2. DIESEL EMISSIONS CHARACTERIZATION, ATMOSPHERIC TRANSFORMATION, AND EXPOSURES

2.1. INTRODUCTION

This chapter provides background information relating to the diesel engine, the pollutants it emits, the history of its use in highway vehicles and railroad locomotives, diesel exhaust composition and emissions trends, and air pollution regulatory standards for diesel engines in the United States. The chapter also provides specific information about physical and chemical composition of diesel exhaust, descriptions of its atmospheric transformations, observations of measured and modeled ambient concentrations (considered alone and as a component of atmospheric particles in general), and some estimates of population exposures. In addition, this chapter gives background information that is used in conjunction with the toxicology and epidemiology data to formulate the conclusions about human health hazards that are discussed in later chapters of this document. The exposure information does not represent a formal or rigorous exposure assessment; it is intended only to provide a context for the health effects data and health hazard findings.

The diesel engine was patented in 1892 by Rudolf Diesel, who conceived it as a prime mover that would provide much improved fuel efficiency compared with spark-ignition engines. To the present day, the diesel engine's excellent fuel economy remains one of its strongest selling points. In the United States, the diesel engine is used mainly in trucks, buses, agricultural and other off-road equipment, locomotives, and ships.

The chief advantages of the diesel engine over the gasoline engine are its fuel economy and durability. Diesel engines, however, emit more particulate matter per mile driven compared with gasoline engines of a similar weight class. Over the past decade, modifications of diesel engine components have substantially reduced particle emissions from both diesel and gasoline engines (Hammerle et al., 1994; Sawyer and Johnson, 1995).

The diesel engine compresses air to high pressure and temperature. Fuel, when injected into this compressed air, autoignites, releasing its chemical energy. The expanding combustion gases do work on the piston before being exhausted to the atmosphere. Power output is controlled by the amount of injected fuel rather than by throttling the air intake. Compared to its spark-ignition counterpart, the diesel engine's superior efficiency derives from a higher compression ratio and no part-load throttling. To ensure structural integrity for prolonged reliable operation at the higher peak pressures brought about by a higher compression ratio and autoignition, the structure of a diesel engine generally is more massive than its SI counterpart.

Diesel engines (also called compression-ignition) may be broadly identified as being either two- or four-stroke cycle, injected directly or indirectly, and naturally aspirated or supercharged.

1   They also are classified according to service requirements such as light-duty (LD) or heavy-duty

2   (HD) automotive/truck, small or large industrial, and rail or marine.

3   All diesel engines use hydraulic fuel injection in one form or another. The fuel system

4   must meet four main objectives if a diesel engine is to function properly over its entire operating

5   range. It must: (1) meter the correct quantity of fuel, (2) distribute the metered fuel to the

6   correct cylinder, (3) inject the metered fuel at the correct time, and (4) inject the fuel so that it is

7   atomized and mixes well with the in-cylinder air. The first two objectives are functions of a

8   well-designed injection pump, and the last two are mostly functions of the injection nozzle. Fuel

9   injection systems are moving toward the use of electronic components for more flexible control

10   than is available with purely mechanical systems to obtain lower exhaust emissions without

11   diminishing fuel efficiency.

12   Both the fuel and the lubricants that are used to service diesel engines are highly finished

13   petroleum-based products combined with chemical additives. Diesel fuel is a mixture of many

14   different hydrocarbon molecules from about C_7 to about C_{35}, with a boiling range from roughly

15   350 °F to 650 °F. Many of the fuel and oil properties, such as its specific energy content (which

16   is higher than gasoline), ignition quality, and specific gravity, are related to its hydrocarbon

17   composition. Therefore, fuel and lubricant composition affects many aspects of engine

18   performance, including fuel economy and exhaust emissions.

19   Complete and incomplete combustion of fuel in the diesel engine results in the formation

20   of a complex mixture of gaseous and particulate exhaust. Because of concerns over health effects

21   associated with diesel particulate emissions, EPA began regulating emissions from diesel engines

22   in 1970 (for smoke) and then added regulations for gaseous emissions. EPA first regulated

23   particulate emissions from HD diesels in 1988.

24   For the purposes of this document, carbonaceous matter, diesel exhaust, diesel particulate

25   matter (DPM), elemental carbon (EC), organic carbon (OC), soluble organic fraction (SOF), and

26   soot are defined as listed below.

27   **Carbonaceous matter**: Carbon-containing compounds, includes organic carbon and

28   elemental carbon that are associated with particulate matter in diesel exhaust. In this

29   document, the term carbonaceous matter includes all organic and elemental carbon-

30   containing compounds that are found in the particle phase. In other documents, this term

31   is sometimes used interchangeably to refer to the insoluble fraction of diesel particulate

32   matter or the soot fraction.

33

34   **Diesel exhaust (DE)**: Gaseous and particle phase emissions resulting from the

35   combustion of diesel fuel in an internal combustion engine (e.g., compression ignition

engine). Diesel exhaust includes emissions from a diesel engine or diesel vehicle (inclusive of aftertreatment devices) but does not include emissions from brake and tire wear.

Diesel particulate matter: The particle-phase compounds emitted in diesel exhaust. DPM can refer to both primary emissions as well as secondary particles that are formed by atmospheric processes. In this document, DPM refers to primary particles. Primary diesel particles are considered fresh after being emitted and undergo aging (oxidation, nitration, or other chemical and physical changes as discussed in Section 2.3) in the atmosphere. As used in this document, DPM refers to both fresh and aged diesel particulate matter unless a distinction is made.

Elemental carbon: Carbon that has undergone pyrolysis (e.g., has been stripped of hydrogen). In pure form, elemental carbon contains only carbon atoms although elemental carbon as it exists in combustion particulate matter is likely to contain some hydrogen atoms. In this document, the terms elemental carbon and organic carbon are used to refer to the carbon-containing components of DPM, and collectively they are referred to as the carbonaceous fraction of a diesel particle.

Organic carbon: Carbon- and hydrogen-containing molecules emitted in diesel exhaust largely as the result of unburned diesel fuel and to a lesser extent resulting from engine lubrication oil. Organic carbon compounds can also contain oxygen, nitrogen, and sulfur as well as other elements in small quantities. In this document, the terms elemental carbon and organic carbon are used to refer to the carbon-containing components of DPM, and collectively they are referred to as the carbonaceous fraction of a diesel particle.

Soluble organic fraction: The portion of DPM that can be extracted from the particle matrix into solution. Extraction solutions and procedures vary and are described in Section 2.2.8.1.

Soot: Agglomerations of elemental carbon and organic carbon particles. Often characterized as the insoluble portion of DPM.

This chapter begins with the history of dieselization for on-road vehicles and locomotives, followed by an introductory discussion of the formation of primary diesel emissions to assist the

1 reader in understanding the complex factors that influence the formation of particulate matter

2 (PM) and other diesel exhaust emissions. The next section is a summary of EPA emission

3 standards for on-road and locomotive diesel engines and a description of the national trends in

4 emissions from on-road and nonroad diesel engine sources based on inventory modeling. The

5 chapter continues with a discussion of diesel fuel use and the impact of fuel properties on

6 emissions. The chronological assessment of emissions factors is presented in summaries of chassis

7 and engine dynamometer testing and tunnel tests. This is followed by a description of engine

8 technologies and their effect on emissions and a description of the chemical and physical nature of

9 emissions. The data describing the important atmospheric transformations of diesel exhaust are

10 summarized. The chapter concludes with a summary of the available literature regarding

11 atmospheric concentrations of diesel particulate matter and exposures to diesel exhaust. EPA has

12 assessed national and urban-area annual average exposure to diesel particulate matter using the

13 Hazardous Air Pollutant Exposure Model - Mobile Sources version 3 model, and this assessment

14 is presented in Section 2.4.3. A full exposure assessment including the distribution of ambient

15 diesel exhaust exposures in different geographic regions and among different demographic

16 groups; the most highly exposed (90th percentile); exposures in microenvironments for short and

17 long durations; and the maximum exposure range (98th percentile) and number of maximum-

18 exposed individuals is not currently available. EPA is developing tools to provide a more

19 complete exposure assessment.

20

21 **2.2. PRIMARY DIESEL EMISSIONS**

22 **2.2.1. History of Dieselization**

23   Information regarding diesel engine use including market share, vehicle miles traveled

24 (VMT) and fleet turnover are important aspects in understanding potential health effects of past

25 and present diesel exhaust exposure. In this section, the dieselization of the on-road truck fleet

26 and locomotives are discussed.

27

28 **2.2.1.1.** *Dieselization of the On-Road Fleet*

29   Because of their durability and fuel economy, the use of diesel engines, particularly in

30 long-distance applications, has increased over the years. The Census of Transportation, Truck

31 Inventory and Use Survey (TIUS) indicates that among Class 3-8 trucks, diesel engine use has

32 increased more rapidly than gasoline engine use in the past 20 years. Truck classes are defined by

33 gross vehicle weight as described in Table 2-1. Dieselization first occurred among Class 7 and 8

34 (HHD) trucks. The TIUS indicates that 81.5% of diesel trucks on the road in 1963 were Class 7

35 or 8 (HHD) trucks (Table 2-2). Class 7 sales became predominantly (e.g., >50%) diesel in the

36 1970s and Class 8 sales became predominantly diesel in the 1960s. Diesels did not comprise a

majority of class 5 and 6 sales until the 1990s (Figures 2-1 and 2-2). Heavy-duty trucks (LHD and HHD) have historically constituted the majority of diesel sales and mileage. However, an increasing number of light-duty (LD) diesel trucks have been sold domestically in recent years. In the 1990s, approximately one in three diesel trucks sold were Class 1 and Class 2 vehicles. Diesel trucks have historically been driven more miles per truck than gasoline trucks. For example, the TIUS indicates that 59% of diesel trucks were driven more than 50,000 miles in 1963, compared to 3% of gasoline trucks. Among combination trucks, consisting of tractor-trailers and single-unit trucks with trailers, diesel vehicles have driven a majority of the miles since at least 1963, the earliest year in which TIUS was conducted (Figure 2-3).

The longevity of diesel trucks is an important factor to understand past, current, and projected exposures to diesel exhaust because older vehicles are subject to less stringent regulations and may remain in use for several decades after their manufacture. American Automobile Manufacturers Association publications (AAMA, 1927-1997) indicate that 53% of trucks from model years 1947-1956 were still on the road after 14 years. The proportion of trucks in use after 14 years was 63% for model years 1974-1983, suggesting that the lifespan of trucks built in later years is longer. According to the 1997 TIUS, vehicles older than 10 years make up 40% of Class 7 and 8 (HHD) trucks and drove 16% of Class 7-8 VMT (Figures 2-4 and 2-5). Almost all HDD trucks were diesel vehicles in the period 1982-1997 (93% in 1982 and 99% in 1997).

2.2.1.2. *Dieselization of Railroad Locomotive Engines*

Early in the 20th century the political and economic pressure on the railroads to replace steam locomotives was substantial. Railroads were losing business to other forms of transport. The diesel-electric locomotive provided 90% in-service time, compared with only 50% for steam locomotives, and had three times the thermal efficiency (Klein, 1991; Kirkland, 1983). Additionally, several cities had passed laws barring steam locomotives within the city limits because the large quantities of smoke obscured visibility, creating a safety hazard. The first prototype diesel locomotive was completed in 1917. By 1924 General Electric (GE) was producing a standard line of switching locomotives on a production basis. Electro-Motive Corporation was founded the same year to produce diesel locomotives in competition with GE. This company was purchased in 1929 by General Motors (GM) and became the Electro-Motive Division. After this acquisition, GM began to develop the two-stroke engine for this application. Up to this time, all locomotive diesel engines were four-stroke. Two-strokes offered a much higher power-to-weight ratio, and GM's strategy was to get a large increase in power by moving to the two-stroke cycle. The first true high-speed two-stroke diesel-electric locomotives were produced by GM in 1935. However, because of the economic climate of the Great Depression,

1   few of these were sold until after the Second World War. At the end of the war most locomotives
2   were still steam-driven but were more than 15 years old, and the railroads were ready to replace
3   the entire locomotive fleet. Few if any steam locomotives were sold after 1945 because the entire
4   fleet was converted to diesel (Coifman, 1994).

5   The locomotive fleet has included significant percentages of both two- and four-stroke
6   engines. The four-stroke diesel engines were naturally aspirated in the 1940s and 1950s. It is
7   unlikely that any of the two-stroke engines used in locomotive applications were strictly naturally
8   aspirated. Nearly all two-stroke diesel locomotive engines are uniflow scavenged, with a positive-
9   displacement blower for scavenging assistance. In 1975, it was estimated that 75% of the
10 locomotives in service were two-stroke, of which about one-half used one or more turbochargers
11 in addition to the existing positive-displacement blower for additional intake boost pressure.

12 Almost all of the four-stroke locomotive engines were naturally aspirated in 1975.
13 Electronic fuel injection for locomotive engines was first offered in the 1994 model year (U.S.
14 EPA, 1998b). All locomotive engines manufactured in recent years are turbocharged, aftercooled
15 or intercooled four-stroke engines. In part, this is because of the somewhat greater durability of
16 four-strokes, although impending emissions regulations may have also been a factor in this shift.
17 The typical lifespan of a locomotive has been estimated to be more than 40 years (U.S. EPA,
18 1998b). Many of the smaller railroads are still using engines built in the 1940s, although the
19 engines may have been rebuilt several times since their original manufacture.

20

21 **2.2.2. Diesel Combustion and Formation of Primary Emissions**
22 A basic understanding of diesel combustion processes can assist in understanding the
23 complex factors that influence the formation of DPM and other diesel exhaust emissions. Unlike
24 spark-ignition combustion, diesel combustion is a fairly nonhomogenous process. Fuel is sprayed
25 at high pressure into the compressed cylinder contents (primarily air with some residual
26 combustion products) as the piston nears the top of the compression stroke. The turbulent mixing
27 of fuel and air that takes place is enhanced by injection pressure, the orientation of the intake
28 ports (e.g., inducement of intake-swirl tangential to the cylinder wall), piston motion, and piston
29 bowl shape. In some cases, fuel and air mixing is induced via injection of the fuel into a
30 turbulence-generating pre-chamber or swirl chamber located adjacent to the main chamber
31 (primarily in older, higher speed engines and some LD diesels). Examples of typical direct
32 injection and indirect injection combustion systems are compared in Figure 2-6. Diesel
33 combustion can be considered to consist of the following phases (Heywood, 1988; Watson and
34 Janota, 1982):

35

1. An ignition delay period, which starts after the initial injection of fuel and continues until the initiation of combustion. The delay period is governed by the rate of fuel and air mixing, diffusion, turbulence, heat transfer, chemical kinetics, fuel vaporization, and fuel composition. Fuel cetane rating is an indication of ignition delay.

2. Rapid, premixed burning of the fuel and air mixture from the ignition delay period.

3. Diffusion-controlled burning, where the fuel burns as it is injected and diffuses into the cylinder.

4. A very small amount of rate-controlled burning during the expansion stroke, after the end of injection.

Engine speed and load are controlled by the quantity of fuel injected. Thus, the overall fuel-to-air ratio varies greatly as engine speed and load vary. On a macro scale, the cylinder contents are always fuel-lean. Depending on the time available for combustion and the proximity of oxygen, the fuel droplets are either completely or partially oxidized. At temperatures above 1,300 K, much of the unburned fuel that is not oxidized is pyrolized (stripped of hydrogen) to form elemental carbon (Dec and Espey, 1995). In addition to elemental carbon, other carbonaceous matter is present, largely from unburned fuel. The agglomeration of elemental and organic carbon (OC) forms particles that are frequently referred to as "soot" particles. In this document, the terms "elemental carbon" and "organic carbon" are used to refer to the carbon-containing components of diesel particulate matter, and collectively, they are referred to as the carbonaceous fraction of a diesel particle.

Carbonaceous particle formation occurs primarily during the diffusion-burn phase of combustion, and it is highest during high load and other conditions consistent with high fuel-air equivalence ratios. Most of the carbonaceous matter formed (80% to 98%) is oxidized during later stages of combustion, most likely by hydroxyl radicals formed during combustion (Kittelson et al., 1986; Foster and Tree, 1994). The remainder of the carbonaceous particulate leaves as a component of DPM emissions from the engine.

DPM is defined by the measurement procedures summarized in the Code of Federal Regulations Title 40 CFR, Part 86, Subpart N (CFR 40:86.N). These procedures define DPM emissions as the mass of material collected on a filter at a temperature of 52 °C or less after dilution of the exhaust with air. As the exhaust is diluted and cooled, nucleation, condensation, and adsorption transform volatile material to solid and liquid DPM. Diesel exhaust particles are aggregates of primary spherical particles consisting of solid carbonaceous material and ash and containing adsorbed organic and sulfur compounds (sulfate) combined with other condensed material (Figure 2-7). These particles have a very large surface area per gram of mass, which

1 make them an excellent carrier for adsorbed inorganic and organic compounds that can effectively

2 reach the lowest airways of the lung. The elemental carbon core has a high specific surface area

3 of approximately 30–50 m^2/g (Frey and Corn, 1967). Because of this high surface area, the

4 elemental carbon core is able to adsorb large quantities of ash, organic compounds, and sulfate.

5 Pierson and Brachaczek (1976) report that after the extraction of adsorbed organic material, the

6 surface area of the diesel particle core is approximately 90 m^2/g.

7   The organic material associated with diesel particles originates from unburned fuel, engine

8 lubrication oil, and small quantities of partial combustion and pyrolysis products. This is

9 frequently quantified as the soluble organic fraction, which is discussed in much more detail in

10 Section 2.2.7. The formation of sulfate in diesel exhaust depends primarily on fuel sulfur content.

11 During combustion, sulfur compounds present in the fuel are oxidized to sulfur dioxide (SO_2).

12 Approximately 1% to 4% of fuel sulfur is oxidized to SO_3, which combines with water vapor in

13 the exhaust to form sulfuric acid (H_2SO_4) (Wall et al., 1987; Khatri et al., 1978; Baranescu, 1988;

14 Barry et al., 1985). Upon cooling, sulfuric acid and water condense into an aerosol that is

15 nonvolatile under ambient conditions. The mass of sulfuric acid DPM is more than doubled by the

16 mass of water associated with the sulfuric acid under typical DPM measurement conditions (50%

17 relative humidity, 20–25 °C) (Wall et al., 1987).

18   Oxide of nitrogen (NO_x) emissions from combustion engines, primarily (at least initially) in

19 the form of NO, are generally thought to be formed via the Zeldovich mechanism, which is highly

20 temperature dependent. High combustion temperatures cause reactions between oxygen and

21 nitrogen to form NO and some NO_2. The majority of NO_2 formed during combustion is rapidly

22 decomposed. NO can also decompose to N_2 and O_2, but the rate of decomposition is very slow

23 because of the rapidly decreasing temperatures from the expansion of combustion gases during

24 the expansion stroke (Heywood, 1988; Watson and Janota, 1982). Thus, almost all of the NO_x

25 emitted is NO.

26   Some organic compounds from unburned fuel and from lubricating oil consumed by the

27 engine can be trapped in crevices or cool spots within the cylinder and thus are not sufficiently

28 available to conditions that would lead to their oxidation or pyrolysis. These compounds are

29 emitted from the engine and either contribute to gas-phase organic emissions or to DPM

30 emissions, depending on their volatility. Within the exhaust system, temperatures are sufficiently

31 high that these compounds are entirely present within the gas phase (Johnson and Kittelson,

32 1996). Upon cooling and mixing with ambient air in the exhaust plume, some of the less volatile

33 organic compounds can adsorb to the surfaces of the elemental carbon agglomerate particles.

34 Lacking sufficient elemental carbon adsorption sites, the organic compounds may condense on

35 sulfuric acid nuclei to form a heterogeneously nucleated organic aerosol (Abdul-Khalek et al.,

36 1999).

1   While not unique to diesel exhaust, the high content of elemental carbon associated with

2   typical DPM emissions has long been used by some investigators to distinguish diesel engine

3   sources of this particle from other combustion aerosols. Diesel particles from newer HD engines

4   are typically composed of ~75% elemental carbon (EC can range from 33-90%), ~20% organic

5   carbon (OC can range from 7-49%), and small amounts of sulfate, nitrate, trace elements, water,

6   and unidentified components (Figure 2-8). Metallic compounds from engine component wear,

7   and from compounds in the fuel and lubricant, contribute to DPM mass (1% to 5% of mass is

8   attributed to metals as discussed in more detail below). Ash from oil combustion also contributes

9   trace amounts to DPM mass.

10   In contrast to the composition of diesel PM2.5, ambient PM2.5 measured in the eastern

11   United States is dominated by sulfate (34%), while ambient PM2.5 in the western United States is

12   dominated by organic carbon (39%) (Table 2-3) (U.S. EPA, 1996a). The organic carbon fraction

13   of DPM is increasingly being used to assist investigators in identifying the contribution of diesel

14   engine emissions to ambient PM2.5. In particular, hopane and sterane compounds (aromatic

15   compounds, $>C_{30}$) have been used in addition to other polycyclic aromatic HCs (PAHs) and long

16   chain alkanes to distinguish DPM from other mobile source PM and from ambient PM (Schauer et

17   al., 1996; Fujita et al., 1998). While PAH compounds comprise 1% or less of DPM mass, diesel

18   emissions have been observed to have elevated concentrations of methylated naphthalenes and

19   methylated phenanthrene isomers compared to other combustion aerosols (Benner et al., 1989;

20   Lowenthal et al., 1994; Rogge et al., 1993). Enrichment of benzo[a]anthracene and

21   benzo[a]pyrene in DPM has also been observed under some conditions and has been used to

22   assess the relative contribution of diesel exhaust to ambient PM.

23   While specific organic carbon species are being identified to help distinguish DPM

24   aerosols from other combustion aerosols, up to 90% of the organic fraction associated with DPM

25   is currently classified as unresolvable complex material. While accounting for the majority (50%

26   to 90%) of the number of particles, ultrafine DPM (5–50 nm) accounts for only 1% to 20% of the

27   mass of DPM. A study conducted by Gertler (1999) in the Tuscarora Mountain tunnel

28   demonstrated an increase in 20 nm diameter particles as the fraction of diesel vehicles in the

29   tunnel increased from 13% to 78%. The contribution of nuclei mode particles from a freeway on

30   an ambient aerosol size distribution was reported by Whitby and Sverdrup (1980).

31   In general, the major factors that distinguish DPM from ambient PM are: (1) the high

32   portion of elemental carbon, (2) the large surface area associated with the carbonaceous particles

33   in the 0.2 μm size range, (3) enrichment of certain polycyclic organic compounds, and (4)

34   50%–90% of the number of DPM particles in diesel engine exhaust are in the nuclei mode size

35   range, with a mode of 20 nm. The physical and chemical composition of DPM and changes in

36   DPM chemical composition are discussed in more detail in Section 2.2.8.

2.2.3. Diesel Emission Standards and Emission Trends Inventory

EPA set a smoke standard for on-road HD diesel engines beginning with the 1970 model year and then added a carbon monoxide (CO) standard and a combined hydrocarbon (HC) and NO_x standard for the 1974 model year, as detailed in Table 2-4. Beginning in the 1979 model year, EPA added a HC standard while retaining the combined HC and NO_x standard. All of the testing for HC, CO, and NO_x was completed using a steady-state test procedure. Beginning in the 1985 model year, EPA added a NO_x standard (10.7 g/bhp-hr), dropped the combined HC and NO_x standard, and converted from steady-state to transient testing for HC, CO, and NO_x emissions. EPA introduced a particulate standard for 1988 model year diesel engines using the transient test (0.6 g/bhp-hr). Transient testing involves running an engine on a dynamometer over a range of load and speed set points.

Since the 1985 model year, only the NO_x and particulate standards have been tightened for on-road diesel engines. For truck and bus engines, the particulate standard was reduced to 0.25 g/bhp-hr in 1991, and it was reduced again in 1994 for truck engines to 0.1 g/bhp-hr. For urban bus engines, the particulate standard was reduced in 1994 to 0.07 g/bhp-hr and again in 1996 to 0.05 g/bhp-hr. The NO_x standard was reduced to 4.0 g/bhp-hr in 1998 for all on-road diesel engines (bus and truck engines). For 2004, the standards were further lowered in a 1997 rulemaking, with limits on nonmethane hydrocarbon (NMHC) and NO_x combined, but no further reductions in CO, PM, or smoke. These lower NMHC-plus-NO_x levels are under examination as part of EPA's 1996 technology review. EPA has proposed further reductions in NO_x, NMHC, and PM for the post-2004 timeframe.

In December 1997, EPA adopted emission standards for NO_x, HC, CO, PM, and smoke for newly manufactured and remanufactured railroad locomotives and locomotive engines. The rulemaking, which takes effect in the year 2000, applies to locomotives originally manufactured in 1973 or after, and any time they are manufactured or remanufactured (locomotives originally manufactured before 1973 are not regulated). Three sets of emission standards have been adopted (Tier 0, 1, and 2); they apply to locomotives and locomotive engines originally manufactured from 1973 through 2001 (Tier 0), from 2002 through 2004 (Tier 1), and in 2005 and later (Tier 2) (Table 2-5; see EPA web page at http://www.epa.gov/omswww/ or http://www.dieselnet.com/standards/ for current information on mobile source emission standards). The emissions are measured over two steady-state test cycles that represent two different types of service, including the line-haul (long-distance transport) and switch (involved in all transfer and switching operations in switch yards) locomotives.

Emission standards for nonroad equipment are not as stringent as current standards for on-road equipment and are being phased in within the next decade. Currently, Federal PM standards exist for nonroad equipment of several horsepower ratings. For equipment between

1 175 and 750 horsepower, the PM standard was set at 0.4 g/bhp-hr in 1996 and will decrease to

2 0.15 g/bhp-hr between 2001 and 2003 depending on the power rating (Table 2-6). This

3 equipment includes construction, agricultural, and industrial equipment such as bulldozers,

4 graders, cranes, and tractors. The current PM standard for this equipment is only slightly lower

5 than the 0.6 g/bhp-hr PM standard in place for on-road HD diesel engines in the late 1980s.

6   The EPA emission trends report (U.S. EPA, 2000a) provides emission inventories for

7 criteria pollutants (PM10, PM2.5, SO_2, NO_x, volatile organic compounds [VOC], CO, Pb, and

8 NH_3) from point, area, and mobile sources, which indicate how emissions have changed from

9 1970 to 1997. The emission trends are based on the EPA mobile source inventory models

10 MOBILE, PART5, and the draft NONROAD model. PART5 derives particulate emission rates

11 for HD diesel vehicles using data generated for new engine certification purposes. PART5 is

12 currently being modified to account for deterioration, in-use emissions, poor maintenance, and

13 tampering effects, all of which would increase emission factors. PM, SO_2, NO_x, and VOC

14 emissions trends from the report are discussed below. Ambient urban/suburban PM samples

15 rarely reflect the large fraction of natural and miscellaneous sources suggested by the national

16 inventory due to removal of a large portion of these emissions close to their source as well as

17 dispersion from these sources to urban/suburban sites. The removal of natural and miscellaneous

18 PM10 (largely fugitive dust) near their source is a result of the lack of inherent thermal buoyancy,

19 low release height, and interaction with their surroundings (impaction and filtration by

20 vegetation). For the summaries presented here, natural and miscellaneous sources are excluded

21 from the national PM and NO_x inventories.

22   Mobile sources of PM include both gasoline- and diesel-powered on-road vehicles and a

23 variety of nonroad equipment. Nonroad diesel engine sources include construction equipment,

24 agricultural equipment, marine vessels, locomotives, and other sources. The EPA emission trends

25 report (U.S. EPA, 2000a) indicates that, excluding natural and miscellaneous (mainly fugitive

26 emissions) sources, mobile sources were responsible for 25% of PM10 emissions in 1998. Diesel

27 engines (on-road and nonroad combined) were estimated to contribute 72% of mobile source

28 PM10 emissions and 18% of total PM10 in 1998 (excluding natural and miscellaneous emissions).

29 Due to the high concentration of fine particles in engine emissions, diesel engines (on-road and

30 nonroad combined) were estimated to contribute 77% of mobile source PM2.5 emissions and

31 23% of total PM2.5 in 1998 (excluding natural and miscellaneous emissions). If natural and

32 miscellaneous PM2.5 sources are included in the inventory, diesel PM2.5 contributes 6% to the

33 national inventory.

34   Gram per mile particulate emissions from diesel vehicles are much greater than those from

35 gasoline-fueled vehicles, accounting for the large contribution of diesel engine emissions to the

36 national inventory in spite of the smaller number of diesel engines in use. Particulate emissions

1　(PM10) from gasoline-fueled engines decreased dramatically in 1975 with the widespread

2　introduction of unleaded gasoline. Particulate emissions from diesel highway vehicles have

3　decreased recently because of EPA emission standards for new model year HD diesel trucks that

4　were first implemented in 1988 and became increasingly stringent in 1991 and 1994, as presented

5　in Table 2-4. A decrease in on-road HD DPM emissions since the mid-1980s is confirmed by in-

6　use vehicle testing, as described in Section 2.2.5. Due to the implementation of existing

7　regulations, DPM emissions from on-road sources are expected to decrease 37% from 1998 to

8　2007; however, nonroad DPM emissions are expected to increase 15% in the same time period

9　(Figure 2-9).

10　　　　The EPA emission trends report (U.S. EPA, 2000a) indicates that annual on-road vehicle

11　PM10 emissions decreased from 397,200 tons to 257,080 tons from 1980 to 1998.[1] Passenger

12　car particulate emissions decreased 53% (from 119,000 to 56,000 tons) in this timeframe, while

13　on-road diesel vehicle PM10 emissions decreased 27% (from 208,000 to 152,000 tons) (Figure 2-

14　9). Nonroad diesel engine PM10 emissions increased 17% (from 314,000 tons in 1980 to

15　369,000 tons in 1998). Emissions data for PM2.5 are available only for the period from 1990 to

16　1998. Between 1990 and 1998, PM2.5 emissions from mobile sources decreased by 14%, largely

17　as the result of decreased on-road emissions. Diesel engines also contribute to secondary PM

18　formation from NO_x and SO_2 emissions that are converted to nitrate and sulfate. VOCs from

19　diesel engines also contribute to secondary particle formation.

20　　　　In 1998, 53% of total emitted NO_x came from mobile sources, with diesels responsible for

21　57% of the mobile source contribution. Overall, NO_x emissions from mobile sources have

22　remained relatively constant over time, increasing an estimated 7% from 1980 to1998. While

23　NO_x from LD gasoline vehicles decreased from 1980 to 1998, resulting in an overall decrease in

24　on-road NO_x emissions of 9%, NO_x from diesel trucks and buses increased 7% (from 2,463,390

25　tons in 1980 to 2,630,120 tons in 1998) owing to the use of NO_x control defeat devices as

26　discussed in Section 2.2.5. NO_x emissions from nonroad diesel engines (including commercial

27　marine and locomotives) have increased 46% (from 3,251,600 tons in 1980 to 4,752,800 tons in

28　1998) (Figure 2-10).

29　　　　About 7% of SO_2 came from mobile sources in 1998, with diesels responsible for 74% of

30　that total. EPA regulations on fuel sulfur have significantly reduced SO_2 emissions from highway

[1]Exhaust emissions constitute the majority of PM emissions from mobile sources, with tire and brake wear
contributing the remainder. To compare trends estimates from past years with future projections (which are
provided for exhaust emissions only), the fraction of brake and tire wear would need to be omitted from these
estimates as reported in the emission trends report (U.S. EPA, 2000a). On average in the late 1990s 39% and 64%
of gasoline vehicle particulate emissions originated from exhaust and 95% and 98% of on-road diesel emissions
originated from exhaust for PM10 and PM2.5, respectively.

diesels. SO_2 emissions from highway diesel engines have decreased 72% (from 303,000 tons in 1980 to 85,000 tons in 1998) (Figure 2-11). Similar trends are not apparent for nonroad diesels, although in 1998, nonroad diesel engines, excluding commercial marine vessels, emitted 785,000 tons of SO_2, comprising 56% of mobile source SO_2 emissions in 1998.

Diesel engines are not a large source of VOC emissions compared to gasoline engines. VOC emissions from diesel engines in 1998 were estimated at 2% of the total emissions from all sources. VOC emissions from diesel mobile sources decreased 9% (from 779,000 tons in 1980 to 721,000 tons in 1998) (Figure 2-12).

Diesel engines are also not a large source of CO emissions compared to gasoline engines. In 1998, mobile sources emitted 79% of all CO and diesel engines accounted for 4% of the mobile source CO. CO emissions from on-road diesel vehicles increased 34% between 1980 and 1998, during which time nonroad diesel emissions of CO increased 45% (Figure 2-13).

2.2.4. Historical Trends in Diesel Fuel Use and Impact of Fuel Properties on Emissions

Use of diesel fuel has increased steadily in the second half of this century. According to statistics from the Federal Highway Administration (1995, 1997), in 1949 diesel fuel was approximately 1% of the total motor fuel used, and in 1995 it was about 18%. Over the same time, diesel fuel consumption increased from about 400 million gallons to 26 billion gallons per year in the United States, an increase by a factor of more than 60 (Figures 2-14 and 2-15).

The chemistry and properties of diesel fuel have a direct effect on emissions of regulated pollutants from diesel engines. Researchers have studied the NO_x and DPM effect of sulfur content, total aromatic content, polyaromatic content, fuel density, oxygenate content, cetane number, and T90 on emissions of regulated pollutants. T90 is the 90% distillation point temperature. An increase in T90 has been observed to cause an increase in DPM emissions (Cunningham et al., 1990; Sienicki et al., 1990). Cetane number is a measure of the ignition quality, or ignition delay time, of a diesel fuel. The percent of cetane (less commonly referred to as hexadecane, $C_{16}H_{34}$) by volume in a blend with alpha-methylnaphthalene ($C_{10}H_7CH_3$) defines the cetane number that provides the same ignition delay time as the fuel in use.

The chemical makeup of diesel fuel has changed over time, in part because of new regulations and in part because of technological developments in refinery processes. EPA currently regulates on-road diesel fuel and requires sulfur content to be less than 500 ppm for on-road applications and cetane index (a surrogate for actual measurements of cetane number) to be greater than or equal to 40, or the maximum aromatic content to be 35% or less (CFR 40:80.29). California has placed additional restrictions on the aromatic content of diesel fuel (California Code of Regulations, Title 13, Sections 2281-2282) and requires a minimum cetane number of 50 and an aromatics cap of 10% by volume, with some exceptions for small refiners and alternative

1 formulations as long as equivalent emissions are demonstrated. Diesel fuel from larger refiners is

2 limited to 10% aromatic content, and for three small refiners (a small fraction of diesel sales) to

3 20% aromatic content.   The refiners can also certify a fuel with higher aromatic content as being

4 emissions-equivalent to the 10% (or 20%) aromatic content fuels by performing a 7-day engine

5 dynamometer emissions test. This method is chosen by most, if not all, California refiners, and so

6 a typical California diesel fuel has an aromatic content above 20%. Emissions equivalence has

7 been obtained through use of cetane enhancers, oxygenates, and other proprietary additives.

8 Nonroad diesel fuel is not regulated, and consequently, cetane index, aromatic content, and sulfur

9 content vary widely with nominal values for cetane number around 43, 31% aromatics, and sulfur

10 approximately 3,000 ppm.

11   Before 1993, diesel fuel sulfur levels were not federally regulated in the United States,

12 although the State of California had such regulations. Industry practices that were in place (e.g.,

13 the ASTMD 975 specification for No. 2 oils) limited sulfur to 0.5%. During the years 1960 to

14 1986, fuel sulfur content showed no chronological increasing or decreasing trends and ranged

15 from 0.23 to 0.28 wt% (NIPER, 1986). A maximum allowable diesel fuel sulfur content in the

16 United States for on-road diesel fuel was established at 0.05 mass % in 1993, in advance of the

17 1994 0.10 g/bhp-hr PM standard for HD on-highway trucks. Nationally, on-road fuels averaged

18 0.032% sulfur in 1994 while nonroad fuels averaged 10-fold the sulfur level of on-road fuel, or

19 0.32% (Dickson and Sturm, 1994). The reduction in diesel fuel sulfur reduced total DPM mass

20 emissions through reduction of sulfate PM (primarily present as sulfuric acid). Approximately 1%

21 to 4% of fuel sulfur is oxidized to SO_3, which rapidly forms sulfuric acid in the presence of water

22 vapor in the exhaust (Wall et al., 1987; Khatri et al., 1978; Baranescu, 1988). Considerably

23 higher sulfuric acid PM emissions are possible with diesel exhaust aftertreatment systems

24 containing precious metals (oxidation catalysts, lean NO_x catalysts, catalyzed DPM traps). At

25 temperatures over 350 °C to 500 °C (depending on device), SO_2 in the exhaust can be oxidized to

26 SO_3 and increase sulfuric acid PM emissions (McClure et al., 1992; McDonald et al., 1995; Wall,

27 1998). Sulfur content remains at unregulated levels for off-highway diesel fuels and fuels used in

28 railroad locomotives.

29   The average cetane number of U.S. diesel fuel declined steadily from 50.0 to 45.1, or

30 about 0.2 per year, from 1960 to 1986 (NIPER, 1986). The decline in cetane number was likely

31 accompanied by an increase in aromatic content and density (Lee et al., 1998). A number of

32 EPA-sponsored studies refer to fuels with nominally 22% aromatics content as "national average

33 fuel" during the 1970s (Hare, 1977; Springer, 1979), while by the 1980s a so-called national

34 average fuel contained 30% aromatics (Martin, 1981a,b). Shelton (1979, 1977) has reported a

35 trend of increasing T90 from 1960 through the late 1970s, which is consistent with increasing

36 density, aromatic content, and polyaromatic content. Unfortunately, aromatic content was not

1   commonly measured before the 1980s. The reason for the decline in cetane number and increase

2   in aromatics is that as diesel demand grew, straight-run diesel became a smaller part of the pool

3   and light-cycle oil from catalytic cracking became available to make up for the increased demand.

4   Light-cycle oil is high in aromatics and PAHs.

5   Studies measuring the emissions impact of changes in cetane number and aromatic content

6   for roughly 1990 model year engine technology find that increasing the aromatic content from

7   20% to 30%, with an accompanying decrease in the cetane number from 50 to 44, results in a 2%

8   to 5% increase in NO_x and a 5% to 10% increase in total DPM (McCarthy et al., 1992; Ullman et

9   al., 1990; Sienicki et al., 1990; Graboski and McCormick, 1996). These ranges may be

10   reasonable upper bounds for the effect of changes in fuel quality on NO_x and DPM emissions

11   during the years 1960–1990.

12   In the northern United States during wintertime, on-road No. 2 diesel may contain some

13   percentage of No. 1 diesel to improve cold-flow properties. Discussions with refiners indicate

14   that a typical wintertime No. 1 diesel blending level is 15 volume percent; however, this number

15   must be taken as a rough estimate. Blending of No. 1 may lower the aromatic content, resulting

16   in improved emissions performance. Nationally, on-highway No. 1 fuels averaged 17% aromatic

17   content in 1994 (Dickson and Sturm, 1994). Thus, there may also be some small but perceptible

18   seasonal changes in emissions from diesel engines.

19   Railroad-grade diesel fuel is significantly different from on-road fuel and is not required to

20   meet the ASTM specification for No. 2 oils. Diesel fuel oil surveys (Shelton, 1979) show that

21   railroad grade diesels have lower cetane number, higher density, and higher T90. Also, the cetane

22   index for these fuels can be as much as 9 cetane units higher than the cetane number, an indication

23   of a high aromatic content in railroad grade diesels.

24   Fuel chemistry is also important for emission of particle-associated PAHs. In studies

25   performed over more than a decade, Williams and Andrews of the University of Leeds have

26   shown that the solvent extractable PAHs from diesel particulate originate almost entirely in the

27   fuel (Williams et al., 1987; Andrews et al., 1998). The PAH molecules are relatively refractory so

28   that a significant fraction survive the combustion process and condense onto the DPM. These

29   studies have been confirmed by other research groups (Crebelli et al., 1995; Tancell et al., 1995).

30   There is a consensus among these researchers that pyrosynthesis of PAHs occurs only at the

31   highest temperature operating conditions in a diesel engine. Under these conditions, most of the

32   DPM and other pyrolysis products are ultimately burned before exiting the cylinder. These results

33   indicate that emissions of PAHs are more a function of the PAH content of the fuel than of engine

34   technology. For a given refinery and crude oil, diesel fuel PAH correlates with total aromatic

35   content and T90. Representative data on aromatic content for diesel fuels in the United States do

36   not appear to be available before the mid-1980s. However, the decreasing trend in cetane

1   number, increasing trend in T90, and the increasing use of light cycle oil from catalytic cracking

2   beginning in the late 1950s suggest that diesel PAH content has increased over the past 40 years.

3   Historical trends in PAH-measured emissions are discussed in Section 2.2.8.2.

4

5   **2.2.5. Chronological Assessment of Emission Factors**

6   **2.2.5.1. *On-Road Vehicles***

7   Numerous studies have been conducted on emissions from in-use on-road HD diesel

8   vehicles. HD vehicles are defined as having a rated gross vehicle weight (GVWR) of greater than

9   8,500 lb, and most over-the-road trucks have a GVWR of 80,000 lb. Emissions of regulated

10   pollutants from these studies have been reviewed (Yanowitz et al., 2000); the review findings,

11   which encompass vehicles from model years 1976 to 1998, are summarized below. In addition, a

12   large amount of engine dynamometer data on HD diesel engines have been published since the

13   mid-1970s. These data are used below to confirm and expand upon the findings from in-use

14   vehicle testing.

15   Figure 2-16 shows chassis dynamometer data for more than 200 different vehicles

16   (approximately one-half of which are transit buses), reported in 20 different published studies, as

17   well as a large amount of additional data collected by West Virginia University (Yanowitz et al.,

18   1999; Warner-Selph and Dietzmann, 1984; Dietzmann et al., 1980; Graboski et al, 1998a;

19   McCormick et al., 1999; Clark et al., 1997; Bata et al., 1992; Brown and Rideout, 1996, Brown

20   et al., 1997; Clark et al., 1995; Dunlap et al., 1993; Ferguson et al., 1992; Gautam et al., 1992;

21   Katragadda et al., 1993; Rideout et al., 1994; Wang et al., 1993, 1994; Williams et al., 1989;

22   Whitfield and Harris, 1998; Graboski et al., 1998b; West Virginia University data available on the

23   World Wide Web at www.afdc.nrel.gov). The results from vehicles tested more than once using

24   the same test cycle, and without any additional mileage accumulated between tests, are averaged

25   and reported as one data point. Buses were tested using the Central Business District (CBD)

26   cycle, while most trucks were tested using the Urban Dynamometer Driving Schedule (UDDS),

27   also known as the Schedule 1d cycle. Some of the trucks were tested using the West Virginia 5-

28   peak cycle, which generates considerably lower g/mi emissions than the CBD or UDDS

29   (Yanowitz et al., 1999). Emissions results from vehicles tested under different test cycles or at

30   different points in the engine's life cycle have been reported as separate data points. Note that all

31   NO_x mass emissions data are reported as equivalent NO_2.

32   Table 2-7 compares the make-up of the fleet of trucks that was tested with the in-use

33   truck fleet according to the 1997 Vehicle Inventory and Use Survey (U.S. Bureau of the Census,

34   1999a). The tested fleet is mostly vehicles in the 33,000-60,000 lb range. Analysis of the tested

35   fleet also shows that the model year distribution is skewed toward newer vehicles. The 1997

36   Vehicle Inventory and Use Survey indicates a flat distribution with roughly the same number of

1   in-use vehicles for each of the model years in the decade preceding 1997. The 1992 Truck

2   Inventory and Use Survey (U.S. Bureau of the Census, 1995) shows the same trend, as shown in

3   Figure 2-1. Analysis of odometer mileage for the tested fleet shows that 45% of the vehicles had

4   less than 50,000 miles at the time of testing. Only 10% of the vehicles had more than 250,000

5   miles. While the mileage distribution of the in-use fleet is unknown, it seems unlikely to be as

6   heavily weighted to low mileage vehicles. Because of the relatively low-mileage of most of the

7   vehicles tested, deterioration of emissions may not be reflected in the results. Yanowitz and co-

8   workers (2000) report that average emissions of regulated pollutants for vehicles of the different

9   classes listed in Table 2-7 are approximately the same. This is clearly a reflection of the small

10   number of vehicles in the lighter weight classes for this dataset, but it also indicates no real

11   difference in emissions for vehicles in Classes 6–8. The data are mainly for vehicles of 19,500 lb

12   and greater GVWR (Classes 6 and 7 and heavier), and predominantly for vehicles of 33,000 lb

13   and greater GVWR (Class 8 trucks and buses).

14   Figure 2-16 shows emissions trends in g/mi.   Least-squares linear regressions and 95%

15   confidence intervals are plotted on each graph and yield the following equations for predicting

16   emissions trends (applicable to the years 1976–98):

17

18   $\text{Log NO}_x \text{ (g/mile)} = (\text{Model year} * -0.008) + 16.519 \quad R^2 = 0.024$ (2-1)

19   $\text{Log PM (g/mile)} = (\text{Model year} * -0.044) + 88.183 \quad R^2 = 0.28$ (2-2)

20   $\text{Log HC (g/mile)} = (\text{Model year} * -0.055) + 109.39 \quad R^2 = 0.27$ (2-3)

21   $\text{Log CO (g/mile)} = (\text{Model Year} * -0.041) + 82.876 \quad R^2 = 0.22$ (2-4)

22

23   As shown in Figure 2-16, changes in NO_x emissions have been relatively small, with an

24   emission rate averaging about 26 g/mi. The data reported in Figure 2-16 are real-world, in-use

25   emissions measurements and therefore more accurately reflect emission factors than engine test

26   data during this time period. There are two potential causes for the relative constancy of NO_x

27   emissions as described by Figure 2-16. The first is emissions deterioration due to engine wear.

28   Weaver and Klausmeier (1988) have shown that diesel engine deterioration results in lower NO_x

29   emissions and higher DPM emissions, and this finding has recently been confirmed by McCormick

30   and co-workers (2000). Wear of mechanical devices that limit smoke, fuel pumps, and fuel

31   injectors alters the effective injection timing to decrease NO_x. Since deterioration is more a

32   function of maintenance than vehicle age or mileage, deterioration introduces a wide range in NO_x

33   emission factors measured in the chassis dynamometer studies. The lack of a decreasing trend in

34   NO_x emissions can also be attributed to the use of illegal emissions control defeat devices, an issue

35   addressed by EPA in its recent settlement with the diesel engine manufacturers. The defeat

devices produced low NO_x emissions on the transient test (HD FTP) but operated in a high NO_x/high fuel economy mode in-use under highway cruise type conditions.

Figure 2-17 shows engine certification data for NO_x emissions reported in the many studies that have employed the transient test over the past 25 years. The engine testing data are also listed in Table 2-8. The data compiled in Figure 2-17 show a significant decline in NO_x emissions, and all engines would appear to meet the regulatory standards for their year of manufacture due to the defeat devices. During the period from 1980 to 1997, the EPA emissions trends report (U.S. EPA, 1998a) predicted a decline in NO_x emissions from HD diesel vehicles since these data are based on engine test data. The emissions trend includes the growth in vehicle miles traveled over time as well as changes in emission factors. The more recent trends inventory (U.S. EPA, 2000a, discussed earlier), accounts for the defeat devices and accordingly demonstrates a slight increase in NOx emissions from on-road HD diesel vehicles in the period from 1990 to 1998.

DPM, CO, and THC emissions, although widely variable within any model year, have shown a pronounced declining trend (Figure 2-16). DPM emissions from chassis dynamometer tests decreased from an average of 3-4 g/mi in 1977 to an average of about 0.5 g/mi in 1997, suggesting a decrease in DPM emissions of a factor of about 6. Note that these data are for vehicles or engines tested on in-use or industry average fuel at the time they were tested. Indications are that the observed decline in DPM is caused primarily by changes in engine technology that often result from emission standards, as well as by the lowering of on-road diesel fuel sulfur content in 1993.

While a substantial decreasing trend in DPM emissions from in-use chassis dynomometer testing and engine testing (Figure 2-18) is evident, these data reflect a wide range in emission factors within any given model year. For example, emission factors for model year 1996 range from less than 0.1 g/mi to over 1 g/mi (Yanowitz et al., 2000; Graboski et al., 1998b). The high variability in DPM emissions measured in the chassis dynamometer tests is observed due to several factors, including differences in measurement methods and test conditions at the various testing facilities, deterioration, and engine-to-engine variation. While there can be excellent agreement between chassis dynamometer testing facilities (Graboski et al., 1998a), there is no standard HD chassis dynamometer Federal test procedure, and no detailed procedures for such testing are described in any authoritative source such as the Code of Federal Regulations, which does contain such procedures for engine dynamometer testing used for EPA emission regulations. Therefore, each facility has developed its own approach to HD testing. Clark et al. (1999) report that the test cycle can have a substantial effect on DPM emissions, with higher DPM emissions reported from test cycles that incorporate full power accelerations. Test cycles incorporating full power accelerations reflect urban HD vehicle driving for several types of vehicles (garbage trucks,

1   buses) operating in urban areas. Clark et al. (1999) also report that aggressive acceleration

2   produces higher DPM emission rates compared to conservative acceleration, and Clark and co-

3   workers suggest that real in-use driving is more likely to mimic aggressive acceleration. While

4   currently unquantified, it is generally believed that the majority of DPM is generated under

5   transient conditions such as heavy acceleration.

6   Weaver and Klausmeier (1988) have examined potential causes and frequency of DPM

7   emissions deterioration for in-use HD diesel vehicles. Potential causes include manufacturing

8   defects and malfunctions such as retarded timing, fuel injector malfunction, smoke limiting

9   mechanism problems, clogged air filter, wrong or worn turbocharger, clogged intercooler, engine

10   mechanical failure, excess oil consumption, and electronics that have been tampered with or have

11   failed. The recent report by McCormick and co-workers (2000) indicates that many of these

12   malfunctions can have very large effects on DPM emissions, resulting in DPM increases of

13   typically 50% to 100%. While Yanowitz and co-workers (1999) found that DPM emissions were

14   positively correlated with odometer mileage for a fleet of 21 vehicles, it is more likely that the

15   vehicle state of maintenance will be more important for determining the degree of emissions

16   deterioration than mileage. In fact, in a similar analysis performed on the chassis dynamometer

17   results included in the review of Yanowitz et al. (2000), DPM emissions could not be correlated

18   with odometer mileage. Differences in testing methods between various facilities, as well as

19   varying states of maintenance for vehicles of the same mileage and model year probably account

20   for this lack of correlation.

21   It is difficult, given current information, to quantitatively assess the contribution of high-

22   emitting or smoking diesel vehicles to ambient DPM. Emission models used to prepare diesel

23   particulate emission inventories presently do not account for deterioration. The relative

24   contribution of high-emitting diesel vehicles to the total mass and overall chemical composition of

25   diesel particulates is presently being quantified. Some studies report numerous smoking diesel

26   trucks. A study of the smoke opacity based inspection and maintenance program in California

27   found failure rates of 20% and higher, suggesting that high-emitting vehicles are not uncommon

28   (CARB/EEAI, 1997). In the Northeast, smoke opacity testing conducted on 781 HD trucks

29   found that 15% of the vehicles failed the smoke standard (40% opacity for 1991 and newer HD

30   diesel vehicles and 50% opacity for pre-1991 HD diesel vehicles) (Cooper, 1999). While the

31   correlation between smoke and particulate emissions tends to be qualitative or semiquantitative

32   (discussed below), there is a good correlation between opacity and elemental carbon

33   concentrations, and it is expected that high-emitting diesel vehicles may be an important part of

34   the DPM emission inventory.

35   Others have attempted to determine if the effects of deterioration could be detected for

36   in-use vehicles. In a study of 21 vehicles (Yanowitz et al., 1999), a linear multivariate regression

1   analysis found that DPM emissions were positively correlated with odometer mileage (several

2   other correlation factors were also identified, including model year). A similar analysis performed

3   on the chassis dynamometer results included in the review of Yanowitz et al. (2000) found that

4   DPM emissions could not be correlated with odometer mileage, probably because of differences

5   in testing methods between the various facilities.

6   Other approaches for measuring emissions from in-use on-road diesel vehicles include

7   tunnel tests and remote sensing, the latter of which measures gaseous, but not DPM, emissions.

8   The literature reports of those studies are summarized in Tables 2-9 and 2-10. Several tunnel test

9   studies have reported DPM emission factors (Pierson and Brachaczek 1976; Szkarlat and Japar

10 1983; Pierson et al., 1983; Kirchstetter et al., 1999; Gertler et al., 1995, 1996).

11 The method for determining emission rates for vehicles traveling through a tunnel are

12 explained in detail by Pierson et al. (1996). Briefly, the emissions of a species are determined by

13 measuring the concentration of a pollutant entering and leaving a tunnel along with knowledge of

14 the cross section of the tunnel and measurements of the wind flux at the inlet and outlet of the

15 tunnel. The emission rate is calculated by dividing the mass of the pollutant by the number of

16 vehicles that passed through the tunnel and the length of the tunnel. The diesel and gasoline

17 vehicle contributions to the total emission of the pollutant are separated by a simple regression

18 analysis where the intercepts (100% HD and 100% LD) are the diesel and gasoline emission rates,

19 respectively.

20 Emission factors from tunnel studies provide a snapshot of real-world emissions under

21 driving conditions experienced in the tunnel and reflect emission factors representative of the mix

22 of in-use vehicles and the atmospheric dilution and short-term transformation processes of diesel

23 exhaust. Emission factors derived from tunnel studies are often used as one source of information

24 to study the impact of improved technology and fleet turnover on emissions because they allow

25 random sampling of large numbers of vehicles, including a range of ages and maintenance

26 conditions. However, tunnel studies are limited in that they represent driving conditions on a

27 single roadway passing through a tunnel and represent mostly steady-state driving conditions,

28 whereas most DPM is generated during transient modes of operation; also tunnel studies do not

29 include cold-start operations. Both of these factors need to be assessed to understand emission

30 rates for DPM to which people are exposed (U.S. EPA 1992, 1995). DPM emission factors from

31 in-use fleets derived from tunnel studies in the 1970s and 1980s compared with the 1990s suggest

32 approximately a fivefold decrease in DPM mass emission factors, with the most recent data from

33 1999 reporting an emission factor of 0.29 g/mi for the on-highway HD diesel fleet (Figure 2-19).

34 Emission factors vary substantially for the various tunnels, with NO_x emissions ranging

35 from 9.7 to 23.8 g/mi in the 1990s, CO emissions ranging from 6 to 14 g/mi, and THC emissions

36 ranging from 0.16 to 2.55 g/mi.

1   Remote sensing reports emission factors in terms of pollutant emissions per unit of fuel,
2 not on a per-mile basis. Agreement between remote sensing and tunnel studies for NO_x emissions
3 is reasonably good for the fleet as a whole, suggesting an average level for the fleet of about 130
4 g/gal, comparable to the average emissions factor measured in chassis dynamometer studies
5 (remote sensing can measure emissions from an individual vehicle, while tunnel studies measure
6 emissions from the fleet as a whole). Generally, chassis dynamometer tests and engine
7 dynamometer test results are corrected for ambient humidity, in accordance with the Federal Test
8 Procedure (CFR 40, Subpart N). Tunnel tests and remote sensing tests have typically not
9 included corrections for humidity. Appropriate humidity corrections for NO_x and DPM can be
10 greater than 20% and 10%, respectively (or a total difference of more than 45% and 20%,
11 respectively, between low- and high-humidity areas), under normally occurring climatic
12 conditions. Additionally, the remote sensing literature has not addressed how to determine the
13 correct value for the NO/NO_x ratio, and there is reason to believe that this value may differ
14 systematically from site to site, although almost all of the NO_x is NO as it leaves the vehicle.
15   In addition to the humidity correction discussed above, several factors must be taken into
16 account when comparing DPM measurements from tunnel tests to chassis dynamometer
17 measurements (Yanowitz et al., 2000): (1) Chassis testing measures only tailpipe emissions;
18 tunnel tests can include emissions from other sources (tire wear, etc.), and (2) tunnel tests
19 typically measure emissions under steady-speed freeway conditions, whereas most chassis
20 dynamometer tests are measured on cycles that are more representative of stop-and-go urban
21 driving conditions. This latter limitation also applies to remote sensing readings, which measure
22 instantaneous emissions versus emissions over a representative driving cycle.
23   Because THC emissions for diesel vehicles are very low in total mass in comparison to
24 gasoline vehicles, tunnel test results for THC have a high degree of uncertainty. A regression
25 analysis to determine the contribution of the limited number of HD vehicles to THC emissions is
26 unstable; small errors in the total measurements can change estimates substantially. Similarly, CO
27 emissions are comparable to automobile emissions on a per-vehicle-mile basis, but since there are
28 generally many more automobiles than HD diesels in tunnel tests, CO measurements from diesels
29 may also have a high degree of uncertainty.
30   As the discussion above indicates, there is a reasonable amount of data upon which to base
31 emission factor estimates for late 1970s and later HD vehicles. However, almost no transient test
32 data are available on engines earlier than the mid-1970s. Nevertheless, there are engine design
33 factors that allow reasonable assumptions to be made about emissions from engines in the mid-
34 1950 to 1970 timeframe. For example, the same means of controlling the engine's air-fuel ratio
35 was used over the period from 1950 to 1970. That is, air-fuel ratios richer than the "smoke limit"
36 of about 22:1 were avoided by fuel system control. This air-to-fuel ratio control, in essence,

1 formed an "upper limit" on DPM emissions and was implemented before the advent of EPA

2 smoke standards for customer satisfaction reasons. There is only a qualitative correlation

3 between smoke (measured as smoke opacity) and particle emissions over the transient driving

4 cycle, but there is semiquantitative correlation between smoke and particle emissions over

5 steady-state operating modes (McGuckin and Rykowski, 1981). Additionally, there is good

6 correlation between smoke and elemental carbon emissions (Alkidas, 1984). The fact that

7 engines, turbocharged or not, were controlled to avoid smoky operation makes it reasonable to

8 assume that they had emissions roughly at the mid-1970s level for many years before this

9 timeframe. Other than the increased use of turbochargers, HD diesel engine technology was

10 reasonably stable since the 1950s, with most engines having direct injection and a nearly constant

11 fraction of two-stroke versus four-stroke engines. Thus, it is likely that the emission factors

12 reported above for mid-1970s engines adequately represent the engines in use in the 1950–70

13 timeframe. Note that the impact of engine technology developments on emissions is specifically

14 discussed in Section 2.2.6.

15

16 **2.2.5.2. *Locomotives***

17 Locomotive engines generally range from 1,000 horsepower up to 6,000 horsepower.

18 Similar to the much smaller truck diesel engines, the primary pollutants of concern are NO_x,

19 DPM, CO, and HC. Unlike truck engines, most locomotive engines are not mechanically coupled

20 to the drive wheels. Because of this decoupling, locomotive engines operate in specific steady-

21 state modes rather than the continuous transient operation normal for trucks. Because the

22 locomotive engines operate only at certain speeds and torques, the measurement of emissions is

23 considerably more straightforward for locomotive engines than for truck engines. Emissions

24 measurements made during the relatively brief transition periods from one throttle position to

25 another indicate that transient effects are very short and thus could be neglected for the purposes

26 of overall emissions estimates.

27 Emissions measurements are made at the various possible operating modes with the engine

28 in the locomotive, and then weighting factors for typical time of operation at each throttle

29 position are applied to estimate total emissions under one or more reasonable operating scenarios.

30 In the studies included in this analysis, two scenarios were considered: line-haul (movement

31 between cities or other widely separated points) and switching (the process of assembling and

32 disassembling trains in a switchyard).

33 The Southwest Research Institute made emissions measurements for three different

34 engines in locomotives in 1972 (Hare and Springer, 1972) and five more engines in locomotives

35 using both low- and high-sulfur fuel in 1995 (Fritz, 1995). Two engine manufacturers (the

36 Electro-Motive Division of GM, and GE Transportation Systems) tested eight different engine

1 models and reported the results to EPA (U.S. EPA, 1998b). All available data on locomotives are

2 summarized in the regulatory impact assessment and shown in Figure 2-20.

3

4 **2.2.6. Engine Technology Description and Chronology**

5 NO_x emissions, DPM emissions, and brake-specific fuel consumption (BSFC) are among

6 the parameters that are typically considered during the development of a diesel engine. Many

7 engine variables that decrease NO_x can also increase DPM and BSFC. One manifestation of the

8 interplay among NO_x, DPM, and BSFC is that an increase in combustion temperatures will tend to

9 increase NO formation via the Zeldovich mechanism. Higher temperatures will also often

10 improve thermal efficiency, can improve BSFC, and can increase the rate of DPM oxidation, thus

11 lowering DPM emissions. One example of this is the tradeoff of DPM emissions and BSFC

12 versus NO_x emissions with fuel injection timing. Many recent advances in reducing the emissions

13 of diesel engines without aftertreatment are combinations of technologies that provide incremental

14 improvements in the tradeoffs among these emissions and fuel consumption. The sum total,

15 however, can be considerable reductions in regulated emissions within acceptable levels of fuel

16 consumption.

17 The majority of current HD diesel truck engines certified for use in the United States

18 utilize:

19 • A four-stroke cycle

20 • Direct-injection, high-pressure (1,200 bar to >2,000 bar) fuel injection systems with

21 electronic control of injection timing and, in some cases, injection rate

22 • Centrally located multihole injection nozzles

23 • Three or four valves per cylinder

24 • Turbochargers

25 • In many cases, air-to-air aftercooling

26 • In some cases, the use of an oxidation catalyst.

27

28 These features have phased into use with HD truck engines because they offer a relatively

29 good combination of fuel consumption, torque-rise, emissions, durability, and the ability to better

30 "tune" the engines for specific types of applications. Fuel consumption, torque-rise, and

31 drivability have been maintained or improved while emissions regulations have become more

32 stringent. Many Class 8a and 8b diesel truck engines are now capable of 700,000 to 1,000,000

33 miles of driving before their first rebuild and can be rebuilt several times because of their heavy

34 construction and the use of removable cylinder liners. These engines are expected to last longer

35 and therefore have a useful life longer than the regulatory estimate of full useful life for HD

36 engines (~1,000,000 miles) previously used by EPA (for 1980 engines that were driven less than

1 300,000 miles between rebuilds and were rebuilt up to three times). Current four-stroke

2 locomotive engines use engine technology similar to on-highway diesel engines, except that

3 electronic controls have only recently been introduced.

4   It is difficult to separate the components of current high-speed diesel engines for

5 discussion of their individual effects on emissions. Most of the components interact in numerous

6 ways that affect emissions, performance, and fuel consumption.

7

8 **2.2.6.1.** *Indirect and Direct Injection High-Speed Diesel Engines*

9   Prior to the 1930s, diesel engine design was limited to relatively low-speed applications

10 because sufficiently high-pressure fuel injection equipment was not available. With the advent of

11 high-speed and higher pressure pump-line-nozzle systems, introduced by Robert Bosch in the

12 1930s, it became possible to inject the fuel directly into the cylinder for the first time, although

13 indirect injection (IDI) diesel engines continued in use for many years. As diesels were introduced

14 into the heavy truck fleet in the 1930s through the 1950s, both IDI and direct injection (DI)

15 naturally aspirated variants were evident. A very low-cost rotary injection pump technology was

16 introduced by Roosa-Master in the 1950s, reducing the cost of DI systems and allowing their

17 introduction on smaller displacement, higher speed truck engines. After this time, only a small

18 fraction of truck engines used an IDI system.

19   DI diesel engines have now all but replaced IDI diesel engines for HD on-highway

20 applications.[2] IDI engines typically required much more complicated cylinder head designs but

21 generally were capable of using less sophisticated, lower pressure injection systems with less

22 expensive single-hole injection nozzles. IDI combustion systems are also more tolerant of lower

23 grades of diesel fuel. Fuel injection systems are likely the single most expensive component of

24 many diesel engines. Caterpillar continued producing both turbocharged and naturally aspirated

25 IDI diesel engines for some on-highway applications into the 1980s. Caterpillar and Deutz still

26 produce engines of this type, primarily for use in underground mining applications. IDI

27 combustion systems are still used in many small-displacement (<0.5 L/cylinder), very high-speed

28 (>3,000 rpm rated speed) diesel engines for small nonroad equipment (small imported tractors,

29 skid-steer loaders), auxiliary engines, and small generator sets, and they were prevalent in diesel

30 automotive engines in the 1980s; IDI designs continue to be used in automotive diesel engines.

31   IDI engines have practically no premixed burn combustion and thus are often quieter and

32 have somewhat lower NO_x emissions than DI engines. Electronic controls, high-pressure

33 injection (e.g., GM 6.5), and four-valve/cylinder designs (e.g., the six-cylinder Daimler LD

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[2]The GM Powertrain/AM General 6.5L electronically controlled, turbocharged IDI-swirl chamber engine, certified
as a light HD diesel truck engine, is the last remaining HD on-highway IDI engine sold in the United States.

1 engine) can be equally applied to IDI diesel engines as in DI, but they negate advantages in cost

2 over DI engines. DI diesel engines of the same power output consume 15% to 20% less fuel than

3 IDI engines (Heywood, 1988). Considering the sensitivity of the HD truck market to fuel costs,

4 this factor alone accounts for the demise of IDI diesel engines in these types of applications.

5 Throttling and convective heat transfer through the chamber-connecting orifice, and heat rejection

6 from the increased surface area of IDI combustion systems, decrease their efficiency and can

7 cause cold-start difficulties when compared to DI designs. Most IDI diesel engine designs require

8 considerably higher than optimum compression ratios (from an efficiency standpoint) to aid in

9 cold-starting (19:1 to 21:1 for IDI engines vs. ~15:1 to 17:1 for DI engines).   Because of the

10 early introduction of DI technology into truck fleets, it is likely that by the end of the 1960s, only

11 a small fraction of the HD diesel engines sold for on-highway use were IDI engines. It is unlikely

12 that the shift from IDI to DI engine designs through the 1950s and 1960s occurred rapidly and

13 likely that this shift had little significant impact on emissions. Springer (1979) reports a

14 comparison of nearly identical Caterpillar 3406 engines (turbocharged and aftercooled) in DI and

15 IDI configurations tested on an engine dynamometer under steady-state conditions, which limits

16 the usefulness of these data. There is no significant difference in emissions of DPM, soluble

17 organic fraction (SOF), aldehydes, or DPM-associated benzo[a]pyrene (Table 2-8). Note that

18 IDI designs continue to be used in automotive diesel engines.

19

20 **2.2.6.2. *Injection Rate***

21   Decreasing the duration of diffusion combustion and promoting elemental carbon

22 oxidation during the expansion stroke can reduce formation of elemental carbon agglomerates

23 (Stone, 1995) and reduce the particulate carbon fraction at high load (Needham et al., 1989).

24 Both of these effects are enhanced by increasing the fuel injection rate. The primary means of

25 accomplishing this is by increasing fuel injection pressure. In 1977 Robert Bosch introduced a

26 new type of high-pressure pump capable of producing injection pressures of 1,700 bar at the

27 nozzle (Voss et al., 1977). This increased fuel injection pressure by roughly a factor of 10. Unit

28 injection, which combines each fuel injection nozzle with individual cam-driven fuel pumps, can

29 achieve very high injection pressures (>2,000 bar). The first combination of unit injectors with

30 electronically controlled solenoids for timing control was offered in the United States by Detroit

31 Diesel Corporation in the 1988 model year (Hames et al., 1985). Replacement of the injection

32 cam with hydraulic pressure, allowing a degree of injection rate control, was made possible with

33 the hydraulic-electronic unit injection jointly developed by Caterpillar and Navistar, introduced on

34 the Navistar T444E engine (and variants) in 1993.

35   It is widely known that high fuel injection pressures have been used to obtain compliance

36 with the PM standards that went into effect in 1988 (Zelenka et al., 1990). Thus, it is likely that a

1 transition to this technology began in the 1980s, with the vast majority of new engine sales

2 employing this technology by 1991, when the 0.25 g/bhp-hr Federal PM standard went into effect.

3   The use of electronic control of injection rate is rapidly increasing on medium HD diesel

4 engines. Engines are currently under development, perhaps for 2002–2004 introduction, that use

5 common-rail fuel injection systems with even more flexible control over injection pressure and

6 timing than previous systems.

7   Increased injection rate and pressure can significantly reduce elemental carbon emissions,

8 but it can also increase combustion temperatures and cause an increase in NO_x emissions

9 (Springer, 1979; Watson and Janota, 1982; Stone, 1995). Low NO_x, low DPM, and relatively

10 good BSFC and brake mean engine pressure (BMEP) are possible when combined with

11 turbocharging, aftercooling, and injection timing retard.

12

13 **2.2.6.3. *Turbocharging, Charge-Air Cooling, and Electronic Controls***

14   Use of exhaust-driven turbochargers to increase intake manifold pressure has been applied

15 to both IDI and DI diesel engines for more than 40 years. Turbocharging can decrease fuel

16 consumption compared to a naturally aspirated engine of the same power output. Turbocharging

17 utilizes otherwise wasted exhaust heat and pressure to generate intake boost. The boosted intake

18 pressure effectively increases air displacement and increases the amount of fuel that can be

19 injected to achieve a given fuel-air equivalence ratio. Turbocharging increases the power density

20 of an engine. Boosting intake pressure via turbocharging and reducing fuel-to-air ratio at a

21 constant power can significantly increase both intake temperatures and NO_x emissions. Increased

22 boost pressure can significantly reduce ignition delay, which reduces VOC and DPM SOF

23 emissions (Stone, 1995) and increases the flexibility in selection of injection timing. Injection

24 timing on turbocharged engines can be retarded further for NO_x emission control with less of an

25 effect on DPM emissions and fuel consumption. This allows a rough parity in NO_x emissions

26 between turbocharged (non-aftercooled) and naturally aspirated diesel engines (Watson and

27 Janota, 1982).

28   Turbocharging permits the use of higher initial injection rates (higher injection pressure),

29 which can reduce particulate emissions. Although this may offer advantages for steady-state

30 operation, hard accelerations can temporarily cause overly fuel-rich conditions because the

31 turbocharger speed lags behind a rapid change in engine speed (turbo-lag). This can cause

32 significant increases in DPM emissions during accelerations. Before the advent of electronic

33 controls, the effect of acceleration on DPM emissions could be limited by mechanically delaying

34 demand for maximum fuel rate with a "smoke-puff eliminator." Since this device also limited

35 engine response, there was considerable incentive for the end-users to remove or otherwise render

36 the device inactive. Charge-air cooling, for example, using an air-to-air aftercooler (air-cooled

1   heat exchanger) between the turbocharger compressor and the intake manifold, can greatly reduce

2   intake air and peak combustion temperatures. When combined with injection timing retard,

3   charge-air cooling allows a significant reduction in NO_x emissions with acceptable BSFC and

4   DPM emissions when compared to either non-aftercooled or naturally aspirated diesel engines

5   (Hardenberg and Fraenkle, 1978; Pischinger and Cartellieri, 1972; Stone, 1995). The use of

6   charge-air cooling effectively shifts the NO_x-DPM tradeoff curve, as shown in Figure 2-21.

7   Electronic control of fuel injection timing allowed engine manufacturers to carefully tailor

8   the start and length of the fuel injection events much more precisely than through mechanical

9   means. Because of this, newer on-highway turbocharged truck engines have virtually no visible

10   smoke on acceleration (although emissions of DPM are substantial during this driving mode).

11   Electronic controls also allowed fuel injection retard under desirable conditions for NO_x

12   reduction, while still allowing timing optimization for reduced VOC emissions on start-up,

13   acceptable cold-weather performance, and acceptable performance and durability at high altitudes.

14   Previous mechanical unit injected engines (e.g., the 1980s Cummins L10, the non-DDEC DDC

15   6V92) were capable of reasonably high injection pressures, but they had fixed injection timing that

16   only varied based on the hydraulic parameters of the fuel system. Many other engines with

17   mechanical in-line or rotary injection pumps had only coarse injection timing control or fixed

18   injection timing.

19   Precise electronic control of injection timing over differing operating conditions also

20   allowed HD engine manufacturers to retard injection timing to obtain low NO_x emissions during

21   highly transient urban operation, similar to that found during emissions certification. HD engine

22   manufacturers also advanced injection timing during less transient operation (such as freeway

23   driving) for fuel consumption improvements (~3% to 5%) at the expense of greatly increased NO_x

24   emissions (approximately three to four times regulated levels). This particular situation resulted

25   in the recent consent decree settlements between the Federal Government and most of the HD

26   engine manufacturers to assure effective NO_x control in all driving conditions, including on-

27   highway high speed steady-state driving.

28   Turbocharged engines entered the market very slowly beginning in the 1960s. Data for

29   DPM emissions from naturally aspirated engines of model years 1976 to 1983 are compared with

30   DPM emissions from turbocharged engines in Figure 2-22. It is apparent that there is no

31   consistent difference in DPM emissions between turbocharged and naturally aspirated engines.

32   While not plotted, the data also show no difference in emissions of NO_x, DPM SOF, or DPM-

33   associated benzo[a]pyrene and 1-nitropyrene.

34   Charge-air cooling was introduced during the 1960s and was initially performed in a heat

35   exchanger using engine coolant. Cooling of the charge-air using ambient air as the coolant was

36   introduced into heavy trucks by Mack in 1977 with production of the ETAY(B)673A engine

1   (Heywood, 1988). Use of ambient air allowed cooling of the charge-air to much lower

2   temperatures. Most HD diesel engines sold today employ some form of charge-air cooling, with

3   air-to-air aftercooling being the most common. Johnson and co-workers (1994) have presented a

4   comparison of similar engines that differ in that the charge-air is cooled by engine coolant (1988

5   engine) and by ambient air, with a higher boost pressure for the second (1991 engine). The 1991

6   engine also used higher pressure fuel injectors. The 1991 engine exhibited both lower DPM

7   emissions (50% lower than the 1988 engine) and lower NO_x emissions. Higher injection pressure

8   is likely to have enabled the reduced DPM emissions, while the lower charge-air temperature and

9   the ability to electronically retard the injection timing under some conditions likely enabled the

10   lower NO_x emissions.

11   It is apparent on the basis of both the literature and certification data that turbochargers

12   with aftercoolers can be used in HD engines in conjunction with other changes to produce a

13   decrease in emissions. Upon the advent of a NO_x standard in 1985, NO_x was probably reduced on

14   the order of 10% to 30% in turbocharged aftercooled engines with retarded injection timing. This

15   decrease in emissions is not evident in the in-use chassis testing data because of deterioration and

16   the use of illegal defeat devices as described above. Overall, it is expected that engines in the

17   1950 to mid-1970s timeframe would have similar DPM emission rates, while post-1970 engines

18   would have somewhat lower DPM emission rates.

19

20   **2.2.6.4. *Two-Stroke and Four-Stroke High-Speed Diesel Engines***

21   A detailed discussion of the two- and four-stroke engine cycles can be found in the

22   literature (Heywood, 1988; Taylor, 1990; Stone, 1995). Nearly all high-speed two-stroke diesel

23   engines utilize uniflow scavenging assisted by a positive-displacement blower (Figure 2-23).

24   Uniflow-scavenged two-stroke diesels use poppet exhaust valves similar to those found in four-

25   stroke engines. The intake air enters the cylinder through a pressurized port in the cylinder wall.

26   A crankshaft-driven, positive-displacement blower (usually a roots-type) pressurizes the intake

27   port to ensure proper scavenging. A turbocharger may be added to the system to provide

28   additional boost upstream of the blower at higher speeds and to reduce the size and parasitic

29   losses associated with the positive-displacement blower.

30   Two-stroke diesel engines can achieve efficiency comparable to four-stroke counterparts

31   and have higher BMEP (torque per unit displacement) (Heywood, 1988). It is useful to note that

32   the two-stroke cycle fires each cylinder once every revolution, while the four-stroke cycle fires

33   every other revolution. Thus, for a given engine size and weight, two-strokes can produce more

34   power. However, two-stroke diesel engines are less durable than their four-stroke counterparts.

35   Lubricating oil is transferred from the piston rings to the intake port, which causes relatively high

36   oil consumption relative to four-stroke designs. Durability and low oil consumption are desirable

1 for on-highway truck applications. This may be why four-stroke engines have been favored for

2 these applications since the beginning of dieselization in the trucking industry, with the notable

3 exception of urban bus applications. Although it is no longer in production, the Detroit Diesel

4 6V92 series of two-stroke diesel engines is still the most popular for urban bus applications,

5 where the high power density allows the engine to be more easily packaged within limited spaces.

6 The primary reason that two-stroke engines like the 6V92 are no longer offered for urban bus

7 applications is excessive DPM emissions. The lubricating oil control with two-strokes tends to be

8 lower for two-stroke engines, and therefore, emissions have higher VOC and organic DPM

9 emissions relative to four-stroke designs. This was particularly problematic for urban bus

10 applications because urban bus engines must meet tighter Federal and California PM emissions

11 standards. The current urban bus PM standard (0.05 g/bhp-hr) is one-half of the current on-

12 highway HD diesel engine PM standard, although EPA is in the process of proposing more strict

13 standards for HD diesel truck engines along with further reductions in diesel fuel sulfur levels. No

14 two-stroke diesel engine designs have been certified to meet the most recent urban bus PM

15 emissions standards, and Detroit Diesel Corporation has not certified a two-stroke diesel engine

16 for on-highway truck use since 1995.

17 A comprehensive review of emissions from hundreds of vehicles (1976–98 model years)

18 that had been tested on chassis dynamometers found that DPM emissions vary substantially within

19 a given model year and that within that variation there are no discernable differences in DPM

20 emissions between two- and four-stroke vehicles (Figure 2-24) (Yanowitz et al., 2000). DPM

21 emission factors reported for engine tests also indicate that two- and four-stroke engines have

22 comparable emission factors, since these engines all had to meet the same regulatory standard

23 (Figure 2-25). In contrast to DPM emissions, evidence suggests that mid-1970s two-stroke

24 engines exhibited very high SOF levels compared to four-stroke engines during that timeframe

25 with later model years showing similar SOF emissions for two- and four-stroke engines (Figure 2-

26 26). For aldehydes, benzo[a]pyrene, and 1-nitropyrene, data are available for only one two-stroke

27 engine, but they indicate no significant difference in emissions from comparable model year four-

28 stroke engines. Overall, regulated emissions changes due to changing proportions of two- and

29 four-stroke engines in the in-use fleet do not appear to have influenced DPM emission levels, but

30 the transition to four-stroke engines in the 1970s would have decreased the fraction of SOF

31 associated with the DPM. It appears that the proportion of two-stroke engines in the in-use fleet

32 was relatively constant until the late 1980s when it began to decline.

33

2.2.7. Air Toxic Emissions

Heavy-duty diesel vehicle exhaust contains several substances that are known, likely, or possible human or animal carcinogens, or that have serious noncancer health effects. These substances include, but are not limited to, benzene, formaldehyde, acetaldehyde, 1,3-butadiene, acrolein, dioxin, PAH and nitro-PAH (the complete list of chemically characterized compounds present in diesel exhaust is provided in Section 2.3.1). Very few historical data are available to examine changes in emission rates over time. In this section, trends in aldehyde emissions over time and a summary of dioxin emission factors are presented. PAH and nitro-PAH emission factors are discussed in Section 2.2.8.2.

2.2.7.1. *Aldehyde Emissions*

Among the gaseous components emitted by diesel engines, the aldehydes are a particularly important component because they comprise an important fraction of the gaseous emissions and they are probable carcinogens that also produce noncancer health effects. Formaldehyde comprises the majority of the aldehyde emissions (65% to 80%), with acetaldehyde being the second most abundant aldehyde in HD diesel emissions. Total aldehyde emissions reported from chassis dynamometer testing suggest that aldehyde emissions have declined since 1980; however, only two tests reported aldehydes from engines made after 1985 (Figure 2-27). Engine dynamometer studies also suggest a downward trend in the emissions of aldehydes in the time period from 1976 to 1994 (Figure 2-28). Engine dynamometer studies report aldehyde emission levels of 150–300 mg/bhp-hr for late 1970s engines with no significant effect of turbocharging, or IDI versus DI. High-pressure fuel injection may have resulted in a marginal increase in aldehyde emissions (Springer, 1979). By comparison, 1991 model year engines (DI, turbocharged) exhibited aldehyde emissions in the 30–50 mg/bhp-hr range (Mitchell et al., 1994).

2.2.7.2. *Dioxin and Furans*

Ballschmiter et al. (1986) reported detecting polychlorinated dibenzo-p-dioxins (CDDs) and polychlorinated dibenzofurans (CDFs) in used motor oil and thus provided some of the first evidence that CDDs and CDFs might be emitted by the combustion process in diesel-fueled engines. Incomplete combustion and the presence of a chlorine source in the form of additives in the oil or the fuel were speculated to lead to the formation of CDDs and CDFs. Since 1986, several studies have been conducted to measure or estimate CDD/CDF concentrations in emissions from diesel-fueled vehicles. These studies can be characterized as direct measurements from the engine exhaust and indirect measurements as indicated by the sampling of air within transportation tunnels.

1   Table 2-11 is a summary of various CDD/CDF emission characterization studies reported

2   in the United States and Europe for diesel-fueled cars and trucks. Hagenmaier et al. (1990)

3   reported an emission factor for LD diesel vehicles of 24 pg TEQ per liter of diesel fuel consumed.

4   TEQ, or the toxic equivalency factor, rates each dioxin and furan relative to that of 2,3,7,8-

5   TCDD, which is arbitrarily assigned a TEQ of 1.0. Schwind et al. (1991) and Hutzinger et al.

6   (1992) studied emissions of CDDs/CDFs from German internal combustion engines running on

7   commercial diesel fuels and reported a range of CDD/CDF emission rates across the test

8   conditions (in units of pg TEQ per liter of diesel fuel consumed) of 10–130 pg TEQ/L for diesel

9   car exhaust and 70–81 pg TEQ/L for diesel truck exhaust.

10   In 1994, Hagenmaier reported CDD/CDF emissions from a diesel-fueled bus and found no

11   detectable levels in the exhaust (at a detection limit of 1 pg /L of fuel consumed) for individual

12   congeners. In 1987, the California Air Resources Board (CARB) produced a draft report of a

13   HD engine tested under steady-state conditions indicating a TEQ emission factor of 7,290 pg/L of

14   fuel burned (or 1,300 pg/km driven) if nondetected values are treated as one-half the detection

15   limit. Treating nondetected values as zeros yields a TEQ concentration equivalent to 3,720 pg/L

16   of fuel burned (or 663 pg/km driven) (Lew, 1996). Norbeck et al. (1998c) reported emission

17   factors for dioxin and furans from a Cummins L10 HD diesel engine running on pre-1993 fuel of

18   0.61 pg/L and 0.41 pg/L for the same engine running on reformulated fuel. The low emission

19   factors reported by Norbeck et al. (1998c) were attributed to losses of dioxin and furan

20   compounds to the dilution tunnel walls.

21   EPA has directly sampled the exhaust from a HD diesel truck for the presence and

22   occurrence of CDDs/CDFs (Gullett and Ryan, 1997). The average of five tests (on highway and

23   city street driving conditions) was 29.0 pg TEQ/km with a standard deviation of 38.3 pg

24   TEQ/km; this standard deviation reflects the 30-fold variation in the two city driving route tests.

25   Tunnel studies are an indirect means of measuring contaminants that may be associated

26   with emissions from cars and trucks. In these studies, scrapings of carbonaceous matter from the

27   interior walls of the transportation tunnel or the tunnel air are sampled and analyzed for the target

28   contaminants. Several European studies and one recent U.S. study evaluated CDD/CDF

29   emissions from vehicles by measuring the presence of CDDs/CDFs in tunnel air. This approach

30   has the advantage that it allows random sampling of large numbers of vehicles passing through the

31   tunnel, including a range of ages and maintenance levels. The disadvantage of this approach is

32   that it relies on indirect measurements (rather than tailpipe measurements), which may introduce

33   unknown uncertainties into the interpretation of results.

34   Oehme et al. (1991) reported the emission rates associated with HD diesel trucks as

35   follows: uphill = 9,500 pg TEQ/km; downhill = 720 pg TEQ/km; mean = 5,100 pg TEQ/km.

36   The mean values are the averages of the emission rates corresponding to the two operating

1   modes: vehicles moving uphill on a 3.5% incline at an average speed of 37 mi/hr and vehicles

2   moving downhill on a 3.5% decline at an average speed of 42 mi/hr.

3   Wevers et al. (1992) measured the CDD/CDF content of air samples taken during the

4   winter of 1991 inside a tunnel in Antwerp, Belgium. The results obtained indicated that the tunnel

5   air had a dioxin TEQ concentration about twice as high as the outside air (80.3 fg TEQ/m^3 for

6   tunnel air vs. 35 fg TEQ/m^3 for outside air for one set of measurements and 100 fg TEQ/m^3 for

7   tunnel air vs. 58 fg TEQ/m^3 for outside air for a second set of measurements).

8   During October/November 1995, Gertler et al. (1996, 1998) measured CDDs/CDFs in the

9   Fort McHenry Tunnel in Baltimore, Maryland. The emission factors calculated, assuming that all

10   CDDs/CDFs emitted in the tunnel were from HD vehicles, are presented in Table 2-12. The

11   average TEQ emission factor was reported to be 172 pg TEQ/km. The major uncertainties in the

12   study were tunnel air volume measurement, sampler flow volume control, and analytical

13   measurement of CDDs/CDFs (Gertler et al., 1996, 1998).

14   The relative strengths of the Gertler et al. (1996; 1998) study include: (1) The study is a

15   recent study conducted in the United States and thus reflects current U.S. fuels and technology;

16   (2) virtually no vehicle using the tunnel used leaded gasoline, which is associated with past

17   emissions of CDDs and CDFs from gasoline-powered vehicles; (3) the tunnel walls and streets

18   were cleaned 1 week before the start of sampling, and in addition, the study analyzed road dust

19   and determined that resuspended road dust contributed only about 4% of the estimated emission

20   factors; (4) HD vehicles made up, on average, a relatively large percentage (25.7%) of vehicles

21   using the tunnel; and (5) a large number of HD vehicles, approximately 33,000, passed through

22   the tunnel during the sampling period, which generates confidence that the emission factor is

23   representative of interstate trucks.

24   The EPA Office of Research and Development's dioxin source emission inventory

25   estimates that 33.5 g of dioxin TEQ (total 2,3,7,8-TCDD equivalents) were emitted from HD

26   U.S. trucks in 1995. This is a very small contribution(1.2 %) compared with the national annual

27   emission of 2,800 g CDDs/CDFs.

28

29   **2.2.8. Physical and Chemical Composition of Diesel Exhaust Particles**

30   DPM is defined by the measurement procedures summarized in Title 40 CFR, Part 86,

31   subpart N. These procedures define DPM emissions as the mass of material collected on a filter

32   at a temperature of 52 °C or less after dilution of the exhaust. As the exhaust is diluted and

33   cooled, nucleation, condensation, and adsorption transform volatile material to solid and liquid

34   DPM. As a consequence of this process, diesel exhaust particles are aggregates of primary

35   spherical particles that consist of solid carbonaceous material and ash and that contain adsorbed

36   organic and sulfur compounds (sulfate) combined with other condensed material. The organic

1   material includes unburned fuel, engine lubrication oil, and low levels of partial combustion and

2   pyrolysis products.

3   The organic material is absorbed to the elemental carbon core and is also found in a

4   heterogeneously nucleated aerosol. This fraction of the DPM is frequently quantified as the SOF,

5   (i.e., the fraction that can be extracted by an organic solvent). Because of the toxicological

6   significance of the organic components associated with DPM, it is important to understand to the

7   extent possible, the historical changes in the composition of SOF and potential changes in the

8   fraction of SOF associated with DPM.

9   Various researchers have attempted to apportion the SOF to unburned oil and fuel sources

10   by thermogravimetric analysis and have found that the results vary with test cycle and engine

11   (Abbass et al., 1991; Wachter, 1990). Kittelson (1998) estimates that a typical composition of

12   SOF is about one-fourth unburned fuel and three-fourths unburned engine lubrication oil. Partial

13   combustion and pyrolysis products represented a very small fraction of the SOF on a mass basis

14   (Kittelson, 1998), which is confirmed in numerous other studies.

15   A number of investigators have tried to separate the organic fraction into various classes

16   of compounds. Schuetzle (1983) analyzed the dichloromethane extract of DPM from a LD diesel

17   engine and found that approximately 57% of the extracted organic mass is contained in the

18   nonpolar fraction. About 90% of this fraction consists of aliphatic HCs from approximately C_{14} to

19   about C_{40} (Black and High, 1979; Pierson et al., 1983). PAHs and alkyl-substituted PAHs

20   account for the remainder of the nonpolar mass. The moderately polar fraction (~9% w/w of

21   extract) consists mainly of oxygenated PAH species, substituted benzaldehydes, and nitrated

22   PAH). The polar fraction (~32% w/w of extract) is composed mainly of n-alkanoic acids,

23   carboxylic and dicarboxylic acids of PAH, hydroxy-PAH, hydroxynitro-PAH, and nitrated N-

24   containing heterocyclic compounds (Schuetzle, 1983; Schuetzle et al., 1985).

25   Rogge et al. (1993) reported the composition of the extractable portion of fine DPM

26   emitted from two HD diesel trucks (1987 model year). The DPM filters were extracted twice

27   with hexane then three times with a benzene/2-propanol mixture. The extract was analyzed by

28   capillary gas chromatography/mass spectrometry (GC/MS) before and after derivatization to

29   convert organic acids and other compounds having an active H atom to their methoxylated

30   analogues. Unidentified organic compounds made up 90% of the eluted organic mass and were

31   shown to be mainly branched and cyclic HCs. From the mass fraction that was resolved as

32   discrete peaks by GC/MS, ~42% were identified as specific organic compounds. Most of the

33   identified resolved organic mass (~60%) consisted of n-alkanes, followed by n-alkanoic acids

34   (~20%). PAH accounted for ~3.5% and oxy-PAH (ketones and quinones) for another ~3.3%.

35   The distribution of the emissions between the gaseous and particulate phases is determined

36   by the vapor pressure of the individual species, by the amount and type of the DPM present

1 (adsorption surface available), and by the temperature (Ligocki and Pankow, 1989). Two-ring

2 and smaller compounds exist primarily in the gas phase (e.g., naphthalene), while five-ring and

3 larger compounds (e.g., benzo[a]pyrene) are almost completely adsorbed on the particles. Three-

4 and four- ring compounds are distributed between the two phases. The vapor pressures of these

5 intermediate PAHs can be significantly reduced by their adsorption on various types of surfaces.

6 Because of this phenomenon, the amount and type of DPM present play an important role,

7 together with temperature, in the vapor-particle partitioning of semivolatile organic compounds

8 (SOCs).

9 The measurements of gas/particulate phase distribution are often accomplished by using a

10 high-volume filter followed by an adsorbent such as polyurethane foam (PUF), Tenax, or XAD-2

11 (Cautreels and Van Cauwenberghe, 1978; Thrane and Mikalsen, 1981; Yamasaki et al., 1982).

12 The pressure drop behind a high-volume filter or cascade impactor can contribute to volatilization

13 of the three- to five-ring PAHs from the PM (e.g., "blow-off") proportional to their vapor

14 pressures. The magnitude of this blow-off artifact depends on a number of factors, including

15 sampling temperature and the volume of air sampled (Van Vaeck et al., 1984; Coutant et al.,

16 1988). Despite these problems from volatilization, measurements with the high-volume filters

17 followed by a solid adsorbent have provided most estimates of vapor-particle partitioning of

18 SOCs in ambient air, as well as insights into the factors influencing SOC adsorption onto aerosols.

19 Significant fractions of phenanthrene, anthracene, and their alkylated derivatives, along with

20 fluoranthene and pyrene, exist in the gas phase. PAHs with molecular weight greater than that of

21 pyrene are typically not observed on PUF samples. During the collection of particulate organic

22 compounds, adsorption of semivolatile PAHs can also occur as well as chemical transformation of

23 the semivolatile compounds (Schauer et al., 1999; Cantrell et al., 1988; Feilberg et al., 1999;

24 Cautreels and Van Cauwenberghe, 1978).

25 Most of the sulfur in the fuel is oxidized to SO_2, but a small amount (1% to 4%) is

26 oxidized to SO_3 and converted to sulfate and sulfuric acid in the exhaust. Sulfate emissions are

27 roughly proportional to sulfur in the fuel. Since the reduction of the allowable sulfur content in

28 diesel fuel in 1993, sulfate emissions have declined from roughly 10% of the DPM mass to around

29 1%. Particulate emissions from numerous vehicles tested using low sulfur fuel were found to

30 have a sulfate content of only about 1% (Yanowitz et al., 1999). Water content is on the order of

31 1.3 times the amount of sulfate (Wall et al., 1987).

32 Metal compounds and other elements in the fuel and engine lubrication oil are exhausted

33 as ash. Hare (1977) examined 1976 Caterpillar 3208 and DDC 6V-71 engines and found the

34 most abundant elements emitted from the 6V-71 engine were silicon, copper, calcium, zinc, and

35 phosphorus. From the Caterpillar engine the most abundant elements were lead, chlorine,

36 manganese, chromium, zinc, and calcium. Calcium, phosphorus, and zinc were present in the

engine lubrication oil. The two-stroke 6V-71 engine had higher engine lubrication oil emissions
and therefore emitted higher levels of zinc, calcium, and phosphorus than the Caterpillar 3208
engine. Other elements may have been products of engine wear or contaminants from the exhaust
system. Springer (1979), in his study of 1977 Mack ETAY(B)673A and Caterpillar 3208 (EGR)
engines, found that calcium was the most abundant metallic element in DPM samples, with levels
ranging from 0.01 to 0.29 wt% of the DPM. Phosphorus and silica were the next most abundant
elements reported, and sodium, iron, nickel, barium, chromium, and copper were either present at
very low levels or were below detection limits. Roughly 1 wt% of the total DPM was represented
by the analyzed metals. There was no consistent difference in metal emissions between the
engines tested by Springer or between modes. Springer tested both engines on a 13-mode steady-
state test. Dietzmann and co-workers (1980) examined metal emission rates from four HD
vehicles tested using the UDDS chassis cycle. For the single two-stroke engine tested (1977
DDC 8V-71), calcium, phosphorus, and zinc emission rates were more than 10 times higher than
metal levels observed for three 1979 model year four-stroke engines because of higher engine
lubrication oil emissions. Metals accounted for 0.5% to 5% of total DPM, depending on engine
model. In addition to these studies, other source profiles for HD diesel engine emissions report
levels of chromium, manganese, mercury compounds, and nickel at levels above the detection
limit (Cooper et al., 1987).

        In more recent studies, Hildemann and co-workers (1991) examined metals in DPM from
the same two 1987 trucks (four-stroke engines) studied by Rogge and co-workers (1993).
Aluminum, silicon, potassium, and titanium were the only metals observed at statistically
significant levels. Taken together these made up less than 0.75 wt% of total DPM mass.
Lowenthal and co-workers (1994) also report metals emission rates for a composite sample of
several diesel vehicles. The most abundant metals were zinc, iron, calcium, phosphorus, barium,
and lanthanum. Together these represented less than 0.3% of total DPM mass, with an emissions
rate of 3.3 mg/mi. Norbeck and co-workers (1998b) report engine transient test emissions of
metals for a 1991 Cummin L10 engine. Silicon, iron, zinc, calcium, and phosphorus were
observed and together made up about 0.5% of total DPM, with an emissions rate of 1.2 mg/bhp-
hr.

2.2.8.1. *Organic and Elemental Carbon Content of Particles*

2.2.8.1.1. *Measurement of the organic fraction.* Various methods have been used to quantify
the organic fraction of DPM. The most common method has been Soxhlet extraction with an
organic solvent. Following extraction, the solvent can be evaporated and the mass of extracted
material (the SOF) determined, or alternatively the PM filter is weighed before and after
extraction and the extracted material can be further analyzed to determine concentrations of

1   individual organic compounds. Vacuum oven sublimation is used to measure a comparable

2   quantity, the volatile organic fraction (VOF), which can be further speciated by GC with a flame

3   ionization detector. Other methods have also been employed, including thermal methods,

4   microwave extraction, sonication with an organic solvent, supercritical fluid extraction,

5   thermogravimetric analysis, and thermal desorption GC.   Abbass et al. (1991) compared various

6   methods, including vacuum oven sublimation and 8 hours of Soxhlet extraction, with 4:1

7   benzene/methanol solvent for determination of SOF and found reasonably good agreement

8   between the two methods. The VOF value was typically 10% higher; however, this variation was

9   less than the coefficient of variation between measurements using the same method.

10   Thermal methods of organic carbon analysis include thermal optical reflectance (TOR) and

11   thermal optical transmittance (TOT). The extractable portion of total carbon, although commonly

12   used as a measure of organic compound content, is not equivalent to the organic carbon fraction

13   as measured by TOR or TOT. Japar et al. (1984) reported an average ratio of organic compound

14   measured by TOR to extractable mass of 0.70 ± 0.05, when the extraction solvent was a

15   toluene/propanol-1 mixture. This ratio may have resulted from the presence of both oxygenated

16   organic compounds and inorganic sulfate in the extracted mass.

17   Levson (1988) reviewed literature regarding the extraction efficiency of various solvents

18   and found contradictory results in many cases. He concluded that there is strong evidence that

19   the most commonly used solvent, dichloromethane, leads to poor recoveries of higher molecular

20   weight PAH. More recently, Lucas et al. (1999) reported the effect of varying

21   dichloromethane/benzene ratios in the solvent (from 25% to 100% dichloromethane) and

22   changing extraction times and found that the most effective extraction (i.e., the largest extracted

23   mass) utilized a 70% dichloromethane/30% benzene mixture and extraction times several times

24   longer than the commonly used 8-hour extraction period. Extractions of 70 hours using pure

25   dichloromethane were found to result in about twice as much SOF as extractions of only 12

26   hours. Between 6 and 24 hours of extraction time (the typical range of extraction times used), the

27   SOF recovered increased by about one-third. Using the most effective extraction conditions

28   (Soxhlet, 70 hours, 70:30 dichloromethane:benzene ratio), Lucas et al. (1999) were able to

29   extract over 90% of the total particulate mass.

30   Other researchers have investigated the relative quantities of mass removed by sequential

31   extraction by polar, moderately polar, and nonpolar solvents. The extracted nonpolar fraction

32   (cyclohexane) ranged from 56% to 90% of the SOF, the moderately polar (dichloromethane) from

33   6% to 22%, and the polar fraction (acetonitrile) from 4% to 29% (Dietzmann et al., 1980).

34   Water and sulfate are not soluble in cyclohexane or dichloromethane but are soluble in

35   acetonitrile.

1   Although the reports on the extraction efficiencies for PAHs are in part contradictory, it

2   appears that Soxhlet extraction and the binary solvent system composed of aromatic solvent and

3   alcohol yield the best recovery of PAHs, as determined by C-B[a]P[14] (benzo[a]pyrene) spiking

4   experiments (Schuetzle and Perez, 1983). Limited recovery studies have shown that there is little

5   degradation or loss of diesel POM on the HPLC column. More than 90% of the mass and 70% to

6   100% of the Ames *S. typhimurium*-active material injected onto the column have been recovered

7   (Schuetzle et al., 1985).

8   The solvent polarity and extraction time used for measuring the SOF can have a significant

9   effect on the quantity reported. In the discussion that follows, every effort has been made to

10   compare only studies using comparable methods and to state what extraction methods were

11   employed.

12

13   **2.2.8.1.2. *Trends in SOF emissions.*** SOF emission values are highly dependent on the test cycle

14   used. Various studies have shown that SOF generally increases at light engine loads and high

15   engine speeds because these conditions lead to low exhaust temperatures, where fuel and oil are

16   not as effectively oxidized (Scholl et al., 1982; Kittleson, 1998; Springer, 1979; Schuetzle and

17   Perez, 1983; Martin, 1981b; Shi et al., 2000).   These conditions are more typically observed in

18   LD diesel vehicle applications, and thus DPM from these vehicles typically emits DPM with a

19   higher SOF component than HD diesel vehicles (Norbeck et al., 1998c). Acceleration modes

20   normally cause increased emission of elemental carbon and an increase in total DPM emissions,

21   while organic components are more dominant when motoring (Wachter, 1990). Additionally,

22   cold-start test emissions of SOF have been shown to be approximately 25% higher than hot-start

23   emissions (Wachter, 1990).

24   The quantity of sulfur in diesel fuel has been suggested to have a role in the quantity of

25   SOF emitted (Sienicki et al., 1990; Tanaka et al., 1998). Sienicki et al. (1990) reported an

26   approximate 25% increase in SOF when sulfur concentrations are increased from 0.08% to

27   0.33%. The cause is unclear but several explanations have been put forth, including increased

28   absorption of organic compounds from the vapor phase onto the DPM by sulfates or sorbed

29   sulfuric acid. Alternately, it has been proposed that the measured SOF may include some sulfate,

30   so that the apparent increase in organic material is due instead to sulfate. Other fuel effects

31   include an increase in SOF emissions with a higher T90 (or T95) and with an increase in aromatic

32   content (Barry et al., 1985; Sienicki et al., 1990; Tanaka et al., 1998; Rantanen et al., 1993).

33   Figures 2-29 and 2-30 show SOF emissions as a function of year for transient emissions

34   tests on chassis and engines, respectively. Both figures suggest a significant decline in SOF

35   emissions, on the order of a factor of 5 since about 1980. The highest SOF emissions are for two-

36   stroke engines built in the 1970s. These data indicate that SOF emission factors for newer model

year vehicles are lower than SOF emission factors for pre-1990 model year vehicles and that this decrease is similar to that observed for emissions of total DPM by model year.

Steady-state testing conducted on late 1970s engines reported SOF at levels between 0.1 and 0.9 g/bhp-hr, while engines from the late 1980s and 1990s all emit 0.03 g/bhp-hr or less (Table 2-8). Hori and Narusawa (1998) measured emissions from engines produced two decades apart, using identical analytical procedures, and found that SOF emission factors and the percent contribution of SOF to DPM were lower in the new engine compared with the old engine, under all tested engine load and speed conditions, and with different fuels. The authors reported that the decrease in SOF was due to lower emissions of both lubricating oil and unburned fuel. It is evident that to meet the 1991 and 1994 U.S. emission standards, SOF emission rates would need to be reduced from the levels of the previous decade, although one may expect differences in SOF fractions of DPM with transient cycles used to determine compliance with emission standards verus steady-state conditions used in earlier test programs (Kawatani et al., 1993; Wachter, 1990). Finally, in the past three decades for economic reasons, engine manufacturers have made efforts to reduce oil consumption and increase the fuel efficiency of diesel engines, both of which would be expected to reduce SOF emissions. Problems in achieving SOF reductions from two-stroke engines have been one factor leading to the phase-out of these engines for on-road use during the 1990s. No data are available prior to 1976 on SOF emissions from HD diesel vehicles. The engine technology changes that occurred between the mid-1950s and mid-1970s (high pressure direct injection and turbocharging, primarily) might be expected to increase the efficiency of combustion and thereby reduce fuel-related SOF. SOF emissions levels in the mid- to late 1970s may be used as a conservative (low) estimate of SOF emissions during the preceding two decades.

The fraction of DPM attributed to SOF from chassis dynamometer studies also shows a decreasing trend over time from SOFs that ranged up to approximately 50% in the 1980s to 20% SOF or less in the 1990s (Figure 2-31). The wide range in SOF as a percent of DPM displayed in Figure 2-31 is suspected to result from factors such as engine deterioration and test cycle. The vehicle emissions data reported in Figure 2-31 do not overrepresent buses that are likely to emit DPM with a greater fraction of SOF than other vehicles. Figure 2-32 presents SOF as a fraction of DPM from the same engine dynamometer studies reported in Figure 2-30. These data do not reflect a downward trend in SOF as a fraction of DPM. Since similar extraction methods were used in reports of the SOF in both the chassis and engine dynamometer studies, this does not appear to be a source of the wide variability observed in the fraction of SOF reported. In some of the engine studies, improved air:fuel ratio control was tested in an attempt to lower carbonaceous DPM formation. Therefore, substantial differences in SOF as a percent of total DPM could be the result of different engine technology or test conditions. The engine dynamometer results

1 presented in Figures 2-30 and 2-32 are from new, or relatively new, engines, that is, engines with

2 no deterioration, whereas the older engines tested on a chassis dynamometer may have

3 experienced significant deterioration that would increase SOF emissions as a percent of DPM.

4 One of the main differences suspected for the lack of a decreasing trend in the percent of SOF in

5 the engine dynamometer studies is the test cycle used. The engine dynamometer tests typically

6 include test modes, such as high speed and low load, or low speed lugging modes, which produce

7 much higher SOF relative to DPM than the driving cycles used on the chassis tests.

8 It appears that as a fraction of total DPM, SOF from new model year HD diesel vehicles is

9 lower than that from older (pre-1990) HD diesel vehicles. However, as with total DPM

10 emissions, a wide range in the fraction of SOF can be observed under different driving conditions

11 and from vehicles with extensive engine wear. In general, DPM emissions have a lower fraction

12 of organic matter compared to gasoline PM (Table 2-13). Recent testing of HD engines at the

13 Desert Research Institute suggests that the organic carbon fraction of DPM is approximately

14 19%, while earlier studies reported in the U.S. EPA SPECIATE database suggest a slightly higher

15 organic fraction of DPM from HD diesel vehicles ranging from 21% to 36%. The SPECIATE

16 database represents older vehicles that, as discussed above, tend to have higher SOF emissions.

17 The organic carbon emissions from LD diesel vehicles recently reported by Norbeck et al. (1998c)

18 and those reported by the U.S. EPA SPECIATE suggest that LD diesel vehicles emit DPM with a

19 slightly higher organic content than HD diesel vehicles, ranging from 22% to 43%. Gasoline

20 engine PM emissions have recently been analyzed at the Desert Research Institute by Fujita et al.

21 (1998) and Watson et al. (1998) for hot stabilized, visibly smoking vehicles, and cold-starts.

22 These data all indicate that LD gas vehicles emit PM with a higher fraction of organic matter than

23 diesel vehicles, with the highest organic content measured from smoking and high-emitting

24 gasoline vehicles (averaging 76% organic carbon). One new finding from the data reported by

25 Fujita et al. (1998) is the roughly equivalent emission of organic and elemental carbon from cold-

26 start emissions of gasoline vehicles. Additional information is needed to characterize a range of

27 organic carbon for DPM from smoking and high-emitting diesel vehicles as well as cold-start HD

28 diesel vehicles.

29

30 **2.2.8.1.3.** *Trends in EC content.* The EC content of ambient PM samples is one component of

31 the source profile commonly used to determine the contribution of diesel vehicles to ambient PM

32 samples (i.e., in source apportionment via chemical mass balance modeling). EC is not, strictly

33 speaking, a regulated pollutant, and so EC emissions are not routinely measured in tests of diesel

34 vehicles and engines. The scant data available on measured EC emissions from HD diesel vehicles

35 are plotted in Figure 2-33. Approximately one-half of these data, from the study of Norbeck et al.

36 (1998b), are for pickup trucks equipped with light and medium HD diesel engines which represent

1 a small portion of the diesel vehicle fleet. All of the 1994 and later model year pickup trucks are

2 equipped with diesel oxidation catalysts that oxidize the SOF component of DPM. EC emissions

3 from these vehicles are uniformly low. Results for the other three studies, all performed on HD

4 trucks, suggest a decline in EC emission rates by model year since the early 1980s. In a study

5 conducted in 1992, four HD vehicles of unknown vintage were tested and a combined EC

6 emission rate of 0.81 g/mi was reported, which consistent with the 1990 timeframe in Figure 2-33

7 (Lowenthal et al., 1994). EC as a percentage of total DPM in these studies ranged from 30% to

8 90%, most likely as a result of different testing cycles and different engines.

9   Figure 2-34 presents these data as a fraction that EC comprises of total carbonaceous

10 matter in the emitted DPM. The carbonaceous matter attributable to EC varied widely in the

11 1980s from approximately 20% to 90%, while in more recent years, the data suggest a smaller

12 range in the EC fraction from approximately 50% to 90% (with one data point at 30%). Recent

13 emission profiles for HD diesel vehicles suggest that 75% ± 10% of the DPM is attributable to

14 EC, whereas approximately 25% of gasoline PM is composed of EC, except for PM emissions

15 during gasoline vehicle cold-starts, which were found to have an EC content of approximately

16 42% (Table 2-13). These data also provide evidence that newer model year HD engines generally

17 emit DPM that is more rich in EC than older HD engines.

18 **2.2.8.2. *PAHs and Nitro-PAH Emissions***

19   PAHs, nitro-PAHs, and oxidized derivatives of these compounds have attracted

20 considerable attention because of their known mutagenic and, in some cases, carcinogenic

21 character (National Research Council, 1982). In this section, PAH and nitro-PAH concentrations

22 and emission rates and trends in emissions over time are presented.

23

24 **2.2.8.2.1. *PAHs identified in diesel exhaust.*** At least 32 PAHs have been identified in the

25 exhaust of LD diesel vehicles and HD diesel vehicles (Table 2-14) (Watson et al., 1998; Zielinska

26 et al., 1998). Table 2-15 lists the PAHs and thioarenes identified in three LD diesel vehicles'

27 DPM extracts, reported as ng/g of DPM (Tong et al., 1984). SOF fractions accounted for 11%

28 to 15% of the total DPM mass for the LD diesel vehicles reported by Tong et al. (1984), which is

29 lower than the LD diesel vehicles organic fraction reported by Norbeck et al. (1998c) in Table 2-

30 13. Among the PAHs reported by Watson et al. (1998) and Zielinska et al. (1998), the higher

31 molecular weight compounds (pyrene through coronene) that are expected to partition to the

32 particle phase have emission rates from HD diesel vehicles ranging from below detection limits up

33 to 0.071 mg/mi. HD diesel vehicle emission rates for the lower molecular weight PAHs ranged

34 up to 2.96 mg/mi for dimethylnaphthalenes. In general, among the vehicles tested, PAH emission

35 rates were higher for LD diesel vehicles compared to HD diesel vehicles. Table 2-16 presents

36 emission rates of four representative particle-phase PAHs from HD diesel vehicles, LD diesel

1   vehicles, and gasoline (with and without catalytic converter) engines. Emission rates for

2   benzo[a]pyrene were higher in diesel emissions compared with gasoline emissions, except for the

3   report by Rogge et al. (1993), who used extraction methods different from those in other studies

4   (discussed above).

5

6   **2.2.8.2.2. *Nitro-PAHs identified in diesel exhaust.*** Positive isomer identification for 16 nitro-

7   PAHs has been made utilizing the GC retention times of authentic standards and low- and high-

8   resolution mass spectra as identification criteria. These include 1-nitropyrene; 2-methyl-1-

9   nitronaphthalene; 4-nitrobiphenyl; 2-nitrofluorene; 9-nitroanthracene; 9-methyl-10-

10   nitroanthracene; 2-nitroanthracene; 2-nitrophenanthrene; 1-methyl-9-nitroanthracene; 1-methyl-3-

11   nitropyrene; 1-methyl-6-nitropyrene; 1-methyl-8-nitropyrene; 1,3-, 1,6-, and 1,8-dinitropyrene;

12   and 6-nitrobenzo[a]pyrene. In addition, two nitrated heterocyclic compounds were identified, 5-

13   and 8-nitroquinoline. Forty-five additional nitro-PAHs were tentatively identified in this diesel

14   particulate extract (Paputa-Peck et al., 1983). The concentration of nitro-PAHs adsorbed on

15   diesel particles varies substantially from sample to sample. Usually 1-nitropyrene is the

16   predominant component, and concentrations ranging from 7 to 165 μg/g of particles are reported

17   (Levsen, 1988).

18   Table 2-17 gives the approximate concentrations of several of the abundant nitro-PAHs

19   quantified in the early 1980s LD diesel particulate extracts (with the exception of 3-

20   nitrobenzanthrone, reported recently) in μg/g of particles. Concentrations for some of the nitro-

21   PAHs identified range from 0.3 μg/g for 1,3-dinitropyrene to 8.6 μg/g for 2,7-dinitro-9-

22   fluorenone and 75 μg/g for 1-nitropyrene. More recent nitro-PAH and PAH data for HD diesel

23   engines are reported in units of g/bhp-hr or mass/volume of exhaust, making it impossible to

24   directly compare them to the older data (Norbeck et al., 1998; Bagley et al., 1996, 1998;

25   Baumgard and Johnson, 1992; Opris et al., 1993; Hansen et al., 1994; Harvey et al., 1994;

26   Kantola et al., 1992; Kreso et al., 1998b; McClure et al., 1992; Pataky et al., 1994).

27

28   **2.2.8.2.3. *PAH and nitro-PAH emission changes over time.*** It is difficult to compare PAH

29   emissions from different studies because not all investigators analyze for total PAH or the same

30   suite of PAH compounds. Most studies have reported emissions of benzo[a]pyrene (B[a]P), or 1-

31   nitropyrene (1-NP) due to their toxicological activity. The results of chassis dynamometer studies

32   in which B[a]P or 1-NP were measured are displayed in Figure 2-35. Dietzmann and co-workers

33   (1980) examined four vehicles equipped with late 1970s turbocharged DI engines. Emissions of

34   B[a]P from particle extracts ranged from 1.5 to 9 μg/mi. No correlation with engine technology

35   (one of the engines was two-stroke) was observed. Rogge and co-workers (1993) reported total

36   particle-associated PAH and B[a]P emissions from two 1987 model year trucks (averaged

together, four-stroke and turbocharged engines). The total particle-phase PAH emission rate was 0.43 mg/mi and the B[a]P emission rate was 2.7 μg/mi. Particle-phase PAH in the Rogge et al. (1993) study accounted for approximately 0.5% of total DPM mass. Schauer and co-workers (1999) recently reported a particle-phase PAH emission rate of 1.9 mg/mi (accounting for about 0.7% of total DPM mass) for a 1995 MD turbocharged and intercooled truck. B[a]P emissions were not reported, but emissions of individual species of similar molecular weight were approximately 10 μg/mi. Schauer et al. (1999) also reported gas-phase PAH emission rate of 6.9 mg/mi for the same truck. Measurements of particle- and gas-phase PAHs conducted for the Northern Front Range Air Quality Study in Colorado (Zielinska et al., 1998) showed an average B[a]P emission rate of 13 μg/mi for 15 vehicles ranging from 1983-1993 model years. The combined gas- and particle-phase PAH emission rate reported for the NFRAQS study was 13.5 mg/mi. B[a]P emissions from chassis studies are summarized in Figure 2-35. Zielinska (1999) reports a decreasing trend in particle-associated diesel exhaust PAH from 11 measurements made on vehicles from model year 1984 to 1993 with a low correlation coefficient of 0.29.

B[a]P emissions reported from diesel engine dynamometer studies are summarized in Figure 2-36. Springer (1979) compared B[a]P emissions from naturally aspirated and turbocharged engines and found that naturally aspirated engines emitted about 1 μg B[a]P/bhp-hr, and DI and IDI engines emitted about 0.15 μg B[a]P/bhp-hr (Table 2-8). The difference between 1 and 0.15 μg/bhp-hr could not be attributed to specific technology changes.   The majority of engine test data indicate that B[a]P emissions have generally ranged from approximately 1 to 4 μg/bhp-hr over the past 25 years.

Emissions reported for 1-NP from diesel engines tested by chassis dynamometer ranges from 0.1 to 12 μg/mi (Figure 2-35), and diesel engines dynamometer studies report 1-NP emission factors ranging from 1 to 4 μg/bhp-hr (Figure 2-36). Too few measurements are available to discern trends in the emission rates of these compounds.

As discussed in Section 2.2.4, Williams et al. (1987) and Andrews et al. (1998) of the University of Leeds have demonstrated that the solvent-extractable PAH from diesel particulate originates primarily in the fuel. PAH molecules are relatively refractory so that a significant fraction survives the combustion process and is exhausted as DPM. These studies have been confirmed by other research groups (Crebelli et al., 1995; Tancell et al., 1995) that included the use of isotopic labeling of fuel PAH. Additionally, engine oil was found to be a reservoir for PAH that originates in the fuel. Pyrosynthesis of PAH occurs during very high temperature conditions in a diesel engine, and under these conditions much of the DPM and other pyrolysis products are ultimately oxidized before exiting the cylinder. Thus, pyrogenic formation of PAH is thought to contribute a small fraction of the total PAH in diesel engine exhaust. As discussed above, fuel PAH content is expected to have slowly increased over a 30-year period until 1993, after which

1   PAH content of diesel fuel is expected to have remained constant. Increasing use of catalytic

2   cracking over time may lead to increasing proportions of PAH in distillates; however, fuel

3   standards limit the aromaticity of fuel to 35%.

4   Recently, Norbeck et al. (1998a) reported on the effect of fuel aromatic content on PAH

5   emissions. Three diesel fuels were used in a Cummins L10 engine: pre-1993 fuel containing 33%

6   aromatic HC and 8% PAH; low aromatic fuel containing a maximum content of 10% aromatic

7   HC and maximum of 1.4% PAH; and a reformulated fuel containing 20% to 25% aromatic HC

8   and 2% to 5% PAH. The investigators found that emission rates for the low molecular weight

9   PAHs (PAHs $\leq$ 3 rings) were significantly lower when the engine was tested using the low

10   aromatic fuel compared to when the engine was run on the pre-1993 or reformulated fuel (Table

11   2-18). While emission rates reported for several higher molecular weight (particle-associated)

12   PAHs were lower (ranging from four to28% lower) for the low aromatic fuel compared with the

13   other two fuels, the differences were not statistically significant except for coronene.

14   On the basis of these limited data it is difficult to draw a precise, quantitative conclusion

15   regarding how PAH, B[a]P or 1-NP emissions have changed over time and in response to fuel and

16   engine changes. A decrease in the range of PAH emission factors from post-1990 model year

17   vehicles and engines compared to pre-1990 vehicles and engines is suggested by the data;

18   however, the data also suggest that differences in a vehicles' engine type and make, general

19   engine condition, fuel composition, and test conditions can influence the emissions levels of PAH.

20

21

22   **2.2.8.3.** *Particle Size*

23   Figure 2-37 shows a generic size distribution for diesel particulate based on mass and

24   particle number. Approximately 50% to 90% of the number of particles in diesel exhaust are in

25   the ultrafine size range (nuclei mode), with the majority of diesel particles ranging in size from

26   0.005 - 0.05 µm and the mode at about 0.02 µm. These are believed to be aerosol particles

27   formed from exhaust constituents during cooling and to consist of sulfuric acid droplets, ash

28   particles, condensed organic material, and perhaps primary carbon spherules (Abdul-Khalek et al.,

29   1998; Baumgard and Johnson, 1996). While accounting for the majority of the number of

30   particles, ultrafine DPM accounts for only 1% to 20% of the mass of DPM.

31   Approximately 80% to 95% of diesel particle mass is in the size range from 0.05 to 1.0

32   µm, with a mean particle diameter of about 0.2 µm. These particles have a very large surface area

33   per gram of mass, which make them an excellent carrier for adsorbed inorganic and organic

34   compounds that can effectively reach the lowest airways of the lung. The elemental carbon core

35   has a high specific surface area of approximately 30 to 50 m^2/g (Frey and Corn, 1967), and

Pierson and Brachaczek (1976) report that after the extraction of adsorbed organic material, the surface area of the diesel particle core is approximately 90 m^2/g.

Considerable caution is required when reporting particle size measurements from diesel engine exhaust because dilution conditions during the measurement process significantly affect size distributions (e.g., the size distribution is largely a function of how it was measured), and DPM size distributions obtained in dilution tunnel systems may not be relevant to size distributions resulting from the physical transformation of engine exhaust in the atmosphere. Measurements made on diluted diesel exhaust typically show higher numbers of nuclei mode particles than do measurements made on raw exhaust because of condensation to form nuclei mode aerosol upon cooling of the exhaust. Dilution ratio, sampling temperature, humidity, relative concentrations of carbon and volatile matter, and other sampling factors can therefore have a large impact on the number and makeup of nuclei mode particles (Abdul-Khalek et al., 1999; Shi and Harrison, 1999; Lüders et al., 1998). Dilution air temperature and humidity can have a large effect on particle number and size distribution especially in the size range below 0.05 µm (also referred to as nanoparticles). Shi and Harrison (1999) report that a high dilution ratio and high relative humidity favor the production of ultrafine particles in diesel engine exhaust. Abdul-Khalek et al. (1998) report that an increase in the residence time of the exhaust during dilution resulted in an increase in the number of particles in exhaust. Khatri et al. (1978) report increased gas-phase HC condensation to DPM with a decrease in dilution air temperature. Some studies report no peak in diesel particles in the ultrafine size range (Kleeman et al., 2000). Kittelson (2000) reports that nanoparticle formation can be prevented by an oxidizing catalyst, which burns organic components of the exhaust, making them unavailable for nucleation or condensation to form an aerosol.

While dilution tunnel conditions clearly do not simulate what occurs when a diesel exhaust plume enters the atmosphere, Gertler (1999) demonstrated an increase in 0.02 µm particles as the fraction of diesel vehicles in the Tuscarora Mountain tunnel increased from 13% to 78%. These data suggest that the mode at 0.02 µm for ultrafine DPM from diesel exhaust is evidenced under real-world conditions.

Several groups have shown that decreasing sulfur content decreases the number of nuclei mode particles measured in the exhaust, assuming temperature is low enough and residence time is long enough for nucleation and condensation of sulfate aerosol and water in the dilution tunnel (Baumgard and Johnson, 1992, 1996; Opris et al., 1993; Abdul-Khalek et al., 1999). The application of this finding to real-world conditions is difficult to predict, as the number of nuclei mode particles formed from sulfate and water in the atmosphere will be determined by atmospheric conditions, not by dilution tunnel conditions. With all other factors held constant, it appears that reducing fuel sulfur content reduces the number of sulfate nuclei mode particles.

Thus the reduction in on-road fuel sulfur content that occurred in 1993 is expected to have reduced the number of sulfate particles emitted by diesel vehicles, or formed secondarily in the atmosphere from diesel exhaust in many urban areas. As discussed above, the contribution of sulfate to total DPM mass ranges from 1% to 5% and is therefore not a substantial portion of DPM mass.

More controversial is the suggestion that the DPM emission size distribution from newer technology engines (1991 and later) may be shifted to have a much higher number concentration of nuclei mode particles, independent of fuel sulfur content (Kreso et al., 1998b; Abdul-Khalek et al., 1998; Baumgard and Johnson, 1996; Bagley et al., 1996). For example, Kreso and co-workers (1998b) compared emissions from a 1995 model year engine with measurements made on 1991 and 1988 model year engines in earlier studies (Bagley et al., 1993, 1996). Nuclei mode particles made up 40% to 60% of the number fraction of DPM emissions for the 1988 engine and 97%+ of the DPM from the 1991 and 1995 engines. Number concentrations were roughly two orders of magnitude higher for the newer engines. SOF made up 25% to 30% of DPM in the 1988 engine and 40% to 80% of DPM for the newer engines. Total DPM mass was significantly reduced for the newer engines. It was suggested that increased fuel injection pressure leads to improved fuel atomization and evaporation, leading to smaller primary carbonaceous particles. Dilution conditions (relatively low temperature, low primary dilution ratio, long residence time of more than 3 seconds) strongly favor the formation of nucleation products. The 1991 and 1988 engines were tested with 100 ppm sulfur fuel while the 1995 engine was tested with 310 ppm sulfur fuel, which may confound the results to some extent.

The results of Kreso and co-workers (1998b) and of Bagley and co-workers (1993, 1996) have been called into question because the high level of SOF emitted by the 1991 engine, particularly at high-load test modes, was inconsistent with SOF values measured for other engines using similar types of technology (Last et al., 1995; Ullman et al., 1995). Kittelson (1998) notes that there is far less carbonaceous DPM formed in newer engines. Accumulation mode particles may have provided a high surface area for adsorption of sulfate and unburned organic compounds. In the absence of this surface area for adsorption, higher number concentrations of small particles are formed from nucleation of HCs and sulfuric acid.

A study performed at EPA by Pagan (1999) suggested that increased injection pressure can lead to the formation of more nuclei mode particles in the exhaust. Particle size distributions were measured for diluted exhaust from an engine in which injection pressure could be varied from roughly 35 to 110 MPa (about 5,000–16,000 psi), comparable to pressures obtained with injection technology introduced in the 1980s. The dilution system and particle size measurement set-up were identical in all experiments, removing some of the uncertainty in earlier studies that compared engine tests performed years apart. The results showed a clear increase in the number

1 of nuclei mode particles and a decrease in the number of accumulation mode particles as injection

2 pressure was increased. This shift did not occur, however, at high engine speeds and loads but

3 only at low to intermediate speeds and loads. The increase in number concentration of nuclei

4 mode particles was much lower than the two orders of magnitude increase reported by Kreso et

5 al. (1998b) or Bagley et al. (1996). One must use caution in applying the results of Pagan to

6 modern high-injection pressure diesel engines with turbocharging/charge-air cooling because the

7 engine used by Pagan was a naturally aspirated engine to which high-pressure common rail

8 injection was applied. This would likely preclude this particular engine from meeting current

9 on-highway PM or NO_x standards. While some studies have suggested that increased injection

10 pressure can lead to elevated ultrafine DPM number counts, Kittelson et al. (1999) cite a German

11 study that reported a decrease in ultrafine DPM number and mass with increasing injection

12 pressure.

13   While the majority of particles in diesel exhaust from modern on-road diesel engines are in

14 the ultrafine size range, evidence regarding a change in the size distribution over time is unclear.

15 To understand the size distribution of DPM to which people are exposed will require

16 measurements under conditions that more closely resemble ambient conditions.

17

18 **2.3. ATMOSPHERIC TRANSFORMATION OF DIESEL EXHAUST**

19   Primary diesel emissions are a complex mixture containing hundreds of organic and

20 inorganic constituents in the gas and particle phases, the most abundant of which are listed in

21 Table 2-19. The more reactive compounds with short atmospheric lifetimes will undergo rapid

22 transformation in the presence of the appropriate reactants, whereas more stable pollutants can be

23 transported over greater distances. A knowledge of the atmospheric transformations of gaseous

24 and particulate components of diesel emissions and their fate is important in assessing

25 environmental exposures and risks. This section describes some of the major atmospheric

26 transformation processes for gas-phase and particle-phase diesel exhaust, focusing on the primary

27 and secondary organic compounds that are of significance for human health. For a more

28 comprehensive summary of the atmospheric transport and transformation of diesel emissions, see

29 Winer and Busby (1995).

30

31 **2.3.1. Gas-Phase Diesel Exhaust**

32   Gas-phase diesel exhaust contains organic and inorganic compounds that undergo various

33 chemical and physical transformations in the atmosphere depending on the abundance of reactants

34 and meteorological factors such as wind speed and direction, solar radiation, humidity,

35 temperature, and precipitation. Gaseous diesel exhaust will primarily react with the following

36 species (Atkinson, 1988):

1   • Sunlight, during daylight hours

2   • Hydroxyl (OH) radical, during daylight hours

3   • Ozone (O_3), during daytime and nighttime

4   • Hydroperoxyl (HO_2) radical, typically during afternoon/evening hours

5   • Gaseous nitrate (NO_3) radicals or dinitrogen pentoxide (N_2O_5), during nighttime

6   hours

7   • Gaseous nitric acid (HNO_3) and other species such as nitrous acid (HONO) and

8   sulfuric acid (H_2SO_4).

9

10   The major loss process for most of the diesel exhaust emission constituents is oxidation,

11   which occurs primarily by daytime reaction with OH radical (Table 2-20). For some pollutants,

12   photolysis, reaction with O_3, and reactions with NO_3 radicals during nighttime hours are also

13   important removal processes. The atmospheric lifetimes do not take into consideration the

14   potential chemical or biological importance of the products of these various reactions. For

15   example, the reaction of gas-phase PAHs with NO_3 appears to be of minor significance as a PAH

16   loss process, but it is more important as a route of formation of mutagenic nitro-PAHs. The

17   reaction products for some of the major gaseous diesel exhaust compounds are listed in Table 2-

18   21 and are discussed briefly below.

19

20   **2.3.1.1. *Organic Compounds***

21   The organic fraction of diesel is a complex mixture of compounds, very few of which have

22   been characterized. The atm exhaust ospheric chemistry of several organic constituents of diesel

23   exhaust (which are also produced by other combustion sources) has been studied. A few of these

24   reactions and their products are discussed below. For a complete summary of the atmospheric

25   chemistry of organic combustion products, see Seinfeld and Pandis (1998).

26   Acetaldehyde forms peroxyacetyl nitrate, which has been shown to be a direct-acting

27   mutagen toward *S. typhimurium* strain TA100 (Kleindienst et al., 1985) and is phytotoxic.

28   Benzaldehyde, the simplest aromatic aldehyde, forms peroxybenzoyl nitrate or nitrophenols

29   following reaction with oxides of nitrogen (Table 2-21).

30   For those PAHs present in the gas phase, reaction with the OH radical is the major

31   removal route, leading to atmospheric lifetimes of a few hours in daylight. The gas-phase reaction

32   of PAHs containing a cyclopenta-fused ring such as acenaphthene, acenaphthylene, and

33   acephenanthrylene with the nitrate radical may be an important loss process during nighttime

34   hours. Relatively few data are available concerning the products of these gas-phase reactions. It

35   has been shown that, in the presence of NO_x, the OH radical reactions with naphthalene, 1- and 2-

36   methylnaphthalene, acenaphthylene, biphenyl, fluoranthene, pyrene, and acephenanthrylene lead to

1   the formation of nitroarenes (Arey et al., 1986; Atkinson, 1986, 1990; Zielinska et al., 1988,

2   1989a; Arey, 1998). In addition, in a two-step process involving OH radical reaction and NO_2

3   addition, 2-nitrofluoranthene and 2-nitropyrene can be formed and eventually partition to the

4   particle phase, as will other nitro-PAHs.

5   The addition of the NO_3 radical to the PAH aromatic ring leads to nitroarene formation

6   (Sweetman et al., 1986; Atkinson et al., 1987, 1990; Zielinska et al., 1989a). The gas-phase

7   reactions of NO_3 radical with naphthalene, 1- and 2-methylnaphthalene, acenaphthene,

8   phenanthrene, anthracene, fluoranthene, and pyrene produce, in general, the same nitro-PAH

9   isomers as the OH radical reaction, but with different yields (Arey et al., 1989; Sweetman et al.,

10   1986; Atkinson et al., 1987, 1990; Zielinska et al., 1986, 1989a). For example, the same 2-

11   nitrofluoranthene is produced from both OH radical and NO_3 gas-phase reactions, but the reaction

12   with NO_3 produces a much higher yield. The production of several nitroarene compounds has

13   been studied in environmental chambers (Arey et al., 1989; Zielinska et al., 1990; Atkinson and

14   Arey, 1994; Arey, 1998; Feilberg et al., 1999), and generally the same nitro-PAH isomers formed

15   from reaction with OH and NO_3 radicals are observed in ambient air samples. Secondary

16   formation of nitroarenes through the gas-phase reactions of the 2-, 3-, and 4-ring PAHs is the

17   major source for many of the nitroarenes observed in ambient air (Pitts et al., 1985a, b, c; Arey et

18   al., 1986; Zielinska et al., 1988). Photolysis is the major removal pathway for nitroarenes with

19   lifetimes of approximately 2 hours (Feilberg et al., 1999; Nielsen and Ramdahl, 1986).

20

21   **2.3.1.2. *Inorganic Compounds***

22   SO_2 and oxides of nitrogen (primarily NO) are emitted from diesel engines. SO_2 is readily

23   oxidized by the OH radical in the atmosphere, followed by formation of the HO_2 radical and

24   HSO_3, which rapidly reacts with water to form H_2SO_4 aerosols. Because SO_2 is soluble in water,

25   it is scavenged by fog, cloud water, and raindrops. In aqueous systems, SO_2 is readily oxidized to

26   sulfate by reaction with hydrogen peroxide (H_2O_2), O_3, or O_2 in the presence of a metal catalyst

27   (Calvert and Stockwell, 1983). Sulfur emitted from diesel engines is predominantly (~98%) in the

28   form of SO_2, a portion of which will form sulfate aerosols by the reaction described above.

29   Nonroad equipment, which typically uses fuel containing 3,300 ppm sulfate, emits more SO_2 than

30   on-road diesel engines, which use fuels currently containing an average of 340 ppm sulfur because

31   of EPA regulations effective in 1993 decreasing diesel fuel sulfur levels. EPA estimates that

32   mobile sources are responsible for about 7% of nationwide SO_2 emissions, with diesel engines

33   contributing 74% of the mobile source total (the majority of the diesel SO_2 emissions originate

34   from nonroad engines) (U.S. EPA, 1998b).

35   NO is also oxidized in the atmosphere to form NO_2 and particulate nitrate. The fraction of

36   motor vehicle NO_x exhaust converted to particulate nitrate in a 24-hour period has been

1 calculated using a box model to be approximately 3.5% nationwide, a portion of which can be

2 attributed to diesel exhaust (Gray and Kuklin, 1996). EPA estimates that in 1997, mobile sources

3 were responsible for about 50% of nationwide NO_x emissions, with diesel engines being

4 responsible for approximately one-half of the mobile source total (U.S. EPA, 1998b).

5

6 **2.3.1.3. *Atmospheric Transport of Gas-Phase Diesel Exhaust***

7 Gas-phase diesel exhaust can be dry deposited, depending on the deposition surface,

8 atmospheric stability, and the solubility and other chemical properties of the compound. Dry

9 deposition of organic species is typically on the order of weeks to months, with dry deposition

10 velocities of approximately 10^{-4} cm/sec (Winer and Busby, 1995). In contrast, inorganic species

11 such as SO_2 and nitric acid have relatively fast deposition rates (0.1–2.5 cm/sec) and will remain

12 in the atmosphere for shorter time periods compared with the organic exhaust components. Some

13 gas-phase species will also be scavenged by aqueous aerosols and potentially deposited via

14 precipitation. These processes can greatly reduce the atmospheric concentration of some vapor-

15 phase species. Atmospheric lifetimes for several gas-phase components of diesel exhaust are on

16 the order of hours or days, during which time atmospheric turbulence and advection can disperse

17 these pollutants widely.

18

19 **2.3.2. Particle-Phase Diesel Exhaust**

20 Particle-associated diesel exhaust is composed of primarily carbonaceous material (organic

21 and elemental carbon) with a very small fraction composed of inorganic compounds and metals.

22 The organic carbon fraction adsorbed on DPM is composed of high-molecular-weight

23 compounds, such as PAHs, which are generally more resistant to atmospheric reactions than

24 PAHs in the gas phase. The elemental carbon component of diesel exhaust is inert to atmospheric

25 degradation, while the PAH compounds are degraded by reaction with the following species:

26

27 •   Sunlight, during daylight hours

28 • O_3, during daytime and nighttime

29 • NO_3 and N_2O_5 during nighttime hours

30 •   OH and HO_2

31 • NO_2, during nighttime and daytime hours

32 • H_2O_2

33 • HNO_3 and other species such as HONO and H_2SO_4.

34

35 Since many of the PAH derivatives formed by reaction with some of the reactants listed

36 above have been found to be highly mutagenic, a brief discussion of PAH photolysis, nitration,

1 and oxidation follows. Some of the major degradation products from particulate diesel exhaust

2 and their biological impact are listed in Table 2-22.

3

4 **2.3.2.1. *Particle-Associated PAH Photooxidation***

5 Laboratory studies of photolysis of PAHs adsorbed on 18 different fly ashes, carbon black,

6 silica gel, and alumina (Behymer and Hites, 1985, 1988) and several coal stack ashes (Yokely et

7 al., 1986; Dunstan et al., 1989) have shown that the extent of photodegradation of PAHs depends

8 very much on the nature of the substrate to which they are adsorbed. The dominant factor in the

9 stabilization of PAHs adsorbed on fly ash was the color of the fly ash, which is related to the

10 amount of black carbon present. It appears that PAHs were stabilized if the carbon black content

11 of the fly ash was greater than approximately 5%. On black substrates, half-lives of PAHs studied

12 were on the order of several days (Behymer and Hites, 1988). The environmental chamber

13 studies of Kamens et al. (1988) on the daytime decay of PAHs present on residential wood smoke

14 particles and on gasoline internal combustion emission

15 particles showed PAH half-lives of approximately 1 hour at moderate humidities and

16 temperatures. At very low angle sunlight, very low water vapor concentration, or very low

17 temperatures, PAH daytime half-lives increased to a period of days. The presence and

18 composition of an organic layer on the aerosol seems to influence the rate of PAH photolysis

19 (Jang and McDow, 1995; McDow et al., 1994; Odum et al., 1994).

20 Because of limited understanding of the mechanisms of these complex heterogeneous

21 reactions, it is currently impossible to draw any firm conclusion concerning the photostability of

22 particle-bound PAHs in the atmosphere. Because DPM contains a relatively high quantity of

23 elemental carbon, it is reasonable to speculate that PAHs adsorbed onto these particles might be

24 relatively stable under standard atmospheric conditions, leading to an anticipated half-life of 1 or

25 more days.

26

27 **2.3.2.2. *Particle-Associated PAH Nitration***

28 Since 1978, when Pitts et al. (1978) first demonstrated that B[a]P deposited on glass-fiber

29 filters exposed to air containing 0.25 ppm NO_2 with traces of HNO_3 formed nitro-B[a]P,

30 numerous studies of the heterogeneous nitration reactions of PAHs adsorbed on a variety of

31 substrates in different simulated atmospheres have been carried out (Finlayson-Pitts and Pitts,

32 1986). PAHs deposited on glass-fiber and Teflon-impregnated glass-fiber filters react with

33 gaseous N_2O_5, yielding their nitro derivatives (Pitts et al., 1985b,c). The most abundant isomers

34 formed were 1-NP from pyrene, 6-nitro-B[a]P from B[a]P, and 3-nitroperylene from perylene.

35 The formation of nitro-PAHs during sampling may be an important consideration for DPM

36 collection because of the presence of NO_2 and HNO_3 (Feilberg et al., 1999). However, Schuetzle

1 (1983) concluded that the artifact formation of 1-NP was less than 10% to 20% of the 1-NP

2 present in the diesel particles if the sampling time was less than 23 min (one FTP cycle) and if the

3 sampling temperature was not higher than 43 °C. The formation of nitroarenes during ambient

4 high-volume sampling conditions has been reported to be minimal, at least for the most abundant

5 nitropyrene and nitrofluoranthene isomers (Arey et al., 1988).

6   DPM contains a variety of nitroarenes, with 1-NP being the most abundant among

7 identified nitro-PAHs. The concentration of 1-NP was measured in the extract of particulate

8 samples collected at the Allegheny Mountain Tunnel on the Pennsylvania Turnpike as 2.1 ppm

9 and ~5 ppm by mass of the extractable material from diesel and SI vehicle PM, respectively.

10 These values are much lower than would be predicted on the basis of laboratory measurements for

11 either diesel or SI engines (Gorse et al., 1983). Several nitroarene measurements have been

12 conducted in airsheds heavily affected by motor vehicle emissions (Arey et al., 1987; Atkinson et

13 al., 1988; Zielinska et al., 1989a,b; Ciccioli et al., 1989, 1993). Ambient PM samples were

14 collected at three sites in the Los Angeles Basin during two summertime periods and one

15 wintertime period. Concentrations of 1-NP ranged from 3 pg/m^3 to 60 pg/m^3 and 3-

16 nitrofluoranthene was also present in DPM at concentrations ranging from not detectable to 70

17 pg/m^3.

18

19 **2.3.2.3. *Particle-Associated PAH Ozonolysis***

20   Numerous laboratory studies have shown that PAHs deposited on combustion-generated

21 fine particles and on model substrates undergo reaction with O_3 (Katz et al., 1979; Pitts et al.,

22 1980, 1986; Van Vaeck and Van Cauwenberghe, 1984; Finlayson-Pitts and Pitts, 1986). The

23 dark reaction toward O_3 of several PAHs deposited on model substrates has been shown to be

24 relatively fast under simulated atmospheric conditions (Katz et al., 1979; Pitts et al., 1980, 1986).

25 Half-lives on the order of 1 to several hours were reported for the more reactive PAHs, such as

26 B[a]P, anthracene, and benz[a]anthracene (Katz et al., 1979).

27   The reaction of PAHs deposited on diesel particles with 1.5 ppm O_3 under high-volume

28 sampling conditions has been shown to be relatively fast, and half-lives on the order of 0.5 to 1

29 hour have been reported for most PAHs studied (Van Vaeck and Van Cauwenberghe, 1984).

30 The most reactive PAHs include B[a]P, perylene, benz[a]anthracene, cyclopenta[cd]pyrene, and

31 benzo[ghi]perylene. The benzofluoranthene isomers are the least reactive of the PAHs studied,

32 and benzo[e]perylene is less reactive than its isomer B[a]P. The implications of this study for the

33 high-volume sampling ambient POM are important: reaction of PAHs with O_3 could possibly

34 occur under high-volume sampling conditions during severe photochemical smog episodes, when

35 the ambient level of O_3 is high. However, the magnitude of this artifact is difficult to assess from

36 available data.

1 **2.3.2.4.** *Atmospheric Transport of Diesel Exhaust Particulate Matter*

2   Ultrafine particles emitted by diesel engines undergo nucleation, coagulation, and
3 condensation to form fine particles. DPM can be removed from the atmosphere by dry and wet
4 deposition. Particles of small diameter (<1 μm), such as DPM, are removed less efficiently than
5 larger particles by wet and dry deposition and thus have longer atmospheric residence times. Dry
6 deposition rates vary depending on the particle size. Because of their small size, diesel exhaust
7 particles have residence times of several days (dry deposition velocities of approximately 0.01
8 cm/sec) (Winer and Busby, 1995). Diesel particulates may be removed by wet deposition if they
9 serve as condensation nuclei for water vapor deposition or are scavenged by precipitation in- or
10 below-cloud.

11   In a study designed to assess the atmospheric concentrations and transport of diesel
12 exhaust particles, Horvath et al. (1988) doped the sole source of diesel fuel in Vienna with an
13 organometallic compound of the heavy earth element dysprosium. The authors found that in
14 some of the more remote sampling areas, DPM composed more than 30% of the particulate mass,
15 indicating that DPM can be dispersed widely.

16

17 **2.3.3. Diesel Exhaust Aging**
18   After emission from the tailpipe, diesel exhaust undergoes dilution, reaction, and transport
19 in the atmosphere. The primary emission is considered "fresh," while "aged" diesel exhaust is
20 considered to have undergone chemical and physical transformation and dispersion over a period
21 of a day or two. Laboratory dilution tunnel measurements represent a homogeneous environment
22 compared to the complex and dynamic system into which real-world diesel exhaust is emitted.
23 The physical and chemical transformation of diesel exhaust will vary depending on the
24 environment into which it is emitted. In an urban or industrial environment, diesel exhaust may
25 enter an atmosphere with high concentrations of oxidizing and nitrating radicals as well as
26 nondiesel organic and inorganic compounds that may influence the toxicity, chemical stability, and
27 atmospheric residence time.

28   In general, secondary pollutants formed in an aged aerosol mass are more oxidized, and
29 therefore have increased polarity and water solubility (Finlayson-Pitts and Pitts, 1986). Kamens
30 et al. (1988) reported that photooxidation of particle-bound PAH is enhanced as relative humidity
31 is increased. Weingartner et al. (1997a) evaluated the hygroscopic growth of diesel particles and
32 found that freshly emitted diesel particles demonstrated minimal hygroscopic growth (2.5%) while
33 aged particles subjected to UV radiation and ozonolysis exhibited greater hygroscopic growth. In
34 addition, increasing sulfur content in the fuel has been observed to result in greater water
35 condensation onto diesel particles. Dua et al. (1999) reported that unlike many other types of
36 particles, diesel particles do not appear to undergo hygroscopic growth once emitted to the

1 atmosphere. To the extent that diesel exhaust components are oxidized or nitrated in the

2 atmosphere, they may be removed at rates different from their precursor compounds and may

3 exhibit different biological reactivities.

4 In a recent experiment, the biological activity of DPM exposed to 0.1 ppm ozone for 48

5 hours was compared with that of DPM not exposed to ozone (Ghio et al., 2000). Instillations of

6 the ozonated DPM in rat lung resulted in an increase in biological activity (neutrophil influx,

7 increased protein, and lactate dehydrogenase activity) compared with DPM that had not been

8 treated with ozone. These data suggest that ambient levels of ozone can alter DPM constituents

9 causing an increase in toxicity compared with nonozonated DPM.

10 In addition to changes in particle composition with aging, particle size distributions may

11 vary depending on aggregation and coagulation phenomena in the aging process. People in

12 vehicles, near roadways (e.g., cyclists, pedestrians, people in nearby buildings), and on

13 motorcycles will be exposed to more fresh exhaust than the general population. In some settings

14 where emissions are entrained for long periods through meteorological or other factors, exposures

15 would be expected to include both fresh and aged diesel exhaust. The complexities of transport

16 and dispersion of emission arising from motor vehicles have been the subject of extensive

17 modeling and experimental studies over the past decades and have been summarized by Sampson

18 (1988); exposures to DPM are discussed in the next section of this chapter.

19 The major organic constituents of diesel exhaust and their potential degradation pathways

20 described above provide evidence for (1) direct emission of PAHs, (2) secondary formation of

21 nitroarenes, and (3) secondary sulfate and nitrate formation. Since nitro-PAH products are often

22 more mutagenic than their precursors, the formation, transport, and concentrations of these

23 compounds in an aged aerosol mass are of significant interest.

24

25 **2.4. AMBIENT DIESEL EXHAUST CONCENTRATIONS AND EXPOSURES**

26 **2.4.1. Diesel Exhaust Gases in the Ambient Atmosphere**

27 Although emissions of several diesel exhaust components have been measured, few studies

28 have attempted to elucidate the contribution of diesel-powered engines to atmospheric

29 concentrations of these components. The emission profile of gaseous organic compounds is

30 different for diesel and SI vehicles; the low-molecular-weight aromatic HCs and alkanes ($<C_9$) are

31 more characteristic of SI engine emissions, whereas the heavier alkanes ($>C_{10}$) and aromatic HCs

32 (such as naphthalene, methyl- and dimethyl- naphthalenes, methyl- and dimethyl-indans) are more

33 characteristic of diesel engine emissions. These differences were the basis for apportionment of

34 gasoline- and diesel-powered vehicle emissions to ambient nonmethane hydrocarbon (NMHC)

35 concentrations in the Boston and Los Angeles (South Coast Air Basin) urban areas.

1   The chemical mass balance receptor model (described below) was applied to ambient

2   samples collected in these areas, along with appropriate fuel, stationary, and area source profiles

3   (Fujita et al., 1997). The average of the sum of NMHC attributed to diesel exhaust, gasoline-

4   vehicle exhaust, liquid gasoline, and gasoline vapor was 73% and 76% for Boston and the South

5   Coast Air Basin (SoCAB), respectively. The average source contributions of diesel exhaust to

6   NMHC concentrations were 22% and 13% for Boston and the SoCAB, respectively. Diesel

7   vehicles emit lower levels of NMHC in the exhaust compared to gasoline vehicles. The relative

8   contribution of diesel exhaust clearly depends on several factors, including fleet composition,

9   sampling location (e.g., near a bus station vs. near a highway or other sources), and the

10 contribution from point and area sources. The contribution of diesel exhaust to ambient NMHC

11 showed large variations among sampling sites in the Boston area. The source apportionment in

12 the Fujita et al. (1997) study indicates that mobile vehicle-related emissions account for the

13 majority of ambient NMHC in the two urban areas studied and the results can likely be

14 extrapolated to other urban areas with similar source compositions. Other source apportionment

15 methods such as those used by Henry et al. (1994) have been applied to speciated HC data to

16 separate the mobile source direct emission from gasoline evaporative emissions. This method

17 uses a combination of graphical analysis (Graphical Ratio Analysis for Composition Estimates,

18 GRACE) and multivariate receptor modeling methods (Source Apportionment by Factors with

19 Explicit Restrictions, SAFER) and was not used to identify the diesel engine contribution to the

20 HCs measured.

21

22 **2.4.2. Ambient Concentrations of Diesel Particulate Matter**

23   Since DPM is chemically complex, an assessment of ambient DPM concentrations relies

24 primarily on (1) studies that collect ambient samples and adequately characterize their chemical

25 composition or (2) modeling studies that attempt to recreate emissions and atmospheric

26 conditions. Ambient concentrations of DPM also have been reported from studies using

27 surrogate species. The results of these studies are summarized below. Studies conducted in

28 Europe and Japan were reviewed but for the most part were not included because of questions

29 surrounding the applicability of measurements in locations that use different diesel technology and

30 control measures from those in the United States.

31

32 **2.4.2.1. *Source Apportionment Studies***

33   Receptor models are used to infer the types and relative contributions of sources to

34 pollutant measurements made at a receptor site. Receptor models assume that the mass is

35 conserved between the source and receptor site and that the measured mass of each pollutant is a

36 sum of the contributions from each source. Receptor models are referred to as "top-down" in

1 contrast to "bottom-up" methods, which use emission inventory data, activity patterns, and
2 dispersion modeling from the source to predict concentrations at a receptor site.
3   The most commonly used receptor model for quantifying concentrations of DPM at a
4 receptor site is the chemical mass balance (CMB) model. Input to the CMB model includes
5 measurements of PM mass and chemistry made at the receptor site as well as measurements made
6 of each of the source types suspected to impact the site. Because of problems involving the
7 elemental similarity between diesel and gasoline emission profiles and their co-emission in time
8 and space, chemical molecular species that provide markers for separation of these sources have
9 been identified (Lowenthal et al., 1992).   Recent advances in chemical analytical techniques have
10 facilitated the development of sophisticated molecular source profiles, including detailed
11 speciation of PM-associated organic compounds that allow the apportionment of PM to gasoline
12 and diesel sources with increased confidence. CMB analysis that uses speciation of organic
13 compounds in the source profiles is typically referred to as extended species CMB. Older studies
14 that made use of only elemental carbon, total organic carbon, trace elements, and major ions in
15 the source profiles (conventional CMB) have been published and are summarized here, but they
16 are subject to more uncertainty. It should be noted that since receptor modeling is based on the
17 application of source profiles to ambient measurements, estimates of DPM concentration
18 generated by this method include the contribution from on-road and nonroad sources to the extent
19 the source profiles are similar (which would include military sources depending on the sampling
20 locations and fleet composition). In addition, this method identifies sources of primary emissions
21 of DPM only, and the contribution of secondary aerosols is not attributed to sources.
22   The CMB model has been used to assess concentrations of DPM in areas of California,
23 Phoenix, Denver, and Manhattan (Table 2-23). DPM concentrations reported by Schauer et al.
24 (1996) for samples collected in California in 1982 ranged from 4.4 $\mu g/m^3$ in west Los Angeles to
25 11.6 $\mu g/m^3$ in downtown Los Angeles. The average contribution of PM to total PM mass ranged
26 from 13% in Rubidoux to 36% in downtown Los Angeles. As mentioned above, this model
27 accounts for primary emissions of DPM only; the contribution of secondary aerosol formation
28 (both acid and organic aerosols) is not included. In sites downwind from urban areas, such as
29 Rubidoux in this study, secondary nitrate formation can account for a substantial fraction of the
30 mass (25% of the fine mass measured in Rubidoux was attributed to secondary nitrate), a portion
31 of which comes from diesel exhaust (Gray and Kuklin, 1996).
32   The California Environmental Protection Agency (Cal EPA) reported ambient DPM
33 concentrations for 15 air basins in California based on ambient measurements taken statewide
34 from 1988 to 1992 across California (Cal EPA, 1998a). Cal EPA used CMB analysis of ambient
35 measurements from the San Joaquin Valley (1988-89), South Coast (1986), and San Jose (winters
36 for 1991–92 and 1992–93) to determine mobile source contributions and then applied the

1   California 1990 PM10 emissions inventory to determine the fraction of mobile source PM10
2   attributable to diesel emissions. The results of this analysis indicate that annual average basin-
3   wide levels of direct DPM may be as low as 0.2 μg/m^3 and may range up to 2.6 μg/m^3 for basins
4   that are largely nonurban but may have one or more densely populated areas (such as Palm
5   Springs in the Salton Sea basin). DPM concentrations for air basins that are moderately or largely
6   urbanized ranged from 1.8 μg/m^3 to 3.6 μg/m^3.
7   Two studies using CMB analysis have been conducted in the Phoenix area that report
8   DPM concentrations. A wintertime study conducted in the Phoenix area in 1989–90 reported
9   DPM concentrations for nonurban areas ranging from 2 μg/m^3 to 5 μg/m^3 and DPM
10   concentrations for central and south Phoenix urban areas ranging from 10 μg/m^3 to 13 μg/m^3
11   (Chow et al., 1991). Chow et al. (1991) reported that DPM levels on single days can range up to
12   22 μg/m^3 at the central Phoenix site. A more recent study conducted from November 1994
13   through March 1995 reported DPM concentrations for Phoenix averaging 2.4 μg/m^3 and reaching
14   5.3 μg/m^3 (Maricopa Association of Governments, 1999). The extended species CMB was used
15   for this study, providing a more confident identification of DPM separate from gasoline PM
16   emissions than the earlier Phoenix study. DPM accounted for an average 15% of ambient PM2.5,
17   and gasoline PM accounted for an average of 52% of ambient PM2.5 in the 1994–95 Phoenix
18   study.
19   During the winter of 1997, a study was conducted that assessed DPM concentrations at
20   two urban sites in the Denver area (Fujita et al., 1998). The Northern Front Range Air Quality
21   Study (NFRAQS), initiated to assess the sources of the "brown cloud" observed along Colorado's
22   Front Range, conducted air quality sampling during the winter of 1996, summer of 1996, and
23   winter of 1997. For a 60-day period from December 1996 through January 1997, ambient
24   samples collected at two urban Denver sites were analyzed for organic carbon species for use in
25   the extended species CMB. The average DPM concentrations reported for the urban site at
26   Welby, CO, and the suburban site at Brighton, CO, were 1.7 μg/m^3 and 1.2 μg/m^3, respectively.
27   During the study period, DPM concentrations exceeded 5 μg/m^3 on two occasions in Welby, with
28   reported DPM concentrations of 5.7 μg/m^3 and 7.3 μg/m^3. DPM accounted for an average of
29   10% of ambient PM2.5, and gasoline PM accounted for an average of 27% of ambient PM2.5.
30   One of the major claims from the NFRAQS was a substantial contribution of EC from
31   gasoline-powered vehicles, mainly from cold-start and high-emitting gasoline vehicles. At the
32   Welby site, the contribution of diesel and gasoline emissions to EC measurements was 52% and
33   42%, respectively. At the Brighton site, the contribution of diesel and gasoline emissions to EC
34   measurements was 71% and 26%, respectively. The findings from the NFRAQS are compelling
35   and suggest the need for further investigations to quantify the contribution from cold-start and
36   high-emitting vehicle emissions for both gasoline and diesel vehicles. Geographical, temporal, and

1 other site-specific parameters that influence PM concentrations, such as altitude, must be

2 considered when extrapolating the NFRAQS findings to other locations.

3   In addition to the need for urban and rural average DPM concentrations, an assessment of

4 potential health effects resulting from DPM exposure includes an assessment of people in

5 environments with potentially elevated levels of DPM. Limited data are available to allow a

6 characterization of DPM concentrations in "hotspots" such as near heavily traveled roadways, bus

7 stations, train stations, and marinas. Only one CMB study has attempted to apportion PM

8 measured in an urban hotspot. Wittorff et al. (1994) reported results of conventional CMB

9 performed on PM samples collected in the spring of 1993 over a 3-day period at a site adjacent to

10 a major bus stop on Madison Avenue in midtown Manhattan. Buses in this area idle for as long

11 as 10 minutes, and PM emissions are augmented by the elevated levels of DPM emitted during

12 acceleration away from the bus stop (discussed in Section 2.2.5). DPM concentrations reported

13 from this study ranged from 13.0 $\mu g/m^3$ to 46.7 $\mu g/m^3$. This study attributed, on average, 53% of

14 the PM10 to diesel exhaust. The DPM concentrations resulting from the source apportionment

15 method used in this study require some caution since the CMB model overpredicted PM10

16 concentrations by an average 30%, which suggests that additional sources of the mass were not

17 accounted for in the model. The relevance of the Manhattan bus stop concentrations and

18 potential exposure for large urban populations provides strong motivation for further studies in

19 the vicinity of such hotspots.

20   In summary, source apportionment studies of ambient samples collected before 1990

21 suggest that seasonal and annual average diesel PM concentrations for nonurban areas ranged

22 from 2 $\mu g/m^3$ to 5 $\mu g/m^3$. DPM concentrations reported from CMB studies for urban areas in the

23 pre-1990 timeframe ranged from 4.4 $\mu g/m^3$ to 13 $\mu g/m^3$ with concentrations on individual days

24 ranging up to 22 $\mu g/m^3$.   Source apportionment applied to ambient measurements taken in 1990

25 or later suggest that seasonal or annual average DPM levels in suburban/nonurban locations can

26 range from 0.2 $\mu g/m^3$ to 2.6 $\mu g/m^3$ with maximum reported values ranging up to 3.4 $\mu g/m^3$. DPM

27 concentrations reported from CMB studies in urban areas during 1990 or later range from 1.7

28 $\mu g/m^3$ to 3.6 $\mu g/m^3$ with maximum concentrations up to 7.3 $\mu g/m^3$. The highest DPM

29 concentrations reported from CMB analysis of ambient measurements were those in the vicinity of

30 a bus stop in midtown Manhattan, which ranged from 13.2 $\mu g/m^3$ to 46.7 $\mu g/m^3$.

31

32 **2.4.2.2.** *EC Surrogate for Diesel Particulate Matter*

33   EC is a major component of diesel exhaust, contributing approximately 50% to 85% of

34 diesel particulate mass, depending on engine technology, fuel type, duty cycle, engine lubrication

35 oil consumption, and state of engine maintenance (Graboski et al., 1998b; Zaebst et al., 1991;

36 Pierson and Brachaczek, 1983; Warner-Selph et al., 1984). In urban ambient environments, diesel

1   exhaust is one of the major contributors to EC, with other potential sources including spark-

2   engine exhaust; combustion of coal, oil, or wood; charbroiling; cigarette smoke; and road dust.

3   While coldstart emissions from gasoline combustion vehicles were reported to be an important

4   source of EC in wintertime samples collected in two cities in the Denver area (Fujita et al., 1998),

5   it is currently unclear to what extent these results are transferable to other locations. It is

6   noteworthy that the EC content of the cold-start emissions from gasoline combustion vehicles was

7   lower than that from diesel combustion engines in the same study by almost a factor of 2.

8   Fowler (1985) evaluated several components of diesel exhaust and concluded that EC is

9   the most reliable overall measure of ambient diesel exhaust exposure. Because of the large

10   portion of EC in DPM, and the fact that diesel exhaust is one of the major contributors to EC in

11   many ambient environments, DPM concentrations can be bounded using EC measurements.

12   Surrogate calculations of DPM have been based on the fraction of ambient EC measured in a

13   sample that is attributable to diesel engine exhaust and the fraction of the diesel particle mass

14   accounted for by EC. In the recent Multiple Air Toxics Exposure Study in the South Coast Air

15   Basin (MATES-II, SCAQMD, 2000), EC measurements were used to estimate DPM

16   concentrations by the following relationship: approximately 67% of fine EC in the ambient air in

17   the Los Angeles area originates from diesel engine exhaust (Gray, 1986), and the average EC

18   fraction of diesel particles measured was 64%. Therefore, in the MATES-II study, the South

19   Coast Air Quality Management District calculated DPM concentrations from EC measurements

20   by multiplying a measured EC concentration by 67% and dividing by the fraction of DPM mass

21   accounted for by EC of 64%, for example, DPM concentration = (EC * 0.67)/0.64, or DPM =

22   HC * 1.04. This calculation relies on data collected in the 1982 timeframe and may not accurately

23   represent the current day contributions of diesel engines to the ambient EC inventory.

24   An alternative calculation can be derived using more recent studies. The fraction of EC

25   attributable to diesel exhaust can be estimated from detailed source profiles applied to a CMB

26   model as discussed above. The contribution of diesel engines to EC averaged 68% ± 20% for

27   Brighton, CO, and 49% ± 26% at Welby, CO, as part of the winter 1996-1997 NFRAQS. In

28   Phoenix, diesel engine exhaust was estimated to account for approximately 46% ± 22% of the

29   ambient EC. For some environments, such as certain occupational settings in which diesel

30   engines are in proximity to workers, all the EC may realistically be attributed to diesel exhaust as

31   a reasonable upper bound estimate of DPM concentrations.

32   As discussed in Section 2.2, the EC content of DPM can vary widely depending on engine

33   type, load conditions, and the test cycle. However, typical profiles for HD and LD diesel engines

34   have been determined and the typical EC fraction of DPM ranges from approximately 52% to

35   75%.

Ambient EC attributed to diesel exhaust in the studies described above ranges from 46% to 68%. A lower bound estimate of DPM from ambient EC measurements in areas with similar source contributions to those in the Phoenix and Denver areas can be estimated using the equation:

$$DPM = (EC * 0.46)/0.75 \text{ or } DPM = HC * 0.62$$

An upper bound estimate uses the equation:

$$DPM = (EC * 0.68)/0.52 \text{ or } DPM = HC * 1.31$$

Using the average of the ranges provides the equation:

$$DPM = HC * 0.89.$$

Clearly the choice of a point estimate can provide a surrogate calculation of DPM that can vary by at least a factor of 2. To assess the usefulness and applicability of the surrogate calculation, the average DPM concentration predicted by extended CMB analysis can be compared with DPM concentrations predicted by the EC surrogate calculation. The average DPM concentrations reported by CMB for the Colorado and Phoenix sites are within the range of DPM concentrations estimated by the EC surrogate method (Table 2-24).

While a recommended surrogate DPM calculation method is not provided here, it is evident that on an annually averaged basis, a surrogate calculation such as the one used above may provide a reasonable estimate of DPM that bounds the actual concentration in those ambient environments with similar source contributions to those in the Denver and Phoenix areas. The surrogate DPM calculation is used here to illustrate the usefulness of this approach for estimating DPM in the absence of a more sophisticated receptor modeling analysis for locations where fine PM EC concentrations are available.

One source of variability in EC concentrations reported for ambient studies is the measurement method used to quantify EC. As discussed in Section 2.2.8.1, EC and OC are operationally defined. Ambient samples are typically analyzed for EC using thermal optical reflectance or thermal optical transmittance. The measurement technique for the studies discussed here is noted since TOR methods often report higher EC levels compared to TOT analyses (Birch, 1998; Norris et al., 2000).

Table 2-25 provides a lower and upper bound DPM estimate from annual average EC concentrations for three urban areas in addition to DPM concentrations reported from EC measurements for the MATES- II (SCAQMD, 2000). Under an EPA research grant with the

1 Northeastern States for Coordinated Air Use Management (NESCAUM), PM2.5 samples were

2 collected every 6 days for 1 year (1995) in Boston (Kenmore Square), MA, and Rochester, NY,

3 and were analyzed for EC using TOT (Salmon et al., 1997). DPM concentrations are estimated

4 to be in the range from 0.8 µg/m^3 to 1.7 µg/m^3 in Boston, and from 0.4 µg/m^3 to 0.8 µg/m³ in

5 Rochester (Table 2-25).

6 The Interagency Monitoring of Protected Visual Environments (IMPROVE) project being

7 conducted by the National Park Service includes an extensive aerosol monitoring network mainly

8 in rural or remote areas of the country (national parks, national monuments, wilderness areas,

9 national wildlife refuges, and national seashores), and also in Washington, DC (Sisler, 1996).

10 PM2.5 samples, collected from March 1992 through February 1995 twice weekly for 24-hour

11 duration at 43 sites (some co-located in the same rural park area), were analyzed for a suite of

12 chemical constituents, including EC (using TOR). EC concentrations in these rural locations may

13 have EC source contributions quite different from those in the urban areas in which the fraction of

14 EC attributable to diesel exhaust has been reported. The lack of information regarding EC

15 sources in these rural locations makes the application of the EC surrogate highly uncertain. It is

16 noteworthy that annual average EC concentrations in the rural and remote regions reported as

17 part of the IMPROVE network range from 0.1 µg/m³ for Denali National Park, AK, to 0.9 µg/m³

18 for the Lake Tahoe, CA, area. In Washington, DC, the annual average EC concentration of 1.7

19 µg/m³ is estimated as an annual average DPM concentration of 1.4 µg/m³.

20 The annual average EC measurements in Washington, DC, suggest that the DPM

21 concentrations are in the range from 1.0 µg/m^3 to 2.2 µg/m³, accounting for 5% to 12% of

22 ambient PM2.5. Seasonally averaged data for the Washington, DC, site indicates that EC

23 concentrations and, by extension, DPM concentrations at this site peak in the autumn and winter

24 (2.0 µg/m^3 and 0.9 µg/m³ EC, respectively).

25 DPM concentrations reported recently as part of the MATES-II study at eight locations

26 ranged from 2.4 µg/m^3 to 4.5 µg/m³. DPM concentrations at Huntington Park and Pico Rivera,

27 CA, were higher than other DPM concentrations in the South Coast Air Basin, potentially due to

28 higher diesel truck traffic, proximity to nonroad diesel sources, or nondiesel sources of EC,

29 including gasoline vehicle traffic.

30

31 **2.4.2.3. *Dispersion Modeling Results***

32 Dispersion models estimate ambient levels of PM at a receptor site on the basis of

33 emission factors for the relevant sources and parameters that simulate atmospheric processes such

34 as the advection, mixing, deposition, and chemical transformation of compounds as they are

35 transported from the source to the receptor site(s). Cass and Gray (1995), Gray and Cass (1998),

1   and Kleeman and Cass (1998) have applied dispersion models to the South Coast Air Basin to

2   estimate DPM concentrations. The models used by these investigators applied emission factors

3   from 1982 and consequently are representative of concentrations prior to the implementation of

4   DPM emission controls. Dispersion modeling has also been performed as part of the EPA

5   National Air Toxics Assessment (NATA) using the Assessment System for Population Exposure

6   Nationwide (ASPEN) to estimate ambient concentrations of DPM from on-road and nonroad

7   sources. The results from this analysis will be available in 2000. In addition to offering another

8   approach for estimating ambient DPM concentrations, dispersion models can provide the ability to

9   distinguish on-highway from nonroad diesel source contributions and have presented an approach

10   for quantifying the concentrations of secondary aerosols from diesel exhaust.

11   Cass and Gray (1995) used a Lagrangian particle-in-cell model to estimate the source

12   contributions to atmospheric fine carbon particle concentrations in the Los Angeles area,

13   including diesel emission factors from on-highway and off-highway sources. Their dispersion

14   model indicates that for 1982, the annual average ambient concentrations of DPM ranged from

15   $1.9 \ \mu g/m^3$ in Azusa, CA, to $5.6 \ \mu g/m^3$ in downtown Los Angeles (Table 2-26). The contribution

16   of on-highway sources to DPM ranged from 63.3% in downtown Los Angeles to 89% in west

17   Los Angeles. Of the on-highway diesel contribution, the model predicted that for southern

18   California, HD trucks made up the majority (85%) of the DPM inventory, and overall they

19   contributed 66% of the DPM in the ambient air. Nonroad sources of diesel exhaust include

20   pumping stations, construction sites, shipping docks, railroad yards, and heavy equipment repair

21   facilities. Cass and Gray (1995) also report that wintertime peaks in DPM concentrations can

22   reach $10 \ \mu g/m^3$.

23   Kleeman and Cass (1998) developed a Lagrangian model that examines the size and

24   chemical evolution of aerosols including gas-to-particle conversion processes during transport.

25   This model was applied to one well-characterized episode in Claremont, CA, on August

26   27-28, 1987. The model provided reasonable predictions of PM10 (overpredicting PM10 13%),

27   EC, and OC, and it adequately reconstructed the size distribution of the aerosols. The model

28   indicated that on August 27-28, 1987, the PM2.5 concentration was $76.7 \ \mu g/m^3$, 13.2% of which

29   $(10.1 \ \mu g/m^3)$ was attributable to diesel engine emissions. This estimate includes secondary

30   aerosol formation for sulfate, ammonium, nitrate, and organic compounds, which accounted for

31   $4.9 \ \mu g/m^3$ of the total estimated DPM mass. The secondary organic aerosol was estimated to be

32   $1.1 \ \mu g/m^3$, or 31% of the total secondary aerosol mass, with the remainder composed of nitrate,

33   ammonium, and sulfate aerosols.

34

35   **2.4.3. Exposures to Diesel Exhaust**

1   Ultimately, personal exposure determines health impacts. To understand the distribution

2   of risk in the population, the distribution of exposures among the general population and more

3   highly exposed groups needs to be assessed. An exposure assessment addresses the exposure

4   profile for the general public, including the distribution of ambient diesel exhaust exposures in

5   different geographic and demographic regions; the most highly exposed (90th percentile),

6   exposures in microenvironments for short and long durations, and the maximum exposure range

7   (98th percentile) and number of maximum exposed individuals. Because diesel exhaust is a

8   mixture of particles and gases, one must choose a measure of exposure (i.e., dosimeter); $\mu g/m^3$ of

9   DPM has historically been used in many studies as the dosimeter for the entire diesel exhaust

10   mixture. Because of the lack of data, a comprehensive exposure assessment cannot be completed

11   at this point. Exposure models are under development at EPA and elsewhere and personal

12   exposure monitoring is being conducted that will improve this assessment of the distribution of

13   exposures to DPM.

14   In the following sections, modeled average exposures and some information reflecting

15   potential exposures for those who spend a large portion of their time outdoors are presented.

16   Occupational exposures to DPM are summarized for the variety of workplaces in which diesel

17   engines are used. These occupational exposures are placed into context with equivalent

18   environmental exposures to understand the potential for overlap in average occupational and

19   average ambient exposures.

20

21   **2.4.3.1. *Occupational Exposure to Diesel Exhaust***

22   The National Institute for Occupational Safety and Health (NIOSH, 1988) estimates that

23   approximately 1.35 million workers are occupationally exposed to diesel exhaust emissions.

24   Workers exposed to diesel exhaust emissions include mine workers, railroad workers, bus and

25   truck drivers, truck and bus maintenance garage workers, loading dock workers, fire fighters,

26   heavy equipment operators, and farm workers.

27   Measurements of DPM exposure in occupational environments have included respirable

28   particulate (<3.5 μm), smoking-corrected respirable particulate, combustible particulate, and EC

29   among other methods. Occupational exposures to DPM as well as breathing zone concentrations

30   of DPM have been described in some detail by Watts (1995), Hammond (1998), the World Health

31   Organization (1996), and Birch and Cary (1996) and are briefly, but not comprehensively,

32   summarized here.

33   The highest occupational exposures to DPM are for workers in coal mines and noncoal

34   mines using diesel-powered equipment. These exposures, reported by several investigators, range

35   from approximately 10 $\mu g/m^3$ to 1,280 $\mu g/m^3$ (Table 2-27). Rogers and Whelan (1999) report

1   exposures to specific DPM-associated PAHs (including naphthalene, fluorene, phenanthrene,
2   pyrene, and benz[a]anthracene) for mine workers using diesel fuels containing low and high levels
3   of sulfur, aliphatic, and aromatic compounds. Results of this study indicate that the composition
4   of DPM to which workers were exposed varies considerably based on engine condition, fuel, and
5   other operating parameters. Mine worker exposures to PAH compounds were highest for
6   naphthalene, ranging from 1,312 μg/g to 3,228 μg/g of organics and exposures were lowest for
7   benz[a]anthracene, ranging from less than 3 μg/g up to 18 μg/g of organics.
8   Other investigators have reported DPM-associated PAH concentrations that do not
9   necessarily represent personal exposures but are a snapshot of short periods of elevated
10   concentration that make up a portion of a worker's daily exposure. Bagley et al. (1991, 1992)
11   reported levels of B[a]P ranging from below the detection limit of 0.05 ng/m^3 to 61 ng/m^3
12   collected only during periods of mining activity. Watts (1995) reported DPM concentrations in
13   four mines collected during significant diesel activity, which range from 850 μg/m^3 to 3,260
14   μg/m^3. Heino (1978) reports DPM concentrations for locomotive engineers reaching 2,000
15   μg/m^3.
16   In a study of four railroads, Woskie et al. (1988) reported concentrations of respirable
17   dust (corrected for cigarette smoke particulate) that ranged from 39 μg/m^3 for engineers/firers to
18   134 μg/m^3 for locomotive shop workers and 191 μg/m^3 for hostlers. Woskie et al. (1988) also
19   reported smoking-corrected respirable dust for railroad clerks (17 μg/m^3) who are considered to
20   be not exposed to diesel exhaust.   Although these exposures may have included nondiesel PM
21   (background respirable dust levels have been estimated to have contributed approximately 10
22   μg/m^3 to 33 μg/m^3 for this study), the majority of the respirable PM is believed to have originated
23   from the diesel locomotive emissions. DPM exposures reported for firefighters operating diesel
24   engine vehicles range from 4 μg/m^3 to 748 μg/m^3, which also encompasses the range of DPM
25   exposures reported for airport ground crew and public transportation system personnel (7 μg/m^3
26   to 98 μg/m^3).
27   Studies reporting diesel exhaust exposure among fire station employees typically report
28   particulate levels below 100 μg/m^3 (ranging from 4 μg/m^3 to 79 μg/m^3) (NIOSH, 1992; Birch and
29   Cary 1996). In a study by Froines et al. (1987), DPM exposures for firefighters in two stations
30   ranged from 39 μg/m^3 to 73 μg/m^3. DPM were also reported for airport ground crew and public
31   transit workers by Birch and Cary (1986), ranging from 7 μg/m^3 to 15 μg/m^3 for airport ground
32   crews and 15 μg/m^3 to 98 μg/m^3 for public transit workers. Dock workers using diesel-powered
33   forklifts have been reported to have DPM exposures ranging from 6 μg/m^3 to 61 μg/m^3 (NIOSH
34   1990; Zaebst et al., 1991). In studies by NIOSH (1990), and Fowler (1985), the organic material
35   measured accounted for about one-half to almost all of the carbonaceous DPM exposures,

1   providing evidence that some pieces of nonroad equipment (forklifts and construction equipment)

2   emitted DPM with a significant OC fraction in the 1980s and early 1990 timeframe.

3   Zaebst et al. (1991) also reported DPM exposures for mechanics, road drivers, and local

4   drivers for 8-hour shifts at each of six large hub truck terminals. Residential background and

5   highway background samples at fixed sites were also collected during warm-weather and cold-

6   weather periods, and the geometric mean for DPM concentrations ranged from 1 μg/m^3 to 5

7   μg/m^3. DPM exposures for road and local truckers in warm- and cold-weather periods ranged

8   from 2 μg/m^3 to 7 μg/m^3, while exposure levels for mechanics were reported between 5 μg/m^3

9   and 28 μg/m^3 (geometric means).

10   Kittelson et al. (2000) are measuring DPM exposures for bus drivers, parking garage

11 attendants, and mechanics. Personal exposures for bus drivers on four different routes range from

12 1 μg/m^3 to 3 μg/m^3, and exposure among parking ramp attendants averaged 2 μg/m^3. These

13 results are preliminary, and data for the mechanics have not yet been analyzed. This study will

14 also characterize PAH compounds to which these workers are exposed.

15   Bus garage workers have also been assessed for exposure to diesel exhaust using

16 biomarkers for particle-associated benzene exposure (Muzyka et al., 1998) and urinary excretion

17 of 8-oxo-2'-deoxyguanosine (Loft et al., 1999). Other biomarkers of diesel exhaust exposure in

18 occupational workers have included measurements of urinary 1-hydroxypyrene, adducts of DNA

19 and hemoglobin, and 8-hydroxyguanosine in lung tissue (Nielsen et al., 1996; Tokiwa et al., 1999;

20 Zwirner-Baier and Neumann, 1999; Hara et al., 1997).

21   To estimate an environmental exposure that is equivalent to an occupational lifetime

22 exposure, the fraction of lifetime worker inhalation exposure (calculated as the amount of air

23 breathed on the job multiplied by the typical amount of time spent on the job) is calculated relative

24 to 70-year lifetime inhalation exposure: (10 m^3/shift/20m^3/day) * (5 days/7days) * (48 weeks/52

25 weeks) * (45-year career/70-year lifetime) = 0.21. Using this calculation, 21% of an annual

26 average occupational lifetime exposure is roughly equivalent to a 70-year annual average lifetime

27 environmental exposure. The equivalent environmental exposures for the occupational exposures

28 presented in Table 2-28 range from 0.6 μg/m^3 to14 μg/m^3 for truckers, dock workers, and

29 mechanics, and from 2 μg/m^3 to 269 μg/m^3 for miners. The low end of the range of

30 environmental equivalent exposures for several of the occupational settings overlap with average

31 exposures predicted from the HAPEM model for on-road sources (described below) and with

32 ambient concentrations from all sources reported for DPM in urban areas in the 1990–96

33 timeframe. The overlap between some occupational exposures and environmental exposures as

34 well as the small difference between occupational environmental equivalent exposures and

35 environmental exposures are a significant concern and suggest the potential for significant risk in

1   the general population. The potential for cancer risk in the general population is discussed in

2   Section 8.3.

3

4   **2.4.3.2.** *Ambient Exposure to Diesel Exhaust*

5   Modeled estimates of population exposures to DPM integrate exposure in various indoor

6   and outdoor environments and also account for the demographic distribution, time-activity

7   patterns, and DPM concentrations in the various environments, including job-related exposures.

8   Two modeling efforts have been developed to determine DPM exposures in the general

9   population: the Hazardous Air Pollutant Exposure Model–Mobile Sources, version 3 (HAPEM-

10   MS3), and the California Population Indoor Exposure Model (CPIEM). EPA is currently

11   developing version 4 of the HAPEM, which will provide State-specific average exposures for

12   DPM.

13

14   **2.4.3.2.1.** *The Hazardous Air Pollutant Exposure Model – Mobile Sources, version 3*. To

15   estimate population exposures to DPM, EPA currently uses HAPEM-MS3 (U.S. EPA, 1999c).

16   This model provides national and urban-area specific exposures to DPM from on-road sources

17   only. HAPEM-MS3 is based on the CO probabilistic National Ambient Air Quality Standards

18   (NAAQS) exposure model (pNEM/CO), which is used to estimate the frequency distribution of

19   population exposure to CO and the resulting carboxyhemaglobin levels (Law et al., 1997).

20   HAPEM simulates the CO exposure scenario of individuals in 22 demographic groups for 37

21   microenvironments. CO concentrations are based on ambient measurements made in 1990 and

22   are related to exposures of individuals in a 10 km radius around the sampling site. DPM

23   exposures are calculated as in Equation 2-4, using a ratiometric approach to CO.

24

25 $$DPM_{mg/m^3} = (CO_{mg/m^3} / CO_{g/mi}) \times DPM_{g/mi} \hspace{2cm} (2\text{-}5)$$

26   Data provided to the model includes CO monitoring data for 1990; time-activity

27   data collected in Denver, Washington, DC, and Cincinnati from 1982 to 1985;

28   microenvironmental data; and 1990 census population data. Motor vehicle DPM and CO

29   emission rates reported by EPA (1999c) are used to calculate mobile-source DPM exposures, and

30   exposures in future years are projected based on the increase in vehicle miles traveled. EPA's

31   PART5 model is used to estimate DPM emission rates (g/mi) for the fleet as a whole in any given

32   calendar year. PART5 is currently being modified to account for deterioration, actual in-use

33   emissions, poor maintenance, and tampering effects, all of which increase emission factors. As a

34   result, HAPEM-MS3 exposure estimates based on PART5 emission factors may underestimate

1   true exposures from on-road sources. A comparison of PART5 HD diesel vehicle emission
2   factors with those presented earlier in this chapter suggest that PART5 may underestimate HD
3   diesel vehicle emissions by up to 50%.
4   HAPEM-MS3 assumes that the highway fleet (gasoline plus diesel) emissions ratio of CO
5   to DPM can be used as an adjustment factor to convert estimated CO personal exposure to DPM
6   exposure estimates. This assumption is supported by the observation that even though gasoline
7   vehicles emit the large majority of CO, gasoline and diesel highway vehicles travel on the same
8   roadways, albeit with somewhat different spatial and temporal patterns. DPM and CO are both
9   relatively long-lived atmospheric species (1–3 days) except under certain conditions; therefore the
10   model does not account for chemical and physical differences between the DPM and CO, and the
11   model assumes that for the average person in a modeled air district, CO and DPM are well mixed.
12   Exposure in microscale environments in which these assumptions may not be valid were not
13   modeled.
14   A validation study conducted for the pNEM/CO model on which HAPEM-MS3 is based
15   indicates that CO exposures for the population in the 5th percentile were overestimated by
16   approximately 33%, while those with exposures in the 98th percentile were underestimated by
17   about 30%. This validation study is considered applicable to the HAPEM-MS3 model. To
18   address the underestimate of exposures for the most highly exposed, Brodowicz (1999) used CO
19   concentrations relevant to the most highly exposed populations to determine DPM exposures for
20   different demographic groups within this population; the results are discussed below.
21   Annual average DPM exposures from on-road vehicles nationwide for the general
22   population, rural and urban population, outdoor workers, and urban children are reported for
23   1990 and 1996 and projected for 2007 and 2020 in Table 2-29. The modeled annual average
24   DPM exposure nationwide (urban and rural areas) in 1996 from on-road sources only was 0.7
25   $\mu g/m^3$. The annual average exposure in urban areas for the same year was 0.7 $\mu g/m^3$, and the
26   modeled exposure for rural areas was 0.3 $\mu g/m^3$. Among the demographic groups modeled,
27   urban outdoor workers in general were found to have the highest average exposure to DPM,
28   averaging 0.8 $\mu g/m^3$ from on-road sources in 1996. DPM exposures attributable to on-road
29   sources are projected to decrease until approximately 2007 due to fleet turnover and the full
30   implementation of Federal regulations that are currently in place. After 2007, the increase in
31   vehicle miles traveled will offset reductions in PM emissions, and consequently, exposure to DPM
32   will begin to increase. Nationally in 1996, 97% of DPM exposure from on-road vehicles was
33   attributable to HD diesel vehicles, and the rest was generated mainly by LD diesel trucks. If the
34   modeled increase in diesels in the LD truck fleet occurs, projected DPM exposures in 2007 are
35   expected to increase 38% on average over 1996 exposures.

1   Since diesel vehicle traffic, and therefore exposure to DPM, varies for different urban
2   areas, HAPEM-MS3 was used to estimate annual average population exposures for 10 urban
3   areas. Modeled 1996 DPM exposures in the cities ranged from 0.5 μg/m^3 in Chicago and St.
4   Louis to 1.2 μg/m^3 in Phoenix (Table 2-30). In 1996, estimated average DPM exposure from on-
5   road sources was higher than the national average in five cities: Atlanta, Minnneapolis, New
6   York, Phoenix, and Spokane.
7   Since HAPEM-MS3 is suspected to underestimate exposures in the highly exposed
8   populations, 1990 CO concentrations relevant to the most highly exposed populations were used
9   to determine 1990 DPM exposures for different demographic groups in this population.   The
10   highest DPM exposures ranged from 0.8 μg/m^3 for outdoor workers in St. Louis to 2.0 μg/m^3 for
11   outdoor workers in Spokane and up to 4.0 μg/m^3 for outdoor children in New York (Table 2-30).
12   The highest exposed demographic groups were those who spend a large portion of their time
13   outdoors. It is important to note that these exposure estimates are lower than the total exposure
14   to DPM since they reflect only DPM from on-road sources and do not yet reflect exposure to
15   non-road DPM emissions.
16   Exposure estimates provided by HAPEM-MS3 for the general population in 1996 are
17   lower than the ambient DPM concentrations reported for urban areas in Section 2.4.2.1 that
18   ranged from 1.2 μg/m^3 to 3.6 μg/m^3 in a similar timeframe. Since most people in the general
19   population spend a large portion of time indoors, average exposures to DPM are expected to be
20   lower than ambient concentrations.
21
22   **2.4.3.2.2. *Personal Exposures: Microenvironments/Hotspots*** Personal monitoring for DPM
23   exposure has focused on occupationally exposed groups, including railroad workers, mine
24   workers, mechanics, and truck drivers. While some studies have measured personal exposures to
25   ambient PM, none have conducted detailed chemical analysis to quantify the portion of PM
26   attributable to diesel exhaust (e.g., using extended species CMB, discussed above). Elemental
27   carbon concentrations have been reported for some microenvironments and are discussed in this
28   section. Microenvironmental exposures of significant concern include in-vehicle exposures such
29   as school buses and passenger cars as well as near highways and in urban canyons. Since DPM
30   from mobile sources is emitted into the breathing zone of humans, this source has a greater
31   potential for human exposure (per kg of emissions) compared to combustion particulates emitted
32   from point sources.
33   Recent EC measurements reported for enclosed vehicles driving on Sacramento roadways
34   ranged from below detection limits up to 10 μg/m^3 and from 3 μg/m^3 to 40 μg/m^3 on Los Angeles
35   roadways. Elevated levels of PM2.5 and EC were observed when the vehicle being followed was

1   powered by a HD diesel truck or bus (Cal EPA, 1998b). These measurements are likely to

2   include some EC from gasoline vehicles. The SHEDS (Stochastic Human Exposure and Dose

3   Simulation) model for PM predicts that although the typical person only spends approximately 5%

4   of his or her time in a vehicle, this microenvironment can contribute on average 20% and as much

5   as 40% of a person's total PM exposure (Burke et al., 2000).

6   The California Air Resources Board also collected EC near the Long Beach Freeway for

7   4 days in May 1993 and 3 days in December 1993 (Cal EPA, 1998a).   Using emission estimates

8   from their EMFAC7G model and EC and OC composition profiles for diesel and gasoline

9   exhaust, tire wear, and road dust, CARB estimated the contribution of the freeway to DPM

10 concentrations. For the 2 days of sampling in December 1993, diesel exhaust from vehicles on the

11 nearby freeway were estimated to contribute from 0.7 μg/m^3 to 4.0 μg/m^3 excess DPM above

12 background concentrations, with a maximum of 7.5 μg/m^3.

13   In 1986, EC concentrations were measured in Glendora, CA, during a carbonaceous

14 aerosol intercomparison study (Cadle and Mulawa, 1990; Hansen and Novakov, 1990). One

15 technique used during the study reported EC concentrations in 1-minute intervals, reflecting the

16 impact from diesel vehicles 50 m from the study site. The diesel vehicles were estimated to

17 contribute up to 5 μg/m^3 EC above the background concentration.

18   In a study designed to investigate relationships between diesel exhaust exposure and

19 respiratory health of children in the Netherlands, EC measurements were collected in 23 schools

20 located from 47 m to 377 m from a freeway and in 8 schools located at a distance greater than

21 400 m from a freeway (Brunekreef, 1999). EC concentrations in schools near freeways ranged

22 from 1.1 μg/m^3 to 6.3 μg/m^3, with a mean of 3.4 μg/m^3, and EC concentrations in schools more

23 than 400 m from freeways ranged from 0.8 μg/m^3 to 2.1 μg/m^3, with a mean of 1.4 μg/m^3.

24 Brunekreef et al. (2000), using a reflectance method to report "soot" or carbonaceous particulate

25 concentrations as a surrogate for EC, found a statistically significant increase in carbonaceous

26 particle concentrations inside and outside of the schools with increasing truck traffic

27 (predominantly diesel), with decreasing distance between the school and the highway, and with an

28 increase in the percent of time the school was downwind of the highway.

29   While currently there is little quantitative information regarding personal exposure to

30 DPM, certain exposure situations are expected to result in higher than average exposures. Those

31 in the more highly exposed categories would generally include people living in urban areas in

32 which diesel delivery trucks, buses, and garbage trucks frequent the roadways, but also included

33 would be people living near freeways, bus stations, construction sites, train stations, marinas

34 frequented by diesel-powered vessels, and distribution hubs using diesel truck transport. One

35 study using the 1-hydroxypyrene biomarker of diesel exhaust exposure reported diesel exhaust

1   exposure among most (76%) of the 26 adolescents sampled in Harlem (Northridge et al., 1999).

2   In a follow-on study, Kinney et al. (1999) reported EC concentrations from personal monitors

3   worn by study staff on sidewalks at four Harlem intersections that ranged from 1.5 μg/m^3 to 6

4   μg/m^3. The EC concentrations were found to be associated with diesel bus and truck counts such

5   that spatial variations in sidewalk concentrations of EC were attributed to local diesel sources in

6   Harlem.

7   In any situation in which diesel engines operate and a majority of time is spent outdoors,

8   personal exposures to diesel exhaust are expected to exceed average exposures. Since a large but

9   currently undefined portion of DPM is emitted during acceleration, those living and working in

10   the vicinity of sources operating in this transient mode could experience highly elevated levels of

11   DPM. DPM enriched in soluble organic material (as opposed to EC) is emitted from LD vehicles,

12   some nonroad equipment, on-road diesel engines during cold-start and motoring conditions, and

13   poorly maintained vehicles. The potential health effects of acute exposures to elevated DPM

14   levels as well as health effects resulting from chronic exposures are discussed in subsequent

15   chapters in this document.

16

17   **2.4.3.2.3. *The California Population Indoor Exposure Model.*** CPIEM, developed under

18   contract to the CARB, estimates Californians' exposure to DPM using distributions of input data

19   and a Monte Carlo approach (Cal EPA, 1998a). This model uses population-weighted outdoor

20   DPM concentrations in a mass balance model to estimate DPM concentrations in four indoor

21   environments: residences, office buildings, schools, and stores/retail buildings. The model takes

22   into account air exchange rates, penetration factors, and a net loss factor for deposition/removal.

23   In four additional environments (industrial plants, restaurants/lounges, other indoor places, and

24   enclosed vehicles), assumptions were made about the similarity of each of these spaces to

25   environments for which DPM exposures had been calculated. Industrial plants and enclosed

26   vehicles were assumed to have DPM exposures similar to those in the outdoor environment;

27   restaurant/lounges were assumed to have DPM concentrations similar to stores; and other indoor

28   places were assumed to have DPM concentrations similar to offices. The estimated DPM

29   concentrations in the indoor and outdoor environments range from 1.6 μg/m^3 to 3.0 μg/m^3 (Table

30   2-31).

31   The DPM concentrations reported in Table 2-31 were used as input to CPIEM, and time-

32   activity patterns for children and adults were used to estimate total indoor and total air exposures

33   to DPM. Overall, total indoor exposures were estimated to be 2.0 ± 0.7 μg/m^3, and total air

34   exposures (indoor and outdoor exposures) were 2.1 ± 0.7 μg/m^3 (Table 2-32). The South Coast

1   Air Basin and the San Francisco Bay Area were also modeled using CPIEM, where total air

2   exposures to DPM were estimated to be 2.5 ± 0.9 μg/m^3 and 1.7 ± 0.9 μg/m^3, respectively.

3   Exposure estimates were also made by Cal EPA (1998a) for 1995, 2000, and 2010 using a

4   ratiometric approach to 1990 exposures. Total air exposures reported for 1995 and projected for

5   2000 and 2010 were 1.5 μg/m^3, 1.3 μg/m^3, and 1.2 μg/m^3, respectively.

6

7   **2.5. SUMMARY**

8   This chapter summarizes information regarding the history of the use of diesel engines,

9   technological developments and their impact on emissions over time, Federal standards on diesel

10 exhaust, the chemical and physical character of diesel exhaust, atmospheric transformations of

11 diesel exhaust, and ambient diesel exhaust concentrations and exposures. The aspects of each of

12 these topics that are most relevant to the discussion of health effects in later chapters of this

13 document are summarized here. Since the majority of information regarding the chemical

14 composition and historical changes in diesel exhaust pertains to on-road diesel engines, these data

15 are discussed in greater detail than diesel emissions from nonroad equipment. Where possible,

16 nonroad emissions were discussed in Chapter 2 and are briefly summarized here.

17

18 **2.5.1. History of Diesel Engine Use, Standards, and Technology**

19   The use of diesel engines in the trucking industry began in the 1940s, and diesel engines

20 slowly displaced gasoline engines among heavy HD trucks comprising 36% of new HD truck

21 sales in 1960, 85% of sales in 1970, and almost 100% of sales in 1997. It is estimated that in

22 2000, HD diesel vehicles will travel over 224 billion miles (U.S. EPA, 2000b). In 1997, on-

23 highway HD diesel engines contributed 66% of the PM2.5 emitted by on-highway vehicles.

24   To understand changes in emissions over time, it is important to note the difference

25 between model year emission trends and calendar year emission trends. Emission trends by model

26 year refer to the year in which an engine was made; the emission rate is specific to the technology

27 and regulations in effect for that year. Emissions in a specific calendar year refer to aggregate

28 emissions due to the mix of model year engines on the road. Due to the time required for fleet

29 turnover, emission rates for the on-road fleet in any calendar year are not as low as the most

30 recent model year emission rate. In 1997, 40% of the HD vehicles on the road were at least 10

31 years old and traveled approximately 17% of HD vehicle miles traveled.

32   EPA set a smoke standard for on-road HD diesel engines beginning with the 1970 model

33 year. In the ensuing years, standards for PM from diesel engines for on-road applications

34 decreased from 0.6 g/bhp-hr in 1988 to 0.1 g/bhp-hr for trucks in 1994-1995 and 0.05 g/bhp-hr

35 for buses in 1996-1997. Calendar year emission contributions of PM from diesel engines to

36 national PM10 inventories reflect decreases expected to result from Federal regulations since the

1   emission factor models (MOBILE5 and PART5) used to provide emission estimates for mobile

2   sources largely use engine test data required for certification. The U.S. EPA Trends Report

3   estimates that PM10 emissions attributed to on-road diesel vehicles decreased 27% in the period

4   between 1980 and 1998. DPM emission factors (g/mi by model year) measured from in-use

5   vehicles have, on average, decreased by a factor of six in the period from the mid-1970s to the

6   mid-1990s.

7   It is important to note that in spite of the decreasing trend in DPM emission factors by

8   model year, a wide range in emission factors from in-use testing are reported, even for newer

9   model year HD vehicles (from less than 0.1 g/mi to over 1 g/mi for model year 1996 vehicles).

10 The high variability in DPM emissions within one model year has been attributed to deterioration[3]

11 and differences in measurement methods and test conditions at the various testing facilities.

12 Studies in which consistent testing methods were used suggest that deterioration (even for newer

13 model year engines) causes some of the variability in emission factors, while other studies clearly

14 demonstrate the important influence of test conditions and driving protocols (e.g., aggressive

15 driving) on DPM emission factors.

16   While significant reductions in DPM from diesel vehicle emissions for on-road applications

17 have been realized, diesel engines (nonroad and on-road combined) are still significant

18 contributors to 1998 inventories of particulate matter, contributing approximately 23% of PM2.5

19 emissions (not including the contribution from natural and miscellaneous sources). As the result

20 of fleet turnover and full implementation of Federal emission standards currently in place, DPM

21 emissions from on-road diesel engines are projected to decrease until 2007, at which time

22 increases in vehicle miles traveled offset current emission standards and the DPM emissions begin

23 to increase.

24   Technology innovations that impact diesel engine emissions have occurred in the years

25 since 1960, in particular the advent of turbocharging with charge air cooling and direct injection

26 engines. The use of these new technologies tends to lower emissions from on-road diesel engines;

27 until the late 1970s, however, engines were optimized for performance rather than emissions, so

28 the effect on emissions prior to this time was small. Overall, it is expected that on-road engines in

29 the 1950 to 1970 timeframe would have DPM emissions similar to those of the mid-1970 engines

30 that were not yet controlled for particulates.

31   Limited data are available to assess the changes in emission rates from locomotive, marine,

32 or other nonroad diesel engine sources over time. It is expected that since the typical lifespan of a

---

[3]Deterioration includes increases in emission rates (g/bhp hr) due to normal wear as well as manufacturing defects and malfunctions such as retarded timing, fuel injector malfunction, smoke limiting mechanism problems, clogged air filter, wrong or worn turbocharger, clogged intercooler, engine mechanical failure, excess oil consumption, and electronics that have been tampered with or have failed.

1   locomotive engine is at least 40 years and since PM regulations for these engines do not take

2   effect until 2000, PM emission rates by model year from locomotives are not likely to have

3   changed substantially since the introduction of the diesel engine into the railroad industry in the

4   early 1950s.

5   Particulate matter regulations for nonroad diesel equipment are not as stringent as PM

6   regulations for on-road diesel engines. While PM emissions have declined for on-road trucks, it is

7   estimated that PM10 emissions from nonroad diesel engines increased 17% between 1980 and

8   1998. DPM emissions from nonroad diesel engines are expected to continue to increase from

9   current levels in the absence of new regulations. No information is available regarding changes in

10   the chemical composition of nonroad engine emissions over time.

11

12   **2.5.2. Physical and Chemical Composition of Diesel Exhaust**

13   Complete and incomplete combustion of fuel in the diesel engine results in the formation

14   of a complex mixture of hundreds of organic and inorganic compounds in the gas and particle

15   phases. Among the gaseous components of diesel exhaust, the aldehydes are particularly

16   important because of their health effects and because they comprise an important fraction of the

17   gaseous emissions. Formaldehyde comprises the majority of the aldehyde emissions (65%-80%)

18   from diesel engines, with the next most abundant aldehydes being acetaldehyde and acrolein.

19   Other gaseous components of diesel exhaust that are notable for their health effects include

20   benzene, 1,3-butadiene, PAH, and nitro-PAH. Dioxin compounds have also been detected in

21   trace quantities in diesel exhaust and currently account for 1.2% of the national inventory. Dioxin

22   compounds are known to accumulate in certain foods, e.g., beef, vegetables, and diary products.

23   It is unknown whether deposition of diesel exhaust emissions has an impact on food chains in

24   local areas.

25   DPM contains EC, OC, and small amounts of sulfate, nitrate, metals, trace elements,

26   water, and unidentified compounds. DPM is typically composed of over 50% to approximately

27   75% EC depending on the age of the engine, deterioration, HD versus LD, fuel characteristics,

28   and driving conditions. The OC portion of DPM originates from unburned fuel, engine

29   lubrication oil, and low levels of partial combustion and pyrolysis products and typically ranges

30   from approximately 19%-43%, although the range can be broader depending on many of the same

31   factors that influence the EC content of DPM. Polyaromatic hydrocarbons generally comprise

32   less than 1% of the DPM mass. Metal compounds and other elements in the fuel and engine

33   lubrication oil are exhausted as ash and typically comprise 1%-5% of the DPM mass. Elements

34   and metals detected in diesel exhaust include barium, calcium, chlorine, chromium, copper, iron,

35   lead, manganese, mercury, nickel, phosphorus, sodium, silicon, and zinc. The composition of

36   DPM contrasts strongly with the typical chemical composition of ambient DPM2.5 that is

1 dominated by sulfate for aerosols measured in the eastern United States and by nitrate,

2 ammonium, and organic carbon in the western United States.

3 Approximately 1%-20% of the mass of diesel particulate matter in diesel exhaust is in the

4 ultrafine size range (nuclei mode), with the majority of particles ranging in size from 0.005-0.05

5 microns and having a mean diameter of about 0.02 microns. These particles account for 50%-

6 90% of the number of particles. These ultrafine particles are largely composed of sulfate and/or

7 sulfate with condensed organic carbon.

8 Evidence regarding an increase in the number of ultrafine particles from new HD engines

9 is inconclusive. The dilution conditions used to measure the size distribution of diesel exhaust

10 have a large impact on the number of ultrafine particles quantified. To understand the size

11 distribution of DPM to which people are exposed will require measurements under conditions that

12 more closely resemble ambient conditions.

13 Approximately 80%-95% of the mass of particles in diesel exhaust is in the size range

14 from 0.05-1.0 microns, with a mean particle diameter of about 0.2 microns, and are therefore in

15 the fine PM size range. Diesel particles in the 0.05-1.0 micron range are aggregates of primary

16 spherical particles consisting of an EC core, adsorbed organic compounds, sulfate, nitrate and

17 trace elements. These particles have a very large surface area per gram of mass, which make them

18 an excellent carrier for adsorbed inorganic and organic compounds that can effectively reach the

19 lowest airways of the lung. The elemental carbon core has a high specific surface area of

20 approximately 30-90 m^2/g.

21 Due to the potential toxicological significance of the organic components associated with

22 DPM, it is important to understand, to the extent possible, the historical changes in the amount

23 and composition of the DPM-associated organic fraction. The organic component of DPM has

24 typically been characterized by extraction with organic solvents, although other techniques such

25 as thermogravimetric methods have also been used. Results from studies using similar extraction

26 methods were compared to characterize historical changes in the SOF emission rates, the

27 percentage of DPM comprised by SOF, and the composition of SOF. Data from both engine and

28 chassis dynamometer tests suggest that SOF emission rates have decreased by model year from

29 1975 to 1995. When expressed as a percentage of total DPM, the contribution of SOF to total

30 DPM demonstrates a wide range of variability that may be attributed to different test cycles,

31 different engine types, and different deterioration rates among the vehicles tested. Currently, LD

32 diesel engines emit DPM with a higher fraction of SOF than HD engines.

33 Chassis dynamometer tests demonstrate an overall decrease in the mass percentage

34 contribution of SOF to DPM ranging from 10%-60% in the 1980s and ~5%-20% in the 1990s. In

35 contrast, engine dynamometer tests demonstrate that typically 10%-50% of DPM mass is soluble

36 organic matter for engines in model years 1980-1995. The higher SOF fraction of DPM from

1 1990s model year engine dynamometer tests is attributed primarily to the differences in the engine
2 and chassis dynamometer driving cycles. The engine dynamometer testing includes high- speed
3 and low-load or low-speed lugging test modes in the engine Federal Test Procedure that produce
4 DPM with a high SOF fraction.

5 The chassis dynamometer data are considered to reflect real-world trends in emissions
6 from heavy HD vehicles by model year since vehicles from different model years, with different
7 mileage and different levels of deterioration, are represented. Thus it is expected that the
8 percentage of SOF from new (1990 or later) model year heavy HD diesel vehicles is lower than
9 that from older vehicles. This expectation is supported by data demonstrating an overall increase
10 in the fraction of EC in the carbonaceous component of DPM. The important observation from
11 the engine test data is that some driving modes occurring in real-world applications even with new
12 (post-1990) engines may produce DPM with a high SOF component (up to 50%).

13 PAH and nitro-PAH are present in DPM from both new and older engine exhaust. There
14 is no information to suggest that the overall PAH composition profile for DPM has changed.
15 There are too few data to speculate on the changes in emissions of total PAH, nitro-PAH, or PAH
16 and nitro-PAH components such as BaP and 1-NP. The data suggest that differences in a
17 vehicles' engine type and make, general engine condition, fuel composition, and test conditions
18 can influence the emissions levels of PAH. Some studies suggest that fuel composition is the
19 most important determinant of PAH emissions. There is limited evidence that gas-phase PAH
20 emission rates increase with higher fuel PAH content and that some particle-phase PAH emission
21 rates increase with higher fuel PAH content. These data suggest that during the period from 1960
22 to 1986, when the aromatic content of fuel increased, PAH emissions may have increased until the
23 aromatic content of diesel fuel was capped in 1993. The aromatic content of nonroad diesel fuel
24 is not federally regulated and is typically greater than 30%. PAH emissions from nonroad
25 equipment would also be expected to vary with the PAH content of the fuel.

26 Currently, information regarding emission rates, chemical composition, and relative
27 contribution of DPM from high-emitting HD diesel vehicles is not available and may significantly
28 change the current understanding of DPM composition to which people are exposed. Some
29 studies have reported a substantial number of smoking diesel trucks in the in-use fleet. While the
30 correlation between smoke and particulate concentration varies with the driving cycle and
31 measurement method, the results of smoke opacity tests suggest that high-emitting HD diesel
32 vehicles may be important contributors to ambient diesel exhaust and DPM concentrations.

33 The chemical composition of DPM to which people are currently exposed is determined
34 by a combination of older and newer technology on-road and nonroad engines. Consequently, the
35 decrease in the SOF of DPM by model year does not directly translate into a proportional
36 decrease in DPM-associated organic material to which people are currently exposed. In addition,

1   the impact from high-emitting and/or smoking diesel engines is not quantified at this time.

2   Because of these uncertainties, the changes in DPM composition over time cannot presently be

3   quantified. The data clearly indicate that toxicologically significant organic components of DE

4   (e.g., PAHs, PAH derivatives, nitro-PAHs) were present in DPM and DE in the 1970s and are

5   still present in DPM and DE as a whole.

6   While a significant fraction of ambient DPM (e.g., over 50% is possible) is also emitted by

7   nonroad equipment, there are no data available to characterize changes in the chemical

8   composition of DPM from nonroad equipment over time.

9   Some analysts project that diesel engines will increase substantially in the LD fleet in

10   coming years. While LD engines currently emit DPM with higher SOF than HD engines of the

11   same model year, recently promulgated Tier 2 standards will require control measures in the

12   2004-2007 timeframe that will reduce PM emissions from these vehicles. These control measures

13   provide some assurance that even if LD diesel use increases, DPM emitted from these vehicles

14   will likely have a smaller SOF component than they currently emit.

15

16   **2.5.3. Atmospheric Transformation of Diesel Exhaust**

17   An understanding of the physical as well as chemical transformations of diesel exhaust in

18   the atmosphere is necessary to fully understand the impact of this complex chemical mixture on

19   human health. In the past two decades, data acquired from laboratory and ambient experiments

20   have provided information regarding the atmospheric loss processes and transformation of diesel

21   exhaust, but knowledge concerning the products of these chemical transformations is still limited.

22   A recent study has suggested that DPM exposed to ambient levels of ozone is sufficiently altered

23   to increase the rat lung inflammatory effect compared with DPM not exposed to ozone.

24   Studies investigating the chemical and physical changes of diesel exhaust emissions

25   suggest that there is little or no hygroscopic growth of primary diesel particles, but that as they

26   undergo oxidation, hygroscopicity increases. Increased solubility can increase the removal

27   efficiency of secondary diesel particles compared with their precursor compounds. Secondary

28   aerosols from diesel exhaust may also exhibit different biological reactivities than the primary

29   particles. For example, there is evidence for nitration of some PAH compounds resulting in the

30   formation of nitroarenes that are often more mutagenic than their precursors.

31

32   **2.5.4. Ambient Concentrations and Exposure to Diesel Exhaust**

33   Due to changes in engine technology and DPM emissions over time, ambient

34   concentrations reported from studies before 1990 are compared here to those reported after 1990.

35   There are no studies in which direct comparisons can be made due to different analytical and

36   modeling tools used to assess DPM ambient levels.

1   DPM concentrations reported from CMB and dispersion modeling studies in the 1980s

2   suggest that in urban and suburban areas (Phoenix, AZ, and Southern California), annual average

3   DPM concentrations ranged from 2-13 $\mu g/m^3$, with possible maximum daily values in Phoenix,

4   AZ, of 22 $\mu g/m^3$. In these studies, the average contribution of DPM in urban areas to total

5   ambient PM ranged from 7% in Pasadena, CA, to 36% in Los Angeles, CA.

6   In the 1990 timeframe, annual or seasonal average DPM concentrations reported in CMB

7   studies and from EC measurements for urban and suburban areas range from 1.2-4.5 $\mu g/m^3$. The

8   contribution of DPM to ambient PM at these sites averaged 10%-15% on a seasonal or annual

9   basis, with contributions up to 38% on individual days (Brighton, CO). Dispersion modeling on

10 individual days in Southern California in the 1990s predicts DPM concentrations ranging from

11 1.9-4.4 $\mu g/m^3$ (8%-12% of ambient PM). On individual days at a major bus stop in New York

12 City, DPM concentrations were reported to reach 46.7 $\mu g/m^3$ and averaged 53% of ambient PM,

13 highlighting the important influence of diesel bus traffic in an urban street canyon.

14 In non-urban and rural areas in the 1980s, DPM concentrations reported range from 1.4 -

15 5 $\mu g/m^3$ and on average comprised 5%-12% of the ambient aerosol. In the 1990s, non-urban air

16 basins in California were reported to have DPM concentrations ranging from 0.2-2.6 $\mu g/m^3$.

17 While estimates from emissions models suggest that DPM emissions from on-road sources

18 decreased during the 1990s, the atmospheric data available do not provide a clear indication of

19 trends in DPM concentrations but are likely to be more a reflection of the choice in sampling sites,

20 source apportionment methods, and modeling techniques. In general, from the limited number of

21 studies available it appears that DPM concentrations averaged over at least a season in the 1990s

22 typically ranged from 1-4 $\mu g/m^3$. These data can be used in model-monitor comparisons and to

23 provide an indication of long-term average exposures in some urban areas. Additional work is

24 needed to assess ambient DPM and DE concentrations in several urban environments, to assess

25 microenvironments, and to evaluate the relative impact of nonroad and on-road sources on

26 concentrations.

27 A comprehensive exposure assessment cannot currently be conducted due to the lack of

28 data. Information regarding DPM in occupational environments suggests that exposure ranges up

29 to approximately 1,280 $\mu g/m^3$ for miners, with lower exposure measured for railroad workers

30 (39-191 $\mu g/m^3$), firefighters (4-748 $\mu g/m^3$), public transit personnel who work with diesel

31 equipment (7-98 $\mu g/m^3$), mechanics and dockworkers (5-65 $\mu g/m^3$), truck drivers (2-7 $\mu g/m^3$),

32 and bus drivers (1-3 $\mu g/m^3$). Work area concentrations at fixed sites are often higher than

33 measured exposures, especially for mining operations or other enclosed spaces. For several

34 occupations involving DE exposure, an increased risk of lung cancer has been reported by

35 epidemiological studies (discussed in Chapter 7). An estimate of the 70-year lifetime

36 environmental exposure equivalent to these occupational exposures provides one means of

1   comparing the potential overlap between occupational exposures and exposures modeled for the

2   general public. The estimated 70-year lifetime exposures equivalent to those for the occupational

3   groups discussed above range from 0.4-2 $\mu g/m^3$ on the low end to 2-269 on the high end.

4   The EPA has performed a national-scale exposure assessment for DPM from on-road

5   sources. Current national exposure modeling using the HAPEM-MS3 model suggests that in

6   1996, annual average DPM exposure from on-road diesel exhaust sources in urban areas was 0.7

7   $\mu g/m^3$, while in rural areas, exposures were 0.3 $\mu g/m^3$. Among 10 urban areas in which DPM

8   exposures were modeled, 1996 annual average exposure from on-road diesel exhaust sources

9   ranged from 0.5 $\mu g/m^3$ to 1.2 $\mu g/m^3$. Outdoor workers and children who spend a large amount of

10 time outdoors were estimated to have elevated DPM exposures in 1990, ranging up to 4.0 $\mu g/m^3$

11 from on-road sources only. Based on the national inventory, DPM exposure that includes the

12 contribution from nonroad emission sources could contribute at least twice the on-road exposure.

13 Additional national-scale exposure modeling efforts have been initiated at EPA and are being

14 refined to initially provide information regarding average exposures and eventually to provide

15 more informed estimates of exposures for more highly exposed individuals.

16   Low-end exposures for many of the occupational groups overlap 1990 and 1996

17 exposures from on-road sources modeled for the general population (0.7-0.8 $\mu g/m^3$) and for the

18 more highly exposed groups. This potential overlap or small difference between occupational and

19 ambient exposures presents a concern that health effects observed in occupational groups may

20 also be evidenced in the general population. The potential magnitude of this risk is discussed in

21 Chapter 8.

22   In different exposure environments, the types of diesel vehicles, their mode of operation,

23 maintenance, atmospheric transformation and many additional factors influence the chemical

24 nature and quantity of DPM to which people are exposed. The potential health consequences of

25 both short- and long-term exposures to diesel exhaust are discussed in the following chapters of

26 this document.

Table 2-1. Vehicle classification and weights for on-road trucks

Class	Gross vehicle weight (lb)
1	<6,000
2	6,001–10,000
3	10,001–14,000
4	14,001–16,000
5	16,001–19,500
6	19,501–26,000
7	26,001–33,000
8A[a]	33,001–60,000
8B[a]	>60,000
Medium duty (MD)	10,001–19,500 (same as Classes 3–5)
Light-heavy duty (LHD)	19,501–26,000 (same as Class 6)
Heavy-heavy duty (HHD)	>26,001 (same as Class 7–8)

[a]Class 8A and Class 8B are often considered together.

Table 2-2. Total (gas and diesel) and diesel trucks in the fleet in 1992

Truck class	1992 gas and diesel trucks	1992 diesel trucks	% Diesels
Class 1 and 2 (Light duty)	55,193,300	1,387,600	3
Class 3, 4, and 5 (Medium duty)	1,258,500	326,300	26
Class 6 (Light heavy-duty)	732,300	273,800	37
Class 7 and 8 (Heavy heavy-duty)	2,016,600	1,725,300	86

Source: Census of Transportation (1995)

Table 2-3. Typical chemical composition of fine particulate matter

	Eastern U.S.	Western U.S.	Diesel PM2.5
Elemental carbon	4%	15%	75%
Organic carbon	21%	39%	19%
Sulfate, nitrate, ammonium	48%	35%	1%
Minerals	4%	15%	2%
Unknown	23%	–	3%

Source: U.S. EPA, 1999a.

Table 2-4. U.S. emission standards: HD highway diesel engines

Model year	Pollutant (g/bhp-hr)					Smoke[a]
	HC	CO	NO$_x$	HC + NO$_x$	Particulate (PM) t=truck, b=bus, ub=urban bus	
1970	—	—-	—-	—-	—	A:40%; L:20%
1974	—	40	—-	16[b]	—	A:20%; L:15%; P:50%
1979	1.5	25	—-	10[b]	—	A:20%; L:15%; P:50%
1985[c]	1.3	15.5	10.7	—	—	A:20%; L:15%; P:50%
1988	1.3	15.5	10.7	—	0.60	A:20%; L:15%; P:50%
1990	1.3	15.5	6.0	—	0.60	A:20%; L:15%; P:50%
1991	1.3	15.5	5.0	—	0.25	A:20%; L:15%; P:50%
1993	1.3	15.5	5.0	—	0.25 t, 0.10 b	A:20%; L:15%; P:50%
1994	1.3	15.5	5.0	—	0.10 t, 0.07 ub	A:20%; L:15%; P:50%
1996	1.3	15.5	5.0	—	0.10 t, 0.05 ub	A:20%; L:15%; P:50%
1998	1.3	15.5	4.0	—	0.10 t, 0.05 ub	A:20%; L:15%; P:50%
2004	1.3	15.5	—	2.4 NMHC[d]	0.10 t, 0.05 ub	A:20%; L:15%; P:50%

[a]Emissions measured in percent opacity during different operating modes: A=acceleration; L=lug; P=peaks during either mode.
[b]Total HC.
[c]In 1985, test cycle changed from steady-state to transient operation for HC, CO, and NO$_x$ measurement and in 1988 for PM.
[d]Or 2.5 plus a limit of 0.5 nonmethane hydrocarbon (NMHC).

Table 2-5. U.S. emission standards: locomotives (g/bhp-hr)

	Year[a]	CO	HC	NO$_x$	PM
Line-haul	1973-2001 (Tier 0)	5.0	1.0	9.5	0.6
Switch	1973-2001 (Tier 0)	8.0	2.1	14.0	0.72
Line-haul	2002-2004 (Tier 1)	2.2	0.55	7.4	0.45
Switch	2002-2004 (Tier 1)	2.5	1.2	11.0	0.54
Line-haul	2005 + (Tier 2)	1.5	0.3	5.5	0.20
Switch	2005 + (Tier 2)	2.4	0.6	8.1	0.24

[a]Date of engine manufacture.

Table 2-6. U.S. emission standards for nonroad diesel equipment (g/bhp-hr)

Power rating	Model year	Pollutant (g/bhp-hr)					Smoke %[a]
		HC	CO	NO$_x$	NMHC + NO$_x$	PM	
11 < hp	2000	—	6.0	—	7.8 (ABT)	0.74 (ABT)	
	2005+	—	6.0	—	5.6 (ABT)	0.60 (ABT)	
11≤ hp < 25	2000	—	4.9	—	7.0 (ABT)	0.60 (ABT)	
	2005+	—	4.9	—	5.6 (ABT)	0.60 (ABT)	
25≤ hp < 50	2000	—	4.1	—	7.0 (ABT)	0.60 (ABT)	
	2005+	—	4.1	—	5.6 (ABT)	0.44 (ABT)	
50≤ hp <100	1998+	—	—-	6.9 (ABT)	—--	—	20/15/50
	2004	—	3.7		5.6 (ABT)	0.30 (ABT)	
	2008+	—	3.7		3.5 (ABT)	—	
100≤ hp <175	1997+	—	—-	6.9 (ABT)	—	—	20/15/50
	2003	—	3.7	—	4.9 (ABT)	0.22 (ABT)	
	2007+	—	3.7	—	3.0 (ABT)	—	
175≤ hp < 750	1996+	1.0	8.5	6.9 (ABT)	—	0.4	20/15/50
175≤ hp < 300	2003	—	2.6	—	4.9 (ABT)	0.15 (ABT)	
	2006+	—	2.6	—	3.0 (ABT)	—	
300≤ hp < 600	2001	—	2.6	—	4.8 (ABT)	0.15 (ABT)	
	2006+	—	2.6	—	3.0 (ABT)	—	
600≤ hp < 750	2002	—	2.6	—	4.8 (ABT)	0.15 (ABT)	
	2006+	—	2.6	—	3.0 (ABT)	—	
≥750 hp	2000+	1.0	8.5	6.9 (ABT)	—	0.4	20/15/50
	2006+	—	2.6	—	4.8 (ABT)	0.15 (ABT)	

[a]Emissions measured in percent opacity during different operating modes: Acceleration/lug/peaks during either mode.

ABT=average banking and trading.

Note: The standards for engines less than 50 hp also apply to diesel marine engines.

Table 2-7. Comparison of in-use truck fleet with truck fleet tested on chassis dynamometer, percent of total vehicles

Class	In-use trucks, 1995 census	Tested trucks
3	17.7	1
4 & 5	13.3	0
6 & 7	25.0	17
8A	20.9	52
8B	23.1	30

Table 2-8. Diesel engine emissions data from engine dynamometer tests

Reference	Engine[a]	Year	Test[b]	NO_x g/bhp-hr	PM g/bhp-hr	CO g/bhp-hr	THC g/bhp-hr	SOF g/bhp-hr	SOF Meth[c]	Total Aldehyde, mg/bhp-hr	B[a]P (PAH) ug/bhp-hr[d]	1-NP (NPAH) ug/bhp-hr[e]
Hare, 1977	Cat 3208 (NA)	1976	SS	7.98	0.871	4.04	1.11	0.103	c-hexane		0.76	
	DDC 6V71 (blower)	1976	SS	10.24	1.92	6.55	0.71	0.937	c-hexane		0.24	
Springer, 1979	Mack ETAY(B)673A (DI, TC,AC)	1977	SS	6.613	0.61	1.588	0.476	0.098	Benz/cyc	65	2.23	
	Cat 3208 (EGR, NA)	1977	SS	3.747	2.21	6.200	1.163		Benz/cyc	161	1.72	
	Cat 3406 (DI, TC, AC)	1977	SS	9.79	0.35	2.34	0.35	0.063	Benz/cyc	73	0.15	
	Cat 3406 (DI, TC, AC, EGR)	1977	SS	5.49	0.93	4.81	0.17	0.181		80	0.08	
	Cat 3406 (IDI, TC, AC)	1977	SS	5.14	0.28	1.26	0.12	0.031	Benz/cyc	80	0.11	
	DB OM-352A (DI, TC, AC)	1977	SS	8.93	0.56			0.190	Benz/cyc	280	0.87	
	DB OM-352A (DI, NA)	1977	SS	7.46	0.99			0.287	Benz/cyc	280	1.07	
Perez, 1980	Cat (DI, NA)	1978	SS	8.12	0.77	5.92	0.77	0.19	DCM		1.08	
	Cat (DI, EGR)	1978	SS	5.16	1.21	5.37	0.57	0.079	DCM		4.34	
	Cat (DI, TC, AC)	1978	SS	7.66	0.33	2.20	0.27	0.037	DCM		0.34	
Martin, 1981a	Cat 3208	1978	T	7.83	1.06							
	Cummins NTC350	1976	T	11.41	0.81							
	DDC 6V92T (2S)	1978	T	9.55	0.72							
	Cummins NTCC350	1979	T	6.58	0.52							
	DDC 8V71N (2S)	1978	T	7.15	0.92							
	DDC 6V92TA (2S)	1979	T	7.80	0.65							
	IH DTI466B	1979	T	7.46	0.48							
	Mack ETAY(B)673A	1979	T	9.01	0.77							
	Mack ETSX676-01	1980	T	6.90	0.85							
	Cummins VTB-903	1979	T	8.10	0.53							
	Cat 3406	1979	T	11.28	0.69							
	Cat 3406PCTA	1979	T	7.24	0.49							
	Cummins BigCam NTC350	1979	T	9.97	0.54							
	IH DT466	1979	T	7.91	0.71							
	DDC 6V92TA (2S)	1979	T	11.66	0.73							
	DDC 8V71TA (2S)	1979	T	9.81	0.51							
	Cummins NTC290	1979	T	11.10	0.78							
	Cummins NH-250	1979	T	10.87	0.97							
Martin, 1981b	Cummins VTB-903	1980	T	5.59	0.67	2.0	2.23	0.228	DCM			
	DDC 8V71TA (2S)	1980	T	7.91	0.44	2.28	0.73	0.176	DCM			
	IH DTI466B	1980	T	4.41	0.62	2.35	0.87	0.186	DCM			
Ullman, 1984	DDAD 6V-71 (2S)	1980	T	6.09	0.56	3.86	1.42	0.298	DCM	23	--	
Martin et al., 1984	Cummins NTC300	1981	T	8.13	0.45	2.70	1.36	--				
	DDC 8V-92 TA (2S)	1980	T	8.15	0.45	2.61	0.53	--				
Barry et al., 1985	Cat 3406B	1985	T	6.58	0.48	2.1	0.5	0.061	DCM	70	1	

Table 2-8. Diesel engine emissions data from engine dynamometer tests (continued)

Reference	Engine[a]	Year	Test[b]	NOx g/bhp-hr	PM g/bhp-hr	CO g/bhp-hr	THC g/bhp-hr	SOF g/bhp-hr	SOF Meth[c]	Total Aldehyde, mg/bhp-hr	B[a]P (PAH) ug/bhp-hr[d]	1-NP (NPAH) ug/bhp-hr[e]
			SS	6.64	0.36	1.83	0.38	0.0255				
Enga et al., 1985	DDC 8V-71 TAC (2S)	1984	T	5.85	1.26	2.99	1.48	--		--	--	
Baines et al., 1986	Cummins NTCC-400	1985	T	4.62	0.55	3.21	0.53					
Wachter et al., 1990	Iveco 8460	1991	T		0.22			0.0957	?			
McCarthy et al., 1992	Navistar DTA466 ES210	1993	T	4.93	0.082	1.3	0.28	0.0237	SFE			
Perez and Williams, 1989	Engine 1	1982	T		0.93			0.179	DCM		26	0.83
	Engine 2	1982	T		0.86			0.145	DCM		5.8	--
	Engine 3	1982	T		0.59			0.185	DCM		4.9	0.89
	Engine 4	1982	T		0.96			0.325	DCM		26	1.2
	Engine 5	1982	T		1.06			0.076	DCM		5.3	--
	Engine 6	1982	T		0.88			0.344	DCM			
Needham et al., 1989	Average of 16 engines	1988	T		0.37			0.12	DCM			
	Average of 3 engines	1991	T		0.24			0.10	DCM			
Kreso et al., 1998b	Cummins L10-300	1988	SS	5.15	0.103		0.26	0.030	DCM			
	Cummins L10-310	1991	SS	4.70	0.035		0.067	0.022	DCM			
	Cummins M11-330E	1995	SS	3.82	0.037		0.16	0.016	DCM			
Bagley et al., 1998	Cat 3304 (IDI, NA) non-road	1983	SS		0.56			0.319	Benz/cyc		1.5(133)	2.2
Graboski, 1998	DDC 6V-71N-77 (MUI, 2S)	1977	T	9.96	0.83	3.59	2.01	0.729	DCM			
(and references therein)	DDC 6V-92TA-91 (DDECII)	1991	T	4.23	0.197	1.51	0.72	0.0788	?			
	DDC-6V-92TA-87 (2S)	1987	T	10.77	0.59	0.71	--	--				
	DDC-6V92TA-83 (MUI, 2S)	1983	T	5.62	0.265	1.19	0.435	0.133	DCM			
	DDC 6V-92TA -88 (DDECII, 2S)	1988	T	8.52	0.2	1.6	0.6	0.116	Tol/EtOH			
	DDC 6V-92TA-91 (DDECII, 2S)	1991	T	4.4	0.276	1.65	0.42	0.07	Tol/EtOH			
	DDC 6V-71N-77 (MUI, 2S)	1977	T	11.72	0.282	3.18	0.86	0.212	DCM			
	DDC 6V-92TA-81/89 (MUI, 2S)	1981	T	10.06	0.268	2.16	0.42	0.144	DCM		--	--
	DDC 6V-92TA-91 (DDECII, 2S)	1991	T	4.84	0.227	1.51	0.44	--		--	--	
	DDC 6V-92TA-89 (DDECII, 2S)	1989	T	4.855	0.338	2.499	0.526	--		--	--	
	DDC Series 60-91 DDECII	1991	T	4.635	0.300	4.458	0.164	--				
	Cummins L-10-87 (MUI)	1987	T	5.64	0.309	2.33	0.89	--				
	DDC Series 60-91 (DDECII)	1991	T	4.68	0.220	2.26	0.08	0.066	DCM			
	Cummins N-14-87 (MUI)	1987	T	6.32	0.369	2.20	0.58	0.100	?			
	DDC Series 60-89 (DDECII)	1989	T	5.128	0.252	4.008	0.154	--				--
	DDC Series 60-91 (DDECII)	1991	T	4.303	0.182	2.004	0.392	0.061	Tol/EtOH	--	--	
	Cummins B5.9	1995	T	4.37	0.106	1.47	0.30	0.05	DCM		0.24((18.5)	
Norbeck et al., 1998b	Cummins L10	1991	T	4.77	0.224	2.26	0.53	--		80	20(1725)	1.95(4.92)
Spreen et al., 1995	Navistar DTA466	1994	T	4.779	0.090	0.989	0.181	0.035	DCM	26		
	DDC Series 60	1994	T	4.89	0.112	1.402	0.065	0.043	DCM	17		
Sienicki et al., 1990	Navistar DTA466	1991	T	5.25	0.22	--	0.23	0.05	DCM			

Table 2-8. Diesel engine emissions data from engine dynamometer tests (continued)

Reference	Engine[a]	Year	Test[b]	NO$_x$ g/bhp-hr	PM g/bhp-hr	CO g/bhp-hr	THC g/bhp-hr	SOF g/bhp-hr	SOF Meth[c]	Total Aldehyde, mg/bhp-hr	B[a]P (PAH) ug/bhp-hr[d]	1-NP (NPAH) ug/bhp-hr[e]
Ullman et al., 1990	DDC Series 60	1991	T	4.552	0.188	2.102	0.508	--				
Kado et al., 1998	Cat 3406E	1997	T						DCM		0.07(30)	0.34
Ullman et al., 1988	Cummins NTCC400	1988	T	4.47	0.42	2.22	0.53					
Mitchell et al, 1994	DDC Series 60	1994	T	4.43	0.111	2.17	0.22	0.021	DCM	34	(141)	0.04(0.12)
	Navistar DTA466	1994	T	4.86	0.099	1.10	0.34	0.046	DCM	56	0.11(242)	0.3(0.6)
Tanaka et al, 1998	Unknown	1994	SS	4.934	0.143	0.807	0.352	0.036	DCM		.076	
Rantanen et al, 1993	Scania	1990	SS	9.30	0.157			0.031	DCM			
	Valmet	1990	SS	8.67	0.157							
	Volvo	1990	SS	9.87	0.262							
	Volvo	1995	SS	4.56	0.135							

[a]NA=naturally aspirated. TC=turbochared (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).

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

[c]SOF extraction method. SFE=Supercritical fluid extraction. All others by Soxhlet extraction using the indicated solvents (? for unreported). DCM=dichloromethane. Tol/EtOH=toluene/ethanol mixture. Benz/cyc=benzene/cyclohexane mixture. C-hexane=cyclohexane.

[d]Number in parentheses is the total PAH emission obtained by summing emissions of all PAHs reported.

[e]Number in parentheses is the total NPAH emission obtained by summing emissions of all NPAHs reported.

Table 2-9. HD diesel emissions results from tunnel tests (adapted from Yanowitz et al., 1999)

Test	Tunnel location, year of study	Fuel efficiency (mi/gal)	NO_x[a] (g/mi)	NMHC (g/mi)	CO (g/mi)	DPM (g/mi)	CO_2 (g/mi)	NO_x[a] (g/gal)	NMHC (g/gal)	CO (g/gal)	DPM (g/gal)
Pierson and	Allegheny, 1974	5.42[b]				.90-1.80					4.9-9.8
Brachaczeck, 1983	Allegheny, 1975					1.75 ± 0.19					9.49±1.03
	Allegheny, 1976					1.5 ± 0.10					8.1 ± 0.54
	Allegheny, 1976					1.4 ± 0.07					7.6 ± 0.4
	Tuscarora, 1976					1.3 ± 0.19					7.0 ± 1.0
	Tuscarora, 1976					1.39 ± 26					7.5 ± 1.40
	Allegheny, 1977					1.3 ± 0.08					7.0 ± 0.43
	Allegheny, 1979					1.2 ± 0.03					6.5 ± 0.16
	Allegheny, 1979					1.4 ± 0.04					7.6 ± 0.19
Rogak et al., 1998	Cassiar Tunnel, 1995, Vancouver	8.03[b]	19.50 ± 4.22	-0.16 ± 0.88	6.79 ± 11.78		1,280 ± 40	157 ± 34	-1 ± 7	55 ± 95	
Miguel et al., 1998	Caldecott Tunnel, 1996, San Francisco	5.42[c]	23.82 ± 4.17			1.67 ± 0.24[d]		129 ± 23			9.0 ± 1.3[d]
Weingartner et al., 1997	Gubrist Tunnel, 1993, Zurich	5.60[e]				0.62 ± 0.02[f]					3.5 ± 0.1[f]
Pierson et al., 1996	Fort McHenry Tunnel, downhill, 1992, Baltimore	11.46[b]	9.66 ± 0.32	0.92 ± 0.21	6.8 ± 1.5		897 ± 48	111 ± 4	11 ± 2	78 ± 17	
Pierson et al., 1996	Fort McHenry Tunnel, uphill, 1992, Baltimore	5.42[b]	22.50 ± 1.00	2.55 ± 1.05	14.3 ± 5.5		1,897 ± 168	122 ± 5	14 ± 6	78 ± 30	
Pierson et al., 1996	Tuscarora Tunnel 1992, Pennsylvania	6.44[b]	19.46 ± 0.85	0.68 ± 0.20	6.03 ± 1.61		1,596 ± 78	125 ± 5	4 ± 1	39 ± 10	
Kirchstetter et al., 1999	Caldecott Tunnel, 1997, San Francisco	5.42[c]	23.82 ± 2.98			1.43 ± 0.12[g]		129 ± 16			7.7 ± 0.6[g]
Gertler,1999	Tuscarora Tunnel, 1999, Pennsylvania					0.29					

[a]NO_x reported as NO_2.

[b]Calculated from observed CO_2 emissions assuming fuel density 7.1 lb/gal and C is 87% of diesel fuel by weight.

[c]Since CO_2 emissions not available, fuel efficiency assumed to be the same as in slightly uphill tunnel (Fort McHenry).

[d]Reported as black carbon, assumed that 50% of total PM emissions are BC.

[e]Slope of tunnel unknown, so used average fuel efficiency for the United States.

[f]PM_3.

[g]$PM_{2.5}$.

[h]Uncertainty reported as ±1.0 standard deviation, except where literature report did not specify standard deviation; in those cases uncertainty listed as reported.

Table 2-10. Remote sensing results for HD vehicles

	Reference	Year study conducted	Emissions (g/gal)
NO_x	Jimenez et al., 1998	1997	150 [a,b,c]
	Cohen et al., 1997	1997	108 [a,b,c]
	Countess et al., 1999	1998	187 [a,b,c]
CO	Bishop et al., 1996	1992	59 [b]
	Cohen et al., 1997	1997	54 [b]
	Countess et al., 1999	1998	85 [b]
THC	Bishop et al., 1996	1992	0.002 HC/CO_2 mole ratio [d]
	Cohen et al., 1997	1997	0.00073 HC/CO_2 mole ratio [d]

[a]Remote sensing measures NO. The reported value was corrected to a NO_x (as NO_2) value by assuming 90% (mole fraction) of NO_x is NO.

[b]Emissions in g/gal calculated by assuming that fuel density is 7.1 lb/gal and C is 87% by weight of fuel.

[c]No humidity correction factor is included.

[d]In order to calculate emissions in g/gal, an average molecular weight is needed.

Source: Yanowitz et al., 1999.

Table 2-11. Summary of CDD/CDF emissions from diesel-fueled vehicles

Study	Country	Vehicle tested	Number of test vehicles	Emission factor (pg TEQ/km driven)	Driving cycle; sampling location
CARB, 1987a; Lew, 1996	United States	Diesel truck	1	663–1,300	6-hr dynamometer test at 50 km/hr
Marklund et al., 1990	Sweden	Diesel truck	1	not detected (<18)[a]	U.S. Federal mode 13 cycle; before muffler
Hagenmaier et al., 1990	Germany	Diesel car	1	2.4[a]	Comparable to FTP-73 test cycle; in tailpipe
Hagenmaier et al., 1994	Germany	Diesel bus	1	not detected (< 1 pg/L)	On-the-road testing
Oehme et al., 1991 (tunnel study)	Norway	—	(b)	520[c] 38[c] avg = 280 9,500[c] 720[c] avg = 5,100	Cars moving uphill (3.5% incline) at 60 km/hr Cars moving downhill (3.5% decline) at 70 km/hr Trucks moving uphill (3.5% incline) at 60 km/hr Trucks moving downhill (3.5% decline) at 70 km/hr
Schwind et al., 1991 Hutzinger et al., 1992	Germany	Diesel car Diesel truck	1 1	5.0–13[a] 13–15[a]	Various test conditions (i.e., loads and speeds) Various test conditions (i.e., loads and speeds)
Gertler et al., 1996 (tunnel study)	United States	Diesel trucks	(d)	mean = 172	Mean of seven 12-hour samples
Gullett and Ryan, 1997	United States	Diesel truck	1	mean - 29.0	Mean of five sample routes

[a]Results reported were in units of pg TEQ/liter of fuel. For purposes of this table, the fuel economy factor used by Marklund et al. (1990), 10 km/L or 24 miles/gal, was used to convert the emission rates into units of pg TEQ/km driven for the cars. For the diesel-fueled truck, the fuel economy factor reported in CARB (1987a) for a 1984 heavy-duty diesel truck, 5.5 km/L (or 13.2 miles/gal), was used.
[b]Tests were conducted over portions of 4 days, with traffic rates of 8,000-14,000 vehicles/day. Heavy-duty vehicles (defined as vehicles over 7 meters in length) ranged from 4% to 15% of total.
[c]Emission factors are reported in units of pg Nordic TEQ/km driven; the values in units of I-TEQ/km are expected to be about 3% to 6% higher.
[d]Tests were conducted over 5 days with heavy-duty vehicle rates of 1,800-8,700 vehicles per 12-hour sampling event. Heavy-duty vehicles accounted for 21% to 28% of all vehicles.

Table 2-12. Baltimore Harbor Tunnel Study: estimated CDD/CDF emission factors for HD vehicles

Congener/congener group	Run-specific emission factors							Mean emission factors (pg/km)
	Run no. 2 (pg/km)	Run no. 3 (pg/km)	Run no. 5 (pg/km)	Run no. 6 (pg/km)	Run no. 8 (pg/km)	Run no. 9 (pg/km)	Run no. 10 (pg/km)	
2,3,7,8-TCDD	24.5	61.6	0.0	21.2	37.8	40.1	54.9	34.3
1,2,3,7,8-PeCDD	40.2	20.6	15.4	5.6	38.4	0.0	83.0	29.0
1,2,3,4,7,8-HxCDD	18.2	25.2	46.5	8.3	64.5	0.0	123	40.8
1,2,3,6,7,8-HxCDD	37.5	28.2	64.3	19.6	153	71.1	186	80.0
1,2,3,7,8,9-HxCDD	53.6	56.5	91.6	48.4	280	126	370	147
1,2,3,4,6,7,8-HpCDD	0	401	729	111	2,438	963	2,080	960
OCDD	0	3,361	3,382	1,120	9,730	5,829	7,620	4,435
2,3,7,8-TCDF	0	94.3	67.6	152.8	155.8	73.4	61.7	86.5
1,2,3,7,8-PeCDF	0	48.9	72.6	23.6	53.3	0.0	43.3	34.5
2,3,4,7,8-PeCDF	24.5	75.7	131	46.6	85.0	63.9	108	76.4
1,2,3,4,7,8-HxCDF	15.4	139	204	93.8	124	164	166	129
1,2,3,6,7,8-HxCDF	0.3	75.1	73.7	51.0	61.3	54.4	95.5	58.8
1,2,3,7,8,9-HxCDF	27.7	14.8	75.6	0	20.6	37.2	63.5	34.2
2,3,4,6,7,8-HxCDF	15.2	82.5	152	55.7	93.0	86.8	111	85.2
1,2,3,4,6,7,8-HpCDF	12.6	280	445	154	313	354	308	267
1,2,3,4,7,8,9-HpCDF	0	58.5	60.8	31.1	25.0	2.3	34.9	30.4
OCDF	0	239	401	175	416	534	370	305
Total 2,3,7,8-CDD	174	3,954	4,328	1,335	12,743	7,028	10,515	5,725
Total 2,3,7,8-CDF	95.7	1,108	1,684	784	1,347	1,371	1,362	1,107
Total TEQ	73.8	175	170	96	235	153	303	172
Total TCDD	245	0	140	165	311	109	97.3	152
Total PeCDD	110	21.9	83.3	35.6	174	0.0	165	84.2
Total HxCDD	677	0	753	54.5	2,009	1,666	2,971	1,162
Total HpCDD	0	802	1,498	142	5,696	1,933	4,377	2,064
Total OCDD	0	3361	3,382	1,120	9,730	5,829	7,620	4,435
Total TCDF	0	901	1,314	656	2,416	1,007	687	997
Total PeCDF	124	119	1,152	78.4	1,055	282	626	491
Total HxCDF	136	319	852	67.6	444	719	619	451
Total HpCDF	0	223	814	144	513	354	637	384
Total OCDF	0	239	401	175	416	534	370	305
Total CDD/CDF	1,291	5,987	10,390	2,638	22,766	12,434	18,168	10,525
HD vehicles as % of total vehicles	21.2	22.0	22.6	34.0	28.8	24.2	27.4	25.7

Notes:
(1) Listed values are based on the difference between the calculated chemical mass entering the tunnel and the mass exiting the tunnel.
(2) All calculated negative emission factors were set equal to zero.
(3) All CDD/CDF emissions were assumed to result from heavy-duty diesel-fueled vehicles. The table presents in the last row the percent of total traffic that was heavy-duty vehicles.

Source: Gertler et al., 1996.

Table 2-13. Organic and elemental carbon fractions of diesel and gasoline engine PM exhaust

Engine type	% Organic carbon	% Elemental carbon
HD diesel engines [a]	19 ± 8	75 ± 10
HD diesel engines (SPECIATE)[b]	21-36	52-54
LD diesel engines[c]	30 ± 9	61 ± 16
LD diesel engines (SPECIATE)[b]	22-43	51-64
Gasoline engines (hot stabilized)[a]	56 ± 11	25 ± 15
Gasoline engines (smoker and high emitter)[a,c]	76 ± 10	7 ± 6
Gasoline engines (cold start)[a]	46 ± 14	42 ± 14

[a] Fujita et al., 1998, and Watson et al., 1998.
[b] U.S. EPA SPECIATE database.
[c] Norbeck et al., 1998c.

Table 2-14. Emission rates of PAH (mg/mi) from LD and HD diesel vehicles

PAH	Light-duty diesel	Heavy-duty diesel
Naphthalene	5.554 ± 0.282	2.451 ± 0.154
2-Menaphthalene	3.068 ± 0.185	2.234 ± 0.152
1-Menaphthalene	2.313 ± 0.134	1.582 ± 0.103
Dimethylnaphthalenes	5.065 ± 0.333	2.962 ± 0.488
Biphenyl	0.743 ± 0.041	0.505 ± 0.037
2-Methylbiphenyl	0.203 ± 0.015	0.049 ± 0.024
3-Methylbiphenyl	1.048 ± 0.063	0.401 ± 0.036
4-Methylbiphenyl	0.447 ± 0.028	0.144 ± 0.021
Trimethylnaphthalenes	6.622 ± 0.563	1.940 ± 0.221
Acenaphthylene	0.422 ± 0.024	0.059 ± 0.087
Acenaphthene	0.096 ± 0.008	0.030 ± 0.040
Phenanthrene	1.411 ± 0.072	0.084 ± 0.011
Fluorene	0.442 ± 0.038	0.066 ± 0.022
Methylfluorenes	1.021 ± 0.091	0.071 ± 0.055
Methylphenanthrenes	1.115 ± 0.064	0.124 ± 0.069
Dimethylphenanthrenes	0.637 ± 0.047	0.090 ± 0.096
Anthracene	0.246 ± 0.025	0.052 ± 0.016
9-Methylanthracene	0.013 ± 0.002	0.434 ± 0.082
Fluoranthene	0.213 ± 0.014	0.044 ± 0.026
Pyrene	0.245 ± 0.020	0.071 ± 0.017
Methyl(pyrenes/fluoranthenes)	0.548 ± 0.045	0.022 ± 0.082
Benzonaphthothiophene	0.002 ± 0.002	0.001 ± 0.027
Benz[a]anthracene	0.020 ± 0.005	0.066 ± 0.046
Chrysene	0.029 ± 0.005	0.009 ± 0.021
Benz[b+j+k]fluoranthene	0.056 ± 0.005	0.009 ± 0.022
Benzo[e]pyrene	0.019 ± 0.003	0.010 ± 0.014
Benzo[a]pyrene	0.013 ± 0.004	0.013 ± 0.044
Indeno[1,2,3-cd]pyrene	0.010 ± 0.003	0.001 ± 0.037
Dibenzo[a]anthracene	0.002 ± 0.003	0.000 ± 0.053
Benzo[b]chrysene	0.001 ± 0.002	0.001 ± 0.027
Benzo[ghi]perlyne	0.018 ± 0.004	0.013 ± 0.048
Coronene	0.006 ± 0.006	0.001 ± 0.095

Table 2-15. Polycyclic aromatic hydrocarbons identified in extracts of diesel particles from LD diesel engine exhaust

Compound	Molec. wt.	Concentration ng/mg extract
Acenaphthylene	152	30
Trimethylnaphthalene	170	140–200
Fluorene	166	100–168
Dimethylbiphenyl	182	30–91
C_4-Naphthalene	184	285–351
Trimethylbiphenyl	196	50
Dibenzothiophene	184	129–246
Phenanthrene	178	2,186–4,883
Anthracene	178	155–356
Methyldibenzothiophene	198	520–772
Methylphenanthrene	192	2,028–2,768
Methylanthracene	192	517–1,522
Ethylphenanthrene	206	388–464
4H-Cyclopenta[*def*]phenanthrene	190	517–1,033
Ethyldibenzothiophene	212	151–179
2-Phenylnaphthalene	204	650–1,336
Dimethyl(phenanthrene/anthracene)	206	1,298–2,354
Fluoranthene	202	3,399–7,321
Benzo[*def*]dibenzothiophene	208	254–333
Benzacenaphthylene	202	791–1,643
Pyrene	202	3,532–8,002
Ethylmethyl(phenanthrene/anthracene)	220	590–717
Methyl(fluoranthene/pyrene)	216	1,548–2,412
Benzo[*a*]fluorene/benzo[*b*]fluorene	216	541–990
Benzo[*b*]naphtho[2,1-*d*]thiophene	234	30–53
Cyclopentapyrene	226	869–1,671
Benzo[*ghi*]fluoranthene	226	217–418
Benzonaphthothiophene	234	30–126
Benz[*a*]anthracene	228	463–1,076
Chrysene or triphenylene	228	657–1,529
1,2-Binapthyl	254	30–50
Methylbenz[*a*]anthracene	242	30–50
3-Methylchrysene	242	50–192
Phenyl(phenanthrene/anthracene)	254	210–559
Benzo[*j*]fluoranthene	252	492–1,367
Benzo[*b*]fluoranthene	252	421–1,090
Benzo[*k*]fluoranthene	252	91–289
Benzo[*e*]pyrene	252	487–946
Benzo[*a*]pyrene	252	208–558
Benzo[*ah*]anthracene	278	50–96
Indeno[1,2,3-[*cd*]pyrene	276	30–93
Benzo[*ghi*]perylene	276	443–1,050
Dibenzopyrene	302	136–254

Source: Tong et al., 1984.

Table 2-16. Emission rates of particle-bound PAH (μg/mi) from diesel and gasoline engines

PAH	Diesel engines					Gasoline engines			
	HDD			LDD		Noncatalyst		Catalyst	
	(a)	(b)	(c)	(a)	(d)	(c)	(e)	(a)	(c)
Pyrene	71	17.6	36.2	245	66	49.6	45	248	4.0
Fluoranthene	44	27.2	20.8	213	50	77.3	32	196	3.6
Benzo[a]pyrene	13	<0.1	2.1	13	NA	69.6	3.2	1.0	3.0
Benzo[e]pyrene	10	0.24	4.2	19	NA	73.3	4.8	1.0	3.6

(a) Watson et al., 1998 included gas-phase PAH .

(b) Westerholm et al., 1991.

(c) Rogge et al., 1993.

(d) Smith, 1989; 1986 Mercedes Benz.

(e) Alsberg et al., 1985.

Table 2-17. Concentrations of nitro-PAHs identified in LD diesel particulate extracts

Nitro-PAH[a]	Concentration (µg/g of particles)
4-nitrobiphenyl	2.2
2-nitrofluorene	~1.8
2-nitroanthracene	4.4
9-nitroanthracene	1.2
9-nitrophenanthrene	1.0
3-nitrophenanthrene	4.1
2-methyl-l-nitroanthracene	8.3
1-nitrofluoranthene	1.8
7-nitrofluoranthene	0.7
3-nitrofluoranthene	4.4
8-nitrofluoranthene	0.8
1-nitropyrene	18.9; 75[b]
6-nitrobenzo[a]pyrene	2.5
1,3-dinitropyrene[b]	0.30
1,6-dinitropyrene[b]	0.40
1,8-dinitropyrene[b]	0.53
2,7-dinitrofluorene[c]	4.2; 6.0
2,7-dinitro-9-fluorenone[c]	8.6; 3.0
3-nitrobenzanthrone[d]	0.6 to 6.6

[a]From Campbell and Lee (1984) unless noted otherwise. Concentrations recalculated from µg/g of extract to µg/g of particles using a value of 44% for extractable material (w/w).
[b]From Paputa-Peck et al, 1983.
[c]From Schuetzle, 1983.
[d]From Enya et al., 1997 (Isuzu Model 6HEL 7127cc).

Table 2-18. Average emission rates for polycyclic aromatic hydrocarbons for different fuel types (units are mg/mi)

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

Source: Norbeck et al., 1998c.

Table 2-19. Classes of compounds in diesel exhaust

Particulate phase		Gas phase	
Heterocyclics, hydrocarbons (C_{14}-C_{35}), and PAHs and derivatives:		Heterocyclics, hydrocarbons (C_1-C_{10}), and derivatives:	
Acids	Cycloalkanes	Acids	Cycloalkanes, Cycloakenes
Alcohols	Esters	Aldehydes	Dicarbonyls
Alkanoic acids	Halogenated cmpds.	Alkanoic acids	Ethyne
n-Alkanes	Ketones	n-Alkanes	Halogenated cmpds.
Anhydrides	Nitrated cmpds.	n-Alkenes	Ketones
Aromatic acids	Sulfonates	Anhydrides	Nitrated cmpds.
	Quinones	Aromatic acids	Sulfonates
			Quinones
Elemental carbon		Acrolein	
Inorganic sulfates and nitrates		Ammonia	
Metals		Carbon dioxide, carbon monoxide	
Water		Benzene	
		1,3-Butadiene	
		Formaldehyde	
		Formic acid	
		Hydrogen cyanide, hydrogen sulfide	
		Methane, methanol	
		Nitric and nitrous acids	
		Nitrogen oxides, nitrous oxide	
		Sulfur dioxide	
		Toluene	
		Water	

Sources: Mauderly, 1992, which summarized the work of Lies et al., 1986; Schuetzle and Frazier, 1986; Carey, 1987; Zaebst et al., 1988, updated from recent work by Johnson, 1993; McDonald, 1997; Schauer et al., 1999.

Table 2-20. Calculated atmospheric lifetimes for gas-phase reactions of selected compounds present in automotive emissions with important reactive species

Compound	Atmospheric lifetime resulting from reaction with:				
	OH[a]	O_3[b]	NO_3[c]	HO_2[d]	hv[e]
NO_2	1.3 days	12 h	24 min	2 h	2 min
NO	2.5 days	1 min	1.2 min	20 min	—
HNO_3	110 days	—	—	—	—
SO_2	16 days	>200 years	>1.4×10^4 years	>600 years	—
NH_3	90 days	—	—	—	—
Propane	12 days	>7,000 years	—	—	—
n-Butane	5.6 days	>4,500 years	3.6 years	—	—
n-Octane	1.9 days	—	1.2 years	—	—
Ethylene	1.9 days	9 days	1.2 years	—	—
Propylene	7 h	1.5 days	6 days	—	—
Acetylene	19 days	6 years	>5.6 years	—	—
Formaldehyde	1.9 days	>2 - 104 years	84 days	23 days	4 h
Acetaldehyde	0.6 day	>7 years	20 days	—	60 h
Benzaldehyde	1.2 days	—	24 days	—	—
Acrolein	0.6 day	60 days	—	—	—
Formic acid	31 days	—	—	—	—
Benzene	11 days	600 years	>6.4 years	—	—
Toluene	2.5 days	300 years	3.6 years	—	—
m-Xylene	7 h	75 years	0.8 years	—	—
Phenol	6 h	—	8 min	—	—
Naphthalene[f]	6.8 h	>80 days	1.5 years	—	—
2-Methylnaphthalene[f]	2.8 h	>40 days	180 days		—
1-Nitronaphthalene[f]	2.3 days	>28 days	1 8 years		1.7 h
Acenaphthene[f]	1.5 h	>30 days	1.2 h	—	—
Acenaphthylene[f]	1.3 h	~43 min	6 min	—	—
Phenanthrene[f]	11.2 h	41 days	4.6 h	—	—
Anthracene[f]	8.6 h	—	—	—	—
Fluoranthene[f]	~2.9 h	—	~1 year	—	—
Pyrene[f]	~2.9 h	—	~ 120 days	—	—

[a] For 12-h average concentration of OH radical of 1.6×10^6 molecule/cm^3 (Prinn et al., 1992).

[b] For 24-h average O_3 concentration of 7×10^{11} molecule/cm^3.

[c] For 12-h average NO_3 concentration of 5×10^8 molecule/cm^3 (Atkinson, 1991).

[d] For 12-h average HO_2 concentration of 10^8 molecule/cm^3.

[e] For solar zenith angle of $0°$.

[f] Lifetimes from Arey (1998), for 12-h concentration of OH radical of 1.9×10^6 molecule/cm^3.

Source: Winer and Busby, 1995, unless noted otherwise.

Table 2-21. Major components of gas-phase diesel engine emissions, their known atmospheric transformation products, and the biological impact of the reactants and products

Gas-phase emission component	Atmospheric reaction products	Biological impact
Carbon dioxide	—	Major contributor to global warming.
Carbon monoxide	—	Highly toxic to humans; blocks oxygen uptake.
Oxides of nitrogen	Nitric acid, ozone	Nitrogen dioxide is a respiratory tract irritant and major ozone precursor. Nitric acid contributes to acid rain.
Sulfur dioxide	Sulfuric acid	Respiratory tract irritation. Contributor to acid rain.
Hydrocarbons:		
Alkanes ($\leq C_{18}$)	Aldehydes, alkyl nitrates, ketones	Respiratory tract irritation. Reaction products are ozone precursors (in the presence of NO_x).
Alkenes ($\leq C_4$) (e.g., 1,3-butadiene)	Aldehydes, ketones	Respiratory tract irritation. Some alkenes are mutagenic and carcinogenic. Reaction products are ozone precursors (in the presence of NO_x).
Aldehydes:		
Formaldehyde	Carbon monoxide, hydroperoxyl radicals	Formaldehyde is a probable human carcinogen and an ozone precursor (in the presence of NO_x).
Higher aldehydes (e.g., acetaldehyde, acrolein)	Peroxyacyl nitrates	Respiratory tract and eye irritation; causes plant damage.
Monocyclic aromatic compounds (e.g., benzene, toluene)	Hydroxylated and hydroxylated-nitro derivatives[a]	Benzene is toxic and carcinogenic in humans. Some reaction products are mutagenic in bacteria (Ames assay).
PAHs (≤ 4 rings) (e.g., phenanthrene, fluoranthene)[b]	Nitro-PAHs (4 rings)[c]	Some of these PAHs and nitro-PAHs are known mutagens and carcinogens.
Nitro-PAHs (2 and 3 rings) (e.g., nitronaphthalenes)	Quinones and hydroxylated-nitro derivatives	Some reaction products are mutagenic in bacteria (Ames assay).

[a]Some reaction products expected to partition into the particle phase.
[b]Nitro-PAHs with more than two rings will partition into the particle phase.
[c]PAHs containing four rings are usually present in both the vapor and particle phases.

Source: Health Effects Institute, 1995.

Table 2-22. Major components of particle-phase diesel engine emissions, their known atmospheric transformation products, and the biological impact of the reactants and products

Particle-phase emission component	Atmospheric reaction products	Biological impact
Elemental carbon	—	Nuclei adsorb organic compounds; size permits transport deep into the lungs (alveoli)
Inorganic sulfate and nitrate	—	Respiratory tract irritation
Hydrocarbons (C_{14}-C_{35})	Little information; possibly aldehydes, ketones, and alkyl nitrates	Unknown
PAHs ($\geq$4 rings) (e.g., pyrene, benzo[a]pyrene)	Nitro-PAHs ($\geq$4 rings)[a] Nitro-PAH lactones	Larger PAHs are major contributors of carcinogens in combustion emissions. Many nitro-PAHs are potent mutagens and carcinogens.
Nitro-PAHs ($\geq$3 rings) (e.g., nitropyrenes)	Hydroxylated-nitro derivatives	Many nitro-PAHs are potent mutagens and carcinogens. Some reaction products are mutagenic in bacteria (Ames assay).

[a]Nitro-PAHs with more than two rings will partition into the particle phase.

Source: Health Effects Institute, 1995.

Table 2-23. Ambient DPM concentrations reported from chemical mass balance modeling

Ref.	Location	Year of sampling	Location type	Diesel PM$_{2.5}$ μg/m^3 mean, (range)	Average DPM % of total PM (range)	Source profile used
a	West LA, CA	1982, annual average (~60 samples at each site)	Urban	4.4	18	EC, OCS, elements
	Pasadena, CA		Urban	5.3	19	
	Rubidoux, CA		Urban	5.4	13	
	Los Angeles, CA		Urban	11.6	36	
b	West Phoenix, AZ	1989-90, winter 11 days at each site	Urban	13 (max. 22)	18	EC, OCT, MI, elements
	Central Phoenix, AZ		Urban	13 (max. 16)	20	
	South Scottsdale, AZ		Urban	10 (max. 12)	17	
	Estrella Park, AZ		Nonurban	5	9	
	Gunnery Park, AZ		Nonurban	3	10	
	Pinnacle Peak, AZ		Nonurban	2	12	
c	California, 6 air basins	1988-92, annual	Urban✣	1.8–3.6*	†	EC, OCT, MI, elements
	California, 9 air basins		Nonurban✣	0.2–2.6*	†	EC, OCT, MI, elements
d	Manhattan, NY	1993, spring 3 days	Urban	29.2(13.2–46.7) *	53 (31–68)	EC, OCT, MI, elements
e	Phoenix, AZ	1994–95, winter 12 days	Urban	2.4 (0–5.3)	15 (0–27)	EC, OCS, MI, elements
f	Welby, CO	1996–97, winter 60 days	Urban	1.7 (0–7.3)	10 (0–26)	EC, OCS, MI, elements
	Brighton, CO		Suburban	1.2 (0–3.4)	10 (0–38)	

*PM10.   †Not available.

EC:Elemental carbon; OCT:Organic carbon total; OCS: Organic carbon species; MI: Major ions including nitrate, sulfate, chloride and, in some cases, ammonium, sodium, potassium

✣Urban air basins are qualitatively defined as those areas that are moderately or largely urbanized, and nonurban air basins are those areas that are largely nonurban, but may have one or more densely populated areas.

[a] Schauer et al., 1996.

[b] Chow et al., 1991.

[c] California Environmental Protection Agency, 1998.

[d] Wittorff et al., 1994.

[e] Maricopa Association of Governments, 1999.

[f] Fujita et al., 1998.

Table 2-24. Comparison of DPM concentrations reported by CMB and EC surrogate calculation

Location	Number of samples	Average DPM, μg/m^3 (CMB)	DPM, μg/m^3 EC surrogate[a] (lower-upper bound estimate)
Brighton, CO	67	1.1 ± 0.8	0.8-1.6
Welby, CO	61	1.7 ± 1.4	1.4-3.1
Phoenix, AZ	12	2.4 ± 1.6	1.1-2.4

[a] Lower-bound estimate: DPM=EC*0.62; Upper bound estimate: DPM=EC*1.31.

Table 2-25. Ambient diesel particulate matter concentrations from elemental carbon measurements in urban locations

Ref.	Year of sampling	Location	DPM$_{2.5}$ μg/m^3 lower-upper bound range (point estimate)[*]	DPM % of total PM
a	1995, annual	Boston, MA	0.8–1.7 (1.1)	6-12
		Rochester, NY		0.4-0.8
b	1992-1995, annual	Washington, DC		1.0-2.2
		MATES II †	Diesel PM$_{2.5}$ μg/m^3 avg± std dev.	
c	1995-6, annual	Anaheim, CA	2.4 ± 1.8	‡
		Burbank, CA	3.3 ± 1.9	‡
		Los Angeles, CA	3.5 ± 1.9	‡
		Fontanta, CA	3.4 ± 2.3	‡
		Huntington Park, CA	4.5 ± 2.4	‡
		Long Beach, CA	2.5 ± 1.7	‡
		Pico Rivera, CA	4.4 ± 2.2	‡
		Rubidoux, CA	3.4 ± 2.0	‡

*Lower-bound range: DPM=EC*0.62; upper-bound range: DPM=EC*1.31;
  point estimate: DPM=EC*0.89
† Not available.
‡The Multiple Air Toxics Exposure Study in the South Coast Air Basin reported DPM calculated from EC concentrations as DPM=EC*1.04. Standard deviations are reported.

[a] Salmon et al., 1997.

[b] Sisler, 1996.

[c] South Coast Air Quality Management District, 1999.

Table 2-26. Ambient diesel particulate matter concentrations from dispersion modeling

Ref.	Location	Year of sampling	Location type	DPM$_{2.5}$ μg/m^3 (mean)	DPM % of total PM
a	Azusa, CA	1982, annual	Nonurban	1.4[a]	5
	Anaheim, CA	1982, annual	Nonurban	2.7[a]	12
	Lennox, CA	1982, annual	Nonurban	3.8[a]	13
	Pasadena, CA	1982, annual	Urban	2.0[a]	7
	Long Beach, CA	1982, annual	Urban	3.5[a]	13
	Downtown LA, CA	1982, annual	Urban	3.5[a]	11
	West LA, CA	1982, annual	Urban	3.8[a]	16
b	Claremont, CA	18-19 Aug 1987	Nonurban	2.4 (4.0)[a,b]	8 (6)[b]
c	Long Beach, CA	24 Sept 1996	Urban	1.9(2.6)[b]	8 (7)[b]
	Fullerton, CA	24 Sept 1996	Nonurban	2.4(3.9)[b]	9 (8)[b]
	Riverside, CA	25 Sept 1996	Suburban	4.4(13.3)[b]	12 (13)[b]

[a] On-road diesel vehicles only; all other values are for on-road plus nonroad diesel emissions.
[b] Value in parenthesis includes secondary DPM (nitrate, ammonium, sulfate and hydrocarbons) due to atmospheric reactions of primary diesel emissions of NO_x, SO_2 and hydrocarbons. For the fraction of ambient PM attributable to DPM, the value in parenthesis reports total DPM (primary plus secondary) as a fraction of total ambient PM (primary plus secondary).

Refences:
[a] Cass and Gray, 1995.
[b] Kleeman and Cass, 1999.
[c] Kleeman et al., 1999.

Table 2-27. Occupational exposure to DPM

Author	Year of sample	Location/job type Typical work schedule of 8 hours	n	Sample type	Range in DPM $\mu g/m^3$
Gangal and Dainty, 1993[a]	NA	Noncoal mine workers	~200	RCD	100–900
Säverin, 1999	1992	Noncoal mine workers	255[b]	RTC	38–1,280
Rogers and Whelan, 1999	1990-99	Coal mine workers	>1,300	DPSMM	10–640
Haney, 1990[a]	1980s	Coal mine workers (five mines)	NA	SJI	180–1,000
Ambs, 1991a[a]	NA	Coal mine workers (four mines)	NA	PDEAS	750–780
Woskie et al., 1988	3-year period in mid-1980s	Railroad engineer/frier	128	ARP	39–73
		Railroad braker/conductor	158	ARP	52–191
		Railroad shop workers	176	ARP	114–134
Froines et al., 1987	1985	Firefighters (two stations)	238	TSP	63–748
NIOSH 1992[a]	NA	Firefighters (three stations)	18	EC	6–70
Birch and Cary, 1996	NA	Firefighters	NA	EC	20–79
	NA	Fire station employees (four stations)	NA	EC	4–52
Birch and Cary, 1996	NA	Airport ground crew	NA	EC	7–15
	NA	Public transit workers	NA	EC	15–98
NIOSH, 1990	1990	Diesel forklift dockworkers	24	EC	12–61
Zaebst et al., 1991	1990	Dockworkers	75	EC	9–20
		Mechanics	80	EC	5–28
		Long- and short-haul truckers	128	EC	2–7
Kittelson et al., 2000	1999-2000	Bus drivers	39	EC	1–3
		Parking ramp attendants	12	EC	2 ± 0.4

[a]Cited in Watts (1995).   NA: not available.
[b] Personal exposure and area samples were not reported separately for this study.
RCD: respirable combustible dust; RTC: respirable total carbon SPM: submicrometer PM; DPSMM: diesel particulate submicron mass (two-stage impaction sampler used to separate PM by size); EC: elemental carbon; SJI: single-jet impactor agreed within 10% with simultaneous PDEAS measurements; PDEAS: personal diesel exhaust aerosol sampler collects DPM <0.8μm, McCartney and Cantrell (1992); SPM: particulate matter; ARP: respirable particulate adjusted to remove the influence of cigarette smoke; TSP: total suspended particulate matter.

Table 2-28. Ranges of occupational exposure to diesel particulate matter by job category with estimates of equivalent environmental exposures

Year of sampling	Occupations	Occupational DPM, μg/m^3	Environmental equivalent[a] exposure, μg/m^3
1980s and 1990s	Miners	10–1,280	2–269
1980s	Railroad workers	39–191	8–40
1985 and later	Firefighters	4–748	1–157
NA	Airport crew, public transit workers	7–98	2–21
1990	Dockworkers, mechanics	5–61	1–13
1990	Long- and short-haul truckers	2–7	0.4–2

[a]Environmental equivalent exposure is calculated as the occupational exposure * (10m^3/shift / 20m^3/day) * (5 days / 7days) * (48 weeks / 52 weeks) * (45 year career / 70 year lifetime), or occupational exposure * 0.21 (discussed in section 2.4.3.1.

Table 2-29. Annual average nationwide DPM exposure estimates (µg/m³) from on-road sources for rural, urban, and urban demographic groups in 1990, 1996, 2007, and 2020 using HAPEM-MS3

Demographic group	1990	1996	2007	2020
50-State population	0.8	0.7	0.4	0.4
Rural population	0.5	0.3	0.2	0.2
Urban population	0.9	0.7	0.4	0.4
Urban outdoor workers	1.1	0.8	0.5	0.5
Urban children (0-17)	0.9	0.7	0.4	0.4

Source: U.S. EPA, 1999c, adjusted to reflect HDDV VMT described in U.S. EPA, 2000b.

Table 2-30. Annual average DPM exposures for 1990 and 1996 in the general population and among the highest exposed demographic groups in nine urban areas and nationwide from (on-road sources only) using HAPEM-MS3

Urban area	1990 Population average exposure, $\mu g/m^3$	1996 Population average exposure, $\mu g/m^3$	Highest DPM exposure in 1990, $\mu g/m^3$ (demographic group experiencing this exposure)
Nationwide	*0.8*	*0.7*	*NA*
Atlanta, GA	0.8	0.8	NA
Chicago, IL	0.8	0.5	1.3 (outdoor workers)
Denver, CO	0.7	0.7	1.2 (outdoor workers)
Houston, TX	0.6	0.7	0.8 (outdoor workers)
Minneapolis, MN	1.0	0.8	1.5 (outdoor workers)
New York, NY	1.6	1.0	4.0 (outdoor children)
Philadelphia, PA	0.7	0.6	1.2 (outdoor children)
Phoenix, AZ	1.4	1.2	2.4 (nonworking men 18-44)
Spokane, WA	1.3	1.0	2.0 (outdoor workers)
St. Louis, MO	0.6	0.5	0.8 (outdoor workers)

NA - Not available.

Source: U.S. EPA, 1999c, adjusted to reflect HDDV VMT described in U.S. EPA, 2000b.

Table 2-31. Modeled and estimated concentrations of DPM in microenvironments for California for all sources

Microenvironment	Estimated mean DPM (stdev), $\mu g/m^3$
Residences	1.9 (0.9)
Offices	1.6 (0.7)
Schools	1.9 (0.8)
Stores/public/retail bldgs	2.1 (0.9)
Outdoor places	3.0 (1.1)
Industrial plants[a]	3.0 (1.1)
Restaurants/lounges[a]	2.1 (0.9)
Other indoor places[a]	1.6 (0.7)
Enclosed vehicles[a]	3.0 (1.1)

[a]Concentrations assumed based on similarity with modeled environments.

Source: California EPA, 1998a.

Table 2-32. Estimated indoor air and total air exposures to DPM in California in 1990

Exposed population	Total indoor exposure (stdev), µg/m^3	Total air exposure, (stdev), µg/m^3
All Californians	2.0 (0.7)	2.1 (0.8)
South Coast Air Basin	2.4 (0.9)	2.5 (0.9)
San Francisco Bay Area	1.7 (0.9)	1.7 (0.9)

Source: California EPA, 1998a.
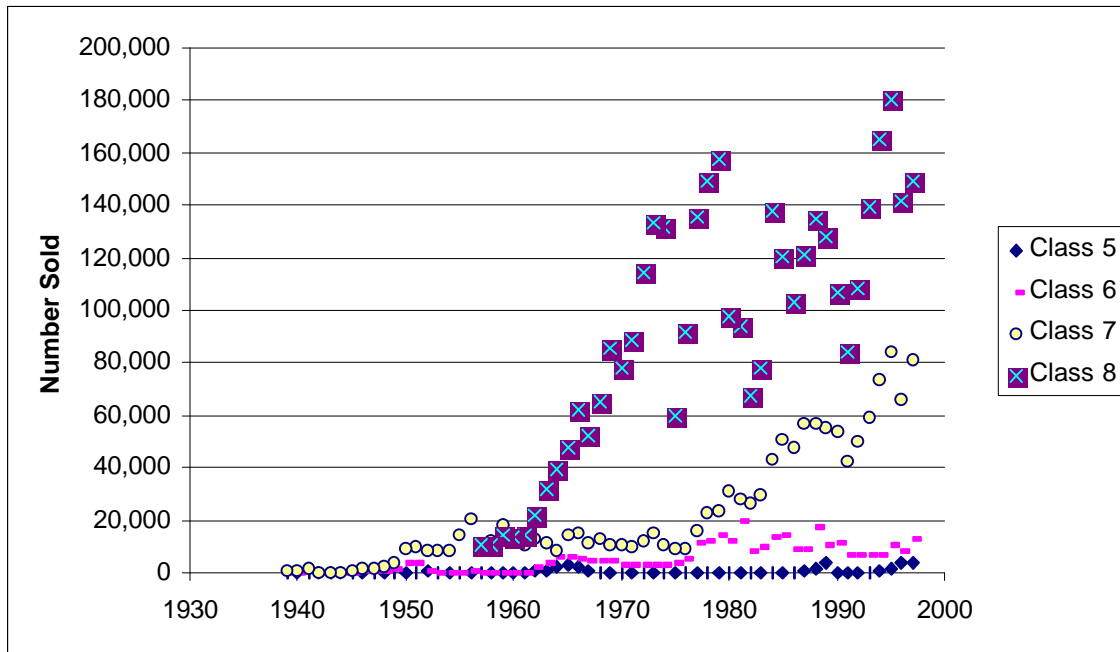
Figure 2-1. Diesel truck sales (domestic) for the years 1939-1997.

Source: AAMA Motor Truck Facts.
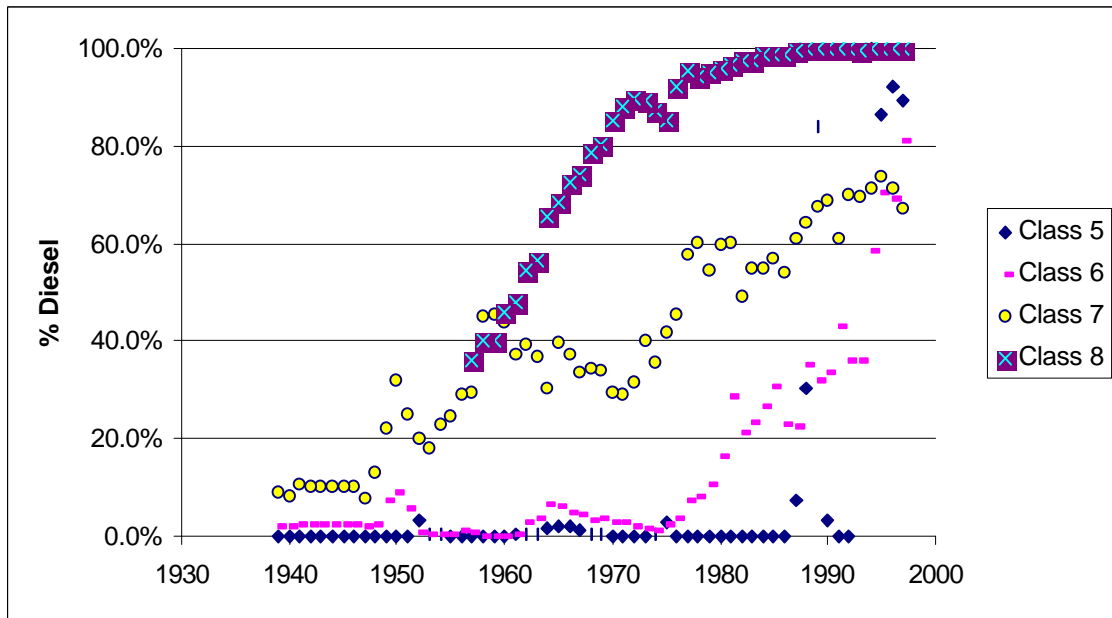
Figure 2-2. Diesel truck sales as a percentage of total truck sales for the years 1939-1997.

Source: AAMA Motor Truck Facts.

	1963	1967	1972	1977	1982	1987	1992	1997
Total Trucks	12.1%	10.9%	16.7%	14.1%	16.8%	17.2%	14.4%	15.6%
Combination Trucks	53.9%	50.5%	83.2%	94.2%	89.1%	91.5%	89.8%	92.4%
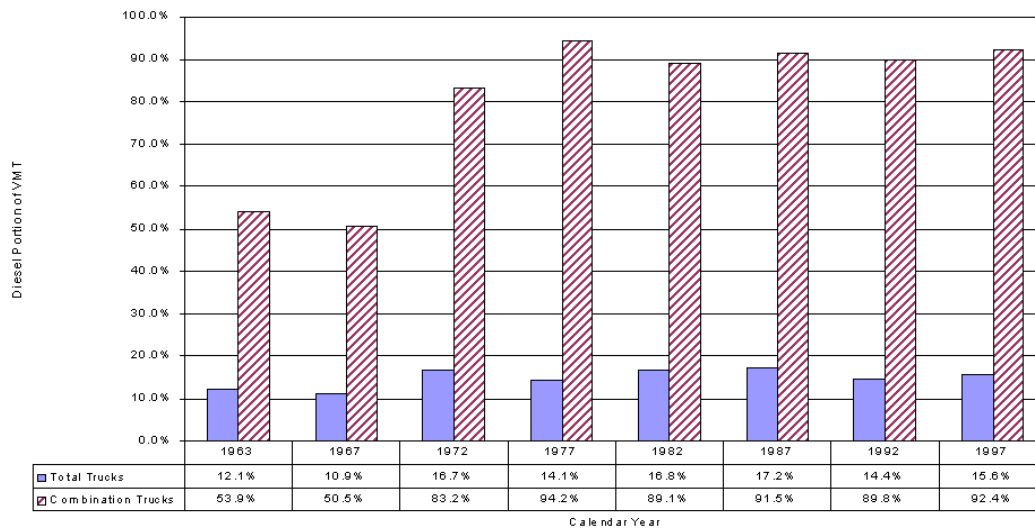
Figure 2-3. Percentage of truck miles attributable to diesel trucks. VMT = vehicle miles traveled.

Source: U.S. Bureau of the Census, 1999b.
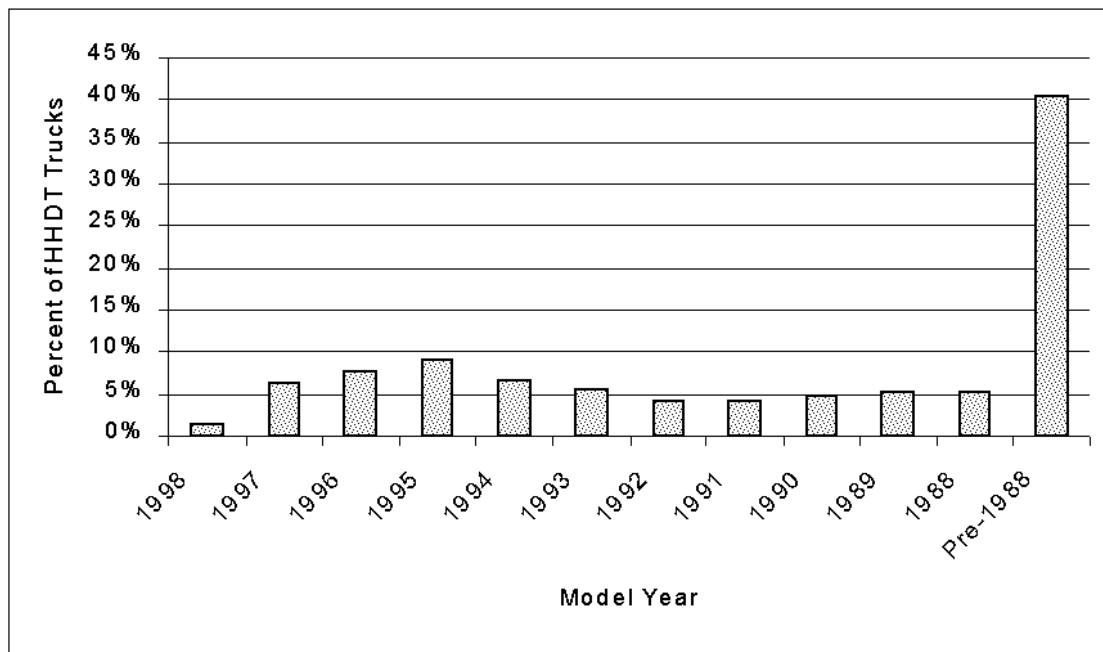
Figure 2-4. Model year distribution of in-use heavy HD truck fleet in 1997.

Source: U.S. Bureau of the Census, 1999b.
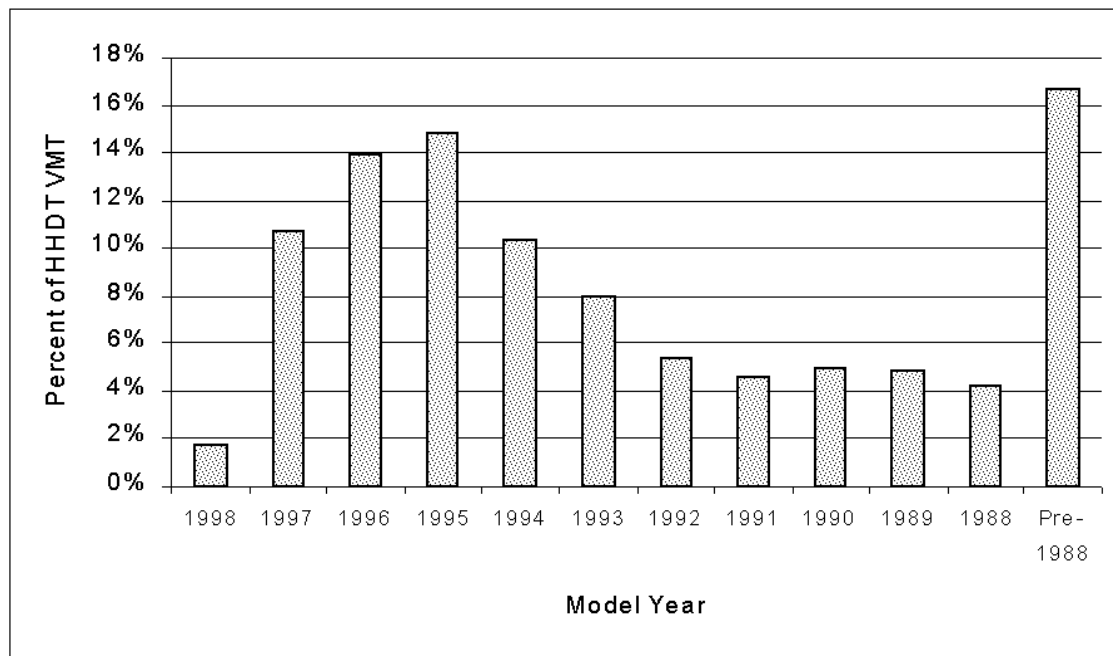
Figure 2-5. Model year distribution of vehicle miles traveled by the in-use heavy HD truck fleet in 1997.

Source: U.S. Bureau of the Census, 1999b.
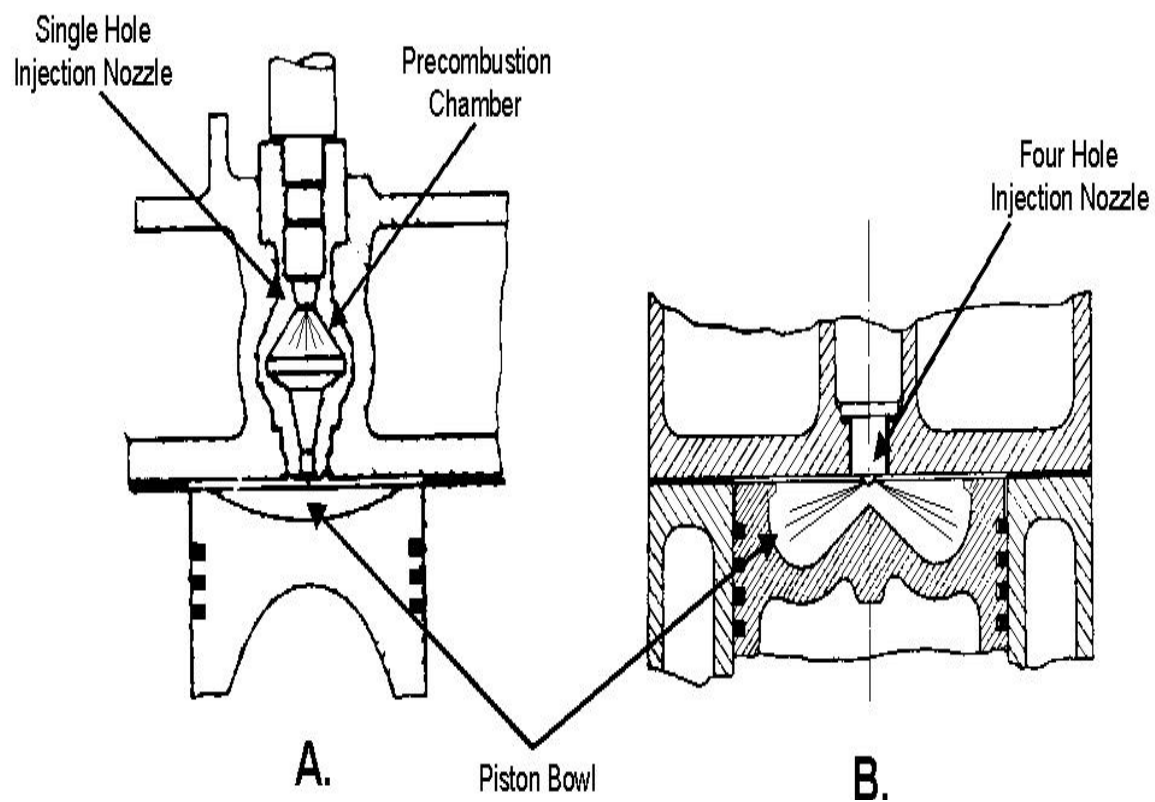
Figure 2-6. A comparison of IDI (A) and DI (B) combustion systems of high-speed HD diesel truck engines. DI engines almost completely replaced IDI engines for these applications by the early 1980s.

**Solid Carbonaceous/Ash Particle
with adsorbed hydrocarbon/sulfate layer**

Sulfuric Acid Particles

Hydrocarbon/Sulfate Particles

0.2 μm
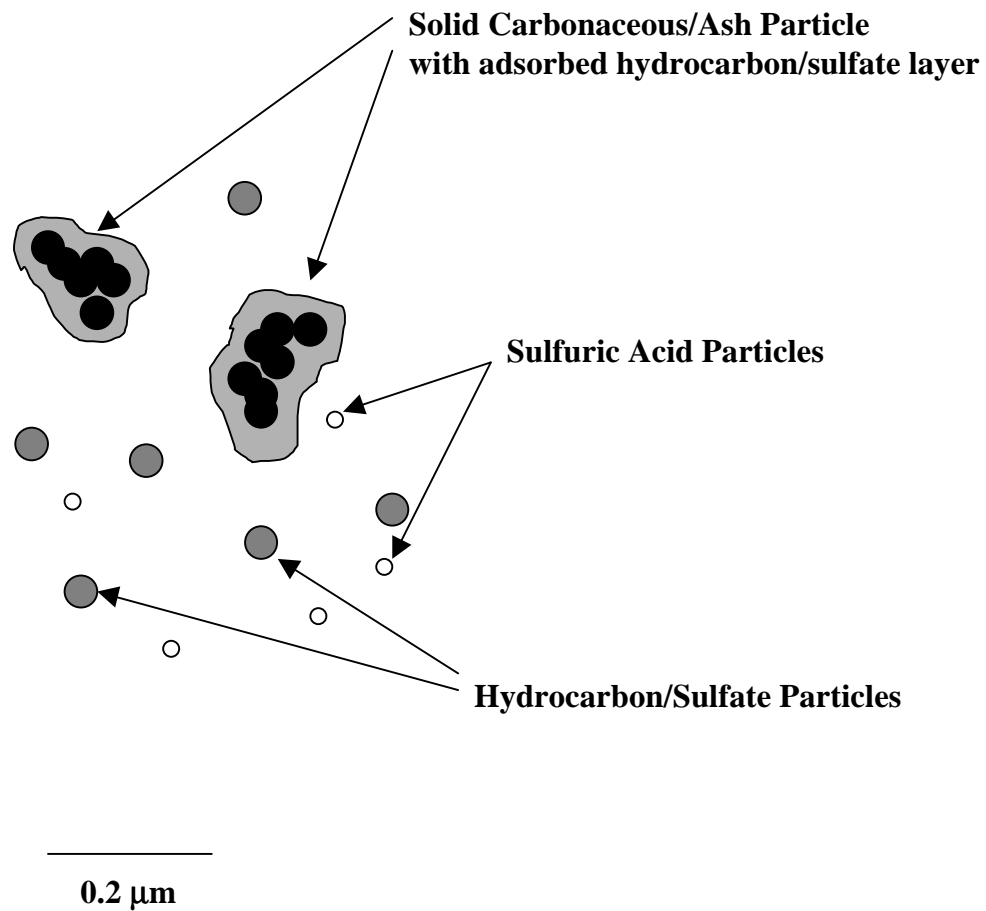
Figure 2-7. Schematic diagram of diesel engine exhaust particles.

Source: Modified from Kittelson, 1998.

Diesel PM2.5 Chemical Composition

Metals & Elements 2% (1-5%)

Other 3% (1-10%)

Sulfate, Nitrate 1% (1-4%)

Organic Carbon 19% (7-49%)

Elemental Carbon 75% (33-90%)
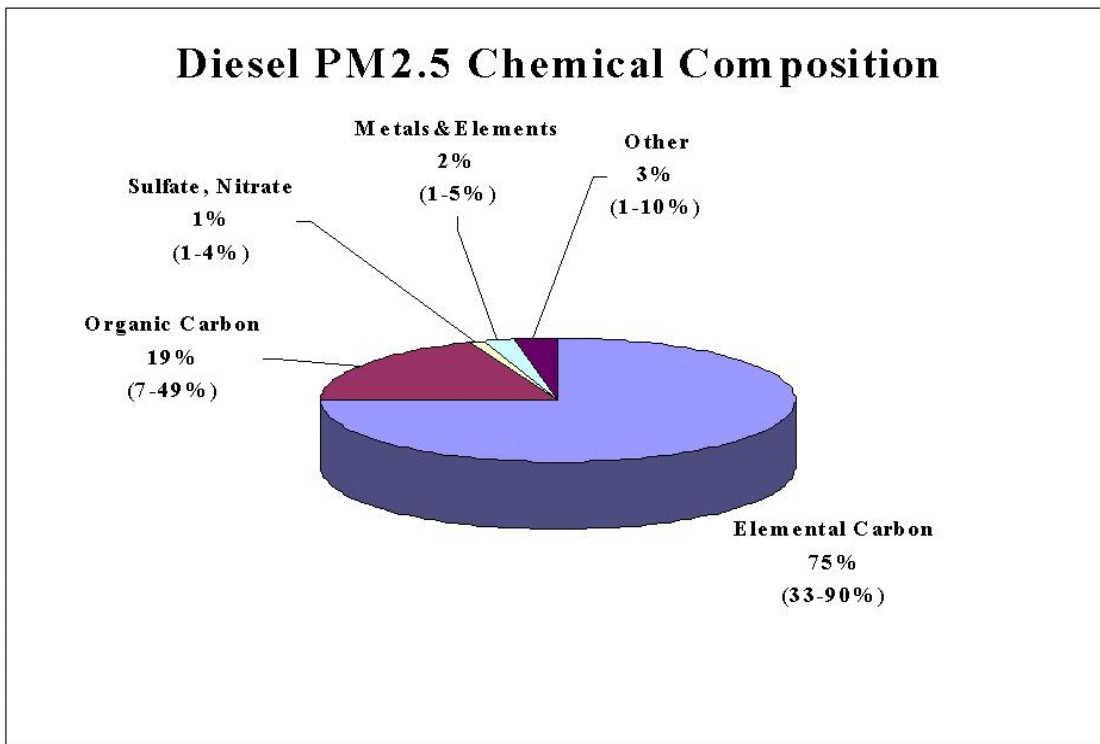
Figure 2-8. Typical chemical composition for diesel particulate matter (PM2.5) from new (post-1990) HD diesel vehicle exhaust.
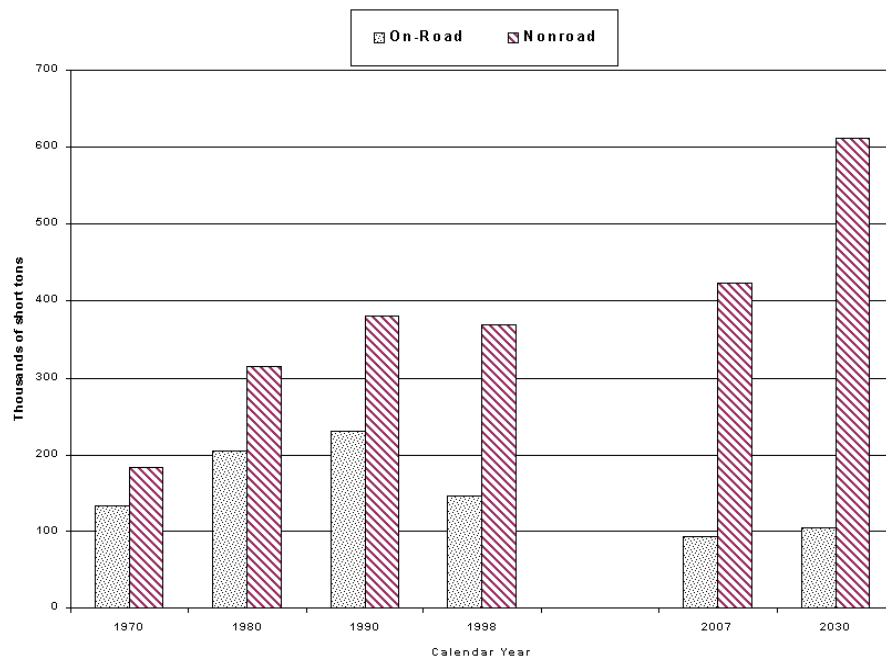
Figure 2-9. Trends in PM10 emissions from on-road and nonroad diesel engines from 1970 to 1998 and projections of emissions to 2007 and 2030.

Source: U.S. EPA, 2000a, National air pollutant emission trends, 1900-1998.
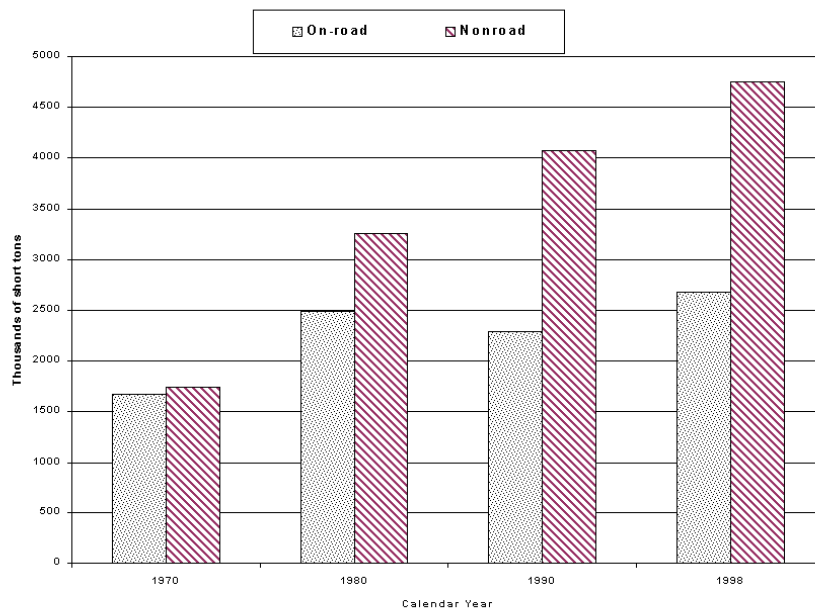
Figure 2-10. Trends in NO$_x$ emissions from on-road and nonroad diesel engines from 1970 to 1998.

Source: U.S. EPA, 2000a, National air pollutant emission trends, 1900-1998.
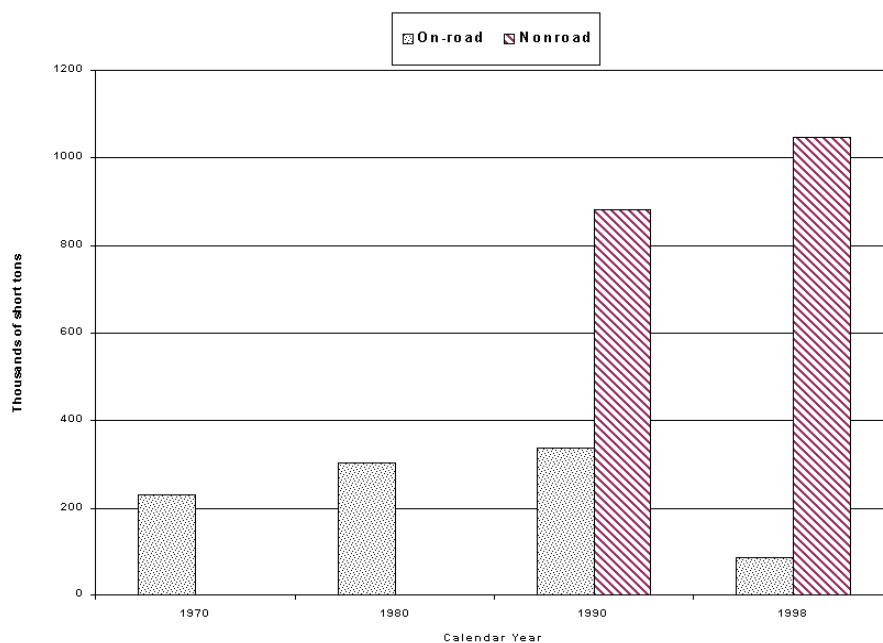
Figure 2-11. Trends in SO$_2$ emissions from on-road diesel engines from 1970 to 1998 and nonroad diesel engines from 1990 to 1998.

Source: U.S. EPA, 2000a, National air pollutant emission trends, 1900-1998.
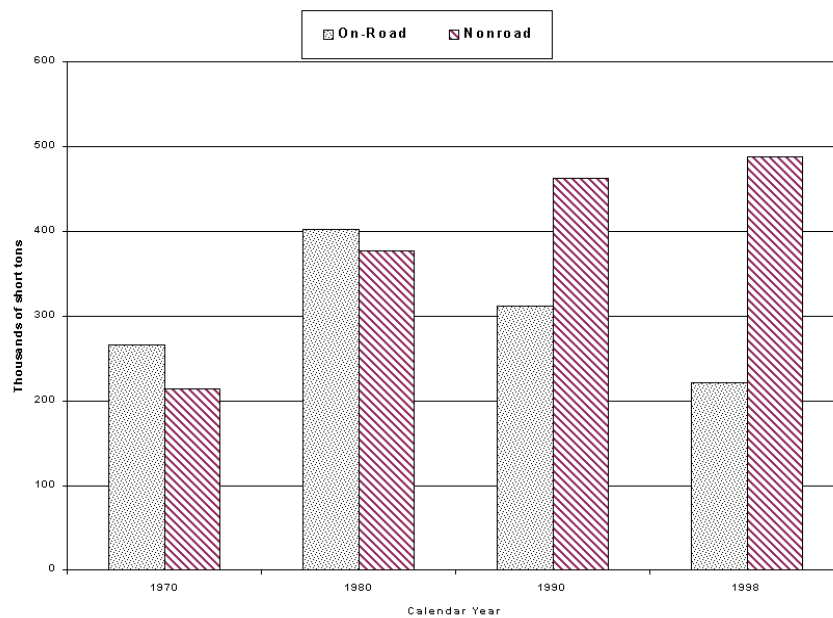
Figure 2-12. Trends in VOC emissions from on-road and nonroad diesel engines from 1970 to 1998.

Source: U.S. EPA, 2000a, National air pollutant emission trends, 1900-1998.
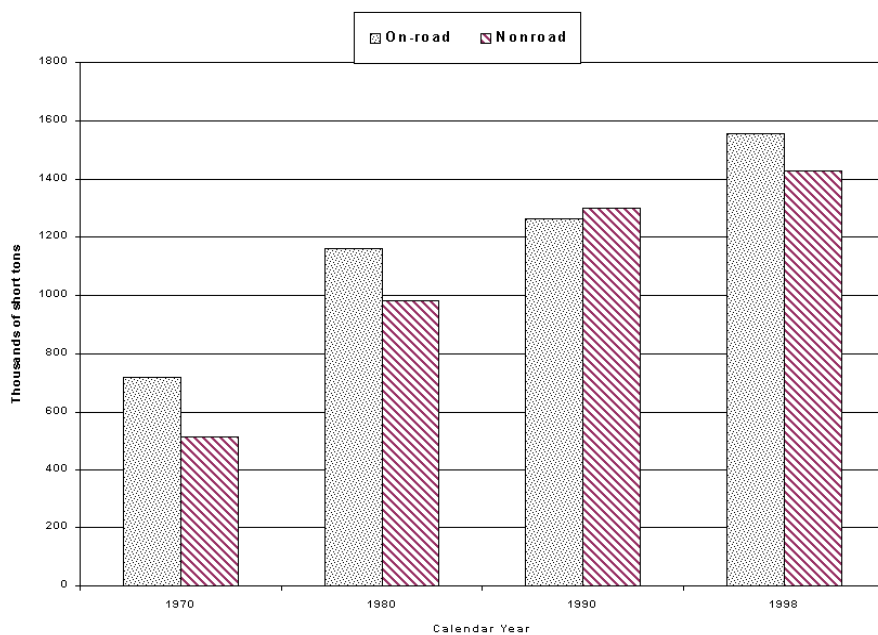
Figure 2-13. Trends in CO emissions from on-road and nonroad diesel engines from 1970 to 1998.

Source: U.S. EPA, 2000a, National air pollutant emission trends, 1900-1998.
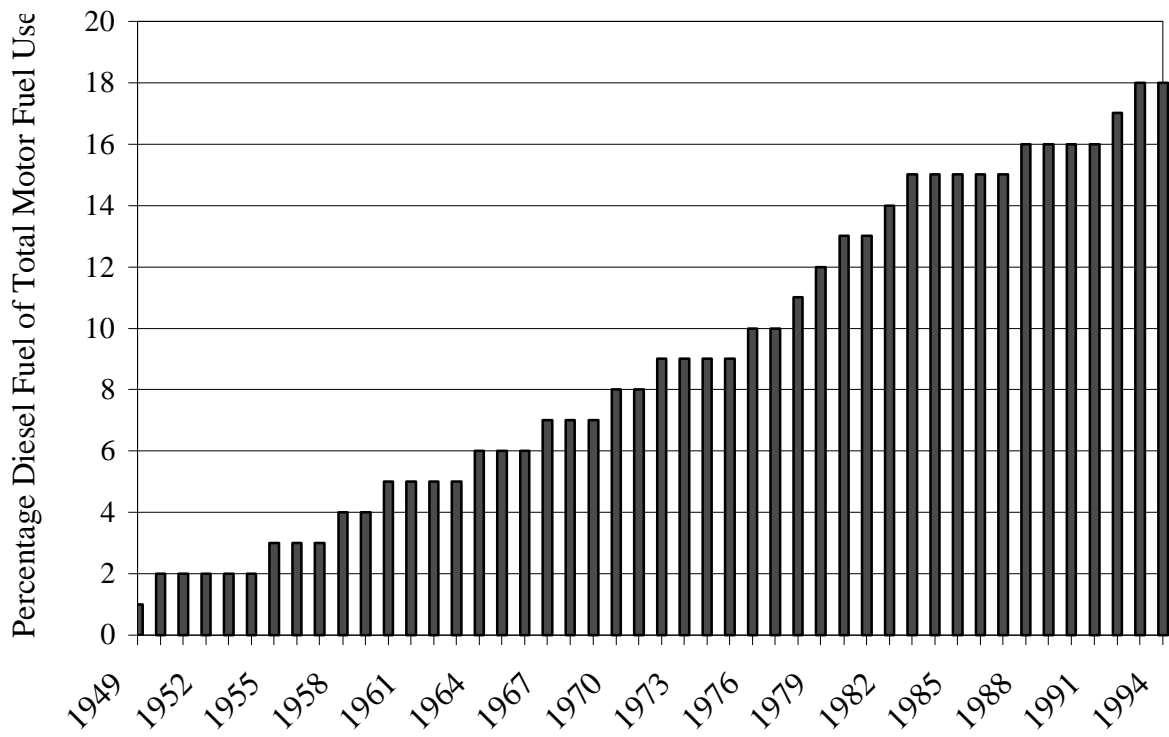
Figure 2-14. Percentage of total motor fuel use that is on-road diesel fuel since 1949.

Source: Federal Highway Administration, 1995.
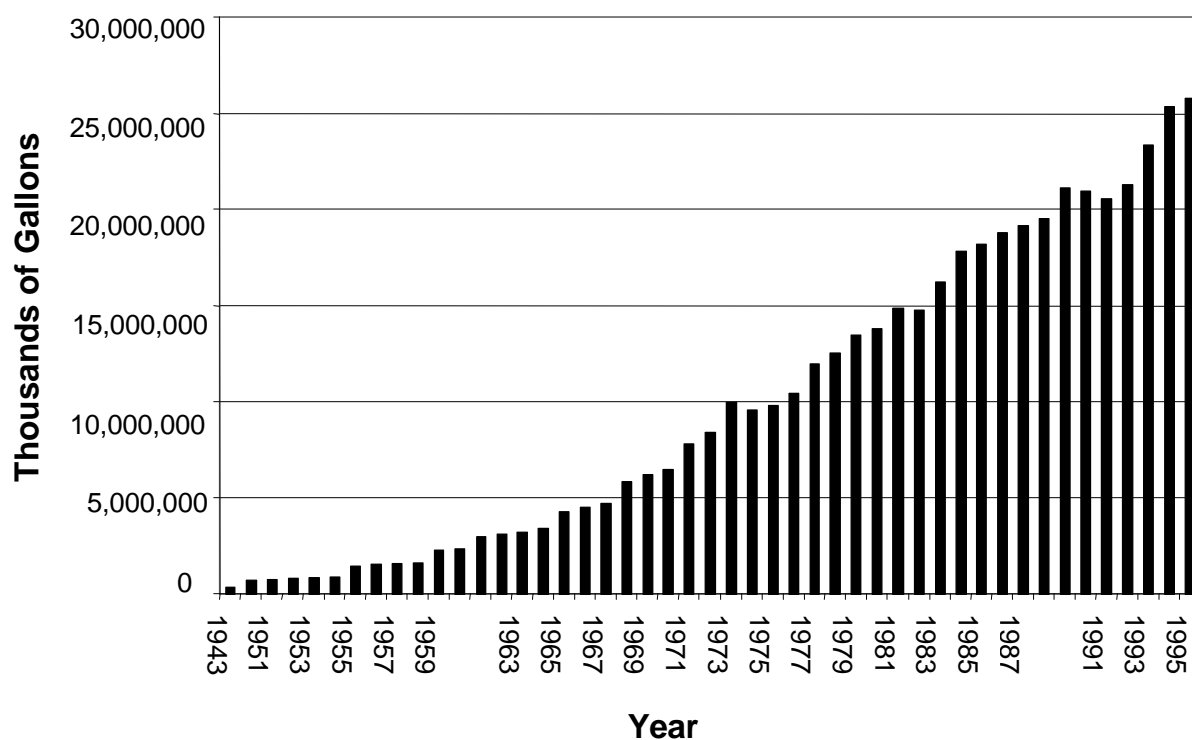
Figure 2-15. On-highway diesel fuel consumption since 1943, values in thousands of gallons.

Source: Federal Highway Administration, 1995.
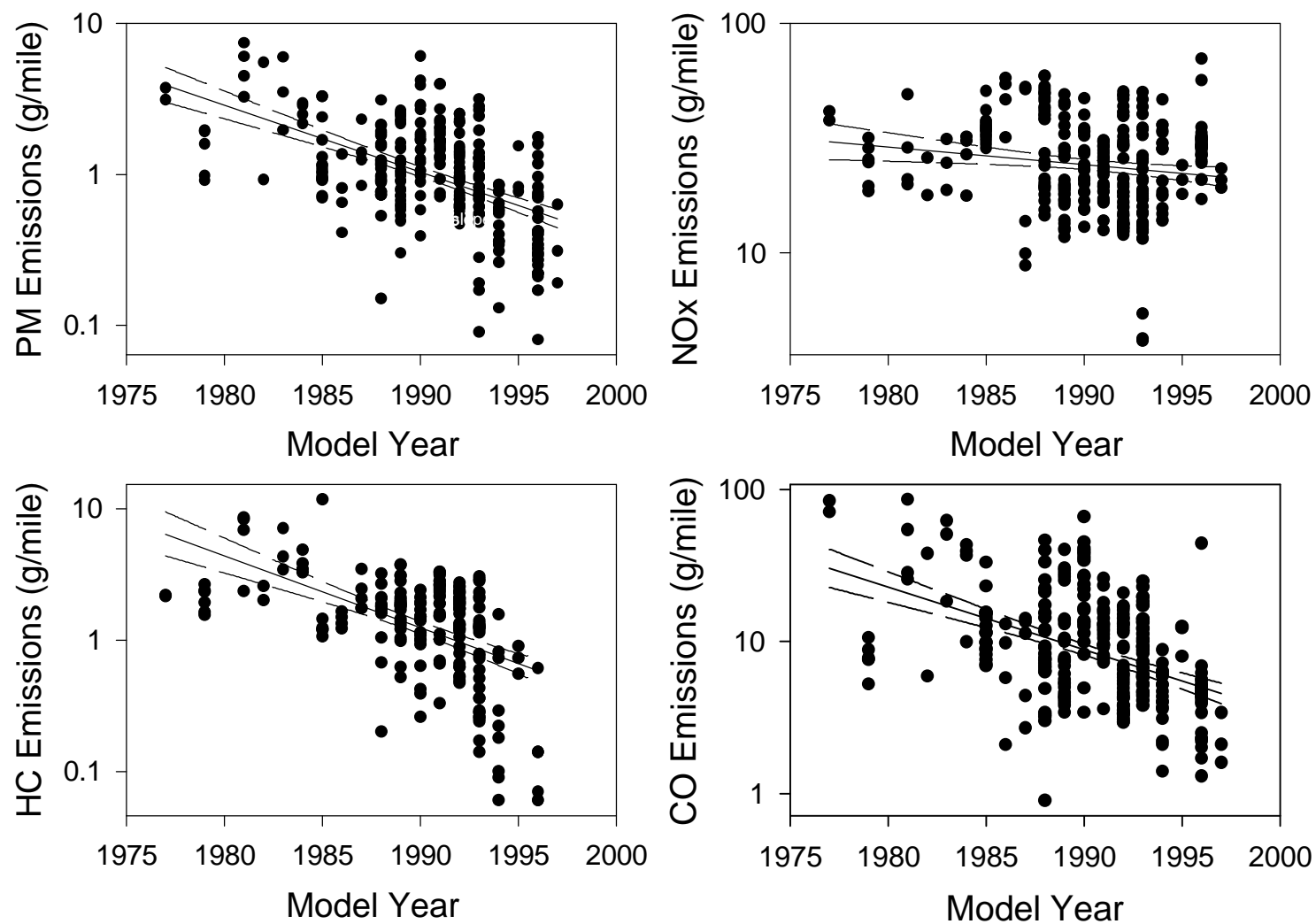
Figure 2-16. Model year trends in PM, NO$_x$, HC, and CO emissions from HD diesel vehicles (g/mile).

Source: Yanowitz et al., 2000.
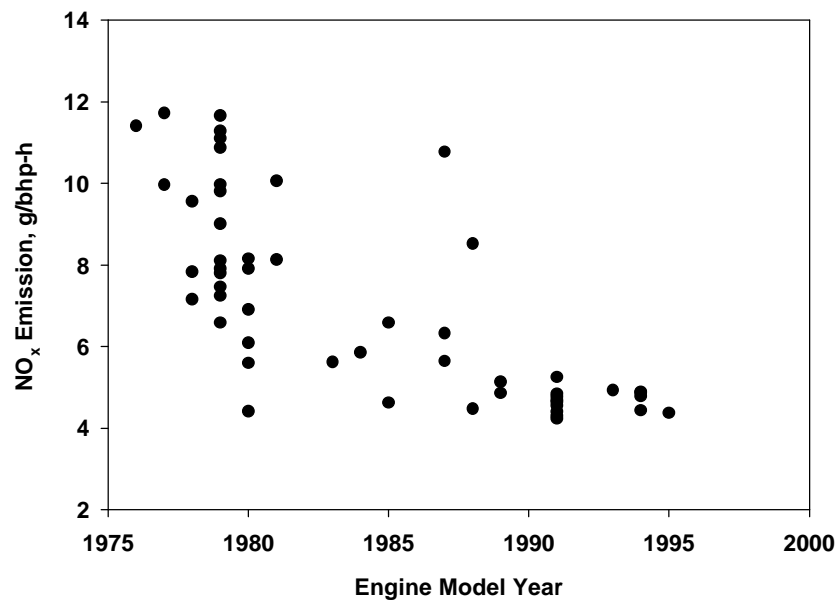
Figure 2-17. Diesel engine certification data for NOx emissions as a function of model year.

Source: Data are from the transient test results provided in Table 2-8.
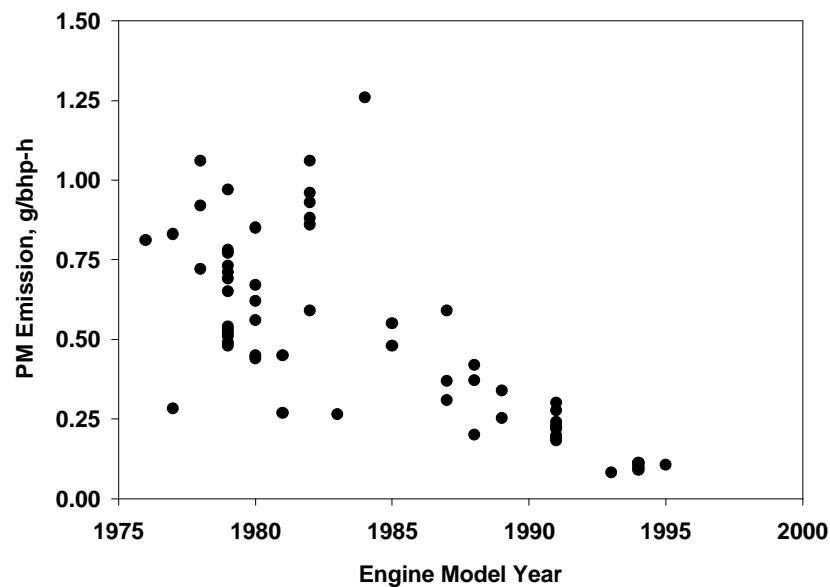
Figure 2-18. Diesel engine certification data for PM emissions as a function of model year.

Source: Data are from the transient test results provided in Table 2-8.
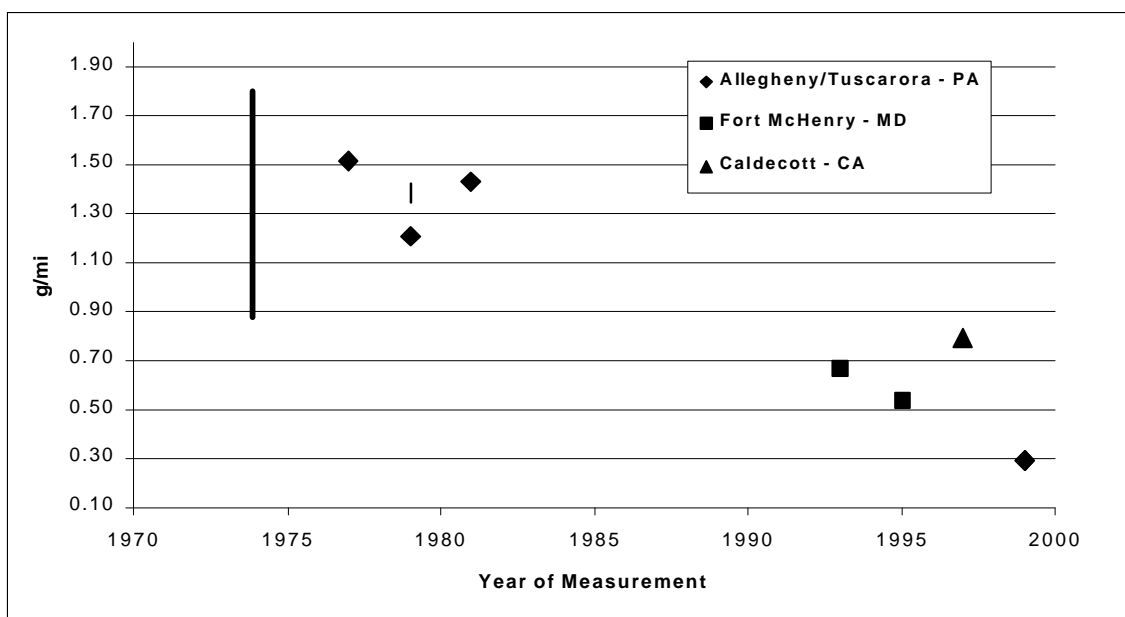
Figure 2-19. Emission factors from HD diesel vehicles from tunnel studies.

Source: Data from Pierson and Brachaczek, 1976; Szkarlat and Japar, 1983; Pierson et al., 1983; Kirchstetter et al., 1999; Gertler et al., 1995, 1996; Gertler, 1999.
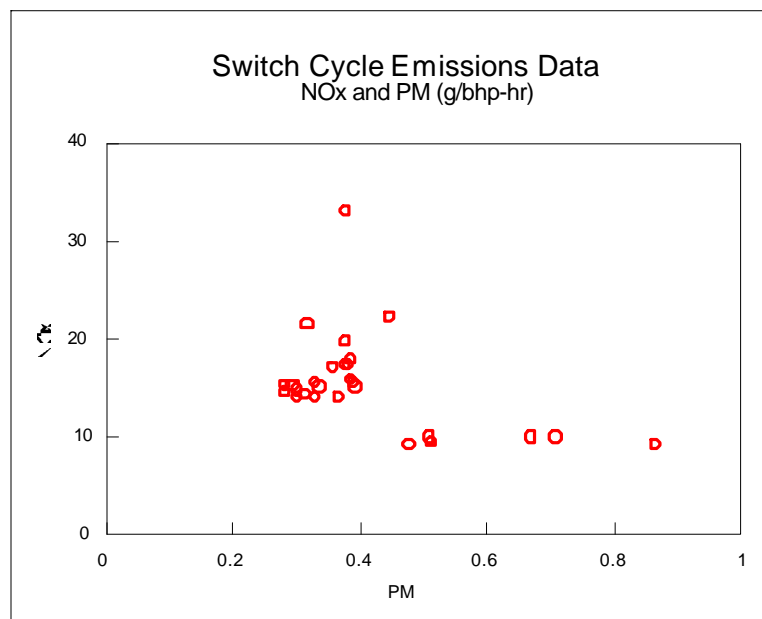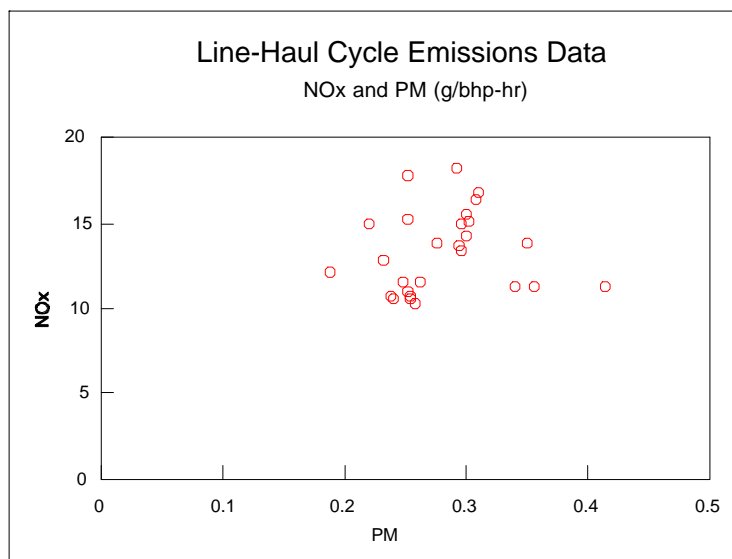
Figure 2-20. Line-haul and switch emissions data.

Source: U.S. EPA, 1998a.
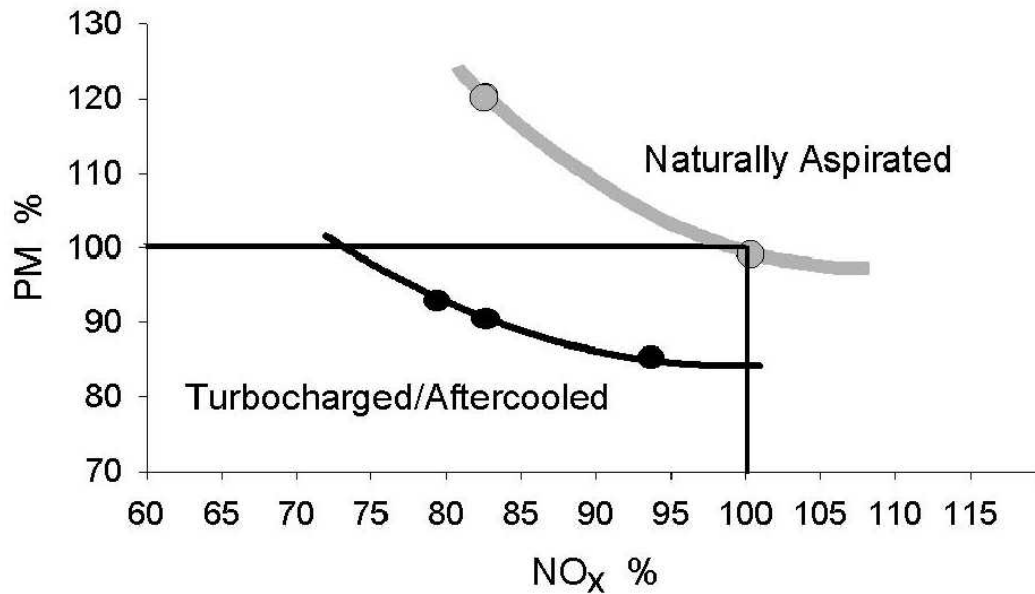
Figure 2-21. Effect of turbocharging and aftercooling on NO$_x$ and PM.

Source: Mori, 1997.
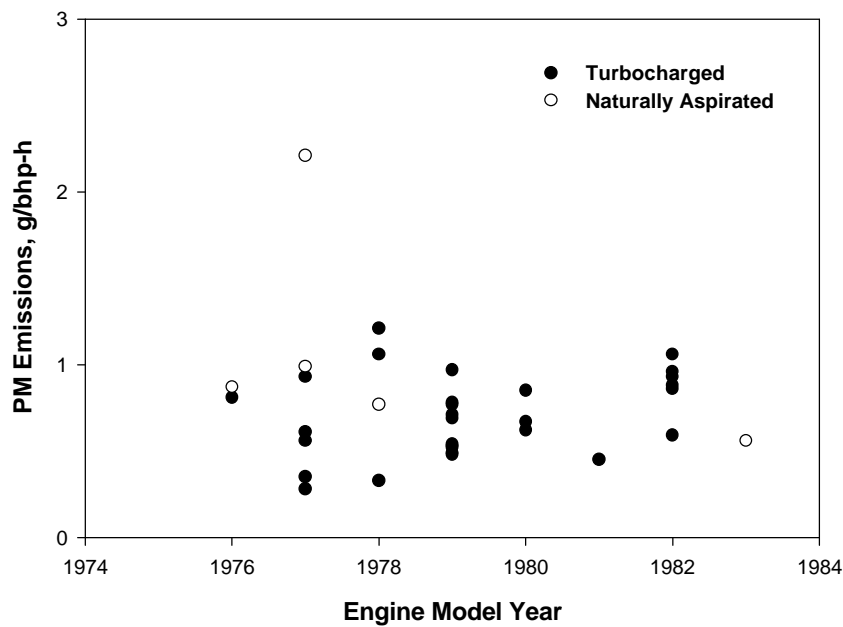
Figure 2-22. Comparison of diesel engine dynamometer PM emissions for 4-stroke, naturally aspirated and turbocharged engines.

Source: Data are from Table 2-8.
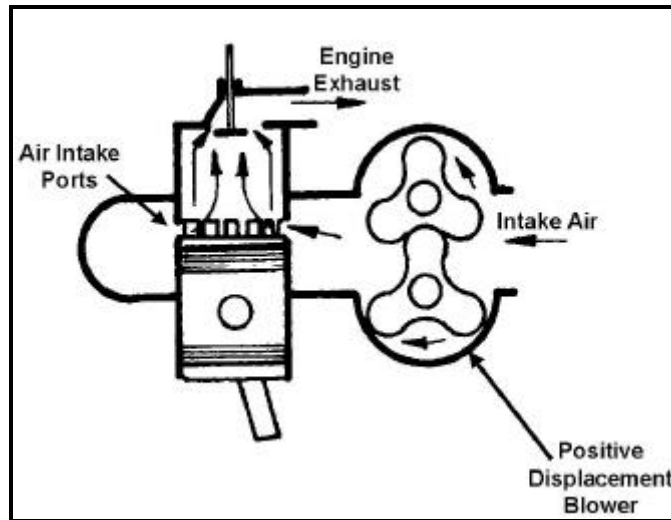
Figure 2-23. An example of uniflow scavenging of a two-stroke diesel engine with a positive displacement blower. Scavenging is the process of simultaneously emptying the cylinder of exhaust and refilling with fresh air.

Source: Adapted from Taylor, 1990.
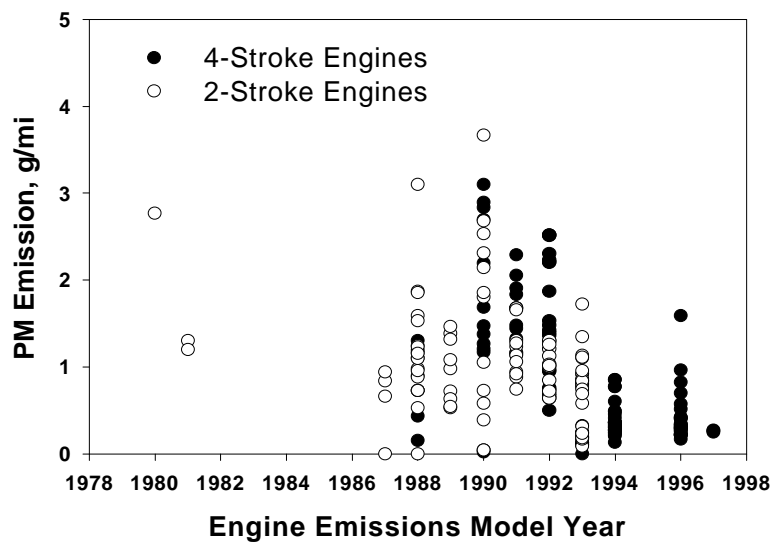
Figure 2-24. Comparison of two- and four-stroke vehicle diesel PM emissions from chassis dynamometer studies.

Source: Yanowitz et al., 2000.
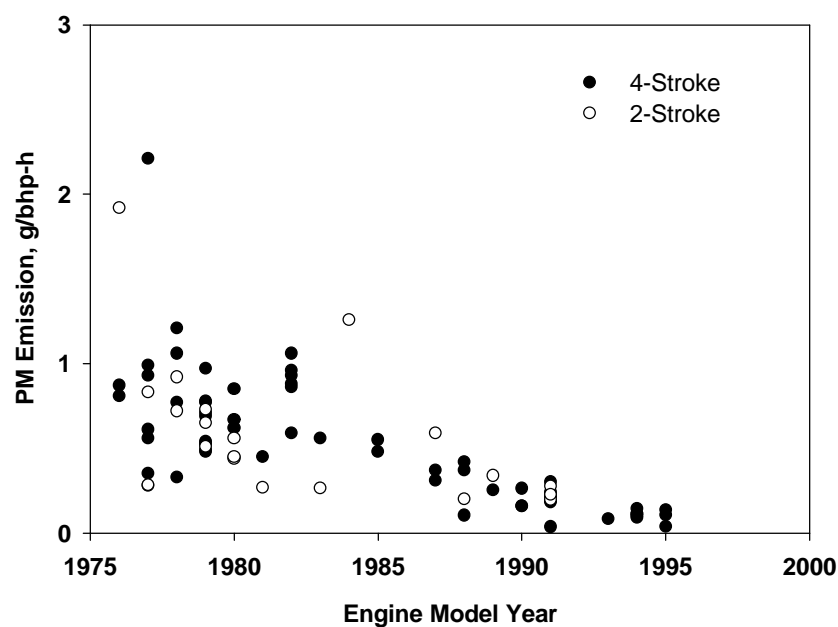
Figure 2-25. Comparison of two- and four-stroke engine diesel PM emissions from engine dynamometer studies.

Source: Data are from Table 2-8.
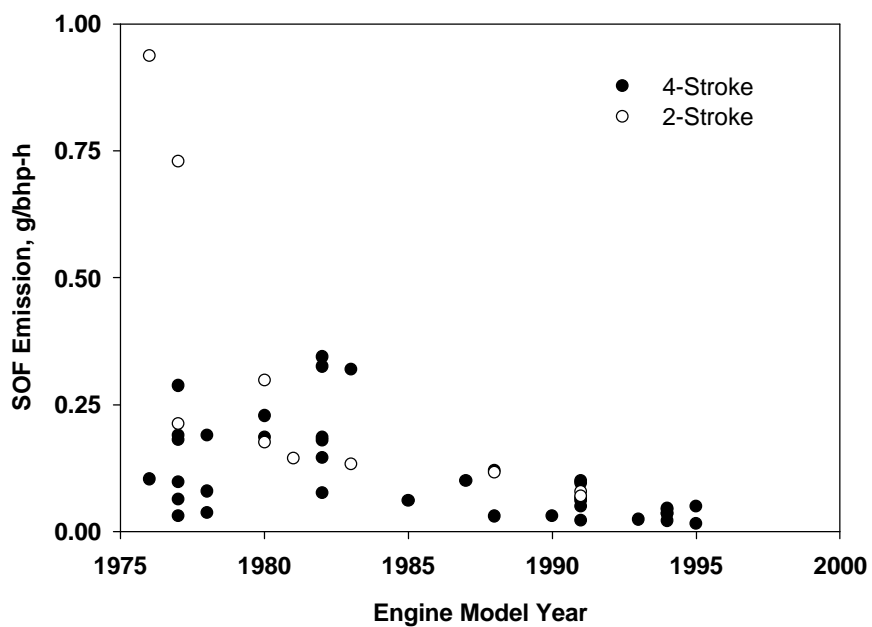
Figure 2-26.   Diesel engine dynamometer SOF emissions from two- and four-stroke engines. SOF obtained by dichloromethane extraction in most studies.
Source: Data are from Table 2-8.
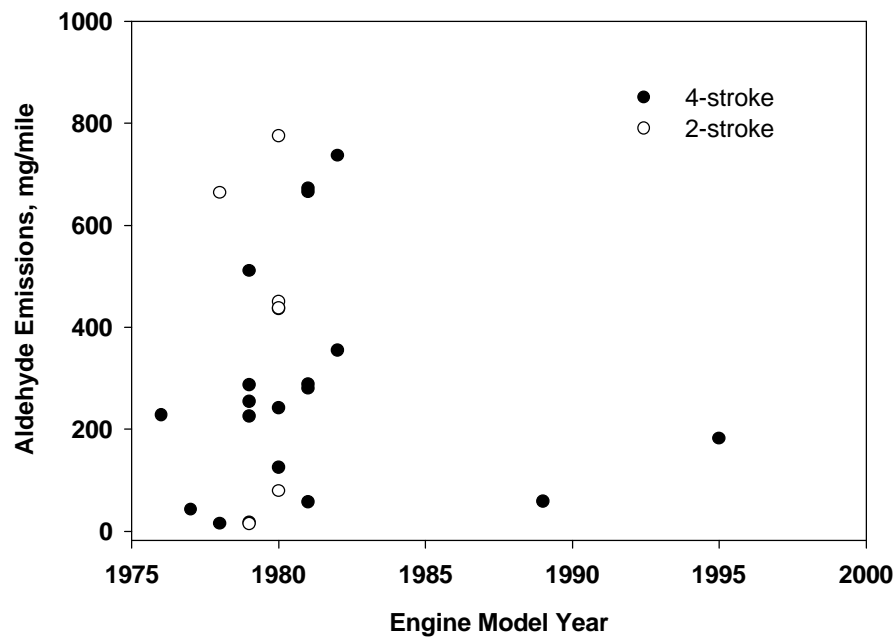
Figure 2-27. Diesel engine aldehyde emissions measured in chassis dynamometer studies.

Source: Data are from Warner-Selph and Dietzmann, 1984; Schauer et al., 1999; Unnasch et al., 1993.
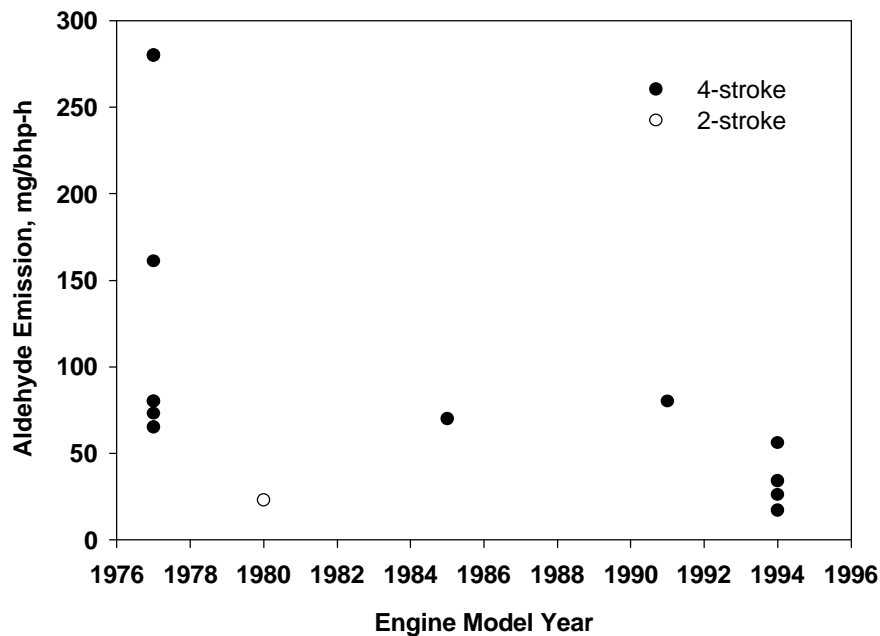
Figure 2-28. Diesel engine aldehyde emissions from engine dynamometer studies.

Source: Data from Table 2-8.

Figure 2-29. Trend in SOF emissions based on chassis dynamometer testing of heavy-duty diesel vehicles. Warner-Selph and coworkers: dichloromethane for 8 hours. Dietzman and coworkers: hexane followed by dichloromethane, extraction times not reported. Graboski and coworkers: VOF by vacuum sublimation at 225 C for 2.5 to 3 hours. Rogge and coworkers: cyclohexane followed by a benzene/2-propanol mixture that may extract significantly more organic matter.

Figure 2-30. Trend in SOF emissions for transient engine dynamometer testing of HD diesel engines. Various extraction methods used; see Table 2-8.

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Figure 2-31. Trend in SOF emissions as a percent of total PM based on chassis dynamometer testing of HD diesel vehicles. Warner-Selph and coworkers: dichloromethane for 8 hours. Dietzman and coworkers: hexane followed by dichloromethane, extraction times not reported. Graboski and coworkers: VOF by vacuum sublimation at 225 C for 2.5 to 3 hours. Rogge and coworkers: cyclohexane followed by a benzene/2-propanol mixture, that may extract significantly more organic matter.
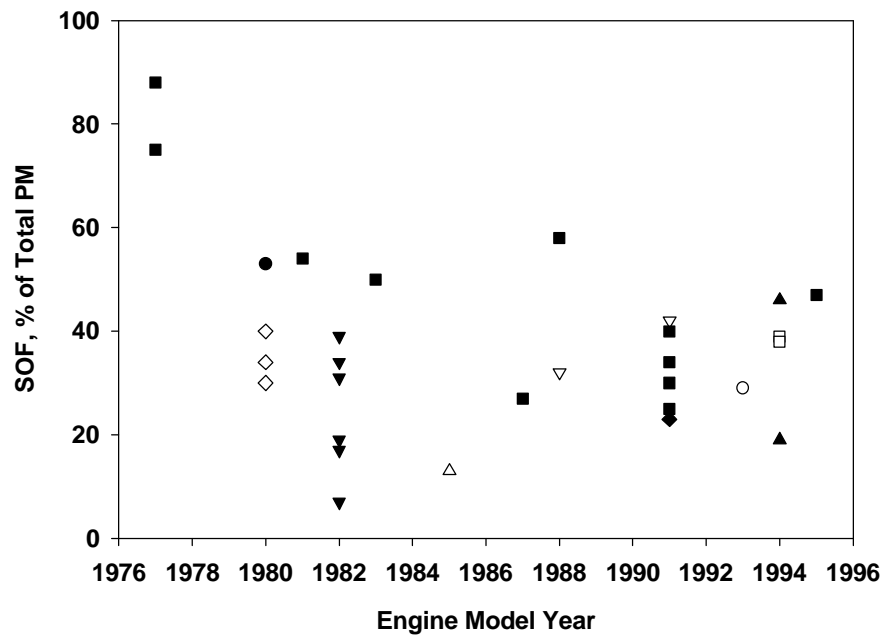
Figure 2-32. Trend in SOF emissions as a percentage of total PM from engine dynamometer testing. Data are from Table 2-8.
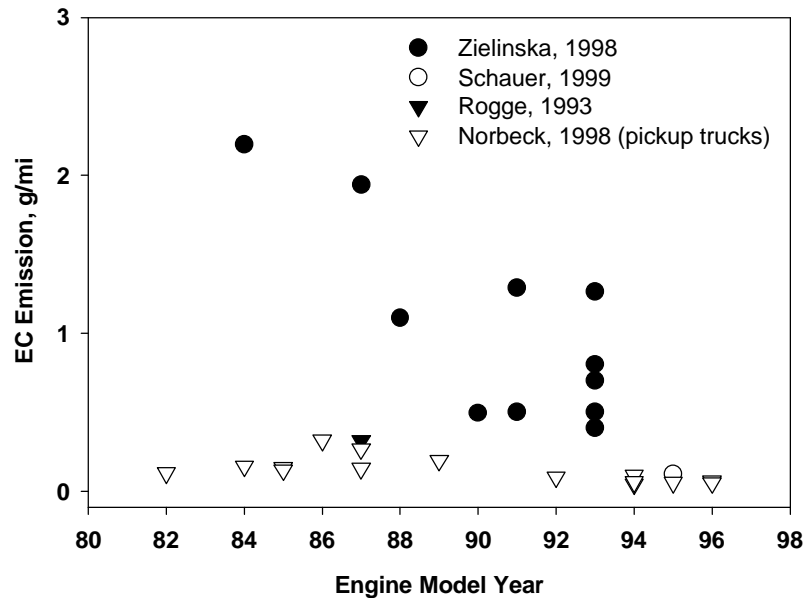
Figure 2-33. EC emission rates for diesel vehicles. All studies employed TOR for measurement of EC. Vehicles tested by Norbeck and co-workers (1998) were all light and medium HD pickup trucks.
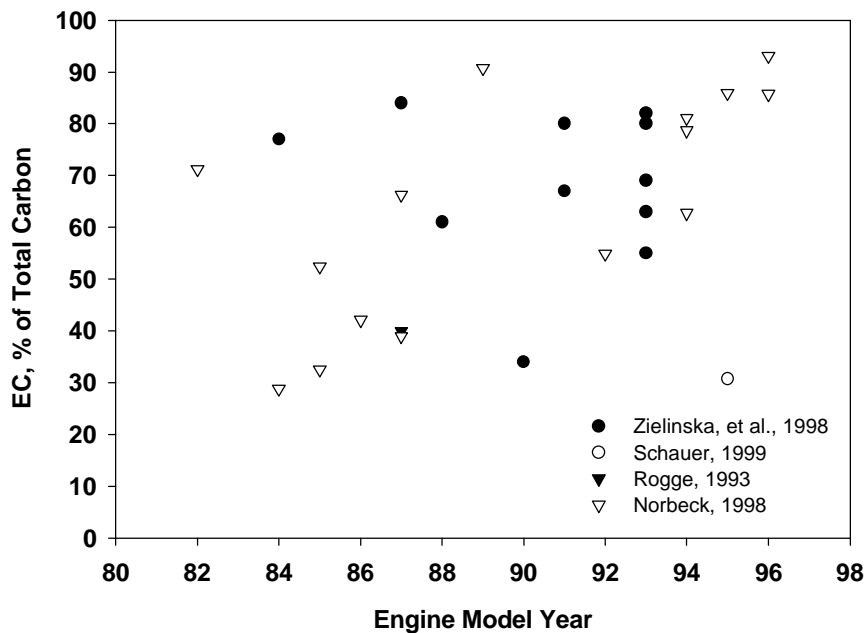
Figure 2-34. EC content as percent of total carbon content for DPM samples obtained in chassis dynamometer studies.
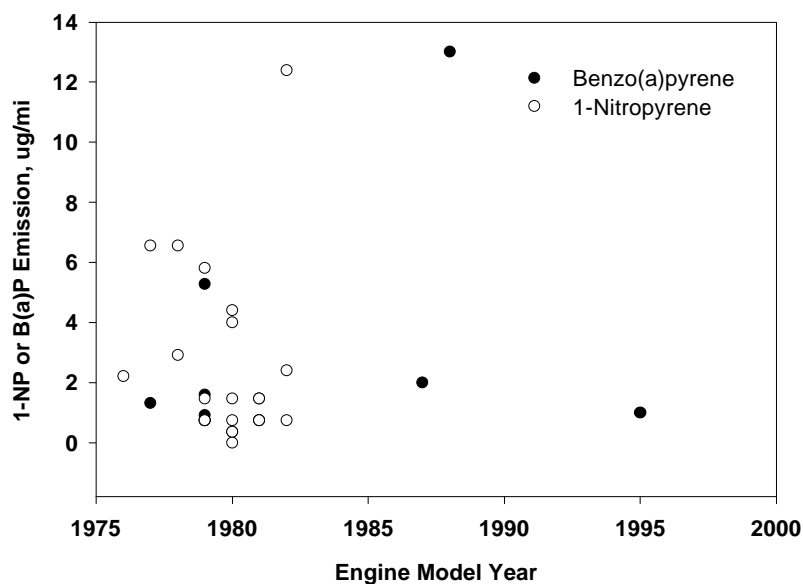
Figure 2-35. Diesel engine emissions of benzo[a]pyrene and 1-nitropyrene measured in chassis dynamometer studies.

Source: Schuetzle and Perez, 1983; Zielinska et al., 1988; Kado et al., 1996; Dietzmann et al., 1980; Warner-Selph and Dietzmann, 1984; Rogge et al., 1993; Schauer et al., 1999.
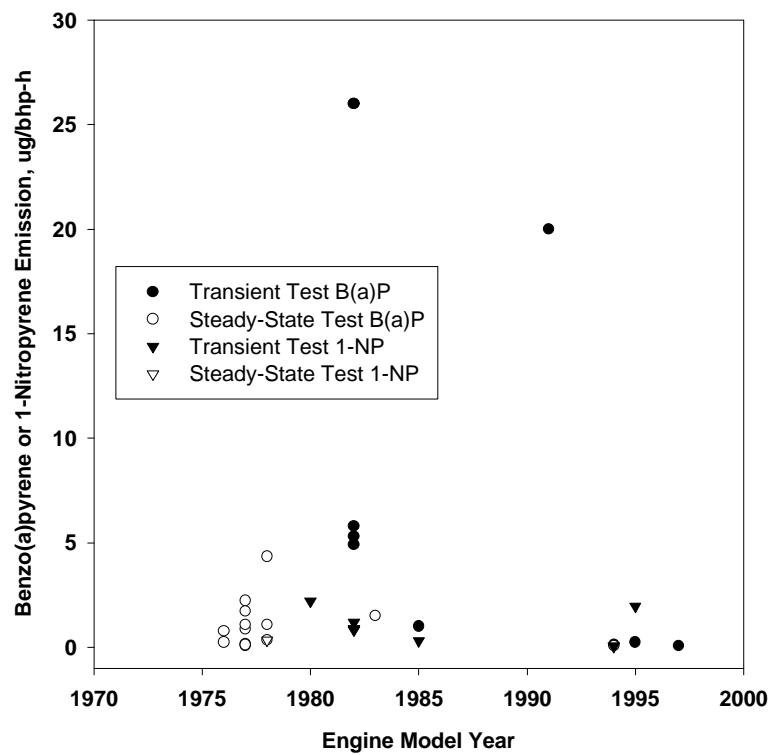
Figure 2-36. Diesel engine dynamometer measurements of benzo[a]pyrene and 1-nitropyrene emissions from HD diesel engines.

Source: Data are from Table 2-8.
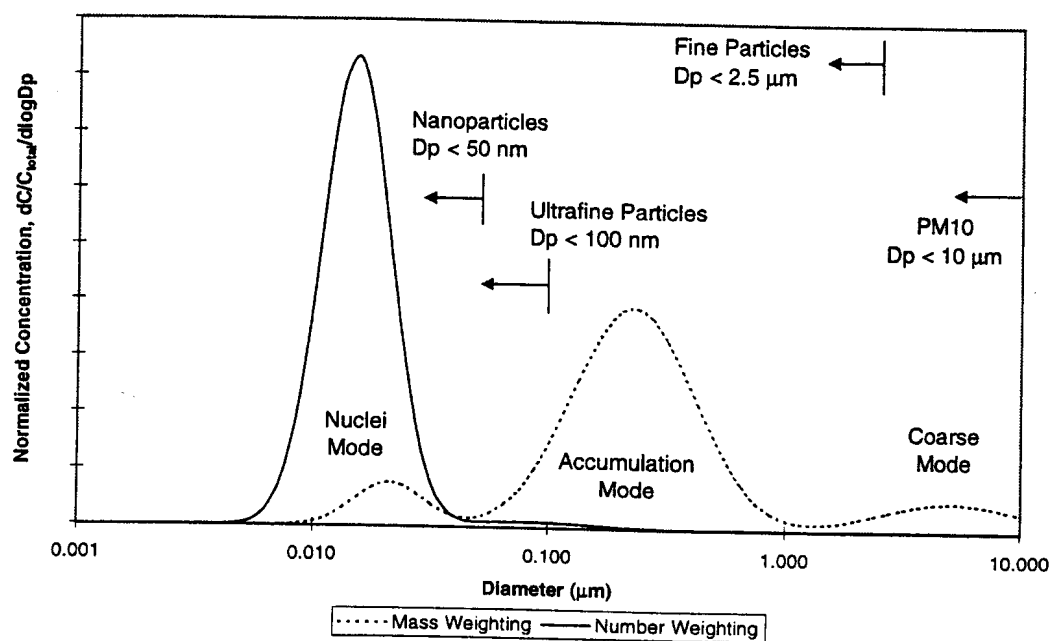
Figure 2-37. Particle size distribution in diesel exhaust.

Source: Kittelson, 1998.

2.6. REFERENCES

Abbass, MK; Andrews, GE; Ishaq, RB; et al. (1991) A comparison of the particulate composition between turbocharged and naturally aspirated DI diesel engines. SAE Technical Paper Ser. No. 910733.

Abdul-Khalek, IS; Kittelson, DB; Graskow, BR; et al. (1998) Diesel exhaust particle size: measurement issues and trends. SAE Technical Paper Ser. No. 980525.

Abdul-Khalek, IS; Kittelson, DB; Brear, F. (1999) The influence of dilution conditions on diesel exhaust particle size distribution measurements. SAE Technical Paper Ser. No. 1999-01-1142.

Alkidas, AC. (1984) Relationships between smoke measurements and particulate measurements. SAE Technical Paper Ser. No. 840412.

American Automobile Manufacturers Association (AAMA). (1975-1998) Motor vehicle facts and figures.

Andrews, GE; Ishaq, RB; Farrar-Khan, JR; et al. (1998) The influence of speciated diesel fuel composition on speciated particulate SOF emissions. SAE Technical Paper Ser. No. 980527 (and references therein).

Arey, J. (1998) Atmospheric reactions of PAHs including formation of nitroarenes. In: The handbook of environmental chemistry, Vol. 3, Part I. PAHs and related compounds. Nielsen, AH, ed. Berlin/Heidelberg, Germany: Springer-Verlag, pp. 347-385.

Arey, J; Zielinska, B; Atkinson, R; et al. (1986) The formation of nitro-PAHs from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO_x. Atmos Environ 20:2339-2345.

Arey, J; Zielinska, B; Atkinson, R; et al. (1987) Polycyclic aromatic hydrocarbon and nitroarene concentrations in ambient air during a wintertime high-NO_x episode in the Los Angeles Basin. Atmos Environ 21:1437-1444.

Arey, J; Zielinska, B; Atkinson, R; et al. (1988) Formation of nitroarenes during ambient high-volume sampling. Environ Sci Technol 22:457-462.

Arey, J; Zielinska, B; Atkinson, R; et al. (1989) Nitroarene products from the gas-phase reactions of volatile polycyclic aromatic hydrocarbons with OH radical and N_2O_5. Int J Chem Kinet 21:775-799.

Atkinson, R. (1986) Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. Chem Rev 86:69-201.

Atkinson, R. (1988) Atmospheric transformation of automotive emissions. In: Air pollution, the automobile and public health. Watson, AY; Bates, RR; Kennedy, D, eds. Washington, DC: National Academy Press, pp. 99-132.

Atkinson, R. (1991) Kinetics and mechanisms of the gas-phase reactions of the NO_3 radical with organic compounds. J Phys Chem Ref Data 20:459-507.

Atkinson, R; Arey, J. (1994) Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: formation of atmospheric mutagen. Environ Health Perspect 102(Suppl. 4):117-126.

Atkinson, R; Arey, J; Zielinska, B; et al. (1987) Kinetics and products of the gas-phase reactions of OH radicals and N_2O_5 with naphthalene and biphenyl. Environ Sci Technol 21:1014-1022.

Atkinson, R; Arey, J; Winer, AM; et al. (1988) A survey of ambient concentrations of selected polycyclic aromatic hydrocarbons (PAH) at various locations in California. Final report prepared under contract no. A5-185-32 for California Air Resources Board, Sacramento, CA.

Atkinson, R; Arey, J; Zielinska, B; et al. (1990) Kinetics and nitro-products of the gas-phase OH and NO_3 radical-initiated reactions of naphthalene-d_8 fluoranthene-d_{10} and pyrene. Int J Chem Kinet 22:999-1014.

Automobile Manufacturers Association (AMA). (1927-1974) Motor truck facts. Motor Truck Committee.

Bagley, ST; Baumgard, KJ; Gratz, LD. (1991) Comparison of in-min and laboratory-generated diesel particulate matter, biological activity, and polynuclear aromatic hydrocarbon levels. In: Proceedings of the Third Symposium of Respirable Dust in the Mineral Industries. Franz, RL; Ramini, RV, eds. Littleton, CO: Society for Mining, Metallurgy, and Exploration, pp. 61-70.

Bagley, ST; Baumgard, KJ; Gratz, LD. (1992) Polynuclear aromatic hydrocarbons and biological activity associated with diesel particulate matter collected in underground coal mines. IC9324. Pittsburgh, PA: Bureau of Mines, pp. 40-48.

Bagley, ST; Gratz, LD; Leddy, DG; et al. (1993) Characterization of particle and vapor phase organic fraction emissions from a HD diesel engine equipped with a particle trap and regeneration controls. Health Effects Institute, Research Report No. 56. Cambridge, MA: HEI.

Bagley, ST; Baumgard, KJ; Gratz, LD; et al. (1996) Characterization of fuel and aftertreatment effects on diesel emissions. Health Effects Institute, Research Report No. 76. Cambridge, MA: HEI.

Bagley, ST; Gratz, LD; Johnson, JH; et al. (1998) Effects of an oxidation catalytic converter and a biodiesel fuel on the chemical, mutagenic, and particle size characteristics of emissions from a diesel engine. Environ Sci Technol 32:1183-1191.

Baines, TM. (1986) Correlation testing of Cummins NTCC-400. EPA-AA-SDSB-87-1.

Ballschmiter, K.; Buchert, H.; Niemczyk, R.; et al. (1986) Automobile exhausts versus municipal waste incineration as sources of the polychloro-dibenzodioxins (PCDD) and -furans (PCDF) found in the environment. Chemosphere 15(7):901-915.

Baranescu, RA. (1988) Influence of fuel sulfur on diesel particulate emissions. SAE Technical Paper Ser. No. 881174.

Barry, EG; McCabe, LJ; Gerke, DH; et al. (1985) Heavy-duty diesel engine/fuels combustion performance and emissions--a cooperative research program. SAE Technical Paper Ser. No. 852078.

Bata, R; Wang, W; Gautam, M; et al. (1992) Fleet-site measurements of exhaust gas emissions from urban buses. ASME, ICE. New Dev Off-Highway Eng 18:185-196.

Baumgard, KJ; Johnson, JH. (1992) The effect of low sulfur fuel and a ceramic particle filter on diesel exhaust particle size distributions. SAE Technical Paper Ser. No. 920566.

Baumgard, KJ; Johnson, JH. (1996) The effect of fuel and engine design on diesel exhaust particle size distributions. SAE Technical Paper Ser. No. 960131.

Behymer, TD; Hites, RA. (1985) Photolysis of polycyclic aromatic hydrocarbons adsorbed on simulated atmospheric particulates. Environ Sci Technol 19:1004-1006.

Behymer, TD; Hites, RA. (1988) Photolysis of polycyclic aromatic hydrocarbons adsorbed on fly ash. Environ Sci Technol 22:1311-1319.

Benner, BA; Gordon, GE; Wise, SA. (1989) Mobile sources of atmospheric PAH: a roadway tunnel study. Environ Sci Technol 23:1269-1278.

Birch, ME. (1998) Analysis of carbonaceous aerosols: interlaboratory comparison. Analyst 123:851-857.

Birch, ME; Cary, RA. (1996) Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Sci Technol 25:221-241.

Bishop, GA; McLaren, SE; Stedman, DH; et al. (1996) Method comparisons of vehicle emissions measurements in the Fort McHenry and Tuscarora Mountain Tunnels. Atmos Environ 30:2307.

Black, F; High, L. (1979) Methodology for determining particulate and gaseous diesel hydrocarbon emissions. SAE Technical Paper Ser. No. 790422.

Brodowicz, P. (1999) Determination of the demographic groups with the highest annual average modeled diesel PM exposure. Memorandum. U.S. Environmental Protection Agency, National Fuel and Vehicle Emissions Laboratory.

Brown, KF. (1998) Diesel aftertreatment technologies. In: Proceedings of the SAE Topical Technical Seminar Diesel Technology for the New Millennium. Schaumburg, IL, April 22, 1998.

Brown, KF; Rideout, GR; Turner, JE. (1997) Urban driving cycle results of retrofitted diesel oxidation catalysts on heavy duty vehicles: one year later. SAE Technical Paper Ser. No. 970186.

Brown, DF; Rideout, GR. (1996) SAE Technical Paper Ser. No. 960134.

Brunekreef, B. (1999) Environmental diesel exhaust exposure and respiratory health of children in the Netherlands. Presented at the Health Effects Institute Diesel Workshop: Building a Research Strategy to Improve Risk Assessment. Stone Mountain, GA, March 7-9, 1999.

Brunekreef, B; Janssen, NAH; van Vliet, PHN; et al. (2000) Particulate matter concentrations in relation to degree of urbanization and proximity to highways in the Netherlands. Presented at: PM2000: Particulate Matter and Health – The Scientific Basis for Regulatory Decision-Making. Specialty Conference and Exhibition. January 24-28, 2000, Charleston, SC.

Burke, JB; Aufall, M; Ozkaynak, H; et al. (2000) Predicting population exposures to PM: The importance of microenvironmental concentrations and human activities. Presented at: PM2000: Particulate Matter and Health – The Scientific Basis for Regulatory Decision-Making. Specialty Conference and Exhibition. January 24-28, 2000, Charleston, SC.

Cadle, SH; Mulawa, PA. (1990) Atmospheric carbonaceous species measurement methods comparison study: General Motors results. Aerosol Sci Technol 12(1):128-141.

California Air Resources Board (CARB). (1987) Determination of PCDD and PCDF emissions from motor vehicles. Draft report. October 1987. Test report no. C-86-029.

California Air Resources Board and Energy and Environmental Analysis Inc. (1997) Regulatory Amendments to California's heavy-duty inspection program (HDVIP) and periodic smoke inspection program (PSIP). August 1997.

California Environmental Protection Agency. (1998a) Report to the California Air Resources Board on the proposed identification of diesel exhaust as a toxic air contaminant. Appendix III, part A: Exposure assessment. April 1998. http://www.arb.ca.gov/regact/diesltac/diesltac.htm.

California Environmental Protection Agency. (1998b) Measuring concentrations of selected air pollutants inside California vehicles. Final report.

Calvert, JG; Stockwell, WR. (1983) Acid generation in the troposphere by gas-phase chemistry. Environ Sci Technol 17:428A-443A.

Campbell, RM; Lee, ML. (1984) Capillary column gas chromatographic determination of nitro polycyclic aromatic compounds in particulate extracts. Anal Chem 56:1026-1030.

Cantrell, BK; Salas, LJ; Johnson, WB; et al. (1988) Phase distributions of low volatility organics in ambient air. Prepared for the U.S. Environmental Protection Agency, Washington, DC, under EPA contract no. 68-02-3748.

Carey, PM. (1987) Air toxics emissions from motor vehicles. U.S. Environmental Protection Agency, Washington, DC, Office of Mobile Sources, Report No. EPA/AA-TSS-PA-86-5.

Cass, GR; Gray, HA. (1995) Regional emissions and atmospheric concentrations of diesel engine particulate matter: Los Angeles as a case study. In: Diesel exhaust: a critical analysis of emissions, exposure, and health effects. A special report of the Institute's Diesel Working Group. Cambridge, MA: Health Effects Institute, pp. 125-137.

Cautreels, W; Van Cauwenberghe, K. (1978) Experiments on the distribution of organic pollutants between airborne particulate matter and the corresponding gas phase. Atmos Environ 12:1133-1141.

Chow, JC; Watson, JG; Richards, LW; et al. (1991) The 1989-1990 Phoenix PM10 study. Volume II: source apportionment. Final report. DRI Document No. 8931.6F1. Prepared for Arizona Department of Environmental Air Quality, Phoenix, AZ, by Desert Research Institute, Reno, NV.

Ciccioli, P; Cecinato, A; Brancaleoni, E; et al. (1989) Evaluation of nitrated PAH in anthropogenic emission and air samples: a possible means of detecting reactions of carbonaceous particles in the atmosphere. Aerosol Sci Technol 10:296-310.

Ciccioli, P; Cecinato, A; Cabella, R; et al. (1993) The contribution of gas-phase reactions to the nitroarene fraction of molecular weight 246 present in carbon particles sampled in an urban area of northern Italy. Atmos Environ 27A:1261.

Clark, N; Messer, JT; McKain, DL; et al. (1995) Use of the West Virginia University truck test cycle to evaluate emissions from Class 8 trucks. SAE Technical Paper Ser. No. 951016.

Clark, N; Gautam, M; Lyons, D; et al. (1997) Natural gas and diesel transit bus emissions: review and recent data. SAE Technical Paper Ser. No. 973203.

Clark, NN; Gautam, M; Rapp, BL; et al. (1999) Diesel and CNG transit bus emissions characterization by two chassis dynamometer laboratories: results and issues. SAE Technical Paper Ser. No.1999-01-1469.

CFR, Code of Federal Regulations, 40 CFR Subpart N; Vol. 40.

CFR, Code of Federal Regulations, Title 40, Section 80.29.

Cohen, LH; Countess, RJ; Countess, SJ. (1997) Advanced remote sensing technology demonstration. Mobile Sources Air Pollution Review Committee.

Coifman, B. (1994) Evolution of the diesel locomotive in the United States. http://www.cyberus.ca/~yardlimit/guide/locopaper.html

Cooper, C. (1999) Heavy-duty diesel smoke enforcement program in the Northeast. Presented at the Mobile Sources Technical Review Subcommittee, July 1999.

Cooper, JA. et al. and NEA, Inc. (1987) PM10 source composition library for the South Coast Air Basin, volumes I and II. Prepared for the South Coast Air Quality Management District, El Monte, CA. July 15, 1987.

Countess, R; Countess, S; Cohen, R. (1999) Remote sensing of heavy duty diesel trucks revisited. 9th Coordinating Research Council On-Road Vehicle Emissions Workshop, San Diego, CA.

Coutant, RW; Grown, L; Chuang, JC; et al. (1988) Phase distribution and artifact formation in ambient air sampling for polynuclear aromatic hydrocarbons. Atmos Environ 22:403-409.

Crebelli, R; Conti, L; Crochi, B; et al. (1995) The effect of fuel composition on the mutagenicity of diesel engine exhaust. Mutat Res 346:167-172.

Cunningham, LF; Henly, TJ; Kulinowski, AM. (1990) The effects of diesel ignition improver in low-sulfur fuels on heavy-duty diesel emissions. SAE Technical Paper Ser. No. 902173.

Dec, JE; Espey, C. (1995) Ignition and early soot formation in a diesel engine using multiple 2-D imaging diagnostics. SAE Technical Paper Ser. No. 950456.

Dickson, CL; Sturm, GP. (1994) Diesel fuel oils, 1994. National Institute for Petroleum and Energy Research. NIPER-187 PPS 94/5.

Dietzmann, HE; Parness, MA; Bradow, RL. (1980) Emissions from trucks by chassis version of 1983 transient procedure. SAE Technical Paper Ser. No. 801371.

Dua, SK; Hopke, PK; Raunemaa, T. (1999) Hygroscopicity of diesel aerosols. Water Air Soil Pollut 112:247-257.

Dunlap, LS; Pellegrin, V; Ikeda, R; et al. (1993) Chassis dynamometer emissions testing results for diesel and alternative-fueled transit buses. SAE Technical Paper Ser. No. 931783.

Dunstan, TDJ; Mauldin, RF; Jinxian, Z; et al. (1989) Adsorption and photodegradation of pyrene on magnetic, carbonaceous, and mineral subfractions of coal stack ash. Environ Sci Technol 23:303-308.

Engler, BH. (1998) Catalytic reduction of NO_x with hydrocarbons under lean diesel exhaust conditions. SAE Technical Paper Ser. No. 980189.

Enya, T; Suzuki, H; Watanabe, T; et al. (1997) 3-Nitrobenzanthrone, a powerful bacterial mutagen and suspected human carcinogen found in diesel exhaust and airborne particles. Environ Sci Technol 31:2772-2776.

Federal Highway Administration (FHA). (1995) Motor fuel use, 1919-1995. U.S. Department of Transportation: www.fhwa.dot.gov/ohim/Summary95/section1.html; Vol. MF221.

Federal Highway Administration. (1997) Highway statistics summary to 1995. U.S. Department of Transportation. FHWA-PL-97-009.

Feilberg, A; Kamens, RM; Strommen, MR; et al. (1999) Modeling the formation, decay, and partitioning of semivolatile nitro-polycyclic aromatic hydrocarbons (nitronaphthalenes) in the atmosphere. Atmos Environ 33:1231-1243.

Ferguson, DH; Gautam, M; Wang, WG; et al. (1992) Exhaust emissions from in-use heavy duty vehicles tested on a transportable transient chassis dynamometer. SAE Technical Paper Ser. No. 922436.

Finlayson-Pitts, BJ; Pitts, JN, Jr. (1986) Atmospheric chemistry: fundamentals and experimental techniques. New York: John Wiley & Sons.

Foster, DE; Tree, DR. (1994) Optical measurements of soot particle size, number density and temperature in a direct injection diesel engine as a function of speed and load. SAE Technical Paper Ser. No. 940270.

Fowler, DP. (1985) Industrial hygiene/environmental sampling program to develop qualitative and quantitative data for diesel exhaust emission exposure. Final report. Coordinating Research Council-APRAC Project No. CAPM-24-78.

Frey, JW; Corn, M. (1967) Diesel exhaust particulates. Nature 216:615-616.

Friones, JR; Hinds, WC; Duffy, RM; Lafuente, EJ; Liu, WV. (1987) Exposure of firefighters to diesel emissions in fire stations. A.m Ind. Hyg. Assoc. J. 48:202-207.

Fritz, SG. (1995) Emission measurements--locomotives. Prepared by Southwest Research Institute under U.S. EPA Contract no. 68-C2-0144.

Fujita, EM; Lu, Z; Sheetz, L; et al. (1997) Determination of mobile source emission source fraction using ambient field measurements. Final report. Prepared for Coordinating Research Council, Atlanta, GA, by Desert Research Institute, Reno, NV, under CRC Project No. E-5-1.

Fujita, E; Watson, JG; Chow, JC; et al. (1998) Northern Front Range Air Quality Study, volume C: source apportionment and simulation methods and evaluation. Prepared for Colorado State University, Cooperative Institute for Research in the Atmosphere, by Desert Research Institute, Reno, NV.

Gautam, M; Ferguson, D; Wang, WG; et al. (1992) In-use emissions and performance monitoring of heavy duty vehicles using a transportable transient chassis test facility. SAE Technical Paper Ser. No. 921751.

Gertler, AW. (1999) Real-world measurements of diesel particulate matter. Presentation to CASAC-Mobile Sources Technical Review Subcommittee, October 13, 1999.

Gertler, AW; Sagebiel, JC; Dippel, WA; et al. (1996) A study to quantify on-road emissions of dioxins and furans from mobile sources: phase 2. Reno, NV: Desert Research Institute.

Gertler, AW; Sagebiel, JC; Dippel, WA; et al. (1998) Measurements of dioxin and furan emission factors from HD diesel vehicles. J Air Waste Manage Assoc 48:276-278.

Ghio, AJ; Richards, JH; Dailey, LA; et al. (2000) The effects of oxidants on modifying the toxicity of ambient PM. Society of Toxicology Annual Meeting.

Gorse, RA, Jr.; Riley, TL; Ferris, FC; et al. (1983) 1-Nitropyrene concentration and bacterial mutagenicity in on-road vehicle particulate emissions. Environ Sci Technol 17:198-202.

Graboski, MS; McCormick, RL. (1996) Effect of diesel fuel chemistry on emissions at high altitude. SAE Technical Paper Ser. No. 961947.

Graboski, MS; McCormick, RL; Alleman, T. (1998a) Testing of natural gas and diesel buses for comparison with WVU mobile dynamometer. Colorado Institute for Fuels and High Altitude Engine Research, Colorado School of Mines, Golden, CO.

Graboski, MS; McCormick, RL; Yanowitz, J; et al. (1998b) HD diesel testing for the Northern Front Range Air Quality Study. Colorado Institute for Fuels and Engine Research, Colorado School of Mines, Golden, CO. http://nfraqs.cira.colostate.edu/index2.html.

Gray, HA. (1986) Control of atmospheric fine primary carbon particle concentrations. Ph.D. thesis, California Institute of Technology.

Gray, HA; Kuklin, A. (1996) Benefits of mobile source NO_x related paticulate matter reductions. Final report. Prepared by Systems Applications International for U.S. Environmental Protection Agency. SYSAPP-96/61.

Gray, HA; Cass, GR. (1998) Source contributions to atmospheric fine carbon particle concentrations. Atmos Environ 32(22):3805-3825.

Gullett, BK; Ryan, JV. (1997) On-road sampling of diesel engine emissions of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran. Organohalogen Compounds 32:451-456.

1   Hagenmaier, H. (1994) Contributions of diesel-powered vehicles and wood burning to overall PCDD/PCDF
2   emissions. Organo Comp 20:267-270.
3
4   Hagenmaier, H; Dawidowsky, V; Weber, UB; et al. (1990) Emission of polyhalogenated dibenzodioxins and
5   dibenzofurans from combustion-engines. Organo Comp 2:329-334.
6
7   Hames, RJ; Straub, RD; Amann, RW. (1985) DDEC Detroit Diesel electronic control. SAE Technical Paper
8   Series No. 850542.
9
10   Hammerle, RH; Schuetzle, D; Adams,W. (1994) A perspective on the potential development of environmentally
11   acceptable light-duty diesel engines. Environ Health Perspect (Suppl.) 102:25-30.
12
13   Hammond, SK. (1998) Occupational exposure to diesel exhaust. Presented at the Scientific Review Panel Meeting,
14   California Air Resources Board, March 11, 1998.
15
16   Hansen, ADA; Novakov, T. (1990) Real-time measurement of aerosol black carbon during the carbonaceous
17   species methods comparison study. Aerosol Sci Technol 12(1):194-199.
18
19   Hansen, KF; Bak, F; Andersen, EM; et al. (1994) The influence of an oxidation catalytic converter on the chemical
20   and biological characteristics of diesel exhaust emissions. SAE Technical Paper Ser. No. 940241.
21
22   Hara, K; Hanaoka, T; Yamano, Y; et al. (1997) Urinary 1-hydroxypyrene levels of garbage collectors with low-
23   level exposure to polycyclic aromatic hydrocarbons. Sci Total Environ 199:159-164.
24
25   Hardenberg, H; Fraenkle, G. (1978) The effect of charge air cooling on exhaust emissions and power output of
26   turbocharged engines. Institute of Mechanical Engineers Paper No. C71/78.
27
28   Hare, CT. (1977) Characterization of diesel gaseous and particulate emissions. Final report. Prepared by
29   Southwest Research Institute under contract no. 68-02-1777.
30
31   Hare, CT. (1985) Study of the effects of fuel composition, and injection and combustion system type and
32   adjustment, on exhaust emissions from light-duty diesels. Final report. Prepared by Southwest Research Institute
33   for Project CAPE-32-80.
34
35   Hare, CT; Springer, KJ. (1972) Exhaust emissions from uncontrolled vehicles and related equipment using internal
36   combustion engines. Part I, locomotive diesel engines and marine counterparts. Southwest Research Institute under
37   contract no. EHS 70-108.
38
39   Harvey, GD; Baumgard, KJ; Johnson, JH; et al. (1994) Effects of a ceramic particle trap and copper fuel additive
40   on HD diesel emissions. SAE Technical Paper Ser. No. 942068.
41
42   Hawker, P; Myers, N; Huethwohl, G; et al. (1997) Experience with a new particulate trap technology in Europe.
43   SAE Technical Paper Ser. No. 970182.
44
45   Hawker, P; Huethwohl, G; Henn, J; et al. (1998) Effect of a continuously regenerating diesel particulate filter on
46   non-regulated emissions and particle size distribution. SAE Technical Paper Ser. No. 980189.
47
48   Health Effects Institute. (1995) Diesel exhaust: a critical analysis of emissions, exposure, and health effects.
49   Cambridge, MA.
50
51   Heino, M. (1978) Work conditions and health of locomotive engineers. Scand J Work Environ Health 4:314.
52
53   Henry, RC; Lewis, CW; Collins, JF. (1994) Vehicle-related hydrocarbon source compositions from ambient data:
54   the GRACE/SAFER method. Environ Sci Technol 28:823-832.
55
56   Heywood, JB. Internal combustion engine fundamentals. New York: McGraw-Hill, Inc., 1988.

Hildemann, LM; Markowski, GR; Cass, GR. (1991) Chemical composition of emissions from urban sources of fine organic aerosol. Environ Sci Technol 25:744-759.

Hori, S; Narusawa, K. (1998) Fuel composition effects on SOF and PAH exhaust emissions from a DI diesel engine. SAE Technical Paper Ser. No. 980507.

Horvath, H; Kreiner, I; Norek, C; et al. (1988) Diesel emissions in Vienna. Atmos Environ 22:1255-1269.

Hutzinger, O; Essers, U.; Hagenmaier, H. (1992) Untersuchungen zur emission halogenierter dibenzodioxine und dibenzofurane aus verbrennungsmortoren beim betrieb mit handelsüblichen betriebsstoffen. Universities of Bayreuth, Stuttgart and Tübingen, Germany. GSF-Forschungszentrum, Munich, Germany, ISSN 0937-9932.

Jang, M; McDow, SR. (1995) Benz[a]anthracene photodegradation in the presence of known organic constituents of atmospheric aerosols. Environ Sci Technol 29:2654.

Japar, SM; Szkarlat, AC; Gorse, RA; et al. (1984) Comparison of solvent extraction and thermal-optical carbon analysis methods: application to diesel vehicle exhaust aerosol. Environ Sci Technol 18:231-234.

Jimenez, J; McRae, G; Nelson, D; et al. (1998) Remote sensing of HD diesel truck NO$_x$ emissions using TILDAS. 8th Coordinating Research Council On-Road Vehicle Emissions Workshop: San Diego, CA, pp. 7-45‒7-61.

Johnson, JE. (1993) Hydrocarbon oxidation in a diesel oxidation catalytic converter. MS thesis, University of Minnesota.

Johnson, JE; Kittelson, DB. (1996) Deposition, diffusion and adsorption in the diesel oxidation catalyst. Appl Catal B: Environ 10:117-137.

Johnson, JH; Bagley, ST; Gratz, LD; et al. (1994) A review of diesel particulate control technology and emissions effects--1992 Horning Memorial Award Lecture. SAE Technical Paper Ser. No. 940233.

Kado, NY; Okamoto, RA; Kuzmicky, PA. (1996) Chemical and bioassay analyses of diesel and biodiesel particulate matter: pilot study. Final report to Montana State Department of Environmental Quality and the U.S. Department of Energy by Department of Environmental Toxicology, University of California, Davis.

Kado, NY; Kuzmicky, PA; Kiefer, KL; et al. (1998) Emissions from biodiesel fuel combustion: bioassay and chemical analyses of the particle and semi-volatile emissions from hydrogenated biodiesel fuels. Final report to U.S. Department of Energy by Department of Environmental Toxicology, University of California, Davis.

Kakoi, Y; Tsutsui, Y; Ono, N; et al. (1998) Emission reduction technologies applied to high-speed direct injection diesel engine. SAE Technical Paper Ser. No. 980173.

Kamens, RM; Guo, Z; Fulcher, JN; et al. (1988) Influence of humidity, sunlight, and temperature on the daytime decay of polyaromatic hydrocarbons on atmospheric soot particles. Environ Sci Technol 22:103-108.

Kantola, TC; Bagley, ST; Gratz, LD; et al. (1992) The influence of a low sulfur fuel and a ceramic particle trap on the physical, chemical, and biological character of HD diesel emissions. SAE Technical Paper Ser. No. 920565.

Katragadda, S; Bata, R; Wang, WG; et al. (1993) A correlation study between two HD vehicle chassis dynamometer emissions testing facilities. SAE Technical Paper Ser. No. 931788.

Katz, M; Chan, C; Tosine, H; et al. (1979) Relative rates of photochemical and biological oxidation (in vitro) of polycyclic aromatic hydrocarbons. In: Polynuclear aromatic hydrocarbons: Third International Symposium on Chemistry and Biology–Carcinogenesis and Mutagenesis, October 1978, Columbus, OH. Jones, PW; Leber, P, eds. Ann Arbor, MI: Ann Arbor Science Publishers, Inc., pp. 171-189.

1   Kawatani, T, Mori, K, Fukano, I, Sugawara, K, Koyama, T. (1993) Technology for meeting the 1994 USA exhaust
2   emission regulations on heavy-duty diesel engine. SAE Technical Paper Ser. No. 932654.
3
4   Khatri, NJ; Johnson, JH; Leddy, DG. (1978) The characterization of the hydrocarbon and sulfate fractions of
5   diesel particulate matter. SAE Technical Paper Ser. No. 780111.
6
7   Kirchstetter, TW; Harley, RA; Kreisberg, NM; et al. (1999) On-road measurement of fine particle and nitrogen
8   oxide emissions from light- and HD motor vehicles. Atmos Environ 33:2955-2968.
9
10 Kirkland, JF. (1983) Dawn of the diesel age. Glendale, CA: Interurban Press.
11
12 Kittelson, DB. (1998) Engines and nanoparticles: a review. J Aerosol Sci 29:575-588.
13
14 Kittelson, DB. (2000) What do we know about the nature of the nanoparticles emitted by diesel engines?
15 Coordinating Research Council, January 2000.
16
17 Kittelson, DB; Pipho, ML; Ambs, JL; et al. (1986) Particle concentrations in a diesel cylinder: comparison of
18 theory and experiment. SAE Technical Paper Ser. No. 861569.
19
20 Kittelson, DB; Winthrop, W; Baltensperger, R; et al. (1999) Diesel aerosol sampling methodology. University of
21 Minnesota Center for Diesel Research. http://www.me.umn.edu/centers/cdr/Proj_EPA.html.
22
23 Kittelson, D; Watts, W; Ramachandran, G. (2000) Exposures to diesel exhaust aerosol: relationship between 6-
24 hour time weighted average personal exposures to EC/OC and real-time variations in aerosol properties. Health
25 Effects Institute Annual Conference 2000: exploring exposure and risk issues. April 9-11, 2000, Atlanta, GA.
26
27 Kleeman, MJ; Cass, GR. (1998) Source contributions to the size and composition distribution of urban particulate
28 air pollution. Atmos Environ 32(16):2803-2816.
29
30 Kleeman, MJ; Schauer, JJ; Cass, GR. (2000) Size and composition distribution of fine particulate matter emitted
31 from motor vehicles. Environ Sci Technol 34:1132-1142.
32
33 Klein, M. (1991) The diesel revolution. Am Heritage Invention Technol 6.
34
35 Kleindienst, TE; Shepson, PB; Edney, EO; et al. (1985) Peroxyacetyl nitrate: measurement of its mutagenic
36 activity using the Salmonella/mammalian microsome reversion assay. Mutat Res 157:123-128.
37
38 Kreso, AM; Johnson, JH; Gratz, LD; et al. (1998a) A study of the vapor- and particle-phase sulfur species in the
39 HD diesel engine EGR cooler. SAE Technical Paper Ser. No. 981423.
40
41 Kreso, AM; Johnson, JH; Gratz, LD; et al. (1998b) A study of the effects of exhaust gas recirculation on HD diesel
42 engine emissions. SAE Technical Paper Ser. No. 981422.
43
44 Ladomatos, N; Abdelhalim, SM; Zhao, H; et al. (1996-1997) The dilution, chemical, and thermal effects of
45 exhaust gas recirculation on diesel engine emissions–parts 1, 2, 3, and 4. SAE Technical Paper Ser. No.
46
47 Last, RJ; Krueger, M; Duernholz, M. (1995) Emissions and performance characteristics of a 4-stroke, direct
48 injected diesel engine fueled with blends of biodiesel and low sulfur diesel fuel. SAE Technical Paper Ser. No.
49 950054.
50
51 Law, PL; Lioy, PJ; Zelenka, MP; et al. (1997) Evaluation of a probabilistic exposure model applied to carbon
52 monoxide (pNEM/CO) using Denver personal exposure monitoring data. J Air Waste Manage Assoc 47:491-500.
53
54 Lee, R; Hobbs, CH; Pedley, JF. (1998) Fuel quality impact on heavy duty diesel emissions: literature review. SAE
55 Technical Paper Ser. No. 982649.
56

Leet, JA; Friesen, T; Shadbourne, A. (1998) EGR's effect on oil degradation and intake system performance. SAE Technical Paper Ser. No. 980179.

Levson, K. (1988) The analysis of diesel particulate. Fresenius Z Anal Chem 331:467-478.

Lew, G. (1996) Letter to G. Schweer (Versar, Inc.) dated January 11, 1996. Sacramento, CA: State of California Air Resources Board, Engineering and Laboratory Branch. Available for inspection at: U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington, DC.

Lies, KH; Hartung, A; Postulka, A; et al. (1986) Composition of diesel exhaust with particular reference to particle bound organics including formation of artifacts. In: Carcinogenic and mutagenic effects of diesel engine exhaust. London: Elsevier Science Limited, pp. 65-82.

Ligocki, MP; Pankow, JF. (1989) Measurements of the gas/particle distributions of atmospheric organic compounds. Environ Sci Technol 23:75-83.

Loft, S; Poulsen, HE; Vistisen, K; et al. (1999) Increased urinary excretion of 8-oxo-2'-deoxyguanosine, a biomarker of oxidative DNA damage, in urban bus drivers. Mutat Res 441:11-19.

Lowenthal, DH; Chow, JC; Watson, JG; et al. (1992) The effects of collinearity on the ability to determine aerosol contributions from diesel- and gasoline-powered vehicles using the chemical mass balance model. Atmos Environ 26A(13):2341-2351.

Lowenthal, DH, Zielinska, B., Chow, JC, Watson, JG, Gautam, M., Ferguson, DH, Neuroth, GR, Stevens, KD (1994) Characterization of heavy-duty diesel vehicle emissions. Atmos. Environ. 28:731-743.

Lucas, A; Duran, A; Carmona, M; et al. (1999) SAE Technical Paper Ser. No. 1999-01-3532.

Lüders, H; Stommel, P; Backes, R. (1997) Applications for the regeneration of diesel particulate traps by combining different regeneration systems. SAE Technical Paper Ser. No. 970470.

Lüders, H, Kruger, M, Strommel, P, Luers, B (1998) The role of sampling conditions in particle size distribution measurements. SAE Technical Paper Ser. No. 981374.

Maricopa Association of Governments (1999) The 1999 Brown Cloud Project for the Maricopa Association of Governments Area, Final Report, December 1999.

Marklund, S.; Andersson, R.; Tysklind, M.; Rappe, C.; Egeback, K.E.; Bjorkman, E.; Grigoriadis, V. (1990) Emissions of PCDDs and PCDFs in gasoline and diesel fueled cars. Chemosphere 20(5):553-561.

Martin, S. (1981a) Emissions from heavy-duty engines using the 1984 transient test procedure. Volume II–diesel. EPA/460/3-81/031.

Martin, S. (1981b) Diesel particulate by 1986 HD transient Federal test procedure. Final report. Prepared by Southwest Research Institute under contract no. 68-03-2603.

Martin, S. (1984) Emissions from two in-use heavy-duty diesel engines. Final report. Prepared by Southwest Research Institute. EPA/460/3-84/017.

Mauderly, J. (1992) Diesel exhaust. In: Environmental toxicants: human exposures and their health effects. Lippmann, M, ed. New York: Van Nostrand Reinhold, pp. 119-162.

McCarthy, CI; Slodowske, WJ; Sienicki, EJ; et al. (1992) Diesel fuel property effects on exhaust emissions from a heavy duty diesel engine that meets 1994 emissions requirements. SAE Technical Paper Ser. No. 922267.

McClure, BT; Bagley ST; Gratz, LD. (1992) The influence of an oxidation catalytic converter and the fuel composition on the chemical and biological characteristics of diesel exhaust emissions. SAE Technical Paper Ser. No. 920854.

McCormick, RL; Ryan, LBA; Daniels, TL; et al. (1998) Comparison of chassis dynamometer in-use emissions with engine dynamometer FTP emissions for three HD diesel vehicles. SAE Technical Paper Ser No. 982653.

McCormick, RL; Graboski, MS; Alleman, TL; et al. (1999) In-use emissions from natural gas fueled HD vehicles. SAE Technical Paper Ser. No. 1999-01-1507.

McCormick, RL; Alleman, TL; Graboski, MS; et al. (2000) Quantifying the emissions benefit of opacity testing and repair of heavy-duty diesel vehicles. Proceedings of the 10th Coordinating Research Council On-Road Vehicle Emissions Workshop, March 27-29, 2000, San Diego, CA.

McDonald, JF. (1997) The emissions and combustion characteristics of a soy-methyl-ester biodiesel fuel in a naturally aspirated indirect injection diesel engine. MS thesis, University of Minnesota.

McDonald, J; Purcell, DL; McClure, BT. (1995) Methyl ester oxygenated fuels for diesel mining applications. In: Proceedings of the 7th U.S. Mine Ventilation Symposium, Society for Mining, Metallurgy, and Exploration, Inc.

McDow, SR; Sun, Q; Vartiainen, M; et al. (1994) Effect of composition and state of organic components on polycyclic aromatic hydrocarbon decay in atmospheric aerosols. Environ Sci Technol 28:2147.

McGuckin, J; Rykowski, R. (1981) Correlation between smoke and particulate emissions from HD diesel engines. Technical Report, Office of Mobile Sources, U.S. Environmental Protection Agency, Washington, DC.

McKinley, TL. (1997) Modeling sulfuric acid condensation in diesel engine EGR coolers. SAE Technical Paper Ser. No. 970636.

Miguel, AH; Kirchstetter, TW; Harley, RA; et al. (1998) On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles. Environ Sci Technol 32:450-455.

Mitchell, K; Steere, DE; Taylor, JA; et al. (1994) Impact of diesel fuel aromatics on particulate, PAH, and nitro-PAH emissions. SAE Technical Paper Ser. No. 942053.

Mori, K. (1997) Worldwide trends in HD diesel engine exhaust emission legislation and compliance technologies. SAE Technical Paper Ser. No. 970753.

Muzyka, V; Veimer, S; Schmidt, N. (1998) On the carcinogenic risk evaluation of diesel exhaust: benzene in airborne particles and alterations of heme metabolism in lymphocytes as markers of exposure. Sci Total Environ 217:103-111.

National Institute for Occupational Safety and Health (NIOSH). (1988) Carcinogenic effects of exposure to diesel exhaust. Current Intelligence Bulletin 50. No. 88-116. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, OH.

National Institute for Occupational Safety and Health (NIOSH). (1990) Health hazard evaluation report. Prepared by Yellow Freight System, Inc. HETA 90-088-2110.

National Institute for Occupational Safety and Health (NIOSH). (1992) Health Hazard Evaluation Report: City of Lancaster, Division of Fire, Lancaster, OH. NIOSH Report No. HHE HETA 92-0160-2360, NTIA No. PB-94140142. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, OH.

National Institute for Petroleum and Energy Research (NIPER). (1986 and earlier years) Diesel fuel oils, annual survey.

National Research Council. (1982) Diesel cars: benefits, risks and public policy. Final report of the Diesel Impacts Study Committee. Washington, DC: National Academy Press.

Needham, JR; Doyle, DM; Faulkner, SA; et al. (1989) Technology for 1994. SAE Technical Paper Ser. No. 891949.

Nielsen, T; Ramdahl, T. (1986) Discussion on determination of 2-nitrofluoranthene and 2-nitropyrene in ambient particulate matter: evidence for atmospheric reactions. Atmos Environ 20:1507.

Nielsen, PS; Andreassen, A; Farmer, PB; et al. (1996) Biomonitoring of diesel exhaust-exposed workers. DNA and hemoglobin adducts and urinary 1-hydroxypyrene as markers of exposure. Toxicology Letters 86:27-37.

Noorkhoek, J; Bos, RP. (1995) 1-Nitropyrene as a marker for the mutagenicity of diesel exhaust derived particulate matter in workplace atmospheres. Environ Mol Mutagen 25:134.

Norbeck, JM; Truex, TJ; Smith, MR; et al. (1998a) Evaluation of factors that affect diesel exhaust toxicity. Final report, prepared under Contract No. 94-312, for California Air Resources Board, by the Center for Environmental Research and Technology, College of Engineering, University of California, Riverside, CA.

Norbeck, JM; Durbin, TD; Truex, TJ; et al. (1998b) Characterizing particulate emissions from medium- and light heavy-duty diesel-fueled vehicles. Final report. Prepared for South Coast Air Quality Management District by for California Air Resources Board by the Center for Environmental Research and Technology, College of Engineering, University of California, Riverside, CA, under contract no. 97031.

Norbeck, JM; Durbin, TD; Truex, TJ. (1998c) Measurement of primary particulate matter emissions from light-duty motor vehicles. Prepared for Coordinating Research Council, Inc., and South Coast Air Quality Management District, by Center for Environmental Research and Technology, College of Engineering, University of California, Riverside, CA, 1998.

Norris, GA; Birch, ME; Tolocka, MP; et al. (2000) Comparison of particulate organic and elemental carbon measurements made with the IMPROVE and NIOSH method 5040 protocols. Aerosol Sci Technol, in press.

Northridge, ME; Yankura, J; Kinney, PL; et al. (1999) Diesel exhaust exposure among adolescents in Harlem: a community-driven study. Am J Public Health 89:998-1002.

Odum, JR; McDow, SR; Kamens, RM. (1994) Mechanistic and kinetic studies of the photodegradation of benz[a]anthracene in the presence of methoxyphenols. Environ Sci Technol 28:1285.

Oehme, M; Larssen, S; Brevik, EM. (1991) Emission factors of PCDD/CDF for road vehicles obtained by a tunnel experiment. Chemosphere 23:1699-1708.

Opris, CN; Gratz, LD; Bagley, ST; et al. (1993) The effects of fuel sulfur concentration on regulated and unregulated HD diesel emissions. SAE Technical Paper Ser. No. 930730.

Pagan, J. (1999) Study of particle size distributions emitted by a diesel engine. SAE Technical Paper Ser. No. 1999-01-1141.

Paputa-Peck, MC; Marano, RS; Schuetzle, D; et al. (1983) Determination of nitrated polynuclear aromatic hydrocarbons in particulate extracts by capillary column gas chromatography with nitrogen selective detection. Anal Chem 55:1946-1954.

Pataky, GM; Baumgard, KJ; Gratz, LD; et al. (1994) Effects of an oxidation catalytic converter on regulated and unregulated diesel emissions. SAE Technical Paper Ser. No. 940243.

Perez, JM. (1980) Measurement of unregulated emissions--some heavy-duty diesel engine results. Health Effects of Diesel Engine Emissions, EPA/600/9-80/057a.

Perez, JM; Williams, RL. (1989) A study of particulate extracts from 1980s heavy duty diesel engines run on steady-state and transient cycles. SAE Technical Paper Ser. No. 892491.

Peters, A; Langer, H-J; Joki, B; et al. (1998) Catalytic NO_x reduction on a passenger car diesel common rail engine. SAE Technical Paper Ser. No. 980191.

Pierson, WR; Brachaczek, WW. (1976) Particulate matter associated with vehicles on the road. SAE Trans 85:209-227.

Pierson, WR; Brachaczek, WW. (1983) Particulate matter associated with vehicles on the road. Aerosol Sci Tech 2:1-40.

Pierson, WR; Gertler, AW; Robinson, NF; et al. (1996) Real-world automotive emissions--summary of studies in the Fort McHenry and Tuscarora mountain tunnels. Atmos Environ 30:2233-2256.

Pischinger, R; Cartellieri, W. (1972) Combustion system parameters and their effect on diesel engine exhaust emissions. SAE Technical Paper Ser. No. 720756.

Pitts, JN, Jr; Van Cauwenberghe, KA; Grosjean, D; et al. (1978) Atmospheric reactions of polycyclic aromatic hydrocarbons: facile formation of mutagenic nitro derivatives. Science 202:515-519.

Pitts, JN, Jr; Lokensgard, DM; Ripley, PS; et al. (1980) Atmospheric epoxidation of benzo[a]pyrene by ozone: formation of the metabolite benzo[a]pyrene-4,5-oxide. Science 210:1347-1349.

Pitts, JN, Jr; Sweetman, JA; Zielinska, B; et al. (1985a) Determination of 2-nitrofluoranthene and 2-nitropyrene in ambient particulate matter: evidence for atmospheric reaction. Atmos Environ 19:1601-1608.

Pitts, JN, Jr; Zielinska, B; Sweetman, JA; et al. (1985b) Reaction of adsorbed pyrene and perylene with gaseous N_2O_5 under simulated atmospheric conditions. Atmos Environ 19:911-915.

Pitts, JN, Jr; Sweetman, JA; Zielinska, B; et al. (1985c) Formation of nitroarenes from the reaction of polycyclic aromatic hydrocarbons with dinitrogen pentoxide. Environ Sci Technol 19:1115-1121.

Pitts, JN, Jr; Paur, HR; Zielinska, B; et al. (1986) Factors influencing the reactivity of polycyclic aromatic hydrocarbons adsorbed on filters and ambient POM with ozone. Chemosphere 15:675-685.

Prinn, R; Cunnold, D; Simmonds, P; et al. (1992) Global average concentration and trend for hydroxyl radicals deduced from ALE/GAGE trichloroethane (methyl chloroform data for 1978-1990). J Geophys Res 97:2445-2461.

Rantanen, L; Mikkonen, S; Nylund, L; et al. (1993) Effect of fuel on the regulated, unregulated and mutagenic emissions of DI diesel engines. SAE Technical Paper Ser. No. 932686.

Rideout, G; Kirshenblatt, M; Prakash, C. (1994) Emissions form methanol, ethanol, and diesel powered urban transit buses. SAE Technical Paper Ser. No. 942261.

Rogak, SN; Pott, U; Dann, T; et al. (1998) Gaseous emissions from vehicles in a traffic tunnel in Vancouver, British Columbia. J Air Waste Manage Assoc 48:604-615.

Rogers, A; Whelan, B. (1999) Exposures in Australian mines. Health Effects Institute Number 7. March 7-9, 1999 Stone Mountain, GA.

Rogge, WF; Hildemann, LM; Mazurek, MA; et al. (1993) Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and HD diesel trucks. Environ Sci Technol 27:636-651.

Salmon, LG; Cass, GR; Pedersen, DU; et al. (1997) Determination of fine particle concentration and chemical composition in the northeastern United States, 1995. Progress Report to Northeast States for Coordinated Air Use Management (NESCAUM), October 1997.

Sampson, PJ. (1988) Atmospheric transport and dispersion of air pollutants associated with vehicular emissions. In: Air pollution, the automobile and public health. Watson, AY; Bates, RR; Kennedy, D, eds. Washington, DC: National Academy Press, pp. 77-97.

Säverin, R. (1999) German potash miners: cancer mortality. Health Effects Institute Number 7. March 7-9, 1999 Stone Mountain, GA. pp. 220-229.

Sawyer, RF; Johnson, JH. (1995) Diesel emissions and control technology. In: Diesel exhaust: a critical analysis of emissions, exposure, and health effects. Cambridge, MA: Health Effects Institute, pp. 65-81.

Schauer, JJ; Rogge, WF; Hildemann, LM; et al. (1996) Source apportionment of airborne particulate matter using organic compounds as tracers. Atmos Environ 30(22):3837-3855.

Schauer, JJ; Kleeman, MJ; Cass, GR; et al. (1999) Measurement of emissions from air pollution sources. 2. C_1 through C_{30} organic compounds from medium duty diesel trucks. Environ Sci Technol 33:1578-1587.

Scholl, JP; Bagley, ST; Leddy, DG; et al. (1982) Study of aftertreatment and fuel injection variables for particulate control in heavy-duty diesel engines. EPA-460/3-83-002.

Schuetzle, D. (1983) Sampling of vehicle emissions of chemical analysis and biological testing. Environ Health Perspect 47:65-80.

Schuetzle, D; Frazier, JA. (1986) Factors influencing the emission of vapor and particulate phase components from diesel engines. In: Carcinogenic and mutagenic effects of diesel engine exhaust. London: Elsevier Science Limited, pp. 41-63.

Schuetzle, D; Perez, JM. (1983) Factors influencing the emissions of nitrated-polynuclear aromatic hydrocarbons (nitro-PAH) from diesel engines. J Air Pollut Control Assoc 33:751-755.

Schuetzle, D; Jensen, TE; Ball, JC. (1985) Polar polynuclear aromatic hydrocarbon derivatives in extracts of particulates: biological characterization and techniques for chemical analysis. Environ Int 11:169-181.

Schwind, K-H; Thoma, H; Hutzinger, O; et al. (1991) Emission halogenierter dibenzodioxine (PXDD) und dibenzofurane (PXDF) aus verbrennungsmotoren. UWSF-Z. Umweltchem. Oekotox. 3, 291-298. [English translation]

Seinfeld, JH; Pandis, SN. (1998) Atmospheric chemistry and physics: from air pollution to climate change. New York: John Wiley & Sons, Inc.

Shelton, EM. (1977) Diesel fuel oils. BERC/PPS-77/5.

Shelton, EM. (1979) Diesel fuel oils. BETC/PPS-79/5.

Shi, JP; Harrison, RM. (1999) Investigation of ultrafine particle formation during diesel exhaust dilution. Environ Sci Technol 33:3730-3736.

Shi, JP; Mark, D; Harrison, RM. (2000) Characterization of particles from a current technology heavy-duty diesel engine. Environ Sci Technol 34:748-755.

Sienicki, EJ; Jass, RE; Slodowske, WJ; et al. (1990) Diesel fuel aromatic and cetane number effects on combustion and emissions from a prototype 1991 diesel engine. SAE Technical Paper Ser. No. 902172.

Sisler, JF. (1996) Spatial and seasonal patterns and long term variability of the composition of the haze in the United States: an analysis of data from the IMPROVE network. Cooperative Institute for Research in the Atmosphere. Colorado State University. ISSN: 0737-5352-32.

South Coast Air Quality Management District (SCAQMD). (2000) Multiple air toxics exposure study (MATES-II). Final Report and Appendices, March 2000.

Spreen, KB; Ullman, TL; Mason, RL. (1995) Effects of fuel oxygenates, cetane number, and aromatic content on emissions from 1994 and 1998 prototype heavy-duty diesel engines. Final report. Prepared by Southwest Research Institute under Contract No. VE-10.

Springer, KJ. (1979) Characterization of sulfates, odor, smoke, POM and particulates from light and heavy duty engines--part IX. Prepared by Southwest Research Institute. EPA/460/3-79/007.

Springer, KJ; White, JT; Domke, CJ. (1974) Emissions from in-use 1970-1971 diesel-powered trucks and buses. SAE Technical Paper Ser. No. 741006.

Stone, R. (1995) Introduction to internal combustion engines. Warrendale, PA: Society of Automotive Engineers.

Sweetman, JA; Zielinska, B; Atkinson, R; et al.(1986) A possible formation pathway for the 2-nitrofluoranthene observed in ambient particulate organic matter. Atmos Environ 20:235-238.

Tamanouchi, M; Morihisa, H; Araki, H; et al. (1998) Effects of fuel properties and oxidation catalyst on exhaust emissions for heavy duty diesel engines and diesel passenger cars. SAE Technical Paper Ser. No. 980530.

Tanaka, S; Takizawa, H; Shimizu, T; et al. (1998) Effect of fuel compositions on PAH in particulate matter from DI diesel engines. SAE Technical Paper Ser. No. 982648.

Tancell, PJ; Rhead, MM; Trier, CJ; et al. (1995) The sources of benzo[a]pyrene in diesel exhaust emissions. Sci Total Environ 162:179-186.

Taylor, CF. (1990) The internal combustion engine in theory and practice - volume 1. Cambridge, MA: MIT Press.

Thrane, KE; Mikalsen, A. (1981) High-volume sampling of airborne polycyclic aromatic hydrocarbons using glass fibre filters and polyurethane foam. Atmos Environ 15:909-918.

Tokiwa, H; Sera, N; Nakanishi, Y; et al. (1999) 8-Hydroyguanosine formed in human lung tissues and the association with diesel exhaust particles. Free Rad Biol Med 27:1251-1258.

Tong, HY; Sweetman, JA; Karasek, FW; et al. (1984) Quantitative analysis of polycyclic aromatic compounds in diesel exhaust particulate extracts by combined chromatographic techniques. J Chromatogr 312:183-202.

Ullman, TL; Hare, CT; Baines, TM. (1984) Preliminary particulate trap tests on a 2-stroke diesel bus engine. SAE Technical Paper Ser. No. 840079.

Ullman, TL. (1988) Emissions evaluation of two heavy-duty diesel engines on two low-sulfur fuels with variation in aromatics. Final report. Prepared by Southwest Research Institute for California Air Resources Board under contract no. A4-132-32.

Ullman, TL; Mason, RL; Montalvo, DA. (1990) Effects of fuel aromatics, cetane number, and cetane improver on emissions from a 1991 prototype heavy-duty diesel engine. SAE Technical Paper Ser. No. 902171.

Ullman, TL; Spreen, KB; Mason, RL. (1995) Effects of cetane number on emissions from a prototype 1998 HD diesel engine. SAE Technical Paper Ser. No. 950251.

U.S. Bureau of the Census. (1995) Truck inventory and use survey. 1992 Census of Transportation, TC92-T-52.

U.S. Bureau of the Census. (1999a) 1997 Economic census, vehicle inventory and use survey. EC97TV-US.

U.S. Bureau of the Census. (1999b) Truck inventory and use survey. 1997 Census of Transportation, EC97-TV-US.

U.S. EPA. (1992) Highway vehicle emission estimates. Office of Mobile Sources.

U.S. EPA. (1995) Highway vehicle emissions estimates. Office of Mobile Sources.

U.S. EPA. (1998a) National air pollutant emission trends update, 1970-1997. EPA/454/E-98-007.

U.S. EPA. (1998b) Locomotive emission standards. Office of Mobile Sources Regulatory Support Document.

U.S. EPA. (1999a) Air quality criteria for particulate matter. External review draft, October 1999.

U.S. EPA. (1999b) Fleet characterization data for MOBILE6: development and use of age distributions, average annual mileage accumulation rates and projected vehicle counts for use in MOBILE6. EPA/420/P-99-011.

U.S. EPA. (1999c) Analysis of the Impacts of control programs on motor vehicle toxic emissions and exposure in urban areas and nationwide: volume I and II. Prepared for EPA by Sierra Research, Inc. and Radian International Corporation/Eastern Research Group, November 30, 1999. Report Nos. EPA/420/R-99/029 and EPA/420/R-99/030.

U.S. EPA. (2000a) National air pollutant emission trends, 1900-1998. EPA-454/R-00-002, March 2000.

U.S. EPA. (2000b) Proposed heavy-duty engine and vehicle standards and highway diesel fuel sulfur control requirements. Draft regulatory impact analysis. Office of Transportation and Air Quality. EPA420-D-00-001.

Unnasch, S; Lowell, D; Lonyai, F; et al. (1993) Performance and emissions of clean fuels in transit buses with Cummins L10 engines. SAE Technical Paper Ser. No. 931782.

Van Vaeck, L; Van Cauwenberghe, K. (1984) Conversion of polycyclic aromatic hydrocarbons on diesel particulate matter upon exposure to ppm levels of ozone. Atmos Environ 18:323-328.

Van Vaeck, L; Van Cauwenberghe, K; Janssens, J. (1984) The gas-particle distribution of organic aerosol constituents: measurements of the volatilisation artifact in hi-vol cascade impactor sampling. Atmos Environ 18:417-430.

Voss, JR; Vanderpoel, RE. (1977) The shuttle distributor for a diesel fuel injection pump. SAE Technical Paper Ser. No. 770083.

Wachter, WF. (1990) Analysis of transient emission data of a model year 1991 heavy duty diesel engine. SAE Technical Paper Ser. No. 900443.

Wall, JC. (1998) Diesel fuel composition for future emissions regulations. Cummins Engine Co. panel discussion, SAE International Fall Fuels and Lubricants Meeting and Exposition, October 21, 1998.

Wall, JC; Shimpi, SA; Yu, ML. (1987) Fuel sulfur reduction for control of diesel particulate emissions. SAE Technical Paper Ser. No. 872139.

Wang, W; Gautam, M; Sun, X; et al. (1993) Emissions comparisons of twenty-six HD vehicles operated on conventional and alternative fuels. SAE Technical Paper Ser. No. 932952.

Wang, WG; Lyons, D; Bata, R; et al. (1994) In-use emissions tests of alternatively fueled HD vehicles by a chassis dynamometer testing facility. SAE Technical Paper Ser. No. 945124.

Warner-Selph, MA; Dietzmann, HE. (1984) Characterization of HD motor vehicle emissions under transient driving conditions. Prepared by Southwest Research Institute. EPA/600/3-84/104.

Watson, N; Janota, MS. (1982) Turbocharging the internal combustion engine. New York: John Wiley and Sons.

Watson, JG; Fujita, EM; Chow, JC; et al. (1998) Northern Front Range Air Quality Study final report. Prepared by Desert Research Institute for Colorado State University, Cooperative Institute for Research in the Atmosphere, 1998.

Watts, FW, Jr. (1995) Assessment of occupational exposure to diesel emissions. In: Diesel exhaust: a critical analysis of emissions, exposure, and health effects. Cambridge, MA: Health Effects Institute, pp. 107-123.

Weaver, CS, Klausmeier, RF. (1988) Heavy-duty diesel vehicle inspection and maintenance study. Final Report Vol. 1: Summary Report to California Air Resources Board, Contract No. A4-151-32.

Weingartner, E; Burtscher, H; Baltensperger, U. (1997a) Hygroscopic properties of carbon and diesel soot particles. Atmos. Environ. 31:2311-2327.

Weingartner, E; Keller, C; Stahel, WA; et al. (1997b) Aerosol emissions in a road tunnel. Atmos Environ 31(3):451-462.

Wevers, M; De Fre, R; Rymen, T. (1992) Dioxins and dibenzofurans in tunnel air. In: Sources of exposure. Extended Abstracts, vol. 9. Organo Comp 9:321-324.

Whitby, KT; Sverdrup, GM. (1980) California aerosols: their physical and chemical characteristics. In: Hidy, GM; Mueleeer, PD; Grosjean, D; et al., eds. The character and origins of smog aerosols: a digest of results from the California Aerosol Characterization Experiment (ACHEX). New York, NY: John Wiley & Sons, Inc., pp. 477-517. (Advances in environmental science and technology: v.9).

Whitfield, JK; Harris, DB. (1998) Comparison of HD diesel emissions from engine and chassis dynamometers and on-road testing. 8th Coordinating Research Council On-Road Vehicle Emissions Workshop: San Diego, CA.

Williams, PT; Andrews, GE; Bartle, KD. (1987) The role of lubricating oil in diesel particulate and particulate PAH emissions. SAE Technical Paper Ser. No. 872084.

Williams, DJ; Milne, JW; Quigley, SM; et al. (1989) Particulate emissions from in-use motor vehicles. II. Diesel vehicles. Atmos Environ 23(12):2647.

Wittorff, DN; Gertler, AW; Chow, JC; et al. (1994) The impact of diesel particulate emissions on ambient particulate loadings. Air & Waste Management Association 87th Annual Meeting, Cincinnati, OH, June 19-24, 1994.

Winer, AM; Busby, WF, Jr. (1995) Atmospheric transport and transformation of diesel emissions. In: Diesel exhaust: a critical analysis of emissions, exposure, and health effects. Cambridge, MA: Health Effects Institute, pp. 84-105.

Woskie, SR; Smith, TJ; Hammond, SK; et al. (1988) Estimation of the diesel exhaust exposures of railroad workers. I. Current exposures. Am J Ind Med 13:381-394.

Yamasaki, H; Kuwata, K; Miyamoto, H. (1982) Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. Environ Sci Technol 16:189-194.

Yanowitz, J; Graboski, MS; Ryan, LBA; et al. (1999) Chassis dynamometer study of emissions from 21 in-use HD diesel vehicles. Environ Sci Technol 33:209-216.

Yanowitz, J; McCormick, RL; Graboski, MS. (2000) Critical review: in-use emissions from HD diesel vehicles. Environ Sci Technol. 34:729-740.

Yokely, RA; Garrison, AA; Wehry, EL; et al. (1986) Photochemical transformation of pyrene and benzo[a]pyrene vapor-deposited on eight coal stack ashes. Environ Sci Technol 20:86-90.

Zaebst, DD; Blad, LM; Morris, JA; et al. (1988) Elemental carbon as a surrogate index of diesel exhaust exposure. In: Proceedings of the American Industrial Hygiene Conference, May 15-20, 1988, San Francisco, CA.

Zaebst, DD; Clapp, DE; Blake, LM; et al. (1991) Quantitative determination of trucking industry workers' exposures to diesel exhaust particles. Am Ind Hyg Assoc J 52:529-541.

Zelenka, P; Kriegler, W; Herzog, PL; et al. (1990) Ways toward the clean HD diesel. SAE Technical Paper Ser. No. 900602.

Zielinska, B. (1999) Changes in diesel engine emissions over the last two decades. Diesel workshop: building a research strategy to improve risk assessment. Health Effects Institute Number 7. March 7-9, 1999, Stone Mountain, GA.

Zielinska, B; Arey, J; Atkinson, R; et al. (1986) Reaction of dinitrogen pentoxide with fluoranthene. J Am Chem Soc 108:4126-4132.

Zielinska, B; Arey, J; Atkinson, R; et al. (1988) Nitration of acephenanthrylene under simulated atmospheric conditions and in solution and the presence of nitroacephenanthrylene(s) in ambient air. Environ Sci Technol 22:1044-1048.

Zielinska, B; Arey, J; Atkinson, R; et al. (1989a) Formation of methylnitronaphthalenes from the gas-phase reactions of 1- and 2-methylnaphthalene with OH radicals and N_2O_5 and their occurrence in ambient air. Environ Sci Technol 23:723-729.

Zielinska, B; Arey, J; Atkinson, R; et al. (1989b) The nitroarenes of molecular weight 247 in ambient particulate samples collected in southern California. Atmos Environ 23:223-229.

Zielinska, B; Arey, J; Atkinson, R. (1990) The atmospheric formation of nitroarenes and their occurrence in ambient air. In: Proceedings of the Fourth International Conference on N-Substituted Aryl Compounds: Occurrence, Metabolism and Biological Impact of Nitroarenes. Cleveland, OH, July 1989.

Zielinska, B; McDonald, J; Hayes, T; et al. (1998) Northern Front Range Air Quality Study, volume B: source measurements. Desert Research Institute.

Zwirner-Baier, I; Neumann, H-G. (1999) Polycyclic nitroaarenes (nitro-PAHs) as biomarkers of exposure to diesel exhaust. Mut Res 441:135-144.