Report to the Air Resources Board
on the Proposed Identification of Diesel Exhaust as a Toxic Air Contaminant

Part A

Exposure Assessment

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REPORT TO THE AIR RESOURCES BOARD ON DIESEL EXHAUST

Part A - Public Exposure To, Sources and Emissions of
Diesel Exhaust in California

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I.
SUMMARY

This document, prepared by staff of the Air Resources Board (ARB), contains the staff's evaluation of atmospheric exposure to diesel exhaust in California. It is Part A of the Technical Support Document Proposed Identification of Diesel Exhaust as a Toxic Air Contaminant, and was developed under the authority of California's Toxic Air Contaminant (TAC) Program (Assembly Bill 1807: Health and Safety Code sections 39660-39662).

This report contains the staff evaluation of diesel exhaust PM_{10} and $PM_{2.5}$ (particulate matter equal to or less than 10 and 2.5 microns in diameter, respectively) emissions, outdoor ambient and indoor air concentrations, potential near source exposures, statewide population-weighted exposures including an estimate of total exposure, and atmospheric persistence and fate.

Diesel exhaust is a complex mixture of inorganic and organic compounds that exist in gaseous, liquid, and solid phases. As with other fuel combustion sources, the primary gaseous components are nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), and water vapor (H_2O). Some of the exhaust components, like arsenic, benzene, and nickel, are known to cause cancer in humans. Over 40 components of the exhaust, including suspected human carcinogens benzo[a]pyrene, 1,3-butadiene, and formaldehyde, have been listed as TACs by the ARB, and as hazardous air pollutants by the U.S. EPA.

One of the main characteristics of diesel exhaust is the release of particles at a rate of about 20 times greater than from gasoline-fueled vehicles (WHO, 1996). Diesel exhaust particles carry many of the harmful organics and metals present in the exhaust. The particles are typically smaller than 1 micrometer [(μm) 1 millionth of a meter] in diameter, and are easily inhaled into the bronchial and alveolar regions of the lung.

The combustion of diesel fuel in an internal combustion engine produces diesel exhaust. Approximately 2.1 billion gallons of diesel fuel were burned in internal combustion engines in California during 1995. The future estimated diesel fuel consumption is predicted to increase in California from current levels up to 2.3 billion gallons in 2000 to 2.9 billion gallons in 2010.

Three major sources emit diesel exhaust in California: mobile sources (on-road vehicles and other mobile sources), stationary area sources (i.e. oil and gas production facilities, shipyards, repair yards), and stationary point sources (i.e., chemical manufacturing, electric utilities). Emissions of carbon monoxide (CO), oxides of nitrogen (NO_x), oxides of sulfur (SO_x), reactive organic gases (ROG), PM_{10}, and $PM_{2.5}$ are estimated in this report. For 1995, emissions of diesel exhaust CO are estimated to be about 188,000 tons per year (tpy); NO_X to be about 415,000 tpy; SO_x to be about 28,000 tpy; and ROG to be about 41,000 tpy. Diesel exhaust PM_{10} and $PM_{2.5}$ emissions during 1995 were estimated to be about 27,000 tpy and 26,000 tpy, respectively.

Statewide emission estimates for other substances found in diesel exhaust are not known (i.e. list of TACs in Table III-1). Further research is needed to estimate emissions from these substances.

In this report, California's population exposure to fine diesel exhaust particulate matter (PM_{10}) is discussed in more detail because more is known about the particulate fraction, and many researchers believe that the diesel exhaust particles contain many of the toxic components of the exhaust. However, the exposure actually experienced in most health studies, particularly the human studies, has been to the overall exhaust. Until more research is done to identify the specific causes of toxicity in diesel exhaust, the identification of whole diesel exhaust is consistent with the basis of health studies.

To estimate Californian's outdoor ambient exposures to diesel exhaust PM_{10}, ARB staff used receptor modeling techniques, which includes chemical mass balance model results from several studies, ambient 1990 PM_{10} monitoring network data, and 1990 PM_{10} emissions inventory data. The staff used the 1990 PM_{10} inventory and monitoring data as the basis for calculating the statewide exposure to diesel exhaust PM_{10} because it would best represent the emission sources in the years when the ambient data were collected for the studies used to estimate 1990 diesel exhaust PM_{10} outdoor concentrations. The staff estimated a population-weighted average outdoor diesel exhaust PM_{10} exposure concentration in California in 1990 to be 3.0 micrograms per cubic meter ($\mu g/m^3$). The staff have also estimated outdoor exposure concentrations for 1995 based on linear extrapolations from the base year 1990 to the 1995 emissions inventories. The estimated 1995 outdoor ambient concentration in California is 2.2 $\mu g/m^3$.

Near-source exposures to diesel exhaust may occur near busy roads and intersections where diesel vehicles are operating. In December 1993, the ARB conducted a study to determine diesel exhaust PM_{10} concentrations due to emissions of diesel exhaust particles near a freeway. Results indicate that diesel exhaust PM_{10} concentrations may be up to five times above 1995 average outdoor ambient concentrations of 2.2 $\mu g/m^3$ and about six times above the 1995 total air exposure concentration of 1.5 $\mu g/m^3$.

To estimate Californian's indoor and total air exposure to diesel exhaust particles, the staff used the 1990 population-weighted outdoor ambient concentration estimates in a model that can estimate indoor air concentrations and total air exposure. The exposure modeling results indicate that, in 1990, Californian's were exposed to average diesel exhaust particle concentrations of 2.0 $\mu g/m^3$ and 2.1 $\mu g/m^3$ for indoor and total air exposure scenarios, respectively. The staff have also estimated indoor and total air exposure concentrations for 1995. These estimates were not developed using the model used in calculating the 1990 indoor and total air exposure estimates. Instead, the staff used the ratios of indoor and total air exposure concentrations to outdoor ambient exposure concentrations and applied these to the 1995 outdoor ambient concentration estimate to calculate 1995 indoor and total air exposure concentrations. The estimated 1995 indoor and total air exposure concentrations are 1.47 $\mu g/m^3$ (rounded to 1.5 $\mu g/m^3$) and 1.54 $\mu g/m^3$ (rounded to 1.5 $\mu g/m^3$), respectively.

As mentioned above, diesel exhaust is a complex mixture of substances, and each substance will remain in the air or react with other substances according to the substance's individual chemical properties. The diesel particles are typically smaller than 1 micron and are expected to remain in the air for about 10 days.

Over the past 20 years, several advances in engine design and fuel formulation have been made in reducing diesel exhaust emissions as a result of control measures that have been adopted by the ARB and U.S. EPA. For example, as part of California's overall program to reduce harmful exposures to particulate matter, current and in the future, the ARB and the U.S. EPA have adopted a series of mobile source standards and regulations to reduce diesel exhaust PM_{10} emissions (see Chapter IV). As a measure of the effectiveness of these standards and regulations, statewide diesel exhaust PM_{10} emissions from on-road mobile sources are expected to be reduced by approximately 80 percent between 1990 and 2010 or about 60 percent from 1995 to 2010.

The U.S. EPA has also adopted a National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$ (particulate matter equal to or less than 2.5 microns in diameter). The federal Clean Air Act requires that the U.S. EPA establish NAAQS' and reassess, at least every five years, whether adopted standards are adequate to protect public health based on current scientific evidence. After review, the U.S. EPA's Clean Air Scientific Advisory Committee (CASAC) found that current PM_{10} standards do not adequately protect public health. For this reason, on July 18, 1997, the U.S. EPA adopted an annual $PM_{2.5}$ federal standard of 15 micrograms per cubic meter ($\mu g/m^3$) and a 24-hour federal standard of 65 $\mu g/m^3$. The addition of the $PM_{2.5}$ standards will result in substantially more health protection than the current federal PM_{10} standards alone. We are looking at how this standard may affect the need for further diesel engine exhaust particle controls, realizing that a larger percentage of the fine $PM_{2.5}$ inventory (as compared to PM_{10} inventory) is due to petroleum-based fuel combustion sources.

Diesel exhaust is in the identification (risk assessment) phase of our air toxics program. While no new control measures specific to the toxicity of diesel exhaust are being proposed at this time, a number of existing sources of diesel engine exhaust are already subject to California regulations requiring reductions of criteria air pollutants contained in diesel exhaust. If diesel exhaust is identified as a TAC, the ARB will begin a full, open public process to evaluate the need, feasibility, and cost of control to determine if any regulatory action is necessary to reduce the risk of exposure to diesel exhaust.

II.
INTRODUCTION

This report (Part A) consists of the ARB staff evaluation of the public exposures to, sources and emissions of diesel exhaust in California. It provides the exposure assessment portion of the evaluation of diesel exhaust as a toxic air contaminant (TAC), pursuant to California's Toxic Air Contaminant Program (Health and Safety Code section 39660). The Office of Environmental Health Hazard Assessment (OEHHA) has developed a comprehensive health evaluation of diesel exhaust (Part B report). Together, these documents serve as the basis for ARB's proposed identification of diesel exhaust as a TAC.

Diesel exhaust entered into the identification program in October 1989. In March 1990, the ARB sponsored a conference on the risk assessment of diesel exhaust. On June 17, 1994, the first draft report was released to the public for a six month comment period. On September 14, 1994, a public workshop was held to discuss the report. On January 29-30, 1996, the OEHHA, ARB, Health Effects Institute, National Institute for Occupational Safety and Health, World Health Organization, and the U.S. EPA sponsored a scientific workshop to discuss the application of human health study data in developing quantitative cancer risk estimates for diesel exhaust. A second version of the draft report was released for public comment in May 1997. On July 1, 1997, a third public workshop was held to discuss the second draft of the report.

This version of the report reflects the public comments received on the exposure assessment during the first and second public comment periods and at the September 1994, January 1996, and July 1997 workshops. Currently, the SRP is planning to hold a special public meeting in early March 1998 to hear from invited scientists, with expertise in the study of diesel exhaust, to hear their research and perspectives on diesel exhaust health effects. It is the SRP's view that the material presented and discussed at this meeting will assist in a better understanding of the science regarding the health effects of diesel exhaust. After this meeting, and the end of the third comment period, the report, along with the comments received and any revisions resulting from the comments, will be formally discussed with the SRP at a duly noticed meeting. We anticipate that this meeting will occur in late April 1998. If the SRP approves the report, the report, and a proposal to formally list diesel exhaust as a TAC, will be presented to the ARB at a public hearing, after a 45-day comment period.

III.

CHEMICAL AND PHYSICAL PROPERTIES OF DIESEL EXHAUST

Diesel exhaust is a complex mixture that contains thousands of inorganic and organic substances (IARC, 1989) which occur in the form of gases and fine particles (composed of liquid and solid materials). The composition of this mixture will vary depending on engine type, operating conditions, fuel, lubricating oil, and whether an emission control system is present. Many of the individual exhaust constituents remain unidentified. Appendix A contains a list of substances and substance groups that have been either positively identified in diesel exhaust, detected (but not quantified in the exhaust), found in the fuel and/or lubricating oil and expected to be emitted in the exhaust, or theorized to be present in the exhaust based on known chemical reactions. Further research is needed to estimate many of these components contribution to whole diesel exhaust and the resulting atmospheric concentrations.

A. Diesel Exhaust's Primary Component Groups

Diesel engines operate with excess air (around 25-30 parts air to 1 part fuel: Lassiter and Milby, 1978). Consequently, the primary gaseous components of whole diesel exhaust are nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), and water vapor (H_2O).

Diesel exhaust also contains substances such as carbon monoxide, oxides of nitrogen, sulfur dioxide, hydrocarbons, particulate matter, aldehydes, ketones, sulfates, cyanides, phenols, metals, and ammonia (Volkswagen, 1989). These substances are unburned fuel and lubricant components, products of incomplete combustion, or are a result of engine wear or trace contaminants in the fuel and lubricating oil.

Emissions from diesel engines have and continue to be regulated to reduce emissions of carbon monoxide, nitrogen oxides, sulfur oxides, hydrocarbons, and particulate matter (see Chapter IV, section D) as part of the effort to control emissions of criteria pollutants in California. Emissions of many toxic species in diesel exhaust are correspondingly being reduced as the existing criteria pollutant standards and regulations are implemented.

B. Toxic Air Contaminants in Diesel Exhaust

Diesel exhaust contains substances formally listed as toxic air contaminants (TACs) by the State of California and as hazardous air pollutants by the U.S. EPA. Section 39655 of California's Health and Safety Code defines a TAC as an air pollutant which "may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health."

Table III-1 is a list of TACs that have either been identified in diesel exhaust, or are predicted to be in diesel exhaust based on observed chemical reactions and/or their presence in the fuel or lubricating oil. Further research is needed to determine the contribution of many of these substances to atmospheric diesel exhaust exposures. The exhaust constituents arsenic, benzene, and nickel are known to cause cancer in humans (IARC, 1987). These three constituents, in addition to 1,3-butadiene, cadmium, dioxins/dibenzofurans, and formaldehyde, have been listed by the ARB as TACs under California's air toxics identification program (Health and Safety Code section 39660). At least 35 other diesel exhaust components and component groups were identified by the ARB as TACs in April 1993, under Assembly Bill (AB) 2728 (Tanner, 1992; Health and Safety Code section 39656). AB 2728 required all federally-listed hazardous air pollutants to be identified as TACs by the ARB.

C. Gas Phase Components

The composition of diesel exhaust gases is similar to that of gasoline engine gases, but because of the relatively higher air to fuel ratio which causes engines to have more complete combustion at increased temperatures, carbon monoxide (CO) and hydrocarbons (HC) occur in lower concentrations in diesel exhaust. However, the emissions of oxides of nitrogen (NO_x), PM, and sulfur compounds is higher (the latter due to the higher sulfur content of the fuels).

As mentioned above, diesel exhaust is composed of both gaseous and particle phase compounds. The gas, or vapor phase, contains typical combustion gases N_2, O_2, CO_2, and volatile hydrocarbon species (Zaebst, 1991). They include classes of compounds such as aldehydes (e.g. formaldehyde, acetaldehyde), alkanes, alkenes, and aromatic compounds (e.g. benzene, toluene, 1,3-butadiene), many of which are known or potential carcinogens.

These gas phase compounds primarily originate from the unburned fuel and lubricating oil, although some may be formed during the combustion process and by reaction with catalysts (Johnson, et al. 1994). The emissions of some of the individual organic components and classes of compounds, summarized as total hydrocarbons, have been measured by a number of researchers for the individual gaseous substances such as 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, benzene, toluene, ethylbenzene, and xylenes (Volkswagen, 1989; Egeback & Bertilsson, 1983; Hamerle et al., 1994).

Other gas phase components of diesel exhaust, as well as other fuel combustion sources, are low-relative molecular mass PAH and nitro-PAH derivatives (volatile 2- to 4-ring PAH and 2-ring nitro-PAH). Atmospheric reactions of these gas phase PAH and nitro-PAH derivatives may lead to the formation of several mutagenic nitro-PAH, and nitro-PAH compounds, including nitrodibenzopyranones, 2-nitroflouranthene and 2-nitropyrene (Atkinson and Arey, 1994;

Table III-1
Substances in Diesel Exhaust Listed by the ARB as Toxic Air Contaminants*

TACs identified under Health and Safety Code section 39660

arsenic
benzene
1,3-butadiene
cadmium
dioxins and dibenzofurans
formaldehyde
nickel
inorganic lead

TACs identified under Health and Safety Code section 39656

acetaldehyde
acrolein
aniline
antimony compounds
beryllium compounds
biphenyl
bis[2-ethylhexyl]phthalate
chlorine
chlorobenzene
**chromium compounds
cobalt compounds
cresol isomers
cyanide compounds
dibutylphthalate
ethyl benzene
hexane
manganese compounds
mercury compounds
methanol
methyl ethyl ketone
naphthalene
4-nitrobiphenyl
phenol
phosphorus
***POM, including PAHs and their derivatives
propionaldehyde
selenium compounds
styrene
toluene
xylene isomers and mixtures
o-xylenes
m-xylenes
p-xylenes

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* Further research is needed to quantify the concentrations of many of these substances before one can assess the contribution of each of these substances to atmospheric diesel exhaust exposures.

** The valence state of exhaust chromium is unknown, but a portion of total chromium emitted may be in the +VI valence state. Chromium VI is a known human carcinogen and has been identified by the ARB as a TAC.

*** POM (polycyclic organic matter) represents a large group of compounds having at least two benzene rings and a boiling point greater than or equal to 100 degrees Celsius. The PAHs (polycyclic aromatic hydrocarbons) are a subset of POM, and also represent a large number of compounds. Several PAHs can be converted to more potent substances in the exhaust stream or in the atmosphere. For example, benzo[a]pyrene can be converted to 3-nitro-benzo[a]pyrene, a potentially powerful mutagen (Finlayson-Pitts and Pitts, 1986; IARC, 1989).

Arey et al., 1987; Atkinson et al., 1988). It is also believed that the majority of the ambient nitro-PAH are now thought to be formed in the atmosphere from gas phase reactions of PAH of four or less rings (Atkinson and Arey, 1994).

Although the above studies provided some quantitative estimates on the compounds mentioned, further research is needed to quantify the gaseous components of diesel exhaust from a variety of engines and test conditions before quantitative estimates of many of the gas phase components can be made.

D. Particulate Matter

Diesel exhaust is characterized by a significantly higher content of particulate matter than that of a gasoline-fueled vehicle (Volkswagon, 1989; Williams, 1989; WHO, 1996). The amount and composition of particles emitted from various diesel engines varies greatly, depending on factors like engine design, load, operating speed, fuel composition, and engine emission controls. In general, newer heavy-duty trucks emit about 20 times more particulate than catalyst-equipped gasoline- fueled vehicles (WHO, 1996). However, depending on operating conditions, fuel composition, and engine control technology, light-duty diesel engines can emit 50 to 80 times and heavy-duty diesel engines 100 to 200 times more particulate mass than typical catalytically equipped gasoline engines (McClellan, 1986).

In urban areas, mobile sources are major contributors to ambient PM_{10} concentrations. Several studies have demonstrated the importance of these sources (Watson et al., 1988; Chow et al., 1991; Wittorff et al., 1994; Gertler et al., 1995; Chow et al., 1996). Chow et al. (1991) looked at PM_{10} and $PM_{2.5}$ source contributions in Phoenix in the winter of 1989-1990. Chemical characteristics of source emissions and ambient concentrations were used as input data to the chemical mass balance (CMB) receptor model which calculates the contributions to the atmospheric PM_{10}. Results indicated that primary motor vehicles contributed up to 52 percent of the observed ambient PM_{10} concentrations, of which, at least 50 percent was derived from diesel engine exhaust. In a similar study done in Bullhead City, Arizona during 1988-1989, Gertler et al. (1995) estimated that primary motor vehicle emissions contribute a yearly average of 17 percent of the measured ambient PM_{10} concentrations. In another study, Wittorf et al. (1994) used the CMB receptor model to apportion the sources of ambient PM_{10} observed at a site heavily impacted by diesel emissions. Results showed that primary diesel exhaust emissions contributed an average of about 53 percent of the ambient PM_{10} mass observed. In a study done by Chow et al., (1996) in Santa Barbara, California, aerosol samples were analyzed chemically using standard methods, and source contributions to PM_{10} were determined using the CMB model. Results showed that primary motor vehicle emissions were responsible for up to 42 percent of the PM_{10} mass.

1. Particle Formation

Studies have shown that the primary soot particles in diesel exhaust are formed in the combustion chamber by nucleation of heavy relative molecular weight PAH (Johnson et al., 1994), with a large percentage of these being oxidized during the expansion stroke (Luo et al., 1989). The particles that survive oxidation typically agglomerate together to form the long chain aggregates or clusters associated with diesel particles (Kittleson et al. 1985). The final particle processes occur in the atmosphere. These are mainly photochemical reactions and to a lesser extent particle surface reactions. It is also possible to have gas-to-particle conversion due to the nucleation of hydrocarbons, oxides of nitrogen, or oxides of sulfur (Baumgard and Johnson, 1996).

2. Particle Size Distribution

Studies have shown that the particle size distribution of diesel exhaust is bi-modal with a nuclei mode (0.0075 to 0.042 μm in diameter) and an accumulation mode (0.042 to 1.0 μm in diameter) (Baumgard and Johnson, 1996), most of which occur in aerodynamic diameters ranging from 0.1 to 0.25 μm (Groblicki and Begeman, 1979; Dolan et al., 1980; National Research Council, 1982; Williams, 1982). Approximately 98 percent of the particles emitted from diesel engines are less than 10 microns in diameter, 94 percent less than 2.5 microns in diameter, and 92 percent less than 1.0 microns in diameter (see Table III-2) (ARB, 1997). The light absorbing black portion of these particles, commonly referred to as elemental carbon (EC), is determined to be a major contributor to reduced visibility in urban areas (Gray, 1986; Trijonis et al., 1990).

Table III-2
Diesel Exhaust Particle Size Distribution*

$\leq$ 1.0 *u*m	$\leq$ 2.5 *u*m	$\leq$ 10 *u*m
92%	94%	98%

* Based on ARB 1995 emission inventory (ARB, 1997)

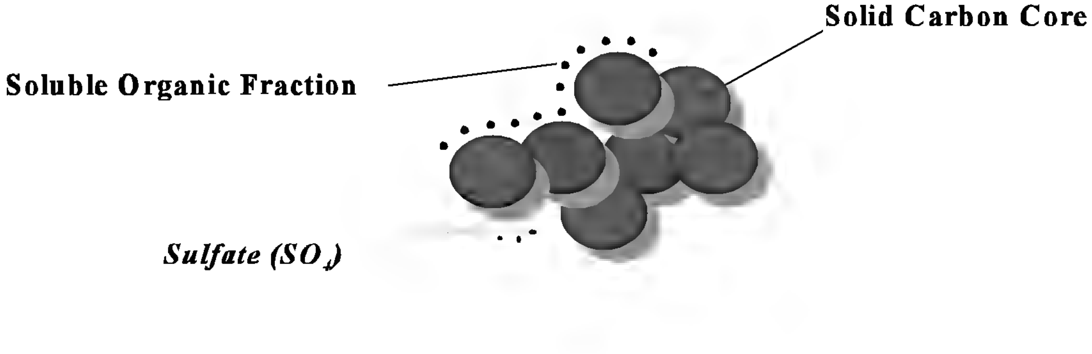
3. Particle Composition

The particles emitted from diesel engines are mainly aggregates of spherical carbon particles coated with organic and inorganic substances (Figure III-1) with the composition of the particles being predominantly, 80 to 90 percent, organic and inorganic carbon (Lowenthal et al., 1994). The inorganic fraction consists of small solid carbon particles, ranging from 0.01 to 0.08 micrograms (McClellan, 1986), and sulfur, oxygen, carbon, sulfate (SO_4), CO and NO_x (Johnson et al., 1994). The amount of the solid carbon, or EC, in the average particle will typically range from approximately 64 percent (Gray, 1986) to 71 percent (Volkswagen, 1989). The fine EC aerosol is formed during the combustion process, and is not found in the atmosphere by reactions involving gaseous hydrocarbon precursors. Therefore, the entire concentration of EC observed in the atmosphere is from primary emission sources.

The characteristic sponge-like structure and large surface area (50 to 200 m^2/gram of soot: Volkswagen, 1989) of particles emitted from diesel engines make it an excellent carrier for organic compounds of low volatility. These compounds reside on the particle surface (as a liquid) or are included inside the particle, or both. Organic compounds present inside the particles may be protected against photolysis and chemical reaction, while organic compounds present on the surface of the particles can volatilize or react with other compounds from the particle surface (described in more detail in Chapter VI).

The organic fraction of the diesel particle contains compounds such as aldehydes, alkanes and alkenes, aliphatic hydrocarbons, and PAH and PAH-derivatives (Zielinska, 1990; Johnson et al., 1994). The organic fraction comes from the unburned fuel and lubricating oil (see section F), and from partially oxidized fuel and oil (Williams et al., 1987). The majority of the organic fraction is adsorbed onto the surface of the solid carbon core. This fraction is called the soluble organic fraction (SOF) because of its solubility in solvents such as dichloromethane (Bagely et al., 1993). Also associated with the total particle mass (TPM) of the particulate matter may be droplets of liquid, condensed hydrocarbons, and SO_4 particles (Johnson et al., 1994). These hydrocarbons collected with the TPM are not volatile enough to exist in the vapor phase and may not be adsorbed onto the solid fraction due to low solid levels, but will also be removed by an organic solvent as the SOF (Johnson et al., 1994). The National Research Council (1983) has shown that approximately 25 percent of the particle mass may be extracted using organic solvents but, depending on the engine conditions and testing cycle, the contribution of organics to the TPM is between 10 and 90 percent (Williams et al., 1989).

Figure III-1
Diesel Exhaust Particles are Mainly Aggregates of Carbon Particles



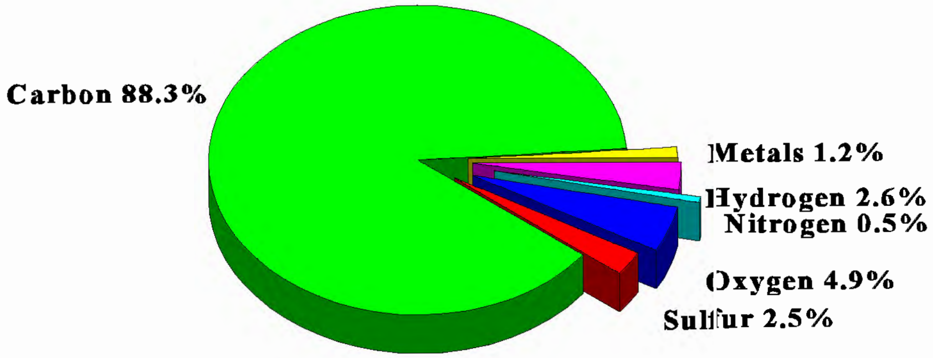
The SO_4 fraction of diesel exhaust TPM is composed primarily of the sulfuric acid formed when sulfur trioxide (SO_3) reacts with water vapor (Truex et al., 1980). SO_3 is formed from the oxidation of SO_2, which is produced during the combustion process by the oxidation of sulfur in the fuel (Bagely et al., 1993). This portion can contribute up to 14 percent of the diesel exhaust particle (Lowenthal et al., 1994).

Recently, a study conducted by Bagely et al. (1996), characterized the physical and chemical composition of emissions from a 1988 heavy-duty diesel engine equipped with a ceramic particulate trap, and a 1991 heavy-duty diesel engine equipped with an oxidation catalytic converter. The investigators determined the number and size of particles within the exhaust of the two engines tested. The results show that, despite a substantial reduction in the weight of the total particulate matter, the total number of particles from the more advanced 1991-model engine was 15 to 35 times greater than the number of particles from the 1988 engine when both engines were operated without emission control devices. This suggests that more fine particles, a potential health concern, could be formed as a result of new technologies. Further study is needed since the extent of these findings only measured exhaust from two engines and engine technologies.

Finally, diesel vehicle exhaust particles yield an average composition (by weight) of carbon (88.3 percent), oxygen (4.9 percent), hydrogen (2.6 percent), sulfur (2.5 percent), metals (1.2 percent) and nitrogen (0.5 percent) (Volkswagen, 1989). Figure III-2 depicts this information.

Engines running under low load typically produce fewer particles with a higher proportion of organic compounds associated with the available particle mass. Conversely, engines under high load typically produce more particulate matter with a lower proportion of organic compounds associated with the available particles. Kishi et al. (1992) found that exhaust gas temperature was an important determinant for particle composition; low exhaust gas temperatures produced particulate matter with more adsorbed soluble organics than did particulate matter produced in a high exhaust gas temperature environment.

Figure III-2
Carbon is the Primary Element in a Diesel Exhaust Particle
(adapted from Volkswagen, 1989)



Inorganic exhaust components are products of engine and component wear, or are trace contaminants of the fuel and/or lubricant oil. The inorganic compounds associated with the particles are primarily trace fuel contaminants such as antimony, arsenic, barium, beryllium, cobalt, and strontium. These substances usually vaporize in the combustion chamber and then "plate" themselves to particles in the exhaust stream. Inorganic exhaust particles can also act as condensation nuclei for vapor-phase exhaust components.

E. PAH and PAH-derivatives

Over that last 10-15 years, several researchers have investigated the health effects of PAH emissions and their atmospheric transformation products. The focus for this attention arose from observed mutagenic and carcinogenic effects of this important class of compounds and their nitro-derivatives. Diesel engine emissions are one of several sources of PAH and nitro-PAH emissions found in the ambient atmosphere. This section focuses on the PAH and PAH-derivatives found in diesel exhaust.

PAH and PAH-derivatives present in the atmosphere are distributed between the gas and particle phases mainly due to their liquid-phase vapor pressure (Bidleman, 1988). They are most likely to be formed by incomplete combustion of hydrocarbons at high temperatures (Kittleson et al., 1985; Tokiwa and Ohnishi, 1986). They are also formed from the reaction of parent hydrocarbons with nitrogen oxides in ambient air. Possible sources of PAH in diesel exhaust are unburnt PAH from the fuel, electrophylic nitration of PAH during combustion, crankcase oils, and engine or systems deposits.

A wide spectrum of gas- and particle-phase PAH and PAH-derivatives are emitted in diesel exhaust (National Research Council, 1983; Jensen and Hites, 1983; Barbella et al., 1988). Many of the PAH that can be extracted from the exhaust particle mass are unburned fuel and/or lubricant oil components (Obuchi et al., 1987; Barbella et al., 1989) like the fuel components naphthalene, fluorene, phenanthrene and their alkyl derivatives (Williams et al., 1986). PAH may also be formed in the combustion chamber during the combustion of diesel fuel (Tancell et al., 1995).

Methylated PAH appear to be the most abundant PAH-derivatives in diesel exhaust. Schuetzle et al. (1981) identified over 100 oxy-PAH in the moderately polar fractions of a diesel exhaust extract. The extract also contained hydroxy-, ketone-, quinone-, acid anhydride-, nitro-, and carboxaldehyde-PAH-derivatives.

The nitro-PAH compounds are recognized mutagens and can be formed by the nitration of PAH by NO_2 in an acid environment (Pitts et al., 1979). More than 50 nitro-PAH have been identified in diesel exhaust, including mononitro-PAH, mononitro-alkyl-PAH, di- and trinitro-PAH, and oxygenated nitro-PAH (Schuetzle et al., 1982; Paputa-Peck et al., 1983; Robbat et al., 1986). The major nitro-PAH observed in diesel exhaust are isomers of the parent PAH derivatives, formed by electrophilic nitration (Schuetzle, 1983; Nielsen, 1984). The most abundant nitro-PAH in diesel exhaust are 1-nitropyrene and 2-nitrofluorene (Schuetzle and Perez, 1983; Beje and Moller, 1988). Henderson et al. (1984) suggested that the active nitrogen oxide species in the exhaust stream could be a limiting factor in nitro-PAH formation.

Kittelson et al. (1985) measured concentrations of select PAH and 1-nitropyrene in the cylinder and exhaust manifold of an operating diesel engine. They observed that the PAH concentrations were higher in the cylinder than in the exhaust manifold, but the 1-nitropyrene concentrations were higher in the exhaust manifold than in the cylinder. This suggests that most of the nitro-PAH in the exhaust are probably formed during the expansion/exhaust process rather than during combustion.

Nitro-PAH can also be formed during transport through the atmosphere by reactions of adsorbed PAH with nitric acid, by gas-phase radical-initiated reactions in the presence of oxides of nitrogen (Atkinson and Arey, 1994; Pitts, 1983), and the artifactual formation of nitro-PAH during high volume sampling of ambient air (Arey et al., 1988).

In a recent study, researchers detected a new class of compounds that have direct mutagenic activity in organic extracts of both diesel exhaust and airborne particles. Specifically, 3-nitrobenzanthrone was isolated and studied. Its mutagenicity compares with that of 1,8-dinitropyrene, which is one of the strongest direct acting mutagens by Ames assay. 3-nitrobenzanthrone is formed during the combustion process of fossil fuels and from reaction between benzanthrone and lower oxides of nitrogen (Enya and Suziki, 1997).

F. Contribution of Lubricating Oil to Diesel Exhaust Particulate Matter

The contribution of lubricating oil to diesel exhaust PM emissions can be substantial. Researchers have reported that from 2 to 48 percent of the diesel exhaust PM mass, depending on speed and load, consisted of material from lubricating oil. Of this material, lubricating oil can contribute up to 88 percent of the SOF of a diesel exhaust particle (Mayer, et al., 1980; Cartillieri and Tritthart, 1984; Williams, et al, 1989; Rogge, et al., 1992). This contribution is important since several studies show that portions of the SOF of the diesel exhaust particle contains substances which are mutagenic, carcinogenic, or both (Pierson et al., 1983; Dorie et al., 1987; Rasmussen, 1988; NIOSH, 1988; Hsieh et al., 1993).

G. Current Research on Diesel Exhaust Emissions

The 1988 ARB diesel fuel regulation which became effective October 1, 1993, mandated reformulated diesel fuel that limited the maximum sulfur content to 0.05 percent, the minimum cetane index to 40, and the maximum aromatic content to 10 percent. Since lowering the aromatic content to levels under 10 percent would dramatically increase the production costs, ARB decided to allow alternative fuels with a higher aromatic content as long as equivalent emissions reductions could be demonstrated. The diesel fuel regulation was adopted for the purpose of reducing particulate matter (PM) and oxides of nitrogen (NO_x) (criteria pollutants), and was not specific to toxic components of diesel exhaust.

To investigate the effects that diesel fuel composition may have on the toxic exhaust constituents from diesel engines, ARB funded a study by the College of Engineering, Center for Environmental Research and Technology (CE-CERT) at the University of California, Riverside. The primary purpose of this study was to obtain a preliminary assessment of the potential impact of diesel fuel formulation on toxic components and on the speciation of hydrocarbons in diesel exhaust. The test was conducted on a Cummins L10 engine (represented the most-used heavy-duty diesel engine in California) operating on pre-October 1993 California diesel fuel, on fuel with lower than the 10 percent aromatic content requirement, and on a mix of alternative fuels with higher aromatic content that comply with ARB's regulation. Testing was conducted from December 1996 to January 1997 and results became available in spring of 1998.

The results from the CE-CERT draft final report show comparable criteria pollutant reductions to those estimated in the ARB staff report for the 1988 diesel fuel regulation. The low aromatic and typical in-use fuels produced particulate matter and NO_x exhaust emissions that met the diesel fuel regulation requirements. For more deatiled information on these and other measured substances, see *Evaluation of Factors that Affect Diesel Exhaust Toxicity* (draft final report), ARB Contract No. 94-312 (CE-CERT, 1998).

The contract was planned as a scoping study. It should be emphasized that the study design did not allow the resulting data to be used to obtain statistically robust conclusions (due to use of one engine and the limited number of data points for each target analyte/fuel combination). In particular, additional data would need to be collected from other types of engines and driving conditions. Rather, the data collected was intended to be used to characterize the influence of diesel fuel formulation on the emissions of toxic species and to assist in the design of more comprehensive studies.

Total Hydrocarbons (THC), NO_x, and Carbon Monoxide (CO)

Emissions of THC and NO_x show the following order of emissions rate with fuel type: pre-1993 > alternative > low aromatic. The emissions rate for THC and NOx from the use of the alternative fuel was approximately six and three percent lower, respectively, than from use of the pre-1993 fuel.

The use of the low aromatic fuel resulted in an increase, and the alternative fuel in a decrease, in the CO emission rates compared to use of the pre-1993 fuel.

PM_{10}, and $PM_{2.5}$

The use of low aromatic and alternative formulation fuels resulted in reductions in PM emission rates of approximately 20 percent compared to use of the pre-1993 fuel, comparable to what ARB staff predicted from implementation of our 1988 reformulated diesel fuel regulation.

More than 99 percent of the particulate mass measured fell within the PM_{10} (particulate matter 10 microns or less) range and greater than 95 percent in the $PM_{2.5}$ (particulate matter 2.5 microns or less) range. These estimates are similar to previous estimates as already indicated in Table III-2. The ARB emissions inventory for 1995 estimates that 98 percent of diesel exhaust PM is less than 10 microns and 94 percent is less than 2.5 microns.

The size distribution of PM_{10} and $PM_{2.5}$ emissions were found to be similar among the three different fuels used.

Elemental and Organic Carbon, Ion, and Elemental Analysis

The low aromatic and alternative fuels exhibited lower total carbon emission rates than the pre-1993 fuel. Elemental and organic carbon dominated the composition of the particulate matter for all fuels, representing more than 97 percent of the total identified mass. Organic carbon as a percent of total carbon is relatively constant for all three fuels and ranged from 33 to 40 percent. These numbers agree fairly well with previous estimates as discussed in section D.

Carbonyls

The use of alternative fuel resulted in similar emissions rates for the targeted carbonyls (formaldehyde, acetaldehyde, acrolein, and propionaldehyde) as from use of the pre-1993 fuel.

Speciated Hydrocarbons

Differences in emission rates among the speciated hydrocarbons were small between the pre-1993 and alternative fuel for 1,3-butadiene, benzene, toluene, ethylbenzene, o-xylene, m- & p-xylene, styrene, and naphthalene.

Particle-Phase PAHs

Many of the PAHs analyzed showed little difference in emissions rates with fuel type. However, four PAHs that ARB has identified as TACs did exhibit significant reductions in the alternative formulation blend and low-aromatic fuel compared to the pre-1993 fuel. These four PAHs were: anthracene, benz[a]anthracene, chrysene (co-eluted with triphenylene), and dibenzo[a,h]pyrene.

Nitro-PAHs

1-Nitropyrene, 6-nitrobenzo[a]pyrene, 9-nitroanthracene, and 1- and 2-nitronaphthalene were measured in the emissions from all three fuel types. 1-Nitropyrene was the most abundant nitro-PAH measured and the emission rate was similar among the three fuel types.

Vapor-Phase PAHs

Of all vapor phase PAHs analyzed, naphthalene emission rates were the highest for all three fuels. A comparison of the emission profiles using three different fuels showed a similar distribution of volatile alkyl-PAHs but at significantly different emission rates. Individual alkyl-PAH emission rates showed the following order with fuel type: pre-1993 > alternative > low aromatic. Lower emissions of volatile alkyl-PAHs may lead to a decreased potential for the atmospheric formation of highly mutagenic nitro-PAHs and nitro-PAH lactones.

Nitrosamines

The pre-1993 fuel emission rate for N-nitrosodimethylamine was similar to the alternative formulation fuel (the low aromatic fuel was not analyzed for nitrosamines). One pre-1993 fuel emission sample and one alternative formulation fuel emission sample contained measurable levels of N-nitrosodipropylamine. No other nitrosamines, such as N-nitrosomorpholine, were detected in any of the samples.

Previous studies have reported nitrosamine emissions from diesel and gasoline powered vehicles. Most of these studies have centered on emissions from catalyst equipped vehicles. N-nitrosodimethylamine has been detected from malfunctioning catalyst equipped vehicles.

Dioxins

Standardized testing procedures are not available for polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in engine emissions. A major objective of this study was to develop improved methods to collect, identify, and quantify dioxins from engines. However, the results are qualitative only and indicate the need for further method development. Hence, results are not presented in Table III-3.

Isomers of PCDD and PCDF were detected in the emissions from the alternative formulation blend and pre-1993 fuel. The most toxic isomers, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), 1,2,3,7,8-PCDD, and 2,3,4,7,8-PCDF were not detected in the emissions from the pre-1993 nor the alternative formulation fuels.

Bioassay

Mutagenic activity was detected in the particle- and vapor-phase emissions from all fuels tested. Higher mutagenic activity was observed in both the particle phase and vapor phase samples collected from pre-1993 fuel than from the low aromatic and alternative formulation fuel. However, the differences are not statistically significant. The calculated emission rate for particle and vapor-phase sample mutagenic activity (reported as revertants per brake horsepower per hour) was higher in the pre-1993 fuel than the low aromatic and alternative formulated fuels. Emission samples were chemically fractionated using high performance liquid chromotography (HPLC). Nine individual fractions were collected from each fuel and these fractions were tested in the bioassay. The most mutagenic fraction for the particulate matter is in a fraction (with unidentified constituents) that differs from (is more polar than) the fractions containing the PAHs and nitro-PAHs.

Table III-3
Average Emission Rates[1]
(mg/bhp-hr)

Substance(s)	Pre-1993	Alt. Formulation	Low-Aromatic
Formaldehyde	57.12	59.83	58.75
Acetaldehyde	18.15	19.93	19.10
Acrolein	2.14	2.42	5.79
Propionaldehyde	3.69	4.13	3.92
1,3-Butadiene	1.80	1.84	2.46
Benzene	5.90	5.81	8.03
Toluene	1.93	1.86	2.26
Ethylbenzene	1.22	1.18	0.67
o-Xylene	0.78	0.88	0.61
m- & p-Xylene	2.09	2.14	1.24
Styrene	1.27	1.45	1.58
Naphthalene	2.41	1.95	1.45
Emissions in μg/bhp-hr			
Anthracene	38.89	26.16	18.54
Benz[a]anthracene	16.42	10.96	10.57
Chrysene + Triphenylene	17.36	12.20	10.38
Benzo[b+j+k]fluoranthene	31.05	29.18	23.17
Benzo[a]pyrene	20.46	20.59	16.48
Dibenz[a,h + a,c]anthracene	1.54	1.48	0.87
Dibenzo[a,l]pyrene	2.84	2.31	1.25
Dibenzo[a,e]pyrene	1.10	1.13	0.61
Dibenzo[a,i]pyrene	0.91	0.71	0.27
Dibenzo[a,h]pyrene	1.33	0.84	0.75
5-Nitroacenaphthene	<0.5	<0.5	<0.5
2-Nitrofluorene	<0.3	<0.3	<0.3
1-Nitropyrene	1.95	1.64	2.07
4-Nitropyrene	<0.06	<0.06	<0.06
6-Nitrochrysene	<0.1	<0.1	<0.1
Biphenyl	410	333	90
N-Nitrosodimethylamine	6.41	7.92	
N-Nitrosomorpholine	<7.8	<7.8	

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[1] The emission rate among the individual substances may reflect averages from multiple test cycles (two hot starts) or the complete test matrix [1/7(cold start) + 6/7(hot start)].

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IV.
PRODUCTION, USES, EMISSIONS, AND EMISSIONS PROJECTIONS

Diesel engines are used to power passenger cars, trucks, buses, ships, railway locomotives, in nonroad equipment used for farming and construction, and in almost every kind of industry.

A. Production

The combustion of diesel fuel in an internal combustion engine produces diesel exhaust. Approximately 2.1 billion gallons of diesel fuel were burned in internal combustion engines in California during 1995 (BOE, 1996). The State predicts that diesel fuel use will increase in California from current levels up to 2.3 billion gallons in 2000 and 2.9 billion gallons in 2010 (CEC, 1998).

B. Uses

The staff is not aware of any commercial or industrial use of diesel exhaust in California. Small amounts are used in research.

C. Emissions

Diesel engine emissions have changed dramatically over the last 20 years because of improvements in engine technology, emissions controls, and fuel formulation. Emissions of NO_x and PM_{10} are significantly lower than those from older uncontrolled engines. Emissions of reactive organic gases (ROG) and CO have also declined as a result of engine emissions standards.

In this report, diesel exhaust PM_{10} emissions and air concentration estimates are used to represent exposure to diesel exhaust. The total emissions of toxic diesel exhaust species have not been estimated because inadequate analytical methods, in conjunction with excessive costs, prevent the detection and quantification of the many individual toxic and potentially toxic species and their atmospheric contribution. Diesel exhaust particulate matter is extremely fine (over 90 percent of the particles are smaller than 1 micrometer [μm] in diameter), readily respirable, and is the primary carrier for many of the hydrocarbons and metals found in the exhaust, many of which are known or suspected mutagens and carcinogens. Because the 1990 year emissions inventory is used in our ambient concentrations analysis (see Chapter V), the primary focus will be on the 1990 emissions inventory. We have, however, included emissions estimates for 1995 to indicate the decrease in emissions that have occurred as a result of recent diesel regulations and estimates of the future trends in diesel engine emissions.

Three major source categories emit diesel exhaust in California: mobile sources (on-road vehicles and other mobile sources), stationary area sources, and stationary point sources. Table IV-1 through Table IV-6 breaks the three major source categories into individual emission groups, and lists the individual groups' emissions in tons per year (TPY), both for base year 1990 (inventory year used for ambient exposure analysis) and for year 1995 for diesel exhaust PM_{10}, $PM_{2.5}$, NO_x, SO_x, CO, and ROG.

Table IV-1
Diesel Exhaust PM_{10} Emitted into California's Air for Years 1990 & 1995 [1]

	PM_{10} Emissions in Tons/Year	
	1990	**1995**
Mobile Sources		
On-Road Vehicles (Diesel Only)		
Heavy-duty Trucks	25, 220	14,730
Light-duty Passenger Cars	1,230	540
Urban Buses	170	110
Light/Medium-duty Trucks	630	300
Total On-Road	**27,250**	**15,680**
Other Mobile (Diesel Only)		
Off-road Vehicles	640	440
Ships	1,030	1,080
Trains	1,440	1,090
Mobile Equipment	10,700	7,220
Total Other Mobile	**13,810**	**9,820**
Stationary Area Sources		
Total Area Sources	**1,360**	**1,370**
Stationary Point Sources		
Total Point Sources	**4**	**30**
TOTAL ALL SOURCES	**42,424**	**26,900**

Notes: 1) Data from California Emission Forecasting System, 1993 Base year trends (run date: 1/5/98).

Table IV-2
Diesel Exhaust $PM_{2.5}$ Emitted Into California's Air for Years 1990 & 1995[1]

	$PM_{2.5}$ Emissions in Tons/Year	
	1990	**1995**
Mobile Sources		
On-Road Vehicle (Diesel Only)		
Heavy-duty Trucks	24,555	14,315
Light/Medium-duty Trucks	600	280
Light-duty Passenger Cars	1,170	510
Urban Buses	165	105
Total On-Road	**26,490**	**15,210**
Other Mobile (Diesel Only)		
Off-road Vehicles	610	425
Ships	1,005	1,040
Trains	1,220	1,065
Mobile Equipment	9,665	7,050
Total Other Mobile	**12,500**	**9,580**
Stationary Sources		
Total Stationary Sources	**1,330**	**1,360**
TOTAL ALL SOURCES	**40,320**	**26,150**

Notes: 1) Data from California Emission Forecasting System, 1993 Base year trends (run date: 4/29/98).

Table IV-3
Diesel Exhaust NO_x Emitted into California's Air for Years 1990 & 1995 [1]

	NO_x Emissions in Tons/Year	
	1990	**1995**
Mobile Sources		
On-Road Vehicles (Diesel Only)		
Heavy-duty Trucks	221,600	174,900
Light-duty Passenger Cars	5,570	2,690
Urban Buses	6,610	6,370
Light/Medium-duty Trucks	2,530	1,310
Total On-Road	**236,310**	**185,270**
Other Mobile (Diesel Only)		
Off-road Vehicles	6,660	7,130
Ships	16,640	15,360
Trains	65,040	54,350
Mobile Equipment	177,030	136,560
Total Other Mobile	**265,370**	**213,400**
Stationary Area Sources		
Total Area Sources	**16,900**	**16,060**
Stationary Point Sources		
Total Point Sources	**60**	**380**
TOTAL ALL SOURCES	**518,640**	**415,110**

Notes: 1) Data from California Emission Forecasting System, 1993 Base year trends (run date: 1/2/98).

Table IV-4
Diesel Exhaust SO_x Emitted into California's Air for Years 1990 & 1995 [1]

	SO_x Emissions in Tons/Year	
	1990	**1995**
Mobile Sources		
On-Road Vehicles (Diesel Only)		
Heavy-duty Trucks	22,300	8,060
Light-duty Passenger Cars	1,180	180
Urban Buses	580	190
Light/Medium-duty Trucks	620	90
Total On-Road	**24,680**	**8,520**
Other Mobile (Diesel Only)		
Off-road Vehicles	880	830
Ships	8,540	10,090
Trains	6,100	2,650
Mobile Equipment	27,550	5.070
Total Other Mobile	**43,070**	**18,640**
Stationary Area Sources		
Total Area Sources	**1,230**	**1,250**
Stationary Point Sources		
Total Point Sources	**7**	**30**
TOTAL ALL SOURCES	**68,987**	**28,440**

Notes: 1) Data from California Emission Forecasting System, 1993 Base year trends (run date: 1/2/98).

Table IV-5
Diesel Exhaust CO Emitted into California's Air for Years 1990 & 1995 [1]

	CO Emissions in Tons/Year	
	1990	**1995**
Mobile Sources		
On-Road Vehicles (Diesel Only)		
Heavy-duty Trucks	111,440	106,480
Light-duty Passenger Cars	6,070	3,960
Urban Buses	780	700
Light/Medium-duty Trucks	2,780	1,900
Total On-Road	**121,070**	**113,040**
Other Mobile (Diesel Only)		
Off-road Vehicles	2,590	1,990
Ships	1,650	1,920
Trains	9,030	8,040
Mobile Equipment	53,700	58,000
Total Other Mobile	**66,970**	**69,950**
Stationary Area Sources		
Total Area Sources	**4,590**	**4,620**
Stationary Point Sources		
Total Point Sources	**10**	**100**
TOTAL ALL SOURCES	**192,640**	**187,710**

Notes: 1) Data from California Emission Forecasting System, 1993 Base year trends (run date: 1/2/98).

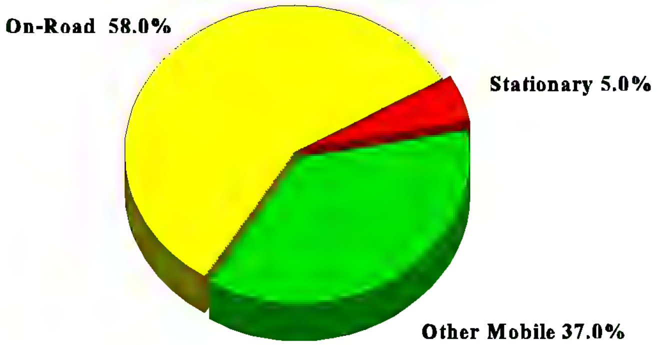
Table IV-6
Diesel Exhaust ROG Emitted into California's Air for Years 1990 & 1995 [1]

	ROG Emissions in Tons/Year	
	1990	**1995**
Mobile Sources		
On-Road Vehicles (Diesel Only)		
Heavy-duty Trucks	27,190	21,780
Light-duty Passenger Cars	1,260	660
Urban Buses	600	630
Light/Medium-duty Trucks	590	350
Total On-Road	**29,640**	**23,420**
Other Mobile (Diesel Only)		
Off-road Vehicles	1,440	1,090
Ships	1,160	1,550
Trains	2,780	2,470
Mobile Equipment	16,680	12,190
Total Other Mobile	**22,060**	**17,300**
Stationary Area Sources		
Total Area Sources	**530**	**570**
Stationary Point Sources		
Total Point Sources	**4**	**50**
TOTAL ALL SOURCES	**52,234**	**41,340**

Notes: 1) Data from California Emission Forecasting System, 1993 Base year trends (run date: 1/2/98).

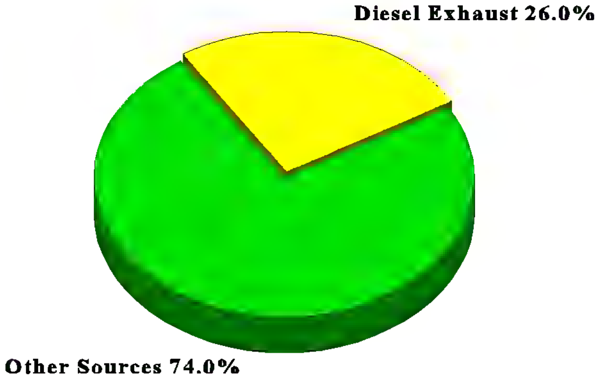
Figure IV-1 illustrates that on-road mobile sources (heavy-duty trucks, light-duty passenger cars and trucks, and urban buses) emit the majority, or about 58 percent of the diesel exhaust PM_{10} in California for 1995. Other mobile sources contribute about 37 percent, and stationary sources emit about 5 percent.

Figure IV-1
1995 Statewide Diesel Exhaust PM_{10} Emissions



Fuel combustion sources include those sources that use various fuels (e.g. solid-liquid combustion material, gasoline, diesel fuel, natural gas, jet fuel, wood and waste combustion) in their production or use. These sources include stationary sources such as oil and gas production facilities, electric utilities, and manufacturing/industrial plants, and mobile sources such as motor vehicles, ships, trains, and aircraft. Figure IV-2 illustrates that diesel exhaust PM_{10} contributes approximately 26 percent of the total statewide PM_{10} from fuel combustion sources. The remaining non-diesel fuel combustion sources contribute the remaining 74 percent (ARB, 1997a, 1998a).

Figure IV-2
1995 Statewide PM_{10} Emissions from
Fuel Combustion Sources



The ARB staff also estimates that emissions from diesel exhaust contribute about 3 and 8 percent of the total PM_{10} and $PM_{2.5}$ inventories, respectively (ARB, 1997b). Diesel exhaust particulate matter is a larger percentage of the Statewide $PM_{2.5}$ inventory, primarily because the $PM_{2.5}$ inventory targets smaller particles emitted from combustion sources (see Figures IV-3 and IV-4). For both PM_{10} and $PM_{2.5}$ inventories, emissions from non-diesel mobile on-road sources include gasoline-powered vehicles, tire wear, and brake dust; non-diesel other mobile emissions include sources such as trains, ships, and mobile equipment; and non-diesel stationary (point and area) emissions include sources such as petroleum refining, mineral processes, residential fuel combustion, farming operations, construction and demolition, entrained road dust, and fugitive windblown dust (ARB, 1998a,b).

1. Mobile Sources

a. On-Road Vehicles

Heavy-duty trucks, urban buses, passenger cars, and light-duty trucks emitted an estimated 27,250 tons (approximately 64 percent of the total emissions) of diesel exhaust PM_{10} statewide during 1990 (ARB, 1998a). Emissions from on-road vehicles has declined to 15,680 tons (approximately 58 percent of the total emissions) in 1995 due to engine emission standards and the introduction of reformulated diesel fuel (see Table IV-1).

b. Other Mobile Sources

Other diesel-fueled mobile sources emitted an estimated 13,810 tons of engine exhaust PM_{10} (approximately 33 percent of the total) statewide during 1990 and 9,820 tons (approximately 37 percent of the total) in 1995. This category includes off-road transportation equipment and mobile industrial equipment such as construction and road equipment, mobile refrigeration units, ships, heavy-duty farm equipment, trains, and recreational and commercial boats (ARB, 1998a).

2. Stationary Sources

Stationary sources emitted an estimated 1,364 tons of diesel exhaust PM_{10} statewide during 1990 (approximately 3 percent of the total) and 1,400 tons (approximately 5 percent of the total) in 1995 (ARB, 1998a).

Most districts in California do not have a complete inventory of their stationary diesel engines. Consequently, the statewide emissions of diesel exhaust PM_{10} from stationary sources are likely higher than those reported here (which are based on available emission inventories).

a. Stationary Area Sources

Stationary area sources of diesel exhaust include shipyards, warehouses, heavy equipment repair yards, and oil and gas production operations where exhaust emissions are emitted from multiple locations within the site. Stationary area sources emitted an estimated 1,360 and 1,370 tons of diesel exhaust PM_{10} in California during 1990 and 1995, respectively (ARB, 1998a).

Figure IV-3
1995 Statewide PM_{10} Emissions

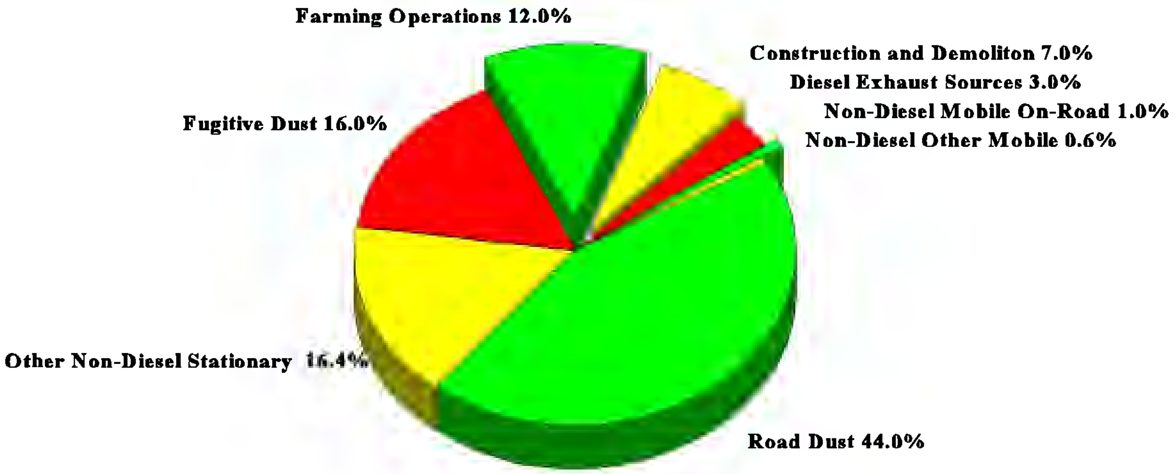
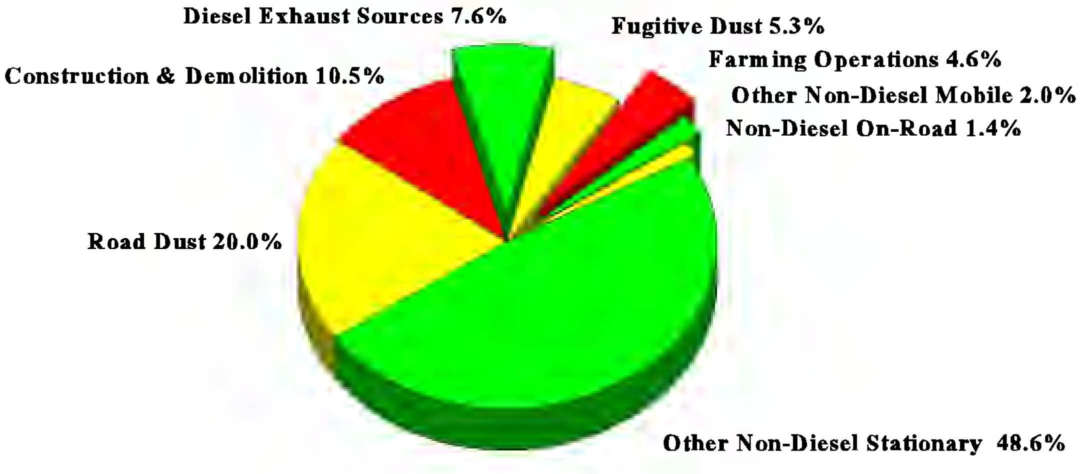


Figure IV-4
1995 Statewide $PM_{2.5}$ Emissions



b. Stationary Point Sources

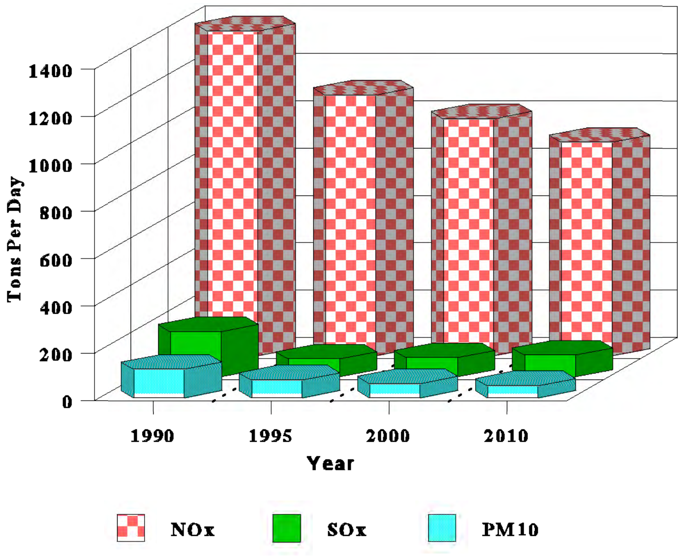
Stationary point sources generate diesel exhaust emissions from specific, fixed locations. These sources include chemical manufacturing, stone, clay, and glass manufacturing, mining, public administration, and utility and water services. Stationary point sources emitted an estimated 4 and 30 tons of diesel exhaust PM_{10} in California during 1990 and 1995, respectively (ARB, 1998a).

D. Emission Projections

1. Mobile Sources

There have been significant advances in the development of technology to control diesel particulate matter emissions. Some of these efforts included engine design modifications, the use of aftertreatment devices, and improvements in fuel formulations. All of these improved technologies were developed to comply with engine emission standards and fuel modifications adopted to date by ARB and the U.S. EPA. Figure IV-5 illustrates emission estimates for PM_{10}, NO_x, and SO_x for the years 1990 and 1995, and emissions projections for years 2000 and 2010.

Figure IV-5
Diesel Exhaust Mobile Source Emissions and Projections
(1990 - 2010)



Emissions of diesel exhaust PM_{10} from mobile sources in California are expected to decrease about 60 percent from 1990 to 2010 as a result of mobile source emission standards and regulations already adopted by the ARB and the U.S. EPA through 1997.

The use of low sulfur fuel (0.05% by mass) has led to additional reductions in total particulate matter levels of diesel exhaust. Since 1990, sulfur oxide (SO_x) emissions from diesel-fueled vehicles have decreased about 60 percent due to the use of this fuel (sold beginning October 1993). However, from now until 2010, SO_x emissions are expected to increase slowly due to increases in population, traffic congestion, and VMT.

Nitrogen oxides (NO_x) emissions from diesel powered mobile sources are expected to decrease from now until about 2010. The U.S. EPA is proposing a new NO_x heavy-duty engine emission standard to be implemented in 2004 which will cut emissions of NO_x from diesel engines statewide by about 18 percent each year thereafter.

a. Particulate Matter

In order to address particulate matter pollution, the U.S. EPA and the ARB have established ambient air quality standards for PM_{10} (U.S. EPA: 24-hr - 150 $\mu g/m^3$, annual arithmetic mean - 50 $\mu g/m^3$; ARB: 24-hr - 50 $\mu g/m^3$, annual geometric mean - 30 $\mu g/m^3$). The U.S. EPA has also adopted a new National Ambient Air Quality Standard for $PM_{2.5}$ to address concerns regarding the health effects of fine particles. On July 18, 1997, the U.S. EPA adopted an annual $PM_{2.5}$ standard of 15 $\mu g/m^3$ and a 24-hour standard of 65 $\mu g/m^3$. To assist in meeting these standards, the ARB and the U.S. EPA are addressing diesel exhaust PM_{10} emissions through a series of on-road and other mobile source emission standards and regulations. The diesel exhaust PM_{10} standards and regulations for on-road and other mobile sources adopted by the ARB and the U.S. EPA include:

On-Road Mobile Sources

- ☞ emission standards that limit the gram per mile (g/mi) of PM that can be emitted from 1982 and newer light- and medium-duty on-road diesel vehicles (1985: 0.4 g/mi; 1986-88: 0.2 g/mi; and 1989 and newer: 0.08 g/mi.);

- ☞ PM emission standards for 1988, 1991, and 1994 and newer diesel powered heavy-duty vehicles of 0.60, 0.25, and 0.10 grams per brake-horsepower-hour (g/bhp-hr), respectively, except for urban bases;

- ☞ PM emission standards that limit new 1991 through 1993 urban bus engines from emitting more than 0.10 g/bhp-hr. 1994-1995 model year urban bus engines are required to meet a 0.07 g/bhp-hr interim in-use standard. Beginning in 1996, new urban buses are restricted from emitting more than 0.05 g/bhp-hr;

- ☞ the roadside testing of heavy-duty on-road vehicles for excessive smoke opacity (1991);

- use of low sulfur/low aromatics diesel fuel (October 1993) that helps reduce PM emissions from mobile sources (excluding locomotives and marine vessels);

- continuation of the fleet inspection and maintenance program for heavy-duty vehicles (anticipated implementation in early 1998);

Other Mobile Sources

- PM emission standards for 1995 and newer utility diesel engines rated under 25 horsepower (1995-98: 0.9 g/bhp-hr; 1999 and newer: 0.25 g/bhp-hr);

- hydrocarbon (HC) + NO_x emission standards for 1995 and newer utility diesel engines rated under 25 horsepower (1995-98: 12.0 g/bhp-hr for engines less than 225 cubic centimeters (cc) and 10.0 g/bhp-hr for engines greater than or equal to 225 cc; 1999 and newer: 3.2 g/bhp-hr for all engines under 25 horsepower);

- PM emission standards for certain heavy-duty off-road diesel engines rated from 175 to 750 horsepower (1996-2000: 0.4 g/bhp-hr; 2001 and newer: 0.16 g/bhp-hr);

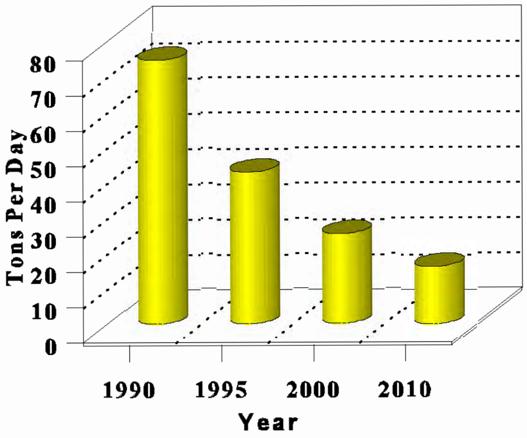
- NO_x emission standards for certain heavy-duty off-road diesel engines rated from 175 to 750 horsepower (1996-2000: 6.9 g/bhp-hr; 2001 and newer: 5.8 g/bhp-hr);

- PM emission standards for certain heavy-duty off-road diesel engines rated above 750 horsepower (2000 and newer: 0.4 g/bhp-hr); and

- NO_x emission standards for certain heavy-duty off-road diesel engines rated above 750 horsepower (2000 and newer: 6.9 g/bhp-hr).

As a result of these control measures, statewide diesel exhaust PM_{10} emissions from on-road diesel vehicles are expected to be reduced by approximately 80 percent over the period 1990-2010 (Figure IV-6). The expected reduction is due to adopted diesel vehicle emission and fuel regulations (listed above), even though both the number and VMT of heavy-duty trucks are expected to increase substantially during this period.

Figure IV-6
Diesel Exhaust On-Road Vehicle
PM_{10} Emissions Projections



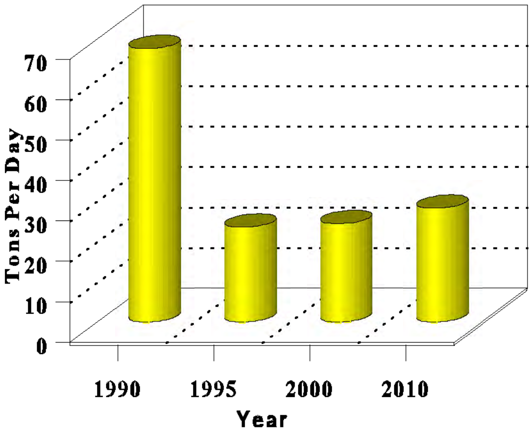
b. Sulfur Oxides

Sulfur is a component of diesel fuel, and is emitted in diesel exhaust as sulfur oxides. Approximately 98 percent of the sulfur is emitted as sulfur dioxide (SO_2) and 2 percent of particulate sulfate (Pierson et al., 1978; Truex et al., 1980). Sulfur oxide (SO_x) inhalation can cause bronchial tube constriction and exacerbation of preexisting respiratory or pulmonary disease (Blumenthal, 1985). Additionally, SO_x emissions from diesel-fueled engines, which may undergo chemical reactions in the atmosphere to form acidic sulfates, can contribute to acid deposition in California. The principle chemical transformation of SO_2 in the atmosphere is reaction with the OH radical followed by the formation of sulfuric acid (Stockwell and Calvert, 1983). SO_x may also react with other compounds in the atmosphere to form particles which contribute to PM emissions.

Since October 1993, diesel fuel sold in California for combustion in mobile sources (excluding locomotives and marine vessels) has been reformulated to be a low aromatic/low sulfur diesel fuel. Use of this reformulated fuel has resulted in lower emissions of SO_x, NO_x and PM, and lower ambient air concentrations of SO_x in areas impacted by diesel exhaust emissions. Low sulfur diesel fuel has been required in the South Coast Air Basin since 1985.

Statewide SO_x emissions from on-road diesel vehicles are expected to have decreased by about 64 percent from 1990 to 1995, and increase slowly after that due to growth in vehicles and VMT (see Figure IV-7).

Figure IV-7
Diesel Exhaust On-Road Vehicle
SO_x Emissions Projections



c. Nitrogen Oxides

Diesel engines produce nitrogen oxides (NO_x, primarily nitrogen monoxide) as a result of a high-temperature combustion process that uses large amounts of air. NO_x is the sum of nitric oxide (NO), nitrogen dioxide (NO_2), and other nitrogen oxide components. This makes controlling both NO_x and particulate matter emissions for a diesel engine difficult, because the decrease of one usually results in the production of the other. NO_x inhalation can cause constriction of the bronchial tubes, exacerbation of preexisting lung disease, and an increased susceptibility to respiratory infections (Blumenthal, 1985). Additionally, NO_x emissions from diesel-fueled engines contribute to acid deposition and tropospheric ozone formation.

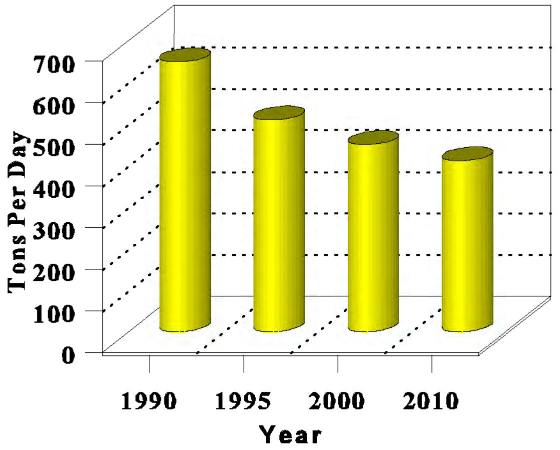
Diesel exhaust contains mutagenic substances that are a result of NO_x radical reaction. For example, the major nitro-PAHs observed in diesel exhaust are formed by electrophilic reaction of the parent PAHs with NO_x radicals (see Chapter III). A reduction in the amount of NO_x in the exhaust stream should result in lower exhaust pipe/stack emissions of mutagenic nitro-compounds.

Since 1991, new heavy-duty diesel trucks and buses in California have been restricted from emitting more than 5.0 grams of NO_x per brake horsepower hour (g/bhp-h). As a result of the diesel fuel regulations adopted by the ARB in 1993, NO_x emissions from diesel-powered motor vehicles have reduced NO_x emissions by about 7 percent (70 tons per day). In 1996, the NO_x standard for new heavy-duty urban buses became 4.0 g/bhp-h. In 1998, new heavy-duty trucks will be required to meet the same standard. In addition, and as part of California’s plan to address heavy-duty diesel vehicle pollutants, the U.S. EPA, ARB, and the leading manufacturers of heavy-duty diesel engines signed a historical agreement to reduce emissions of NO_x and hydrocarbons. In this "Statement of Principles," signed on July 11, 1995, the signatories agreed to pursue new heavy-duty diesel engine standards from future trucks and buses on a nationwide basis by proposing a national non-methane hydrocarbon (NMHC) plus NO_x standard of 2.4 g/bhp-hr, or a combined NMHC plus NO_x standard of 2.5 g/bhp-hr with an NMHC cap of 0.5 g/bhp-hr. The U.S. EPA formally proposed these standards in a Notice of Proposed Rulemaking on June 2, 1996. The final rule was published in the Federal Register in October 1997. The new standards are proposed to be implemented beginning in 2004, and are predicted to decrease NO_x emissions by approximately 71 tons per year or about 18 percent. The ARB staff is proposing to adopt a similar emission standard at a ARB public hearing in April 1998.

Lower emissions of NO_x from affected sources will result in lower ambient air concentrations of NO_x in areas impacted by diesel exhaust emissions. Since NO_x is an ozone precursor, this would decrease the amount of ozone formed in the atmosphere.

As a result of the regulations mentioned above, the ARB projects that statewide NO_x emissions from on-road diesel vehicles will decrease by about 19 percent from now until 2010 (Figure IV-8).

Figure IV-8
Diesel Exhaust On-Road Vehicle
NO_x Emissions Projections



2. Stationary Sources

Diesel exhaust emissions from stationary sources are increasing with the increase in California's population. Emission regulations that will slow the increase in diesel exhaust PM and NO_x emissions from these types of sources have been addressed or may be addressed by the local air pollution control districts.

E. Indoor Sources of Diesel Exhaust

Indoor non-occupational environments will not typically have sources of indoor diesel exhaust. The presence of diesel exhaust indoors will normally result from infiltration of outdoor air contaminated with diesel exhaust. Industrial workplaces such as fire stations and loading docks are potential sources of indoor exposures. These environments may have occasional indoor sources such as diesel-powered tools, machinery, forklifts, and vehicles. Such sources may be used in enclosed work spaces near outdoor air intakes that draw the exhaust in and deliver it to indoor work spaces. Exposure to diesel exhaust indoors is discussed in more detail in Chapter V.

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V.
EXPOSURE TO DIESEL EXHAUST

The main focus of this chapter is to provide an estimate of near source and total exposure to diesel exhaust PM_{10} in California. It also includes: a discussion of monitoring methods used by other researchers to predict ambient concentrations of diesel exhaust PM_{10}, a description of ARB's method for estimating outdoor ambient concentrations, ARB staff projections for future ambient diesel exhaust PM_{10} concentrations, an estimate of indoor exposures, and a discussion of other routes of exposure (multipathway).

A. Monitoring for Diesel Exhaust

Diesel exhaust is a complex mixture of thousands of gases and particles. Because of its complex mixture and that many of the individual constituents of diesel exhaust may be emitted from other combustion sources, whole diesel exhaust has not been directly monitored or quantified in the atmosphere.

The most common approach to monitoring diesel exhaust has been to select a surrogate measure or measures of exposure that are representative of the exhaust as a whole. Although diesel exhaust markers (substances unique to diesel exhaust that could be used to qualify and quantify its presence in the atmosphere) have not been found, fine particles and elemental carbon have been used as surrogates of exposure to diesel exhaust particulate matter. Consequently, ambient diesel exhaust PM concentrations are often used by researchers to represent the public's exposure to whole diesel exhaust.

The ARB staff estimated diesel exhaust concentrations using a PM-based exposure method. Although there are several diesel exhaust PM estimation methods (discussed on following pages), the staff of the ARB used a PM-based exposure estimation method for the following reasons:

we have a comprehensive emissions inventory and ambient concentrations data base for diesel exhaust-derived PM in California;

diesel exhaust PM contains many of the toxic components of the exhaust; and

> diesel exhaust PM has been shown to contribute a significant portion of the exposure to the whole exhaust. The PM has been associated with approximately 50 (Hsieh et al., 1993) to 90 (Schuetzle, 1983) percent of the mutagenic potency of whole diesel exhaust, (NIOSH, 1988)*.

Toxic gas-phase exhaust constituents like acetaldehyde, benzene, 1,3-butadiene, and formaldehyde are not directly included in a PM-based exposure estimation because they are not typically carried on or in the particles. The ARB and others have initiated research to improve and refine the estimates of exposure to the gas-phase portion of the exhaust.

Until more sophisticated estimation methods can be devised, PM-based estimation methods provide a useful tool to develop diesel exhaust exposure estimates.

Table V-1, adapted from Krieger et al. (1994), lists ambient diesel exhaust PM concentration estimates developed by a number of researchers using a variety of data bases and estimation methods. Most of the estimations presented in the Table are not California-specific, and represent only general diesel exhaust PM air concentrations (California-specific data are presented later in this Chapter). Based on the information shown in Table V-1, ambient diesel exhaust PM concentrations range from 0.2 to 23 $\mu g/m^3$.

As discussed, several diesel exhaust PM estimation methods have been developed. These include the use of the following:

tracers;
modeled exhaust emissions; and
source apportionment.

1. Tracers

Although diesel exhaust may not contain markers that can be used to qualify and quantify its presence in the atmosphere, it does contain substances predominately emitted from diesel-fueled engines (tracers) which can be used to estimate its presence and concentrations. Tracer substances are consistently emitted from diesel-fueled engines, and can be consistently monitored in the air. Diesel exhaust tracers that have been suggested by various researchers include particle-associated diesel fuel additives, elemental carbon, PAH and PAH ratios, and lubricating oil combustion products. Known quantities of substances not normally found in the atmosphere can also be added to the fuel as artificial tracers.

In an effort to quantify atmospheric concentrations of diesel exhaust in Vienna, Austria, researchers added a small amount of the rare element dysprosium to the area's entire diesel fuel supply. Dysprosium is not normally detected in ambient air, and its quantifiable presence in Vienna's atmosphere during the 4-week study period allowed scientists to successfully qualify and quantify its carrier (diesel exhaust PM) in the atmosphere through PM sampling and analysis.

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* The OEHHA's discussion and evaluation of diesel exhaust's toxicity is contained in the Part B *Health Risk Assessment for Diesel Exhaust.*

Table V-1
Estimates of Diesel Exhaust Ambient PM Concentrations by Selected Researchers

Conditions/Method	for Year	Concentrations ($\mu g/m^3$)	Reference
Ambient Concentration Estimates Using:			
Dysprosium Tracer - range	1988	5 - 23	Horvath, et al., 1988
- typical	1988	11	
Lead Surrogate - range	1995	0.7 - 3.9	U.S. EPA, 1983
Elemental Carbon - range Surrogate	1982	3.4 - 5.7	Adapted from Denton, et al., 1992
NAAQS Exposure Model - range	1995	3.1 - 3.7	U.S. EPA, 1983
NAAQS Exposure Model modified	1986	2.6	Ingalls, 1985
Source Apportionment - Urban Areas	1991	4 - 22	Chow et al. 1991
Ambient Concentration Estimates (considering only light-duty diesel vehicles) Using Various Dispersion Models:			
Urban residents - typical	1995	0.2	Cuddihy, et al., 1981 & McClellan, 1986
- near freeway	1995	2.0	
Street Canyon - range	1989	3.9 - 8.8	Volkswagen, 1989
Expressway - range	1989	2.6 (100m) - 7.1 (4m)	Volkswagen, 1989

Horvath et al. (1988) found that from 12 to 33 percent of the PM suspended in Vienna's atmosphere was diesel exhaust PM, in concentrations that varied with the density and flow of traffic. The diesel exhaust PM mixed well in the atmosphere, and there were no dramatic differences in ambient concentrations between busy commercial areas and calm residential areas. Diesel exhaust PM concentrations during the study ranged between 5 and 23 μg/m^3, with typical concentrations around 11 μg/m^3. The researchers observed that the diesel exhaust PM concentrations increased 5.5 μg/m^3 above ambient levels for every 500 diesel-fueled vehicles passing near a monitoring site per hour.

2. Modeled Exhaust Emissions

Researchers at Volkswagen (1989) estimated air concentrations of vehicle exhaust PM in urban street canyons and near U.S. expressways. The researchers used emission factors for on-road gasoline- and diesel-fueled vehicles, estimates of the numbers and types of vehicles on the road, diurnal activity patterns, and mathematical simulation models of a typical U.S. street canyon and expressway. Emissions from heavy-duty on-road vehicles were not included in the researchers' calculations.

The researchers estimated that vehicle exhaust PM concentrations in the street canyon would range from 3.9 to 8.8 μg/m^3, while PM concentrations near the expressway would range from 7.14 μg/m^3 at 4 meters from the side of the road, to 2.57 μg/m^3 at 100 meters from the side of the road.

3. Source Apportionment

Source apportionment is a technique for identifying the sources and source emissions which contribute to the total ambient air concentrations of a pollutant in a specific area. PM source apportionment typically employs a chemical mass balance (CMB) model to match the chemical profiles of ambient PM samples with known chemical profiles of PM from specific types of sources. Source apportionment can be used to calculate diesel exhaust PM concentrations in a specific area for which adequate emissions inventory and PM ambient air data are available. With this information, future year diesel exhaust PM concentrations can be estimated from future year emission inventories (see section D).

a. PM$_{10}$ Source Apportionment

Zielinska (1991) reported that a PM$_{10}$ source apportionment study conducted by the Desert Research Institute during the winter of 1989-1990 (Chow et al., 1991) produced estimates of motor vehicle exhaust concentrations for West Phoenix, Central Phoenix, and South Scottsdale, Arizona. The results of this study indicated that primary motor vehicle exhaust is the second highest contributor to PM$_{10}$ at all sampling sites, and that diesel-fueled motor vehicle exhaust was determined to be responsible for at least half of the motor vehicle-derived PM$_{10}$.

The calculated diesel exhaust PM$_{10}$ concentrations for the winter study period ranged from approximately 4 μg/m^3 (at all three sites), to 14 μg/m^3 (in South Scottsdale) and 22 μg/m^3 (in Central Phoenix).

b. Elemental Carbon Source Apportionment

As previously mentioned, elemental carbon (EC) has been used by researchers to estimate ambient diesel exhaust PM concentrations. Gray (1986) used fine particulate EC ambient data (particle sizes below 2.1 in diameter) collected in the Los Angeles area in 1982 and emissions inventory data to determine source contributions from diesel engine emissions. Results indicated that diesel engine emissions were responsible for approximately 67 percent of the fine EC mass in the Los Angeles area atmosphere, and that the exhaust particles averaged about 64 percent EC. Average annual fine EC concentrations ranged from 3.03 to 5.04 μg/m^3. From this information, we derived approximate concentrations of fine PM attributed to diesel exhaust by multiplying the EC concentrations measured during the study by 67 percent and dividing the result by 64 percent. In addition, Gray estimates that the fine PM constitutes about 93 percent of the PM$_{10}$ mass for diesel emissions. This percentage is then divided by the fine diesel exhaust PM concentration to determine total diesel exhaust PM$_{10}$ concentrations. Therefore, diesel exhaust PM concentrations, calculated as described above, ranged from approximately 3.4 to 5.7 μg/m^3 (See Table V-1).

In another study, diesel exhaust PM$_{10}$ concentrations were estimated in the South Coast from ambient PM$_{10}$ measurements taken throughout 1986 and source apportioned using the CMB model (Gray et al., 1989; reported in 1991). The results of the study indicate the following: The average diesel exhaust PM concentrations due to light-duty diesel emissions ranged from 3.6 to 5.6 μg/m^3 across the eight sites in the study area (averaging 4.6 μg/m^3). The highest average 24-hour diesel exhaust PM concentrations in the study area ranged from 6.2 to 22.0 μg/m^3 (averaging 14.3 μg/m^3).

B. ARB Staff Method for Estimating Diesel Exhaust PM$_{10}$ Outdoor Ambient Concentrations in California

Staff of the ARB estimated diesel exhaust PM$_{10}$ concentrations for California's 15 air basins (see Figure V-1) using receptor modeling techniques, which include chemical mass balance model results from several studies. This method provides a means to apportion sources of primary PM$_{10}$ on a site-by-site basis, and is used to estimate population-weighted annual averaged outdoor concentrations statewide. Studies from the San Joaquin Valley (1988-89), South Coast (1986), and San Jose (winters of 1991-1992 and 1992-1993) were used to obtain speciated PM$_{10}$ ambient data. The ARB staff used these studies along with the ambient PM$_{10}$ monitoring network data, and the 1990 PM$_{10}$ emissions inventory, in a receptor model approach to estimate statewide outdoor concentrations of diesel exhaust PM$_{10}$.

In each of the studies used to estimate diesel exhaust PM$_{10}$ concentrations, researchers used a chemical mass balance model to apportion primary sources of PM$_{10}$ to diesel exhaust. Using their methods and results along with several assumptions, staff of the ARB were able to extract the diesel exhaust PM$_{10}$ concentrations from the San Joaquin Valley, South Coast (including the Southeast Desert), and San Jose areas.

Calculations for the other 12 air basins in California were based on the DRI SJV source apportionment study results to estimate average fractions for rural and urban exposures (DRI, 1990). Air monitoring data for California were extracted from the 1988 through 1992 versions of the California Air Quality Data Summary, Air Quality Data Gaseous & Particulate Pollutants Report (CAQDS report), published by the ARB's Technical Support Division. The 1990 PM_{10} Emission Inventory for diesel exhaust analysis and the CAQDS report were used to extrapolate the PM_{10} concentrations from diesel exhaust in the San Joaquin Valley (SJV) to the other 12 air basins. The SJV is used as a surrogate because the chemical mass balance results are the most recent and inclusive of rural and urban areas. By using each basin's inventory, basin-specific results were obtained (see Appendix B of this report).

Figure V-1
California's 15 Air Basins

Using an interpolation model and population distribution model, staff calculated the population-weighted annual average diesel exhaust PM_{10} concentration for all the air basins using 1990 census data for California (Appendix B).

With the sources of data outlined above, a number of assumptions were made. Some of the assumptions include: 1) using diesel exhaust PM_{10} as a subset of the primary motor vehicle category of the chemical mass balance results, 2) the diesel exhaust subset may be determined from the motor vehicle emission inventory, and 3) the sampling sites within the SJV can be characterized as rural or urban and this characterization can be further extrapolated to other air basins where source apportionment data are not available (See Appendix B for a detailed discussion of the approach taken and the assumptions used). The results of our analysis have been extensively discussed at public workshops and have incorporated public comments. We believe our approach used to estimate Californians' outdoor ambient exposure to diesel exhaust PM_{10} reflects the best available science and methods.

C. Estimated Concentrations of Outdoor Ambient Diesel Exhaust PM_{10} in California

Table V-2 summarizes the ARB staff-estimated ambient concentrations of diesel exhaust PM_{10} in California. The statewide population-weighted annual outdoor average diesel exhaust PM_{10} concentration is 3.0 $\mu g/m^3$. The basin-wide average diesel exhaust PM_{10} concentrations range from 0.2 $\mu g/m^3$ (Great Basin Valleys Air Basin) to 3.6 $\mu g/m^3$ (South Coast Air Basin). These concentrations are within the range of estimates given by other researchers (see Table V-1). The statewide population-weighted annual outdoor average diesel exhaust PM_{10} concentration estimate represents, in general, what most Californians may be exposed to, although 14 out of the 15 air basins with less population have values below the statewide average.

The ARB staff have also estimated 1995 outdoor ambient exposure concentrations based on linear extrapolations from the 1990 to the 1995 emissions inventories using linear rollback techniques. Linear rollback techniques are used to estimate the projected ambient concentrations of primary sources with respect to the base year emissions inventory. For this technique, a one-to-one correspondence between basin-wide emissions and source contributions at a given site is assumed. It is assumed that the changes in a specific source category, due to growth or emission control, will not greatly alter the distribution of emissions from that source category, and thus affect the outdoor ambient concentration estimate. Using this technique, we estimated 1995 outdoor ambient concentration of diesel exhaust PM_{10} in California of 2.2 $\mu g/m^3$.

Table V-2
Average Ambient Outdoor Concentrations of Diesel Exhaust PM_{10}
in California for 1990

Air Basin	Air Basin Population	Diesel Exhaust PM_{10} ($\mu g/m^3$)
Great Basin Valleys	29,000	0.2
Lake County	51,000	0.3
Lake Tahoe	21,000	1.0
Mojave Desert	557,000	0.8
Mountain Counties	485,000	0.6
North Central Coast	622,000	1.4
North Coast	564,000	1.2
Northeast Plateau	80,000	1.1
Sacramento Valley	2,219,000	2.5
Salton Sea	330,000	2.6
San Diego	2,504,000	2.9
San Francisco Bay Area	5,967,000	2.5
San Joaquin Valley	2,658,000	2.6
South Central Coast	1,232,000	1.8
South Coast	12,809,000	3.6
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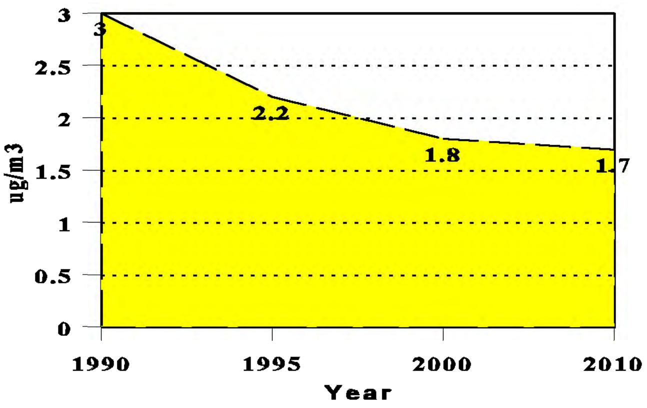
Statewide Population-Weighted Concentration	**30,131,000**	**3.0**

D. Diesel Exhaust PM_{10} Outdoor Ambient Air Concentration Projections

As with the 1995 estimated outdoor ambient exposure estimation, linear rollback techniques are used to project the ambient diesel exhaust PM_{10} concentration for the years 2000 and 2010. Figure V-2 shows the estimated and projected PM_{10} outdoor ambient concentrations based on the emissions inventory from diesel exhaust emissions for the base year, 1990 and 1995, and the projected years 2000, and 2010. Based on the emissions inventory projections, staff estimates that outdoor ambient diesel exhaust PM_{10} concentrations decreased from 3.0 $\mu g/m^3$ in 1990 to 2.2 $\mu g/m^3$ in 1995. By 2000 and 2010, concentrations are projected to be 1.8 $\mu g/m^3$ and 1.7 $\mu g/m^3$, respectively.

Figure V-2
Estimated PM_{10} Concentrations
Attributed to Emissions from Diesel Exhaust
for 1990, 1995, 2000, 2010



E. Near-source Emissions and Exposures

Approximately 60 percent of California's diesel exhaust PM_{10} is emitted on roadways by heavy-duty trucks, buses, and light-duty passenger vehicles. People living and/or working near busy roadways or intersections are exposed to higher-than-average concentrations of diesel exhaust.

The ARB staff conducted a study in 1993 to determine the PM_{10} concentrations due to the primary emissions from diesel engine exhaust near the Long Beach Freeway. Ambient carbon data was collected for three days in December 1993 on both sides of the freeway as well as on the roof of a school gymnasium located 1.5 miles away to obtain background concentrations. The measured carbon data, elemental and organic, were then used to estimate near-freeway diesel exhaust PM_{10} concentrations. In addition, information from other studies on motor vehicle EC/OC source profiles, ARB's emission estimates from its EMFAC7G model, and a system of equations were used to estimate the concentrations. Results indicate that near-roadway concentrations of diesel exhaust PM_{10} may be as high as 8 $\mu g/m^3$ above ambient concentrations for one 24-hour period (ARB, 1996; Appendix C of this report).

This estimate is similar to the result that researchers at Volkswagen (1989) obtained from dispersion models to estimate typical U.S. roadway exhaust PM concentrations that would result from light-duty vehicle emissions. PM emissions from heavy-duty diesel vehicles were not included in the models. The researchers estimated that the vehicle-derived PM concentrations near an expressway could be as high as 7.1 $\mu g/m^3$ (4 meters from the road), while PM concentrations in an urban street canyon could be as high as 8.8 $\mu g/m^3$ (1 meter from the curb). Even without adding the contribution of heavy-duty vehicles, near-road PM concentrations estimated in this study for typical U.S. roadways are about twice the average ambient statewide population-weighted diesel exhaust PM_{10} concentration of 3.0 μg/m^3.

Diesel exhaust drifting away from stationary sources can significantly increase outdoor diesel exhaust concentrations (and the resulting public risk) in impacted areas. Higher-than-average exposures to diesel exhaust can occur near powerplants, oil production facilities, pumping stations, construction sites, shipping docks, railroad yards, truck parks, heavy equipment repair facilities, bus terminals, and other point or area emission sources where heavy-duty diesel engine operation is common.

1. Occupational Exposure

Occupational exposure studies have certain advantages over environmental studies conducted in outdoor ambient atmosphere. The diesel exhaust concentrations are generally higher, the exposed workplace population is better defined, duration of exposure more predictable, and sources of diesel exhaust are usually definable.

For example, Froines et al. (1987) reported PM concentrations (primarily diesel exhaust PM) inside urban fire stations from less than 100 μg/m^3 to as high as 480 μg/m^3, depending on the number of runs during the sampling period (8-hour). Personal sampling was used to measure total airborne particulate in several fire stations in New York, Boston, and Los Angeles. The authors sought the participation of nonsmokers to reduce the potential for elevated results due to the particles emitted from tobacco smoke. The fire stations acted as emission sources as the exhaust escaped from the buildings; the researchers reported outdoor PM concentrations ranging from 30 to 120 μg/m^3. The study also estimated a “worst-case” scenario. In a Los Angeles fire station, concentrations as high as 748 μg/m^3 were found. This represents an upper bound for the concentration of particles likely to be found in fire stations.

Recent industrial surveys of miners, forklift truck operators, truck drivers and railroad workers indicate a wide range of daily occupational exposures to PM in diesel exhaust (4 to 1,700 μg/m^3). Mine workers in enclosed spaces were exposed to the highest concentrations. NIOSH estimates that approximately 1.35 million people are exposed to diesel exhaust in the workplace. The 8-hour average measured concentrations of diesel particulate range from 100 to 1,000 μg/m^3 and levels in excess of 2,000 μg/m^3 have been reported (NIOSH, 1988).

In another study, and as part of a case control mortality study of trucking industry workers, exposures to diesel aerosol, via elemental carbon, were measured among four exposed job groups (road drivers, local drivers, dockworkers, and mechanics). In this study, eight industrial hygiene surveys were conducted at eight U.S. terminals and truck repair shops. A single-stage personal impactor was used to collect submicrometer-sized diesel particulates. All of the samples were taken over a full shift (approximately 8 hours) to maximize sensitivity. Results from these surveys indicated that overall average exposures to EC ranged from 5.1 μg/m^3 in road (long distance) drivers to 26.6 $\mu g/m^3$ in mechanics. These were significantly higher than average background concentrations, measured at the same locations where workers were sampled, of 3.4 $\mu g/m^3$ on major highways and 1.4 $\mu g/m^3$ in residential areas (Zaebst, et al. 1991). By assuming that the percentage of diesel exhaust-derived EC in Los Angeles (approximately 67 percent) and that diesel exhaust particles are about 64 percent EC (Gray et al., 1986) applies to other urban areas, we calculated approximate concentrations of diesel exhaust PM to range from 5.3 to 27.8 $\mu g/m^3$.

As part of the epidemiology studies used to estimate exposures to railroad workers, measurements were made to characterize workers' exposure to diesel exhaust. Personal samples to respirable particulate matter for over 530 workers in 39 jobs in four U.S. railroads over a three-year period were made. The samples were adjusted to remove the fraction of cigarette smoke, or called the adjustable respirable particulate (ARP). The geometric mean exposures to the ARP ranged from 17 $\mu g/m^3$ for clerks to 134 $\mu g/m^3$ for locomotive shop workers (Woskie et al., 1988).

F. Indoor and Total Air Exposure

People spend a majority of their time indoors. To accurately estimate the population's exposure to toxic air pollutants, risk assessors must consider both the amount of time people spend in different environments and the concentrations of the pollutants of interest in those environments.

To estimate Californians' exposures to diesel exhaust particles, ARB staff used estimates of population-weighted ambient diesel exhaust particle concentrations (discussed in sections B and C of this Chapter and in detail in Appendix B) in a model that can estimate indoor air concentrations, population indoor air exposure, and total air exposure. The model, called the California Population Indoor Exposure Model (CPIEM), was recently developed under contract to the ARB to improve estimates of population exposures to toxic air pollutants (Koontz et al., 1995). The model generally uses distributions of data (rather than single values) as inputs, and a Monte Carlo (repeated random sampling) simulation approach. ARB's model estimates developed using CPIEM are summarized here and discussed in more detail in Appendix D.

Because representative data on indoor concentrations of diesel exhaust particles are not available, population-weighted outdoor concentrations of diesel exhaust particles plus other inputs (such as distributions of California building air exchange rates) were used in a mass-balance model (provided as one of two modules in CPIEM) to estimate indoor air concentrations of diesel exhaust particles for different indoor environments. Using these indoor air concentration distribution estimates, the second module of CPIEM that combines adults and children's activity pattern data and air concentration data was used to estimate Californians' exposures to diesel exhaust particles across all enclosed environments. In addition, CPIEM was used to provide estimates of the population's total air exposure to diesel exhaust particles by combining indoor and outdoor air exposure estimates.

In estimating indoor air concentrations for different indoor environments, input data and various assumed values for six parameters were entered into the mass balance model. The six parameters were: the outdoor concentration distributions of diesel exhaust particles; air exchange rates; penetration factor; volume of the indoor space; indoor source emissions rate (set to zero); and a net loss factor that accounts for removal of particles from the indoor space. The statewide population-weighted annual average outdoor diesel exhaust particle concentration estimate of 3.0 ± 1.1 $\mu g/m^3$ (standard deviation) was used as the outdoor concentration input distribution. The mass-balance module was used to estimate indoor diesel exhaust particle concentrations for the four indoor environments (residences, office buildings, schools, and stores/retail buildings) in CPIEM for which specific data for one or more of the input parameters are available. Estimated indoor concentrations for these environments are shown in Table V-3 and range from 1.6 ± 0.7 $\mu g/m^3$ to 2.1 ± 0.9 $\mu g/m^3$. These and other estimates developed using CPIEM are discussed further in Appendix D.

No data for input parameters were found for the other enclosed environments used in the exposure module of CPIEM; consequently, those environments were assigned surrogate diesel exhaust particle distributions equal to the distributions estimated for similar types of buildings or environments. As shown in Table V-3, industrial plants and enclosed vehicles were assigned the population-weighted average outdoor concentration values, restaurants and lounges were assumed to have levels similar to those found in stores and retail buildings, and “other indoor places” were assumed to have levels similar to those in office buildings.

The distributions of indoor concentration estimates shown in Table V-3 were used as inputs in the exposure module of CPIEM, which combines concentration data and data on Californians’ activity patterns to develop time-weighted population exposure estimates. The results, shown in Table V-4, indicate that Californians were are exposed to average diesel exhaust particle concentrations of 2.0 + 0.7 $\mu g/m^3$ in indoor environments in 1990. The population time-weighted average total air exposure concentration across all environments (including outdoor) is 2.1 + 0.8 $\mu g/m^3$. This is about two-thirds of the population-weighted ambient average concentration. The integrated exposure estimates in Table V-4 predict the average exposure to diesel exhaust particles experienced by Californians indoors and across all environments. Both the integrated exposure estimates and the average air exposure concentration estimates take into account the differences in air concentrations in different environments and the time spent by Californians in those environments.

Table V-3
Estimated Statewide Air Concentrations of Diesel Exhaust Particles used as Exposure Module Inputs (μg/m^3)*

Environment	Estimated Mean (+ std dev)	Surrogate Mean (+ std dev)
Residences	1.9 ± 0.9	
Offices	1.6 ± 0.7	
Schools	1.9 ± 0.8	
Stores/Public/Retail Bldgs.	2.1 ± 0.9	
Outdoor Places	3.0 ± 1.1	
Industrial Plants		3.0 ± 1.1 (outdoors)
Restaurant/Lounges		2.1 ± 0.9 (retail)
Other Indoor Places		1.6 ± 0.7 (office)
Enclosed Vehicles		3.0 ±1.1 (outdoors)

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* Values significant to one digit (whole micrograms); calculated values shown here are rounded to two digits for informational purposes.

Similar indoor concentration and exposure calculations were conducted for the South Coast Air Basin and the San Francisco Bay Area. For the South Coast, the population-weighted outdoor concentration input distribution was 3.6 + 1.4 μg/m^3; the resulting estimated population average indoor exposure concentration was 2.4 + 0.9 μg/m^3, and the population average total exposure concentration was 2.5 + 0.9 μg/m^3. The input population-weighted outdoor concentration distribution use for the San Francisco Bay Area was 2.5 + 1.6 μg/m^3; the resulting estimated population average indoor exposure concentration was 1.7 + 0.9 μg/m^3, and the population average total exposure concentration was 1.7 + 0.9 μg/m^3.

Table V-4
Estimated Exposure of Californians to Diesel Exhaust Particles for 1990

	Time in Environment (Mean hours)	Integrated Daily Exposure (μg-hr/m^3)	Average Air Exposure Conc. (μg/m^3)*
Total Indoor (Enclosed) Exposure	22.5	48 ± 18	2.0 ± 0.7
Total Air Exposure	24	53 ± 18	2.1 ± 0.8

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* Values significant to one digit (whole numbers); calculated values shown here are rounded to two digits for informational purposes.

It is important to note that these estimates are population estimates based on very limited input data and a number of assumptions. These estimates are “improved” over previous estimates because they incorporate into the exposure calculation both Californians’ activity patterns and the reduced air concentrations of diesel exhaust particles in indoor environments relative to levels measured at ambient monitoring stations. However, they include notable uncertainty and do not adequately reflect the great variability of exposures that Californians are likely to experience over time. Of particular concern is the fact that higher exposures (the upper tail of the distribution) are likely to be underestimated and are not fully identified in this type of analysis, largely because the primary input (the annual average outdoor concentration calculated from ambient station data) does not necessarily reflect elevated diesel exhaust particle levels in “hot spot” locations and data are not available for environments such as inside vehicles where levels typically would be elevated. Individuals whose occupation or leisure activities keep them in close proximity to diesel exhaust for extended periods would be exposed to much higher levels of diesel exhaust particles than are reflected by the average estimated levels (and the distributions) shown in Tables V-3 and V-4.

1. Indoor and Total Air Exposure Estimates for 1995, 2000, and 2010

The estimated average indoor air exposure concentration associated with the 1995, 2000, and 2010 estimated outdoor average population-weighted exposure concentrations of 2.2 $\mu g/m^3$, 1.8 $\mu g/m^3$, and 1.7$\mu g/m^3$, respectively, is estimated to be approximately 1.47 $\mu g/m^3$ for 1995, 1.2 $\mu g/m^3$ for 2000, and 1.13 $\mu g/m^3$ for 2010. The average total air exposure concentration for the years 1995, 2000, and 2010 is estimated to be about 1.54 $\mu g/m^3$, 1.26 $\mu g/m^3$, and 1.19 $\mu g/m^3$, respectively (see Table V-5). The discussion below demonstrates how these estimates were made using the method for calculating 1995 estimates as an example.

These estimates were not developed by using the CPIEM model as were the earlier estimates for the 1990 baseline year. Because of the uncertainties associated with the outdoor ambient population-weighted average exposure concentrations for 1995, 2000, and 2010, and the lack of distributional information (such as a standard deviation) for these estimates, it is not appropriate to use the CPIEM to develop detailed indoor and total air exposure concentration estimates. Instead, to provide parallel average indoor and total air exposure estimates for 1995, 2000, and 2010, the ratios of the 1990 average indoor and total air exposure estimates to the 1990 population-weighted average outdoor concentration estimate were calculated and applied to the corresponding 1995, 2000, and 2010 outdoor estimates. The ratio of the 1990 estimated average indoor air exposure concentration to the 1990 population-weighted outdoor average concentration is 2.0/3.0. Using this ratio, we calculated the time-weighted average indoor exposure concentrations for 1995, 2000, and 2010. Two-thirds of 2.2 $\mu g/m^3$ (the 1995 outdoor population-weighted average estimate), 1.8 $\mu g/m^3$ (2000) and 1.7 $\mu g/m^3$ (2010) equals 1.47 $\mu g/m^3$, 1.2 $\mu g/m^3$ and 1.13 $\mu g/m^3$, respectively. The ratio of the 1990 baseline total air exposure to the population-weighted outdoor average concentration is 2.1/3.0. Taking 2.1/3 times the corresponding population-weighted outdoor levels for 1995, 2000, and 2010, we estimate average total air exposure concentrations to be 1.54 $\mu g/m^3$ for 1995, 1.26 $\mu g/m^3$ for 2000, and 1.19 $\mu g/m^3$ for 2010. These calculations assume that the ratios of the indoor and total air exposure concentrations relative to the estimated population-weighted ambient levels do not change over time, which may or may not be true due to changes in activity patterns and other factors. These estimates are approximations only, and are provided to allow some comparison to the 1990 baseline estimates.

These total exposure estimates are believed to underestimate, to an unknown extent, Californians' actual exposures to diesel exhaust particles. This is because insufficient data are available for concentrations inside vehicles and along roadways to allow such near-source, elevated exposures to be estimated for the population. Instead, in estimating total exposure, in-vehicle and roadway concentrations were assumed to equal the ambient outdoor population-weighted concentration. The few roadside data available indicate that in-vehicle and roadside levels would typically be several times higher than those measured at nearby ambient stations. Thus, because adult Californians spend an average of seven percent of their time inside vehicles, and at least one percent of their time walking or biking along roadways, elevated concentrations in those environments would increase the population's total exposure.

Table V-5
Estimated Exposure of Californians to Diesel Exhaust Particles for 1995, 2000, 2010

	Estimated Average Air Exposure Concentration - 1990 $\mu g/m^3$ (std. dev.)	**1990 Ratio**	**Estimated Average Air Exposure Concentration $\mu g/m^3$**		
			1995	**2000**	**2010**
Ambient Estimate	3.0 (1.1)		2.2	1.8	1.7
Total Indoor Exposure Estimate	2.0 (0.7)	2.0/3.0	2/3 x 2.2 = 1.47*	2/3 x 1.8 = 1.20*	2/3 x 1.7 = 1.13*
Total Air Exposure Estimate	2.1 (0.8)	2.1/3.0	2.1/3 x 2.2 = 1.54*	2.1/3 x 1.8 = 1.26*	2.1/3 x 1.7 = 1.19*

* Significant to two figures

G. Relevant Indoor Air Quality Studies

Data from a variety of studies were reviewed by ARB staff to develop the inputs to CPIEM to estimate diesel exhaust particle concentrations in indoor environments for use in exposure modeling. Except for indoor elemental carbon data collected for one study of southern California museums, there are no data available that can be used to directly estimate diesel exhaust particle concentrations inside enclosed environments. However, there is a small but increasing number of studies on building air exchange rates, particle penetration factors, indoor particle deposition and sink effects, and other factors that can be used, in combination with outdoor diesel exhaust particle concentration estimates, to estimate concentrations of diesel exhaust particles in indoor environments. Some of those studies were conducted in California and provide California-specific data. The major studies used in the modeling work described in the previous section are discussed briefly below. All of the studies reviewed for the modeling work and the specific data from those studies used to develop the model inputs are discussed in Appendix D of this report.

1. Residential Studies

The Particle Total Exposure Assessment Methodology (PTEAM) Study provided important input data for residential air exchange rates, particle outdoor-to-indoor penetration factors, and indoor particle removal rates for modeling residential concentrations of diesel particles. In the PTEAM study, investigators measured PM_{10} and $PM_{2.5,}$ metals, and other pollutants in 178 homes in southern California in the summer and fall of 1990 (Clayton et al., 1993). The air exchange rates (number of air changes of the volume of air in the house with outdoor air per hour) measured in those homes averaged 1.25 with a standard deviation of 1.02, and thus covered a broad range of air exchange situations that would be expected (Ozkaynak et al., 1994). The penetration factor calculated by the investigators for $PM_{2.5}$ was estimated to equal one, meaning that essentially all of the fine particles present in the outdoor air that entered the homes made it past the building shell. The indoor particle removal rate (due to indoor deposition and sink effects) was estimated to be about 0.4 per hour.

These PTEAM estimates were relied upon more heavily than estimates from other studies in modeling residential indoor concentrations of diesel exhaust particles for several reasons. The PTEAM data were collected from California homes, they are fairly recent, and they are based on a reasonable sample size. Most important, the investigators examined the relationships among air exchange rate, penetration factor, and indoor removal rate and provided estimates for all of these variables. Because these factors are inter-related, a data set such as that provided by PTEAM is somewhat more reliable for modeling purposes than data sets that provide information on only one of these factors.

In addition to the PTEAM study, a number of other California studies have included measurements of air exchange rates in homes in various regions of the state and during different seasons. Together, they provide a useful body of data for estimating annual air exchange rates for California homes. Air exchange rate measurements obtained during winter or from newer, more air-tight, California homes were available for over 1000 California homes; the average rates ranged from about 0.5 to 0.9 (Sheldon et al., 1993; BSG, 1990; Wilson et al., 1993; Wilson et al., 1986; Pellizzari et al., 1989). The average air exchange rates measured in a total of about 500 California homes during the summer ranged from about 0.7 to 2.8 (BSG, 1990; Wilson et al., 1986; ADM, 1990; Pellizarri et al., 1989). Data for fall and spring values, which fall somewhere in between the summer and winter values, were available from more than 700 California homes (BSG, 1990; Wilson et al., 1993; Wilson et al., 1986). The use of the data from these studies to develop a distribution of air exchange rates is described in Appendix D.

Penetration factor estimates for residences were based on a review of studies that provide modeled penetration factors based on various measured values. In the major California study discussed above, PTEAM investigators estimated a penetration factor of one for $PM_{2.5}$ and nearly one for PM_{10} (Ozkaynak et al., 1994). Other field study investigators have estimated penetration factors of less than one in residences. In a large field study of 394 homes, Koutrakis et al., (1992) estimated a penetration factor of about 0.84 for particles smaller than 2.5 microns. Results from smaller studies of 68 and 47 homes indicated penetration factors of 0.7 to 0.85 (Suh et al., 1994; Dockery and Spengler, 1981). In a winter study of 10 homes in Boise, Idaho conducted for the U.S. EPA's Integrated Air Cancer Project, investigators estimated an infiltration factor of about 0.5 for fine particles and 1.0 for VOCs, based on indoor/outdoor ratios of pollutants in homes with very low air exchange rates (0.2 - 0.8).

In a single, two-story California home, Thatcher and Layton (1995) investigated in detail the relationships among penetration, deposition, resuspension, and airborne particle concentrations indoors. The deposition velocities for particles were measured by raising the particle concentration indoors and simultaneously measuring air infiltration rates and particle concentration decay rates. Based on sampling results on different days, the indoor deposition rate for particles from 1 to 3 μm in diameter ranged from about 0.25 to 0.75 per hour, and deposition rates for particles 3 to 10 μm in diameter ranged from about 0.75 to 1.78 per hour. The investigators estimated the penetration factor for both particle fractions based on the experimentally determined deposition velocities and indoor/outdoor particle concentration ratios. For both particle fractions, the penetration factor was calculated to be nearly one; the investigators indicated that this shows that the building shell is not effective at removing particles as air enters the building. These test home results are consistent with the field study estimates obtained by Ozkaynak et al. (1994). Because Thatcher and Layton and Ozkaynak et al. both accounted for indoor deposition in their calculation of penetration factor, results from these studies were weighed more heavily in developing estimates of penetration factor and net indoor removal for the model, as discussed in Appendix D to this report.

2. Studies of Commercial and Public Buildings

Air exchange rate data for commercial and public buildings are provided by three studies, only one of which is a California study. Grot (1995) measured air exchange rates in 49 non-residential buildings located throughout the State of California. These buildings included 14 schools, 22 office buildings and 13 retail buildings. The measurements were taken for the buildings when their air handling systems were purposely set at minimum damper settings. Therefore, the data represent the natural infiltration rates of the buildings with a minimum influence from the air handling systems, and thus provide conservative (low) estimates of the typical in-use air exchange rates. The school buildings had the highest mean air exchange rate at 2.45 air changes per hour. The mean rate for retail buildings was 2.22, and the mean rate for office buildings was 1.35. For both office and retail buildings, large buildings were shown to have lower air exchange rates than small buildings.

In a second study, the National Institute of Standards and Technology conducted over

3000 measurements of air exchange rates in 14 U.S. office buildings (Persily, 1989). These included 2- to 15-story buildings which were mechanically ventilated by different types of heating, ventilating, and air conditioning (HVAC) systems. Investigators monitored each building for about a year under a range of weather and building operation conditions. The mean air exchange rate of all the measurements was 0.94 air changes per hour. The mean air exchange rate of individual buildings ranged from 0.29 to 1.73 (medians ranged from 0.25 to 1.65). In a third study, Turk et al. (1987) obtained air exchange measurements ranging from 0.3 to 4.1 in 38 buildings in the Pacific Northwest. The mean air exchange rate was 1.5.

Penetration factor data were not available for common public and commercial buildings. Because many public and commercial buildings have central HVAC systems that actively bring in outdoor air and filter the outdoor air, re-circulated indoor air, or both, distributions of penetration factors were estimated for different types of buildings. A single study provided information on the percent of different types of buildings that have active air filtration. BSG (1993) conducted a telephone survey to gather information about HVAC systems of non-residential buildings in California. Participants were specifically asked whether a filtration system was used in their air handling units. Complete information was provided on 88 buildings. These included 26 office buildings, 28 retail buildings and 34 schools. About 76% of school buildings, 64% of retail buildings and 73% of office buildings in the survey had filtered air. Approximately 20% of the buildings surveyed had only unfiltered air.

Data from several studies on filter efficiencies and the fraction of air filtered (Sinclair et al., 1990 and 1992; Weschler et al., 1983 and 1995; Ligocki et al., 1993) were used in combination with the BSG (1993) data to estimate distributions of penetration factors for different types of buildings. These data are very limited, but cover a range of building types including museums, telecommunications buildings, and manufacturing plants. The use of these studies to estimate particle penetration for public and commercial buildings is described in Appendix D and in Tables C4 and C5 of Appendix D.

In one of these studies, the investigators examined elemental carbon levels indoors in museums. Their results showed that indoor concentrations of elemental carbon vary with the air exchange rate and with the type of HVAC system used and the extent of particle filtration. Ligocki, et al. (1993) measured elemental carbon concentrations in and around five museums in Southern California during the summer of 1987 and the winter of 1987-1988. The five museums were the Getty Museum in Malibu, the Norton Simon Museum in Pasadena, the Scott Gallery in San Marino, the Southwest Museum in Los Angeles, and the Sepulveda House in downtown Los Angeles. The first three museums are modern buildings with custom heating, ventilation, and air conditioning (HVAC) systems with particle filtration. The Southwest Museum has a HVAC system in the hall, but no particle filtration system. The Sepulveda House is a historical museum with no HVAC system--when the weather is warm it is often operated with the doors and windows open. Seasonal averages for elemental carbon in the museums ranged from approximately 0.14 $\mu g/m^3$ at the Getty Museum during the summer, to 7.4 $\mu g/m^3$ at the Sepulveda House during the winter. The ratios of indoor to outdoor air concentrations of fine particles ranged from approximately 1:5 at the Norton Simon Museum (with the best HVAC system) to approximately 1:1 at the Sepulveda House (Nazaroff et al., 1990; Ligocki, et al., 1993).

As reported earlier in this Chapter (see 3.b. Elemental Carbon Source Apportionment), Gray (1986) determined that diesel exhaust contributes 67 percent of the Los Angeles area's airborne EC, and that an average diesel exhaust particle is about 64 percent EC. If this is the case, then the indoor diesel exhaust PM concentrations in the museums may have ranged from approximately 0.15 $\mu g/m^3$ (in the buildings with modern HVAC systems) to 7.7 $\mu g/m^3$ (in the Sepulveda House with no HVAC). Corresponding outdoor diesel exhaust particulate matter concentrations may have ranged from approximately 0.03 to 7.7 $\mu g/m^3$.

H. Other Routes of Diesel Exhaust Exposure (Multipathway)

Exposure assessment also involves determining concentrations of the various pollutants in media by which humans are exposed. Air emissions contaminate not only the air, but deposit onto water, soil, and vegetation. These media represent the additional possible pathways of exposure to ambient diesel exhaust concentrations. In order to estimate long-term exposures resulting from ambient concentrations, the risk assessment must address both inhalation and non-inhalation pathways of exposure.

Multiple exposure pathways may contribute to the total exposure to a pollutant. For humans, the primary pollutant exposure pathways are inhalation, ingestion of dirt and contaminated food products, water ingestion, and dermal absorption of pollutants or contaminated dirt deposited on the skin. The secondary pathways are a result of the assimilation of the pollutant into a food source.

In order to assess non-inhalation pathways, substance and site-specific data are needed. Since the specific parameters for diesel exhaust are not known for these pathways, a multi-pathway assessment for diesel exhaust exposure was not done. More research is needed in this area for diesel exhaust.

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VI.
ATMOSPHERIC PERSISTENCE AND FATE OF DIESEL EXHAUST

Diesel exhaust contains thousands of gas, particle, and particle- associated constituents, including carbon dioxide, carbon monoxide, water vapor, oxides of nitrogen, saturated and unsaturated aldehydes and ketones, alkanes, alkenes, monocyclic aromatic hydrocarbons, carbon-core particles, gas- and particle-phase polycyclic aromatic hydrocarbons (PAH) and PAH-derivatives, and metals (see Chapter III). This wide range of substances has an even wider range of atmospheric fates. For example, diesel exhaust contains the atmospherically-reactive animal carcinogen benzo[a]pyrene (BaP). Van Cauwenberghe et al. (1979) tentatively identified at least nine BaP derivatives after reaction with tropospheric ozone. Many of these derivatives are direct-acting mutagens (Finlayson-Pitts and Pitts, 1986).

Diesel exhaust's constituents can react with atmospheric radicals to form new species, combine with other substances to form more complex species, and/or be deposited onto surfaces. In this chapter, we provide a general discussion of what is known about the atmospheric lifetimes and fates of diesel exhaust's major component groups: particles, particle-associated organic compounds, gas and particle-associated PAH and PAH-derivatives, and gaseous species.

Diesel exhaust contributes to global warming because it contains substances such as methane and carbon dioxide. Diesel exhaust also contributes to acid deposition because it contains nitric and sulfuric acids, as well as other substances which can be transformed to acidic PM in the atmosphere. Diesel exhaust is not known to contribute to stratospheric ozone depletion.

A. Atmospheric Fate of Diesel Exhaust Particles

The two most important processes affecting diesel exhaust particles in the atmosphere are:

- ☞ dry and wet deposition (physical removal) of the particles, and
- ☞ atmospheric transformations of species adsorbed to the particles.

1. Physical Removal

Physical removal of diesel exhaust PM from the atmosphere is usually accomplished through accretion of the particles, atmospheric fall-out (dry deposition), and atmospheric removal by rain (wet deposition).

A particle's atmospheric lifetime due to dry deposition is a function of the particle's diameter (Graedel and Weschler, 1981). Diesel exhaust particles, generally smaller than 1 μm (Pierson et al., 1983), are expected to remain in the atmosphere from 5 to 15 days.

Rain events result in almost complete wash-out of particles 0.1 to 10 μm in diameter from the atmosphere (Leuenberger et al., 1985; Ligocki et al., 1985a,b). Since diesel exhaust particles are in this size range, they are expected to be efficiently washed from the atmosphere when it rains.

2. Atmospheric Reactions of Particle-Associated Organic Compounds

Organic compounds absorbed by the particles in the exhaust stream may be protected from photolysis and/or chemical reaction. Organic species coating the surface of the particles may be expected to primarily react with sunlight (through photolysis), ozone (O_3), gaseous nitric acid (HNO_2), and nitrogen dioxide (NO_2). Organic compounds coating the surface of the particles can also volatilize from the particle and become more susceptible to photolysis and/or chemical reaction.

B. Atmospheric Transformations of PAH and PAH-derivatives

This section describes the reactions to PAH in general, keeping in mind that PAH are a product of incomplete combustion from a number of sources. Both gas- and particle-phase PAH are found in the atmosphere. Naphthalene and other 2-ring PAH are present in the gas phase in ambient air, while the 5- or more-ring PAH (such as the 5-ring benzo[a]pyrene) are particle-associated (Coutant et al., 1988; Arey et al., 1987, 1989a; Atkinson et al., 1988). A similar distribution between gas and particle phase occurs for the PAH-derivatives, with, for example, nitro-PAH with 4- or more-rings being particle-associated.

In contrast to the PAH (with no atmospheric formation pathways), PAH-derivatives can be formed in the atmosphere from the gas- and adsorbed-phase reactions of the parent PAH. Some of the PAH-derivatives studied in the laboratory have been found to be highly mutagenic (Arey et al., 1986; Atkinson et al., 1990; Atkinson and Arey, 1994).

PAH adsorbed to particles can be transformed into PAH-derivatives by a number of atmospheric reaction processes, including photolysis and reaction with O_3, NO_2 and/or HNO_3, sulphur dioxide (SO_2), and dinitrogen pentoxide (N_2O_5) (Pitts et al., 1978, 1980). For example, particle-associated PAH may photolyze in ambient atmospheres. The extent to which this occurs depends on the properties of the absorbent. Researchers investigating photooxidation and photolysis of PAH on various surfaces (Korfmacher et al., 1980a,b; Blau and Gusten, 1981; Behymer and Hites, 1985, 1988; Kamens et al., 1985a,b, 1986; Yokley et al., 1986; Valerio et al., 1987) have concluded that photolysis rates are highly substrate dependent, with darker substrates leading to lower photolysis rates (presumably due to stabilization of the PAH incorporated in the particles). Cope and Kalkwarf (1987) investigated the photooxidation of certain adsorbed oxy-PAH and found them to be generally stable in sunlight, but to decay under the influence of light and O_3.

Gas-phase PAH appear to dominate over particle-phase PAH in the formation of nitro-PAH and other PAH-derivatives in the atmosphere (Arey et al., 1987, 1989a, 1990a; Atkinson et al., 1988; Zielinska et al., 1989b, Atkinson and Arey, 1994). Most of the atmospheric transformation products of the gas-phase PAH remain unidentified.

1. Loss Processes for the Gas-phase PAH and PAH-derivatives

Gas-phase PAH and PAH-derivatives undergo wet and dry deposition, photolysis, and reaction with OH radicals, NO_3 radicals, and O_3.

a. Wet and Dry Deposition

Gas-phase PAH have washout ratios ranging from 10^2 to 10^4, while particle-associated PAH generally have washout ratios around $10^{5\pm1}$ (Ligocki et al., 1985a; Bidleman, 1988). Comparison of the washout ratios for gas-phase PAH with the time-scale of gas-phase chemical reactions suggest that rain will not effectively remove them from the atmosphere. Dry deposition is also expected to be of minor importance (Eisenreich et al., 1981).

b. Reaction with the OH Radical

OH radical reactions with the PAH and PAH-derivatives proceed by OH radical addition to the aromatic ring (forming an initially energy-rich hydroxycyclohexadienyl-type radical), or by OH radical interaction with the substituent groups (either through H atom abstraction from C-H or O-H bonds or OH radical addition to >C=C< bonds: Atkinson, 1986; Atkinson, 1989).

The observed products of OH radical-initiated reactions (in the presence of NO_x) with PAH and PAH-derivatives are hydroxy- and nitro-arenes (Atkinson et al., 1987). The available (and limited) data indicate that yields of the hydroxyarenes are significantly higher than those of the nitroarenes.

c. NO_3 Radical Reactions

Reactions involving the initial addition of a NO_3 radical to the aromatic ring of a PAH lead to the formation of nitroarenes (Pitts et al., 1985a; Sweetman et al., 1986; Atkinson et al., 1987, 1990; Zielinska et al., 1989a; Arey et al., 1989b). Reactions involving NO_3 radical interaction with the substituent group(s) do not lead to the formation of nitroarenes (Atkinson, 1990). The other products of this type of reaction are not known with any certainty, although they may include hydroxynitro-PAH.

d. O_3 Reactions

For the gas-phase PAH studied to date, only acenaphthylene has been observed to react with O_3 (Atkinson and Aschmann, 1988), but reaction is also expected to occur for acephenanthrylene (Zielinska et al., 1988). These PAHs react with O_3 by addition of O_3 at the cylcopenta-fused ring >C=C< bond (Atkinson and Aschmann, 1988).

e. Photolysis

No evidence has been observed for the gas-phase photolysis of the 2- to 4-ring PAH (Atkinson et al., 1984; Biermann et al., 1985; Atkinson and Aschmann, 1986, 1988). However, photolysis of 1- and 2-nitronaphthalene and 2-methyl-1-nitronaphthalene has been observed under ambient outdoor sunlight conditions (Atkinson et al., 1989; Arey et al., 1990b).

C. Atmospheric Lifetimes of Gas-phase PAH and PAH-derivatives

Photolysis and reaction rate data have been combined with the ambient radiation flux and ambient concentrations of OH and NO_3 radicals, NO_2 and O_3 to estimate the lifetimes for some of the PAH and PAH-derivatives. These lifetime data are given in Table VI-1.

The ambient concentrations of NO_3 radicals in the lower troposphere over continental areas vary widely, in contrast to O_3 and OH radical concentrations which stay at reasonably consistent day-to-day ambient levels (Logan, 1985; Prinn et al., 1987; Arey et al., 1989a).

For the PAH that don't contain cyclopenta-fused rings, the dominant tropospheric loss process is by reaction with the OH radical, with calculated lifetimes of 1 day or less (the OH radical reaction only occurs during daylight hours).

The PAH containing cyclopenta-fused rings (such as acenaphthene, acenaphthylene, and acephenanthrylene) are expected to react with NO_3 radicals at a significant rate. NO_3 radical addition to the fused rings of the PAH is not significant as a tropospheric loss process for the PAH. PAH like acenaphthylene, having unsaturated cyclopenta-fused rings, are also expected to react with O_3 at a significant rate.

The dominant tropospheric removal process for the gas-phase PAH appears to be by daytime reaction with the OH radical, leading to lifetimes of about 1 day or less.

Many of the nitroarenes observed in ambient air are only formed in the atmosphere through the gas-phase reactions of the 2- 3- and 4-ring PAH (Pitts et al., 1985b; Nielsen and Ramdahl, 1986; Sweetman et al., 1986; Arey et al., 1986, 1987, 1989a,b, 1990a; Ramdahl et al, 1986; Zielinska et al., 1988, 1989a,b; and Atkinson et al., 1988).

The presence of the nitro-substituent group in the nitroarenes leads to a marked decrease in their reactivity towards the OH radical. Photolysis may be the dominant tropospheric removal process for these compounds, with calculated lifetimes of about 2 hours.

Table VI-1

The Atmospheric Lifetimes of Selected PAH and PAH-derivatives due to Photolysis and Gas-phase Reaction with OH and NO_3 Radicals, and O_3

PAHs	Lifetime due to reaction with			
	OH^a	$NO_3{}^b$	$O_3{}^c$	Photolysis[d]
Naphthalene	8.6 hrs	100 days	>80 days	
1-Methylnaphthalene	3.5 hrs	50 days	>125 days	
2-Methylnaphthalene	3.6 hrs	40 days	>40 days	
2,3-Dimethylnaphthalene	2.4 hrs	25 days	>40 days	
Biphenyl	2.1 days	>20 yrs	>80 days	
Acenaphthene	1.8 hrs	2.5 hrs	>30 days	
Acenaphthylene	1.7 hrs	13 mins	~43 mins	
Phenanthrene	6.0 hrs			
Anthracene	1.4 hrs			
Fluoranthene	~3.7 hrs[e]	~85 days		
Pyrene	~3.7 hrs[e]	~30 days		
1-Nitronaphthalene	2.9 days	3.6 yrs	>28 days	1.7 hrs
2-Nitronaphthalene	2.8 days	4.0 yrs	>28 days	2.2 hrs
1,4-naphthoquinone	5.0 days	100 days	>80 days	~2.6 hrs
2-Methyl-1-nitro-naphthalene	1.8 days	4.0 yrs	>55 days	2.1 hrs

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[a] For a 12-hr daytime average OH radical concentration of 1.5×10^6 molecule cm^{-3} (Prinn et al., 1987).

[b] For a 12-hr average nighttime NO_3 radical concentration of 2.4×10^8 molecule cm^{-3} and an NO_2 concentration of 2.4×10^{12} molecule cm^{-3} (Atkinson et al., 1986).

[c] For a 24-hr average O_3 concentration of 7×10^{11} molecule cm^{-3} (Logan, 1985).

[d] For an average 12-hr daytime NO_2 photolysis rate of $J_{NO2} = 5.2. \times 10^{-3}\ s^{-1}$.

[e] Using estimated OH radical reaction rate constant correlation with ionization potential (Biermann et al., 1985; Arey et al., 1990b; Atkinson et al., 1990).

D. Atmospheric Reactions of Gaseous Species

Gaseous diesel exhaust species (such as benzene or formaldehyde) can react in the atmosphere with other pollutants and/or sunlight to form new species. For example, 1,3-butadiene can react in the atmosphere with OH radicals and O_3 to form formaldehyde, acrolein, and/or radicals (ARB, 1992). Gaseous diesel exhaust species will primarily react with the following:

sunlight (through photolysis),
O_3,
the OH radical (during the daylight hours),
the NO_3 radical (during the nighttime hours),
gaseous HNO_3,
NO_2, and
the HO_2 radical (mainly during afternoon/evening hours).

The important reaction processes for most of the gas-phase organics are photolysis and reaction with O_3 and the OH and NO_3 radicals. For a limited number of compounds, one or more of the other reactive chemical species (HO_2, NO_2, and/or HNO_3) may react with them at significant rates. For example, HO_2 radicals react with formaldehyde, acetaldehyde, and glyoxal; NO_2 reacts with conjugated dienes; and gaseous HNO_3 reacts with the amines.

Gaseous species absorbed by particles may be unavailable for further chemical reaction. Gaseous species adsorbed to particles may be degraded by photolysis and reaction with tropospheric O_3, N_2O_5, NO_2, HNO_3, nitrous acid (HONO), sulfuric acid (H_2SO_4), and hydrogen peroxide (H_2O_2).

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APPENDIX A

SPECIES/SPECIES GROUPS IDENTIFIED OR TENTATIVELY IDENTIFIED IN DIESEL EXHAUST

Appendix A

Species/Species Groups Identified or Tentatively Identified in Diesel Exhaust

The substances below have either been detected in diesel exhaust or presumed to be in diesel exhaust based on observed chemical reactions and/or their presence in the fuel or lubricating oil. Further research is needed to estimate their contribution to diesel exhaust as a whole, and to diesel exhaust related atmospheric exposures.

Species/Species Groups Identified or Tentatively Identified in Diesel Exhaust

acenapthene (references: 1, 12)
acenaphthenequinone (11)
acenaphthylene (1, 4, 12)
acetaldehyde (1, 11)
acetone (11)
acetylene (11)
acrolein (1, 3, 4, 11)
aldehydes (11)
alkanes (3)
alkylanthraquinone (2)
alkylbenzenes (10)
alkyl-4H-cyclopenta[def]phenanthren-4-one isomers (6)
alkyl-9-fluorenones (2, 6)
alkyl-9-fluorenone isomers (6)
alkylnaphthaldehyde (2)
alkylnaphthaldehyde isomers (6)
alkylnaphthofuran carboxaldehyde (2)
C -alkylnitroanthracene isomer (6)
aluminum (7)
ammonia (4, 7, 11)
aniline (4)
anthanthrene (11)
anthracene (1, 4, 5, 6, 10, 12)
anthracene-x-aldehyde (11)
anthracene carboxaldehydes (5, 10)
anthracene-9-carboxaldehyde (2)
anthracene dicarboxylic acid anhydrides (10)
anthracene quinones (5, 10)
9,10-anthracenedione (13)
anthraldehyde isomer (6)

anthraquinone (2, 11)
9,10-anthraquinone (6)
anthrones(2, 5, 10)
antimony (7)
arsenic (1, 7)
barium (4, 7)
benzacenaphthylene (4)
benzacridines (4)
benzaldehyde (11)
benz[a]anthracene (1, 2, 4, 10, 11, 13)
benz[a]anthracene carboxaldehydes (10)
benz[a]anthracenedione (2)
benz[a]anthracene-7,12-dione (11)
7H-benz[de]anthracene-7-one (2, 11)
benz[de]anthracenone (2)
benzanthrone isomers (6, 10, 13)
7H-benz[de]anthrone-7-one (2, 11, 13)
benzene (1, 11)
benzo[c]cinnoline (12)
benzo[def]dibenzothiophene (4)
benzofluoranthene (12, 13)
benzo[b]fluoranthene (1, 4, 11)
benzo[ghi]fluoranthene (4, 10, 11, 12, 13)
benzo[j]fluoranthene (4)
benzo[k]fluoranthene (1, 4, 11)
benzofluorene isomer (6)
benzo[a]fluorene (4)
benzo[b]fluorene (4)
benzo[x]fluorene-y-one (11)
benzofluorenone (2)
benzo[a]fluorenone (2)
11-benzo[a]fluorenone (13)
benzoic acid (4)
benzonaphthothiophene (4)
benzo[b]naphtho[2,1-d]thiophene (4, 13)
benzo[b]naphtho[2,1-d]thiophene isomers (13)
benzo[ghi]perylene (1, 4, 11, 12)
benzo[c]phenanthrene (11)
1-benzopyran-2-one (12)
benzopyrenes (13)
benzopyrene ketones (2)
benzo[a]pyrene (1, 4, 8, 10, 11)
benzo[e]pyrene (4, 11)

benzo[xy]pyrene-z-one (11)
6H-benzo[cd]pyrenone isomers (6, 11)
benzo[cd]pyrenone (2)
6-H-benzo[cd]pyrene-6-one (11)
beryllium (1)
1,2-binaphthyl (4)
2,2-binaphthyl (4)
biphenyl (12)
biphenyl carboxaldehydes (5, 13)
biphenylene (12)
bis[ethylhexyl]phthalate isomer (6)
bromine (7)
1,3-butadiene (1, 3)
cadmium (1, 7)
calcium (7)
carbon dioxide (11)
carbon monoxide (1, 11)
carbonate ion (7)
chlorine (1, 7)
chlorobenzene (1)
chromium (1, 7)
chrysene (1, 4, 10, 11, 12, 13)
cobalt (7)
copper (1, 7)
coronene (4, 11)
cresols (4)
crotonaldehyde (11)
cyanides (11)
cyclopenta[cd]benzo[ghi]perylene (9)
cyclopenta[jk]naphtho[1,8,7-efg]pyrene (9)
cyclopentaphenanthrene-5-one (12)
4H-cyclopenta[def]phenanthrene (4)
4H-cyclopenta[def]phenanthren-4-one (2, 5, 6, 11)
cyclopenta[cd]pyrene (4, 9, 10, 11)
cyclopenteno[cd]pyrene (12)
dibenzacridines (4)
dibenz[a,c]anthracene (11)
dibenz[a,h]anthracene (1, 4, 11)
dibenz[a,j]anthracene (11)
dibenzofurans (12)
dibenzofuran carboxaldehydes (10)
dibenzopyrene or -[def,p]chrysene (4)
dibenzothiophene (4, 5, 13)

dibutyl phthalate (2)
2,3-dihydro-inden-1-one (12)
dihydroxyfluorenes (5)
1,3-dihydroxynitropyrene (4)
dihydroxyphenanthrenes (5)
dimethylanthracenes (4, 10)
dimethylanthracene carboxaldydes (1, 10)
dimethylanthrones (10)
dimethylbiphenyl (4)
1,9-dimethylfluorene (5)
dimethylfluorene quinones (10)
dimethylfluorenones (10)
dimethyhydroxyfluorene (10)
dimethylnaphthalene carboxaldehydes (10)
dimethylnaphthalene dicarboxylic acid anhydrides (10)
dimethylphenanthrene (4)
dimethylphenanthrenes (10)
dimethylphenanthrene carboxaldehydes (10)
dimethylphenanthrones (10)
4,4-dinitrobiphenyl (11)
2,5-dinitrofluorene (4)
2,7-dinitrofluorene (4)
2,7-dinitro-9-fluorenone (4)
dinitronaphthalene (4)
1,3-dinitropyrene (4)
1,6-dinitropyrene (4)
1,8-dinitropyrene (4)
dioxins (1)
elemental carbon (4, 7)
ethane (3, 11)
ethylbenzene (1)
ethyldibenzothiophene (4)
ethylene (3, 11)
ethylmethylphenanthrene (4)
2- or 9-ethylphenanthrene (4)
fluoranthene (1, 4, 5, 10, 11, 12, 13)
fluoranthene carboxaldehydes (10, 13)
fluoranthene quinones (10)
fluoranthones (10)
fluorene (1, 4, 5, 12)
fluorene carboxaldehydes (10)
fluorene quinones (5, 10, 12)
fluorenones (10, 13)

9-fluorenone (2, 11, 12)
fluoren-9-one (5)
9-fluorenone isomers (6)
formaldehyde (1, 11)
formic acid (4)
furans (1)
gallium (7)
heptane (3)
hexane (1, 3)
hexanaldehyde (11)
hydrogen (11)
hydrogen chloride (1)
hydrogen cyanide (11)
hydrogen sulfide (11)
hydroxyanthracenes (10)
hydroxychrysene/triphenylene (2)
hydroxydimethylanthracenes (10)
hydroxydimehtylphenanthrenes (10)
hydroxyfluoranthene (2)
hydroxyfluorene (10)
hydroxyfluorenone (10)
hydroxymethylanthracenes (10)
hydroxymethylphenanthrenes (10)
hydroxyphenanthrenes (5, 10)
hydroxypyrene (2)
hydroxyxanthene (10)
hydroxyxanthone (10)
indeno[1,2,3-cd]pyrene (1, 4, 11)
indium (7)
iron (4, 7, 11)
isobutyraldehyde (11)
lanthanum (7)
lead (1, 7)
manganese (1, 7, 11)
mercury (1, 7)
methane (3, 11)
methanol (4, 11)
methyl ethyl ketone (11)
methylanthracenes (10)
2-methylanthracene (4)
methylanthracene carboxaldehydes (2, 10)
methylanthracene-9-carboxaldehyde (2)
methylanthracene quinones (10)

methyl-9,10-anthracenedione (13)
methylanthraldehyde isomer (6)
methylanthraquinone (2)
x-methylanthraquinone (11)
methylanthrones (10)
methylbenz[a]anthracene (4)
7-methylbenzofuran (12)
methylbiphenyl carboxaldehydes (13)
9-methylcarbazole (4)
3-methylchrysene (4)
methyl-4H-cyclopenta[def]phenanthren-4-one isomer (6)
x-methyl-4-H-cyclopenta[def]phenanthrene-4-one (11)
methyldibenzothiophene (4)
methylfluoranthenes (4, 10, 13)
methylfluorenes (13)
9-methylfluorene (5)
methylfluorene carboxaldehydes (10)
methylfluorene quinones (10)
methylfluorenones (10, 13)
2-methylfluorenone (13)
methyl-9-fluorenone (2, 12)
methyl-9-fluorenone isomers (6, 11)
methylhydroxyfluorene (10)
methylnaphthaldehyde (2, 13)
methylnaphthaldehyde isomers (6)
6-methyl-2-naphthaldehyde (13)
methylnapthalene (12)
methylnaphthalene dicarboxylic acid anhydrides (10)
methylnitroanthracene isomer (6)
methylnitrofluoranthenes (10)
x-methyl-9-nitroanthracene (11)
x-methyl-1-nitronaphthalene (4)
methylnitropyrenes (6, 10)
methylphenanthrenes (10)
1-methylphenanthrene (5, 13)
2-methylphenanthrene (4, 5, 13)
3-methylphenanthrene (4, 13)
4-methylphenanthrene (13)
9-methylphenanthrene (5, 13)
methylphenanthrene carboxaldehydes (2, 10, 13)
methylphenanthrene-9-carboxaldehyde (2)
methylphenanthrene quinones (2, 10)
methylphenanthrones (10)

methylphenylnapthalenes (13)
methylpyrenes (4, 10, 12, 13)
1-methylpyrene (4)
methylthioxanthones (10)
methylxanthones (10)
molybdenum (7)
1-napthaldehyde (13)
2-napthaldehyde (13)
napthaldehyde isomers (6)
naphthalene (1, 5, 12)
naphthalene carboxaldehydes (5)
naphthalene dicarboxaldehydes (10)
naphthalene dicarboxylic acids (5)
1,8-naphthalene dicarboxylic acid (11)
naphthalene dicarboxylic acid anhydrides (5, 10)
naphthoic acid (4)
1-naphthol (4)
2-naphthol (4)
naphtho[1,8-cd]pyrene 1,3-dione (10, 12)
nickel (1, 7)
nitrates (7)
nitric acid (4)
nitric oxide (4)
nitro-PAHs (2)
1-nitro-3-acetoxypyrene (4)
nitroanthracenes (6, 10)
nitroanthracene isomer (6)
9-nitroanthracene (4, 8)
2-nitroanthracene (4)
(1 or 3)-nitrobenzo[a]pyrene (8)
(3 or 1)-nitrobenzo[a]pyrene (8)
6-nitrobenzo[a]pyrene (4, 8, 11)
x-nitrobenzoquinoline (4)
2-nitrobiphenyl (4)
3-nitrobiphenyl (4)
4-nitrobiphenyl (4)
1-nitrochrysene (4)
nitrochrysene isomer (6)
x-nitrodibenzothiophene isomers (4)
x-nitro-y,z-dimethylanthracene (4)
nitrofluoranthenes (10, 13)
nitrofluoranthene isomers (6)
1-nitrofluoranthene (4)

3-nitrofluoranthene (4, 11)
7-nitrofluoranthene (4)
8-nitrofluoranthene (4)
nitrofluorenes (10)
2-nitrofluorene (4, 11)
2-nitro-9-fluorene (4)
3-nitro-9-fluorene (4)
nitrogen (1, 11)
nitrogen oxides (1, 4, 11)
1-nitro-3-hydroxypyrene (4)
9-nitro-1-methylanthracene (4)
10-nitro-1-methylanthracene (4)
10-nitro-9-methylanthracene (4)
x-nitro-y-methylanthracene (4)
1-nitro-2-methylnaphthalene (4)
3-nitro-1-methylpyrene (4)
6-nitro-1-methylpyrene (4)
8-nitro-1-methylpyrene (4)
1-nitronaphthalene (4)
2-nitronaphthalene (4)
3-nitro-1,8-naphthalic acid anhydride (4)
2-nitrophenanthrene (4)
nitrophenanthrenes (6, 10)
nitropyrenes (5, 6, 10, 12, 13)
1-nitropyrene (4, 8, 11)
5-nitroquinoline (4)
8-nitroquinoline (4)
x-nitroterphenyl (4)
x-nitro-y,z,z'-trimethylanthracene [6 isomers] (4)
x-nitrotrimethylnaphthalene [3 isomers] (4)
nitrous acid (4)
octane (3)
organic Carbon (7)
4-oxapyrene-5-one(I) (8)
oxygen (11)
oxy-PAHs (2, 5)
PAHs (1, 2, 4, 5, 9, 10, 11)
PAH derivatives (2, 4, 5, 11)
PAH anhydrides (4, 5)
PAH carboxaldehydes (4, 5)
PAH coumarin (11)
PAH epoxides (2)
PAH esters (4)

PAH ketones (4, 5, 10)
PAH quinones (4)
PAH sulfonates (4)
palladium (7)
pentane (3)
perylene (11, 13)
1-H-phenalene-1-one (11)
phenanthrenes (1, 4, 5, 6, 7, 12, 13)
phenanthrene-x-aldehyde (11)
phenanthrene carboxaldehydes (5, 10, 13)
phenanthrene-9-carboxaldehyde (2)
2-phenanthrene carboxaldehyde (13)
phenanthrene dicarboxylic acid anhydrides (10)
phenanthrene quinones (5, 10, 12)
phenanthrene-9,10-quinone (11)
phenanthroic acid (4)
phenanthrones (2, 5, 10)
5H-phenanthro[4,5-bcd]pyran-5-one (8)
phenol (4, 11)
phenylbenzaldehyde isomers (6)
phenylnaphthalene (5, 13)
2-phenylnaphthalene (4)
1-phenylphenanthrene (4)
9-phenylphenanthrene (4)
phenylphenanthrene or -anthracene (4)
phosphorus (1, 7)
phthalate (11)
phthalate Anhydride (12)
phthalic acid (4)
platinum (4, 11)
POM [Polycyclic Organic Matter] (8)
potassium (7)
propane (1, 3)
propionaldehyde (11)
propylene (3)
pyrene (1, 4, 5, 6, 10, 11, 12, 13)
pyrene carboxaldehydes (10, 13)
1,12-pyrenedicarboxylic acid anhydride (11)
pyrene-3,4-dicarboxylic acid anhydride (2, 9)
pyrene quinones (10)
pyridine (4)
pyrones (10)
quercetin (8)

rhodium (11)
rubidium (7)
selenium (1, 7)
silicon (7)
siloxane (6)
silver (7)
sodium (7)
strontium (7)
styrene (3)
sulfates (7, 11)
sulfur (1, 7, 11)
sulfur dioxide (11)
sulfuric acid (4)
n-tetradecane (12)
tetramethylnaphthalene (4)
thioxanthen-9-one (5)
9H-thioxanthen-9-one (2)
thioxanthones (10)
tin (7)
titanium (7)
toluene (1, 11)
trimethylbiphenyl (4)
2,2,4-trimethyl-1,3-diol diisobutyrate (6)
trimethylnaphthalene (4)
trimethylnaphthalene carboxaldehydes (10)
2,4,7-trinitro-9-fluorenone (4)
triphenylene carboxaldehydes (10)
vanadium (7)
water vapor (11)
xanthene carboxaldehydes (10)
xanthen-9-one (5)
9H-xanthen-9-one (2)
xanthones (10)
xylenes (1)
yttrium (7)
zinc (1, 4, 7)
zirconium (7)

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