

Internal Combustion Engine (ICE) Air Toxic Emissions

Final Report

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Table of Acronyms

ADR 36	Australian Design Rules Procedure 36
AQIRP	Auto/Oil Air Quality Improvement Research Program - Joint program of major US car manufacturers and oil industries
API	American Petroleum Institute
AL	Adaptive Learning
BCB	Braunschweig City Bus Driving Cycle, used by the Swedish for HD vehicles
CAA	Clean Air Act
CARB	California Air Resource Board
CBD	Central Business District
CDPF	Catalyzed Diesel Particulate Filters
CE-CERT	The University of California, Riverside, College of Engineering-Center for Environmental Research and Technology
CFR	Code of Federal Regulation
CIFER	Colorado Institute for Fuels and High Altitude Engine Research
CNG	Compressed Natural Gas
CRC	Coordinating Research Council
CRT™	Johnson-Matthey Continuously Regenerating Technology
CSHVC	City Suburban Heavy Vehicle Cycle
CUE	Congested Urban Expressway Cycle
CUEDC	Composite Urban Emissions Drive Cycle
D13	The Japan Diesel 13 Mode Cycle
DD	Detroit Diesel
DISI	Direct Injection Spark Ignition Engine
DOE	Department of Energy
DPF	Diesel Particulate Filters
DPX™	Engelhard Catalytic Soot Filter
DRI	Desert Research Institute
E85	Ethanol /gasoline fuel - Ethanol/gasoline blend (here 85% Ethanol by weight)
ECD	Emission Control Diesel
ECE	Economic Commission for Europe
EGR	Gas Recirculation
EPA	Environmental Protection Agency
ETBE	Ethyl tertiary butyl ether - Fuel additive
FTP	Federal Test Procedure - Exhaust emission test procedure used commonly in the USA and widely documented
HAP	Hazardous air pollutant, also known as air toxics
HC	Hydrocarbon
HD	Heavy-Duty
HDDV	Heavy-Duty Diesel Vehicles
HDGV	Heavy-Duty Gasoline Vehicles
HDTC	Heavy-Duty Transient Cycle
HWFET	Highway Fuel Economy Test

IARC	International Agency for Research on Cancer
ICE	Internal Combustion Engines
I/M	Inspection and Maintenance Programs
IUATS	Integrated Urban Air Toxics Strategy
LD	Light-Duty
LDDV	Light-Duty Diesel Vehicle
LDGV	Light-Duty Gasoline Vehicle
LED	low emission diesel, S<15ppm
LEV	Low Emission Vehicle - Class of vehicles according to their exhaust emissions as defined in US /California legislation
LPG	Liquid Petroleum Gas
M85	Methanol /gasoline fuel - Methanol/gasoline blend (here 85% methanol by weight)
MSATs	Mobile Source Air Toxics
MATES	Multiple Air Toxics Exposure Study
MTBE	Methyl tertiary butyl ether Blending component for fuels
MIR	Maximum Incremental Reactivity - Reactivity Factors of emissions components regarding ozone formation potential
NC	Non Catalyst Vehicle
NEDC	New European Driving Cycle
NLEV	National Low Emission Vehicle
NMHC	Non methane Hydrocarbons - Group of total hydrocarbons with methane removed
NMOG	Non methane Organic Gases - Group of total organic gases with methane removed, in other words NMHC + oxygen-containing materials (aldehydes, ketones & alcohols)
NO _x	Nitrogen Oxides
NRC	National Research Council
NREL	The National Renewable Energy Laboratory
NYCC	New York City Cycle
OC	The Oxidation Catalyst
OEHHA	Office of Environmental Health Hazard Assessment
PAH	Polycyclic Aromatic Hydrocarbon
PFI	Port Fuel Injected Engine
PM	Particulate matter
RfC	Inhalation Reference Concentration
RFG	The Reformulated Gasoline
SAB	EPA's Scientific Advisory Board
SAPRC	Statewide Air Pollution Research Center at University of California, Riverside
SCAQMD	South Coast Air Quality Management District
SOF	Soluble Organic Fraction
SET	Sulfur Emissions Test
SS	Steady State
SwRI	Southwest Research Institute
TAC	Toxic Air Contaminant

THC	Total Hydrocarbon
TLEV	Transitional Low Emission Vehicle - Class of vehicles according to their exhaust emissions as defined in US /California legislation
TLV	Threshold Limit Value - Concentration limit value of a chemical component, depends on legislation
TWC	Three-Way Catalyst
UC	Unified Cycle
UDDS	Urban Dynamometer Driving Schedule
ULEV	Ultra Low Emission Vehicle - Class of vehicles according to their exhaust emissions as defined in US /California legislation
ULSD	Ultra-Low Sulfur Diesel
U.S.	The United States
VOC	Volatile Organic Compounds
WHO	World Health Organization
WVT	West Virginia University
ZEV	Zero Emission Vehicle Class of vehicles according to their exhaust emissions as defined in US /California legislation

Executive Summary

The emission rates of gas-phase airborne toxic compounds, as well as particulate matter (PM), have steadily been reduced during the past decade as a result of the introduction of reformulated gasoline and diesel fuel, advances in engine design and fuel metering systems, and the implementation of highly efficient exhaust aftertreatment control devices. As regulatory standards have gotten increasingly stringent, it is important to understand how air toxic emission rates have changed over the years in order to gauge the expected improvement in air quality. In this work, the available literature for studies dealing with the air toxic, PM, and PAH emissions from on-road, off-road, and stationary diesel, gasoline, and natural gas internal combustion engines (ICEs) is reviewed and evaluated. This review focuses on toxic emission studies using typical dynamometer source testing methods, and near-source ambient sampling (e.g., tunnel studies) of ICE emissions.

Gas-phase toxics (formaldehyde, acetaldehyde, acrolein, benzene, and 1,3-butadiene), PAHs, and PM are formed by the incomplete oxidation of hydrocarbons during combustion and are associated with adverse health effects. Formaldehyde, acetaldehyde, acrolein, and 1,3-butadiene all react rapidly with free radicals in the air. The ambient concentrations of benzene, 1,3-butadiene, and acetaldehyde are considerably below the EPA threshold. The ambient concentrations of formaldehyde are at the EPA threshold. Acrolein is the only compound that has ambient concentrations above the EPA threshold.

Both gas-phase toxics and PM emissions from mobile sources have been investigated in a number of dynamometer studies dating back to the 1970s and early 1980s. Data reported here showed large reductions in the airborne toxic and PM emissions from gasoline- and diesel-powered vehicles over the years as a result of improved emissions control technology and the introduction of cleaner fuels. These trends are observed in chassis dynamometer, engine dynamometer, and tunnel studies. It is expected that the emissions of these compounds will continue to be reduced further in the future with the introduction and proliferation of even more advanced technology vehicles.

Of all the engine and vehicle technologies, the catalytic converter provides the greatest emission reductions. For gas-phase toxics, the reductions were about 50 to 80% for oxidation catalysts and 80 to 99%+ for three-way catalyst (TWC) vehicles compared to non-catalyst (NC) vehicles, with conversion efficiencies for today's modern vehicle reducing toxics by >98%. For diesel vehicles, a decrease of 69 to 85% in gas-phase air toxic emissions was observed for diesel vehicles equipped with oxidation catalysts (OCs) compared to uncontrolled diesel vehicles. Gas-phase toxics and PM emissions also showed a strong dependence driving cycles.

There is a wide range of toxics and PM emission rates for different heavy-duty vehicle class/model year categories. Toxics and PM emission rates from properly functioning, catalyst-equipped gasoline vehicles are considerably less than those from

uncontrolled diesel vehicles. PM mass emission rates from smoking gasoline-fueled vehicles; on the other hand, can be comparable to those observed for diesel vehicles. Diesel vehicles with DPFs and low sulfur diesel fuel show the highest PM reduction potential of 90 to 99% compared to diesel vehicles having no exhaust aftertreatment. The reduction of gas-phase air toxic emissions is more than 70% for diesel vehicle equipped with catalyzed DPF. It is anticipated that diesel vehicles with DPFs will be able to meet up coming regulatory limits with tightening PM control.

CNG vehicles generally exhibit reductions in PM and PAHs compared to uncontrolled diesel vehicles. CNG vehicles also generally have low gas-phase air toxic emissions, with the exception of formaldehyde, which is usually higher for CNG vehicles. The use of DPFs can reduce PM and other gas-phase emissions from diesel applications to levels comparable to those of CNG vehicles. The combustion of alcohol fuels tends to increase formation of aldehydes such as formaldehyde for methanol fuels and acetaldehyde for ethanol based fuels.

Fuel properties can also effect the emissions of air toxics, although this can depend on the specific vehicle and engine. General fuel effects are smaller than those that can be obtained with more advanced aftertreatment. Exhaust benzene and PAH content increase with both fuel benzene and fuel aromatics content. Reducing fuel olefin content and T90 lowers exhaust 1,3-butadiene emissions. Aldehyde emissions increase with fuel olefins, paraffins, and oxidation content. For PM emissions, significant reductions are found when fuel sulfur is reduced in the range between 3000 and 500 ppm, but changes in fuel sulfur below 500 ppm have a small impact on PM. Low fuel sulfur level s are also critical for the operation of many aftertreatment devices. Fuel aromatics do not appear to effect PM emissions when decoupled from density, although reducing PAH content does reduce PM in older engines. The effect of cetane number on PM emissions is engine dependent, with many engines showing no effect. There are a number of advanced/alternative diesel fuels that show promise in providing further PM reductions, including Fischer-Tropsch diesel, biodiesel, and ethanol diesel blends.

1. Introduction

Air borne toxic compounds (Air Toxics), also known as hazardous air pollutants (HAPs), are of interest for a variety of health related and ecological reasons (U.S. EPA, 2001a and b). California's statewide comprehensive air toxics program was established in the early 1980's. The Toxic Air Contaminant Identification and Control Act (Assembly Bill 1807) created California's program to reduce the potential health effects from air toxic substances and protect the public health of Californians. The California Air Resources Board (CARB) and the Office of Environmental Health Hazard Assessment (OEHHA) identified toxic air contaminants (TACs) in California that included benzene, 1,3-butadiene, formaldehyde, acetaldehyde and acrolein. In September 1987, the California Legislature established the air toxics "Hot Spots" program (Assembly Bill 2588). It required facilities to report their air toxics emissions, ascertain health risks, and to notify nearby residents of significant risks. The "Hot Spots" Act was amended in September 1992 to require facilities that pose a significant health risk to the community to reduce their risk through a risk management plan. In 1993, the California Legislature amended the AB 1807 program for the identification and control of TACs and required the ARB to identify the 189 federal hazardous air pollutants as TACs. Later in 1998, CARB identified diesel particulate matter (PM) emission as a Toxic Air Contaminant (CARB, 1999a). Findings of the risk assessment revealed that diesel PM can cause health problems ranging from respiratory illness, heart problems, asthma, cancer and even death.

South Coast Air Quality Management District (SCAQMD), the air quality control agency in Southern California, conducted a series major air toxic evaluation programs, referred as Multiple Air Toxics Exposure Studies (MATES I in 1980's, MATES II in 1990's, and up coming MATES III) to quantify the current magnitude of population exposure risk from existing sources of selected air toxic contaminants for the South Coast Air Basin. The study identified PM emissions from diesel engines as an important cancer risk factor. According to the MATES II study, diesel PM accounted for 71% of the total cancer risk associated with the air pollutants that were investigated. Other cancer risk contributors, primarily from gasoline engines and other non-diesel sources, included 1,3-butadiene at 8% of the risk, benzene at 7%, carbonyls (including formaldehyde and acetaldehyde) at 3%, and other pollutants (primarily from stationary sources) at 11% (SCAQMD, 1997). Overall, the study showed that motor vehicles and other mobile sources accounted for about 90% of the cancer risk and industries and other stationary sources the remaining 10%. The study also confirmed that the cancer risk from some air toxics in Southern California has declined by as much as 75% over the last decade.

Air quality in California has improved dramatically over the past 25 years, largely due to continued progress in controlling pollution from motor vehicles. In 1990, CARB approved standards for Cleaner Burning Fuels and Low and Zero Emission Vehicle (LEV and ZEV). California Phase I reformulated gasoline (RFG) came to market in 1992 and Phase II in 1996 (CARB, 2003a). These reduced airborne toxic chemicals emissions, especially for benzene. CARB enacted new standards for cleaner diesel fuel in 1993,

which resulted in a reduction of diesel PM and other emissions. Then in 1998, CARB adopted its LEVII emission standards that provided additional reductions for passenger car and light-duty trucks emissions beginning in 2004. Most federal and California mobile source emission control programs have focused on HC, nitrogen oxides (NO_x), and CO emissions and were not designed to reduce toxics emission specifically. However, these standards nevertheless helped to reduce the emission of gas phase toxics since many toxic air pollutants are HCs or formed from HC precursors.

Since mid-1980s, the United States (U.S.) Environmental Protection Agency (EPA) has a growing concern over the potential health effects of air toxics. In 1985, the U.S.EPA conducted a Six-Month Study with a goal of gaining a better understanding of the magnitude and causes of health problems attributed to outdoor exposure to air toxics. This study included quantitative estimates of the cancer risks posed by selected air pollutants and their sources (U.S. EPA, 1985). The estimates of upper bound cancer incidence ranged from 1300 to 1700 cases annually nationwide for all pollutants combined and the results further indicated that mobile sources might be responsible for a large portion of the aggregate cancer incidence. Based on this study, another study about air toxics was conducted, which for the first time placed more emphasis on motor vehicle emissions (Adler, 1989). In 1990, EPA's Office of Air Quality sponsored a five-city study to define the multi-source, multi-pollutant nature of the urban air toxics problem in different areas in U.S., with the goal of determining what reductions were likely to occur as a result of ongoing regulatory activities, and investigating what further reductions might be possible with additional controls (E.H. Pechan & Associates, Inc. 1990). Around the same time, EPA's Office of Air Quality also sponsored a study to update the 1985 Six-Month Study of cancer risks in the U.S. from outdoor exposures to air toxic pollutants. Motor vehicles accounted for almost 60% of total cancer incidence according to source categories examined in this study (U.S. EPA, 1990).

To address concerns about the potentially serious impacts of HAPs on public health and the environment, the 1990 Clean Air Act (CAA) Amendments included a number of provisions that allowed EPA to control these toxic emissions as appropriate. The CAA Amendments specifically targeted reductions in HAPs from mobile sources. These mobile source HAPs include benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and particulate matter (PM). This led to a set of EPA programs that have resulted or were projected to result in substantial reductions in HAP emissions from both the mobile sources and the stationary sources. Examples of these programs include the development of stationary source standards, the lead phase-out program, the reformulated gasoline (RFG) program, the national low emission vehicle (NLEV) program, the vehicle inspection and maintenance (I/M) programs, Tier 2 motor vehicle emissions standards, the gasoline sulfur control requirement, heavy-duty engine and vehicle standards, and emission standards for nonroad vehicles and equipment (locomotives, recreational marine engines, and aircraft). All these programs have substantially reduced air toxics emissions, especially in urban areas that often have high levels of ambient air toxics.

In 1993, EPA conducted a motor vehicle-related air toxics study, which estimated levels of several mobile source pollutants believed to pose the greatest risk to public

health, including the main HAPs from motor vehicles (U.S. EPA, 1993). The study also explored air toxics emissions from alternative fuel vehicles and nonroad engines. To support possible regulatory action required by CAA Section 202(1) and update EPA 1993 motor vehicle-related air toxics study, a follow-up study to estimate motor vehicle toxic emissions and exposure in selected urban areas was conducted in 1999 (U.S. EPA, 1999). This study, named as the EPA's Integrated Urban Air Toxics Strategy (IUATS), assessed motor vehicle air toxics emissions, and analyzed the impacts of control programs on motor vehicles toxic emissions. The analysis of toxic emissions was performed for benzene, acetaldehyde, formaldehyde, 1,3-butadiene, tert-butyl methyl ether (MTBE), and diesel PM. EPA conducted another study that addressed emissions of HAPs from mobile sources and their fuels (U.S. EPA, 2000a). In this study, they identified those compounds that should be considered MSATs, and examined the mobile source contribution to national inventories of these compounds. They also analyzed environmental impacts of existing and newly promulgated mobile source control programs and evaluated whether additional mobile source air toxics controls are technologically feasible.

The contribution of PM to ambient air quality has received considerable attention over the past decade, with studies showing that increases in human mortality and morbidity can be associated with particulate pollution levels lower than those previously believed to affect human health. In view of the potential risks of exposure to excess levels of ambient PM, there has been an increased emphasis on understanding which sources make the most significant contribution to the emissions inventory. Although it is generally agreed that PM emissions from diesel vehicles account for a significantly disproportionate amount of the mobile source PM emissions inventory when compared to their fraction of miles traveled, our current state of knowledge on diesel PM is limited. In particular, there is still debate regarding in the contribution of diesel vehicles to the emissions inventory and more information is required to define the chemical composition, size distributions, and number counts of particulate phase emissions from diesel vehicles of different technology categories.

The emission rates of gas-phase airborne toxic compounds, as well as PM, have steadily been reduced during the past decade as a result of the introduction of reformulated gasoline and diesel fuel, advances in engine design and fuel metering systems, and the implementation of highly efficient exhaust aftertreatment control devices. As regulatory standards have gotten increasingly stringent, it is important to understand how air toxic emission rates have changed over the years in order to gauge the expected improvement in air quality.

In this work, a comprehensive literature search was conducted to identify available data on gas-phase air toxics and particulate mass emission rates from dynamometer and on-road testing. Nearly 400 documents were identified in this survey regarding gas-phase air toxics and PM emissions from diesel, gasoline, and natural gas internal combustion engines (ICEs). This review focused on toxic emission studies using typical dynamometer source testing methods, and near-source ambient sampling (e.g., tunnel or roadway studies) of ICE emissions. The effects of various factors such as fuel

type, driving conditions, cycle type or application, and emissions standards on TACs and PM were also examined.

2. Brief Overview of MSATs: Health Effects and Properties

The Toxic Air Contaminant Identification and Control Act (AB 1807, Tanner 1983) created California's program to reduce exposure to air toxics. In 1983, the California Legislature established a two-step process of risk identification and risk management to address the potential health effects from air toxic substances and protect the public health of Californians. During the first step (identification), the ARB and the OEHHA determines if a substance should be formally identified as a TAC in California. The CARB staff assesses the potential for human exposure to a substance and the OEHHA staff evaluates the health effects. In the second step (risk management), the ARB reviews the emission sources of an identified TAC to determine if any regulatory action is necessary to reduce the risk. The analysis includes a review of controls already in place, the available technologies and associated costs for reducing emissions, and the associated risk. Public outreach is an essential element in the development of a control plan and any control measure to ensure that the ARB efforts are cost-effective and appropriately balance public health protection and economic growth.

In 1993, the California Legislature amended the AB 1807 program for the identification and control of toxic air contaminants (TACs) (AB 2728). Specifically, AB 2728 required the ARB to identify the 189 federal HAP as TACs. For those substances that have not previously been identified under AB 1807 and identified under AB 2728, health effects values will need to be developed. This report will serve as a basis for that evaluation. For substances that were not identified as TACs and are on the TAC Identification List, this report will provide information to evaluate which substances may be entered into the air toxics identification process.

In December 1999, the CARB completed the final report and update the Toxic Air Contaminant List. The List represents priorities for identifying and regulating substances as directed by State law. The Toxic Air Contaminant List is a list of 244 substances that have either been identified by the CARB as Toxic Air Contaminants (TACs) in California or are known or suspected to be emitted in California and have potential adverse health effects. The list is available at <http://www.arb.ca.gov/toxics/cattable.htm>. The List is used by the ARB to identify which substances should be evaluated as toxic air contaminants in California and which TACs should be evaluated for health effects. The list categorizes by priority, the substances for review under the Assembly Bill 1807 Toxic Air Contaminant Program.

The 1990 CAA Amendments designated a list of 188 air contaminants on the basis of their potential adverse health and/or environmental effects and specifically targeted reductions of five mobile source air toxics (MSATs) from mobile sources (benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and polycyclic aromatics). The U.S. EPA also identified 33 compounds as posing the greatest concern to human health in urban areas in EPA's IUATS in 1999. These compounds are a subset of the 188 air toxics contained in the 1990 CAA Amendments. MSATs are associated with on- and off-road motor vehicles and engines. They are formed by combustion processes or emitted into the atmosphere directly from gasoline and diesel evaporates. The U.S. EPA, in their proposal

for Control of Emissions of Hazardous Air Pollutants from Mobile Sources, identified 21 MSATs in 2000. The 21 MSATs is provided in Table 2-1.

Table 2-1. List of MSATs from EPA's Control of Emissions of Hazardous Air Pollutants from Mobile Sources.

Acetaldehyde*	Diesel Particulate Matter + Diesel Exhaust Organic Gases (DPM + DEOG)	MTBE
Acrolein*	Ethylbenzene	Naphthalene
Arsenic Compounds*	Formaldehyde*	Nickel Compounds ^{1*}
Benzene*	n-Hexane	POM ^{3*}
1,3-Butadiene*	Lead Compounds ^{1*}	Styrene
Chromium Compounds ^{1*}	Manganese Compounds ^{1*}	Toluene
Dioxin/Furans ²	Mercury Compounds ^{1*}	Xylene

¹ Although the different metal compounds generally differ in their toxicity, the on-road mobile source inventory contains emissions estimates for total metal compounds (i.e., the sum of all forms).

² This entry refers to two large groups of chlorinated compounds. In assessing their cancer risks, their quantitative potencies are usually derived from that of the most toxic, 2,3,7,8-tetrachlorodibenzodioxin.

³ Polycyclic Organic Matter includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100 degrees centigrade. A group of seven polynuclear aromatic hydrocarbons, which have been identified by EPA as probable human carcinogens, (benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, 7,12-dimethylbenz(a)anthracene, and indeno(1,2,3-cd)pyrene) are used here as surrogates for the larger group of POM compounds.

* Included in the 33 Urban HAPs list.

Five organic gas-phase species from Table 2-1 were selected to report on here. EPA has targeted these compounds for specific control based on the estimated toxicity and concern of high concentrations and human exposure. These compounds are benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and acrolein. PM emissions are also surveyed along with some information on polycyclic aromatics. They are also on the TAC List identified by CARB. All of them are included in the list of both MSATs and Urban HAPs. Of these five compounds only benzene is not formed to any large degree by photochemical processes. It has a longer residence time in the atmosphere compared with the other compounds. Other compounds, such as formaldehyde, acetaldehyde, and acrolein, can be formed by photochemical reactions of other hydrocarbon species in the atmosphere. Photochemical processes can also remove MSATs. Thus, the relationship between emission rates and ambient concentrations is not always straightforward. It is important to note that in urban areas, the ambient concentrations of benzene, 1,3-butadiene, and acetaldehyde are considerably below the EPA threshold (Zhu & Norbeck, 2003). The ambient concentrations of formaldehyde are at the EPA threshold. Acrolein is the only compound that has ambient concentrations above the EPA threshold. Because of its serious potential health effects, especially for fine PM, we included PM emissions in this report.

The following is a brief description of the chemical and physical properties and potential exposure effects of these compounds.

2.1 Formaldehyde

Traffic emissions are one of the most important sources of formaldehyde in air in urban areas including both primary formaldehyde (emitted directly from vehicles) and secondary formaldehyde (formed from photo oxidation of other VOCs emitted from vehicles) (U.S. EPA, 1993). Formaldehyde is the most prevalent aldehyde in vehicle exhaust and is produced as a by-product in the incomplete combustion process. Formaldehyde is not found in evaporative emissions (U.S. EPA, 1993). Formaldehyde is very reactive and reacts rapidly with free radicals in air. The half-life time in sunlight is a few hours (World Health Organization (WHO), 1989). The EPA in 1987, classified formaldehyde as a probable human carcinogen, based on nasal cancers in rats and limited evidence for carcinogenicity in humans. Formaldehyde has been identified by the ARB as a TAC. Epidemiological studies in occupationally exposed workers suggest that long-term inhalation of formaldehyde may be associated with tumors of the nasopharyngeal cavity, nasal cavity, and sinus (Vaughan et al., 1986). Both long-term and short-term effects on humans from exposure to formaldehyde are irritation of the eyes, nose, and respiratory tract. The threshold of irritation is considered to be 0.1 mg/m^3 for the average population (International Agency for Research on Cancer, 2002; World Health Organization, 1989). The potential lifetime cancer unit risk of formaldehyde is 6.0 E-6 per $\mu\text{g/m}^3$ (CARB, 2002).

2.2 Acetaldehyde

Acetaldehyde is found in both gasoline and diesel vehicle exhaust and is formed as a result of incomplete combustion of fuel. Acetaldehyde is not a component of evaporative emissions. Similar to formaldehyde, acetaldehyde also can also formed through a secondary process in which motor vehicle pollutants undergo chemical reactions in the atmosphere. The summer residence time of acetaldehyde in the atmosphere is on the order of hours but winter residence time is on the order of days. Acetaldehyde is classified as a probable human carcinogen based on sufficient evidence of carcinogenicity in experimental animals and limited human data (U.S. EPA, 1999). Acetaldehyde induced tumors in the nasal cavities in rats after long-term exposure by inhalation (Feron et al., 1982). Short-term exposure at low to moderate levels of acetaldehyde results in irritation of the eyes, skin and respiratory tract (Ligocki, 1991a and b). The potential lifetime cancer unit risk of acetaldehyde is 2.7 E-6 per $\mu\text{g/m}^3$ (CARB, 2002).

2.3 Benzene

Benzene is an aromatic hydrocarbon that is present as a gas in both exhaust and evaporative emissions from motor vehicles as well as from the burning of coal and oil. Some exhaust benzene is unburned fuel benzene. Some benzene also forms from engine combustion of non-benzene aromatics and even non-aromatic fuel hydrocarbons. Mobile

sources benzene emissions vary depending on both the benzene and aromatic content in the fuel. The benzene residence time in the atmosphere ranges from 2-4 days under summer, clear-sky conditions, to several months under winter, cloudy-sky conditions (U.S. EPA, 1993). Benzene is an important chemical from a health risk perspective. Benzene has been shown to cause cancer in both animals and humans; and is classified as a known human carcinogen (Group A) by the U.S. EPA. The primary source of human exposure to benzene is respiration. Drowsiness, dizziness, headache and unconsciousness have been reported at benzene levels between 160 and 480 mg/m³ (Larsen, 1998). There are also blood disorders such as preleukemia and aplastic anemia because of bone marrow depression, which have been associated with low-dose, long-term exposure to benzene, in some cases at exposure levels as low as 4-7mg/m³ (Larsen, 1998). The short-term exposure effects include respiratory tract, skin, and eye irritation. The potential lifetime cancer unit risk of acetaldehyde is 2.9 E-5 per µg/m³ (CARB, 2002).

2.4 1,3-Butadiene

The primary source of 1,3-butadiene in ambient air is traffic exhaust. Incomplete combustion of gasoline and diesel fuel results in 1,3-butadiene in vehicle exhaust. It is not present in vehicle evaporative and refueling emissions. The photochemical atmosphere reaction of 1,3-butadiene can produce a number of potentially toxic compounds such as acrolein and formaldehyde. In the daytime during the summer, the residence time of 1,3-butadiene in atmosphere is estimated to be less than one hour, while in the winter on cloudy days it may exceed a day (U.S. EPA, 1993). EPA classified 1,3-butadiene as a probable human carcinogen in 1985 based on evidence from animal studies. The Environmental Health Committee of EPA's Scientific Advisory Board recommended the designation of 1,3-butadiene as a known human carcinogen in 1998 based on a growing body of evidence of carcinogenic effects in humans and evidence of tumors in animals. Short-term exposure by inhalation results in irritation of the respiratory track, skin, as well as blurred vision, fatigue, and headaches at exposure levels of several thousand ppm (CARB, 2002). The potential lifetime cancer unit risk of acetaldehyde is 1.7 E-4 per µg/m³ (CARB, 2002).

2.5 Acrolein

Acrolein is a highly toxic and corrosive substance and is a more potent irritant than formaldehyde. Acrolein is produced by partial combustion of gasoline and diesel engines (IARC, 1985). EPA estimates that acrolein comprises 0.05 to 0.4% of exhaust TOG, depending on control technology and fuel composition. Acrolein is not a component of evaporative emissions (U.S. EPA, 1993). Acrolein is a byproduct of fires and is one of several acute toxicants, which firefighters must endure. It is also formed by atmospheric reactions of 1,3-butadiene. In ambient air, the most important removal mechanism for acrolein is the reaction with hydroxyl radicals (half life 15-20 hours). Acrolein may be removed from the atmosphere by precipitation. The atmospheric chemistry of acrolein is expected to be similar in many respects to that of formaldehyde and acetaldehyde.

Inhalation of acrolein can cause moderate to severe eye, nose, and respiratory system irritation. Higher concentrations can cause immediate and/or delayed lung injury including pulmonary edema and respiratory insufficiency. Fatal reactions have occurred upon exposure as low as 10 ppm (22.9 mg/m³). Acrolein is a powerful lachrymator, and eye contact with acrolein liquid or vapor can cause severe burns. Acrolein is mutagenic in bacteria but does not cause increased tumor incidence in animals exposed chronically by injection or inhalation. Chronic exposure to low level acrolein caused inflammatory changes in lungs, liver, kidneys, and brains of experimental animals. Acrolein was identified as a national non-cancer hazard driver in the National-Scale Air Toxics Assessment and was estimated to pose the highest potential on a nationwide basis for significant chronic noncancer effects (U.S. EPA, 2002). It was estimated that more than 10% of the U.S. population lives in census tracts where the typical exposure exceeded the reference concentration for this compounds (U.S. EPA, 2001b). EPA has classified acrolein as a possible human carcinogen, based on limited animal and mutagenicity data. A formal cancer risk characterization has not been conducted due to this limited data set (U.S. EPA, 1994).

2.6 PM

Numerous studies have been conducted to characterize airborne particles in the atmosphere and to identify their sources (Kittelson, 1978; Gertler et al., 2002a). PM emissions are primarily produced by automotive traffic and especially by diesel engines and heavy-duty (HD) diesel trucks. PM emission is a complex mixture consisting of solid carbon spheres with adsorbed compounds that include organics, metals, and sulfate. There is a general concern over possible health impacts of PM, especially diesel PM. U.S. CARB, EPA and many other agencies (World Health Organization, International Agency for Research on Cancer, National Institute of Occupational Health Sciences) have also reviewed health effects of diesel PM. In 1998, CARB identified Particulate emissions from diesel-fueled engines as a Toxic Air Contaminant. Derived from diesel exhaust, the California Office of Environmental Health Hazard Assessment (OEHHA) concluded that diesel PM is a known carcinogen with a unit risk of 3 excess deaths in 10,000 people per µg/m³ diesel PM lifetime exposure (CARB, 2002). Noncancer effects of diesel PM include enhanced allergic responses, exacerbation of asthma, and childhood illness.

2.7 PAHs

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in our environment and arise mainly from incomplete combustion of fossil fuels, organic materials, and wood. PAHs are also found in petroleum (NRC, 1983). Emissions from incomplete combustion can be categorized as mobile (e.g., gasoline and diesel engine exhausts) and stationary (e.g., coal-fired power plant, residential heating) sources. PAH emission from stationary sources has been decreasing since the 1950s due to a change in fuel usage from coal to petroleum and enhanced emission controls (Latimer and Quinn, 1996; U.S. EPA, 2000c). The increasing vehicle traffic associated with population growth in metropolitan areas can be responsible for increasing PAH concentrations and consequent degradation of air, soil and watershed quality (Van Metre et al., 2000). PAHs are a major health concerns in

most urban areas due to their high concentrations, and carcinogenic and mutagenic properties (IARC, 1983).

3. Gas-Phase Air Toxic Emissions

Over the past two decades, a number of studies have been conducted in an effort to measure air toxic emission rates from gasoline and diesel engines and vehicles. These have included chassis dynamometer tests of gasoline and diesel vehicles, engine dynamometer tests of gasoline and diesel engines, as well as on-road measurements. In the following section, these data have been compiled, collated, and evaluated. A comparison of emission rates for different vehicle classes is also made. Additionally, a brief summary of the impacts of technological advances on air toxics emissions is given.

Chassis dynamometer and engine dynamometer testing are extensively used to measure vehicle exhaust emissions. A chassis dynamometer is capable of simulating driving situations on the road while remaining in a controlled environment (laboratory). Most of vehicle emission studies have used the Federal Test Procedure (FTP) driving cycle to simulate city driving (Code of Federal Regulations 40 § 86.). Engine dynamometers are used to determine how well the engine, fuel system, and emissions control system work together by measuring the engine's speed and load, the fuel system's air-fuel ratio, and the concentration of constituents in the exhaust before and after treatment by the emissions control system.

In this study, only Class 7 and Class 8 vehicles are included in the heavy-duty vehicle section, others are included in the light-duty vehicle section.

3.1 Gasoline Engines and Vehicles

3.1.1 Gasoline Vehicles

Some of the earliest emission measurements of gas-phase toxics were conducted in the early 1980s by EPA to help provide initial data of gaseous toxics from vehicles. These studies included a range of the older vehicle technologies including non-catalyst (NC) as well as early catalyst vehicles. From a historical standpoint, the emissions measurements from the non-catalyst vehicles are important since they provide a baseline for comparison as to how toxics emissions have evolved over the years. In addition to these early studies, a number of researchers have also included non-catalyst vehicles to track the development of emissions control technology (Seizinger et al., 1986; Sigsby et al., 1987; Bogdonoff et al., 1988; Marshall, 1988; Marshall and Gurney 1989, Zafonte and Lyons, 1989; Boekhaus, et al., 1991a and; Stump et al., 1989, 1990a, 1990b, 1992, and 1994; Warner-Selph and Harvey, 1990; Hoekman, 1992; Jemma et al., 1992). The resulting toxic emission rates for NC vehicles over the FTP from these studies are summarized in Table 3-1. These results indicate that emissions rates for the different air toxics ranged widely. Air toxic emission rates varied from below 1 to 45 mg/mi for 1,3-butadiene, 47 to 156 mg/mi for benzene, 32.5 to 122 mg/mi for formaldehyde, and 7.1 to 27 mg/mi for acetaldehyde. Based on these studies, the average emissions rates were 17 mg/mi for 1-3 butadiene, 109 mg/mi for benzene, 70 mg/mi for formaldehyde, 16 mg/mi for acetaldehyde, and 8 mg/mi for acrolein.

Table 3-1. Experimental Values of Gas-Phase Toxics from Non-Catalyst-Equipped Vehicles on FTP Driving Cycle (mg/mi)

Year	Make	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolien	TOG (g/mi)	Ref
1970	Olds Delta 88 (Carb)	NA	82.19	51.28	7.18	NA	2.38	1
1970	Dodge Challenger (Carb)	NA	86.54	14.98	5.55	NA	2.84	1
1970	Chev Monte Carlo (Carb)	NA	91.10	107.43	10.84	NA	3.41	1
1970	Ford Fairlane (Carb)	NA	85.46	34.26	2.28	NA	3.9	1
1977	AMC Pacer (Carb)	NA	64.00	15.62	3.78	NA	1.21	1
1976	Toyota Celica	NA	26.16	77.64	19.68	3.98	0.88	2
1977	AMC Hornet	NA	112.89	121.84	20.63	4.18	6.31	2
1977	Datsun F-10	NA	21.44	84.80	20.69	4.19	1.98	2
1979	Mazda RX-7	NA	20.83	65.68	14.76	2.99	1.29	2
1980	Olds Cutlass	NA	42.77	9.74	12.75	2.58	2.07	2
1974	Chevy Impala (Carb) (0 MTBE)	60.40	421.00	84.10	19.50	NA	8.31	3
1974	Chevy Impala (Carb) (16.4% MTBE)	58.20	240.00	100.00	21.60	NA	6.30	3
	16 vehicles average	5.49	95.85	60.67	12.51	NA	3.14	4
1987	Volkswagen Golf (95 RON)	14.20	178.00	32.50	7.10	NA	2.90 ^a	5
1987	Volkswagen Golf (EC-P)	18.60	74.80	47.10	14.40	NA	2.73 ^a	5
1989	Volvo 740 (95 RON)	8.57	108.00	40.20	12.40	NA	1.52 ^a	5
1989	Volvo 740 (EC-P)	9.20	50.90	42.30	22.50	NA	1.41 ^a	5
1990	Rover 2000 (95 RON)	11.20	103.00	55.80	19.90	NA	2.06 ^a	5
1990	Rover 2000 (EC-P)	12.20	49.60	75.20	26.90	NA	2.07 ^a	5
70-78	4 vehicles average	2.96	156.18	73.25	19.74	11.62	3.16 ^a	6
70-78	4 vehicles average (RFG)	1.81	138.48	85.24	21.72	13.20	2.94 ^a	6
1984	GM Buick Century (40°F, Base)	34.35	108.25	105.44	23.32	NA	3.61 ^a	7
1984	GM Buick Century (40°F, MTBE)	28.95	74.50	108.91	20.76	NA	3.04 ^a	7
1984	GM Buick Century (75°F, Base)	36.83	85.83	100.73	22.27	NA	3.12 ^a	7
1984	GM Buick Century (75°F, MTBE)	34.53	61.07	111.89	22.47	NA	2.78 ^a	7
1984	GM Buick Century (90°F, Base)	44.80	46.52	103.54	23.71	NA	2.99 ^a	7
1984	GM Buick Century (90°F, MTBE)	34.65	64.90	108.37	21.80	NA	2.70 ^a	7
1976	Ford Pinto (RFG II)	16.23	49.20	99.12	26.17	5.23	1.72 ^a	8

Table 3-1. Continued

Year	Make	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	TOG (g/mi)	Ref
	2 vehicles average	NA	756.8	1414.4	481.6	6.11	NA	9
	Average (not include ref 9) ^b	16.57	103.29	69.45	16.10	8.74	3.02	

1. Urban, 1980a and 1981 (EPA-460/3-80-003, 81-020);
2. Sigsby et al., 1987 (46 car study);
3. Warner-Selph and Harvey, 1990;
4. CARB Butadiene Study, 1991;
5. Jemma et al., 1992; 95 RON is a typical European gasoline with Octane Number of 95. EC-P is a first generation of reformulated gasoline (ARCO EC-P) with 2% oxygen as MTBE;
6. Hoekman, 1992; The reference fuel is a typical Los Angeles premium gasoline, RFG contained 11 vol % MTBE;
7. Stump et al., 1994; Two fuel were used in this study, one was a summer grade unleaded regular fuel and the other one was a summer grade regular fuel with an 87 octane value and 9.5 % MTBE content; The vehicle operated at three different temperature to simulate ambient driving conditions.
8. Jones et al., 2001
9. Schauer et al., 2002. (2 vehicles: 1970 Volkswagen Vancamper and 1969 Chevy Camaro)

NA=not available; ^a HC data; ^b Because of the extremely high toxics emission rates from reference 9, these high values are not included to calculate the average emission rates.

The introduction of catalyst technology vehicles has been an important driver in reducing air toxic emission rates on a per vehicle basis. The earliest catalyst technologies were the oxidation catalysts (OC) introduced beginning in 1975 through the early 1980s when NO_x standards required the implementation of three-way catalysts (TWC). A summary of results from a range of different studies that have included test results for OC vehicles over the FTP is presented in Table 3-2. Although the toxic emissions also show a range of values for the OC catalysts, these values are typically well below those of the NC vehicles. Specifically, the average values obtained from these studies were 8 mg/mi for 1-3 butadiene, 43 mg/mi for benzene, 23 mg/mi for formaldehyde, 8 mg/mi for acetaldehyde, and 2 mg/mi for acrolein. Overall, the averaged emission rates of all species of air-borne toxics decrease by factors of about 70 to 80% for OC vehicles compared to NC vehicles.

A number of studies have included comparisons between different OC catalyst and NC vehicles (Sigsby et al., 1987; Warner-Selph and Harvey, 1990; Hoekman et al., 1992). Hoekman (1992) conducted exhaust tests with NC and OC catalyst vehicles, in addition to TWC, and TWC with adaptive learning vehicles as well as two fuels. Significant benzene emission decreases were observed for OC vehicles with reductions of 84% for traditional gasoline and 82% for reformulated gasoline, for the OC vehicles compared with the NC vehicles. Compared to NC vehicles, the 1,3-butadiene emission rates for the OC vehicles decreased by 99% using traditional gasoline and 82% using

reformulated gasoline. Hoekman also found formaldehyde emissions of the OC vehicles had reductions of 60% in comparison to NC vehicles and acetaldehyde emissions had reductions of 45%.

In addition to general comparisons between fleets of NC and OC catalyst equipped vehicles, some studies have also made direct measurements of toxics with and w/o OCs. Stump et al. (1990b) found that removing the OC catalyst from a 1984 GM Buick Century increased the emission rates of 1,3-butadiene by 5 to almost 100 times, of benzene by 3 to 12 times, of formaldehyde by 5 to 11 times, and of acetaldehyde by 3 to 7 times. A later study by Jones et al. (2001) presents emission values of individual toxics for a 1976 Ford Pinto without catalyst and with a new OC. These researchers found that the OC catalyst was effective at removing 98% of 1,3-butadiene, 93% of benzene, 97% of formaldehyde, and 95% of acetaldehyde from the exhaust. Stump et al. (1994) also found removing an OC from a 1984 GM Buick Century significantly increased the 1,3-butadiene, benzene, formaldehyde, and acetaldehyde emission rates (Table 3-1 and Table 3-2).

Table 3-2. Experimental Values of Gas-Phase toxics from Oxidation Catalyst-equipped Vehicles on FTP Driving Cycle (mg/mi)

Year	Make	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	TOG (g/mi)	Ref
1978	Chevy Malibu	N.A.	26.56	1.77	0.50	NA	0.51	1
1978	Ford Granada	N.A.	12.80	4.65	0.23	NA	0.44	1
1978	Ford Mustang II	N.A.	22.40	2.54	1.01	NA	0.52	1
1977	Oldsmobile Cutlass (Carb)	N.A.	9.01	4.18	0.64	NA	0.34	2
1977	Volkswagen Rabbit (FI)	N.A.	14.64	0.64	0.00	NA	0.23	2
1979	Chevy Chevette (Carb)	N.A.	53.96	7.55	2.45	0.50	1.25	3
1978	Ford LTD Wagon (Carb)	N.A.	17.77	18.47	7.63	1.54	0.74	3
1979	Ply Volare (Carb)	N.A.	80.25	12.74	6.17	1.25	2.12	3
1978	Ford Mustang (FI)	N.A.	144.62	68.10	18.91	3.83	4.78	3
1980	VW Scirocco (FI)	N.A.	8.83	4.01	2.94	0.60	0.45	3
1976	Olds Starfire (Carb)	N.A.	6.51	18.99	12.08	2.44	2.86	3
1976	Olds Regency (Carb)	N.A.	58.50	17.04	8.13	1.65	2.22	3
1977	Buick Skyhawk (Carb)	N.A.	29.70	16.30	7.24	1.47	1.51	3
1975	Ply Valiant (Carb)	N.A.	30.65	35.76	10.66	2.16	1.55	3
1978	Pont Phoenix (Carb)	N.A.	46.45	17.02	11.21	2.27	1.95	3
1979	Toyota Corolla (Carb)	N.A.	29.45	27.36	9.73	1.97	1.61	3
1980	Buick Electra (Carb)	N.A.	12.06	16.36	7.66	1.55	0.78	3
1977	Chevy Chevette (Carb)	N.A.	24.90	9.33	5.51	1.12	0.70	3
1978	Ply Volare (Carb)	N.A.	34.02	18.57	5.57	1.13	1.86	3
1978	Datsun 200SX (Carb)	N.A.	18.51	129.95	25.98	5.26	1.55	3
1979	Ford Fairmont (Carb)	N.A.	25.57	19.54	8.63	1.75	2.26	3
1980	Mazda GLC (Carb)	N.A.	23.56	48.75	14.29	2.89	1.92	3
1981	Chevy Chevette (Carb)	N.A.	20.12	3.89	2.93	0.59	0.83	3
1975	Olds Cutlass (Carb)	N.A.	87.36	92.82	22.73	4.60	5.36	3
1980	Chev Citation (Carb)	N.A.	6.71	5.84	2.46	0.50	0.37	3
1980	Ford Fairmont (Carb)	N.A.	39.10	78.46	19.20	3.89	1.78	3
1981	Crys Lebaron (Carb)	N.A.	10.36	6.33	3.67	0.74	0.41	3
1981	AMC Concord (Carb)	N.A.	27.31	8.68	6.79	1.37	1.38	3
1980	Crys Lebaron (Carb)	N.A.	10.36	6.60	2.82	0.57	0.38	3
1978	Buick Regal (Carb)	N.A.	86.53	14.21	2.61	NA	1.74	4
1978	Ford Granada (Carb)	N.A.	59.66	8.66	1.83	NA	1.77	4
1978	Ford Granada (Carb)	N.A.	53.34	11.86	2.70	NA	1.83	4
1978	Olds Cutlass (Carb)	N.A.	51.26	1.82	3.44	NA	0.88	4
1978	Olds Cutlass (Carb)	N.A.	43.71	1.96	1.95	NA	0.78	4

Table 3-2. Continued

Year	Make	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	TOG (g/mi)	Ref
1978	Chevy Malibu (Carb)	N.A.	33.87	10.23	2.14	NA	0.65	4
1978	Chevy Malibu (Carb)	N.A.	33.52	12.36	1.35	NA	0.67	4
1978	Chevy Monte C (Carb)	N.A.	17.94	8.54	0.00	NA	0.46	4
1978	Chevy Monte C (Carb)	N.A.	48.46	2.04	0.48	NA	0.85	4
1978	Ford Fiesta (Carb)	N.A.	12.51	2.74	0.00	NA	0.65	4
1978	Ford Fiesta (Carb)	N.A.	9.81	2.16	0.00	NA	0.56	4
1978	Chy N Yorker (Carb)	N.A.	209.41	27.37	4.54	NA	4.65	4
1978	Chy N Yorker (Carb)	N.A.	67.25	9.35	0.29	NA	1.36	4
1987	Chy Caravelle (FI)	0.80	16.08	2.46	1.32	NA	0.41	5
1984	Chevrolet Suburban (Carb)	1.89	20.36	22.66	9.09	NA	0.58	6
1983	Ford F-150 (Carb)	4.64	32.62	25.16	7.67	NA	1.09	6
1984	Chevrolet Suburban (15.0MTBE)	1.83	18.53	33.75	10.62	NA	0.58	6
1983	Ford F-150 (15.0MTBE)	6.30	32.13	60.80	9.03	NA	1.03	6
1980	Chevrolet Monza (Carb)	4.30	42.10	8.90	0.60	NA	1.42	7
1980	Chevrolet Monza (9.0% MTBE)	1.10	42.10	8.90	0.60	NA	1.44	7
1977	Mercury Marquis (Carb)	1.50	17.30	31.70	10.90	NA	0.92	8
1977	Mercury Marquis (16.4% MTBE)	1.70	12.60	100.00	21.60	NA	1.11	8
	7 vehicles average	0.28	38.04	19.29	5.93	NA	1.38	9
1976	Pinto	0.39	3.52	2.68	1.31	0.26	0.19 ^a	10
75-82	5 vehicles average	0.02	25.57	28.50	11.15	3.74	0.58	11
75-82	5 vehicles average (RFG)	0.33	25.01	35.83	11.76	3.75	0.57	11
1984	GM Buick Century (40°F)	5.75	40.30	17.39	7.08	NA	1.57 ^a	12
1984	GM Buick Century (40°F, 9.5% MTBE)	3.10	29.15	18.30	7.31	NA	1.48 ^a	12
1977	Ford Mustang (40°F)	99.10	271.80	37.36	23.49	NA	11.53 ^a	12
1977	Ford Mustang (40°F, 9.5% MTBE)	19.85	189.50	45.21	21.33	NA	6.96 ^a	12
1980	GM Chevrolet Citation (40°F)	8.35	32.55	20.71	7.70	NA	1.98 ^a	12
1980	GM Chevrolet Citation (40°F, 9.5% MTBE)	6.33	55.17	36.77	9.52	NA	2.40 ^a	12
1984	GM Buick Century (75°F)	0.80	7.10	10.16	3.72	NA	0.62 ^a	12

Table 3-2. Continued

Year	Make	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	TOG (g/mi)	Ref
1984	GM Buick Century (75°F, 9.5% MTBE)	0.35	7.80	22.46	6.49	NA	0.70 ^a	12
1977	Ford Mustang (75°F)	42.95	188.65	15.90	18.59	NA	7.87 ^a	12
1977	Ford Mustang (75°F, 9.5% MTBE)	9.05	136.25	25.34	13.25	NA	4.47 ^a	12
1980	GM Chevrolet Citation (75°F)	3.30	12.14	17.49	5.01	NA	0.75 ^a	12
1980	GM Chevrolet Citation (75°F, 9.5% MTBE)	2.40	16.70	33.00	7.05	NA	0.78 ^a	12
1984	GM Buick Century (90°F)	0.73	7.03	9.29	3.45	NA	0.59 ^a	12
1984	GM Buick Century (90°F, 9.5% MTBE)	0.35	7.10	17.17	4.97	NA	0.69 ^a	12
1977	Ford Mustang (90°F)	27.95	152.48	13.19	18.28	NA	6.92 ^a	12
1977	Ford Mustang (90°F, 9.5% MTBE)	6.27	120.27	17.90	12.54	NA	3.70 ^a	12
1980	GM Chevrolet Citation (90°F)	2.20	13.93	17.66	4.67	NA	0.64 ^a	12
1980	GM Chevrolet Citation (90°F, 9.5% MTBE)	1.90	13.85	30.55	6.16	NA	0.69 ^a	12
	Average	7.66	42.73	22.70	7.57	2.38	1.59	

1. Urban, 1980a (EPA-460/3-80-003);
2. Springer, 1979 (EPA-460/3-79-007);
3. Sigsby et al., 1987 (46 car study);
4. Smith, 1981 (EPA-460/3-81-024)
5. Stump et al., 1989;
6. Auto/Oil Study;
7. Boekhaus, et al., 1991. (Arco91-03)
8. Warner-Selph and Smith, 1991 (EPA-460/3-91-02);
9. CARB Butadiene Study, 1991;
10. Jones et al., 2001;
11. Hoekman, 1992;
12. Stump et al., 1994; Two fuel were used in this study, one was a summer grade unleaded regular fuel and the other one was a summer grade regular fuel with an 87 octane value and 9.5 % MTBE content; The vehicle operated at three different temperature to simulate ambient driving conditions.

NA=not available; ^a HC value

As TWCs were introduced into the fleet and then became the predominant component of the fleet, studies of TAC emissions from vehicles continued. In the late 1980s and early 1990s, one of the most important drivers for studying toxics from vehicles was the need to better understand how fuel properties affected toxics. This was particularly important in view of the CAA requirements for improvements in fuel quality. Among the groups that studied fuel effects on toxics were Auto/Oil Air Quality Improvement Research Program (AQIRP), Coordinating Research Council (CRC), California Air Resource Board (CARB), Arco Products Co., American Petroleum Institute (API), and others. For this section, we are focused primarily on the body of data collected on toxic emissions for a range of different vehicle types. The actual effects of fuel on TACs will be discussed further in fuel effect section.

A summary of the results of various studies of TWC-equipped vehicles is provided in Table 3-3. For these studies, airborne toxics emission rates from TWC vehicles over FTP averaged at 2, 18, 4, 2, and 1 mg/mi for 1,3-butadiene, benzene, formaldehyde acetaldehyde and acrolein, respectively. Although the toxic emissions also show a range of values for the TWC catalysts, these values are typically well below those of the NC and OC vehicles. The emission rates of all species of air-borne toxics decrease by factors of 85 to 95% for TWC vehicles when compared to NC vehicles.

Significant declines in air borne toxic emissions with catalyst-equipped vehicles have been shown by a number of studies (Seizinger et al., 1986; Jemma et al., 1992; Hoekman, 1992; Stump et al., 1994, Jones et al., 2001; Schauer et al., 2002). Seizinger et al. (1986) found that the TWC conversion efficiencies for benzene and total HC were essentially the same, ranging from 74% to 95% for benzene and 82% to 91% for total HC. Jemma et al. (1992) made measurements of tailpipe emissions on a 1989 model year Volvo 740 with and without a TWC catalyst. These researchers observed that benzene emissions were substantially reduced by TWCs on the gasoline vehicle (by 82% for a typical European gasoline and 72% for California reformulated gasoline). The reduction of 1,3-butadiene emission was about 88% and reductions of formaldehyde and acetaldehyde were about 92 to 95%.

Hoekman (1992) conducted exhaust tests with two fuels (regular and reformulated) and four vehicle technology types (NC, OC, TWC, and TWC with AL) on 17 vehicles. For both traditional and reformulated gasolines, significant benzene emission reductions were observed for OC, TWC, and AL vehicles by factors of 84, 88, 88% for traditional gasoline and 82, 89, 85% for reformulated gasoline, respectively, in comparison to NC vehicles. Compared to the NC vehicles, the 1,3-butadiene emission rates decreased by 99, 98, 100% for an OC, TWC, and TWC with AL using traditional gasoline and 82, 97, and 92% for an OC, TWC, and TWC with AL using reformulated gasoline. The authors also found formaldehyde emissions of the vehicles with an OC, TWC and TWC plus AL had reductions of 60, 91, 92%, respectively, in comparison to NC vehicles while reductions of 45, 80, and 81%, respectively, were found for acetaldehyde.

Stovell et al. (1999) from University of Texas conducted tests on a 1998 Toyota Corona with a Direct Injection Spark Ignition Engine (DISI) and a 1999 port fuel injected (PFI) Toyota Corolla. The DISI vehicle had two close-coupled TWCs and an underfloor NO_x trap. The PFI vehicle has a single TWC located underfloor. Overall, the DISI vehicle had higher benzene and formaldehyde emissions than the PFI vehicle. In contrast to PFI engine, the HC emissions for the DISI engine are not dominated by the first 1-2 minutes of operation. The engine out and tailpipe HCs and gas-phase toxics are higher throughout most of the FTP for the DISI than for the PFI vehicle. This is due to a large increase in engine-out HCs for late injection for the DISI engine.

Zhu and Norbeck (2003) reviewed LDGV toxic emissions trends during the last thirty years. The vehicles were stratified according to seven main technology categories, in order of increasing sophistication, are NC, OC, TWC, TLEV, LEV, ULEV, and SULEV vehicles. The typical emission rates of all MSATs for each technology group are shown in Figure 3-1. All these species in the figure are CARB TACs. In general, in comparison to NC vehicles, the emission rates of benzene were reduced by factors of about 70%, and 85% for the OC, and TWC vehicles, respectively, and above 98% for LEVs, ULEVs, and SULEVs. Compared to NC vehicles, the 1,3-butadiene emission rates decreased by 76, 85, and 95%, for OC, TWC, and TLEV vehicles, and more than 98% for LEV, ULEV, and SULEV vehicles. Compared to NC vehicles, the formaldehyde emission rates decreased by 81, 94, and 95%, for OC, TWC, and TLEV vehicles, and more than 99% for LEV, ULEV, and SULEV vehicles. The acetaldehyde emission rates decreased by 70, 87, and 95%, for OC, TWC, and TLEV vehicles, and more than 98% for LEV, ULEV, and SULEV vehicles.

Table 3-3. Experimental Values of Gas-Phase toxics from Three Way -Catalyst Vehicles on FTP Driving Cycle (mg/mi)

Year	Make	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	TOG (g/mi)	Ref
1989	5 vehicles average	2.00	15.40	5.20	2.26	NA	0.31	1
1989	5 vehicles average (5.5% MTBE)	1.93	8.68	5.14	2.45	NA	0.31	1
81-90	16 vehicles average	2.32	40.61	6.08	2.58	NA	0.72	1
1990	10 vehicles average	2.38	19.95	1.38	0.90	NA	0.34	1
81-90	29 vehicles average (9.0% MTBE)	3.03	24.50	5.92	2.32	NA	0.58	1
81-90	13 vehicles average (9.0% MTBE)	3.14	15.56	5.58	2.08	NA	0.53	1
1990	10 vehicles average (15.0% MTBE)	1.59	8.45	1.55	0.78	NA	0.23	1
1990	10 vehicles average (15.0% MTBE)	1.59	10.21	1.56	0.69	NA	0.24	1
1989	9 vehicles average	0.89	11.49	1.58	1.16	NA	0.20	2
1989	9 vehicles average (15.0% MTBE)	0.99	12.17	1.90	0.96	NA	0.22	2
1989	20 vehicles average	0.94	11.80	1.78	0.93	NA	0.22 ^a	3
1989	20 vehicles average (INDAVG)	0.84	10.80	1.75	1.23	NA	0.22 ^a	3
1989	20 vehicles average (CERT)	0.70	6.80	1.52	0.76	NA	0.20 ^a	3
	38 vehicles average	1.97	25.74	3.78	1.80	NA	0.46	4
1989	Volvo 740	1.03	19.40	1.7	0.90	NA	0.27 ^a	5
1989	Volvo 740 (RFG)	1.07	14.40	3.4	0.89	NA	0.2 ^a	5
83-90	5 vehicles average	0.07	19.39	7.27	4.43	1.11	0.43	6
83-90	5 vehicles average (RFG)	0.05	15.69	7.61	3.64	0.74	0.33	6
86-89	5 vehicles average (TWC+AL)	0.00	19.77	4.87	3.07	0.81	0.39	6
86-89	5 vehicles average (TWC+AL) (RFG)	0.14	20.39	8.43	4.71	1.16	0.39	6
1993	Taurus FFV (RFG)	0.40	3.70	2.50	0.90	NA	0.12 ^b	7
1993	Taurus FFV (M85)	0.00	1.80	14.90	0.20	NA	0.30 ^b	7
1998	Toyota Corona	0.38	5.07	2.20	0.68	NA	NA	8
1999	Toyota Corolla	0.36	1.85	1.14	1.05	NA	NA	8
1997	Mitsubishi Legnum	14.96	47.10	NA	NA	NA	NA	9
1995	Dodge Neon	1.74	14.94	NA	NA	NA	NA	9
	Average	1.62	18.24	3.85	1.80	0.96	0.38	

1. Boekhaus et al., 1991 (Arco study);

2. Auto/Oil Study;
 3. Gorse et al., 1991; INDAG: industry average; CERT: emissions certification fuel;
 4. CARB Butadiene Study, 1991;
 5. Jemma et al., 1992;
 6. Hoekman, 1992; AL: adaptive-learning
 7. Black et al., 1998;
 8. Stovell et al., 1999;
 9. Cole et al., 1998;
- a. HC; b. NMHC; NA=not available.

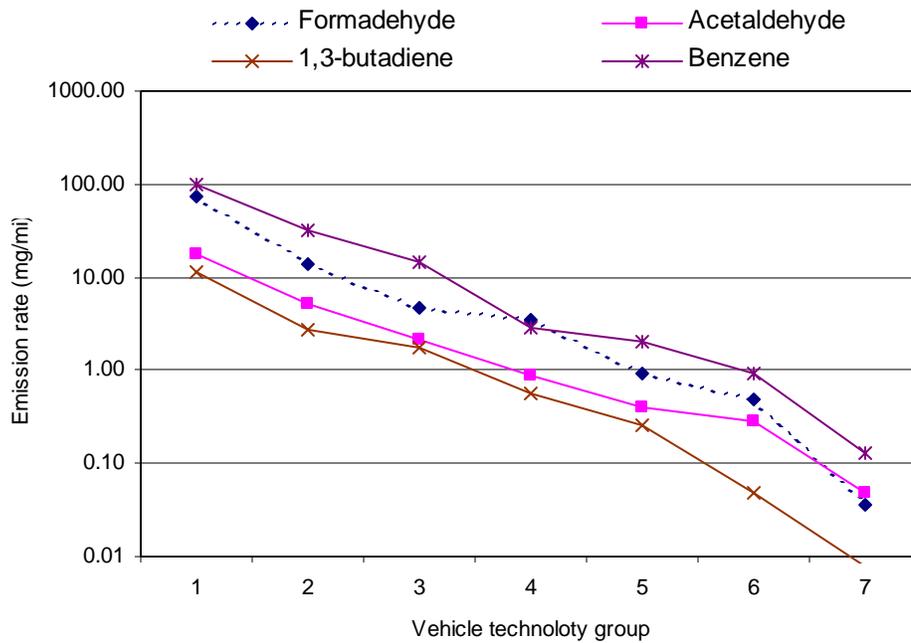


Figure 3-1. MSATs Emission Rates with Different Emission Categories

Emission category:

1. Non-catalyst (NC),
2. Oxidation catalyst (OX),
3. Three-way catalyst (TWC),
4. Transitional – Low Emission Vehicles (TLEVs),
5. Low Emission Vehicles (LEVs),
6. Ultra-Low Emission Vehicles (ULEVs), and
7. Super Ultra-Low Emission Vehicles (SULEV).

Schifter et al. (2000) from the Mexico Instituto Mexicano del Petróleo investigated toxic emissions from 18 vehicles with model years 1984-1990, 15 vehicles with model years from 1991-1996, and 17 vehicles with model year 1997-1999 in the Metropolitan Area of Mexico City. It was found that newer emission control technologies have decreased considerably the emission rates of 1,3-butadiene, benzene, formaldehyde, and acetaldehyde (Table 3-4). However, when compared with other studies, even the 1997 to 1999 model year vehicles in the Mexico City showed emission rates similar to those of 1989 model year vehicles in the US.

Ahlvik (2002) from Sweden Ecotraffic measured benzene emissions on two gasoline-fueled passenger cars and two diesel-fueled passenger cars with 2001 model year over the New European Driving Cycle (NEDC). The gasoline cars included a Peugeot 307 and a VW Golf with 1.6 liter engine. As a function of temperature, benzene emissions were found to increase at lower temperatures, with the increase roughly proportional to the increase in HC emissions.

Table 3-4. Toxic Emissions from Light-Duty Vehicles

Model year	Cycle	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	HC	Note
		mg/mi	mg/mi	mg/mi	mg/mi	g/mi	Mexico
18 vehicles, 1984-1990	FTP	42.97	85.78	23.66	9.98	NA	Mexico
15 vehicles, 1991-1996	FTP	2.41	23.17	2.74	0.97	NA	Mexico
17 vehicles 1997-1999	FTP	0.80	7.89	2.25	1.29	NA	Mexico
2001 Peugeot 307	NEDC at 22 °C		0.95			0.08	Sweden
2001 Peugeot 307	NEDC at -7°C		3.72			0.32	Sweden
2001 VW Golf	NEDC at 22 °C		1.66			0.13	Sweden
2001 VW Golf	NEDC at -7°C		9.87			0.84	Sweden

NEDC: the New European Driving Cycle.

3.1.2 Heavy-Duty Gasoline Vehicles

MSAT emissions from heavy-duty gasoline vehicles have not been studied extensively. Springer (1979) conducted one of the earliest studies using a Chevrolet 366 gasoline fueled engine over a 23 mode test cycle. The emission rates were 349 mg/kw-hr for benzene, 105 mg/kw-hr for formaldehyde, and 21 mg/kw-hr for acetaldehyde. Emission rates for 1,3-Butadiene were not available.

3.2 Diesel Vehicles

Due to their power, durability, fuel economy and efficiency, diesel vehicles are used extensively in transportation. Emissions of gaseous air toxics from diesel vehicles overall are less well characterized than those of gasoline vehicles.

3.2.1 Light-Duty Diesel Vehicles

Springer (1977 and 1979) made some of the first measurements of unregulated emissions from light-duty diesel vehicles. He measured emissions for five 1974 to 1975 model year light-duty diesel vehicles (LDDVs) and two 1976 to 1977 model year LDDVs. Several other studies of air toxics emissions from diesel vehicles were conducted in the late 1980s to early 1990s (Weidmann et al., 1988; Schuermann et al., 1990; Jemma et al. 1992). The results of these studies are provided in Table 3-5. Air toxic emission rates from light-duty diesel vehicles varied from 2 to 13 mg/mi for 1,3-butadiene, 2 to 19 mg/mi for benzene, 4 to 129 mg/mi for formaldehyde, and 2 to 51 mg/mi for acetaldehyde. Based on these studies, the average emissions rates were 8 mg/mi for 1-3 butadiene, 9 mg/mi for benzene, 52 mg/mi for formaldehyde, 20 mg/mi for acetaldehyde, and 5 mg/mi for acrolein.

When comparisons were made to similar uncontrolled vehicles powered by gasoline-fueled vehicles, the average emission values for diesel-fuelled vehicles are generally much lower. Several studies conducted emission testing for both gasoline- and diesel-fuelled vehicles (Springer, 1979; Schuermann et al., 1990; Jemma et al., 1992). Schuermann et al. (1990) conducted a comparison between gasoline vehicles without catalyst, gasoline vehicles with TWCs, and uncontrolled diesel vehicles. The test fleet included 18 VW/Audi production cars with model years from 1978 to 1986 and four to five-cylinder, 1.4 to 2.2 liter engines with power outputs from 37 to 101 kW. The gasoline fuelled cars without catalyst, the gasoline fueled cars with TWC and diesel cars emitted total aldehydes on average in the ratio of 20:1:10. Jemma et al. (1992) compared a gasoline-fuelled 1989 Volvo 740 with and without a TWC and an uncontrolled diesel-fueled 1990 Mercedes Benz 250. These researchers found formaldehyde and acetaldehyde emission rates from diesel cars were much higher than those from TWC gasoline cars. The toxics emission ratios for the gasoline-fueled car without catalysts, the gasoline-fueled car with TWC and the diesel car were 25:2.5:1 for 1,3-butadiene, 50:10:1 for benzene, 20:1:4 for formaldehyde, and 11:1:2 for acetaldehyde.

Table 3-5. Experimental Values of Gas-Phase Toxics from Non-Catalyst-Equipped Vehicles on FTP Driving Cycle (mg/mi)

Year	Make	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	TOG (g/mi)	Ref
1974	Peugeot 204D	NA	NA	18.10	6.89	NA	1.16	1
1974	Perkins 6-247	NA	15.38	61.42	16.89	NA	0.76	1
1975	Mercedes 220D	NA	9.77	4.05	1.61	NA	0.19	1
1975	Mercedes 240D	NA	NA	6.37	1.82	NA	0.30	1
1975	Mercedes 300D	NA	4.04	6.11	1.79	NA	0.17	1
1976	Cutlass	NA	18.66	25.42	10.46	NA	0.80	2
1977	Rabbit	NA	8.21	25.74	8.05	NA	0.39	2
1990	MB250	3.8	2.20	7.50	1.90	NA	0.11 ^a	3
NA	Ford transit	NA	2.03	NA	NA	NA	0.13 ^a	4
78-85	7 vehicles average	NA	5.92	NA	NA	NA	0.18 ^a	5
NA	Peugeot 406	NA	6.03	57.92	21.92	NA	0.18 ^a	6
1983	Ford F-250 PU (CARB)	12.71	8.59	125.56	51.49	NA	1.28 ^a	7
1983	Ford F-250 PU(ARCO-ECD)	8.92	4.77	99.49	44.04	8.76	0.77 ^a	7
1983	Ford F-250 PU (W.E. Biodiesel)	12.21	7.77	125.68	47.32	6.59	1.13 ^a	7
1983	Ford F-250 PU (Soygold)	13.07	8.26	128.82	41.03	11.46	1.07 ^a	7
1983	Ford F-250 PU(OxyG)	9.14	5.63	104.50	41.71	9.32	0.77 ^a	7
1989	Chevy 2500 PU(CARB)	6.39	10.75	41.06	17.37	8.86	0.43 ^a	7
1989	Chevy 2500 PU(ARCO-ECD)	5.55	10.33	31.27	13.01	2.59	0.29 ^a	7
1989	Chevy 2500 PU(W.E. Biodiesel)	8.43	13.39	61.01	24.76	2.02	0.60 ^a	7
1989	Chevy 2500 PU (Soygold)	7.96	11.49	58.99	24.45	3.16	0.60 ^a	7
1989	Chevy 2500 PU(OxyG)	6.80	10.97	45.09	18.67	4.3	0.48 ^a	7
1999	Ford F-250 PU(CARB)	2.30	5.18	33.56	14.21	3	0.52 ^a	7
1999	Ford F-250 PU(ARCO-ECD)	2.41	5.65	31.81	14.26	1.14	0.47 ^a	7
1995	2 vehicles average	0.5	4.38	35.68	66.88	5.44	0.14 ^a	8
	Average	4.37	7.05	34.58	20.58	4.69	0.36	

1. Springer, 1977 (EPA-460/3-76-034).
2. Springer, 1979 (EPA-460/3-79-077).
3. Jemma et al., 1992.
4. Lepperhoff et al., 1994.
5. Neumann et al., 1999.
6. Blanchard et al., 2002.
7. Zhu et al., 2002; five fuels used in this study including CARB diesel, ARCO-ECD, and three 20% biodiesel blends; PU: Pickup truck.

8. Schauer et al., 1999.
NA=not available; ^a: HC value.

Several studies have also evaluated airborne toxics emission rates for 1990 vintage diesel vehicles (Hammerle, 1994 and 1995; Schauer et al 1999; Siegl et al., 1999; Neumann et al., 1999). The results of these studies are provided in Table 3-6. Siegl et al. (1999) conducted emission tests on a 1992 MB 250 and found the emission rates for airborne toxics were 1.6, 14.8, and 5.6 mg/mi, respectively, for benzene, formaldehyde, and acetaldehyde. Schauer et al (1999) conducted tests on a 1995 model year Isuzu diesel truck and a GMC Vandura 3500 van driven on the FTP driving cycle. The emission rates for the individual toxic species were 0.5, 4.4, 35.7, and 66.9 mg/mi, respectively, for 1,3-butadiene, benzene, formaldehyde, and acetaldehyde.

Environment Australia made measurements of the toxic emissions from both light-duty and heavy-duty diesel vehicles over the Composite Urban Emissions Drive Cycle (CUEDC) (Anyon et al., 2003). The CUEDC drive cycle consists of four segments: congested, minor roads, arterial roads and highway/freeway. These researchers found that the newer vehicles (with model years after 1990) had lower toxic emission rates compared to the old vehicles. The results generally showed the highest emission rates for the congested segment with progressively lower emissions for the minor roads, arterial roads, and highway/freeway. The decrease in emission rates for various segments was generally repeatable for each vehicle.

Currently, aftertreatment systems are becoming more prevalent for controlling diesel emissions. This has resulted in more studies of the effects of both OCs and diesel particulate filters (DPF) on diesel toxics (Oyama and Kakegawa, 2000; Fanick et al., 2001; Schubert et al., 2002; Blanchard et al., 2002; Zhu et al., 2002). These studies have shown significant declines in airborne toxic emissions for aftertreatment-equipped vehicles.

OCs may be fitted to either gasoline or diesel cars. Gaseous hydrocarbons, CO and the soluble organic fraction of diesel PM are reduced by oxidation over precious metal catalysts. Jemma et al. (1992) measured toxic emissions for a 1990 model year Mercedes Benz 250 with and without OC over the FTP driving cycle. The emissions rates of 1,3-butadiene, benzene, formaldehyde, and acetaldehyde decreased by 87%, 36%, 69%, and 47%, respectively, using the OC. Neumann et al. (1999) compared diesel emissions from 7 NC vehicles and two OC equipped vehicles and found that reductions of benzene emissions were 81% and the reductions of aldehydes and ketones emissions were at least 50%. The emissions of 1,3-butadiene were virtually undetectable in the exhaust gas of two modern diesel passenger cars with OC.

Table 3-6. Experimental Values of Gas-Phase Toxics from Oxidation Catalyst Equipped Vehicles on FTP Driving Cycle (mg/mi)

Year	Make	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	TOG (g/mi)	Ref
1990	MB250	<0.5	1.40	2.30	1.00	NA	0.034 ^a	1
NA	Audi 80	NA	4.41	NA	NA	NA	0.087 ^a	2
NA	VW Golf ECO	NA	1.66	NA	NA	NA	0.055 ^a	2
1997	2 vehicles average	NA	1.12	NA	NA	NA	0.050 ^a	3
1999	Volkswagen Golf GL TDI (D2)	NA	0.20	3.00	2.70	0.1	0.04 ^a	4
1999	Volkswagen Golf GL TDI (S-2)	NA	0.10	1.50	2.30	0.1	0.03 ^a	4
2000	Dodge Ram 2500HD (D2)	0.80	1.44	18.24	8.80	1.13	0.1 ^a	5
2000	Dodge Ram 2500HD (CARB)	0.32	1.44	17.60	7.68	0.32	0.1 ^a	5
2000	Dodge Ram 2500HD (Swedish)	0.80	1.28	16.00	9.60	0.32	0.1 ^a	5
2000	Dodge Ram 2500HD (F-T)	0.64	0.96	12.80	5.44	0.32	0.1 ^a	5
	5 passenger cars and 1 LDDT	NA	<5.6	<14.4	NA	NA	NA	6
1992	Mercedes Benz 250 (MVEG)	NA	1.60	14.77	5.62	NA	0.039 ^a	7
1995	2 vehicles average	0.50	4.38	35.68	66.88	5.47	NA	8
	Average (not include ref 8)*	0.64	1.42	10.78	5.39	0.38	0.065	

1. Jemma et al., 1992;
2. Lepperhoff et al., 1994
3. Neumann et al., 1999;
4. Schubert et al., 2002; Two fuels conventional D2 diesel and syntroleum S-2 produced from natural gas were used in this study.
5. Fanick et al., 2001; Fuels include D2 diesel, CARB diesel, Swedish diesel, and F-T diesel.
6. Hammerle, 1994;
7. Siegl et al., 1999; MVEG: Motor vehicle emissions group cycle
8. Schauer et al., 1999.

* Average value was calculated based on reference 1 to 7.

NA=not available.

Under the Japan Clear Air Program (JCAP), Oyama and Kakegawa (2000) investigated the effectiveness and future direction of diesel emission control technologies and diesel fuel properties. Eight new passenger cars with different emission control technologies were tested using 13 different diesel fuels. All vehicle tests were over Japan 10-15 mode driving cycle. The 10-15 mode cycle is currently used in Japan for emission certification and fuel economy for light duty vehicles. It is derived from the 10-mode

cycle by adding another 15-mode segment of a maximum speed of 70 km/h. The effects on the reduction of 1,3-butadiene, benzene, formaldehyde, and acetaldehyde varied widely among the vehicles, with significant effects observed from the use of certain catalysts. One vehicle was equipped with several different catalysts including one highly oxidative Pt catalyst. While these catalysts reduced toxics, they also resulted in increased emissions of N₂O, which is a potent greenhouse gas. There were no clear effects observed from the fuels in the vehicle tests. The results of this study were summarized in Table 3-7.

Table 3-7. Experimental Values of Gas-Phase Toxics from Different Oxidation Catalyst Equipped Vehicles on 10-15 mode (mg/mi)^a

Vehicle		Emission control	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	HC (g/mi)
id	Description						
K	Direct injection, 3.0L	EGR+cat	NA	0.97	9.17	4.83	0.12
S	IDI, 2.0L (OC, Pt 2.5g/l)	EGR+cat	NA	NA	0.48	NA	0.17
S	IDI, 2.0L (dummy cat)	EGR	3.38	6.11	16.25	4.99	0.16
T	IDI, 2.0L	EGR	1.29	1.29	8.37	3.22	0.13
U	IDI, 2.2L	EGR+cat	NA	0.51	2.41	0.97	0.077

^a Oyama and Kakegawa, 2000. S: Passenger vehicle; T: high fuel sensitive vehicle; U: low fuel sensitive vehicle. Toxics emission rates presented in the table are for a No.2 grade diesel fuel in Japan, although the study included 13 fuels.

The Coordinating Research Council (CRC) Advanced Vehicle, Fuel, Lubricant (AVFL) Committee funded project AVFL-3 to explore the nature of exhaust downstream of a diesel OC (Shaw, 2003). A 1999 Mercedes-Benz C220 CDI equipped with a 2.2L OM611 diesel engine was tested over the FTP, US06 and steady state conditions with a low sulfur diesel fuel (15 ppm sulfur level). This vehicle is manufactured for sale in Europe and is calibrated to meet ECE 15/EUDC emission standards. The vehicle was tested with a catalyst loaded with 20, 70, 120 g/ft² of platinum and without catalyst. Benzene, formaldehyde, and acetaldehyde were reduced significantly with the addition of the catalyst with more significant reductions with the increased catalyst loading. Compared to uncontrolled vehicles, the reductions of benzene, formaldehyde, and acetaldehyde emissions were 68 to 78% for the vehicle with a catalyst loaded with 20 g/ft² of platinum, and 88 to 91% for the vehicle with a catalyst loaded with 70 g/ft² of platinum, and 91 to 94% for the vehicle with a catalyst loaded with 120 g/ft² of platinum.

Diesel particulate filters (DPF) can also provide significant reductions in air toxics for diesel vehicles. Durbin et al. (2003) and Zhu et al. (2002) conducted vehicle emission tests on four medium-duty diesel vehicles over the FTP driving cycle. The authors found that the 1999 Ford F-250 pickup equipped with DPF reduced 1,3-butadiene, benzene, formaldehyde, and acetaldehyde by factors of 89, 70, 12, and 27%, when compared with another 1999 Ford F-250 pickup not equipped with DPF. The lower reductions in formaldehyde for the DPF could be due to the higher use of Pt in the DPF that is less effective in eliminating formaldehyde than Pd and the relatively low temperatures over the light-duty FTP. Interestingly, studies of heavy-duty vehicles over

different cycle patterns have shown greater reductions in carbonyl emissions with DPFs (Lev-On et al., 2002b). In comparison with a 1983 Ford F-250 pickup truck not equipped with DPF, the reduction factors were up to 98, 80, 78, 80%, and 98%, respectively, for 1,3-butadiene, benzene, formaldehyde, acetaldehyde, and acrolein. The individual toxic species emission rates are summarized in Table 3-8.

Table 3-8. Experimental Values of Gas-Phase Toxics on FTP Driving Cycle from non-catalyst vehicles and DPF equipped vehicle (mg/mi).

Year	Make	Fuel used	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC
1983	Ford F-250 PU	CARB	12.71	8.59	125.56	51.49	8.76	1.28
1983	Ford F-250 PU	ARCO-ECD	8.92	4.77	99.49	44.04	6.59	0.77
1999	Ford F-250 PU	CARB	2.30	5.18	33.56	14.21	1.14	0.52
1999	Ford F-250 PU	ARCO-ECD	2.41	5.65	31.81	14.26	1.45	0.47
1999	Ford F-250 PU	ECD1+DPF	0.26	1.70	27.87	10.45	0.18	0.14

Zhu et al., 2002

Swedish National Road Administration conducted emissions tests on gasoline and diesel passenger cars with 2001 model years over the NEDC at two different temperatures (Ahlvik, 2002). The diesel vehicles included a Peugeot 307 with EGR, OC and DPF and a VW Golf with EGR and OC. The benzene levels were lower for the diesel cars than gasoline cars. All cars, but the diesel car with a DPF, showed a distinct increase of benzene by lowering the temperature. At the low ambient temperature (-7 °C), the aldehyde emissions from the diesel cars increased from below the detection limit (1.5 mg/km) to a level about two times higher than the detection limit.

Understanding gaseous air toxics under different driving conditions is also important. Recently, Southwest Research Institute and Syntroleum Corp. have conducted emission studies with diesel vehicles operated over different driving cycles and different fuels. Schubert et al. (2002) conducted emission tests using a light-duty passenger car and Fanick et al. (2001a) conducted emission tests using a light heavy-duty truck with a Cummins B-series engine. Both studies were conducted over the FTP, the US06, and the Highway Fuel Economy Test (HFET) driving cycles. The detailed driving cycle descriptions are given in the Appendix A. The results showed that the FTP driving cycle had highest emission rates of gas-phase toxics, followed by the US06, and the HFET. These differences are due to the characteristics of the driving cycles. The FTP driving cycle includes a cold start phase and represents moderate driving done in urban areas. The US06 was designed to represent real-world driving conditions with the more extreme high-speed, high-acceleration driving behavior observed during the FTP Review Project (Diesel net, 2000). The HFET test characterizes more steady-state conditions of highway driving. The higher FTP emissions can primarily be attributed to the cold start. The results of this study are summarized in Table 3-9.

Table 3-9. Toxics Emission Rates from Light-Duty Diesel Vehicles over Different Driving Cycles.

Vehicle	Model	Fuel	Cycle	1,3-Butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC	Ref
Year				mg/mi	mg/mi	mg/mi	mg/mi	mg/mi	g/mi	
1999	Volkswagen Golf GL TDI	D2	FTP	NA	0.20	3.00	2.70	0.1	0.04	1
		D2	US06	NA	0.00	1.30	1.50	0.1	0.02	1
		D2	HFET	NA	0.00	0.80	0.80	0.0	0.01	1
		S2	FTP	NA	0.10	1.50	2.30	0.0	0.03	1
		S2	US06	NA	0.00	0.80	1.30	0.1	0.01	1
		S2	HFET	NA	0.00	0.50	0.70	NA	0.01	1
2000	Dodge Ram 2500HD	D2	FTP	0.80	1.44	18.24	8.80	1.13	0.39	2
			US06	0.32	0.64	7.20	3.52	0.16	0.19	2
			HFET	0.16	0.32	6.24	2.72	0.16	0.19	2
		Carb	FTP	0.32	1.44	17.60	7.68	0.32	0.34	2
			US06	0.32	0.64	7.04	3.52	0.16	0.18	2
			HFET	0.16	0.64	5.60	2.40	0.16	0.16	2
		Swedish	FTP	0.80	1.28	16.00	9.60	0.32	0.34	2
			US06	0.48	0.64	7.68	4.48	0.16	0.18	2
			HFET	0.32	0.32	5.92	2.72	0.16	0.16	2
		F-T	FTP	0.64	0.96	12.80	5.44	0.16	0.26	2
			US06	0.48	0.16	7.04	3.84	0.16	0.16	2
			HFET	0.32	0.32	5.60	2.72	0.16	0.14	2
1995	Nissan Navara	Australia commercial diesel (0.17% sulfur)	Congested	0.14	3.74	42.24	23.84	NA	NA	3
			Minor	0.19	3.41	22.24	12.32	NA	NA	3
			Arterial	0.15	2.98	17.76	9.82	NA	NA	3
			Freeway	0.17	1.89	5.76	3.54	NA	NA	3
1986	Toyota LX Turbo	Australia commercial diesel (0.17% sulfur)	Congested	4.32	25.60	48.00	36.80	NA	NA	3
			Minor	0.11	8.96	1.92	2.08	NA	NA	3
			Arterial	0.08	8.80	4.64	2.40	NA	NA	3
			Freeway	0.06	6.24	2.88	0.90	NA	NA	3

1. Schubert et al., 2002

2. Fanick et al., 2001

3. Anyon et al., 2003

Table 3-9. Continued

Vehicle	Model	Fuel	Cycle	1,3-Butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC	Ref
Year				mg/mi	mg/mi	mg/mi	mg/mi	mg/mi	g/mi	
1993	Toyota Hilux	Australia commercial diesel (0.17% sulfur)	Congested	0.14	11.68	27.20	10.88	NA	NA	3
			Minor	0.21	7.20	13.28	5.92	NA	NA	3
			Arterial	0.07	5.44	12.80	5.44	NA	NA	3
			Freeway	0.12	3.84	6.56	2.56	NA	NA	3
1995	Ford Econovan Maxi	Australia commercial diesel (0.17% sulfur)	Congested	0.13	25.60	38.40	19.20	NA	NA	3
			Minor	0.70	15.52	6.40	3.04	NA	NA	3
			Arterial	0.18	14.08	19.20	8.48	NA	NA	3
			Freeway	0.18	12.16	10.08	4.64	NA	NA	3
1990	Mitsubishi Canter	Australia commercial diesel (0.17% sulfur)	Congested	2.09	20.92	225.30	91.73	NA	NA	3
			Minor	0.18	13.84	33.80	17.70	NA	NA	3
			Arterial	0.19	14.81	49.89	22.53	NA	NA	3
			Freeway	0.03	5.31	12.23	6.12	NA	NA	3
1990	Toyota Dyna	Australia commercial diesel (0.17% sulfur)	Congested	11.99	48.28	540.72	196.33	NA	NA	3
			Minor	0.27	15.88	102.35	39.11	NA	NA	3
			Arterial	0.00	15.29	97.36	36.53	NA	NA	3
			Freeway	0.23	9.09	27.68	12.13	NA	NA	3
1993	Toyota Hilux	Australia commercial diesel (0.17% sulfur)	Congested	0.21	7.72	4.07	3.48	NA	0.10	3
			Minor	0.00	4.83	0.54	0.74	NA	0.04	3
			Arterial	0.00	6.00	0.47	0.51	NA	0.04	3
			Freeway	0.00	4.33	0.04	0.28	NA	0.02	3
1993	Toyota Hilux	Euro 2	Congested	0.28	7.21	7.03	4.70	NA	0.05	3
			Minor	0.00	4.73	1.72	1.27	NA	0.02	3
			Arterial	0.04	4.36	1.92	1.63	NA	0.02	3
			Freeway	0.03	3.49	0.96	0.99	NA	0.02	3
1993	Toyota Hilux	Euro 3	Congested	0.00	6.37	3.25	0.96	NA	0.04	3
			Minor	0.00	5.26	1.75	1.40	NA	0.04	3
			Arterial	0.00	4.54	2.35	1.25	NA	0.04	3
			Freeway	0.09	2.99	1.87	1.00	NA	0.03	3

3. Anyon et al., 2003

Table 3-9. Continued

Vehicle	Model	Fuel	Cycle	1,3-Butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC	Ref
Year				mg/mi	mg/mi	mg/mi	mg/mi	mg/mi	g/mi	
1993	Toyota Hilux	Euro 4	Congested	0.02	9.06	2.03	6.58	NA	0.06	3
			Minor	0.00	5.87	2.41	2.78	NA	0.04	3
			Arterial	0.00	4.23	2.69	2.72	NA	0.04	3
			Freeway	0.00	4.62	0.85	1.58	NA	0.04	3
1993	Toyota Hilux	World wide fuel Charter	Congested	0.00	6.98	8.38	5.23	NA	0.06	3
			Minor	0.00	7.42	4.92	2.19	NA	0.06	3
			Arterial	0.00	6.20	3.27	1.52	NA	0.06	3
			Freeway	0.00	4.31	2.54	1.27	NA	0.04	3
1993	Toyota Hilux	CARB	Congested	0.18	7.39	5.23	0.79	NA	0.08	3
			Minor	0.02	5.38	3.17	1.10	NA	0.04	3
			Arterial	0.01	4.70	2.54	0.77	NA	0.05	3
			Freeway	0.01	3.40	1.67	0.66	NA	0.03	3
2001	Peugeot 307, 2.0L with DPF	EC1 at 22°C	NEDC	NA	0.27	ND	ND	NA	0.02	4
		EC1 at -7°C	NEDC	NA	0.40	3.18	2.95	NA	0.02	4
2001	VW Golf, 1.9L	EC1 at 22°C	NEDC	NA	0.24	1.56	ND	NA	0.02	4
		EC1 at -7°C	NEDC	NA	1.30	2.95	3.09	NA	0.04	4
1999	Mercedes-Benz	Low sulfur diesel ^a	FTP	NA	2.10	15.50	8.20	NA	0.066	5
			US06	NA	ND	0.50	0.10	NA	0	5
		Low sulfur diesel ^b	FTP	NA	0.60	6.10	3.70	NA	0.026	5
			US06	NA	ND	0.20	0.20	NA	0	5
		Low sulfur diesel ^c	FTP	NA	0.60	5.30	1.90	NA	0.015	5
			US06	NA	0.40	0.20	0.10	NA	0	5
Low sulfur diesel ^d	FTP	NA	6.50	70.40	30.00	NA	0.59	5		
	US06	NA	1.90	13.90	5.20	NA	0.12	5		

3. Anyon et al., 2003;

4. Ahlvik, 2002; EC1: the Swedish Environmental Class 1, the EC 1 has a low sulfur content (<10ppm) and it is essentially free from PAH. NEDC: the New European Driving Cycle. ND: below the detection limit, the detection level is 2.41 mg/mi for formaldehyde and acetaldehyde.

5. Shaw, 2003; ^a with 20g/ft² catalyst, ^b with 70g/ft² catalyst, ^c with 120g/ft² catalyst, ^d without catalyst.

ND: not detected; NA: not available.

3.2.2 Heavy-Duty Diesel Vehicles and Diesel Buses

For heavy-duty diesel vehicles (HDDV), Springer et al. (1979) conducted one of the earliest studies of MSATs. This study included two HDDVs. The emission rates averaged 13.2, 33.2, and 11.4 mg/kw-hr for benzene, formaldehyde, and acetaldehyde, respectively. Emissions rates for 1,3-butadiene were not available. These values were very low when compared to non-catalyst HDGVs' emission results from same study, with emission rates of benzene, formaldehyde, and acetaldehyde being about 4, 32, and 54% of those for the HDGVs.

Several more recent studies have evaluated airborne toxics emission rates for HDDVs and diesel buses and results are summarized in Table 3-10 and Table 3-11 (Levon et al., 2002; Storey et al., 2003; Ullman et al., 2003; Zhu et al., 2003). The emission rates of airborne toxics from HDDVs varied widely from clean new technology vehicles to the old vehicles: from under the detection limits to 13.8 mg/mi for 1,3-butadiene, 0.3 to 3 mg/mi for benzene, under the detection limits to 4901 mg/mi for formaldehyde, and under the detection limits to 3049 mg/mi for acetaldehyde. The emission rates of airborne toxics for buses varied 0.8 to 11.1 mg/mi for 1,3-butadiene, 0.2 to 4.7 for benzene, 0.2 to 41 for formaldehyde, and 0.05 to 15.0 for acetaldehyde.

To quantify the uncertainty in in-use emission rates and the influence of tampering and malmaintenance on heavy-duty vehicle emissions, West Virginia University (WVU), the Desert Research Institute (DRI) and the California Trucking Association characterized the emissions from a total of 25 HDDV vehicles in Phase 1 of the CRC E-55/E-59 study (Gautam et al., 2003). Vehicles were procured in the Los Angeles area, based on model years specified by the sponsors and by engine types determined from a survey. Emissions measurement was conducted using one of the WVU Transportable Heavy-Duty Vehicle Emissions Testing Laboratories. The first three class eight vehicles were evaluated both under the US Department of Energy (DOE) "Gasoline/Diesel PM Split Study" and the CRC E-55/E-59 study. The overlap vehicles were sampled for both regulated and unregulated emissions. The next ten vehicles were subjected to regulated emissions characterization and sampling for unregulated species, with the samples archived for possible future analysis. Only regulated emissions and PM₁₀ emissions were taken for the remaining vehicles. The three class 8 trucks were operated on a transportable chassis dynamometer over CARB's heavy heavy-duty diesel truck (HHDDT) driving cycle. The HHDDT test cycle includes four modes: an cold start/idle mode, a very low speed or "creep" mode, an intermediated speed or "transient" mode, and a relatively high speed "cruise" mode. The creep mode generated higher toxics emissions on a per-mile basis.

CE-CERT also measured toxic emissions from HDDVs over HHDDT driving cycle (Zhu et al., 2003). For this cycle, the Creep phase provided significantly higher toxic emissions in comparison to transient and cruise phases. The gas-phase toxic compounds emitted per mile of driving with the creep mode was equivalent to driving 3-7 miles in the transient phase or driving 13-23 miles in cruise phase. Of the gas-phase

MSATs, formaldehyde had the highest emissions for each of the vehicle/driving cycle combinations, with acetaldehyde having the second-highest emissions. Formaldehyde also was found to be the most prevalent carbonyl, accounting for 39 to 50% of total identified carbonyl emissions. The results were consistent with the CRC E-55/E-59 study. This affirms that urban congestion is a contributor to air pollution.

McCormick et al. (2001) conducted vehicle emissions tests to quantify the benefits of a smoke opacity based inspection and maintenance program (I/M) over Heavy-Duty Transient Truck Cycle. A total of 26 vehicles exhibiting visible smoke emissions were recruited in this study, including 17 pre-1991 trucks and 9 1991 and later model year trucks. McCormick found that aldehyde levels for the smoking vehicles were extremely high and were reduced dramatically by repair. The average formaldehyde emissions declined from 114 mg/mi pre-repaired vehicles to 72 mg/mi for post-repaired vehicles and acetaldehyde emissions declined from 168 mg/mi for pre-repair vehicles to 97 mg/mi for post-repaired vehicles.

Environment Australia measured toxic emissions from both buses and heavy-duty diesel trucks over the Composite Urban Emissions Drive Cycle (Anyon et al., 2003). The results for buses and heavy-duty trucks showed a trend of decreasing emissions from the Congested phase to Freeway phase, which was similar to the trend for light-duty vehicles, as discussed above. These results are included in Table 3-11.

Several studies have also evaluated the effects of aftertreatment technologies such as OCs and DPFs on HDDV toxic emissions. Ahlvik and Brandberg (2000) of Sweden evaluated the emissions from city buses without aftertreatment, with OCs, and with DPFs. The OC and the DPF significantly impacted 1,3-butadiene emissions, with 70% and 60% reductions, respectively, compared with no aftertreatment. About a 70% reduction of benzene emissions was observed for vehicles with an OC and DPF. The OC had a relatively small impact on aldehyde emissions. On the other hand, the DPF had a much higher efficiency in oxidizing the aldehydes resulting in the lowest aldehyde emissions. The difference in catalyst formulation between the OC and the DPF and the larger catalyst volume for the latter could explain the difference. The most significant reduction of cancer risk was obtained by using the DPF. The 1,3-butadiene accounts for most of the contribution from the toxic compounds. The impact of the catalyst formulation is also important and a DPF without a catalytic component does not give as favorable results for the volatile emission components.

Lev-On et al. (2002a, b) performed a chemical characterization study for four class 8 diesel vehicles. The vehicles were tested with the original exhaust system and subsequently fitted with DPFs provided by Engelhard (DPXTM) and Johnson Matthey (CRTTM). Benzene, formaldehyde, and acetaldehyde emissions significantly decreased for all vehicles with the DPF control technology, but no significant reductions in 1,3-butadiene were found. In most cases, the total NMHC emissions were reduced by 70% for diesel-fueled vehicles with DPFs, Aldehyde emissions were reduced by over 95% for diesel-fueled vehicles with DPF compared to the baseline.

Ullman et al. (2003) found that acetaldehyde, benzene, formaldehyde, and acrolein emissions for a conventional diesel bus were significantly different and higher in value than for a diesel bus equipped with a catalyzed DPF. The emissions for the low emission diesel bus were significantly lower in value than for the uncontrolled compressed natural gas (CNG) bus configuration.

Table 3-10. Gas-Phase Toxics Emission Rates from Buses

Vehicle	Engine	Engine size	Emission control	Fuel	Cycle	1,3-Butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC	Ref	
		L				mg/mi	mg/mi	mg/mi	mg/mi	mg/mi	g/mi		
1998 AT	2001 IN DT530	8.7	NC	D2	CSHVC	ND	4.7	27	9.5	3.3	0.39	1	
1998 AT	2001 IN DT530	8.7	CDPF	LED	CSHVC	1.3	ND	5.2	2.7	0.45	0 ^a	1	
1998 AT	IN 530E	8.7	None	CARB	CSHVR	1.18	2.98	33.2	12.7	0.35	0.072 ^b	2	
			None	ECD	CSHVR	1.17	2.18	35.9	13.8	0.61	0.056 ^b	2	
			None	ECD-1	CSHVR	1.19	2.28	40.8	15	0.58	0.071 ^b	2	
			None	FT	CSHVR	3.55	1.72	35.8	14.8	0.58	0.048 ^b	2	
			DPX	CARB	CSHVR								2
			DPX	ECD	CSHVR	3.55	0.19	0.186	0.112	0	0.013 ^b	2	
			DPX	ECD-1	CSHVR	2.36	0.19	0.185	0.103	0	0.016 ^b	2	
			DPX	FT	CSHVR	ND	0.3	0.222	0.0469	0	0.024 ^b	2	
1998 New Flyer	DD Series 50	8.5	None	CARB	CBD	0.84	3.6	26.4	10.5	0.258	0.043 ^b	2	
			None	ECD-1	CBD	ND	1.44	18.6	4.28	0.322	0.028 ^b	2	
			CRT	ECD	CBD	2.52	0.21	0.219	0.0764	0	0.027 ^b	2	
			CRT	ECD-1	CBD	2.12	0.2	0.206	0.196	0	0.018 ^b	2	
			NC		BCB	27.84	3.2	46.4	32	NA	0.73	3	
			Cat		BCB	8.352	0.96	24	22.4	NA	0.088	3	
			DPF		BCB	11.136	0.96	4.64	4.8	NA	0.059	3	
			DPF+EGR		BCB	11.136	0.96	4.64	4.8	NA	0.059	3	

- Ullman et al., 2003. AT: American Transportation; IN: International; LED: low emission diesel, S<15ppm; CSHVC: city suburban heavy vehicle cycle; ND: Not detected; detection limits are 2 mg/mi for 1,3-butadiene and 1 mg/mi for benzene.
 - Lev-On et al., 2002a and 2002b. DD: Detroit Diesel; CBD: Central Business District cycle.
 - Ahlvik and Brandberg, 2000; BCB: Braunschweig City Bus Driving Cycle, used by the Swedish for HD vehicles.
 - Anyon et al., 2003;
- ^a: Background sample HC was higher than dilute exhaust gas sample HC. The value reported as zero.
^b: The value here is NMHC and is estimated from figures.

Table 3-10. Continued

Vehicle	Engine	Displacement	Emission control	Fuel	Cycle	1,3-Butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC	Ref
		L				mg/mi	mg/mi	mg/mi	mg/mi	mg/mi	g/mi	
1998	Volvo B10	10.5		Australia commercial diesel (0.17% sulfur)	Congested	0.00	9.72	15.27	7.79	NA	NA	4
					Minor	0.00	3.96	4.17	2.98	NA	NA	4
					Arterial	0.00	5.23	7.77	6.68	NA	NA	4
					Freeway	0.00	3.04	3.19	3.03	NA	NA	4
1996	Scania L113C RL	11.0		Australia commercial diesel (0.17% sulfur)	Congested	0.00	9.41	7.35	7.92	NA	NA	4
					Minor	0.00	3.96	2.00	4.01	NA	NA	4
					Arterial	0.00	5.63	4.25	4.80	NA	NA	4
					Freeway	0.00	3.51	2.82	4.18	NA	NA	4

4. Anyon et al., 2003

Table 3-11. Gas-Phase Toxics Emission Rates from Heavy-Duty Diesel Vehicles

Vehicle	Engine	Displacement	Emission control	Fuel	Cycle	1,3-Butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC	Ref
MY		L				mg/mi	mg/mi	mg/mi	mg/mi	mg/mi	g/mi	
1999 Sterling AT9513	Detroit Diesel Series 60	12.7	None	CARB	CSHVR	4.97	2.12	48.10	14.80	NA	0.064 ^a	1
			None	ECD-1	CSHVR	13.80	2.82	55.20	19.50	NA	0.080 ^a	1
			CRT	ECD	CSHVR	4.32	0.35	0.18	0.095	NA	0.024 ^a	1
			CRT	ECD-1	CSHVR	1.32	0.28	0.44	0.14	NA	0.028 ^a	1
1999 Sterling AT9513	Detroit Diesel Series 60	12.7	DPX	ECD-1	CSHVR	ND	0.592	0.000001	0	NA	0.038 ^a	1
1995 Isuzu 900SUR		NA		Australia commercial diesel (0.17% sulfur)	Congested	0.26	51.50	482.79	225.30	NA	NA	2
			Minor		1.61	17.70	257.49	111.04	NA	NA	2	
			Arterial		0.76	19.31	96.56	56.33	NA	NA	2	
			Freeway		0.51	10.62	51.50	28.97	NA	NA	2	
1996 Mitsubishi Superframe		NA		Australia commercial diesel (0.17% sulfur)	Congested	0.53	24.14	321.86	120.70	NA	NA	2
			Minor		0.00	11.10	114.26	46.67	NA	NA	2	
			Arterial		0.00	9.82	94.95	38.62	NA	NA	2	
			Freeway		0.27	8.85	62.76	25.75	NA	NA	2	
1998 Iveco INT9200		NA		Australia commercial diesel (0.17% sulfur)	Congested	0.00	16.58	13.34	9.99	NA	NA	2
			Minor		0.00	5.84	1.79	3.97	NA	NA	2	
			Arterial		0.00	6.68	1.53	2.90	NA	NA	2	
			Freeway		0.00	3.25	0.08	1.75	NA	NA	2	
1998 Hino Ranger 50		NA		Australia commercial diesel (0.17% sulfur)	Congested	3.41	37.98	70.97	32.83	NA	NA	2
			Minor		0.00	10.89	14.98	6.50	NA	NA	2	
			Arterial		0.00	11.04	11.84	4.31	NA	NA	2	
			Freeway		0.00	5.10	4.38	3.67	NA	NA	2	

1. Lev-on et al., 2002a and 2002b. DD: Detroit Diesel; CSHVC: city suburban heavy vehicle cycle

2. Anyon et al., 2003.

^a: The value here is NMHC and is estimated from figures.

Table 3-11. Continued

Vehicle	Engine	Displac_ement	Emission control	Fuel	Cycle	1,3-Butadiene	Benzene	Formald ehyde	Acetalde hyde	Acrole in	HC	Ref
		L				mg/mi	mg/mi	mg/mi	mg/mi	mg/mi	g/mi	
		NA										
1995 Isuzu 900SUR				Commer_ cial 2	Congested	0.47	41.84	83.20	53.43	NA	2.83	2
					Minor	0.00	13.63	25.43	16.41	NA	1.19	2
					Arterial	0.00	13.84	16.25	11.78	NA	1.02	2
					Freeway	0.00	9.29	7.55	7.15	NA	0.71	2
				Euro 2	Congested	0.00	29.29	98.01	50.85	NA	1.99	2
					Minor	0.00	11.76	51.34	23.98	NA	1.10	2
					Arterial	0.00	11.02	28.00	14.84	NA	0.90	2
					Freeway	0.00	8.64	21.08	11.15	NA	0.67	2
				Euro 3	Congested	0.49	35.24	113.46	32.51	NA	1.83	2
					Minor	0.00	14.39	37.34	13.07	NA	1.27	2
					Arterial	0.00	13.95	35.73	11.70	NA	0.95	2
					Freeway	0.00	8.46	14.84	6.69	NA	0.67	2
				Euro 4	Congested	0.31	34.44	72.90	11.92	NA	1.62	2
					Minor	0.67	13.66	35.57	9.95	NA	0.88	2
					Arterial	0.00	14.82	22.21	4.28	NA	0.74	2
					Freeway	0.00	9.58	19.96	5.49	NA	0.54	2
				World wide fuel Charter	Congested	0.00	34.76	57.61	9.06	NA	1.62	2
					Minor	0.00	12.71	30.09	8.19	NA	0.89	2
					Arterial	0.00	13.57	21.56	4.84	NA	0.71	2
					Freeway	0.00	8.75	15.29	4.92	NA	0.56	2
			CARB	Congested	0.39	29.77	64.85	0.00	NA	2.13	2	
				Minor	0.00	12.63	0.35	2.00	NA	1.01	2	
				Arterial	0.00	11.59	10.80	0.76	NA	0.82	2	
				Freeway	0.00	8.32	12.54	2.24	NA	0.63	2	

2. Anyon et al., 2003.

Table 3-11. Continued

Vehicle	Engine	Displacement	Emission control	Fuel	Cycle	1,3-Butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC	Ref
		L				mg/mi	mg/mi	mg/mi	mg/mi	mg/mi	g/mi	
1994	Detroit Diesel Series 60	12.7		In-use fuel	UDDS	0.24	2.56	26.08	4.20	0.00	0.24	3
					Idle (mg)	8.14	12.12	259.79	102.57	0.00	1.02	3
					Creep	37.76	47.97	874.71	352.68	0.00	5.15	3
					Transient	1.43	5.84	70.56	28.83	0.55	0.47	3
					Cruise	0.05	1.55	1.54	0.03	0.00	0.17	3
1995	Caterpillar 3406B	14.60		In-use fuel	UDDS	4.57	7.35	74.43	29.02	0.90	0.84	3
					Idle (mg)	24.90	60.41	425.70	158.64	5.08	2.30	3
					Creep	36.24	61.67	609.10	222.35	7.34	7.00	3
					Transient	7.57	9.88	146.21	59.31	0.67	1.52	3
					Cruise	0.44	3.92	3.73	0.07	0.00	0.36	3
1985	Cummins NTCC-300	14.02		In-use fuel	Idle (mg)	77.44	59.15	1076.06	432.43	19.60	4.83	3
					Creep	126.15	81.72	1407.80	387.75	10.32	21.75	3
					Transient	30.69	22.29	378.87	135.70	4.85	5.18	3
					Cruise	7.85	9.65	47.77	1.55	1.78	1.77	3
Average of 12				ECD	Idle (mg)	14.10	16.59	353.17	95.54	5.24	1.96	4
					Creep	25.65	29.76	760.30	290.77	16.01	4.75	4
					Transient	5.48	6.47	231.64	85.81	2.39	0.98	4
					Cruise	1.71	2.34	38.28	12.55	0.82	0.35	4

3. Gautam et al., 2003. The unit for idle mission rates is mg/cycle. UDDS: Urban Dynamometer Driving Schedule.

4. Zhu et al, 2003; All vehicle are class 8 HHDDV.

3.2.3 Diesel engines

While diesel engines have been extensively tested over the years, there are relatively few data on the air toxics emissions from modern diesel engines. In an early study, the individual toxic species present in emissions from diesel-fueled engines were measured by Dietzmann and Lee (1984). They also analyzed the effect of induced faults on diesel forklift engines. Increasing the intake air restriction increased the aldehyde values dramatically from 167 mg/kWh under standard conditions to 2682 mg/kWh. Formaldehyde emissions were highest at low load conditions (34 mg/kWh at 2 % load vs. 1 mg/kWh at 100% load). Gautam et al. (1996) measured hydrocarbon speciation from a heavy-duty diesel engine under a steady state mode cycle. The emission rates for 1,3-butadiene were about 0.2 to 0.6 mg/kWh and the emission rates for benzene were about 0.6 to 1.3 mg/kWh. The highest mass emission rate of 1,3-butadiene was at an intermediate speed and 100% load (I100) and the highest benzene emission rate was at an intermediate speed and 50% load (I50).

To reduce emissions, the effects of an OC on diesel engine emissions reductions were studied recently. Mogi et al. (1999) from Japan Hino Motors investigated the effects of OCs with different Pt loading. A Japanese 1994 emission regulation engine was used and the Japan Diesel 13 (D13) mode cycle was used as the test cycle. The HC, CO, and toxic emissions except PM declined as Pt loading (i.e. oxidation activity) of the catalyst increased. They found that Pt is very effective in reducing benzene and aldehyde emissions. The reason is that for catalysts with high oxidation activity, the complete oxidation of HCs that contain the unregulated emissions is promoted even at low temperature. Benzene, formaldehyde, and acetaldehyde emissions increase for catalysts with lower oxidation activities. To reduce benzene, formaldehyde, and acetaldehyde emissions effectively, it was found that the Pt loading of the catalyst should be 0.2 g/l or higher.

Oyama and Kakegawa (2000) from Japan Nippon Mitsubishi Oil Corp. and Hino Motors also found that catalysts with high oxidation activity were effective in reducing PM, THC, CO and toxic emissions. The effects of catalysts on benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and acrolein emission varied widely among the engines, with significant effects observed from the use of certain catalysts. Compared to the same engine without a catalyst, an engine equipped with a highly oxidative catalyst (Pt 1.5 g/l) decreased 1,3-butadiene emissions from about 7 mg/kWh to below the detection limit, benzene emissions from 9 mg/kWh to 3 mg/kWh, formaldehyde emissions from 83 to 9 mg/kWh, and acetaldehyde emissions from 33 mg/kWh to 5 mg/kWh.

Sharp et al. (2000) performed detailed chemical speciation measurements for three modern diesel engines with and without OCs using three test fuels including a biodiesel fuel, a diesel fuel (S<0.05 wt%), and a blend of 20% biodiesel by volume in the diesel fuel. They found that the 1,3-butadiene emission declined about 30% with the OC for the neat biodiesel and the blend when compared to the values without a catalyst for

the same fuel. For neat diesel fuel, however, no clear reduction was observed for engines with a catalyst.

One of the earliest studies with DPFs was conducted by Danis et al. (1985). Danis did experiments with three different ceramic monolith particulate filter types on a single-cylinder, indirect injection diesel engine under steady-state conditions. All DPFs showed no effect on aldehyde emissions, while increasing the equivalence ratio from 0.35 to 0.75 decreased the aldehyde concentration in the exhaust from 15 to 2 ppm for formaldehyde and 27 to 5 ppm for acetaldehyde. The equivalence ratio is the ratio of the actual fuel-air ratio to the stoichiometric fuel-air ratio. It is interesting that the acetaldehyde concentrations were higher than formaldehyde concentrations. The authors explained the decrease in aldehyde emissions when increasing equivalence ratios as enhanced hydrocarbon oxidation caused by an increase of the exhaust gas temperature.

Recently, there have been a number of studies to evaluate DPFs (Oyama and Kakegawa, 2000; Warner et al., 2003). Japanese researchers Oyama and Kakegawa (2000) did not find a significant reduction of air toxics for an engine installed with an uncatalyzed DPF. With use of a catalyzed DPF, the toxic emissions are expected to be lower because the catalytic material should have the same apparent effects on toxics emissions as discussed above. This is demonstrated by Warner (2003). Warner conducted diesel engine tests with a 375 ppm sulfur fuel over the EPA old 13-mode steady state test cycle. The engine was equipped with manually controlled exhaust gas recirculation (EGR) and a catalyzed DPF (coated with a platinum catalyst (5g/ft³)). The results showed significant decreases in aldehyde emissions for each of the operating conditions with use of the catalyzed DPF. The formaldehyde emissions decreased about 20 to 74% and acetaldehyde emissions decreased about 43 to 63%.

The load of the engine is also an important factor for toxic emissions. Taiwan researchers Chao et al. (2000) conducted a study on the emissions of carbonyl compounds from a heavy-duty diesel engine over both cold-start and hot-start Transient Cycle tests and for both low-load and high-load steady-state tests. Results showed that emission rates of total carbonyl compounds for cold-start runs were only 12% higher compared to those for hot-start runs and formaldehyde, acetaldehyde and acrolein for cold-start runs were 18 to 26% higher than those for hot-start runs. In contrast, for steady-state tests, the calculated emission rates of the carbonyl compounds for low-load runs were drastically higher than those for high-load runs. Specifically, formaldehyde and acetaldehyde for low-load runs were 11.3 and 6.6 times higher than those for high load runs on g/kWh basis. Authors also found that in either transient cycle tests or steady-state tests, the use of either a 10% or 15% methanol-containing additive resulted in a significant increase in the emissions of acrolein, benzaldehyde, isovaleraldehyde, and valeraldehyde. The emissions of these four compounds were at least 1.90 times higher than for those without the use of methanol-containing additive. The effects of methanol additive to carbonyls emissions will be discussed in more detail in Chapter 6. The results of the studies discussed in this subsection are summarized in Table 3-12.

Table 3-12. Gas-Phase Toxics Emission Rates from Diesel Engines

Year	Engine	Engine Size	Emission control	Fuel	Cycle	1,3-Butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC	Ref
		Liters				mg/kWh	mg/kWh	mg/kWh	mg/kWh	mg/kWh	g/kWh	
	VW dummy	8.2	NC	D1	13-mode	7.4	7.8	84.4	33.1	NA	0.74	1
			NC	MD6	13-mode	6.6	8.8	82.4	32.1	NA	0.73	
			NC	MD13	13-mode	6.8	9.1	80.6	33	NA	0.69	
	V	9.2	OC	D1	13-mode	N.D.	N.D.	10.5	5.6	NA	0.13	
	V		OC	MD6	13-mode	N.D.	N.D.	10	5.9	NA	0.12	
	V		OC	MD7	13-mode	N.D.	N.D.	10.4	4.9	NA	0.13	
	V		OC	MD8	13-mode	N.D.	2.6	9	4.9	NA	0.13	
	V		OC	MD9	13-mode	N.D.	N.D.	10.3	5.9	NA	0.13	
	V		OC	MD10	13-mode	N.D.	N.D.	9.1	5.3	NA	0.14	
	V		OC	MD11	13-mode	N.D.	N.D.	9.1	5.5	NA	0.17	
	V		OC	MD12	13-mode	N.D.	N.D.	4.9	4.6	NA	0.10	
	V		OC	MD13	13-mode	N.D.	N.D.	2.9	3	NA	0.08	
	W	10.2	OC	D1	13-mode	4.3	6.1	81.2	34.8	NA	0.48	
	W		OC	MD6	13-mode	3.5	7.7	81.5	32.6	NA	0.48	
	W		OC	MD7	13-mode	3.9	6.6	80.3	33	NA	0.48	
	W		OC	MD8	13-mode	3.4	8.6	81.1	31.4	NA	0.50	
	W		OC	MD9	13-mode	3.9	7	85.2	34.6	NA	0.46	
	W		OC	MD10	13-mode	3.4	7.1	76.9	30.9	NA	0.48	
	W		OC	MD11	13-mode	3.8	7.7	98.3	38.2	NA	0.65	
	W		OC	MD12	13-mode	3.1	6	69.9	29.6	NA	0.45	
	W		OC	MD13	13-mode	3.1	4.7	38.6	26.1	NA	0.40	

1. Oyama and Kakegawa, 2000; V: Engine equipped with highly oxidative catalyst; W: Engine equipped with oxidation catalyst for 0.05%S. VW dummy: Dummy of V and W catalyst. D1~MD13: Diesel fuel with different aromatics (mono-, di-, and tri-) content and the cetane number adjusted to within a fixed range (53-58).

Table 3-12. Continued

Year	Engine	Engine Size	Emission control	Fuel	Cycle	1,3-Butadiene	Benzen e	Formald ehyde	Acetald ehyde	Acrolein	HC	Ref
		Liters				mg/kWh	mg/kWh	mg/kWh	mg/kWh	mg/kWh	g/kWh	
	X	8		D1	13-mode	8.2	7.7	120.5	48.1	NA	1.16	1
	X		MD6	13-mode	8.9	11.5	122.4	48.5	NA	1.20		
	X		MD7	13-mode	9.6	10.3	122.5	50.1	NA	1.07		
	X		MD8	13-mode	9.5	11.9	139.3	54.7	NA	1.35		
	X		MD9	13-mode	8.6	9.8	107.2	45.3	NA	1.07		
	X		MD10	13-mode	10.6	10.3	129.9	54.4	NA	1.13		
	X		MD11	13-mode	14.8	12.7	237.6	97	NA	2.18		
	X		MD12	13-mode	8.2	11.6	112.2	43.7	NA	1.13		
	X		MD13	13-mode	10.8	11.2	133	55	NA	1.14		
	Y	21.2		D1	13-mode	3	3	39.8	15.5	NA	0.33	
	Y		MD6	13-mode	2.9	3.2	38.3	15.2	NA	0.33		
	Y		MD7	13-mode	2.6	3.3	39.3	15.5	NA	0.30		
	Y		MD8	13-mode	2.4	3.6	37.8	15	NA	0.33		
	Y		MD9	13-mode	2.7	3.3	35.5	14.2	NA	0.33		
	Y		MD10	13-mode	2.8	3.4	38.4	15	NA	0.32		
	Y		MD11	13-mode	2.7	3.4	43.8	17.4	NA	0.43		
	Z		DPF	D1	13-mode	10.3	9.4	120.3	49.4	NA	1.64	
	Z		DPF	MD6	13-mode	9.5	11.9	115.8	44.1	NA	1.65	
	Z		DPF	MD7	13-mode	9	10.2	108.6	44.1	NA	1.42	
	Z		DPF	MD-11	13-mode	7.3	8.4	98.9	23.4	NA	1.67	
	Z dummy			D1	13-mode	9.7	8.8	119.5	44.9	NA	3.50	
	Z dummy			MD6	13-mode	8.6	11.7	106.5	41.1	NA	3.21	

1. Oyama and Kakegawa, 2000. X: High fuel sensitivity engine; Y: Low fuel sensitivity engine; Z: DPF equipped engine; Z dummy: Dummy of DPF.

Table 3-12. Continued

MY	Engine Size	Engine Size Liters	Emission control	Fuel	Cycle	1,3-Butadiene mg/kWh	Benzene mg/kWh	Formaldehyde mg/kWh	Acetaldehyde mg/kWh	Acrolein mg/kWh	HC g/kWh	Ref
1999	Cummins "B-series"	5.9		D2	Transient	2.00	1.60	20.30	7.90	3.90	0.10	2
				Carb	Transient	1.30	1.60	15.00	6.00	1.30	0.10	
				Swedish	Transient	1.50	1.70	18.20	7.40	3.40	0.10	
				F-T	Transient	1.60	1.10	13.00	5.20	1.70	0.10	
		7	Euro 1		ECE R49	3.63	3.58	25.79	12.41	NA	0.29	3
		12.7	Euro 2		ECE R49	1.07	5.97	12.26	5.86	NA	0.097	
	Valmet 620 DWRE	6.6		EC-1	Idle at 700rpm	0.35	1.91	0.47	1.4	0.06	0.13	4
				FT		0.025	0.49	0.46	0.41	0.01	0.11	
1997	Cummins N14	14.0		B100	Transient	1.50	1.19	12.16	4.09	3.34	NA	5
				B20	Transient	1.85	1.80	15.26	5.74	1.89	NA	
				2D	Transient	1.77	1.25	17.92	6.37	1.93	NA	
1997	DDC series 50	8.5	NC	B100	Transient	0.54	0.84	12.77	4.53	3.00	NA	
			OC		Transient	0.15	1.01	14.17	8.77	2.40	NA	
			NC	B20	Transient	1.07	0.98	16.16	6.11	3.14	NA	
			OC		Transient	0.72	1.03	19.12	11.29	4.14	NA	
			NC	2D	Transient	0.28	0.98	18.20	9.21	2.75	NA	
			OC		Transient	0.74	0.99	17.22	6.65	3.39	NA	
1995	Cummins B5.9	5.9	NC	B100	Transient	3.11	5.34	31.66	9.90	5.82	NA	
			OC		Transient	1.81	4.65	38.46	15.70	5.90	NA	
			NC	B20	Transient	3.29	3.82	40.99	13.49	5.08	NA	
			OC		Transient	2.08	2.76	44.31	19.31	3.31	NA	
			NC	2D	Transient	3.00	3.70	48.95	22.19	7.16	NA	
			OC		Transient	4.30	4.40	55.89	21.50	10.50	NA	

2. Fanick et al., 2001

3. Reynolds et al., 1999

4. Nord and Haupt, 2002

5. Sharp et al., 2000

Table 3-12. Continued

	Engine	Engine Size	Emission control	Fuel	Cycle	1,3-Butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC	Ref
MY		Liters				mg/kWh	mg/kWh	mg/kWh	mg/kWh	mg/kWh	g/kWh	
	AWM D - 916-6				I100	0.58	1.18	NA	NA	NA	NA	6
					R100	0.21	NA	NA	NA	NA	NA	
					I50	0.29	1.29	NA	NA	NA	NA	
					R50	0.24	0.64	NA	NA	NA	NA	
					Idle	NA	12.95	NA	NA	NA	NA	
	DI engine	5.78		Fuel 1	1600rpm (50%load)	0.00	0.00	1.45	0.60	NA	NA	7
				Fuel2		0.00	0.00	0.00	2.36	NA	NA	
				Fuel 3		0.00	0.00	0.00	1.90	NA	NA	
1991	Series 60 DI			Fuel 2	Hot start transient	1.34	0.80	20.92	7.78	NA	0.15	
				Fuel 4		2.01	0.94	36.48	12.74	NA	0.27	
				Fuel 5		1.21	0.80	22.13	7.51	NA	0.26	
	Cummins L10	10		Pre-1993	Cold start	2.79	8.70	83.58	27.13	2.18	0.56	8
					Hot start	2.35	7.78	75.44	23.88	2.13	0.52	
					Weighted	2.41	7.91	76.60	24.34	2.14	0.53	
				Low aromatic fuel	Cold start	2.94	9.78	73.42	23.68	5.49	0.41	
			Hot start		3.35	10.93	79.68	25.93	5.84	0.48		
			Weighted		3.30	10.77	78.78	25.61	5.79	0.47		
				Reformulated fuel	Cold start	2.31	9.09	80.04	26.95	2.52	0.47	
			Hot start		2.51	7.58	80.26	26.69	2.41	0.50		
			Weighted		2.47	7.79	80.23	26.73	2.42	0.50		

6. Gautam et al., 7th CRC. Fuel: 27.7% aromatic content and 46.9 cetane number. Cycle: 8-mode steady state cycle. I100: Intermediate speed, 100%load; R100: Rated speed 100%load; I50: Intermediate speed, 50%load; R50: Rated speed 50%load.

7. Gonzalez et al. 2001. Fuel 1: reference fuel (aromatic content < 10 wt%, sulfur content 300ppmw); Fuel 2: base fuel (aromatic content 18.4 wt%, sulfur content 0.28 wt %); Fuel 3: base fuel with 10% water; Fuel 4: water12%; Fuel 5: water12%.

8. Truex et al., 1998. Cycle: transient cycle.

Table 3-12. Continued

	Engine	Engine Size	Emission control	Fuel	Cycle	1,3-Butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC	Ref
MY		Liters				mg/kWh	mg/kWh	mg/kWh	mg/kWh	mg/kWh	g/kWh	
	Mitsubishi i 6D 14	6.557			Transient cold start			114.12	90.25	12.73	NA	9
					Transient hot start			88.37	74.43	10.37	NA	
					Transient weighted			91.99	76.71	10.70	NA	
					Steady state low load			449.24	96.55	4.59	NA	
					Steady state high load			39.83	14.75	1.09	NA	

9. Chao et al., 2000

3.3 Alternative Fuel Vehicles and Engines

Compressed natural gas (CNG) has been one of the most widely researched fuels proposed to replace liquid petroleum based fuels. Under certain conditions, the use of CNG fuel has proven its potential to reduce regulated emissions compared to conventionally fueled engines. Regulated non-methane hydrocarbon emissions are often lower than hydrocarbon emissions from conventional liquid fuels because of the absence of heavier hydrocarbons in the fuel.

3.3.1 Light-Duty Engines and Vehicles

Some of the earliest studies of emissions from CNG engines and vehicles were conducted in the 1980s. Fleming and O'Neal (1985) tested the effect of the equivalence ratio and the compression ratio on the aldehyde emissions from a single cylinder research engine fuelled with CNG. It was reported that aldehyde emissions decrease while equivalence ratio is increased from lean to stoichiometric conditions. No effect of the compression ratio could be identified because the absolute aldehyde values were near to the detection limit of the analysis equipment.

DeLuchi et al. (1988) compared the aldehyde emissions from a CNG vehicle with a gasoline fuelled vehicle and reported no great differences in the total aldehyde emissions for gasoline and CNG cars. They observed total aldehyde emissions were about 0.03-0.05 g/mi without the catalyst system and 0-0.004 g/mi with the catalyst system for both types of fuel.

The use of CNG as a fuel in engines was reviewed by Weaver (1989). It is reported that the principal aldehyde in the exhaust of a CNG engine is formaldehyde, because natural gas consists mainly of methane (CH₄), the lowest carbon-number hydrocarbon, and the effect of higher hydrocarbons in the natural gas on aldehyde formation is negligible. Wagner et al. (1996) compared the aldehyde emissions from a CNG vehicle with a gasoline fueled vehicle and found an increase of 20% in the formaldehyde value when the engine was fueled with natural gas. Newkirk and Bass (1995) also found that formaldehyde emissions from CNG vehicles without catalysts could be rather high compared to gasoline vehicles.

Kelly et al. (1996) of NREL investigated toxic emissions from 37 CNG vehicles compared to 38 gasoline vehicles. All test vehicles were 1992-1994 Dodge B250 vans with 5.2-liter V8 engines. The CNG contained 93% methane. California Phase 2 RFG was used in the control vehicles. They found in all cases except for formaldehyde, the results show that levels of toxic compounds emitted from the CNG vans are substantially lower, on average, than those from the gasoline vans. The reductions of toxic emissions from CNG vehicles were 94.8%, 96%, and 61.8% for 1,3-butadiene, benzene, and acetaldehyde, respectively, when compared with RFG vehicles. While the average formaldehyde emission rate increased by 48% compared to average RFG vehicles.

A research program at West Virginia University (Nine et al., 1997) sought to identify and quantify the individual hydrocarbon species present in CNG exhaust. A Hercules GTA 3.7 liter medium duty CNG spark ignited engine was tested at different load and speed set points. The results of this study are summarized in Table 3-13. The emission rates of 1,3-butadiene varied from under the detection limit to 0.0092 g/mode. The intermediate speed with light load (I10) produced the highest 1,3-butadiene emissions. Benzene emission rates varied from under the detection limits to 0.0067 g/mode. Rated speed modes had higher benzene emissions than intermediate speed modes.

Table 3-13. Emission Rates of Air Toxics over Different Test Modes

Mode		Lambda Value	1,3-butadiene (g/mode)	Benzene (g/mode)
I50	1600 rpm, 50% load	1.32	0.0029	0.0034
I50	1600 rpm, 50% load	1.55	0.0025	NP
I50	1600 rpm, 50% load	1.10	NP	0.0048
I10	1600 rpm, 10% load	1.32	0.0092	0.0024
R50	2500 rpm, 50% load	1.32	NP	0.0055
R10	2500 rpm, 10% load	1.32	NP	0.0053
I100	1600 rpm, 100% load	1.32	NP	0.0015
Idle	790 rpm	1.32	NP	0.0021
R100	2500 rpm, 100% load	1.32	NP	0.0067

Nine et al., 1997; NP=no peak detected.

Later, Black and Tejada (1999) reported that FTP toxic compound emissions from a variety of vehicle technologies using RFG, methanol (15%) (M85), ethanol (15%) (E85), and CNG. The aldehydes emissions were greater with M85 and E85 fuels than with RFG fuel, and less with CNG fuel than RFG fuel. The most abundant toxic compound was benzene with RFG fuel, formaldehyde with M85 fuel, acetaldehyde with E85 fuel, and formaldehyde with CNG fuel.

Winebrake and Deaton (1999) conducted emission tests with conventional fuels, CNG, and some other alternative fuels. CNG vehicles showed significant reductions for benzene, 1,3-butadiene, and acetaldehyde emissions when compared to RFG vehicles with reductions of 96%, 94%, and 77%, respectively. While formaldehyde emissions rates from CNG vehicles were on the same order of magnitude or slight higher compared to RFG vehicles.

In Europe, Ahlvik and Brandberg (2003) from Sweden Ecotraffic conducted light-duty vehicle tests over the new European driving cycle (NEDC). The fuels investigated in this study were ethanol (E85), methanol (M85), CNG, biogas and diesel oil. The researchers found that the emissions of formaldehyde and acetaldehyde are a drawback for alcohol fuels. E85 had the highest formaldehyde emissions. The high

emissions during cold start at low ambient temperature was one reason for this trend. The gasoline and CNG fuels had very low aldehyde emissions, whereas the diesel test showed considerably higher aldehyde levels.

Nylund and Lawson (2000) from the Finland VTT Technical Research Centre and GFC Control Systems, Inc., Canada conducted a study of exhaust emissions from natural gas vehicles. This study covered emission testing of natural gas vehicles as well as fuel properties, engine technology effects. The results of this study are summarized in Table 3-14. For a gasoline, the TWC reduced 1,3-butadiene, benzene and formaldehyde emissions by a factor of more than 10. For those three compounds, LPG and CNG give lower emissions than gasoline and M85. M85 exhaust contains unburned methanol. Nylund and Aakko (2003) also found E85 had higher aldehyde emissions than CNG and gasoline. CNG gave extremely low formaldehyde emissions, especially at low temperature. Acetaldehyde emissions are high with E85. Only trace 1,3-butadiene was emitted from CNG vehicles. Gasoline and E85 produced equivalent 1,3-butadiene levels.

Table 3-14. Emission Rates of Air Toxics over FTP Cycle for Different Fuels and Vehicle Technologies (mg/km)

	1,3-Butadiene	Benzene	Formaldehyde	Methanol
Gasoline w/o cat	11.8	55	43	0
0Gasoline	0.6	4.7	2.5	0
M85	<0.5	1.5	5.8	79
LPG	<0.5	<0.5	<2	0
CNG	<0.5	0.6	<2	0
Diesel	1	1.5	12	0

3.3.2 Heavy-Duty CNG Engines and Vehicles

Lev-On et al. (2002a) conducted vehicle emission tests on two CNG transit buses and a diesel transit bus with and without DPF. These researchers found that CNG buses had benzene emissions on the same order of magnitude as the diesel transit bus without aftertreatment. For the transit buses fueled by CNG, the emissions of both formaldehyde and acetaldehyde were an order of magnitude higher than for any of the diesel-fueled transit buses. The results of these studies are summarized in Table 3-15.

Ullman et al. (2003) and Slodowske (2003) found that compared to a conventional diesel bus, a CNG bus had higher emissions of 1,3-butadiene, formaldehyde, and acetaldehyde. Compared to a low emission diesel bus (with a DPF), the CNG bus had higher levels of formaldehyde, acetaldehyde, and benzene emissions. The CNG also had the highest emissions of total aldehydes and ketones.

Over the past three years, the California Air Resources Board (CARB) has investigated the tailpipe emissions from three different late-model, in-use heavy-duty

transit buses (Ayala et al., 2003a; Ayala et al., 2003b). The impact of OC control for both diesel and CNG buses and a passive DPF were evaluated over multiple driving cycles. The diesel bus was a 1998 model year bus powered by a DDC-S50 engine. This bus was equipped with a diesel OC and a catalyst-based DPF. CNG-1 was a 2000 model year bus powered by a DDC S-50G engine. This bus was tested in two configurations, without after-treatment and with an OC. The second CNG bus (CNG-2) was a 2001 model year vehicle powered by a Cummins Westport C Gas Plus engine. This bus is equipped with an OC by the OEM. Carbonyl emissions from the uncontrolled CNG bus were highest among all test bus configurations over the Central Business District (CBD) driving cycle. These emissions were dominated by formaldehyde, ranging from approximately 86% to 92% of all carbonyl emissions measured over time. The CNG OC reduced formaldehyde significantly by 96% for the DDC bus. The lowest carbonyl emissions came from the Diesel bus with DPF. The second largest contributor to carbonyl emissions was acetaldehyde. Some reductions in acetaldehyde levels from the OC were also observed for the CNG buses. Similar trends were observed over the Steady State tests. Carbonyl emissions for the DDC bus over the Steady State were less than half of those measured over the CBD cycle. Again, dramatic reductions with the OC, on the order of 96%, were found for formaldehyde emissions. Benzene emissions were reduced with the OC also. The lowest emissions of benzene corresponded to the Diesel (DPF) and the CNG (OC) configurations. Emissions of 1,3-butadiene were only detected in the exhaust from the uncontrolled CNG bus over CBD cycle and these measurements exhibited high variability. The application of an OC resulted in 1,3-butadiene levels below detection for both CBD and SS cycles.

In Europe, the application of CNG to heavy-duty buses and other engines is considered by some to be one of the best options in reducing diesel emissions (Ahlvik and Brandberg, 2000; Seguelong, 2003; Ahlvik, 2003). Some results comparing CNG and diesel vehicles are summarized in Table 3-15. Ahlvik and Brandberg (2000) of Sweden evaluated the emissions from city buses with CNG, diesel fuel and ethanol. They found that the aldehydes from CNG mainly consist of formaldehyde. This is consistent with other studies. Emission rates of 1,3-butadiene were also, to some extent, higher from the methane in the CNG.

Table 3-15. Average Air Toxics Emissions by Driving Cycle (mg/mi)

Year	Make	Tech	Cycle	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC (g/mi)	Ref
2000	CNG, DDC-S50G	None	SS	0.1	1.47	357	12.7	NA	3.32	1
		None	CBD	0.39	2.24	860	50.7	NA	6.21	1
		None	CBD	1.2*	4.4*	710*	80*	NA	10*	1
		None	CBD	3.5	3.2	780	90.0	NA	6.09	1,2
		OC	SS	ND	0.21	7.8	4.8	NA	0.45	1
		OC	CBD	ND	0.60	38.4	32.6	NA	6.15	1
2001	Cummins-Westport C-Gas Plus	OC	SS	ND	ND	24.6	6.20	NA	5.31	1
		OC	CBD	ND	1.29	56.8	19.4	NA	14.13	1
2000	Blue Bird, John Deere	None	CSHVC	4.5	4.3	500	24.0	4.9	9.34	3
2000	New Flyer, DD-S50G	None	CBD	ND	2.74	583	23.1	0.31	NA	4
2001	New Flyer, DD-S50G	None	CBD	ND	1.71	657	17.9	0	NA	4

1. Ayala et al., 2003b; 9th Diesel Engine Emissions Reduction Conference; CBD: central business cycle; SS: steady state; * Estimated from figure;

2. Ayala et al., 2001, Presentation to South Coast Air Quality Management District;

3. Ullman, et al., 2003, CSHVC: Suburban Heavy Vehicle Cycle;

4. Lev-On, et al., 2002a and 2002b. ND: Non detect.

3.4. Stationary Sources.

The Western States Petroleum Association (1990) conducted emission tests of oil field combustion sources in Fresno and Ventura counties. This study consisted of stack sampling from a drilling rig IC engine and a workover rig IC engine. CARNOT, formerly the California Division of Energy Systems Associates, measured emissions in support of emission inventory reports by Western States Petroleum Association for the Air Toxics “Hot Spots” program. A total of eleven sites were measured, however, only two sites performed hydrocarbon speciation tests and carbonyl tests including a bank of six crude oil fired steam generators and a diesel fired 350 HP IC engine. The results of these studies are summarized in Table 3-16.

CE-CERT is currently measuring emissions from backup generators (BUGs) in a project sponsored by the California Energy Commission (Miller et al, 2002 and 2003). CARB is also involved in this program and has an interest in obtaining data on the performance of certain emission control technologies for stationary generators. The 5-mode steady-state test cycle was selected for this test matrix. The 5-mode steady-state test cycle is a simplified version of the UN-ECE R49 13-mode steady-state test cycle.

The results are summarized in Table 3-17 and the final report is expected the summer of 2004.

Table 3-16. Air Toxics Emission Rates from Stationary Sources (lb/MMBtu)

Device	Rating	Fuel	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC	Ref
Drilling rig IC engine	850 hp	Diesel		7.76E-04	7.89E-05	2.52E-05	7.88E-06	2.35E-02	1
Workover rig IC engine	350 hp	Diesel		1.33E-03	9.87E-04	4.64E-04	1.32E-04	1.15E-01	1
IC engine	350 hp, Chevron	Diesel	<3.91E-05	5.36E-04	1.38E-03	1.07E-03	<5.3E-05	1.17E-01	2

1. Western States Petroleum Association, 1990.
2. CARNOT, 1990, report for Western States Petroleum Association.

Table 3-17. Air Toxics Emission Rates from Backup Generators (mg/kw-hr)

	Generator Type	Catalyst	Fuel	Load	Formaldehyde	Acetaldehyde	Acrolein	HC (g/kw-hr)
1996 CAT 3406C	Primary	No	RFD#2	10	NA	NA	NA	0.65
				25	14.01	5.38	0.0	0.23
				50	12.90	4.90	0.65	0.08
				75	11.85	3.16	0.54	0.04
				100	15.61	3.07	0.32	0.06
1991 CAT 3406B	Backup	No	RFD#2	10	37.75	8.31	0.82	0.45
				25	18.73	5.03	0.60	0.25
				50	16.36	2.84	0.32	0.16
				75	15.87	2.59	0.47	0.11
				100	24.24	3.02	0.91	0.07
1991 DDC8 V 92	Backup	No	RFD#2	10	89.6	18.5	3.9	2.7
				25	26.7	6.3	0.5	1.1
				50	16.0	3.3	0.3	0.6
				75	16.0	2.7	0.4	0.4
				100	21.8	2.5	0.9	0.4

4. PM Emissions

Over the past two decades, a number of studies have been conducted in an effort to measure particulate emission rates from diesel engines and vehicles. These have included engine dynamometer tests of heavy-duty diesel engines, chassis dynamometer tests of heavy- and light-duty diesel vehicles, as well as on-road measurements. In the following section, these data have been compiled, collated, and evaluated. A comparison of emission rates for different vehicle classes is also made. Additionally, a brief summary of the impacts of technological advances on PM emissions is given. A more detailed review of other aspects of PM emissions, including size distributions, sampling and measurement techniques, is provide elsewhere (Durbin et al., 2004).

4.1 Light-Duty Vehicles

4.1.1 Light-Duty Gasoline Dynamometer Testing

A number of studies have been conducted on light-duty gasoline vehicles over the years. A summary of chassis dynamometer results for light-duty gasoline vehicles is presented in Table 4-1. These studies show that particulate emissions from light-duty gasoline vehicles have decreased significantly over the years. Emission rates from early non-catalyst gasoline vehicles tested on leaded fuel were typically greater than 100 mg/mi. The introduction of catalysts and unleaded fuel reduced this value significantly. The EPA summarized the early available literature for different technology gasoline vehicles and found average emission rates of 24.3 mg/mi for vehicles equipped with oxidation catalysts without air injection, 30.4 mg/mi for vehicles with air injected oxidation catalysts, and 14.2 mg/mi for vehicles equipped with both three-way and oxidation catalysts with air injection (U.S. EPA, 1993).

PM emissions from modern vehicles re relatively low, with emission rates of 5 mg/mi or less (Zinbo, 1995; Siegl, 1994; Hammerle, 1992). FTP exhaust PM emission rates from properly-functioning, late-model LDGVs, in many case have been shown to be low, on the order of 2 mg/mi, even at high mileage (Chase et al., 1998; Ball, 1997; Mulawa et al., 1997; Mulawa and Dasch, 1995; Zinbo et al., 1995; and Siegl et al., 1994; Maricq et al., 1999b).

It is important to note that while most modern gasoline-fueled vehicles are low PM emitters, PM emission rates from high CO emitting and visibly smoking gasoline vehicles can be significantly higher than general gasoline vehicles. Several recent studies have shown that visibly smoking and high CO emitting vehicles can have emissions on the order of hundreds or thousands of mg/mi (Cadle et al., 1995, 1996; Durbin et al., 1999). Thus, high emitters can have a significant impact on the particulate emissions inventory for light-duty vehicles (Durbin et al., 1999). A smoking vehicle study in the SCAQMD (Durbin et al., 1999) found that 18 gasoline smokers had an average FTP PM emission rate of 408 mg/mi. Similarly, studies in Nevada (Sagebiel et al., 1997) and Orange County, California (Cadle, et al., 1998) found that smoking vehicle PM emission

rates averaged 558 and 400 mg/mi., respectively, on the IM240 driving cycle. These two studies also found that vehicles recruited for testing due to their high on-road HC and CO emission rates, had PM emission rates averaging 51 and 94 mg/mi in Nevada and Orange County, respectively.

Because of the wide range of PM emission rates from in-use vehicles and the small number of vehicles that have been tested, estimates of their contribution to the PM inventory were very uncertain in the mid to later 1990s. The Coordinating Research Council (CRC) sponsored studies of light-duty vehicle PM exhaust emissions at the University of California, Riverside, College of Engineering-Center for Environmental Research and Technology (CE-CERT) (Norbeck et al., 1998), the Northern Front Range Air Quality Study (NFRAQS) in Denver, Colorado (Cadle et al., 1998), and the Southwest Research Institute (SwRI) (Whitney 1998). A total of 361 gasoline-fueled vehicles and 49 diesel-fueled vehicles at three different locations were tested using the FTP-UDDS (urban dynamometer driving schedule) during these studies. The results were summarized by Cadle et al. (1999). Vehicle model years ranged from 1965 to 1997. Particle size distribution, particle number, and bulk composition of the particulate were made on a subset of the vehicles at each location. The average PM emission rates were 3.3, 79.9, 384 and 558 mg/mi for 1991-97 model year LDGVs, pre-1981 LDGVs, smoking LDGVs and the diesel vehicles, respectively.

Another large study that is near completion is a Department of Energy sponsored study to investigate the source apportionment of gasoline/diesel PM (Fujita et al., 2004; Lawson et al., 2004). This study included measurements of 59 light-duty vehicles over the Unified Driving Cycle. The vehicles tested included 51 light-duty gasoline vehicles in 9 groups of model years and mileages, 6 gasoline-smoking vehicles, and 2 light duty diesel vehicles. Overall PM emission rates averaged 19 mg/mi with a median emission rate of 5 mg/mi and a maximum emission rate of 185 mg/mi. The results of this study have yet to be released in a report, but a report is expected in the Summer 2004 timeframe.

Other studies have also looked at emission rates from vehicles under non-standard FTP test conditions, including different driving cycles and temperatures. Maricq et al. (1999b) measured the emissions rates of 8 vehicles over the FTP and US06. The US06 emission rates varied from 1.2 to 9.6 mg/mi and were similar in magnitude to the emission rates observed during bag 1 of the FTP. Norbeck et al. (1998) measured 12 1986 and newer vehicles over the Unified Cycle (UC) and found emission rates of 4.5 mg/mi, comparable to typical values over the FTP. Direct comparisons between FTP and UC cycles in this same studied, however, showed that UC cycle PM emissions were consistently higher than those from the FTP. Cadle et al. (1998) found significantly higher emissions when vehicles were tested under winter ambient conditions (24.9 mg/mi for 1991-1996 vehicles) in comparison with FTPs on the same vehicles tested indoors (3.51 mg/mi for 1991-1996). In a follow-up study, Cadle et al. (2001) showed that emission rates for properly functioning Tier 0 and Tier 1 vehicles averaged 6.1 mg/mi over an FTP conducted at 35°F. REPO5 and hot UC cycles were also conducted on these same vehicles with average emission rates of 12.7 and 3.6, respectively. Mulawa et al.

(1997) also investigated PM emission rates from 10 1977-1994 in-use vehicles at 20, 0 and -20°F in conjunction with the Alaska Department of Environmental Conservation. These vehicles also showed increases in PM emissions with decreasing temperatures for both an oxygenated and non-oxygenated fuel.

In Europe, Department of the Environment, Transport and the Regions (DETR), UK, SMMT and CONCAWE conducted a PM research program to investigate the effects of vehicle/engine technology level, fuel specification and various operating conditions on emissions of particle mass, number and size for light-duty vehicles (Andersson et al., 2001). The authors concluded that, in general, PM mass emissions from the multipoint injection gasoline vehicles were below 0.001 g/km for both cold start transient cycles and steady state conditions, while emissions from gasoline direct injection vehicle were at least 10 times greater than this.

The association of European automobile manufactures (ACEA) conducted programs on fine particulate emissions from light-duty gasoline and diesel passenger cars and heavy-duty vehicle (ACEA, 2002; Stein, 2002; Carli, 2002; Mohr et al., 2003). During ACEA study (2002), four gasoline cars were tested; one of them (a Ford Fiesta) was naturally aspirated with multi-point injection. The other three were equipped with direct injection systems (Renault Megae iDE), with two of them utilized lean burn combustion (Volvo V40 GDI, VW Lupo FSI). All four vehicles were equipped with TWC. The results showed that gravimetry was able to reliably measure very low PM emissions. A large variation is observed depending on the combustion concept and higher emissions were found for stratified combustion compared to stoichiometric combustion. One vehicle also showed a load dependence of the PM emissions. The PM emissions from gasoline vehicles remain substantially below the typical diesel level.

Ahlvik (2002) of Sweden also showed that two gasoline vehicles over the New European Driving Cycle (NEDC) had an increase in PM emissions from 0.7 to 1.3 mg/km at 22°C to 2.1 to 5.3 mg/km at -7°C. Kokko et al. (2000) from Finland Fortum Oil and Gas Oy measured exhaust emissions from cars using reformulated gasoline and found PM emissions were reduced on average by 30% at 22 °C and 40% at -7 °C compared to the European 2000 regulations gasoline.

Table 4-1. Light-Duty Gasoline Vehicle Particulate Emission Rates-
Dynamometer Tests

Make/Model	Test cycle	Emission Rate	Reference	Comments
		mg/mi		
High Emitters				
3 high emitting cars	FTP	27.4	Cadle, 2001	35°F
3 high emitting trucks	FTP	268	Cadle, 2001	35°F
3 high emitting cars	Hot UC	26.2	Cadle, 2001	35°F
3 high emitting trucks	Hot UC	69	Cadle, 2001	35°F
3 high emitting cars	REP05	56.9	Cadle, 2001	35°F
3 high emitting trucks	REP05	52.6	Cadle, 2001	35°F
31 smoking vehicles	FTP	384	Cadle, 1999	smokers
18 gasoline vehicles	FTP	avg.=408 64-2323	Durbin, 1999	smokers
	IM240	avg.=349 13-1807	Durbin, 1999	smokers
17 High CO vehicles MY 1976-90	IM240	avg.=50.8 5.6-221.4	Cadle, 1995	Nevada
6 smoking vehicles MY 1976-89	IM240	avg.=558 59-1342	Cadle, 1995	Nevada
86 High CO vehicles ages 6-22 yrs	IM240	avg.=94 3-475	Cadle, 1996	Orange County
17 smoking vehicles ages 8-21 yrs	IM240	avg.=395 19-1097	Cadle, 1996	Orange County
31 scrap vehicles/ MY 1964-71	FTP	avg.=1500 100-16,760	Unocal Scrap Project	
Catalyst/Unleaded				
Gasoline Peugeot and Golf	NEDC	0.7-1.3 mg/km	Ahlvik, 2002	22°C
Gasoline Peugeot and Golf	NEDC	2.1-5.3 mg/km		-7°C
21 1994-1997 vehicles	FTP	<2	Maricq, 1999a	
11 1995-1998 vehicles	FTP	<2	Maricq, 1999b	
8 1995-1998 vehicles	US06	1.2-9.6	Maricq, 1999b	
109 LDGVs MY 1991-97	FTP	3.3	Cadle, 1999	
4 - 1991-4L Ford Explorers/ 5-105K mi & 4 -1991-1.9L Ford Escorts/5-105K mi	6 consecutive FTP cycle	2.5	Hammerle, 1992	
		4	Hammerle, 1992	w/ MMT
1990 Ford Taurus	FTP	2.0-4.4	Zinbo, 1995	
8 Tier 1 cars	FTP	4.43	Cadle, 2001	35°F
4 Tier 1 trucks	FTP	6.58	Cadle, 2001	35°F
8 Tier 0 cars	FTP	10.3	Cadle, 2001	35°F
4 Tier 0 trucks	FTP	19.1	Cadle, 2001	35°F
8 Tier 1 cars	Hot UC	1.72	Cadle, 2001	35°F
4 Tier 1 trucks	Hot UC	2.54	Cadle, 2001	35°F

Table 4-1. - Continued

Make/Model	Test cycle	Emission Rate	Reference	Comments
		mg/mi		
8 Tier 0 cars	Hot UC	4.01	Cadle, 2001	35°F
4 Tier 0 trucks	Hot UC	6.93	Cadle, 2001	35°F
8 Tier 1 cars	REP05	7.46	Cadle, 2001	35°F
4 Tier 1 trucks	REP05	11.4	Cadle, 2001	35°F
8 Tier 0 cars	REP05	14.7	Cadle, 2001	35°F
4 Tier 0 trucks	REP05	25.3	Cadle, 2001	35°F
12 cars and trucks/ MY 1986-90	FTP	6.7±5.9 cars	Mulawa and Dasch	
		8.4±1.1 trucks		
1989 Ford Taurus	4 FTPs back/back	5.80	Siegl, 1994	
1987 Ford Taurus		25.5-40.5	Siegl, 1994	"high emitter"
12 1986+ vehicles	UC	4.5	Norbeck, 1998	
7 1981-1985 vehicles	UC	20.0	Norbeck, 1998	
Seven vehicles MY 1977-83	FTP	18	Hildemann, 1991	
66 LDGVs MY Pre-1981	FTP	79.9	Cadle, 1999	
Sixteen vehicles (MY 1975-1981)	FTP	31.7±44.1	Lang, 1981	
Five - 1978-79 cars w/ catalysts		14.5	Muhlbaier, 1982	low altitude
Five - 1975-78 cars w/catalysts		19	Muhlbaier, 1982	high altitude
15 vehicles		avg.=21 5.9-36.0	Zweidinger, 1981	
Avg. of data from eight 1980-81 refs.		18	Schuetzle, 1983	
Nine 1978-79 vehicles (exclude New Yorker)	FTP	39.6	Smith, 1981	
Four 1978 vehicles	FTP	9.1	Urban, 1980a	unmodified
Three 1978 3-way cat vehicles	FTP	16.8	Urban, 1980b	unmodified
1973 & 1974 oxy cat vehicles	FTP	4 and 9	Cadle, 1979	
1977 production oxy cat w/air	FTP	8.5	Cadle, 1979	
Catalyst/Unleaded				
4 1975-1980 vehicles	UC	47.1	Norbeck, 1998	
1978 production 3-way cat	FTP	10	Cadle, 1979	
(1977 VW Rabbit/1977Olds. Cutlass)	FTP	6.18/9.06	Springer, 1977	
	FTP (cold start)	8.0/13.5	Springer, 1977	
	FTP (hot start)	4.85/5.7	Springer, 1977	
	SET	2.62/15.6	Springer, 1977	
	HWFET	2.5/22.0	Springer, 1977	
Five 1975 cars w/ catalyst		21±8	Braddock, 1977	
1970 Chevy V-8 engine dyno test	7-mode Fed. Test	13.00	Laresgoiti, 1977	Indolene, 0.1%S
Noncatalyst/Unleaded				
1974 Chevy Impala	FTP	22.7±0.46	Mulawa and Dasch	

Table 4-1. - Continued

Make/Model	Test cycle	Emission Rate	Reference	Comments
		mg/mi		
1977 AMC Pacer w/ air pump	FTP	50.4	Urban, 1980a	
1973 & 1974 noncat/unlead gas. Vehs	FTP	26 and 31	Cadle, 1979	
1970 Ford Fairlane (V-8 engine)	72 Fed.-cold start	24	Miller, 1976	
5-cars	7-mode Fed. cycle	197	Ter Harr, 1972	
3 cars w/<1000 mi	7-mode Fed. cycle	165	Ter Harr, 1972	
Noncatalyst/Leaded				
Six vehicles MY 1965-76	FTP (cold start)	95	Hildemann, 1991	
Ave. of data from eight 1980-81 refs.		100	Schuetzle, 1983	
4 non cat. cars (1970-1978)		119	Muhlbaier, 1982	low altitude
4 Vehicles (MY 1970-1979)	FTP	102.5±36	Lang, 1981	
4 vehicles		ave=102	Zweidinger, 1981	
		49-128	Zweidinger, 1981	
1970 Ford Fairlane (V-8 engine)	72 Fed.-cold start	167	Miller, 1976	
16 - 1966 cars w/>30,000 mi	7-mode Fed. cycle	339	Ter Haar, 1972	
6 cars w/<1000 mi	7-mode Fed. cycle	152	Ter Haar, 1972	
Other				
22 Vehicles MY 1965-1983	ADR 37	ave=110 50-320	Williams, 1989b	FTP75
European studies				
Ford Fiesta w/TWC	SS 120km/h	0.2 mg/km	ACEA, 2002	
	SS 100km/h	0.1 mg/km	ACEA, 2002	
	SS 50km/h	0.2 mg/km	ACEA, 2002	
Renault Megane iDE w/TWC	SS 120km/h	1.9 mg/km	ACEA, 2002	
	SS 100km/h	0.8 mg/km	ACEA, 2002	
	SS 50km/h	0.3 mg/km	ACEA, 2002	
Volvo V40 GDI w/TWC/NO _x storage Cat	SS 120km/h	0.4 mg/km	ACEA, 2002	
	SS 100km/h	3.7 mg/km	ACEA, 2002	
	SS 50km/h	3.8 mg/km	ACEA, 2002	
VW Lupo FSI w/TWC/NO _x storage Cat	SS 120km/h	0.4 mg/km	ACEA, 2002	
	SS 100km/h	0.2 mg/km	ACEA, 2002	
	SS 50km/h	0.6 mg/km	ACEA, 2002	
Euro II with underfloor TWC	Cold start transient	0.4-0.5 mg/km	Andersson, 2001	
	SS 120km/h	0.7-2.2 mg/km	Andersson, 2001	
Euro III with 2 OC and underfloor lean-NO _x trap	Cold start transient	7.5-14.5 mg/km	Andersson, 2001	
	SS 120km/h	1.4-2.2 mg/km	Andersson, 2001	

FTP=Federal Test Procedure; HWFET=Highway Fuel Economy Test; IM240=IM240 driving cycle; SET=Sulfate Emissions Test; 72 Fed.=1972 Federal Mass Emission Cycle; 7-mode Fed. cycle=7-mode Federal Emissions Test Cycle; ADR 37=Australian Design Rules Procedure 37; SS=Steady State. Smoking vehicles have a very small percentage in the total fleet.

4.1.2 Light-Duty Diesel Dynamometer Testing

PM emissions testing for light-duty diesel vehicles has predominantly focused on chassis dynamometer measurements. The data are limited and confined to isolated tests of small numbers of vehicles. A summary of chassis dynamometer emissions test results for light-duty diesel vehicles is presented in Table 4-2. Some of this work was conducted during the late 1970s and early 1980s, when interest in diesel vehicles peaked as a result of escalating gasoline prices and fuel shortages. Emission rates ranged from about 200 to 1,000 mg/mi for the diesel vehicles tested in these earlier studies.

The effect of using different chassis dynamometer test cycles on particulate emissions was examined in some of these early studies. Braddock and Gabele (1977) found that particulate emissions were on average 42% greater for a Peugeot diesel vehicle when it was run over the Federal Test Procedure (FTP) cycle, as compared to either the highway fuel economy test (HWFET) or the sulfur emissions test (SET). They attributed this to the fact that the engine operates under greater load during the FTP as opposed to the quasi-steady state HWFET or SET that are characterized by partial load operation.

Gabele et al. (1981) conducted more extensive studies using six different cycles, including the FTP, HWFET, Congested Urban Expressway Cycle (CUE), New York City Cycle (NYCC), a specially designed cycle, and a 45 minute steady-state cycle. These researchers found that the particulate emission rates for all vehicles were highest for the NYCC. Given the low average speed of the NYCC and its stop and go nature, high emission rates can be expected when emissions are expressed in terms of grams per mile. Braddock and Perry (1986) also found that PM emission rates were higher for more rigorous test cycles, i.e., ones with more stop and go driving and lower average speeds. In contrast to these results, Lang et al. (1981), using gasoline vehicles, found that particulate emissions for the HWFET were higher than those from either the NYCC or the FTP. However, this trend was not well defined over the set of vehicles examined in this study.

Although interest in emissions testing of light-duty diesel vehicles subsided after the early 1980s, several recent programs have examined emissions from diesel vehicles. The CRC E-24 program was one of the largest programs for measurement of diesel PM emissions from light/medium-duty vehicles. The PM emission rates at the different sites were relatively high at 811 mg/mi for Denver in the summer, 460 mg/mi for Denver in the winter, 381 mg/mi at SwRI, and 561 mg/mi at CE-CERT. These emission rates were for older technology diesel vehicles, however, with the average model years for the Denver winter and CE-CERT studies being early 1980s and the average model years for the Denver summer and SwRI studies being in the mid-1980s. The particulate emissions of five diesel vehicles with model years ranging from 1979 to 1984 were measured as part of a program to characterize the emissions of smoking vehicles in the LA Air Basin

(Norbeck et al., 1996). For these five vehicles, FTP emission rates averaged 366.3 mg/mi and ranged from 190.6 mg/mi to 756.3 mg/mi. Norbeck et al. (1996) measured emission from two diesel vehicles, a 1982 Chevrolet C-10 and a 1994 Ford F250 and found emission rates of 150.6 and 287.7 mg/mi, respectively. PM emissions from 2 diesel vehicles are also being characterized as part of an on-going DOE gasoline/diesel PM split study (Fujita et al., 2004; Lawson et al., 2004).

Maricq et al. (2002) measured PM emissions from a 1997 light-duty diesel truck designed to meet Euro II standards at steady state speeds of 40 mph, 70 mph, and 70 mph with a 3% grade, with and without a catalyst, and with sulfur levels of 4 and 350 ppm. The results showed that emission rates varied from 51 to 190 mg/mi over the test conditions. With respect to PM mass, the most significant effect was observed for operating conditions, with the 70 mph 3% grade tests having the highest emissions and the 40 mph test having the lowest emissions for all fuel sulfur and catalyst conditions.

While these older studies of light/medium-duty diesel vehicles provide some information on older technologies, diesel technologies of the future are expected to have considerably lower PM emission rates due to the tightening of standards to the level where diesel particulate filters will be required. Several newer studies have investigated the emission rates from light/medium-duty vehicles with DPFs and found substantial reductions in emissions. The particulate emissions of four medium-duty diesel vehicles with model years ranging from 1998 to 1999 were measured with or without DPFs (Durbin et al., 2003). Tests on vehicles operating with DPFs showed reductions ranged from 89% to 98% for PM.

Other studies of advanced technology passenger cars have demonstrated that PM emissions <10 mg/mi can also be achieved for light-duty diesel vehicles. McDonald and Bunker (2002) found that PM emissions from a Toyota Advensis could be reduced to a level of 5.7 mg/mi for the FTP and 5 mg/mi for the US06 with Toyota's Diesel Particulate – NO_x Reduction (DPRN) system (Nakatani et al., 2002). Maricq (2003) found that a diesel vehicle with a DPF could achieve PM levels of ~1 mg/mi over the FTP. Similar results were also found by Sluder and West (2000) from Oak Ridge National Laboratory (ORNL). It should be noted that both Cummins (Stang et al., 2001) and Detroit Diesel Corporation (Hakim et al., 2000) have programs to develop light-duty diesel trucks with PM emissions <10 mg/mi.

While European studies focused more on PM size/number, several studies have also characterized PM emission rates from 1990s vintage diesel vehicles. Kerminen et al. (1997) of the Finnish Meteorological Institute examined the mass and particle number of a 1.9 l Volkswagen Passat diesel and found an emission rate of 0.07 g/km, comparable to the 1996 European standard limits. Several studies have also investigated catalyst technology together with factors that may influence catalyst performance for light-duty diesel vehicles to meet South American and European PM emission levels (Wilkins et al., 1998; Ntziachristos and Samaras, 2000).

Mohr et al. (2000) from Swiss Federal Laboratories for Materials Testing and Research conducted emission tests using a diesel vehicle and three gasoline vehicles with model year 1995 to 1997 and found all three gasoline vehicles produced significantly less particulates in mass and number than a common diesel vehicle. Increased PM emissions were observed for the direct injection vehicle during the driving cycles and for the premixed engines for rich air-fuel equivalence ratios.

Ahlvik (2002) from Sweden Ecotraffic compared results for a gasoline and an advanced diesel vehicle with a DPF at 22°C and -7°C for the Swedish National Road Administration. These results showed diesel PM emission levels were controlled to 0.3 mg/km while those for the gasoline vehicle varied from 0.7 to 1.3 mg/km at 22°C and 2.1 to 5.3 mg/mi at -7°C.

The Oil Companies' European Organization for Environmental and Health Protection (CONCAWE) investigated the mass and the number of light duty diesel and gasoline exhaust PM emissions (Hall et al., 1998). PM emissions measured from LDDVs were much higher than from LDGVs. The emission rate was 40-85 mg/km for LDDVs over steady-speed and MVEG driving cycle tests. The largest vehicle technology effect on PM emissions was the gasoline/diesel effect. However, technology effects were evident within the gasoline car set, the advanced TWC vehicle tending to give the lowest emissions. Vehicle differences within the diesel set were less pronounced. PM emissions were lower under fully warmed-up conditions than for cold engines because more large particles are produced during a cold test.

DETR, SMMT and CONCAWE conducted a PM research program to investigate the effects of vehicle/engine technology level, fuel specification and various operating conditions on emissions of particle mass, number and size for light-duty vehicles (Andersson et al., 2001b). The authors concluded that in general, when comparing conventional diesel, gasoline direct injection, multipoint injection gasoline and DPF equipped diesel vehicles together, vehicle technology effects were larger than fuel effects for PM mass emissions. Mass emissions from Euro III DPF equipped diesel passenger car were considerably lower than those from either the Euro III diesel passenger car or the Euro II light commercial diesel vehicle. The reduction in mass emissions between Euro III passenger car and Euro III passenger car equipped DPF was about 90%.

During European ACEA (2002) PM emissions study, exhaust emissions from three diesel passenger cars were measured. One of the cars was equipped with a DPF and other two cars with OCs. The DPF cars had significantly lower PM emissions than other two cars. The results are summarized in Table 4-2.

Table 4-2. Light-Duty Diesel Vehicle Particulate Emission Rates-Dynamometer Tests (mg/mi)

Make/Model	Test cycle	Emission Rate	Reference	Comments
Toyota Advensis w/ DPNR	FTP	5.7±0.8	McDonald/Bunker	2002
	US06	5±3		
	SC03	7±2		
	HWFET	2±1		
	NYCC	7±2		
2.5 L diesel car w/DPF	10-15 mode	9-13 mg/km	Saegusa/Senda, 2003	
2.0 L diesel car w/DPF+NSR	10-15 mode	1-3 mg/km		
DI diesel vehicle w/ DPF	FTP	~1	Maricq, 2003	
Peugot 307 diesel w/DPF	NEDC	0.3 mg/km	Ahlvik, 2002	22°C
	NEDC	0.3 mg/km		-7°C
VW Golf TDI wo/DPF	NEDC	22.1 mg/km		22°C
	NEDC	32.4 mg/km		-7°C
1999 Ford F250	FTP	302-339	Durbin, 2003	Without DPF
1999 Ford F250	FTP	7.0-26.4		With DPF
1998 Ford F450	FTP	180-218		Without DPF
1998 Ford F450	FTP	24.0		With DPF
1982 Chevy C-10	FTP	150.6	Norbeck, 1996	
1994 Ford F250	FTP	287.7		
Ten vehicles (Denver, summer)	FTP	811	Cadle, 1999	
Twelve vehicles (Denver, winter)	FTP	460		
Eight vehicles (San Antonio)	FTP	381		
Nineteen vehicles (CE-CERT)	FTP	561		
1978 production 5.7 L diesel	FTP	710		
1977 experimental 5.7 L diesel	FTP	595 and 960		
1979 production 4.3 L diesel	FTP	850		
5 diesel vehicles	FTP	avg.= 366.3	Durbin, 1999	
		190.6-756.3		
	IM240	avg.=334.6		
		129.2-597.1		
Eight light-duty diesel vehicles	FTP	~145~420	Stradling, 1993	
Six diesel vehicles: 48 to 125 hp	FTP	avg.=478 290-700	Bouffard, 1981	
Two vehicles (Rabbit/Oldsmobile)	FTP	430/540	Gabele, 1981	
	HWFET	540/580		
	CUE	610/530		
	NYCC	640/680		
	Special Cycle	480/530		

Table 4-2. Continued (mg/mi)

Make/Model	Test cycle	Emission Rate	Reference	Comments
	45 ss	350/390		
Six light-duty diesel vehicles	FTP	avg.= 607 307 -1070	Zweidinger,1981	
1975 diesel Peugeot 504D (Nat. Ave. D#2)	FTP	397	Braddock & Gabele, 1977	
	HWFET	264		
	SET	298		
average 5 fuels		avg. = 345		
19 diesel vehicles MY 1977-1980	FTP	avg.=607 320-1070	Gibbs, 1980	
Two Vehicles (Rabbit/Cutlass)	FTP	293/923	Springer, 1977	
	FTP (cold start)	325/1011		
	FTP (hot start)	266/842		
	SET	259/580		
	HWFET	253/480	Springer, 1977	
Foreign Tests				
Alfa Romeo 1.9JTD w/OC	SS 120km/h	39 mg/km	ACEA, 2002	
	SS 100km/h	30 mg/km	ACEA, 2002	
	SS 50km/h	12 mg/km	ACEA, 2002	
VW Bora TDI w/OC	SS 120km/h	32 mg/km	ACEA, 2002	
	SS 100km/h	26 mg/km	ACEA, 2002	
	SS 50km/h	11 mg/km	ACEA, 2002	
Peugeot 607 HDi	SS 120km/h	1 mg/km	ACEA, 2002	
	SS 100km/h	1 mg/km	ACEA, 2002	
	SS 50km/h	1 mg/km	ACEA, 2002	
Peugot 307 diesel w/DPF	NEDC	0.3 mg/km	Ahlvik, 2002	22°C
	NEDC	0.3 mg/km	Ahlvik, 2002	-7°C
VW Golf TDI wo/DPF	NEDC	22.1 mg/km	Ahlvik, 2002	22°C
	NEDC	32.4 mg/km	Ahlvik, 2002	-7°C
2.5 L diesel car w/DPF	10-15 mode	10.1-25.6 mg/km	Oyama/Kakagawa, 2003	
2.0 L diesel car w/DPF+NSR	10-15 mode	1.3-4.7 mg/km	Oyama/Kakagawa, 2003	
car w/ 2.1 L engine	ECE-15 + EUDC	~80~330	Betts, 1992	
18 commercial & passenger cars	ADR37 (FTP)	avg.=596 290-1401	Williams, 1989b	1975 FTP
Euro III, with underfloor OC and proportional EGR	Cold start transient	15-23 mg/km	Andersson, 2001	
	SS 120km/h	43-110 mg/km	Andersson, 2001	
Duro II, with NC and mechanical EGR	Cold start transient	50-70 mg/km	Andersson, 2001	
	SS 120km/h	40-50 mg/km	Andersson, 2001	
Euro III with OC, DPF and cerium additive	Cold start transient	1-3 mg/km	Andersson, 2001	
	SS 120km/h	10-41 mg/km	Andersson, 2001	

FTP=Federal Test Procedure
HWFET=Highway Fuel Economy Test

45 ss=45 mph steady state test
SET=Sulfate Emissions Test

IM240=IM240 driving cycle
NYCC=New York City Cycle

CUE=Congested Urban Expressway Cycle
SS=Steady State

The Australia National Environment Protection Council conducted a comprehensive diesel emissions research and testing program (Anyon et al., 2000). A clear downward trend of PM emissions rates for newer diesel passenger vehicles was found. PM emission rates decreased from 0.7g/km for 1980 to 1989 model year vehicles to less than 0.3 g/km for 1996 to 1999 model year vehicles.

Oyama and Kakegawa (2003) of Japan Nippon Oil Corporation and Hino Motors, respectively, found that PM emissions were reduced to 10-20 mg/km for a vehicle with a DPF and to <5 mg/km for a diesel vehicle with a DPF + a NO_x storage reduction catalyst over a 10-15 mode cycle. Similar results were also found by Saegusa and Senda (2003) of Nissan and the Nippon Oil Corporation, respectively.

4.1.3 Light-Duty Alternative Fuel Dynamometer Testing

The National Renewable Energy Laboratory (NREL) conducted tests of PM emissions from alternative fueled vehicles at CE-CERT and the SwRI. Durbin et al. (1998) measured PM from 5 1994 CNG vans, and 5 1994 flexible fuel M85 Ford Taurus and 5 gasoline control vehicles for both of these technologies. The FTP emissions rates for the CNG vans and M85 vehicles were 1.4 and 0.7 mg/mi, respectively. PM emissions increased over the US06 to 7.8 mg/mi and 3.6 mg/mi, respectively, for the CNG vans and M85 vehicles. PM emissions for the gasoline control vehicles for both the FTP and US06 were essentially the same as those found for the alternative fuel vehicles of the same technology. Whitney (1997) tested a 1994 Ford Taurus configured to operate on Federal RFG, LPG, CNG, E85, and M85. This vehicle was tested over the FTP at room temperature and 20°F. For all fuels but M85, the room temperature PM emission rates were 2-3 mg/mi. For the RFG vehicle, PM emissions at 20°F were 6 times higher than those at room temperature, while PM emissions for the alcohol fueled vehicles were 2-3 times higher than at room temperature. The CNG and LPG fuels had the same PM emission rates at room temperature and 20°F. Overall, these results suggest that the PM emission rates for light-duty alternative fuel vehicles are very similar to those from more traditional gasoline technologies, with the possibility of some differences observed at low temperatures.

Ahlvik and Brandberg (2003) from Sweden Ecotraffic conducted light-duty vehicle tests over the new European driving cycle (NEDC). The fuels investigated in this study were ethanol (E85), methanol (M85), CNG, biogas and diesel oil. The researchers found that PM emissions for all alternative fuels are considerably lower than for diesel fuel. Alcohols generated little or no soot under rich operating conditions at cold start at low temperature and CNG did not need much enrichment at cold start. This was a considerable advantage for alternative fuels for emissions.

Nylund and Lawson (2000) from Finland VTT Technical Research Centre and GFC Control Systems, Inc., Canada conducted a study of exhaust emissions from natural gas vehicles. This study covered emission testing of natural gas vehicles as well as fuel

properties, engine technology effects. PM emission rates for Europe Stage 1 and 2 vehicles (model year 1993 to 1996) were 11 mg/km for CNG, 6 mg/km for LPG, 9 mg/mi for gasoline, and 84 mg/mi for diesel.

Aakko and Nylund (2003) from Finland VTT studied the effects of temperature on PM emissions for light-duty vehicles using different fuels (gasoline, diesel, E85, CNG, and LPG). Authors also found that PM emissions from CNG vehicles were near detection limits. PM mass and number emissions increased in the order of CNG vehicles, E85 vehicles, gasoline vehicles, and diesel vehicles. The effects of temperature were dependent on the engine technology. Significant increases in PM mass and number emissions were seen with some technologies when -7°C temperature was compared to the room temperature test. The CNG car did not show any significant PM emissions at normal or low temperatures. The PM mass emissions were highest with diesel cars and increased as test temperature decreased.

4.1.4 PM Chemical Composition and PAHs from Light Duty-Vehicles

The composition of the PM is important in understand its health impacts and toxicity. A number of studies mid- to late 1990s extensively characterized the PM emissions from a range of vehicle technologies. Numerous studies have shown that the composition of gasoline and diesel PM is predominantly carbonaceous in nature, with the ratios of elemental and organic carbon varying significantly from vehicle-to-vehicle (Owring, 2004; Westerholm, et al., 1999; Watson et al. 1994, Gillies and Gertler 2000, Hildemann et al. 1991). From a toxicity perspective, PAHs are the most significant concern of the PM constituents. Sagebiel et al. (1997) measured PAHs from 23 vehicles over the IM240 in Nevada, including 6 vehicles that were visible smokers. PAH emission rates were in the range of 10-200 mg/mi with naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene being the most prominent semi-volatile PAHs. For most PAH compounds, the smoker emission rates were on the order of 2-10 times higher than the non-smokers.

A larger sample of PM emission rates were collected as part of the E-24 program at Colorado, CE-CERT and SwRI. Results from this study are presented in Tables 4-3 and 4-4 for gasoline and diesel vehicles. It should be noted that the samples are not necessarily designed to represent the latest technology for gasoline and diesel vehicles. Again, the profiles show that semi-volatile PAHs are the most prominent, with the lower volatility particle bound PAHs representing only a small fraction of the total PAHs. The PAH emission rates are relatively similar between the different locations, noting the most prominent PAH (naphthalene) was not included for the Colorado samples. Very large differences were found for some of the compounds from the low gasoline emitters. For example, the 2-methylnaphthalene and anthracene emission rates for Denver were 0.734 and 0.022 mg/mi, while they were 0.067 and 0.00006 mg/mi for San Antonio. It is not known if these differences represent analytical errors at the low concentrations present in these samples or real differences. An additional diesel PM split is also in progress and scheduled for completion in Summer of 2004.

Table 4-3. PAH Gasoline Vehicle Emission Rates

Compound	Denver	San An.	SCAQMD	Denver	San An.	SCAQMD
	Low	1994-97	Low	High	Pre-81	High
	mg/mi			mg/mi		
Naphthalene	*	0.063	5.41	*	1.39	6.63
2-Methylnaphthalene	0.734	0.067	2.78	2.76	1.49	3.14
Acenaphthylene	0.027	0.031	0.184	0.424	1.09	0.291
Acenaphthene	0.015	trace	0.0399	0.047	0.109	0.0670
Fluorene	0.025	0.020	0.0881	0.147	0.290	0.106
Phenanthrene	0.010	0.032	0.120	0.086	0.389	0.181
Anthracene	0.0220	0.00006	0.0384	0.0572	0.126	0.0552
Fluoranthene	0.0483	0.00039	0.0299	0.0701	0.118	0.0660
Pyrene	0.0556	0.00078	0.0421	0.0840	0.172	0.0917
Benzo(a)anthracene	0.0016	0.0016	0.0032	0.0082	0.0250	0.0065
Chrysene	0.0013	0.0012	0.0028	0.0085	0.0072	0.0060
Benzo(b,j,k)fluoranthene	0.00007	0.0035	0.0054	0.0125	0.022	0.0154
Benzo(e)pyrene	0.00035	0.0010	0.0029	0.0098	0.0080	0.0062
Benzo(a)pyrene	0.00052	0.0024	0.0023	0.0107	0.014	0.0052
Indeno(1,2,3-cd)pyrene	0.00033	0.00064	0.0012	0.0079	0.0061	0.0033
Dibenz(a,h)anthracene	0.00007b	0.00003	0.0001b	0.00087b	0.00008	0.0002b
Benzo(g,h,i)perylene	0.00089	0.0013	0.0053	0.0183	0.0303	0.0148
Sum	0.942	0.227	8.76	3.75	5.286	10.7
Sum Chrysene: Benzo(ghi)perylene	0.0035	0.010	0.020	0.069	0.088	0.051
PM	6.1	6.1	17.1	70.8	148.5	49.7

a) Benzo(bj,k)fluoranthene

b) Dibenz(ah+ac)anthracene

Table 4-4. PAH Diesel Vehicle Emission Rates

Compound	Denver	San Antonio	SCAQMD
	mg/mi		
Naphthalene	*	2.56	2.06
2-Methylnaphthalene	6.05	2.81	0.431
Acenaphthylene	0.773	2.43	0.545
Acenaphthene	0.180	0.243	0.048
Fluorene	0.758	0.844	0.214
Phenanthrene	1.412	1.103	0.594
Anthracene	0.562	0.338	0.102
Fluoranthene	0.896	0.369	0.301
Pyrene	1.050	0.694	0.387
Benzo(a)anthracene	0.0768	0.0450	0.027
Chrysene	0.153	0.033	0.032
Benzo(b,j,k)fluoranthene	0.115	0.038	0.088
Benzo(e)pyrene	0.059	0.019	0.030
Benzo(a)pyrene	0.039	0.024	0.025
Indeno(1,2,3-cd)pyrene	0.048	0.015	0.012
Dibenz(a,h)anthracene	0.0038 ^b	0.00004	0.001 ^b
Benzo(g,h,i)perylene	0.083	0.054	0.030
Sum	12.26	11.62	4.93
Sum Chrysene: benzo(ghi)perylene	0.50	0.181	0.22
PM	1447	381	561

a) Benzo(b,k)fluoranthene

b) Dibenz(ah+ac)anthracene

In Europe, a comprehensive literature review of PAH in automotive exhaust emissions and fuels was conducted by CONCAWE (Hall et al., 1998). The authors found that all aftertreatment devices reduce PAH emissions; however, the effectiveness of the aftertreatment systems varied depending on the technology. For gasoline, the presence of a 3-way catalyst effectively reduces PAH emissions to an immeasurably low level. For diesel, the presence of an oxidation catalyst shows a more variable efficiency for PAH reduction. Some alternative fuels provided some reductions in PAH exhaust emissions.

4.2 Heavy-Duty Vehicles

4.2.1. Dynamometer Studies

Heavy-duty vehicles make a disproportionately large contribution to the PM emissions inventories in the State and elsewhere. Based on on-road emissions from EMFAC2002, 2000 estimates for mobile sources in California (www.arb.ca.gov) indicate the on-road medium and heavy heavy-duty diesel vehicles contribute 18.4 tons per day to the inventory. For comparison, light-duty gasoline and diesel vehicles, which have a considerably larger population, contribute approximately 11.0 tons per day of exhaust PM.

To date, the largest body of emissions testing for heavy-duty vehicles is available for engine testing, as opposed to chassis dynamometer testing, as many class 8 trucks incorporate engines from a third party manufacturer. Much of these data are from certification testing of new engines. A summary of the progressively more stringent emission standards for diesel engine certification is provided in Table 4-5.

Table 4-5 California and EPA on-road heavy-duty diesel standards (gm/bhp-hr)

Model Year	Federal Standards			California Standards		
	NO _x	PM	HC +NO _x	NO _x	PM	HC +NO _x
1973	---	---	---	---	---	16
1974	---	---	16	---	---	16
1975-76	---	---	16	---	---	10
1977-80	---	---	10 ^a	7.5	---	---
1981-83	---	---	10	6.0	---	---
1984-87	10.7 ^b	---	---	5.1	---	---
1988-90	10.7	0.60	---	6.0	0.60	---
1991-93	5.0	0.25	---	5.0	0.25	---
1994-97	5.0	0.10	---	5.0	0.10	---
1998-02	4.0	0.10	---	4.0	0.10	---
2003+	2.0	0.10	---	2.0	0.10	---
2007	0.20	0.01	---	0.20	0.01	---

^aAs of 1979; ^bAs of 1985

While engine dynamometer test data is more widely available for different engine types, it has limitations for the development of emissions factors for modeling. The load put on an engine, for example, will depend on the application in which the engine is used. A comprehensive review of PM emissions data from engine heavy-duty engine dynamometer data will not be addressed here. A partial summary of engine test data compiled by EPA (2002) is provided in Table 4-6. Overall, these data show a trend of declining PM emissions with newer engine model years and technology.

Table 4-6. Diesel Engine PM Emissions Data from Engine Dynamometer Tests
(g/bhp-hr)

Make/Model	Year	Test cycle	Emission Rate	Reference	Comments
Cat 3208 (NA)	1976	SS	0.87	Hare, 1977	
DDC 6V71 (blower)	1976	SS	1.92		
Mack ETAY(B)673A (DI, TC, AC)	1977	SS	0.61	Springer, 1979	
Cat 3208 (EGR, NA)	1977	SS	2.21		
Cat 3406 (DI, TC, AC)	1977	SS	0.35		
Cat 3406 (DI, TC, AC, EGR)	1977	SS	0.93		
Cat 3406 (IDI, TC, AC)	1977	SS	0.28		
DB OM-352A (DI, TC, AC)	1977	SS	0.56		
DB OM-352A (DI, NA)	1977	SS	0.99		
Cat (DI, NA)	1978	SS	0.77	Perez, 1980	
Cat (DI, EGR)	1978	SS	1.21		
Cat (DI, TC, AC)	1978	SS	0.33		
Cat 3208	1978	T	1.06	Martin, 1981a	
Cummins NTC350	1976	T	0.81		
DDC 6V92T (2S)	1978	T	0.72		
Cummins NTCC350	1979	T	0.52		
DDC 8V71N (2S)	1978	T	0.92		
DDC 6V92TA (2S)	1979	T	0.65		
IH DTI466B	1979	T	0.48		
Mack ETAY(B)673A	1979	T	0.77		
Mack ETSX676-01	1980	T	0.85		
Cummins VTB-903	1979	T	0.53		
Cat 3406	1979	T	0.69		
Cat 3406PCTA	1979	T	0.49		
Cummins BigCam NTC350	1979	T	0.54		
IH DT466	1979	T	0.71		
DDC 6V92TA (2S)	1979	T	0.73		
DDC 8V71TA (2S)	1979	T	0.51		
Cummins NTC290	1979	T	0.78		
Cummins NH-250	1979	T	0.97		
Cummins VTB-903	1980	T	0.67	Martin, 1981b	
DDC 8V71TA (2S)	1980	T	0.44		
IH DTI466B	1980	T	0.62		
DDAD 6V-71 (2S)	1980	T	0.56	Ullman et al., 1984	
Cat 3406B	1985	T	0.48	Barry et al., 1985	
DDC 8V-92 TA (2S)	1980	T	0.45		
		SS	0.36		
DDC 8V-71 TAC (2S)	1984	T	1.26	Enga et al., 1985	
Iveco 8460	1991	T	0.22	Wachter, 1990	
Average of 16 engines	1988	T	0.37	Needham et al., 1989	
Average of 3 engines	1991	T	0.24		
Navistar DTA466 ES210	1993	T	0.082	McCarthy et al., 1992	

Table 4-6. Continued (g/bhp-hr)

Make/Model	Year	Test cycle	Emission Rate	Reference	Comments
Engine 1	1982	T	0.93	Perez and Williams, 1989	
Engine 2	1982	T	0.86		
Engine 3	1982	T	0.59		
Engine 4	1982	T	0.96		
Engine 5	1982	T	1.06		
Engine 6	1982	T	0.88		
Cummins L10-300	1988	SS	0.10	Kreso et al., 1998	
Cummins L10-310	1991	SS	0.035		
Cummins M11-330E	1995	SS	0.037		
Cat 3304 (IDI, NA) non-road	1983	SS	0.56	Bagley et al., 1998	
DDC 6V-71N-77 (MUI, 2S)	1977	T	0.83	Graboski, 1998b	
DDC 6V-92TA-91 (DDECII)	1991	T	0.197		
DDC-6V-92TA-87 (2S)	1987	T	0.59		
DDC-6V92TA-83 (MUI, 2S)	1983	T	0.265		
DDC 6V-92TA -88 (DDECII, 2S)	1988	T	0.2		
DDC 6V-92TA-91 (DDECII, 2S)	1991	T	0.276		
DDC 6V-71N-77 (MUI, 2S)	1977	T	0.282		
DDC 6V-92TA-81/89 (MUI, 2S)	1981	T	0.268		
DDC 6V-92TA-91 (DDECII, 2S)	1991	T	0.227		
DDC 6V-92TA-89 (DDECII, 2S)	1989	T	0.338		
DDC Series 60-91 DDECII	1991	T	0.300		
Cummins L-10-87 (MUI)	1987	T	0.309		
DDC Series 60-91 (DDECII)	1991	T	0.220		
Cummins N-14-87 (MUI)	1987	T	0.369		
DDC Series 60-89 (DDECII)	1989	T	0.252		
DDC Series 60-91 (DDECII)	1991	T	0.182		
Cummins B5.9	1995	T	0.106		
Navistar DTA466	1994	T	0.090	Spren et al., 1995	
Cummins L10	1991	T	0.224	Norbeck et al., 1998d	
DDC Series 60	1994	T	0.112		
Navistar DTA466	1991	T	0.220	Sienicki et al., 1990	
DDC Series 60	1991	T	0.188	Ullman et al., 1990	
DDC Series 60	1994	T	0.111	Mitchell et al., 1994	
Navistar DTA466	1994	T	0.099		
Unknown	1994	SS	0.143	Tanaka et al., 1998	
Scania	1990	SS	0.157	Rantanen et al., 1993	
Valmet	1990	SS	0.157		
Volvo	1990	SS	0.262		
Volvo	1995	SS	0.135		

Data Summary from EPA (2002)

NA=naturally aspirated. TC=turbocharged (engines not designated as NA or TC are turbocharged). AC=aftercooled. DI=direct injection. IDI=indirect injection. EGR=exhaust gas recirculation. 2S=two-stroke (engines not designated as 2S are four-stroke). MUI=mechanical unit injector (not electronically controlled). DDEC=Detroit Diesel Corporation's engine control module (electronic control).

SS=various single or multimode steady-state tests. T=heavy-duty FTP (transient test).

To better understand diesel PM emissions under on-road conditions, there has been increased interest in heavy-duty chassis dynamometer testing in an effort to obtain an assessment of emissions from actual vehicles under typical driving conditions. Several facilities around the nation are presently equipped with heavy-duty chassis dynamometer facilities, including CARB HDDV laboratory located in Los Angeles, CA, the Colorado Institute for Fuels and Engine Research, which is now under the direction of NREL, the Southwest Research Institute in Texas, and the New York City Department of Environmental Protection in New York City, NY. West Virginia University has also been actively conducting research in this area and has developed and constructed two transportable laboratories capable of measuring emissions from heavy-duty vehicles (Clark et al., 1994a; Lyons et al., 1992; Gautam et al., 1991). The transportable emissions testing laboratory consists of two trailers, one of which houses a dynamometer while the other houses the data acquisition and emission analysis systems. CE-CERT (Cocker et al., 2004) and the US EPA (Brown, 2001) also have diesel trailers that are equipped for making on road measurements from class 8 diesel trucks. A more detailed description of these test facilities is provided in the companion document to this report (Durbin et al., 2004).

The database of chassis dynamometer PM emissions for heavy-duty trucks and buses is extensive, and has been the subject of several reviews (Yanowitz et al., 2000; Prucz et al., 2001). Yanowitz et al. (2000) examined over 250 chassis dynamometer test records for 1976 to 1998 model years from over 20 references. They examined the trends in PM emissions with model year and found steadily declining emissions for later model years/new technologies, consistent with the changes in emissions standards. The variability in emission rate observed in most categories is significant, however. It should be noted, however, that some earlier versions of electronic controls were also designed to use special injection timing and other parameters to pass the certification tests, while reverting to more polluting operation during actual use, especially for NO_x. The model year trends from this work are provided in Table 4-2 for PM as well as the other emissions components. A partial, but not comprehensive, summary of chassis dynamometer testing results for heavy-duty vehicles is presented in Table 4-7, including some data from Yanowitz and other identified sources. This table presents results from heavy-duty diesel trucks and buses and heavy-duty gasoline vehicles. Vehicles are separated into groups based on vehicle type (truck, bus, and gasoline) and model year. The model year periods are based on the introduction of stricter emissions standards in 1988, 1991, and 1994 (the emission standards for these and other years are shown in Table 4-4). Diesel buses with particulate traps have also been separated out.

Figure 4-1 shows chassis dynamometer data for more than 200 different vehicles (approximately one-half of which are transit buses), as summarized by Yanowitz et al. (2000). These data were obtained from 20 different published studies, as well as a large amount of additional data collected by West Virginia University (Yanowitz et al., 1999; Warner-Selph and Dietzmann, 1984; Dietzmann et al., 1980; Graboski et al., 1998a,b; McCormick et al., 1999; Clark et al., 1995, 1997; Bata et al., 1992; Brown and Rideout,

1996, Brown et al., 1997; Dunlap et al., 1993; Ferguson et al., 1992; Gautam et al., 1992; Katragadda et al., 1993; Rideout et al., 1994; Wang et al., 1993, 1994; Williams et al., 1989; Whitfield and Harris, 1998; West Virginia University data available on the World Wide Web at www.afdc.nrel.gov). The results from vehicles tested more than once using the same test cycle, and without any additional mileage accumulated between tests, are averaged and reported as one data point. Buses were tested using the Central Business District (CBD) cycle, while most trucks were tested using the Urban Dynamometer Driving Schedule (UDDS). Some of the trucks were tested using the West Virginia 5-peak cycle, which generates considerably lower g/mi emissions than the CBD or UDDS (Yanowitz et al., 1999). Emissions results from vehicles tested under different test cycles or at different points in the engine's life cycle were reported as separate data points. Consistent with the engine data, a declining trend in PM emissions for newer model years is found.

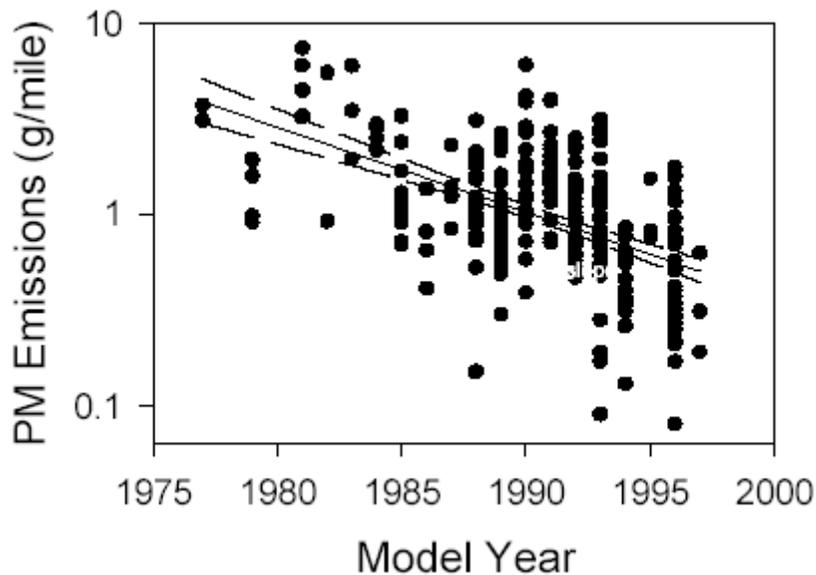


Figure 4-1. Model Year Trends in PM Emissions from HD Diesel Vehicles (g/mile) (Source Yanowitz et al., 2000)

Some of the more extensive chassis dynamometer studies of heavy-duty diesel emissions have been conducted by researchers at West Virginia University. Test data from a range of West Virginia University programs are available at http://www.ctts.nrel.gov/heavy_vehicle/emissions.html#truckemissions. This website includes over 300 test records for the heavy-duty trucks and over 300 test records for heavy-duty buses. These records are incorporated, in part, in the work conducted by Yanowitz and were not examined separately for this study. From their test data, Prucz et al. (2001) examined the trends in emissions from Detroit Diesel Corporation Transit Buses. This comparison showed that the most dramatic emission reductions were for PM, which had declined 70% over the years as there was a transition between the 6V-92TA to

the Series 60 models. Gajendran and Clark (2003) also examined the effects of truck operating weight on heavy-duty diesel emissions and found that PM emissions were a strong function of weight during transient operation, but were relatively insensitive during steady-state operation. Clark et al. (2003) have also developed emissions model based on vehicle specific power, using time resolved CO emissions to develop the distribution of PM emissions throughout the cycle. Other studies incorporating West Virginia University chassis dynamometer testing are discussed further below.

McCormick et al.(1998) compared chassis dynamometer emissions and engine dynamometer FTP emissions for three heavy-duty diesel vehicles. Chassis testing was performed using the Central Business District (CBD) cycle and the EPA Urban Dynamometer Driving Schedule for heavy-duty vehicles (heavy-duty transient or HDT cycle). Researchers found that both driving cycle and inertial load had a significant effect on g/mi PM emissions. However, the influence of these factors on PM is reduced if emissions are viewed on a g/gal fuel basis. The results of this study are summarized in Table 4-7.

Other recent studies showed driving cycle has a significant impact on emissions on a g/mi basis (Yanowitz et al.,1999; Zhu et al., 2003). Yanowitz et al. (1999) measured PM emissions from 21 in-use heavy-duty diesel vehicles on chassis dynamometer via three driving cycles including CBD, the EPA Urban Dynamometer Driving Schedule for heavy-duty vehicles (heavy-duty transient or HDT cycle), and West Virginia University cycle (WVT). The authors found that the average emissions followed the sequence CBD>HDT>WVT. On a g/mi basis, it was clear that vehicles that produced high emissions on the CBD also produced high emissions on the HDT and WVT cycles. For emissions of PM, driving cycle still has an effect on a g/gal basis but much less than for g/mi. Starting temperature also has some impact on emission from heavy-duty vehicles. Yanowitz et al. (1999) found PM emissions increase from an average of 1.96 g/mi for hot starts to 2.18 g/mi for cold starts, an 11% increase.

Zhu et al. (2003) measured 11 in-use heavy-duty diesel vehicles over the CARB combined HHDDV driving cycle which include four modes: cold start idle, creep, transient, and cruise. The average PM emissions followed the sequence: creep > transient > cruise. The per mile PM emissions on the creep mode corresponded 1.5 miles driving in the transient mode or 5 miles of driving in the cruise mode. Vora et al (2004) from WVU also reviewed emissions data from the 5-mode CARB HHDDV schedule, UDDS Schedule, and a steady-state cycle. PM emissions were highest for the Transient Mode because of energy requirements and the production of a PM “puff”. The PM “puff” occurred when the turbocharger does not reach full boost pressure at the onset of increasing engine load.

The Department of Energy sponsored study discussed above to investigate the source apportionment of gasoline/diesel PM (Fujita et al., 2004; Lawson et al., 2004), also includes PM measurements from heavy-duty diesel vehicles. A total of 32 heavy-duty diesel vehicles and two transit buses were measured in the study on the West Virginia Heavy-Duty Diesel Dynamometer. The test cycles used included the

city/suburban, highway, idle, and Manhattan. The results of this study are expected to be available in the Summer 2004 timeframe.

PM emissions control from diesel engines are one of the major concerns in the urban areas in California. A working group comprised of representative from government, industry and academia was assembled to evaluate the low-sulfur emissions control diesel (ECD) in vehicle fleets operating in southern California. This program demonstrated a retrofit solution using ECD fuel in combination with passive particulate filter systems (Chatterjee et al., 2001; Vertin et al., 2000; LeTavec et al., 2000; Clark et al., 2000). A select number of vehicles were retrofitted with either the Engelhard catalytic soot filter (DPXTM) or the Johnson-Matthey continuously regenerating technology (CRTTM). All the studies in this program found that trucks retrofitted with DPFs and fueled with ECD emitted 91 to 99% less PM compared to CARB-fueled trucks having no exhaust filter equipment. HC and CO emissions were also significantly reduced (90 to 99%). This validation program was completed in 2001. Then in 2003, additional round of emission testing was performed by NREL on a small subset of vehicles in the Ralphs Grocery Truck fleet that demonstrated continued robust emissions performance to evaluate long-term durability of passive DPFs on heavy-duty vehicles. The results showed that with a NO_x/PM ratio better than 20:1 and exhaust gas temperatures above 250°C, the DPFs provided robust long-term performance with emission reductions of 99% PM, 85% HC, and 65% CO in a heavy-duty application (Kimura et al., 2004). The results of these studies are summarized in Table 4-7.

In Europe, there are a number of studies about DPFs for HDDV (Biancotto et al., 2004; Mayer, et al., 2002; Salvat, 2000; SAEFL, 2000). Reduction of Emissions of Diesel Engines (Verminderung der Emissionen von Realmaschinen im Tunnelbau) (VERT) is a joint project of several European environmental and occupational health agencies. The project established a trap-verification protocol that adapts industrial filtration standards to include catalytic effects and trap regeneration phenomena. DPF system continue to improve in order to be implemented on more recent urban buses, such as EURO 3, and extend the DPF system technology to the whole EURO 1 and EURO 2 urban bus fleet. The results showed the DPF efficiency was above 95% for PM emissions.

TNO Automotive conducted tests on several different heavy-duty diesel engines over a steady-state 13 mode test (Ling and Helden, 2003). The engine types ranged in power output from 160 to 240 KW and included an LPG engine with a TWC, a natural gas engine with an OC, a natural gas engine with a TWC, a diesel engine with a platinum-based DPF, and a diesel engine with no exhaust aftertreatment. The PM mass emissions for all of the gaseous-fueled engines and the diesel engine with the DPF were several orders of magnitude lower than those found for the diesel engine without a DPF. The diesel engine with the DPF did show relatively high numbers of nanoparticles, however, even with a fuel with an ultralow sulfur content. The ratio of NO₂ to NO_x was also found to increase from 10% to 50% when a DPF was used.

Table 4-7. Heavy-Duty Particulate Emission Rates-Dynamometer Tests (g/mi)

Vehicle description	Test Cycle	Emission Rate	Reference	Comments
Equipped with Particulate Trap				
1 HD Diesel Bus MY 1987	CBD	0.3	Dunlap, 1993	Before/after trap regen.
	CBD	0.4	Dunlap, 1993	During trap regen.
3 HD Buses MY 1990-1992 (Jet A) (DDC-6V-92TA)	CBD	~0.3	Ferguson, 1992	
2 HD buses, Jet A w additive	CBD	0.103	Lowenthal, 1994	PM-2.5
bus, Jet A and diesel No. 2	CBD	0.373	Lowenthal, 1994	
1988 TMC bus	CBD	~0.3--~0.4	Gautam, 1992	
Trucks 1997+				
Eleven trucks 1997-2001	Idle	0.30 (g/cycle)	Zhu, 2004	On road tests
	Creep	0.98		
	Transient	0.68		
	Cruise	0.21		
Five Arco fuel delivery trucks 1995-96				
				Before/after DPF
CARB fuel	CSHVR	0.75	Chatterjee, 2001	
ECD fuel	CSHVR	0.70	Chatterjee, 2001	
ECD & CRDPF	CSHVR	0.026	Chatterjee, 2001	
Five LA city refuse/sanitation trucks 1999				
CARB fuel	CBD	0.50	Chatterjee, 2001	
ECD fuel	CBD	0.45	Chatterjee, 2001	
ECD & CRDPF	CBD	0.011	Chatterjee, 2001	
ECD1 & CRDPF	CBD	0.007	Chatterjee, 2001	
CARB fuel	Orange city	0.40	Chatterjee, 2001	
ECD fuel	Orange city	0.50	Chatterjee, 2001	
ECD & CRDPF	Orange city	0.022	Chatterjee, 2001	
ECD1 & CRDPF	Orange city	0.028	Chatterjee, 2001	
Five Ralphs grocery trucks 1998				
CARB fuel	CSHVR	0.20	Chatterjee, 2001	
ECD fuel	CSHVR	0.21	Chatterjee, 2001	
ECD & DPX	CSHVR	0.003	LeTavec, 2000	
ECD & CRDPF	CSHVR	0.003	Chatterjee, 2001	
Two San Diego School District school bus				
				Before/after DPF
CARB fuel	CSHVR	0.22	LeTavec, 2000	
ECD fuel	CSHVR	0.19	LeTavec, 2000	
ECD & DPX	CSHVR	0.00	LeTavec, 2000	
ARCO tanker truckers				
CARB fuel	CSHVR	0.58	LeTavec, 2000	
ECD fuel	CSHVR	0.56	LeTavec, 2000	

Table 4-7. Continued (g/mi)

Vehicle description	Test Cycle	Emission Rate	Reference	Comments
ECD & CRDPF	CSHVR	0.026	LeTavec, 2000	
Three Ralphs grocery trucks 1998				
CARB fuel	5 Mile Route	0.089	LeTavec, 2000	
ECD fuel	5 Mile Route	0.11	LeTavec, 2000	
ECD & DPX	5 Mile Route	0.003	LeTavec, 2000	
ECD & CRDPF	5 Mile Route	0.008	LeTavec, 2000	
Three Ralphs grocery trucks 1998				
Johnson Matthey CRT, 2000	CSHVR	0.005	Kimura, 2004	DPF with accumulated mileage over 220,000mi at 2002 and 340,000 mi at 2003
2001	CSHVR	0.000	Kimura, 2004	
2002	CSHVR	0.003	Kimura, 2004	
2003	CSHVR	0.002	Kimura, 2004	
Johnson Matthey CRT, 2000	CSHVR	0.000	Kimura, 2004	
2001	CSHVR	0.008	Kimura, 2004	
2002	CSHVR	0.020	Kimura, 2004	
2003	CSHVR	0.002	Kimura, 2004	
Engelhard DPX, 2000	CSHVR	0.000	Kimura, 2004	
2001	CSHVR	0.008	Kimura, 2004	
2002	CSHVR	0.006	Kimura, 2004	
2003	CSHVR	0.001	Kimura, 2004	
Smoking Trucks				
Seventeen 1986-1990, pre repaired	UDDS	5.57	Kado, 2001	
Seventeen 1986-1990, post repaired	UDDS	3.27		
Nine 1991-1999, pre repaired	UDDS	2.20		
Nine 1991-1999, post repaired	UDDS	1.26		
Trucks 1994+				
Ten Trucks 1994-1995 (Diesel #1)	CBD	0.275 0.2-0.35	Gautam, 1996	
Two 1994 KW Trucks (DDC 60)	WVU truck	0.31 and 0.34	Gertler, 1995b	
Buses 1994+				
Six Buses MY 1994	CBD	1.1 0.1-3.31	Gautam, 1996	
Buses 1993				
RTD Bus 5079/DDC S-50/1993	HDTC	0.73	McCormick, 1998	
	CBD	0.82		
RTD Bus 5079/DDC S-50/1993	HDTC	0.73		
	CBD	0.61		
Truck 1993				
CDOT Plow Truck/Navistar DTA-466/1993	HDT	0.72		

Table 4-7. Continued (g/mi)

Vehicle description	Test Cycle	Emission Rate	Reference	Comments
Trucks 1991-1993				
4 1992 MY Trucks	CBD	0.89 0.5-1.73	Gautam, 1996	
1993 NVSTR Truck (DDC-6V-92)		0.77	Gertler, 1995b	
1993 INTL Truck (DDC-60)		0.28	Gertler, 1995b	
1992 GMC Truck (DDC 6V-92)		0.71	Gertler, 1995b	
1992 FI Truck (Cummins)		0.67	Gertler, 1995b	
Buses 1991-1993				
Twelve Buses MY 1992-1993 (DDC 6V-92)	CBD	1.0 0.64-1.35	Gautam, 1996	
Two 1992 Flexible Buses (Cum. LTA-10)	CBD	1.77 and 1.93	Wang, 1993	
1992 Transpt. (DDC 6V-92)		0.386	Wang, 1993	
1991 Orion Bus (DDC 6V-92)		1.5	Wang, 1993	
1991 NPLN Bus (DDC 6V92/Jet A)		1.19	Wang, 1993	
1992 Ikarus Bus (Cat. 3176)	CBD	Diesel #2=0.84 Clean Diesel=0.59	Bata, 1992	
Two 1991 Buses (DDC 6V-92)	CBD	~1.3--~1.8	Ferguson, 1992	
Trucks 1988-1990				
Two 1989 Mack Truck (Mack E-6)	WVU truck	1.48 and 1.61	Gertler, 1995b	
Two 1989 FL Truck (Cummins)		0.49 and 0.8	Gertler, 1995b	
		g/mi		
Buses 1988-1990				
14 Buses MY 1988-1990 (DDC-6V92) (Diesel #1, Bio Diesel, Diesel #2)	CBD	1.6 0.69-3.67	Gautam, 1996	
12 Buses MY 1988-90	NYBC	0.95	CARB, 1995	
1989 Bus (DDC 6V-92)	CBD	1.0 and 1.4	Dunlap, 1993	
Two 1988 Buses (DDC 6V-92)		1.1 and 1.9	Dunlap, 1993	
1988 Bus (Cummins L10)		1.3	Dunlap, 1993	
6 Buses MY 1989-1990 (Jet A, D#1, D#2) (DDC-6V92 & Cum. LTA-10)	CBD	avg.=1.08 0.28-1.71	Wang, 1993	
1989 TMC bus (DDC 6V-92)	CBD	1.24 (WVU)	Katragadda, 1993	
Two 1988 Buses (DDC 6V-92) (Jet A)	CBD	~1.2 and ~2.3	Ferguson, 1992	
1990 Bus (Diesel and Jet A fuel)	CBD	~2.3--~6	Gautam, 1992	
Trucks Pre-1988				
Four Trucks MY1982 and 1985 (Diesel #2)	WVU truck & CBD	1.12 0.92-1.69	Gautam, 1996	
1985 FL Truck (Cat. 3306B)	WVU truck	1.15	Gertler, 1995b	
Refuse Truck (Diesel & Jet A)	CBD	~1.1--~1.3	Gautam, 1992	
GMC Tractor (Diesel & Jet A)	CBD	~1.6--~2.1	Gautam, 1992	
Two-1986 heavy-duty GMC Trucks	HDCC	1.3 and 1.6	Fritz, 1992	
1983 GMC Bus (DDC-92TA)	CBD	Diesel #2=1.87 Clean Diesel=1.31	Bata, 1992	

Table 4-6. Continued

Vehicle description	Test Cycle	Emission Rate	Reference	Comments
Two-1987 Trucks	SC	0.65	Hildemann, 1991	finest (<2 μ m)
8 Diesel Trucks MY 1977-1984 (Class 2B and 6)	HDTC	avg.=1.27 0.422-2.218	Braddock and Perry, 1986	
	Durham Road Route	avg.=1.063 0.287-1.941	Braddock and Perry, 1986	
5 Heavy-Duty Tractors (1979-1981)	Special Cycle	avg.=1.69 1.26-2.17	Dietzmann, 1985	
Buses Pre-1988				
20 pre-1984 Buses	NYBC	1.78	CARB, 1995	
Two 1981 Diesel Buses (DDC 6V-92)	CBD	1.2 and 1.3	Dunlap, 1993	
1985 FLX Bus (DDC 6V92)	CBD	0.37	Wang, 1993	
1982 Bus (DDC 6V-92)	CBD	~5.6	Ferguson, 1992	
GMC 1980 Bus (DDC 6V-71N)	Special Cycle	2.06	Dietzmann, 1985	
Other				
132 tests on 96 vehicles, predominantly buses, Diesel #1, engine MY 1990-1994	CBD Modified CBD WVU truck	0.8 0.1-3.7	Clark, 1996	
94 tests on 56 vehicles, predominantly buses, Diesel #2, engine MY 1990-1994	CBD Modified CBD WVU truck	1.4 0.0-5.9	Clark, 1996	
4 Trucks, diesel No. 2 fuel	CBD	1.263	Lowenthal, 1994	PM-2.5
5 Trucks and buses, diesel No. 2 fuel		1.416	Lowenthal, 1994	
8 Trucks and buses, Jet A fuel		1.021	Lowenthal, 1994	
13 HD vehicles	ADR 36 cycle	1.29-11.51 avg. = 3.37	Williams, 1989	Australian
Ave. of data from eight 1980-81 refs.	Dynamometer	1.67	Schuetzle, 1983	
Four heavy-duty diesel vehicles	Proposed (83) FTP	0.9 - 3.33	Zweidinger, 1981	
Gasoline Vehicles				
6 gasoline trucks MY 1972-1983 (Class 2B,5, 6)	HDTC	avg.=0.229 0.092-0.516	Braddock & Perry, 1986	
	Durham Road Route	avg.=0.199 0.088-0.460	Braddock & Perry, 1986	
6 gasoline trucks MY 1973-1980 (Class 2B-6)	HDTC	avg.=0.648 0.210-2.11	Black, 1984	inertia= 1/2 rated load

CBD=Central Business District driving cycle
WVU truck=WVU truck driving cycle
HDTC=Heavy-Duty Transient Cycle
ADR 36=Australian Design Rules Procedure 36
NYBC=New York Bus Cycle

4.2.2 Heavy-Duty Alternative Fuel Dynamometer Testing

A number of studies have investigated PM emissions from alternative fueled heavy-duty vehicles. A summary of CNG fueled bus chassis dynamometer test results is provided in Table 4-8.

The 1991 Federal and state heavy-duty engine emission standards, and the South Coast Air Quality Management District (SCAQMD) potential requirements for fleet use of cleaner fuels, motivated the Los Angeles County Transportation Authority and Orange County Transportation Authority to evaluate clean fuels for use in transit buses (Dunlap et al., 1993; Unnasch et al., 1993). During the studies, emissions from alternative fueled (CNG, liquefied petroleum gas, and methanol) and diesel fueled transit buses and heavy-duty trucks were compared. The overall results showed that CNG buses either with catalyst or without catalyst exhibited much lower emissions of PM than a conventional diesel bus.

Tuner et al. (2000) compared in-use emissions from diesel and CNG trucks and buses. Diesel trucks had average in-use PM emissions of 0.23 g/bhp-hr over the WVU 5-mile cycle and diesel buses had average in-use PM emissions of 0.13 g/bhp-hr over the CBD cycle. While CNG trucks and buses had average PM emissions 0.016 g/bhp-hr that was about 90% lower than the diesel trucks and buses.

Emissions of six 32-passenger transit buses were tested using one of the West Virginia University (WVU) and Transportable Heavy Duty Emissions Testing Laboratories and the fixed base chassis dynamometer at the Colorado Institute for Fuels and High Altitude Engine Research (CIFER) (Clark et al., 1999). Three of the buses were powered with 1997 Cummins diesel engines, and three were powered with a 1997 Cummins CNG counterpart. Both laboratories found that PM emissions were substantially lower for the CNG buses (0.1 g/mi) than for the diesel buses (below 0.7g/mi). WVU found that for non-aggressive driving CNG PM was well below 0.1 g/mi, diesel PM averaged approximately 0.38 g/mi, and the two diesel buses with catalysts averaged at 0.1 g/mi. The researchers from WVU and CIFER also found that PM emissions were higher for the aggressive driving style in the CBD.

CARB reported emissions data from a CNG 40-passenger New Flyer bus equipped with a 2000 DDC Series 50G engine and a diesel 40-passenger New Flyer bus equipped with a 1998 DDC Series 50 engine with a catalyzed muffler and the same vehicle with a CRT DPF (Ayala et al., 2002). The cycles used in this study included idle operation, a 55 mph steady-state cruise condition, the Central Business District Cycle (CBD), and the New York City Bus Cycle (NYBC). The CNG bus had significantly lower PM emissions compared to the baseline diesel bus across all cycles (Table 4-8). The CRT equipped diesel bus had lower average PM emissions compared to the non-catalyzed CNG bus. The CRT was able to achieve an average reduction of 85% across all cycles. More recently, CARB has investigated the effectiveness of OC control for CNG bus applications (Ayala et al., 2003). These observations are consistent with a study by

SwRI (Ullman et al., 2003) and New York State Department of Environmental Conservation (Lanni et al., 2003). In the work by Lanni et al. (2003), the NYBC was the most rigorous driving schedule and had the highest PM emissions rates averaging at 631 mg/mi for OC diesel vehicle and 96 mg/mi for the DPF vehicle. The effect of driving cycle on CNG total PM emissions was similar to the diesel results in that the NYBC cycle had the highest PM emissions (92 to 102 mg/mi).

There are number of studies of alternative vehicle emissions in Europe (Ahlvik and Brandberg, 2000; Ahlvik, 2003; Seguelong, 2003; Anderson and Wedekind, 2001), Australia (Watt, 2003; Butler, 2000; Stott, 2000), and Canada (Lythgo, 2001; Colavincenzo, 1998). These studies showed comparable results for CNG vehicles compared to US studies. Seguelong (2003) conducted a comparative study on exhaust emission from diesel- and CNG-powered buses and found that CNG bus PM emission rates were 1/10 of PM emission rates from diesel buses. Seguelong also found that diesel buses with DPFs have lower PM emission rates than CNG buses and have around a 98% reduction of PM over the RATP cycle compared to same buses without DPF.

Table 4-8. PM Emissions from CNG Buses (g/mi)

Bus	Engine	Emission Control	Test cycle	Fuel	PM
Unnasch et al., 1993					
Gillig Model 40TB96	Cummins L10	None	CBD	CNG	0.05
Gillig Model 40TB96	Cummins L10	OC	CBD	CNG	0.025
Clark et al., 1999 (CIFER data)					
1997World Tans 300	Cummins CSB-175	OC	CBD	Diesel	0.29
1997World Tans 300	Cummins CSB-175	OC	CBD (aggressive)	Diesel	0.69
1997World Tans 300	Cummins CSB-175	OC	CBD (aggressive)	Diesel	1.02
1997World Tans 300	Cummins CSB-175	OC	CBD (aggressive)	Diesel	0.50
1997World Tans 300	Cummins B5.9G	OC	CBD (aggressive)	CNG	0.024
1997World Tans 300	Cummins B5.9G	OC	CBD (aggressive)	CNG	0.015
1997World Tans 300	Cummins B5.9G	OC	CBD	CNG	0.044
1997World Tans 300	Cummins B5.9G	OC	CBD (aggressive)	CNG	0.006
Clark et al., 1999 (WVU data)					
1997World Tans 300	Cummins CSB-175	OC	CBD	Diesel	0.19
1997World Tans 300	Cummins CSB-175	OC	CBD	Diesel	0.63
1997World Tans 300	Cummins CSB-175	OC	CBD (aggressive)	Diesel	1.45
1997World Tans 300	Cummins CSB-175	OC	CBD	Diesel	0.31
1997World Tans 300	Cummins B5.9G	OC	CBD	CNG	0.020
1997World Tans 300	Cummins B5.9G	OC	CBD	CNG	0.004
1997World Tans 300	Cummins B5.9G	None	CBD	CNG	0.10
Ayala et al., 2002					
2000 New Flyer	DD Series 50G	None	CBD	CNG	0.040
			Steady State	CNG	0.023
			NYBC	CNG	0.092
			UDDS	CNG	0.023
2000 New Flyer	DD Series 50G	None	CBD	CNG	0.033
			Steady State	CNG	NA
			NYBC	CNG	0.10
			UDDS	CNG	0.023
1998 New Flyer	DD Series 50	OC	CBD	ULSD	0.12
			Steady State	ULSD	0.23
			NYBC	ULSD	0.63
			UDDS	ULSD	0.091
1998 New Flyer	DD Series 50	CRT	CBD	ULSD	0.014
			Steady State	ULSD	0.0034
			NYBC	ULSD	0.096
			UDDS	ULSD	0.016
Ayala et al., 2003					
2000 New Flyer	DD Series 50G	None	Steady State	CNG	0.013
			CBD	CNG	0.028
2000 New Flyer	DD Series 50G	OC	Steady State	CNG	0.011
			CBD	CNG	0.021
2001 New Flyer	Cummins Westport C Gas plus	OC	Steady State	CNG	0.015
			CBD	CNG	0.021
Ullman et al., 2003					
1998 AT	International	None	CSHVC	CD	0.184
1998AT	International	CDPF	CSHVC	ULSD	0.010
2000 Blue Bird	John Deere	None	CSHVC	CNG	0.052

Table 4-8. Continued (g/mi)

Bus	Engine	Emission Control	Test cycle	Fuel	PM
Lanni et al., 2003					
1999 New Flyer	DDC Series 50 G	None	CBD	CNG	0.017
1999 New Flyer	DDC Series 50 G	None	CBD	CNG	0.013
1999 New Flyer	DDC Series 50 G	None	CBD	CNG	0.019
1999 Orion V	DDC Series 50	CRDPF	CBD	ULSD	0.035
1999 Orion V	DDC Series 50	CRDPF	CBD	ULSD	0.047
1999 New Flyer	DDC Series 50 G	None	NYBC	CNG	0.065
1999 New Flyer	DDC Series 50 G	None	NYBC	CNG	0.040
1999 New Flyer	DDC Series 50 G	None	NYBC	CNG	0.055
1999 Orion V	DDC Series 50	CRDPF	NYBC	ULSD	0.04
1999 Orion V	DDC Series 50	CRDPF	NYBC	ULSD	0.05
European studies					
Ahlvik et al., 2000					
City bus from Scania			Bus cycle ^a	CNG	0.024
Seguelong, 2003					
RVI AGORA		OC	RATP	CNG	0.058
Volvo CNG		OC	RATP	CNG	0.040
Mercedes CNG*		TWC	RATP	CNG	0.042

DD: Detroit Diesel; ULSD: Ultra-low sulfur diesel. NYBC: New York City Bus Cycle; AT: American Transportation; *: Stoichiometric combustion.; a: Braunschweig city bus cycle.

4.2.3 PM Composition and PAHs from Heavy-Duty Vehicles

PAH compounds have attracted considerable attention because of their known mutagenic and, in some cases, carcinogenic character (National Research Council, 1982). A number of investigators have tried to separate the organic fraction into various classes of compounds. In the 1980s, several studies were conducted to measure PAHs in extracts from diesel particulate emissions (Schuetzle, 1983; Eisenberg et al., 1984; Schuetzle et al., 1985). More recently, Collier et al. (1998) described a technique applicable to simultaneous collection and measurement of both vapor phase and particulate bound PAH in exhaust emissions.

In the 1990s, Rogge et al. (1993) reported the composition of the extractable portion of fine diesel PM emitted from two HD diesel trucks (1987 model year). PAH accounted for ~3.5% and oxy-PAH (ketones and quinones) for another ~3.3% of identified organic compounds. DRI researchers studied 32 PAHs in the exhaust HDDVs (Watson et al., 1998; Zielinska et al., 1998). The higher molecular weight compounds (pyrene through coronene) that are expected to partition to the particle phase had emission rates from HD diesel vehicles ranging from below the detection limits up to 0.071 mg/mi. HD diesel vehicle emission rates for the lower molecular weight PAHs ranged up to 2.96 mg/mi for dimethylnaphthalenes. In general, among the vehicles tested, PAH emission rates were higher for LD diesel vehicles compared with HD diesel vehicles. The results of this study are summarized in Table 4-9.

Table 4-9. PAH Emission Rates from HDDVs

Compound	Emission Rates (mg/mi)
Naphthalene	2.451 ± 0.154
2- Menaphthalene	2.234 ± 0.152
1-Menaphthalene	1.582 ± 0.103
Dimethylnaphthalenes	2.962 ± 0.488
Bipheny	0.505 ± 0.037
2-Methylbiphenyl	0.049 ± 0.024
3-Methylbiphenyl	0.401 ± 0.036
4-Methylbiphenyl	0.144 ± 0.021
Trimethylnaphthalenes	1.940 ± 0.221
Acenaphthylene	0.059 ± 0.087
Acenaphthene	0.030 ± 0.040
Phenanthrene	0.084 ± 0.011
Fluorene	0.066 ± 0.022
Methylfluorenes	0.071 ± 0.055
Methylphenanthrenes	0.124 ± 0.069
Dimethylphenanthrenes	0.090 ± 0.096
Anthracene	0.052 ± 0.016
9-Methylanthracene	0.434 ± 0.082
Fluoranthene	0.044 ± 0.026
Pyrene	0.071 ± 0.017
Methyl(pyrenes/fluoranthenes)	0.022 ± 0.082
Benzenaphthothiophene	0.001 ± 0.027
Benz[a]anthracene	0.066 ± 0.046
Chrysene	0.009 ± 0.021
Benz[b+j+k]fluoranthene	0.009 ± 0.022
Benzo[e]pyrene	0.010 ± 0.014
Benzo[a]pyrene	0.013 ± 0.044
Indeno[1,2,3-cd]pyrene	0.001 ± 0.037
Dibenzo[a]anthracene	0.000 ± 0.053
Benzo[b]chrysene	0.001 ± 0.027
Benzo[ghi]perlyne	0.013 ± 0.048
Coronene	0.001 ± 0.095

Ref: Watson et al., 1998 and Zielinska et al., 1998.

Norbeck et al. (1998a) reported on the effect of fuel aromatic content on PAH emissions. As we mentioned earlier, three diesel fuels were used in a Cummins L10 engine: a pre-1993 fuel containing 33% aromatics and 8% PAHs; a low aromatic fuel containing a maximum content of 10% aromatics and maximum of 1.4% PAHs; and a reformulated fuel containing 20% to 25% aromatics and 2% to 5% PAHs. The investigators found that emission rates for the low molecular-weight PAHs (PAHs with three or fewer rings) were significantly lower when the engine was tested using the low aromatic fuel compared to when the engine was run on the pre-1993 or reformulated fuel (Table 4-10). Although emission rates reported for several higher molecular weight (particle-associated) PAHs were lower (ranging from 4% to 28% lower) for the low

aromatic fuel compared with the other two fuels, the differences were not statistically significant except for coronene.

Recently, several studies have reported the PAHs emissions from CNG buses including DOE “Gasoline/Diesel PM Split Study” program and ARCO ECD program on DPFs (Fujita et al., 2004; Lawson et al., 2004; Ullman et al., 2003; Lanni et al., 2003; Ayala et al., 2001; Chatterjee et al., 2001; Ahlvik and Brandberg, 2000). Lanni et al. (2003) found that similar PAH emissions were observed for CNG buses and diesel buses (Table 4-11), although CNG as a fuel contains much lower levels of PAHs than diesel fuel. Much lower PAH emissions were observed for DPF (CRTTM) buses. Ullman et al. (2003) also found that for conventional diesel configuration PAH emission levels were significantly higher than the ULSD with CDPF or CNG bus configuration (Table 4-12). The ULSD with CDPF had lower levels of all PAHs than the CNG bus. This observation agrees with the higher PAH emissions from CNG buses reported by Ahlvik and Brandberg (2000) and Schauer et al. (1999). It may be due to possible lube oil burning or thermal synthesis during CNG combustion.

On the basis of these limited data it is difficult to draw a quantitative conclusion regarding how PAH emissions have changed over time and in response to fuel and engine changes. However, the data suggest that differences in a vehicle’s engine type and make, general engine condition, fuel composition, and test conditions can influence the emission levels of PAH.

Table 4-10. PAHs Emission Rates for Different Fuel Types

Compound	Pre-1993 diesel	Low aromatic diesel	Reformulated diesel
	Cetane No.>40 Aromatics 33% v. PAH 8% wt. ($\mu\text{g}/\text{bhp-hr}$)	Cetane No.>48 Aromatics 10% v. PAH 1.4% wt. ($\mu\text{g}/\text{bhp-hr}$)	Cetane No.50-55 Aromatics 20-25% v. PAH 2%-5% wt. ($\mu\text{g}/\text{bhp-hr}$)
2,3,5-trimethyl naphthalene	283.68 \pm 5.27	14.77 \pm 2.42	56.21 \pm 2.82
Phenanthrene	336.71 \pm 9.08	160.92 \pm 15.54	220.73 \pm 52.68
Anthracene	38.89 \pm 1.43	18.54 \pm 2.13	26.16 \pm 6.86
Methylphenanthrenes/anthracenes	331.32 \pm 16.07	25.17 \pm 1.41	111.98 \pm 28.74
Fluoranthene	128.45 \pm 7.60	132.36 \pm 18.30	123.07 \pm 26.21
Pyrene	193.03 \pm 16.51	211.19 \pm 37.35	206.82 \pm 39.04
Benzo[c]phenanthrene	3.03 \pm 0.24	1.74 \pm 0.14	1.54 \pm 0.26
Benzo[ghi]fluoranthene	24.84 \pm 2.68	18.93 \pm 2.14	16.94 \pm 2.31
Cyclopenta[cd]pyrene	21.44 \pm 4.11	26.15 \pm 3.12	21.25 \pm 3.46
Benz[a]anthracene	16.42 \pm 1.67	10.57 \pm 1.15	10.96 \pm 2.42
Chrysene + triphenylene	17.36 \pm 1.66	10.38 \pm 0.54	12.20 \pm 2.72
Benzo[b+j+k]fluoranthene	31.05 \pm 4.17	23.17 \pm 1.98	29.18 \pm 7.93
Benzo[e]pyrene	16.71 \pm 2.72	14.55 \pm 1.34	18.99 \pm 5.58
Benzo[a]pyrene	20.46 \pm 3.27	16.48 \pm 1.56	20.59 \pm 5.75
Perylene	4.32 \pm 0.88	3.71 \pm 0.74	4.18 \pm 1.16
Indeno[1,2,3-cd]fluoranthene	0.34 \pm 0.07	0.21 \pm 0.02	0.17 \pm 0.00
Benzo[c]chrysene	0.29 \pm 0.05	0.18 \pm 0.05	0.14 \pm 0.04
Dibenz[a,h]anthracene	0.93 \pm 0.05	0.55 \pm 0.10	0.67 \pm 0.09
Indeno[1,2,3-cd]pyrene	19.45 \pm 2.71	14.04 \pm 1.99	22.16 \pm 9.11
Dibenz[a,h+a,c]anthracene	1.54 \pm 0.15	0.87 \pm 0.12	1.48 \pm 0.67
Benzo[b]chrysene	0.40 \pm 0.01	0.15 \pm 0.05	0.27 \pm 0.05
Benzo[ghi]perylene	49.17 \pm 9.63	39.81 \pm 7.22	60.74 \pm 26.60
Coronene	9.49 \pm 3.13	4.93 \pm 0.47	7.48 \pm 1.59
Dibenzo[a,l]pyrene	2.84 \pm 0.45	1.25 \pm 0.15	2.31 \pm 0.48
Dibenzo[a,e]pyrene	1.10 \pm 0.29	0.61 \pm 0.06	1.13 \pm 0.15
Dibenzo[a,i]pyrene	0.91 \pm 0.21	0.27 \pm 0.09	0.71 \pm 0.15
Dibenzo[a,h]pyrene	1.33 \pm 0.25	0.75 \pm 0.07	0.84 \pm 0.20

Ref: Norbeck et al., 1998a.

Table 4-11 Comparison PAH Emissions from CNG Buses and Diesel Buses

(mg/mi)

Bus type	Three 1999 CNG buses			Two 1999 Diesel			
Engine	DDC series 50G			DDC series 50			
Exhaust system	OEM	OEM	OEM	OEM	CRT	OEM	CRT
Fuel sulfur	-	-	-	30	30	30	30
With CBD driving cycle							
Acenaphthylene	0.0057	0.0053	0.023	0.0136	0.0012	0.0102	0.0006
Acenaphthene	0.0058	0.005	0.007	0.0036	0.0018	0.0019	0.0016
Fluorene	0.0107	0.0113	0.0103	0.0076	0.0033	0.0084	0.0032
2-Me-Fluorene	0.0042	0.0041	0.0049	0.0041	0.0012	0.0044	0.0014
Phenanthrene	0.0198	0.0188	0.028	0.0234	0.0069	0.0277	0.0062
Anthracene	0.0045	0.0028	0.0036	0.0016	0.0008	0.0053	NA
Fluoranthene	0.0032	0.0026	0.005	0.0043	0.0013	0.0051	0.0014
Pyrene	0.0032	0.0037	0.0075	0.0045	0.0009	0.0055	0.0012
Total PAHs	0.057	0.054	0.102	0.063	0.0173	0.0687	0.0161
With New York Bus driving cycle							
Fuel sulfur	-	-	-	300	30		
Acenaphthylene	0.0189	0.0114	0.0565	0.0366	0.0041		
Acenaphthene	0.0242	0.0144	0.021	0.0133	0.0036		
Fluorene	0.037	0.0279	0.0325	0.0299	0.0075		
2-Me-Fluorene	0.0188	0.0123	0.0182	0.0094	0.0032		
Phenanthrene	0.0684	0.0509	0.0798	0.0805	0.0164		
Anthracene	0.0166	0.0155	0.01	0.0031	0.001		
Fluoranthene	0.0146	0.0062	0.0163	0.0142	0.0005		
Pyrene	0.0118	0.0079	0.0248	0.0142	0.0005		
Total PAHs	0.21	0.146	0.291	0.201	0.042		

Ref: Lanni et al., 2003

Table 4-12. PAH Emission Rates from CNG and Diesel Buses (mg/mi)

Compound	CD	ULSD with CDPF	CNG
Bus	1998 American Transportation		2000 Blue Bird
Engine	International		John Deere
Sulfur, ppm	371	14	-
Aromatics, wt%	33.1	30.9	-
PNAs, wt%	13.3	7.6	-
Naphthalene	0.73000	0.06900	0.07400
2-Methylnaphthalene	1.20000	0.00310	0.02700
Acenaphthylene	0.12000	0.00027	0.01900
Acenaphthene	0.05000	0.00000	0.00250
Fluorene	0.19000	0.00037	0.00770
Phenanthrene	0.41000	0.00052	0.02100
Anthracene	0.03700	0.00019	0.00310
Fluoranthene	0.03100	0.00130	0.00240
Pyrene	0.05900	0.00120	0.00300
Benzo(a)anthracene	0.00110	0.00008	0.00056
Chrysene	0.00240	0.00008	0.00081
Benzo(b)fluoranthene	0.00052	0.00001	0.00014
Benzo(k)fluoranthene	0.00073	0.00002	0.00021
Benzo(e)pyrene	0.00085	0.00002	0.00037
Benzo(a)pyrene	0.00055	ND	0.00019
Perylene	0.00017	ND	0.00006
Indeno(1,2,3-cd)pyrene	0.00032	ND	0.00011
Dibenz(a,h)anthracene	0.00006	ND	ND
Benzo(g,h,i)perylene	0.00084	ND	0.00056
1-Nitropyrene	0.00083	0.00001	0.00019
Sum PAH	2.8	0.076	0.16
PM (g/mi)	0.184	0.010	0.0052

Ref: Ullman et al., 2003. Detection limits for PAHs were 0.00002 mg/mi, for 1-Nitropyrene it was 0.000002 mg/mi. CD: conventional diesel; ULSD: ultra-low sulfur diesel; CDPF: catalyzed diesel particulate filter

4.3 The Impacts of Technological Advances on Particulate Emissions Levels

With changes in vehicle technology, it is important to understand how technological advances can contribute to changes in PM mass emission rates. Among the factors that must be considered are engine technology, fuel composition, and aftertreatment controls. The effects of engine design changes are briefly discussed in the following subsection, with the focus being on diesel engines. The impact of aftertreatment controls is discussed in a companion report to this (Durbin et al., 2004). The effects of fuel composition are discussed in section 6.3.

Engine manufacturers to date have primarily relied on engine modifications to meet existing and past emissions standards. These changes have been discussed in previous review papers for the standards of the late 1980s and early 1990s (Khair, 1992; Zelenka et al., 1990; Kawatani, 1993; Richards and Sibley, 1988) and in recent CARB

and EPA documents for more recent regulatory standards (CARB, 1998, 1999; EPA, 1998, 2000). Currently, the engine control measures include turbocharging, aftercooling, optimizing combustion chamber design, retarding injection timing, and high-pressure fuel injection. One of the disadvantages of strictly engine control measures is that there is a tradeoff between PM and NO_x emissions in some cases. PM emissions, for example, are reduced when improved combustion is achieved. Improved combustion can lead to higher combustion temperatures, however, which can lead to higher NO_x emissions.

The geometry of the combustion chamber and the air-intake port effect the air motion in the combustion chamber, and hence influence air/fuel mixing and emissions. In direct injection engines, the distribution of air in the combustion chamber can be improved by reducing the crevice volumes where air utilization is poor. PM emissions have been reduced by design changes to the combustion chamber, such as a re-entrant lip on the piston bowl (Khair, 1988). The swirl characteristics in the combustion chamber have been improved by optimizing the shape of the intake port. Reducing oil consumption is also important for reducing SOF particulate. Measures to control oil consumption include bore honing and ring pack design (Zelenka et al., 1990; Khair, 1992). Oil can also enter the combustion chamber through the exhaust and intake valve guides and the turbine and turbocharger seals.

The injection system is one of the most important components for engine designers. To optimize fuel delivery, a number of parameters must be matched, including injection timing, injection rate, injection duration, and nozzle hole configuration. Using electronically controlled fuel injection systems, injection timing is optimized to improve the trade-off between NO_x and particulate emissions. Retarding the injection timing is one of the most effective methods of controlling NO_x emissions, but can have an adverse effect on PM emissions. Increased injection pressure is one of the measures that has been implemented over the years to improve PM emissions (Zelenka et al., 1990). Changes in injection pressure can lead to changes in the fuel injection rate, injection duration, atomization and penetration. Other improvements in fuel injection systems include common-rail fuel systems and advanced electronically controlled injectors. Improved systems allow greater control of the injection process or injection rate shaping that can be used to reduce peak flame temperatures without increasing fuel consumption. Rate shaping methods include the use of pilot or split injections. Injection rate shaping has been shown to simultaneously reduce NO_x by 20% and PM by 50% under some conditions (Dickey et al., 1998).

The configuration of the nozzle is also considered important in controlling PM emissions. Important factors with respect to nozzle configuration include minimizing the nozzle sac volume to reduce the soluble organic fraction (SOF) (Richards and Sibley, 1988), selecting a nozzle diameter to provide proper fuel atomization, and choosing the length of the nozzle based on fuel utilization considerations (Khair, 1992). SOF PM have been reduced by lowering the spill rates or dribble at the end of fuel injection and by preventing the fuel spray from adhering to the cold surface of the cylinder walls (Kawatani et al., 1993).

Turbochargers are used to increase the pressure of the air entering the engine. This allows more fuel to be used, increasing the power output. Aftercooling with turbocharging can be used to decrease the temperatures of the charged air after it has been compressed by the turbocharger. This improves the filling of the combustion chamber because the higher-density cool air sinks faster than hotter air (Lloyd and Cackette, 2001). The combination of turbocharging and aftercooling allows flexibility in the controlling emissions and injection timing and pressure. The combination of turbocharging with aftercooling allows corresponding reductions in both NO_x and PM.

Exhaust gas recirculation (EGR) is a technique where the intake air is diluted with recirculated exhaust gas. This dilution process reduces the peak flame temperatures and hence NO_x emissions. Studies have shown that laboratories can reduce NO_x emissions by up to 90% at light load and up to 60% at full load near the rated speed (Dickey et al., 1998). EGR played an important role in achieving the US 2002/2004 NO_x standard (2.0 g/bhp-hr). Some of the technical challenges addressed in the development of EGR included reliable components and control systems and limitations on engine rating and fuel consumption. Higher EGR rates are considered an important option for meeting 2007 standards (0.2 g/bhp-hr). Recent work by Richardo, and other, has indicated that a well developed combustion system, using perhaps 50-60% higher levels of EGR than the 2002 engines could achieve the 2007 levels for NO_x without aftertreatment (Weller, 2003; Ryan, 2003; Cummins, 2003; Bertola et al., 2003).

Homogeneous charge compression ignition (HCCI) is another technique that can be used in reducing emissions (Duffy et al., 2003). HCCI systems utilize fuel and air premixed prior to entering the combustion chamber. Ignition is still induced through compression. This process eliminates some of the locally rich and lean zones that cause high NO_x and PM. Thermal efficiencies of HCCI engines are comparable to those of conventional diesel engines at part loads, but can have lower efficiencies for certain diesel engines. Some issues related with HCCI systems include control of the combustion rate, formation of the correct fuel air mixture, and achieving stable combustion at high load.

5. Tunnel studies

Highway and road tunnel studies have been used to measure the real world emissions of large numbers of motor vehicles. Tunnel Studies, compared to individual vehicle tests on a dynamometer, have the advantage on their simplicity, cost effectiveness and robustness of sample size. Tunnel studies can provide important real-world emission data from mobile sources since the measurements occur under actual operation on the highway. Tunnel studies monitor only a limited number of operating modes, however.

5.1 Air toxics emission

There are a number of tunnel studies of on-road emissions from motor vehicles in highway and roadway tunnels. Of these tunnel studies, a few have identified toxic emission factors from vehicles. Brief descriptions of these tunnels are listed in Table 5-1, including the Fort McHenry Tunnel experiment in Baltimore Harbor, Maryland (Pierson et al., 1996) and the Tuscarora Mountain Tunnel in Pennsylvania (Sagebiel et al., 1996); the Van Nuys tunnel in Los Angeles, California (Harley, 1993; Fraser, 1998); the Caldecott Tunnel in San Francisco Bay area, California (Kirchstetter, 1996; Kirchstetter, 1999a, 1999b, and 1999c) and other tunnels studies.

A summary of literature data for toxic emission factors performed in tunnels is presented in Table 5-1. For all highway tunnel studies listed in the Table 5-1, only the study by Pierson and coworkers at the Fort McHenry and Tuscarora Mountain Tunnels included separate calculations of carbonyl emission factors for LD and HD vehicles (Pierson et al 1996; Sagebiel et al 1996; Zielinska et al 1996). The other studies provided emission data for the entire fleet including heavy-duty trucks. For the combined emission factors, the fleet average gaseous toxic emission factors are generally dominated by light-duty vehicles because the percentages of heavy-duty vehicles were very low in the overall fleet. Heavy-duty vehicle also represented less than 5% of traffic for the Van Nuys, Sepulveda Boulevard, and Callahan tunnels. High percentages of LDVs (>99.7%) in the Caldecott tunnel were observed since HDVs were required to use other tunnel bores.

The gaseous toxics emission rates have a wide range and show changes between different years. For all tunnel studies, the range of 1,3-butadiene emission factors was 0.69 (Lincoln Tunnel, 1996) to 5.98 mg/mi (Deck Park Winter, 1995). The benzene emission rates varied from 13.73 (Tuscarora Mountain Tunnel, HD, 1992) to 97.58 mg/mi (Van Nuys, 1993). The emission rates of formaldehyde varied from 4.15 (Tuscarora Mountain Tunnel, LD, 1999) to 52.7 mg/mi (Fort McHenry HD, 1992). The range of emission rates of acetaldehyde varied from 1.03 (Tuscarora Mountain Tunnel, LD, 1999) to 32 mg/mi (Fort McHenry HD, 1992).

For the Fort McHenry and Tuscarora Mountain Tunnel studies, comparisons were made between LD and HD vehicles. In comparing LD and HD vehicles, on a distance-traveled basis, total toxic emission factors ratios (HD versus LD) were 2.98 in Fort McHenry at 1992 and 2.65 for Tuscarora Mountain Tunnel (not including acetaldehyde).

Benzene and 1,3-butadiene emission rates were comparable for LD and HD vehicles. However, much higher emission rates of formaldehyde and acetaldehyde were observed for HD vehicles than LD vehicles. The HD (class 7-8)/LD formaldehyde emission factor ratios were 7.6 for Fort McHenry in 1992 and 6.9 for Tuscarora Tunnel in 1992, decreased to 2.6 for Tuscarora Tunnel in 1999. The HD 7-8/LD acetaldehyde emission factor ratios were 16 for Fort McHenry Tunnel in 1992 and 6.1 in Tuscarora Tunnel in 1999.

Comparing the emission factors in the same tunnel but in different study years, the fleet average benzene emission factors measured in Van Nuys Tunnel were 62% lower in 1995 than in 1993. The average vehicle fleet toxic emission factors in Caldecott Tunnel declined significantly between 1999 and 1994. The emission factor for 1,3-butadiene in 1997 was 26% lower than in 1995 and 66% lower than in 1994. A significant decrease in benzene occurred between 1995 and 1996 for LD vehicles because most of the changes to gasoline composition occurred at that time. Benzene emissions in Caldecott tunnel had decreased by 66% from 1994 to 1997. Formaldehyde and acetaldehyde emission rates had similar trends between 1994 and 1999 with reductions of 52% and 58%, respectively. For Tuscarora Mountain tunnel, the LD formaldehyde emission factors measured at 1999 were 33% lower than those measured at 1992 and the HD formaldehyde emission factors in 1999 were 75% lower than in 1992. The primary reason for reductions in the on-road toxics emissions is the replacement of older vehicles with newer ones. The impact of fleet turnover on vehicle emissions is anticipated because newer vehicles have more advanced emission controls and need to meet increasingly more stringent emissions standards. With the continuing improvements in vehicle control technology, fleet turnover, and cleaner fuels (for example formulated gasoline), it is expected that the long-term trend of toxic emission rates should be downward.

HD vehicle emission factors measured in more recent tunnel studies were also lower than reported in previous tunnel studies. The toxic emission reductions of HD vehicles were larger than similar reductions from LD vehicles. HD vehicle emission rates were 4 times lower in Tuscarora Mountain tunnel in 1999 than in 1992 for formaldehyde and 5 times lower for acetaldehyde (Tuscarora Mountain tunnel, 1999 versus Fort McHenry, 1992).

For studies conducted in the same year but different tunnels, the emission rates of toxics vary considerably. It may reflect differences in fuel composition, fleet age, fleet composition, mean speed and acceleration, deceleration, and proportion of high emitters for some toxics. For example, the LD formaldehyde emission factors measured in 1999 in Caldecott tunnel were lower than those previously measured in the Caldecott Tunnel (Kirchstetter et al., 1996, 1999a, and 1999b) but were essentially same, within the stated uncertainties, as those measured in 1992 in the Tuscarora Mountain and Fort McHenry Tunnels (Pierson et al., 1996; Zielinska et al., 1996). Of all tunnel studies, the Van Nuys tunnel (1993) in Los Angeles had highest fleet emission rates of benzene and formaldehyde. The CO and VOC emission rates in Van Nuys tunnel (1993) were also higher than reported for studies in highway tunnels in other cities (Fraser et al 1998). One possibility is that an unusually large amount of unburned gasoline is either being emitted

from the tailpipe because the vehicle fleet in the Van Nuys Tunnel on average was older and running rich or was leaking from vehicle fuel systems (Fraser et al 1998).

It is important to point out that tunnel studies examine only a limit number of driving modes. Because of the locations of the tunnels, the vehicles measured in tunnel studies are not likely to be in cold-start mode. The emission factors measured in tunnel studies are also generally for vehicles operated in hot-stabilized mode with little or no off-cycle emissions. As such, tunnel results may represent lower limits from vehicle emissions of toxics that may occur in urban areas, with higher contributions coming from cold starts, and stop-and-go traffic or off cycle driving.

5.2 PM emissions

5.2.1 Road Studies of Light-Duty Vehicles

Emissions factors for light-duty vehicles developed in conjunction with tunnel studies at Fort McHenry, Allegheny, Van Nuys, and Tuscarora are presented in Table 5-3. The results are generally consistent with the PM emissions obtained through dynamometer testing, but are highly variable. One of the problems with using tunnel studies to determine particulate emissions from light-duty vehicles is that these emission rates must be separated from the emission rates of heavy-duty vehicles that have substantially higher emission rates. The light-duty fleet is also composed of a small fraction of diesel vehicles that are difficult to disaggregate. It should be noted that PM emissions measurements were also incorporated into a tunnel study conducted in Los Angeles by the Desert Research Institute (DRI) (Fraser, 1998). The traffic volume through these tunnels is composed of almost entirely light-duty vehicles.

Table 5-1. Tunnel Descriptions

Tunnel	Location	Speed (mph)	Tunnel Descriptions	Studied date
Fort McHenry	Baltimore, Maryland	49±4	Four-bore, two lanes per bore, on interstate 95 east-west in a wide curve under Baltimore Harbor. Down grade and upgrade for both eastbound and westbound traffic are ±3.76%. 2195m in length westbound and 2174m eastbound.	June 18-24 1992
Tuscarora Mountain	Pennsylvania	56.3±2.2	Two-bore tunnel, two lanes per bore, on the Pennsylvania Turnpike (Interstate 76) east-west through Tuscarora Mountain in south central Pennsylvania at an altitude of approximately 305m. 1623.2m long and almost flat with a grade of +0.3%.	Sep 2-8 1992 May 18-21 1999
Van Nuys	L.A. California	40 (1993) 43.6±5.4 (1995)	Two-bore, 3 lanes per bore, urban tunnel, 222m in length, running east/west under the runway of the Van Nuys Airport.	Sep 21, 1993 June 9-12, 1995
Sepulveda Boulevard	L.A. California	45.7±8.0	A covered roadway with the top portion being part of airplane runway and taxiway for LAX. Two-bore, 3 lanes per bore with a sidewalk on the right side of each bore. 582m	October 3-4, 1995
Callahan	Boston	26.4±5.4	The eastbound of a pair of tunnels carrying traffic between North Boston and East Boston and Logan International Airport. One-bore tunnel with two lanes in the bore. Most light vehicles 1545m	September 19, 1996
Lincoln	N.Y.	27.1±4.3	Three-bore tunnel with two lanes per bore running under the Hudson River between Weehawken, New Jersey and Manhattan Island. 2440 long.	August 18, 1996
Deck Park	Phoenix	59.7±5.7	Three-bore tunnel urban freeway tunnel 804m in length running east/west under Deck Park. Center bore is unused. Five lanes and two emergency lanes in the south and north bore.	July 25-27, 1995
Caldecott	San Francisco, California	32.5 ~44.4	Located east of San Francisco Bay on state highway 24. It runs in the east-west direction with three two-lane traffic bores and 1100m long. It has a roadway grade of +4.2% in the eastbound direction and steady acceleration throughout tunnel.	1994-1997 July 20 to Aug 5 1999

Table 5-2. On-Road Gas-Phase Air Toxics Emission Rates (mg/vehicle-mi)

	Vehicle	Fleet composition	1,3-butadiene	Benzene	Formaldehyde	Acetaldehyde	Acrolein	HC (g/mi)	Ref
Fort (1992) McHenry	LD	83% LD	2.81±0.45	23.79±1.76	6.94±1.79	2.0±5.0	NA	0.62	Pierson, 1996 and Sagebiel, 1996
	HD	17%HD, 80%diesel	1.90±2.36	19.36±9.19	52.7±9.36	32±3	NA	1.54	
Tuscarora Mountain (1992)	LD	82%LD	2.01±0.58	14.75±1.49	6.24±2.20	NA	NA	0.29	Pierson et al 1996 and Sagebiel, 1996
	HD	18%HD	3.94±1.91	13.73±4.91	43.25±7.27	NA	NA	0.69	
Tuscarora Mountain (1999)	LD	71.3% LD	NA	NA	4.15±1.69	1.03±0.43	0.17	0.65	Grosjean, 2001
	HD	28.7% HD	NA	NA	10.83±3.28	6.36±0.95	1.16	2.40	
Van Nuys (1993) ^b	Fleet	96.1%LD 3.9%HD	NA	97.58	32.67	7.41	NA	NA	Fraser et al 1998
Van Nuys (1995)	Fleet	97.2%LD 2.8%HD	NA	37.45±11.61	NA	NA	NA	1.04 ^h	Gertler et al. 1997
Sepulveda (1995)	Fleet	97.6%LD 2.4%HD	4.64±1.96	29.53±3.55	NA	NA	NA	0.89 ^h	Gertler et al. 1997
Callahan (1996)	Fleet	96.3%LD 3.7%HD	1.59±0.61	17.23±5.50	NA	NA	NA	0.63 ^h	Gertler et al. 1997
Lincoln (1996)	Fleet	86.7%LD13.3%HD	0.69±0.91	26.07±11.25	NA	NA	NA	0.98 ^h	Gertler et al. 1997
Deck Park (1995)	Fleet Summer	94.5%LD 5.5%HD	4.67±1.03	33.92±6.94	NA	NA	NA	0.87 ^h	Gertler et al. 1997
	Fleet Winter		5.98±1.58	33.90±7.95	NA	NA	NA	0.87 ^h	
Caldecott, 94 Aug ^c	LD	99.8%LD 0.2%HD	2.67±1.78 ^a	45.28±5.66	11.43±0.47	2.66±0.21	NA	0.78 ^g	Kirchstetter, 1996 ^d
Caldecott, 94 Oct ^c	LD	99.8%LD 0.2%HD	2.38±1.12 ^a	34.38±1.98	12.87±0.47	2.77±0.47	NA	0.78 ^g	Kirchstetter, 1996 ^d
Caldecott, 1995 ^c	LD	99.8%LD 0.2%HD	4.48±1.14	38.14±2.63	11.36±0.51	2.35±0.16	NA	0.71 ^g	Kirchstetter, 1999
Caldecott, 1996 ^c	LD	99.7%LD 0.3%HD	2.56±0.63	17.48±1.52	11.46±0.82	1.93±0.16	NA	0.55 ^g	Kirchstetter, 1999
Caldecott, 1997 ^c	LD	99.8%LD 0.2%HD	3.09±0.38	15.42±1.10	6.71±0.93	1.48±0.21	NA	0.45 ^g	Kirchstetter, 1999
Caldecott, 1999	LD	99.9%LD 0.1%HD	NA	NA	6.00±0.74	1.54±0.16	0.21±0.02	NA	Grosjean, 2001 ^g ; Kean, 2001

^a: The number shown here are the low limits because of losses of 1,3-butadiene in the stainless steel canister.

^b: Results reported by authors in mg/L of fuel consumed (no SD given) and converted to mg/km using a fuel economy of 6.3 km/L (Fraser and Cass 1998)

^c: Results reported by authors in mg/L of fuel consumed and converted to mg/mi using fuel economies of 8.3 km/L (1994, 1995) and 8.5 km/L (1996, 1997) (Kirchstetter et al 1996, 1999)

^d: Oxygen content of gasoline increased from 0.3 in August, 1994 to 2.0% in October, 1994 by weight.

^f: HD means class 7-8 vehicles.

^g: NMOC value; ^h: NMHC.NA: Not available.

Table 5-3. On-Road Particulate Emission Factors for Light-Duty Vehicles

Make/Model	Emission Factor g/mi	Reference
Caldecott, 1997	0.17	Allen, 2001
Sepulveda, 1996	0.11	Gillies, 2001
Van Nuys 1993 ^a	0.125±0.016	Fraser, 1998
Fort McHenry	0.015±0.060	Gertler, 1995a
Tuscarora Mountain, 1999	0.023±0.021 ^b	Gertler, 2002
	0.016±0.018 ^c	
Allegheny July 1975	~0.048	Pierson, 1983
Allegheny May-June, 1976	0.027±0.027	
Allegheny August 1976	0.01±0.021	
Allegheny July, August 1977	0.048±0.019	
Allegheny May, June 1979	0.048±0.018	
Allegheny August, October 1979	0.01	
Tuscarora August 1976	0.04±0.018	
Tuscarora June, July 1977	0.082±0.048	
For the year of 1981	0.040±0.035	
Allegheny 1970-1974	<0.1	Pierson, 1976

^a Results reported by authors in mg/L of fuel consumed (no SD given) and converted to mg/km using a fuel economy of 6.3 km/L (Fraser and Cass 1998). Emission factor here was for overall fleet include 96.1%LD 3.9%HD; ^bPM_{2.5}; ^cPM₁₀.

5.2.2 Road Studies of Heavy-Duty Vehicles

Researchers at the Ford Motor Company were among the first to measure on-road particulate emission rates at tunnel exits. These experiments were conducted throughout the 1970s and into the 1980s at the Allegheny and Tuscarora Mountain tunnels in Pennsylvania (Pierson and Brachaczek, 1976, 1983). Emission rates from these and more recent studies are presented in Table 5-4 for heavy-duty vehicles. The emission rates derived from these early tunnel studies correlated relatively well with the dynamometer test results of the time (see Pierson and Brachaczek, 1976) and provide a baseline from which the effects of technological advances on emissions rates can be compared.

Ingalls et al. (1989) conducted a similar experiment in 1987 in the Sherman Way tunnel under the Van Nuys Airport as part of the Southern California Air Quality Study. For this study, average PM emission rates of all vehicles varied between 30 and 180 mg/mi depending on the sampling period. These raw values represent a range of vehicle technology classes, including light-, medium-, and heavy-duty vehicles, powered by both gasoline and diesel fuels, and hence cannot be compared directly with dynamometer test results.

Gertler et al. (1995b) measured the fleet average of PM₁₀ emission rates of heavy-duty vehicles passing through the Ft. McHenry Tunnel during July of 1993. The heavy-duty fleet average emission rates of PM-10 were 0.67±0.13 g/mi. This emission factor compares relatively well with chassis dynamometer tests from that era. For comparison, tests were conducted over the West Virginia 5 Peak Cycle on eleven diesel-powered trucks with model years ranging from 1982 to 1994. The resulting average PM emission rate was 0.78 g/mi. The Ft. McHenry emission factors are about a factor of two lower than those obtained by Pierson and co-workers in earlier tunnel studies. This is probably due to improvements in diesel technology and the use of cleaner diesel fuels. Other tunnel studies have also shown similar emission reductions from the levels reported in early tunnel studies (Rogak, 1996). Kirchstetter et al (1999) interestingly found heavy-duty PM emission rates similar to those early tunnel studies in the Caldecott tunnel in 1999. Gertler et al. (2002) studied on-road emissions from vehicles in the Tuscarora Mountain Tunnel from May 18 through 23, 1999. Compared the data in 1976, a downward trend in HD PM emissions was observed from approximately 1.38 g/mi to 0.21 g/mi (reported as PM_{2.5}). It is noted that this emission level is consistent with HDDTs operated over highway cruise type of cycles, but that stop-and go transient operation trends to produce substantially higher PM emissions.

Table 5-4. On-Road Particulate Emission Factors for Heavy-Duty Vehicles

Tunnel	Emission Factor g/mi	Reference
Caldecott Tunnel, 1997	1.43±0.12 ^a	Kirchstetter, 1999
Vancouver Cassair, 1995	0.58±0.3	Rogak, 1996
Vancouver Cassair, 1994	0.47	Rogak, 1996
Fort McHenry, 1993	0.67±0.13 ^a	Gertler, 1995a
Tuscarora, May 1999	0.21 ^a	Gertler, 2002
Allegheny 1970-1974	0.9016-1.803	Pierson, 1983
Allegheny July 1975	1.376±0.256	Pierson, 1983
Allegheny May-June, 1976	1.2±0.104	Pierson, 1983
Allegheny August 1976	1.25±0.072	Pierson, 1983
Tuscarora August 1976	1.38±0.184	Pierson, 1983
Tuscarora June, July 1977	1.33±0.256	Pierson, 1983
Allegheny July, August 1977	1.36±0.08	Pierson, 1983
Allegheny May, June 1979	1.54±0.032	Pierson, 1983
Allegheny August, October 1979	1.74±0.0352	Pierson, 1983
Allegheny July 10-20, 1981	1.344±0.144	Szkarlat, 1983

^aPM 2.5; ^bPM 3;

5.3 Foreign Tunnel Studies

There have been several tunnel studies in Taiwan, South Korea, France, Australia and Switzerland over the years. In Taiwan, the tunnel study was first conducted in the southern Taiwan area by Tsai et al. (1998) and Hsu et al., (2001) using the Chung-Cheng tunnel in Kao-Hsiung city. This tunnel is relatively short, however, and thus the entrance effect becomes a major concern. Later on, an experiment was carried out in the Lishin and Zefun tunnel of Taipei County for the emissions of volatile aromatic compounds from the combined traffic composed by motorcycles and LD vehicles. Recently, Hwa et al. (2002) from National Taiwan University conducted an in situ field experiment in a highway road tunnel in the Taipei City to determine the motor vehicle VOCs emission factors. In another study, motor vehicle emission factors of carbon monoxide (CO) and NMHCs were estimated inside the Chung-Cheng Tunnel of Kaohsiung in Taiwan (Hsu et al., 2001). The results of these studies are summarized in Table 5-5.

Na et al. (2002) from Korea Institute of Science and Technology measured 45 hydrocarbon species in Seoul tunnel in winter, spring, and summer, 2000. The average concentration of HC in the tunnel air varied significantly with highest concentration level of 2274.9 ppbC in Spring, followed by 1090.1 ppbC in Summer, and 1087.5 ppbC in Winter. The Benzene had concentrations of 13.2 ppb in Spring, 6.6 ppb in Winter, and 4.3 ppb in Summer. Vehicle emission factors were not calculated in this paper.

Weingartner et al. (1996) measured aerosol emissions in the Gubrist tunnel, a 3250 m long freeway tunnel near Zfirich, Switzerland, from September 20 to 26 1993. The particles in the respirable size range were found to be mainly tail pipe emissions with very small amount of tire wear and road dust. Thirty-one percent of the PM < 3 μ m emissions from diesel vehicles were black carbon and 0.86% were particle bound PAHs. The emission rates of particle bound PAHs were 0.19 mg/mi for LD vehicles and 3.84 for HD vehicles.

The concentrations of individual hydrocarbon species in the Sydney Harbor Tunnel were measured and used to estimate the average composition of emissions from motor vehicles in the Sydney urban area (Duffy and Nelson, 1996). The mean concentrations for benzene and 1,3-butadiene were 45 and 13 ppbv, respectively, which in turn represented 5.2% and 1.0% by weight of the total non-methane C₂-C₁₀ hydrocarbons in the tunnel air.

The concentrations of semi-volatile PAHs, HCs, PM and total suspended particles (TSPs) were measured in a traffic tunnel in Gothenburg, Sweden (Wingfors et al., 2001). Emission factors were also calculated. It was shown that the majority of particle-associated PAHs were found on particles with an aerodynamic diameter of <1 μ m. The concentrations of PAHs were one order higher in magnitude in air samples from the tunnel than in air samples at two urban locations. The total emission rates were 1.17 mg/mi for PAHs and 0.81 mg/mi for total suspended PM. Notably, there was no significant change in the total emissions when the proportion of heavy-duty vehicle and light-duty vehicle varied. Concentrations of dibenzothiophene, phenantrene, anthracene and

monomethyl-derivatives of phenantrene and anthracene were all correlated to the proportion of HDVs. The concentrations of naphthalene, some mono- and dimethylnaphthalenes and most large PAHs (with 5–7 fused rings) were correlated to the proportion of LDVs.

Recently, Laschober et al. (2004) studied PM emissions from on-road vehicles in the Kaisermühlen tunnel (Vienna, Austria). The emission factors found in the Kaisermühlen tunnel were remarkably lower compared to earlier tunnel studies such as in the Caldecott tunnel (Allen et al., 2002), in the Sepulveda tunnel (Gillies et al., 2001) and in two road tunnels in Gothenborg, Sweden (Sternbeck et al., 2002).

Table 5-5. On-Road Emission Factors from Foreign Tunnels

Tunnel	Benzene	1,3-Butadiene	NMHC	PM	Reference
	mg/mi	mg/mi	g/mi	g/mi	
Taipei, Taiwan	19.65±5.25	4.12±2.59	0.71		Hwa, 2002
Chung-Cheng, Taiwan			2.43		Hsu, 2001
Gubrist, Switzerland					
LD			0.74		John, 1999
HD			0.47		John, 1999
All vehicles	16.70±3.77	2.59±0.34	0.71		John, 1999
LD				0.013.7 ^a	Weingartner, 1996
HD				0.617.2 ^a	
HD				0.620a	Stahelin, 1996
All vehicles				0.0898	Weingartner, 1997
Kaisermühlen tunnel, Austria				0.07532	Laschober, 2004
Tauern tunnel, Austria				0.122	Schmid, 2001
Tingstad tunnel, Sweden				0.174	Sternbeck, 2002
Lundby tunnel, Sweden				0.833	Sternbeck, 2002

^aPM₃.

Table 5-6. Emission Factors for PAHs in the Lundby Tunnel and Baltimore Harbour Tunnel. ($\mu\text{g}/\text{mi}$)

Species	Lundby tunnel			Baltimore harbor
	PUFs	Filters	PUF+filter	
Naphthalene	180.2		180.2	
2-Methylnaphthalene	170.6		170.6	
1-Methylnaphthalene	103.0		103.0	
Biphenyl	53.1		53.1	
2,6-Dimethylnaphthalene	35.4		35.4	
Acenaphthylene	11.9		11.9	
Acenaphthene	11.1		11.1	
2,3,5-Trimethylnaphthalene	8.0		8.0	
Fluorene	69.2	1.8	72.4	
Dibenzothiophene	2.3	0.4	2.7	
Phenanthrene	225.3	41.8	267.1	61.2
Anthracene	10.3	8.4	19.3	9.7
2-Methylanthracene	1.3	5.0	6.3	3.2
1-Methylphenanthrene	13.0	6.1	19.3	12.9
1-Methylanthracene	12.7	5.3	17.7	
Fluoranthene	20.9	62.8	82.1	12.9
Pyrene	19.3	77.2	96.6	12.9
Retene		0.3	0.3	
Benzo[a] anthracene		3.2	3.2	3.2
Chrysene		3.4	3.4	4.8
Benzo[b] fluoranthene		1.1	1.1	4.8
Benzo[k] fluoranthene		0.1	0.1	
Benzo[e] pyrene		0.9	0.9	1.6
Benzo[a] pyrene		0.9	0.9	3.2
Perylene		0.3	0.3	
Indeno[1,2,3,cd]pyrene		0.4	0.4	1.6
Dibenzo[a,h] anthracene		0.2	0.2	
Benzo[ghi] perylene		1.4	1.4	3.2
Coronene		0.5	0.5	
SPAH, gas phase	946.3			
SPAH, particle phase		222.1		
SPAH, gas+particles			1168.4	130.4

6. Fuel effects

Effects of fuel composition on the TACs have been reported in a number of studies. A summary of the results of some of studies for each individual MSAT species is provide below for both gasoline and diesel vehicles.

6.1 Gasoline Engines and Vehicles Air Toxic Emissions

6.1.1 Benzene

Fuel precursor relationships were most clearly defined for benzene. Exhaust benzene content increases with both fuel benzene and fuel aromatics content, with the effect of fuel benzene being about 10 times that of an equal fraction of an alkyl aromatic compound.

Some of the earliest emission studies of benzene were conducted in the middle – 1980s with a focus on fuel effects on benzene emissions (Seizinger et al., 1986; Bogdonoff et al., 1988; Marshall, 1988; Marshall and Gurney 1989, Zafonte and Lyons, 1989; Boekhaus, et al., 1990). The data showed the benzene level in the exhaust was linearly related to both benzene and total aromatics in the test fuels. The regression coefficients reported in these studies are summarized in Table 6-1.

Table 6-1. Fuel Effects on Benzene Emission

Study	Regression coefficient for wt. % benzene in exhaust				Increase factor ^a	Fuels used	Vehicle tested
	Benzene	C7	C7+	C8+			
Seizinger et al., 1986	0.77		0.13		0.9 %	8	5
Marshall, 1988	0.97		0.087			10	5
Boekhaus, et al., 1990	0.90	0.09		0.07		9	2
Bogdonoff et al., 1988					0.60% 0.96% ^b	2	41

^a: The percent of increment in exhaust benzene of total exhaust HC (wt %) for each 1 vol.% increase in fuel benzene content.

^b: The increase in engine emissions by each 1 vol.% increase in fuel benzene content.

For each 1 vol.% increase in fuel benzene content, Seizinger et al. (1986) found the average increment in exhaust benzene was about 0.9 wt% of the total exhaust hydrocarbon (HC). Bogdonoff et al. (1988) found that the average increment in tailpipe

benzene was 0.6% for total HC, or 1.05 mg/mile and the increment in engine-out benzene emission was 0.96% by each 1 vol.% increase in fuel benzene content. Zafonte and Lynos (1989) measured benzene in the exhaust and in the fuel. The average benzene fraction in the exhaust was 4.5% while that in the fuel was 1.8%, with the exhaust benzene to fuel benzene ratio being 2.5. The exhaust fractions for toluene, ethylbenzene, and xylenes were all about equal to their fractions in the fuels.

The contribution of other specific aromatic compounds to exhaust benzene formation was varied and lower than benzene. Marshall and Gurney (1989) measured the contribution of specific aromatic compounds to exhaust benzene formation using ten fuels with aromatics content ranging from 23 to 49 vol. %. They found that each 1 vol.% increment in benzene in the fuels produced on average about 12 times more benzene in the exhaust than a 1 vol.% increment in the other aromatic compounds. With the 10 fuels, exhaust benzene averaged about 4 wt.% of total engine-out hydrocarbons and about 3 wt.% of tailpipe hydrocarbons. The effect of ethylbenzene was the smallest and statistically insignificant. With one fuel containing alkylates alone without benzene and only 0.2 vol.% of other aromatics, exhaust benzene averaged 0.3 wt.%, showing that some benzene might also be formed from non-aromatic precursors. Boekhaus, et al. also observed a good correlation of exhaust benzene with fuel benzene, toluene, and C7+ aromatics. These researchers found a 44% decrease in the exhaust benzene for five vehicles tested on EC-1 with 21 wt.% aromatics and 0.8 wt.% benzene in comparison with a reference gasoline having 34 wt.% aromatics and 1.8 wt.% benzene.

Effects of reformulated gasolines on the toxic air pollutants have been reported in a number of studies. Reformulated gasolines have the potential of the reduce benzene emissions because of reductions of both benzene and aromatics content of reformulated gasolines (Warner-Selph and Harvey, 1990; Boekhaus et al., 1990; Stump et al., 1990a, b ; Schoonveld and Marshall, 1991). Warner-Selph and Harvey (1990) found that exhaust benzene decreased about 25% or more with three oxygenated fuels (MTBE, ETBE, and ethanol) over the five vehicle test fleet when aromatic content was reduced by 35 to 48% and the corresponding benzene content was reduced by 16 to 28%. Boekhaus et al. (1990) found a 44% decrease in the exhaust benzene fraction on EC-1 with 21 wt.% aromatics and 0.8 wt.% benzene in comparison with a reference gasoline having 34 wt.% aromatics and 1.8 wt. % benzene. Schoonveld (1991) found an average decrease of 40% in the benzene fraction of exhaust on a reformulated gasoline with 20 vol.% aromatics and 0.9 vol.% benzene in comparison with a base fuel having 31 vol.% aromatics and 1.4 vol.% benzene.

Stump and coworkers also examined evaporative emissions as part of their test program to evaluate the influence of oxygenated fuels on emissions at varying temperatures. These studies included a 1988 (Stump et al., 1990a) and a 1987 (Stump et al., 1990b) GM Corsica. For the 1988 GM Corsica, evaporative tests were conducted for an 8.1% ethanol and a 16.2% MTBE blend. Benzene evaporative emissions were also measured in these studies. The 1988 Corsica showed a consistent trend of increasing benzene emissions for the ethanol blend for all diurnal and hot soak evaporative tests. For the 1987 Corsica, on the other hand, the evaporative benzene emissions did not show any

clear trend, although there was a considerable decrease in benzene emissions for the diurnal 84-108°F for the ethanol blend.

Work by the Auto/Oil Air Quality Improvement Research (AQIRP) has highlighted fuel parameters, which are important for the development of reformulated gasoline (Gorse et al., 1991; Koehl et al. 1991; Reuter et al., 1992). These studies evaluated the gasoline fuel compositional variables including aromatic content, MTBE content, olefin content, and the 90% distillation temperature (T90). Regression analyses were performed for a “current fleet” of 20 vehicles with model years of 1989 and an “old fleet” of 14 vehicles with model year from 1983 to 1985. The results were summarized in Table 6-2. Regression analysis for 20 vehicles with 1989 model year showed that reducing fuel aromatic content from 45% to 20% lowered benzene emissions by 42%. Reducing T90 lowered benzene emissions by 11%. Addition of MTBE or a reduction of fuel olefins did not significantly affect benzene emissions. Gorse et al. (1991) found that for older vehicles reducing aromatic content or adding MTBE resulted in lowered benzene emissions by 31 and 11%, respectively. Changes in T90 or olefin content did not significantly affect benzene emissions. Gorse et al. also evaluated interactions affecting benzene emissions and found that reducing olefins lowered benzene only when aromatics were low.

Table 6-2. Fuel Effects of Changes in Fuel Variables on Benzene Emissions
(Percent Change)

		Aromatics 45%→20%	MTBE 0→15%	Olefins 20%→5%	T90 360°F→280°F
1989 vehicles					
Main effects		-41.8±4.5	-5.5±5.6	-3.0±5.6	-10.8±6.1
Interactive effects	Low Olefins	-46.8±6.3			
	High Olefins	-35.1±6.3			
	Low aromatics			-9.3±7.9	
	High aromatics			6.9±7.9	
1983-1985 vehicles					
Main effects		-30.9±6.2	-10.5±7.0	-6.1±7.1	-1.3±8.4
Interactive effects	Low T90		-19.9±9.9		
	High T90		-1.7±9.9		
	Low MTBE				11.4±11.9
	High MTBE				-8.2±11.9

Gorse et al., 1991.

Koehl et al. (1991) reviewed the effect of gasoline composition and physical properties on automotive exhaust and evaporative emissions. Exhaust benzene content was found to decrease with both decreasing benzene and aromatics content. The effect of fuel benzene is about ten times that of non-benzene aromatics.

Thummadetsak et al. (1999) from Petroleum Authority of Thailand conducted exhaust emission tests in 6 vehicles operating on 15 fuels. Eight fuel parameters were examined: RVP, T50 and content of aromatics, olefins, benzene, MTBE, ethanol and sulfur. Reducing aromatics or benzene from 45% to 20% in fuel decreased benzene in exhaust by factors of 36.3% for catalyst vehicles and 27.5% for NC vehicles.

Work by Jemma et al. (1992) from Ricardo Consulting Engineers Ltd. on speciation of hydrocarbon emissions from European vehicles showed significant benzene reductions in exhaust using California reformulated gasoline compared to a typical European gasoline. Hoekman (1992) conducted experiments with conventional and reformulated gasolines from different emission control technology vehicles. The results showed that the reformulated fuel reduced total toxics from TWC vehicles (by 12%) as a consequence of the large benzene reductions from these vehicles (by 19%). For OC vehicles, the reformulated fuel increased aldehyde emissions offsetting the benzene decrease resulting in a net increase of total toxics. UK researchers Perry and Gee (1995) from Imperial College also observed that the emissions of benzene were dependant upon the aromatic content of the gasoline, with benzene forming between 4 and 7% of the total hydrocarbon emissions.

In a study by Rueter et al. (1992), the impact of ethanol, MTBE, and ethyl tertiary butyl ether (ETBE) on toxic emissions was measured for twenty 1989 vehicles. Each of these three oxygenates showed a significant reduction in benzene. The reduction factors were 11.5% for ethanol, 11.2% for MTBE, and 8.1% for ETBE. The combined effect of the three oxygenates was approximately a 10.5% reduction in benzene. This is probably due, in part, to the lower benzene concentration in these fuels compared to the non-oxygenated fuels. These results are consistent with a previous study by Gorse et al. (1991) and a more recent study (Winebrake and Deaton, 1999).

Mayotte et al. (1994 a and b) conducted a series of tests comparing the effects of oxygenates and other parameters such as RVP, T90, and sulfur on TACs. The results from these studies for ethanol showed benzene emissions decreased about 28% with ethanol addition for normal emitters vehicles and around 39% for high emitter vehicles.

In Europe, CONCAWE investigated the influence of gasoline benzene and aromatics content on benzene exhaust emissions from noncatalyst and catalyst equipped cars (McArragher et al., 1996). This study was based on data from CONCAWE member companies and an Italian industry programme, and included the results of emission tests on 21 conventional non-catalyst and 34 catalyst cars. If benzene emissions are expressed as a percentage of total hydrocarbons emitted, then the effect of gasoline benzene content and other aromatics varies between vehicle type. More specifically, the influence of fuel benzene content was found to be over 18 times greater than that of non-benzene aromatics for non-catalyst cars. For catalyst-equipped cars, the effect of benzene content was 10 times greater than that of other aromatics. Moreover, benzene exhaust emissions from catalyst cars were substantially lower. On average, emissions were reduced by around 85%, demonstrating the efficient control provided by the catalysts employed.

6.1.2. 1,3-Butadiene

1,3-Butadiene has rarely been found in gasoline, but it is found in exhaust as a combustion product of other hydrocarbons. Exhaust 1,3-butadiene appears related to non-aromatic fuel hydrocarbons, but specific precursors have not been identified. The data on precursor hydrocarbons of 1,3-butadiene are rather limited. Warner-Selph and DeVita (1989) found that 1,3-butadiene comprised 0.26 and 0.49 wt. % of the total FTP exhaust hydrocarbons from a 1987 and a 1986 vehicle, respectively. Stump et al. (1989 and 1990a) conducted emission measurements for 20 1984 to 1987 model cars tested with two different fuels. The fuels had 4.6 and 12.7% olefins and 30 and 44% aromatics, respectively. They found that during bag 1 of the FTP and in idle tests, the average concentrations of 1,3-butadiene were 0.07 to 0.13% of total HC emissions with 9 of the vehicles and 0.28 to 0.55% with the other 11 vehicles. There was no significant difference in 1,3-butadiene emissions between the two test fuels. The emission rates of 1,3-butadiene for gasoline vehicles are summarized in chapter 3. The wide variation observed in 1,3-butadiene values may be due to variation in fuel composition, engine operating conditions, and analytical difficulties.

Dempster and Shore (1990) found that isooctane alone or blended with benzene or toluene produced only one-fifth as much 1,3-butadiene as a conventional gasoline. They theorize that 1,3-butadiene formation requires precursors that can produce linear four-carbon fragments. Emissions of 1,3-butadiene from their test gasoline were sensitive to air-fuel ratio and increased 60-80% at lean or rich conditions, while isooctane based fuels showed no significant response. Koehl et al. (1991) reviewed the effect of gasoline composition and physical properties on automotive exhaust and evaporative emissions. Koehl found that exhaust 1,3-butadiene appeared to be related to non-aromatic fuel hydrocarbons, but specific precursors were not defined. Auto/Oil AQIRP data also showed that reducing fuel-aromatic content (increasing non-aromatic content) increased 1,3-butadiene emissions.

The effects of reformulated gasoline on 1,3-butadiene emission were studied in detail in Auto/Oil AQIRP. The reduction of 1,3-butadiene emission has been seen in Auto/Oil studies (Gorse et al., 1991 and 1992; Reuter et al., 1992). As mentioned before, Gorse et al (1991) made regression analysis of 1,3-butadiene on the gasoline fuel compositional variables for a fleet of 20 vehicles with 1989 model years and a fleet of 14 vehicles with model years from 1983 to 1985. The results were summarized in Table 6-3. The results showed reducing fuel olefin content lowered exhaust 1,3-butadiene by about 31%, and the reduction of T90 lowered 1,3-butadiene emissions by 37% for all vehicles. The addition of MTBE lowered 1,3-butadiene by 9% for vehicles with 1989 model year and 3% for older vehicles. Reducing fuel aromatic content raised the level of 1,3-butadiene by 11% for "current fleet" vehicles with model years 1989, but had no effect for older vehicles.

Table 6-3. Fuel Effects of Changes in Fuel Variables on 1,3-butadiene Emissions
(Percent Change)

		Aromatics 45%→20%	MTBE 0→15%	Olefins 20%→5%	T90 360°F→280°F
1989 vehicles					
Main effects		11.3±4.5	-8.8±6.4	-31.6±4.9	-36.8±5.4
Interactive effects	W/O MTBE	-4.2±10.1			
	With MTBE	19.3±10.1			
	Low aromatics		-2.3±10.1		
	High aromatics		-14.7±10.1		
	Low T90			-36.6±6.9	
	High T90			-26.4±6.9	
	Low Olefins				-40.9±7.7
	High Olefins				31.5±7.7
1983-1985 vehicles					
Main effects		-0.6±14.8	-3.3±14.6	-31.3±12.0	-37.4±13.3
Interactive effects	Low T90	18.3±20.9			
	High T90	-15.8±20.9			
	Low T90		-22.4±20.6		
	High T90		19.3±20.6		
	Low aromatics, W/O MTBE				-7.9±26.6
	High aromatics W/O MTBE				-34.4±26.6
	Low aromatics with MTBE				-40.1±26.6
	High aromatics with MTBE				57.4±26.6

Gorse et al., 1991.

Aliphatic compounds could be a more effective source of 1,3-butadiene than aromatic compounds (Jemma, 1992). Other previous work has also shown that fuel-alkenes are a source of alkenes including 1,3-butadiene in the exhaust (Pelz et al., 1990; Lachowicz, et al., 1992). Perry and Gee (1995) observed that olefins were a primary source of 1,3-butadiene, contributing between 0.7% and 1.75% of the total hydrocarbon emissions. This finding is in agreement with Auto/Oil AQIRP (Koehl et al., 1991) studies.

The impact of ethanol, MTBE, and ETBE on toxic emissions has been widely studied (Stump et al., 1990b; Rueter et al., 1992; Auto/Oil study; Perry and Gee, 1995). Stump et al (1990b) conducted emission tests with four different fuels and found no significant differences in 1,3-butadiene emissions between a gasoline fuel without oxygenates, a gasoline with 8.1% ethanol and a gasoline with 16.2% MTBE. Rueter et

al., 1992 found that each of the oxygenates reduced 1,3-butadiene, although only the ethanol response and the combined oxygenate response were statistically significant with reduction factors of 5.7% and 4.2%, respectively. However, several studies compared the effects of ethanol and found no statistically significant changes for 1,3-butadiene (Mayotte et al., 1994a and b; Warner-Selph and Harvey, 1990).

6.1.3 Formaldehyde, Acetaldehyde and Acrolein

Formaldehyde is the lowest molecular weight aldehyde molecule with 1 carbon number and acetaldehyde is the next largest aldehyde compound after formaldehyde with 2 carbon atoms. Formaldehyde does not occur in fuels but is a product of the incomplete oxidation of several fuel components or additives. Formaldehyde is the primary oxidation product of the incomplete combustion of methanol. Acetaldehyde is not present in gasoline, but occurs in exhaust emissions as a partial oxidation product of fuel components and as the primary partial oxidation production of ethanol, and possibly of ETBE, and other fuel additives containing an exposed ethyl group.

In early studies, Wigg (1972) found that formaldehyde increases parallel with decreasing aromatics. Wigg also observed that increasing olefins (alkenes and alkadienes) and paraffins (alkanes) increase formaldehyde emissions. Later, many studies observed that fuels containing MTBE had higher emissions of formaldehyde because of the MTBE containing a methoxy group (Boekhaus, 1990; Warner-Selph and Harvey, 1990; Shoonveld and Marshall, 1991; Jemma, 1992). Boekhaus (1990) found a 15% increase in formaldehyde emissions from non-catalyst cars and an 8% increase in formaldehyde for catalyst-equipped vehicles by fuels with 11 vol.% lower aromatics and 5.5% added MTBE.

Shoonveld and Marshall (1991) measured aldehydes from several reformulated gasolines and found that both formaldehyde and acetaldehyde increased for the reformulated gasoline. The increases for formaldehyde were 20% for non-catalyst vehicles, 58% for OC vehicles, 4% for TWC vehicles, and 48% for TWC vehicles with AL. Acetaldehyde also showed some tendency to increase for the reformulated fuel with a 25% increase for NC vehicles, a 19% increase for OC vehicles, and a 33% increase for TWC vehicles, although an 8% decrease was observed for TWC vehicles with AL. The principal changes in the fuels that may have affected aldehydes were a decrease in aromatics from 31 to 20% while simultaneously increasing the MTBE by 5.3 vol.%.

In several Auto/Oil AQIRP studies, formaldehyde and acetaldehyde exhaust emissions were both raised when aromatics were reduced (Koehl et al., 1991; Gorse et al., 1991). The results are summarized in Table 6-4. Exhaust formaldehyde emissions increased when MTBE was blended in fuels (Koehl et al., 1991; Reuter et al., 1992). Warner-Selph and Harvy (1990) also reported that increased MTBE in the fuel would significantly increase formaldehyde emissions. These increases ranged from 19 to 100% with a 15% MTBE fuel. Acetaldehyde was found to increase when fuels contain ethanol or ETBE (Koehl et al., 1991 and 1992; Reuter et al., 1992). Reuter et al. (1992) also observed that acetaldehyde increased when ethanol or ETBE were blended with gasoline

while the reduction of Reid vapor pressure of fuel had no significant effect on formaldehyde and acetaldehyde emissions. Work by Jemma (1992) on speciation of hydrocarbon emissions from European vehicles also showed emissions of formaldehyde increased for reformulated gasoline.

Table 6-4. Fuel Effects of Changes in Fuel Variables on Formaldehyde and Acetaldehyde Emissions (Percent Change)

Compounds		Aromatics	MTBE	Olefins	T90
		45%→20%	0→15%	20%→5%	360°F→280°F
1989 vehicles					
Formaldehyde	Main effects	23.5±14.4	26.8±14.6	1.3±12.8	-25.7±12.6
Acetaldehyde	Main effects	19.5±10.5	-1.9±9.5	-3.7±9.2	-23.9±9.5
Formaldehyde Interactive effects	Low MTBE	-8.4±20.4			
	High MTBE	41.3±20.4			
	Low aromatics		45.3±20.6		
	High aromatics		11.5±20.6		
1983-1985 vehicles					
Formaldehyde	Main effects	18.8±16.4	18.1±19.2	-2.3±14.5	-2.3±17.1
Acetaldehyde	Main effects	32.8±21.9	4.0±19.2	-6.7±17.8	-9.3±20.2

Gorse et al., 1991.

The results of the studies discussed above strongly show that fuel composition has an effect on the exhaust emissions. However, in these experiments more than one fuel parameter was changed. Studies where only one parameter in the fuel was changed were conducted by Oberdorfer (1967) and Shore et al. (1993). In average exhaust emissions of a car fleet tested on pure single component hydrocarbon fuels (benzene, toluene, o-xylene, cyclo-hexane, isooctane, di-isobutylene), Oberdorfer found increases in total aldehyde emissions in the following order: aromatics < cycloalkane < paraffins < olefins. Shore et al., investigated single fuel parameter changes and conducted experiments with toluene (aromatic), isooctane (branched paraffins/alkane) and di-isobutylene (branched olefins/alkene). These fuels were burned in an early 90's engine. Formaldehyde emissions for aliphatic fuels were five times higher than for the aromatic fuel. Acetaldehyde, acrolein and methacrolein emissions showed the same tendency, with the emissions from olefins being higher than those from the paraffins.

The effects of ethanol addition to gasoline on unregulated emissions have also been studied (Hare and White, 1991; Reuter et al., 1992; Stump et al., 1996; White et al., 1997). These studies found that a great amount of acetaldehyde is formed in the combustion process. SI engines show 2-3 times higher emissions of acetaldehyde with 10% ethanol blends (Hare and White, 1991; Reuter et al., 1992; Stump et al., 1996). While, for two-stroke engine snowmobiles using a 10% ethanol blend, 4.3-5.6 times higher emissions of acetaldehyde have been reported (White et al., 1997). An increase of formaldehyde emissions at low ethanol blends was seen in some studies (Stump et al.,

1996; White et al., 1997), while others showed no significant increase (Reuter et al., 1992).

Fuel effects on toxic exhaust emissions were also measured for a fleet of high emitting vehicles (Knepper et al., 1993). These results actually showed some increases in formaldehyde although there was considerable variation in the test results observed for the higher emitters. Mayotte et al. (1994a and b) also conducted a series of tests on regular emitting vehicles and high emitting vehicles as part of their work discussed above. In the first series of tests, acetaldehyde emissions were found to increase with ethanol addition by 88.9% for normal emitters and 137.9% for high emitters (Mayotte et al., 1994a). Changes in formaldehyde emissions were mixed and not statistically significant. The results of the second series of tests were similar to those from the initial test program, with acetaldehyde emissions increasing by 54.3% for normal emitters and 64.3% for high emitters (Mayotte et al., 1994b). No statistically significant changes were found for formaldehyde.

Stump and coworkers (1990a and b) also examined toxic emissions as part of their work discussed above. Overall, the strongest trends were observed for increased acetaldehyde emissions with the ethanol blend. This trend was observed for both vehicles tested and at all temperatures. In addition to the studies discussed above, the trend of increasing acetaldehyde emissions for ethanol blends has also been observed in several other studies. This includes studies by Environment Canada (Graham, 2002, Kirshenblatt et al., 1993), API (1994), and Knapp et al. (1998).

Recently, Pouloupoulos et al. (2001) from Greece National Technical University of Athens found that acetaldehyde production through the partial oxidation of ethanol seems to be highly dependent on oxygen concentration. In the case of 10% ethanol, the oxygen content of the fuel favors the oxidation of the produced acetaldehyde during the combustion process. Moreover, ethanol seems to be converted primarily to ethylene (the typical dehydration process of ethanol) than to acetaldehyde, since generally higher ethylene engine out emissions were observed for 10% ethanol gasoline. After the catalytic converter, the differences in acetaldehyde emissions between the base and 10% ethanol fuel were insignificant, while low catalytic efficiency in acetaldehyde oxidation was observed for the 3% ethanol fuel.

Magnusson and Nilsson (2002) from Swedish University of Agricultural Sciences investigated carbonyl emissions from a two-stroke chain saw engine using gasoline, an ethanol-blended gasoline, and a pure ethanol. Magnusson and Nilsson found that formaldehyde and acetaldehyde were the most abundant carbonyls in the exhaust. Acetaldehyde dominated for all ethanol-blended fuels, and formaldehyde dominated for gasoline. Acetaldehyde emissions were about 5 times higher for 15% ethanol blend fuel than regular gasoline. When using pure ethanol fuel, the acetaldehyde emissions were as much as 35-44 times higher as compared to regular gasoline, depending on the relative air/fuel ratio (λ) where the comparison was made. The formaldehyde emissions were not so easily correlated to the ethanol content. Formaldehyde emissions had an increase of about 30 to 50% when 50% ethanol was added to the regular gasoline, except for at the

highest λ where the increase was about 95%. This agrees with some earlier studies (Stump et al., 1996; White et al., 1997). However, when adding more ethanol to the fuel, there was no change or there was a decrease in formaldehyde emissions.

6.2 Diesel Engines and Vehicles Air Toxic Emissions

The effects of diesel composition have been reported by a number of studies (Weidmann, et al, 1988; Truex et al., 1998; Oyama and Kakegawa, 2000; Fanick et al., 2001; Schubert et al., 2002; Blanchard et al., 2002; Zhu et al., 2002). These studies have shown that the diesel fuel composition has an effect on the airborne toxics emission rates. The use of biodiesel fuel and synthetic diesel fuels as substitutes for conventional petroleum fuel in diesel engines has also received increased attention and been the subject of a number of studies (Graboski and McCormick, 1998; Durbin et al., 1998; Fanick et al., 2001; Schubert et al, 2002; Nord and Haupt, 2002; Lev-on et al., 2002a and 2002b; EPA, 2002; CARB, 2003). This interest is based on a number of properties of biodiesel including the fact that it is produced from a renewable resource, its biodegradability, and its potential beneficial effects on exhaust emissions. Recently, a number of studies investigated ethanol or water use in diesel as oxygenate (Ahlvik and Brandberg, 2000; Chao et al., 2000; He et al., 2003).

6.2.1 Benzene

To evaluate the emissions impact of fuel changes on the complex speciation of the gas-phase, semi-volatile, and particle-phase components and specifically on emissions of toxic components present in diesel exhaust, CE-CERT and the Statewide Air Pollution Research Center (SAPRC) at University of California, Riverside, as well as the Department of Environmental Toxicology at UC Davis conducted a diesel toxicity study (Truex et al., 1998). For this study, three diesel fuels: a pre-93 fuel (sulfur <5000 ppm Wt, aromatic 33 vol. %), a research fuel with low aromatic content (sulfur <500 ppm Wt., aromatic <10 vol. %), and a reformulated fuel (sulfur 100-300 ppm Wt., aromatic 20-25 vol. %) were tested on a Cummins L10, 6-cylinder inline, turbocharged, 4-stroke direct injected diesel engine over the heavy-duty transient test cycle. They found benzene emission rates for cold and hot start tests were very similar for all fuels and ranged from 5.65 to 8.15 mg/Bhp-hr. Neumann et al. (1999), on the other hand, found that the fuel has a significant influence on the emissions of the gas phase toxic emissions when comparing a reference diesel (sulfur content 0.041 %w/w and aromatics 27.0% w/w) and a clean diesel fuel (sulfur content <0.001 %w/w and aromatics <5.0% w/w). The emissions of benzene, which are already very low in modern diesel passenger cars, were reduced by about 30% with the clean diesel.

Fanick et al. (2001) compared diesel exhaust emissions from four different diesel fuels with different aromatics and sulfur content, a conventional low sulfur D2 diesel (0.03% sulfur, 28% aromatics), a CARB diesel (0.015% sulfur, 8% aromatics), a "Swedish" diesel (<0.001% sulfur, 4% aromatics), and a Fischer-Tropsch (F-T) diesel (<0.0001% sulfur, <0.1% aromatics) fuel. Testing was conducted using a light heavy-duty truck with a Cummins B-series engine operating on a chassis dynamometer and on

an engine dynamometer. The benzene emissions were equivalent with the CARB diesel and the Swedish diesel regardless of operating cycle and significantly lower benzene emissions were observed for the F-T diesel fuel.

Schubert et al (2002) conducted vehicle emission tests with a focus on comparing currently available conventional diesel fuel (aromatic 30.7 mass % and polynuclear aromatics 12.0 mass %) to a synthetic F-T diesel fuel free of aromatics and sulfur. In general, the individual air toxics were lower with synthetic diesel fuel than with conventional diesel fuel for all four toxic compounds and benzene was 50% lower for synthetic diesel fuel than conventional diesel fuel for FTP cycles.

Nord and Haupt (2002) from Sweden compared the emissions from a heavy-duty, Valmet, diesel engine running on a commercially available F-T fuel and a Swedish environmental class 1 diesel fuel. The reduction of emissions when the engine was running on F-T fuel was between 30% and 95% for benzene because of the low aromatic content in FT fuel.

Lev-on et al. (2002a and 2002b) performed a chemical characterization study on four diesel vehicles (two bus and two grocery trucks), using a representative California diesel fuel (sulfur 114.5 ppm, aromatics 16.1 % w/w), emission control diesel no.1 (ECD-1) (sulfur 12.7 ppm, aromatics 17.5 % w/w), and ECD (4.1 ppm, aromatics 7.7 % w/w), all with and without DPFs. One diesel vehicle was also tested with F-T diesel fuel (sulfur <1.0 ppm, aromatics 0.16 % w/w). Two vehicles showed higher benzene emissions for CARB fuel than for other fuels. The other two vehicles had similar benzene emissions for all fuels without aftertreatment.

6.2.2 1,3-Butadiene

Truex et al (1998) conducted testing on three diesel fuels: a pre-1993 fuel, a low aromatic fuel, and a reformulated diesel fuel. The ultra low aromatic fuel had higher 1,3-butadiene emissions (2.46 mg/Bhp-hr) than the pre-1993 fuel (1.8 mg/Bhp-hr) and the reformulated diesel fuel (1.84 mg/Bhp-hr). Ahlvik and Brandberg (2000) from Sweden evaluated the emissions from city buses with diesel fuel and ethanol. Emissions of 1,3-butadiene emission rates were higher for the ethanol than from the diesel fuel.

Sharp et al. (2000) performed detailed chemical speciation measurements for three modern diesel engines with and without OCs using three test fuels including a neat biodiesel fuel, a neat diesel fuel (cetane number 45.2, aromatics, 39.1 wt%), and a blend of 20% biodiesel by volume in the diesel fuel. The authors found that the neat biodiesel reduced 1,3-butadiene emissions by 60% to 80% for OC engines, and the 20% biodiesel blend also reduced 1,3-butadiene mass emissions, but to a lesser extent due to the smaller amount of biodiesel present in the fuel. No significant reductions of 1,3-butadiene emissions were found for engines without OCs.

Zhu et al. (2002) also measured toxics emission rates from four medium-duty diesel powered vehicles using a California diesel fuel, a low sulfur low aromatic diesel

fuel, and some selected bio-diesel fuels and blends. The ultra low sulfur diesel fuel had an aromatic content considerably lower than that of the in-use California diesel fuel and a higher cetane number. They found the ultra low sulfur diesel fuel had lowest 1,3-butadiene emission rates by between 13% to 30% when compared to California diesel fuel.

González et al. (2001) evaluated diesel fuels on a 1991 Series 60 heavy-duty diesel engine in the hot-start transient cycles. The fuels included a diesel fuel with less than 10 wt% aromatic content, and two diesel fuel microemulsions containing 12 vol% of water. The microemulsion with 12 vol% water, which had the highest cetane number, showed a 10% reduction for 1,3-butadiene.

Lev-on et al. (2002 a and b) performed a chemical characterization study with F-T diesel fuel (sulfur <1.0 ppm, aromatics 0.16 % w/w) and some petroleum diesel fuels using a school bus. The F-T diesel fuel showed lower 1,3-butadiene emissions than other fuels.

Fanick et al. (2001) compared diesel exhaust emissions from four different diesel fuels with different aromatic levels and sulfur contents, a conventional low sulfur D2 diesel, a CARB diesel, a “Swedish” diesel, and a F-T diesel fuel on a light heavy-duty truck. The 1,3-butadiene emissions were lower with the CARB diesel (1.3 mg/kW-hr for engine tests and 0.2 mg/km for vehicle tests over FTP cycle) than other diesel fuels (1.5 to 2.0 mg/kW-hr for engine tests and 0.4 to 0.5 mg/km for vehicle tests over FTP cycle).

6.2.3 Formaldehyde, Acetaldehyde and Acrolein

Diesel fuel composition has a large effect on the aldehyde emissions. Weidmann et al (1988) investigated the effect of diesel fuel composition on aldehyde exhaust emissions from a 1.6 liter engine in a naturally aspirated and a turbocharged version on an engine dynamometer over the FTP engine transient cycle. With increasing cetane number (decreasing aromatic content), the ignition quality increased and the aldehyde emissions decreased. Since increasing density decreases cetane number and increasing aromatic content decreases cetane number, they concluded the optimum diesel fuel should have a low density and a low aromatic content to produce minimal aldehyde emissions.

CE-CERT conducted a study of the Evaluation of Factors that Affect Diesel Exhaust Toxicity (Truex et al., 1998). They found carbonyl emission rates for cold and hot start tests are very similar for all fuels, with formaldehyde > acetaldehyde > acrolein. The low aromatic fuel had lower formaldehyde and acetaldehyde emission rates during cold start by about 13%. During the hot start, the pre-1993 fuel had approximately 10% lower acetaldehyde emissions than the low aromatic and reformulated fuels.

Neumann et al. (1999) found that fuel has a significant influence on the emissions of the gas phase toxic emissions in comparing a reference diesel and a clean diesel. The

emissions of formaldehyde and acetaldehyde were reduced by around 40% and 36%, respectively, with clean fuel.

Recently, there are a number of studies of biodiesel fuels, ethanol, and synthetic diesel fuels (Sharp et al., 2000; Ahlvik and Brandberg, 2000; Durbin, et al., 2002; He et al., 2003; Schubert et al., 2002; Nord and Haupt, 2002; Corkwell et al., 2003). Sharp et al. (2000) investigated the effect of biodiesel fuel on transient exhaust emissions from three modern diesel engines with and without an oxidation catalyst. Generally, toxics emissions were lower with biodiesel than with diesel fuel, but reductions were usually small. The level of reduction observed with a biodiesel blend was much more dependent on the test engines. The makeup of aldehyde emissions was similar on all fuels. Generally, about 75% of the total aldehyde mass was made up of formaldehyde, acetaldehyde, and acrolein.

Durbin et al. (2002) conducted emission tests with California diesel fuel, an ultra low sulfur diesel (ECD), and several 20% biodiesel blends. Compared to CARB fuel, no significant reductions were observed for several biodiesel blends, while the reduction for ECD fuel of formaldehyde and acetaldehyde was about 20% for two 1980s vintage diesel vehicles.

Cardone et al. (2002) from Italy investigated biodiesel performance on a turbocharged direct injection passenger car diesel engine fueled with 100% biodiesel. They observed that the higher mean temperatures reached in the cylinder at the higher engine load level (lower values of λ) caused a decrease in both PAH and carbonyl compound emissions levels.

Schubert et al. (2002) from Syntroleum Corp. conducted vehicle emission tests and compared the emission characteristics of conventional, hydrotreated, and F-T diesel fuels in a heavy-duty diesel engine. They found all air toxics were lower from the engine with the hydrotreated fuel and F-T diesel fuel when compared with the conventional diesel fuel. Formaldehyde emissions were the most significant contributor to the lower air toxics. The formaldehyde and acetaldehyde emissions were lower with the hydrotreated fuel and the synthetic diesel fuel than with the conventional diesel fuel. Synthetic diesel fuel produced about 50% less formaldehyde than the conventional diesel fuel during the FTP and about 15% less acetaldehyde during the FTP.

Recently, a number of studies investigated ethanol or water use in diesel as oxygenate (Ahlvik and Brandberg, 2000; Chao et al., 2000; He et al., 2003). Ahlvik and Brandberg (2000) evaluated emissions from city buses with diesel fuel and pure ethanol. They found ethanol had the highest total aldehyde emissions of all fuel options and acetaldehyde (136.8 mg/mi) comprised most of the aldehydes. Formaldehyde emissions from ethanol were actually lower than from diesel fuel. The explanation is that acetaldehyde is more difficult to oxidize than formaldehyde.

Chao et al. (2000) from National Cheng-Kung University, Taiwan studied the effect of a methanol-containing additive on the emission of carbonyl compounds from a

heavy-duty diesel engine over both cold-start and hot-start transient cycle tests and for both low-load and high-load steady-state tests. In either transient cycle tests or steady-state tests, the use of either the 10% or 15% methanol-containing additive caused a significant increase in the emissions of carbonyls.

Chinese researchers He et al. (2003) from Tsinghua University investigated the effect of ethanol blended diesel fuel on combustion. The authors found that the addition of ethanol to fuel has little effect on formaldehyde emissions since formaldehyde is an intermediate of oxygenating diesel fuel. However, acetaldehyde emissions increase sharply with the increase in ethanol content, which means that acetaldehyde emissions are converted from ethanol in the blends. The acetaldehyde emission ratio is about 1:2:4 for a diesel engine fueled with pure diesel and ethanol blended diesel fuels containing 10% and 30% ethanol by volume.

6.3 PM Emissions

A number of fuel studies have investigated the possibility of reducing PM emissions. Among the parameters investigated include sulfur level, aromatics content, cetane number and oxygen content. A brief review of some of the basic properties of diesel fuel and their effects of PM emissions is provided in the following subsection.

6.3.1 Sulfur

The reduction of fuel sulfur was considered to be one of the more important fuel variables in reducing PM to the emissions standards that were required during the 1990s. It has been observed that between 1-3% of fuel sulfur is converted to sulfate which contributes to the total PM mass, while the remainder is exhausted as sulfur dioxide (Baranescu, 1988). A number of studies have demonstrated that, at sulfur levels between 3,000 and 500 ppm, decreasing sulfur levels can have a significant impact in reducing total PM, with reductions ranging from 0.0166 to as high as 0.0328 g/HP-hr per 0.1% wt. % sulfur reduction (Baranescu, 1988; Wall et al., 1987; Wall and Hoekman, 1984; Ullman, 1989; Zelenka et al., 1990). In 1993, federal regulations went into effect limiting the sulfur content of diesel fuel to no more than 0.05% by weight. Fuel sulfur has been limited to these same levels in the Los Angeles Air Basin since 1985. These changes were considered critical to meeting the 1994 particulate standard of 0.1 g/BHP-hr. For example, assuming a pre-1993 fuel sulfur level of 0.3% by weight, sulfates would represent 28% and 70%, respectively, of the total particulate matter at the 1991 and 1994 particulate standard levels of 0.25 g/bhp-hr and 0.10 g/bhp-hr (Richards and Sibley, 1988). The reduction of fuel sulfur has also facilitated the use of aftertreatment technologies, such as oxidation catalysts.

As part of EPA’s Heavy-Duty Engine Working Group, Lee et al. (1998) reviewed the effects of fuel sulfur, focusing on engines designed to meet 1991 through 1998 US standards. These authors observed that the reduction of diesel fuel sulfur levels from 3,000 to 500 ppm resulted in relatively large PM benefits (~0.04-0.08 g/bhp-hr). In contrast to the results at higher sulfur levels, Lee et al. (1998) found reducing the sulfur level below 500 ppm had a smaller impact on PM reduction for current or older engines (~0.006-0.013 g/bhp-hr). A graph of PM as a function of fuel sulfur level for different studies is included in figure 6-1.

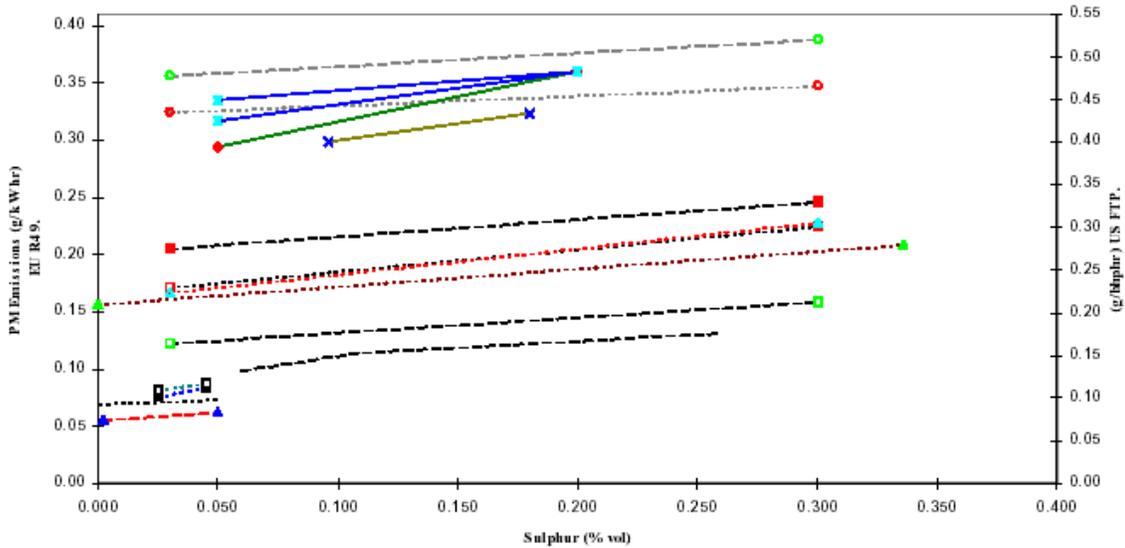
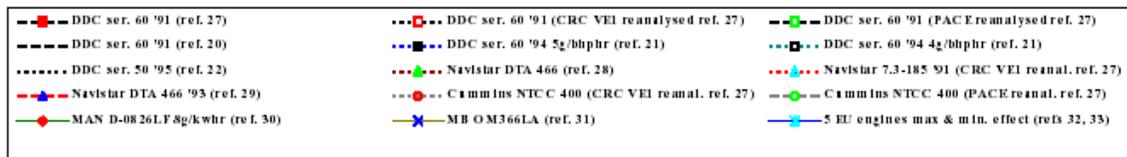


Figure 6-1: Effect of Sulfur on Particulate Emissions



Considerably lower fuel sulfur levels, on the order of 15 ppm, are required for the use of diesel aftertreatment systems such as DPFs and NO_x aftertreatment, either for engines meeting future 2007 standards or engines being retrofitted with DPFs. DOE has sponsored two relatively large efforts to examine the effects of diesel fuel sulfur levels on diesel aftertreatment systems. The Diesel Emissions Control – Sulfur Effects Project (DECSE) was the first of these major programs (see NREL). The DECSE program investigated DPFs, lean NO_x catalysts, DOCs, and NO_x adsorber catalysts. These technologies were tested on several engines of 1998/1999 vintage with fuels with fuel sulfur levels of 3, 30, 150, and 350 ppm and 16 and 78 ppm for the NO_x adsorber catalyst project. The results showed that increasing fuel sulfur level from 3 to 350 ppm produced an essentially linear 29% increase in engine out PM. Fuel sulfur also significantly increased PM emissions after the DPF. In particular, the PM reduction efficiency dropped from 95% at 3 ppm to 73% at 30 ppm to 0% at 150 ppm to a >100% increase at 350 ppm.

NO_x adsorber catalysts had the best performance for NO_x reduction with efficiencies of >90% over a temperature window of 300-450°C while maintaining a fuel economy penalty of less than 4%. The NO_x adsorber experienced a reduction in efficiency when aged on the 3, 16, and 30 ppm fuels, with the greatest reductions observed for the 30 ppm (to about 20%) and the best efficiencies for the 3 ppm fuel (about 70-80%). This technology was recommended as the most promising for meeting future NO_x standards.

The Advanced Petroleum-Based Fuels-Diesel Emissions Control (APBF-DEC) program is a series of 5 different programs, including a study of 2 types of integrated selective catalytic reduction (SCR)/DPF systems at SwRI, 3 separate test programs examining integrated NO_x/DPF systems for a passenger car at FEV Technology, a light-duty truck at SwRI, and heavy-duty engine at Richardo (Thornton, M, 2003). The fuels include sulfur levels of 3 ppm, 8 ppm, 15 ppm, and 30 ppm. For most of the tasks, it appears that the development of the integrated emissions control systems has been completed and the programs have advanced to the stage of durability testing (Tomazic and Tatur, 2003; Webb and Weber, 2003; May, 2003). This program is scheduled for completion by the end of 2004.

During European ACEA diesel PM studies (Vogt, 2002; Mohr, et al., 2003), four fuels with different sulfur contents were tested (gasoline fuel with <10 ppm sulfur content; gasoline fuel with 175 ppm sulfur content; diesel fuel with <10 ppm sulfur content; diesel fuel with 250 ppm sulfur content). A higher fuel sulfur content was found to clearly increase PM emissions from diesel and gasoline vehicles for higher load. The increase in emissions was due to the contribution of condensed material and most of it could be clearly related to sulfur compounds.

6.3.2 Aromatics

A number of early studies have shown that reductions in aromatic content lead to reductions in PM emissions (Bouffard and Beltzer, 1981; Wall and Hoekman, 1984; Burley and Rosebrock, 1979; Hilden et al., 1982; Ullman, 1989; Bertoli et al., 1993). In many of these studies, however, the effects of aromatics were not decoupled from other variables such as density, cetane or other changes. Given the complexity of diesel fuel formulations, it is difficult to isolate the effects of aromatics from those of other fuel parameters. Other researchers have argued that aromatics do not directly affect PM emissions but rather influence these emissions via their effect on the density of the fuel (Lang, 1991; Cowley et al., 1993; Barry et al., 1985; Betts et al., 1992). In the review by Lee et al. (1998), it was observed that, when density was decoupled from aromatics, it had a significant impact in reducing PM emissions from high emitting diesel engines, but little impact on PM emissions from low emitting engines. The reduction of total aromatics by itself was not found to have any impact on PM emissions when isolated from density. Polycyclic aromatics as a fully decoupled fuel parameter have shown a consistent benefit in PM emissions for older engines, but for more modern, lower emitting engines reducing polyaromatics does not have a significant effect on PM emissions.

6.3.3 Cetane Number

The cetane number of diesel fuel is another important fuel parameter that influences emissions. Cetane number indicates the ease with which diesel fuel ignites, with higher cetane number fuels requiring lower temperatures to ignite. The effect of cetane number on PM emissions, however, appears to be very engine dependent (Nikanjan, 1993; Ullman et al., 1994, 1995; Lange, 1991; Sienicki et al. 1990; Cowley et al. 1993; Den Ouden et al. 1993). For many engines, cetane number did not have an influence on PM emissions. In some engines, a small reduction in PM emissions has been observed (Cowley et al. 1993; Den Ouden et al. 1994) while PM emissions were found to increase with increasing cetane number in other engines (Signer et al. 1996; Stradling et al., 1997). Overall, Lee et al. (1998) observed that the effect of increasing cetane number on PM emissions was neutral. The EPA Heavy-Duty Engine Working Group also conducted some additional testing on fuels with different cetane numbers although this was primarily for its potential effects on NO_x (EPA, 1998).

6.3.4 Biodiesel

Several fuels with enhanced levels of oxygen have been introduced that have the potential to reduce engine out PM emissions. The use of biodiesel fuels has expanded considerably in recent years due to its emission reduction potential and renewability. An earlier review of biodiesel emissions was conducted by Graboski and McCormick (1998). EPA conducted an extensive review of emissions test results of biodiesel (EPA, 2002). As part of this work, EPA conducted a correlation analysis to determine the average impacts of biodiesel, although the data showed considerable scatter. For a 20% biodiesel blend, it was found that approximately a 10.1% reduction in PM could be expected compared to a standard federal diesel. Given the more stringent regulations for diesel fuel in California, the emissions benefits relative to California fuels may be different (CARB, 2003).

6.3.5 Fisher Tropsch

Most F-T diesel fuels share a set of common properties – near zero sulfur content, high cetane number, and low aromatic content. The end result of these properties is a fuel that is conducive to reduced emissions compared to conventional diesel fuel. Ultra-low sulfur fuel not only reduces PM emissions, but also enables state-of-the-art aftertreatment technologies. A number of studies have collected emissions data from F-T diesel and F-T/conventional diesel fuel blends in engine and chassis dynamometers. In almost every case, PM emissions were reduced with neat F-T diesel fuel. These reductions have been shown on a variety of light and heavy-duty vehicles and engines. A review of exhaust emissions of diesel engines operating on F-T diesel fuels was recently conducted by

Alleman and McCormick (2003). Average PM reductions were about 26% compared to conventional diesel fuel and average NO_x reductions were 13%.

6.3.6 Ethanol

Ethanol is another oxygenate that is being researched and used in some more limited fleet applications. Ethanol has a relatively low cetane level so typically an additive is needed to bring the cetane level of the blend to an appropriate level. Ethanol diesel blends also have a lower flashpoint than diesel fuel and a higher vapor formation potential in confined spaces, hence, appropriate precautions must be taken to ensure safe use of the blend. A review of exhaust emissions of diesel engines operating on ethanol diesel fuel blends was recently conducted by Corkwell et al. (2003). They found that the changes in PM emissions with ethanol ranged from an increase of 65% to a decrease of 72%. When separated by category, a decrease of 20% in PM emissions was the most frequently observed category and the average reductions were found to be 13% when blended with ethanol at 10% by volume.

6.3.7 EPEFE / Europe

The European Programme on Emissions, Fuels and Engine Technologies (EPEFE) was a cooperative effort between the European Motor Industry (represented by ACEA) and the European Oil Industry (represented by EUROPIA) (Hublin et al., 1996; Cuvelier et al., 2002; Stradling et al., 2004). The EPEFE programme was designed to extend the information on relationships between fuel properties and engine technologies and to quantify the reduction in on-road emissions that can be achieved by combining advanced fuels with advanced vehicle/engine technologies of the time.

The relationships found among fuel properties, engine technologies, and exhaust emissions were found to be complex in the program. Changes in a given fuel property may lower the emissions of one pollutant but may increase those of another (i.e., decreasing aromatics content in gasolines lowers CO and HC emissions but can increase NO_x emissions). In some cases, engines in different vehicle categories, such as heavy duty and light duty vehicles, have disparate responses to changes in fuel properties (i.e., increasing cetane number in diesel fuels lowers NO_x emissions only on heavy duty and light duty DI engines, but not on light duty IDI engines.) A summary of some of the conclusions from the EPEFE program is provided in Table 6-5 and as follows:

Gasoline Fuels / Gasoline Vehicles

- The effect of reducing gasoline sulfur on regulated emissions was generally linear over the range studied. The relative distribution of HC species in the exhaust gases was unaffected by the fuel sulfur content. However, the absolute benzene emissions (g/km) were reduced with sulfur reduction by an amount equivalent to the reduction measured for the total HC emissions. The other three toxics, 1,3-butadiene, formaldehyde and acetaldehyde were unaffected by changes in the sulfur content of the fuel.

- Fuel effects were generally larger for the aromatics matrix than for the sulfur matrix, and were, in many cases, non-linear. Over the ECE cycle, HC emissions increased with increasing aromatic content. Benzene emissions decreased with decreased aromatic content. Formaldehyde and acetaldehyde emissions showed a slight decrease with increasing aromatic content.
- Individual vehicles showed substantial variation in response to fuel properties, especially over the EUDC driving sequence. The vehicles fitted with catalysts containing palladium were more sensitive to sulfur content than those equipped with Pt/Rh catalysts
- The effect of technology on speciated emissions tended to follow that of total HC emissions. There were also some indications that catalyst formulation can have an effect on the conversion efficiencies for aldehydes.

Diesel Fuels / Diesel Vehicles / Heavy Duty Engines

- Reducing fuel density decreased PM emissions in LD vehicles. No significant effect was seen in HD engines. Reducing fuel density also decreased HC, benzene, 1,3-butadiene, formaldehyde and acetaldehyde emissions in LD vehicles.
- Reducing PAH content reduced PM emissions in both LD vehicles and HD engines. Reducing PAH content also reduced HC emissions in HD engines and formaldehyde and acetaldehyde emissions in LD vehicles, but increased benzene emissions in LD vehicles.
- Increasing Cetane Number increased PM in LD vehicles with no significant effect from HD engines, but decreased benzene, 1,3-butadiene, formaldehyde and acetaldehyde emissions from LD vehicles.
- Decreasing T95 increased formaldehyde and acetaldehyde emissions from LD vehicles but decreased PM emissions from LD vehicles.
- Individual vehicle and engines showed a wide range of response to the fuel properties investigated. The impact of the vehicle/engine set on emissions was larger than that of the matrix of fuel properties except for NO_x emissions for HD engines. DI and IDI light-duty vehicles showed the same trend concerning the effect of fuel properties on regulated emissions except for the NO_x response to cetane number.
- The lowest sensitivity to fuel property changes was associated with LD IDI engines and mechanical injection controls. Vehicles equipped with IDI engines achieved consistently lower absolute emission levels (g/km). Interest with DI technology for application on LD vehicles is, however, growing for its performance in terms of fuel consumption.

Following EPEFE, CONCAWE conducted a rigorous test program to examine exhaust emissions from 3 LD vehicles and 2 HD engines representing Euro-3 technology levels (Cuvelier et al., 2002). Cuvelier et al. found that increasing cetane number (from 53 to 58) directionally reduced HC and CO emissions but had no significant effect on PM emissions in either the HD engines or LD vehicles tested.

Table 6-5. Diesel Vehicles Emissions Comparison of Ranges of Fuel

	Light-duty vehicles		Heavy-duty engines	
	HC	PM	HC	PM
Average Emission rate	0.140 g/km	0.049 g/km	0.369 g/km	0.130 g/km
Density 855 - 828 g / l	-0.018 g / km -18.9 %	-0.012 g / km -19.4 %	+0.0332 g/kWh +14.25 %	-0.002 g/kWh -1.59 % ns
Poly aromatics 8 - 1 %	+0.005 g / km 5.5 %	-0.003 g / km -5.2 %	-0.0093 g/kWh -4.02 %	-0.0045 g/kWh -3.58 %
Cetane 50-58	-0.026 g / km -26.3 %	+0.003 g / km +5.2 %	-0.014 g/kWh -6.25 %	0 g/kWh 0 ns
T-95 370-325 °C	+0.003 g / km +3.4 %	-0.004 g / km -6.9 %	+0.0306 g/kWh +13.22 %	0 g/kWh 0 ns

Note : Fuel effects have been described through regression equations. When these are linear it is possible to express these effects on both absolute values and percentage from a baseline. ns : Not Significant. (Diesel density = 855; Poly aromatics = 8 %; Cetane number = 50; T95 = 370C).

7.0 Summary and Conclusions

Since the mid-1980s, there has been a growing concern over the potential health effects of air toxics and PM from internal combustion engines. To reduce these pollutants, California has developed the nation's most extensive and stringent mobile source emission controls and fuels programs. As a result of these programs, air quality in California has improved dramatically over the past 25 years. These continued programs include standards for Cleaner Burning Fuels and Cleaner Diesel Fuel, California Phase I RFG and Phase II RFG, California LEV and ZEV standards, and California LEV II emission standards.

As regulatory standards have gotten increasingly stringent, it is important to understand how air toxic and PM emission rates have changed over the years in order to gauge the expected improvement in air quality. As part of this program, a comprehensive literature search was conducted to review and evaluate emissions of gas-phase air toxics and PM mass and chemical species for gasoline, diesel and alternative internal combustion engines and vehicles. Studies included chassis, engine, and on-road measurements. Nearly 400 documents were identified as part of this survey. A summary of the major conclusions and accomplishments of this project are:

- Gas-phase air toxics (formaldehyde, acetaldehyde, acrolein, benzene, and 1,3-butadiene), PAHs and diesel PM are associated with adverse health effects. Gas-phase toxics and PAHs are formed by the incomplete oxidation of hydrocarbons during combustion. Formaldehyde, acetaldehyde, acrolein, and 1,3-butadiene react rapidly with free radicals in the air. Ambient concentrations of benzene, 1,3-butadiene, and acetaldehyde are considerably below the EPA threshold and CARB chronic reference level. The ambient concentrations of formaldehyde are at the CARB chronic reference level. Acrolein is the only compound that has ambient concentrations above the EPA threshold.
- Data reported here showed large reductions in the airborne toxic and PM emissions from light-duty gasoline- and diesel-powered vehicles over the years as a result of improved emissions control technology and the introduction of cleaner fuels. It is expected that the emissions of these compounds will be further reduced in the future with the introduction of even more advanced technology vehicles.
- Of all the engine and vehicles technologies, the catalytic converter provides the greatest reductions in gas-phase air toxics. For gasoline vehicles, toxic species reductions were about 50 to 70% for oxidation catalysts, 80 to 95% for TWC vehicles, 95%+ for advanced LEVs compared to NC vehicles. For diesel vehicles, a decrease of 70 to 85% in gas-phase air toxic emissions was observed for diesel vehicles equipped with OCs compared to uncontrolled diesel vehicles.
- There is a wide range of toxics and PM emission rates for different heavy-duty vehicle class/model year categories. Toxics and PM emission rates from properly functioning, catalyst-equipped gasoline vehicles are considerably less than those from

uncontrolled diesel vehicles. PM mass emission rates from smoking gasoline-fueled vehicles; on the other hand, can be comparable to those observed for diesel vehicles.

- Diesel vehicles with DPF and low sulfur diesel fuel have significantly reduced PM levels and emit 90 to 99% less PM compared to vehicles having no exhaust aftertreatment. The reduction of gas-phase air toxic emissions is more than 70% for diesel vehicle equipped with catalyzed DPF. Future light-duty diesel vehicles with DPFs should be expected to comply with the light-duty vehicle PM standard of 0.01 g/mile.
- Tunnel studies show significant reductions of gas-phase air toxics and PM emissions due to advances in vehicle technology, fuel composition (i.e., reformulated gasoline), and fleet turnover.
- The most abundant aldehyde in ICE exhaust emissions is formaldehyde, followed by acetaldehyde. In comparison with gasoline, methanol or gasoline/methanol blend engines produce more formaldehyde and ethanol or gasoline/ethanol blend engines produce more acetaldehyde.
- CNG vehicles generally exhibit reductions in PM and PAHs compared to uncontrolled diesel vehicles. CNG vehicles also generally have low gas-phase air toxic emissions, with the exception of formaldehyde, which is usually higher for CNG vehicles. The use of DPFs can reduce PM and other gas-phase emissions from diesel applications to levels comparable to those of CNG vehicles.
- Fuel properties can also effect the emissions of air toxics. Exhaust benzene and PAH content increase with both fuel benzene and fuel aromatics content. Reducing fuel olefin content and T90 lower exhaust 1,3-butadiene emissions. Aldehyde emissions increase with fuel olefins, paraffins, and oxidation content.
- For PM emissions, significant reductions are found when fuel sulfur is reduced in the range between 3000 and 500 ppm. The reduction in the sulfur content below 500 ppm produces smaller PM emission reductions. In California, the reduction of fuel sulfur from 140 to 10 ppm is expected to reduce PM emissions by 4% before aftertreatment. Fuel aromatics do not appear to effect PM emissions when decoupled from density, although reducing PAH content does reduce PM in older engines. The effect of cetane number on PM emissions is engine dependent, with many engines showing no effect. There are a number of advanced/alternative diesel fuels that show promise in providing further PM reductions, including Fischer-Tropsch diesel, biodiesel, and ethanol diesel blends.

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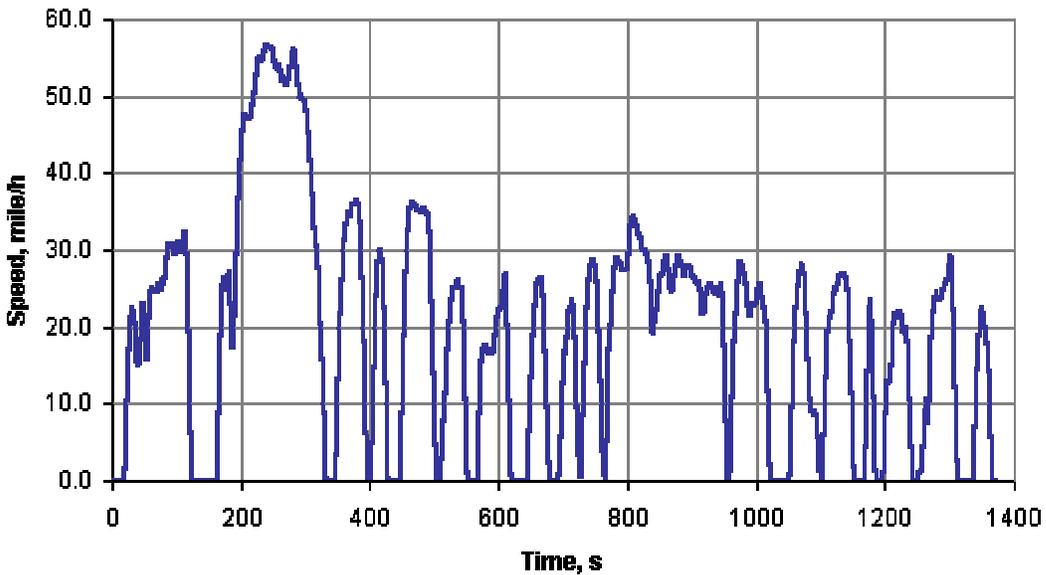
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Attachment A: Testing Cycles

Federal Test Procedure (FTP72)

The U.S. FTP-72 (Federal Test Procedure) cycle is also called Urban Dynamometer Driving Schedule (UDDS) or LA-4 cycle [CFR 40, 86, App.I]. The same engine driving cycle is known in Sweden as A10 or CVS (Constant Volume Sampler) cycle and in Australia as the ADR 27 (Australian Design Rules) cycle.

The cycle simulates a urban route of 12.07 km (7.5 mi) with frequent stops. The maximum speed is 91.2 km/h (56.7 mi/h) and the average speed is 31.5 km/h (19.6 mi/h).



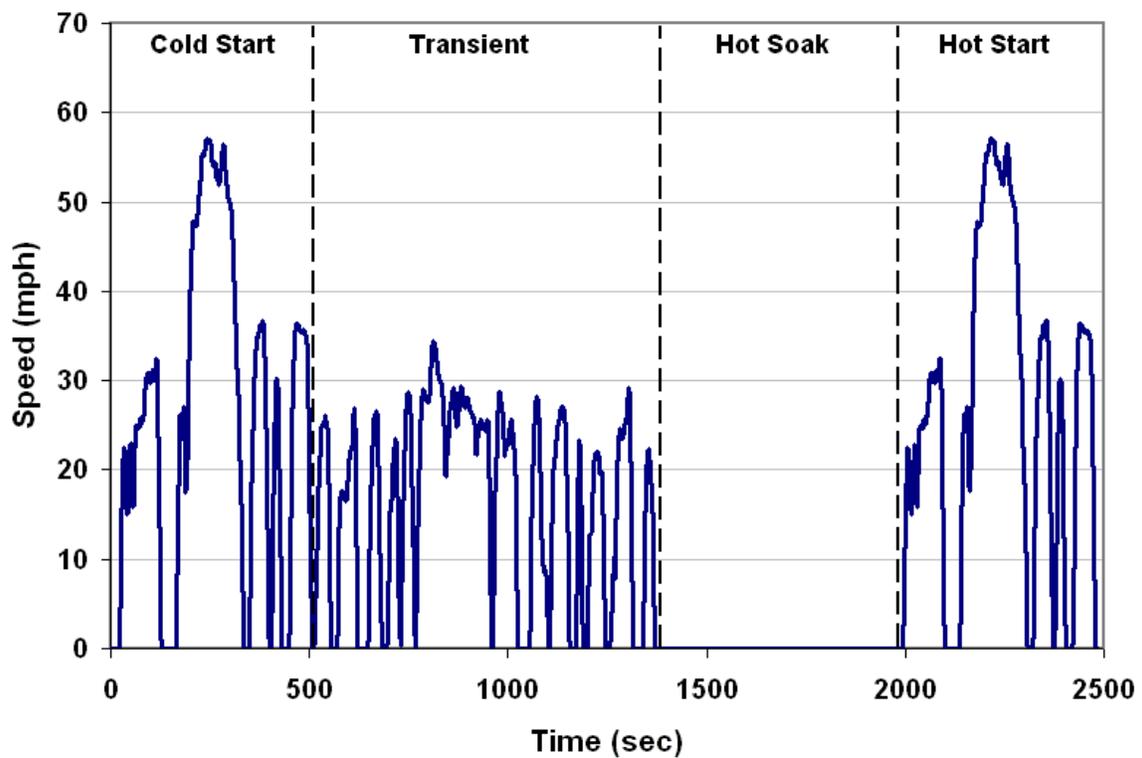
Federal Test Procedure (FTP75)

The FTP is a three-phase cycle designed to represent emissions under cold start conditions, hot stabilized operating conditions over an urban route, and hot start conditions.

Distance traveled: 11.04 miles

Duration: 1874 s

Average speed: 21.2 mph



The US06 Supplemental Federal Test Procedure (SFTP)

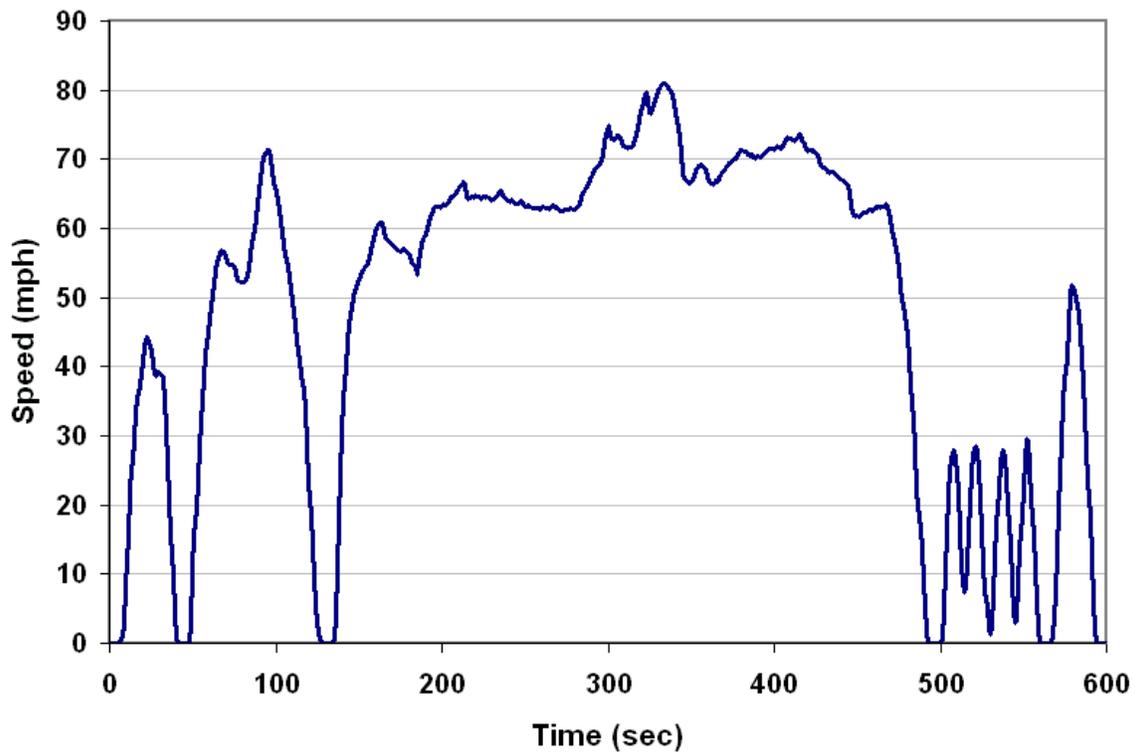
US06 was developed to address the shortcomings with the FTP 75 test cycle in the representation of aggressive, high speed and/or high acceleration driving behavior, rapid speed fluctuations, and driving behavior following startup.

Distance traveled: 8.01 miles

Duration: 596 s

Average speed: 48.4 mph

Maximum speed: 80.3 mph



EPA New York City Cycle (NYCC)

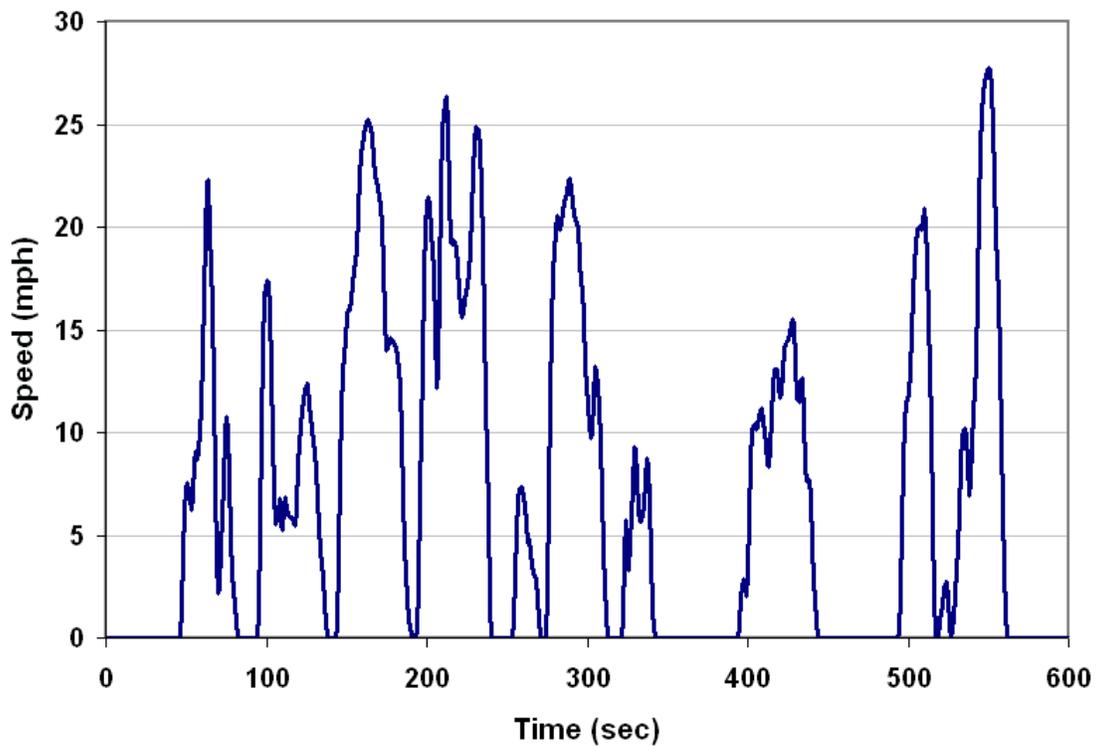
The EPA NYCC simulates low-speed urban driving with frequent stops.

Distance traveled: 1.18 miles

Duration: 598 s

Average speed: 7.1 mph

Maximum speed: 27.7 mph



Highway Fuel Economy Cycle

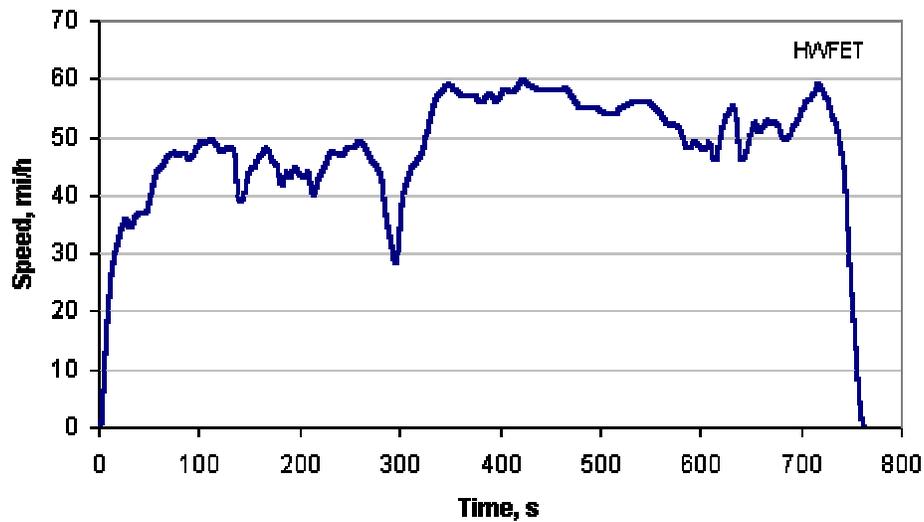
The HWFET cycle is a chassis dynamometer driving schedule, developed by the US EPA for the determination of fuel economy of light duty vehicles.

The following are some characteristic parameters of the cycle:

Duration: 765 seconds

Total distance: 10.26 miles (16.45 km)

Average Speed: 48.3 mi/h (77.7 km/h)



HD UDDS schedule

The EPA UDDS schedule has been developed for chassis dynamometer testing of heavy-duty vehicles (*CFR 40, 86, App.I*). Sometimes referred to as “cycle D”. It should not be confused with the FTP-72 cycle for light-duty vehicles, which is also termed UDDS.

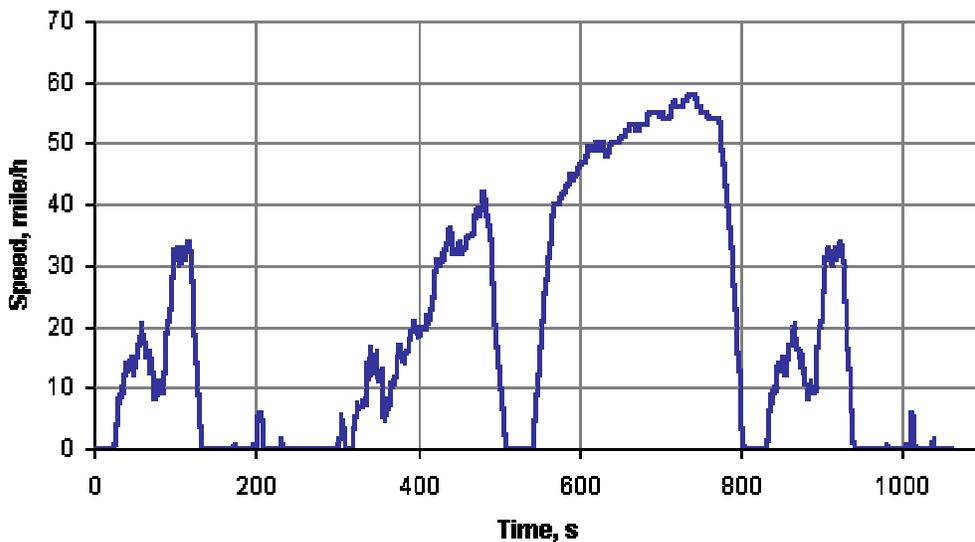
The following are basic parameters of the cycle:

Duration: 1060 seconds

Distance: 5.55 miles = 8.9 km

Average speed: 18.86 mi/h = 30.4 km/h

Maximum speed: 58 mi/h = 93.3 km/h



HD Central Business District (CBD)

The Central Business District (CBD) Cycle is a chassis dynamometer testing procedure for heavy-duty vehicles (*SAE J1376*). The CBD cycle represents a “sawtooth” driving pattern, which includes 14 repetitions of a basic cycle composed of idle, acceleration, cruise, and deceleration modes. The following are characteristic parameters of the cycle:

Duration: 560 s

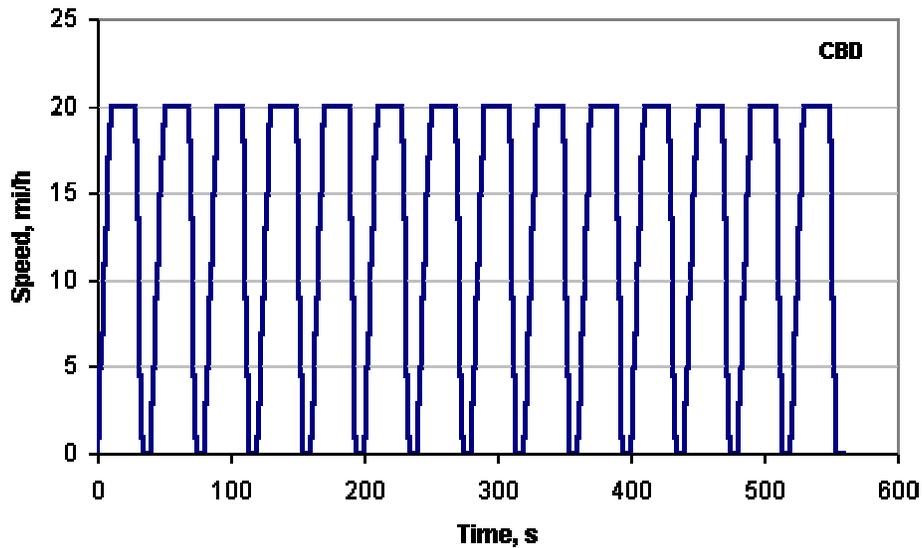
Average speed: 20.23 km/h

Maximum speed: 32.18 km/h (20 mph)

Driving distance: 3.22 km

Average acceleration: 0.89 m/s²

Maximum acceleration: 1.79 m/s²



HD CSC and CSHVR

The City Suburban Cycle (CSC) is a chassis dynamometer test for heavy-duty vehicles developed by the West Virginia University. The CSC is also abbreviated as CSHVC (City Suburban Heavy Vehicle Cycle).

The test is also available in a “route” version—the City Suburban Heavy Vehicle Route (CSHVR)—where the vehicle speed is given as a function of travelled distance, rather than time.

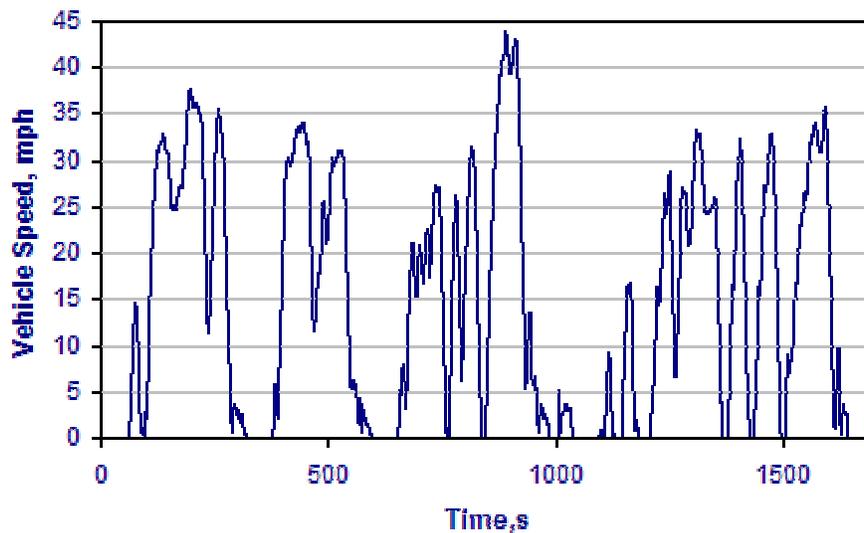
The following are selected parameters of the CSC cycle:

Duration: 1700 s

Total distance: 10.75 km (6.68 mi)

Maximum speed: 70.55 km/h (43.84 mph)

Average speed: 22.77 km/h (14.15 mph)



Australia CUEDC driving cycle

To provide a method of testing vehicles that closely replicates actual on-road driving conditions, the National Environment Protection Council (NEPC) commissioned a study in 1998 (DNEPM Project 2.1) to instrument a range of vehicles and record their actual speed/acceleration profiles in congested, minor roads, arterial and highway driving conditions.

The recorded data was then statistically analyzed and synthesized into drive cycle segments that most accurately reflected the speed-time patterns for each of these four driving conditions, and subsequently combined into a Composite Urban Emissions Drive Cycle (CUEDC). Because vehicles of different types have varying driving patterns, a different CUEDC was developed for each of the six major vehicle categories used for certification in Australia:

MC off-road passenger vehicle

NA light commercial < 3.5 t gross vehicle mass (GVM)

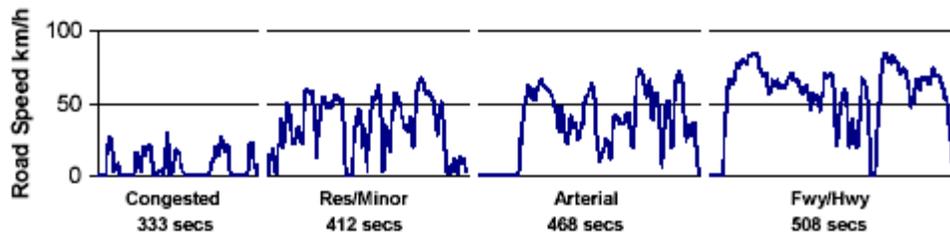
NB medium commercial 3.5 – 12.5 t GVM

NC rigid truck 12.5 – 25 t GVM

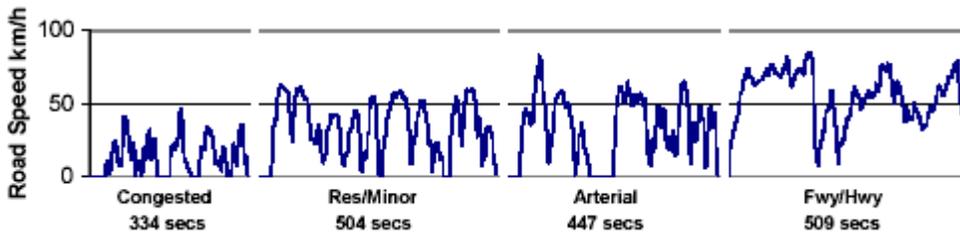
NC-H articulated truck > 25 t GVM

ME bus > 5 t GVM

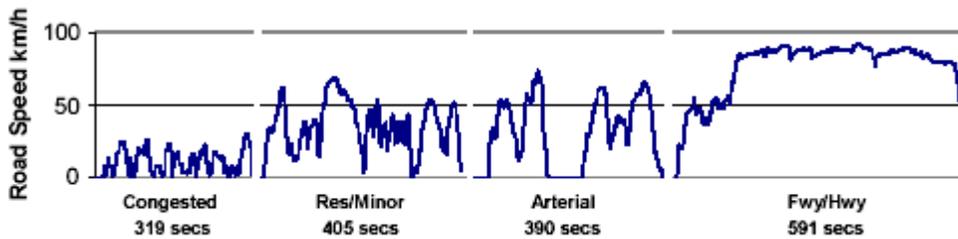
CUEDC for MC Category Vehicles



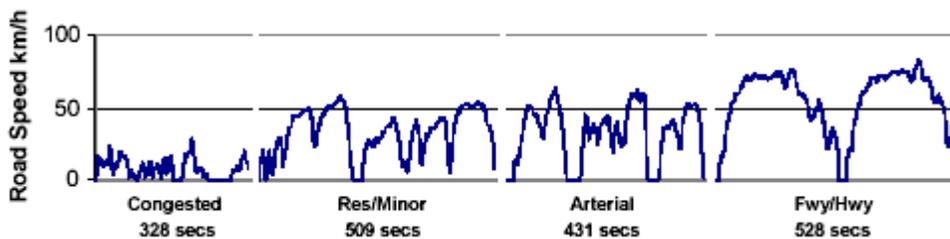
CUEDC for NA Category Vehicles



CUEDC for NB Category Vehicles



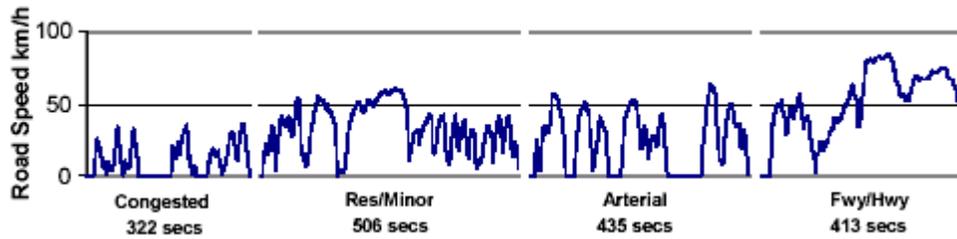
CUEDC for NC Category Vehicles



CUEDC for NCH Category Vehicles



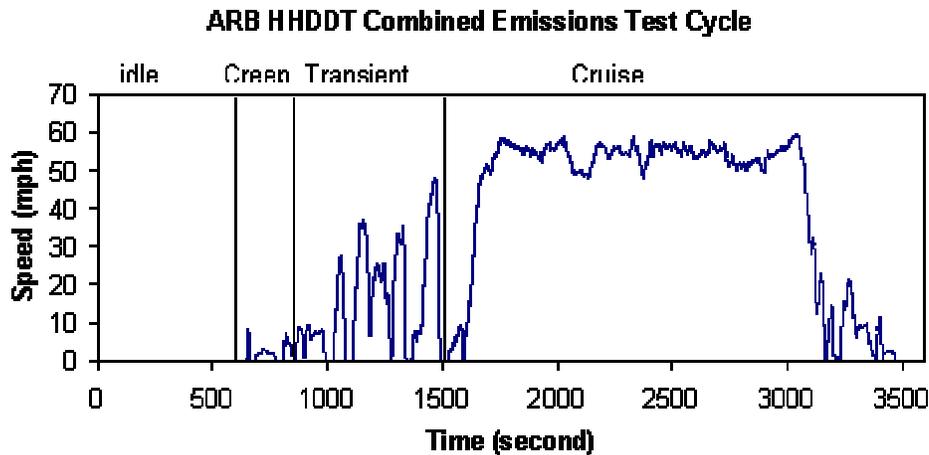
CUEDC for ME Category Vehicles



HHDDT Driving Cycle

Heavy-duty diesel truck (HHDDT) test cycle has been developed by California ARB using real-world driving data. (Maldonado, 2002) The ARB HHDDT test cycle includes four modes: an cold start/idle mode, a very low speed or “creep” mode, an intermediated speed or “transient” mode, and a relatively high speed “cruise” mode. Cold start/idle is a cold-start followed by a ten minute idle. Creep simulates slow driving such as that in a parking lot, a highway weigh station, or heavily congested traffic. The transient phase simulates driving on arterial type roads with light to medium traffic. The cruise phase simulates highway driving.

Mode/cycle	Average speed (mph)	Duration (s)	Distance (mi)
Idle		600	0
Creep	1.8	253	0.12
Transient	15.4	668	2.85
Cruise	39.9	2083	23.1

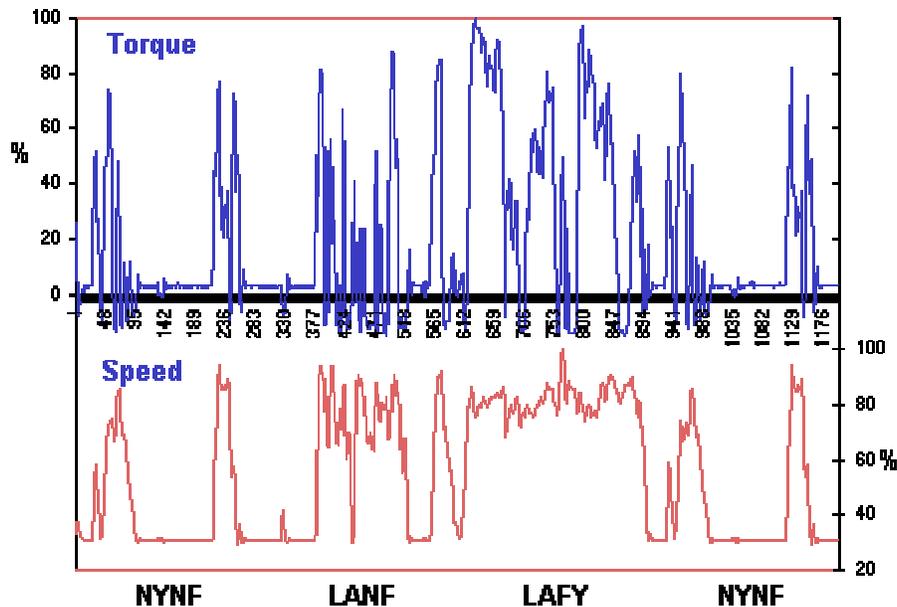


HD FTP Transient Cycle

The FTP (Federal Test Procedure) heavy-duty transient cycle is currently used for emission testing of heavy-duty on-road engines in the USA [CFR Title 40, Part 86.1333]. The transient test was developed to take into account the variety of heavy-duty truck and buses in American cities, including traffic in and around the cities on roads and expressways.

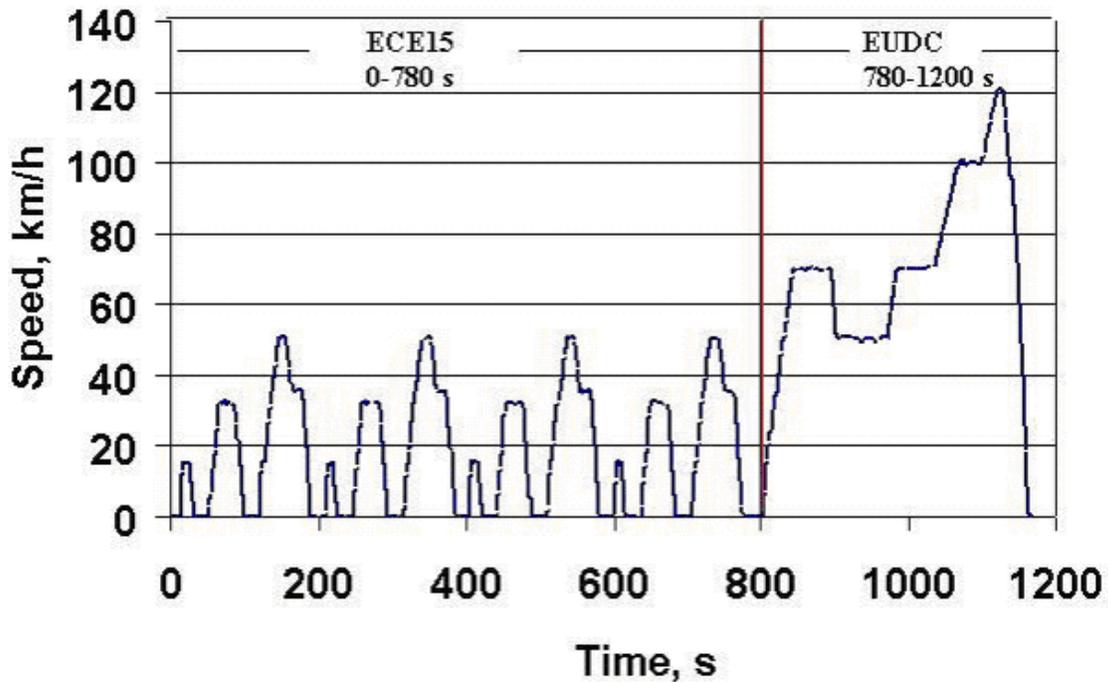
The transient cycle consists of four phases: the first is a NYNF (New York Non Freeway) phase typical of light urban traffic with frequent stops and starts, the second is LANF (Los Angeles Non Freeway) phase typical of crowded urban traffic with few stops, the third is a LAFY (Los Angeles Freeway) phase simulating crowded expressway traffic in Los Angeles, and the fourth phase repeats the first NYNF phase. It comprises a cold start after a parking overnight, followed by idling, acceleration and deceleration phases, and a wide variety of different speeds and loads sequenced to simulate the running of the vehicle that corresponds to the engine being tested. There are few stabilized running conditions, and the average load factor is about 20 to 25% of the maximum horsepower available at a given speed.

The cycle is carried out twice and the second repetition is made with a warm start after a stop of 1200 s (20 min) on completion of the first cycle. The equivalent average speed is about 30 km/h and the equivalent distance traveled is 10.3 km for a running time of 1200 s.



European Driving Cycle (EC2000)

The driving cycle consists of two parts, ECE15 and EUDC, that correspond to urban and highway (extra-urban) driving conditions in that order. ECE15 test cycle simulates a 4.052 km urban trip at an average speed of 18.7 km/h and at a maximum speed of 50 km/h. Its duration is 780 seconds. The same part of the ECE15 driving cycle is repeated four times to obtain an adequate driving distance and temperature. The EUDC cycle instead illustrates the aggressive, high speed driving at a maximum speed of 120 km/h. Its duration is 400 seconds and 6.955 km at an average speed of 62.6 km/h.



AVL 8-Mode

The AVL 8-Mode test is a steady-state engine test procedure, designed to closely correlate with the exhaust emission results over the US FTP heavy-duty engine transient cycle. The test involves 8 steady state modes. The composite value is calculated by applying weighing factors on the modal results.

The sequential engine operating points are as follows:

Mode	% Engine Speed*	% Load	Weight factor**
1	0	0	35.00
2	11	25	6.34
3	21	63	2.91
4	32	84	3.34
5	100	18	8.40
6	95	40	10.45
7	95	69	10.21
8	89	95	7.34

* - Normalized speed: 0% = low idle, 100% = rated speed

** - Relative weight factors, not normalized (they do not add to 100%)

Japanese 13 Mode

The 13-mode cycle replaced the older 6-mode cycle for the testing of heavy-duty engines in Japan. The test includes a sequence of 13 steady-state modes. The emissions are averaged over the entire cycle using a set of weighting factors and are expressed in g/kWh. The test emphasizes low-speed driving conditions, is characterized by low average engine loads and low exhaust temperatures. The test parameters for the diesel cycle are listed in Table.

Mode	Speed	Load	Weighting factor
	% of nominal	%	
1	idle	-	0.410/2
2	40	20	0.037
3	40	40	0.027
4	idle	-	0.410/2
5	60	20	0.029
6	60	40	0.064
7	80	40	0.041
8	80	60	0.032
9	60	60	0.077
10	60	80	0.055
11	60	95	0.049
12	80	80	0.037
13	60	5	0.142

Japanese 10-15 Mode

The 10-15 mode cycle is currently used in Japan for emission certification and fuel economy for light duty vehicles. It is derived from the 10-mode cycle by adding another 15-mode segment of a maximum speed of 70 km/h. Emissions are expressed in g/km [*Japanese Industrial Safety and Health Association, JISHA 899, 1983*].

The entire cycle includes a sequence of a 15 minute warm-up at 60 km/h, idle test, 5 minute warm-up at 60 km/h, and one 15-mode segment, followed by three repetitions of 10-mode segments and one 15-mode segment. Emissions are measured over the last four segments ($3 \times 10\text{-mode} + 1 \times 15\text{-mode}$, Figure 1).

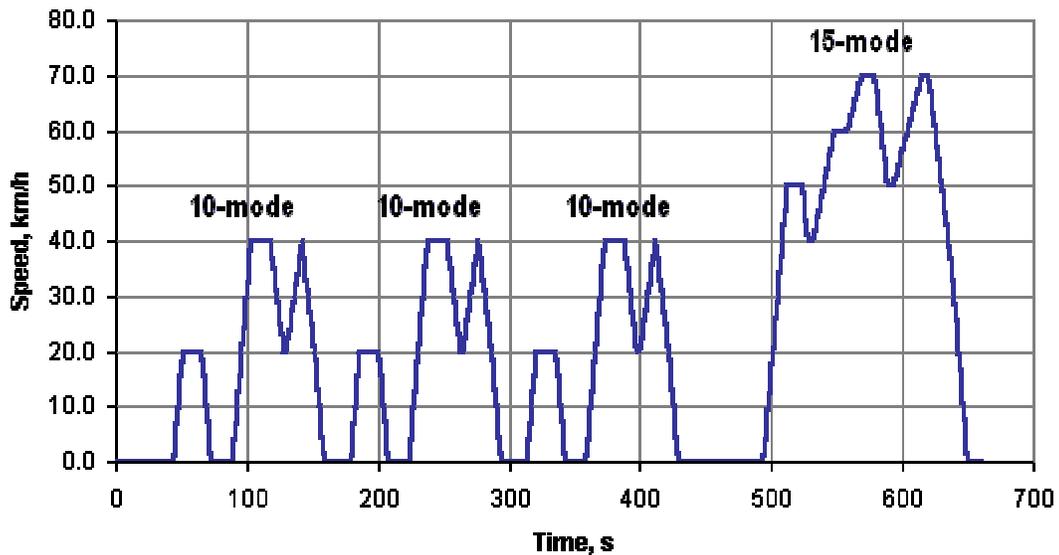


Figure 1. 10-15 Mode Cycle

The distance of the cycle is 4.16 km, average speed 22.7 km/h, duration 660 s (or 6.34 km, 25.6 km/h, 892 s, respectively, including the initial 15 mode segment).