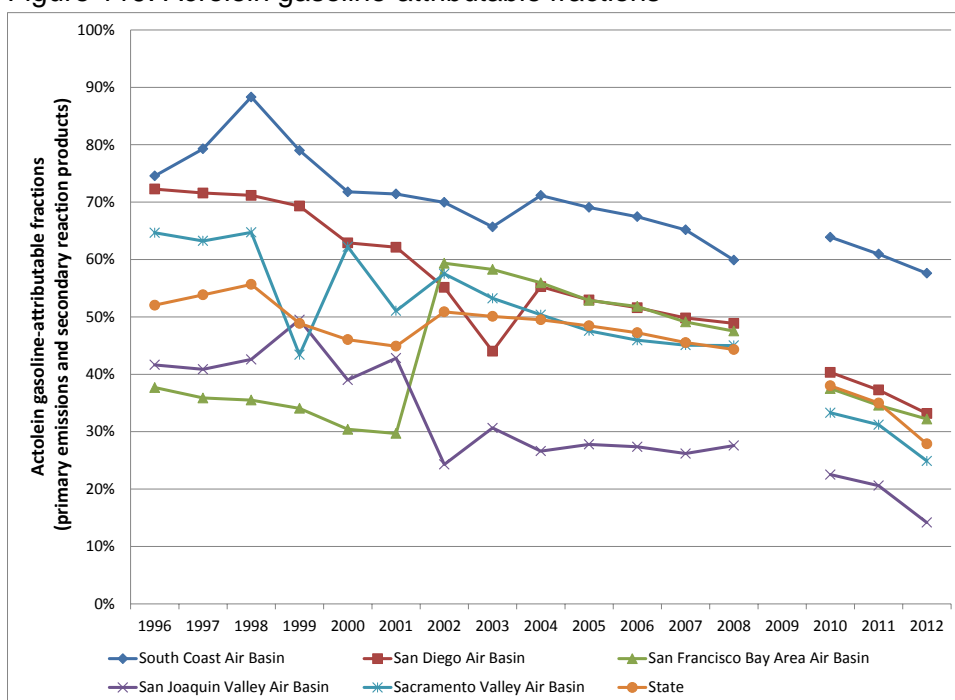
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Table 62. Acrolein gasoline-attributable fractions from primary and secondary reactions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	75%	72%	38%	42%	65%	52%
1997	79%	72%	36%	41%	63%	54%
1998	88%	71%	36%	43%	65%	56%
1999	79%	69%	34%	49%	43%	49%
2000	72%	63%	30%	39%	62%	46%
2001	71%	62%	30%	43%	51%	45%
2002	70%	55%	59%	24%	57%	51%
2003	66%	44%	58%	31%	53%	50%
2004	71%	55%	56%	27%	50%	49%
2005	69%	53%	53%	28%	48%	48%
2006	67%	52%	52%	27%	46%	47%
2007	65%	50%	49%	26%	45%	46%
2008	60%	49%	48%	28%	45%	44%
2009	--	--	--	--	--	--
2010	64%	40%	38%	23%	33%	38%
2011	61%	37%	35%	21%	31%	35%
2012	58%	33%	32%	14%	25%	28%

Note: Mobile source emissions were not available for 2009

Figure 119. Acrolein gasoline-attributable fractions



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Table 63. Population-weighted annual average ambient air concentrations of acrolein (ppb)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
2004	0.54	0.51	0.50	0.49	0.51	0.51
2005	0.59	0.59	0.53	0.50	0.51	0.56
2006	0.57	0.56	0.55	0.58	0.54	0.56
2007	0.60	0.60	0.52	0.54	0.56	0.57
2008	0.67	0.67	0.61	0.61	0.65	0.65
2009	0.71	0.71	0.64	0.68	0.68	0.69
2010	0.66	0.66	0.62	0.62	0.62	0.64
2011	0.87	0.85	0.87	0.87	0.81	0.86
2012	0.73	0.74	0.70	0.71	0.73	0.72
2013	0.69	0.73	0.72	0.69	0.66	0.70
2014	0.68	0.64	0.65	0.62	0.64	0.66

Note: half the limit of detection substituted for non-detects

Table 64. Gasoline-attributable concentrations of acrolein (ppb)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
2004	0.38	0.28	0.28	0.13	0.25	0.25
2005	0.41	0.31	0.28	0.14	0.24	0.27
2006	0.38	0.29	0.28	0.16	0.25	0.26
2007	0.39	0.30	0.25	0.14	0.25	0.26
2008	0.40	0.33	0.29	0.17	0.29	0.29
2009	0.42	0.35	0.30	0.19	0.31	0.30
2010	0.42	0.27	0.23	0.14	0.21	0.24
2011	0.53	0.32	0.30	0.18	0.25	0.30
2012	0.42	0.25	0.22	0.10	0.18	0.20
2013	0.40	0.24	0.23	0.10	0.16	0.19
2014	0.39	0.21	0.21	0.09	0.16	0.18

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

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Figure 120. South Coast Air Basin population-weighted annual average ambient air concentration compared to quartiles of acrolein measurements

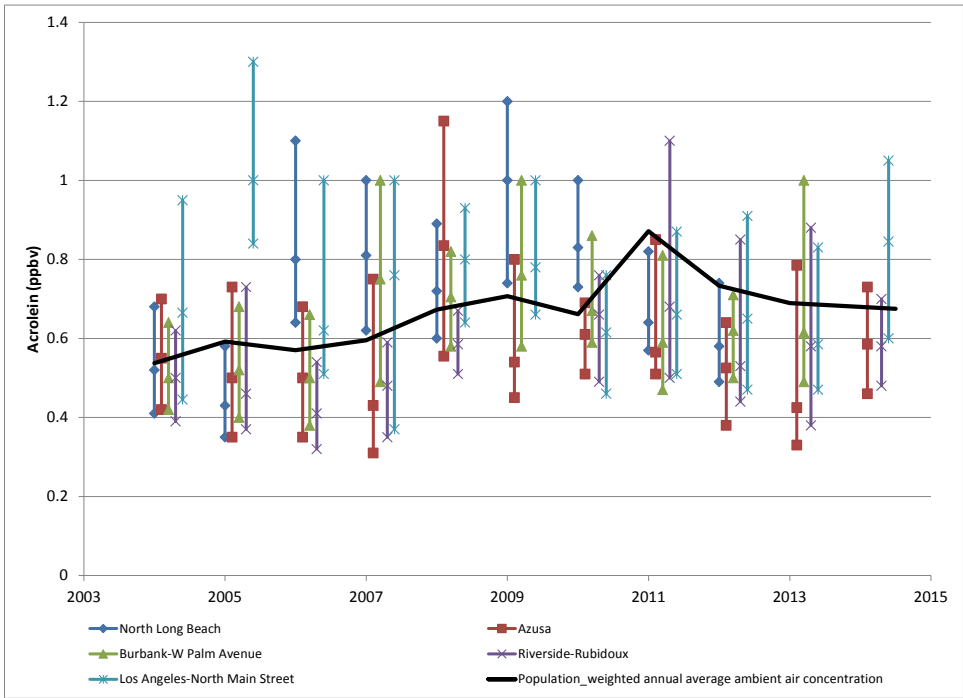
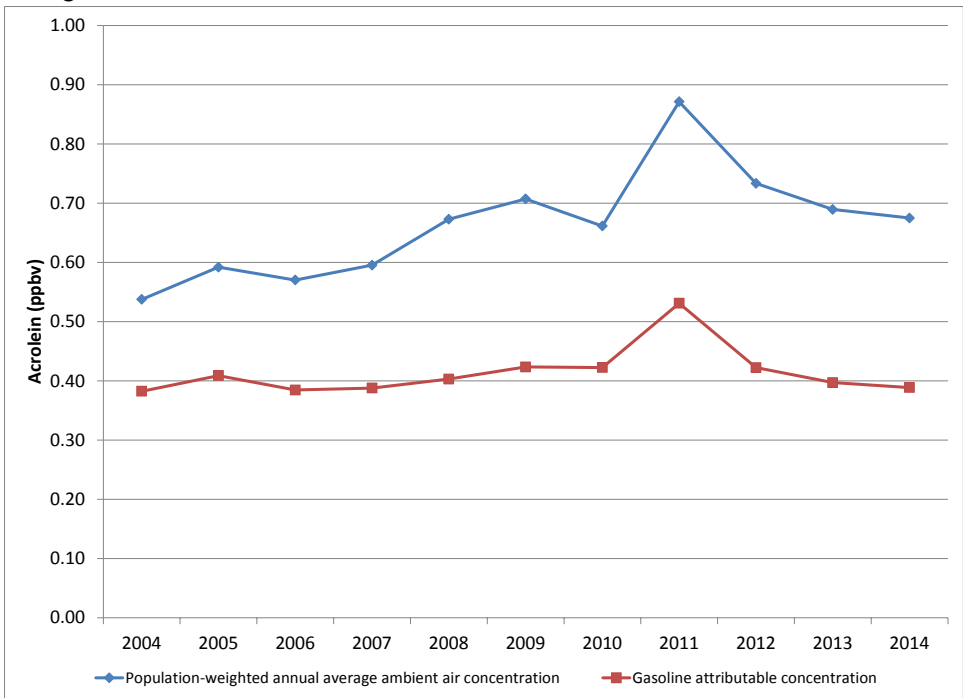


Figure 121. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of acrolein



Benzaldehyde: Exposure and Screening Risk Assessment Results

Benzaldehyde is an aromatic aldehyde that is carcinogenic in mice and has evidence of respiratory toxicity in rats. It had the 62nd highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Benzaldehyde is also formed through secondary atmospheric reactions. Carter (2001) provided formation potentials for aromatic aldehydes, including benzaldehyde, as a group. These formation potentials were used to estimate tons of aromatic aldehydes formed through secondary atmospheric reactions as a group, and we used that information to estimate the gasoline-attributable fraction for benzaldehyde. In 2012, about 46% of the overall emissions of aromatic aldehydes were formed through secondary reactions.

Figure 122 shows that total emissions of aromatic aldehydes declined between 1996 and 2012. Figure 123 shows the emission sources of aromatic aldehydes. Table 65 and Figure 124 show the gasoline-attributable fractions of aromatic aldehydes. Statewide in 2012, 68% of aromatic aldehyde emissions came from gasoline-related sources including cars and light duty trucks. The main non-gasoline-related sources included heavy-duty diesel trucks, off-road equipment and aircraft. Figure 124 shows that gasoline-attributable fractions in the San Joaquin air basin dropped between 2001 and 2003, because estimated emissions from diesel farm equipment, a source of aromatic aldehydes, increased in 2003.

Data collected by the Desert Research Institute (DRI) in the summer of 1996 were used to create a model for estimating ambient air concentrations of benzaldehyde (see Appendix D for details). Table 66 lists the population-weighted annual average ambient air concentrations for the South Coast Air Basin. Figure 125 compares the estimated population-weighted annual average ambient air concentrations of benzaldehyde in the South Coast Air Basin to the DRI data and to benzaldehyde measurements from other studies. It was assumed that the gasoline-attributable fraction of aromatic aldehydes could be used for benzaldehyde. Figure 126 shows that the gasoline-attributable ambient air concentration of benzaldehyde in the South Coast Air Basin declined by 80% between 1996 and 2012.

We located a few studies that could be used to check the estimated population-weighted annual average ambient air concentrations for benzaldehyde. A study funded by OEHHA and conducted at the San Francisco-Oakland Bay Bridge Toll Plaza in April 2001 found benzaldehyde air levels in the range of 0.02-0.04 ppb (Destailats et al., 2002). The US EPA AirData website had 3-hour measurements taken during summer months in Sacramento County, Fresno County and Kern County. CARB NMOC/PAMS benzaldehyde data came from two monitoring sites in the San Joaquin Air Basin. Figure 125 compares our modeled population-weighted ambient air concentrations of benzaldehyde in the South Coast Air Basin to ambient air measurements taken at sites in California.

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We could not estimate cancer risk or a non-cancer hazard quotient for benzaldehyde, because we did not locate a cancer potency or other health reference value.

Figure 122. Emissions of aromatic aldehydes from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

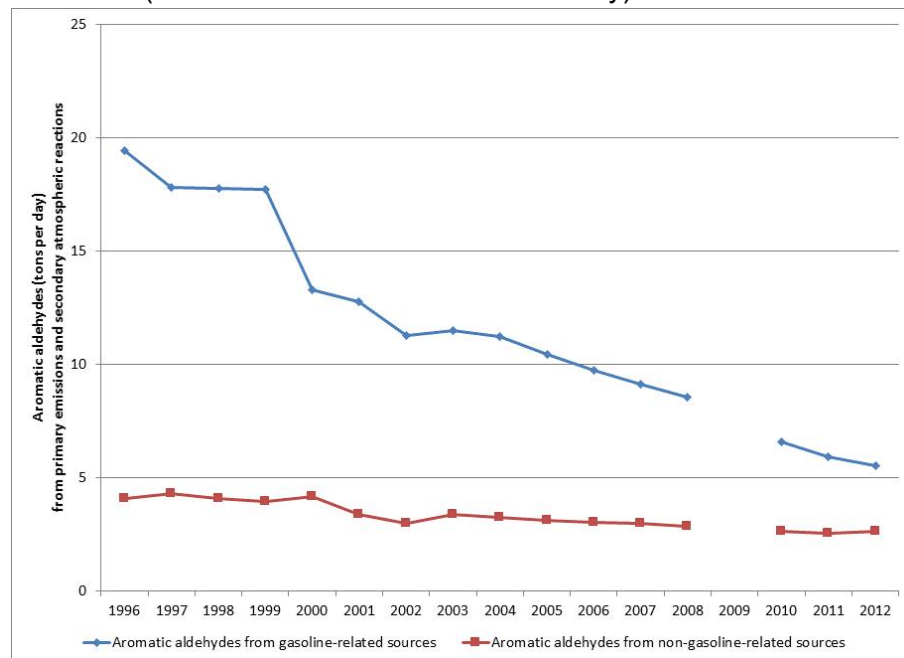
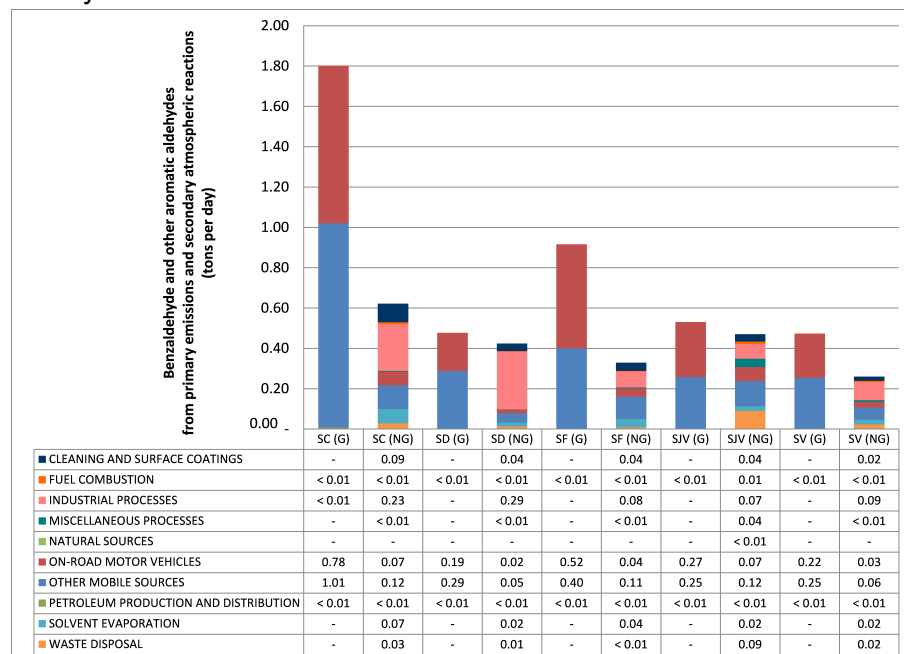


Figure 123. Primary emission sources and sources of secondary formation of aromatic aldehydes in 2012



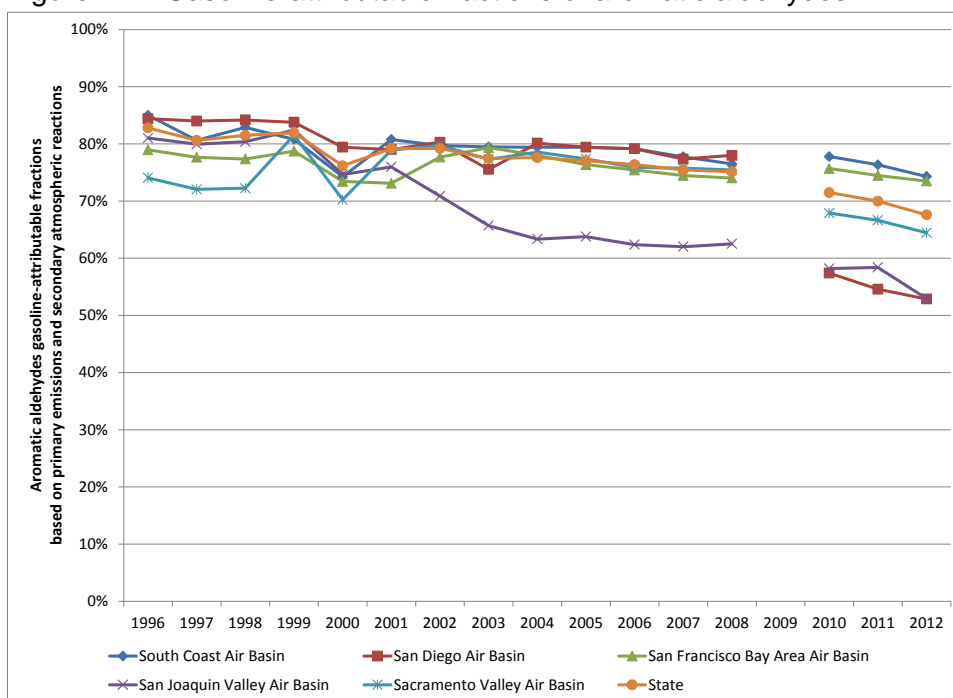
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Table 65. Gasoline-attributable fractions of aromatic aldehydes (including benzaldehyde) from primary and secondary atmospheric reactions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	85%	84%	79%	81%	74%	83%
1997	81%	84%	78%	80%	72%	81%
1998	83%	84%	77%	80%	72%	82%
1999	81%	84%	79%	82%	82%	82%
2000	74%	79%	73%	75%	70%	76%
2001	81%	79%	73%	76%	79%	79%
2002	80%	80%	78%	71%	80%	79%
2003	79%	76%	79%	66%	77%	77%
2004	79%	80%	78%	63%	79%	78%
2005	79%	79%	76%	64%	77%	77%
2006	79%	79%	75%	62%	76%	76%
2007	78%	77%	74%	62%	76%	75%
2008	76%	78%	74%	63%	75%	75%
2009 ^a	--	--	--	--	--	--
2010	78%	57%	76%	58%	68%	71%
2011	76%	55%	74%	58%	67%	70%
2012	74%	53%	74%	53%	64%	68%

Note: Mobile source emissions were unavailable for 2009.

Figure 124. Gasoline-attributable fractions of aromatic aldehydes



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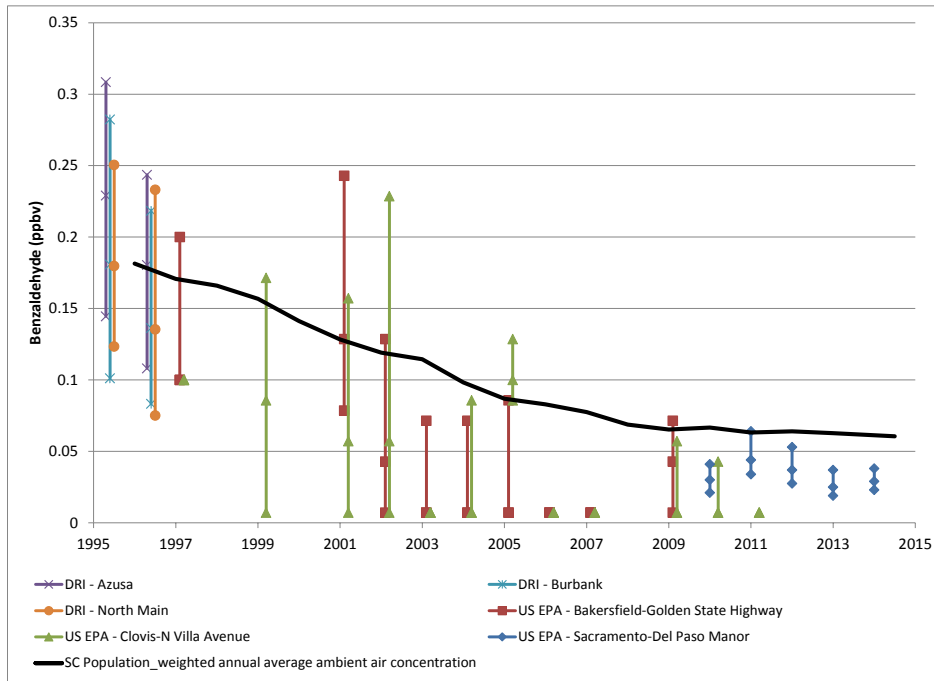
Table 66. Benzaldehyde in the South Coast Air Basin

Year	Population-weighted annual average ambient air concentration (ppbv)	Gasoline-attributable fraction	Gasoline-attributable concentration (ppbv)
1996	0.18	85%	0.15
1997	0.17	81%	0.14
1998	0.17	83%	0.14
1999	0.16	81%	0.13
2000	0.14	74%	0.10
2001	0.13	81%	0.10
2002	0.12	80%	0.095
2003	0.11	79%	0.091
2004	0.098	79%	0.078
2005	0.087	79%	0.069
2006	0.083	79%	0.066
2007	0.078	78%	0.060
2008	0.069	76%	0.053
2009	0.065	76%	0.050
2010	0.067	78%	0.052
2011	0.063	76%	0.048
2012	0.064	74%	0.048
2013	0.063	74%	0.047
2014	0.061	74%	0.045

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

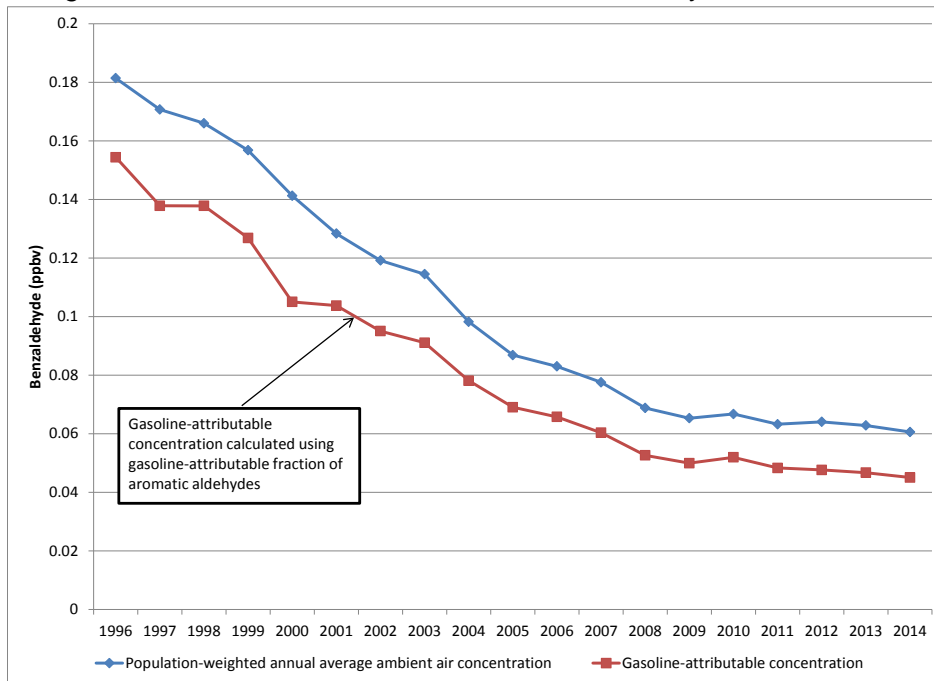
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Figure 125. Comparison of modeled population-weighted ambient air concentration of benzaldehyde in the South Coast Air Basin to measurements from other sites in California.



Note: The plot shows the first quartile, median, and third quartile from each site and year. The data used to calculate the summary statistics were 3-hour samples from summer months.

Figure 126. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of benzaldehyde



Formaldehyde: Exposure and Screening Risk Assessment Results

Formaldehyde is a carcinogen and respiratory toxicant and had the 21st highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Formaldehyde is also formed through secondary atmospheric reactions. Secondary emissions were estimated by applying the formation potential to data from the Emission Inventory (see Appendix E). In 2012, 89% of formaldehyde emissions was formed through these secondary reactions. Figure 127 shows that the overall formaldehyde emissions declined between 1996 and 2012.

Figure 128 shows the emission sources of formaldehyde. Table 67 and Figure 129 show the gasoline-attributable fractions of formaldehyde. Statewide, in 2012, 11% of formaldehyde emissions came from gasoline-related sources. Biogenic sources, wildfires, aircraft, residential combustion and construction and mining equipment were some of the main non-gasoline-related sources of formaldehyde. The gasoline-attributable fractions varied by air basin. In the San Joaquin and Sacramento Valley Air Basins, controlled burning contributed a substantial part of formaldehyde emissions and caused the gasoline-attributable fractions in these two basins to be lower. Gasoline-attributable fractions dropped in San Diego, Sacramento and San Joaquin Valley air basins in 2002, because of an increase in estimated emissions from natural sources.

Population-weighted annual average ambient air concentrations of formaldehyde were estimated for the South Coast, San Diego, San Francisco Bay Area, Sacramento Valley and San Joaquin Valley Air Basins and statewide for the years 1996 to 2014 (see Table 68). The ambient air data used to calculate the population-weighted annual average ambient air concentrations came from the California Toxic Monitoring Network and was supplemented with modeled values at additional locations to produce more robust estimates.

Table 69 tabulates the gasoline-attributable population-weighted annual average ambient air concentrations (referred to as gasoline-attributable concentrations) for all air basins. Figure 130 compares the population-weighted annual average ambient air concentrations of formaldehyde in the South Coast Air Basin to ambient air measurements from monitoring sites within the basin. Figure 131 shows that the gasoline-attributable concentrations of formaldehyde in the South Coast Air Basin declined by 65% between 1996 and 2014.

Cancer risks and hazard quotients for non-cancer health effects were calculated from gasoline-attributable concentrations (see Appendix G for details). The gasoline-attributable cancer risk for formaldehyde in the South Coast Air Basin declined from 6.5×10^{-5} in 1996 to 2.3×10^{-5} in 2014, corresponding to a reduction of 42 estimated cancer cases per 1 million people. The statewide gasoline-attributable cancer risk of formaldehyde declined from 3.9×10^{-5} in 1996 to 6.8×10^{-6} in 2014, or 33 cancer cases per 1 million people.

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The gasoline-attributable hazard quotient for formaldehyde, based on respiratory toxicity, declined from 0.36 in 1996 to 0.13 in 2014 in the South Coast Air Basin. The statewide gasoline-attributable hazard quotient declined from 0.22 in 1996 to 0.042 in 2014.

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Figure 127. Emissions of formaldehyde from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

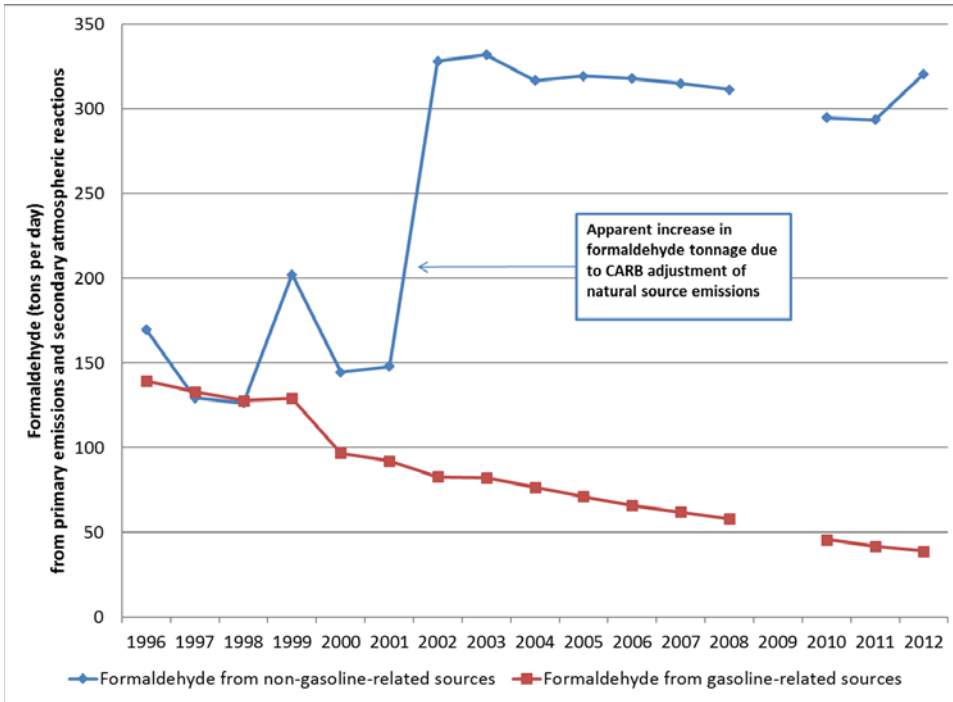
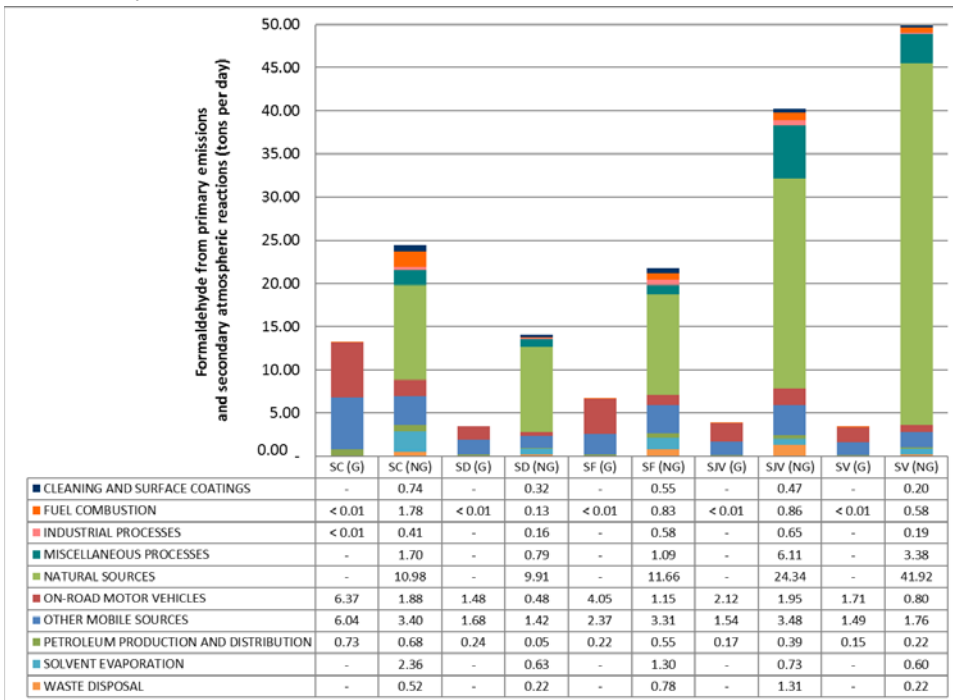


Figure 128. Primary emission sources and sources of secondary formation of formaldehyde in 2012



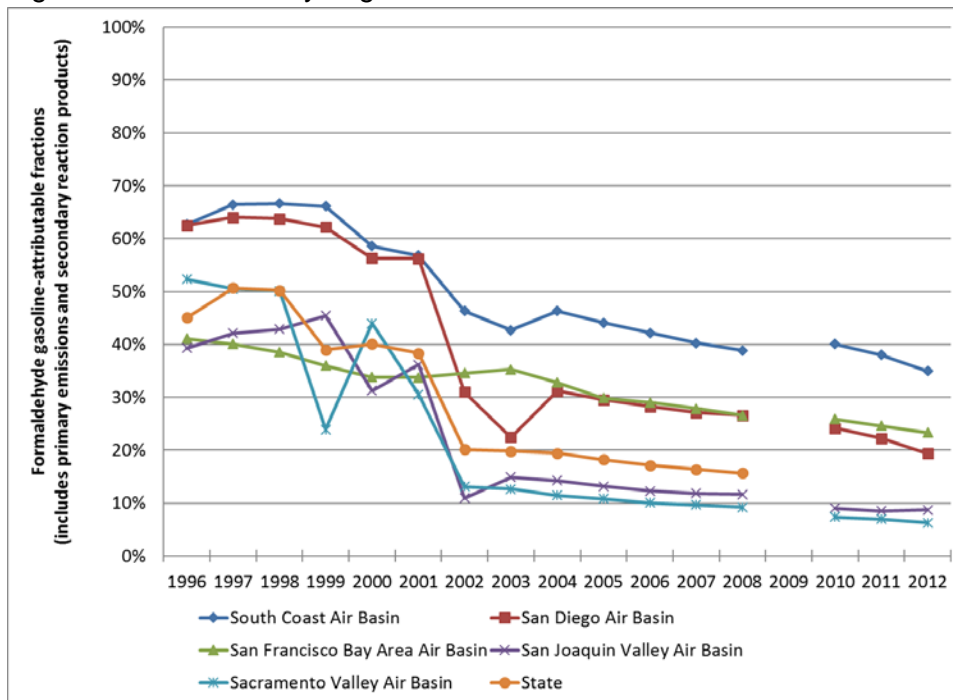
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Table 67. Formaldehyde gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	63%	63%	41%	39%	52%	45%
1997	66%	64%	40%	42%	50%	51%
1998	67%	64%	39%	43%	50%	50%
1999	66%	62%	36%	45%	24%	39%
2000	59%	56%	34%	31%	44%	40%
2001	57%	56%	34%	36%	31%	38%
2002	46%	31%	35%	11%	13%	20%
2003	43%	22%	35%	15%	13%	20%
2004	46%	31%	33%	14%	11%	19%
2005	44%	30%	30%	13%	11%	18%
2006	42%	28%	29%	12%	10%	17%
2007	40%	27%	28%	12%	10%	16%
2008	39%	27%	27%	12%	9%	16%
2009						
2010	40%	24%	26%	9%	7%	13%
2011	38%	22%	25%	9%	7%	12%
2012	35%	19%	23%	9%	6%	11%

Note: Mobile source emissions were unavailable for 2009.

Figure 129. Formaldehyde gasoline-attributable fractions



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Table 68. Population-weighted average concentrations of formaldehyde (ppbv) with half the limit of detection substituted for non-detects

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	4.0	3.1	2.8	2.9	2.7	3.4
1997	3.7	3.0	2.5	2.6	2.5	3.1
1998	3.3	2.7	2.2	2.5	2.3	2.8
1999	3.5	3.2	2.6	3.0	2.8	3.1
2000	2.8	2.5	2.1	2.3	2.1	2.4
2001	3.2	2.9	2.3	2.5	2.2	2.8
2002	3.5	3.3	2.9	2.8	3.0	3.2
2003	3.3	3.0	2.6	2.7	2.9	3.0
2004	3.0	2.6	2.2	2.3	2.4	2.6
2005	3.0	2.8	2.0	2.3	2.4	2.6
2006	2.9	2.6	2.0	2.4	2.5	2.5
2007	2.8	2.6	1.9	2.4	2.6	2.5
2008	2.9	2.5	1.8	2.3	2.4	2.5
2009	2.2	2.2	1.7	2.1	2.1	2.0
2010	2.5	2.3	1.9	2.4	2.3	2.3
2011	2.5	2.4	2.1	2.4	2.3	2.3
2012	2.5	2.4	1.9	2.3	2.3	2.3
2013	2.6	2.4	2.3	2.4	2.5	2.5
2014	2.5	2.4	2.2	2.5	2.4	2.4

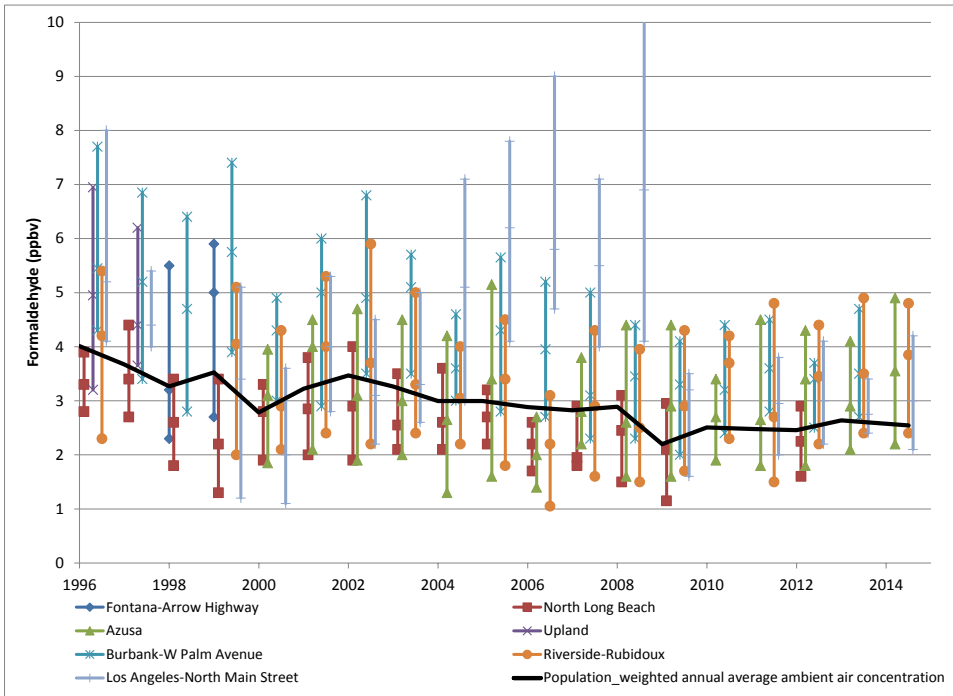
Table 69. Gasoline-attributable concentrations of formaldehyde (ppbv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	2.5	2.0	1.1	1.1	1.4	1.5
1997	2.4	1.9	1.0	1.1	1.3	1.6
1998	2.2	1.7	0.85	1.1	1.2	1.4
1999	2.3	2.0	0.95	1.4	0.68	1.2
2000	1.6	1.4	0.70	0.71	0.93	0.98
2001	1.8	1.6	0.78	0.89	0.68	1.1
2002	1.6	1.01	1.0	0.31	0.40	0.64
2003	1.4	0.67	0.92	0.40	0.37	0.58
2004	1.4	0.80	0.71	0.32	0.27	0.50
2005	1.3	0.82	0.61	0.30	0.25	0.47
2006	1.2	0.73	0.57	0.30	0.25	0.43
2007	1.1	0.70	0.54	0.29	0.25	0.41
2008	1.1	0.67	0.49	0.27	0.23	0.39
2009	0.86	0.59	0.44	0.24	0.20	0.32
2010	1.0	0.56	0.48	0.21	0.17	0.31
2011	0.94	0.53	0.51	0.21	0.16	0.29
2012	0.86	0.47	0.45	0.20	0.15	0.25
2013	0.92	0.47	0.53	0.21	0.16	0.27
2014	0.89	0.46	0.52	0.21	0.15	0.26

Note: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

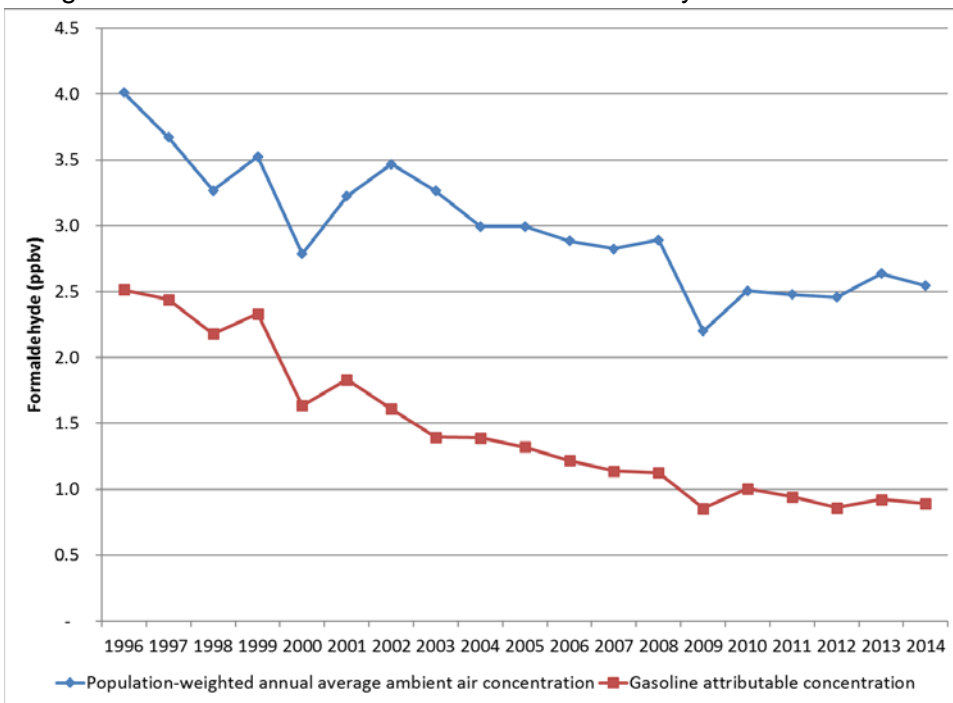
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Figure 130. Population-weighted annual average ambient air concentration of formaldehyde in the South Coast Air Basin



Note: The vertical bars show the annual quartiles at South Coast Air Basin monitoring sites.

Figure 131. South Coast population-weighted annual average ambient air concentration and gasoline-attributable concentration of formaldehyde



Propionaldehyde, Butyraldehyde, and Other Higher Aldehydes: Exposure and Screening Risk Assessment Results

Higher aldehydes are saturated aldehydes with three or more carbon atoms, such as propionaldehyde, butyraldehyde and hexaldehyde. Propionaldehyde, butyraldehyde and hexaldehyde are suspected respiratory toxicants and had the 124th, 161st and 177th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. These aldehydes are also formed through secondary atmospheric reactions. We used direct formation potentials provided by Dr. Carter and data from the Emission Inventory to calculate the secondary atmospheric formation of higher aldehydes as a group (see Appendix E). Statewide, in 2012, we estimated that 82% of higher aldehyde emissions came from these secondary atmospheric reactions. Figure 132 shows that the tons of higher aldehydes emitted from gasoline-related sources or with gasoline-related sources of secondary formation declined between 1996 and 2012. Figure 133 shows the emission sources of higher aldehydes. Table 70 and Figure 134 show the gasoline-attributable fractions of higher aldehydes. Statewide, in 2012, 11% of higher aldehydes came from gasoline-related sources.

Propionaldehyde, butyraldehyde and hexaldehyde were the most common directly emitted higher aldehydes in the Emission Inventory in 2012. Table 71 and Figure 135 display ambient air measurements of propionaldehyde. Ambient air measurements of butyraldehyde are shown in Table 72 and Figure 136. Ambient air measurements of hexaldehyde are shown in Table 73 and Figure 137.

US EPA developed an RfC for propionaldehyde equal to 0.008 mg/m³ (or 3 ppb). Ambient air measurements of propionaldehyde were taken over 3-hour intervals during summer months. For each year, the average of these measurements was calculated. These averages were all below 0.3 ppb, a factor of 10 lower than the RfC.

Hazard quotients were not calculated for butyraldehyde or hexaldehyde due to sparse ambient air monitoring and lack of health reference values.

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Figure 132. Emissions of higher aldehydes from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

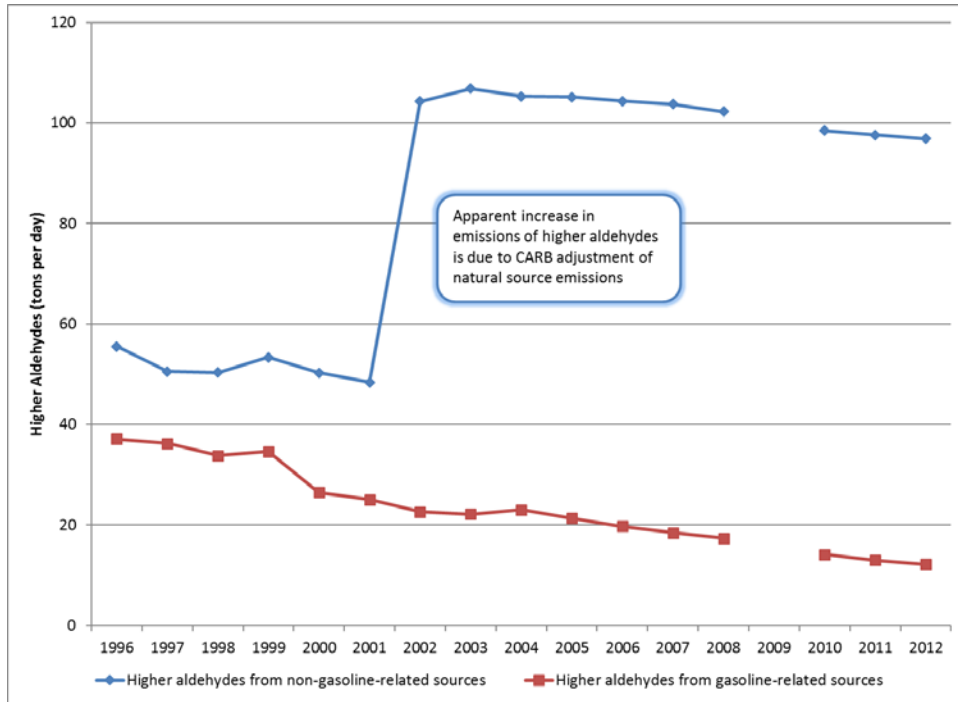
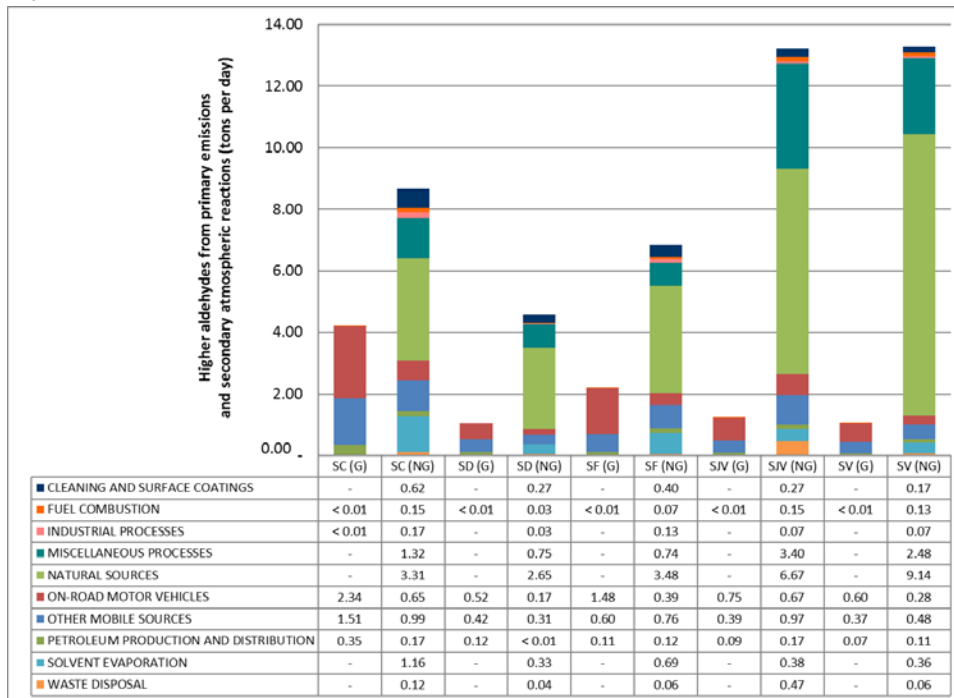


Figure 133. Primary emission sources and sources of secondary formation of higher aldehydes in 2012



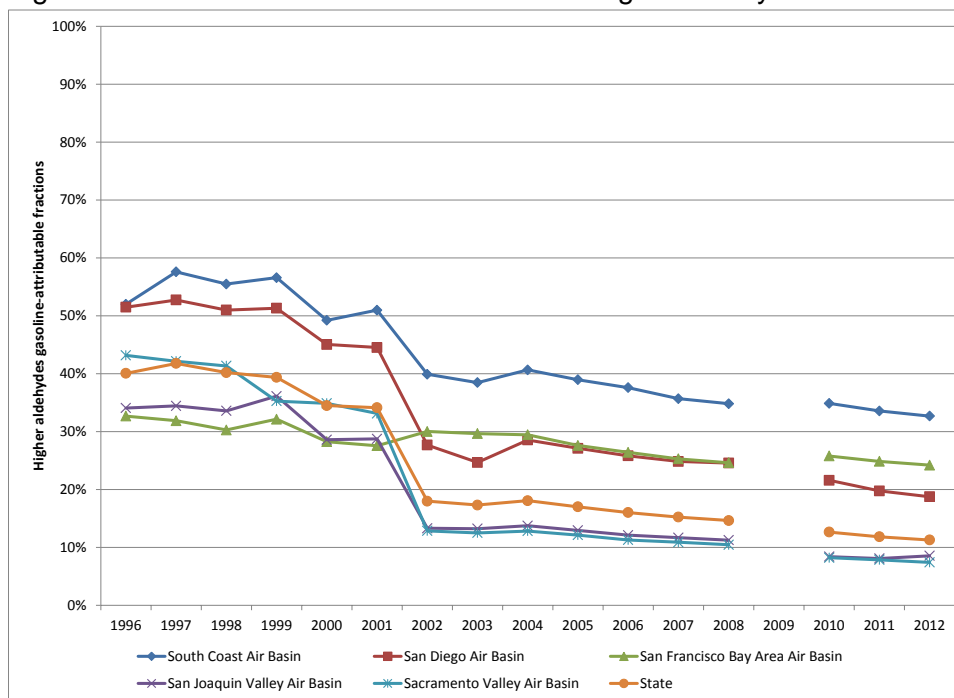
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Table 70. Gasoline-attributable fractions of higher aldehydes

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	52%	51%	33%	34%	43%	40%
1997	58%	53%	32%	34%	42%	42%
1998	55%	51%	30%	34%	41%	40%
1999	57%	51%	32%	36%	35%	39%
2000	49%	45%	28%	29%	35%	34%
2001	51%	45%	28%	29%	33%	34%
2002	40%	28%	30%	13%	13%	18%
2003	38%	25%	30%	13%	12%	17%
2004	41%	28%	29%	14%	13%	18%
2005	39%	27%	28%	13%	12%	17%
2006	38%	26%	26%	12%	11%	16%
2007	36%	25%	25%	12%	11%	15%
2008	35%	25%	25%	11%	10%	15%
2009	--	--	--	--	--	--
2010	35%	22%	26%	8%	8%	13%
2011	34%	20%	25%	8%	8%	12%
2012	33%	19%	24%	8%	7%	11%

Note: Mobile source emissions were unavailable for 2009.

Figure 134. Gasoline-attributable fractions of higher aldehydes



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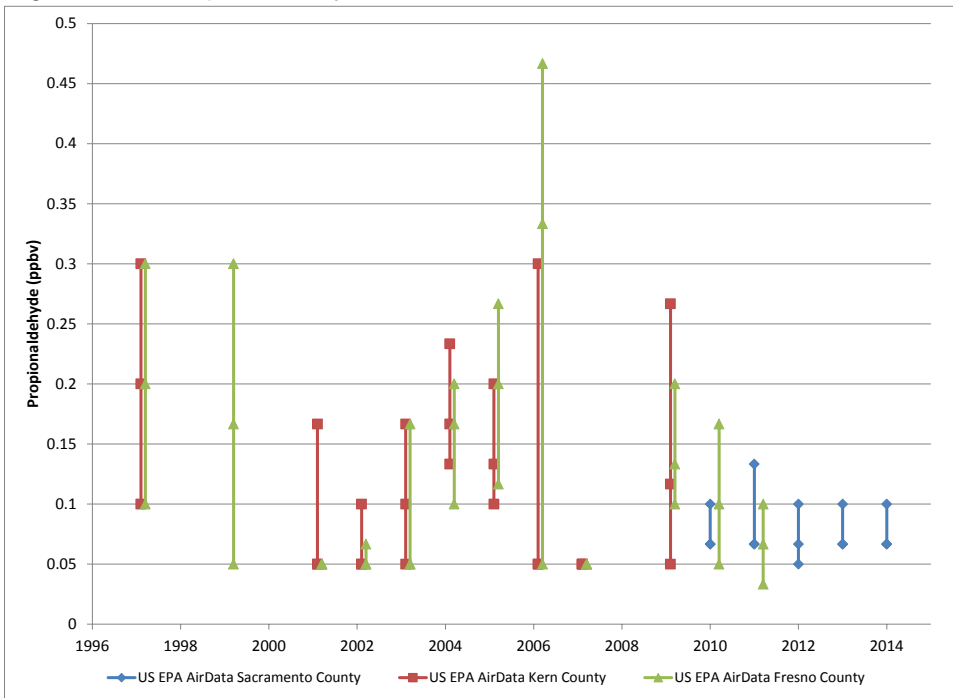
Table 71. Propionaldehyde ambient air measurements

Site Name	Year	N	Average	Standard Deviation	Minimum	First Quartile	Median	Third Quartile	Maximum
Sacramento, Sacramento County	2010	127	0.10	0.071	0.0040	0.067	0.067	0.10	0.43
	2011	134	0.098	0.063	0.0040	0.067	0.067	0.13	0.33
	2012	128	0.088	0.060	0.0055	0.050	0.067	0.10	0.30
	2013	129	0.089	0.054	0.033	0.067	0.067	0.10	0.37
	2014	122	0.086	0.045	0.0035	0.067	0.067	0.10	0.30
Bakersfield, Kern County	1997	98	0.21	0.11	0.10	0.10	0.20	0.30	0.50
	2001	124	0.11	0.099	0.050	0.050	0.050	0.17	0.73
	2002	133	0.080	0.050	0.050	0.050	0.050	0.10	0.23
	2003	131	0.12	0.074	0.050	0.050	0.10	0.17	0.40
	2004	141	0.17	0.082	0.050	0.13	0.17	0.23	0.47
	2005	131	0.16	0.092	0.050	0.10	0.13	0.20	0.40
	2006	136	0.18	0.14	0.050	0.050	0.050	0.30	0.60
	2007	41	0.17	0.30	0.050	0.050	0.050	0.050	1.4
	2009	140	0.17	0.13	0.033	0.050	0.12	0.27	0.57
Clovis, Fresno County	1997	25	0.21	0.095	0.10	0.10	0.20	0.30	0.40
	1999	122	0.21	0.18	0.050	0.050	0.17	0.30	0.67
	2001	113	0.085	0.17	0.050	0.050	0.050	0.050	1.7
	2002	122	0.078	0.055	0.050	0.050	0.050	0.067	0.30
	2003	135	0.17	0.46	0.050	0.050	0.050	0.17	4.2
	2004	133	0.16	0.081	0.050	0.10	0.17	0.20	0.40
	2005	124	0.21	0.12	0.050	0.12	0.20	0.27	0.77
	2006	122	0.30	0.22	0.050	0.050	0.33	0.47	0.93
	2007	121	0.10	0.12	0.050	0.050	0.050	0.050	0.53
	2009	134	0.17	0.10	0.033	0.10	0.13	0.20	0.50
	2010	148	0.13	0.084	0.050	0.050	0.10	0.17	0.57
2011	169	0.082	0.057	0.033	0.033	0.067	0.10	0.30	

Notes: Half the limit of detection was substituted for non-detects.

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Figure 135. Propionaldehyde ambient air measurements



Data are 3-hour measurements from summer months. Vertical bars show the quartiles from each site and year.

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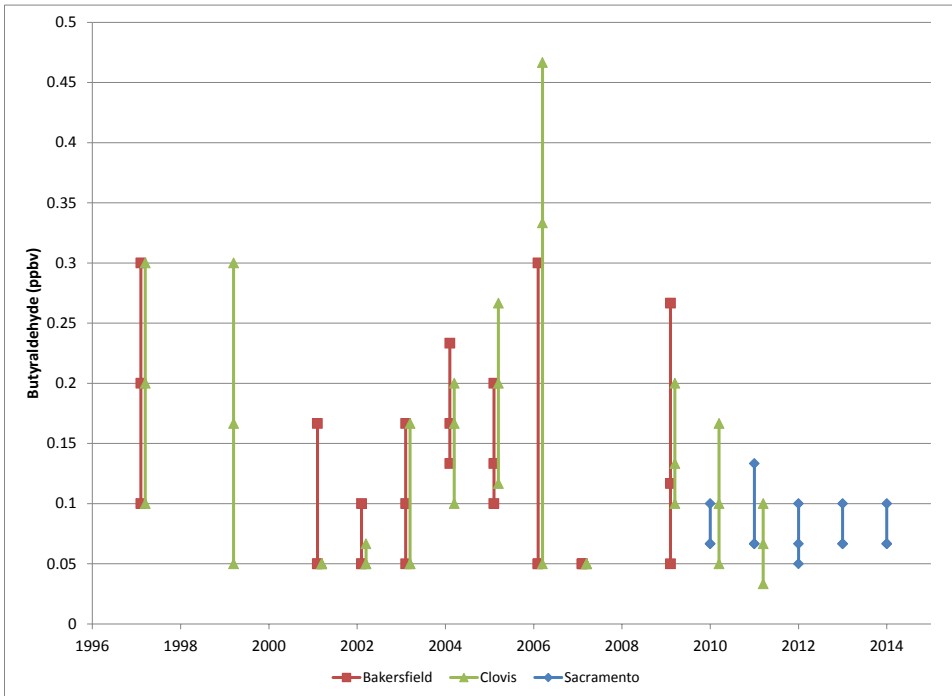
Table 72. Ambient air measurements of butyraldehyde

Site Name	Year	N	Average	Standard Deviation	Minimum	First Quartile	Median	Third Quartile	Maximum
Sacramento, Sacramento County	2010	127	0.10	0.071	0.0040	0.067	0.067	0.10	0.43
	2011	134	0.098	0.063	0.0040	0.067	0.067	0.13	0.33
	2012	128	0.088	0.060	0.0055	0.050	0.067	0.10	0.30
	2013	129	0.089	0.054	0.033	0.067	0.067	0.10	0.37
	2014	122	0.086	0.045	0.0035	0.067	0.067	0.10	0.30
Bakersfield, Kern County	1997	98	0.21	0.11	0.10	0.10	0.20	0.30	0.50
	2001	124	0.11	0.099	0.050	0.050	0.050	0.17	0.73
	2002	133	0.080	0.050	0.050	0.050	0.050	0.10	0.23
	2003	131	0.12	0.074	0.050	0.050	0.10	0.17	0.40
	2004	141	0.17	0.082	0.050	0.13	0.17	0.23	0.47
	2005	131	0.16	0.092	0.050	0.10	0.13	0.20	0.40
	2006	136	0.18	0.14	0.050	0.050	0.050	0.30	0.60
	2007	41	0.17	0.30	0.050	0.050	0.050	0.050	1.4
2009	140	0.17	0.13	0.033	0.050	0.12	0.27	0.57	
Clovis, Fresno County	1997	25	0.21	0.095	0.10	0.10	0.20	0.30	0.40
	1999	122	0.21	0.18	0.050	0.050	0.17	0.30	0.67
	2001	113	0.085	0.17	0.050	0.050	0.050	0.050	1.7
	2002	122	0.078	0.055	0.050	0.050	0.050	0.067	0.30
	2003	135	0.17	0.46	0.050	0.050	0.050	0.17	4.2
	2004	133	0.16	0.081	0.050	0.10	0.17	0.20	0.40
	2005	124	0.21	0.12	0.050	0.12	0.20	0.27	0.77
	2006	122	0.30	0.22	0.050	0.050	0.33	0.47	0.93
	2007	121	0.10	0.12	0.050	0.050	0.050	0.050	0.53
	2009	134	0.17	0.10	0.033	0.10	0.13	0.20	0.50
	2010	148	0.13	0.084	0.050	0.050	0.10	0.17	0.57
2011	169	0.082	0.057	0.033	0.033	0.067	0.10	0.30	

Note: Half the limit of detection was substituted for non-detects.

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Figure 136. Ambient air measurements of butyraldehyde



Note: Data are 3-hour measurements from summer months. Vertical bars show the quartiles from each site and year.

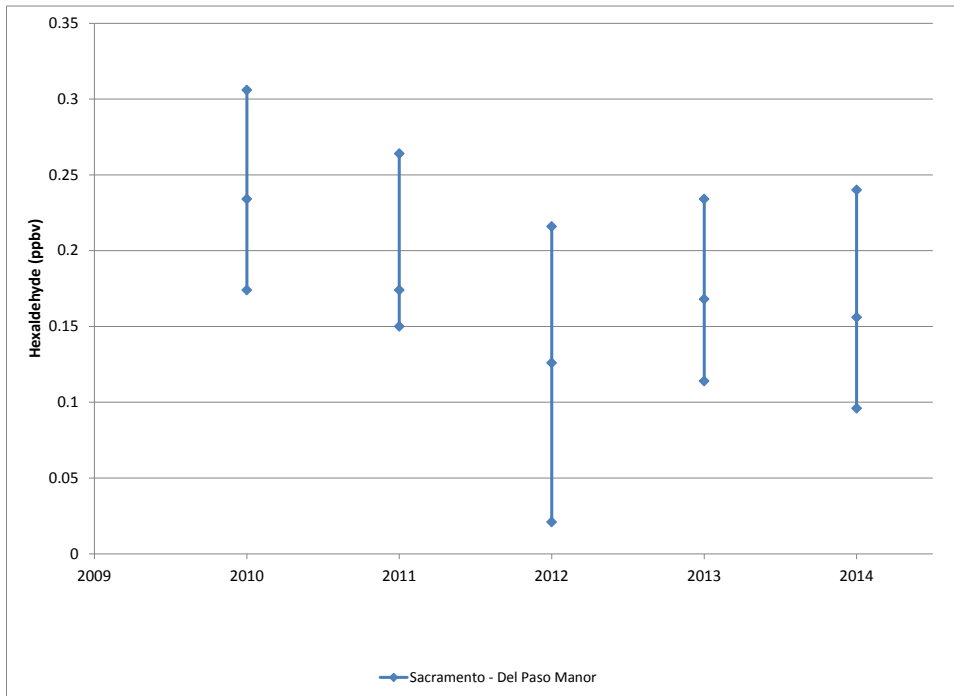
Table 73. Hexaldehyde ambient air measurements (ppbv)

Site Name	Year	N	Average	Standard deviation	Minimum	First quartile	Median	Third quartile	Maximum
Sacramento - Del Paso Manor	2010	127	0.27	0.16	0.072	0.17	0.23	0.31	1.1
	2011	133	0.22	0.15	0.018	0.15	0.17	0.26	0.85
	2012	126	0.19	0.29	0.021	0.021	0.13	0.22	2.2
	2013	129	0.20	0.16	0.021	0.11	0.17	0.23	1.3
	2014	121	0.18	0.12	0.012	0.096	0.16	0.24	0.73

Note: Data are from summer months.

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Figure 137. Hexaldehyde ambient air measurements



Note: Vertical lines show first quartile, median and third quartile of hexaldehyde from summer months

Chemical Profiles: Atmospheric Transformation Products of Gasoline-related Chemicals

The chemicals described in this section are formed primarily through secondary atmospheric reactions of precursor chemicals. The secondary emission tonnage was calculated using the Emission Inventory and formation potentials (Carter, 2001). There were inadequate data to estimate ambient air concentrations or conduct a screening risk assessment for these atmospheric transformation products, so the Chemical Profiles below primarily discuss the estimates for gasoline-attributable fractions.

Cresols: Exposure Assessment Results

Aromatic compounds, such as toluene, are precursors for secondary formation of cresols in the atmosphere (Carter 2001; OEHHA 2006). Cresols are also directly emitted from some non-gasoline-related sources (e.g., solvent evaporation). Secondary reaction tonnage for cresols was calculated using formation potentials as described in Appendix E. Based on our analysis of the 2012 Emission Inventory, more than 99% of total emissions of cresols statewide were formed through secondary atmospheric reactions. The gasoline-related precursor chemicals that contributed most to the formation of cresols were toluene, *m*-xylene, *o*-xylene, 1,2,4-trimethylbenzene, *p*-xylene and ethylbenzene.

The tons of cresols emitted from gasoline-related sources or with gasoline-related sources of secondary formation declined statewide between 1996 and 2012 (Figure 138). Figure 139 displays the gasoline and non-gasoline-related sources of cresols. Cresols formed from gasoline-related on-road motor vehicle emissions exceeded cresols derived from non-gasoline source emissions statewide and in all five air basins analyzed. In 2012, 60% of cresol emissions statewide came from gasoline-related sources (Table 74 and Figure 140).

We did not locate adequate ambient air data for cresols to support the analyses conducted in this report; however, we did identify some literature studies on cresols. Fraser et al. (1998a) collected samples of air from a Los Angeles tunnel in 1993 and detected *m*- and *p*-cresol and *o*-cresol. They noted that cresols are often excluded from profiles of vehicle exhaust in photochemical airshed models. In a separate paper, Fraser et al. (1998b) discussed that the spatial distribution of cresols in ambient air around Los Angeles suggests that a large fraction of cresols are directly emitted. Their conclusion is inconsistent with the results of our analysis that 99% of cresols came from secondary reactions. The work of Fraser et al. prompted OEHHA to investigate which speciation profiles included cresols. None of the gasoline vehicle profiles in the US EPA Speciate database or CARB Emission Inventory included cresols. A profile for diesel exhaust from medium duty diesel trucks in the US EPA's Speciate database²⁷ contained cresols as did speciation profiles for petroleum refining, cigarette smoke, wood burning and pulp and paper mills. Non-gasoline related sources of cresols in the CARB Emission Inventory included solid waste disposal, petroleum marketing (losses from tank trucks and barge loading), and consumer products (e.g., degreasers). Therefore, it appears that cresols are not typically included in primary emissions speciation profiles, particularly those relevant to gasoline-related sources. This suggests that direct

²⁷ Profile number 5295 in the US EPA's Speciate database based on the paper "Comparison of Emissions for Medium-Duty Diesel Trucks Operated on California In-Use Diesel, ARCO's EC-Diesel, and ARCO EC-Diesel with a Diesel Particulate Filter," by Durbin & Norbeck for DOE NREL under Contract # ACL-1-30110-01, 2002.

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emissions are not being captured in the Emission Inventory, and that our estimate that 99% of cresols comes from secondary formation is an overestimate.

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Figure 138. Statewide annual tons of cresols that were directly emitted or formed through secondary atmospheric reactions (data from CARB Emission Inventory)

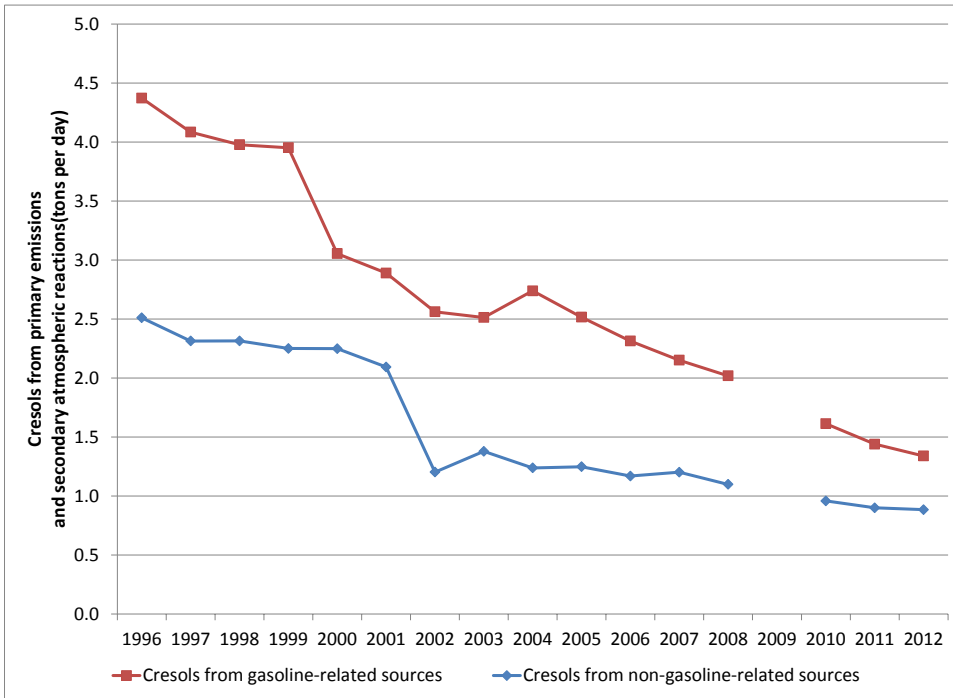
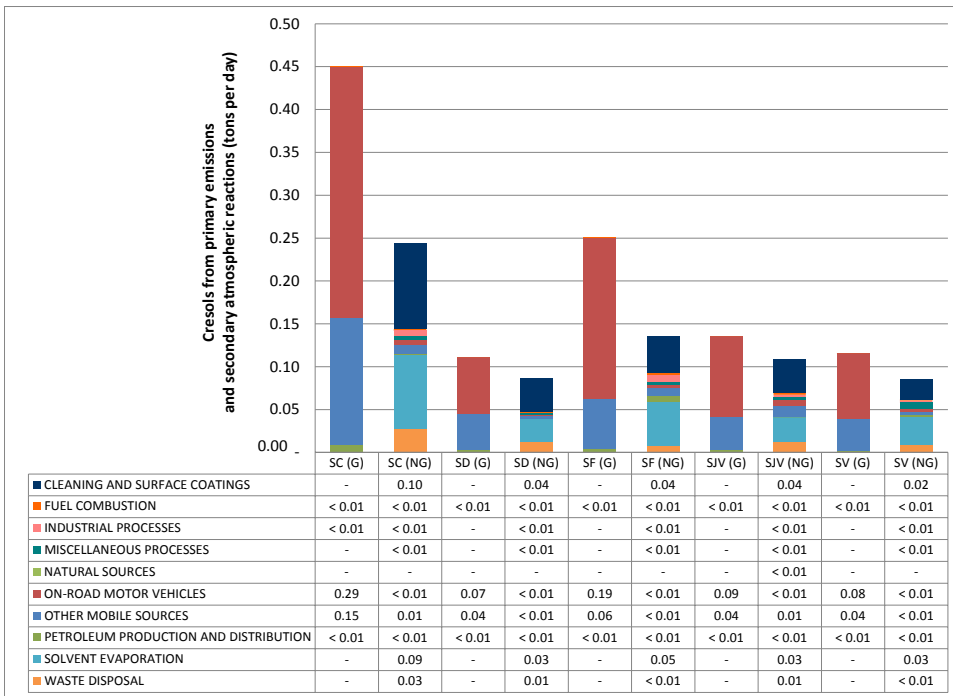


Figure 139. Primary emission sources and sources of secondary formation of cresols in 2012.



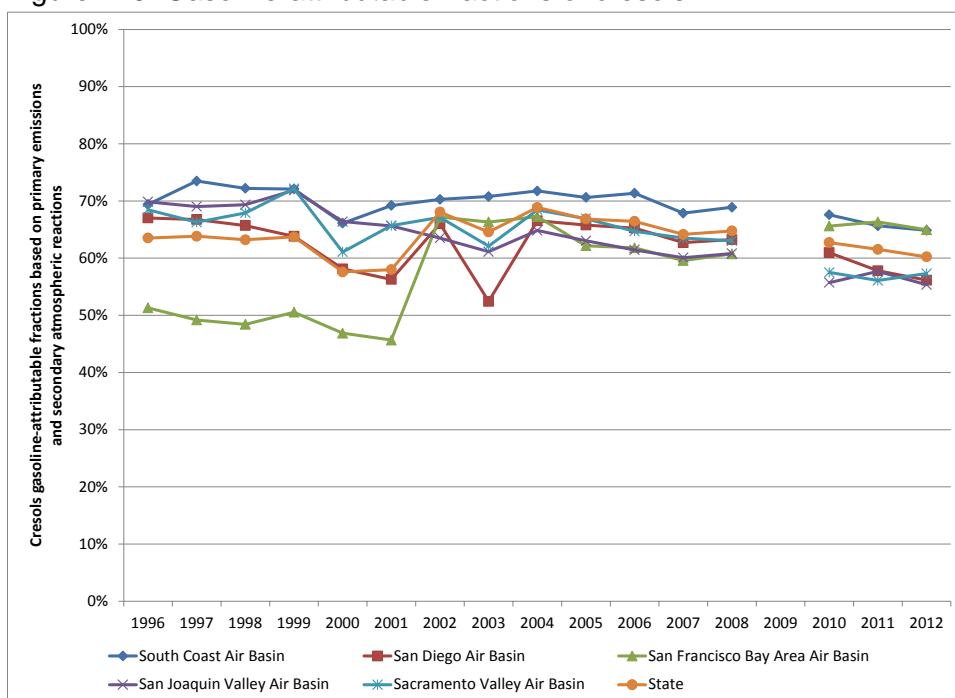
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Table 74. Gasoline-attributable fractions of cresols based on primary emission tonnage and secondary reaction tonnage

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	69%	67%	51%	70%	68%	64%
1997	73%	67%	49%	69%	66%	64%
1998	72%	66%	48%	69%	68%	63%
1999	72%	64%	51%	72%	72%	64%
2000	66%	58%	47%	66%	61%	58%
2001	69%	56%	46%	66%	66%	58%
2002	70%	66%	67%	64%	67%	68%
2003	71%	52%	66%	61%	62%	65%
2004	72%	67%	67%	65%	68%	69%
2005	71%	66%	62%	63%	67%	67%
2006	71%	65%	62%	61%	65%	66%
2007	68%	63%	60%	60%	64%	64%
2008	69%	63%	61%	61%	63%	65%
2009 ^a	--	--	--	--	--	--
2010	68%	61%	66%	56%	58%	63%
2011	66%	58%	66%	58%	56%	62%
2012	65%	56%	65%	55%	57%	60%

Note: Mobile source emissions were unavailable for 2009.

Figure 140. Gasoline-attributable fractions of cresols



Nitrophenols and Aromatic Nitro-compounds: Exposure Assessment Results

Nitrophenols and aromatic nitro-compounds are formed in the atmosphere from aromatic compounds (Carter, 2001; OEHHA, 2006). Fraser et al. (1998a) detected nitrobenzene in ambient air samples collected in 1993 from a Los Angeles tunnel.

The tons of nitrophenols and aromatic nitro-compounds formed from secondary reactions were calculated using formation potentials, as described in Appendix E. Based on these calculations, more than 99% of nitrophenols and aromatic nitro-compounds were formed through secondary atmospheric reactions statewide in 2012.

Based on the application of formation potentials to the Emission Inventory, the gasoline-related precursor chemicals that contributed most to the formation of nitrophenols and aromatic nitro-compounds statewide in 2012 included toluene, *m*-xylene, benzaldehyde, tolualdehyde and *o*-xylene.

Figure 141 shows that tons of nitrophenols and aromatic nitro-compounds directly emitted or formed through secondary atmospheric reactions declined between 1996 and 2012. Figure 142 contains the emissions sources of nitrophenols and aromatic nitro-compounds. Table 75 and Figure 143 show the gasoline-attributable fractions of nitrophenols and aromatic nitro-compounds. Statewide, in 2012, 53% of nitrophenols and aromatic nitro-compounds came from gasoline-related sources.

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Figure 141. Statewide annual tons of nitrophenols and aromatic nitro-compounds that were directly emitted or formed through secondary atmospheric reactions (data from CARB Emission Inventory)

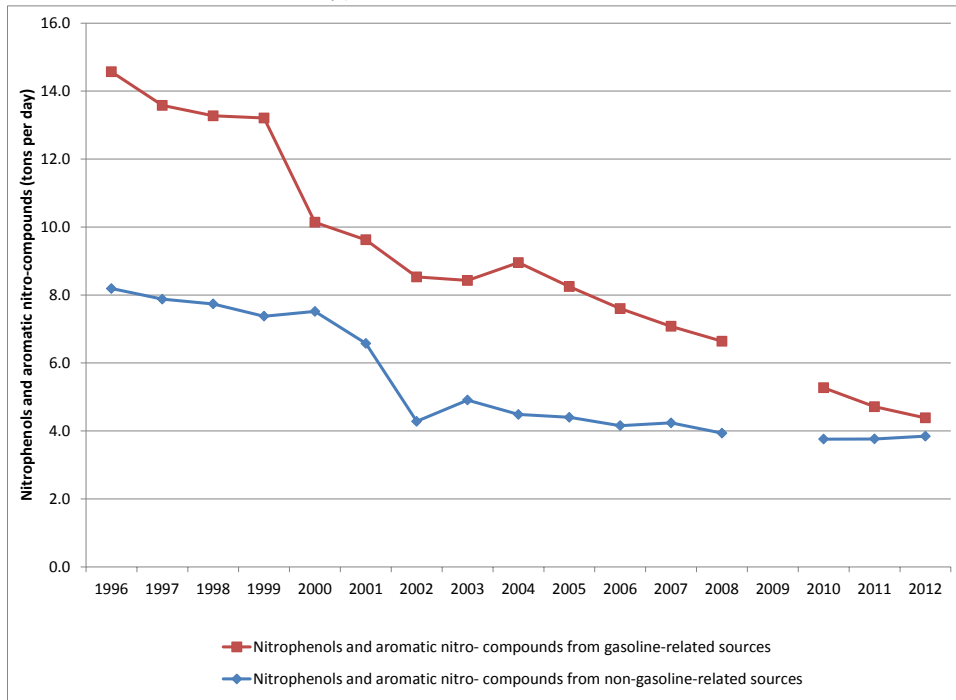
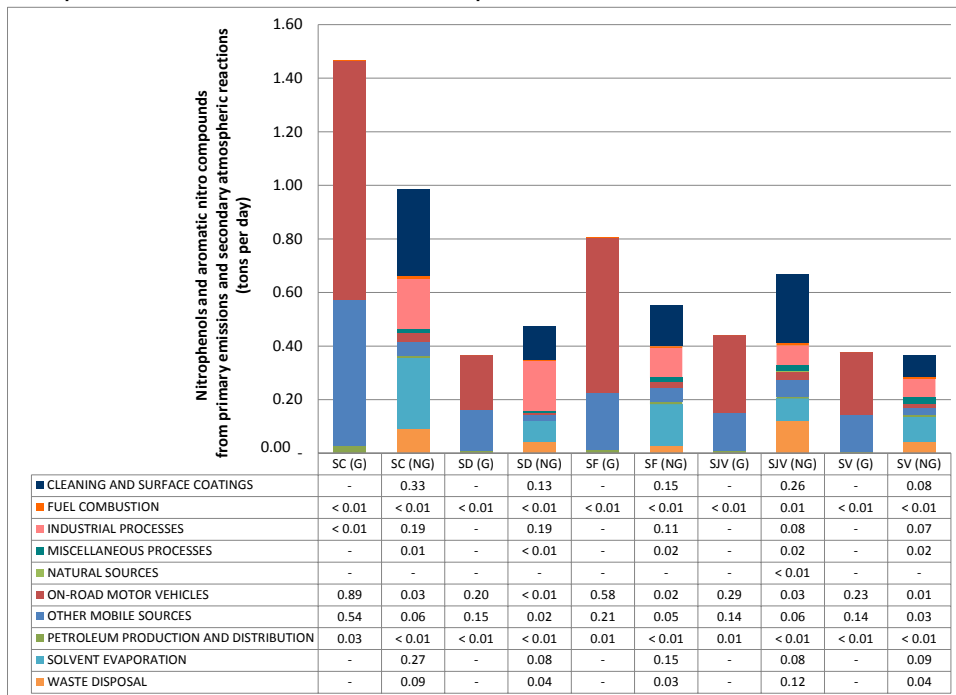


Figure 142. Primary emission sources and sources of secondary of formation of nitrophenols and aromatic nitro-compounds in 2012



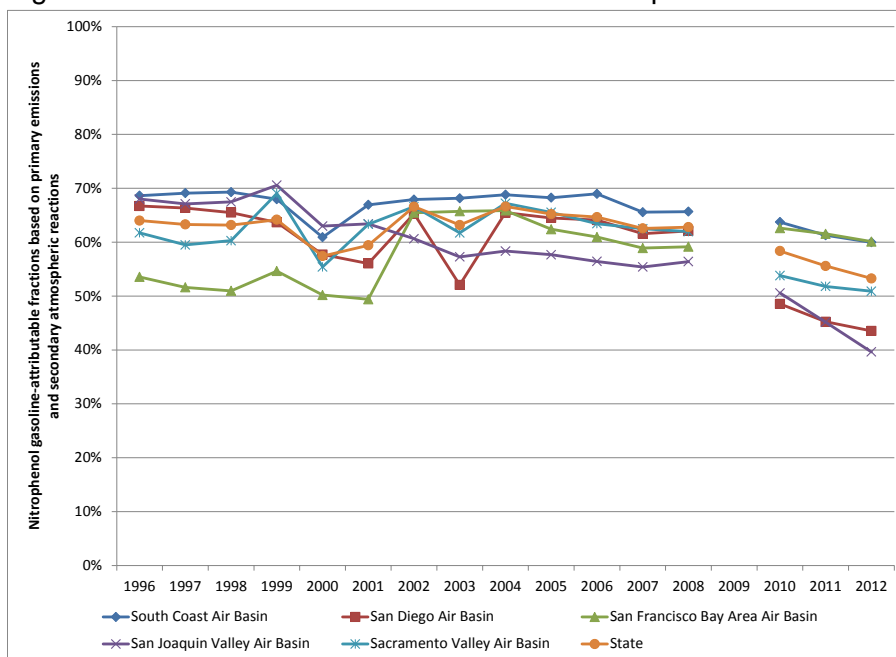
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Table 75. Gasoline-attributable fractions of nitrophenols and aromatic nitro-compounds are based on primary emission tonnage and secondary reaction tonnage.

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	69%	67%	54%	68%	62%	64%
1997	69%	66%	52%	67%	60%	63%
1998	69%	65%	51%	68%	60%	63%
1999	68%	64%	55%	71%	69%	64%
2000	61%	58%	51%	63%	56%	58%
2001	67%	56%	50%	63%	64%	60%
2002	68%	65%	66%	61%	67%	67%
2003	68%	52%	67%	57%	62%	63%
2004	69%	65%	67%	58%	68%	67%
2005	68%	64%	64%	58%	66%	66%
2006	69%	64%	62%	56%	64%	65%
2007	66%	62%	60%	55%	63%	63%
2008	66%	62%	60%	56%	62%	63%
2009	--	--	--	--	--	--
2010	64%	49%	63%	51%	54%	59%
2011	61%	45%	62%	45%	52%	56%
2012	60%	44%	60%	40%	51%	53%

Note: Mobile source emissions were unavailable for 2009.

Figure 143. Gasoline-attributable fractions of nitrophenols and aromatic nitro-compounds



Alkyl Nitrates: Exposure Assessment Results

Gasoline-related precursors of alkyl nitrates include 2,2,4-trimethylpentane and 2,3,4-trimethylpentane (OEHHA, 2006). Based on the Emission Inventory, direct emissions of alkyl nitrates were zero. Tons of alkyl nitrates formed through secondary atmospheric reactions were calculated using formation potentials as described in Appendix E. Based on these calculations, the gasoline-related precursor chemicals that contributed most to the formation of alkyl nitrates statewide in 2012 included isopentane, 2-methylpentane, methylcyclopentane, n-pentane and 2,2,4-trimethylpentane.

Figure 144 shows that the tons of alkyl nitrates emitted from gasoline-related sources or with gasoline-related sources of secondary formation declined between 1996 and 2012.

Figure 145 shows the emission sources of alkyl nitrates. Table 76 and Figure 146 show the gasoline-attributable fractions of alkyl nitrates. Statewide, in 2012, 15% of alkyl nitrates came from gasoline-related sources. The gasoline-attributable fractions declined in 2002 due to an adjustment by CARB to natural source emissions.

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Figure 144. Statewide annual tons of alkyl nitrates that were directly emitted or formed through secondary atmospheric reactions (data from CARB Emission Inventory)

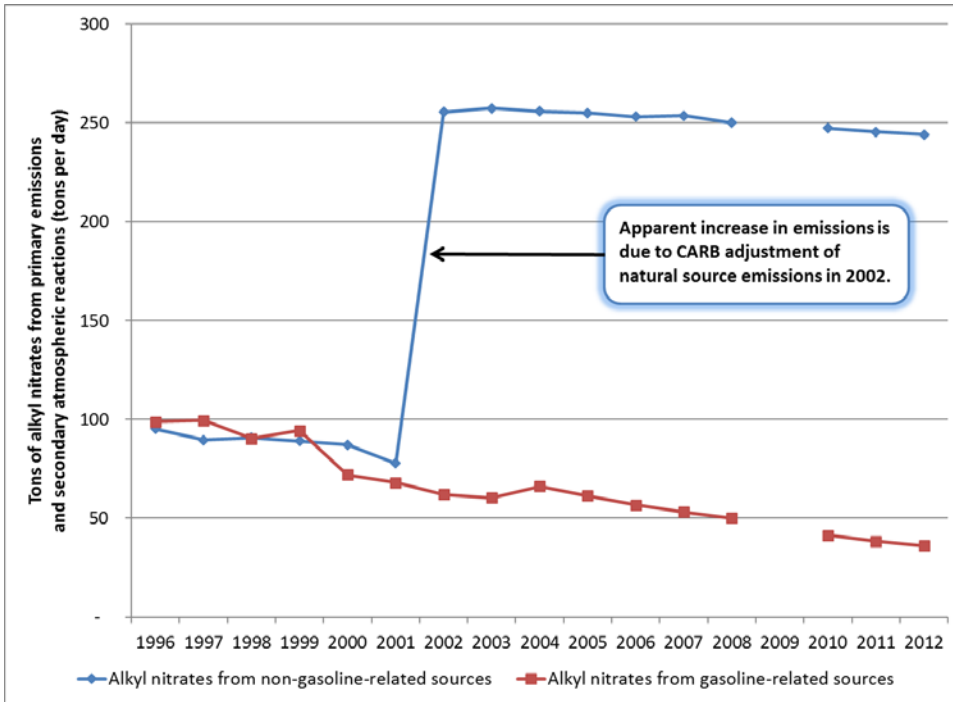
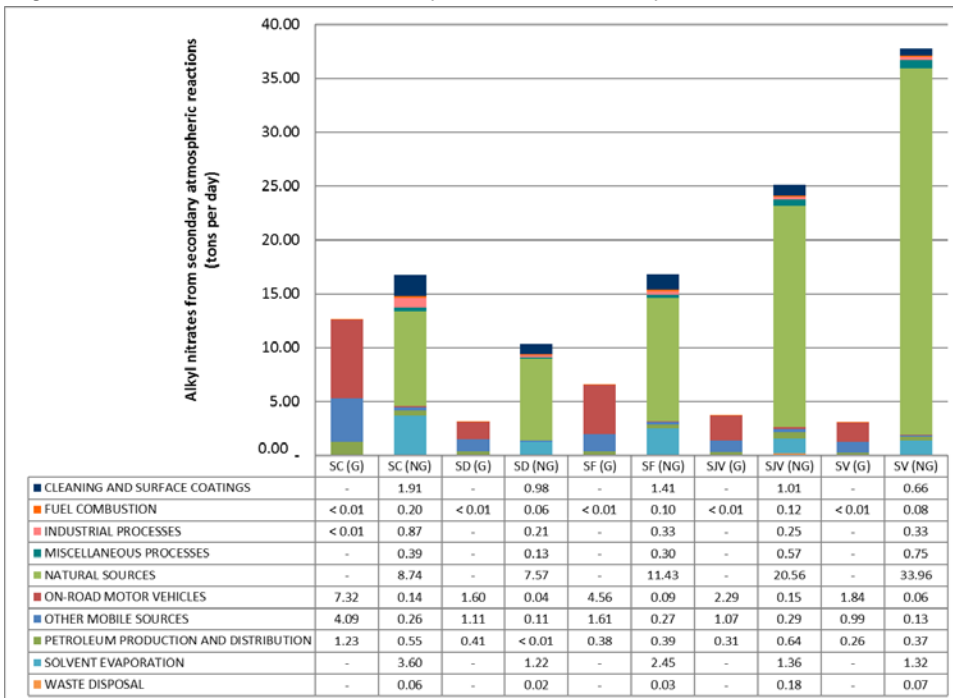


Figure 145. Sources of secondary formation of alkyl nitrates in 2012



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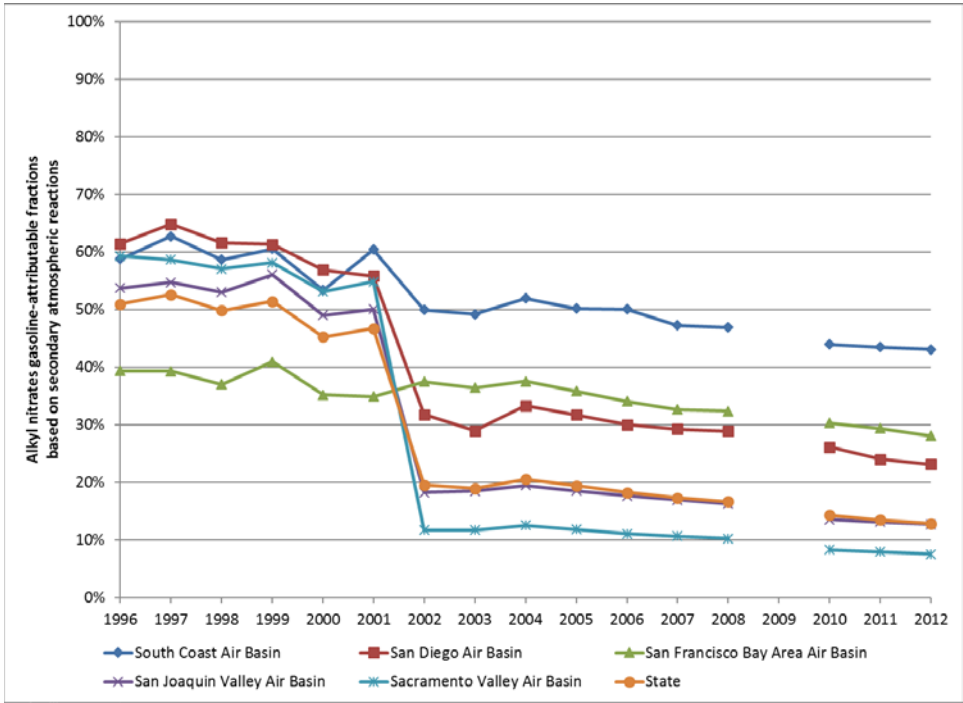
Table 76. Gasoline-attributable fractions of alkyl nitrates based on secondary reaction tonnage only.

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	59%	61%	39%	54%	59%	51%
1997	63%	65%	39%	55%	59%	53%
1998	59%	62%	37%	53%	57%	50%
1999	61%	61%	41%	56%	58%	51%
2000	53%	57%	35%	49%	53%	45%
2001	60%	56%	35%	50%	55%	47%
2002	50%	32%	37%	18%	12%	20%
2003	49%	29%	36%	19%	12%	19%
2004	52%	33%	38%	19%	13%	21%
2005	50%	32%	36%	19%	12%	19%
2006	50%	30%	34%	18%	11%	18%
2007	47%	29%	33%	17%	11%	17%
2008	47%	29%	32%	16%	10%	17%
2009						
2010	44%	26%	30%	14%	8%	14%
2011	43%	24%	29%	13%	8%	13%
2012	43%	23%	28%	13%	8%	13%

Note: Mobile source emissions were unavailable for 2009.

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Figure 146. Gasoline-attributable fractions of alkyl nitrates



Peroxyacetyl Nitrate (PAN): Exposure Assessment Results

PAN, a respiratory toxicant, is formed through secondary atmospheric reactions of hydrocarbons with oxygen and nitrogen dioxide in the presence of light. PAN does not appear in the Emission Inventory and its primary emission tonnage was estimated to be zero. Secondary atmospheric reaction tonnage of PAN was calculated using formation potentials as described in Appendix E. Secondary gasoline-related PAN emissions declined by 65% between 1996 and 2012 (see Figure 147).

The 10 main precursors of PAN were isoprene, ethanol, propylene, ethylene, acetaldehyde, isopentane, ethane, d-limonene, α -pinene and carene (based on all sources in 2012 Emission Inventory and formation potentials). These 10 chemicals react to form 73% of PAN, with 39% formed from isoprene.

The estimated tonnage from secondary atmospheric reactions was used to investigate the sources of PAN. Figure 148 shows the sources of PAN in 2012. In the South Coast Air Basin, in 2012, 45% of PAN were derived from gasoline-related emissions. In the other air basins, a smaller fraction of PAN was derived from gasoline-related sources. In all basins, biogenic sources (e.g., plants) contributed to PAN formation. The gasoline-related precursor chemicals that contributed most to the formation of PAN statewide in 2012 included isopentane, ethanol, propylene, *m*-xylene and toluene.

The secondary tonnage was used to calculate the gasoline-attributable fractions of PAN shown in Figure 149 and Table 77. Statewide, in 2012, 17% of PAN was derived from gasoline-related emissions.

We were not able to estimate ambient air concentrations for PAN, due to lack of adequate data, but did locate some relevant literature. Ambient air measurements of PAN were taken during the 1997 Southern California Ozone Study. The maximum PAN concentrations were 4.8 and 3.0 ppb at Azusa and Simi Valley, respectively (Grosjean et al., 2001). In a review of PAN studies from 1960 to 1997, Grosjean (2003) found that peak concentrations fell from 60-70 ppb to 5-10 ppb in Southern California. He attributed the downward trend to reductions in emissions of NO_x and VOCs that act as ozone precursors. Draft health protective concentrations of 0.6 ppb (annual average) and 1.8 ppb (1 hour) for PAN were previously developed by OEHHA (1999). These values have not been finalized, but do suggest a potential health concern based on PAN concentrations reported in Grosjean's publications.

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Figure 147. Statewide annual tons of PAN formed through secondary atmospheric reactions (data from CARB Emission Inventory)

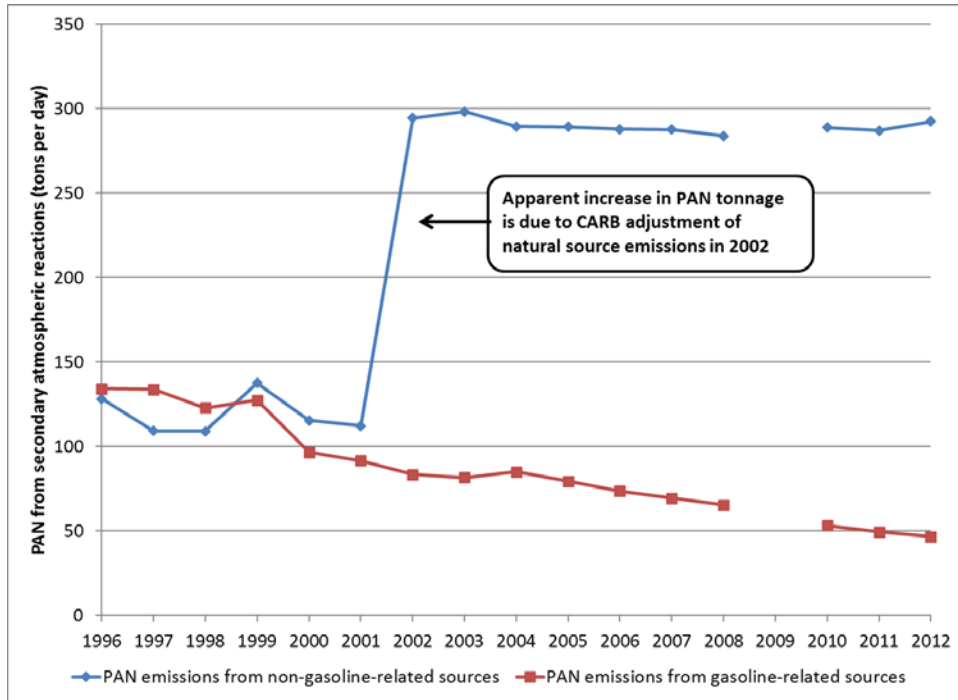
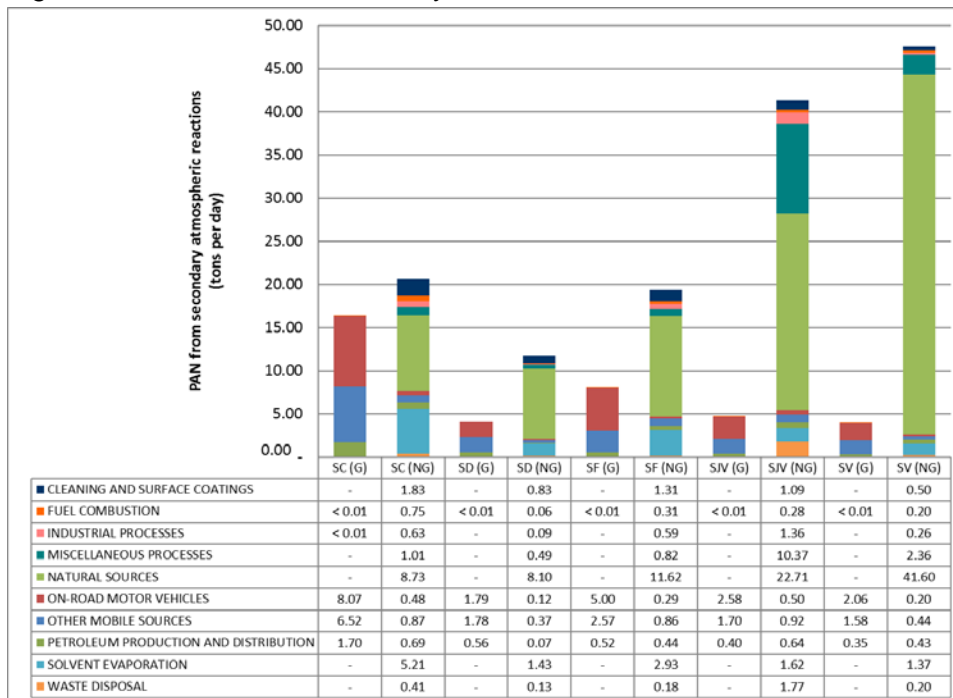


Figure 148. Sources of secondary formation of PAN in 2012



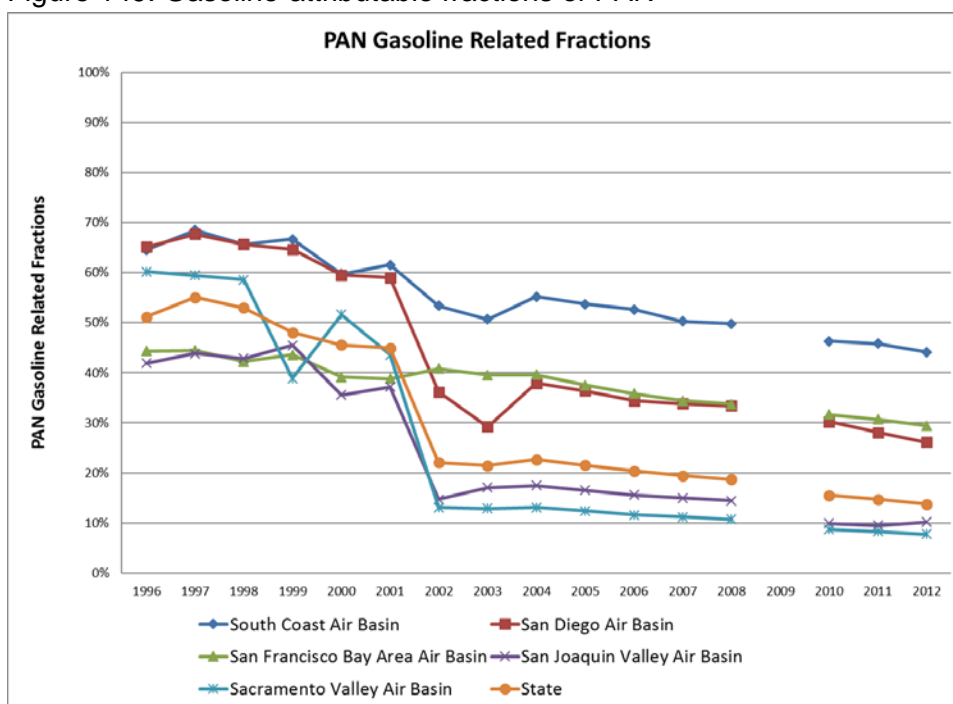
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Table 77. Gasoline-attributable fractions of PAN based on secondary reaction tonnage only.

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	64%	65%	44%	42%	60%	51%
1997	68%	68%	44%	44%	59%	55%
1998	66%	66%	42%	43%	59%	53%
1999	67%	65%	44%	45%	39%	48%
2000	60%	60%	39%	36%	52%	46%
2001	62%	59%	39%	37%	44%	45%
2002	53%	36%	41%	15%	13%	22%
2003	51%	29%	40%	17%	13%	21%
2004	55%	38%	40%	18%	13%	23%
2005	54%	36%	38%	17%	12%	22%
2006	53%	34%	36%	16%	12%	20%
2007	50%	34%	34%	15%	11%	19%
2008	50%	33%	34%	14%	11%	19%
2009	--	--	--	--	--	--
2010	46%	30%	32%	10%	9%	16%
2011	46%	28%	31%	10%	8%	15%
2012	44%	26%	29%	10%	8%	14%

Note: Mobile source emissions were unavailable for 2009.

Figure 149. Gasoline-attributable fractions of PAN



Higher PAN Analogues (Higher Saturated Acyl Peroxynitrates): Exposure Assessment Results

Carter (2001) noted that precursor chemicals of higher PAN analogues include, for example, alkyl-substituted alkenes and alkylbenzenes. Primary emission tonnage of higher PAN analogues was estimated to be zero because they did not appear in the Emission Inventory. Secondary atmospheric reaction tonnage of higher PAN analogues was calculated using formation potentials as described in Appendix E. Based on the Emission Inventory and formation potentials, the gasoline-related precursor chemicals that contributed most to the formation of higher PAN analogues statewide in 2012 included 2-methylpentane, toluene, n-pentane, isopentane, methylcyclopentane.

Figure 150 shows that the statewide gasoline-related tonnage of higher PAN analogues declined between 1996 and 2012. Figure 151 shows the sources of secondary formation of higher PAN analogues. Table 78 and Figure 152 show the gasoline-attributable fractions of higher PAN analogues. Statewide, in 2012, 19% of higher PAN analogues tonnage was formed from gasoline-related emissions.

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Figure 150. Statewide annual tons of higher PAN analogues formed through secondary atmospheric reactions (data from CARB Emission Inventory)

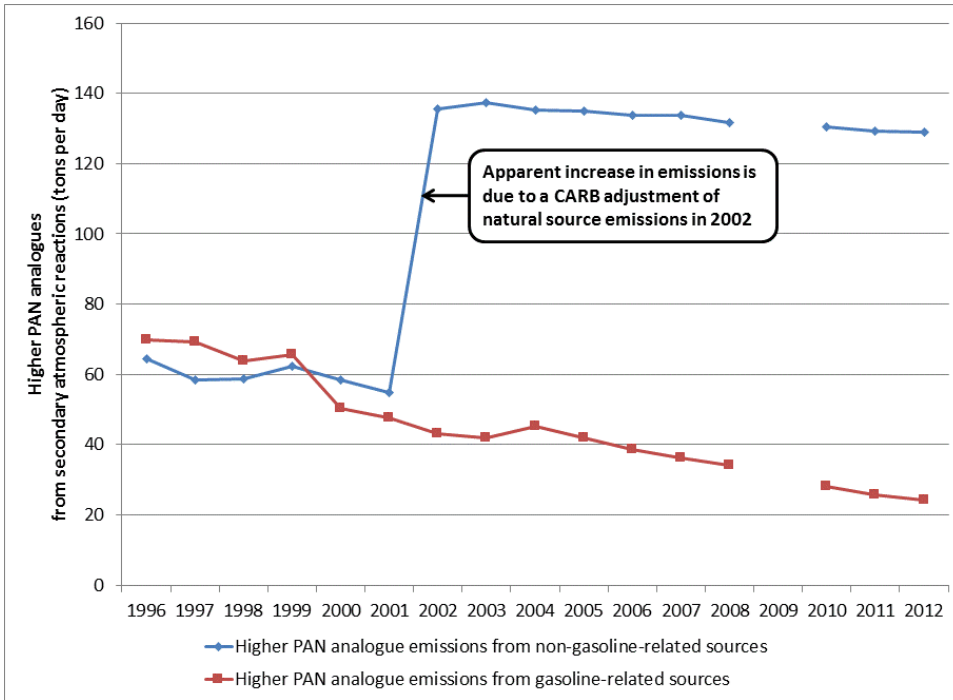
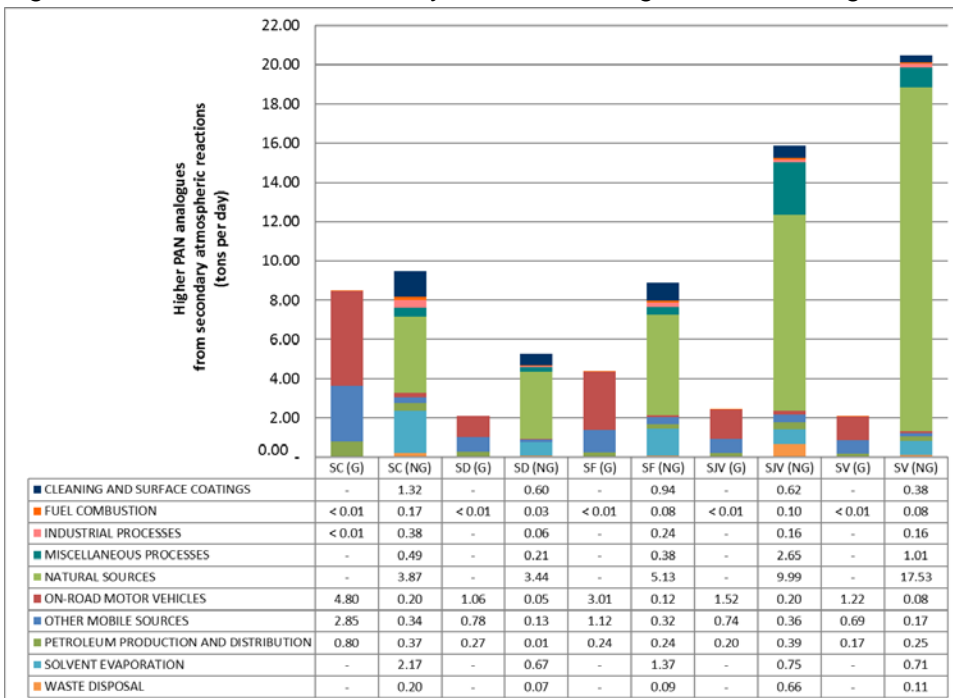


Figure 151. Sources of secondary formation of higher PAN analogues in 2012



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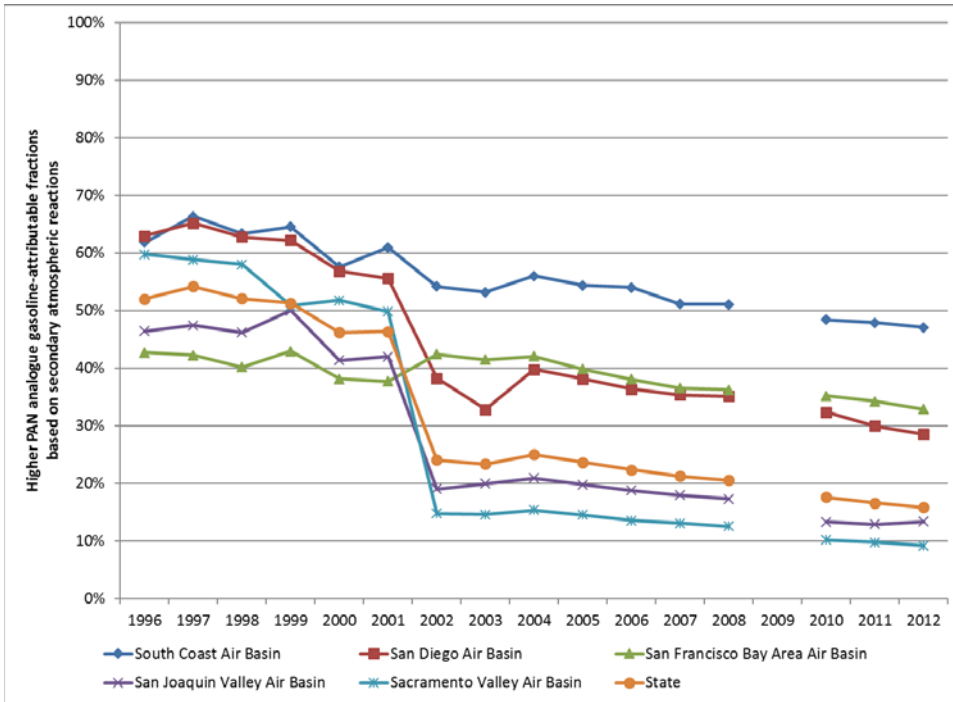
Table 78. Gasoline-attributable fractions of higher PAN analogues based on secondary reaction tonnage

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	62%	63%	43%	46%	60%	52%
1997	66%	65%	42%	47%	59%	54%
1998	63%	63%	40%	46%	58%	52%
1999	65%	62%	43%	50%	51%	51%
2000	58%	57%	38%	41%	52%	46%
2001	61%	56%	38%	42%	50%	46%
2002	54%	38%	42%	19%	15%	24%
2003	53%	33%	41%	20%	15%	23%
2004	56%	40%	42%	21%	15%	25%
2005	54%	38%	40%	20%	15%	24%
2006	54%	36%	38%	19%	14%	22%
2007	51%	35%	37%	18%	13%	21%
2008	51%	35%	36%	17%	13%	21%
2009	--	--	--	--	--	--
2010	48%	32%	35%	13%	10%	18%
2011	48%	30%	34%	13%	10%	17%
2012	47%	29%	33%	13%	9%	16%

Note: Mobile source emissions were unavailable for 2009.

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Figure 152. Gasoline-attributable fractions of higher PAN analogues



Unsaturated PAN Analogues: Exposure Assessment Results

Secondary atmospheric reaction tonnage of unsaturated PAN analogues was calculated by applying formation potentials to Emission Inventory data, as described in Appendix E. In 2012, 9% of the estimated total tonnage of unsaturated PAN analogues in the South Coast Air Basin was formed from gasoline-related emissions, with other air basins having lower percentages.

Precursor chemicals of unsaturated PAN analogues include acrolein and methacrolein, for example (Carter, 2001). The gasoline-related precursor chemicals that contributed most to the formation of unsaturated PAN analogues statewide in 2008 included (listed in order of highest contribution): 1,3-butadiene, acrolein, 2-methyl-2-propenal (methacrolein), crotonaldehyde and isoprene.

Figure 153 shows that estimated statewide tonnage of unsaturated PAN analogues formed from gasoline-related sources declined from 2 tons per day in 1996 to 0.5 tons per day in 2012. Figure 154 illustrates the sources of secondary formation of unsaturated PAN analogues. Table 79 and Figure 155 show the gasoline-attributable fractions of unsaturated PAN analogues.

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Figure 153. Statewide annual tons of unsaturated PAN analogues formed through secondary atmospheric reactions (data from CARB Emission Inventory)

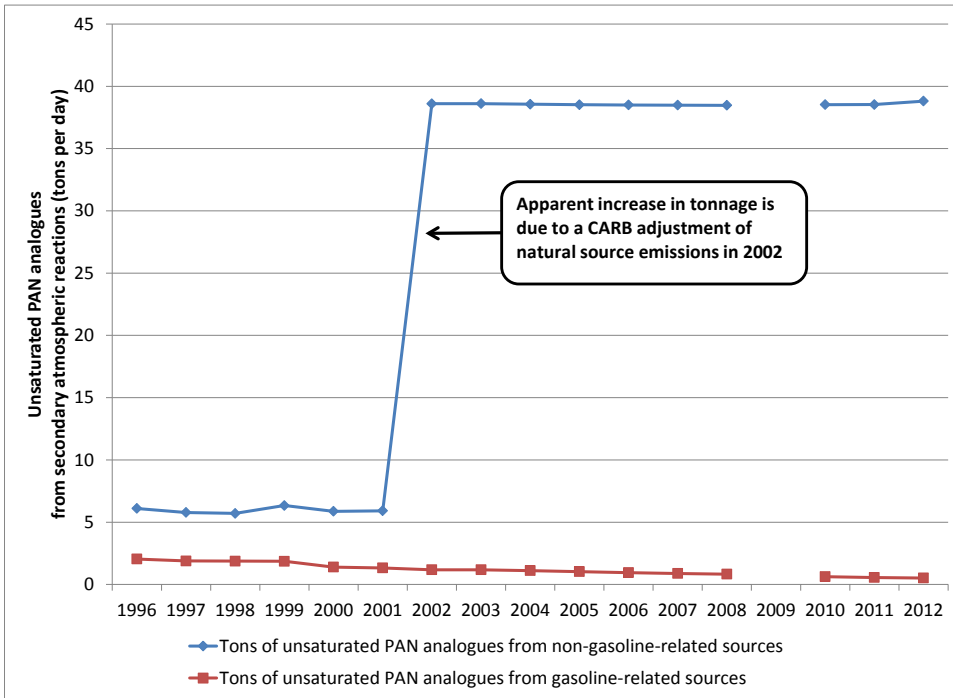
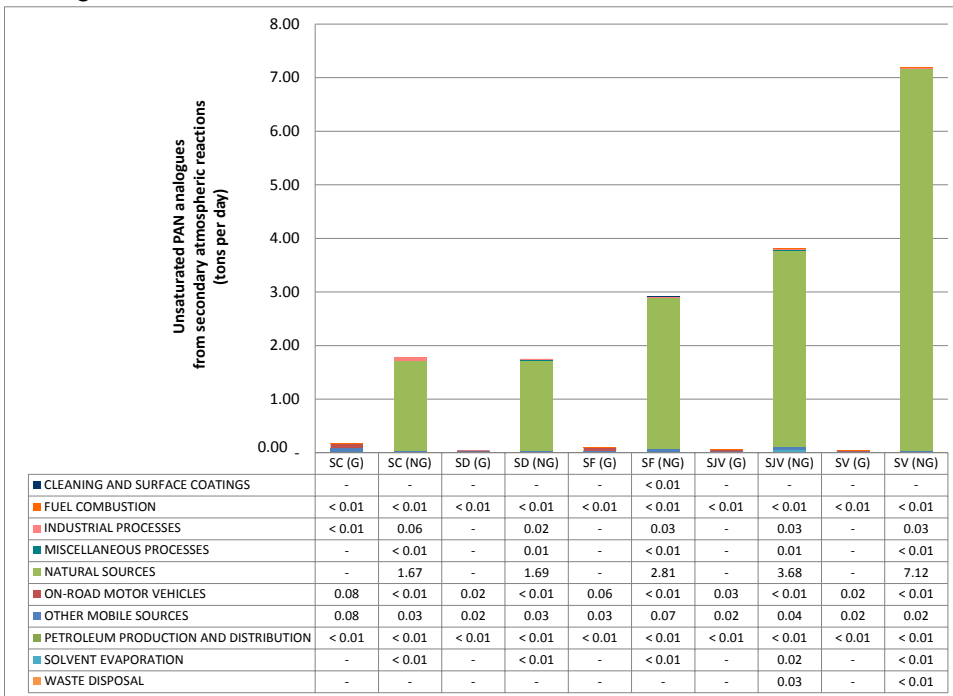


Figure 154. Sources that contributed to secondary formation of unsaturated PAN analogues in 2012



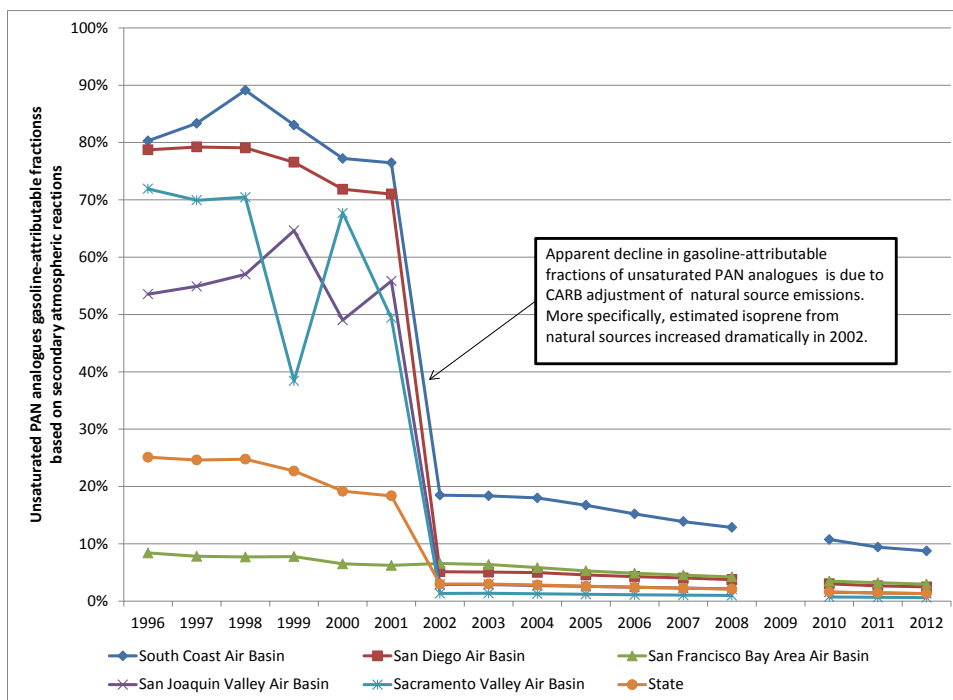
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Table 79. Gasoline-attributable fractions of unsaturated PAN analogues based on secondary reaction tonnage.

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	80%	79%	8%	54%	72%	25%
1997	83%	79%	8%	55%	70%	25%
1998	89%	79%	8%	57%	70%	25%
1999	83%	77%	8%	65%	38%	23%
2000	77%	72%	6%	49%	68%	19%
2001	76%	71%	6%	56%	49%	18%
2002	18%	5%	7%	3%	1%	3%
2003	18%	5%	6%	3%	1%	3%
2004	18%	5%	6%	3%	1%	3%
2005	17%	5%	5%	3%	1%	3%
2006	15%	4%	5%	2%	1%	2%
2007	14%	4%	5%	2%	1%	2%
2008	13%	4%	4%	2%	1%	2%
2009	--	--	--	--	--	--
2010	11%	3%	3%	2%	1%	2%
2011	9%	3%	3%	1%	1%	1%
2012	9%	2%	3%	1%	1%	1%

Note: Mobile source emissions were unavailable for 2009.

Figure 155. Gasoline-attributable fractions of unsaturated PAN analogues



Peroxybenzoyl Nitrate and Other Aromatic PAN analogues (Aromatic Acyl Peroxynitrates): Exposure Assessment Results

Carter (2001) identified alkylbenzenes as precursor chemicals for atmospheric formation of aromatic peroxy nitrates. The top five gasoline-related precursor chemicals that contributed to the formation of aromatic peroxy nitrates statewide in 2012 were toluene, benzaldehyde, tolualdehyde, *m*-xylene and styrene. Secondary atmospheric reaction tonnage of aromatic peroxy nitrates was calculated using formation potentials applied to Emission Inventory data as described in Appendix E.

Figure 156 plots secondary formation tonnage of aromatic peroxy nitrates from gasoline-related sources, which declined between 1996 and 2012. Figure 157 summarizes the sources of secondary formation of aromatic peroxy nitrates. Table 80 and Figure 158 show the gasoline-attributable fractions of aromatic peroxy nitrates. Statewide, in 2012, 49% of secondary formation emission tonnage of aromatic peroxy nitrates came from gasoline-related sources.

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Figure 156. Statewide annual tons of aromatic acyl peroxy nitrates formed through secondary atmospheric reactions (data from CARB Emission Inventory)

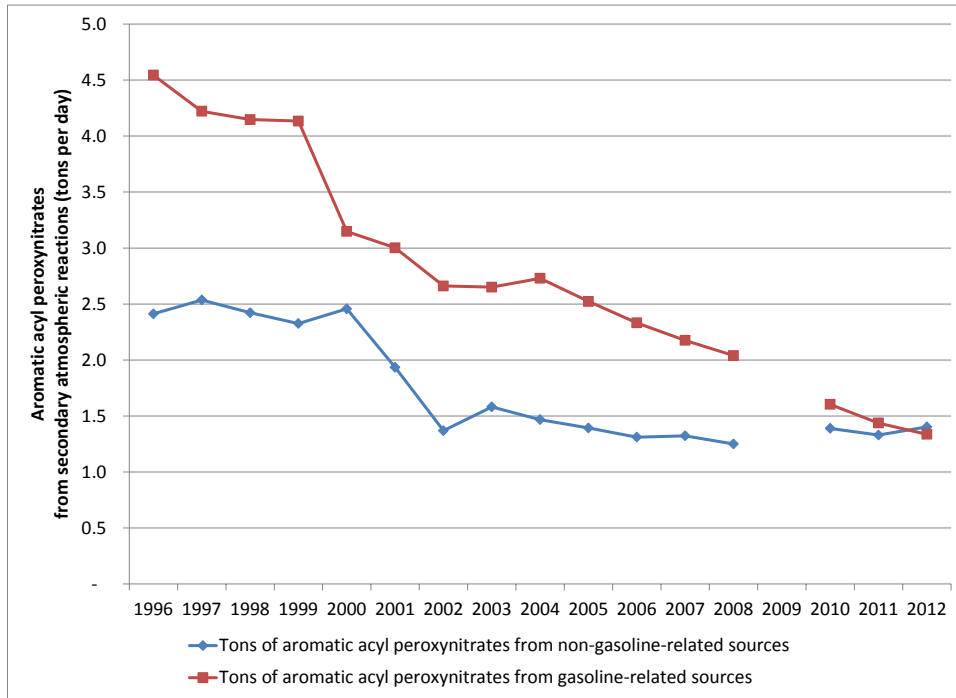
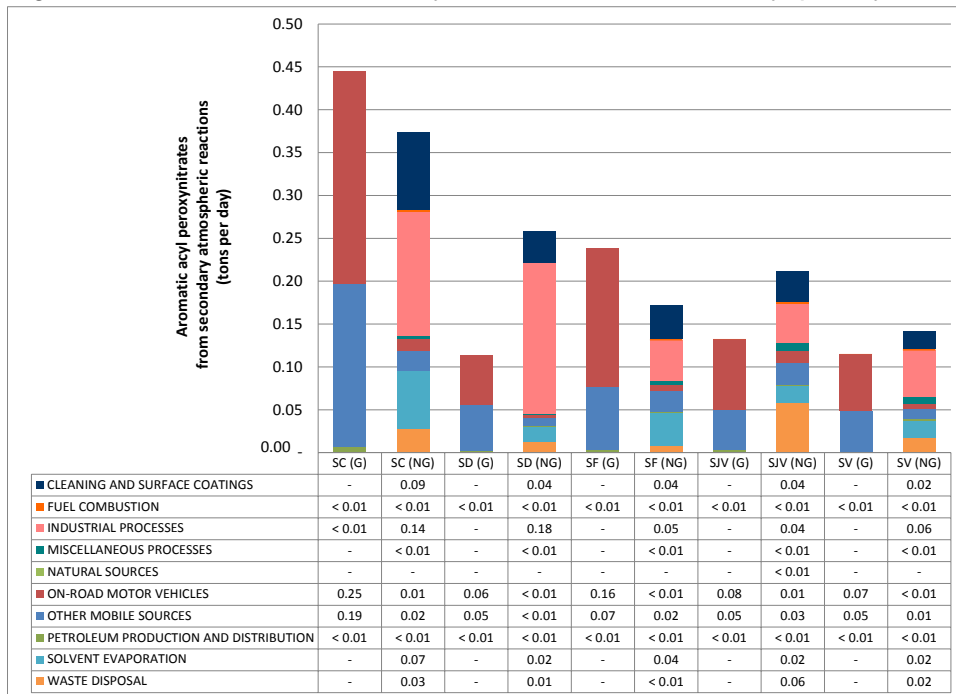


Figure 157. Sources of secondary formation of aromatic acyl peroxy nitrates in 2012



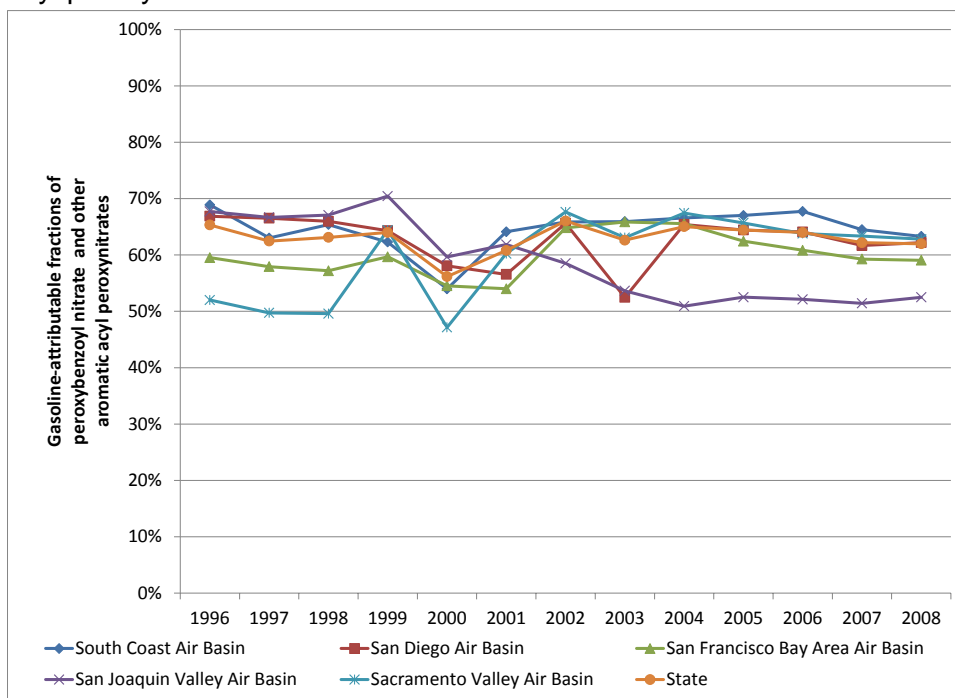
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Table 80. Gasoline-attributable fractions of peroxybenzoyl nitrate and other aromatic acyl peroxy nitrates are based on secondary reaction tonnage only.

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	69%	67%	60%	68%	52%	65%
1997	63%	67%	58%	67%	50%	62%
1998	65%	66%	57%	67%	50%	63%
1999	62%	64%	60%	70%	64%	64%
2000	54%	58%	55%	60%	47%	56%
2001	64%	57%	54%	62%	60%	61%
2002	66%	66%	65%	59%	68%	66%
2003	66%	52%	66%	54%	63%	63%
2004	67%	65%	66%	51%	67%	65%
2005	67%	64%	62%	53%	66%	64%
2006	68%	64%	61%	52%	64%	64%
2007	64%	62%	59%	51%	63%	62%
2008	63%	62%	59%	52%	63%	62%
2009	--	--	--	--	--	--
2010	59%	35%	60%	45%	49%	54%
2011	57%	32%	59%	47%	47%	52%
2012	54%	30%	58%	38%	45%	49%

Note: Mobile source emissions were unavailable for 2009.

Figure 158. Gasoline-attributable fractions of peroxybenzoyl nitrate and other aromatic acyl peroxy nitrates



Chemical Profiles: Gasoline-Related PAHs

This section presents exposure and screening risk assessment results for selected gasoline-related PAHs. We present summary graphs and tables of available ambient air measurements. Population-weighted annual average ambient air concentrations were also calculated for the South Coast Air Basin for selected PAHs.

Sources of ambient air PAH measurements that we located are described below:

- US EPA NATTS measured ambient air concentrations of PAHs from 3 monitoring sites in California: San Jose in Santa Clara County, Rubidoux in Riverside County and Main Street in Los Angeles between 2008 and 2014. The samples were collected over 24-hour periods at six-day intervals throughout the year.
- California Air Toxic Monitoring Network monitored the following particle-bound PAHs: benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[k]fluoranthene, dibenz[ah]anthracene, and indeno[1,2,3-cd]pyrene. Monitoring of these ended in February 2005 because the calculated health risks were low.
- Multiple Air Toxics Exposure Study III (MATES III) measured ambient air concentrations of 16 PAHs at three sites in Southern California between Dec 2004 and March 2005. The monitoring sites are listed in the following table.

Site	Address	City	County	Air Basin
Central Los Angeles	1630 N. Main St.	Los Angeles	Los Angeles	South Coast
Riverside (Rubidoux)	5888 Mission Blvd.	Riverside	Riverside	South Coast
North Long Beach	3648 N. Long Beach Blvd.	Long Beach	Los Angeles	South Coast

- Eiguren-Fernandez et al. (2004) measured ambient air concentrations of PAHs at six schools in Southern California between 2001 and 2002. Particle-bound and vapor phase PAHs were measured. In the tables below, the particle-bound and vapor-phase concentrations are tabulated separately. In the plots of ambient air concentrations that appear in the main report, the particle-bound and vapor-phase concentrations were added. The schools where samples were collected were located in the cities listed in the table below.

City	County
Atascadero	San Luis Obispo
Lompoc	Santa Barbara
San Dimas	Los Angeles
Upland	San Bernardino
Mira Loma	Riverside
Riverside	Riverside

- Additional data sources were available for naphthalene, and are described in the naphthalene section below.

Gasoline-Related PAHs in the Emission Inventory

Naphthalene: Exposure and Screening Risk Assessment Results

Naphthalene is a carcinogen and a respiratory toxicant and had the 95th highest primary emissions from gasoline-related sources in 2012 among all gasoline-related VOCs. Figure 159 shows that the statewide emissions of naphthalene from gasoline-related sources declined between 1996 and 2012. Estimated naphthalene emissions from gasoline-related sources appeared to increase between 2003 and 2004 when the Emission Inventory was changed to account for the phase out of MTBE, but then declined again over the next eight years. Schiffer et al. (2013) examined emissions from high emitting vehicles powered by different gasoline-blends and found that changing from MTBE to ethanol had no impact on naphthalene emissions from high emitting vehicles.

Figure 160 and Figure 161 show the emission sources and gasoline-attributable fractions of naphthalene (see Table 81 also). Statewide, in 2012, 33% of naphthalene emissions came from gasoline-related sources including cars, trucks, motorcycles, lawn and garden equipment and recreational boats. Non-gasoline-related sources of naphthalene included aircraft, construction and mining equipment, consumer products, asphalt paving and concrete production. Gasoline-attributable fractions increased between 2003 and 2004 because mobile source emissions were estimated to contain more naphthalene. The gasoline-attributable fractions for naphthalene in the South Coast and San Francisco Bay Area Air Basins increased between 2008 and 2010 because of a decrease in the modeled naphthalene emissions from solvent evaporation.

In a study of 15 US EPA priority PAHs in Southern California ambient air, Eiguren-Fernandez et al. (2004) found that vapor phase PAHs accounted for more than 99.9% of measured PAH mass and that naphthalene made up 91% of PAH mass.

Naphthalene is not routinely monitored in California, so we searched for available studies that included ambient air measurements of this PAH. We found nine relevant studies, although none of these studies spanned the entire time period of interest for the current report (1996 to 2014). We used two sets of data from the South Coast Air Basin as the basis for modeling naphthalene air concentrations over time, and used the other studies we located for validation. The first model was based on data collected during the summer of 1996 by the Desert Research Institute (DRI) (Zielinska *et al.*, 1999; complete dataset obtained from those authors). The second model was based on data from 2007 to 2014 collected by the NATTS (<https://www3.epa.gov/ttnamti1/natts.html>). The models are described in Appendix D. The population-weighted annual average ambient air concentrations were calculated based on modeled values (Tables 82 and 83). The model based on 1996 DRI data produced population-weighted annual average concentrations that ranged from 0.15 ppb in 1996 to 0.077 ppb in 2014. The model based on 2007-2014 NATTS data gave population-weighted annual averages that ranged from 0.048 ppb in 1996 to 0.014 ppb in 2014. Other measurements of ambient air naphthalene concentrations have been made in and around the South Coast Air Basin, and we used those to compare with our model results (Figure 162). The 1996 model produced

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estimates that are higher than the measured values from more recent studies. The 2007-2014 model seems to underestimate the 1996 ambient air concentrations. Naphthalene annual average concentrations appear to range from about 0.15 ppb in 1996 to 0.016 ppb in 2014.

Cancer risks were calculated based on gasoline-attributable ambient air concentrations (see Appendix G for details). Based on the 1996 modeled values, the gasoline-attributable cancer risk of naphthalene in the South Coast Air Basin was 4.4×10^{-5} in 1996. Based on the 2007-2014 modeled values, the gasoline-attributable cancer risk of naphthalene in the South Coast Air Basin was 4.8×10^{-6} in 2014. Our estimates indicate an approximate reduction of 40 estimated cancer cases per 1 million people between 1996 and 2014 in the South Coast region. There were inadequate data to calculate a statewide hazard quotient for naphthalene.

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Figure 159. Annual naphthalene emissions from gasoline and non-gasoline-related sources in California (data from CARB Emission Inventory)

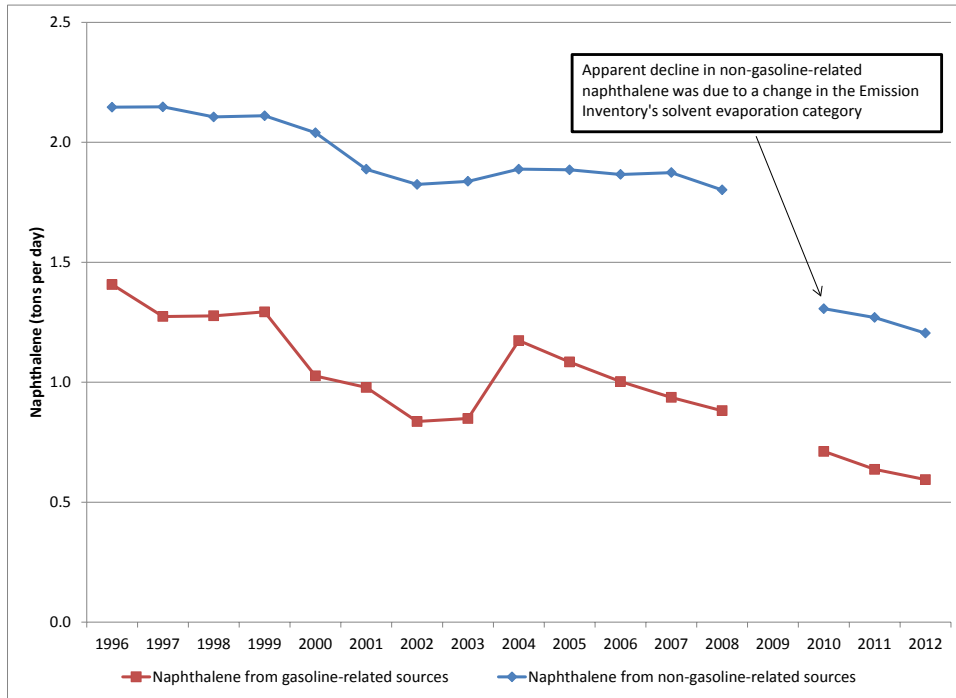
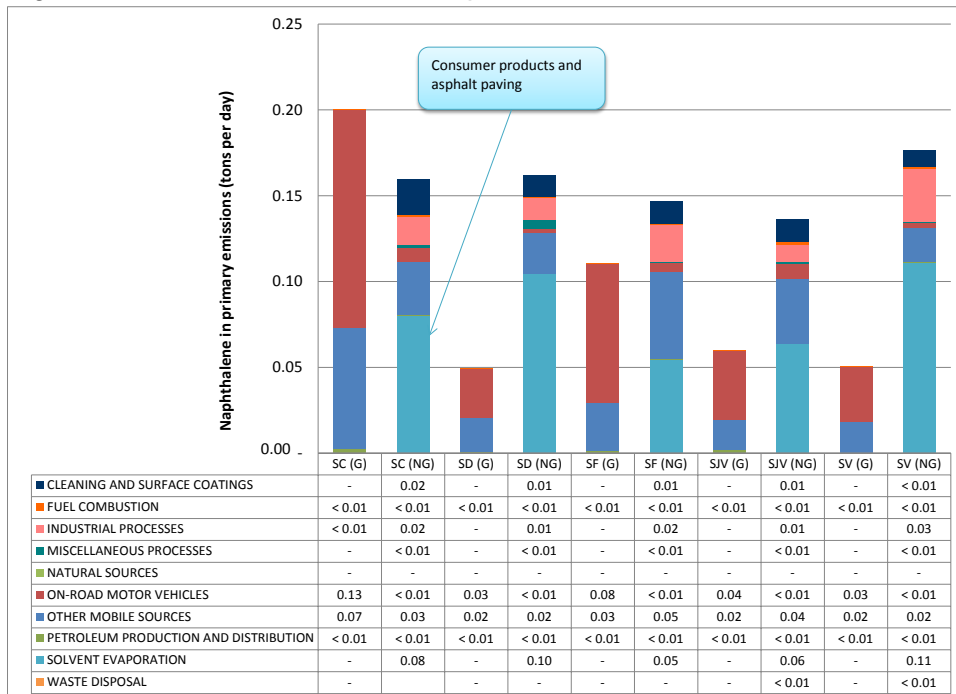


Figure 160. Emission sources of naphthalene in 2012



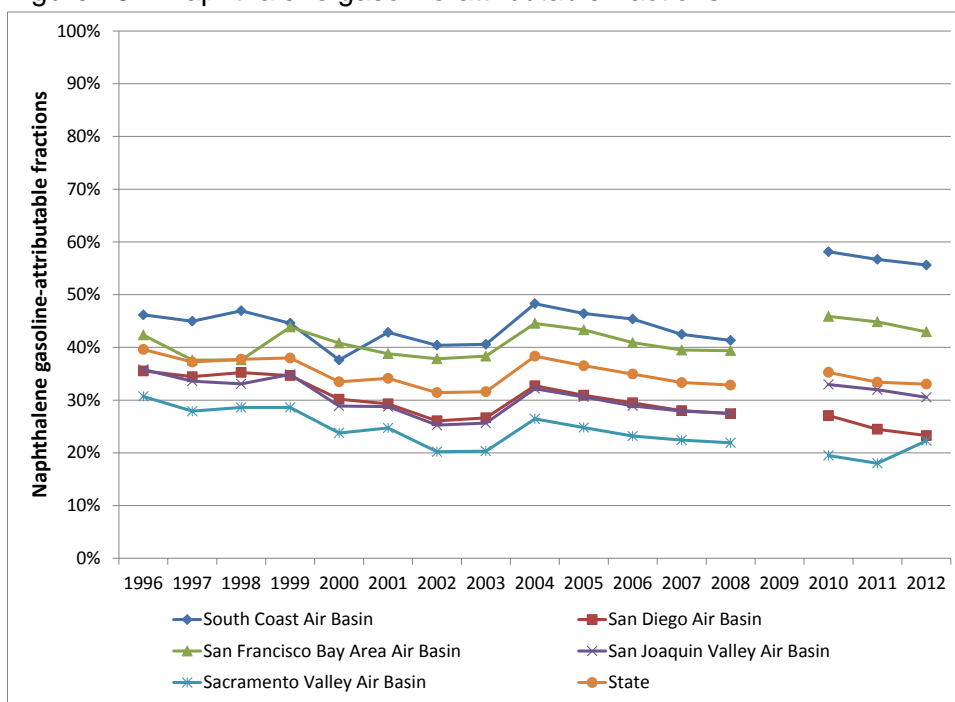
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Table 81. Naphthalene gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	46%	36%	42%	36%	31%	40%
1997	45%	34%	38%	34%	28%	37%
1998	47%	35%	38%	33%	29%	38%
1999	45%	35%	44%	35%	29%	38%
2000	38%	30%	41%	29%	24%	33%
2001	43%	29%	39%	29%	25%	34%
2002	40%	26%	38%	25%	20%	31%
2003	41%	27%	38%	26%	20%	32%
2004	48%	33%	45%	32%	26%	38%
2005	46%	31%	43%	31%	25%	37%
2006	45%	29%	41%	29%	23%	35%
2007	42%	28%	39%	28%	22%	33%
2008	41%	27%	39%	28%	22%	33%
2009	--	--	--	--	--	--
2010	58%	27%	46%	33%	19%	35%
2011	57%	24%	45%	32%	18%	33%
2012	56%	23%	43%	31%	22%	33%

Note: Mobile source emissions were not available for 2009.

Figure 161. Naphthalene gasoline-attributable fractions



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Table 82. Results for naphthalene in the South Coast Air Basin based on 1996 model

Year	Population-weighted average concentration of naphthalene (ng/m ³)	Population-weighted average concentration of naphthalene (ppbv)	Gasoline-attributable fraction	Gasoline-attributable concentration (ppbv)
1996	812	0.15	46%	0.071
1997	778	0.15	45%	0.067
1998	760	0.14	47%	0.068
1999	729	0.14	45%	0.062
2000	680	0.13	38%	0.049
2001	640	0.12	43%	0.052
2002	611	0.12	40%	0.047
2003	596	0.11	41%	0.046
2004	538	0.10	48%	0.050
2005	495	0.094	46%	0.044
2006	482	0.092	45%	0.042
2007	464	0.089	42%	0.038
2008	434	0.083	41%	0.034
2009	418	0.080	41%	0.033
2010	428	0.082	58%	0.047
2011	412	0.079	57%	0.045
2012	418	0.080	56%	0.044
2013	412	0.079	56%	0.044
2014	403	0.077	56%	0.043

Notes: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

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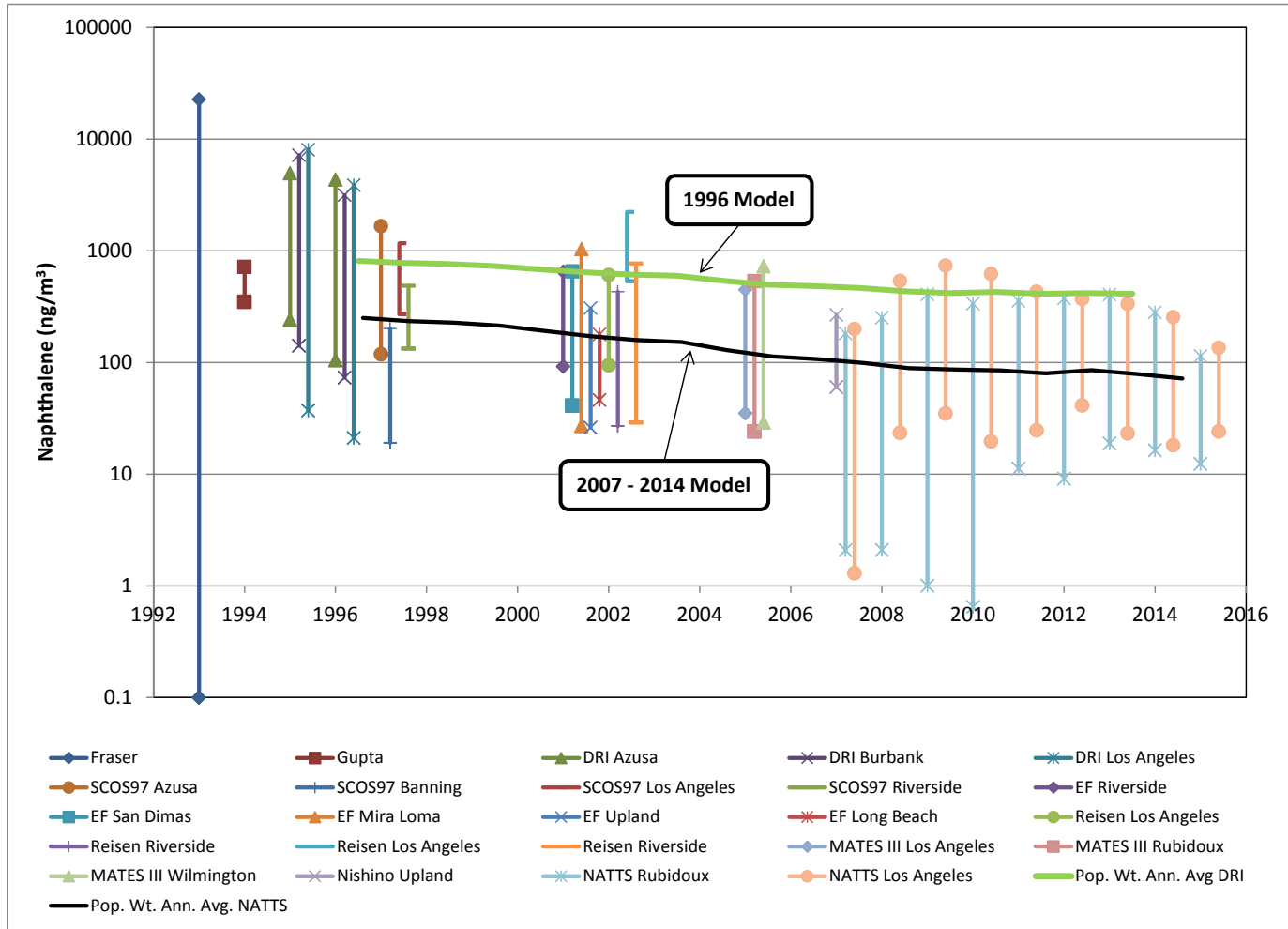
Table 83. Results for naphthalene in the South Coast Air Basin based on 2007-2014 model

Year	Population-weighted average concentration of naphthalene (ng/m ³)	Population-weighted average concentration of naphthalene (ppbv)	Gasoline-attributable fraction	Gasoline-attributable concentration (ppbv)
1996	251	0.048	46%	0.022
1997	234	0.045	45%	0.020
1998	227	0.043	47%	0.020
1999	214	0.041	45%	0.018
2000	191	0.036	38%	0.014
2001	172	0.033	43%	0.014
2002	159	0.030	40%	0.012
2003	152	0.029	41%	0.012
2004	129	0.025	48%	0.012
2005	113	0.022	46%	0.0100
2006	107	0.020	45%	0.0093
2007	99	0.019	42%	0.0080
2008	89	0.017	41%	0.0070
2009	86	0.016	41%	0.0068
2010	85	0.016	58%	0.0094
2011	80	0.015	57%	0.0086
2012	85	0.016	56%	0.0091
2013	79	0.015	56%	0.0083
2014	72	0.014	56%	0.0076

Notes: The 2009 gasoline-attributable concentration was calculated with the 2008 gasoline-attributable fraction. The 2013 and 2014 gasoline-attributable concentrations were calculated with the 2012 gasoline-attributable fraction.

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Figure 162. Comparison of modeled annual average naphthalene concentration to naphthalene measurements from other studies



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Notes for Figure 162:

1. Vertical lines range from minimum to maximum value in the study.
2. The 1996 model is based on naphthalene data collected by the Desert Research Institute (DRI) in 1996 (Zielinska et al., 1999).
3. The 2007-2014 model is based on data collected from the NATTS between 2007 and 2014.
4. References:
 - a. Fraser et al. (1998b) collected naphthalene samples during a smog episode Sept 8-9, 1993
 - b. Gupta et al. (1996) collected 12 naphthalene samples in Oct. 1994
 - c. DRI collected naphthalene samples during summer months of 1995 and 1996 (Zielinska et al., 1999)
 - d. SCOS97 - data collected by Arey as part of Southern California Ozone Study
 - e. EF - data described in Eiguren-Fernandez et al. (2004), summary statistics reported in Lu et al. (2005)
 - f. Reisen - summary statistics from Lu et al. (2005), based on data in Reisen (2003) and Reisen and Arey (2005)
 - g. MATES III – Multiple Air Toxics Exposure Study in the South Coast Air Basin
 - h. Nishino et al. (2008)
 - i. NATTS – Naphthalene (total suspended particulate) data downloaded from <https://aqg.epa.gov/api>

1-Methylnaphthalene: Exposure Assessment Results

The estimated gasoline-related primary emissions of 1-methylnaphthalene increased in 2004, which was associated with the replacement of MTBE with ethanol and reflected in revised speciation profiles in the Emission Inventory.

The estimated statewide gasoline-attributable fraction for 1-methylnaphthalene was at its lowest in 2002-2003 (41%), rising to 98% in 2004 and staying at or above that value since then (Table 84).

We did not locate ambient air measurements for 1-methylnaphthalene in the sources we consulted for ambient air PAH data (see the beginning of the PAH Chemical Profiles for a description of these sources).

Table 84. Statewide tonnage and gasoline-attributable fractions of 1-methylnaphthalene

Year	Gasoline-attributable emissions (tons per day)	Total emissions (tons per day)	Gasoline-attributable fraction
1996	0.012	0.012	100%
1997	0.0047	0.0047	100%
1998	0.0049	0.0049	100%
1999	0.010	0.010	100%
2000	0.021	0.032	66%
2001	0.019	0.030	63%
2002	0.0071	0.018	41%
2003	0.0066	0.016	41%
2004	0.13	0.13	98%
2005	0.12	0.12	98%
2006	0.11	0.11	98%
2007	0.10	0.10	97%
2008	0.095	0.095	100%
2009	--	--	--
2010	0.093	0.093	99%
2011	0.082	0.083	99%
2012	0.078	0.078	99%

Note: Mobile source emissions were unavailable for 2009.

2-Methylnaphthalene: Exposure Assessment Results

The estimated gasoline-related primary emissions of 2-methylnaphthalene increased in 2004 as was true for 1-methylnaphthalene. The increases were associated with the replacement of MTBE with ethanol and reflected in adjustments to speciation profiles in the Emission Inventory.

The estimated statewide gasoline-attributable fractions of 2-methylnaphthalene were about 5% or less until 2004, increasing to close to 20-30% in 2004 and later (Table 85). The fractions are lower for 2-methylnaphthalene compared to 1-methylnaphthalene, because

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2-methylnaphthalene is also part of the mixture “naphtha”, which is emitted by some non-gasoline-related sources.

We did not locate ambient air measurements for 2-methylnaphthalene.

Table 85. Statewide tonnage and gasoline-attributable fractions of 2-methylnaphthalene

Year	Gasoline-attributable emissions (tons per day)	Total emissions (tons per day)	Gasoline-attributable fraction
1996	0.029	0.838	3%
1997	0.011	0.851	1%
1998	0.011	0.838	1%
1999	0.024	0.862	3%
2000	0.049	0.860	6%
2001	0.043	0.808	5%
2002	0.017	0.749	2%
2003	0.016	0.753	2%
2004	0.306	1.057	29%
2005	0.278	1.033	27%
2006	0.252	1.007	25%
2007	0.233	0.993	23%
2008	0.221	0.965	23%
2009	--	--	--
2010	0.206	0.896	23%
2011	0.183	0.856	21%
2012	0.172	0.802	21%

Note: Mobile source emissions were unavailable for 2009.

Other Gasoline-Related PAHs with Some Ambient Air Data

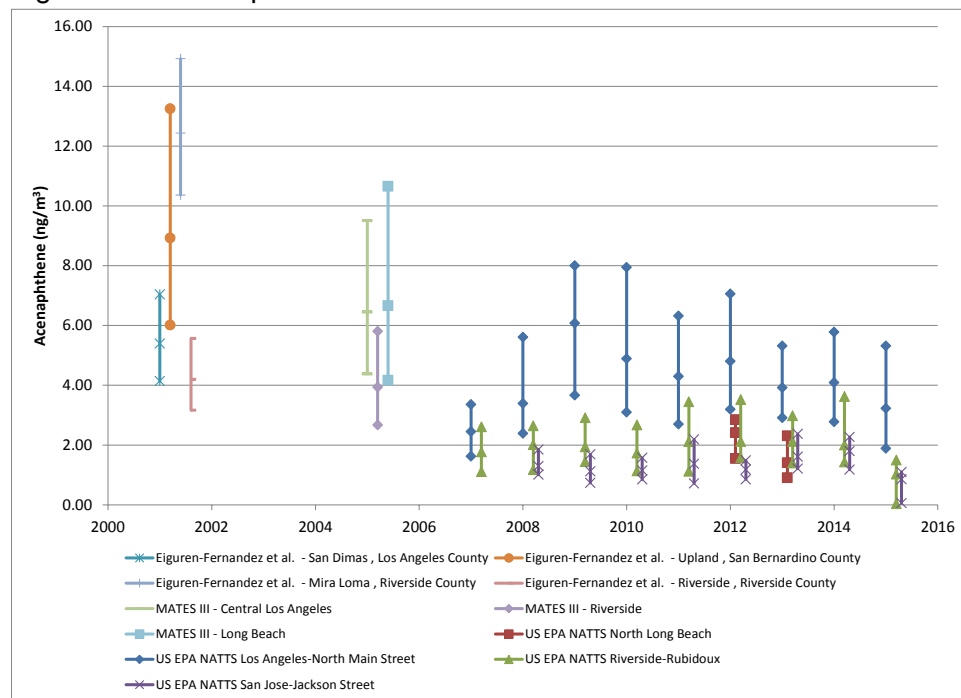
PAHs measured by the California Toxic Monitoring Network were benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene and dibenz[ah]anthracene. We used these measurements to estimate population-weighted annual average ambient air concentrations for the South Coast Air Basin. Measurements from other studies are also included in the discussion below for comparison. We also report cancer risk estimates where possible.

For PAHs not included in the California Toxic Monitoring Network, we located some ambient air measurements and these data are summarized in the relevant sections below.

Acenaphthene: Summary of Ambient Air Measurements

A few studies have measured acenaphthene in ambient air. Descriptions of these studies are on page 247. Figure 163 contains a plot of the first quartile, median and third quartile of these measurements. The data used to create the plot are tabulated below. The annual average and standard deviation from the Eiguren-Fernandez et al. and MATES III studies were used to estimate the quartiles for the plot by assuming the data came from a lognormal distribution.

Figure 163. Acenaphthene ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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The following box provides further details on acenaphthene ambient air measurements displayed in Figure 163.

Eiguren-Fernandez et al. (2004)					
Site	Time	Particle phase (pg/m ³)		Vapor phase (ng/m ³)	
		Average	SD	Average	SD
Atascadero	May 2001-July 2002	2.09	3.61	2.51	2.18
Lompoc	May 2001-July 2002	2.56	2.46	2.16	1.39
San Dimas	May 2001-July 2002	3.17	5.49	5.83	2.39
Upland	May 2001-July 2002	0.39	0.67	10.6	6.78
Mira Loma	May 2001-July 2002	0.76	1.31	12.9	3.55
Riverside	May 2001-July 2002	1.32	2.29	4.58	2

MATES III (ng/m ³)			
Site	Year	Average	SD
Central Los Angeles	2005	7.61	4.76
Riverside	2005	4.65	2.92
North Long Beach	2005	8.49	6.70

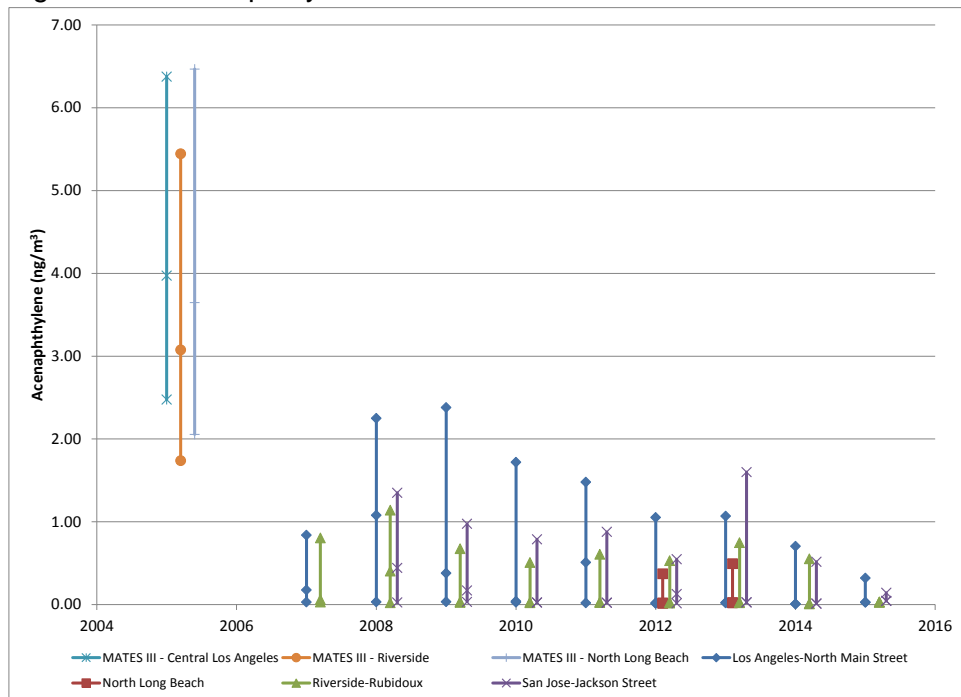
US EPA NATTS (ng/m ³)									
Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average
Los Angeles-North Main Street	2007	39	13%	0.035	1.6	2.4	3.4	9.5	2.7
	2008	61	0%	1.4	2.4	3.4	5.6	17	4.7
	2009	60	2%	0.034	3.7	6.1	8	44	7
	2010	59	0%	0.53	3.1	4.9	8	25	6.1
	2011	59	0%	0.76	2.7	4.3	6.3	15	4.9
	2012	60	0%	1.3	3.2	4.8	7.1	12	5.4
	2013	58	0%	0.63	2.9	3.9	5.3	12	4.3
	2014	56	0%	0.79	2.8	4.1	5.8	9.5	4.4
North Long Beach	2012	26	0%	0.87	1.6	2.4	2.8	3.5	2.2
	2013	29	0%	0.31	0.91	1.4	2.3	4.4	1.7
Riverside-Rubidoux	2007	55	4%	0.055	1.1	1.8	2.6	5.7	2
	2008	71	1%	0.031	1.2	2	2.6	5.6	2.1
	2009	64	2%	0.021	1.4	1.9	2.9	6.3	2.4
	2010	65	2%	0.032	1.1	1.7	2.7	5.8	2.1
	2011	67	0%	0.18	1.1	2.1	3.4	7.8	2.6
	2012	67	0%	0.61	1.6	2.1	3.5	8.2	2.6
	2013	64	0%	0.39	1.4	2.1	3	7.2	2.4
	2014	65	2%	0.048	1.4	2	3.6	6.2	2.5
San Jose-Jackson Street	2008	40	0%	0.56	1	1.3	1.8	3	1.5
	2009	61	2%	0.028	0.73	1.1	1.7	4.8	1.3
	2010	59	0%	0.44	0.85	1.2	1.6	3.9	1.3
	2011	61	0%	0.41	0.72	1.4	2.2	5.3	1.5
	2012	59	0%	0.35	0.85	1.2	1.5	3.2	1.3
	2013	59	0%	0.61	1.2	1.6	2.4	4.1	1.8
	2014	59	2%	0.074	1.2	1.8	2.3	23	2.1
	2015	43	33%	0.054	0.055	0.86	1.1	1.9	0.75

Note: Half the limit of detection substituted for non-detects

Acenaphthylene: Summary of Ambient Air Measurements

A few studies have measured acenaphthylene in ambient air. Descriptions of these studies are on page 247. Figure 164 contains a plot of the first quartile, median and third quartile of these measurements. The data used to create the plot are tabulated below. The annual average and standard deviation from the Eiguren-Fernandez et al. and MATES III studies were used to estimate the quartiles for the plot by assuming the data came from a lognormal distribution.

Figure 164. Acenaphthylene ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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The following box provides further details on acenaphthylene ambient air measurements displayed in Figure 164.

MATES III (2005) (ng/m ³)										
	Average	SD								
Central Los Angeles	5.08	4.05								
Riverside	4.4	4.5								
North Long Beach	5.23	5.38								

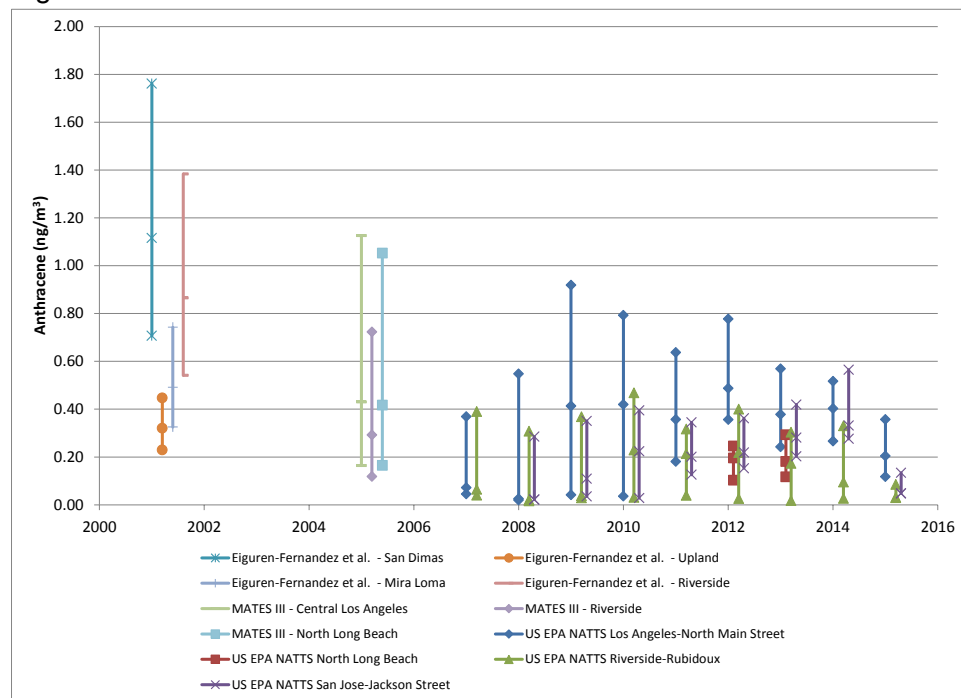
US EPA (ng/m ³)										
Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	41%	0.025	0.03	0.18	0.84	5.2	0.8	1.4
	2008	61	26%	0.019	0.033	1.1	2.2	6.6	1.5	1.6
	2009	60	45%	0.026	0.035	0.38	2.4	11	1.4	2.2
	2010	59	53%	0.016	0.027	0.04	1.7	5.1	0.93	1.3
	2011	59	44%	0.016	0.021	0.51	1.5	7.3	1.2	1.7
	2012	60	53%	0.011	0.014	0.02	1.1	4.2	0.67	1
	2013	58	60%	0.016	0.019	0.024	1.1	5.3	0.78	1.3
	2014	56	64%	0.007	0.0071	0.0089	0.71	4	0.43	0.77
North Long Beach	2012	26	62%	0.013	0.015	0.021	0.37	4.9	0.45	1
	2013	29	66%	0.018	0.021	0.023	0.49	5.4	0.7	1.3
Riverside-Rubidoux	2007	55	51%	0.025	0.03	0.06	0.8	8.4	1	1.9
	2008	71	34%	0.016	0.022	0.4	1.1	3.9	0.82	0.97
	2009	64	55%	0.021	0.027	0.035	0.67	9	0.84	1.8
	2010	65	60%	0.016	0.022	0.028	0.51	7.8	0.58	1.3
	2011	67	64%	0.018	0.023	0.031	0.61	7.5	0.48	1.1
	2012	67	51%	0.014	0.019	0.028	0.53	4	0.5	0.92
	2013	64	55%	0.019	0.023	0.029	0.75	6.2	0.62	1.1
	2014	65	60%	0.0069	0.0084	0.011	0.55	4.4	0.48	0.89
San Jose-Jackson Street	2008	40	33%	0.025	0.026	0.44	1.4	6.1	1.1	1.5
	2009	61	48%	0.03	0.032	0.17	0.98	7.2	1.1	1.9
	2010	59	51%	0.024	0.025	0.026	0.79	8.3	0.69	1.4
	2011	61	56%	0.02	0.021	0.022	0.88	13	1.2	2.6
	2012	59	47%	0.016	0.017	0.13	0.55	7.7	0.86	1.8
	2013	59	51%	0.025	0.026	0.028	1.6	11	1.3	2.3
	2014	59	51%	0.01	0.011	0.012	0.52	8.8	0.81	1.7
	2015	43	74%	0.042	0.044	0.045	0.14	3.4	0.41	0.89

Note: Half the limit of detection substituted for non-detects

Anthracene: Summary of Ambient Air Measurements

A few studies have measured anthracene in ambient air. Descriptions of these studies are on page 247. Figure 165 contains a plot of the first quartile, median and third quartile of these measurements. The data used to create the plot are tabulated below. The annual average and standard deviation from the Eiguren-Fernandez et al. and MATES III studies were used to estimate the quartiles for the plot by assuming the data came from a lognormal distribution.

Figure 165. Anthracene ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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Box below provides more details on ambient air measurements of anthracene in Figure 165

Eiguren-Fernandez et al. (2004)

Site	Time	Particle phase (pg/m ³)		Vapor phase (ng/m ³)	
		Average	SD	Average	SD
Atascadero	May 2001-July 2002	0.16	0.15	0.73	0.29
Lompoc	May 2001-July 2002	2.05	2.62	0.13	0.15
San Dimas	May 2001-July 2002	3.18	3.45	1.4	1.07
Upland	May 2001-July 2002	1.87	1.85	0.36	0.19
Mira Loma	May 2001-July 2002	2.77	4.8	0.59	0.4
Riverside	May 2001-July 2002	2.3	2.6	1.1	0.87

MATES III (2005) (ng/m³)

Site	Average	SD
Central Los Angeles	1.19	3.07
Riverside	0.72	1.62
North Long Beach	1.07	2.53

US EPA National Air Toxics Trend Stations (ng/m³)

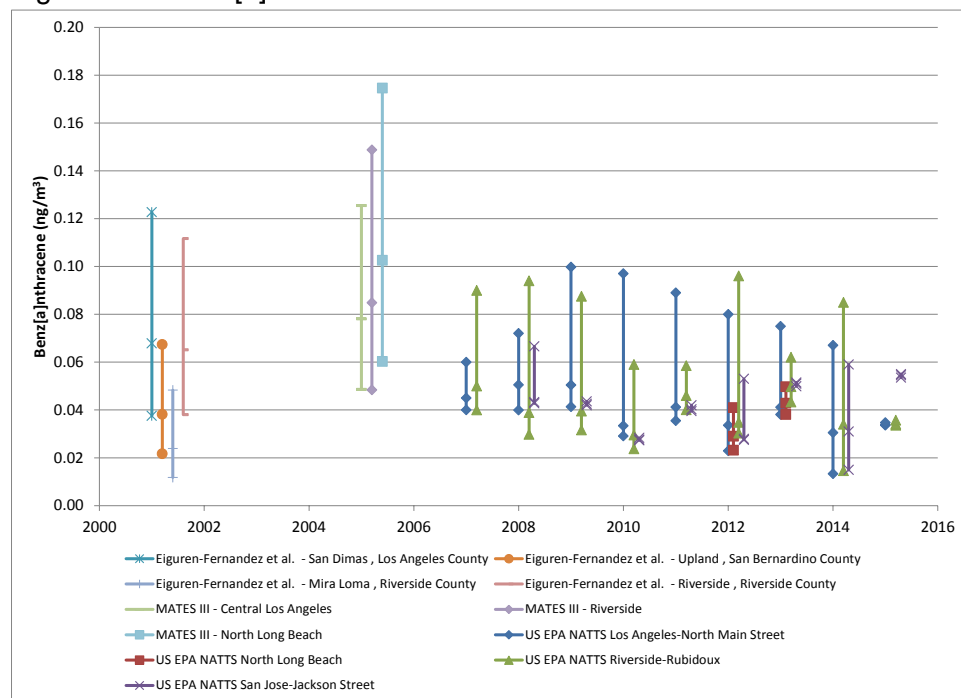
Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	51%	0.03	0.045	0.072	0.37	1.2	0.23	0.28
	2008	61	56%	0.015	0.02	0.026	0.55	2.1	0.35	0.48
	2009	60	37%	0.028	0.042	0.41	0.92	4	0.63	0.8
	2010	59	27%	0.018	0.036	0.42	0.79	13	0.72	1.7
	2011	59	15%	0.019	0.18	0.36	0.64	1.6	0.46	0.38
	2012	60	5%	0.019	0.36	0.49	0.78	1.5	0.54	0.29
	2013	58	14%	0.012	0.24	0.38	0.57	0.98	0.43	0.27
	2014	56	13%	0.023	0.27	0.4	0.52	0.94	0.39	0.23
North Long Beach	2012	26	23%	0.017	0.1	0.2	0.25	0.98	0.23	0.22
	2013	29	21%	0.014	0.12	0.18	0.29	1.2	0.27	0.28
Riverside-Rubidoux	2007	55	60%	0.035	0.04	0.065	0.39	4.5	0.38	0.83
	2008	71	63%	0.014	0.016	0.021	0.31	4.1	0.26	0.65
	2009	64	55%	0.022	0.029	0.038	0.37	4.4	0.32	0.69
	2010	65	31%	0.018	0.031	0.23	0.47	1.6	0.32	0.32
	2011	67	31%	0.018	0.04	0.21	0.32	1.1	0.24	0.24
	2012	67	31%	0.021	0.026	0.22	0.4	6.4	0.38	0.82
	2013	64	38%	0.015	0.018	0.17	0.3	1.3	0.22	0.24
	2014	65	49%	0.023	0.027	0.095	0.33	1.3	0.21	0.26
San Jose-Jackson Street	2008	40	58%	0.021	0.022	0.022	0.28	0.92	0.18	0.24
	2009	61	46%	0.034	0.035	0.11	0.35	2.9	0.32	0.54
	2010	59	25%	0.027	0.028	0.22	0.4	2.8	0.32	0.43
	2011	61	10%	0.027	0.13	0.2	0.35	1.3	0.3	0.29
	2012	59	3%	0.022	0.15	0.22	0.36	1	0.29	0.21
	2013	59	7%	0.018	0.2	0.28	0.42	1.4	0.36	0.28
	2014	59	2%	0.037	0.28	0.33	0.56	1.5	0.45	0.28
	2015	43	53%	0.046	0.048	0.049	0.13	0.78	0.16	0.21

Note: Half the limit of detection substituted for non-detects

Benz[a]anthracene: Summary of Ambient Air Measurements

We located a few studies that measured benz[a]anthracene in ambient air (see page 247 for study descriptions). Figure 166 plots the first quartile, median and third quartile of these measurements. The annual average and standard deviation from the Eiguren-Fernandez et al. and MATES III studies were used to estimate the quartiles for the plot by assuming the data came from a lognormal distribution. Table 86 contains cancer risk estimates based on the average measurement from each site and year. Risks were all well below 1×10^{-6} .

Figure 166. Benz[a]anthracene ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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Box gives more details on ambient air measurements of benz[a]anthracene shown in Figure 166

Eiguren-Fernandez et al. (2004)					
Site	Time	Particle phase (pg/m ³)		Vapor phase (ng/m ³)	
		Average	SD	Average	SD
Atascadero	May 2001-July 2002	24.2	38.1	0.24	0.12
Lompoc	May 2001-July 2002	6.26	8.19	-	-
San Dimas	May 2001-July 2002	29.8	39.5	0.07	0.1
Upland	May 2001-July 2002	24.4	23.3	0.03	0.05
Mira Loma	May 2001-July 2002	41.2	58	-	-
Riverside	May 2001-July 2002	19.6	27.4	0.07	0.08

MATES III (2005) (ng/m ³)		
Site	Average	SD
Central Los Angeles	0.1	0.08
Riverside	0.12	0.12
North Long Beach	0.14	0.13

US EPA National Air Toxics Trend Stations (ng/m ³)										
Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	82%	0.03	0.04	0.045	0.06	0.41	0.075	0.076
	2008	61	72%	0.031	0.04	0.05	0.072	0.39	0.084	0.081
	2009	60	72%	0.033	0.041	0.05	0.1	1.3	0.1	0.17
	2010	59	71%	0.018	0.029	0.033	0.097	0.67	0.076	0.11
	2011	59	69%	0.028	0.036	0.041	0.089	0.29	0.074	0.064
	2012	60	55%	0.018	0.023	0.034	0.08	0.31	0.058	0.052
	2013	58	74%	0.031	0.038	0.041	0.075	0.77	0.083	0.12
	2014	56	32%	0.0093	0.013	0.031	0.067	1.4	0.076	0.19
North Long Beach	2015	39	85%	0.032	0.034	0.034	0.035	1.1	0.077	0.17
	2012	26	77%	0.021	0.023	0.029	0.041	2	0.12	0.38
Riverside-Rubidoux	2013	29	76%	0.035	0.038	0.043	0.05	0.33	0.076	0.08
	2007	55	76%	0.035	0.04	0.05	0.09	0.58	0.095	0.11
	2008	71	69%	0.027	0.03	0.039	0.094	0.76	0.091	0.14
	2009	64	72%	0.027	0.032	0.04	0.088	1.6	0.1	0.21
	2010	65	69%	0.019	0.024	0.03	0.059	0.52	0.063	0.082
	2011	67	88%	0.021	0.04	0.046	0.058	0.34	0.062	0.049
	2012	67	60%	0.023	0.03	0.035	0.096	0.68	0.075	0.095
	2013	64	83%	0.038	0.043	0.05	0.062	1.7	0.097	0.22
2014	65	34%	0.0095	0.015	0.034	0.085	0.66	0.075	0.11	
San Jose-Jackson Street	2015	48	85%	0.032	0.034	0.034	0.036	0.73	0.06	0.1
	2008	40	75%	0.041	0.043	0.043	0.067	0.48	0.076	0.08
	2009	61	79%	0.039	0.042	0.043	0.044	1.8	0.11	0.24
	2010	59	85%	0.027	0.027	0.028	0.028	0.26	0.045	0.049
	2011	61	80%	0.037	0.04	0.04	0.042	0.64	0.085	0.12
	2012	59	75%	0.026	0.028	0.028	0.053	1.2	0.074	0.16
	2013	59	81%	0.049	0.05	0.051	0.051	0.61	0.092	0.11
2014	59	47%	0.014	0.015	0.031	0.059	2	0.12	0.31	
2015	43	91%	0.052	0.054	0.055	0.055	0.28	0.072	0.056	

Note: Half the limit of detection substituted for non-detects

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Table 86. Benz[a]anthracene cancer risk based on various studies

Eiguren-Fernandez et al. (2004)		2001	
Mira Loma, Riverside County		1.6E-08	
Riverside, Riverside County		3.5E-08	
San Dimas, Los Angeles County		3.9E-08	
Upland, San Bernardino County		2.1E-08	

MATES III		2005	
Central Los Angeles, Los Angeles County		3.9E-08	
N. Long Beach, Los Angeles County		5.4E-08	
Rubidoux, Riverside County		4.7E-08	

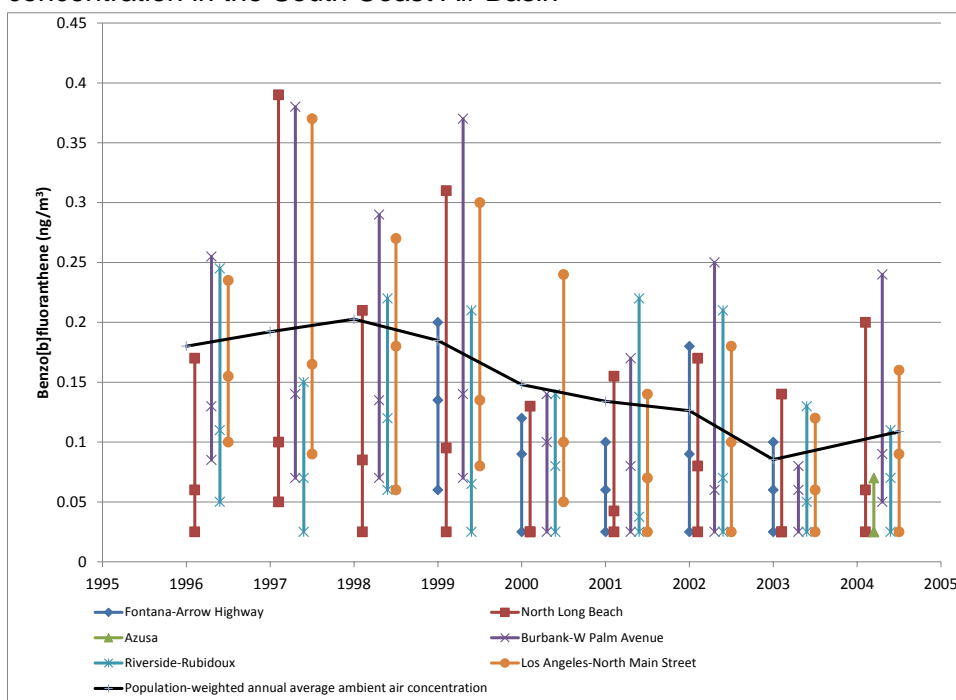
US EPA NATTS	2008	2009	2010	2011	2012	2013	2014
Central Los Angeles, Los Angeles County	3.3E-08	3.9E-08	3.0E-08	2.9E-08	2.3E-08	3.2E-08	3.0E-08
Rubidoux, Riverside County	3.5E-08	3.9E-08	2.5E-08	2.4E-08	2.9E-08	3.8E-08	2.9E-08
San Jose, Santa Clara County	3.0E-08	4.3E-08	1.8E-08	3.3E-08	2.9E-08	3.6E-08	4.7E-08

Benzo[b]fluoranthene: Exposure and Screening Risk Assessment Results

Data from the California Toxic Monitoring Network were used to estimate the population-weighted annual average ambient air concentrations of benzo[b]fluoranthene in the South Coast Air Basin from 1996-2004, the years with data. These results are displayed in Figure 167 and Table 87. Table 87 shows that between 1996 and 2004 the percentage of non-detects increased from 15 to 40%. By default, non-detects were replaced with half the limit of detection. Figure 168 compares the population-weighted annual average to ambient air data collected from other monitoring studies. For Eiguren-Fernandez et al. and MATES III studies, the quartiles were calculated from the reported averages and standard deviations by assuming the data came from a lognormal distribution. Summaries from these studies are presented in tables below. Descriptions of these studies are on page 247.

Table 88 contains cancer risk estimates for benzo[b]fluoranthene based on averages for each site and year. The maximum cancer risk across all sites in the California Toxic Monitoring Network is provided for comparison with the cancer risk based on the South Coast Air Basin population-weighted average.

Figure 167. Benzo[b]fluoranthene population-weighted annual average ambient air concentration in the South Coast Air Basin



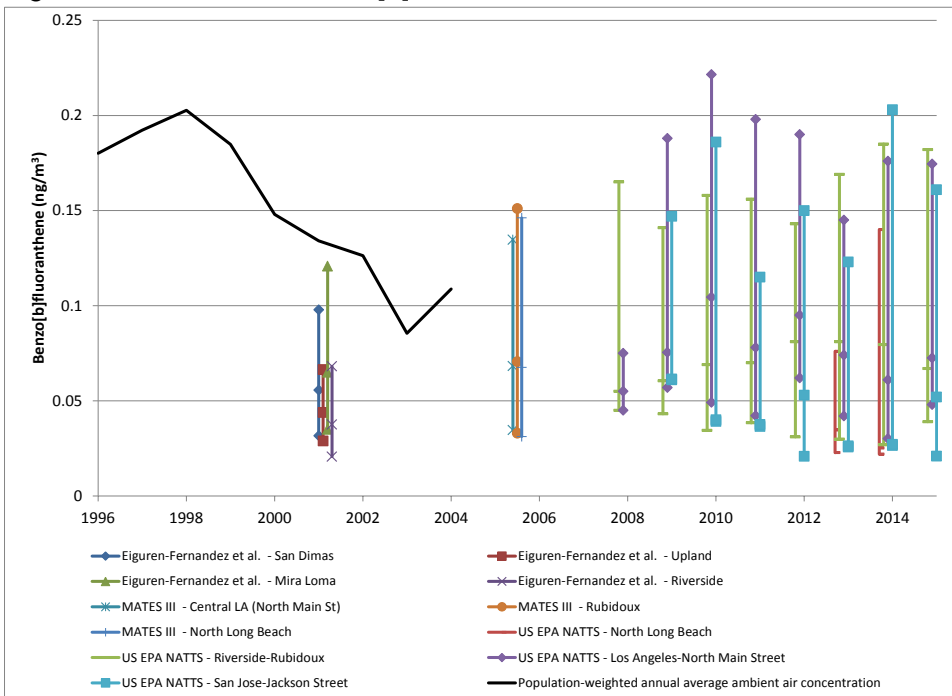
Note: The vertical bars show the quartiles of benzo[b]fluoranthene measurements from South Coast Air Basin monitoring sites in the California Toxic Monitoring Network with 10 or more months of data. Due to the large percentage of non-detects the estimated first quartile and median are the same at some sites.

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Table 87. Population-weighted annual average ambient air concentration of benzo[b]fluoranthene in the South Coast Air Basin

Year	Benzo[b]fluoranthene population-weighted annual average ambient air concentration (ng/m ³)	Percent of measurements that are non-detects
1996	0.18	15%
1997	0.19	19%
1998	0.20	21%
1999	0.18	21%
2000	0.15	34%
2001	0.13	38%
2002	0.13	36%
2003	0.085	41%
2004	0.11	40%

Figure 168. Additional benzo[b]fluoranthene ambient air measurements



Note: The vertical bars show the quartiles of benzo[b]fluoranthene measurements from additional monitoring sites

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The following box provides further details on benzo[b]fluoranthene ambient air measurements displayed in Figure 168.

Eiguren-Fernandez et al. (2004) particle phase PAHs (pg/m³)

Site	Time	Average	SD
Atascadero	May 2001-July 2002	64.8	94.7
Lompoc	May 2001-July 2002	11.7	15.3
San Dimas	May 2001-July 2002	79	79.7
Upland	May 2001-July 2002	53	36
Mira Loma	May 2001-July 2002	99.1	114
Riverside	May 2001-July 2002	55.5	60.4

MATES III (2005) (ng/m³)

Site	Average ¹	SD ²
Central Los Angeles	0.11	0.15
Riverside	0.13	0.21
North Long Beach	0.13	0.21

Notes: Average of benzo[b]fluoranthene was calculated by taking the average of benzo[b+j+k]fluoranthene and dividing by 3. SD of benzo[b]fluoranthene was calculated by taking the SD of benzo[b+j+k]fluoranthene and dividing by $\sqrt{3}$.

US EPA National Air Toxics Trend Stations (ng/m³)

Site	Year	N	Percent non-	Minimum	First Quartile	Median	Third Quartile	Max	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	77%	0.035	0.045	0.055	0.075	0.55	0.1	0.12
	2008	61	59%	0.043	0.057	0.076	0.19	0.72	0.15	0.15
	2009	60	35%	0.031	0.049	0.10	0.22	2.8	0.21	0.37
	2010	59	46%	0.024	0.042	0.078	0.2	0.72	0.14	0.15
	2011	59	14%	0.017	0.062	0.095	0.19	0.6	0.15	0.14
	2012	60	23%	0.017	0.042	0.074	0.15	0.43	0.11	0.089
	2013	58	29%	0.020	0.03	0.061	0.18	0.9	0.14	0.17
North Long Beach	2012	26	58%	0.020	0.023	0.035	0.076	2.5	0.18	0.49
	2013	29	55%	0.018	0.022	0.025	0.14	0.75	0.13	0.2
Riverside-Rubidoux	2007	55	67%	0.035	0.045	0.055	0.17	1.0	0.15	0.2
	2008	71	63%	0.039	0.043	0.061	0.14	0.74	0.12	0.14
	2009	64	45%	0.025	0.034	0.069	0.16	2.9	0.19	0.41
	2010	65	43%	0.025	0.038	0.07	0.16	1.1	0.12	0.16
	2011	67	31%	0.017	0.031	0.081	0.14	0.71	0.11	0.12
	2012	67	36%	0.022	0.03	0.081	0.17	0.74	0.12	0.13
San Jose-Jackson Street	2007	64	34%	0.022	0.027	0.080	0.18	2.0	0.16	0.26
	2008	40	73%	0.058	0.061	0.062	0.15	1.4	0.15	0.23
	2009	61	57%	0.036	0.039	0.040	0.19	3.2	0.23	0.46
	2010	59	59%	0.036	0.037	0.038	0.12	0.59	0.12	0.15
	2011	61	34%	0.020	0.021	0.053	0.15	1.5	0.18	0.31
	2012	59	58%	0.024	0.026	0.026	0.12	1.4	0.13	0.24
	2013	59	54%	0.026	0.027	0.027	0.20	1.4	0.2	0.32
	2014	59	34%	0.019	0.021	0.052	0.16	2.5	0.22	0.44

Note: Half the detection limit substituted for non-detects

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Table 88. Benzo[b]fluoranthene cancer risk

CARB TAC	1996	1997	1998	1999	2000	2001	2002	2003	2004
Maximum risk across all CARB sites	1.9E-07	2.6E-07	2.7E-07	2.2E-07	2.1E-07	2.5E-07	1.9E-07	1.7E-07	2.2E-07
South Coast Air Basin population-weighted average	7.0E-08	7.5E-08	7.9E-08	7.2E-08	5.8E-08	5.2E-08	4.9E-08	3.3E-08	4.2E-08

Eiguren-Fernandez et al. (2004)	2001-2002
Mira Loma, Riverside County	3.9E-08
Riverside, Riverside County	2.2E-08
San Dimas, Los Angeles County	3.1E-08
Upland, San Bernardino County	2.1E-08

MATES III	2005
Central Los Angeles, Los Angeles County	4.4E-08
N. Long Beach, Los Angeles County	5.1E-08
Rubidoux, Riverside County	5.2E-08

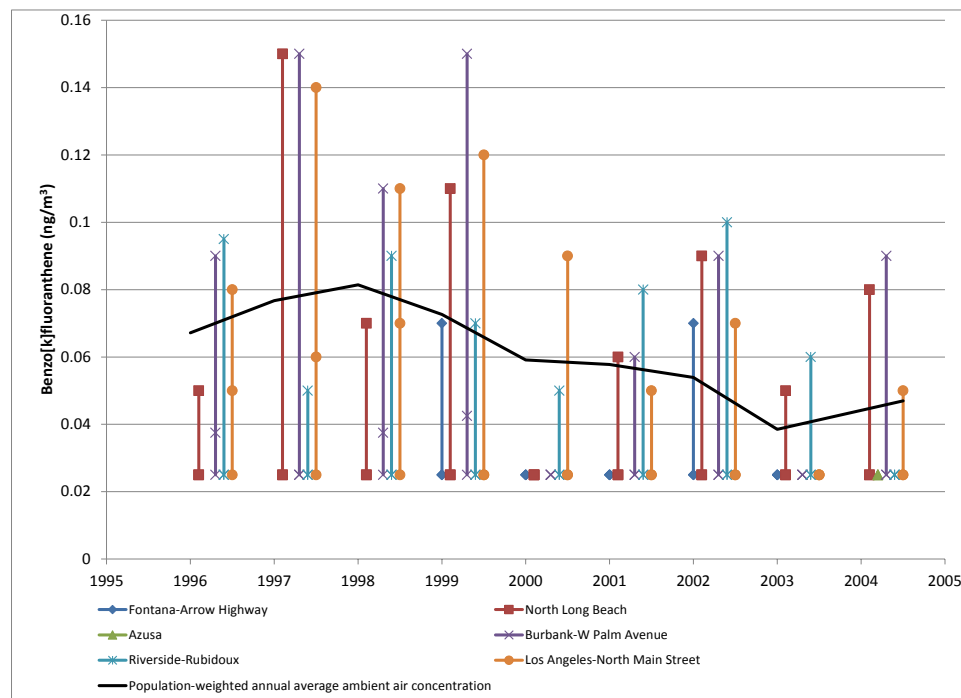
US EPA NATTS	2008	2009	2010	2011	2012	2013	2014
Central Los Angeles, Los Angeles County	5.8E-08	8.2E-08	5.4E-08	5.8E-08	4.3E-08	5.4E-08	5.4E-08
Rubidoux, Riverside County	4.7E-08	7.4E-08	4.7E-08	4.3E-08	4.7E-08	6.2E-08	5.8E-08
San Jose, Santa Clara County	5.8E-08	8.9E-08	4.7E-08	7.0E-08	5.1E-08	7.8E-08	8.6E-08

Benzo[k]fluoranthene: Exposure and Screening Risk Assessment Results

Data from the California Toxic Monitoring Network were used to estimate the population-weighted annual average ambient air concentration of benzo[k]fluoranthene in the South Coast Air Basin from 1996-2004, the years with data. These results are presented in Figure 169 and displayed in Table 89. During this time period, the percent of non-detects varied between 50 and 78% in the South Coast Air Basin. By default, these non-detects were replaced with half the limit of detection. Figure 170 compares the population-weighted annual average ambient air concentration to measurements from other ambient air monitoring studies. For Eiguren-Fernandez et al. and MATES III studies, the quartiles were calculated from the reported averages and standard deviations by assuming the data came from a lognormal distribution. Summaries from these studies are presented in tables below. Descriptions of these studies are on page 247.

Table 90 contains benzo[k]fluoranthene cancer risk estimates. The maximum cancer risk across all California Toxic Monitoring Network sites is provided for comparison with the cancer risk based on the South Coast Air Basin population-weighted average.

Figure 169. Benzo[k]fluoranthene population-weighted annual average ambient air concentration in the South Coast Air Basin



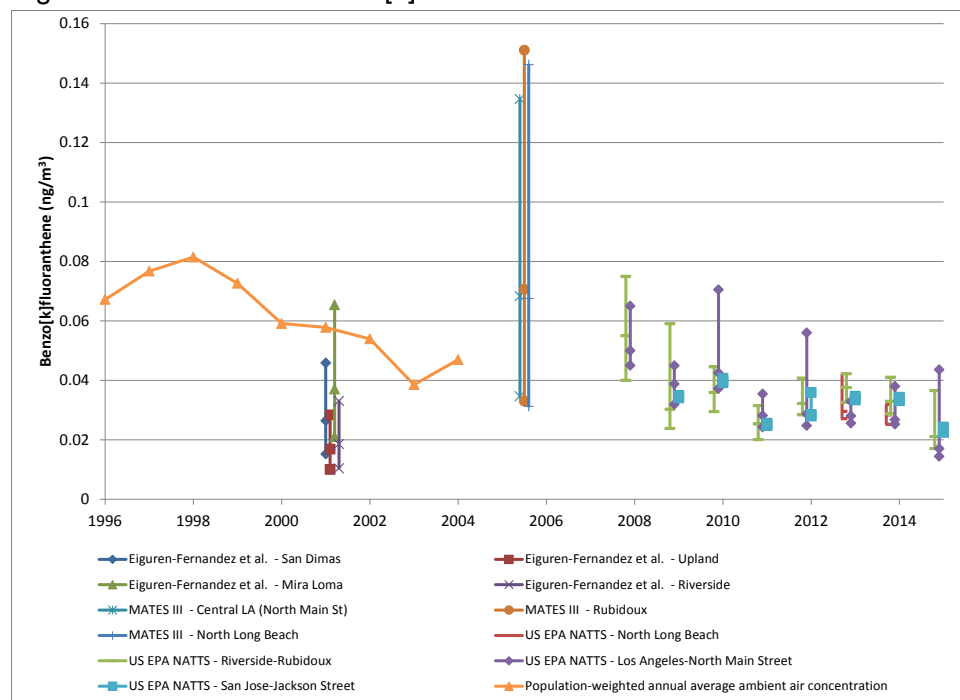
Note: The vertical bars show the quartiles of benzo[k]fluoranthene measurements from South Coast Air Basin monitoring sites in the California Toxic Monitoring Network with 10 or more months of data. Due to the large percentage of non-detects the estimated first quartile and median are the same at some sites.

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Table 89. Population-weighted annual average ambient air concentration of benzo[k]fluoranthene in the South Coast Air Basin

Year	Benzo[k]fluoranthene population-weighted annual average ambient air concentration (ng/m ³)	Percent of measurements that are non-detects
1996	0.067	52%
1997	0.077	54%
1998	0.081	50%
1999	0.073	57%
2000	0.059	75%
2001	0.058	72%
2002	0.054	65%
2003	0.039	78%
2004	0.047	74%

Figure 170. Additional benzo[k]fluoranthene ambient air measurements



Note: The vertical bars show the quartiles of benzo[k]fluoranthene measurements from additional monitoring sites.

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The following box provides further details on benzo[k]fluoranthene ambient air measurements displayed in Figure 170.

Figure-Fernandez et al. (2004) particle phase PAHs (pg/m ³)			
Site	Time	Average	SD
Atascadero	May 2001-July 2002	46.1	68.4
Lompoc	May 2001-July 2002	5.8	7.65
San Dimas	May 2001-July 2002	36.9	36
Upland	May 2001-July 2002	22.7	20.5
Mira Loma	May 2001-July 2002	52.8	53.5
Riverside	May 2001-July 2002	26.8	28

MATES III (2005) (ng/m ³)		
Site	Average ¹	SD ²
Central Los Angeles	0.11	0.15
Riverside	0.13	0.21
North Long Beach	0.13	0.21

Note: Average of benzo[k]fluoranthene was calculated by taking the average of benzo[b+j+k]fluoranthene and dividing by 3. SD of benzo[k]fluoranthene was calculated by taking the SD of benzo[b+j+k]fluoranthene and dividing by $\sqrt{3}$.

US EPA National Air Toxics Trend Stations (ng/m ³)										
Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Max	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	82%	0.035	0.045	0.05	0.065	0.43	0.082	0.091
	2008	61	77%	0.024	0.032	0.039	0.045	0.47	0.062	0.073
	2009	60	80%	0.031	0.037	0.043	0.07	0.65	0.071	0.085
	2010	59	85%	0.016	0.024	0.028	0.035	0.18	0.041	0.034
	2011	59	69%	0.02	0.025	0.029	0.056	0.15	0.046	0.034
	2012	60	92%	0.022	0.026	0.028	0.033	0.23	0.035	0.028
	2013	58	79%	0.02	0.025	0.027	0.038	0.29	0.044	0.047
	2014	56	71%	0.014	0.014	0.017	0.044	0.61	0.042	0.084
North Long Beach	2012	26	88%	0.026	0.027	0.03	0.042	0.78	0.068	0.15
	2013	29	83%	0.023	0.025	0.028	0.032	0.18	0.042	0.039
Riverside-Rubidoux	2007	55	80%	0.035	0.04	0.055	0.075	0.63	0.098	0.12
	2008	71	73%	0.022	0.024	0.03	0.059	0.34	0.059	0.07
	2009	64	80%	0.025	0.029	0.036	0.044	0.77	0.063	0.1
	2010	65	82%	0.016	0.02	0.025	0.031	0.25	0.035	0.034
	2011	67	91%	0.019	0.028	0.032	0.041	0.17	0.04	0.026
	2012	67	91%	0.024	0.033	0.038	0.042	0.25	0.043	0.03
	2013	64	83%	0.025	0.029	0.033	0.041	0.7	0.054	0.086
	2014	65	72%	0.014	0.017	0.021	0.037	0.36	0.047	0.066
San Jose-Jackson Street	2008	40	85%	0.028	0.034	0.035	0.035	0.31	0.05	0.05
	2009	61	79%	0.037	0.039	0.04	0.041	0.98	0.083	0.13
	2010	59	85%	0.024	0.025	0.025	0.026	0.32	0.041	0.049
	2011	61	77%	0.026	0.028	0.029	0.036	0.41	0.06	0.08
	2012	59	85%	0.032	0.033	0.034	0.035	0.54	0.056	0.076
	2013	59	83%	0.032	0.033	0.034	0.034	0.44	0.064	0.076
	2014	59	76%	0.021	0.022	0.023	0.024	0.89	0.073	0.14
2015	43	93%	0.062	0.064	0.065	0.066	0.21	0.074	0.032	

Note: Half the limit of detection substituted for non-detects

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Table 90. Benzo[k]fluoranthene cancer risk

California Toxic Monitoring Network	1996	1997	1998	1999	2000	2001	2002	2003	2004
Maximum risk across all California sites	8.2E-08	1.0E-07	1.2E-07	9.4E-08	8.8E-08	1.1E-07	8.7E-08	8.1E-08	9.9E-08
South Coast Air Basin population-weighted average	2.6E-08	3.0E-08	3.2E-08	2.8E-08	2.3E-08	2.2E-08	2.1E-08	1.5E-08	1.8E-08

Eiguren-Fernandez et al. (2004)	2001-2002
Mira Loma, Riverside County	2.1E-08
Riverside, Riverside County	1.0E-08
San Dimas, Los Angeles County	1.4E-08
Upland, San Bernardino County	8.8E-09

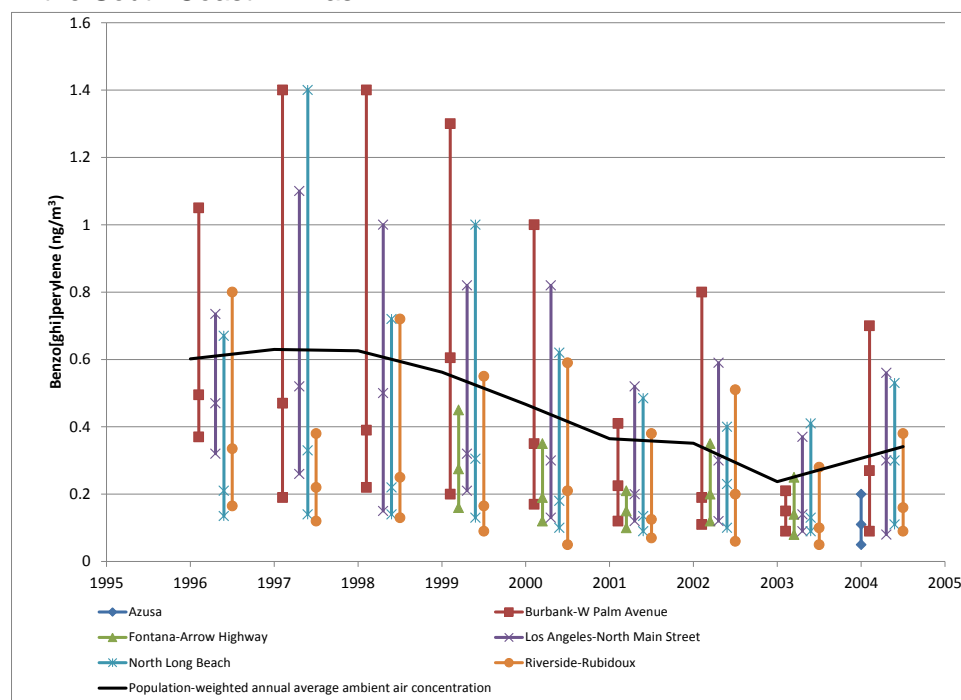
MATES III	2005
Central Los Angeles, Los Angeles County	4.4E-08
N. Long Beach, Los Angeles County	5.1E-08
Rubidoux, Riverside County	5.2E-08

US EPA NATTS	2008	2009	2010	2011	2012	2013	2014
Central Los Angeles, Los Angeles County	2.4E-08	2.8E-08	1.6E-08	1.8E-08	1.4E-08	1.7E-08	1.6E-08
Rubidoux, Riverside County	2.3E-08	2.5E-08	1.4E-08	1.6E-08	1.7E-08	2.1E-08	1.8E-08
San Jose, Santa Clara County	1.9E-08	3.2E-08	1.6E-08	2.3E-08	2.2E-08	2.5E-08	2.8E-08

Benzo[ghi]perylene: Summary of Ambient Air Measurements

Data from the California Toxic Monitoring Network were used to estimate the population-weighted annual average ambient air concentration of benzo[ghi]perylene in the South Coast Air Basin from 1996-2004, the years with data. These results are presented in Table 91 and displayed in Figure 171. Between 1% and 13% of the measurements were non-detects in the South Coast Air Basin during this time period. By default, non-detects were replaced with half the limit of detection. Ambient air measurements from other studies are shown in Figure 172. Summaries from these other ambient air monitoring studies are presented in tables below. Descriptions of these studies are on page 247.

Figure 171. Benzo[ghi]perylene population-weighted annual average ambient air concentration in the South Coast Air Basin



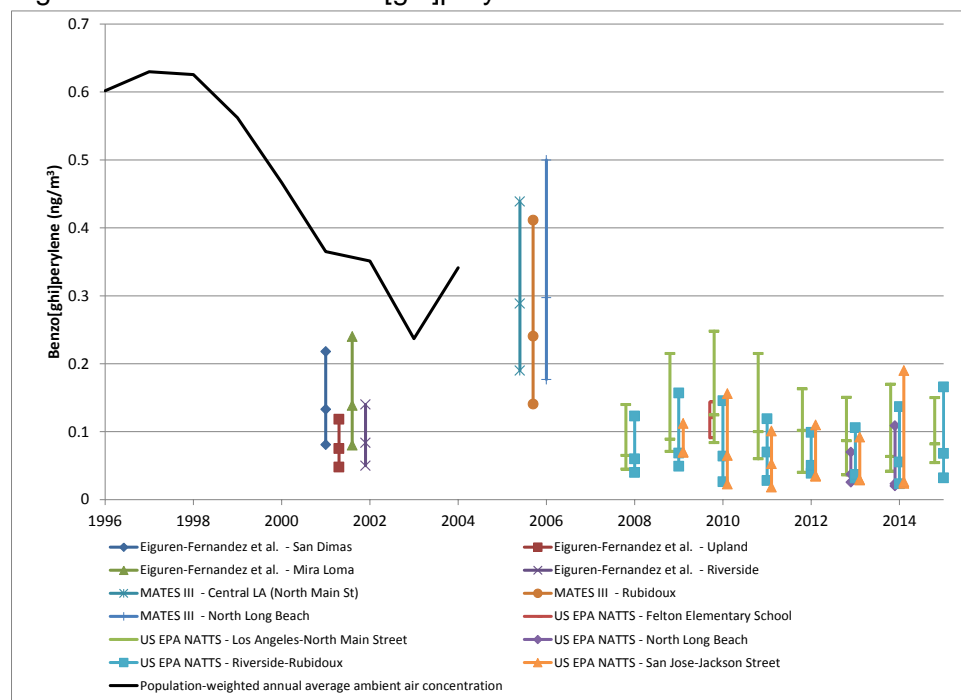
Note: The vertical bars show the quartiles of benzo[ghi]perylene measurements from South Coast Air Basin monitoring sites in the California Toxic Monitoring Network with 10 or more months of data. Due to the large percentage of non-detects the estimated first quartile and median are the same at some sites.

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Table 91. Population-weighted annual average of benzo[ghi]perylene in the South Coast Air Basin

Year	Benzo[ghi]fluoranthene population-weighted annual average ambient air concentration (ng/m ³)	Percent of measurements that are non-detects
1996	0.60	1%
1997	0.63	2%
1998	0.63	2%
1999	0.56	5%
2000	0.47	5%
2001	0.36	6%
2002	0.35	12%
2003	0.24	13%
2004	0.34	11%

Figure 172. Additional benzo[ghi]perylene ambient air measurements



Note: The vertical bars show the quartiles of benzo[ghi]perylene measurements from other studies.

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Box below gives further details on benzo[ghi]perylene ambient air measurements in Figure 172.

Figuren-Fernandez et al. (2004) particle phase PAHs (pg/m ³)										
Site	Time	Average	SD							
Atascadero	May 2001-July 2002	107	128							
Lompoc	May 2001-July 2002	23.3	30.5							
San Dimas	May 2001-July 2002	174	147							
Upland	May 2001-July 2002	94.3	71							
Mira Loma	May 2001-July 2002	193	187							
Riverside	May 2001-July 2002	112	99.6							

MATES III (2005) (ng/m ³)		
Site	Average	SD
Central Los Angeles	0.35	0.24
Riverside	0.33	0.31
North Long Beach	0.4	0.36

US EPA National Air Toxics Trend Stations (ng/m ³)										
Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	51%	0.03	0.045	0.065	0.14	0.75	0.13	0.15
	2008	61	52%	0.05	0.071	0.089	0.22	0.62	0.17	0.14
	2009	60	5%	0.025	0.084	0.12	0.25	1.6	0.21	0.24
	2010	59	10%	0.016	0.06	0.1	0.22	0.56	0.15	0.13
	2011	59	29%	0.026	0.04	0.1	0.16	0.5	0.14	0.12
	2012	60	27%	0.02	0.036	0.087	0.15	1.3	0.12	0.17
	2013	58	19%	0.018	0.042	0.064	0.17	0.39	0.11	0.1
	2014	56	5%	0.016	0.055	0.082	0.15	0.6	0.12	0.11
North Long Beach	2012	26	62%	0.022	0.026	0.037	0.07	0.79	0.09	0.16
	2013	29	52%	0.017	0.02	0.023	0.11	0.68	0.12	0.18
Riverside-Rubidoux	2007	55	65%	0.03	0.04	0.06	0.12	0.74	0.13	0.16
	2008	71	63%	0.044	0.049	0.069	0.16	0.41	0.12	0.096
	2009	64	27%	0.015	0.026	0.064	0.15	1.2	0.14	0.19
	2010	65	25%	0.015	0.028	0.07	0.12	0.68	0.09	0.098
	2011	67	61%	0.029	0.039	0.05	0.099	0.61	0.085	0.093
	2012	67	60%	0.024	0.032	0.037	0.11	0.33	0.074	0.068
	2013	64	38%	0.019	0.023	0.056	0.14	0.67	0.1	0.11
	2014	65	23%	0.014	0.032	0.068	0.17	0.43	0.11	0.12
San Jose-Jackson Street	2008	40	75%	0.067	0.07	0.07	0.11	0.87	0.14	0.15
	2009	61	28%	0.022	0.023	0.065	0.16	1.8	0.16	0.27
	2010	59	36%	0.018	0.018	0.053	0.1	0.53	0.089	0.11
	2011	61	64%	0.033	0.034	0.035	0.11	0.93	0.13	0.2
	2012	59	66%	0.027	0.029	0.029	0.092	0.71	0.095	0.14
	2013	59	51%	0.023	0.024	0.026	0.19	0.7	0.14	0.2
	2014	59	29%	0.018	0.02	0.05	0.14	0.94	0.14	0.21

Note: Half the limit of detection substituted for non-detects

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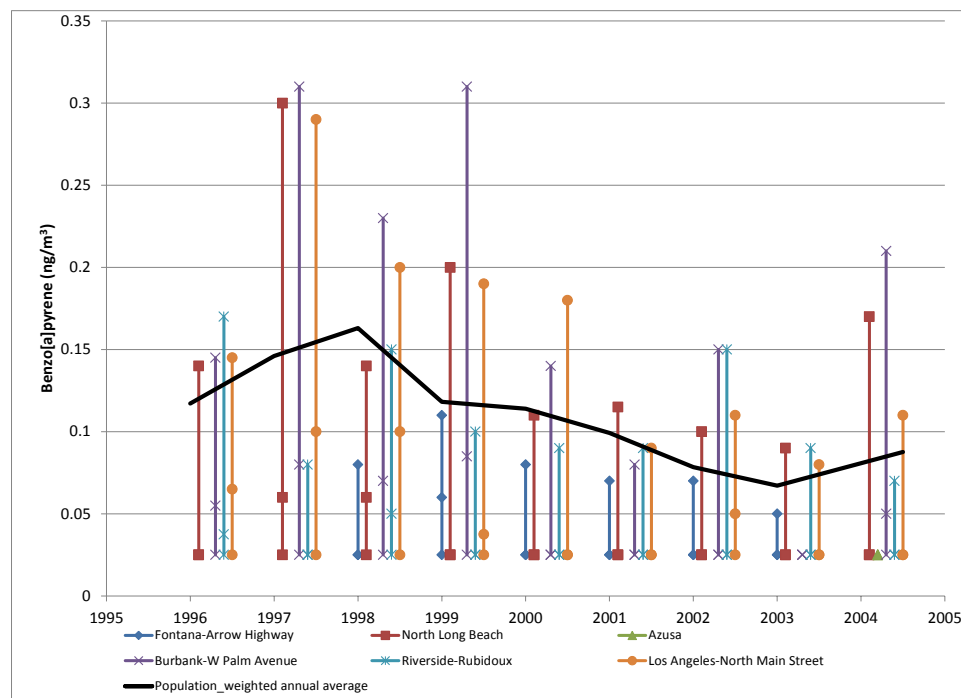
Benzo[a]pyrene: Exposure and Screening Risk Assessment Results

We estimated population-weighted annual average ambient air concentrations of benzo[a]pyrene in the South Coast Air Basin from 1996 to 2004, the years with data from the California Toxic Monitoring Network. Results are shown in Figure 173 and Table 92. Figure 174 compares the population-weighted annual average to ambient air data collected from other monitoring studies. Summaries from these other studies are presented in tables below. Descriptions of these studies are on page 247.

Table 93 contains cancer risk estimates based on the average concentrations of benzo[a]pyrene for each monitoring site and year. The maximum cancer risk based on the highest average measurements across all California Toxic Monitoring Network sites is provided for comparison with the cancer risk based on the South Coast Air Basin population-weighted average. The cancer risk based on the highest observed annual average was slightly elevated with values between 1.6×10^{-6} to 2.7×10^{-6} during the years 1996 to 2004.

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Figure 173. Benzo[a]pyrene population-weighted annual average ambient air concentration in the South Coast Air Basin



Note: The vertical bars show the quartiles of benzo[a]pyrene measurements from South Coast Air Basin monitoring sites in the California Toxic Monitoring Network with 10 or more months of data. Due to the large percentage of non-detects the estimated first quartile and median are the same at some sites.

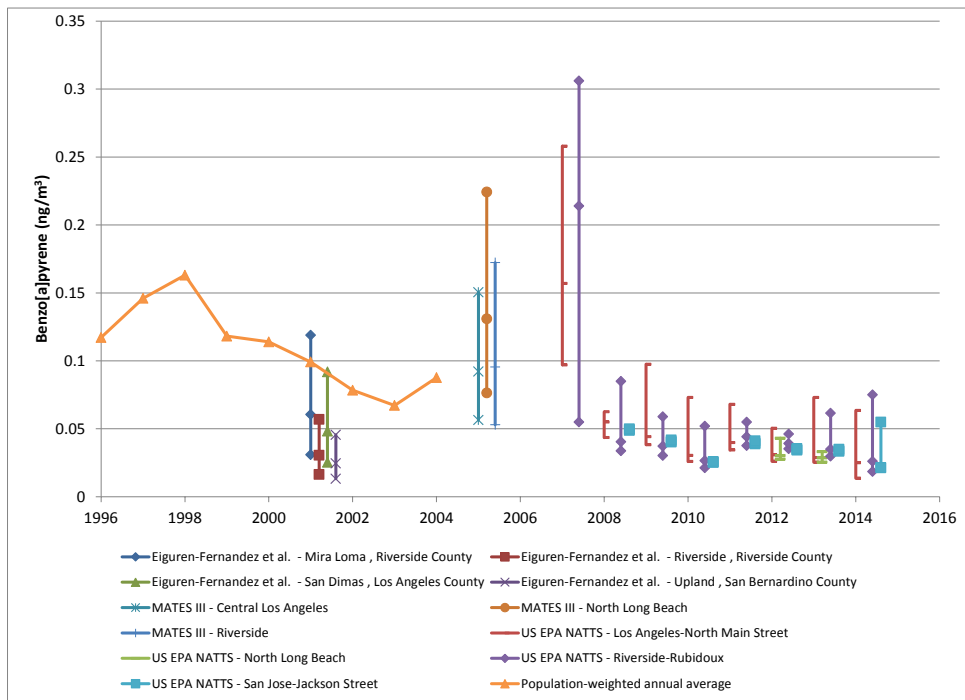
Table 92. Population-weighted annual average ambient air concentration of benzo[a]pyrene in the South Coast Air Basin

Year	Benzo[a]pyrene population-weighted annual average ambient air concentration (ng/m ³)	Percent non-detects
1996	0.12	55%
1997	0.15	54%
1998	0.16	49%
1999	0.12	55%
2000	0.11	61%
2001	0.10	62%
2002	0.078	61%
2003	0.067	65%
2004	0.088	66%

Note: Half the limit of detection was substituted for non-detects.

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Figure 174. Additional benzo[a]pyrene ambient air measurements



Note: The vertical bars show the quartiles of benzo[a]pyrene measurements from additional monitoring studies. For Eiguren-Fernandez et al. and MATES III studies, the quartiles were calculated from the reported averages and standard deviations by assuming the data came from a lognormal distribution.

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The following box provides further details on benzo[a]pyrene ambient air measurements displayed in Figure 174

Eiguren-Fernandez et al. (2004) particle phase PAHs (pg/m ³)										
Site	Time	Average	SD							
Atascadero	May 2001-July 2002	88.1	130							
Lompoc	May 2001-July 2002	9.01	11.9							
San Dimas	May 2001-July 2002	76.2	93.2							
Upland	May 2001-July 2002	37.4	42.9							
Mira Loma	May 2001-July 2002	99.9	131							
Riverside	May 2001-July 2002	46.8	54.2							

MATES III (2005) (ng/m ³)		
Site	Average	SD
Central Los Angeles	0.12	0.10
Riverside	0.14	0.15
North Long Beach	0.18	0.17

US EPA NATTS (ng/m ³)										
Site	Year	N	Percent non-defect	Minimum	First Quartile	Median	Third Quartile	Max	Average	Standard Deviation
Los Angeles-North Main Street	2007	78	21%	0.035	0.097	0.16	0.26	0.47	0.18	0.11
	2008	122	82%	0.035	0.044	0.055	0.063	0.37	0.082	0.078
	2009	120	75%	0.032	0.038	0.044	0.098	1.3	0.1	0.17
	2010	118	75%	0.017	0.026	0.03	0.073	0.99	0.086	0.18
	2011	118	71%	0.028	0.034	0.04	0.068	0.31	0.067	0.06
	2012	120	78%	0.023	0.026	0.031	0.05	0.46	0.054	0.067
	2013	116	69%	0.02	0.025	0.029	0.073	0.63	0.07	0.1
North Long Beach	2012	52	88%	0.026	0.028	0.03	0.043	1.4	0.092	0.27
	2013	58	76%	0.023	0.025	0.029	0.033	0.39	0.067	0.09
Riverside-Rubidoux	2007	110	29%	0.030	0.055	0.21	0.31	0.62	0.21	0.14
	2008	142	73%	0.029	0.034	0.04	0.085	0.34	0.069	0.058
	2009	128	75%	0.025	0.03	0.037	0.059	1.5	0.093	0.2
	2010	130	72%	0.018	0.021	0.027	0.052	0.6	0.05	0.076
	2011	134	94%	0.018	0.038	0.044	0.055	0.44	0.056	0.055
	2012	134	81%	0.029	0.035	0.039	0.046	0.52	0.056	0.063
San Jose-Jackson Street	2007	128	75%	0.025	0.03	0.035	0.062	1.3	0.078	0.17
	2014	130	54%	0.013	0.019	0.026	0.075	0.5	0.071	0.10
	2008	80	88%	0.040	0.049	0.049	0.05	0.55	0.073	0.086
	2009	122	79%	0.038	0.04	0.041	0.042	0.83	0.092	0.13
	2010	118	86%	0.025	0.025	0.025	0.026	0.3	0.043	0.055
	2011	122	80%	0.036	0.039	0.04	0.041	0.99	0.099	0.17
San Jose-Jackson Street	2012	118	85%	0.033	0.034	0.035	0.036	0.92	0.078	0.14
	2013	118	78%	0.033	0.033	0.034	0.035	0.71	0.092	0.14
	2014	118	66%	0.020	0.021	0.022	0.055	1.8	0.12	0.28

Note: Half the limit of detection substituted for non-detects.

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Table 93. Benzo[a]pyrene cancer risk

California Toxic Monitoring Network	1996	1997	1998	1999	2000	2001	2002	2003	2004
Maximum risk across all California sites	2.0E-06	2.4E-06	2.7E-06	2.0E-06	1.8E-06	2.6E-06	1.8E-06	1.6E-06	2.1E-06
South Coast Air Basin population-weighted average	4.6E-07	5.7E-07	6.3E-07	4.6E-07	4.4E-07	3.9E-07	3.1E-07	2.6E-07	3.4E-07

Figuren-Fernandez et al. (2004)	2001-2002
Mira Loma, Riverside County	3.9E-07
Riverside, Riverside County	1.8E-07
San Dimas, Los Angeles County	3.0E-07
Upland, San Bernardino County	1.5E-07

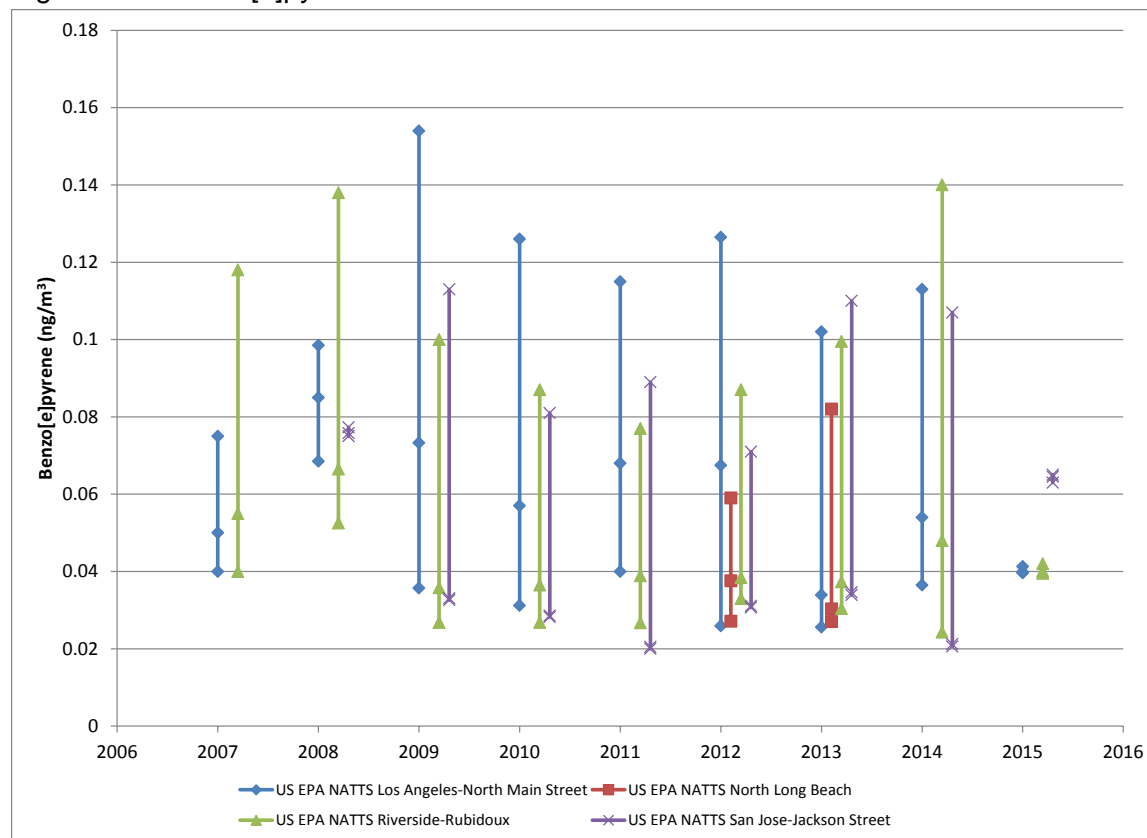
MATES III	2005
Central Los Angeles, Los Angeles County	4.7E-07
N. Long Beach, Los Angeles County	7.0E-07
Rubidoux, Riverside County	5.4E-07

US EPA NATTS	2008	2009	2010	2011	2012	2013	2014
Central Los Angeles, Los Angeles County	3.2E-07	3.9E-07	3.3E-07	2.6E-07	2.1E-07	2.7E-07	2.6E-07
Rubidoux, Riverside County	2.7E-07	3.6E-07	1.9E-07	2.2E-07	2.2E-07	3.0E-07	2.8E-07
San Jose, Santa Clara County	2.8E-07	3.6E-07	1.7E-07	3.9E-07	3.0E-07	3.6E-07	4.7E-07

Benzo[e]pyrene: Summary of Ambient Air Measurements

US EPA National Air Toxics Trend Stations measured benzo[e]pyrene in ambient air. A description of this program is on page 247. Figure 175 contains a plot of these measurements. The data used to create the plot are tabulated below.

Figure 175. Benzo[e]pyrene ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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Benzo[e]pyrene measurements from US EPA National Air Toxics Trend Stations (ng/m³)

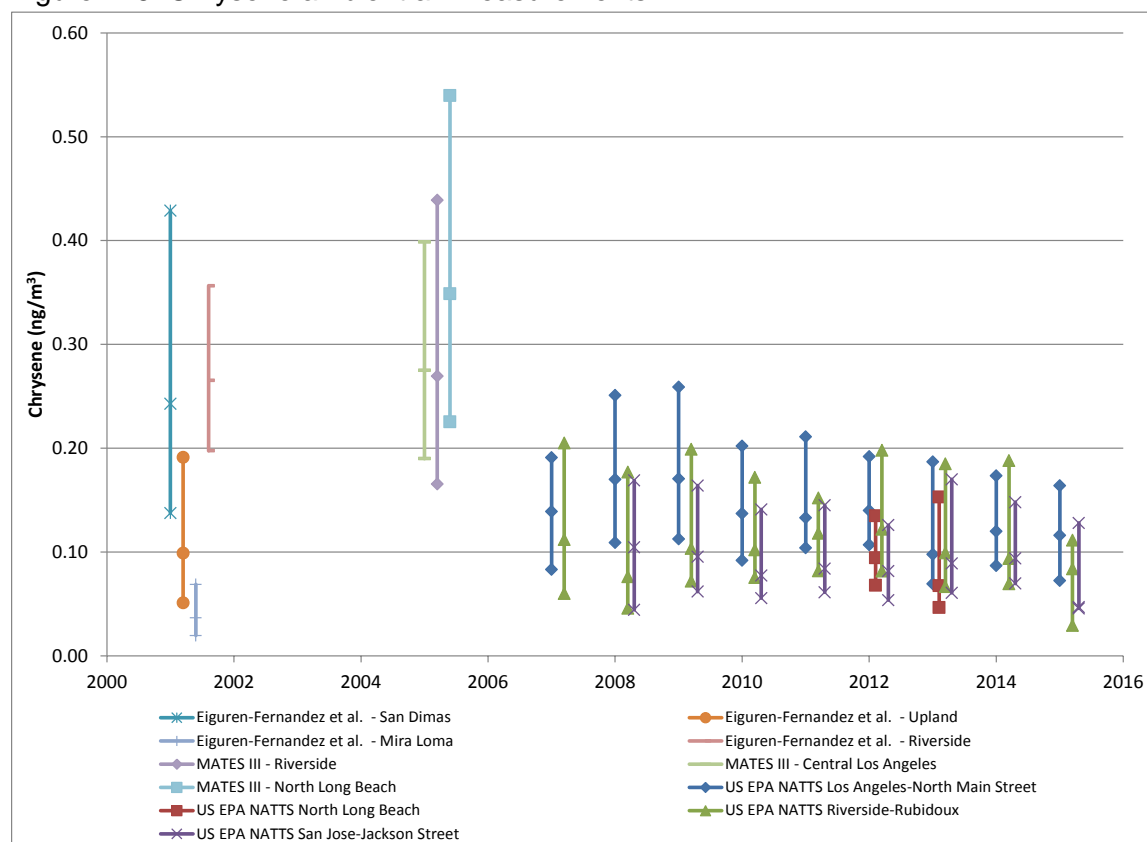
Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	78	74%	0.035	0.04	0.05	0.075	0.44	0.084	0.083
	2008	122	79%	0.054	0.069	0.085	0.099	0.47	0.12	0.1
	2009	120	45%	0.026	0.036	0.073	0.15	1.4	0.13	0.19
	2010	118	53%	0.019	0.031	0.057	0.13	0.76	0.1	0.14
	2011	118	20%	0.016	0.04	0.068	0.12	0.31	0.093	0.079
	2012	120	45%	0.02	0.026	0.068	0.13	2	0.11	0.25
	2013	116	57%	0.021	0.026	0.034	0.1	0.41	0.08	0.083
	2014	112	14%	0.013	0.037	0.054	0.11	0.81	0.092	0.12
North Long Beach	2015	78	79%	0.038	0.04	0.04	0.041	0.5	0.08	0.1
	2012	52	65%	0.023	0.027	0.038	0.059	1.1	0.098	0.22
Riverside-Rubidoux	2013	58	66%	0.024	0.027	0.03	0.082	0.42	0.089	0.11
	2007	110	73%	0.035	0.04	0.055	0.12	0.52	0.1	0.11
	2008	142	72%	0.048	0.053	0.067	0.14	0.37	0.11	0.086
	2009	128	55%	0.021	0.027	0.036	0.1	1.4	0.11	0.2
	2010	130	54%	0.02	0.027	0.037	0.087	0.57	0.071	0.081
	2011	134	51%	0.017	0.027	0.039	0.077	0.4	0.064	0.067
	2012	134	64%	0.026	0.033	0.038	0.087	0.34	0.067	0.059
	2013	128	63%	0.026	0.03	0.037	0.1	0.86	0.083	0.12
	2014	130	31%	0.015	0.024	0.048	0.14	0.62	0.096	0.12
San Jose-Jackson Street	2015	96	85%	0.038	0.04	0.04	0.042	0.45	0.061	0.069
	2008	80	83%	0.073	0.075	0.076	0.077	0.68	0.11	0.11
	2009	122	70%	0.031	0.033	0.033	0.11	1.6	0.12	0.22
	2010	118	69%	0.027	0.028	0.029	0.081	0.34	0.07	0.082
	2011	122	59%	0.019	0.02	0.021	0.089	0.8	0.098	0.16
	2012	118	73%	0.029	0.031	0.031	0.071	0.62	0.079	0.11
	2013	118	63%	0.033	0.034	0.035	0.11	0.58	0.11	0.14
	2014	118	54%	0.019	0.021	0.021	0.11	1.2	0.12	0.22
	2015	86	86%	0.061	0.063	0.064	0.065	0.39	0.094	0.085

Note: half the limit of detection substituted for non-detects

Chrysene: Summary of Ambient Air Measurements

A few studies have measured chrysene in ambient air. Descriptions of these studies are on page 247. Figure 176 contains a plot of the first quartile, median and third quartile of these measurements. The data used to create the plot are tabulated below. The annual average and standard deviation from the Eiguren-Fernandez et al. and MATES III studies were used to estimate the quartiles for the plot by assuming the data came from a lognormal distribution. Chrysene cancer risks are presented in Table 94.

Figure 176. Chrysene ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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Box provides more details on ambient air measurements of chrysene shown in Figure 176

Eiguren-Fernandez et al. (2004)					
Site	Time	Particle phase (pg/m ³)		Vapor phase (ng/m ³)	
		Average	SD	Average	SD
Atascadero	May 2001-July 2002	21.4	25.8	0.38	0.18
Lompoc	May 2001-July 2002	7.98	10.4	-	-
San Dimas	May 2001-July 2002	46.4	40.6	0.3	0.35
Upland	May 2001-July 2002	39.5	26.8	0.12	0.2
Mira Loma	May 2001-July 2002	56.7	66.7	-	-
Riverside	May 2001-July 2002	32	32.9	0.26	0.13

MATES III (2005) (ng/m ³)			
Site	Average	SD	
Central Los Angeles	0.32	0.19	
Riverside	0.35	0.29	
North Long Beach	0.43	0.31	

US EPA (ng/m ³)										
Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	78	23%	0.035	0.083	0.14	0.19	0.63	0.16	0.12
	2008	122	5%	0.037	0.11	0.17	0.25	0.71	0.21	0.14
	2009	120	2%	0.03	0.11	0.17	0.26	2.1	0.23	0.27
	2010	118	5%	0.026	0.092	0.14	0.2	0.95	0.18	0.17
	2011	118	2%	0.018	0.1	0.13	0.21	0.56	0.17	0.11
	2012	120	3%	0.021	0.11	0.14	0.19	1.6	0.18	0.2
	2013	116	2%	0.018	0.069	0.098	0.19	0.81	0.15	0.13
	2014	112	0%	0.04	0.087	0.12	0.17	1.5	0.17	0.21
North Long Beach	2012	52	19%	0.019	0.068	0.094	0.14	2	0.18	0.38
	2013	58	0%	0.028	0.047	0.068	0.15	0.62	0.14	0.16
Riverside-Rubidoux	2007	110	36%	0.03	0.06	0.11	0.21	1	0.17	0.2
	2008	142	34%	0.028	0.046	0.076	0.18	1.1	0.15	0.2
	2009	128	13%	0.018	0.072	0.1	0.2	2.3	0.19	0.31
	2010	130	3%	0.019	0.075	0.1	0.17	0.74	0.15	0.12
	2011	134	9%	0.015	0.082	0.12	0.15	0.53	0.13	0.091
	2012	134	6%	0.024	0.082	0.12	0.2	1.1	0.16	0.16
	2013	128	5%	0.016	0.067	0.099	0.18	1.8	0.15	0.22
	2014	130	2%	0.018	0.069	0.094	0.19	0.96	0.15	0.16
San Jose-Jackson Street	2008	80	33%	0.043	0.044	0.1	0.17	0.9	0.15	0.15
	2009	122	15%	0.026	0.062	0.096	0.16	2.2	0.18	0.3
	2010	118	5%	0.021	0.056	0.077	0.14	0.46	0.11	0.087
	2011	122	2%	0.018	0.061	0.084	0.15	1	0.16	0.19
	2012	118	19%	0.024	0.054	0.082	0.13	1.4	0.14	0.2
	2013	118	0%	0.035	0.061	0.089	0.17	0.86	0.16	0.18
	2014	118	0%	0.039	0.07	0.094	0.15	2.2	0.2	0.33
2015	86	56%	0.044	0.046	0.047	0.13	0.42	0.11	0.1	

Note: Half the limit of detection substituted for non-detects

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Table 94. Chrysene cancer risk

Eiguren-Fernandez et al. (2004)	2001
Mira Loma, Riverside County	2.2E-09
Riverside, Riverside County	1.1E-08
San Dimas, Los Angeles County	1.3E-08
Upland, San Bernardino County	6.2E-09

MATES III	2005
Central Los Angeles, Los Angeles County	1.2E-08
N. Long Beach, Los Angeles County	1.7E-08
Rubidoux, Riverside County	1.4E-08

US EPA NATTS	2008	2009	2010	2011	2012	2013	2014
Central Los Angeles, Los Angeles County	8.2E-09	8.9E-09	7.0E-09	6.6E-09	7.0E-09	5.8E-09	6.6E-09
Rubidoux, Riverside County	5.8E-09	7.4E-09	5.8E-09	5.1E-09	6.2E-09	5.8E-09	5.8E-09
San Jose, Santa Clara County	5.8E-09	7.0E-09	4.3E-09	6.2E-09	5.4E-09	6.2E-09	7.8E-09

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Coronene: Summary of Ambient Air Measurements

The US EPA National Toxic Trend Stations measured coronene in ambient air. A description of this program is on page 247. A summary of the data is presented below. A plot was not produced due to the large percentage of non-detects.

Coronene ambient air measurements from US EPA National Air Toxics Trend Stations (ng/m³)

Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	62%	0.03	0.035	0.05	0.085	0.3	0.071	0.057
	2008	61	80%	0.06	0.074	0.094	0.11	0.37	0.11	0.066
	2009	60	28%	0.023	0.058	0.096	0.18	0.77	0.13	0.12
	2010	59	14%	0.012	0.04	0.065	0.12	0.28	0.084	0.063
	2011	59	63%	0.027	0.035	0.041	0.086	0.27	0.071	0.057
	2012	60	62%	0.021	0.025	0.032	0.07	0.22	0.053	0.041
	2013	58	59%	0.02	0.025	0.032	0.087	0.18	0.057	0.043
	2014	56	9%	0.012	0.043	0.063	0.11	0.24	0.078	0.05
	2015	39	82%	0.038	0.039	0.039	0.04	0.4	0.067	0.07
North Long Beach	2012	26	88%	0.024	0.026	0.028	0.04	0.16	0.042	0.036
	2013	29	69%	0.023	0.027	0.029	0.051	0.25	0.062	0.067
Riverside-Rubidoux	2007	55	78%	0.03	0.035	0.045	0.06	0.34	0.068	0.065
	2008	71	86%	0.053	0.058	0.069	0.087	0.3	0.085	0.046
	2009	64	45%	0.018	0.026	0.049	0.096	0.48	0.082	0.092
	2010	65	35%	0.011	0.017	0.039	0.074	0.26	0.051	0.044
	2011	67	90%	0.01	0.037	0.044	0.055	0.29	0.054	0.038
	2012	67	87%	0.027	0.031	0.036	0.041	0.15	0.041	0.019
	2013	64	73%	0.025	0.029	0.034	0.065	0.2	0.051	0.036
	2014	65	32%	0.012	0.019	0.046	0.11	0.25	0.068	0.059
	2015	48	90%	0.037	0.039	0.04	0.041	0.17	0.048	0.026
San Jose-Jackson Street	2008	40	88%	0.08	0.083	0.084	0.085	0.42	0.1	0.062
	2009	61	69%	0.027	0.029	0.03	0.083	0.98	0.092	0.15
	2010	59	42%	0.015	0.015	0.041	0.063	0.31	0.056	0.061
	2011	61	79%	0.035	0.038	0.039	0.041	0.44	0.078	0.095
	2012	59	81%	0.03	0.032	0.032	0.033	0.32	0.053	0.055
	2013	59	64%	0.032	0.033	0.033	0.089	0.32	0.078	0.079
	2014	59	51%	0.018	0.019	0.02	0.097	0.33	0.073	0.085
	2015	43	91%	0.061	0.063	0.063	0.064	0.32	0.082	0.061

Note: Half the limit of detection substituted for non-detects

Cyclopenta[cd]pyrene: Summary of Ambient Air Measurements

Ambient air concentration data for cyclopenta[cd]pyrene were only available in the US EPA NATTS data set. Ninety percent of the data were less than the limit of detection. A plot was not produced for cyclopenta[cd]pyrene due to the large percentage of non-detects and lack of other data sets for comparison. The table below contains summary statistics based on substituting half the limit of detection for non-detects.

US EPA National Air Toxics Trend Stations (ng/m³)

Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2008	55	95%	0.063	0.078	0.093	0.11	0.39	0.1	0.057
	2009	60	87%	0.034	0.04	0.045	0.059	0.44	0.074	0.077
	2010	59	90%	0.02	0.027	0.033	0.039	0.22	0.045	0.038
	2011	59	83%	0.022	0.027	0.032	0.038	0.25	0.047	0.044
	2012	60	95%	0.028	0.032	0.035	0.041	0.29	0.043	0.036
	2013	58	81%	0.014	0.019	0.019	0.026	0.2	0.034	0.037
	2014	56	84%	0.016	0.017	0.018	0.024	0.14	0.027	0.022
North Long Beach	2012	26	96%	0.032	0.034	0.038	0.049	0.59	0.062	0.11
	2013	29	86%	0.018	0.019	0.021	0.023	0.22	0.034	0.041
Riverside-Rubidoux	2008	59	95%	0.056	0.06	0.066	0.08	0.32	0.08	0.047
	2009	64	86%	0.021	0.032	0.037	0.044	0.44	0.058	0.07
	2010	65	91%	0.019	0.024	0.028	0.034	0.28	0.037	0.037
	2011	67	96%	0.025	0.031	0.036	0.044	0.43	0.047	0.052
	2012	67	99%	0.028	0.041	0.046	0.051	0.17	0.048	0.017
	2013	64	89%	0.019	0.022	0.025	0.03	0.34	0.036	0.043
	2014	65	83%	0.016	0.02	0.023	0.03	0.2	0.037	0.036
San Jose-Jackson Street	2008	40	100%	0.072	0.088	0.088	0.089	0.091	0.088	0.003
	2009	61	89%	0.04	0.043	0.043	0.044	0.52	0.065	0.077
	2010	59	95%	0.029	0.03	0.03	0.031	0.15	0.034	0.017
	2011	61	84%	0.03	0.031	0.032	0.033	0.45	0.055	0.067
	2012	59	95%	0.04	0.042	0.043	0.043	0.26	0.053	0.043
	2013	59	83%	0.024	0.025	0.025	0.026	0.32	0.048	0.064
	2014	59	92%	0.025	0.026	0.027	0.027	0.29	0.036	0.038
	2015	43	95%	0.079	0.082	0.083	0.084	0.26	0.089	0.03

Note: Half the limit of detection substituted for non-detects

Dibenz[ah]anthracene: Exposure and Screening Risk Assessment Results

Ambient air measurements of dibenz[ah]anthracene were available from 4 sources: the California Toxic Monitoring Network, a study by Eiguren-Fernandez et al., the Multiple Air Toxics Exposure Study (MATES III), and the National Air Toxics Trends monitoring stations (NATTS). About 90% of the data from California Toxic Monitoring Network were non-detects where the detection limit was 0.05 ng/m³. The NATTS data had a similarly large fraction of non-detects. Summaries from these ambient air monitoring studies are presented in tables below. Detailed descriptions of the studies are on page 247.

Table 95 summarizes cancer risk estimates based on average concentrations of dibenz[ah]anthracene for each site and year.

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California Toxic Monitoring Network stations – South Coast Air Basin - dibenz[ah]anthracene (ng/m³)

Site	Year	N	Percent non-detect	Third Quartile	Maximum	Average	Standard Deviation
Azusa	2004	30	100%	0.025	0.025	0.025	0
Burbank-W Palm Avenue	1996	24	88%	0.025	0.11	0.031	0.018
	1997	31	94%	0.025	0.06	0.027	0.0087
	1998	30	80%	0.025	0.2	0.046	0.052
	1999	30	90%	0.025	0.57	0.046	0.1
	2000	31	90%	0.025	0.1	0.032	0.022
	2001	30	83%	0.025	0.09	0.033	0.018
	2002	31	87%	0.025	0.08	0.03	0.013
	2003	27	93%	0.025	0.16	0.032	0.027
Fontana-Arrow Highway	2004	31	97%	0.025	0.06	0.026	0.0063
	1999	30	100%	0.025	0.025	0.025	0
	2000	31	100%	0.025	0.025	0.025	0
	2001	29	97%	0.025	0.07	0.027	0.0084
	2002	31	100%	0.025	0.025	0.025	0
Los Angeles-North Main Street	2003	29	100%	0.025	0.025	0.025	0
	1996	24	96%	0.025	0.06	0.026	0.0071
	1997	30	100%	0.025	0.025	0.025	0
	1998	30	97%	0.025	0.05	0.026	0.0046
	1999	30	100%	0.025	0.025	0.025	0
	2000	31	90%	0.025	0.07	0.029	0.013
	2001	30	93%	0.025	0.08	0.028	0.012
	2002	31	94%	0.025	0.06	0.027	0.0076
	2003	31	100%	0.025	0.025	0.025	0
North Long Beach	2004	31	100%	0.025	0.025	0.025	0
	1996	20	95%	0.025	0.05	0.026	0.0056
	1997	31	94%	0.025	0.09	0.028	0.012
	1998	30	87%	0.025	0.14	0.034	0.027
	1999	30	97%	0.025	0.07	0.027	0.0082
	2000	31	94%	0.025	0.13	0.03	0.02
	2001	28	82%	0.025	0.12	0.036	0.026
	2002	31	94%	0.025	0.07	0.028	0.01
	2003	31	97%	0.025	0.05	0.026	0.0045
Riverside-Rubidoux	2004	31	94%	0.025	0.18	0.031	0.028
	1996	24	88%	0.025	0.05	0.028	0.0085
	1997	29	100%	0.025	0.025	0.025	0
	1998	29	93%	0.025	0.29	0.036	0.05
	1999	30	100%	0.025	0.025	0.025	0
	2000	31	97%	0.025	0.06	0.026	0.0063
	2001	30	90%	0.025	0.08	0.029	0.012
	2002	31	87%	0.025	0.07	0.029	0.011
	2003	31	97%	0.025	0.06	0.026	0.0063
2004	31	100%	0.025	0.025	0.025	0	

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Eiguren-Fernandez et al. (2004) particle phase PAHs (pg/m³)

Site	Time	Average	SD
Atascadero	May 2001-July 2002	11.1	18.4
Lompoc	May 2001-July 2002	2.09	2.79
San Dimas	May 2001-July 2002	7.74	10.4
Upland	May 2001-July 2002	5.67	5.63
Mira Loma	May 2001-July 2002	12.1	13.8
Riverside	May 2001-July 2002	5.54	8.73

MATES III (2005) - dibenz[ah]anthracene (ng/m³)

Site	Average	SD
Central Los Angeles	0.03	0.02
Riverside	0.04	0.05
North Long Beach	0.06	0.06

US EPA National Air Toxics Trend Stations, (ng/m³)

Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Max	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	100%	0.03	0.04	0.045	0.05	0.075	0.048	0.0099
	2008	61	97%	0.043	0.051	0.062	0.071	0.12	0.063	0.015
	2009	60	97%	0.026	0.029	0.034	0.041	0.21	0.04	0.026
	2010	59	95%	0.014	0.019	0.023	0.027	0.15	0.029	0.025
	2011	59	100%	0.019	0.027	0.031	0.036	0.056	0.033	0.0068
	2012	60	98%	0.018	0.022	0.024	0.027	0.22	0.03	0.033
	2013	58	93%	0.015	0.018	0.018	0.022	0.085	0.022	0.011
	2014	56	95%	0.012	0.012	0.013	0.016	0.15	0.018	0.02
North Long Beach	2012	26	96%	0.022	0.023	0.025	0.033	0.22	0.035	0.038
	2013	29	93%	0.017	0.018	0.02	0.022	0.053	0.022	0.0084
Riverside-Rubidoux	2007	55	100%	0.035	0.04	0.05	0.065	0.09	0.053	0.013
	2008	71	99%	0.035	0.041	0.045	0.055	0.11	0.051	0.014
	2009	64	97%	0.016	0.024	0.027	0.032	0.18	0.031	0.021
	2010	65	98%	0.014	0.017	0.02	0.023	0.075	0.021	0.0082
	2011	67	100%	0.014	0.034	0.038	0.047	0.1	0.041	0.012
	2012	67	99%	0.019	0.027	0.031	0.034	0.052	0.032	0.0062
	2013	64	98%	0.018	0.021	0.023	0.027	0.18	0.026	0.019
	2014	65	91%	0.012	0.015	0.017	0.021	0.1	0.021	0.015
San Jose-Jackson Street	2015	48	98%	0.035	0.037	0.037	0.038	0.081	0.038	0.0065
	2008	40	98%	0.049	0.06	0.061	0.061	0.13	0.062	0.012
	2009	61	98%	0.03	0.032	0.033	0.033	0.28	0.038	0.032
	2010	59	97%	0.021	0.021	0.021	0.022	0.054	0.023	0.0055
	2011	61	93%	0.019	0.035	0.035	0.036	0.095	0.039	0.013
	2012	59	97%	0.027	0.029	0.029	0.029	0.11	0.031	0.011
	2013	59	88%	0.023	0.024	0.024	0.025	0.069	0.028	0.012
	2014	59	88%	0.018	0.019	0.02	0.02	0.27	0.032	0.042
	2015	43	100%	0.057	0.058	0.06	0.06	0.061	0.059	0.001

Note: Half the limit of detection substituted for non-detects

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Table 95. Dibenz[ah]anthracene cancer risk

CARB TAC	1996	1997	1998	1999	2000	2001	2002	2003	2004
Maximum risk across all California sites	1.9E-07	2.5E-07	2.6E-07	3.2E-07	2.9E-07	3.9E-07	3.4E-07	3.4E-07	3.8E-07
South Coast Air Basin population-weighted average	1.1E-07	1.1E-07	1.4E-07	1.2E-07	1.2E-07	1.3E-07	1.1E-07	1.1E-07	1.1E-07

Eiguren-Fernandez et al. (2004)	2001
Mira Loma, Riverside County	4.9E-08
Riverside, Riverside County	2.3E-08
San Dimas, Los Angeles County	3.2E-08
Upland, San Bernardino County	2.3E-08

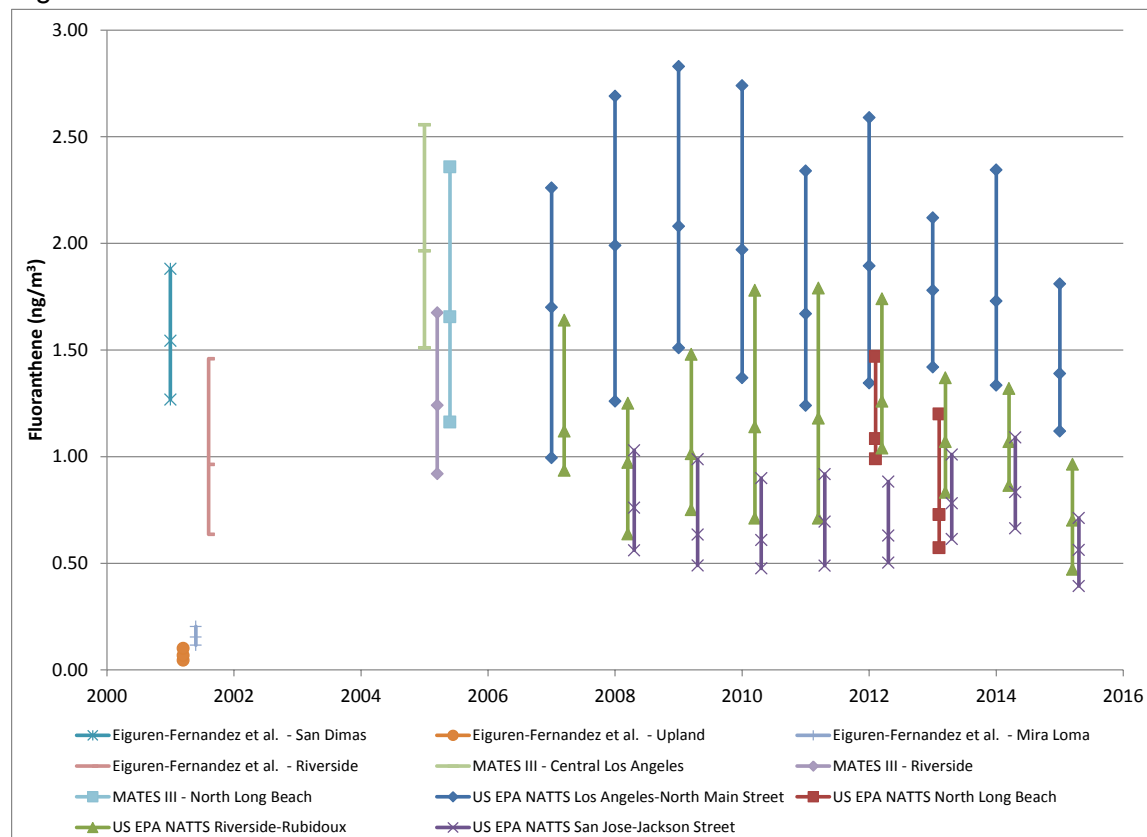
MATES III	2005
Central Los Angeles, Los Angeles County	1.2E-07
N. Long Beach, Los Angeles County	2.5E-07
Rubidoux, Riverside County	1.6E-07

US EPA NATTS	2008	2009	2010	2011	2012	2013	2014
Central Los Angeles, Los Angeles County	2.58E-07	1.64E-07	1.19E-07	1.35E-07	1.23E-07	9.00E-08	7.36E-08
Rubidoux, Riverside County	2.09E-07	1.27E-07	8.59E-08	1.68E-07	1.31E-07	1.06E-07	8.59E-08
San Jose, Santa Clara County	2.54E-07	1.55E-07	9.41E-08	1.6E-07	1.27E-07	1.15E-07	1.31E-07

Fluoranthene: Summary of Ambient Air Measurements

A few studies have measured fluoranthene in ambient air. Descriptions of these studies are on page 247. Figure 177 contains a plot of the first quartile, median and third quartile of these measurements. The data used to create the plot are tabulated below. The annual average and standard deviation from the Eiguren-Fernandez et al. and MATES III studies were used to estimate the quartiles for the plot by assuming the data came from a lognormal distribution.

Figure 177. Fluoranthene ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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Box below gives more details on fluoranthene ambient air data show in Figure 177

Eiguren-Fernandez et al. (2004)

Site	Time	Particle phase (pg/m ³)		Vapor phase (ng/m ³)	
		Average	SD	Average	SD
Atascadero	May 2001-July 2002	6.11	13.7	0.82	2.14
Lompoc	May 2001-July 2002	4.51	7.29	b	b
San Dimas	May 2001-July 2002	31.1	41.7	1.58	0.48
Upland	May 2001-July 2002	40.8	16.7	0.04	0.05
Mira Loma	May 2001-July 2002	47.9	70.2	0.12	0.02
Riverside	May 2001-July 2002	24.3	35.4	1.14	0.79

MATES III (2005) (ng/m³)

Site	Average	SD	Min	Max
Central Los Angeles	2.12	0.86	0.48	4.37
Riverside	1.37	0.64	0.33	3.09
North Long Beach	1.9	1.07	0.54	4.84

US EPA National Air Toxics Trend Stations (ng/m³)

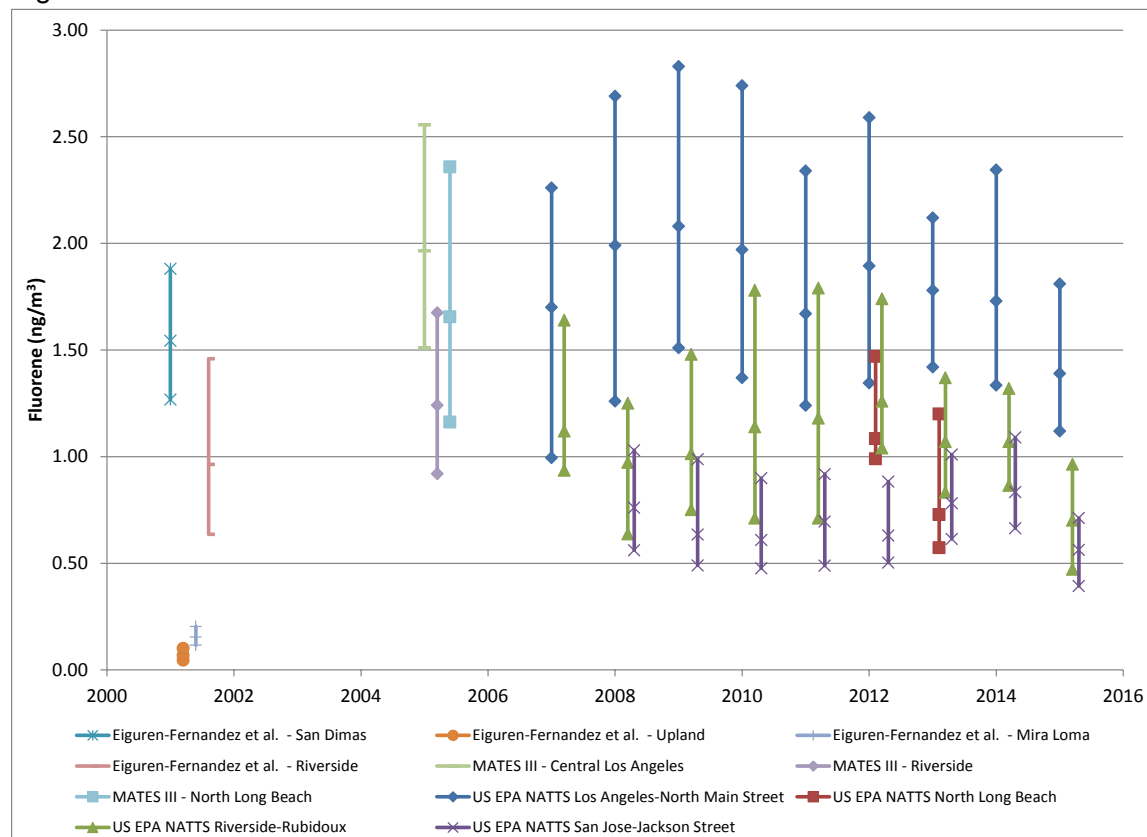
Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	13%	0.025	1	1.7	2.3	3	1.6	0.88
	2008	61	0%	0.06	1.3	2	2.7	4.9	2	1
	2009	60	0%	0.51	1.5	2.1	2.8	6.2	2.4	1.3
	2010	59	0%	0.34	1.4	2	2.7	5.4	2.3	1.2
	2011	59	0%	0.48	1.2	1.7	2.3	5.1	1.9	0.95
	2012	60	0%	0.67	1.3	1.9	2.6	4.6	2	0.88
	2013	58	0%	0.3	1.4	1.8	2.1	4.6	1.8	0.83
	2014	56	0%	0.43	1.3	1.7	2.3	6.5	1.9	0.94
North Long Beach	2012	26	0%	0.61	0.99	1.1	1.5	5.7	1.3	0.96
	2013	29	0%	0.35	0.57	0.73	1.2	2.3	0.93	0.56
Riverside-Rubidoux	2007	55	4%	0.04	0.94	1.1	1.6	2.8	1.2	0.55
	2008	71	0%	0.081	0.64	0.97	1.2	11	1.2	1.5
	2009	64	2%	0.023	0.75	1	1.5	5.4	1.2	0.75
	2010	65	2%	0.019	0.71	1.1	1.8	3.2	1.3	0.7
	2011	67	0%	0.17	0.71	1.2	1.8	3.6	1.3	0.77
	2012	67	0%	0.25	1	1.3	1.7	4.3	1.4	0.74
	2013	64	0%	0.32	0.83	1.1	1.4	4.2	1.2	0.57
	2014	65	0%	0.4	0.86	1.1	1.3	2.3	1.1	0.37
San Jose-Jackson Street	2015	48	0%	0.29	0.47	0.7	0.96	2	0.78	0.38
	2008	40	0%	0.37	0.56	0.76	1	1.6	0.81	0.32
	2009	61	0%	0.28	0.49	0.64	0.99	4.3	0.85	0.61
	2010	59	0%	0.31	0.48	0.61	0.9	1.9	0.72	0.35
	2011	61	0%	0.23	0.49	0.7	0.92	2.3	0.78	0.39
	2012	59	0%	0.29	0.5	0.63	0.88	3.5	0.77	0.48
	2013	59	0%	0.31	0.61	0.78	1	2.4	0.86	0.4
2014	59	0%	0.39	0.66	0.83	1.1	9	1.1	1.3	
2015	43	0%	0.29	0.39	0.56	0.71	1.3	0.61	0.27	

Note: Half the limit of detection substituted for non-detects

Fluorene: Summary of Ambient Air Measurements

A few studies have measured fluorene in ambient air. Descriptions of these studies are on page 247. Figure 178 contains a plot of the first quartile, median and third quartile of these measurements. The data used to create the plot are tabulated below. The annual average and standard deviation from the Eiguren-Fernandez et al. and MATES III studies were used to estimate the quartiles for the plot by assuming the data came from a lognormal distribution.

Figure 178. Fluorene ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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Box below gives more details on fluorene ambient air data displayed in Figure 178

Eiguren-Fernandez et al. (2004)

Site	Time	Particle phase (pg/m ³)		Vapor phase (ng/m ³)	
		Average	SD	Average	SD
Atascadero	May 2001-July 2002	5.91	10.2	3.03	2.37
Lompoc	May 2001-July 2002	8.39	11.2	4.04	4.52
San Dimas	May 2001-July 2002	9.85	14.8	4.02	3.79
Upland	May 2001-July 2002	4.89	4.55	21.4	21.1
Mira Loma	May 2001-July 2002	2.35	4.07	22.8	20.7
Riverside	May 2001-July 2002	7.68	10.2	5.45	1.43

MATES III (ng/m³)

Site	Time	Average	SD
Central LA (North Main St)	2005	2.12	0.86
Rubidoux	2005	1.37	0.64
North Long Beach	2005	1.9	1.07

US EPA National Air Toxics Trend Stations (ng/m³)

Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	8%	0.04	2.2	3.4	4.6	8.3	3.4	2
	2008	61	0%	2.2	3.2	4.8	6.8	16	5.5	3
	2009	60	0%	2.1	4.6	6.2	8.5	37	7.5	5.3
	2010	59	0%	0.98	4.1	6	8.8	24	6.9	4.3
	2011	59	0%	1.3	3.9	5	6.9	14	5.6	2.7
	2012	60	0%	2.1	4.3	6.7	10	19	7.7	4.2
	2013	58	2%	0.026	4.8	5.8	6.7	13	5.7	2.2
	2014	56	7%	0.036	3.4	5.4	6.5	11	5	2.4
North Long Beach	2012	26	0%	1.7	2.3	3.5	3.8	5	3.3	1
	2013	29	10%	0.026	1.2	2.1	3.7	5.4	2.4	1.6
Riverside-Rubidoux	2007	55	4%	0.06	2.2	3.3	4.7	7.2	3.4	1.6
	2008	71	1%	0.04	2.1	3.3	4.2	7.1	3.3	1.7
	2009	64	3%	0.019	2.5	3.6	4.5	9.4	3.6	1.9
	2010	65	0%	0.078	2.2	3.7	5.1	8.3	3.7	1.9
	2011	67	0%	0.5	2.1	4	5.5	9.5	4.1	2.2
	2012	67	0%	0.79	3.1	4.1	5.4	9	4.4	1.9
	2013	64	17%	0.028	2	3.5	4.5	10	3.2	2.1
	2014	65	25%	0.037	1.3	3	4.1	7.8	2.9	2
San Jose-Jackson Street	2008	40	0%	1	1.7	2	2.9	4.7	2.4	0.95
	2009	61	0%	0.7	1.3	1.8	2.9	7.6	2.3	1.3
	2010	59	0%	0.82	1.5	2	2.8	6	2.3	1.1
	2011	61	0%	0.98	1.6	2.3	3.5	5.9	2.6	1.3
	2012	59	0%	0.86	1.4	1.9	2.9	6.1	2.3	1.2
	2013	59	17%	0.034	1.4	2.4	3.3	6.2	2.4	1.6
	2014	59	24%	0.056	1	2.8	3.7	18	2.8	2.8
	2015	43	40%	0.12	0.13	1.5	2.4	3.9	1.4	1.2

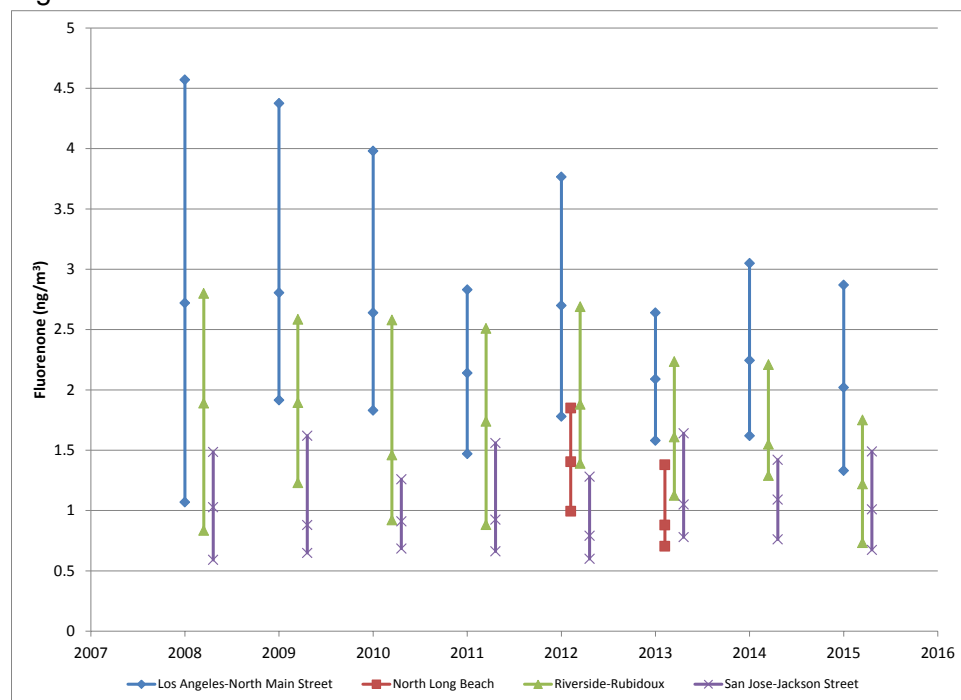
Note: Half the limit of detection substituted for non-detects

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Fluorenone: Summary of Ambient Air Measurements

US EPA National Air Toxics Trend Stations measured fluorenone in ambient air. A description of this program is on page 247. Figure 179 contains a plot of these measurements. The data used to create the plot are tabulated below.

Figure 179. Fluorenone ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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Fluorenone ambient air measurements from US EPA National Air Toxics Trend Stations (ng/m³)

Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2008	55	18%	0.028	1.1	2.7	4.6	9.7	2.9	2.4
	2009	60	0%	0.46	1.9	2.8	4.4	29	3.8	3.9
	2010	59	0%	0.5	1.8	2.6	4	9.3	3.2	1.9
	2011	59	0%	0.46	1.5	2.1	2.8	7.2	2.4	1.4
	2012	60	0%	0.61	1.8	2.7	3.8	8.1	3	1.6
	2013	58	0%	0.33	1.6	2.1	2.6	5.6	2.2	1.1
	2014	56	0%	0.51	1.6	2.2	3	6.8	2.5	1.3
	2015	39	3%	0.56	1.3	2	2.9	5.5	2.2	1.2
North Long Beach	2012	26	0%	0.67	0.99	1.4	1.8	2.8	1.5	0.59
	2013	29	0%	0.34	0.7	0.88	1.4	3.3	1.2	0.81
Riverside-Rubidoux	2008	59	14%	0.025	0.84	1.9	2.8	4.8	1.9	1.3
	2009	64	2%	0.023	1.2	1.9	2.6	7.1	2	1.2
	2010	65	3%	0.027	0.92	1.5	2.6	7.5	1.9	1.3
	2011	67	0%	0.15	0.88	1.7	2.5	5.2	1.8	1.1
	2012	67	0%	0.21	1.4	1.9	2.7	4.6	2.1	0.99
	2013	64	0%	0.32	1.1	1.6	2.2	4.9	1.7	0.81
	2014	65	0%	0.49	1.3	1.6	2.2	4	1.8	0.77
	2015	48	0%	0.29	0.73	1.2	1.8	4.1	1.4	0.78
San Jose-Jackson Street	2008	40	23%	0.037	0.59	1	1.5	2.5	1	0.71
	2009	61	0%	0.28	0.65	0.88	1.6	5.1	1.2	0.83
	2010	59	2%	0.031	0.69	0.91	1.3	4	1.1	0.69
	2011	61	0%	0.28	0.66	0.92	1.6	3.3	1.2	0.67
	2012	59	0%	0.36	0.6	0.79	1.3	2.8	1	0.56
	2013	59	0%	0.45	0.78	1	1.6	4.6	1.3	0.8
	2014	59	0%	0.45	0.76	1.1	1.4	3.6	1.2	0.68
	2015	43	0%	0.42	0.67	1	1.5	3.8	1.2	0.68

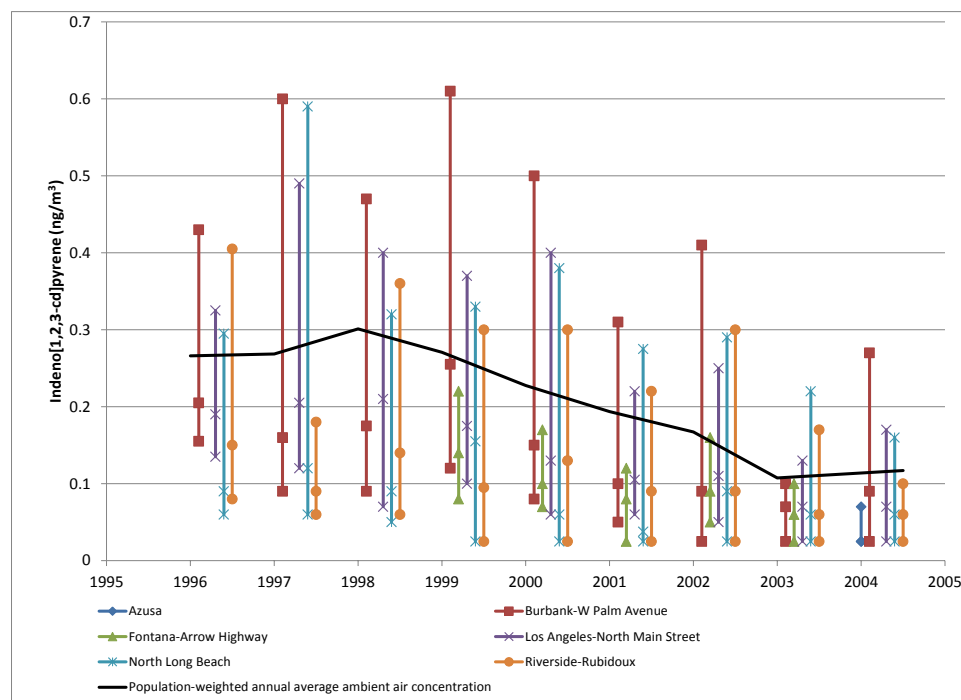
Note: Half the limit of detection substituted for non-detects

Indeno[1,2,3-cd]pyrene: Exposure and Screening Risk Assessment Results

Data from the California Toxic Monitoring Network were used to estimate of the population-weighted annual average ambient air concentration of indeno[1,2,3-cd]pyrene in the South Coast Air Basin from 1996-2004, the years with data. These results are displayed in Figure 180 and Table 96 below. Between 1996 and 2004, the percentage of non-detects increased from 2% to 40% in the South Coast Air Basin. By default, non-detects were replaced with half the limit of detection. Figure 181 compares measurements from other ambient air monitoring studies to the population-weighted annual average. Summaries from these other ambient air monitoring studies are presented in tables below. Descriptions of these studies are on page 247.

Table 97 contains indeno[cd]pyrene cancer risk estimates based on averages for each site and year.

Figure 180. Indeno[1,2,3-cd]pyrene population-weighted annual average ambient air concentration in the South Coast Air Basin



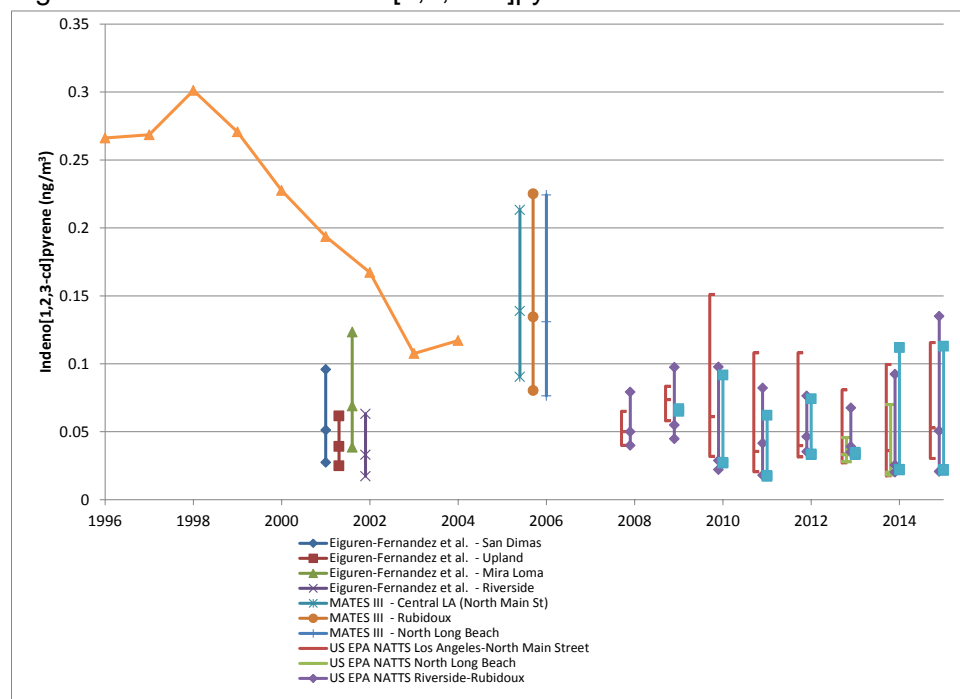
Note: The vertical bars show the quartiles of indeno[1,2,3-cd]pyrene measurements from South Coast Air Basin monitoring sites in the California Toxic Monitoring Network with 10 or more months of data. Due to the large percentage of non-detects the estimated first quartile and median are the same at some sites.

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Table 96. Indeno[1,2,3-cd]pyrene population-weighted annual average ambient air concentration in the South Coast Air Basin

Year	Indeno[1,2,3-cd]pyrene population-weighted annual average ambient air concentration (ng/m ³)	Percent of measurements that are non-detects
1996	0.27	2%
1997	0.27	11%
1998	0.30	14%
1999	0.27	15%
2000	0.23	23%
2001	0.19	31%
2002	0.17	33%
2003	0.11	38%
2004	0.12	42%

Figure 181. Additional indeno[1,2,3-cd]pyrene ambient air measurements



Note: The vertical bars show the quartiles of indeno[1,2,3-cd]pyrene measurements from additional monitoring sites

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Box below provides more details on data used in Figure 171.

Figuren-Fernandez et al. (2004) particle phase PAHs (pg/m³)

Site	Time	Average	SD
Atascadero	May 2001-July 2002	86.5	129
Lompoc	May 2001-July 2002	12.3	15.9
San Dimas	May 2001-July 2002	78.8	91.9
Upland	May 2001-July 2002	49.1	37
Mira Loma	May 2001-July 2002	100	105
Riverside	May 2001-July 2002	52.4	64.4

MATES III (2005) (ng/m³)

Site	Average	SD
Central Los Angeles	0.17	0.12
Riverside	0.18	0.16
North Long Beach	0.18	0.17

US EPA National Air Toxics Trend Stations (ng/m³)

Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Max	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	77%	0.035	0.04	0.05	0.065	0.49	0.084	0.1
	2008	61	79%	0.046	0.058	0.074	0.084	0.4	0.11	0.093
	2009	60	43%	0.021	0.032	0.061	0.15	1.6	0.13	0.21
	2010	59	47%	0.011	0.021	0.036	0.11	0.39	0.076	0.085
	2011	59	56%	0.023	0.031	0.04	0.11	0.32	0.085	0.08
	2012	60	60%	0.022	0.027	0.034	0.081	0.34	0.062	0.057
	2013	58	47%	0.013	0.018	0.036	0.1	0.46	0.074	0.09
	2014	56	21%	0.013	0.03	0.053	0.12	0.88	0.093	0.13
North Long Beach	2012	26	81%	0.025	0.028	0.033	0.046	0.97	0.087	0.19
	2013	29	59%	0.015	0.018	0.02	0.07	0.44	0.075	0.11
Riverside-Rubidoux	2007	55	75%	0.035	0.04	0.05	0.079	0.55	0.094	0.11
	2008	71	76%	0.041	0.045	0.055	0.098	0.41	0.086	0.072
	2009	64	56%	0.017	0.022	0.029	0.098	1.3	0.1	0.19
	2010	65	42%	0.013	0.018	0.042	0.082	0.63	0.065	0.085
	2011	67	70%	0.014	0.035	0.046	0.076	0.38	0.066	0.058
	2012	67	72%	0.028	0.035	0.039	0.068	0.32	0.061	0.051
	2013	64	53%	0.018	0.02	0.025	0.092	0.94	0.078	0.12
	2014	65	37%	0.014	0.021	0.051	0.14	0.49	0.098	0.12
San Jose-Jackson Street	2008	40	78%	0.063	0.065	0.066	0.067	0.76	0.11	0.13
	2009	61	67%	0.025	0.027	0.027	0.092	1.9	0.12	0.26
	2010	59	58%	0.017	0.017	0.018	0.062	0.38	0.062	0.088
	2011	61	74%	0.031	0.033	0.034	0.074	0.74	0.11	0.17
	2012	59	80%	0.032	0.033	0.034	0.035	0.54	0.079	0.11
	2013	59	58%	0.021	0.022	0.022	0.11	0.74	0.11	0.17
	2014	59	56%	0.02	0.022	0.022	0.11	1.3	0.14	0.26
	2015	43	84%	0.053	0.055	0.056	0.057	0.41	0.087	0.086

Note: Half the limit of detection substituted for non-detects

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Table 97. Indeno[1,2,3-cd]pyrene cancer risk

California Toxic Monitoring Network	1996	1997	1998	1999	2000	2001	2002	2003	2004
Maximum across all CARB sites	2.0E-07	2.6E-07	3.0E-07	2.3E-07	2.2E-07	2.6E-07	2.0E-07	1.7E-07	2.0E-07
South Coast Air Basin population-weighted annual average	1.0E-07	1.0E-07	1.2E-07	1.1E-07	8.9E-08	7.5E-08	6.5E-08	4.2E-08	4.6E-08

Eiguren-Fernandez et al. (2004)	2001
Mira Loma, Riverside County	3.9E-08
Riverside, Riverside County	2.0E-08
San Dimas, Los Angeles County	3.1E-08
Upland, San Bernardino County	1.9E-08

MATES III	2005
Central Los Angeles, Los Angeles County	6.6E-08
N. Long Beach, Los Angeles County	7.0E-08
Rubidoux, Riverside County	7.0E-08

US EPA NATTS	2008	2009	2010	2011	2012	2013	2014
Central Los Angeles, Los Angeles County	4.3E-08	5.1E-08	3.0E-08	3.3E-08	2.4E-08	2.9E-08	3.6E-08
Rubidoux, Riverside County	3.3E-08	3.9E-08	2.5E-08	2.6E-08	2.4E-08	3.0E-08	3.8E-08
San Jose, Santa Clara County	4.3E-08	4.7E-08	2.4E-08	4.3E-08	3.1E-08	4.3E-08	5.4E-08

Note: The maximum cancer risk across all sites in the California Toxic Monitoring Network is provided for comparison with the South Coast Air Basin cancer risk.

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Perylene: Summary of Ambient Air Measurements

US EPA National Air Toxics Trend Stations measured perylene in ambient air. A description of this program is on page 247. A summary of the data is presented below. A plot was not created due to the large fraction of non-detects.

Perylene ambient air measurements from US EPA National Air Toxics Trend Stations (ng/m³)

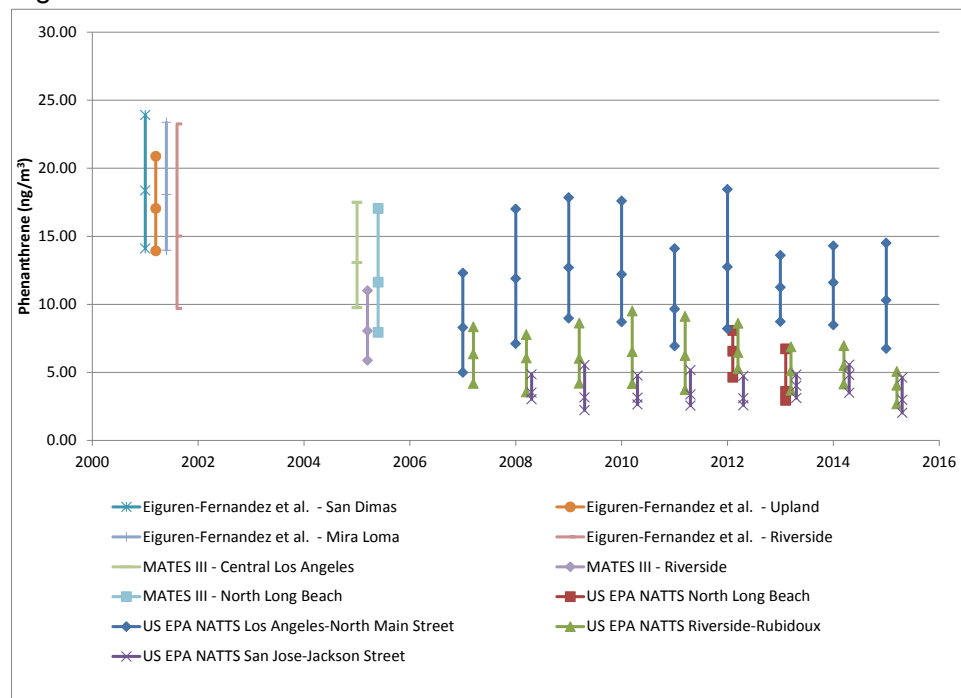
Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	100%	0.035	0.04	0.045	0.055	0.075	0.049	0.0099
	2008	61	97%	0.038	0.047	0.055	0.065	0.24	0.06	0.03
	2009	60	75%	0.015	0.018	0.022	0.042	0.21	0.037	0.038
	2010	59	78%	0.014	0.019	0.023	0.033	0.52	0.075	0.12
	2011	59	98%	0.021	0.03	0.035	0.039	0.078	0.036	0.0091
	2012	60	92%	0.022	0.026	0.028	0.034	0.23	0.038	0.033
	2013	58	93%	0.015	0.018	0.018	0.022	0.17	0.024	0.022
	2014	56	96%	0.016	0.016	0.017	0.021	0.29	0.024	0.037
	2015	39	97%	0.026	0.027	0.027	0.027	0.27	0.037	0.044
North Long Beach	2012	26	96%	0.026	0.028	0.03	0.039	0.39	0.047	0.07
	2013	29	90%	0.017	0.018	0.02	0.022	0.066	0.024	0.012
Riverside-Rubidoux	2007	55	100%	0.035	0.04	0.05	0.065	0.095	0.054	0.014
	2008	71	100%	0.032	0.038	0.041	0.05	0.082	0.046	0.01
	2009	64	77%	0.012	0.014	0.018	0.022	0.25	0.034	0.042
	2010	65	80%	0.013	0.017	0.02	0.025	0.42	0.059	0.1
	2011	67	99%	0.016	0.036	0.042	0.051	0.11	0.046	0.015
	2012	67	99%	0.023	0.033	0.037	0.041	0.11	0.038	0.011
	2013	64	97%	0.018	0.021	0.023	0.027	0.35	0.029	0.041
	2014	65	94%	0.016	0.019	0.023	0.027	0.13	0.026	0.016
	2015	48	98%	0.026	0.027	0.027	0.028	0.13	0.03	0.015
San Jose-Jackson Street	2008	40	98%	0.045	0.055	0.055	0.056	0.11	0.056	0.0092
	2009	61	84%	0.018	0.019	0.019	0.02	0.21	0.034	0.037
	2010	59	75%	0.021	0.021	0.021	0.043	0.4	0.058	0.083
	2011	61	93%	0.021	0.038	0.038	0.039	0.17	0.044	0.024
	2012	59	95%	0.033	0.034	0.034	0.035	0.18	0.039	0.022
	2013	59	90%	0.023	0.024	0.024	0.025	0.14	0.03	0.021
	2014	59	88%	0.024	0.026	0.026	0.026	0.42	0.042	0.06
	2015	43	100%	0.042	0.043	0.044	0.044	0.045	0.043	0.0008

Note: Half the limit of detection substituted for non-detects

Phenanthrene: Summary of Ambient Air Measurements

A few studies have measured phenanthrene in ambient air. Descriptions of these studies are on page 247. Figure 182 contains a plot of the first quartile, median and third quartile of these measurements. The data used to create the plot are tabulated below. The annual average and standard deviation from the Eiguren-Fernandez et al. and MATES III studies were used to estimate the quartiles for the plot by assuming the data came from a lognormal distribution.

Figure 182. Phenanthrene ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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Eiguren-Fernandez et al. (2004)

Site	Time	Particle phase (pg/m ³)		Vapor phase (ng/m ³)	
		Average	SD	Average	SD
Atascadero	May 2001-July 2002	4.63	6.83	11.4	3.43
Lompoc	May 2001-July 2002	1.46	1.86	7.32	1.75
San Dimas	May 2001-July 2002	23.8	14.7	19.8	8.07
Upland	May 2001-July 2002	32.6	25.5	17.8	5.48
Mira Loma	May 2001-July 2002	36.5	29	19.4	7.69
Riverside	May 2001-July 2002	27.3	21.9	18.5	13.4

MATES III (2005) (ng/m³)

Site	Average	SD
Central Los Angeles	14.35	6.52
Riverside	8.96	4.39
North Long Beach	13.65	8.4

US EPA National Air Toxics Trend Stations (ng/m³)

Site	Year	N	Percent non-	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	13%	0.045	5	8.3	12	29	8.8	6
	2008	61	0%	3.9	7.1	12	17	36	13	7.4
	2009	60	0%	3.6	9	13	18	63	16	10
	2010	59	0%	2	8.7	12	18	45	15	8.7
	2011	59	0%	2.5	6.9	9.6	14	31	11	6.2
	2012	60	0%	2.7	8.2	13	18	36	15	7.8
	2013	58	0%	2.2	8.7	11	14	28	11	5.1
	2014	56	0%	2.4	8.5	12	14	28	12	4.9
North Long Beach	2012	26	0%	3.4	4.6	6.6	8.1	14	6.7	2.4
	2013	29	0%	1.6	2.9	3.6	6.7	11	4.8	2.8
Riverside-Rubidoux	2007	55	4%	0.08	4.2	6.3	8.4	18	6.6	3.4
	2008	71	1%	0.074	3.6	6.1	7.8	32	6.7	5
	2009	64	0%	0.084	4.2	6	8.6	23	6.7	3.9
	2010	65	0%	0.16	4.2	6.5	9.5	18	6.9	3.8
	2011	67	0%	0.71	3.7	6.2	9.1	18	6.9	3.9
	2012	67	0%	1.3	5.3	6.5	8.6	15	7.1	3.2
	2013	64	0%	1.4	3.7	5.1	6.9	14	5.5	2.4
	2014	65	0%	1.8	4.1	5.5	7	10	5.7	2.1
San Jose-Jackson Street	2008	40	0%	1.8	3	3.5	4.9	8.3	4.1	1.6
	2009	61	0%	1.2	2.2	3.2	5.5	20	4	2.8
	2010	59	0%	1.5	2.6	3.1	4.8	9.4	3.9	1.9
	2011	61	0%	1.6	2.6	3.4	5.2	9.7	4	2
	2012	59	0%	1.5	2.6	3.1	4.7	9.9	3.7	1.7
	2013	59	0%	1.5	3.1	4	4.8	11	4.2	1.8
	2014	59	0%	2	3.5	4.8	5.6	37	5.2	4.5
	2015	43	0%	1.2	2	3	4.6	8	3.4	1.7

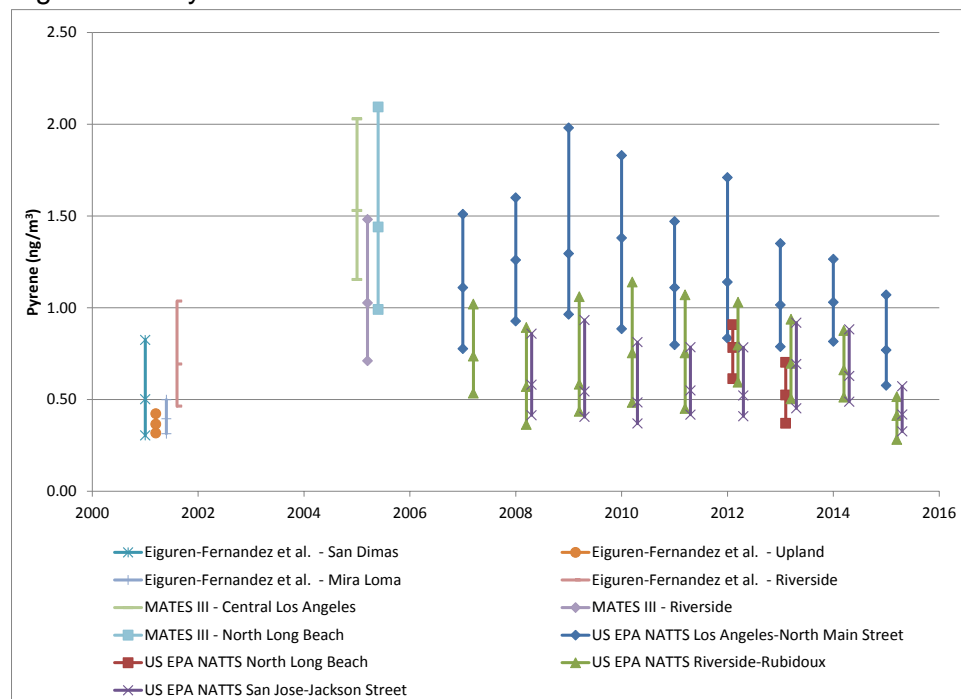
Note: Half the limit of detection substituted for non-detects

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Pyrene: Summary of Ambient Air Measurements

A few studies have measured pyrene in ambient air. Descriptions of these studies are on page 247. Figure 183 contains a plot of the first quartile, median and third quartile of these measurements. The data used to create the plot are tabulated below. The annual average and standard deviation from the Eiguren-Fernandez et al. and MATES III studies were used to estimate the quartiles for the plot by assuming the data came from a lognormal distribution.

Figure 183. Pyrene ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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Box below gives more details on pyrene ambient air measurements displayed in Figure 183

Eiguren-Fernandez et al. (2004)					
Site	Time	Particle phase (pg/m ³)		Vapor phase (ng/m ³)	
		Average	SD	Average	SD
Atascadero	May 2001-July 2002	17.3	1.26	1.68	0.44
Lompoc	May 2001-July 2002	5.51	5.6	-	-
San Dimas	May 2001-July 2002	48	21.1	0.61	0.56
Upland	May 2001-July 2002	54.2	11.2	0.32	0.08
Mira Loma	May 2001-July 2002	69.5	50.1	0.35	0.14
Riverside	May 2001-July 2002	37.7	21.3	0.79	0.54

MATES III (2005) (ng/m ³)		
Site	Average	SD
Central Los Angeles	1.67	0.73
Riverside	1.19	0.7
North Long Beach	1.68	1.01

US EPA National Air Toxics Trend Stations (ng/m ³)										
Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2007	39	13%	0.03	0.78	1.1	1.5	2.6	1.1	0.64
	2008	61	0%	0.36	0.93	1.3	1.6	3.2	1.3	0.61
	2009	60	0%	0.35	0.96	1.3	2	4.8	1.6	0.89
	2010	59	0%	0.24	0.89	1.4	1.8	3	1.4	0.69
	2011	59	0%	0.25	0.8	1.1	1.5	2.7	1.2	0.56
	2012	60	0%	0.45	0.83	1.1	1.7	4.6	1.3	0.65
	2013	58	0%	0.21	0.79	1	1.4	2.4	1.1	0.49
	2014	56	0%	0.28	0.82	1	1.3	4	1.1	0.54
North Long Beach	2015	39	3%	0.27	0.58	0.77	1.1	2	0.85	0.4
	2012	26	0%	0.37	0.61	0.78	0.91	3.7	0.88	0.63
Riverside-Rubidoux	2013	29	0%	0.24	0.37	0.52	0.7	2.6	0.78	0.68
	2007	55	4%	0.045	0.53	0.74	1	2.5	0.85	0.47
Riverside-Rubidoux	2008	71	3%	0.033	0.36	0.57	0.89	6.8	0.81	1
	2009	64	2%	0.03	0.44	0.58	1.1	4.1	0.83	0.68
	2010	65	2%	0.019	0.48	0.75	1.1	2.3	0.86	0.48
	2011	67	0%	0.11	0.45	0.75	1.1	2.2	0.81	0.45
	2012	67	0%	0.14	0.59	0.8	1	2.8	0.9	0.5
	2013	64	0%	0.21	0.5	0.7	0.94	3.2	0.77	0.43
	2014	65	0%	0.24	0.51	0.66	0.88	1.9	0.72	0.31
	2015	48	0%	0.15	0.28	0.41	0.52	1.4	0.44	0.24
San Jose-Jackson Street	2008	40	0%	0.25	0.41	0.58	0.86	1.6	0.68	0.33
	2009	61	0%	0.23	0.41	0.54	0.93	4	0.75	0.6
	2010	59	0%	0.29	0.37	0.48	0.81	1.8	0.62	0.33
	2011	61	0%	0.18	0.42	0.55	0.78	2.3	0.68	0.41
	2012	59	0%	0.2	0.41	0.52	0.78	2.6	0.64	0.4
	2013	59	0%	0.24	0.45	0.69	0.92	1.9	0.77	0.4
	2014	59	0%	0.31	0.49	0.63	0.88	4.5	0.85	0.74
2015	43	0%	0.26	0.33	0.42	0.57	1.3	0.51	0.26	

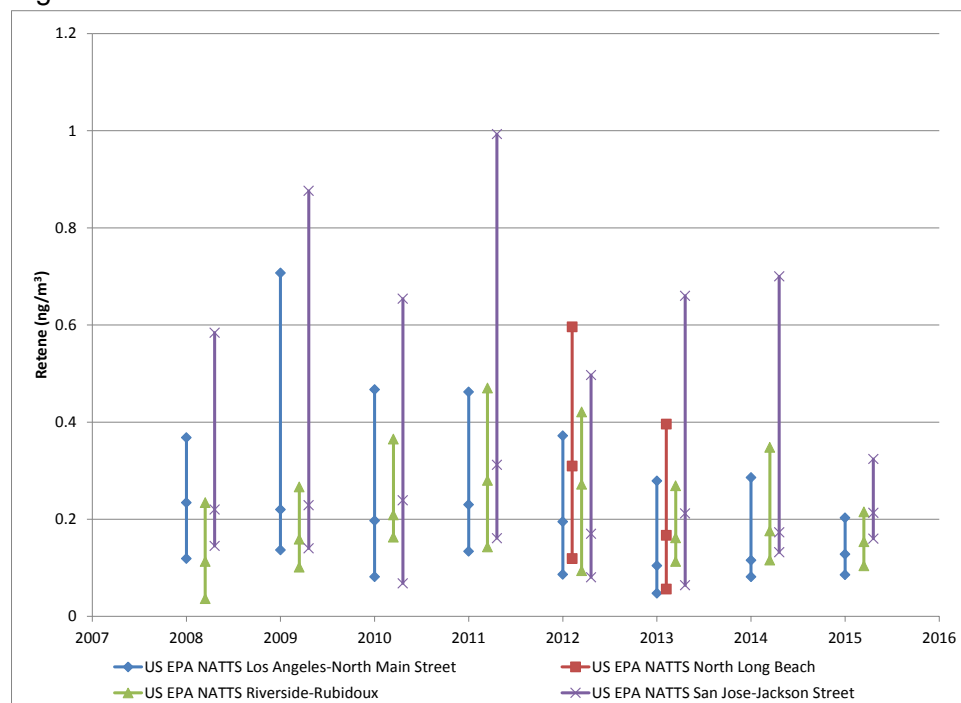
Note: Half the limit of detection substituted for non-detects

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Retene: Summary of Ambient Air Measurements

US EPA National Air Toxics Trend Stations measured retene in ambient air. A description of this study is on page 247. Figure 184 contains a plot of these measurements. The data used to create the plot are tabulated below.

Figure 184. Retene ambient air measurements



Note: Vertical bars show first quartile, median and third quartile

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Retene ambient air measurements from US EPA National Air Toxics Trend Stations (ng/m³)

Site	Year	N	Percent non-detect	Minimum	First Quartile	Median	Third Quartile	Maximum	Average	Standard Deviation
Los Angeles-North Main Street	2008	55	5%	0.032	0.12	0.23	0.37	3.1	0.37	0.52
	2009	60	7%	0.034	0.14	0.22	0.71	8.5	0.59	1.2
	2010	59	36%	0.058	0.082	0.2	0.47	1.6	0.36	0.39
	2011	59	2%	0.022	0.13	0.23	0.46	2.1	0.39	0.39
	2012	60	28%	0.053	0.086	0.2	0.37	1.4	0.29	0.29
	2013	58	47%	0.038	0.048	0.1	0.28	1.7	0.26	0.36
	2014	56	2%	0.01	0.082	0.12	0.29	1.5	0.24	0.3
North Long Beach	2012	26	27%	0.061	0.12	0.31	0.6	5.2	0.67	1.1
	2013	29	45%	0.044	0.056	0.17	0.4	4.3	0.54	0.97
Riverside-Rubidoux	2008	59	29%	0.026	0.036	0.11	0.23	2.7	0.24	0.42
	2009	64	8%	0.025	0.1	0.16	0.27	4	0.33	0.58
	2010	65	17%	0.044	0.16	0.21	0.36	1.5	0.29	0.26
	2011	67	1%	0.023	0.14	0.28	0.47	3	0.39	0.44
	2012	67	31%	0.07	0.094	0.27	0.42	1.6	0.36	0.34
	2013	64	25%	0.051	0.11	0.16	0.27	0.89	0.22	0.17
	2014	65	0%	0.055	0.12	0.18	0.35	2	0.28	0.29
San Jose-Jackson Street	2008	40	10%	0.039	0.15	0.22	0.58	8.3	0.82	1.6
	2009	61	8%	0.038	0.14	0.23	0.88	9	0.79	1.4
	2010	59	29%	0.066	0.068	0.24	0.65	3.8	0.55	0.72
	2011	61	0%	0.07	0.16	0.31	0.99	4.4	0.69	0.88
	2012	59	49%	0.077	0.08	0.17	0.5	2.7	0.36	0.48
	2013	59	32%	0.061	0.064	0.21	0.66	2	0.48	0.58
	2014	59	3%	0.014	0.13	0.17	0.7	2.5	0.49	0.61
	2015	43	9%	0.062	0.16	0.21	0.32	1.6	0.35	0.37

Note: Half the limit of detection substituted for non-detects

Chemical Profiles: Gasoline-Related Criteria Air Pollutants

Nitrogen Dioxide: Exposure

Nitrogen oxides (NO_x) are formed during combustion and are emitted by on-road vehicles, other mobile sources and stationary sources (like manufacturing and industrial plants, oil and gas production facilities and electric utilities). Nitrogen oxides react to form nitric acid, which contributes to secondary PM formation (Shepherd, 2003). They also contribute to the formation of ground-level ozone (US EPA, 2016a; CARB, 1997).

The Emission Inventory had estimates for NO_x. These data were used to identify sources of NO_x and to calculate the gasoline-attributable fractions. Sources of NO_x were identified in CARB's 2012 Emission Inventory and are summarized in Table 98 below. A substantial portion (about 19%) of NO_x came from gasoline-related on-road mobile sources. Non-gasoline-related sources of NO_x include large diesel trucks, ocean-going vessels and construction and mining equipment.

Figure 185 shows that gasoline-attributable fractions of NO_x declined between 1996 and 2012. There is an apparent increase in gasoline-attributable fractions between 2008 and 2010 because the 2010 Emission Inventory had lower estimates of NO_x emissions from non-gasoline-related on-road mobile sources and other mobile sources. Gasoline-attributable fractions for NO_x differed among air basins, ranging in 2012 from 14% in the San Joaquin Valley Air Basin to about 30% in the South Coast and San Diego Air Basins (see Table 99).

Ambient air monitoring data of nitrogen dioxide was available from 1996 to 2013. Population-weighted annual average ambient air concentrations for nitrogen dioxide declined during this time period (see Table 100). Gasoline-attributable fractions for NO_x were applied to calculate the gasoline-attributable concentrations of nitrogen dioxide. In the South Coast Air Basin and statewide, the gasoline-attributable nitrogen dioxide concentration declined by about 70% over this time period (see Table 101 and Figure 186).

Despite declines in ambient concentrations, nitrogen dioxide levels still pose health concerns in California, as demonstrated by a number of studies (see for example, Coker et al., 2016; Jerrett et al., 2013; Ritz et al., 2006).

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Table 98. Statewide sources of NO_x in 2012

Source Category	Percentage of NO _x (by weight) from gasoline-related sources	Percentage of NO _x (by weight) from non-gasoline-related sources
On-Road Motor Vehicles	18.8%	29.9%
Other Mobile Sources	2.2%	31.6%
Fuel Combustion	< 0.1%	9.9%
Miscellaneous Processes	-	3.2%
Industrial Processes	-	2.6%
Natural Sources	-	1.3%
Petroleum Production And Marketing	< 0.1%	0.3%
Waste Disposal	-	0.2%
Cleaning And Surface Coatings	-	< 0.1%
Solvent Evaporation	-	-
Total	21.0%	79.0%

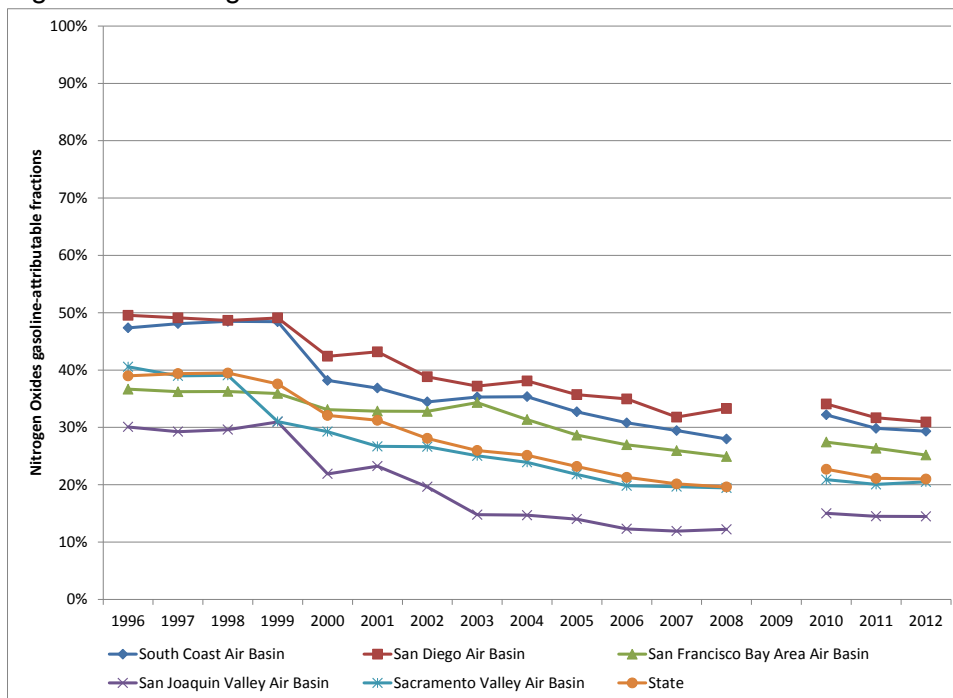
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Table 99. Gasoline-attributable fractions of nitrogen oxides.

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	47%	50%	37%	30%	41%	39%
1997	48%	49%	36%	29%	39%	39%
1998	48%	49%	36%	30%	39%	39%
1999	48%	49%	36%	31%	31%	38%
2000	38%	42%	33%	22%	29%	32%
2001	37%	43%	33%	23%	27%	31%
2002	34%	39%	33%	20%	27%	28%
2003	35%	37%	34%	15%	25%	26%
2004	35%	38%	31%	15%	24%	25%
2005	33%	36%	29%	14%	22%	23%
2006	31%	35%	27%	12%	20%	21%
2007	29%	32%	26%	12%	20%	20%
2008	28%	33%	25%	12%	19%	20%
2009	--	--	--	--	--	--
2010	32%	34%	27%	15%	21%	23%
2011	30%	32%	26%	14%	20%	21%
2012	29%	31%	25%	14%	20%	21%

Note: Mobile source emissions were not available for 2009. Note that these fractions are based on emissions of NO_x not nitrogen dioxide

Figure 185. NO_x gasoline-attributable fractions



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Table 100. Population-weighted average concentration of nitrogen dioxide (ppmv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	0.033	0.022	0.020	0.019	0.015	0.025
1997	0.032	0.022	0.019	0.018	0.013	0.024
1998	0.032	0.021	0.019	0.018	0.014	0.024
1999	0.034	0.024	0.020	0.020	0.015	0.026
2000	0.031	0.022	0.018	0.018	0.015	0.024
2001	0.030	0.020	0.018	0.017	0.014	0.022
2002	0.028	0.020	0.017	0.018	0.014	0.022
2003	0.027	0.020	0.015	0.017	0.013	0.021
2004	0.025	0.018	0.014	0.015	0.013	0.019
2005	0.023	0.017	0.014	0.015	0.012	0.018
2006	0.023	0.018	0.014	0.015	0.012	0.018
2007	0.022	0.016	0.014	0.014	0.012	0.017
2008	0.021	0.016	0.013	0.014	0.011	0.017
2009	0.021	0.015	0.013	0.013	0.010	0.016
2010	0.018	0.014	0.012	0.011	0.008	0.014
2011	0.017	0.013	0.013	0.011	0.009	0.014
2012	0.016	0.013	0.012	0.012	0.009	0.013
2013	0.016	0.013	0.013	0.012	0.009	0.014

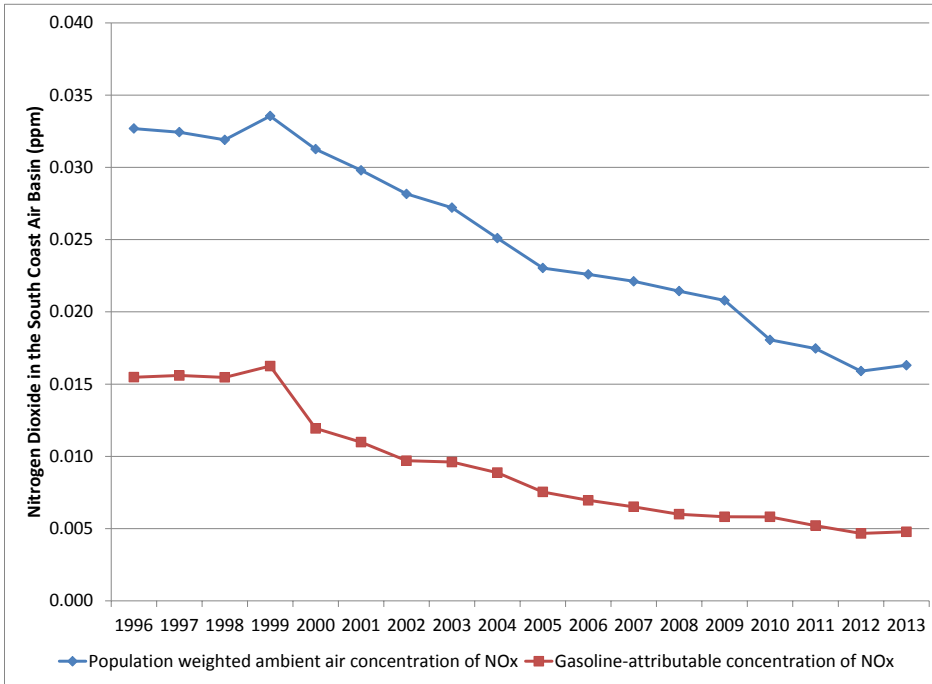
Table 101. Gasoline-attributable concentration of nitrogen dioxide (ppmv)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	0.015	0.011	0.0073	0.0058	0.0062	0.0097
1997	0.016	0.011	0.0068	0.0054	0.0052	0.0096
1998	0.015	0.0100	0.0068	0.0054	0.0056	0.0095
1999	0.016	0.012	0.0072	0.0063	0.0046	0.0096
2000	0.012	0.0093	0.0061	0.0040	0.0044	0.0076
2001	0.011	0.0087	0.0059	0.0040	0.0037	0.0070
2002	0.0097	0.0078	0.0055	0.0035	0.0038	0.0061
2003	0.0096	0.0073	0.0052	0.0024	0.0033	0.0053
2004	0.0089	0.0069	0.0045	0.0022	0.0030	0.0048
2005	0.0075	0.0062	0.0042	0.0021	0.0026	0.0042
2006	0.0070	0.0062	0.0039	0.0018	0.0024	0.0038
2007	0.0065	0.0052	0.0035	0.0017	0.0023	0.0035
2008	0.0060	0.0055	0.0033	0.0017	0.0021	0.0033
2009	0.0058	0.0051	0.0032	0.0016	0.0019	0.0031
2010	0.0058	0.0047	0.0033	0.0017	0.0018	0.0032
2011	0.0052	0.0041	0.0033	0.0017	0.0018	0.0030
2012	0.0047	0.0039	0.0029	0.0017	0.0018	0.0028
2013	0.0048	0.0039	0.0032	0.0017	0.0019	0.0028

Note: calculated with NO_x gasoline-attributable fractions.

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Figure 186. Ambient air concentrations of nitrogen dioxide in the South Coast Air Basin



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PM_{2.5}: Exposure Assessment Results

Particulate matter (PM) can be emitted directly from a variety of sources (primary PM) and can also be formed from gas-phase chemicals (secondary PM). Particulate matter up to 2.5 µm in diameter is known as PM_{2.5}, which is the form addressed in this Chemical Profile.

Based on the 2012 statewide Emission Inventory, more than 98% of *primary* PM_{2.5} comes from non-gasoline-related sources such as burning (woodstoves, fireplaces, agricultural burning, wildfires), road dust, farming operations, and exhaust from diesel engines. Exhaust from gasoline vehicles makes only a small contribution to primary PM_{2.5}. Table 102 shows the fractions by weight of primary PM_{2.5} that came from non-gasoline-related sources and gasoline-related sources in 2012.

Table 102. Statewide sources for primary PM_{2.5} in 2012

Source category	Percentage of <i>primary</i> PM _{2.5} (by weight) from non-gasoline-related sources	Percentage of <i>primary</i> PM _{2.5} (by weight) from gasoline-related sources
Miscellaneous processes		
Residential fuel combustion	6.4%	--
Fugitive windblown dust	6.1%	--
Managed burning and disposal	3.8%	--
Cooking	3.3%	--
Unpaved road dust	3.2%	--
Paved road dust	3.1%	--
Farming operations	3.0%	--
Construction and demolition	1.9%	--
Fires	0.1%	--
Other (miscellaneous processes)	< 0.05%	--
Natural sources (wildfires)	48.9%	--
On-road motor vehicles	5.2% ¹	0.4%
Other mobile sources	4.2%	1.1%
Industrial processes	4.8%	--
Fuel combustion	3.4%	< 0.05%
Waste disposal	0.4%	--
Cleaning and surface coatings	0.3%	--
Petroleum production and marketing	0.3%	< 0.05%
Solvent evaporation	< 0.05%	--
Total	98.4%	1.6%

1. This is primarily from brake wear, a non-gasoline-related source associated with motor vehicles.

We researched possible approaches for estimating the fraction of *total* PM_{2.5} (i.e., primary plus secondary) attributable to gasoline-related sources. One aspect of this calculation is understanding the proportion of total PM_{2.5} coming from primary sources versus secondary

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formation. Another consideration is the composition of secondary PM_{2.5}, which is known to include sulfate, nitrate, ammonium and secondary organic aerosols (SOA). A number of studies have examined the estimated contributions to ambient PM_{2.5} from gasoline-related sources, the proportion of PM_{2.5} attributable to primary sources versus secondary formation, and the composition of secondary PM_{2.5} (see for example, Rogge et al., 1993; Schauer et al., 1996; Watson et al., 1998; Gertler et al. 2000; Held et al., 2005; Fine et al., 2008; Ying and Kleeman, 2006; Hu et al., 2014a,b, 2015). Some of this work is briefly discussed below.

Based on preliminary results from a simulation study of PM_{2.5}, Hu et al. (2014b, 2015) reported that primary PM_{2.5} accounted for about 70% of total PM_{2.5} in Los Angeles and Fresno, suggesting that secondary formation could account for about 30%. However, there are shortcomings with models of secondary PM_{2.5}, and this proportion is likely to vary by region, meteorological parameters, proximity to sources, and other factors. Calculations based on California data from the Chemical Speciation Network indicate higher percentages of secondary PM_{2.5} (see Table 104 below).

Gasoline-related aromatic VOCs like toluene, xylenes and trimethylbenzenes are important precursors of SOA (Fine et al. 2008, Pandis 2003). Ensberg et al. (2014) noted that current atmospheric models tend to underpredict SOA levels in urban areas. They concluded that either vehicle emissions are not the main contributors to SOA formation, or that the models of SOA formation from vehicle emissions are inadequate. Jathar et al. (2014) found that 10% to 20% of emissions from gasoline exhaust, diesel exhaust and biomass burning are not adequately characterized, and the failure to account for them in emission inventories significantly hinders studies of SOA formation. There are also conflicting results on the relative contributions of gasoline versus diesel vehicles to ambient particulate matter (Gertler et al., 2005), and to the formation of SOA. For example, Bahreini et al. (2012) estimated that very little ambient SOA was derived from diesel combustion and recommend focusing on reducing emissions from gasoline vehicles in order to reduce SOA. However, Gentner et al. (2012) found that diesel emissions were responsible for 65 to 90% of vehicle-derived SOA.

Gasoline-related sources emit NO_x and, to a lesser extent, SO_x and ammonia, which are also precursors of PM_{2.5}. Rogge et al. (1993) found that ammonium, nitrate, and sulfate made up 40% and 50% of total PM_{2.5} at two sites in the South Coast Air Basin. In a review of findings from a PM research program (the "Supersites Program") and related studies, Fine et al. (2008) reported that ammonium, nitrate, and sulfate typically make up 50% of total PM_{2.5} mass, and that the percentage can increase to 70% in the winter in the western US. These studies are useful, but cover a limited geographic region and do not capture short-term variability in the percentages.

A few studies have modeled the estimated contributions from various sources, including gasoline-related sources, to total PM_{2.5} and its components in California. Held et al. (2005) estimated that gasoline-engines used in transportation contributed about 10% to 20% to total PM_{2.5} based on a three-day simulation study in 1993 for four sites in the South Coast Air Basin. Ying and Kleeman (2006) estimated that about 30% of nitrate and about 20% of ammonium in

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secondary PM_{2.5} came from gasoline engines used in transportation, based on a simulation for a three-day period in 1996 in the South Coast Air Basin.

Given the limited information available in the literature, we settled on a method for estimating gasoline-attributable fractions for PM_{2.5} that relies on data from the Emission Inventory and the Chemical Speciation Network²⁸. The approach, described in the section below, involves calculating gasoline-attributable fractions for primary PM_{2.5}, and using proxies to estimate the gasoline-attributable fractions for components of secondary PM_{2.5} (NO_x as a proxy for ammonium nitrate; SO_x as a proxy for ammonium sulfate, and ROG as a proxy for SOA). There are a number of uncertainties and limitations to this approach, which are also summarized below.

Gasoline-Attributable Fractions for PM_{2.5}

Using the methods described in Appendix E and data from the Emission Inventory we first estimated the gasoline-attributable fractions for *primary* PM_{2.5} (shown in Table 103). The fractions range from 0.6% to 8.4% for PM_{2.5} depending on the year and air basin.

Table 103. Gasoline-attributable fractions for *primary* PM_{2.5} based on the Emission Inventory

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1996	4.5%	3.8%	3.3%	1.3%	1.6%	1.8%
1997	6.6%	4.2%	3.5%	1.4%	1.6%	2.4%
1998	6.9%	4.5%	3.7%	1.6%	1.7%	2.5%
1999	8.0%	4.8%	3.3%	2.4%	0.7%	1.8%
2000	5.8%	3.7%	3.6%	1.0%	1.5%	1.1%
2001	5.7%	3.8%	3.9%	1.5%	1.0%	1.8%
2002	6.0%	3.9%	4.0%	0.6%	1.9%	2.0%
2003	2.1%	1.9%	4.1%	1.2%	2.0%	1.7%
2004	7.8%	5.0%	4.2%	1.5%	1.8%	2.5%
2005	8.0%	5.1%	3.0%	1.6%	1.9%	2.5%
2006	8.4%	5.4%	4.5%	1.7%	1.9%	2.8%
2007	8.1%	5.3%	4.5%	1.7%	2.0%	2.8%
2008	8.2%	5.7%	4.7%	1.8%	2.1%	2.9%
2009	--	--	--	--	--	--
2010	5.9%	3.6%	4.3%	1.0%	1.4%	2.0%
2011	5.7%	3.8%	4.1%	1.0%	1.4%	1.9%
2012	4.7%	2.8%	4.4%	1.1%	1.2%	1.6%

Note: Mobile source emissions were unavailable for 2009.

²⁸ See <https://www.arb.ca.gov/aqd/pm25/pmfmom.htm> for a description of the PM_{2.5} monitoring and speciation network in California. PM_{2.5} speciation data are available from CARB.

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Data from the Chemical Speciation Network were used to estimate the average proportions of PM_{2.5} components by air basin over the period 2000 to 2014. These percentages are shown in Table 104 below. Note that the PM_{2.5} speciation data are from only a small number of sites in each air basin, and the results may not represent the air quality over the entire region.

Table 104. Average percentages of PM_{2.5} components based on data from Chemical Speciation Network (2000-2014).

Air Basin	Primary PM _{2.5} (%)	Secondary PM _{2.5} components		
		Ammonium sulfate (%)	Ammonium nitrate (%)	SOA (%)
South Coast	26.7%	16.8%	43.6%	12.9%
San Diego	32.3%	21.9%	26.7%	19.1%
San Francisco Bay Area	39.6%	14.1%	24.1%	22.2%
San Joaquin Valley	34.5%	11.1%	37.6%	16.8%
Sacramento Valley	46.0%	10.6%	20.0%	23.3%

Table Notes: Speciation data for PM_{2.5} samples collected at sites within the Network were obtained for 2000 to 2014. The calculation of the percentages uses data on the total mass of the PM_{2.5} sample, and the speciated masses of organics, sulfate and nitrate. Nitrate and sulfate are assumed to be fully neutralized by ammonium (Buzcu-Guven et al., 2007), and half the organics are attributed to secondary formation (Fine et al., 2008). The values shown in the Table represent averages for each basin over the full time period.

We then applied the following equation to estimate gasoline-attributable fractions for total PM_{2.5}, accounting for both primary and secondary components:

$$PM_{2.5}GAF(y, AB) = (a\%)PrimaryPM_{2.5}GAF(y, AB) + (b\%)SO_xGAF(y, AB) + (c\%)NO_xGAF(y, AB) + (d\%)ROGGAF(y, AB)$$

Where:

PM_{2.5} GAF (y, AB) = Gasoline-attributable fraction for PM_{2.5} in year y and air basin AB

a% = Fraction of total PM_{2.5} from primary sources

PrimaryPM_{2.5}GAF(y,AB) = Gasoline-attributable fraction of primary PM_{2.5} based on the Emission Inventory for year y and air basin AB

b% = Fraction of total PM_{2.5} assumed to be ammonium sulfate

SO_xGAF(y,AB) = Gasoline-attributable fraction of SO_x used as a proxy for the gasoline-attributable fraction for ammonium sulfate

c% = Fraction of total PM_{2.5} assumed to be ammonium nitrate

NO_xGAF(y,AB) = Gasoline-attributable fraction of NO_x used as a proxy for the gasoline-attributable fraction for ammonium nitrate

d% = Fraction of total PM_{2.5} assumed to be SOA

ROGGAF(y,AB) = Gasoline-attributable fraction of ROG used as a proxy for the gasoline-attributable fraction for SOA

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The estimated gasoline-attributable fractions for total PM_{2.5} based on the above equation are shown in Table 105 on the next page. There are many limitations to the approach we applied, including the following:

- Using gasoline-attributable fractions for NO_x, SO_x and ROG as proxies for the gasoline-attributable fractions of ammonium nitrate, ammonium sulfate and SOA is inherently uncertain. For example, the relationship between NO_x and nitrate is complex and likely does not follow the linear relationship assumed in the above equation (Mysliwiec et al., 2002). Also, the formation of SOA depends on a number of factors, such as the composition of VOCs emitted and atmospheric conditions, and is not well understood (Lurmann et al., 2006). To estimate the percentages in Table 104 above, a 50/50 split between primary and secondary organic aerosol was assumed (Fine et al., 2008). The actual ratio will vary by season and location. These complexities have not been incorporated into the method for approximating PM_{2.5} gasoline-attributable fractions.
- The average percentages of the secondary components presented in Table 104 were estimated over the period 2000 to 2014, but these percentages likely vary seasonally and over time. Further, the data used to calculate these values came from a few monitoring sites in each air basin, which were located in areas with poor air quality as required under the State Implementation Plan²⁹ for California. For example, there are only two PM_{2.5} speciation monitoring sites (downtown Los Angeles and Riverside) in the South Coast Air Basin. Therefore, the PM_{2.5} speciation data used to calculate the percentages in Table 104 are likely not representative of the overall air quality in each air basin.

²⁹ A State Implementation Plan is a comprehensive plan that describes how an area will attain National Ambient Air Quality Standards. For more information, see <https://www.arb.ca.gov/planning/sip/background.htm>.

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Table 105. Estimated PM_{2.5} gasoline-attributable fractions

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin
1996	31%	28%	21%	19%	23%
1997	33%	29%	21%	19%	23%
1998	33%	28%	21%	19%	22%
1999	33%	30%	21%	21%	21%
2000	26%	24%	19%	15%	19%
2001	26%	25%	19%	16%	16%
2002	24%	22%	20%	11%	11%
2003	23%	18%	20%	10%	11%
2004	25%	22%	19%	10%	10%
2005	24%	21%	17%	9%	10%
2006	23%	21%	17%	8%	9%
2007	22%	19%	16%	8%	9%
2008	21%	20%	16%	8%	9%
2009	--	--	--	--	--
2010	23%	20%	16%	8%	8%
2011	22%	19%	16%	8%	8%
2012	21%	17%	16%	8%	8%

Note: Mobile source emissions were unavailable for 2009.

Population-Weighted and Gasoline-Attributable Air Concentrations of PM_{2.5}

PM_{2.5} ambient air concentration data were available from 1999 through 2013. Population-weighted annual average ambient air concentrations of PM_{2.5} are shown in Table 106. To produce the gasoline-attributable concentrations, the estimated fractions (see Table 105) were multiplied by the population-weighted annual average ambient air concentrations. The results are provided in Table 107 below.

Table 106. Population-weighted annual average concentrations of PM_{2.5} (µg/m³)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin	State
1999	23	17	16	23	16	19
2000	21	15	13	19	12	17
2001	22	17	13	18	12	18
2002	21	15	14	21	14	17
2003	19	14	10	17	11	15
2004	18	13	11	16	11	15
2005	16	12	10	16	11	13
2006	15	12	10	17	12	13
2007	15	13	9.7	17	11	13
2008	14	13	9.7	17	12	12
2009	13	11	8.3	15	8.9	11
2010	11	9.8	7.7	13	7	9.5
2011	11	10	8.8	14	9.1	10
2012	11	10	7.4	14	7.2	9.7
2013	11	9.9	9.2	16	8.6	10

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Table 107. PM_{2.5} Gasoline-attributable concentrations (µg/m³)

Year	South Coast Air Basin	San Diego Air Basin	San Francisco Bay Area Air Basin	San Joaquin Valley Air Basin	Sacramento Valley Air Basin
1999	7.6	5.0	3.4	4.7	3.4
2000	5.4	3.7	2.4	2.8	2.2
2001	5.8	4.2	2.4	2.8	1.9
2002	5.2	3.3	2.7	2.2	1.6
2003	4.4	2.5	2.0	1.6	1.2
2004	4.5	2.9	2.1	1.5	1.2
2005	3.8	2.4	1.7	1.5	1.1
2006	3.5	2.5	1.7	1.4	1.1
2007	3.4	2.4	1.6	1.4	0.96
2008	2.9	2.5	1.5	1.4	1.0
2009	2.7	2.2	1.3	1.2	0.78
2010	2.5	1.9	1.3	1.1	0.57
2011	2.5	1.9	1.4	1.2	0.71
2012	2.3	1.8	1.2	1.2	0.56
2013	2.3	1.7	1.4	1.4	0.67

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Appendix A Brief History of CARB's Regulation of Gasoline Formulation

Phase I California Cleaner Burning Gasoline (CBG), sold beginning in 1992, reduced volatility, phased out lead, and required additives to prevent engine deposits. Phase II CBG, also known as California Reformulated Gasoline 2 (CaRFG2), was introduced for year-round use in California in 1996. In comparison to the reformulated gasoline mandated under federal regulations, CaRFG2 had a lower vapor pressure, lower aromatic content, reduced olefin content, substantially lower sulfur content, and reduced distillation temperature. Neither federal nor state law mandated the use of a particular oxygenate to meet the oxygen content requirements for fuel. In formulating CaRFG2, refiners favored methyl *t*-butyl ether (MTBE) based on its ability to meet performance and regulatory requirements at the lowest cost.

In the late 1990s, mounting evidence that MTBE was contaminating groundwater and surface water in California and other states prompted debate over its continued use as a fuel oxygenate. In March 1999, California Governor Gray Davis issued Executive Order D-5-99, which required removal of MTBE from California's gasoline by December 31, 2002 (the deadline was later extended to December 31, 2003). The Executive Order directed state agencies to facilitate the phase out of MTBE without reducing the emissions benefits of the existing CaRFG2 program. The Governor also requested that CARB and the State Water Resources Control Board (SWRCB) conduct an environmental fate and transport analysis of gasoline containing ethanol, a likely substitute for MTBE. OEHHA was directed to prepare an analysis of the health risks or benefits posed by substituting ethanol for MTBE in gasoline. CARB, SWRCB and OEHHA completed the report entitled "Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate" in December of 1999 (CARB, OEHHA and SWRCB, 1999).

CARB approved Phase 3 reformulated gasoline (CaRFG3) regulations in 1999, to take effect December 31, 2002 (Board Resolution 99-39). The new gasoline was designed to maintain the air quality benefits of CaRFG2 without the use of MTBE. By 2004, most California gasoline contained 5.7% ethanol by weight, replacing MTBE. The Federal Renewable Fuels Standard prompted refiners to add more ethanol to gasoline, and most California gasoline now contains 10% ethanol by weight, the maximum allowed under CaRFG3.

More recently, CARB has begun to address climate change impacts of transportation fuels, as required by the California Global Warming Solutions Act of 2006 (AB 32). In 2009, CARB adopted the Low Carbon Fuel Standard with the purpose of reducing the carbon intensity of fuels by 10% by 2020.

Appendix A. Brief History of CARB's Regulation of Gasoline Formulation

Appendix A References

CARB, OEHHA, and SWRCB (1999). Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate. Report to the California Environmental Policy Council in Response to Executive Order D-5-99. Health effects section available at: <http://oehha.ca.gov/air/cnr/potential-health-risks-ethanol-gasoline>

Appendix B Fuel-Related Research Conducted by OEHHA

As noted in the Introduction to this report, OEHHA was charged with proactively evaluating the human and environmental health impacts of motor vehicle fuels. We have undertaken a number of activities and written several reports to fulfill our responsibilities for conducting fuels research, including:

- Developed the “Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate” (one section in the California Air Resources Board 1999 report).
- Convened a scientific meeting in 2000 on “Approaches to Assessing Health Impacts of Gasoline-Related Exposures in California” and wrote a meeting summary report (OEHHA, 2000).
- Convened a scientific meeting in 2001 on “Issues in the Assessment of Health Impacts of Gasoline Emissions in California” at the University of California, Los Angeles.
- Sponsored research by Drs. Roger Atkinson and Janet Arey at UC Riverside to identify atmospheric transformation products, and developed a report on “Atmospheric Chemistry of Gasoline-Related Emissions: Formation of Pollutants of Potential Concern” (OEHHA, 2006).
- Funded a follow-up Interagency Agreement with UC Riverside to measure selected atmospheric transformation products of potential concern in chamber studies and ambient air (findings reported in Arey et al., 2009, Nishino et al., 2008, Obermeyer et al., 2009).
- Contracted with Dr. William Carter at UC Riverside to develop formation potentials for selected atmospheric transformation products (Carter, 2001).
- Contracted with Dr. Judith Charles at UC Davis to develop an improved method for analyzing acrolein in ambient air and to measure selected carbonyls in ambient air (Destailats et al., 2002).
- Published papers on the respiratory health of children attending schools located near busy roads including:
 - Proximity of California public schools to busy roads (Green et al., 2004)
 - Residential traffic and children’s respiratory health (Kim et al., 2008)
- Developed fact sheets about the impact of traffic-related air pollution on children’s health:
 - Air Pollution from Nearby Traffic and Children’s Health: Information for Schools (OEHHA, 2004)
 - Air Pollution from Nearby Traffic and Children’s Health Information for Parents (OEHHA, 2004)
- Participates in the Fuels Multimedia Working Group (MMWG), within the California Environmental Protection Agency. The MMWG reviews the potential multimedia impacts of new fuel formulations. For example, an evaluation of PuriNOx was conducted in 2004 (CARB, DTSC, OEHHA and SWRCB, 2004).

Appendix B

Fuel-Related Research Conducted by OEHHA

- Identified constituents of potential concern in biogas and developed health protective standards for those constituents as part of a joint analysis with CARB (CARB and OEHHA, 2013) for the California Public Utilities Commission.
- Assisted the California Council on Science and Technology with portions of the Senate Bill 4 study related to human and environmental risk, including: identification of well stimulation treatment chemical hazards; definition of possible exposure pathways; and development of quantitative screening criteria for ranking these hazards. OEHHA also coordinated public participation activities.
- Preparing to assist CARB in a project to monitor neighborhood air quality near oil and gas facilities by:
 - Identifying chemical hazards and potential risks to California communities from oil and gas production activities and from unanticipated events, such as the natural gas leak at Aliso Canyon.
 - Advising on the use of CalEnviroScreen to inform selection of monitoring sites.
 - Assessing chemicals lacking current RELs and providing input on additional chemicals that should be monitored.

Appendix B References

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Appendix B
Fuel-Related Research Conducted by OEHHA

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Appendix C Primary Emissions Rankings

The following table contains a list of gasoline-related chemicals ranked by statewide primary emission tonnage in 1996 and 2012, based on CARB's Emission Inventories for those years. Gasoline-related chemicals were identified from the Emission Inventory based on material code 1100, per CARB. The table also shows the fractions emitted by gasoline-related sources for each chemical (gasoline-attributable fractions), based on primary emissions only. In the individual Chemical Profiles, we accounted for secondary formation where possible, but these calculations are not reflected in the following table. See Appendix E for details on the methods used to calculate gasoline-attributable fractions. The table also includes anthropogenic gasoline-attributable fractions that were calculated by excluding primary emissions from natural sources, like wildfires and biogenic sources.

Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
Isopentane	78-78-4	1	1	109.73	84%	86%
Ethanol	64-17-5	89	2	39.04	22%	22%
Toluene	108-88-3	4	3	38.29	48%	48%
Methane	74-82-8	2	4	36.97	1%	1%
Ethylene	74-85-1	5	5	31.27	11%	43%
2-Methylpentane	107-83-5	8	6	29.90	88%	90%
<i>n</i> -Pentane	109-66-0	7	7	27.64	61%	63%
2,2,4-Trimethylpentane	540-84-1	16	8	25.60	90%	91%
<i>m</i> -Xylene	108-38-3	9	9	22.34	76%	76%
<i>n</i> -Butane	106-97-8	6	10	20.15	32%	37%
3-Methylpentane	96-14-0	15	11	17.25	90%	92%
Methylcyclopentane	96-37-7	12	12	17.16	82%	83%
Propylene	115-07-1	10	13	16.24	22%	57%

Appendix C
 Primary Emissions Rankings

Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
2,3-Dimethylpentane	565-59-3	20	14	15.36	55%	57%
Benzene	71-43-2	13	15	13.88	63%	63%
3-Methylhexane	589-34-4	26	16	12.90	61%	63%
Acetylene	74-86-2	14	17	12.10	11%	50%
Hexane	110-54-3	17	18	10.85	57%	57%
2,3-Dimethylbutane	79-29-8	22	19	9.59	92%	94%
2-Methylhexane	591-76-4	58	20	9.58	77%	77%
Formaldehyde	50-00-0	18	21	8.84	22%	22%
<i>o</i> -Xylene	95-47-6	21	22	8.82	52%	52%
Ethyl benzene	100-41-4	23	23	8.35	78%	78%
2,4-Dimethylpentane	108-08-7	35	24	8.17	58%	59%
Isobutene	115-11-7	11	25	7.67	86%	86%
2,3,4-Trimethylpentane	565-75-3	33	26	7.20	95%	96%
1,2,4-Trimethylbenzene	95-63-6	25	27	7.16	77%	77%
2,2-Dimethylbutane	75-83-2	29	28	6.02	92%	93%
1-Methyl-3-ethylbenzene	620-14-4	27	29	5.78	83%	83%
Ethane	74-84-0	24	30	5.77	1%	2%
<i>n</i> -Heptane	142-82-5	36	31	5.74	39%	39%
Methylcyclohexane	108-87-2	32	32	5.43	31%	31%
Cyclopentane	287-92-3	39	33	5.24	68%	70%
2-Methyl-2-butene	513-35-9	30	34	4.91	97%	97%
3-Methylheptane	589-81-1	37	35	4.84	77%	77%
Cyclohexane	110-82-7	31	36	4.31	60%	61%

Appendix C
Primary Emissions Rankings

Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
2,4-Dimethylhexane	589-43-5	52	37	3.88	53%	54%
2-Methylheptane	592-27-8	49	38	3.69	64%	64%
2,2,5-Trimethylhexane	3522-94-9	53	39	3.67	79%	83%
Isobutane	75-28-5	19	40	3.58	11%	12%
2,5-Dimethylhexane	592-13-2	50	41	3.43	95%	96%
2,3,3-Trimethylpentane	560-21-4	136	42	3.36	99%	99%
<i>trans</i> -2-Pentene	646-04-8	41	43	3.19	97%	97%
2,3-Dimethylhexane	584-94-1	60	44	2.92	88%	89%
1,3-Butadiene	106-99-0	38	45	2.87	26%	52%
1,3,5-Trimethylbenzene	108-67-8	44	46	2.78	86%	86%
Acetaldehyde	75-07-0	45	47	2.78	6%	12%
<i>n</i> -Octane	111-65-9	48	48	2.63	34%	34%
1-Butene	106-98-9	40	49	2.56	11%	44%
<i>trans</i> -2-Butene	624-64-6	42	50	2.50	81%	81%
<i>trans</i> -1,3-Dimethylcyclopentane	1759-58-6	56	51	2.48	73%	73%
1-Methyl-4-ethylbenzene	622-96-8	46	52	2.47	84%	84%
<i>cis</i> -1,3-Dimethylcyclopentane	2532-58-3	61	53	2.44	76%	76%
<i>p</i> -Xylene	106-42-3	146	54	2.37	29%	29%
3-Methyloctane	2216-33-3	51	55	2.36	67%	71%
2-Methyl-1-butene	563-46-2	43	56	2.15	99%	99%
3-Ethylpentane	617-78-7	54	57	1.94	54%	56%
1-Methyl-2-ethylbenzene	611-14-3	55	58	1.90	76%	76%
<i>cis</i> -2-Butene	590-18-1	47	59	1.82	84%	84%

Appendix C
 Primary Emissions Rankings

Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
4-Methylheptane	589-53-7	73	60	1.73	75%	75%
3-Methyl-1-butene	563-45-1	66	61	1.72	47%	93%
Benzaldehyde	100-52-7	59	62	1.70	64%	64%
<i>m</i> -Tolualdehyde	620-23-5	57	63	1.70	100%	100%
<i>n</i> -Propylbenzene	103-65-1	64	64	1.61	83%	83%
<i>cis</i> -2-Pentene	627-20-3	65	65	1.52	97%	97%
Acetone	67-64-1	63	66	1.45	1%	2%
1-Propyne	74-99-7	62	67	1.43	24%	84%
4-Methyloctane	2216-34-4	68	68	1.41	60%	64%
1-Pentene	109-67-1	67	69	1.32	48%	48%
Propane	74-98-6	28	70	1.32	2%	3%
1,2,3-Trimethylbenzene	526-73-8	69	71	1.32	64%	64%
Ethylcyclopentane	1640-89-7	76	72	1.30	61%	61%
1-Methyl-3 <i>n</i> -propylbenzene	1074-43-7	72	73	1.23	98%	98%
<i>cis</i> -1, <i>trans</i> -2,3-Trimethylcyclopentane	15890-40-1	109	74	1.12	94%	95%
Methanol	67-56-1	34	75	1.12	1%	14%
<i>trans</i> -1,2-Dimethylcyclopentane	822-50-4	168	76	1.11	99%	99%
Cyclopentene	142-29-0	70	77	1.11	98%	98%
<i>n</i> -Nonane	111-84-2	74	78	1.08	22%	22%
1,2-Propadiene	463-49-0	71	79	1.07	69%	69%
2-Methyl-2-pentene	625-27-4	81	80	9.43E-01	99%	99%
1,2-Dimethyl-4-ethylbenzene	934-80-5	83	81	9.19E-01	75%	75%
1,3-Dimethyl-5-ethylbenzene	934-74-7	82	82	8.80E-01	80%	80%

Appendix C
 Primary Emissions Rankings

Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
<i>trans</i> -2-Hexene	4050-45-7	77	83	8.76E-01	99%	99%
2,6-Dimethylheptane	1072-05-5	75	84	8.45E-01	44%	46%
2-Methyloctane	3221-61-2	132	85	7.78E-01	57%	59%
1-Hexene	592-41-6	105	86	7.52E-01	72%	72%
2,2-Dimethylhexane	590-73-8	102	87	7.28E-01	96%	97%
3,5-Dimethylheptane	926-82-9	78	88	7.27E-01	69%	74%
2-Methylnonane	871-83-0	84	89	6.57E-01	42%	42%
Indan	496-11-7	90	90	6.56E-01	64%	64%
Isoprene	78-79-5	79	91	6.54E-01	0%	98%
2-Methyl-2-propenal	78-85-3	88	92	6.06E-01	95%	95%
Styrene	100-42-5	85	93	6.04E-01	12%	12%
Acrolein	107-02-8	86	94	5.97E-01	29%	29%
Naphthalene	91-20-3	107	95	5.94E-01	33%	33%
1,2,4-Trimethylcyclopentene	2815-58-9	80	96	5.86E-01	92%	94%
1,3-Dimethyl-4-ethylbenzene	874-41-9	98	97	5.80E-01	82%	82%
1,4-Dimethyl-2-ethylbenzene	1758-88-9	100	98	5.50E-01	75%	75%
<i>n</i> -Decane	124-18-5	87	99	5.48E-01	7%	7%
4-Methyl- <i>trans</i> -2-pentene	674-76-0	101	100	5.16E-01	99%	99%
<i>trans</i> -1,4-Dimethylcyclohexane	9/8/7942	110	101	5.13E-01	38%	38%
<i>trans</i> -1-Methyl-3-ethylcyclopentane	2613-65-2	91	102	5.04E-01	81%	83%
<i>trans</i> -1,3-Dimethylcyclohexane	8/28/7942	116	103	4.99E-01	15%	16%
<i>cis</i> -1,3-Dimethylcyclohexane	638-04-0	92	104	4.90E-01	18%	18%
3,3-Dimethylpentane	562-49-2	159	105	4.85E-01	88%	88%

Appendix C
Primary Emissions Rankings

Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
1,3-Diethylbenzene (meta)	141-93-5	115	106	4.53E-01	88%	88%
<i>cis</i> -1, <i>trans</i> -2,4-Trimethylcyclopentane		200	107	4.50E-01	100%	100%
<i>cis</i> -1,2-Dimethylcyclopentane	1192-18-3	201	108	4.48E-01	100%	100%
2-Methyl-1-pentene	763-29-1	99	109	4.40E-01	95%	95%
1,2,3,5-Tetramethylbenzene	527-53-7	120	110	4.37E-01	63%	63%
Vinylacetylene	689-97-4	97	111	4.25E-01	100%	100%
1,4-Diethylbenzene (para)	105-05-5	96	112	4.24E-01	87%	87%
2,2,3-Trimethylpentane	564-02-3	192	113	4.20E-01	97%	97%
2,2,4-Trimethylhexane	16747-26-5	108	114	4.17E-01	72%	77%
2,5-Dimethylheptane	2216-30-0	205	115	4.16E-01	51%	52%
2,2,5-Triethylheptane	20291-95-6	94	116	4.14E-01	33%	33%
<i>cis</i> -2-Hexene	7688-21-3	118	117	4.13E-01	99%	99%
2-Methylindan	824-63-5	121	118	4.08E-01	100%	100%
2,3,5-Trimethylhexane	1069-53-0	134	119	3.92E-01	83%	86%
3-Methylcyclopentene	1120-62-3	95	120	3.90E-01	99%	99%
2,4-Dimethylheptane	2213-23-2	104	121	3.84E-01	52%	54%
3-Methyl-1-pentene	760-20-3	93	122	3.80E-01	99%	99%
Isobutylcyclopentane	3788-32-7	208	123	3.73E-01	99%	99%
Propionaldehyde	123-38-6	111	124	3.67E-01	4%	4%
3,4-Dimethylheptane	922-28-1	127	125	3.66E-01	78%	82%
5-Methylindan	874-35-1	124	126	3.66E-01	45%	45%
1-Methyl-2-isopropylbenzene	527-84-4	113	127	3.63E-01	96%	96%
Crotonaldehyde	4170-30-3	114	128	3.52E-01	24%	24%

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Primary Emissions Rankings

Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
<i>trans</i> -3-Hexene	13269-52-8	112	129	3.46E-01	99%	99%
1,3,5-Trimethylcyclohexane	1839-63-0	106	130	3.43E-01	52%	52%
<i>cis</i> -1-Methyl-3-ethylcyclopentane	2613-66-3	117	131	3.35E-01	81%	82%
1,2,4,5-Tetramethylbenzene	95-93-2	130	132	3.22E-01	62%	62%
Cyclohexene	110-83-8	103	133	3.20E-01	100%	100%
Ethylcyclohexane	1678-91-7	149	134	3.07E-01	16%	16%
<i>trans</i> -3-Heptene	14686-14-7	119	135	3.05E-01	100%	100%
2-Methyl-3-ethylpentane	609-26-7	182	136	2.99E-01	78%	79%
2,3,4-Trimethylhexane	921-47-1	213	137	2.84E-01	100%	100%
1,1,4-Trimethylcyclohexane	7094-27-1	214	138	2.71E-01	66%	66%
3,3-Dimethyloctane	4110-44-5	123	139	2.69E-01	37%	41%
Cumene	98-82-8	133	140	2.63E-01	46%	46%
4-Methyl-1-pentene	691-37-2	138	141	2.63E-01	100%	100%
2,2,4-Trimethylheptane	14720-74-2	122	142	2.59E-01	35%	39%
3-Methyl- <i>cis</i> -2-hexene	10574-36-4	135	143	2.56E-01	100%	100%
2,6-Dimethyloctane	2051-30-1	126	144	2.49E-01	20%	22%
2,3-Dimethylheptane	3074-71-3	185	145	2.48E-01	85%	86%
2,4-Dimethyloctane	4032-94-4	128	146	2.41E-01	9%	10%
<i>trans</i> -1, <i>cis</i> -2,3-Trimethylcyclopentane		--	147	2.39E-01	100%	100%
2,5-Dimethyloctane	15869-89-3	137	148	2.37E-01	38%	42%
Isovaleraldehyde	590-86-3	125	149	2.30E-01	71%	71%
3-Methyl- <i>cis</i> -2-pentene	922-62-3	196	150	2.27E-01	98%	98%
3-Methyl-3-ethylpentane	1067-08-9	216	151	2.15E-01	100%	100%

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 Primary Emissions Rankings

Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
2,2,3-Trimethylbutane	464-06-2	156	152	2.10E-01	68%	69%
3,4-Dimethylhexane	583-48-2	176	153	2.10E-01	62%	62%
3-Ethylhexane	619-99-8	223	154	2.06E-01	43%	43%
Methyl ethyl ketone {2-butanone}	78-93-3	131	155	2.06E-01	2%	2%
<i>n</i> -Undecane	1120-21-4	142	156	1.99E-01	4%	4%
1,2-Dimethyl-3-ethylbenzene	933-98-2	155	157	1.91E-01	98%	98%
3,3-Dimethylhexane	563-16-6	184	158	1.89E-01	98%	99%
<i>cis</i> -1,2-Dimethylcyclohexane	8/6/7942	157	159	1.87E-01	63%	63%
2,4-Dimethyl-2-pentene	625-65-0	129	160	1.87E-01	100%	100%
Butyraldehyde	123-72-8	139	161	1.81E-01	6%	6%
<i>trans</i> -1,2-Dimethylcyclohexane	6876-23-9	218	162	1.80E-01	75%	75%
2,2,3,Trimethylhexane	16747-25-4	219	163	1.80E-01	100%	100%
<i>cis</i> -1, <i>cis</i> -2,3-Trimethylcyclopentane	2613-69-6	220	164	1.79E-01	100%	100%
2-Methyl- <i>trans</i> -3-hexene	692-24-0	141	165	1.77E-01	100%	100%
3,3-Dimethyl-1-pentene	3404-73-7	199	166	1.72E-01	100%	100%
2-Methyl naphthalene	91-57-6	208	167	1.72E-01	21%	21%
1-Methyl-2 <i>n</i> -propylbenzene	1074-17-5	140	168	1.69E-01	91%	91%
<i>trans</i> -2-Heptene	14686-13-6	153	169	1.69E-01	99%	99%
<i>cis</i> -2-Heptene	6443-92-1	154	170	1.66E-01	99%	99%
1,2,3,4-Tetramethylbenzene	488-23-3	144	171	1.66E-01	93%	93%
<i>trans</i> -2-Ethylmethylcyclopentane		224	172	1.64E-01	100%	100%
Dimethylcyclopentane	28729-52-4	225	173	1.64E-01	87%	87%
1-Methylcyclopentene	693-89-0	201	174	1.58E-01	100%	100%

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Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
1-Methyl-4n-propylbenzene	1074-55-1	212	175	1.49E-01	26%	26%
3-Methyl- <i>trans</i> -2-pentene	616-12-6	169	176	1.49E-01	99%	99%
Hexaldehyde	66-25-1	143	177	1.47E-01	2%	3%
1-Methyl-4-ethylcyclohexane	6236-88-0	145	178	1.46E-01	54%	54%
1,2-Butadiene {methylallene}	590-19-2	150	179	1.41E-01	94%	94%
1-Methyl-3-isopropylbenzene	535-77-3	148	180	1.40E-01	28%	28%
2,3-Dimethyloctane	7146-60-3	147	181	1.39E-01	15%	16%
3-Ethylheptane	15869-80-4	228	182	1.38E-01	49%	49%
1,3-Dipropylbenzene	17171-72-1	163	183	1.38E-01	100%	100%
3,3-Dimethylheptane	4032-86-4	229	184	1.34E-01	100%	100%
<i>trans</i> -1,3-Pentadiene	2004-70-8	151	185	1.30E-01	100%	100%
2,2-Dimethylpentane	590-35-2	190	186	1.29E-01	79%	80%
3-Methyl- <i>trans</i> -2-hexene	20710-38-7	208	187	1.22E-01	100%	100%
<i>cis</i> -3-Hexene	7642093	193	188	1.12E-01	99%	99%
3-Methylnonane	5911046	221	189	1.09E-01	24%	24%
1-Nonene	124-11-8	161	190	1.08E-01	55%	55%
<i>n</i> -Pentylbenzene	538-68-1	160	191	1.08E-01	98%	98%
Propylcyclopentane	2040-96-2	232	192	1.05E-01	60%	60%
4-Methylindan	824-22-6	170	193	1.05E-01	58%	58%
1-Ethyl-2n-propylbenzene	16021-20-8	179	194	1.03E-01	81%	81%
2,2-Dimethyloctane	15869-87-1	158	195	1.03E-01	38%	42%
(2-Methylpropyl)benzene	538-93-2	175	196	9.47E-02	41%	41%
<i>n</i> -Dodecane	112-40-3	177	197	9.20E-02	3%	3%

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Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
1,3-Dimethyl-2-ethylbenzene	11/28/9757	165	198	8.67E-02	28%	28%
4-Methyl- <i>trans</i> -2-hexene	3683-22-5	162	199	8.50E-02	99%	99%
1-Methyl-2- <i>n</i> -butylbenzene	1595-68-1	166	200	8.20E-02	87%	87%
1,2,4-Triethylbenzene	887-44-1	197	201	8.18E-02	99%	99%
2-Methyl-2-hexene	2738-19-4	152	202	8.02E-02	100%	100%
1-Methyl-1-ethylcyclohexane	4926-90-3	236	203	7.96E-02	99%	99%
<i>n</i> -Butylbenzene	104-51-8	225	204	7.80E-02	86%	86%
3-Methyl- <i>trans</i> -3-hexene	3899-36-3	180	205	7.77E-02	98%	98%
1-Methylnaphthalene	90-12-0	225	206	7.76E-02	99%	99%
1-(1,1-Dimethylethyl)-3,5-dimethylbenzene	98-19-1	167	207	7.62E-02	98%	98%
<i>cis</i> -1, <i>cis</i> -3,5-Trimethylcyclohexane	1795-27-3	236	208	7.47E-02	10%	10%
4,4-Dimethylheptane	1069-19-5	235	209	7.46E-02	100%	100%
2,3-Dimethyl-1-butene	563-78-0	174	210	7.37E-02	70%	70%
1,2-Diethylbenzene (ortho)	135-01-3	188	211	6.92E-02	30%	30%
2,4,4-Trimethylhexane	16747-30-1	171	212	6.91E-02	82%	85%
1,1,2-Trimethylcyclopentane	4259-00-1	244	213	6.16E-02	24%	24%
<i>n</i> -Butylcyclopentane	2040-95-1	245	214	5.97E-02	99%	99%
4,4-Dimethyl-2-pentene	690-08-4	221	215	5.97E-02	100%	100%
<i>cis</i> -1, <i>trans</i> -2, <i>trans</i> -4-Trimethylcyclohexane	7667-60-9	245	215	5.97E-02	100%	100%
1-Methyl-4-isopropylbenzene	99-87-6	178	217	5.41E-02	49%	49%
4-Methyl- <i>cis</i> -2-pentene	691-38-3	206	218	5.19E-02	95%	95%
1,3,5-Triethylbenzene	102-25-0	203	219	4.86E-02	99%	99%

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Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
1,4-Isodipropylbenzene	577-55-9	230	220	4.77E-02	100%	100%
1-Methyl-4- <i>n</i> -pentylbenzene		230	220	4.77E-02	100%	100%
5-Methylnonane	15869-85-9	236	222	4.76E-02	97%	97%
<i>n</i> -Propyl alcohol	71-23-8	245	223	4.72E-02	3%	3%
<i>cis</i> -2-Octene	7642048	181	224	4.41E-02	99%	99%
2,4-Dimethyl-1-pentene	2213-32-3	189	224	4.41E-02	50%	50%
2,2-Dimethylpropane	463-82-1	164	226	4.22E-02	41%	41%
<i>trans</i> -2-Octene	13389-42-9	191	227	4.17E-02	96%	96%
1,3-Butadiyne	460-12-8	186	228	4.00E-02	100%	100%
2,3-Dimethyl-2-pentene	10574-37-5	186	228	4.00E-02	100%	100%
3,3-Dimethyl-1-butene	558-37-2	183	230	3.72E-02	1%	1%
1-Methyl-4- <i>t</i> -butylbenzene	98-51-1	243	231	3.58E-02	75%	75%
1,1,3-Trimethylcyclohexane	3073-66-3	253	232	3.32E-02	5%	5%
2-Ethyl-1-butene	760-21-4	206	233	3.30E-02	99%	99%
3- <i>n</i> -Dipropylbenzene		234	234	3.28E-02	100%	100%
3-Methyl- <i>cis</i> -3-hexene	4914-89-0	233	235	3.25E-02	100%	100%
1,1-Dimethylcyclohexane	590-66-9	252	236	3.21E-02	12%	12%
2,4-Dimethylnonane	17302-24-8	--	237	3.20E-02	25%	26%
Isopropylcyclohexane	696-29-7	253	238	3.12E-02	2%	2%
Pentamethylbenzene	700-12-9	245	239	3.11E-02	100%	100%
3-Ethyl-2-pentene	816-79-5	211	240	3.09E-02	100%	100%
1,1-Methylethylcyclopentane	16747-50-5	172	241	3.05E-02	33%	33%
1,1,2-Trimethylcyclohexane	7094-26-0	253	242	2.98E-02	31%	31%

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Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
(1-Methylpropyl)benzene	135-98-8	236	243	2.98E-02	17%	17%
s-Pentylbenzene	29316-05-0	236	243	2.98E-02	100%	100%
Trimethylcyclohexane	30498-63-6	253	243	2.98E-02	4%	4%
1-Octene	111-66-0	173	246	2.56E-02	20%	20%
2-Butyne	503-17-3	195	247	2.12E-02	84%	84%
5-Methyl-1-hexene	3524-73-0	253	248	2.01E-02	100%	100%
<i>trans</i> -3-Nonene	20063-92-7	253	249	1.76E-02	100%	100%
3,4-Dimethyl-2-pentene	24910-63-2	245	250	1.68E-02	100%	100%
<i>tert</i> -Amyl methyl ether (TAME)	994-05-8	217	251	1.65E-02	99%	99%
3-Ethyl-octane	5881-17-4	253	252	1.63E-02	12%	13%
Butylcyclohexane	1678-93-9	253	253	1.62E-02	2%	2%
2-Methyl-1-octene	4588-18-5	253	254	1.60E-02	100%	100%
3-Ethyl-nonane	17302-11-3	253	255	1.56E-02	98%	99%
<i>cis</i> -3-Nonene	20237-46-1	245	256	1.51E-02	100%	100%
4-Methyl-1-hexene	3769-23-1	245	257	1.50E-02	100%	100%
<i>trans</i> -4-Octene	14850-23-8	253	258	1.49E-02	100%	100%
Dihydronaphthalene		253	258	1.49E-02	100%	100%
1,3-Cyclopentadiene	542-92-7	253	258	1.49E-02	100%	100%
5-Methyl- <i>cis</i> -2-hexene	3404-62-4	253	258	1.49E-02	100%	100%
3,6-Dimethyloctane	15869-94-0	253	258	1.49E-02	10%	10%
2,3-Dimethyl-2-octene	19781-18-1	253	258	1.49E-02	100%	100%
<i>n</i> -Hexylbenzene	1077-16-3	253	258	1.49E-02	100%	100%
Ethylindan		--	265	1.41E-02	100%	100%

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Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
2,2-Dimethylheptane	1071-26-7	285	266	1.30E-02	4%	4%
<i>trans</i> -1,2- <i>cis</i> -4-Trimethylcyclopentane	4850-28-6	280	267	1.28E-02	77%	79%
Unidentified	99-99-9	--	268	1.25E-02	0%	0%
1,1,3-Trimethylcyclopentane	4516-69-2	275	269	1.16E-02	2%	2%
1,2,4-Trimethylcyclopentane	99-07-3	273	270	1.15E-02	1%	1%
3,4-Dimethyl-1-pentene	7385-78-6	194	271	1.08E-02	100%	100%
2-Methyldecane	6975-98-0	--	272	9.57E-03	1%	1%
<i>cis</i> -1-Ethyl-3-methylcyclopentane	99-07-1	289	273	9.24E-03	35%	35%
1-Methyl-2- <i>tert</i> -butylbenzene	1074-92-6	198	274	8.01E-03	100%	100%
<i>trans</i> -1,3-Diethylcyclopentane		--	275	7.47E-03	100%	100%
c11-Aromatics		--	276	7.39E-03	91%	91%
3,3-Diethylpentane	1067-20-5	--	277	7.29E-03	99%	99%
c10-Olefins		--	278	7.26E-03	4%	4%
Dimethylheptanes	98-09-1	241	279	7.01E-03	4%	5%
1,2-Isodipropylbenzene	100-18-5	276	280	6.51E-03	100%	100%
1-Ethyl-4-isopropylbenzene	4218-48-8	271	281	6.33E-03	4%	4%
<i>trans</i> -1-Ethyl-3-methylcyclopentane	99-08-5	289	282	6.24E-03	26%	26%
1,2,3-Trimethylcyclopentane	99-07-4	274	283	5.86E-03	1%	1%
2-Methyl-1-hexene	6094026	--	284	5.66E-03	100%	100%
Indene	95-13-6	--	285	5.44E-03	14%	14%
1-Methyl-3-butylbenzene	99-08-4	270	286	5.07E-03	12%	12%
4-Methylnonane	17301-94-9	--	287	4.96E-03	1%	1%
1-Ethyl-2-isopropylbenzene		271	288	4.95E-03	29%	29%

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Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
<i>trans</i> -1-Methyl-2-propylcyclopentane	932-44-5	--	289	4.63E-03	100%	100%
Trimethylcyclopentane	30498-64-7	278	290	4.56E-03	9%	9%
tert-Pentylbenzene	2049-95-8	--	291	4.32E-03	100%	100%
3-Ethyl-3-methylheptane	17302-01-1	--	292	4.19E-03	100%	100%
t-Butylbenzene	98-06-6	--	293	3.83E-03	0%	0%
2-Ethyl-1-pentene	3404-71-5	--	294	3.68E-03	100%	100%
<i>cis</i> -1-Ethyl-2-methylcyclopentane	930-89-2	288	295	3.52E-03	9%	9%
2,3,3-Trimethyl-1-butene	594-56-9	--	296	3.07E-03	98%	98%
<i>trans</i> -3-Octene	14919-01-8	--	297	2.99E-03	100%	100%
t-1-Butyl-4-ethylbenzene		276	298	2.98E-03	100%	100%
3-Methyl-5-ethylheptane		--	299	2.96E-03	100%	100%
1-Methyl-4-(1-methylpropyl)benzene	1595-16-0	--	300	2.79E-03	100%	100%
Dimethylcyclopentene		--	301	2.54E-03	18%	18%
<i>cis</i> -3-Heptene	7642106	--	302	2.52E-03	100%	100%
<i>trans,trans</i> -1,2,4-Trimethylcyclohexane	2234-75-5	--	303	2.23E-03	0%	0%
Isopropylcyclopentane	3875-51-2	--	304	2.20E-03	98%	98%
2,7-Dimethyloctane	1072-16-8	--	305	2.19E-03	3%	3%
<i>cis</i> -1, <i>trans</i> -2, <i>cis</i> -4-Trimethylcyclohexane		--	306	2.15E-03	100%	100%
<i>trans</i> -1-Ethyl-4-methylcyclohexane	99-08-2	--	307	1.90E-03	1%	1%
Trimethylindan	36541-18-1	--	308	1.80E-03	100%	100%
1-Methyl-4-isobutylbenzene		--	309	1.75E-03	3%	3%
2-Methyl-2-octene	16993-86-5	--	310	1.70E-03	5%	5%
1-Ethyl-3-methylcyclopentane	99-04-8	281	311	1.47E-03	1%	1%

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Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
1-Ethyl-2-methylcyclopentane	99-08-3	281	311	1.47E-03	1%	1%
2,6-Dimethylnaphthalene	581-42-0	--	313	1.44E-03	100%	100%
2-Methyl- <i>cis</i> -3-hexene	15840-60-5	--	314	1.39E-03	100%	100%
<i>cis</i> -1,4-Dimethylcyclohexane	624-29-3	283	315	1.38E-03	1%	1%
<i>n</i> -Tridecane	629-50-5	--	316	1.16E-03	0%	0%
2-Methylundecane	7045-71-8	--	317	7.82E-04	0%	0%
1-Heptene	592-76-7	--	318	7.22E-04	0%	0%
Unidentified (SAROAD 43381)		--	319	5.72E-04	100%	100%
Unidentified (SAROAD 43384)		--	320	5.58E-04	100%	100%
Unidentified (SAROAD 43382)		--	321	5.35E-04	100%	100%
2,3-Dimethyl-1-hexene	16746-86-4	--	322	4.36E-04	100%	100%
<i>cis</i> -Bicyclo[3.3.0]octane	694-72-4	287	323	4.29E-04	1%	1%
Dimethylindene		--	324	4.16E-04	100%	100%
Ethylmethylcyclohexanes	90-08-3	--	325	4.11E-04	0%	0%
2-Undecene, (e)-	693-61-8	--	326	4.10E-04	100%	100%
3-Ethyl-3-hexene	16789-51-8	--	327	3.31E-04	100%	100%
3-Methyl-1-hexene	3404-61-3	--	328	2.52E-04	30%	30%
<i>n</i> -Tetradecane	629-59-4	--	329	2.48E-04	0%	0%
<i>trans</i> -1, <i>cis</i> -2,3-Trimethylcyclopentane		215	330	2.01E-04	29%	30%
2,3-Dimethyl-2-heptene	3074-64-4	--	331	1.83E-04	100%	100%
Ethylmethylhexane	90-08-2	279	332	1.67E-04	1%	1%
Isobutylcyclohexane	1678-98-4	--	333	1.52E-04	0%	0%
Unidentified (SAROAD 43383)		--	334	1.26E-04	100%	100%

Appendix C
 Primary Emissions Rankings

Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
1,4-Dimethyl-1-cyclohexene	70688-47-0	--	335	1.26E-04	100%	100%
<i>trans</i> -4-Nonene	10405-85-3	--	336	8.90E-05	100%	100%
2,2,3,3-Tetramethylpentane	7154-79-2	284	337	7.61E-05	0%	0%
Propenylcyclohexane	90-10-5	--	338	7.43E-05	0%	0%
Propylcyclohexane	1678-92-8	--	339	6.57E-05	0%	0%
<i>trans,cis</i> -1,2,4-Trimethylcyclohexane	99-07-5	--	340	6.32E-05	0%	0%
Methylheptyne		--	341	6.29E-05	100%	100%
<i>trans,trans</i> -1,3,5-Trimethylcyclohexane	99-07-6	--	342	5.94E-05	0%	0%
Methyl biphenyl	28652-72-4	--	343	5.79E-05	100%	100%
Tetramethylcyclopentane	90-09-8	--	344	5.35E-05	0%	0%
Unidentified (SAROAD 43385)		--	345	4.72E-05	100%	100%
<i>cis</i> -1-Ethyl-3-methylcyclohexane	19489-10-2	--	346	4.15E-05	0%	0%
1,2,3-Trimethylcyclohexane	1678-97-3	--	347	3.77E-05	0%	0%
<i>trans</i> -2-Nonene	6434-78-2	--	348	3.14E-05	100%	100%
<i>cis,trans</i> -1,2,4-Trimethylcyclohexane	99-07-9	--	349	2.64E-05	0%	0%
<i>trans</i> -1-Ethyl-3-methylcyclohexane	99-08-0	--	350	2.17E-05	0%	0%
<i>n</i> -Pentadecane	629-62-9	--	351	2.09E-05	0%	0%
1,2-Dimethylcyclopentane	2452-99-5	--	352	1.43E-05	0%	0%
<i>cis</i> -Bicyclo[4.3.0]nonane	4551-51-3	--	353	1.41E-05	0%	0%
<i>cis,cis</i> -1,2,4-Trimethylcyclohexane	99-05-4	--	354	1.23E-05	0%	0%
<i>trans</i> -1-Ethyl-2-methylcyclohexane	4923-78-8	--	354	1.23E-05	0%	0%
<i>cis,trans</i> -1,2,3-Trimethylcyclohexane	20348-72-5	--	356	8.51E-06	0%	0%
Ethylhexane	90-08-1	286	357	4.78E-06	0%	0%

Appendix C
 Primary Emissions Rankings

Chemical name	CASRN	1996 Rank by tonnage	2012 Rank by tonnage	2012 Gasoline-related primary emissions (tons/day)	2012 Statewide gasoline-attributable fraction	2012 Statewide gasoline-attributable fraction (anthropogenic)
<i>cis</i> -1-Ethyl-4-methylcyclohexane	3728-56-1	--	358	4.69E-06	0%	0%
<i>cis</i> -1-Ethyl-2-methylcyclohexane	4923-77-7	--	358	4.69E-06	0%	0%
1,1-Dimethylcyclopentane	1638-26-2	--	360	1.24E-06	0%	0%
4-Ethyldecane	99-04-9	291	361	1.14E-06	0%	0%
Methyl <i>t</i> -butyl ether (MTBE)	1634-04-4	3	362	1.04E-06	0%	0%
1-Methyl-2- <i>n</i> -butylbenzene	1595-11-5	204	--	--	--	--
2,4,4-Trimethyl-2-pentene	107-40-4	242	--	--	--	--

Appendix D Calculation of Population-Weighted Ambient Air Concentrations

This appendix describes how California ambient air monitoring data and census data were used to estimate population-weighted ambient air concentrations for selected pollutants. The first step was to calculate the annual average concentration of the pollutant at monitoring sites. When there were enough sites with data, these averages were combined to calculate a population-weighted annual average ambient air concentration. The following sections describe:

- The ambient air monitoring data sources
- How annual averages were calculated and/or modeled at monitoring sites
- How monitoring site averages were interpolated to census tracts
- How census tract estimates were combined to get population-weighted annual averages for an air basin and state
- How decennial census tract values were interpolated

Sources of Ambient Air Monitoring Data

Ambient Air Monitoring Data from California Air Resources Board

CARB collects ambient air measurements from monitoring stations throughout California. The data for this analysis were primarily taken from CARB's 2015 Air Quality Data DVD. Additional data were available on the CARB website for download. A brief description of each data file follows.

- Carbon monoxide (CO) data were taken from the dlygas_csv.txt data file, which was downloaded from the CARB website. It contained data on criteria pollutants by monitoring station from 1995-2011. There were data from throughout the state and from nearly each day in each year. For 2012 to 2014, hourly data were converted to daily averages and appended to the daily data. The data file co20102014.txt, from the CARB website, was used for 2012 and 2013 data and "2014 AQMIS Extraction 20150310.accdb" from the DVD was used for 2014.
- Nitrogen dioxide daily averages came from the Access database "AQDVD2015_Daily Data.accdb" on the DVD. The 2014 NO₂ data was incomplete and not used.
- The California Toxic Monitoring Network data file (DailyToxcis_3-6-2014.accdb) contained the daily average concentrations of TACs for the years 1990-2014. There were data from two or three days in each month. The detectors used to measure the concentrations of chemicals in the air have minimum levels of detection. When the actual concentration fell below this limit of detection, CARB put one-half the limit of detection in the data file.
- The PAMS hourly data file (NMOC_PAMS 3-hr data 1994-2014.accdb) contained data on non-methane organic compounds collected by the Photochemical Assessment Monitoring Station (PAMS) monitoring network. It included hourly concentrations of non-methane organic compounds by monitoring station 1994-2014. The data were from July through October of each year. There were 0 to 8 measurements per day.

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Calculation of Population-Weighted Ambient Air Concentrations

- The PAMS 24 hour data set (NMOC 24 Hour.accdb) contained data on non-methane organic compounds collected by the Photochemical Assessment Monitoring Stations (PAMS). It included 24-hour average concentrations of non-methane organic compounds by monitoring station from the years 1994-2014. The data were from throughout the year. The number of data points varied by site and year. Many sites had 50 to 60 data points per year. The South Coast Air Basin data from 2012 to 2014 was very limited.
- The PM₁₀ data file (PM10StdDaily20150302.xlsx) contained the daily average concentration of PM₁₀ from 1996 to 2014. The 2014 data were incomplete and not used. For many sites data were collected every sixth day resulting in 50 to 60 measurements annually. The data in the file were at standard temperature and pressure. There was a separate data file with measurements recorded at local conditions. The local conditions data file was not used because data were either missing or very sparse for 1998 and earlier.
- The PM_{2.5} data file (PM25Daily20150302.xlsx) contained daily average concentrations of PM_{2.5} from 1998 to 2014. The data from 1998 and 2014 were incomplete and not used. Measurements were recorded at local conditions.
- The location data file (location.dat) contained monitoring station information such as name, air basin, county, address, latitude and longitude.

DRI Ambient Air Measurements

The DRI data file (dri_rfg9596.xls) was created by Desert Research Institute (DRI) (Zielinska et al., 1999). It contained ambient air measurements from summer months in 1995 and 1996. There were two readings per day and the samples were collected over a 3-hour period. The data came from four monitoring stations in Southern California but the bulk of the data are from three of these sites: Azusa, Burbank and Los Angeles.

US EPA AirData

- PAH data collected by three California monitoring stations in the National Air Toxics Trend Stations (NATTS) system were downloaded from the US EPA AirData website³⁰.
- Benzaldehyde, butyraldehyde, ethanol and propionaldehyde data were downloaded from the US EPA AirData website.

³⁰ <https://ofmext.epa.gov/AQDMRS/aqdmrs.html>

Methods for Estimating the Annual Average Concentration at Each Monitoring Site

Introduction

This section describes how air quality monitoring data was used to calculate the annual average ambient air concentrations of chemicals at sites within an air quality monitoring network. The method used depended on the amount of data available for the chemical. The general procedures used are described in the sections immediately below. Details for individual chemicals are provided after the general methods. Data sources were described in the previous section. The annual average from each monitoring site was used at a later stage to calculate the population-weighted average of the chemical; this procedure is explained in detail later in this appendix. The estimated population-weighted annual averages are presented in the Chemical Profiles section beginning on page 85.

Method 1 – Dense Monitoring Networks

This method was used for nitrogen dioxide and particulate matter (PM_{2.5} and PM₁₀). The annual average concentration at a monitoring station was calculated as the average of the observed daily average concentrations from one year. The site had to have 10 or more months of data to be included. Details about nitrogen dioxide and particulate matter are provided below in individual sections

Method 2 – California Toxic Monitoring Network

The California Toxic Monitoring Network collected ambient air data from multiple air basins. Data from 1996 through 2014 were used. The five most populated air basins (SC, SD, SFB, SJV, and SV) had between two and six monitoring stations active annually between 1996 and 2014. The South Coast Air Basin had the most monitoring stations with five to six stations collecting data at any time. The annual average was calculated at each site from daily average data. The annual averages were retained provided they were based on 10 or more months of data. These observed annual averages were supplemented with modeled annual averages at additional locations. The observed and modeled annual averages were then used to calculate the population-weighted averages for the five basins and for the state.

The model for the concentration of a toxic contaminant took into account the year the measurement was made and the level of carbon monoxide at the site:

$$SqC_{ik} = Intercept + \beta_{1996} Year_{1996} + \dots + \beta_{2013} Year_{2013} + \beta_{SqCO} SqCO_{ik} + Site_i + Error_{ik}$$

Where

- SqC_{ik} is the square root of the k^{th} daily average ambient air concentration of the TAC from site i .
- $Year_{1995+j}$ is an indicator function that indicates if the measurement was made in the year 1995+j. For example, $Year_{1996}$ equals 1 if the measurement was taken in year 1996 and

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equals zero otherwise. There were 18 indicator variables Year₁ to Year₁₈, one for each year between 1996 and 2013. 2014 was the reference year.

- SqCo_{ik} is the square root of the kth daily average carbon monoxide concentration at site i.
- Site_i is a random effect for site i. Site_i is assumed to have a normal distribution with mean zero and standard deviation σ_{Site} . Site_i and Site_j are assumed to be independent when $i \neq j$.
- Error_{ik} is the error term that is assumed to have a normal distribution with mean zero and standard deviation σ_{error} . Error_{ik} is assumed to be independent of Site_j for all j and independent of Error_{i'k'} unless $i=i'$ and $k=k'$.

The model accounts for annual changes in TAC levels and uses observed levels of carbon monoxide to account for spatial and temporal differences within a year. Random effects are included to account for the repeated measurements made at the monitoring sites. A square root transformation was used in order to reduce uneven spread about the average response. A log transformation was not used because some of the measurements were near zero and a log transformation introduced uneven spread at these small values.

When the ambient air concentration of the chemical fell below the device's limit of detection, one-half the limit of detection was put in the data file as a placeholder by CARB. The handling of non-detects is discussed separately for each chemical below.

A model for predicting the annual average of a chemical from the annual average of carbon monoxide was considered but ultimately rejected since, for some chemicals, large numbers of non-detects in the data made calculating the annual averages directly from the data questionable.

A data file containing the annual traffic volume near each monitoring site was obtained from Environmental Health Investigations Branch of the California Department of Public Health. An attempt was made to include the traffic volume as an additional predictor of benzene. Traffic volume did not significantly contribute to the model (i.e., carbon monoxide tended to be higher in areas with more traffic), and was excluded from the final models that were used.

A data file was obtained that contained a land use description of each monitoring site. The data file was obtained from the US EPA web site. An attempt was made to include land use code as an additional predictor of benzene ambient air concentration. Land use codes did not significantly contribute to the model and were excluded from the final models.

Once the model was fit, the best linear unbiased predictor of the square root of the daily average concentration of the toxic chemical was found using the square root of the daily average concentration of carbon monoxide at sites in California. These values were squared to get an estimate of the daily average concentration of the chemical. The daily averages from a site were combined to get an annual average for the monitoring site. A modeled annual average was retained provided it was based on 300 or more daily average estimates. When possible, the

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measured annual average concentration from a monitoring site was used instead of the modeled concentration. The criterion for using the observed annual average from a monitoring site instead of the modeled annual average concentration was that there needed to be 10 or more months of data used to calculate the observed annual average.

Method 3 – Photochemical Assessment Monitoring Stations (PAMS) 24 hour data file

The Photochemical Assessment Monitoring Stations (PAMS) had daily average concentrations from nine sites in the South Coast Air Basin from 1996 to 2011. Data were collected every sixth day. However, the number of daily averages available throughout the year varied by monitoring site and year. Seven of these sites also had carbon monoxide data.

The model for the concentration of a PAMS chemical included an annual trend term and the observed level of carbon monoxide:

$$SqC_{ik} = Intercept + \beta_{Trend}Trend + \beta_{SqCO}SqCO_{ik} + Site_i + Error_{ik}$$

Where

- SqC_{ik} is the square root of the k^{th} daily average ambient air concentration of the chemical from site i .
- Trend is the value of a third degree polynomial with slope set to zero in the years 1996 and 2014. More precisely, let 'year' be the year the measurement was made and $y = \text{year} - 1995$, then $Trend = y^3 - 30*y^2 + 57$.
- Let $SqCO_{ik}$ be the square root of the k^{th} daily average carbon monoxide concentration at site i .
- Let $Site_i$ be a random effect for site i , which is assumed to have a normal distribution with mean zero and standard deviation σ_{Site} . $Site_i$ and $Site_j$ are assumed to be independent when $i \neq j$.
- Let $Error_{ik}$ be the error term, which is assumed to have a normal distribution with mean zero and standard deviation σ_{Error} . $Error_{ik}$ is assumed to be independent of $Site_i$ for all i and independent of $Error_{i'k'}$ unless $i=i'$ and $k=k'$.

The reasons for modeling the annual trend this way included: (1) Some years had sparse data which led to erratic estimates when a separate intercept was included for each year (as was done for the California Toxic Monitoring Network data); (2) The South Coast PAMS data ended in 2011 and OEHHA wanted to extrapolate to 2014; and (3) A review of the PAMS data sets indicated that the annual trend in concentrations between 1996 and 2011 had roughly a backward S shape that could be modeled by this type of polynomial. The appropriateness of the model was checked for each chemical by comparing the estimated population-weighted averages to the observed values (see plots in the Chemical Profiles section of this report).

The model was used to calculate the best linear unbiased predictors of the square root of the daily average chemical concentrations at each monitoring site in the South Coast Air Basin with carbon monoxide data. The square root values were squared to get estimates of the daily average concentrations. These daily averages were combined into annual averages. An

estimated annual average was retained provided it was based on 300 or more daily average estimates. The annual average concentration of the chemical at a site was calculated directly from the PAMS data instead of from the modeled values provided there were at least 10 months of data available from the monitoring site.

Method 4 – Three Hour Data Files

The hourly PAMS data file and DRI data file are described above. Both of these files contained measurements of ambient air concentrations of chemicals collected for 3-hour periods during the summer months. Data from these files were used to estimate chemical concentrations in the South Coast Air Basin using the model described below.

The model for the three-hour average concentration of a chemical was

$$SqC_{ik} = Intercept + \beta_1 SqCO_{ik} + Site_i + Error_{ik}$$

Where

- SqC_{ik} is the square root of the kth three-hour average concentration of the chemical from site i
- $SqCO_{ik}$ is the square root of the kth three-hour average concentration of carbon monoxide from site i.
- $Site_i$ is a random effect for the ith monitoring site. It is assumed to follow a normal distribution with mean 0 and standard deviation σ_{Site} . Random effects are included to account for the repeated measurements made at the monitoring sites. $Site_i$ and $Site_j$ are independent.
- $Error_{ik}$ is random error. $Site_j$ and $Error_{ik}$ are independent for all j. $Error_{ik}$ and $Error_{i'k'}$ are independent unless $i=i'$ and $t=t'$.

The model was used to calculate the best linear unbiased predictors of the square root of the daily average chemical concentrations at each monitoring site in the South Coast Air Basin with carbon monoxide data. These hourly predictions were combined into daily averages and then annual averages for the monitoring site. The annual averages from the monitoring sites were used to create a population-weighted average for the whole air basin.

Acetaldehyde

Acetaldehyde data was extracted from the California Toxic Monitoring Network data. The limit of detection for acetaldehyde was 0.1 ppb from 1990 through 2014. There were very few non-detects in the data set. Between 1996 and 2014, the highest percentage of non-detects (2.5%) occurred in 1999. In the data set, ARB substituted non-detects with 0.05 ppbv (one-half the limit of detection). These substituted values were left in for model fitting and the calculation of annual averages. Acetaldehyde measurements were taken two or three times a month at monitoring stations located in each air basin. The exact number of monitoring stations in an air basin depended on the year. Between 1996 and 2014, the South Coast Air Basin had four to five monitoring stations while other air basins had fewer. A model was developed for estimating the

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daily average concentration of acetaldehyde from the carbon monoxide daily average as described in Method 2 – above. The parameter estimates are shown below.

Covariance Parameter	Estimate
σ_{Site}	0.02409
σ_{Error}	0.07402

Parameter	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.5033	0.03539	25	14.22	<.0001
β_{1996}	-0.0603	0.02162	7998	-2.79	0.0053
β_{1997}	-0.0838	0.0218	7998	-3.84	0.0001
β_{1998}	-0.1534	0.02151	7998	-7.13	<.0001
β_{1999}	-0.0821	0.02178	7998	-3.77	0.0002
β_{2000}	-0.1819	0.02187	7998	-8.32	<.0001
β_{2001}	-0.1366	0.0217	7998	-6.29	<.0001
β_{2002}	-0.1029	0.02185	7998	-4.71	<.0001
β_{2003}	-0.0626	0.02135	7998	-2.93	0.0034
β_{2004}	-0.035	0.02152	7998	-1.63	0.1035
β_{2005}	0.02223	0.02146	7998	1.04	0.3003
β_{2006}	-0.0663	0.02212	7998	-3	0.0027
β_{2007}	-0.0547	0.02192	7998	-2.49	0.0127
β_{2008}	-0.0802	0.02189	7998	-3.66	0.0003
β_{2009}	-0.0503	0.02191	7998	-2.3	0.0217
β_{2010}	-0.014	0.02317	7998	-0.6	0.5459
β_{2011}	-0.0183	0.02239	7998	-0.82	0.4137
β_{2012}	0.01412	0.02199	7998	0.64	0.5208
β_{2013}	0.01647	0.02154	7998	0.76	0.4443
β_{SqCO}	0.7351	0.01295	7998	56.76	<.0001

A previous report found that the 1996 South Coast Air Basin population-weighted concentration of acetaldehyde was 1.75 ppbv based on the TAC data and using a different estimation method (CARB, 1999). The method described in this section gave a population-weighted average of 1.7 ppbv for the South Coast.

Acrolein

Acrolein data were extracted from the California Toxic Monitoring Network data. Acrolein was measured from July 2003 onwards. The limit of detection was 0.3 ppbv. The annual percentage of non-detects from all monitoring site were 6%,12%,17%, 13%, 14%, 3%, 2%, 3%, 3%, 4%, 9% and 4% % in the years 2003 to 2014. The percentage of non-detects dropped dramatically in 2008. When the data from individual monitoring sites were reviewed by year, sites with 3-5 non-detects in 2007 tended to have zero non-detects in 2008 reducing the percent of non-detects.

A model was developed for estimating the daily average concentration of acrolein based on the year of observation and the carbon monoxide daily average (see Method 2 – California Toxic

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Monitoring Network) above. When a measurement fell below the limit of detection, the original data set had one-half the limit of detection as a placeholder. No adjustment was made to these values. Only partial data were available from 2003 so the Chemical Profiles section only has results for 2004 through 2014. The parameter estimates are shown below:

Covariance Parameter	Estimate
σ_{Site}	0.00208
σ_{Error}	0.06006

Parameter	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.7171	0.021	19	34.15	<.0001
β_{2003}	-0.0116	0.02335	4178	-0.5	0.6202
β_{2004}	-0.1274	0.01989	4178	-6.4	<.0001
β_{2005}	-0.106	0.01973	4178	-5.37	<.0001
β_{2006}	-0.0944	0.0203	4178	-4.65	<.0001
β_{2007}	-0.0839	0.02018	4178	-4.16	<.0001
β_{2008}	-0.0166	0.0199	4178	-0.83	0.4038
β_{2009}	0.00533	0.01999	4178	0.27	0.7898
β_{2010}	-0.0117	0.02087	4178	-0.56	0.5741
β_{2011}	0.1009	0.02017	4178	5	<.0001
β_{2012}	0.03414	0.02005	4178	1.7	0.0887
β_{2013}	0.01512	0.02031	4178	0.74	0.4567
β_{SqCO}	0.1612	0.01853	4178	8.7	<.0001

Benzaldehyde

Benzaldehyde data were extracted from the DRI data file. The data had units ppbv so no conversion was necessary. The data were collected at four monitoring sites in the summers of 1995 and 1996 although most of the data came from only three of the sites. Only the 1996 data were used. The hourly concentration of benzaldehyde was positively correlated with the hourly concentration of carbon monoxide. A model was developed for estimating the square root of the hourly concentration of benzaldehyde from the square root of the hourly concentration of carbon monoxide as described in Method 4 above. The parameter estimates are shown below.

Covariance Parameter	Estimate
σ_{Site}	0.00164
σ_{Error}	0.00785

Parameter	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.04967	0.02892	3	1.72	0.1844
β_{SqCO}	0.3227	0.01862	226	17.33	<.0001

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The fixed effects from the model were used to estimate the level of benzaldehyde in the South Coast from 1996 through 2014. The results for benzaldehyde were based on this model and should be interpreted with care due to the extrapolation of results from 1996 to later years. Figure 125 on page 207 compares the estimated population-weighted annual average concentration of benzaldehyde in the South Coast to measurements from around California.

Benzene

Benzene concentration measurements were extracted from the California Toxic Monitoring Network data. CARB adjusted the pre-1999 benzene and 1,3-butadiene data to account for a change in the methodology used to measure benzene and 1,3-butadiene. The limit of detection changed over time. From 1/2/1990 – 12/29/1996 the benzene limit of detection was 0.5 ppb. In 1996, nearly half of the measurements were non-detects. From 1/4/1997-4/19/2001, the limit of detection was 0.2 ppb. After that, the limit of detection was 0.05 ppb. Between 1997 and 2000, the annual percent of non-detects was 21%, 15%, 6% and 8%. The higher percentage of non-detects in 1997 and 1998 compared to 1999 and 2000 seemed to indicate that the adjustment made to pre-1999 data introduced an overabundance of non-detects; this speculation was not investigated further. After 2001, the annual percent of non-detects was 0% to 2%. Non-detects were left equal to half the limit of detection. The annual average benzene concentrations at monitoring sites were estimated using method 2, which was described above. The parameter estimates from the model are shown below.

Covariance Parameter	Estimate
σ_{Site}	0.00435
σ_{Error}	0.02257

Parameter	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	-0.0517	0.01642	25	-3.15	0.0042
β_{1996}	0.07685	0.01191	8132	6.45	<.0001
β_{1997}	0.08307	0.01207	8132	6.88	<.0001
β_{1998}	0.0908	0.01196	8132	7.59	<.0001
β_{1999}	0.07751	0.0121	8132	6.41	<.0001
β_{2000}	0.05934	0.01202	8132	4.94	<.0001
β_{2001}	0.0186	0.01209	8132	1.54	0.1239
β_{2002}	0.03217	0.01228	8132	2.62	0.0088
β_{2003}	0.02638	0.01196	8132	2.21	0.0275
β_{2004}	0.01854	0.01199	8132	1.55	0.1222
β_{2005}	0.00366	0.01197	8132	0.31	0.7598
β_{2006}	0.01073	0.01231	8132	0.87	0.3834
β_{2007}	0.00443	0.01235	8132	0.36	0.7195
β_{2008}	0.00181	0.01221	8132	0.15	0.8823
β_{2009}	0.00489	0.01229	8132	0.4	0.6911
β_{2010}	0.02995	0.01267	8132	2.36	0.0181
β_{2011}	0.01275	0.01238	8132	1.03	0.3033
β_{2012}	0.02721	0.01229	8132	2.21	0.0269
β_{2013}	-0.0091	0.01208	8132	-0.75	0.4532
β_{SqCO}	0.9381	0.00701	8132	133.85	<.0001

1,3-Butadiene

1,3-Butadiene concentrations were extracted from the California Toxic Monitoring Network data. CARB changed to a more accurate method for determining the concentration of 1,3-butadiene and benzene in 1999. The benzene and 1,3-butadiene data from 1998 and earlier were adjusted by CARB to account for the discrepancy resulting from the change in methodology. The limit of detection for 1,3-butadiene was 0.04 ppb. The percentage of non-detects increased steadily from 6% in 1996 to 64% in 2014. A model was developed to estimate the concentration of 1,3-butadiene at additional locations. Non-detects were left equal to half the limit of detection when developing the model. Method 2, described above, was used to estimate the concentration of 1,3-butadiene at monitoring sites with carbon monoxide data. Parameter estimates from the model are shown below.

Covariance Parameter	Estimate
σ_{Site}	0.00138
σ_{Error}	0.00846

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	-0.0943	0.00957	25	-9.85	<.0001
β_{1996}	0.08591	0.0073	8135	11.77	<.0001
β_{1997}	0.07542	0.00738	8135	10.22	<.0001
β_{1998}	0.08207	0.00732	8135	11.21	<.0001
β_{1999}	0.04984	0.00741	8135	6.73	<.0001
β_{2000}	0.03801	0.00736	8135	5.16	<.0001
β_{2001}	0.04112	0.0074	8135	5.56	<.0001
β_{2002}	0.03496	0.00752	8135	4.65	<.0001
β_{2003}	-0.0152	0.00733	8135	-2.07	0.0385
β_{2004}	0.00741	0.00734	8135	1.01	0.3133
β_{2005}	-0.0078	0.00733	8135	-1.06	0.289
β_{2006}	-0.0055	0.00754	8135	-0.73	0.4652
β_{2007}	0.00625	0.00756	8135	0.83	0.4085
β_{2008}	-0.002	0.00748	8135	-0.27	0.7849
β_{2009}	0.01037	0.0075	8135	1.38	0.1668
β_{2010}	0.01259	0.00776	8135	1.62	0.1046
β_{2011}	0.0099	0.00758	8135	1.31	0.1916
β_{2012}	-0.0116	0.00754	8135	-1.54	0.1236
β_{2013}	-0.0022	0.0074	8135	-0.29	0.7702
β_{SqCO}	0.5408	0.0043	8135	125.9	<.0001

Appendix D

Calculation of Population-Weighted Ambient Air Concentrations

Since there were a large number of non-detects in the original data file, a sensitivity analysis was conducted to determine the effect of the non-detect values on the estimated population-weighted average concentrations. A data file with non-detects set equal to the limit of detection was created and the model was fit to this data set. The estimated population-weighted averages based on both data sets are presented in the Chemical Profiles section for comparison.

Butyraldehyde

The butyraldehyde data were downloaded from US EPA AirData website. The data had units ppbC and were converted to ppbv by dividing by 4 (the number of carbon atoms in butyraldehyde). The data were 3-hour measurements from summer months. Half the limit of detection was substituted for non-detects. For each year and site, summary statistics were calculated and reported in the Chemical Profile for butyraldehyde.

Cumene (isopropylbenzene)

Cumene data were taken from the PAMS 24-hour data file. The data were in ppbC and were converted to ppbV by dividing each ppbC measurement by 9. Method 3 was used to estimate the annual average of cumene at monitoring sites in the South Coast Air Basin. The estimated parameters from the model are shown below.

Covariance Parameter	Estimate
σ_{Site}	0.00018
σ_{Error}	0.00832

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.1219	0.00848	9	14.37	<.0001
β_{Trend}	2.2×10^{-5}	1.94×10^{-6}	4129	11.11	<.0001
β_{SqCO}	0.1694	0.00604	4129	28.06	<.0001

Ethylbenzene

Ethylbenzene data were taken from the PAMS 24-hour data file. The California Toxic Monitoring Network data also had ethylbenzene data but most of the values were non-detects and so it was not used. The data were in ppbC and were converted to ppbv by dividing each ppbC measurement by 8. Method 3 was used to estimate the annual average of ethylbenzene at monitoring sites in the South Coast Air Basin. The estimated parameters from the model are shown below.

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Calculation of Population-Weighted Ambient Air Concentrations

Covariance Parameters

Covariance Parameter	Estimate
σ_{Site}	0.00191
σ_{Error}	0.01469

Solution for Fixed Effects

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.1343	0.01674	9	8.02	<.0001
β_{Trend}	3.3×10^{-5}	2.51×10^{-6}	4315	13.21	<.0001
β_{SqCO}	0.5174	0.00779	4315	66.41	<.0001

Formaldehyde

Formaldehyde data were extracted from the California Toxic Monitoring Network data. The limit of detection was 0.1 ppbv. Between 1996 and 2008 the annual percentage of non-detects was less than 1%. In the data file, non-detects were replaced with half the limit of detection. These values were not changed or excluded during model fitting. The annual average of formaldehyde was estimated at monitoring sites with carbon monoxide data using Method 2 (described above). The estimated model parameters are shown below.

Covariance Parameter	Estimate
σ_{Site}	0.04856
σ_{Error}	0.1971

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	1.1275	0.0523	25	21.56	<.0001
β_{1996}	-0.0545	0.03522	7998	-1.55	0.1217
β_{1997}	-0.1035	0.03553	7998	-2.91	0.0036
β_{1998}	-0.1932	0.03505	7998	-5.51	<.0001
β_{1999}	-0.0637	0.0355	7998	-1.79	0.0729
β_{2000}	-0.233	0.03564	7998	-6.54	<.0001
β_{2001}	-0.1192	0.03537	7998	-3.37	0.0008
β_{2002}	0.0123	0.03561	7998	0.35	0.7297
β_{2003}	-0.025	0.03479	7998	-0.72	0.4721
β_{2004}	-0.1214	0.03507	7998	-3.46	0.0005
β_{2005}	-0.1056	0.03499	7998	-3.02	0.0026
β_{2006}	-0.0929	0.03606	7998	-2.58	0.01
β_{2007}	-0.0661	0.03574	7998	-1.85	0.0643
β_{2008}	-0.0767	0.03569	7998	-2.15	0.0317

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Calculation of Population-Weighted Ambient Air Concentrations

Effect	Estimate	Standard Error	DF	t Value	Pr > t
β_{2009}	-0.1727	0.03572	7998	-4.84	<.0001
β_{2010}	-0.0751	0.03777	7998	-1.99	0.0469
β_{2011}	-0.0506	0.0365	7998	-1.38	0.1662
β_{2012}	-0.0727	0.03586	7998	-2.03	0.0428
β_{2013}	-0.0135	0.03512	7998	-0.38	0.7007
β_{SqCO}	0.7506	0.02113	7998	35.53	<.0001

n-Hexane

n-Hexane ambient air concentrations were in the PAMS 24 hour data. The data were converted to ppbv by dividing by 6. The annual average *n*-hexane concentrations at monitoring sites in the South Coast Air Basin were calculated using method 3, which was described above. The estimated model parameters are shown below.

Covariance Parameter	Estimate
σ_{Site}	0.00155
σ_{Error}	0.03898

Fixed Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.1786	0.01965	9	9.09	<.0001
β_{Trend}	2.6×10^{-5}	4.01×10^{-6}	4314	6.44	<.0001
β_{SqCO}	0.6759	0.01265	4314	53.42	<.0001

Isobutene

Data were available from the PAMS hourly data file and the DRI data file. The PAMS hourly data file was ultimately used to build the model. The PAMS hourly data file had data from 1994 through 2013 from sites throughout the state. Most of the observations were from July, August and September. Seven sites in the South Coast Air Basin had data. Six of the seven sites only had data from the years 2001 and 2002. The remaining site (Los Angeles-North Main Street) had data from 1994 to 2001. The measurements from North Main Street were higher than those taken at other sites in the basin. The annual average isobutene concentrations at monitoring sites in the South Coast Air Basin were calculated using method 4, which was described above. Data from the sites in the South Coast Air Basin and from 1996 and later were used to build the model. The data were in ppbC and were converted to ppbV by dividing by 4. The estimated model parameters are shown below.

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Calculation of Population-Weighted Ambient Air Concentrations

Covariance Parameter	Estimate
σ_{Site}	0.02842
σ_{Error}	0.02488

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.01161	0.07051	5	0.16	0.8757
β_{SqCO}	0.8236	0.01695	1687	48.58	<.0001

Isobutene data were also extracted from the DRI data file. The data were collected at four monitoring sites in the summers of 1995 and 1996 although most of the data came from only three of the sites. Only the 1996 data were used. The annual average isobutene concentrations at monitoring sites in the South Coast Air Basin were calculated using method 4, which was described above. The population-weighted annual average ambient air concentrations of isobutene were very similar to those estimated from the PAMS data set. The PAMS hourly data was used because it had data from more sites and a large portion of the measurements came from 2001 and 2002 and not just 1996.

Isoprene

Isoprene data were extracted from the PAMS 24-hour data file. Data were available from 1996 to 2011. A model was not developed for isoprene because an annual temporal trend was not apparent and a model based on carbon monoxide levels was not plausible since most isoprene comes from natural sources. Annual monitoring site averages are reported in the Chemical Profiles section for sites with 12 months of data instead of population-weighted annual averages.

Methyl t-Butyl Ether (MTBE)

Data on MTBE was extracted from the California Toxic Monitoring Network data. The limit of detection was 0.3 ppbv. Between 1996 and 2002 the percent of non-detects ranged from 0% to 4%. In 2003 and 2004, MTBE was phased out and the measured levels of MTBE in the ambient air dropped. The percent of non-detects in 2003 and 2004 was 52% and 99%, respectively. The annual average concentration of MTBE was estimated at sites throughout the state using method 2, which was described at the beginning of this section. Only data from 1996 through 2002 were used to fit the model. Non-detects were left equal to half the limit of detection when fitting the model. The parameter estimates from the model are given below where 2002 is the reference year.

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Calculation of Population-Weighted Ambient Air Concentrations

Covariance Parameter	Estimate
σ_{Site}	0.02702
σ_{Error}	0.05622

Effect	Year	Estimate	Standard Error	DF	t Value	Pr > t
Intercept		0.06859	0.03971	21	1.73	0.0988
β_{1996}	1996	0.2335	0.0241	2720	9.69	<.0001
β_{1997}	1997	0.2592	0.02026	2720	12.79	<.0001
β_{1998}	1998	0.09375	0.01611	2720	5.82	<.0001
β_{1999}	1999	0.1041	0.0167	2720	6.23	<.0001
β_{2000}	2000	0.06273	0.01601	2720	3.92	<.0001
β_{2001}	2001	0.0006	0.01625	2720	0.04	0.9706
β_{SqCO}		1.2632	0.01678	2720	75.28	<.0001

Naphthalene

Naphthalene data were extracted from the DRI data file. The data were collected during July, August and September of 1995 and 1996 at four sites in the South Coast Air Basin. Only the data from 1996 were used for modeling since the gasoline formulation changed that year. The samples were collected over a 3-hour period twice a day. One of the sites only had a few measurements; the model is essentially based on measurements from three sites. The data were in ppbC and were converted to ppbV by dividing by 10. Hourly naphthalene concentrations were positively correlated with carbon monoxide. Method 4 (described above) was used to model the 3-hour average concentrations of naphthalene from the 3-hour average concentrations of carbon monoxide. The parameter estimates from the model are given below.

Covariance Parameters		Estimate			
σ_{Site}		0.001775			
σ_{Error}		0.01768			
Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.1515	0.03595	3	4.21	0.0244
β_{SqCO}	0.2137	0.02639	247	8.1	<.0001

Naphthalene measurements were also available from the National Air Toxics Trends Stations (NATTS). These measurements were 24-hour averages and had units ng/m³. The model for the concentration of naphthalene from the NATTS network was similar to Method 4 but used 24-hour averages instead of 3-hour averages:

$$SqC_{ik} = \text{Intercept} + \beta_{\text{SqCO}}SqCO_{ik} + Site_i + Error_{ik}$$

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Calculation of Population-Weighted Ambient Air Concentrations

Where

- SqC_{ik} is the square root of the k^{th} daily average ambient air concentration of the chemical from site i .
- $SqCO_{ik}$ is the square root of the k^{th} daily average carbon monoxide concentration at site i .
- Let $Site_i$ be a random effect for site i , which is assumed to have a normal distribution with mean zero and standard deviation σ_{Site} . $Site_i$ and $Site_j$ are assumed to be independent when $i \neq j$.
- Let $Error_{ik}$ be the error term, which is assumed to have a normal distribution with mean zero and standard deviation σ_{Error} . $Error_{ik}$ is assumed to be independent of $Site_i$ for all i and j and independent of $\epsilon_{i'j'k'}$ unless $i=i'$, $j=j'$ and $k=k'$.

The parameter estimates from this model are shown below.

Covariance Parameter	Estimate
σ_{Site}	0.7421
σ_{Error}	5.3756

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.7122	0.4889	3	1.46	0.241
β_{SqCO}	12.7946	0.3353	1409	38.15	<.0001

Nitrogen Dioxide

Nitrogen dioxide data were extracted from the database AQDVD2015_Daily Data.accdb, which is available on CARB's 2015 Air Quality Data DVD. The data were average concentrations based on samples collected over 24-hour periods. Annual averages at each monitoring site were calculated using Method 1 above. The average was retained provided it was based on at least 10 months of data. The data from 2014 appeared to be incomplete (about half the sites had 10 or more months of data) and was not used. Between 1996 and 2013, there were 92 to 116 monitoring sites each year with at least 10 months of data. Each site had about 330 measurements per year. The annual averages from each site were used to calculate the population-weighted averages.

Other PAHs

PAHs measured by California Toxic Air Contaminant Network

The California Toxic Monitoring Network data file contained the daily average concentrations of particle-bound TAC PAHs from 1990 through February 2005. There were data from two or three days in each month. When the actual concentration fell below the limit of detection, CARB put one-half the limit of detection in the data file (and we did not adjust these values). The annual

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Calculation of Population-Weighted Ambient Air Concentrations

average was calculated by averaging the measurements at each site (i.e., no modelling was done at other locations).

PAHs measured by NATTS

US EPA NATTS measured ambient air concentrations of PAHs from 3 monitoring sites in California: San Jose in Santa Clara County, Rubidoux in Riverside County and Main Street in Los Angeles between 2008 and 2014. The samples were collected over 24-hour periods at six-day intervals throughout the year. In the data files, we replaced non-detects with half the level of detection. The annual average was calculated by averaging the measurements at each site i.e., no modelling was done at other locations.

PM₁₀

PM₁₀ data were taken from the data file PM10StdDaily20150302.xlsx. The annual average at each monitoring site was calculated as described in Method 1 above. The averages were retained provided they were based on 10 or more months of data. There were between 108 and 163 sites with 10 or more months of data between 1996 and 2013. Each site had about 85 measurements per year. These averages were used to determine the population-weighted averages.

PM_{2.5}

PM_{2.5} data was extracted from the file PM25Daily20150302.xlsx available on CARB's 2015 Air Quality Data DVD. The data were available starting in 1998. The 1998 and 2014 data were incomplete and were not used. Method 1 was used to find monitoring site annual averages for 1999 through 2013. The averages were retained provided they were based on 10 or more months of data. There were 70 to 101 sites with 10 or more months of data each year between 1999 and 2013. Each site had about 150 measurements per year. These averages were used to find the population-weighted averages.

Propionaldehyde

Propionaldehyde data were downloaded from US EPA AirData website. Propionaldehyde data had units ppbC and were converted to ppbv by dividing by 3 (the number of carbon atoms in propionaldehyde). The data were 3-hour measurements from summer months. Half the limit of detection was substituted for non-detects. For each year and site, summary statistics were calculated with the data and reported in the Chemical Profile for propionaldehyde.

Propylene

Propylene data were extracted from the PAMS 24-hour data file. The data came from monitoring sites in the South Coast Air Basin. The data were positively correlated with carbon monoxide. Method 3 was used to estimate the annual average concentration of propylene. The parameter estimates from the model are shown below.

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Calculation of Population-Weighted Ambient Air Concentrations

Covariance parameter	Estimate
σ_{Site}	0.0031
σ_{Error}	0.07795

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.2526	0.02778	9	9.09	<.0001
β_{Trend}	3.6×10^{-5}	5.67×10^{-6}	4314	6.44	<.0001
β_{SqCO}	0.9558	0.01789	4314	53.42	<.0001

Styrene

The styrene data in the California Toxic Monitoring Network data had too many non-detects to be useful (more than 70% of the measurements were non-detects for many years). The styrene data from the nmoc24 data file were used instead. This data file only had data from the South Coast Air Basin. Measurements were available from 1996 to 2011. The data were in ppbC and were converted to ppbV by dividing by 8. Method 3 was used to estimate the annual average of styrene at monitoring sites in the South Coast Air Basin. The estimated model parameters are shown below.

Covariance parameter	Estimate
σ_{Site}	0.00015
σ_{Error}	0.01565

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.2074	0.0104	9	19.95	<.0001
β_{Trend}	2.7×10^{-5}	2.51×10^{-6}	4160	10.92	<.0001
β_{SqCO}	0.1854	0.00815	4160	22.75	<.0001

Toluene

Toluene data were extracted from the California Toxic Monitoring Network data file. The limit of detection was 0.2 ppbv from 1996 to 2014. The number of non-detects increased from 1% to 26% between 1996 to 2014. Method 2, which was described above, was used to estimate the annual average concentration of toluene at monitoring sites. Non-detects were set to half the limit of detection. The estimated model parameters are given below.

Covariance parameter	Estimate
σ_{Site}	0.01895
σ_{Error}	0.1021

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Calculation of Population-Weighted Ambient Air Concentrations

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	-0.1112	0.03482	25	-3.19	0.0038
β_{1996}	0.2229	0.0258	7878	8.64	<.0001
β_{1997}	0.2037	0.02622	7878	7.77	<.0001
β_{1998}	0.1561	0.02665	7878	5.86	<.0001
β_{1999}	0.09627	0.02666	7878	3.61	0.0003
β_{2000}	0.2096	0.02626	7878	7.98	<.0001
β_{2001}	0.1868	0.02611	7878	7.15	<.0001
β_{2002}	0.2153	0.02652	7878	8.12	<.0001
β_{2003}	0.1915	0.02583	7878	7.41	<.0001
β_{2004}	0.1677	0.02589	7878	6.48	<.0001
β_{2005}	0.1561	0.02585	7878	6.04	<.0001
β_{2006}	0.1484	0.02655	7878	5.59	<.0001
β_{2007}	0.1298	0.02663	7878	4.87	<.0001
β_{2008}	0.0918	0.02633	7878	3.49	0.0005
β_{2009}	0.08497	0.02641	7878	3.22	0.0013
β_{2010}	0.1198	0.0273	7878	4.39	<.0001
β_{2011}	0.02933	0.0267	7878	1.1	0.272
β_{2012}	0.07524	0.02652	7878	2.84	0.0046
β_{2013}	0.01956	0.02605	7878	0.75	0.4528
β_{SqCO}	1.4201	0.01522	7878	93.31	<.0001

1,2,3-Trimethylbenzene

1,2,3-Trimethylbenzene data were extracted from the PAMS 24-hour data file. We converted the data, originally in units of ppbC, to ppbV by dividing by 9. There were seven monitoring sites with 1,2,3-trimethylbenzene and carbon monoxide data. Most of the data were from 2001 and later. Data from two sites (2166 and 2492) were excluded due to possible errors prior to 2007 per SCAQMD. Method 3 was used to estimate the levels of 1,2,3-trimethylbenzene from the more densely monitored carbon monoxide. The estimated model parameters are shown below.

Covariance parameter	Estimate
σ_{Site}	0.00023
σ_{Error}	0.00669

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.2559	0.00947	7	27.02	<.0001
β_{Trend}	5.7×10^{-5}	2.07×10^{-6}	2940	27.48	<.0001
β_{SqCO}	0.1786	0.00677	2940	26.4	<.0001

1,2,4-Trimethylbenzene

1,2,4-Trimethylbenzene data were extracted from the PAMS 24-hour data file. The data were converted from ppbC to ppbV by dividing by 9. Data from two sites (2166 and 2492) were excluded due to possible errors prior to 2007 per SCAQMD. Model 3 was used to estimate the annual average concentrations of 1,2,4-trimethylbenzene at monitoring sites in the South Coast Air Basin where carbon monoxide data were available.

The model parameter estimates are given below.

Covariance Parameter	Estimate
σ_{Site}	0.00077
σ_{Error}	0.01384

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.3292	0.01458	7	22.58	<.0001
β_{Trend}	0.00009	2.84×10^{-6}	3011	31.8	<.0001
β_{SqCO}	0.3915	0.00949	3011	41.24	<.0001

1,3,5-Trimethylbenzene

1,3,5-Trimethylbenzene data were extracted from the PAMS 24-hour data file. The data were converted from ppbC to ppbV by dividing by 9. Data from two sites (2166 and 2492) were excluded due to possible errors prior to 2007 per SCAQMD. Method 3 was used to estimate the annual average concentration of 1,3,5-trimethylbenzene at sites with carbon monoxide data.

The estimated model parameters are given below.

Covariance Parameter	Estimate
σ_{Site}	0.00053
σ_{Error}	0.0057

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	0.1665	0.01073	7	15.52	<.0001
β_{Trend}	4.5×10^{-5}	1.85×10^{-6}	2999	24.38	<.0001
β_{SqCO}	0.2897	0.00613	2999	47.23	<.0001

m- & p-Xylene

m- & p-Xylene data were extracted from the California Toxic Monitoring Network data file. The limit of detection was 0.6 ppbv between 1996 and early 2001. After that, the limit of detection was 0.2 ppbv. Between 1996 and 2000, the annual fraction of measurements that fell below the limit of detection ranged from 42% to 63%. Between 2001 and 2014, the annual percent of non-detects increased from 2% to 49%. When the concentration fell below the limit of detection, CARB put one-half the limit of detection into the data set as a placeholder. These values were left in the data set for modeling. Three large outliers were dropped from the data set. Method 2 was initially used to calculate the annual average of *m- & p-xylene* at monitoring sites but the resulting population-weighted averages fluctuated too much. Instead, Method 3 was used to estimate the annual average concentration of *m- & p-xylene* at monitoring sites. The parameter estimates for the model are shown below.

Covariance Parameter	Estimate
σ_{Site}	0.0078
σ_{Error}	0.05363

Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	-0.0551	0.02058	25	-2.68	0.0129
β_{Trend}	-1.28×10^{-6}	2.50×10^{-6}	7815	-0.51	0.607
β_{SqCO}	1.0819	0.01102	7815	98.22	<.0001

Since some years of data had a large number of non-detects, a sensitivity analysis was carried out to determine whether the non-detects would have a substantial effect on the estimated population-weighted average concentration of *m- & p-xylene*. A data set was created with the limit of detection, which varied by year, put in for the non-detect values. There were noticeable differences between the analyses done with the two data sets. The population-weighted average results from the two analyses are included in Chemical Profiles for comparison.

o-Xylene

o-Xylene data were extracted from the California Toxic Monitoring Network data file. The limit of detection was 0.1 ppb. Each year between 15% and 43% of the measurements were non-detects; these were recorded as 0.05 ppb. Method 2 was used to estimate the annual average at monitoring sites. The estimated model parameters are in the tables below.

Covariance Parameter	Estimate
σ_{Site}	0.00255
σ_{Error}	0.01754

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Effect	Estimate	Standard Error	DF	t Value	Pr > t
Intercept	-0.0399	0.01366	25	-2.92	0.0073
β_{1996}	0.01221	0.01096	7769	1.11	0.2652
β_{1997}	-0.0389	0.01113	7769	-3.49	0.0005
β_{1998}	-0.0767	0.01137	7769	-6.75	<.0001
β_{1999}	-0.0227	0.0114	7769	-1.99	0.0463
β_{2000}	-0.006	0.01115	7769	-0.53	0.5927
β_{2001}	0.00148	0.01108	7769	0.13	0.8937
β_{2002}	0.06567	0.01125	7769	5.84	<.0001
β_{2003}	0.0435	0.01097	7769	3.97	<.0001
β_{2004}	0.02853	0.01099	7769	2.6	0.0095
β_{2005}	-0.0051	0.01098	7769	-0.46	0.6448
β_{2006}	-0.0013	0.01126	7769	-0.12	0.9069
β_{2007}	0.00386	0.01129	7769	0.34	0.7321
β_{2008}	0.00954	0.01117	7769	0.85	0.3932
β_{2009}	0.02045	0.01121	7769	1.83	0.068
β_{2010}	0.04414	0.01157	7769	3.82	0.0001
β_{2011}	-0.0032	0.01132	7769	-0.28	0.7779
β_{2012}	0.034	0.0114	7769	2.98	0.0029
β_{2013}	0.01557	0.01121	7769	1.39	0.1649
β_{SqCO}	0.642	0.0063	7769	101.96	<.0001

A sensitivity analysis was conducted to determine the effect of the non-detect values on the estimated population-weighted average concentrations. A data set was formed with non-detect values set to 0.1. The same model was fit to the data set and the population-weighted average concentrations were calculated. The estimated population-weighted average concentrations calculated from the data set is included in the Chemical Profiles section of o-xylene for comparison.

Method for Estimating the Annual Average Concentration at Each Census Tract

The annual average concentration of a compound at each census tract was estimated by combining the annual average concentrations from nearby monitoring stations (where nearby is defined to be less than 30 km). The formula for estimating the concentration at the j^{th} census tract from the data from nearby monitoring stations was:

$$c_j = \frac{\sum_{i=1}^{n_j} b_i/d_{ij}^2}{\sum_{i=1}^{n_j} 1/d_{ij}^2}$$

Where:

n_j = number of monitoring stations within 30 km of the j^{th} census tract

b_i = annual average concentration at the i^{th} monitoring station

d_{ij} = distance from the i^{th} monitoring station to the j^{th} census tract

Appendix D

Calculation of Population-Weighted Ambient Air Concentrations

The distance squared weighting was used in a previous report (CARB, 1999). If there were no observations within 30 km of the census tract, then no estimate was made for the population in that census tract.

The distances from the monitoring stations to the census tract centroids were calculated according to the formula below. The formula assumes that the earth is spherical.

$$D = R \cdot \arccos(\sin(L1) \sin(L2) + \cos(L1) \cos(L2) \cos(DG))$$

Where:

R = 6371 km is the average radius of the earth

L1 = latitude at the first point

L2 = latitude at the second point

DG = longitude of the second point minus longitude of the first point

D = computed distance (km)

arccos in radians

Method for Calculating the Population-Weighted Annual Average Concentrations

The annual average concentration of a chemical was estimated at monitoring sites throughout an air basin (p. 360). These annual averages were used to estimate the concentration of the chemical at census tracts in the air basin by using an inverse distance squared weighting scheme to combine the monitoring site averages (p. 379).

A weighted average of the census tract chemical concentration estimates was found using the census tract populations as weights. The air basin population-weighted annual average concentration was calculated according to the formula:

$$\frac{\sum_{i=1}^m [(p_i c_i)]}{\sum_{i=1}^m p_i}$$

Where:

c_i = annual average concentration at each census tract

p_i = population in the census tract

m = number of census tracts (with concentration estimates) in the air basin

Each monitoring station was assigned an air basin in CARB's "location" data file. Census tracts were assigned to air basins by determining which monitoring station the census tract was closest to and assigning the monitoring station's air basin to the census tract.

Where possible a statewide population-weighted average concentration was estimated. The method used depended on the data available.

Methods for Estimating the Census Tract Populations

Every ten years, when the decennial census is done, the boundaries of some census tracts are altered (e.g., a census tract may be split into two separate tracts due to a large population increase). The impact on this study is that some of the 1990 and 2000 and 2010 census tracts do not match up. The US census bureau provides files that map 2000 census results into the 1990 census tracts and 2010 results into 2000 census tracts. The files for mapping 2000 census results to 1990 census tracts and 2010 census results to 2000 census tracts were capop19902000.txt and capop20002010.txt; they were downloaded from the US census website <http://www.census.gov>. The California Department of Finance carried out this mapping for census 2000 and provided the results on their website in the file “1970-1980-1990-2000 comparability file.xls”. The file contained the latitude, longitude, 1990 population and 2000 population of each 1990 census tract. The 2010 populations of the 2010 census tracts were obtained from the US census website. The mapping files were used to add the 2010 populations of the 1990 census tracts to the comparability file. Estimates of the census tract populations for the years 1996 to 2000 were obtained by linearly interpolating between the 1990 and 2000 populations as follows $p_{year,i} = p_{1990,i} + (p_{2000,i} - p_{1990,i}) / 10 \times (year - 1990)$ where $p_{year,i}$ is the population from census tract i for year. A similar method was used to interpolate the 2000 and 2010 census tract populations.

A different approach was used to estimate the census tract populations for 2011 to 2015. The California Department of Finance provides a data file with annual estimates of the California county populations for 2011 to 2015 (E-42015InternetVersion.xls). The 2010 census tract and county populations were used to determine the ratio of each census tract population to its county population. These ratios were then applied to the 2011 county populations to estimate the census tract populations in 2011. The same approach was used to get the 2012-2015 census tract populations.

Appendix E Method for Determining Gasoline-Attributable Fractions

Introduction

The gasoline-attributable fraction of a chemical is the fraction of the ambient air concentration of a chemical that came from gasoline-related sources. It was estimated as the ratio of emission tonnage from gasoline-related sources divided by emission tonnage from all sources:

$$\text{Gasoline-attributable fraction} = \frac{\text{tons of chemical from gasoline-related sources}}{\text{tons of chemical from all sources}}$$

If the chemical had a significant portion of its ambient air concentration coming from secondary atmospheric reactions, then the previous formula was modified as follows:

$$\text{Gasoline-attributable fraction} = \frac{\text{tons of chemical from gasoline-related sources and secondary reactions}}{\text{tons of chemical from all sources and secondary reactions}}$$

If the chemical had all of its ambient air concentration coming from secondary atmospheric reactions, then the previous formula was modified as follows:

$$\text{Gasoline-attributable fraction} = \frac{\text{tons of chemical from gasoline-related secondary reactions}}{\text{tons of chemical from all secondary reactions}}$$

The emission tonnage information came from the CARB's Emission Inventory. Based on input from CARB, all sources with material code equal to 1100 were identified as gasoline-related sources. Some chemicals were emitted directly from the sources, and referred to as primary emission products. The tonnage of these chemicals was derived directly from the Emission Inventory. Other chemicals were formed in significant proportions as both primary emission products and as products of secondary atmospheric reactions. The tonnage from these secondary reactions was calculated using the Emission Inventory and direct formation potential values provided by Carter (2001). A detailed description of how the direct formation potential was used is provided below.

Data Source: Emission Inventory Extracts

A description of CARB's Emission Inventory is available at <https://www.arb.ca.gov/ei/ei.htm>. CARB provided to OEHHA Emission Inventory extracts, which include estimates of the amount of pollutants discharged into the atmosphere by source categories, for each air basin, and within a specified time span. The extracts covered the following years: 1996 to 2006 (data file received in August 2008); 2007 (data file received in August 2009); 2008 (data file received in August 2010); and 2010 to 2012 (data file received in October 2015). Some additional notes on the Emission Inventory extracts are provided below:

- CARB's approach for estimating ROG and TOG emissions from natural sources was changed in 2002, and this affected gasoline-attributable fractions for chemicals like

Appendix E Method for Determining Gasoline-Attributable Fractions

1,3-butadiene and acetaldehyde that had large natural source components. These changes are noted where relevant in the Chemical Profiles.

- Natural source emission estimates were not available for 2009 to 2011, so the 2008 values were used for those years. The statewide ROG and TOG emissions attributed to natural sources differed by about 10% between 2008 and 2012.
- Mobile source emissions were not available for 2009, so gasoline-attributable fractions could not be calculated for that year. Estimates for 2008 were applied as a proxy.

Primary Emission Tonnage

This section describes how the primary emission tonnage of a chemical was calculated.

CARB provided data files that contained the estimated annual tons of total organic gases (TOG) (i.e., gaseous organic compounds including both reactive organic gases and the relatively unreactive organic gases such as methane) emitted by sources throughout California. The data were extracted from CARB's Emission Inventory and covered the years 1996 to 2012. The TOG of an emission source included all the chemicals released as primary emissions from the source. The TOG of each emission source was separated into component primary emission chemicals using the source's chemical speciation profile. These data were aggregated into two lists: The first list had the primary emissions weight of each chemical by air basin and year for all sources. The second list had the primary emissions weight of each chemical by air basin and year for gasoline-related sources only.

Calculating Tonnage of Secondary Formation Products

This section describes how the tonnage of a chemical from secondary atmospheric reactions was calculated.

A formation potential is the percentage of each primary emission chemical that reacts to form another chemical. Under contract with OEHHA, Dr. William Carter determined formation potentials for twelve reaction products: formaldehyde, acetaldehyde, lumped higher aldehydes, benzaldehyde and other aromatic aldehydes, acrolein, cresols, nitrophenols and aromatic nitro-compounds, lumped alkyl nitrates, peroxyacetyl nitrate (PAN), higher saturated acyl peroxy nitrates, peroxybenzoyl nitrate and other aromatic acyl peroxy nitrates (PBzN) and unsaturated PAN analogues such as that formed from methacrolein. The formation potentials were used to determine secondary formation for selected pollutants, described in detail below.

The tons of a secondary product were calculated by finding the amount of secondary product formed from each primary emission product and then adding them up. The rest of this section explains this calculation in detail. Let A_i and C_i be the primary emissions weight of the i th chemical from gasoline-related sources and all sources, respectively. The weight of secondary product j from all sources is referred to here as " D_j ". D_j was calculated by multiplying the primary emissions weight of each chemical C_i by the direct formation potential of the secondary product (f_{ij}) and summing over all chemicals, as follows

Appendix E Method for Determining Gasoline-Attributable Fractions

$$D_j = \sum_{i=1}^n C_i f_{ij}$$

where n is the number of distinct primary emission chemicals from all sources. The weight of secondary product j from gasoline-related sources is referred to here as “ B_j ”. It was calculated as

$$B_j = \sum_{i=1}^n A_i f_{ij}$$

There were direct formation potentials for some chemicals to themselves (e.g., formaldehyde to formaldehyde). These direct formation potentials, where $f_{jj} > 0$, were not used. Chemicals of interest falling in this group included: formaldehyde, higher aldehydes, acetaldehyde, cresol, acrolein and benzaldehyde.

Calculating Gasoline-Attributable Fractions

For chemical i :

A_i = weight of chemical from primary emissions from gasoline-related sources

B_i = weight of chemical formed from secondary reactions
for which the input chemicals were emitted from gasoline-related sources

C_i = weight of chemical from primary emissions from all sources

D_i = weight of chemical formed from secondary reactions
for which the input chemicals were emitted from all sources

The gasoline-attributable fraction for primary emissions only was calculated as A_i/C_i .

The gasoline-attributable fraction for chemicals in primary emissions products and also formed through secondary reactions was calculated as $(A_i + B_i)/(C_i + D_i)$. Acetaldehyde, acrolein, aromatic aldehydes (e.g., benzaldehyde), formaldehyde and higher aldehydes (i.e., propionaldehyde) fell in this category.

Cresols, nitrophenols and aromatic nitrates, lumped alkyl nitrates, peroxyacetyl nitrate (PAN), higher saturated acyl nitrates, aromatic acyl peroxy nitrates (e.g., peroxybenzoyl nitrate) and unsaturated PAN analogues are mostly produced through secondary reactions. Their gasoline-attributable fractions were calculated as B_i/D_i .

Air Basin and Year Specific Gasoline-Attributable Fractions

The Emission Inventory included the air basin where the emissions source was located and the year the emissions occurred. Based on this information, separate gasoline-attributable fractions were calculated for the five most populated air basins by year. The air basins were the South

Appendix E Method for Determining Gasoline-Attributable Fractions

Coast Air Basin, San Diego, San Francisco Bay Area, San Joaquin Valley and Sacramento Valley Air Basins.

Statewide gasoline-attributable fractions were also calculated using Emission Inventory data from all the air basins.

Some Notes on Calculating Gasoline-Attributable Fractions for Specific Chemicals

- Formation potentials were only available for aromatic aldehydes as a group. The Emission Inventory included two aromatic aldehydes: benzaldehyde and tolualdehyde. The primary emission tonnage of “aromatic aldehydes” was calculated by adding the primary emission tonnage of benzaldehyde and tolualdehyde.
- Formation potentials were only available for higher aldehydes as a group. The Emission Inventory included a number of higher aldehydes (hexaldehyde, propionaldehyde, butyraldehyde, isovaleraldehyde, glutaraldehyde, isobutyraldehyde and decanal). The primary emission tonnage of “higher aldehydes” was calculated by adding the primary emission tonnage of these higher aldehydes together.
- Gasoline-attributable fractions were calculated for nitrogen oxides. The ambient air monitoring data were for nitrogen dioxide. It was assumed that the gasoline-attributable fractions for NO_x could be applied to nitrogen dioxide.
- The Emission Inventory did not include secondary formation of particulate matter. Gasoline-attributable fractions of $\text{PM}_{2.5}$ were estimated from source attribution studies of $\text{PM}_{2.5}$ which included both primary emissions and secondary formation of $\text{PM}_{2.5}$. These estimates are described in the Chemical Profile for PM
- Gasoline-attributable fractions of PM_{10} were based on the primary emissions data from the Emission Inventory. Secondary formation of PM_{10} was not included.
- In the Emission Inventory, the emission tonnages of NO_x , $\text{PM}_{2.5}$ and PM_{10} are stored separately from the TOG and so the step (mentioned above) of splitting the TOG into component chemicals based on speciation profiles was not required here.
- Directly emitted cresols in the Emission Inventory came from non-gasoline-related sources and included *o*-cresol and cresylic acid.
- Nitrophenols do not appear in the Emission Inventory. Some aromatic nitro-compounds do appear in the Emission Inventory including nitrobenzene, 2,2-dichloronitroaniline, bromodinitroaniline (2,4-dinitro-6-bromoaniline) and bromodinitrobenzene. These directly emitted aromatic nitro-compounds came from non-gasoline sources that were linked to speciation profiles for industrial processes, mineral products, textile products and organic chemical storage.
- Alkyl nitrates do not appear in the Emission Inventory so direct emissions of alkyl nitrates were estimated to be zero.
- PAN does not appear in the Emission Inventory and its primary emission tonnage was estimated to be zero.

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Method for Determining Gasoline-Attributable Fractions

- Primary emission tonnage of higher saturated acyl peroxy nitrates was estimated to be zero because they did not appear in the Emission Inventory.
- Primary emissions of aromatic acyl peroxy nitrates were estimated to be zero because they do not appear in the Emission Inventory.
- Primary emissions of unsaturated PAN analogues were estimated to be zero because they were not in the Emission Inventory.

Gasoline-Attributable Annual Average Concentration

The gasoline-attributable annual average concentration of a chemical was calculated by multiplying the estimated population-weighted annual average concentration of an air basin by the appropriate gasoline-attributable fraction.

Example Calculation Based on Primary Emissions Only – Benzene

The estimated gasoline-attributable fraction of benzene in the South Coast in 1996 was 0.81, based on primary emissions. The details of this calculation are shown below.

Primary emissions weight of benzene from gasoline-related sources (tons per year)	7,304
Primary emissions weight of benzene from all sources (tons per year)	9,023
Gasoline-attributable fraction for benzene	7,304/9,023 or 0.81

Example Calculation Based on Primary and Secondary Emissions – Formaldehyde

Formaldehyde is found in primary emissions and formed in secondary atmospheric reactions. The estimated gasoline-attributable fraction of formaldehyde in the South Coast in 1996 was 0.63, based on both primary and secondary emissions. The details of this calculation are shown below.

Primary emissions weight of formaldehyde from gasoline-related sources (tons per year) ("A")	4,817
Weight of formaldehyde from secondary reactions from gasoline-related sources (tons per year) ("B")	14,256
Primary emissions weight of formaldehyde from all sources (tons per year) ("C")	9,591
Weight of formaldehyde from secondary reactions from all sources (tons per year) ("D")	20,826
Gasoline-attributable fraction for formaldehyde	$(A+B)/(C+D) = 0.63$

Appendix E
Method for Determining Gasoline-Attributable Fractions

The partial calculation of “B” (defined above) is shown below:

Year	Air basin	Primary emitted VOCs	Tons from gasoline sources (A _i)	Direct formation potential (f _{ij}) of formaldehyde	Formaldehyde secondary product weight
1996	SC	2,2,3-Trimethylbutane	55.0	0.028653846	1.6
1996	SC	Methane	20,725.5	0.000508882	10.5
1996	SC	Ethane	3,210.6	0.005376256	17.3
1996	SC	Ethylene	16,764.9	0.251697436	4,219.7
1996	SC	Propane	2,157.3	0.003547051	7.7
<i>Additional rows for all gasoline-related VOCs - table is truncated for space reasons</i>					
Total formaldehyde from secondary reactions from gasoline-related sources (tons per year)					14,256

The partial calculation of “D” (defined above) is shown below:

Year	Air basin	Primary emitted VOC	Tons from all sources (C _i)	Direct formation potential (f _{ij}) of formaldehyde	Formaldehyde secondary product weight
1996	SC	2,2,3-Trimethylbutane	62.5	0.028653846	1.8
1996	SC	Methane	155,157.7	0.000508882	79.0
1996	SC	Ethane	21,388.3	0.005376256	115.0
1996	SC	Ethylene	24,660.7	0.251697436	6,207.0
1996	SC	Propane	8,588.6	0.003547051	30.5
<i>Table is truncated to save space</i>					
Total formaldehyde from secondary reactions from all sources (tons per year)					20,826

Additional Comments on Gasoline-Attributable Fractions

The source apportionment procedure relied heavily on values tabulated in CARB’s Emission Inventory. Possible problems that could affect the calculated gasoline-attributable fractions include missing sources, inaccurate estimates of pollution tonnage and inaccurate source profiles. The Emission Inventory tabulated primary emissions only.

The chemical profiles include explanations for why the gasoline-attributable fractions of specific chemicals change dramatically. One reason was that the total organic gas (TOG) from a source was updated over time to a much different value. Another reason was that the source was linked to a new source profile. These two changes could cause large changes in the estimated tonnage of a chemical released into the air. In turn, this caused large changes in the estimated

Appendix E Method for Determining Gasoline-Attributable Fractions

gasoline-attributable fraction of the chemical from one year to the next. For example, the tons emitted from natural sources, including wildfires and other biogenic sources were revised in 2002 as part of Western Regional Air Partnership (WRAP) so that estimates in different regions were similar. The revision had a dramatic effect on the gasoline-attributable fraction of many chemicals. After that year, the tonnage was kept constant for many natural sources in the Emission Inventory. Another example is the introduction of new source profiles following the prohibition of MTBE from gasoline.

Appendix F References

Carter WP (2001). Determination of Aldehyde and PAN Formation Potentials for Volatile Organic Compounds. Air Pollution Research Center University of California, Riverside. Prepared under contract with OEHHA.

Appendix F Summary of Research Results from Interagency Agreement with UC Riverside

OEHHA entered into an Interagency Agreement with the University of California Riverside (UCR) from 2006 to 2008 to determine the presence and concentrations of atmospheric reaction products of gasoline-related emissions in ambient air (OEHHA agreement number 06-E0016). Dr. Janet Arey was the principal investigator. The project involved both laboratory methods development work and ambient air analyses. The focus of the work was on measuring atmospheric products of gasoline-related volatile aromatic compounds (such as benzene, ethylbenzene) and PAHs. Arey and colleagues published two papers describing results of the project (Obermeyer et al., 2009; Arey et al., 2009). Research reported in a third paper (Nishino et al., 2008) was partially supported by this agreement.

The project arose out of earlier OEHHA-supported work to describe the atmospheric chemistry of gasoline-related compounds. Atkinson and Arey summarized the known or predicted atmospheric products of gasoline-related VOCs, PAHs and nitro-PAHs or classes of compounds (OEHHA, 2006). The research described in this Appendix was primarily undertaken to determine whether certain toxic products that were predicted to occur from gasoline-related emissions could be measured in ambient air.

Arey et al. (2009) carried out chamber studies to investigate the dicarbonyl reaction products of toluene, xylenes and trimethylbenzenes, all of which are emitted from gasoline-powered vehicles. The dicarbonyls were chosen because of the known and suspected toxicity of these types of compounds. Arey et al. observed glyoxal, methylglyoxal and diacetyl, which are 1,2-dicarbonyls. They also identified 1,4-dicarbonyls such as 1,4-butenedial and 3-hexene-2,5-dione. The 1,4-dicarbonyls were generally observed in lower yield than the 1,2-dicarbonyls.

Obermeyer et al. (2009) reported on ambient air measurements of the carbonyl atmospheric reaction products of aromatic hydrocarbons and other VOCs. They collected ambient air samples in Riverside in 2008. The table below summarizes the carbonyls and dicarbonyls that were identified in the ambient air samples, along with the possible VOC precursors of those atmospheric reaction products.

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Interagency Agreement with UC Riverside

Carbonyls and dicarbonyls identified in ambient air from Riverside, California, November 18-19 2008

(adapted from Obermeyer *et al.*, 2009)

Carbonyl	Structure	Possible VOC precursors
Aromatic carbonyls		
Benzaldehyde	C ₆ H ₅ CHO	Toluene, ethylbenzene
<i>o</i> -Tolualdehyde	<i>o</i> -CH ₃ C ₆ H ₄ CHO	<i>o</i> -Xylene
<i>m</i> -Tolualdehyde	<i>m</i> -CH ₃ C ₆ H ₄ CHO	<i>m</i> -Xylene
<i>p</i> -Tolualdehyde	<i>p</i> -CH ₃ C ₆ H ₄ CHO	<i>p</i> -Xylene
Acetophenone	C ₆ H ₅ C(O)CH ₃	Ethylbenzene
1,2-dicarbonyls		
Glyoxal	(CHO) ₂	Aromatics and other VOCs
Methylglyoxal	CH ₃ C(O)CHO	Aromatics and other VOCs
Diacetyl	CH ₃ C(O)C(O)CH ₃	<i>o</i> -Xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene
Ethylglyoxal ^a	CH ₃ CH ₂ C(O)CHO	Ethylbenzene, ethyltoluenes
Unsaturated 1,4-dicarbonyls		
2-Butenedial (unsaturated form of 1,4-butanedial)	HC(O)CH=CHCHO	Toluene, ethylbenzene, <i>o</i> -xylene, <i>o</i> -ethyltoluene
3-Hexene-2,5-dione ^a	CH ₃ C(O)CH=CHC(O)CH ₃	<i>p</i> -Xylene, 1,2,4-trimethylbenzene
Other dicarbonyls		
Malonaldehyde	HC(O)CH ₂ CHO	<i>n</i> -Butane
3-Oxo-butanal ^a	CH ₃ C(O)CH ₂ CHO	<i>n</i> -Pentane
1,4-Butanedial ^a	HC(O)CH ₂ CH ₂ CHO	<i>n</i> -Butane

^aObermeyer *et al.* (2009) noted that, to their knowledge, these were the first reported observations in ambient air of these compounds.

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Nishino et al. (2008) measured formation yields of nitro products from the atmospheric reactions of toluene, naphthalene and biphenyl, and examined the effect of the nitrogen dioxide concentration. The researchers also measured ambient air concentrations of selected aromatic hydrocarbons and nitrated aromatic hydrocarbons in Upland, California, the location of a South Coast Air Quality Management District (SCAQMD) monitoring station. A key conclusion of this work is that, for nitrogen dioxide concentrations found in urban areas, nitro-PAH formation from atmospheric OH radical-initiated reactions will occur. This conclusion was supported both by the laboratory investigations and the ambient analyses.

The table below summarizes the ambient air measurements taken in 2006 and 2007.

Appendix F Summary of Research Results
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Ambient aromatic, nitroaromatic, and nitrogen dioxide concentrations in Upland, CA in 2006 and 2007 (adapted from Nishino et al., 2008).

Date	10/22/06	10/23/06	10/24/06	10/28/06	9/12/07	9/18/07	9/26/07	10/25/07
	Toluene and PAH (ng m ⁻³)							
Toluene	4400	5890	8980	4510	6276	3643	4956	9404
Naphthalene	60.7	101.1	139.5	100.3	159.3	70.9	104.1	265.5
Biphenyl	6.9	10.2	13.6	8.5	13.8	7.5	9.9	22.3
	Nitroaromatics (pg m ⁻³)							
3-Nitrotoluene	695	753	1723	407	1005	780	488	995
1-Nitronaphthalene	58.3	84.6	78.6	108.3	101.9	38.9	42.9	94.3
2-Nitronaphthalene	71.4	88.7	79.2	91.3	69.5	25.5	39.9	78.7
3-Nitrobiphenyl	22.5	42.8	39.6	21.2	45.0	9.5	23.5	50.9
	Nitrogen dioxide (ppbv)							
Nitrogen dioxide	12	24	28	26	20	17	17 ^a	33 ^a

a. Data not available from Upland, CA. Value given is from Fontana, CA, the nearest downwind SQAQMD monitoring station.

Appendix F References

Arey J, Obermeyer G, Aschmann SM, Chattopadhyay S, Cusick RD, Atkinson R (2009). Dicarbonyl products of the OH radical-initiated reaction of a series of aromatic hydrocarbons. *Environ Sci Technol* 43:683-689.

Nishino N, Atkinson R, Arey J (2008). Formation of nitro products from the gas-phase OH radical-initiated reactions of toluene, naphthalene, and biphenyl: Effect of NO₂ concentration. *Environ Sci Technol* 42:9203-9209.

Obermeyer G, Aschmann SM, Atkinson R, Arey J (2009). Carbonyl atmospheric reaction products of aromatic hydrocarbons in ambient air. *Atmos Environ* 43:3736-3744.

Office of Environmental Health Hazard Assessment (OEHHA, 2006). Atmospheric Chemistry of Gasoline-Related Emissions: Formation of Pollutants of Potential Concern. Reproductive and Cancer Hazard Assessment Section, OEHHA, California Environmental Protection Agency. Available at:
<https://oehha.ca.gov/media/downloads/air/document/atmoschemgas.pdf>

Appendix G Screening Health Risk Assessment Methods For VOCs and PAHs

This Appendix provides additional details on the screening risk assessment used for gasoline-related VOCs and PAHs.

Methods for Estimating Cancer Risks for Gasoline-Related VOCs

Gasoline-attributable cancer risks for gasoline-related VOCs, including naphthalene, were estimated for the South Coast Air Basin and statewide, based on the five most populous air basins (South Coast, San Diego, San Francisco Bay Area, San Joaquin Valley and Sacramento Valley). These five air basins account for approximately 80% of the total California population. The cancer risk calculations take into account early-in-life sensitivity using the method described in OEHHA (2015).

The method for estimating the cancer risk is explained using acetaldehyde as an example. The cancer risk is based on the gasoline-attributable population-weighted annual average ambient air concentration of acetaldehyde (also referred to as gasoline-attributable concentration). The gasoline-attributable concentration of acetaldehyde in the South Coast Air Basin in 1996 was estimated to be 1.1 ppb, which was converted to 1.98×10^{-3} mg/m³ using the conversion factor from Table 108 below. The concentration had to be converted to match the units of the cancer potency values.

Table 108. Conversion factors and cancer potency values for selected VOCs

Chemical	Conversion factor ¹ at 25 ° C and 1 atm	Cancer potency value ² (mg/kg-day) ⁻¹
Acetaldehyde	1 ppm = 1.8 mg/m ³	1.0×10^{-2}
Benzene	1 ppm = 3.2 mg/ m ³	1.0×10^{-1}
1,3-Butadiene	1 ppm = 2.21 mg/ m ³	6.0×10^{-1}
Ethyl benzene	1 ppm = 4.35 mg/ m ³	8.7×10^{-3}
Formaldehyde	1 ppm = 1.24 mg/ m ³	2.1×10^{-2}
Methyl <i>t</i> -butyl ether (MTBE)	1 ppm = 3.6 mg/ m ³	1.8×10^{-3}
Naphthalene	1 ppm = 5.24 mg/ m ³	1.2×10^{-1}
Styrene	1 ppm = 4.26 mg/m ³	2.6×10^{-2}

Notes:

1. Conversion factors for all chemicals except naphthalene came from Appendix B of the report "Air Toxics Hot Spots Risk Assessment Guidelines Part II: Technical Support Document for Cancer Potency Factors" (OEHHA, 2009). The conversion factor for naphthalene came from the NIOSH Pocket Guide to Chemical Hazards.
2. Cancer potency values were obtained from OEHHA (2015).

Appendix G
Screening Health Risk Assessment Calculations

The average daily dose (ADD) for each age range was calculated using the formula:

$$ADD_{\text{age range}} = (\text{Air concentration}) \times (\text{Body weight adjusted breathing rate}_{\text{age range}})$$

The body weight adjusted breathing rates are presented in Table 109.

Table 109. Inhalation rates and age sensitivity factors

Age Range	95th Percentile Inhalation Rate ¹ (L/kg-day)	Age Sensitivity Factor ²
3rd Trimester	361	10
0<2 years	1090	10
2<16 years	745	3
16<70 years	290	1

Notes:

1. OEHHA (2015) Table I-2
2. OEHHA (2015) Table I-4

The calculation of the average daily dose for each lifestage is shown in Table 110 below:

Table 110. Example calculation of average daily dose for acetaldehyde in the South Coast Air Basin in 1996.

Age range	Concentration (mg/m ³)	95th Percentile body weight adjusted breathing rate (L/kg-day)	Average daily dose (mg/kg-day)
3rd trimester	0.00198	361	7.15 x10 ⁻⁴
0<2 years	0.00198	1090	2.16 x10 ⁻³
2<16 years	0.00198	745	1.48 x10 ⁻³
16<70 years	0.00198	290	5.74 x10 ⁻⁴

The cancer risk was calculated using the following formula

$$\text{Cancer risk} = \sum_{\text{age range}} [(ADD_{\text{age range}} \times \text{CPF} \times \text{ASF}_{\text{age range}} \times [\text{fraction of lifetime}])]$$

where $ADD_{\text{age range}}$ is the average daily dose for the age range, CPF is the cancer potency factor, $ASF_{\text{age range}}$ is the age sensitivity factor, and fraction of lifetime is calculated as length of age range divided by 70.

Appendix G
Screening Health Risk Assessment Calculations

The gasoline-attributable cancer risk from exposure to an ambient air concentration of 1.1 ppb acetaldehyde was calculated to be 2.0×10^{-5} as shown in Table 111 below.

Table 111. Example calculation of cancer risk from exposure to acetaldehyde in the ambient air in the South Coast Air Basin in 1996

Age Range	Average daily dose (mg/kg-day)	Cancer Potency Factor	ASF	Duration (years)	Cancer Risk
3rd Trimester	7.15×10^{-4}	0.01	10	0.3	3.1×10^{-7}
0<2 years	2.16×10^{-3}	0.01	10	2	6.2×10^{-6}
2<16 years	1.48×10^{-3}	0.01	3	14	8.9×10^{-6}
16<70 years	5.74×10^{-4}	0.01	1	54	4.4×10^{-6}
Sum					2.0×10^{-5}

Methods for Estimating Cancer Risks For Selected PAHs

This section discusses methods for PAHs other than naphthalene, which is addressed as a VOC in the previous section. A list of PAHs with cancer potency factors or potency equivalency factors was compiled and refined to include only those PAHs with monitoring data in the South Coast Air Basin (see Table 3 on p. 31). It was not possible to calculate gasoline-attributable fractions for these PAHs because, unlike the volatile PAH naphthalene, they are not included in the CARB Emission Inventory. Therefore, we conservatively assumed a gasoline-attributable fraction of 1 and cancer risks were calculated using the total ambient air concentrations. Cancer potency factors and potency equivalency factors (PEF) were obtained from OEHHA (2015) and are listed in Table 112. To determine a cancer potency factor based on a PEF, the benzo[a]pyrene inhalation cancer potency factor was multiplied by the PEF (see Table 116). For details on the cancer risk calculation, see the previous section.

Table 112. Inhalation cancer potency factors for gasoline-related PAHs with ambient air data (OEHHA, 2015)

Chemical	Inhalation cancer potency factor (mg/kg-day) ⁻¹	PEF
Benz[a]anthracene ¹	3.9 E-1	0.1
Benzo[a]pyrene	3.9	--
Benzo[b]fluoranthene ¹	3.9 E-1	0.1
Benzo[k]fluoranthene ¹	3.9 E-1	0.1
Chrysene ¹	3.9 E-2	0.01
Dibenz[ah]anthracene	4.1	--
Indeno[1,2,3-cd]pyrene ¹	3.9 E-1	0.1

Notes:

1. Cancer potency estimated from benzo[a]pyrene potency

Appendix G
Screening Health Risk Assessment Calculations

The sources used for PAH ambient air data are listed below and described on p. 247.

Abbreviation	Data source
Calif. Toxics	CARB's California Toxic Monitoring Network
Eiguren-Fernandez et. al	South Coast Air Basin ambient air study of PAHs (Eiguren-Fernandez et al., 2004)
MATES III	Multiple Air Toxics Exposure Study in the South Coast Air Basin (South Coast Air Quality Management District, 2008)
US EPA NATTS	Ambient air data from the National Air Toxics Trends Network downloaded from the US EPA AirData website (https://aqs.epa.gov/api)

Many of these PAH data sets had a large number of non-detects. Non-detects were set equal to half the limit of detection prior to calculating the annual average.

Methods for Estimating Non-Cancer Hazard Quotients

Gasoline related chemicals were included if a gasoline-attributable concentration was calculated for the South Coast Air Basin and a chronic reference exposure level (cREL) was available.

Statewide hazard quotients were not calculated for respiratory toxicants because it was not possible to estimate a statewide population-weighted average concentration for acrolein, naphthalene, or propylene. The hazard quotients for the South Coast Air Basin should be conservative estimates since the gasoline-attributable concentrations in the South Coast Air Basin are typically higher than those statewide. For example, the average acrolein ambient air concentrations and the gasoline-attributable fractions for acrolein tended to be higher in the South Coast Air Basin compared to other air basins.

Similarly, statewide hazard quotients were not calculated for nervous system toxicants because of data limitations. For two of the neurotoxicants, n-hexane and styrene, data were inadequate to estimate statewide gasoline-attributable concentrations. For the remaining neurotoxicants, benzene, toluene, and xylenes, the hazard quotients for the South Coast Air Basin will be conservative estimates, because the ambient air concentrations of these chemicals are higher in the South Coast compared to statewide values.

Chronic RELs were obtained from OEHHA (2015). The hazard quotient for a chemical was calculated according to the equation below.

$$\text{Gasoline-attributable hazard quotient} = \frac{\text{Gasoline-attributable concentration of chemical}}{\text{cREL}}$$

Table 113 lists the cRELs used in this report and the associated hazard index target organs or systems (OEHHA, 2015).

Appendix G
 Screening Health Risk Assessment Calculations

Table 113. List of cRELS

Chemical	cREL (ppb)	Target Organs/Systems
Acetaldehyde	80	Respiratory
Acrolein	0.15	Respiratory
Benzene	1	Hematologic
1,3-Butadiene	1	Reproductive/development
Ethylbenzene	400	Alimentary; reproductive/development; endocrine; kidney
Formaldehyde	7	Respiratory system
Methyl <i>t</i> -butyl ether (MTBE)	2000	Alimentary; eye; kidney
Naphthalene	2	Respiratory
n-Hexane	2000	Nervous
Propylene	2000	Respiratory
Styrene	200	Nervous
Toluene	70	Reproductive/development; nervous; respiratory
<i>m</i> -, <i>o</i> - and <i>p</i> -Xylene	200	Eye; nervous; respiratory

US EPA (2016) developed an RfC of 6×10^{-2} mg/m³ (12 ppb) for trimethylbenzenes based on increased pain sensitivity. US EPA (1997) also developed an RfC for cumene of 0.4 mg/m³ (80 ppb) based on toxicity to endocrine and urinary systems.

References for Appendix G

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US EPA (1997). Toxicological Review of Cumene. Available at: https://cfpub.epa.gov/ncea/iris/iris_documents/documents/toxreviews/0306tr.pdf

US EPA (2016). Toxicological Review of Trimethylbenzenes (Final Report). Available at: https://cfpub.epa.gov/ncea/iris/iris_documents/documents/toxreviews/1037tr.pdf

Appendix H Gasoline-Related PAHs and Related Compounds

The following table contains a list of PAHs, nitro-PAHs, oxo-PAHs and selected other polycyclic matter that were determined to be gasoline-related. The chemicals are sorted by molecular weight. The footnotes indicate if a cancer potency value (used for calculating cancer risk) has been developed, if a chronic reference exposure level (cREL) has been developed, if a gasoline-attributable fraction was calculated and if ambient air data were available. The main sources used to identify gasoline-related PAHs included: CARB's Emission Inventory and four recent automobile exhaust speciation studies (Schauer et al. 2002, Zielinska et al. 2004, Riddle et al. 2007, and the Department of Energy National Renewable Energy Laboratory Gasoline/Diesel PM Split Study³¹).

CASRN	Chemical name	Molecular weight
91-20-3	Naphthalene ^{1,2,3,4}	128
	Dihydronaphthalenes	130
83-33-0	1-Indanone	132
90-12-0	1-Methylnaphthalene ³	142
91-57-6	2-Methylnaphthalene ³	142
208-96-8	Acenaphthylene ⁴	152
83-32-9	Acenaphthene ⁴	154
	1&2-Ethylnaphthalene	156
	Dimethylnaphthalenes	156
86-73-7	Fluorene ⁴	166
	Methylbiphenyls	168
	C3-Naphthalenes including trimethylnaphthalenes, 1-ethyl-2-methylnaphthalene, 2-ethyl-1-methylnaphthalene	170
86-57-7	1-Nitronaphthalene	173
120-12-7	Anthracene ⁴	178
85-01-8	Phenanthrene ⁴	178
486-25-9	9-Fluorenone ⁴	180
548-39-0	Perinaphthenone; 1H-phenalen-1-one	180
	Methylfluorenes	180

³¹ See for example, Lough et al. 2007 and Fujita et al. 2007. A summary of the Gasoline/Diesel PM Split Study is available at <http://www.arb.ca.gov/research/seminars/doe/doe.htm>. Archived results from Gasoline/Diesel PM Split Study are available at: http://web.archive.org/web/20121010113724/http://www.nrel.gov/vehiclesandfuels/nfti/feat_split_study.html.

Appendix H
Gasoline-Related PAHs and Related Compounds

CASRN	Chemical name	Molecular weight
82-86-0	Acenaphthenequinone	182
132-65-0	Dibenzothiophene	184
	C4-Naphthalenes	184
	Methyl nitronaphthalenes	187
	Methylantracenes	192
	Methylphenanthrenes	192
90-44-8	Anthrone	194
90-47-1	Xanthone	196
	C2-Fluorenes	196
129-00-0	Pyrene ⁴	202
201-06-9	Acephenanthrylene	202
206-44-0	Fluoranthene ⁴	202
	Dimethylphenanthrenes	206
84-65-1	Anthraquinone	208
	Methylpyrene / methylfluoranthene	216
602-60-8	9-Nitroanthracene	223
203-12-3	Benzo[ghi]fluoranthene	226
	Benzo[bjk]fluoranthene	226
195-19-7	Benzo(c)phenanthrene	228
218-01-9	Chrysene ^{1,4}	228
217-59-4	Triphenylene	228
27208-37-3	Cyclopenta[cd]pyrene ⁴	228
56-55-3	Benz(a)anthracene ^{1,4}	228
61523-34-0	Benzonaphthothiophene	234
483-65-8	Retene ⁴	234
	5-Methylchrysene ¹	242
	6-Methylchrysene	242
2541-69-7	7-Methylbenz(a)anthracene	242
892-21-7	3-Nitrofluoranthene	247
5522-43-0	1-Nitropyrene ¹	247
192-97-2	Benzo[e]pyrene (BeP) ⁴	252
198-55-0	Perylene ⁴	252
205-99-2	Benzo[b]fluoranthene ^{1,4}	252
50-32-8	Benzo[a]pyrene (BaP) ^{1,4}	252
207-08-9	Benzo[k]fluoranthene ^{1,4}	252
205-82-3	Benzo[j]fluoranthene ¹	252
2498-66-0	Benz(a)anthracene-7,12-dione	258
500024-84-0	7-Methylbenzo(a)pyrene	266
20268-51-3	7-Nitrobenzo[a]anthracene	273

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Gasoline-Related PAHs and Related Compounds

CASRN	Chemical name	Molecular weight
7496-02-8	6-Nitrochrysene	273
191-24-2	Benzo(ghi)perylene ⁴	276
193-39-5	Indeno[1,2,3-cd]pyrene ^{1,4}	276
193-43-1	Indeno[1,2,3-cd]fluoranthene	276
215-58-7	Dibenz(ac)anthracene	278
53-70-3	Dibenz(ah)anthracene ^{1,4}	278
63041-90-7	6-Nitrobenzo[a]pyrene	297
191-07-1	Coronene ⁴	300
	PAH MW 302 ⁵	302
	PAH MW 326 ⁵	326
	PAH MW 350 ⁵	350
	PAH MW 374 ⁵	374

1. Cancer potency factor or potency equivalency factor available
2. cREL available
3. Gasoline-attributable fraction calculated
4. Ambient air data available
5. Riddle et al. (2007) did not specify more than the molecular weights of these PAHs

Appendix H References

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Zielinska B, Sagebiel J, McDonald JD, Whitney K, Lawson DR. (2004). Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles. *J Air Waste Manag Assoc*, 54(9), 1138-1150.

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