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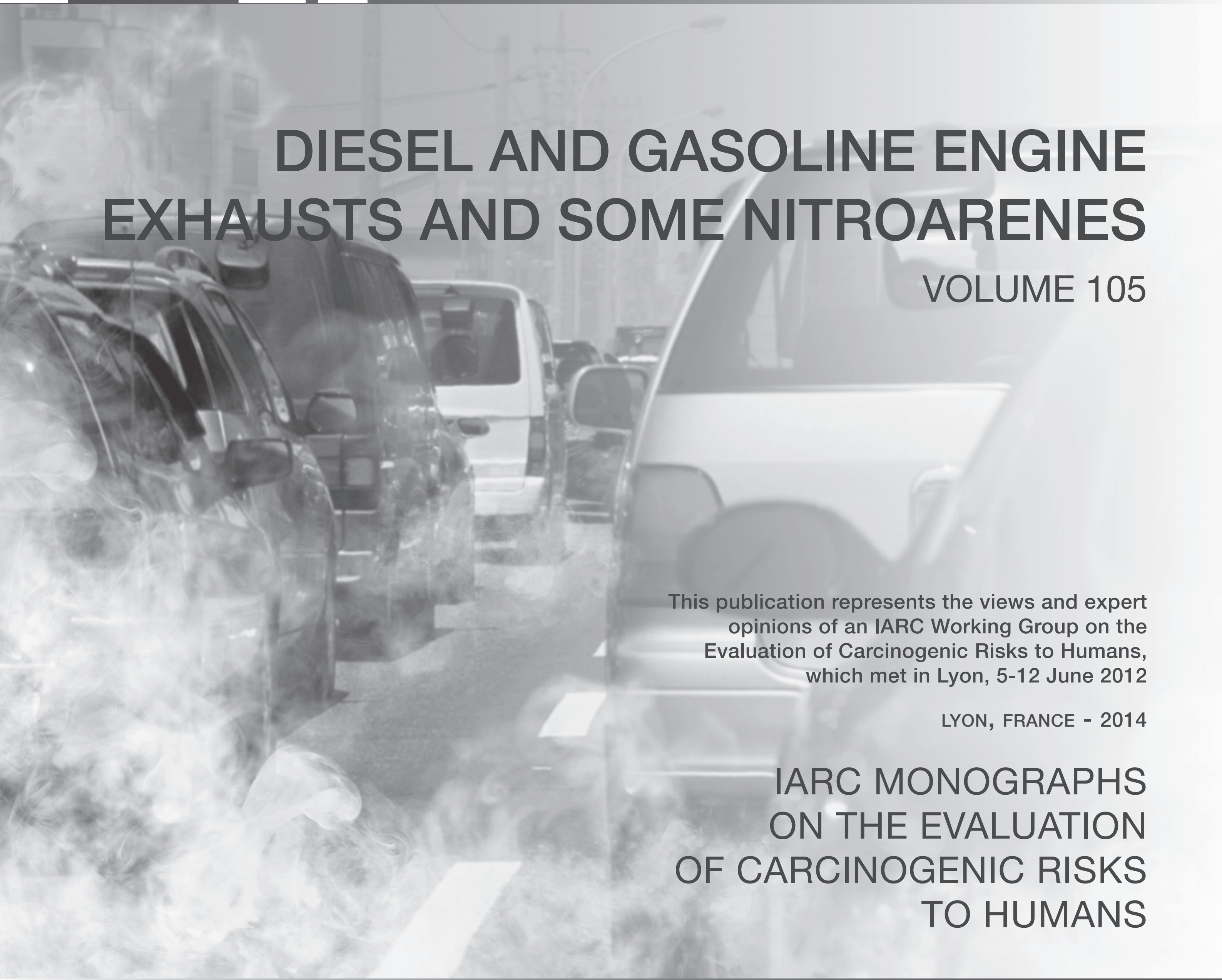

DIESEL AND GASOLINE ENGINE EXHAUSTS AND SOME NITROARENES

VOLUME 105

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International Agency for Research on Cancer

World Health Organization

1. EXPOSURE DATA

Diesel and gasoline engine exhausts were evaluated by a previous IARC Working Group in 1988 (IARC, 1989a). New data have since become available, and these have been taken into consideration in the present evaluation.

1.1 Diesel and gasoline engines and the chemical composition of their exhausts

Diesel and gasoline engines are the major power sources used in motor vehicles. Both are internal, intermittent combustion engines but differ fundamentally in terms of the way in which their mixtures are prepared and ignition (for reviews, see Heywood, 1989; Stone, 1999; Majewski & Khair, 2006).

In diesel engines, air is introduced into the engine and heated by compression to temperatures in excess of 700 °K. The fuel is introduced into the combustion chamber by a high-pressure injection system and is mixed with the hot air until the fuel jet becomes sufficiently hot for auto-ignition to occur. The centre of this burning jet is very rich in fuel, which leads to the formation of elemental carbon (EC), partially burned fuel, polycyclic aromatic hydrocarbons (PAHs) and carbon monoxide (Flynn *et al.*, 1999). At the outer edges of the burning jet, excess air leads to high temperatures and the formation of nitrogen oxides.

In contrast, in port-fuel injection gasoline engines, fuel and air are mixed before entering the cylinder and the mixture of fuel and air is compressed. To prevent auto-ignition (knock), the compression ratio is much lower than that in a diesel engine, leading to slightly reduced efficiency. In a gasoline engine, the mixture is ignited with a spark, and a flame propagates across the combustion chamber. Premixing the fuel and air minimizes local fuel-rich conditions and normal gasoline combustion produces little soot. In contrast, high temperatures in the flame zone lead to the formation of carbon monoxide and nitrogen oxides, and flame quenching near the walls leads to the presence of unburned and partially oxidized hydrocarbons.

The fuels used in diesel and gasoline engines also differ. Diesel fuel is made up of petroleum fractions with a higher boiling range, has a higher density and contains approximately 13% more energy per unit volume of gasoline.

Hydrocarbon combustion by-products include nitrogen oxides, carbon monoxide, unburned and partially burned hydrocarbons, soot (mainly EC and particle-bound organic carbon) and some nitrated species. Engine exhaust also contains partially burned lubricating oil, and ash from metallic additives in the lubricating oil and wear metals. These combustion by-products represent thousands of chemical components present in the gas and particulate phases (Zaebst *et al.*, 1988); some specific chemical species and classes found in engine exhaust are listed in Table 1.1. Agents found in engine exhaust and evaluated by the IARC as group 2B, 2A or 1 are

Table 1.1 Some compounds and classes of compound in vehicle engine exhaust

Gas phase	Particulate phase
Acrolein	Heterocyclics and derivatives[a]
Ammonia	Hydrocarbons (C_{14}–C_{35}) and derivatives[a]
Benzene	Inorganic sulfates and nitrates
1,3-Butadiene	Metals (e.g. lead and platinum)
Formaldehyde	Polycyclic aromatic hydrocarbons and derivatives[a]
Formic acid	
Heterocyclics and derivatives[a]	
Hydrocarbons (C_1–C_{18}) and derivatives[a]	
Hydrogen cyanide	
Hydrogen sulfide	
Methane	
Methanol	
Nitric acid	
Nitrous acid	
Oxides of nitrogen	
Polycyclic aromatic hydrocarbons and derivatives[a]	
Sulfur dioxide	
Toluene	

[a] Derivatives include acids, alcohols, aldehydes, anhydrides, esters, ketones, nitriles, quinones, sulfonates, halogenated and nitrated compounds, and multifunctional derivatives.

From National Research Council (1983), Lies *et al.* (1986), Schuetzle & Frazier (1986), Carey (1987), Johnson (1988), Zaebst *et al.* (1988)

listed in Table 1.2. Diesel emission standards and diesel engine technology are closely linked: standards drive the technology and technology enables more stringent standards. The concentration of a chemical species in vehicle exhaust is a function of several factors, including the type and operating conditions of the engine, the compositions of the fuel and lubricating oil used and the presence of an emission control system (Johnson, 1988).

1.1.1 Diesel engine technology

(a) Historical and technical overview

Rudolf Diesel patented the Diesel engine in 1898. In the early part of the twentieth century, diesel engines were used mainly in marine applications, and were then installed in heavy goods vehicles (HGVs) in Europe in the 1920s. In the 1930s, manufacturers in the USA started to install diesel engines in commercial HGVs, buses and tracked vehicles. The first mass-produced diesel passenger car was introduced in Europe in 1936. Diesel engines had replaced steam power in railroad locomotives by the early 1950s, and had replaced gasoline engines in most HGVs by the 1960s. Today, diesel engines power all types of automotive vehicles: passenger cars (up to 50% of new car sales in some European countries), commercial vehicles, buses, industrial, agricultural and construction equipment, mine vehicles, locomotives, ships and many stationary power applications (Busch-Sulzer, 1913; Cummins, 1967; Hind, 1974; Cummins, 1993; IRSG, 2012a, b).

In a diesel engine, fuel is introduced into the engine by a high-pressure fuel injection system and mixes with air that has been heated by compression. Combustion begins when the fuel–air mixture becomes sufficiently hot for auto-ignition to occur. Common diesel engine configurations include indirect and direct

Table 1.2 Chemicals and metals found in diesel and gasoline engine exhaust and their evaluation by IARC

Agent	CAS No.	Evaluation	Volume (reference)
Metals			
Antimony compounds	1309-64-4 (Trioxide)	2B	47 (IARC, 1989b)
Arsenic and inorganic arsenic compounds	007440-38-2	1	100C (IARC, 2012a)
Beryllium and beryllium compounds	007440-41-7	1	100C (IARC, 2012a)
Cadmium and cadmium compounds	007440-43-9	1	100C (IARC, 2012a)
Chromium (VI)	018540-29-9	1	100C (IARC, 2012a)
Cobalt and cobalt compounds	007440-48-4	2B	52 (IARC, 1991)
Lead compounds	Inorganic/organic	2A/3	87 (IARC, 2006)
Nickel	Metallic/compounds	2B/1	100C (IARC, 2012a)
Organic chemicals			
1,3-Butadiene	106-99-0	1	100F (IARC, 2012b)
Acetaldehyde	75-07-0	2B	71 (IARC, 1999)
Benzene	71-43-2	1	100F (IARC, 2012b)
Bis(ethylhexyl)phthalate	117-81-7	2B	101 (IARC, 2012c)
Ethylbenzene	100-41-4	2B	77 (IARC, 2000)
Formaldehyde	50-00-0	1	100F (IARC, 2012b)
Propylene oxide	75-56-9	2B	60 (IARC, 1994)
Halogenated and other chemicals			
Dioxin/dibenzofurans	1746-01-6 (TCDD)	1	100F (IARC, 2012b)
Polycyclic aromatic hydrocarbons			
Benz[*a*]anthracene	56-55-3	2B	92 (IARC, 2010)
Benzo[*b*]fluoranthene	205-99-2	2B	92 (IARC, 2010)
Benzo[*k*]fluoranthene	207-08-9	2B	92 (IARC, 2010)
Benzo[*a*]pyrene	5-32-8	1	100F (IARC, 2012b)
Chrysene	218-01-9	2B	92 (IARC, 2010)
Dibenz[*a,h*]anthracene	53-70-3	2A	92 (IARC, 2010)
3,7-Dinitrofluoranthene	105735-71-5	2B	This volume
3,9-Dinitrofluoranthene	22506-53-2	2B	This volume
1,3-Dinitropyrene	75321-20-9	2B	This volume
1,6-Dinitropyrene	42397-64-8	2B	This volume
1,8-Dinitropyrene	42397-64-9	2B	This volume
Indeno[1,2,3-*cd*]pyrene	193-39-5	2B	92 (IARC, 2010)
Naphthalene	91-20-3	2B	82 (IARC, 2002)
3-Nitrobenzanthrone	17 117-34-9	2B	This volume
6-Nitrochrysene	7496-02-8	2A	This volume
2-Nitrofluorene	607-57-8	2B	This volume
1-Nitropyrene	5522-43-0	2A	This volume
4-Nitropyrene	57835-92-4	2B	This volume
Styrene	100-42-5	2B	82 (IARC, 2002)

TCDD, 2,3,7,8-tetrachlorodibenzodioxin

injection, and two- and four-stroke cycles (Heywood, 1989; Stone, 1999).

Indirect injection engines cost less and are less efficient than direct injection engines. Fuel is injected into a secondary chamber, where ignition takes place, and a jet of the partially burned fuel–air mixture is discharged into the main combustion chamber, where it is mixed with additional air and combustion is completed. This allows relatively fast and complete combustion without the need for a very high-pressure fuel injection system because most of the energy required for mixing is produced by the hot burning jet. However, significant energy loss occurs due to heat transfer and loss of pressure, which lead to higher fuel consumption. Indirect combustion engines dominated the diesel passenger car market until the mid-1990s and are still used in small engines, such as generator sets and auxiliary power units. Direct injection engines require higher-pressure fuel injection and more precise control of the fuel–air mixing process, but are considerably more fuel efficient. Nearly all modern heavy-duty vehicles are fitted with direct injection engines.

Two- and four-stroke cycles refer to the number of piston strokes required to complete an engine cycle. Two-stroke diesel engines are mechanically simpler but are more complex thermodynamically and aerodynamically than four-stroke engines. In a two-stroke engine, the four phases of an engine cycle (intake, compression, expansion and exhaust) require only one revolution, while two revolutions are required in a four-stroke engine. In a two-stroke engine, intake and compression take place in one stroke, and expansion, exhaust and the beginning of intake take place in the second stroke. Two-stroke diesel engines are generally more compact and have a better power-to-weight ratio than their four-stroke counterparts but are typically less efficient and their emissions are more difficult to control. Two-stroke engines came into general use in the 1930s, first in locomotives, then in military applications, generator sets, HGVs and buses (Sloan, 1964), and were widely used in HGVs and buses until the early 1990s, when it became apparent that increasingly stringent emission standards would be more difficult to meet than with four-stroke engines. However, they are still used to a great extent in large engines in rail, marine and stationary applications. Since the mid-1980s, stringent emission standards and highly competitive performance requirements have caused the design of on-road engines in developed countries to converge on a ‘common diesel engine architecture’ (IRSG, 2012a, b).

In this *Monograph*, diesel engines that are unregulated for particulate emissions are referred to as ‘traditional technology diesel engines’; those that are fitted with wall-flow particulate filters and oxidation catalysts, and use ultra-low sulfur fuel are referred to as ‘new technology diesel engines’; and those that fall in between the two are referred to as ‘transitional diesel engines’. The following section focuses primarily on emission technology for heavy-duty and light-duty diesel engines in Europe and the USA.

(b) Traditional and transitional technology engines

Until the mid-1980s, a wide variety of diesel engine designs and technologies were available, including two-stroke and four-stroke combustion systems, two-valve and four-valve gas exchange systems (or side ports in the case of two-stroke engines), direct and indirect fuel injection systems, and turbocharged and naturally aspirated air induction systems. With increasingly stringent regulations on emissions (see Section 1.3), the industry converged on a common diesel engine architecture: four-stroke combustion, four-valve gas exchange, high-pressure direct fuel injection with electronic control and turbocharged air induction. Other technological changes have ensued: intake air cooling was introduced – first using engine cooling water, then air-to-air heat exchangers – to produce lower peak combustion temperatures to reduce emissions of nitrogen oxides. In 2002, cooled exhaust gas recirculation was introduced an additional control for nitrogen oxides.

Fuel technology also changed when the sulfur content of fuel was reduced from up to 5000 ppm (0.5%) to 500 ppm to enable diesel engines to meet the particulate matter (PM) standards and to introduce cooled exhaust gas recirculation without unacceptable corrosion from sulfuric acid.

Diesel oxidation catalysts were introduced first (Volkswagen, 1989), then diesel exhaust particle filters (DPFs). The catalysts came into relatively wide use in light- and medium-duty applications in the 1990s, and are effective at reducing emissions of carbon monoxide, hydrocarbons and particle-bound organic carbon but have little influence on those of EC or nitrogen oxides.

(c) *New technology engines: aftertreatment of diesel exhaust*

The new PM standards for on-road heavy diesel equipment that were introduced in 2010 in the USA could not be achieved by new developments in combustion alone, and required exhaust aftertreatment from the installation of DPFs and diesel oxidation catalysts, and a reduction in the sulfur content of fuel to a maximum of 15 ppm.

The nitrogen oxide standard also introduced in 2010 led to the further integration of aftertreatment techniques in the form of selective catalytic reduction (SCR) or nitrogen oxide adsorber-based systems.

(i) *Particle filtration*

DPFs were first introduced into European passenger cars in 2000 (Salvat *et al.*, 2000) and in heavy-duty trucks and buses in the USA in 2007.

A variety of types of filter medium are available, including ceramic foams, sintered metal, and wound, knit and braided fibres (Majewski & Khair, 2006). Most of these filters have a qualitatively similar efficiency and differ mainly in durability, cost and packaging. The wall-flow filter is the most common for transportation applications, and comprises a honeycomb-like ceramic structure, the alternate passages of which are blocked. Wall-flow filters typically achieve removal efficiencies for diesel PM of more than 95%. In some applications, so-called partial flow filters are used (Mayer *et al.*, 2009), which have considerably lower collection efficiencies – typically less than 50% – and are designed for applications that have less stringent emission standards or for which emissions are already very low.

As the exhaust passes through the filter, the initial substrate is the filtration medium. However, as soot gradually fills the filter channels, the surface of the filter becomes covered with a layer of soot, which in turn serves as a very efficient filtration medium. The temperatures of diesel exhaust are typically too low for any significant oxidation by the oxygen contained therein. Soot must be removed from the filter by its periodical or continuous burning in a process called regeneration, which can be achieved in three ways: one active and two passive methods.

Passive regeneration is achieved by placing an oxidizing catalyst upstream from the filter or by adding a metallic catalyst (usually some combination of cerium, strontium and iron) to the fuel. Active regeneration systems are used under light load conditions, such as those encountered in congested urban traffic or during prolonged idling (Majewski & Khair, 2006; Twigg & Phillips, 2009). This usually involves spraying fuel onto an oxidizing catalyst upstream from the filter to raise the exhaust temperature to above ~600 °C to initiate oxidation of the collected soot. Active regeneration is initiated typically every few hours.

The efficiency of a freshly regenerated filter at the most penetrating (least efficient) size (100–300 nm) is approximately 90%. As the filter loads and a soot layer builds up on its surface, the efficiency across the size range approaches 100%.

DPFs remove most solid particles by filtration, as well as carbon monoxide and light and semi-volatile hydrocarbons by catalytic oxidation, and by the conversion of nitrogen monoxide to nitrogen dioxide and sulfur dioxide to sulfur trioxide and sulfuric acid. Nucleation mode particles (Kittelson, 1998; Kittelson *et al.*, 2006) formed by engines equipped with a catalysed DPF consist mainly of sulfuric acid or ammonium sulfate particles (Grose *et al.*, 2006).

(ii) Aftertreatment for nitrogen oxides

Diesel engines operate under oxidizing conditions, and the reduction of nitrogen oxides to elemental nitrogen is challenging. The two main types of control system for nitrogen oxides in diesel exhaust are SCR (Gekas *et al.*, 2002) and lean nitrogen oxide traps (Morita *et al.*, 2007) (for a review, see Majewski & Khair, 2006).

SCR is designed to reduce the emissions of nitrogen oxides by their reaction with a reductant over a catalyst to form elemental nitrogen. SCR systems may be used alone or integrated with a catalysed DPF (Cooper *et al.*, 2003; Servati *et al.*, 2005) to form a four-way catalyst (carbon monoxide, hydrocarbon, nitrogen oxides and PM). Ammonia may not be fully consumed in the SCR system, and an ammonia slip catalyst is therefore usually used to reduce ammonia emissions. However, these catalysts may produce emissions of other chemicals (Havenith & Verbeek, 1997).

A lean nitrogen oxide trap involves the storage of nitrogen oxides during lean operations and catalytic reduction and release of nitrogen during rich operations (Yezerets *et al.*, 2007). During lean operations, nitrogen monoxide is oxidized to form nitrogen dioxide by a platinum catalyst and is stored as nitrate on the surface. To reduce nitrogen oxides to nitrogen, all oxygen in the exhaust passing through the catalyst must be eliminated. This is accomplished by temporarily injecting fuel into the exhaust to consume the remaining excess oxygen or by operating the engine briefly in a fuel-rich mode. Similarly to SCR systems, these can be used alone or combined with a particle filter (Xu *et al.*, 2010).

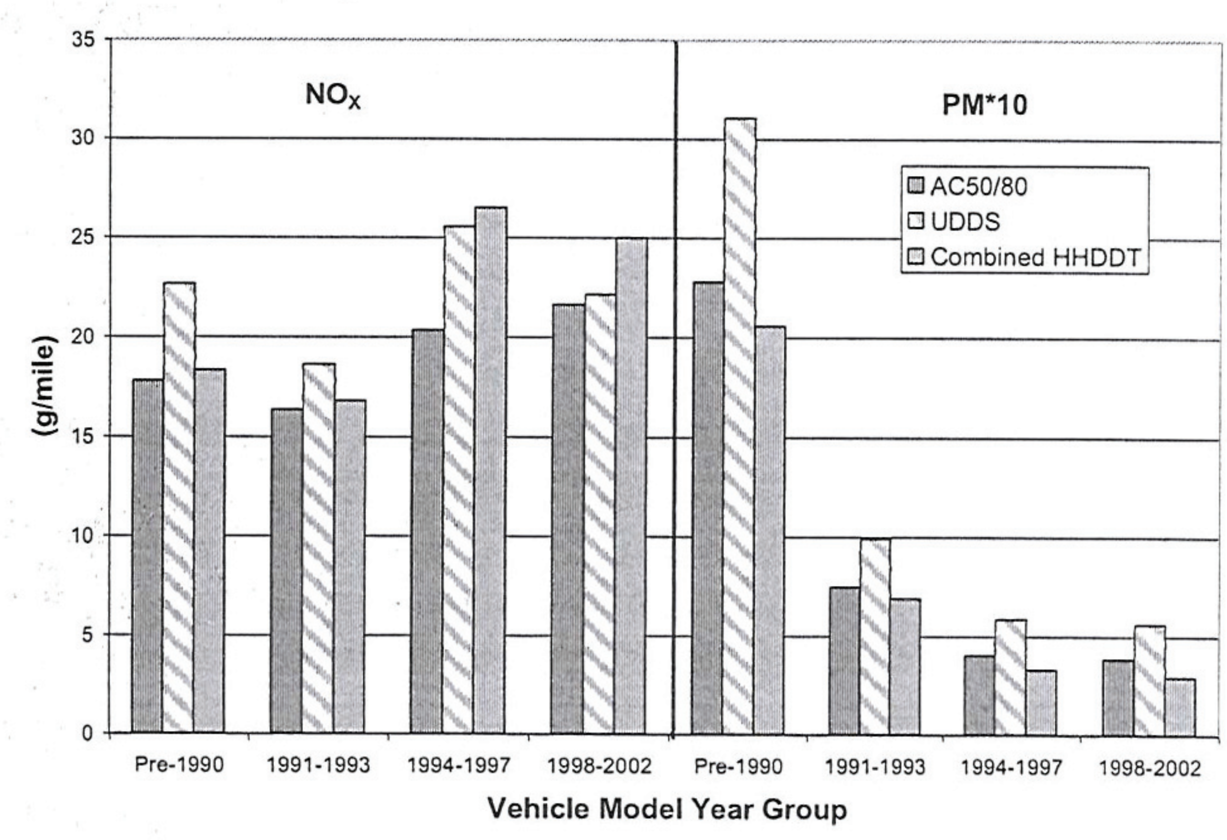
1.1.2 Levels of diesel engine exhaust emissions

(a) Traditional and transitional technology diesel engines

Clark *et al.* (2006) tested a fleet of heavy-duty diesel vehicles using three different driving cycles. Fig 1.1 shows the decreasing trend in PM emissions for vehicle models ranging from pre-1990 through 2002. A similar trend was also apparent from on-road tunnel data (Fig. 1.2; Gertler *et al.*, 2002). Measurements of PM emissions from heavy-duty vehicles in the Tuscarora tunnel were reduced by one order of magnitude between pre-1985 and 1999.

Operating conditions may influence PM emissions from traditional and transitional technology diesel engines. [Particulate mass emissions from new technology diesel engines are very low across the operating range because they are fitted with wall-flow particulate filters.] Clark *et al.* (2002) compared the relative effects of vehicle class and weight, simulated driving cycle, vehicle vocation [application] and driving activity, fuel, aftertreatment [catalytic converter], age [level of technology] and terrain on PM emissions from heavy-duty diesel vehicles (Fig. 1.3). PM emissions varied by 1500% due to differences in the driving cycle alone. Clark *et al.* (2006) tested a fleet of 25 heavy heavy-duty diesel vehicles using a chassis dynamometer and full flow dilution tunnel. Table 1.3 summarizes the influence of driving cycle on PM and hydrocarbon emissions from laden vehicle models from pre-1990 and from 1998 through 2002. The ‘creep’ cycle gave the highest PM and hydrocarbon emissions, while the cruise cycle gave the lowest PM emissions and the transient cycle gave the lowest hydrocarbon emissions. [The idle emissions are not directly comparable with the other cycles

Fig. 1.1 Trends in emissions of nitrogen oxides and particulate matter by model year group, measured on a chassis dynamometer with three different drive cycles



AC50/80, standard driving cycle; HHDDT, heavy heavy-duty diesel truck; NO_x, nitrogen oxides; PM, particulate matter; UDDS, urban dynamometer driving schedule
From Clark *et al.* (2006). Copyright © 2006 SAE International. Reprinted with permission.

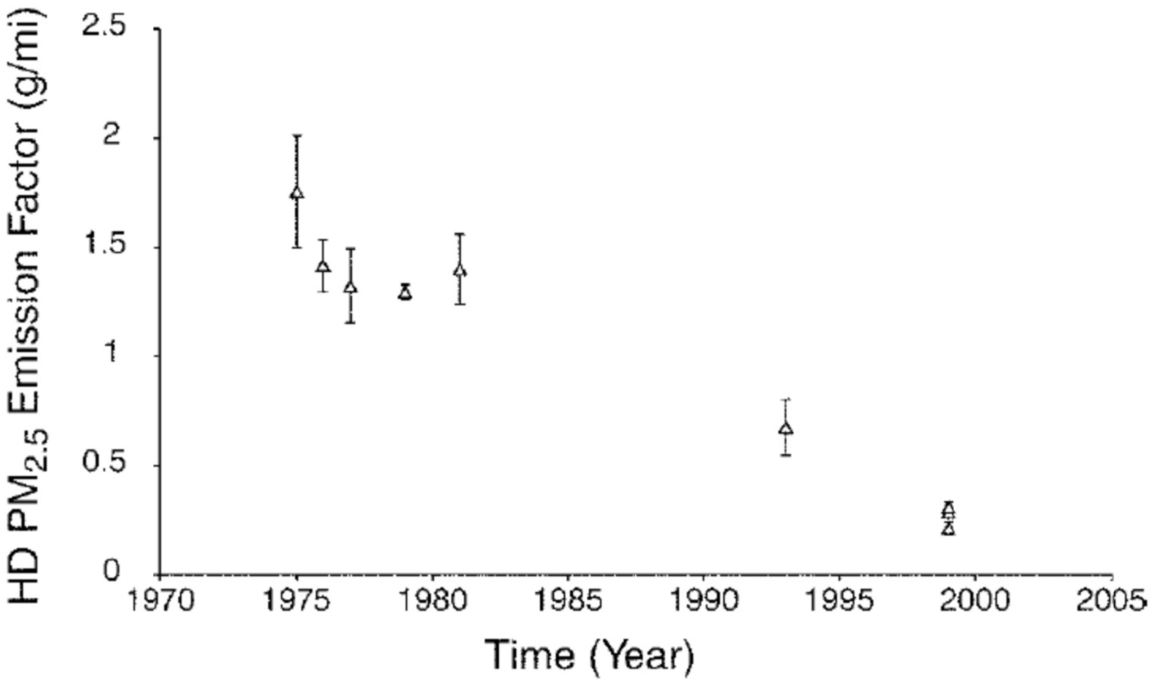
because they are measured in grams per second rather than grams per mile.]

Idle emissions are of particular interest in some exposure situations, e.g. for garage mechanics, and are influenced by engine technology and accessory load, especially air conditioning. Engines with electronic fuel injection systems produce substantially lower carbon monoxide, hydrocarbon and PM emissions but somewhat higher emissions of nitrogen oxides (Khan *et al.*, 2006, 2009).

Kweon *et al.* (2003) examined the impact of engine speed and load on particle-bound organic emissions. A Cummins N14-series single-cylinder research engine was run under the California Air Resources Board eight-mode test cycle. Under high load conditions, most of the particle-phase organic compounds were below the limit of detection in gas chromatography-mass spectrometry (GC-MS); in contrast, most of the 39 organic compounds quantified were detected under idling, light and medium load conditions, which are associated with lower exhaust temperatures. Fig 1.4 shows PAH emissions in relation to exhaust temperature for two speeds.

Kittelson *et al.* (2006) measured size distributions of PM for a variety of heavy-duty engines, both on-road and using engine and chassis dynamometers. Measurements were

Fig. 1.2 Heavy-duty vehicle particulate matter emission factor estimates measured on-road in the Tuscarora tunnel, USA



Note: the markers for 1999 include PM_{10}, $PM_{2.5}$, and $PM_{2.5}$ (reconstructed mass).
HD, heavy duty; PM, particulate matter
From Gertler *et al.* (2002). Reprinted with permission from the Health Effects Institute, Boston, MA.

made using fuels with varying sulfur contents, and with and without a thermal denuder that was used to measure solid particles. Without the thermal denuder, the size distributions were nearly unimodal, whereas the thermal denuder revealed a bimodal structure. Except for the fuel with the highest sulfur content (325 ppm), the size distribution for the high-speed cruise condition showed a single mode – the accumulation mode centred at about 50 nm, which consisted mainly of carbonaceous soot particles. The PM concentration in this mode was nearly two orders of magnitude higher than that under idling conditions. Using fuel with the highest sulfur content, a nucleation mode was found, centred at about 10 nm. Although the formation of this mode was related to the sulfur content of the fuel, other work has shown that it consists mainly of heavy hydrocarbons, primarily from unburned lubricating oil (Sakurai *et al.*, 2003).

Table 1.3 Influence of operating cycle on particulate matter and hydrocarbon emissions by car model year

Driving cycle	Hydrocarbons		Particulate matter	
	Pre-1990	1998–2002	Pre-1990	1998–2002
Idle (g/s)	20.2	7.6	3.7	0.8
Creep (g/mile)	16.3	5.8	7.3	1.5
Transient (g/mile)	3.8	1.3	4.2	0.6
Cruise (g/mile)	1.2	0.4	2	0.2
Urban dynamometer driving schedule (g/mile)	3.2	0.8	3.1	0.6

Adapted from Clark *et al.* (2006)

Fig. 1.3 Relative impact of operating variables on particulate matter emissions

Parameters measured are: class (vehicle class and weight), cycle (simulated driving cycle), vocations (application and driving activity), fuel (type of diesel fuel), aftertreatment (catalytic converter), age (level of technology), terrain (driving terrain) and injection timing.
From Clark *et al.* (2002). Reprinted by permission of the publisher, Taylor & Francis Ltd, http://www.tandf.co.uk/journals/

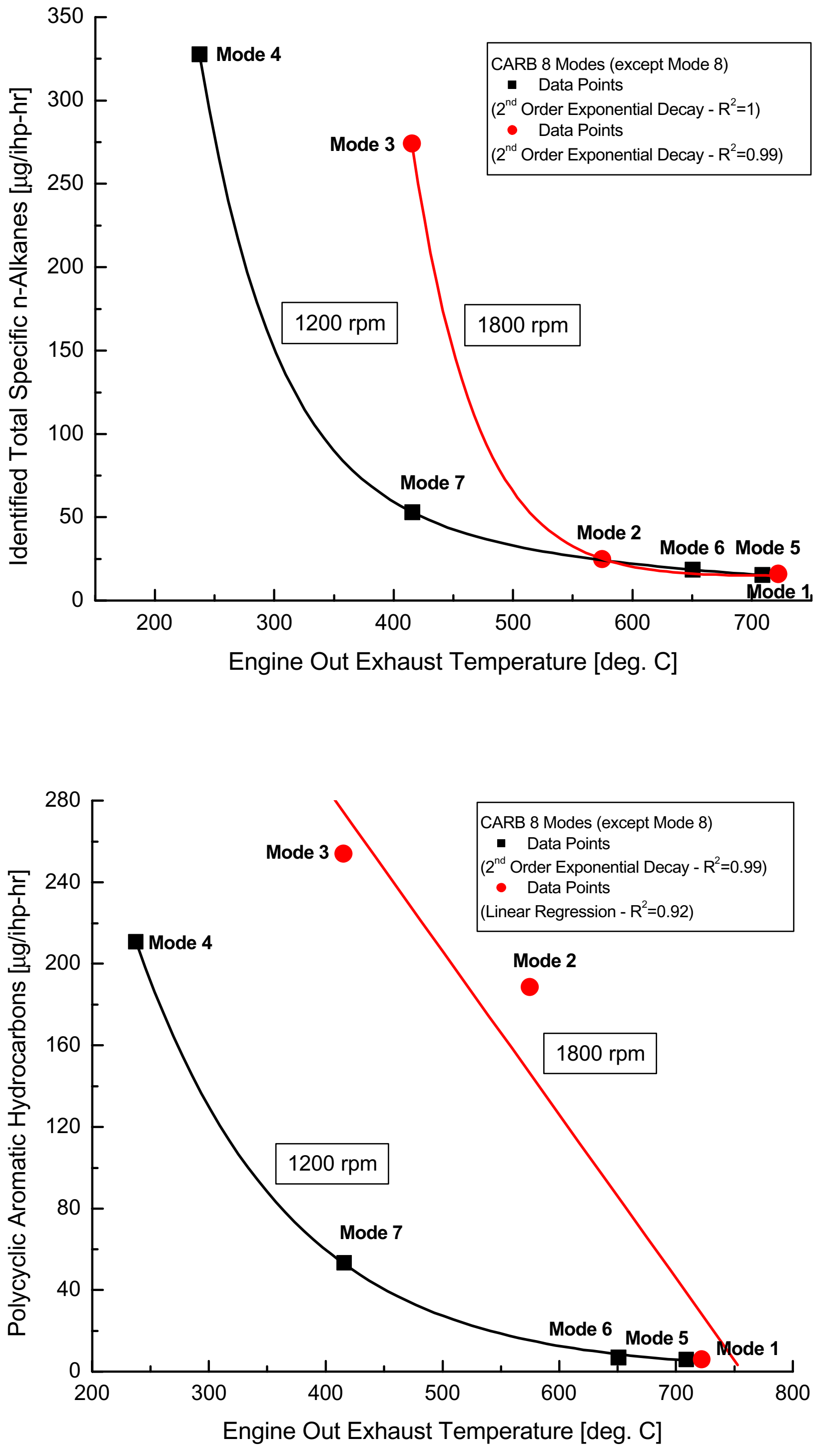
Fig. 1.5 shows a comparison of the average particle size distribution for 2007 model engines with and without regeneration, and for a 2004 model engine without a diesel oxidation catalyst or a DPF. Measurements for the 2007 engines were taken from the exposure chamber for 4-hour segments of the 16-hour cycle; the data were based on 19 repeats with regeneration and 29 repeats without regeneration. Measurements for the 2004 engine were taken from the full-flow constant volume sampling of the Federal Test Procedure (FTP) transient cycle, and were based on six repeats.

(b) New technology diesel engines

Several recent studies have reported on the changes in the composition of diesel exhaust linked to new technology. Emission trends in fluoranthene, pyrene, benzo[*a*]pyrene, benzo[*e*]pyrene and 1-nitropyrene with changing engine technology are shown in Fig. 1.6 as a fraction of the emissions from pre-1999 technology. All compounds showed a marked downward trend. Emissions from the 2000 and 2004 transitional technology engines represented only a fraction (maximum, 40%) of those from the traditional technology engines, and a further decrease occurred with the introduction of new technology engines fitted with catalysed DPFs.

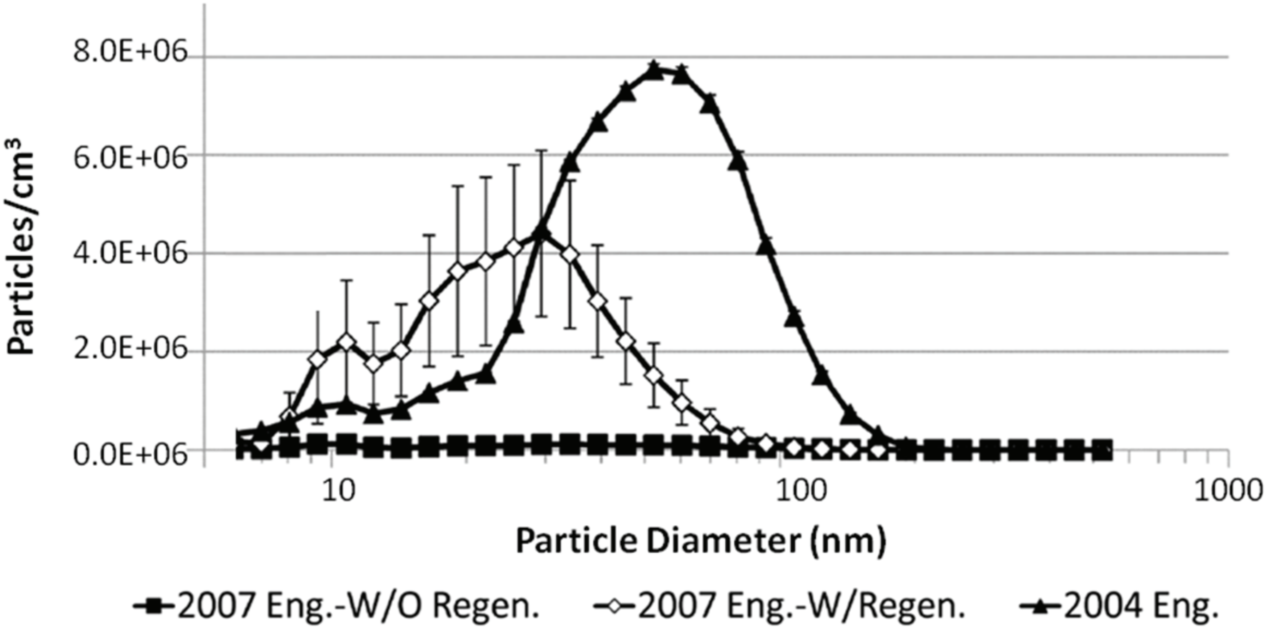
Hesterberg *et al.* (2011) published a comprehensive comparison of emissions from current

Fig. 1.4 Variations in total specific *n*-alkanes (top) and polycyclic aromatic hydrocarbons (bottom) versus engine-out exhaust temperature for CARB 8-mode test cycle



From Kweon *et al.* (2003). Copyright © 2003 SAE International. Reprinted with permission.

Fig. 1.5 Particle size distribution of a 2004 engine and 2007 engines with or without active regeneration



Geometric number mean diameter (GNMD) and geometric standard deviation (GSD):
2007 engine with regeneration: GNMD = 25 nm; GSD = 1.72
2007 engine without regeneration: GNMD = 40 nm; GSD = 1.95
2004 engine: GNMD = 46 nm; GSD = 1.90
From Khalek *et al.* (2011). Reprinted by permission of the publisher, Taylor & Francis Ltd, http://www.tandf.co.uk/journals/

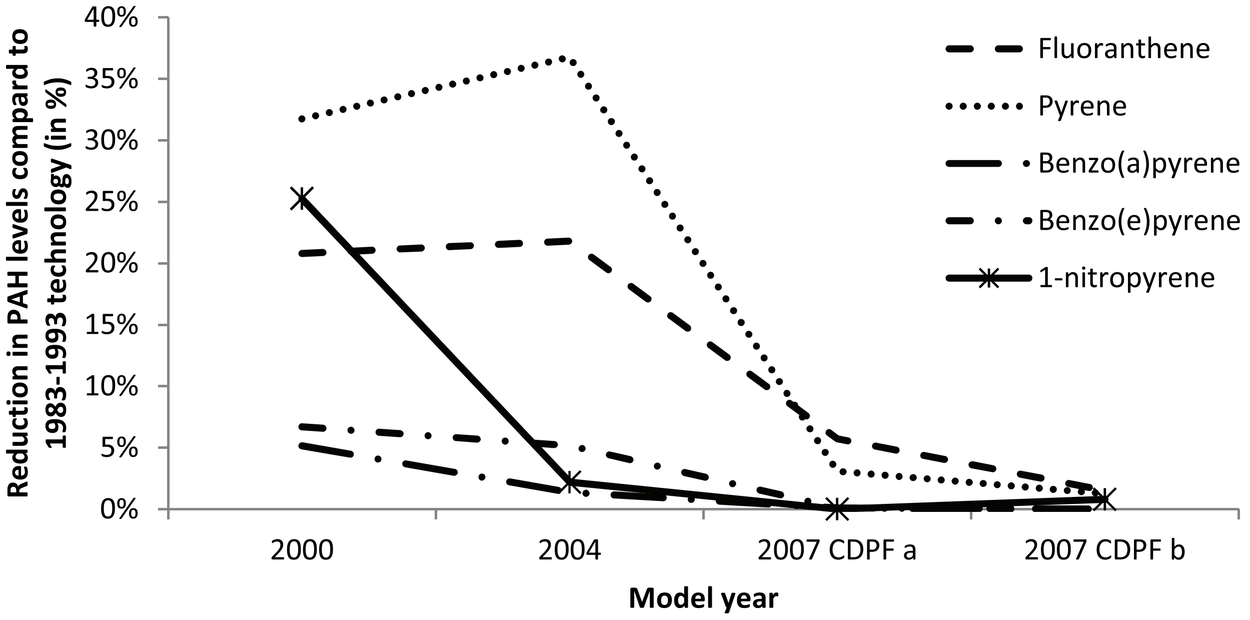
technology diesel engines fitted with and without advanced aftertreatment systems. Large reductions in total emissions of PM, sulfate/nitrate, hydrocarbons, EC and ash were observed. Total reductions in PM emissions of 99% were typical (Liu *et al.*, 2009).

PAH and nitro-PAH emissions have been studied extensively. The reduction in emission levels between transitional and new technology engines for various classes of compounds, for the 39 California Air Resources Board Toxic Air contaminants, and for PAHs and nitro-PAHs is shown in Table 1.4, Table 1.5, and Table 1.6, respectively. Studies generally showed large reductions in PAHs and nitro-PAHs in new technology diesel engines compared with traditional and transitional technology engines (52– > 99%) (Biswas *et al.*, 2009a, b; Khalek *et al.*, 2009, 2011; Liu *et al.*, 2010).

Some studies (Heeb *et al.*, 2008, 2010) showed that uncatalysed filters and filters that did not strongly oxidize carbon and nitrogen monoxides in the exhaust removed PAHs less efficiently than those that strongly oxidized carbon and nitrogen monoxides, with individual PAH removal efficiencies of 37–90% for the former and 75–98% for the latter.

Several recent studies that evaluated the formation of nitro-PAHs in DPFs produced conflicting results (Heeb *et al.*, 2008, 2010; Liu *et al.*, 2010; Khalek *et al.*, 2011). The level of 1-nitrophenanthrene increased by 20% for an uncatalysed DPF with fuel-borne catalysts in one study (Heeb *et al.*, 2008), and by 55 and 91% for low- and high-activity DPFs, respectively, in a later study by the same authors (Heeb *et al.*, 2010). In contrast, Liu *et al.* (2010) observed a 76% decrease in 1-nitrophenanthrene in 2004 model engines compared with 2007 model engines. The

Fig. 1.6 Trends in selected polycyclic aromatic hydrocarbon species with developing technology



Concentrations are plotted as a fraction of the emissions from a group of 1983–93 heavy-duty vehicles reported by Watson *et al.* (1998), except for 1-nitropyrene which was taken as the mid-point of the range of 1–4 mg/brake horse power–h given as typical of 1975–2000 engines by EPA (2002a). 2000 and 2007 CDPF b data from Khalek *et al.* (2011). 2004 and 2007 CDPF a data from Liu *et al.* (2010).

Table 1.4 Unregulated emissions for all 12 repeats of the 16-hour cycles for four 2007 ACES engines and for 2004 technology engines used in CRC E55/E59

Compound	2004 engines (average ± SD, mg/h)	2007 engines (average ± SD, mg/h)	2007 engines[a] (average ± SD, mg/bhp-h)	Average percentage reduction relative to 2004 technology engines
Single-ring aromatics	405.0 ± 148.5	71.6 ± 32.97	0.76 ± 0.35	82
PAHs	325.0 ± 106.1	69.7 ± 23.55	0.74 ± 0.25	79
Alkanes	1030.0 ± 240.4	154.5 ± 78.19	1.64 ± 0.83	85
Hopanes/steranes	8.2 ± 6.9	0.1 ± 0.12	0.0011 ± 0.0013	99
Alcohols and organic acids	555.0 ± 134.4	107.4 ± 25.4	1.14 ± 0.27	81
Nitro-PAHs	0.3 ± 0.0	0.1 ± 0.0	0.0065 ± 0.0028	81
Carbonyls	12 500.0 ± 3535.5	255.3 ± 95.2	2.68 ± 1.00	98
Inorganic ions	320.0 ± 155.6	92.3 ± 37.7	0.98 ± 0.40	71
Metals and elements	400.0 ± 141.4	6.7 ± 3.0	0.071 ± 0.032	98
Organic carbon	1180.0 ± 70.7	52.8 ± 47.1	0.56 ± 0.50	96
Elemental carbon	3445.0 ± 1110.0	22.6 ± 4.7	0.24 ± 0.05	99
Dioxins/furans	NA	$6.2 \times 10^{-5} \pm 5.2 \times 10^{-5}$	$6.6 \times 10^{-7} \pm 5.5 \times 10^{-7}$	99[b]

[a] Data shown in brake-specific emissions for completeness; no comparable data on brake-specific emissions were available

[b] Relative to 1998 technology engines

bhp, brake horse power; h, hour; NA, not applicable; PAHs, polycyclic aromatic hydrocarbons; SD, standard deviation

From Khalek *et al.* (2011)

Table 1.5 Average emissions of the 39 CARB toxic air contaminants for four 2007 ACES engines and for 1994–2000 technology engines[a]

TAC No.	Compound	1994–2000 technology engines[b] (mg/bhp-h)	2007 technology engines[c] (mg/bhp-h)	Percentage reduction
1	Acetaldehyde	10.3	0.61 ± 0.27	93
2	Acrolein	2.7	< 0.01	> 99
3	Aniline	NA	0.000150 ± 0.000075	NA
4	Antimony compounds	NA	< 0.001	NA
5	Arsenic	NA	< 0.0002	NA
6	Benzene	1.82	< 0.01	> 99
7	Beryllium compounds	NA	< 0.0003	NA
8	Biphenyl	NA	0.013780 ± 0.001716	NA
9	Bis(ethylhexyl)phthalate	NA	NR	NA
10	1,3-Butadiene	1.7	< 0.01	> 99
11	Cadmium	NA	< 0.00003	NA
12	Chlorine (chloride)	0.18	< 0.007	> 96
13	Chlorobenzene and derivatives	NA	NR	NA
14	Chromium compounds	NA	0.0007 ± 0.0003	NA
15	Cobalt compounds	NA	< 0.0001	NA
16	Cresol isomers	NA	0.02727 ± 0.01233	NA
17	Cyanide compounds	NA	< 0.05	NA
18	dl-*n*-Butylphthalate	NA	NR	NA
19	Dioxins and dibenzofurans	0.000066	0.00000066 ± 0.000000055	99
20	Ethyl benzene	0.49	0.05 ± 0.04	90
21	Formaldehyde	25.9	1.90 ± 1.01	94
22	Hexane	0.14	< 0.01	> 93
23	Inorganic lead	0.0009	< 0.0001	> 89
24	Manganese	0.0008	< 0.00022	> 73
25	Mercury	NA	< 0.00016	NA
26	Methanol	NA	0.07 ± 0.13	NA
27	Methyl ethyl ketone	NA	< 0.01	NA
28	Naphthalene	0.489	0.0982 ± 0.0423	80
29	Nickel	0.01	0.0002 ± 0.0001	98
30	4-Nitrobiphenyl	NA	< 0.00000001	NA

Table 1.5 (continued)

TAC No.	Compound	1994–2000 technology engines[b] (mg/bhp-h)	2007 technology engines[c] (mg/bhp-h)	Percentage reduction
31	Phenol	NA	0.00905 ± 0.00414	NA
32	Phosphorus	NA	0.0130 ± 0.0064	NA
33	POM, including PAHs and derivatives	See Table 1.6	See Table 1.6	See Table 1.6
34	Propionaldehyde	1.8	0.01	> 99
35	Selenium	NA	< 0.0001	NA
36	Styrene	0.73	< 0.01	> 99
37	Toluene	0.64	0.26 ± 0.28	59
38	Xylene isomers and mixtures	2.2	0.35 ± 0.10	85
39	*ortho*-Xylene	0.99	0.13 ± 0.07	87
40 and 41	*meta*- and *para*-Xylenes	1.21	0.20 ± 0.08	83

[a] Engines run over the Federal Test Procedure transient cycle for all 12 repeats of the 16-hour cycle.

[b] Data on standard deviations were not provided.

[c] The limit of detection is indicated by values marked ‘ < ’.

bhp, brake horse power; h, hour; NA, not applicable; NR, not reported; PAHs, polycyclic aromatic hydrocarbons; POM, polycyclic organic matter; TAC, toxic air contaminant

From Khalek *et al.* (2011)

Table 1.6 Emissions of selected polycyclic aromatic hydrocarbon (PAH) and nitro-PAH compounds from 2000 and 2007 technology engines[a]

PAH/nitro-PAH	2007 technology engines[b] (mg/bhp-h)	2000 technology engines[b, c] (mg/bhp-h)	Percentage reduction
Naphthalene	0.0982 ± 0.0423	0.4829	80
Acenaphthylene	0.0005 ± 0.0005	0.0524	98
Acenaphthene	0.0004 ± 0.0001	0.0215	98
Fluorene	0.0015 ± 0.0009	0.0425	96
Phenanthrene	0.0077 ± 0.0025	0.0500	85
Anthracene	0.0003000 ± 0.0001000	0.0121	97
Fluoranthene	0.0006 ± 0.0006	0.0041	85
Pyrene	0.0005 ± 0.0004	0.0101	95
Benzo[*a*]anthracene	< 0.0000001	0.0004	> 99
Chrysene	< 0.0000001	0.0004	> 99
Benzo[*b*]fluoranthene	< 0.0000001	< 0.0003	> 99
Benzo[*k*]fluoranthene	< 0.0000001	< 0.0003	> 99
Benzo[*e*]pyrene	< 0.0000001	< 0.0003	> 99
Benzo[*a*]pyrene	< 0.0000001	< 0.0003	> 99
Perylene	< 0.0000001	< 0.0003	> 99
Indeno[1,2,3-*cd*]pyrene	< 0.0000001	< 0.0003	> 99
Dibenz[*a,h*]anthracene	< 0.0000001	< 0.0003	> 99
Benzo[*ghi*]perylene	< 0.0000001	< 0.0003	> 99
2-Nitrofluorene	0.0000036 ± 0.0000041	0.000065	94
9-Nitroanthracene	0.0000148 ± 0.0000213	0.0007817	98
2-Nitroanthracene	0.0000004 ± 0.0000009	0.0000067	94
9-Nitrophenanthrene	0.0000211 ± 0.0000209	0.0001945	89
4-Nitropyrene	< 0.0000001	0.0000216	> 99
1-Nitropyrene[d]	0.0000197 ± 0.0000243	0.0006318	97
7-Nitrobenz[*a*]anthracene[d]	0.0000002 ± 0.0000002	0.0000152	99
6-Nitrochrysene	< 0.00000001	0.0000023	> 99
6-Nitrobenzo[*a*]pyrene[d]	< 0.00000001	0.0000038	> 99

[a] Four 2007 ACES engines and some 2000 technology engines were run over the Federal Test Procedure transient cycle for all 12 repeats of the 16-hour cycles.

[b] The limit of detection is indicated by values marked '< '.

[c] Data on standard deviations were not provided

[d] Previous work showed artefact formation during filter collection

bhp, brake horse power; h, hour

From Khalek *et al.* (2011)

level of 2-nitrophenanthrene was also increased by 100% with DPFs in the first study (Heeb *et al.*, 2008), but was decreased by 34 and 81% for low- and high-activity DPFs, respectively (Heeb *et al.*, 2010), and by 91% for 2004 model engines compared with 2007 model engines (Liu *et al.*, 2010). The level of 9-nitrophenanthrene was increased in two studies (Heeb *et al.*, 2010; Liu *et al.*, 2010), whereas a 92% reduction was reported in another study (Khalek *et al.*, 2011). The concentration of 1-nitropyrene was shown to increase in one study (Heeb *et al.*, 2010), but two other studies reported decreases of 99 and 97%, respectively (Liu *et al.*, 2010; Khalek *et al.*, 2011).

[These differences were probably due to a combination of differences in the test cycle and sampling method. The studies by Liu *et al.* (2010) and Khalek *et al.* (2011) both used dilution sampling that is intended to approximate the atmospheric dilution process, while the studies by Heeb *et al.* (2008, 2010) used undiluted sampling of cooled exhaust gases with samples combined from a filter, a condenser and an XAD absorber.]

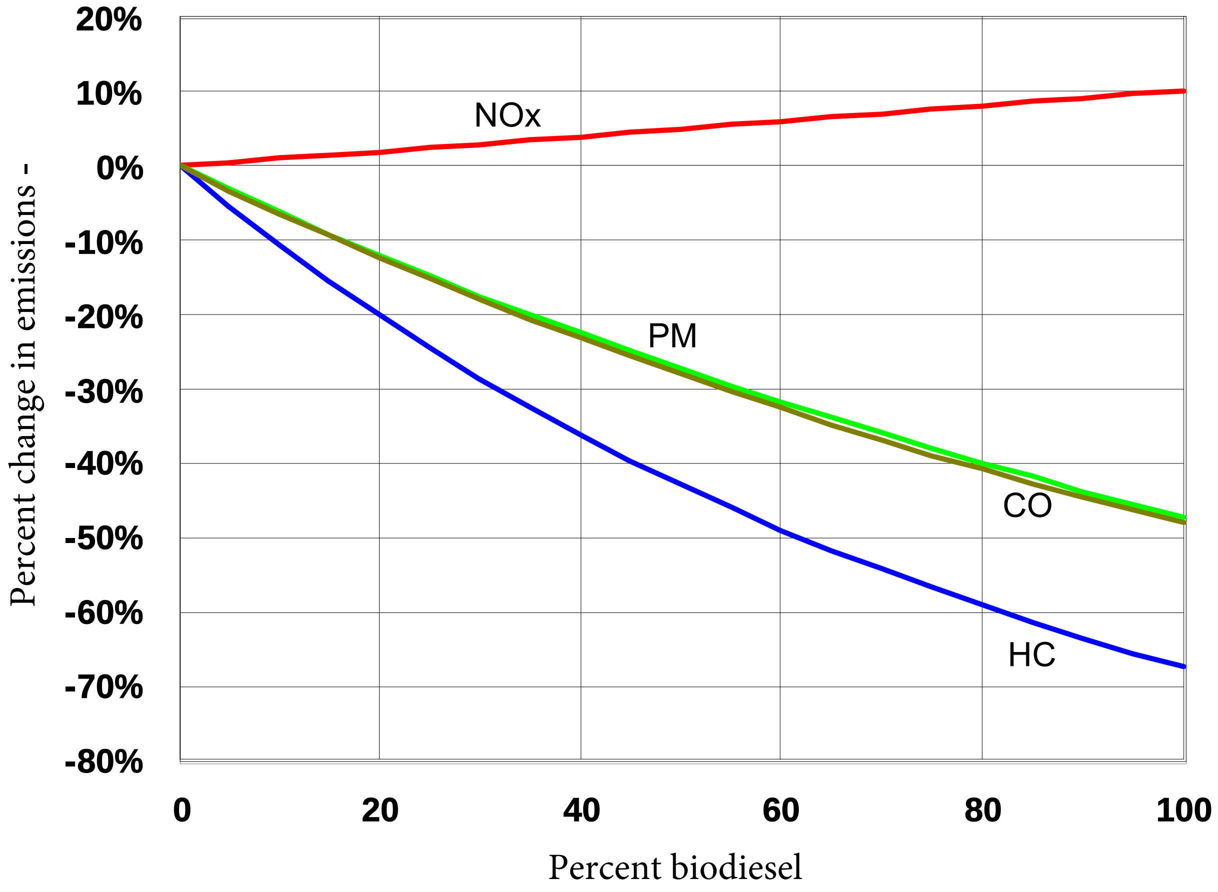
Some studies showed increases in dioxin/furan emissions with the use of copper fuel-borne catalyst materials, in particular in the presence of elevated levels of chlorine in the fuel (Mayer *et al.*, 2003; Heeb *et al.*, 2007); subsequent work by the same investigators (Wenger *et al.*, 2008) reported increases in copper fuel-borne catalysed systems but small absolute values except in one case using fuel with an extremely high chlorine content. Other studies (Table 1.4 and Table 1.5; Khalek *et al.*, 2011) reported a 99% reduction in dioxins/furans with catalysed DPF and SCR systems compared with transitional technology engines. In a comprehensive programme that tested two different 2010 new technology engines with a range of different exhaust aftertreatment configurations chosen for their potential for dioxin/furan formation, Liu *et al.* (2011) showed 60–80% reductions in dioxin/furan emissions for all aftertreatment configurations, and no impact of elevated levels of chlorine content. Dyke *et al.* (2007) reported an approximate 80% reduction in dioxin/furan emissions when a diesel oxidation catalyst was fitted.

Andersson *et al.* (2007) compared six conventional diesel vehicles with six DPF-equipped vehicles. Conventional vehicles emitted 300–700-fold more particles than DPF-equipped vehicles.

Although solid particle emissions are greatly reduced by DPFs, increases in total emissions have been reported with the use of DPFs. Sulfate and ammonium sulfate emissions may be the main constituents of nucleation mode particles, which are formed at higher exhaust temperatures and generally by more heavily catalysed systems (Herner *et al.*, 2011). Kittelson *et al.* (2008) observed the formation of a large nucleation mode and an increase in particle emissions downstream from a continuously regenerating trap (diesel oxidation catalyst upstream of an uncatalysed DPF) when exhaust temperatures exceeded about 350 °C. The DPF was very efficient at removing accumulation mode soot particles but, in the absence of a surface to adsorb the sulfuric acid, the vapours nucleated and grew into a large nucleation mode that contained very little mass but a large number of particles. No detectable nucleation mode formation took place when a catalysed continuously regenerating trap (diesel oxidation catalyst upstream from a catalysed DPF) was used.

Khalek *et al.* (2011) compared particle size and particle emissions from four new technology engines with those from a transitional technology engine, and did not observe the increase in total emissions described above. Total emissions were, respectively, 3.0×10^{14}, 3.3×10^{13} and 3.9×10^{12} particles/brake horse power (bhp)–h for the 2004 engine, the 2007 engines, including regeneration events, and the 2007 engines, not including the regeneration events. Thus, the total emissions were reduced by 89% and 88% of the remaining emissions were produced during the infrequent regeneration events.

Fig. 1.7 Impact of biodiesel blends on emissions



CO, carbon monoxide; HC, hydrocarbon; NO_x, nitrogen oxides; PM, particulate matter
From EPA (2002b)

1.1.3 Biodiesel

Biodiesel is usually a fatty acid methyl ester made by reacting vegetable oils or animal fats with methanol. The most common feedstocks are soya bean, rapeseed and palm oils, and various waste animal fats. In general, biodiesel does not significantly change engine efficiency but leads to slightly higher fuel consumption because of its lower energy content. It is usually used in blends with petroleum diesel, where for example B20 refers to a 20% biodiesel blend.

The US Environmental Protection Agency (EPA) published a comprehensive review of the performance and emissions of biodiesel blends (EPA, 2002b). The emissions are sensitive to engine specifications and aftertreatment systems, but general trends are observed. Fig 1.7 shows the average variation in emissions of nitrogen oxides, carbon monoxide, hydrocarbon and PM from a biodiesel blend fraction for soya methyl ester, based on many engine tests. Emissions may vary depending on feedstock.

Several studies of emissions from biodiesel blends have been reported (Sharp *et al.*, 2000; Turrio-Baldassarri *et al.*, 2004; Arapaki *et al.*, 2007; Cheung *et al.*, 2009; Karavalakis *et al.*, 2009a, b, 2010); most showed trends in regulated emissions similar to those described by the US EPA (2002b), while results for unregulated emissions were mixed. Some showed increases in the levels of PAHs and derivatives with increasing blends, while others showed decreasing trends.

To resolve these inconsistencies, Eckerle *et al.* (2008) studied blends of B0 (i.e. pure conventional diesel fuel), B20 and B100 (pure biodiesel) and isolated the effects of changes in combustion due to the properties of the fuels and changes in emissions due to interactions with the calibration of the engine control system. Their experiments and analysis of combustion indicated little effect of biodiesel blend on combustion at higher loads; however, at lower loads, biodiesel tended to increase the emissions of nitrogen oxides.

A more significant and potentially confusing effect was the interaction between the volumetric energy content of the fuel and the engine control system. Biodiesel blends have a lower volumetric energy content compared with conventional diesel fuel. As a result, the engine requires a higher volumetric fuel flow of biodiesel to produce the same power as conventional diesel, and, depending on the specific engine control calibration, the levels of nitrogen oxides may increase or decrease as a result of this interaction. [The Working Group noted that this would explain to some extent the wide range of responses observed to the effects of biodiesel on emissions of nitrogen oxides that were dependent on the base properties of the fuels, engine operating conditions (especially load factor) and the means of control calibration.]

1.1.4 Spark ignition (gasoline) engines

(a) Historical perspective

Spark ignition engines have been and continue to be the main source of power for passenger cars, motorcycles and scooters, and for most small-scale on-road and off-road applications, e.g. all-terrain vehicles, snowmobiles, outboard motors, garden tractors and lawn mowers. The first operational four-stroke spark ignition engine was developed by Nicolaus Otto in 1876, and named the Otto Cycle. Unfortunately, his early design was unsuitable for automotive applications, and a more practical, single-cylinder automotive engine was developed in 1899 by Gottlieb Daimler (Amann, 1990).

The early development of spark ignition engines was hindered by destructive combustion knock, which limited the compression ratio and thus the power and efficiency of the engine. The discovery in 1921 by Charles Kettering of the anti-knock properties of tetraethyl lead opened the way to engines with higher compression ratios, which were more powerful and efficient. Tetraethyl lead was used as an anti-knock agent until growing concerns about engine emissions led to its gradual phase out (see below) (Amann, 1990).

The reduction of emissions from gasoline-fuelled passenger cars has for many years been focused on gaseous emissions, and led to major changes in spark ignition engine technology. The introduction of catalytic converters – oxidation catalysts in the mid-1970s followed by three-way catalysts in the early 1980s – allowed optimization of the engines for maximum performance while cleaning the exhaust with the catalyst (Twigg, 2011).

(b) Port-fuel injection engine technology

Spark ignition engines are designed to operate with well mixed homogeneous charges at either lean or chemically correct fuel–air mixture ratios. Until the mid-1980s, nearly all automotive spark ignition engines used carburettors (mechanical devices for mixing fuel and air in a predetermined ratio) to provide the fuel–air mixture. However, these were unable to provide the precise mixture control required to meet ever more stringent emission standards, and were replaced by port fuel injection systems (although carburettors are still used in off-road applications, especially in small engines). Today, nearly all passenger car spark ignition engines rely on the injection of fuel into the intake port and are therefore called port fuel injection (PFI) engines. Well mixed homogeneous combustion under lean or chemically correct conditions does not lead to significant particle formation. Thus, particle emissions from PFI spark ignition engines are associated with conditions other than normal premixed combustion – for example, rich combustion during cold starts or at high loads. Engines with excessive oil consumption or an improper fuel–air mixture may also emit high levels of particles.

Regulatory efforts to reduce emissions from gasoline-fuelled vehicles preceded those for diesel-fuelled engines. Standards worldwide gradually reduced and finally eliminated the addition of tetraethyl lead to gasoline (Colucci, 2004; Twigg, 2005). The lower lead content had both direct and indirect impacts on gasoline engine emissions. In addition to decreasing the levels of lead in exhaust, the elimination of tetraethyl lead from gasoline was critical to the use of advanced aftertreatment technologies, such as three-way catalytic converters that reduce the emissions of carbon monoxide, nitrogen oxides and hydrocarbons in exhaust from gasoline-fuelled vehicles. The presence of even trace levels of lead in the exhaust poisoned the catalysts in exhaust treatment systems, and rendered them ineffective. By 2000, lead had been banned in gasoline in most countries around the world. Nevertheless, leaded fuel is still used in some light aircraft applications.

(c) Gasoline direct injection

The gasoline direct injection (GDI), a more fuel-efficient version of the gasoline engine (Maricq *et al.*, 2011; McMahon *et al.*, 2011), entered the marketplace in Japan and Europe in the 1990s and in the USA in 2003. Similarly to the diesel engine, GDI engines inject fuel directly into the combustion chamber (CARB, 2011). This system results in significant reductions in fuel consumption and provides greater power, but increases particle emissions to levels that are intermediate between PFI and diesel engines. In some cases, especially in the stratified charge mode, GDI engines can produce levels of PM emissions similar to those of diesel engines.

1.1.5 Levels of gasoline exhaust emissions

Several tests have been conducted on fleets of vehicles to determine emissions from representative on-road gasoline engines.

Cadle *et al.* (2001) tested a fleet of passenger car and light-duty goods vehicle (24 with normal and six with high emissions) model from years 1990–97 on a chassis dynamometer, using three test cycles and two fuels, one with ethanol (oxygenated) and one without ethanol. The test cycles were a cold-start (35 °F) FTP, a hot-start unified cycle and a hot-start REP05 cycle (high load, high speed cycle). Overall, average PM emissions from normal emitters running on oxygenated fuel were 6.1, 3.2 and 12.7 mg/mile for the FTP, unified cycle and REP05, respectively. Compositions of PM were determined for 12 vehicles (10 normal and two high emitters). For normal emitters, total carbon accounted for approximately 83 and 68% of the PM in the FTP and REP05 tests, respectively, and organic compounds accounted for 36 and 45% of the total carbon in the two tests. Chloride, nitrate and sulfate emission rates were measured, of which sulfate was the highest. These ions accounted for 2.1 and 10.5% of the PM mass in FTP and REP05, respectively. When the water associated with sulfuric acid was included, these compounds accounted for up to 20% of the PM in the REP05. The high particle number emissions observed during the REP05 may have been linked to these sulfuric acid emissions. Fourteen elements were measured using X-ray fluorescence and the major contributors were sulfur, silica, iron, magnesium and zinc. Total elements averaged 2.8 and 15.4% of the PM mass in FTP and REP05, and sulfur (also included in the sulfate mentioned above) was the major contributor. Emissions of PAHs were measured for 20 normal vehicles and four with high emissions. The total PAH emissions were dominated by naphthalene and methylnaphthalene. The FTP PAH emission rates were ~6.5- and 2.3-fold higher than those from the REP05 for normal and high emitters, respectively. Total PAH emission rates were 1.55-fold higher with non-oxygenated than with oxygenated fuel. High emitters exhibited clearly elevated levels of light PAHs, but the pattern for larger four- and five-ring PAHs was less clear.

Zielinska *et al.* (2004) tested a set of models of passenger cars, sport utility vehicles and pick-up HGVs ranging from 1976 to 2000, including both normal and high emitters. Tests were carried out on a chassis dynamometer using the California unified cycle at 72 and 30 °F. Vehicles were classified as NG (new technology gasoline), G and G30 (gasoline, normal emitters at 72 and 30 °F), and WG and BG (gasoline, high-emitting white and black smokers). Average PM emission rates were 2.5, 8.7, 66 and 716 mg/mile for NG, G, BG and WG, respectively, and increased at low temperatures by a factor of about 4. PM emissions were almost entirely carbonaceous, but the ratio of EC to total carbon varied widely: G30 had the highest ratio of ~0.7, G and NG had ratios between 0.4 and 0.5, and WG had the lowest ratio of < 0.05 (presumably mostly lubricating oil). All cars emitted 5 mg/mile or less of total ions; for the G set, sulfate represented 10–20% of the PM emissions. The main elements measured were iron, silica and aluminium, presumably formed from dust ingested by the engine and from engine wear (iron and aluminium). Total elements accounted for 13% of the PM mass from G. Hopanes and steranes are species of high molecular weight and low vapour pressure that are found mainly bound to particles. These species are present mainly in the lubricating oil and are linked to the consumption of engine oil. Most of the PAHs were of low molecular weight and in the gas phase. Gasoline had the highest fraction of high-molecular-weight particle-bound PAHs. The highest total PAH emission rates were from WG, followed by BG and then G. PAH emissions were about 10-fold higher in the low-temperature tests (G30) than at normal temperatures (G). The PAH distributions were very similar to those in used (but not fresh) lubricating oils, which are believed to collect and store partial combustion products. Eight PAHs have been identified as known, probable or possible carcinogens by IARC and/or EPA: benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, chrysene, dibenz[*a*,*h*]anthracene and indeno[1,2,3-*cd*]pyrene. The Working Group calculated the emission levels of the sum of these PAHs, excluding chrysene and dibenz[*a*,*h*]anthracene: 12 and 140 µg/mile from G and G30, respectively; the highest were found from WG (400 µg/mile) and the lowest from NG (3 µg/mile).

Zielinska *et al.* (2004) also measured the levels of nine nitro-PAHs: 1-nitronaphthalene, 2-methyl-nitronaphthalene, methyl-nitronaphthalene, 9-nitroanthracene, 3-nitrofluoranthene, 1-nitropyrene, 7-nitrobenzo[*a*]anthracene, 6-nitrochrysene, and 6-nitrobenz[*a*]pyrene. The sum of their emission rates, excluding 2-methyl-nitronaphthalene and methyl-nitronaphthalene, was calculated by the Working Group. [These two species were excluded to report only those in common with the study by EPA (2008) described below.] Total emission rates of these nitro-PAHs were close to or below the limit of detection from NG [not reported] and were low from the other gasoline vehicles: [0.11], [0.27], [1.29] and [1.02] µg/mile from G30, G, BG and WG, respectively, and were not significantly influenced by temperature.

Fujita *et al.* (2007) tested 57 light-duty gasoline vehicles, two light-duty diesel vehicles and 30 medium- and heavy-duty goods vehicles and buses as part of the DOE Gasoline/Diesel Split Study. The objectives were to determine the relative contributions of gasoline and diesel vehicles to ambient fine PM and to identify suitable markers for diesel and gasoline exhaust. Gasoline vehicle models ranged from earlier than 1980 to 1996 and more recent, and included six 'smoker' [vehicles with high emissions and visible smoke in the exhaust] models from 1969 to 1990. These vehicles were tested using modified cold- and hot-start unified cycles. The trucks included three weight categories (range of model years): seven light-heavy (1989–2000), seven medium-heavy (1988–99) and 16 heavy-heavy (1985–2001). The HGVs were tested using a city suburban and a highway driving cycle. A 1982 and a 1992 transit bus were also tested. PM mass, elements, ions, organic compounds, EC, PAHs, hopanes, steranes, alkanes and polar organic compounds were measured. Total $PM_{2.5}$ emissions of 1995–99 model gasoline vehicles were 3.7 mg/mile for warm starts and 8 mg/mile for cold starts. Average emissions of the entire gasoline fleet (all model years) were 16.9 and 27.2 mg/mile for hot and cold tests, respectively, and were highly skewed; the 10% that were the highest emitters were responsible for about two-thirds of the total emissions. PM emissions from 1997–2000 model light-heavy goods vehicles ranged from 150 to 230 on the city suburban cycle, and from 65 to 90 mg/mile on the highway cycle; for 1995–99 model medium-heavy goods vehicles, the emissions ranged from 70 to 450 and from 60 to 210 mg/mile on the city suburban and highway cycles, respectively; and for 1994–2001 model heavy-heavy goods vehicles, they ranged from 310 to 1130 and from 130 to 520 mg/mile on the city suburban and highway cycles, respectively. Average PM emissions for the HGV fleet were 404 and 187 mg/mile for the city suburban and highway tests, respectively, and were less skewed than those of gasoline vehicles. Emissions of non-carbonaceous materials from both gasoline and diesel engines were relatively small; silicon and ammonium sulfate were the dominant emissions. Elements present in lubricating oil (zinc, calcium and phosphorus) were present in all samples at very variable amounts, probably depending on the consumption of lubricating oil. The EC to total carbon fraction for heavy-duty vehicles ranged from 0.37 to 0.74 and was usually above 0.5; the fraction for gasoline engines was below 0.25 for all samples, except for high black carbon vehicles.

Both low- and high-emitter gasoline vehicles emitted larger amounts of the high-molecular-weight particulate PAHs, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene and coronene, which have been identified as potential markers for gasoline emissions, than diesel vehicles. In contrast, diesel emissions contained higher levels of two- to four-ring semi-volatile PAHs. Total levels of carcinogenic PAHs [see above] were [140] and [180] µg/mile in combined city suburban and highway emissions from combined light-heavy and medium-heavy, and heavy-heavy diesel vehicles, respectively. Emissions of these substances from gasoline vehicles were lower, ranging from [2.6] to [13] µg/mile for low emitters after warm starts and smokers after cold starts. Similar compositions and amounts of hopanes and steranes were present in lubricating oil for both gasoline and diesel vehicles but were negligible in gasoline or diesel fuels. Total hopane and sterane emissions on a mass per mile basis were higher from diesel vehicles, but the relative contribution of hopanes and steranes to total carbon emissions was similar in diesel and gasoline exhausts. Thus, hopane and sterane emission levels were related to the rate of oil consumption. The three high-molecular-weight marker PAHs generated by combustion were found in used gasoline motor oil but not in fresh oil and were negligible in used diesel engine oil (Fujita *et al.*, 2007).

The Kansas City Light-Duty Vehicle Emission Study (EPA, 2008) was designed to evaluate the relative contributions of diesel and gasoline vehicles to $PM_{2.5}$, by taking comprehensive measurements of the emissions of PM, as well as other regulated and unregulated compounds, from a representative sample of light-duty gasoline-powered vehicles in the USA fleet (Fulper *et al.*, 2010). Vehicles were tested on a portable chassis dynamometer under ambient temperature conditions. All tests were run using the LA92 unified cycle, and were conducted in two phases: a summer phase in 2004 with a fleet of 261 vehicles (80 HGVs and 181 passenger cars), and a winter phase in 2005 with a fleet of 235 vehicles (119 HGVs and 116 cars). Each class of vehicles was subdivided into four subgroups by model year: pre-1981 (as old as 1968), 1981–90, 1991–95 and 1996 and more recent (as new as 2004). The PM emissions ranged over more than three orders of magnitude, with a downward trend for more recent vehicles; however, even within a given model year subgroup, emissions ranged over up to two orders of magnitude. The median PM emissions from passenger cars in the summer tests were 45, 7, 5 and 2 mg/mile for the pre-1981, 1981–90, 1991–95 and post-1996 models, respectively. Median PM emissions from HGVs were typically higher by a factor of about two. Median emissions of carcinogenic PAHs (see above) from passenger cars in the summer tests were [120], [25], [15] and [3] µg/mile for the pre-1981, 1981–90, 1991–95 and post-1996 models, respectively. Nineteen nitro-PAHs were measured. Combined emission levels of the seven nitro-PAHs reported in the study by Zielinska *et al.* (2004) from cars in the summer tests were [0.23], [0.70], [0.11] and [0.00] µg/mile for the pre-1981, 1981–90, 1991–95 and post-1996 models, respectively.

Andersson *et al.* (2009) reported the chemical composition of PM from lean-burn GDI engines that meet Euro 4 standards: carbon, 55.8%; all hydrocarbons, 36%; sulfates, 2.2%; nitrate/nitrite, 4%; and water, 3%.

Khalek *et al.* (2010) tested a 2009 GDI engine using three commercially available fuels. Emissions ranged from 0.7 to 3.2 mg/km on the FTP cycle and from 1.3 to 12.8 mg/km on the more aggressive US06 cycle. Zhang & McMahon (2012) tested a fleet of nine 2007–10 model GDI light-duty vehicles and one 2009 model PFI vehicle, all of which met the California LEV II emission standard (see Section 1.3). The vehicles were tested on the FTP cycle and PM emissions ranged from 1 to 5.3 mg/km from the GDI vehicles and were 0.4 mg/km from the PFI vehicle.

1.1.6 Comparison of levels of emissions from current technology diesel and gasoline engines

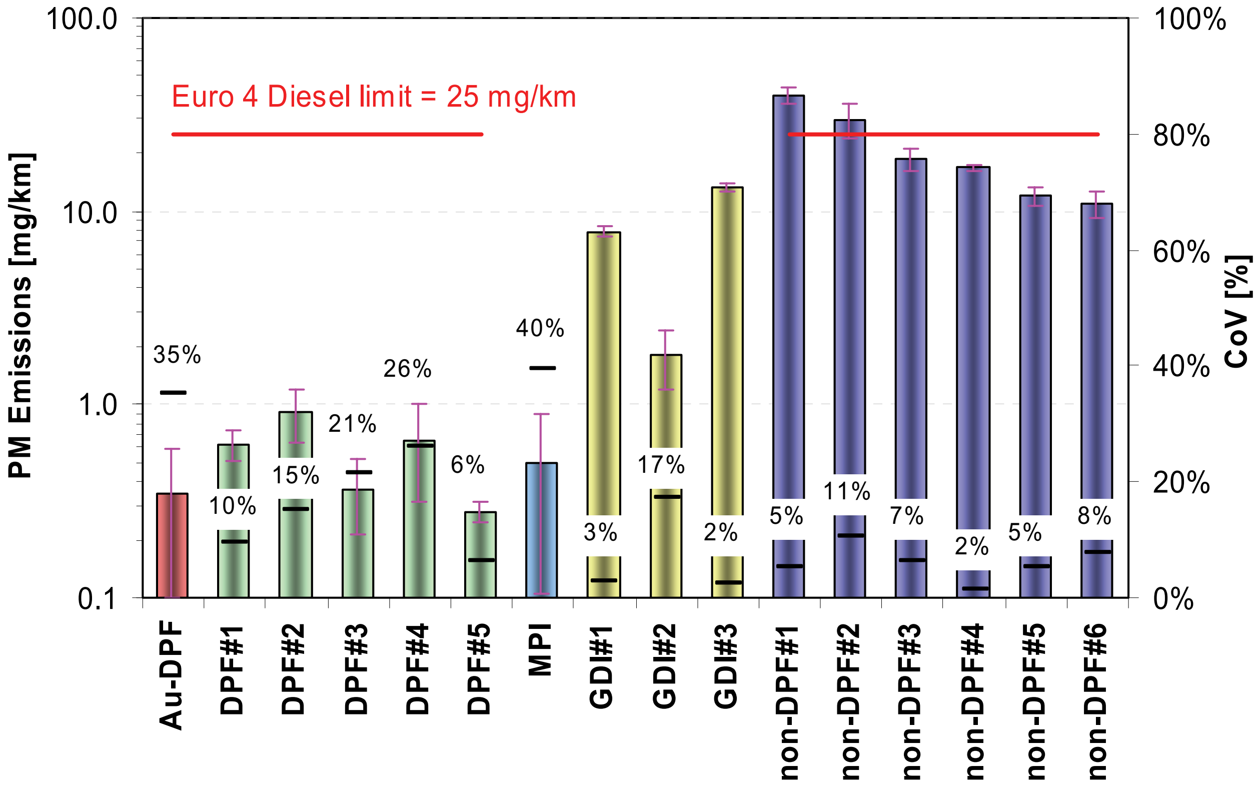
(a) Light-duty vehicles

Only a few studies have compared the emissions from current technology gasoline and diesel light-duty vehicles.

The bulk composition of PM emitted by GDI engines was similar to that of diesel engines without a DPF, i.e. mostly EC and hydrocarbons and other volatile compounds (Andersson *et al.*, 2009). At present, PM emissions from GDI engines are higher than those from PFI gasoline engines and diesel engines with a DPF.

In the 'PARTICULATES' programme, Samaras *et al.* (2005) tested nine diesel cars not fitted with a DPF that met the Euro-3 (model year, 2000) and earlier standards, five diesel cars fitted with a DPF that met the Euro-3+ standards (model year, 2000–05), six gasoline PFI engines that met the Euro-1 (model year, 1992), ultra-low emission vehicle and Euro-3 standards and five GDI cars that met the Euro-3 standards (see the Annex for a definition of the standards). PM emission levels of DPF-equipped vehicles were generally below 3 mg/km, although one vehicle emitted 7 mg/km. Those from GDI vehicles ranged from 4 to 11 mg/km and the majority of measurements were below 10 mg/km. Gasoline PFI vehicles emitted PM in the same range as diesel vehicles fitted with a DPF. The two older gasoline cars that met the ultra-low emission vehicle and Euro-1 standards emitted greater levels than the more recent models, but these were still below 2.5 mg/km. The authors questioned whether the methods used for the measurement of PM were appropriate for such ultra-low emitting vehicles. PAH measurements focused on the sum of 23 'particle-bound' PAHs. For the DPF-equipped

Fig. 1.8 Levels of particulate matter emission for diesel, diesel particle filter (DPF), port fuel-injected (PFI) gasoline and gasoline direct injection (GDI) vehicles measured in the PMP Programme



Au-DPF, golden vehicle (reference); DPF, diesel particle filter; GDI, gasoline direct injection; MPI, part-injected gasoline; PFI, port fuel-injected; PMP Programme, Particle Measurement Programme
Reprinted with permission from Andersson *et al.* (2007)

vehicles, the sum of PAHs ranged from 1.5 to 3 and from 0.2 to 0.6 µg/km during cold-start and motorway cycles, respectively. For gasoline vehicles, the sum of PAHs ranged from < 0.25 µg/km on the motorway cycle to 1.5 µg/km on a cold-start cycle. PAH emissions were very dependent on vehicle technology and driving cycle and increased significantly on cold-start cycles.

During the Particle Measurement Programme (Andersson *et al.*, 2007), a variety of modern vehicles (six conventional diesel, six diesel fitted with a DPF, one PFI gasoline and three GDI engines) was tested in multiple laboratories in Europe and Japan. The test fleet comprised predominantly Euro-4 vehicles, except for two vehicles that were tested in Japan with local calibrations. One of the DPF-fitted diesel vehicles (the so-called golden vehicle) was shipped from laboratory to laboratory while the other vehicles were provided locally. Fig 1.8 shows the average PM emissions on a test cycle that included cold start, urban, suburban and motorway components (New European Driving Cycle). PM emissions ranged from 11 to 40 mg/km for conventional diesel vehicles, from 0.3 to 0.9 mg/km for diesel vehicles with a DPF, and from 1.8 to 13.3 mg/km for GDI vehicles, and were 0.5 mg/km for the PFI gasoline vehicle.

Vouitsis *et al.* (2009) tested two Euro-4 passenger cars, one with a diesel and one with a

PFI gasoline engine. The diesel engine was tested under two configurations: the standard combination of an oxidizing catalyst and an SCR system for the control of nitrogen oxides, and a modified combination in which the oxidizing catalyst was replaced by a DPF. Total PM, carbon, elements, ions and PAHs were measured during four different driving cycles. Total PM ranged from 22 to 37 mg/km for the conventional diesel engine, from 1 to 5 mg/km for the DPF-fitted diesel engine and from 1 to 3 mg/km for the gasoline vehicle. The average chemical profile of the PM was: 97% carbon, 0.08% PAHs, 0.22% elements and 2.76% ions for the conventional diesel engine; 48% carbon, 0.22% PAHs, 1% elements and 51% ions for the DPF-fitted diesel engine; and 89% carbon, 0.26% PAHs, 0.86% elements and 10% ions for the gasoline engine. The principal ions were sulfate, nitrate and ammonium. Four of the six heavy PAHs discussed above (benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*k*]fluoranthene and benzo[*b*]fluoranthene) were measured, the sum of which, depending on the operating cycle, ranged from not detected to 1.8 µg/km for the conventional diesel engine, from not detected to 0.1 µg/km for the DPF-fitted diesel engine and from not detected to 0.3 µg/km for the gasoline engine.

(b) Comparisons on the basis of fuel emissions

Comparisons of light-duty emissions with medium- and heavy-duty emissions that are measured in grams per mile, and heavy-duty emissions that are measured in grams per brake horse power-hour (g/bhp-h) are difficult. A further complication is that the various studies frequently used different test cycles. However, the conversion of emissions to a fuel-specific form – mass emissions per mass of fuel (g/kg$_{\text{fuel}}$) – allows some comparisons to be made. The conversion from grams per mile is:

$$\frac{g}{kg_{fuel}} = \frac{g}{mi} \times \frac{mi}{gallon} \times \frac{gallon}{kg_{fuel}} = 0.31 \frac{mi}{gallon} \times \frac{g}{mi}$$

for a typical fuel density of 0.85 kg/L.

Fuel economy varies with vehicle type from less than four miles per gallon (4 mpg) for some heavy-duty goods vehicles and buses to over 60 mpg for small light-duty vehicles. The conversion for heavy-duty vehicles is:

$$\frac{g}{kg_{fuel}} = \frac{g}{bhp - hr} \times \frac{bhp}{kW} \times \frac{kWh}{kg_{fuel}} = 1.34 \frac{1}{BSFC} \times \frac{g}{bhp - hr}$$

where 1.34 is the conversion from kilowatts (kW) to brake horse power (bhp) and BSFC is the engine brake-specific fuel consumption in kg$_{\text{fuel}}$/kW-h. BSFC values vary from > 1 kg$_{\text{fuel}}$/kW-h at very light loads to < 0.2 kg$_{\text{fuel}}$/kW-h for large diesel engines running at a high load.

The Working Group used the conversions to compare emissions from new technology diesel engines with those from gasoline engines (Table 1.7). [The Working Group noted that these data are for typical operating cycles and for vehicles with the latest technology for both diesel and gasoline engines. Values of miles per gallon and BSFC are the best estimates for a given test cycle and vehicle type when values are not provided by the authors.] The current heavy-duty PM emission standard converts to 34 mg/kg$_{\text{fuel}}$. The values for the four engines tested by Khalek *et al.* (2011) averaged 5 mg/kg$_{\text{fuel}}$; those for the vehicles tested by Herner *et al.* (2009) and Andersson *et al.* (2007) ranged from 2 to 17 mg/kg$_{\text{fuel}}$; and the vehicle retrofitted with a DPF in the study by Vouitsis *et al.* (2009) emitted 47 mg/kg$_{\text{fuel}}$.

For gasoline vehicles, the current light-duty PM emission standards in Europe and in the USA are 78 and 62 mg/kg$_{\text{fuel}}$, respectively. The estimate of emissions from the current in-use gasoline fleet (CARB, 2011) is 25 mg/kg$_{\text{fuel}}$ and the emissions from the various fleets tested ranged

Table 1.7 Comparison of fuel-specific emissions of diesel engines and gasoline engines

Technology	Vehicle type	PM emission level			Assumed	High MW PAHs			1-Nitropyrene		
		(g/bhp-h)	(g/mile)	(g/kg fuel)	(mpg)	(ng/bhp-h)	(ng/mile)	(ng/kg fuel)	(ng/bhp-h)	(ng/mile)	(ng/kg fuel)
New technology diesel engines[a]											
2010 HDV diesel standard		0.01		0.034							
Khalek *et al.* (2011)		0.0014		0.005		0.5		2	20		70
Liu *et al.* (2010)						77		260	0.25		1
Pakbin *et al.* (2009)					8		5.6	7			
Heeb *et al.* (2008)								2			350
Herner *et al.* (2009)	High emitter		0.0140	0.017	6						
Herner *et al.* (2009)	Low emitter		0.0010	0.002	4						
Andersson *et al.* (2007)	Average		0.0010	0.010	35						
Vouitsis *et al.* (2009)	Average		0.0043	0.047	35		44	480			
Traditional diesel engines											
Wail & Hoekman (1984)		Unregulated[b]		NA	6	78 000		220 300			
PFI gasoline											
Current LDV standard (USA)			0.0100	0.062	20						
2009 Euro-5 (EU)			0.0072	0.078	35						
CARB (2011)	LDV fleet		0.0040	0.025	20						
Fujita *et al.* (2007)	Lowest emitter		0.0004	0.002	20		2600	16 000			
EPA (2008)	Latest LDV		0.0020	0.012	20		2700	17 000		0.7	2
Li *et al.* (2006)	SULEV		0.0002	0.001	20						
Andersson *et al.* (2007)	Average		0.0008	0.009	35						

Table 1.7 (continued)

Technology	Vehicle type	PM emission level			Assumed	High MW PAHs			1-Nitropyrene		
		(g/bhp-h)	(g/mile)	(g/kg fuel)	(mpg)	(ng/ bhp-h)	(ng/mile)	(ng/kg fuel)	(ng/ bhp-h)	(ng/mile)	(ng/kg fuel)
Vouitsis *et al.* (2009)	Average		0.0021	0.023	35		216	2400			
GDI											
Andersson *et al.* (2007)	Average		0.0123	0.134	35						
Zhang & McMahon (2012)	Average		0.0039	0.036	30						

[a] Assumed BSFC of 0.4 kg/kWh

[b] Actual BSFC of 0.475 kg/kWh

BSFC, brake-specific fuel consumption; EU, European Union; GDI, gasoline direct injection; HDV, heavy-duty vehicle; LDV, light-duty vehicle; mpg, miles per gallon; MW, molecular weight; NA, not applicable; PAHs, polycyclic aromatic hydrocarbons; PFI, port-fuel injection; PM, particulate matter; SULEV, super ultralow-emitting vehicle from 1 to 23 mg/kg_{fuel}. The average value of PM emissions from the three GDI vehicles tested by Andersson *et al.* (2007) was 130 mg/kg_{fuel}, but engines have evolved rapidly, and the average level of emissions from nine GDI vehicle tested 5 years later by Zhang & McMahon (2012) was 36 mg/kg_{fuel}. Levels of PAHs and 1-nitropyrene were also converted into nanograms per kilogram of fuel. The level of high-molecular-weight particle-bound PAHs ranged from 2 to 480 and from 2400 to 17 000 ng/kg_{fuel} for DPF-fitted diesel and PFI gasoline engines, respectively. Emissions of 1-nitropyrene ranged from 1 to 350 ng/kg_{fuel} for DPF-fitted diesel engines, and those for the only gasoline engine measured were 2 ng/kg_{fuel}.

1.2 Sampling and analysis

Diesel and gasoline engine exhausts are complex mixtures of gaseous and PM species that require special methods for sampling and analysis. The gaseous species of interest are carbon monoxide, nitrogen oxides and various volatile and semi-volatile organic compounds; PM is a complex matrix in involving EC and organic carbon, various ions and metals.

This section reviews the methodologies of sampling and analysis for diesel and gasoline exhausts constituents, as well as the corresponding methodologies for monitoring ambient air and biomonitoring.

1.2.1 Sampling

(a) Experimental settings and testing

Sampling of engine exhaust is typically carried out in specialized laboratories where the engine (usually heavy-duty engines) or the vehicle (usually light-duty passenger vehicles) is operated under prescribed conditions while connected to a dynamometer which simulates the load on the engine. Heavy-duty vehicles can also be tested on chassis dynamometers, and an increasing number of studies have used transportable heavy-duty vehicle chassis dynamometers (Zhen *et al.*, 2009). The dynamometer drive and duty cycles used for the measurement of exhaust emissions generally attempt to replicate the main characteristics of the type of load that the engines may experience during ‘real-life’ use.

The raw exhaust is typically introduced into a constant volume sampling system with a dilution tunnel where it is diluted with air filtered by high-efficiency particulate filters at dilution ratios in the range of 10–100 to avoid condensation before PM and gaseous samples are collected from the diluted sample for analysis. Gaseous and PM species in engine exhaust can be sampled under either raw or dilute conditions. However, particulate sampling must be diluted even when the first sampling step is from undiluted exhaust. The dilution step for particulate sampling is to ensure that hydrocarbon vapours condense onto the particles to simulate ambient exposure conditions. When particulates reach the sample filters, the temperature must be 47 °C ± 5 °C (range, 42–52 °C) (IRSG, 2012a, b). Traditionally, diesel PM has been collected on filter media and then analysed to determine its chemical composition. The most commonly used method to determine the gravimetric PM mass is the sampling technique described by the EPA (2000, 2001) in the USA. Filter sampling is sensitive to thermodynamic and chemical phenomena, and is also accompanied by potential reactions of gases with the PM on the filter or with the filter medium during sampling and the absorption of water from humid air (IRSG, 2012a, b).

Gases (carbon monoxide and carbon dioxide, and nitrogen oxides) and hydrocarbon vapours in dilute exhaust are collected in tedlar bags or Summa canisters sequentially over the test phase(s) and analysed online by dedicated non-dispersive infrared (carbon monoxide and carbon dioxide), chemiluminescence (nitrogen oxides) or flame ionization detectors (total hydrocarbons), respectively. Corresponding measurements are made for the dilution air to correct for any contribution to the diluted exhaust from that source. The dedicated analysers can also be used for taking instantaneous measurements during a test. Carbon dioxide is measured essentially to determine fuel consumption via a carbon balance and may be used to determine the dilution ratio. Volatile organic compounds collected in tedlar bags can later be analysed by GC-MS methods. Carbonyl compounds are absorbed in dinitrophenylhydrazine cartridges while gas- and particle-phase semivolatile PAH and nitro-PAH species are adsorbed onto different media for later chemical analysis.

The details of procedures for testing vehicles and engines are proscribed by various bodies in the USA (EPA, 2000, 2001) and in Europe. The test methods in Europe and in the USA are similar, although the European engine test cycles reflect road and use conditions that differ from those in the USA (CONCAWE, 2006a, b, c).

In contrast to the dilution approach, Heeb *et al.* (2007, 2008, 2010) described a special sampling procedure in which undiluted exhaust was sampled through a device comprising a probe, a cooler, a condensate separator, a filter stage and a two-stage adsorber unit. The procedure was used in the investigation of the secondary effects of 14 different DPFs with respect to PAHs, nitro-PAHs and dioxins/furans.

(b) Ambient air

Carbon monoxide and nitrogen oxides can be monitored continuously in ambient air. Hourly averages are typically recorded. Passive samplers are used for personal exposure in occupational settings (methods 6104 and 6604 for nitrogen oxides and carbon monoxide, respectively; NIOSH, 1994a, 1996). Analysis of organic compounds (volatile organic compounds and PAHs) in ambient air relies on methods similar to those for engine exhaust without dilution, and sampling is typically carried out using Summa canisters rather than tedlar bags.

PM mass concentration is typically determined by methods based on gravimetric filters that can be distinguished by size (e.g. PM_{10}, $PM_{2.5}$ and $PM_{1.0}$) when the sampling apparatus has size-selective inlets designed to exclude particles with aerodynamic diameters greater than the specified number (in micrometres). Compared with dilute exhaust, higher volumes of ambient air need to be sampled due to its lower concentrations. Several techniques provide continuous (real-time) PM concentrations in ambient air with appropriate calibration against reference methods.

1.2.2 Analysis

(a) Particulate matter

The mass concentration, size distribution and chemical composition of Particulate matter (PM) are all important factors from the perspective of health effects in humans. $PM_{2.5}$ has been widely used as a general marker of fine-particle air contaminants (see Section 1.4.2), but is less useful for traffic emissions due to the high background of materials related to regional emissions and because exhaust components comprise only a small fraction of the total mass.

Burtscher (2005) reviewed methods for the physical characterization of particulate emissions from diesel engines in terms of particle mass, number, surface area, density and structure. Particle mass and number counts, together with size distribution, are the more widely used measures. Particle number counts are determined by condensation particle counters. Coagulation, diffusional losses and the variation in lower size limit (between 3 nm and ~15 nm) of different condensation particle count models may account for variations in number counts (Burtscher, 2005). Systems to determine size distributions in the submicron range are based on mobility analysis or impaction – for example, the scanning mobility particle sizer (Wang & Flagan, 1990) or the electrical low pressure impactor (Keskinen *et al.*, 1992). Schlatter (2000) performed a round robin test of 11 scanning mobility particle sizer systems and showed differences of up to 10% in the particle size and 20% in the number concentration of diesel particles; these differences were attributed mainly to inaccurate flow controllers.

The transverse element oscillating microbalance can give mass concentrations in real time for both engine exhausts and ambient air that are in line with gravimetric methods. Ayers *et al.* (1999) reported ~30% lower values compared with gravimetric methods for ambient air measurements in four Australian cities, which they attributed to the loss of semi-volatile aerosol material from the heated sample filter employed on the microbalance. A calibration/correction model has been proposed to resolve this discrepancy (Green *et al.*, 2009).

Portable dust monitors for $PM_{2.5}$ and PM_{10} are used effectively to assess occupational and environmental exposure to aerosols. Cheng (2008) provided comparisons of measurements from gravimetric methods and the transverse element oscillating microbalance, with satisfactory results when appropriately calibrated.

PM in engine exhaust is a complex mixture of EC and organic carbon, metals and sulfate. EC and organic carbon are discussed in a separate section below.

The major elemental components can be analysed by X-ray fluorescence, a non-destructive measurement technique made directly on the filter. However, inductively coupled plasma-MS is necessary for trace and ultra-trace components; this destructive method requires acid digestion to dissolve the sample. Ion chromatography is used for inorganic and organic ionic species (nitrate, nitrite, sulfate, sulfite, elemental anions, ammonium, elemental cations, formate, acetate and oxalate). Capillary electrophoresis is used for the quantitation of organic acid ions and to confirm the results of inductively coupled plasma-MS.

(b) Elemental and organic carbon

The determination of EC and organic carbon components of PM is based on the principle of heating the filter in an inert atmosphere (helium) in which the organic carbon is expected to be removed from the PM on the filter by volatilization and pyrolysis, and then repeating the process in an oxidizing gas (oxygen–helium) in which EC is expected to be converted to carbon dioxide. Changes in the optical properties of PM on the filter, as determined by the reflection or transmittance of laser illumination, govern the temperature ramp and the switch between the inert and oxidizing gas environment. The fractions removed in subsequent temperature intervals are then termed sequentially.

Chow *et al.* (2001) compared the operational protocols used in the IMPROVE and National Institute of Occupational Safety and Health (NIOSH) networks/methodologies. Similarly, ten Brink *et al.* (2004) reported on the comparability of methods used in Europe to measure the concentration of aerosol–carbon. Four methods are available to measure EC/organic carbon, which differ in the times, temperatures and inert versus oxidative environments at different stages of the procedure. Two apply heat in a reduced atmosphere to remove organic carbon and one of these corrects for charring/pyrolysis of the sample with optical correction. The other two use a two-step oxidative method, with a first oxidation step at a lower temperature to remove organic carbon under oxidative conditions, and a second final oxidation step at a high temperature to oxidize EC. Differences between the methods of more than a factor of 3 were observed, but the daily EC concentrations over the sampling period were highly correlated ($r^2 > 0.9$).

(c) Black carbon

The terms 'elemental carbon', 'soot', 'black carbon' and 'light-absorbing carbon' in suspended particles are used loosely and often interchangeably in the literature. The definition of EC is further complicated by the many different methods applied for its quantification, the most commonly applied being thermal evolution, light transmission or reflectance and solvent extraction. Chow *et al.* (2001) compared two studies that applied different protocols (developed for each of these methods) to the same samples with instruments calibrated against common standards. Results for total carbon were usually very consistent between protocols (typically within ~5%). Data for EC were often also reasonably comparable (within ~20% for diesel exhaust samples); however, differences by a factor of 2 or more were observed when ambient samples were measured with different protocols.

The aethalometer is one of the most frequently used techniques to measure real-time black carbon mass concentrations, especially for long-term background measurements. It is based on the attenuation of a broad-band light source (maximum wavelength, < 820 nm) due to particles accumulated on a quartz fibre filter. In one study at an Alpine site, EC and black carbon measurements were in good agreement (Lavanchy *et al.*, 1999).

Hitzenberger *et al.* (1999) compared one thermal and two optical methods that were applied to laboratory-generated aerosols that contained only black carbon. Differences in the measurement of black carbon of 20–30% were observed between the methods.

In the INTERCOM 2000 study (ten Brink *et al.*, 2004), black carbon was measured using three independent methods: the aethalometer, the integrating sphere technique and a third method that determines the difference in light reflection of loaded and unloaded filters. Similar to the observations on EC, the differences between the results for black carbon were considerable; however, the daily concentrations were highly correlated.

The comprehensive Carbonaceous Species Methods Comparison Study was carried out with the participation of 30 different research groups from the USA and Canada (Lawson & Hering, 1990). Special sampling artefact studies were also performed simultaneously with side-by-side ambient sampling to assess the relative magnitude of absorption, volatilization or chemical reaction artefacts under field conditions.

(d) Polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs

Nitro-PAHs are difficult to analyse because they are typically present at low concentrations (typically low or subpicograms per cubic metre in air) and in combination with significant concentrations of other compounds that may interfere with the analysis. Before detection by chemical analysis, these substances were identified and quantified by fractionation of diesel exhaust particulate extracts and subsequent testing in the *Salmonella typhimurium* mutagenicity (Ames) assay (Gibson, 1983; Arey *et al.*, 1988; Kinouchi *et al.*, 1988; Hayakawa *et al.*, 1995). The involvement of nitro compounds was suggested by the appearance of strong direct mutagenicity, which was reduced by addition of a liver enzyme microsome fraction and also by the use of bacterial strains with a low or lack of nitroreductase activity for a comparison with mutagenic activity in the parent strains. Strains with enhanced nitroreductase activity were introduced for the sensitive detection of nitrated mutagens (Scheepers *et al.*, 1991).

The chemical analysis of nitro-PAHs has been reviewed extensively (IPCS, 2003). Zielinska & Samy (2006) reviewed many of these considerations for analysis in air, most methods of which collect the aerosol onto filters (Teflon-coated glass fibre or quartz fibre filters) and sorbents (e.g. XAD-4). The PAH or nitro-PAH species captured on the filter or sorbent media is recovered by solvent extraction. The solvents are typically used in a specialized (Soxhlet, microwave extraction, supercritical fluid extraction or ultrasonication) apparatus and comprise hexane, toluene, dichloromethane, acetone and methanol, used individually or in combination.

Most methods require extensive solvent clean-up of the extracts before analysis. Extraction methods may include Soxhlet, sonication or pressurized fluid extraction. Common approaches include GC-MS and liquid chromatography-MS. However, several other chromatographic methods have been used successfully, many of which required chemical modification (derivatization) of the nitro-PAHs before analysis to enhance affinity for specialized detectors, such as electron capture or fluorescence (Zielinska & Samy, 2006). Immunoaffinity methods have also been used with some success (Zühlke *et al.*, 1998). Negative ion chemical ionization-GC-MS has historically been the method of choice because it provides enhanced sensitivity and selectivity compared with many other methods. Liquid chromatography-MS has not been used as extensively as other techniques.

Pandey *et al.* (2011) reviewed the techniques for the determination of airborne PAHs in the gas and particle phases (Fig. 1.9 and Fig. 1.10), while the review by Zielinska & Samy (2006) focused specifically on nitro-PAHs (Table 1.8). Analytical procedures for the individual nitro-PAHs reviewed in this Volume are presented in their respective *Monographs* and are not discussed further here.

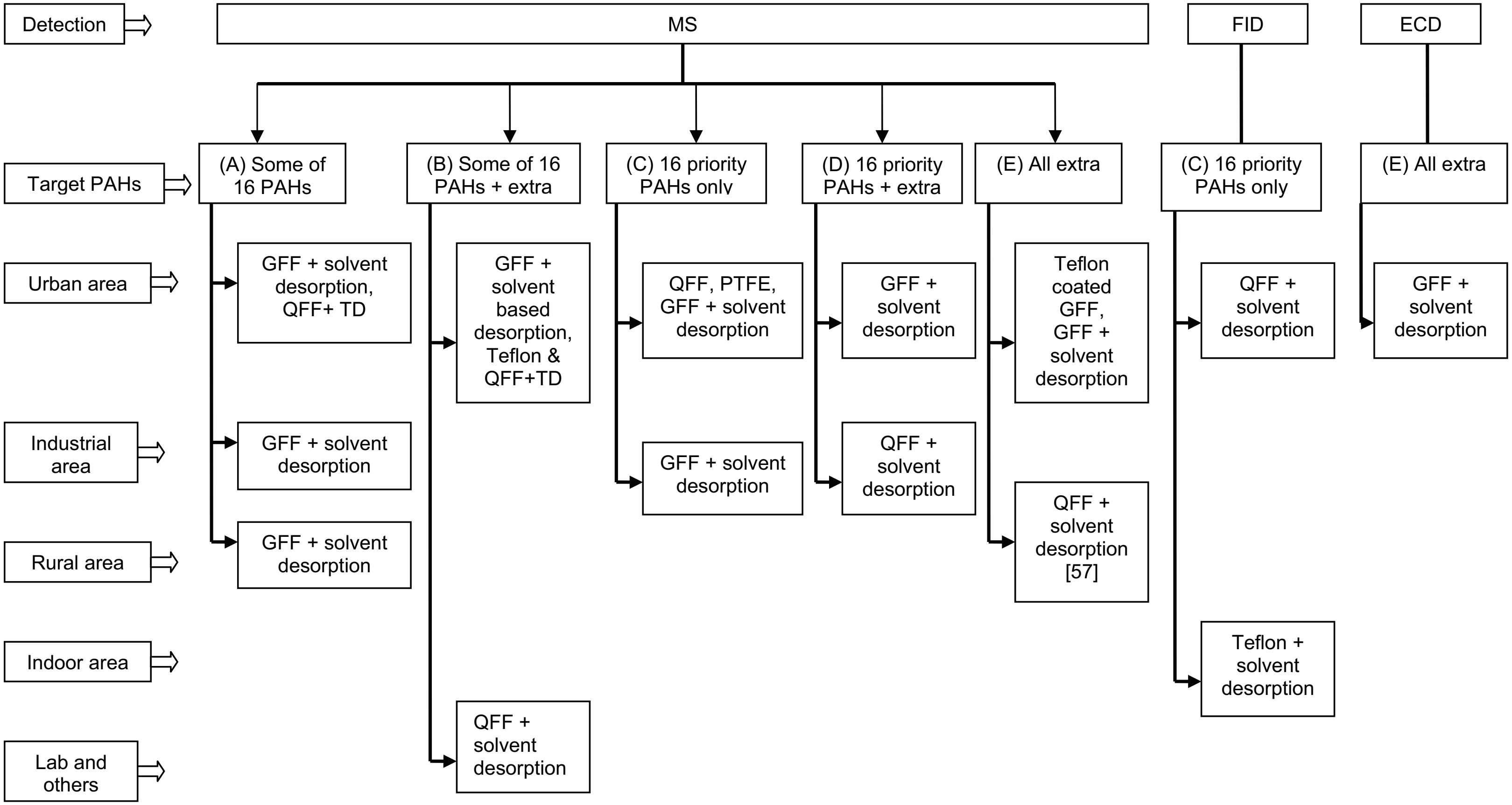
The high-efficiency recovery of all the target species from the filter and sorbent media is an important consideration in these techniques and has been an even greater challenge for nitro-PAH species. Recovery of the target species from the sampling medium is quantified by adding an internal standard (e.g. triphenylene and *para*-quaterphenyl; Schauer *et al.*, 2004) or deuterated nitroarenes that have the same recovery rates as the non-deuterated analogues (Zielinska & Samy, 2006). Albinet *et al.* (2006) reported recovery rates of nitro-PAHs for the whole analytical procedure in the range of 14% (1-nitronaphthalene) to 84% (7-nitrobenz[*a*]anthracene), while those of oxy-PAHs ranged from 5% (1-naphthaldehyde) to 83% (benzo[*b*]fluorenone).

Castells *et al.* (2003) used a two-step supercritical fluid extraction procedure to remove non-polar compounds, such as aliphatic hydrocarbons, using pure carbon dioxide as the extraction fluid in the first step, and extract nitro- and oxy-PAHs with toluene–carbon dioxide in the second, with total recoveries of 68–93% (Table 1.9). The second step represents one- third to half of the total recovery. Total 1-nitropyrene recovery was 72%, with 42% from the second step. An earlier study (Paschke *et al.*, 1992) compared the extraction of PAHs and nitro-PAHs from diesel exhaust particulates and diesel soot using supercritical chlorodifluoromethane, carbon dioxide and carbon dioxide with added modifiers. Supercritical fluid extraction with pure chlorodifluoromethane yielded the highest recovery (117 ± 7%) of 1-nitropyrene and carbon dioxide modified with toluene yielded 97 ± 7%.

‘Reduction’ refers to the process by which nitro-PAH species are reduced to their respective amino-PAHs or other derivatives; this is required for sensitive detection because the parent nitro-PAHs exhibit only very weak fluorescence and chemiluminescence signals (Schauer *et al.*, 2004). ‘On-line’ and ‘off-line’ methods exist for this reduction process; the first requires an additional column packed with a reduction agent before the analysis and the second is achieved using a titanium (III) citrate complex as the reducing agent in a hydrochloric acid medium (Table 1.9).

Although the derivatization process is used mostly for high-performance liquid chromatography (HPLC)-fluorescence detection and HPLC-circular dichroism systems, Brichac *et al.* (2004) reported an application of derivatization with a gas chromatography-electron capture detector (GC-ECD). The measurements of nitro-PAHs in ambient PM involved their reduction to the corresponding amino-PAHs with sodium borohydride, followed by derivatization with

Fig. 1.9 Plot of all possible combinations of sampling and detection methods of polycyclic aromatic hydrocarbons in the particle phase



ECD, electron capture detector; FID, flame ionization detector; GFF, glass fibre filter; MS, mass spectroscopy; PAH, polycyclic aromatic hydrocarbons; PTFE, polytetrafluoroethylene filter; QFF, quartz fibre filter; TD, thermal desorption

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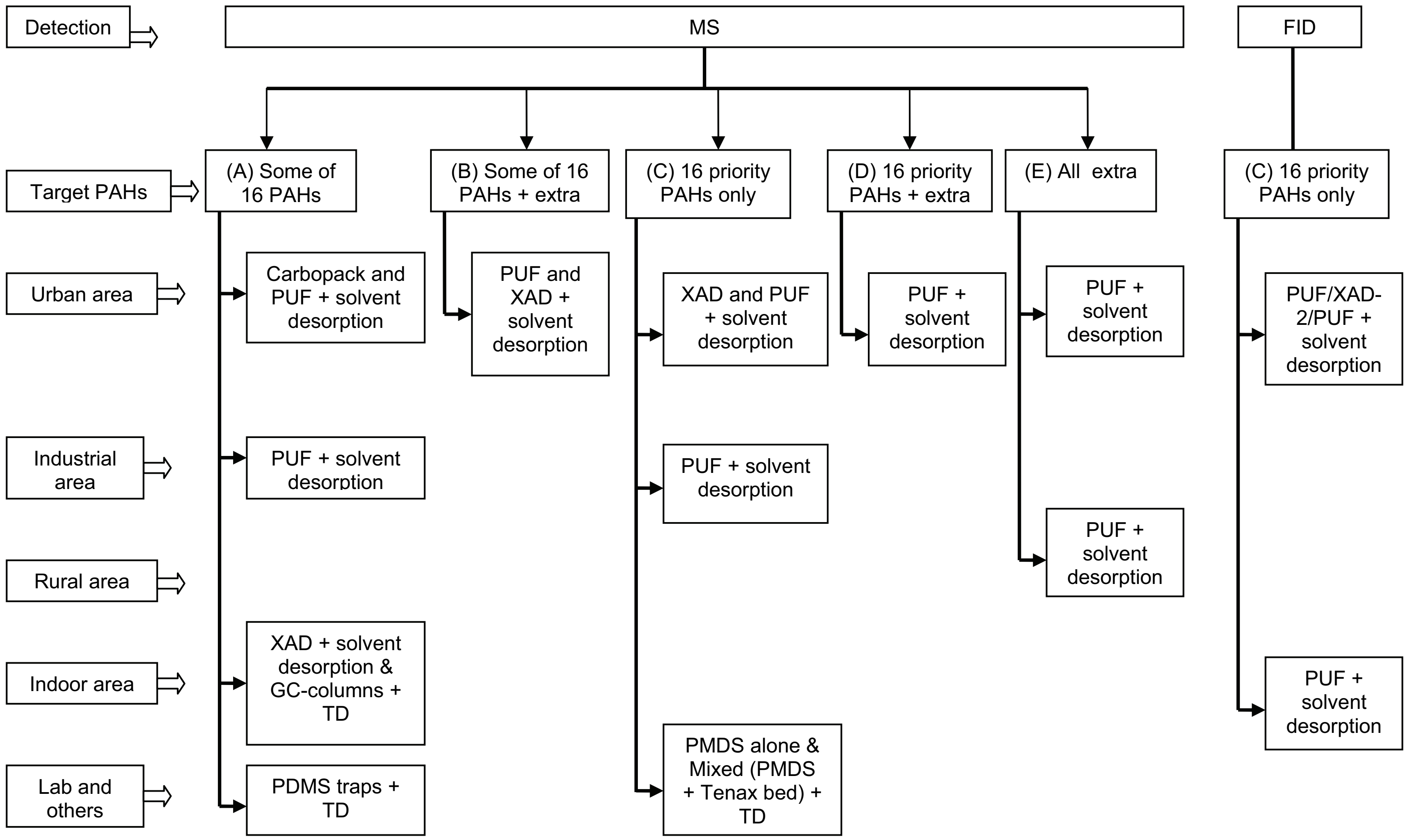
Fig. 1.10 Plot of all possible combinations of sampling and detection methods of polycyclic aromatic hydrocarbons in the vapour phase



FID, flame ionization detector; GC, gas chromatography; MS, mass spectroscopy; PAH, polycyclic aromatic hydrocarbons; PDMS, polydimethylsiloxane foam; PTFE, polytetrafluoroethylene filter; PUF, polyurethane foam; TD, thermal desorption; XAD, polymeric resin
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Table 1.8 Examples of the detection ranges for nitro-polycyclic aromatic hydrocarbons (N-PAHs) associated with particulate matter analysed by gas chromatography/mass spectrometry with various detectors

N-PAH[a]	Detection mode	Extraction technique	Detection range	Sampling environment	Reference
1-NP, 3-NF, 3-NPh, 6-NC, 1,3-DNP, 1,8-DNP	NICI	SE	5–80 ng/m^3, sum for all six species	Industrial workplaces	Chaspoul *et al.* (2005)
1-NP, 2-NP, 7-NBA, 6-NC, 1,3-DNP, 1,6-DNP, 1,8-DNP, 6-NBP, 2-NF, 3-NF, 9-NA, 9-NPh, 2-NFl	NICI	PFE	< 2–282 ng/g	Urban dust (SRM 1649a)	Bamford *et al.* (2003)
19 N-PAHs (see reference for details)	NICI	SE	< 0.1–99 pg/m^3	Urban/suburban (ambient)	Bamford & Baker (2003)
1-NP	EI	SFE	24–104 pg/m^3	Urban (ambient)	Castells *et al.* (2003)
1-NN+2-NN, 14 total MNN	EI	SE	10–1906 pg/m^3	Urban (ambient)	Gupta *et al.* (1996)
1-NN+2-NN	NICI	SE	202–494 pg/m^3	Urban (ambient)	Reisen *et al.* (2003)

[a] 1,3-DNP, 1,3-dinitropyrene; 1,6-DNP, 1,6-dinitropyrene; 1,8-DNP, 1,8-dinitropyrene; MNN, methylnitronaphthalenes; 9-NA, 9-nitroanthracene; 7-NBA, 7-nitrobenz[*a*]anthracene; 6-NBP, 6-nitrobenzo[*a*]pyrene; 7-NBaA, 7-nitrobenz[*a*]anthracene; 6-NC, 6-nitrochrysene; 2-,3-NF, 2- or 3-nitrofluoranthene; 2-NFl, 2-nitrofluorene; 1-,2-NN, 1- or 2-nitronaphthalene; 3-NPh, 3-nitrophenanthrene; 9-NPh, 9-nitrophenanthrene; 1-NP, 1-nitropyrene; 2-NP; 2-nitropyrene

EI, electron ionization/impact; NICI, negative ion chemical ionization; PFE, pressurized fluid extraction; SE, Soxhlet extraction; SFE, supercritical fluid extraction; SRM, standard reference material

From Zielinska & Samy (2006)

heptafluorobutyric anhydride. This procedure adds a polyfluorinated group to the amino-PAH, thus enhancing the sensitivity of electron capture detector analysis by approximately 10-fold in comparison with the GC-ECD analysis of underivatized nitro-PAHs. Murahashi *et al.* (2003a) used a GC-MS method that does not require derivatization (Table 1.10).

(e) Carbon monoxide

Non-dispersive infrared detection is the basis for instruments used to quantify both carbon monoxide and carbon dioxide in exhaust and ambient air, and is a well established method that is widely used.

Gasoline engines typically emit more carbon monoxide per unit quantity of fuel than diesel engines. Thus, carbon monoxide levels have been used as an indicator of emissions from light-duty passenger vehicles. For example, ventilation systems in closed underground garages are typically triggered by carbon monoxide sensors.

NIOSH method 6604 (NIOSH, 1996) describes the analysis of passive sampler media for the measurement of carbon monoxide concentrations in ambient air and occupational settings.

(f) Nitrogen oxides

Chemiluminescent analysers are the principal analytical technology available for determining levels of nitric oxide emissions from combustion sources. Nitric oxide in a gas sample reacts with ozone, which is prepared by an ozone generator in a reaction chamber. The chemiluminescence generated in this reaction is detected with a photomultiplier. The intensity of nitric oxide is in direct proportion to its concentration in a wide range. By switching a three-way valve, the sample gas is passed through a converter to convert nitrogen dioxide to nitric oxide;

Table 1.9 Recoveries obtained for two-step supercritical fluid extraction of spiked[a] urban aerosol samples

Compound	Spiked samples			Non-spiked samples
	Total recovery (%)	RSD (%) ($n = 3$)	Second SFE step[b] (%)	Second SFE step[b]
1,4-Naphthoquinone	84	4	25	ND
2-Methyl-1-nitronaphthalene	68	6	29	ND
2-Nitronaphthalene	70	7	26	ND
9-Fluorenone	76	7	25	28
Acenaphthenequinone	86	3	27	ND
9,10-Anthraquinone	70	7	33	37
1,5-Dinitronaphthalene	89	8	29	ND
2-Methyl-9,10-anthraquinone	78	3	28	26
2-Nitrofluorene	93	5	40	ND
9-Nitroanthracene	89	6	32	ND
Benzanthrone	70	5	37	35
Benz[*a*]anthracene-7,12-dione	78	5	46	48
1-Nitropyrene	72	7	42	39

[a] Spiking conditions: 0.5 mL dichloromethane, incubation time 2 hours

[b] Percentages of the total amount extracted

ND, not detected; RSD, relative standard deviation; SFE, supercritical fluid extraction

From Castells *et al.* (2003)

the concentration of nitrogen oxides (nitric oxide and nitrogen dioxide) can be obtained by measuring the intensity of the chemiluminescence (Bionda *et al.*, 2004). The concentration of nitrogen dioxide in the sample gas can be obtained by calculating the difference between the two measured values. The method is very sensitive and selective for the quantification of nitrogen oxides. Chemiluminescent analysers are usually calibrated with a blend of nitric oxide in a nitrogen balance.

NIOSH method 6014 describes the analysis of passive sampler media for the measurement of concentrations of nitric oxide and nitrogen dioxide in ambient air and occupational settings (NIOSH, 1994a).

Nitric oxide has been used as a marker for HGV exhaust emissions (see Section 1.4.2).

(g) Volatile organic compounds

Volatile organic compounds are typically analysed by GC-MS, although a preconcentration step (by an automated cryogenic concentrator interfaced to the gas chromatograph) is required to achieve adequate detection limits with flame ionization detection. Heavier hydrocarbons (C2–C10) in diesel exhaust are captured on Tenax, solvent extracted and then analysed by GC-flame ionization detection. Aldehydes and ketones are trapped on dinitrophenylhydrazine cartridges. The hydrazones formed on the cartridge are then analysed by HPLC. These methods provide quantitative analysis for about 100 compounds.

1.2.3 Biomarkers of exposure

Sensitive analytical techniques are required to assess the uptake by tissues of chemicals from exhaust emissions.

Table 1.10 Examples of limits of detection (LOD) (per sample) for nitro-polycyclic aromatic hydrocarbon (nitro-PAH)-associated particulate matter analysed by high-performance liquid chromatography with various reduction techniques and detectors

nitro-PAH	LOD (pg) S/N 3	Reduction technique	Detection method	Reference
1-NP, 2-NFl, 6-NC	46, 41, 584	Titanium(III) citrate	FD	Brichac *et al.* (2004)
1-NP, 1,3-DNP, 1,6-DNP, 1,8-DNP	2.20, 1.03, 1.61, 1.71	Electrochemical	FD	Kuo *et al.* (2003)
1-NN, 2-NN, 2-NFl, 9-NPhe, 1-NP, 6-NC, 6-NBaP, 9-NA, 3-NF, 1,6-DNP, 7-NBaA, 1,3-DNP	6–100 (4–80)	Pt (Pt/Rh)	FD	Schauer *et al.* (2004), see also Tejada *et al.* (1986)
3-NBA	2	Raney nickel/ hydrazine	FD	Murahashi *et al.* (2003a)
3-NBA, 2-NTP, 1-NP, 1,8-DNP, 6-NC, 2-NF, 3-NF	5.50, 11.0, 2.0, 6.0, 17.0, 10.0, 3.0	Pt/Rh	CD	Inazu *et al.* (2004)
1-NP, 1,3-DNP, 1,6-DNP, 1,8-DNP	100, 3, 6, 3	Pt/Rh	CD	Hayakawa *et al.* (2001)
1,8-DNN, 9-NA, 3-N-9-Fl, 2,2-DNBphe, 1-NP, 2,7-DNFl, 2,7-DN-9-Fl	1–10	None	MS-NICI	Bonfanti *et al.* (1996)
2-NN, 9-NA, 1-NP	300–1600	Electrochemical	ED	Galceran & Moyano (1993)

CD, chemiluminescence detection; 2,7-DNFl, 2,7-dinitrofluorene; 2,7-DN-9-Fl, 2,7-dinitro-9-fluorene; 2,2-DNBphe, 2,2′–dinitrobiphenyl; 1,8-DNN, 1,8-dinitronaphthalene; 1,3-DNP, 1,3-dinitropyrene; 1,6-DNP, 1,6-dinitropyrene; 1,8-DNP, 1,8-dinitropyrene; ED, electrochemical detection; FD, fluorescence detection; MS, mass spectrometry; 9-NA, 9-nitroanthracene; 7-NBaA, 7-nitrobenz[*a*]anthracene; 3-NBA, 3-nitrobenzanthrone; 6-NBaP, 6-nitrobenzo[*a*]pyrene; 6-NC, 6-nitrochrysene; 2-,3-NF, 2- or 3-nitrofluoranthene; 2-NFl, 2-nitrofluorene; 3-N-9-Fl, 3-nitro-9-fluorene; NICI, negative ion chemical ionization; 1-,2-NN, 1- or 2-nitronaphthalene; 9-NPhe, 9-nitrophenanthrene; 1-NP, 1-nitropyrene; 2-NTP, 2-nitrotriphenylene; Pt/Rh, platinum/rhodium; S/N, signal-to-noise ratio
From Zielinska & Samy (2006)

(a) Biomarkers of exposure to diesel engine exhaust

Organic constituents associated with the particulate phase of diesel exhaust have been proposed as chemical markers of exposure. The measurement of these biomarkers in human body fluids requires sophisticated and ultrasensitive analytical methods. Some of the methods that have been developed to achieve this are discussed below.

(i) Protein and DNA adducts

Nielsen *et al.* (1996) used GC-MS to detect hydroxyethylvaline adducts in haemoglobin as a biomarker to assess exposure to diesel exhaust in garage workers. In addition, they used P1 nuclease extraction of DNA adducts and a butanol method to extract polar DNA adducts from peripheral blood lymphocytes, and detected these adducts using ^{32}P-postlabelling.

Zwirner-Baier & Neumann (1999) detected several nitro-PAH metabolites after hydrolysis of haemoglobin using liquid chromatography equipped with negative ion chemical ionization and MS. [The Working Group noted that this method is based on the hydrolysis of haemoglobin adducts before detection of the free metabolites. It is not certain whether the entire quantity of each of the retrieved (free) metabolites originates from covalent binding to haemoglobin.]

(ii) Urinary metabolites

1-Hydroxypyrene, a urinary metabolite of pyrene, was used as a marker for exposure to diesel exhaust in garage workers (Nielsen *et al.*, 1996). Using GC-MS, Seidel *et al.* (2002) found elevated urinary excretion of 1-Hydroxypyrene and hydroxylated phenanthrene metabolites in salt miners operating diesel-powered equipment. 1-Hydroxypyrene may not be sufficiently specific because it may originate from other combustion sources. A more specific marker for diesel exhaust is 1-nitropyrene (Schuetzle & Perez, 1983; Scheepers *et al.*, 1995a). Urinary metabolites of 1-nitropyrene were measured in humans exposed to diesel exhaust using immunoassays (Scheepers *et al.*, 1994, 1995b). This method is very sensitive but cross-reactivity with other PAH metabolites was reported (Scheepers *et al.*, 1995b). A more specific approach to the analysis of urinary metabolites is HPLC with fluorescence detection.

(b) Biomarkers of exposure to gasoline engine exhaust

Carbon monoxide and lead are the most frequently used biomarkers of exposure to gasoline exhaust emissions (see Section 1.4.1(b)).

(i) Carbon monoxide

Exposure to carbon monoxide can readily be detected using spectrometric principles in exhaled air and also as carboxyhaemoglobin in the blood (Lee *et al.*, 1994; Gourdeau *et al.*, 1995). [The Working Group noted that direct-reading spectrometric instruments may not have the accuracy of most off-line analytical methods used for routine analysis in hospitals.]

(ii) Lead and platinum

The measurement of metals such as lead and platinum in blood or urine requires sensitive inductively coupled plasma-MS methods, which are well established (Iavicoli *et al.*, 2004; Ghittori *et al.*, 2005; Heitland & Köster, 2006).

(iii) Volatile organic compounds

Using GC-MS, organic constituents of gasoline exhaust emissions can be detected with high specificity and sensitivity. Benzene, toluene, ethylbenzene, xylene isomers and other volatile organic compounds have been measured in exhaled air (Jo & Song, 2001), blood (White *et al.*, 1995; Romieu *et al.*, 1999) and urine (Ghittori *et al.*, 2005).

1.3 Regulations and guidelines

1.3.1 Structure and progression of emission standards

There is a strong link between emission standards and engine technology: standards drive the technology and technology enables more stringent standards. Increasing environmental concerns over the past two decades have resulted in regulatory action around the globe to introduce successively more rigorous emission standards. The technological developments and their impact on the characteristics of engines and of vehicle emissions are presented in Section 1.1.

Standard values for different categories of engines and vehicles from several countries are presented in detail in the Annex. The Section below gives an overview of the structure and development of the standards and their penetration into the fleet.

Except for the USA, most countries worldwide have adopted European Union standards, occasionally with small local modifications and at a rate dictated by local economics and other factors. Different test cycles are used by Europe and the USA and across different applications. Emissions are expressed in a variety of units depending upon vehicle type – usually in grams per mile (g/mi) or per kilometre (g/km) when the entire vehicle is tested, and g/bhp-h or per kilowatt-h (g/kW-h) when only the engine is tested. Normally, the engine is tested for heavier commercial and industrial applications, and the vehicle for passenger cars and light goods vehicles. Table 1.11 gives a very approximate relationship between these units. For PM, standards based on both mass and number are shown. The engine or vehicle operating test cycle, the protocol used to measure emissions and the absolute number of

Table 1.11 Equivalent emission standards

Mass emissions					Number emissions			
Heavy-duty vehicles								
g/kWh	g/bhp-h	g/km	g/mile	g/kg fuel	#/kWh	#/bhp-h	#/km	#/mile
0.013	[a]0.0100	0.018	0.029	–	2.7×10^{12}	2.0×10^{12}	3.6×10^{12}	5.8×10^{12}
Light-duty vehicles								
–	–	0.0030	0.0048	0.054	–	–	[a]6.0×10^{11}	9.6×10^{11}

[a] Current standards
bhp, brake horse power; h, hour
Compiled by the Working Group

the emission standard are important to establish the stringency of the standard (see Section 1.2 for details of some of the measurement protocols).

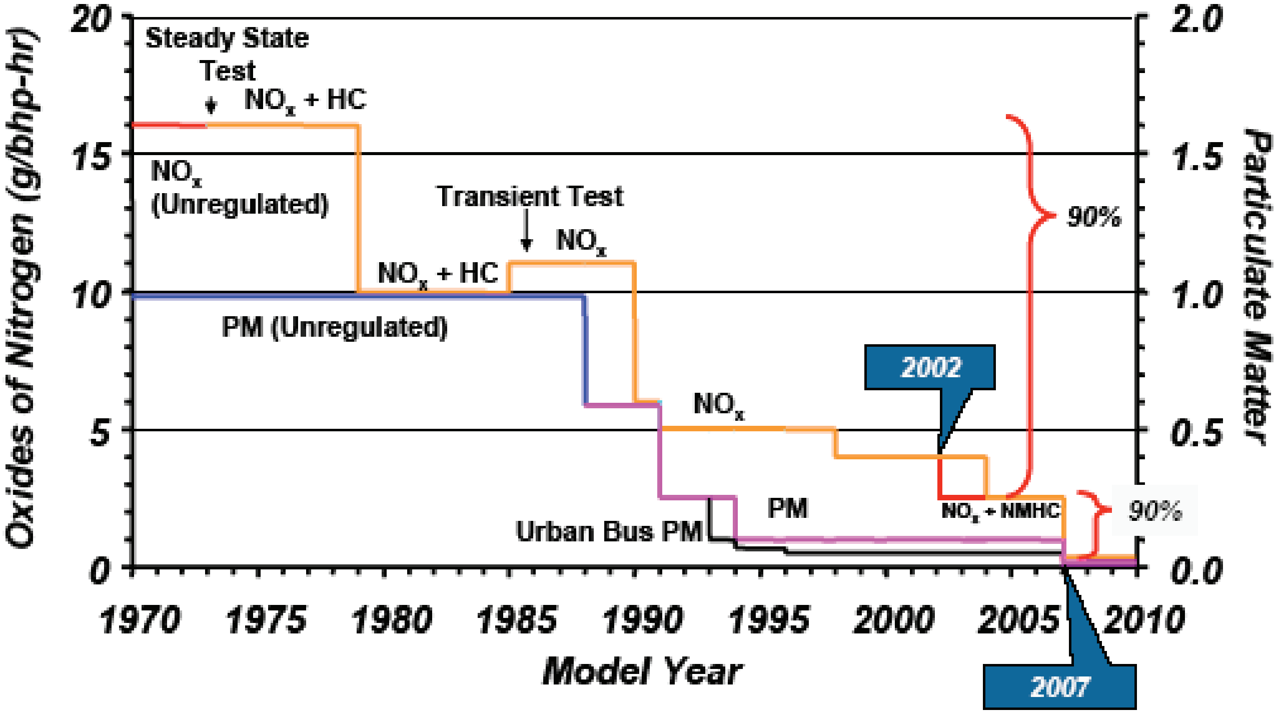
Standards are becoming increasingly more stringent throughout the world. As an example, Fig. 1.11 shows the downward stepwise trend of heavy-duty engine emission standards in the USA, starting from the first Californian standards in 1969. From the unregulated state in the early 1980s to 2010, permitted levels for nitrogen oxides, nitrogen oxides plus hydrocarbons, nitrogen oxides plus non-methane hydrocarbons, and PM have decreased progressively over time, with particulate and nitrogen oxide emission standards being reduced by more than two orders of magnitude.

Particle number standards are more stringent than mass standards, and are intended to result in more effective particulate control technologies. The current European Union light-duty mass emission standard is 4.5 mg/km and the number (#) standard is 6×10^{11} #/km. If one assumes typical diesel particle size distribution with a geometric standard deviation (σ_g) of 1.8, a geometric mean diameter of 60 nm and an effective particle density of 0.6 g/cm^3, this number standard corresponds to approximately 0.19 mg/km. If one assumes larger and more dense particles, with a geometric standard deviation of 2, a geometric mean diameter of 100 nm and a density of 1 g/cm^3, the number standard corresponds to 2.4 mg/km, i.e. about half of the mass standard.

1.3.2 Representative emission standards worldwide

To illustrate the evolution of engine and vehicle emission standards, trends for key categories of diesel-powered mobile sources for several countries are summarized in Fig. 1.12, Fig. 1.13, and Fig. 1.14: on-highway heavy-duty diesel engines, diesel passenger cars and non-road heavy-duty diesel engines. For simplicity, key changes are indicated in terms of US and European standards, even when some countries have their own local equivalents. Each figure indicates the time of introduction of the first emission standard for PM: for on-highway heavy-duty engines, Euro-1/US-1998; for passenger cars, Euro-1/USA Tier 1; and for non-road engines, Tier 1. Before these standards were introduced, particulate emissions from diesel engines were not regulated and the engines were of ‘traditional technology’ (grey area on the left of each chart). An intermediate level was implemented for on-highway heavy-duty diesel engines (Euro-4/USA-1994), representing a reduction of approximately one order of magnitude in PM and nitrogen oxides from unregulated levels, and corresponding to ‘transitional technology’ (see Section 1.1). The next levels of standards, which result in a reduction of two orders of magnitude in PM from unregulated levels and are expected to force the use of ‘new technology diesel engines’ are: on-highway heavy-duty engines, Euro-6/USA-2010; passenger car, Euro-5b/USA Tier 2,

Fig. 1.11 Historical trend in emission standards for heavy-duty engines in the USA



bhp, brake horse power; HC, hydrocarbon; NMHC, non-methane hydrocarbons; NO_x, nitrogen oxides; PM, particulate matter
From Department of Energy (2006)

with particle number standard; and non-road engines, Tier 4.

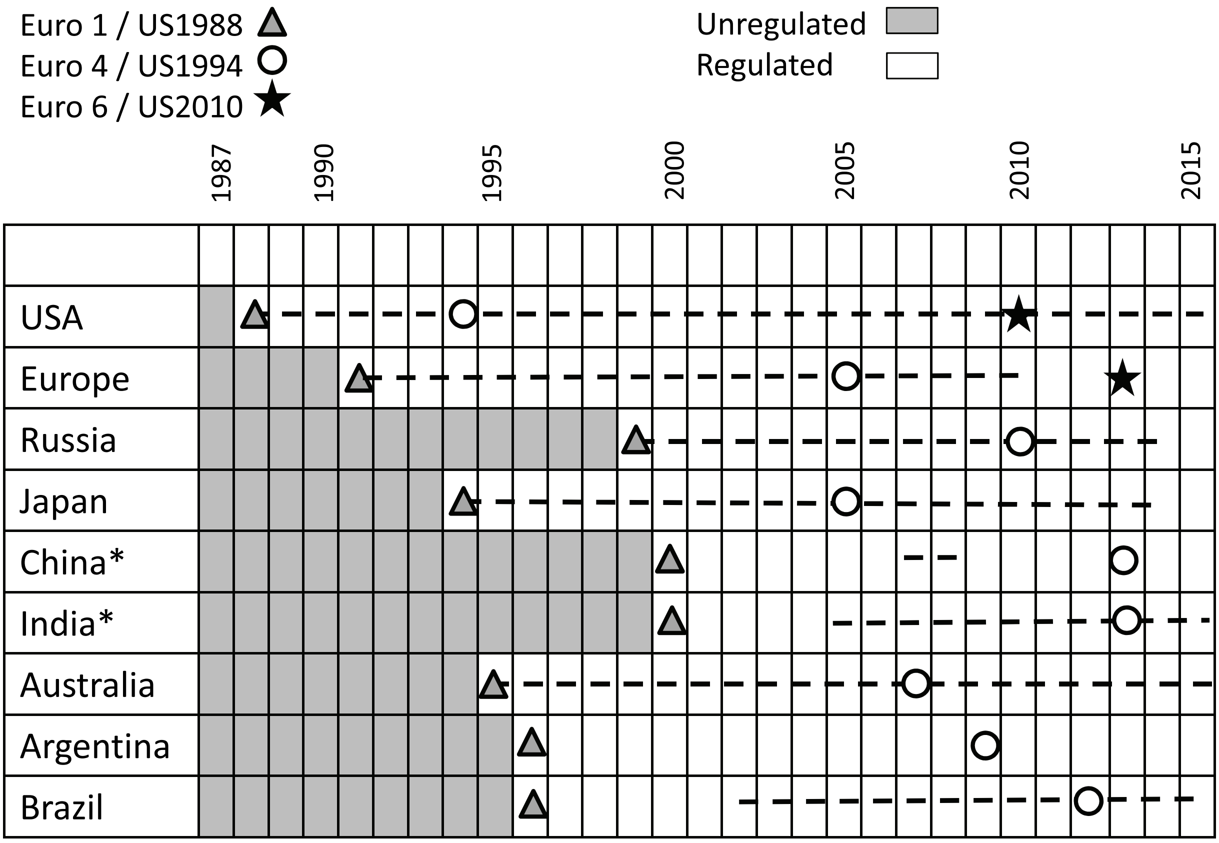
These charts also illustrate the strategy of regulatory agencies to introduce the most stringent emission controls first in on-road applications, and then in non-road and industrial applications at a later date: non-road heavy-duty applications, followed by high- and very low-horse power non-road applications, followed by locomotive and marine engines. Consequently, PM emissions from many non-road applications worldwide are still uncontrolled today.

The rate of development and implementation of technology in any country or market is governed by local regulatory standards for tailpipe emissions and fuel quality. Most countries have implemented at least basic regulations for PM for heavy-duty and light duty on-highway vehicles, although many developing countries lag behind with regard to the technology of heavy-duty and light-duty vehicles. Also, engines in non-road vehicles, especially higher horse power engines in ships and locomotives worldwide, including those in Europe and the USA, are still unregulated for PM emissions.

1.3.3 Availability of engines with new emission control technologies in the fleet/temporal impact of new emission standards

When new emission standards are implemented, all new products must comply but products already in use are generally not required to be upgraded (or 'retrofitted') to the new standard. The exception is a change in fuel standards. Thus, engines that meet new emission standards penetrate the fleet only as fast as new vehicles are

Fig. 1.12 Implementation schedule of on-road heavy-duty diesel emission standards in selected countries



* Nationwide

Compiled by the Working Group

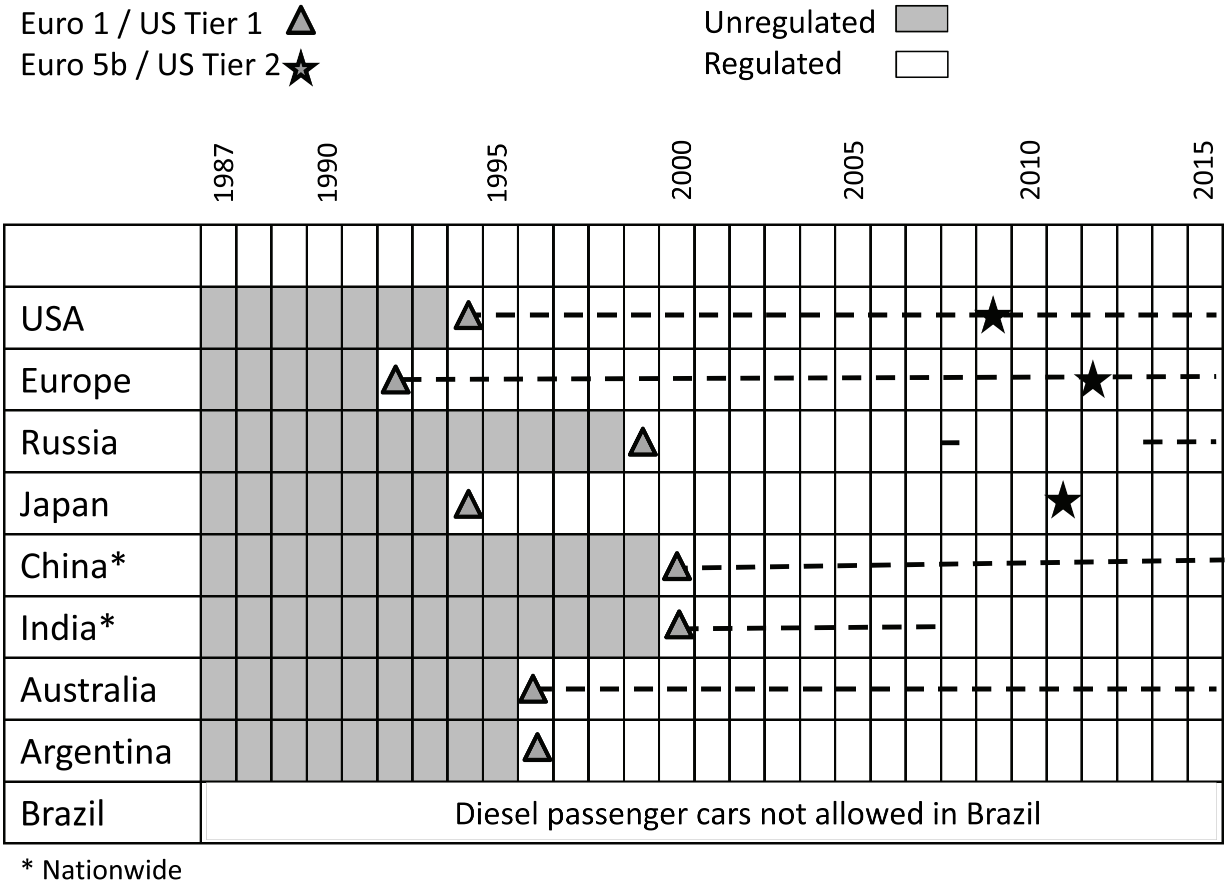
purchased to replace those already in use. For on-highway heavy-duty engines, this transition is slightly accelerated because the highest-annual-mileage applications, generally larger long-haul HGVs, favour most recent vehicles powered by the most recent engines. The US EPA models total mileage accumulation by age of the vehicle for the purposes of emission inventory calculations. The heavy-duty mileage accumulation rates used in the EPA model MOBILE5b indicate that half of the total fleet mileage accumulation is accounted for by vehicles that are 6 years old or more recent, and new vehicles account for 10 times the annual mileage of the oldest vehicles in the fleet (Kremer, 1999).

1.3.4 In-use emission verification programmes

In addition to the emission standards to which new products must comply, several in-use verification tests and practices are applied worldwide to ensure continued compliance with emission standards in service.

Many countries in Europe, 33 states and local jurisdictions in the USA, Japan and other developed and developing countries have implemented inspection and maintenance programmes. To maintain on-road vehicle registration, vehicles are required to pass emission verifications at annual or biannual intervals. The US EPA has also incorporated in-use monitoring

Fig. 1.13 Implementation schedule of passenger car diesel emission standards in selected countries



Compiled by the Working Group

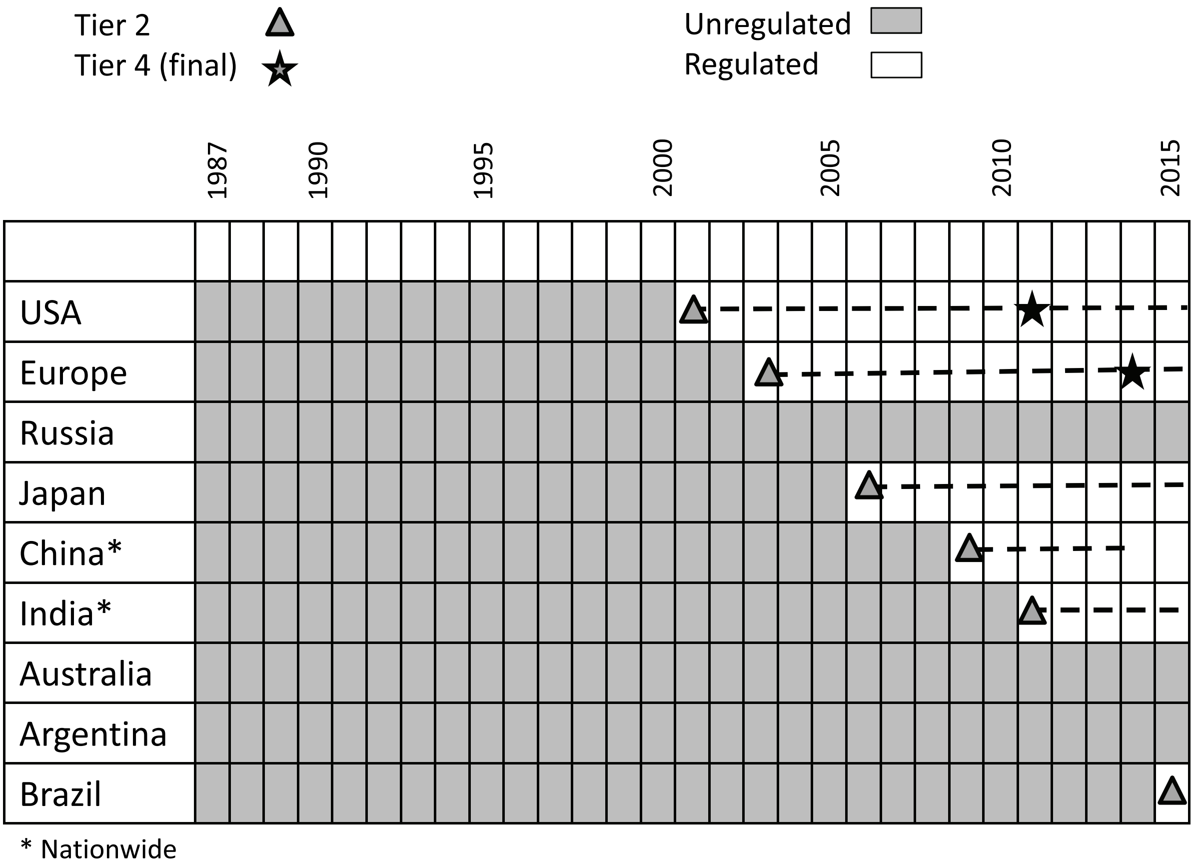
of on-highway heavy-duty vehicle emissions through a programme that requires manufacturer-run in-use testing to validate compliance with not-to-exceed limits (http://www.epa.gov/otaq/regs/hd-hwy/inuse/420f05021.htm). For Euro VI regulations, European commercial vehicle and engine manufacturers must demonstrate in-use conformity with these emission standards.

1.4 Occurrence and exposure

1.4.1 Occupational exposure of workers predominantly exposed to diesel exhaust

It has been estimated that 1.4 million workers in the USA and 3 million workers in Europe are occupationally exposed to diesel engine exhaust (Lewtas & Silverman, 2010). Exposure to diesel engine exhaust through the use of diesel equipment occurs in many different occupational settings, including those in the mining, railroad, construction and transportation industries. Exposures to diesel engine exhaust in

Fig. 1.14 Implementation schedule of off-road heavy-duty diesel emission standards in selected countries



Compiled by the Working Group

occupational and traffic settings are the result of vehicle operations and vehicle mix, and the composition and particle size characteristics of diesel exhaust are known to change depending on the load, fuel–air ratio and exhaust temperature, as summarized in Table 1.12. This affects the quantities of PAHs, EC and hydrocarbons in the particles emitted from the engine, which can influence the qualitative and quantitative nature of exposures in various occupational settings as shown in Table 1.13.

An overview of the levels of exposure to diesel engine exhaust is presented in Table 1.14, Table 1.15, Table 1.16, and Table 1.17 and is an update of the review published by Pronk *et al.* (2009). The exposure levels are summarized by on-road and off-road equipment, and major occupational settings. Data on the components of diesel engine exhaust, such as EC, nitrogen oxides and carbon monoxide are summarized below. Because the exposure data were mainly collected between 1990 and 2005, these measurements predominantly reflect the use of traditional and transitional diesel engines.

(a) On-road vehicles

The conversion of HGVs to diesel engines began in the 1950s and from the 1960s and 1970s predominantly diesel-powered heavy-duty vehicles were sold. In contrast to Europe, where about

Table 1.12 Approximate characteristics[a] of particle emissions defined by diesel engine operating conditions for an uncontrolled diesel engine

Engine operation[b]			Characteristics[b]			
Load	Fuel–air ratio	Exhaust Temperature	PAH, EC and HC	Particulate HC droplets	Soluble organic fraction	Ratio PAH/surface (ng/mm²)[c]
Idle, low and medium load (< 50% max); high acceleration	42–60	Low (< 250 °C)	Highest% PAHs, HC covers EC surface	Higher MW; heavy oil emissions; major nuclei fraction	High (> 40%)	< 0.3
High load (> 50% max) and speed; moderate acceleration	25–30	High (~500 °C)	Low total PAHs and HC; HC partially covers EC surface	Lower MW; limited oil emissions; no nuclei fraction	Low (< 20%)	1–10

[a] These approximate characteristics apply to sustained conditions, not to rapid changes, such as slowing down to a stop after a period of cruising with a heavy load because the exhaust system will remain hot for a period of time.

[b] From Kweon *et al.* (2003) and Kittelson *et al.* (2006)

[c] From Bukowiecki *et al.* (2002)

EC, elemental carbon; HC, hydrocarbon; MW, molecular weight; PAH, polycyclic aromatic hydrocarbon

one-third of all new passenger cars have diesel engines, only very few new passenger cars or taxis in the USA are diesel-fuelled (Lloyd & Cackette, 2001). Workers in occupations that involve the driving, maintenance and unloading of diesel HGVs and, to a lesser extent, diesel cars can be exposed to diesel exhaust. Table 1.14 summarizes the reported levels of exposure to EC, carbon monoxide, nitric oxide and nitrogen dioxide for workers exposed to diesel engine exhaust from on-road vehicles, by agent and by activity.

(i) HGV drivers

Studies performed mainly in the 1990s and 2000s showed that HGV drivers were exposed on average to levels of EC ranging from 1 to 22 µg/m³ [weighted arithmetic mean (AM), 2 µg/m³], and levels of nitric oxide and nitrogen dioxide were around 0.2–0.3 and 0.03–0.04 ppm, respectively.

Several factors appear to influence the levels of exposure of drivers to diesel engine exhaust. For instance, long-haul drivers tended to have lower levels of exposure than local drivers (Garshick *et al.*, 2002). In addition, a comparison of two cross-sectional exposure surveys in the HGV transport industry indicated a two- to threefold decline in the levels of exposure to EC between the 1980s and 2001–05 (Zaebst *et al.*, 1991; Davis *et al.*, 2007; Fig. 1.15). Furthermore, a positive association was found between the age of the vehicle and the levels of EC. This increase in exposure was attributed to a higher seepage of diesel engine exhaust in older HGV cabins due to leaks in their rubber seals (Davis *et al.*, 2007).

(ii) HGV/bus mechanics

Mechanics of heavy-duty diesel equipment (e.g. HGVs and buses) were exposed to levels of EC that were generally higher than those of drivers. Average levels of exposure to EC ranged between 4 and 39 µg/m³ [weighted AM, 29 µg/m³].

(iii) Bus garage and other bus workers

Few studies have addressed exposure to diesel engine exhaust for bus garage and other bus workers. In a study by Ulfvarson *et al.* (1987), levels of carbon monoxide, nitric oxide and nitrogen dioxide in a bus garage varied from 1.7 to 24, 0.3 to 1.0 and 0.2 to 1.1 ppm, respectively.

(iv) Firefighters

Firefighters are frequently exposed to diesel engine exhaust and other combustion products (Froines *et al.*, 1987). Exposures can occur during

Table 1.13 Exposure scenarios, size distributions and composition of diesel emissions under operating conditions in common work settings

	Engine temperature and operation	Exposure scenarios	Particle size characteristics	Composition
Off-road activities				
Maintenance shops for railroads and trucks	Cold engines	Briefly move vehicles in/out of shop; emissions into confined space; slow removal by ventilation	High agglomeration; considerably reduced nuclei and surface area; most in accumulation mode	Lower EC and very high OC from lubricating oils
Railroad operations and exposures of crews	Hot engines; continuous engine operations; frequent idling and steady speed under loads	Emissions into the environment by leading locomotive(s); exposure intensity defined by downwind proximity to source(s)	Low agglomeration Idling: high nuclei level and PM Steady speed: low/no nuclei, reduced surface.	Higher EC and very high OC Moderate EC and lower OC from lubricating oils
Underground mining	Hot engines; steady use, frequent stops and idling, and hard acceleration under load. Fixed engines: hot; steady use	Exposure intensity defined by proximity to vehicles – haulage trucks, loaders; and fixed engines – generators, large equipment; moderate to fast removal by ventilation	High agglomeration; no nuclei and lower surface area.	Higher EC and lower OC from lubricating oils
Above-ground mining	Hot engines; steady use: haulage trucks – limited stops and hard acceleration under load; frequent idling and low load return trips. Fixed engines: hot; steady use	Brief exposure to occasional exhaust from preceding trucks or nearby heavy equipment	Idle: high nuclei level and PM Steady speed: up-hill, low nuclei and low hydrocarbons down-hill, high nuclei and high hydrocarbons	High EC and OC High EC and low OC High EC and OC
On-road vehicle operations (exposure from preceding vehicles)				
City driving	Hot; frequent stops and hard acceleration under load; frequent of idling	Exposure from preceding vehicles depends on traffic density and proximity	Moderate agglomeration; Idle and high acceleration: high nuclei level and PM Steady speed: low nuclei and accumulation mode (depends on proximity).	High EC and OC Moderate EC and low OC
Highway driving	Hot engine; usually heavy load; rare idling or acceleration	Exposure from preceding vehicles depends on traffic density and proximity	Low agglomeration; low nuclei and accumulation mode (depends on proximity)	High EC and low OC

EC, elemental carbon; OC, organic carbon; PM, particulate matter

Table 1.14 Measurements of occupational exposure to diesel exhaust from on-road vehicles: elemental carbon (µg/m³), and carbon monoxide, nitric oxide and nitrogen dioxide (ppm)

Description	Agent	Duration (h)	No.	AM (SD)	GM (GSD)	Location	Year	Reference
Drivers								
Truck – local	EC_S	> 4	56	5 (0.9)	0.9 (4.0)	USA	1980s	Zaebst *et al.* (1991)
Truck – local	EC_S	> 4	576[a]	2 (2.3)	1 (2.8)	USA	2001–05	Davis *et al.* (2007)
Truck – local	EC_R	> 4	5	7[b]	6 (1.6)	USA	1999	Garshick *et al.* (2002)
Truck – local	EC_{NR}	> 4	4 [a]	5 (0.1)	5 (1.0)	USA	1985	NIOSH (1986)
Truck – long haul	EC_S	> 4	72	5 (0.4)	0.4 (3.8)	USA	1980s	Zaebst *et al.* (1991)
Truck – long haul	EC_S	> 4	349[a]	1 (0.8)	1 (2.3)	USA	2001–05	Davis *et al.* (2007)
Truck – long haul	EC_R	> 4	5	5[b]	4 (2.0)	USA	1999	Garshick *et al.* (2002)
Truck – long haul	EC_{NR}	> 4	4[a]	22 (13.2)	19 (2.0)	USA	1985	NIOSH (1986)
HGV	EC_I	1- > 4	3	10 (6.0)	9 (1.8)	USA	1992	NIOSH (1993)
Bus	EC_R	> 4	5	10[b]	9 (1.3)	Estonia	2002[c]	Boffetta *et al.* (2002)
Bus	EC_R	> 4	39	2.0 (1.3)	1.4 (3.3)	USA	2002[c]	Ramachandran *et al.* (2005)
Bus	EC_I	> 4	4	2 > LOD: 11–20		USA	1998	NIOSH (1998)
Bus and HGV[d]	EC_I	> 4	20	11[b]	6 (2.9)	Sweden	2002–04	Lewné *et al.* (2007)
Taxi[d]	EC_I	> 4	8	8[b]	7 (1.6)	Sweden	2002–04	Lewné *et al.* (2007)
Mechanics								
Truck	EC_S	> 4	80	27 (4.1)	4 (12.1)	USA	1980s	Zaebst *et al.* (1991)
Truck	EC_R	> 4	10	4[b]	4 (1.6)	USA	1999	Garshick *et al.* (2002)
Ambulance depot	EC_R	> 4	3	31	29 (1.6)	United Kingdom	2000[c]	Groves & Cain (2000)
Bus	EC_R	> 4	53	39	31 (2.1)	United Kingdom	2000[c]	Groves & Cain (2000)
Bus	EC_R	> 4	15	39[b]	38 (1.3)	Estonia	2002[c]	Boffetta *et al.* (2002)
HGV/bus (+inspection)	EC_I	> 4	40	21[b]	11 (3.2)	Sweden	2002–04	Lewné *et al.* (2007)
Bus	EC_I	> 4	4	ND	ND	USA	1998	NIOSH (1998)
Others								
Firefighter	EC_I	> 4	27	24 (max)		USA	2002[c]	Roegner *et al.* (2002)
Firefighter	EC_I	> 4	18	40 (20.3)	35 (1.7)	USA	1995[c]	Echt *et al.* (1995)
Firefighter	EC_I	> 4	12	10 (max)		USA	1997	NIOSH (1998)
Firefighter	EC_I	< 1	8	ND	ND	US	1998	NIOSH (1998)
Service worker bus	EC_I	> 4	4	2 > LOD: 0.3–15		USA	1998	NIOSH (1998)
Vehicle testing	EC_R	> 4	11	11	11 (1.8)	United Kingdom	2000[c]	Groves & Cain (2000)
Car park attendant (booth)	EC_R	> 4	34[a]	1.1 (0.6)	1.1 (1.8)	USA	2002[c]	Ramachandran *et al.* (2005)

Table 1.14 (continued)

Description	Agent	Duration (h)	No.	AM (SD)	GM (GSD)	Location	Year	Reference
Others								
Bus garage	CO			1.7–24			1987[c]	Ulfvarson *et al.* (1987)
Driver								
Truck – local	NO	> 4	4[a]	0.23 (0.05)	0.22 (1.3)	USA	1985	NIOSH (1986)
Truck – long haul	NO	> 4	4[a]	0.27 (0.10)	0.25 (1.5)	USA	1985	NIOSH (1986)
Others								
	NO			0.3–1.0			1987[c]	Ulfvarson *et al.* (1987)
Driver								
Taxi[d]	NO_2	> 4	12	0.03[b]	0.02 (0.7)	Sweden	2002–04	Lewné *et al.* (2007)
Bus and HGV[d]	NO_2	> 4	30	0.03[b]	0.03 (0.7)	Sweden	2002–04	Lewné *et al.* (2007)
HGV	NO_2	> 4	40	0.04 (0.02)		Sweden	1997–99	Lewné *et al.* (2006)
Taxi	NO_2	> 4	20	0.03 (0.01)		Sweden	1997–99	Lewné *et al.* (2006)
Bus	NO_2	> 4	42	0.03 (0.01)		Sweden	1997–99	Lewné *et al.* (2006)
Mechanics								
HGV/bus (+inspection)	NO_2	> 4	60	0.05[b]	0.05 (0.9)	Sweden	2002–04	Lewné *et al.* (2007)
Bus	NO_2		232	0.24 (0.26)		USA	1987[c]	Gamble *et al.* (1987)
Others								
Bus	NO_2		232	0.2–1.1		Sweden	1987[c]	Ulfvarson *et al.* (1987)

[a] Area sample representative of personal exposure

[b] AM estimated from GM and GSD or from range

[c] Year of publication, year of sampling not available

[d] Mostly diesel powered vehicles

AM, arithmetic mean; CO, carbon monoxide; EC, elemental carbon; EC_I, inhalable; EC_{NR}, not reported; EC_R, respirable; EC_S, submicron; GM, geometric mean; GSD, geometric standard deviation; h, hour; HGV, heavy-goods vehicle; LOD, limit of detection; ND, Not detected; NO, nitrogen oxide; NO_2, nitrogen dioxide; SD, standard deviation

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Table 1.15 Measurements of occupational exposure to diesel exhaust in the mining industry: elemental carbon (µg/m³), and carbon monoxide, nitric oxide and nitrogen dioxide (ppm)

Description	Agent	Duration (h)	No.	AM (SD)	GM (GSD)	Location	Year	Reference
Underground								
Production (NM)	EC_R		6[a]	148 (136)	85 (3.5)	United Kingdom	2004[b]	Leeming & Dabill (2004)
Production (NM)	EC_R	> 4	343	202 (32–144)	111 (1.4–4.8)	USA	2002[b]	Cohen *et al.* (2002)
Production (NM)	EC_S	> 4	38	219 (65–193)		USA	1997[b]	Stanevich *et al.* (1997)
Production (C)	EC_R	> 4	4	241[c]	202 (1.8)	Estonia	2002[b]	Boffetta *et al.* (2002)
Production (M)	EC_R	> 4	15	637 (75–508)		USA	1999	McDonald *et al.* (2002)
Production (NR)	EC_I	< 1–4	12	538 (512)		USA	2007[b]	Burgess *et al.* (2007)
Maintenance (NM)	EC_S	> 4	8	53 (46)		USA	1997[b]	Stanevich *et al.* (1997)
Maintenance (NM)	EC_R	> 4	269	144 (17–462)	66 (1.7–4.6)	USA	2002[b]	Cohen *et al.* (2002)
Mining, NS (C)	EC_R		7[a]	66 (28)	62 (1.5)	United Kingdom	2004[b]	Leeming & Dabill (2004)
Mining, NS (M)	EC_{NR}		27	27		Sweden	2006[b]	Adelroth *et al.* (2006)
Mining, NS (NM)	EC_R	> 4	779	[135] (40–384)		USA	1998–2001	Coble *et al.* (2010)
Surface								
Production/maintenance (NM)	EC_R	> 4	164	13 (2–89)	2 (1.8–6.2)	USA	2002[b]	Cohen *et al.* (2002)
Production/maintenance (NM)	EC_S	> 4	23	23 (15–54)		USA	1997[b]	Stanevich *et al.* (1997)
Production/maintenance (NM)	EC_R	> 4	265	3.5		USA	1998	Coble *et al.* (2010)
Underground								
Production (NM)	CO	1- > 4	5	2.0 (0.6)	1.9 (1.4)	USA	1991	NIOSH (1991)
Mining, NS (NR)	CO	< 4	21	12.4 (0–23)		USA	1978	Holland (1978)
Mining, NS (NM)	CO		≥ 5[a, d]	8.9		USA	1976–77	Attfield (1978)
Mining, NS (M)	CO		≥ 5[a, d]	6.1		USA	1976–77	Attfield (1978)
Underground								
Mining, NS (NI)	NO	< 4	10	10.3 (0.4–57)		USA	1978	Holland (1978)
Production (NM)	NO	> 4	9	14.7 (2.8)	14.5 (1.2)	USA	1991	NIOSH (1991)
Production (NM)	NO	> 4	7	4.2 (1.7)	3.9 (1.5)	USA	1991	NIOSH (1991)
Production (NM)	NO	> 4	6	4.7 (1.0)	4.6 (1.2)	USA	1991	NIOSH (1993)

Table 1.15 (continued)

Description	Agent	Duration (h)	No.	AM (SD)	GM (GSD)	Location	Year	Reference
Mining, NS (M)	NO	> 4	54[a]	11.0 (5.7)		USA	1988	NIOSH (1992)
Mining, NS (M)	NO	> 4	25	0.7 (0.6)		USA	1988	NIOSH (1991, 1992)
Mining, NS (NM)	NO	> 4	666	[0.9] (0.2–1.5)		USA	1998–2001	Coble *et al.* (2010)
Surface								
Production/maintenance (M)	NO	> 4	12	0.3 (0.2)		USA	1988	NIOSH (1992)
Production/maintenance (NM)	NO	> 4	225	[0.07] (0.02–0.11)		USA	1988	Coble *et al.* (2010)
Underground								
Production (NM)	NO_2	> 4	9	2.9 (0.5)	2.9 (1.2)	USA	1991	NIOSH (1991)
Production (NM)	NO_2	> 4	7	0.8 (0.4)	0.7 (1.6)	USA	1991	NIOSH (1991)
Production (NM)	NO_2	> 4	6	0.7 (0.1)	0.7 (1.1)	USA	1991	NIOSH (1993)
Mining, NS (NR)	NO_2	< 4	29	0.8 (0–5.5)		USA	1978	Holland (1978)
Production (NM)	NO_2		183	1.9 (1.6)		USA	1978[b]	Gamble *et al.* (1978)
Production (C)	NO_2	> 4	41	0.2[c]	0.1 (1.5–2.8)	USA	1976–80	Wheeler *et al.* (1981)
Production (C)	NO_2	> 4	76	0.2 (0.1–0.1)		USA	1982[b]	Reger *et al.* (1982)
Production (M)	NO_2		29	0.2		Sweden	2006[b]	Adelroth *et al.* (2006)
Production (M)	NO_2	> 4	54[a]	1.5 (0.9)		USA	1988	NIOSH (1992)
Production (M)	NO_2	> 4	25	5.5 (3.9)		USA	1988	NIOSH (1991)
Mining, NS (C)	NO_2	> 4	60	0.2 (0.1)		USA	1982[b]	Ames *et al.* (1982)
Mining, NS (NM)	NO_2	> 4	689	[0.3] (0.1–0.6)		USA	1998–2001	Coble *et al.* (2010)
Surface								
Production/maintenance (M)	NO_2	> 4	12	0.04 (0.03)		USA	1988	NIOSH (1992)
Production/maintenance (NM)	NO_2	> 4	233	[0.04] (0.01–0.06)		USA	1988	Coble *et al.* (2010)

[a] Area sample representative of personal exposure

[b] Year of publication, year of sampling not available

[c] AM estimated from GM and GSD or from range

[d] At least five samples for all jobs combined in the study

AM, arithmetic mean; C, coal; CO, carbon monoxide; EC, elemental carbon; EC_I, inhalable; EC_{NR}, not reported; EC_R, respirable; EC_S, submicron; GM, geometric mean; GSD, geometric standard deviation; M, metal; NM, non-metal; NO, nitrogen oxide; NO_2, nitrogen dioxide; NR, not reported; NS, job not specified; SD, standard deviation

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Table 1.16 Measurements of occupational exposure to diesel exhaust in the railroad industry: elemental carbon (µg/m³), and carbon monoxide, nitric oxide and nitrogen dioxide (ppm)

Description	Agent	Duration (h)	No.	AM (SD)	GM (GSD)	Location	Year	Reference
Train crew								
Driver, assistant, shunter driver	EC_R	> 4	19	20 (18.7)	16 (2.0)	Russian Federation	2002[a]	Boffetta et al. (2002)
Hostler	$EC_{R/I}$	> 4	5	4 (1.3)	3 (1.5)	Canada	1999–2000	Verma et al. (2003)
Engineer/driver, conductor/trainman	$EC_{R/I}$	> 4	76[b]	5 (1.1–15.8)	3 (1.5–3.5)	Canada	1999–2000	Verma et al. (2003)
Non-operating crew trailing locomotive	EC_I	> 4	47[b]	10 (12)	6	Canada	2003	Seshagiri (2003)
Engineer's operating console	EC_I	1- > 4	49[b]	6	4 (3)	USA	1996–98	Liukonen et al. (2002)
Maintenance								
Rolling equipment	$EC_{R/I}$	> 4	48	5 (4.9–8.8)	3 (2.4–2.7)	Canada	1999–2000	Verma et al. (2003)
Rolling equipment	EC_R	> 4	64	39	17 (1.9)	United Kingdom	2000[a]	Groves & Cain (2000)
Train crew								
Non-operating crew trailing locomotive	CO	> 4	280[b]	4.50 (max)		Canada	2003	Seshagiri (2003)
Locomotive and caboose	CO	> 4	16[b]	< 1		USA	1974–76	Hobbs et al. (1977)
Train crew								
Non-operating crew trailing locomotive	NO	> 4	46[b]	1.13 (0.87)	0.82	Canada	2003	Seshagiri (2003)
Locomotive	NO	> 4	9[b]	0.55		Canada	1996	Verma et al. (1999)
Locomotive and caboose	NO	> 4	16[b]	0.23		USA	1974–76	Hobbs et al. (1977)

Table 1.16 (continued)

Description	Agent	Duration (h)	No.	AM (SD)	GM (GSD)	Location	Year	Reference
Maintenance								
Rolling equipment	NO	> 4	18	0.26		Canada	1996	Verma *et al.* (1999)
Train crew								
Non-operating crew trailing locomotive	NO_2	> 4	181[b]	0.3 (max)		Canada	2003	Seshagiri (2003)
Locomotive on board	NO_2	> 4	9[b]	0.05		Canada	1996	Verma *et al.* (1999)
Locomotive and caboose	NO_2	> 4	16[b]	0.03		USA	1974–76	Hobbs *et al.* (1977)
Maintenance								
Rolling equipment	NO_2	> 4	18	0.10		Canada	1996	Verma *et al.* (1999)

[a] Year of publication, year of sampling not available

[b] Area sample representative of personal exposure

AM, arithmetic mean; CO, carbon monoxide; EC, elemental carbon; EC_I, inhalable; EC_R, respirable; $EC_{R/I}$, respirable/inhalable; GM, geometric mean; GSD, geometric standard deviation; NO, nitrogen oxide; NO_2, nitrogen dioxide; SD, standard deviation

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Table 1.17 Measurements of occupational exposure to diesel exhaust from other off-road vehicles: elemental carbon (µg/m³), and carbon monoxide, nitric oxide and nitrogen oxide (ppm)

Description	Agent	Duration (h)	No.	AM (SD)	GM (GSD)	Location	Year	Reference
Construction								
Tunnel	EC_I	> 4	10	314[a]	163 (1.5–3.0)	Norway	1996–99	Bakke *et al.* (2001)
	EC_I	> 4	12	132[a]	87 (2.5)	Sweden	2002–04	Lewné *et al.* (2007)
Heavy/highway	EC_R	> 4	261	13	8 (2.7)	USA	1994–99	Woskie *et al.* (2002)
Above-ground	EC_I	> 4	22	13[a]	8 (2.8)	Sweden	2002–04	Lewné *et al.* (2007)
Electric utility installation	EC_I	> 4	120	4		USA	1996–97	Whittaker *et al.* (1999)
Tunnel	CO	> 4	78	9[a]	5.7 (1.5–2.6)	Norway	1996–99	Bakke *et al.* (2001)
	CO	> 4	52	5 (3.7)		Sweden	1991[b]	Ulfvarson *et al.* (1991)
Electric utility installation	CO	> 4	27	1 (0.6–0.6)		USA	1996–97	Whittaker *et al.* (1999)
Tunnel	NO	> 4	53	2.6 (1.5)		Sweden	1991[b]	Ulfvarson *et al.* (1991)
Electric utility installation	NO	> 4	27	0.2 (0.2–0.4)		USA	1996–97	Whittaker *et al.* (1999)
Tunnel	NO_2	> 4	18	0.22[a]	0.19 (0.58)	Sweden	2002–04	Lewné *et al.* (2007)
	NO_2	> 4	82	0.86[a]	0.54 (1.5–4.5)	Norway	1996–99	Bakke *et al.* (2001)
	NO_2	> 4	53	0.88 (0.68)		Sweden	1991[b]	Ulfvarson *et al.* (1991)
Above-ground	NO_2	> 4	33	0.02[a]	0.02 (1.06)	Sweden	2002–04	Lewné *et al.* (2007)
Electric utility (outside)	NO_2	> 4	24	0.32 (0.2–0.2)		USA	1996–97	Whittaker *et al.* (1999)
Dock/distribution								
Dock worker	EC_S	> 4	54	24 (0.4–2.5)	2 (1.3–27.2)	USA	1991[b]	Zaebst *et al.* (1991)
	EC_S	> 4	≥ 5[c]		7	USA	1990	Zaebst *et al.* (1992)
Fork-lift truck	EC_R	> 4	39[d]	36[a]	27	United Kingdom	2004[b]	Wheatley & Sadhra (2004)
Dock worker	EC_R	> 4	27	122	66 (3.3)	United Kingdom	2000[b]	Groves & Cain (2000)
	EC_R	> 4	12	9[a]	7 (2)	USA	1999	Garshick *et al.* (2002)
	EC_I	> 4	5	4 (1.8)	4 (1.5)	USA	1992	NIOSH (1993)
	NO_2	> 4	≥ 5[c]		0.18	USA	1990	Zaebst *et al.* (1992)

Table 1.17 (continued)

Description	Agent	Duration (h)	No.	AM (SD)	GM (GSD)	Location	Year	Reference
Airline personnel								
Baggage and screening	EC_I	> 4	72	11 (5.4)		USA	2004	NIOSH (2005)
	CO	> 4	61	2.4[a]		USA	2004	NIOSH (2005)
Mechanics and refuelers	CO	> 4	10	5 (1.5)	4.7 (1.3)	USA	1992	NIOSH (1994b)
Baggage and screening	NO	> 4	40	0.13 (0.07)		USA	2004	NIOSH (2005)
	NO_2	> 4	40	0.12 (0.07)		USA	2004	NIOSH (2005)
Loading/unloading ships								
Marine terminal	EC_I	> 4	168	6 (0.9–9.0)		USA	2003–05	NIOSH (2006)
Ferry	EC_R	> 4	20	49	37 (2.5)	United Kingdom	2000[b]	Groves & Cain (2000)
Marine terminal	CO	> 4	60	2.5		USA	2003–05	NIOSH (2006)

[a] AM estimated from GM and GSD or from range

[b] Year of publication, year of sampling not available

[c] At least five samples for all jobs combined in the study

[d] Area sample representative of personal exposure

AM, arithmetic mean; CO, carbon monoxide; EC, elemental carbon; EC_I, inhalable; EC_R, respirable; EC_S, submicron; GM, geometric mean; GSD, geometric standard deviation; NO, nitrogen oxide; NO_2, nitrogen dioxide; SD, standard deviation

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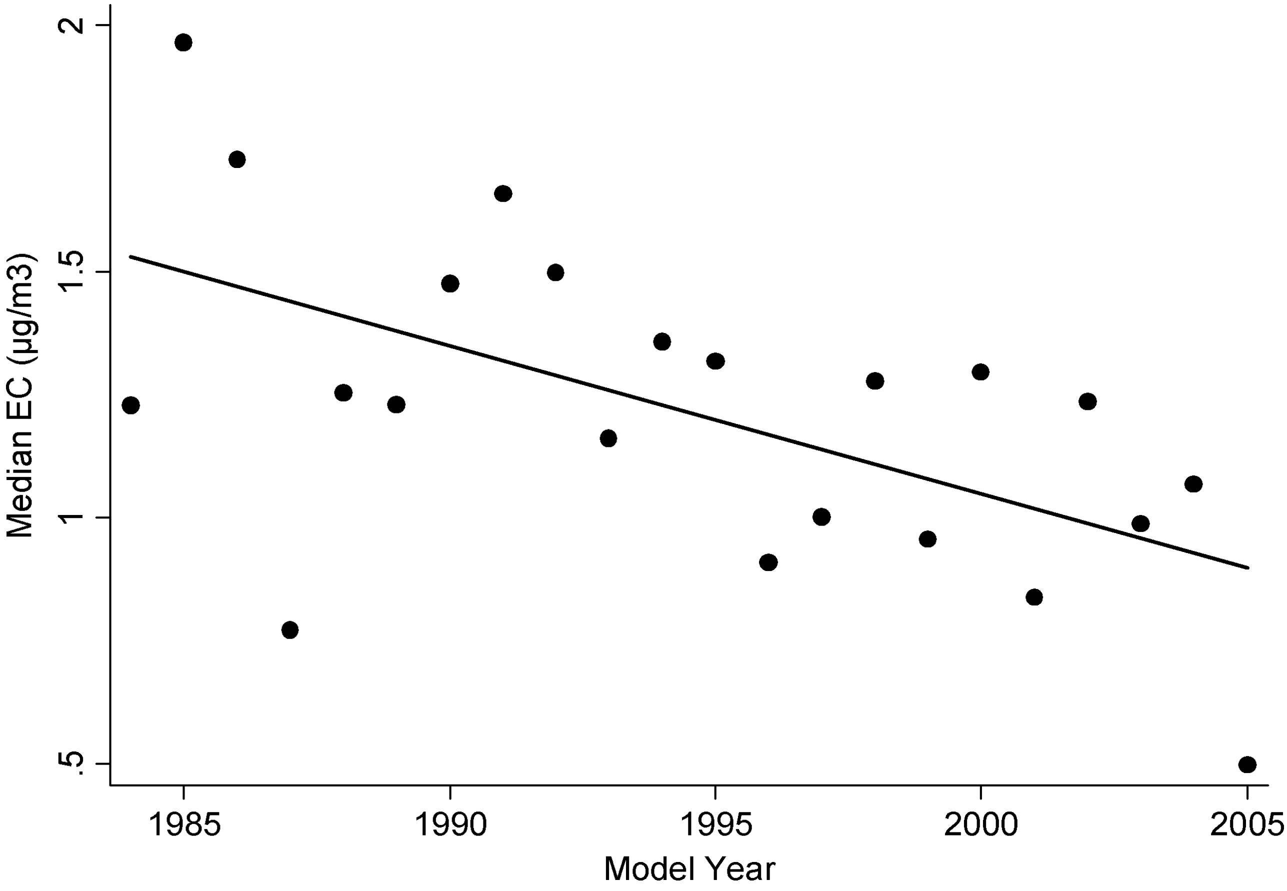
Fig. 1.15 Median levels of exposure to elemental carbon in truck cabins for pick-up and delivery drivers, by model year



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EC, elemental carbon

a response to an incident and in the fire station, and those reported varied considerably between studies. Echt *et al.* (1995) reported average levels of 40 µg/m³ EC, while others reported maximum levels of 24 µg/m³, 10 µg/m³ or non-detectable levels (Roegner *et al.*, 2002; Pronk *et al.*, 2009).

(v) Others

Other occupations with exposure to diesel engine exhaust from on-road vehicles include vehicle testing, parking attendant, toll booth worker, transport terminal worker and traffic police officer. Reported exposures to EC were mostly < 10 µg/m³ (see Table 1.14).

(b) Off-road vehicles

Exposure to exhaust emissions from off-road vehicles can occur in many different industries and occupations (see Table 1.15). The major industries are mining, railroad transport, construction and loading/unloading operations.

(i) Mining

Mining operations can be carried out on the surface or underground. In surface (open-pit) mining, the ore is mined using large excavating equipment, such as load and dump vehicles, drills, graders and utility trucks, and transported using very large dumper trucks.

Diesel equipment in underground mining may include vehicles for the transportation of personnel, haulage trucks, load and dumper vehicles, drills, graders and utility trucks. The first diesel engine-powered vehicles in underground mines were used in Germany in 1927 (Kaplan, 1959). In the 1970s, the use of diesel engines in underground mines greatly increased in the USA. In 1998, the Mine Safety and Health Administration estimated that 18% of the 971 underground coal mines and 78% of the 261 underground metal/non-metal mines in the USA used diesel engines (Pronk *et al.*, 2009).

In addition to underground mining operations, diesel equipment is also used in some surface operations. These include bulldozers for cleaning stockpiles, trucks for the transportation of ore and tailings, and forklift trucks for loading/unloading.

Other potential exposures in mines include airborne particles, from blasting, and the mining and transport of the ore, and gases, such as carbon monoxide and sulfur dioxide. Some other exposures that may occur in mines, depending on the ores extracted, have been evaluated in previous *Monographs*; these include radon (IARC, 2012d), silica, nickel, chromium and asbestos (IARC, 2012a).

Table 1.15 summarizes the levels of exposure to EC, carbon monoxide, nitric oxide and nitrogen dioxide reported for workers exposed to diesel engine exhaust in the mining industry.

(ii) Underground production/mining

Production workers include miners involved in drilling, blasting and hauling ore. Reported levels of exposure to EC varied from 148 to 637 µg/m³ [weighted AM, 135 µg/m³], average levels of nitric oxide varied from < 1 to 15 ppm [weighted AM, 1.8 ppm] and average levels of nitrogen dioxide ranged from 0.2 to 5.5 ppm [weighted AM, 1.9 ppm].

A large exposure survey among non-metal miners in seven mines showed that, in general, the highest levels of exposure to diesel engine exhaust were for miners working in the active face area. Workers in the haulage or travel ways were generally lower exposed than workers at the face. Workers in the underground maintenance shop and offices had the lowest levels of exposure, most probably due to the proximity of these areas to the fresh-air intake shafts (Coble *et al.*, 2010).

(iii) Underground maintenance

Maintenance workers include those in the maintenance shops and underground warehouses, and those involved in the maintenance of travel and haulage routes. The studies that reported the exposure to EC of underground maintenance workers indicated levels between 53 and 144 µg/m³ [weighted AM, 141 µg/m³].

(iv) Surface production

Reported levels of exposure on the surface were much lower than those reported underground. Workers involved in surface activities had levels of exposure to EC between 3.5 and 23 µg/m³ [weighted AM, 8 µg/m³]. Levels of nitric oxide varied from 0.07 to 0.3 ppm [weighted AM, 0.08 ppm], while concentrations of 0.04 ppm nitrogen dioxide were observed.

(v) Railroad transportation

The use of diesel engines in railroad locomotives was first introduced into Canada and the USA in 1928 and into Germany in 1932 (Garshick *et al.*, 1988), and diesel engines largely replaced steam engines between 1945 and the 1960s (Pronk *et al.*, 2009). In the 1960s, second-generation diesel locomotives were introduced that were reported to be cleaner (Woskie *et al.*, 1988). Table 1.16 and Fig. 1.16 summarize the levels of exposure reported in the railroad industry.

(vi) Train crews

A typical train crew comprises a conductor and an engineer and occasionally includes brakers/switchers for local or yard jobs. Several studies measured the exposures of train personnel to diesel engine exhaust. Average levels of exposure to EC varied from 4 to 20 µg/m³ [weighted AM, 8 µg/m³], and concentrations of nitric oxide and nitrogen dioxide ranged from 0.2 to 1.1 and from 0.03 to 0.3 ppm, respectively.

The location of the exhaust stack in relation to the cabin (either in front of or behind the cabin) has been shown to be an important determinant of exposure. In addition, significantly increased levels of exposure to diesel engine exhaust have been reported in the cab when the windows were open compared with when they were closed.

(vii) Maintenance

The levels of exposure of train maintenance personnel to diesel engine exhaust have been reported to be in the same range as those of train crews, with levels of exposure to EC varying from 5 to 39 µg/m³ [weighted AM, 24 µg/m³], and those to nitric oxide and nitrogen dioxide being around 0.3 and 0.1 ppm, respectively.

Woskie *et al.* (1988) conducted an industrial hygiene survey of the US railroad industry. Personal exposure to respirable particles was measured and then corrected for the estimated contribution of cigarette-smoke particulates. Similar to the measurements of EC, these results indicated that the highest exposures occurred for hostlers (yard workers who move trains and rail cars, sometimes using specialized locomotives), electricians, machinists and mechanics. Lower exposures were reported for clerks.

(viii) Construction

Exposure to diesel engine exhaust within the construction industry varies widely (Table 1.17). Many studies have been carried out on exposure during tunnel construction, and indicated that the average levels of exposure to EC were between approximately 100 and 300 µg/m³ [weighted AM, 215 µg/m³]. Similarly, high levels of nitric oxide and nitrogen dioxide were reported (2.6 and 0.22–0.88 ppm, respectively). Construction workers above ground are exposed to much lower levels of diesel engine exhaust, with measured levels of generally around 10 µg/m³ [weighted AM, 13 µg/m³] of EC, 0.2 ppm of nitric oxide and 0.02–0.32 ppm of nitrogen dioxide.

Blute *et al.* (1999) reported several determinants of exposure to diesel engine exhaust at highway construction sites. Regression analyses indicated higher exposures to EC for enclosed versus open worksites, cranes versus other types of diesel-powered equipment, proximity within 10 feet of diesel equipment and greater numbers of diesel sources.

(ix) Loading/unloading operations

Loading and unloading activities can be performed at transport terminals and docks, and on board ships and aircraft.

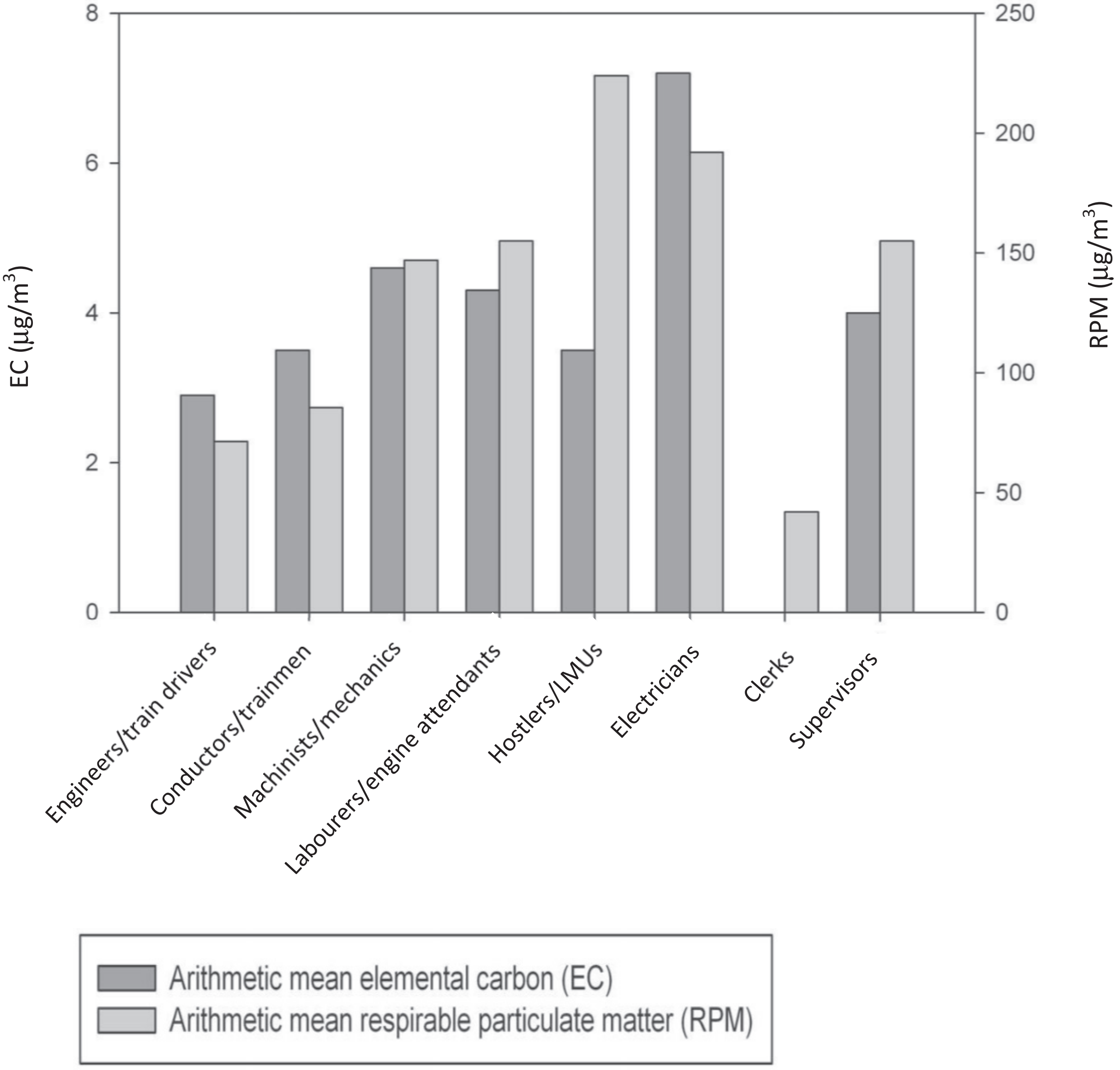
Several studies have measured the average levels of exposure to EC among dock workers (see Table 1.17), and reported that these varied from 4 to 122 µg/m³ [weighted AM, 43 µg/m³]. The sources of exposure for dock workers include diesel-powered forklift trucks and on-road HGVs. Studies at docks where only non-diesel-powered forklifts were used reported low levels of exposure to EC (< 5 µg/m³), indicating that the major contributors to the exposure of dock workers were diesel-powered forklifts (Zaebst *et al.*, 1991).

Similarly, a large variation in exposure to diesel engine exhaust has been reported for people involved in the loading/unloading of ships, for whom levels of EC were reported to range from 6 to 49 µg/m³ [weighted AM, 11 µg/m³].

Little information was available on the exposure of workers who unload baggage from airplanes. The limited data indicated that levels of exposure were around 10 µg/m³ for EC and around 0.1 ppm for nitric oxide and nitrogen dioxide (Schauer, 2003). However, the contribution of jet fuel to the measured levels of EC cannot be excluded.

Fig. 1.17 summarizes measurements of EC, nitric oxide and nitrogen dioxide by major industry/job based on weighted averages. Miners

Fig. 1.16 Average personal exposures to elemental carbon and respirable particulate matter by job title among railroad workers



LMU, labourer moving unit
Compiled by the Working Group

(when mines use diesel engines) and tunnel construction workers have the highest exposures, with average levels of EC above 100 µg/m³. Dock workers, diesel mechanics and maintenance personnel are exposed to average levels of 20–40 µg/m³. Train crews, construction workers and workers involved in unloading airplanes and ships are exposed to levels of ~10 µg/m³ EC. Professional drivers have the lowest average exposure to levels of ~2 µg/m³. However, variations within job titles can be large, and these relative rankings can therefore differ according to specific situations.

1.4.2 Occupational exposure of workers predominantly exposed to gasoline engine exhaust

In occupational settings, gasoline engine exhaust is produced by spark-ignition engines. Four-stroke gasoline-powered engines are mostly used for the propulsion of road vehicles, ranging from motorcycles to small lorries (see Section 1.1.4). Exposures to emissions from road vehicles can occur in occupations such as border inspectors, car mechanics, office workers, car park attendants, professional drivers, service station attendants, shopkeepers, street workers, tollbooth workers and (traffic) policemen.

In addition to road traffic-related sources, gasoline exhaust may also be emitted by engines used in small electric power generators and in small portable equipment (power output, 2–7 kW) used to power chain saws, leaf blowers, hedge trimmers, brush cutters and clearing saws. During these applications, gasoline exhaust may be emitted in the breathing zone of some workers, such as loggers.

(a) Markers of exposure

For exposure assessment, some chemical components, such as inorganic compounds (metals) or some specific organic compounds, are fairly specific for emissions from gasoline engines. Some of these chemical markers of gasoline exhaust exposure are discussed in more detail below.

(i) Lead

Tetraethyl lead was used as an anti-knock agent in gasoline fuel but, during combustion, more than 90% was converted to and emitted as inorganic lead. Within a few hours to days, alkyl lead vapour emitted from the tailpipe is decomposed to lead oxides (IARC, 2006). The use of lead in gasoline was phased out to facilitate the introduction of exhaust catalysts and, in most parts of the world, this use of tetraethyl lead was abolished in the 1990s (IARC, 2006).

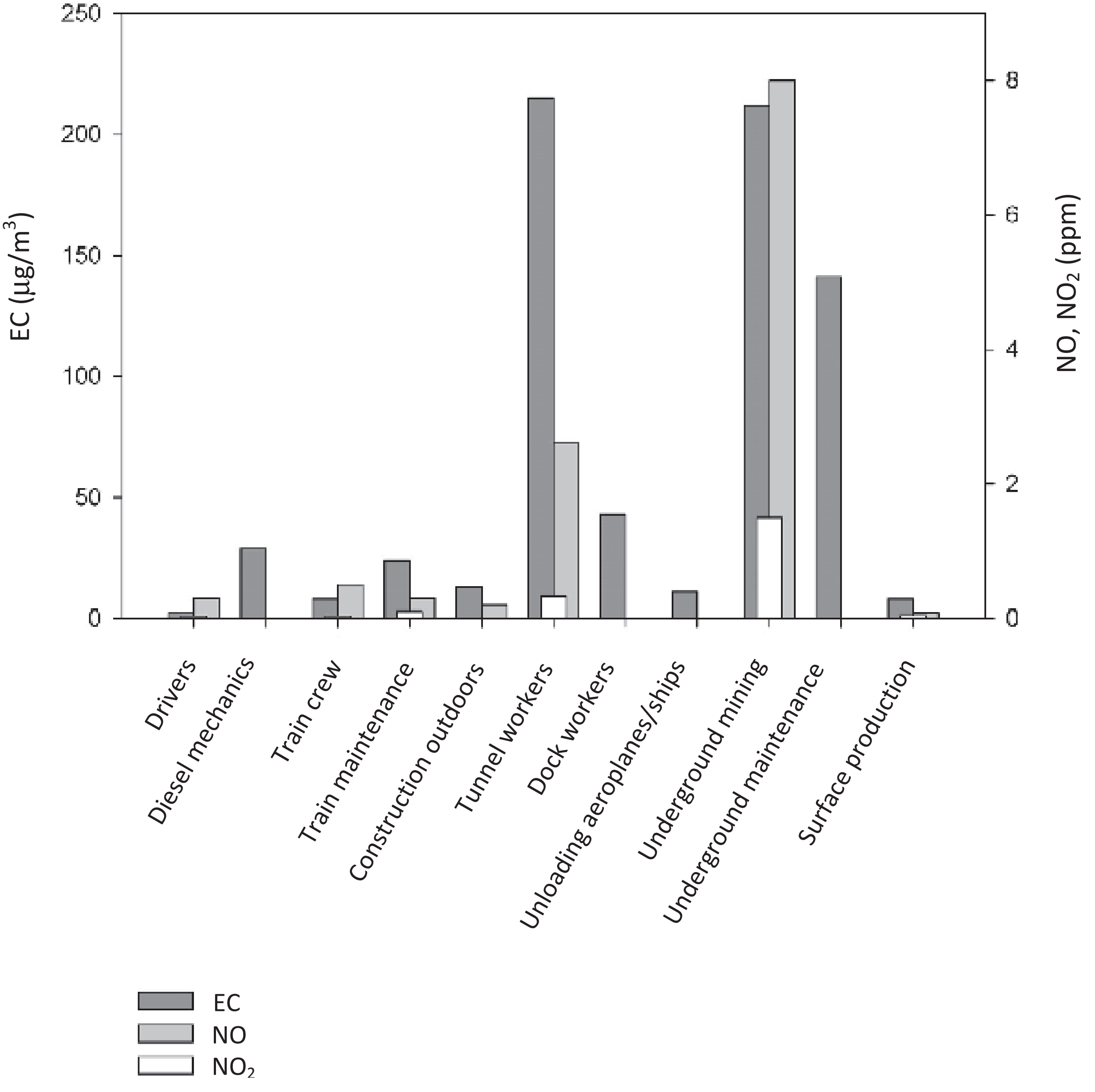
Lead is an important marker to reconstruct historical exposure to gasoline fuel and gasoline exhaust emissions, and appears to be related to exposures to both gasoline vapours and engine exhaust emissions over time (Anttila *et al.*, 1995). Occupational exposure to lead derived from gasoline exhaust emissions is summarized in Table 1.18 and Table 1.19. For exposure assessment in epidemiological studies, blood lead values are a reliable index for long-term exposure to lead. However, the interpretation of airborne lead exposure in relation to lung cancer is complicated due to the particle distribution of lead in airborne dust (Anttila *et al.*, 1995).

(ii) Carbon monoxide

Carbon monoxide in ambient air is a marker for occupational exposures to gasoline exhaust emissions. Especially in outdoor workplaces, ambient carbon monoxide is mostly derived from gasoline-powered engines from road traffic or other uses. In indoor environments, other (incomplete) combustion sources may contribute to elevated concentrations, including tobacco smoking.

Biomonitoring methods can be used to estimate internal exposure. Carbon monoxide can be monitored by determination of the percentage of carboxyhaemoglobin in blood and that of carbon

Fig. 1.17 Average personal exposures to elemental carbon, and nitric oxide and nitrogen dioxide by major occupational group predominantly exposed to exhaust from diesel engines



Compiled by the Working Group
EC, elemental carbon; NO, nitrogen oxide; NO_2, nitrogen dioxide

Table 1.18 Exposure to components from gasoline engine exhaust (mean ± standard deviation)

Type of source	Conditions	CO (ppm)	VOC (ppm)	Benzene (µg/m³)	Formaldehyde (µg/m³)	M*t*BE (µg/m³)	1,3-Butadiene (µg/m³)	NO_2 (ppb)	Respirable dust (µg/m³)	Lead in respirable dust (µg/m³)	Reference
Car mechanics											
Emissions and contaminants from exhaust systems	Indoor exposure in garage A (‘small’)	–	–	–	–	–	–	–	–	53.2 (*n* = 1)[a] [21.7 ± 11.3] (*n* = 8)[b]	Chambers *et al.* (1984)
	Indoor exposure in garage B (100 m²)	–	–	–	–	–	–	–	–	[59.8 ± 31.8] (*n* = 4)[a] [43.7 ± 24.3] (*n* = 12)[b]	
	Indoor exposure in garage C (85 m²)	–	–	–	–	–	–	–	–	[21.7 ± 12.3] (*n* = 3)[a] [17.5 ± 5.9] (*n* = 4)[b]	
Car exhaust emissions	Workers at 7 garages and automobile firms in Stamford, CT, USA (*n* = 37)		0.003–0.053	–	–	108–43 464	–	–	–	–	White *et al.* (1995)
Car exhaust emissions	496 car mechanics working in 76 dealer workshops in Quebec, Canada, during the winter of 1991–92 and 1992–93	< 25 (28.8%) 25–35 (30.7%) 36–50 (19.3%) > 51 (21.2%)	–	–	–	–	–	–	–	–	Gourdeau *et al.* (1995)
Car exhaust emissions	Indoor exposure in garages in South Wales, United Kingdom (*n* = 16)		[0.419 (0.070–1280)]	[3.4 (6–9.3)]			–				Parry *et al.* (1997)
Commuting office workers											
Car exhaust emissions	Officers of South Wales Constabulary, United Kingdom, not considered to be exposed during work hours	–	[0.0589 (0.014–0.336)]	[11 (7–42)]	–						Parry *et al.* (1997)

Table 1.18 (continued)

Type of source	Conditions	CO (ppm)	VOC (ppm)	Benzene (μg/m^3)	Formaldehyde (μg/m^3)	M*t*BE (μg/m^3)	1,3-Butadiene (μg/m^3)	NO$_2$ (ppb)	Respirable dust (μg/m^3)	Lead in respirable dust (μg/m^3)	Reference
Loggers											
Chain saw (two-stroke engine)	Felling, limbing, buckling and manual skidding in snow-free conditions in a thick and dense mixed and pine forest stand at wind speed < 3 m/s and temperature −3 to −8 °C	[29 (36–38)] (n = 4)[d]	15 (7–40) mg/m^3	[700 (300–1800)] (n = 28)	[80 (40–200)] (n = 12)	–	–	–	–	0.8 (0.5–10) (n = 7)	Nilsson *et al.* (1987)
	Felling, limbing, buckling and manual skidding in 50–90-cm deep snow in a sparse pine forest stand at wind speed < 3 m/s and temperature −16 to +1 °C	[17 (8.6–20)] (n = 4)	19 (3–74) (n = 42) mg/m^3	[600 (100–2400)] (n = 42)	[80 (20–100)] (n = 25)	–	–	–	–	2 (0.4–4) (n = 14)	
	Felling only in a thick pine forest stand in 80–100-cm deep snow; wind speed < 4 m/s and temperature −1 to +1 °C	[32 (4–73)] (n = 7)	22.0 (9–69) (n = 8) mg/m^3	[700 (300–2,300)] (n = 8)	[90 (70–100)] (n = 8)	–	–	–	–	–	
	Felling, limbing, buckling and manual skidding in a thick pine forest stand in 80–100-cm deep snow; wind speed < 4 m/s and temperature −1 to +1 °C	[12 (4–21)] (n = 18)	8.0 (2–17) (n = 16) mg/m^3	[300 (70–600)] (n = 16)	[70 (30–90)] (n = 18)	–	–	–	–	–	
Chain saw (two-stroke engine)	Logging during 36 working periods of 2 hours at a snow depth of 80–100 cm in the county of Västerbotten, Sweden; wind speed < 4 m/s and temperature −2 to +3 °C	17 (4–73) (n = 23)	12 (2–69) (n = 23) mg/m^3	–	[63 (28–130)] (n = 23)	–	–	–	–	–	Hagberg *et al.* (1985)

Table 1.18 (continued)

Type of source	Conditions		CO (ppm)	VOC (ppm)	Benzene (µg/m³)	Formaldehyde (µg/m³)	M*t*BE (µg/m³)	1,3-Butadiene (µg/m³)	NO_2 (ppb)	Respirable dust (µg/m³)	Lead in respirable dust (µg/m³)	Reference
Car park attendants^{c}												
Emissions from private cars	Eight-story parking garage for 1400 cars at a hospital and university, Baltimore, MD, USA	Wk d (71 cars/h)	2.6	–	2.7	–	7.4	0.5	–	–	–	Kim *et al.* (2007)
		Wk-ends (6 cars/h)	1.2	–	0.3		0.4	0.2	–	–	–	
Professional drivers												
Traffic emissions	Professional drivers (*n* = 250)		71.2 ± 8.1	–	–	–	–	–	–	–	–	Jovanović *et al.* (1999)
Service station workers												
Traffic emissions	Pavia, Lombardy, Italy (*n* = 26)		–	–	38.81 ± 46.26	10.38 ± 5.49	174.04 ± 258.72	–	–	–	–	Ghittori *et al.* (2005)
Traffic emissions	Mexico City, Mexico (*n* = 24)		–	–	330 (130–770)	–	–	–	–	–	–	Romieu *et al.* (1999)
Shop keepers												
Road traffic	Polishers and repairmen working 10.11 ± 1.44 h/d in shoe stalls in Seoul, South-Korea (*n* = 32), indoor		–	–	732 ± 1640^{d}	–	–	–	57.4 ± 17.1	127.7 ± 44.7	–	Bae *et al.* (2004)
	Outdoor (*n* = 32)		–	–	8 ± 20	–	–	–	58.1 ± 23.2	138.7 ± 43.6	–	
Street workers												
Traffic emissions	Mexico City, Mexico (*n* = 6)		–	–	62 (49–180)	–	–	–	–	–	–	Romieu *et al.* (1999)

Table 1.18 (continued)

Type of source	Conditions	CO (ppm)	VOC (ppm)	Benzene (µg/m³)	Formaldehyde (µg/m³)	M*t*BE (µg/m³)	1,3-Butadiene (µg/m³)	NO_2 (ppb)	Respirable dust (µg/m³)	Lead in respirable dust (µg/m³)	Reference
Toll booth workers											
Road traffic city	Bridge in New York, USA (*n* = 440)	63 (217)[e]	7.9 (29.6)[e]	–	61 (196)[e]	–	–	70 (320)[e]	64	10.6	Ayres *et al.* (1973)
Road traffic on three locations in Boston, MA, USA (*n* = 174)	August 1972	16.0 (4.0–> 130)	6.1 (2.9– > 50)	–	–	–	–	67 (15–220)	90 (< 20–200)	12.9 (1.5–35.5)	Burgess *et al.* (1977)
	March 1973	15.4 (3.0–> 100)	5.7 (3.2–16.6)	–	–	–	–	81 (10–290)	105 (65–150)	12.9 (1.0–33.2)	
	August 1973	33.7 (11.0–> 100)	19.8 (3.9–24.5)	–	–	–	–	100 (< 5–215)	100 (60–105)	15.6 (7.4–36.3)	
	Feb—March 1974	24.3 (6.0–81)	10.1 (7.0–13.0)	–	–	–	–	38 (< 5–119)	105 (55–160)	7.7 (1.0–17.8)	
Baltimore Harbor Tunnel in the summer of 2001;400–5900 vehicles/h and 72 000 vehicles/d	Inside toll booth (average over three shifts)	–	–	4.12 (0.29–14.9)	–	18.8 (0.50–43.8)	1.60 (0.23–8.09)	–	–	–	Sapkota *et al.* (2005)
	Inside toll booth (morning shift)			6.70 ± 1.31			2.91 ± 0.90				
	Inside toll booth (afternoon shift)			3.21 ± 1.20			0.91 ± 0.40				
	Inside toll booth (night shift)			2.42 ± 1.42			0.92 ± 0.51				
	Outside toll booth (average over three shifts)	–	–	13.3 (0.73–35.0)	–	39.6 (0.17–121)	7.24 (0.23–20.5)	–	–	–	
	Outside toll booth (morning shift)			19.8 ± 2.81			10.7 ± 3.20				
	Outside toll booth (afternoon shift)			14.9 ± 4.70			7.23 ± 1.72				
	Outside toll booth (night shift)			4.90 ± 2.21			3.71 ± 0.91				

Table 1.18 (continued)

Type of source	Conditions		CO (ppm)	VOC (ppm)	Benzene (µg/m³)	Formaldehyde (µg/m³)	M*t*BE (µg/m³)	1,3-Butadiene (µg/m³)	NO_2 (ppb)	Respirable dust (µg/m³)	Lead in respirable dust (µg/m³)	Reference
Road traffic Klang Valley Kuala Lumpur, Malaysia (*n* = 90)	Toll booths with air conditioning system	Mon-Sun: 1597 (752–6333) vehicles/d in morning shift	20 (< 34)	–	–	–	–	–	–	–	–	Niza & Jamal (2007)
		Mon-Sun: 1778 (700–3269) vehicles/d in evening shift	30 (< 61)									
Traffic policemen												
Traffic emissions	Wuhan, China		–	–	–	–	–	–	–	–	5.2 ± 2.4 (*n* = 36)	Zhang *et al.* (1994)

Concentrations expressed as time-weighted average exposures in the breathing zone (unless otherwise indicated); range of exposure concentrations in parentheses

[a] Air samples collected in breathing zone

[b] Air samples collected from fixed locations

[c] Air concentrations determined from fixed locations in parking garages; this study was not performed with the explicit aim of assessing exposure of parking attendants

[d] The authors noted that benzene was presumably derived from indoor sources (such as solvents, polish and adhesives) but not from traffic or smoking, since shop keepers did not smoke during business hours.

[e] Average per 30-day period (maximum hourly reading)

–, not determined; CO, carbon monoxide; d, day; M*t*BE, methyl *tertiary* butyl ether; NO_2, nitrogen dioxide; VOC, volatile organic compounds; wk, week

Table 1.19 Biomonitoring of exposures to carbon monoxide and lead in occupations that entail exposure to gasoline engine exhaust (mean ± standard deviation unless otherwise indicated)

Reference	Type of source	Conditions		COHb (%)		CO in end-exhaled air (ppm)		Blood lead (µg/dL)
				Nonsmokers	Smokers	Nonsmokers	Smokers	
Border inspector								
Cohen *et al.* (1971)	Road traffic at border San Ysidro, CA, USA-Mexican Border	All of three shifts	Pre-shift	[1.4 ± 0.61] (*n* = 9)[a]	[4.8 ± 1.1] (*n* = 11)[a]	5.7 ± 1.05 (*n* = 9)	25.5 ± 4.01 (*n* = 11)	-
			Post-shift	[3.6 ± 1.0] (*n* = 9)[a]	[6.4 ± 1.3] (*n* = 11)[a]	18.6 ± 3.27 (*n* = 9)*	35.0 ± 4.93 (*n* = 11)	
		Night and morning shift	Pre-shift	[1.4 ± 0.58] (*n* = 7)[a]	[3.7 ± 0.83] (*n* = 6)[a]	5.0 ± 0.90 (*n* = 7)	19.2 ± 2.34 (*n* = 6)	
			Post-shift	[4.0 ± 1.1] (*n* = 7)1[a]	[7.5 ± 1.6] (*n* = 6)[a]	21.0 ± 3.70 (*n* = 7)*	41.8 ± 6.77 (*n* = 6)**	
Car mechanic								
Tola *et al.* (1976)	Exhaust emissions from repaired cars in Finland (*n* = 165)	In 13 workplaces; highest exposures occurred during cleaning the motor with compressed air		–	–	–	–	27 (10–80)[b]
Gourdeau *et al.* (1995)	Exhaust emissions from repaired cars in Canada (*n* = 496)	Indoor exposure in 76 repair shops involving 287 non-smoking mechanics		< 3.5 (28.6%) 3.5–5.0 (26.8%) 5.1–7.5(32.0%) > 7.6 (12.6%)	–	–	–	–
White *et al.* (1995)	Stamford, CT, USA	Workers at 7 garages and automobile firms (*n* = 37)	Men	1.05 (*n* = 12)	3.80 (*n* = 8)	–	–	–
			Women	0.90 (*n* = 1)	–		–	–
Commuting office worker								
White *et al.* (1995)	Stamford, CT, USA	Workers at 7 garages and automobile firms in Stamford Connecticut, US (*n* = 37)	Men	0.60 (*n* = 7)	2.6 (*n* = 1)	–	–	–
			Women	0.70 (*n* = 4)	4.80 (*n* = 2)	–	–	–
Car park attendant								
Johnson *et al.* (1975)	Parking cars in a garage in Houston, TX, USA	Indoor exposure to slow moving traffic (*n* = 36)		–	–	–	–	28.3 ± 10.33
Professional driver								
Suzuki (1990)	Bandung, Indonesia	Drivers of minibuses who work 12 h/d (*n* = 22)		–	–	–	–	2.5 ± 1.7[c]
Khan *et al.* (1995)	Pakistan	Employees of the governmental transport service in the city of Abbottabad (*n* = 36)		–	–	–	–	51.06[c, d]

Table 1.19 (continued)

Reference	Type of source	Conditions	COHb (%)		CO in end-exhaled air (ppm)		Blood lead (μg/dL)
			Nonsmokers	Smokers	Nonsmokers	Smokers	
Jovanović *et al.* (1999)	Russian Federation	Professional drivers exposed to road traffic (*n* = 250)	[8.9 ± 1.7] (*n* = 97)[e]	[24.6 ± 3.2] (*n* = 153)[e]	–	–	–
Zhou *et al.* (2001)	Shanghai, China	Taxi and bus drivers (*n* = 164)	–	–	–	–	10.9 ± 0.13
Service station worker							
Tola *et al.* (1976)	Traffic emissions and gasoline fuel	Ten different workplaces in Finland entailing exposure to fuel (*n* = 76)	–	–	–	–	20 (11–40)
Hunaiti *et al.* (1995)		Bus drivers in Jordan (*n* = 47)	–	–	–	–	7.6
Naeher *et al.* (2004)		Summer 2002 in Trujillo, Peru (*n* = 17)	–	–	–	–	2.8 ± 1.1[f]
Ghittori *et al.* (2005)		Pavia, Lombardy, Italy (*n* = 26)	–	–	–	–	7.0 ± 1.72 (4.0–10.0)
Zhang *et al.* 1994	Gasoline depot workers	Wuhan, China (*n* = 227)	[1.67 ± 0.79][a] [1.76 ± 0.76][a]				7.28 ± 2.13 7.85 ± 1.97
Shop keeper							
Khan *et al.* (1995)	Traffic emissions	8–10 h/d along busy road in the city of Abbottabad, Pakistan (*n* = 36)	–	–	–	–	52.10
Street worker							
Nordman & Hernberg (1975)	Primarily from automobile exhaust (86 men)	Street sweepers in Finland	–	–	–	–	13.3 (7–29)
Naeher *et al.* (2004)	Summer 2002 Trujillo, Peru	Street vendors (*n* = 3)	–	–	–	–	2.8 ± 0.8[f]
		Newspaper vendors (*n* = 3)	–	–	–	–	3.9 ± 1.5[f]
Toll booth worker							
Ayres *et al.* (1973)	Road traffic in New York city, NY, USA (*n* = 619)	Bridge	2.12 ± 1.08	3.90 ± 2.13	–	–	28 ± 10 (*n* = 360)
		Tunnel	2.93 ± 1.36	5.01 ± 2.25	–	–	
		Square	1.94 ± 0.62	3.84 ± 2.06	–	–	
Burgess *et al.* (1977)	Road traffic on three locations in Boston, MA, USA (*n* = 172)	Tunnel location 1	[4.88 ± 1.48][g]	[8.20 ± 3.26][g]	26.9 ± 9.9 (*n* = 37)	43.5 ± 18.8 (*n* = 56)	30.84 ± 14.98 (*n* = 57)
		Alsston Location 2	[3.82 ± 1.4][g]	[7.82 ± 4.76][g]	21.6 ± 9.5 (*n* = 22)	41.6 ± 26.3 (*n* = 20)	35.11 ± 17.14 (*n* = 28)
		Weston Location 3	[2.78 ± 1.3][g]	[6.02 ± 2.9][g]	16.4 ± 9.0 (*n* = 10)	32.6 ± 17.0 (*n* = 24)	37.75 ± 15.72 (*n* = 24)

Table 1.19 (continued)

Reference	Type of source	Conditions		COHb (%)		CO in end-exhaled air (ppm)		Blood lead (µg/dL)
				Nonsmokers	Smokers	Nonsmokers	Smokers	
Kocasoy & Yalin (2004)	Istanbul Bosphorus Bridge, Turkey	Cashiers on working in 3 shifts of 5–6 h; slowly moving road traffic on bridge	Pre-shift	0.67 ± 0.90 ($n = 236$)	1.99 ± 1.84 ($n = 295$)	4.09 ± 3.52 ($n = 236$)	12.13 ± 10.99 ($n = 295$)	–
			Post-shift	1.25 ± 1.03 ($n = 236$)	3.23 ± 2.19 ($n = 295$)	7.67 ± 6.35 ($n = 236$)	20.09 ± 13.61 ($n = 295$)	
			Increase	0.58 ($n = 236$)	1.24 ($n = 295$)	3.58 ($n = 236$)	7.96 ($n = 295$)	
Niza & Jamal (2007)	Road traffic Klang Valley, Kuala Lumpur, Malaysia	Toll booths with functioning air conditioning system; samples collected Mon-Sun: 1597 (752–6339) vehicles/d in the morning shift		1.0 (ND–18.4) ($n = 66$)	–	–	–	–
Traffic controller and traffic policeman								
Johnson *et al.* (1975)	Traffic emissions Houston, TX, USA	On foot patrol (number not specified)		–	–	–	–	23.1 ± 9.21
Nordman & Hernberg (1975)	Primarily automobile exhaust	($n = 28$)		–	–	–	–	13.5 (9–20)[b]
Suzuki (1990)	Traffic emissions, Indonesia	Working 6 h/d on the road in Bandung, Indonesia ($n = 24$)		–	–	–	–	3.1 ± 1.8
Kamal *et al.* (1991)	Traffic emissions, Egypt	($n = 126$)		–	–	–	–	29.2 ± 7.5
Biava *et al.* (1992)	Traffic emissions, Milan, Italy	Pre-shift		1.5 ($n = 79$)	2.6 ($n = 79$)	-	-	Low 14.2 ± 5.9 Middle 15.3 ± 6.8 High 16.2 ± 6.9
		Post-shift		2.5 ($n = 79$)	4.3 ($n = 79$)			
		Increase		1.0 ($n = 79$)	1.7 ($n = 79$)			
Zhang *et al.* (1994)	Traffic emissions Wuhan, China	Traffic policemen, pre-shift ($n = 36$)		[1.17 ± 0.72][a]				4.36 ± 1.71 4.81 ± 1.64
		Traffic policemen, post-shift ($n = 36$)		[1.25 ± 0.71][a]				
Khan *et al.* (1995)[f]	Traffic emissions, Abbottatabad, Pakistan	8–10 h/d along busy road ($n = 36$)		–	–	–	–	53.43
Potula & Hu (1996)[f]	Traffic emissions, India	($n = 88$)		–	–	–	–	11.2 (0.5–40.2)

Table 1.19 (continued)

Reference	Type of source	Conditions	COHb (%)		CO in end-exhaled air (ppm)		Blood lead (µg/dL)
			Nonsmokers	Smokers	Nonsmokers	Smokers	
Bono *et al.* (2007)	Traffic emissions, Torino, Italy	(*n* = 228)	0.6 ± 0.3 (*n* = 176)	2.4 ± 1.8[h] (*n* = 52)	–	–	–
Iavicoli *et al.* (2004)	Traffic emissions, Rome, Italy	Pre-shift (*n* = 161) Post-shift (*n* = 161)	–	–	–	–	–

* Increase from pre- to post-shift (in all three shifts) $P < 0.01$; afternoon value not reported in abstract

** Increase from pre- to post-shift (only in evening and night shifts) $P < 0.02$

[a] Calculated by Working Group using [%COHb] = 0.43+0.17·[CO] (Cohen *et al.*, 1971)

[b] Median (range)

[c] A positive trend with exposure classification (low – middle – high) was found for male but not female traffic wardens (data not presented).

[d] The value for the group of professional drivers, shop keepers and traffic policemen (*n* = 118) was 52.20 ± 2..88 µg/dL, which was higher than that for controls living in a rural area ($P < 0.001$), see text for further details.

[e] % COHb calculated by the Working group from mmol/L, assuming a concentration of 10 mmol/L haemoglobin (for men and women drivers)

[f] Geometric mean and geometric standard deviation

[g] Calculated from alveolar CO concentrations using the equation of Ringold *et al.* (1962)

[h] COHb was 4.8% for policemen who spent more than 7 days outdoors.

CO, carbon monoxide; COHb, carboxyhaemoglobin; d, day; h, hour; ND, not detected monoxide in alveolar air [the last fraction of the exhaled (end-exhaled) air is usually collected to avoid dilution by the air volume, which does not reach the region of the lung where gas is exchanged with blood]. These parameters of internal exposure are highly correlated (r ~0.99) (Cohen *et al.*, 1971). The background level of carboxyhaemoglobin is substantially higher in smoking than in nonsmoking workers and is dependent on the number of cigarettes smoked and on the time since the last cigarette was smoked. Occupational exposure to carbon monoxide is usually assessed in smokers and nonsmokers separately, and by pre- and post-shift collection of blood or exhaled air. An increase in the percentage of carboxyhaemoglobin over the shift is often correlated to the ambient concentrations of carbon monoxide (Hagberg *et al.*, 1985). Fig 1.18 shows a comparison of exposure to carbon monoxide for the main occupational groups discussed in this section, and Fig. 1.19 shows the corresponding blood values of carboxyhaemoglobin, expressed as a percentage for smokers and nonsmokers.

(iii) Volatile organic compounds

Some volatile organic compounds are highly specific for gasoline engine exhaust, such as methyl *tertiary* butyl ether and 1,3-butadiene. Benzene, toluene, ethylbenzene and xylene have been studied extensively in relation to exposure to traffic emissions. Tobacco smoking leads to important co-exposures to benzene in some workers (White *et al.*, 1995). Occupational exposures to toluene and xylenes can also occur through work-related contact with products such as adhesives, paint, ink and cleaning solvents (Jo & Song, 2001). Fig 1.20 shows concentrations of benzene measured during personal air sampling by job title.

(iv) Formaldehyde and nitrogen oxides

Formaldehyde and nitrogen oxides are often used in the characterization of gasoline exhaust emissions, but these substances are also formed in diesel engines or may originate from alternative sources, such as building materials, or the use of preservative solutions, such as formalin.

(v) Particles

Compared with traditional diesel engines, spark-ignition engines only emit relative small amounts of PM (Murahashi *et al.*, 2003b), parent PAHs and PAH-derivatives such as alkylated, oxygenated and nitrated PAHs (Alsberg *et al.*, 1985; Scheepers & Bos, 1992). Particles emitted from gasoline engines are usually condensates of incompletely combusted fuel constituents and some metal oxides formed by the corrosion of engines and tailpipes.

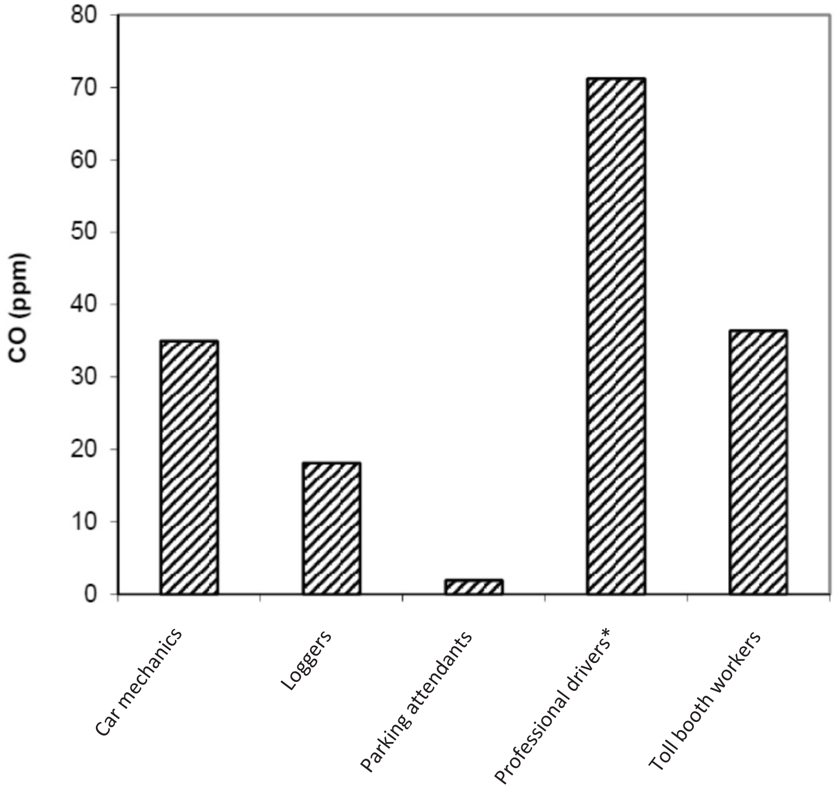
(b) Occupational exposures

Job titles associated with indoor and outdoor exposure to exhaust emissions from gasoline-powered engines are reviewed in this section, and the data are presented in Table 1.18, Table 1.19, Table 1.20, and Table 1.21.

(i) Border inspectors

Cohen *et al.* (1971) studied 26 workers at the border inspection station of San Ysidro, California, which is located at the USA–Mexican border (Table 1.19). Exposure assessment was performed by measuring carbon monoxide in exhaled air after the breath had been held, as described by Jones *et al.* (1958). The percentage of carboxyhaemoglobin was determined from the breath concentrations using a regression equation with a correlation coefficient of 0.99 and an intercept at zero exposure to carbon monoxide of 0.43% carboxyhaemoglobin (see the footnote in Table 1.19). In nonsmoking inspectors (in all shifts), the mean concentration of carbon monoxide increased from pre-shift to post-shift by a factor of 3.3 ($P < 0.01$). For smokers, post-shift carbon monoxide levels were increased but this difference was not statistically significant. However, for combined night and morning shifts, the increase in nonsmokers was fourfold

Fig. 1.18 Personal air concentrations of carbon monoxide by occupational group predominantly exposed to exhaust from gasoline engines



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*Exposure estimated based on 250 samples using a hand-operated pump colorimetric analysis (Jovanović *et al.*, 1999)
CO, carbon monoxide
Compiled by the Working Group

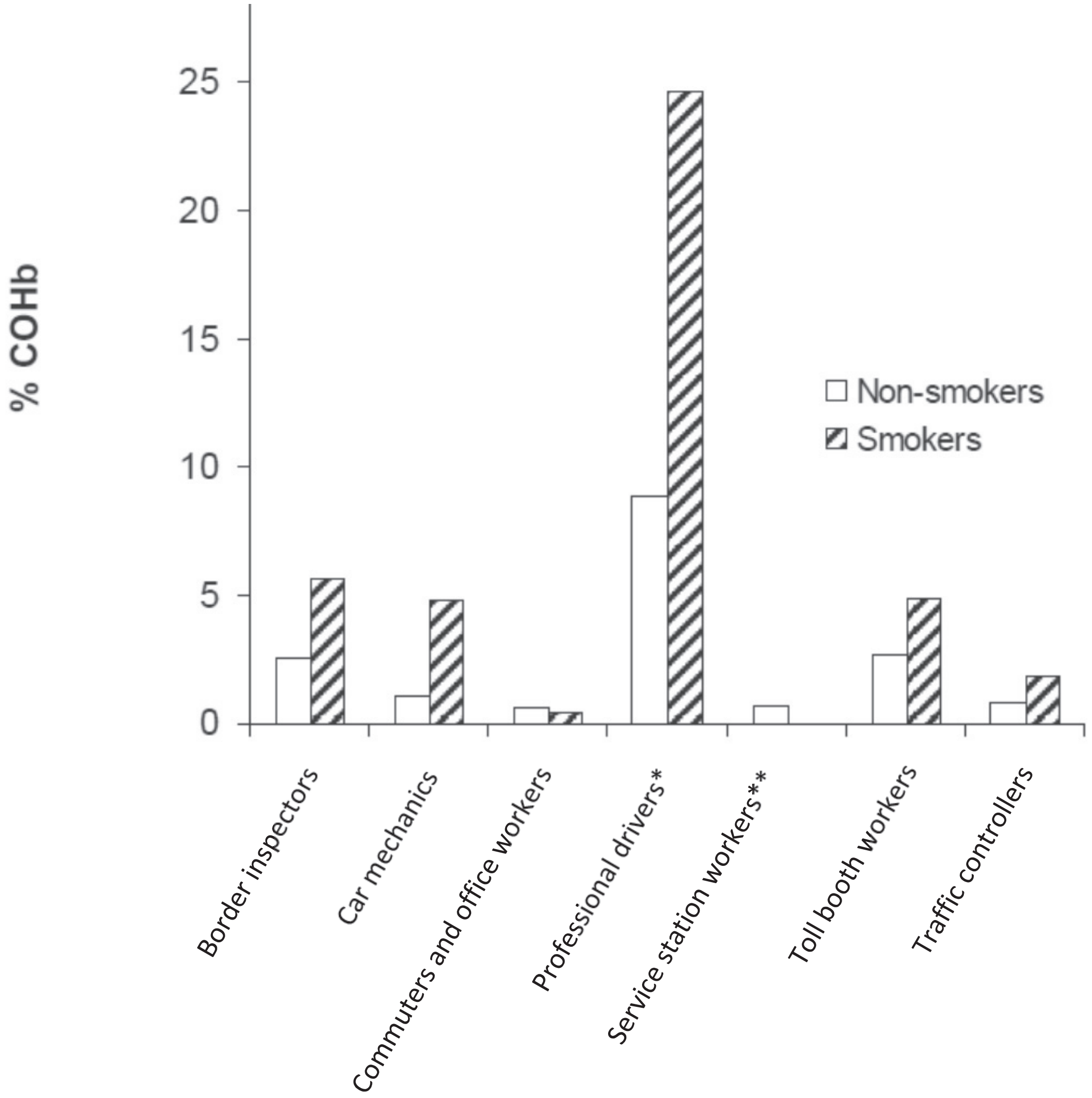
($P < 0.01$) and, for this subgroup, a statistically significant increase was also observed in smokers ($P < 0.02$). In nonsmoking and smoking control subjects (office clerks), no increase was observed (data not presented).

(ii) Office workers

Workers in offices may be exposed to chemicals derived from gasoline-powered road traffic, especially if their workplace is ventilated (either forced or naturally) with unfiltered outdoor air. In Taipei, Taiwan, China, Chan & Lin (1994) showed that differences in exposure to volatile organic compounds can occur, depending on the type of organization and type of office facilities used (see Table 1.20). Office workers are often assumed to have low exposures, but some data suggest they can experience exposures to volatile organic compounds from road traffic comparable with those of traffic policemen, car park attendants and store keepers (Romieu *et al.*, 1999; Jo & Song, 2001).

Office workers commuting to and from work typically have no direct contact with engine exhausts and consequently receive an exposure that is determined by the general air quality, derived primarily from pollution by road traffic. White *et al.* (1995) studied 14 commuters and assessed both environmental exposure by air

Fig. 1.19 Weighted percentage (%) of carboxyhaemoglobin by job title in workers predominantly exposed to exhaust from gasoline engines



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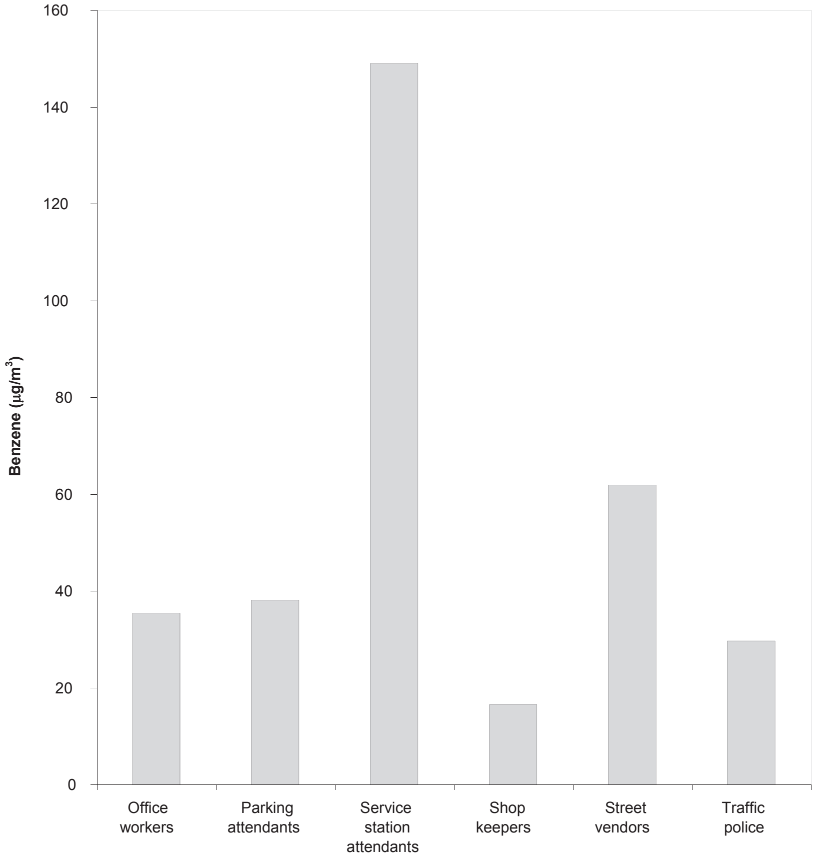
* Calculated from mmol/L assuming a concentration of 10 mmol/L haemoglobin (Jovanović *et al.*, 1999).
** The study of service station workers reported results from three nonsmokers only (White *et al.*, 1995).
COHb, carboxyhaemoglobin
Compiled by the Working Group

sampling and internal exposure by biological monitoring (see Table 1.21). In comparison with car mechanics, the median blood levels of methyl *tertiary* butyl ether of commuting office workers were an order of magnitude lower while the median blood levels of benzene were only 40% lower for nonsmoking men. The percentage of carboxyhaemoglobin of commuting office workers was in the normal range and more than 50% lower than the blood value of car mechanics (see below).

(iii) Car mechanics

Mechanics who work in garages have higher exposures to gasoline engine exhaust than outdoor workers. In most of the smaller

Fig. 1.20 Mean personal air sampling of benzene by job title in workers predominantly exposed to exhaust from gasoline engines



[The Working Group noted that the exposure of service station attendants was probably caused primarily by evaporation from fuels and only to a limited extent from exhaust fumes.]
Compiled by the Working Group

workshops, mechanical general or local exhaust ventilation is rarely available (Chambers *et al.*, 1984). Following the introduction of unleaded gasoline, exposure to lead in repair shops should have been reduced substantially, but no studies were found to confirm this.

Exposures to carbon monoxide from gasoline engine exhaust vary widely among car mechanics. In a study of 287 nonsmoking car mechanics in Canada, approximately 45% of the participants had carboxyhaemoglobin values higher than 5.0% (Gourdeau *et al.*, 1995). A study in Connecticut, USA, showed that the percentage of carboxyhaemoglobin was much lower and did not exceed the range observed in office workers (White *et al.*, 1995). Relatively low exposures to volatile organic compounds and benzene were reported for 16 car mechanics in garages in South Wales, United Kingdom by Parry *et al.* (1997), although these exposures were still much higher than those of office workers (threefold for benzene and about 10-fold for total aromatic compounds and volatile organic compounds).

Table 1.20 Concentrations of volatile organic compounds in occupations with exposure to gasoline engine exhaust (mean ± standard deviation)

Reference	Type of source, location	Conditions	Compound	Personal air concentration during shift (µg/m³)		End-exhaled air concentration (µg/m³)		Benzene metabolites (µg/g creatinine)	
				Smoker	Non-smoker	Pre-shift (*n* = 8–10)	Post-shift (*n* = 8–10)	SPMA	MA
Office worker									
Chan & Lin (1994)	Air pollution mainly from traffic sources in Taipei, Taiwan, China	Office of governmental agency (*n* = 10)	Benzene	25 ± 8		–	–	–	–
			Toluene	125 ± 99					
			Ethylbenzene	16 ± 11					
			m/p-Xylene	30 ± 21					
			o-Xylene	20 ± 14					
		Office of private company (*n* = 12)	Benzene	17 ± 8		–	–	–	–
			Toluene	150 ± 106					
			Ethylbenzene	11 ± 7					
			m/p-Xylene	25 ± 28					
			o-Xylene	14 ± 8					
		Office of research institute (*n* = 10)	Benzene	61 ± 29		–	–	–	–
			Toluene	79 ± 30					
			Ethylbenzene	13 ± 4					
			m/p-Xylene	23 ± 8					
			o-Xylene	15 ± 5					
Car park attendant									
Jo & Song (2001)	Four underground parking garages and four parking garages on ground floor in the city of Taegu, Republic of Korea	Working 8–12 h/d in the garage	Benzene	38.1 ± 19.6	24.6 ± 10.3	20.5 ± 11.4	24.0 ± 11.1	–	–
			Toluene	130 ± 57.6	119 ± 74.9	56.5 ± 26.7	61.4 ± 21.4		
			Ethylbenzene	10.6 ± 2.8	9.2 ± 4.8	5.4 ± 2.4	6.2 ± 2.8		
			p-Xylene	9.5 ± 4.3	8.9 ± 4.4	5.2 ± 2.4	6.4 ± 3.1		
			m-Xylene	7.5 ± 3.7	5.9 ± 3.7	3.7 ± 2.6	4.6 ± 2.6		
			o-Xylene	17.2 ± 8.8	17.3 ± 9.0	8.2 ± 3.9	10.6 ± 4.9		

Table 1.20 (continued)

Reference	Type of source, location	Conditions	Compound	Personal air concentration during shift (µg/m³)		End-exhaled air concentration (µg/m³)		Benzene metabolites (µg/g creatinine)	
				Smoker	**Non-smoker**	**Pre-shift (*n* = 8–10)**	**Post-shift (*n* = 8–10)**	**SPMA**	**MA**
Service station attendant									
Jo & Song (2001)	Five service station located in the city of Taegu, Republic of Korea	Working 6–8 h/d at the service station	Benzene	84.4 ± 33.2	72.1 ± 16.0	26.6 ± 14.5	41.0 ± 14.7[a]	–	–
			Toluene	141 ± 18.2	126 ± 42.0	40.2 ± 17.5	63.6 ± 18.8[a]		
			Ethylbenzene	12.9 ± 3.4	12.1 ± 5.9	6.1 ± 2.8	10.3 ± 4.1[a]		
			p-Xylene	14.6 ± 6.5	13.1 ± 6.3	6.0 ± 2.6	11.0 ± 6.1[a]		
			m-Xylene	14.0 ± 4.9	13.6 ± 6.8	3.5 ± 2.0	6.6 ± 2.8[a]		
			o-Xylene	26.5 ± 8.6	24.0 ± 11.1	8.9 ± 3.8	16.1 ± 5.9[a]		
Service station workers									
Ghittori *et al.* (2005)	Traffic emissions in Pavia, Lombardy, Italy	(*n* = 26)	Benzene	38.81 ± 46.26 (1.71–178.28)	-	-		2.36 ± 1.82 (0.30–6.90)	96.57 ± 53.44 (26.0–215)
Shop keeper									
Jo & Song (2001)	Roadside store near main street with heavy traffic in Taegu, Republic of Korea	Working 9–11 h/d in the store	Benzene	22.4 ± 7.3	16.7 ± 4.9	16.1 ± 8.2	16.8 ± 7.6	–	–
			Toluene	167 ± 230	176 ± 193	48.3 ± 16.9	83.6 ± 48.2[a]		
			Ethylbenzene	5.1 ± 3.4	3.9 ± 2.2	3.1 ± 0.9	3.7 ± 1.0		
			p-Xylene	4.3 ± 2.3	3.6 ± 2.6	2.7 ± 1.1	3.1 ± 1.3		
			m-Xylene	3.8 ± 3.1	3.3 ± 2.4	2.8 ± 1.1	2.7 ± 0.7		
			o-Xylene	7.9 ± 5.1	7.5 ± 5.0	4.9 ± 2.1	5.2 ± 1.8		
	Store near underground entrance or exit in Taegu, Republic of Korea	Working 9–11 h/d in the store	Benzene	23.8 ± 10.4	19.9 ± 15.3	18.8 ± 8.9	19.3 ± 6.5	–	–
			Toluene	175 ± 96.7	197 ± 213	52.6 ± 17.7	93.1 ± 44.7[a]		
			Ethylbenzene	7.8 ± 5.4	7.2 ± 4.6	5.2 ± 1.9	5.3 ± 1.7		
			p-Xylene	4.9 ± 3.4	5.2 ± 2.1	4.4 ± 1.6	4.5 ± 1.5		
			m-Xylene	4.6 ± 2.4	4.2 ± 1.6	2.9 ± 1.4	2.9 ± 1.3		
			o-Xylene	11.1 ± 5.2	9.2 ± 4.5	6.7 ± 3.0	7.0 ± 2.5		

Table 1.20 (continued)

Reference	Type of source, location	Conditions	Compound	Personal air concentration during shift (µg/m^3)		End-exhaled air concentration (µg/m^3)		Benzene metabolites (µg/g creatinine)	
				Smoker	Non-smoker	Pre-shift ($n = 8–10$)	Post-shift ($n = 8–10$)	SPMA	MA
Bae *et al.* (2004)	Polishers and repairmen shoe stalls in Seoul, South-Korea ($n = 32$), outdoor	working 10.11 ± 1.44 h/d in the store ($n = 32$)	Benzene Toluene p-Xylene o-Xylene	8 ± 20 (1–42) 160 ± 120 (33–504) 182 ± 120 (58–431) 139 ± 80 (52–229)		-	-	–	–
Traffic policeman									
Jo & Song (2001)	Traffic emissions in Taegu, Republic of Korea	6–8 h/d standing in dense motor vehicle traffic	Benzene Toluene Ethylbenzene p-Xylene m-Xylene o-Xylene	35.3 ± 14.8 114 ± 57.9 7.8 ± 4.7 6.3 ± 2.5 4.7 ± 2.0 11.1 ± 3.7	24.2 ± 10.0 125 ± 61.9 7.7 ± 4.2 8.4 ± 4.9 5.4 ± 3.7 13.4 ± 8.8	16.8 ± 7.8 27.1 ± 16.2 3.2 ± 1.6 3.0 ± 1.5 1.9 ± 0.9 4.6 ± 2.1	24.9 ± 11.5 46.8 ± 26.4[a] 4.8 ± 1.9[a] 4.9 ± 1.8[a] 2.9 ± 1.1[a] 7.3 ± 2.9[a]	–	–

[a] Statistically significant increase from pre- to post-shift level

d, day; MA, t,t-muconic acid; m-, *meta*; o-, *ortho*; p-, *para*; SPMA, S-phenylmercapturic acid

Table 1.21 Concentrations of volatile organic compounds in occupations with exposure to gasoline engine exhaust (median and range)

Reference	Job title	Location	Conditions	Compound	Breathing zone concentration (µg/m^3)	Blood concentration (µg/L)	
						Pre-shift	Post-shift
White *et al.* (1995)	Car mechanic	Stamford, CT, USA	Post-shift samples collected at 7 garages and automobile firms	Benzene (*n* = 12)*a*	–		0.19 (0.11–0.98)[a]
				M*t*BE (*n* = 21)	–		1.73 (0.17–36.7)
				TBA (*n* = 21)	–		15 (2–50)[b]
	Commuting office worker		Samples collected after arriving at work during the shift in the morning	Benzene (*n* = 7)[a]	–		0.12 (0.10–0.20)[a]
				M*t*BE (*n* = 14)	–		0.11 (< 0.05–2.60)
				TBA (*n* = 14)	–		2.5 (0.5–9)[b]
	Service station attendant		Post-shift samples collected at 7 garages and automobile firms	Benzene (*n* = 3)[a]	–		0.36 (0.32–0.47)[a]
				M*t*BE (*n* = 3)	–		15 (7.6–28.9)
				TBA (*n* = 3)	–		80 (20–90)[b]
Romieu *et al.* (1999)	Service station attendant	Downtown Mexico City, Mexico	(*n* = 23–25)	Benzene	330 (130–770)	0.63 (0.26–2.3)	0.42 (0.13–1.4)
				Ethylbenzene	90 (61–1,400)	0.35 (0.12–1.4)	0.37 (0.12–7.8)
				o-Xylene	100 (65–1,900)	0.39 (0.16–1.2)	0.45 (0.15–6.3)
				m/p-Xylene	290 (180–5,800)	1.4 (0.50–4.7)	1.3 (0.36–16)
				Toluene	610 (410–1,300)	1.3 (0.44–4.1)	1.2 (0.34–4.7)
				M*t*BE	–	7.7 (2.2–48)	6.8 (0.22–25)
				Styrene	–	0.029 (0.022–0.045)	0.024 (0.020–0.093)
	Office worker		(*n* = 7–10)	Benzene	39 (32–67)	0.17 (0.12–0.23)	0.14 (0.12–0.20)
				Ethylbenzene	18 (12–22)	0.12 (0.071–0.18)	0.076 (0.045–0.11)
				o-Xylene	23 (16–28)	0.15 (0.081–0.31)	0.10 (0.073–0.21)
				m/p-Xylene	60 (44–80)	0.55 (0.37–0.81)	0.39 (0.19–0.73)
				Toluene	250 (20–7,100)	0.71 (0.30–1.4)	0.61 (0.38–7.4)
				M*t*BE	–	0.26 (0.22–0.97)	0.24 (0.16–0.57)
				Styrene	–	0.025 (0.022–0.049)	0.023 (0.022–0.027)
	Street vendor		Entire day outdoors (*n* = 5–6)	Benzene	62 (49–180)	0.30 (0.20–0.68)	0.22 (0.14–0.33)
				Ethylbenzene	29 (20–35)	0.13 (0.096–0.31)	0.12 (0.054–0.18)
				o-Xylene	6.0 (2.0–44)	0.18 (0.13–0.30)	0.15 (0.083–0.20)
				m/p-Xylene	95 (71–120)	0.75 (0.41–1.1)	0.53 (0.25–0.70)
				Toluene	170 (110–210)	1.8 (0.39–5.4)	0.51 (0.32–4.6)
				M*t*BE	–	0.47 (0.23–0.80)	0.33 (0.20–0.37)
				Styrene	–	0.028 (0.025–0.18)	0.025 (0.022–0.073)

[a] Nonsmokers

[b] Approximations of values taken from graphs (no table available)

m/p-, *meta-/para-*; M*t*BE, methyl *tertiary* butyl ether; o-, *ortho-*; TBA, tertiary butyl alcohol

(iv) Loggers

Loggers perform a range of tasks, including felling trees, limbing, bucking and manual skidding of trunks, although some of these may be performed mechanically and felling remains the main task (Nilsson *et al.*, 1987). Much of the exposure is dependent on the type, maintenance and operational conditions of the two-stroke engines used in the chain saw. Worn-out chain saw engines may cause increased exhaust emissions. The carburettor settings of the engine can also influence the composition of the exhaust; a lean setting (low fuel–air ratio) increases the emission of aldehydes and nitrogen oxides, whereas a rich setting (high fuel–air ratio) increases carbon monoxide and hydrocarbon emissions (Nilsson *et al.*, 1987).

The work of loggers is particularly strenuous because of the heavy physical workload, high levels of exposure to noise and also high levels of exposure to exhaust emissions. Loggers have high exposures to volatile organic compounds, benzene and formaldehyde. Exposures to carbon monoxide were low, which may be related to the carburettor settings on the chain saw engines (Table 1.18). The highest exposures were observed for loggers who were specifically performing felling operations. In 80–100-cm deep snow, loggers performing felling tasks only were exposed to more than twofold higher exhaust emissions compared with loggers performing all tasks using the same carburettor adjustment on their chain saws and under similar snow conditions. The estimated peak exposures during logging were 1.6 mg/m^3 of aldehydes, 320 ppm of carbon monoxide and 0.2 mg/m^3 of nitrogen oxides. The value for carbon monoxide was close to the short-term exposure levels of 400 ppm [calculated from milligrams per cubic metre by the Working Group] reported in the field (Bünger *et al.*, 1997). The maximum carboxyhaemoglobin level of German loggers exceeded the biological exposure index of the American Conference of Governmental Industrial Hygienists of 3.5%, 2–3 h after the start of the shift, when workers were paid on a piecework basis (Bünger *et al.*, 1997).

(v) Car park attendants

As shown in Table 1.18, the mean levels of exposure to carbon monoxide, benzene and methyl *tertiary* butyl ether of attendants at a university hospital car park in Baltimore, USA, were 2.6 ppm, 2.7 μg/m^3 and 7.4 μg/m^3, respectively, on weekdays (72 cars/h), compared with 1.2 ppm, 0.3 μg/m^3 and 0.4 μg/m^3 at the weekend (6 cars/h), respectively (Kim *et al.*, 2007). Jo & Song (2001) studied the exposure of car park attendants in ground-level and underground parking garages in Taegu, Republic of Korea (see Table 1.20). All garages used mechanical ventilation systems and ground-level garages also benefited from natural ventilation in the entrance/exit area. Exposure to benzene, toluene, ethylbenzene, *meta*-xylene, *para*-xylene and *ortho*-xylene was measured by the collection of personal air samples. In addition, before and after shift (of 8–12 hours), alveolar air samples were collected to determine the concentrations in alveolar air. The mean and median breath concentrations of all components tended to increase across the shift, but no statistically significant differences were observed. Personal air samples were collected from four smoking and four nonsmoking car park attendants (Table 1.20). Both breath and personal air concentrations of benzene, toluene, ethylbenzene, *meta*-xylene, *para*-xylene and *ortho*-xylene were approximately twofold higher in attendants who worked in underground car parks compared with those who worked at ground-level, possibly due to the additional natural ventilation in the entrance/exit area. Personal measurements of concentrations in workplace air correlated significantly with post-shift concentrations in alveolar air for all substances except *meta*-xylene (Spearman correlation coefficients varied from 0.76 to 0.84). Mean and median levels of alveolar air concentrations of benzene, toluene, ethylbenzene, *meta*-xylene, *para*-xylene and *ortho*-xylene were twofold higher in car park attendants compared with the levels reported in a control group of college students (results not presented).

Johnson *et al.* (1975) reported elevated blood lead values of 28.3 ± 10.3 µg/dL in car park attendants in Houston, TX, USA.

(vi) Professional drivers

Drivers represent a heterogeneous group of workers, including taxi drivers and drivers of lorries and buses, who spend most of their time in a vehicle driving mostly in urban areas and on highways (Table 1.18 and Table 1.19). Exposure to carbon monoxide and the percentage of carboxyhaemoglobin were clearly elevated in 250 drivers studied by Jovanović *et al.* (1999) but it is uncertain whether such exposures were derived from exhaust emissions from their own vehicle, which can enter into the interior of the vehicle due to a leaking exhaust system, or from emissions from other road vehicles, which enter the interior of the vehicle through the windows or the ventilation system. [The Working Group noted that the exposure values for carbon monoxide reported in this study were exceptionally high but were nevertheless consistent with the high reported values of carboxyhaemoglobin.] Studies of blood lead levels in professional drivers in China, Indonesia and Pakistan have also indicated elevated exposure originating from gasoline engine exhaust (Suzuki, 1990; Khan *et al.*, 1995; Zhou *et al.*, 2001).

(vii) Service station attendants

Attendants of gasoline stations are primarily exposed to volatile organic compounds from gasoline vapours and also from exhaust emissions from the vehicles of customers and from passing road traffic. These sources of exposure have been investigated in two studies that used both personal air sampling and biological monitoring (Romieu *et al.*, 1999; Ghittori *et al.*, 2005).

Romieu *et al.* (1999) reported the breathing zone concentrations of several PAHs and some chemicals specific for gasoline such as methyl *tertiary* butyl ether. Mexican fuel contains approximately 5% of methyl *tertiary* butyl ether, which resulted in higher blood levels of this compound compared with those of benzene, toluene, ethylbenzene and xylene (see Table 1.21), whereas the benzene content of Mexican fuel is lower (1.5–2%) than that of European gasoline (2–6%) (Romieu *et al.*, 1999). About half of the population smoked, but the blood levels of volatile organic compounds and chemical markers for smoking, such as 2,5-dimethylfuran, were similar in smokers and nonsmokers, suggesting that the data reflected primarily exposure to volatile organic compounds derived from gasoline fuel and exhaust. Overall the levels of exposure to benzene, toluene, ethylbenzene and xylene reported in this study appeared to be higher than those in other available studies (Moolenaar *et al.*, 1994). [The Working Group noted that the higher exposures in the study in Mexico were probably due to high traffic density and the use of old vehicles with poor emission control technology. The median concentrations of markers of exposure to volatile organic compounds in end-of shift blood samples appeared to be somewhat lower than those in pre-shift samples, which may be related to the collection of the pre-shift sample more than half an hour after the start of the shift. Long-term exposure may also contribute to enhanced pre-shift values due to bioaccumulation because of incomplete metabolism/excretion between exposures.]

Ghittori *et al.* (2005) performed a detailed study of service station attendants in Pavia, Italy, who were stratified into three subgroups: cashiers, self-service attendants and fuel dispensers (in Table 1.18, Table 1.19, and Table 1.20, only results of the entire group are presented). Mean exposure to methyl *tertiary* butyl ether in air was significantly higher for fuel dispensers (401.75 ± 302.75 µg/m^3) than for cashiers

(16.28 ± 7.47 µg/m³) and self-service attendants (19.66 ± 5.79 µg/m³). This was reflected in the significantly higher values of methyl *tertiary* butyl ether in the urine of fuel dispensers (3.0 ± 3.2 µg/L) compared with cashiers (0.10 ± 0.06 µg/L) and self-service attendants (0.74 ± 1.69 µg/L). This suggests that primarily fuel-related exposure occurred, although levels of formaldehyde were slightly lower in fuel dispensers (no statistically significant difference with the other job titles). Fuel dispensers also had significantly higher exposure to benzene (88.56 ± 47.64 µg/m³) than cashiers (4.38 ± 2.08 µg/m³) and self-service attendants (19.66 ± 5.79 µg/m³). This pattern was also reflected in the values of urinary excretion of the benzene metabolites, S-phenylmercapturic acid and *t,t*-muconic acid.

Exposures to carbon monoxide were not studied extensively in service station attendants but appeared to be relatively low (White *et al.*, 1995). Except for one report of elevated blood lead (Tola *et al.*, 1976), exposure to lead also appeared to be low relative to other job titles (Hunaiti *et al.*, 1995; Ghittori *et al.*, 2005). Urinary platinum concentrations of 73.8 ± 79.9 ng/L were reported in service station workers in Italy (Ghittori *et al.*, 2005).

(viii) Shop keepers

Jo & Song (2001) studied exposure to traffic emissions by persons tending a shop, either underground or at the street level, in a busy sector of Taegu, Republic of Korea. Vehicle emissions were the primary source of the exposure of shop attendants to ethylbenzene, and *ortho*-, *meta*- and *para*-xylene (Table 1.20) because outdoor and indoor concentrations were found to be in the same range in stores tended by both smoking and nonsmoking shop keepers. No information was provided on the type of ventilation or the distance of these shops from the road. Exposure of store keepers to benzene, toluene, ethylbenzene and xylene was two- to fourfold higher than that reported for a control group of college students (results not presented). A statistically significant increase in the mean and median concentrations of toluene in alveolar air from pre-shift to post-shift was observed in both underground and ground-level shops. Workers in shoe stalls in Seoul, Republic of Korea, were exposed to an average concentration of 8 µg/m³ of benzene (Bae *et al.*, 2004).

[The Working Group noted that, for print shops, the post-shift increase in toluene concentration could be explained by the presence of toluene in the adhesives used for bookbinding. This may also explain the somewhat higher alveolar air levels of toluene observed in keepers of book stores compared with those of keepers of cosmetic and flower shops. This interpretation of the results on toluene is supported by the finding of higher indoor than outdoor levels of toluene in print shops and book shops. Because of the apparent lack of indoor sources of toluene, it may be assumed that, for keepers of flower and cosmetic shops, vehicle emissions were the primary source of exposure to toluene. The concentrations of benzene in alveolar air were higher in smokers, suggesting that exposure from traffic may be masked by active smoking.]

Thirty-six shop keepers who worked 8–10 hours per day along the main roads of Abbottabad, Pakistan had mean blood lead values of 52.10 µg/dL (Khan *et al.*, 1995), which were similar to those of policemen who worked in the same city (see Section 1.4.2 (b, xi)).

(ix) Street vendors and street sweepers

Very limited data were available on street vendors and street sweepers in cities with high road traffic intensity, such as Mexico City (Romieu *et al.*, 1999). Reported exposures to benzene were higher for street vendors than for office workers but much lower than those of service station attendants and also lower than those of shop keepers who worked in outdoor locations (Table 1.18, Table 1.19, and Table 1.20). Street sweepers in Finland had intermediate exposure to lead at a time when tetraethyl lead was still added to gasoline (Tola *et al.*, 1976).

(x) Toll booth workers

The exposure of attendants in toll booths at bridges and tunnels is primarily outdoor and depends on the local infrastructure and weather conditions. Exposure patterns primarily reflect traffic density, weather conditions and emissions during the acceleration of vehicles. One study found that air levels of aldehydes, lead, total hydrocarbons, nitrogen oxides and carbon monoxide followed a similar pattern during the day, suggesting that carbon monoxide could be a useful exposure indicator for toll booth workers (Ayres *et al.*, 1973). The levels of exposure to nitric oxide, respirable PM and lead of toll booth workers were found to be consistently elevated at three different locations near Boston, MA, USA (Burgess *et al.*, 1977). [The Working Group did not take into account lead in hair levels reported by Burgess *et al.* (1977) because of uncertainty whether this represents real uptake or contamination due to external deposition of dust.]

No difference was noted between exposures to carbon monoxide observed in the USA in 1973 (Ayres *et al.*, 1973) and in Boston, USA (Burgess *et al.*, 1977). More recently reported exposures for toll booth workers in Turkey (Kocasoy & Yalin, 2004) and Malaysia (Niza & Jamal, 2007) were in a similar range. These results suggest that control technologies combined with reduced carbon monoxide emissions from car exhaust over a period of three decades have led to substantially lower exposures to carbon monoxide in nonsmokers (but less striking decreases in smokers). Reduction in exposure can also be achieved by ventilation, irrespective of high traffic density and/or high emission levels. Sapkota *et al.* (2005) demonstrated exposures to benzene, methyl *tertiary* butyl ether and 1,3-butadiene two- to fourfold lower in toll booths compared with levels outside the booth (Table 1.18). This was achieved by the supply of filtered air through a set of pre-filters and a box filter as part of an air conditioning unit, which in part recirculated the air.

(xi) Traffic policemen

Exposure to emissions from road traffic has been studied extensively among policemen and similar occupations. Biava *et al.* (1992) observed a small cross-shift increase of the percentage of carboxyhaemoglobin in nonsmoking and smoking traffic wardens in Milan, Italy. Zhang *et al.* (1994) reported similar findings in Wuhan, China (Table 1.19). The contribution of ambient exposure to carbon monoxide on carboxyhaemoglobin levels was significantly higher only in nonsmokers compared with policemen who predominantly worked indoors. In Torino, Italy, Bono *et al.* (2007) also reported relatively low carboxyhaemoglobin values (except for a subgroup of police officers who worked on the street for shifts of more than 7 hours).

The mean and median concentrations of benzene, toluene, ethylbenzene and xylene in alveolar air increased from pre-shift to post-shift in policemen in Taegu, Republic of Korea (Jo & Song, 2001). This increase was statistically significant ($P < 0.05$) for all substances except benzene. Traffic police spent 6–8 hours in dense motor vehicle traffic. No differences in concentrations in the alveolar air between smokers and nonsmokers were observed, suggesting that smoking habits did not mask possible exposure to emissions from road traffic. Concentrations of benzene, toluene, ethylbenzene and xylene in post-shift alveolar air samples correlated significantly with concentrations obtained by personal air sampling (Spearman correlations ranging from 0.65 to 0.86). Mean and median levels of benzene, toluene, ethylbenzene and xylene in alveolar air were up to twofold higher than those reported for a control group of college students (results not presented). One study (Iavicoli *et al.*, 2004) provided data on urinary platinum levels in traffic policemen: the reported pre- and post-shift concentrations of 4.43 ± 2.34 and 4.63 ± 2.47 ng/L, respectively, were markedly lower than those reported for service station workers (Ghittori *et al.*, 2005).

High mean blood lead levels of 52.2 (± 2.88) µg/dL were reported in policemen who worked 8–10 hours per day in Abbottabad, Pakistan (Khan *et al.*, 1995). The mean levels in traffic policemen (53.43 µg/dL) were similar to those observed in shop keepers (52.10 µg/dL) and in employees of the governmental transport service (51.06 µg/dL), and were twofold higher ($P < 0.001$) than those observed in 36 controls from a rural area (24.06 ± 1.70 µg/dL). The elevated exposure to lead in policemen was also reflected in a higher level of urinary 5-amino-levulinic acid dehydrase of 3.68 ± 0.2 mg/dL, compared with 0.8 ± 0.04 mg/dL in the control group ($P < 0.001$).

1.4.3 Exposure of the general population

Exposures of the general population to traffic emissions are a function of proximity to fresh traffic emissions and the presence of aged traffic emissions in regional pollutants. During air transport, atmospheric processes change the contaminants: particles agglomerate, rain out and settle out according to size, chemical reactions affect some components and weather processes remove others (Lippmann *et al.*, 2003).

(a) Exposure from traffic

Source apportionment can be conducted to determine the contribution of traffic to a complex mixture of air pollution (Schauer *et al.*, 1996; Schauer & Cass, 2000; Schauer *et al.*, 2002; Schauer, 2003; Zheng *et al.*, 2005; Zhao *et al.*, 2006; Hopke, 2008; Brinkman *et al.*, 2009). Sources emit correlated sets of individual pollutants in a pattern that is more or less unique. The ability to distinguish sources depends on the components being measured [large numbers of elements can be measured by X-ray fluorescence or neutron activation analysis] plus EC, organic carbon, $PM_{2.5}$ and perhaps ultrafine particles. Table 1.22 summarizes the data of Viana *et al.* (2008) in European source apportionment studies. They noted that overlap among source component emissions and variability in the pattern for a given set of sources, such as for diesel and gasoline engines, may occur and the results may therefore be difficult to interpret. One limitation of the application of organic tracers is that a large sample is required and a very sophisticated analysis must be performed using extremely sensitive equipment. In addition, environmentally stable tracers must be used, wherever possible, to avoid problems with changes during transport which may blur source assignments. Several studies have been conducted in cities and regions around the world, and these are presented in Table 1.23 to illustrate the findings and relative importance of traffic sources in a variety of urban backgrounds.

In urban areas, the $PM_{2.5}$ ranged from 9.5 µg/m³ in Corpus Christi, TX, USA (Karnae & John, 2011) to 231 µg/m³ in Delhi, India (Chowdhury *et al.*, 2007). The corresponding contributions from traffic were about 10% for Corpus Christi and 21% and 9% for diesel and gasoline vehicles, respectively, in Delhi (Table 1.23). Beijing, China, had high $PM_{2.5}$ levels (39–167 µg/m³) with a low contribution from traffic (7% ± 3%) (Zheng *et al.*, 2005), but vehicle ownership has increased rapidly in China. Developing countries have fewer engine emission controls and subsequently may have higher emission levels and exposures depending on the country and traffic density.

(b) Other sources

Source apportionment analyses have been used to determine the amount of emissions from ships in marine ports, from aircraft near airports and from the use of diesel generators.

Table 1.22 Characteristics of the four main source categories identified from the European studies

PM	Source signatures	No. of studies	Source contribution range (%)	Trend	Source interpretations
Source interpretations provided by the different authors					
PM_{10}	C, Fe, Ba, Zn, Cu	23/28	1 (Areao, PT)	Dependent on volume and mixture of traffic emissions	Traffic
$PM_{2.5}$	C, Fe, Ba, Zn, Cu, Pb	19/20	55 (Milan, IT) 5 (Birkenes, NO) 49 (Barcelona, ES)		Vehicle exhaust
PM_{10}	Al, Si, Ca, Fe	24/28	5 (Duisburg, DE)	Marked North to South gradient	Mineral matter
$PM_{2.5}$	Al, Si, Ca, Fe, K	19/20	37 (Huelva, ES) 5 (Helsinki, FI) 30 (Huelva, ES)		City dust
PM_{10}	Na, Cl, Mg	20/28	< 5 inland sites	Gradient from Atlantic coastal sites to continental inland sites	Marine aerosol
$PM_{2.5}$	Na, Cl, Mg	15/20	88 (Areao, PT) < 5 inland sites 15 (Areao, PT)		Sea spray
PM_{10}	V, Ni, SO^{2-}_4	21/28	8 (Barcelona, ES) 37 (Florence, IT)	No clear trend	Oil combustion
$PM_{2.5}$	V, Ni, SO^{2-}_4	16/20	11 (Amsterdam, NL) 43 (Barcelona, ES)		Industry
PM_{10}	SO^{2-}_4, NO^-_3, NH^+_4	9/28	12 (Cork, IE) 46 (Milan, IT)	No clear trend	Secondary aerosols Regional background
$PM_{2.5}$	SO^{2-}_4, NO^-_3, NH^+_4	10/20	17 (Huelva, ES) 57 (Duisburg, DE)		Long-range support
Signatures reported for specific sources identified at single locations					
Source signatures	*Location*	*Source interpretation*	*Study*		
Cu, K, Ca	Estarreja, PT	Copper smelter	Pio *et al.* (1989)		
Cr, Ni, Cu	Estarreja, PT	Oil combustion	Pio *et al.* (1989)		
As, Cu, Pb, Ba, Sb	Huelva, ES	Copper smelter	Alastuey *et al.* (2006), Querol *et al.* (2007a)		

Table 1.22 (continued)

PM	Source signatures	No. of studies	Source contribution range (%)	Trend	Source interpretations
Cr, Ni, Mo, Cu, Co, As	Llodio, ES	Pigment production	Viana *et al.* (2006)		
As, Pb, Zn, Zr, Tl, Cs	L'Alcora, ES	Ceramic frit production	Cruz-Minguillón *et al.* (2007)		
Mn, Zn, Pb, Cd	Llodio, ES; Alasua, ES	Metallurgy	Viana *et al.* (2006), Zabalza *et al.* (2006)		
Si, Al, Fe, Li, Sc	L'Alcora, ES	Ceramic production	Querol *et al.* (2007b)		
K, As	Copenhagen, DK	Biomass burning	Andersen *et al.* (2007)		
K, C, O_3	Monagrega, ES	Biomass burning	Rodríguez *et al.* (2004)		

Al, aluminium; As, arsenic; Ba, barium; C, carbon; Ca, calcium; Cd, cadmium; Cl, chlorine; Co, cobalt; Cr, chromium; Cs, caesium; Cu, copper; Fe, iron; K, potassium; Li, lithium; Mg, magnesium; Mn, manganese; Mo, molybdenum; Na, sodium; NH_4^+, ammonium; Ni, nickel; NO_3^-, nitrate; O_3, ozone; Pb, lead; PM, particulate matter; Sb, antimony; Sc, scandium; Si, silica, SO_4^{-2}, sulfate; Tl, thallium; V, vanadium; Zn, zinc; Zr, zirconium

DE, Germany; DK, Denmark; ES, Spain; FI, Finland; IE, Ireland; IT, Italy; NL, Netherlands; NO, Norway; PT, Portugal

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Table 1.23 Occurrence of diesel and gasoline vehicle exhaust in measurements of urban particulate matter ($PM_{2.5}$) or ultrafine particles

Country, region	Type of sample location	$PM_{2.5}$ concentration ($\mu g/m^3$)	Gasoline exhaust (%)	Diesel exhaust (%)	Ship exhaust (%)	Main monitor activities	References
USA							
Seattle, WA	Urban background or rural	8.97 – 11.57	13 – 31	2 – 9	4–6	3 city, 1 rural, 1 port sites	Kim & Hopke (2008)
Kalmiopsis, OR	Remote location	3.4 ± 3.07	1.9	1.4	–	1 remote site	Hwang & Hopke (2007)
Corpus Christi, TX	Urban background and port	9.45	Traffic 9.7		4.6	1 city site	Karnae & John (2011)
St. Louis, MO	Urban background	16.4	21.1	5.0	–	2 city sites	Lee & Hopke (2006)
New York City area, NY	Urban background	10.7 ± 8.7–13.9 ± 9.0	8–22	3–15	–	3 city sites, 2 suburban	Qin *et al.* (2006)
Raleigh and Chapel Hill, NC	Personal, indoor and outside residences	Personal, 23.0 Indoors, 19.1 Outdoors, 19.3 Ambient, 19.2	Traffic Personal, 10.0 Indoors, 9.4 Outdoors, 17.2 Ambient, 19.4		–	38 suburban homes	Williams *et al.* (2003), Zhao *et al.* (2006)
Los Angeles area, CA	Urban background	Azusa, 14–20 Los Angeles, 14–24	Traffic, 40–50%		–	2 sites	Lough *et al.* (2006)
Los Angeles port area, CA	Ship emissions	10.2 ± 3	–		< 5	4 urban 1 on pier	Arhami *et al.* (2009)
Seattle, WA	Ship emissions	8.05	–		1–2	1 site	Wu *et al.* (2009)
Los Angeles airport, CA	Aircraft emissions	UFP counts 11 900–28 500 during take-off	–		–	Site at blast fence	Zhu *et al.* (2011)
Asia							
Lahore, Pakistan	Urban background	190.5 ± 90.5	7.7 (2-cycle engine)	28.3	–	1 city site	Raja *et al.* (2010)
Delhi, Mumbai, Kolkata, India	Urban background	Delhi, 230.9 Mumbai, 88.9 Kolkata, 304.5 Chandigarth, 29.2	9 6 11 16	21 10 16 13	–	3 city sites, 1 background	Chowdhury *et al.* (2007)[a]

Table 1.23 (continued)

Country, region	Type of sample location	$PM_{2.5}$ concentration (µg/m^3)	Gasoline exhaust (%)	Diesel exhaust (%)	Ship exhaust (%)	Main monitor activities	References
Beijing, China	Urban background	39–167	Traffic, 7 ± 3		–	4 city monitors 1 background	Zheng *et al.* (2005)
Europe							
Erfurt, Germany	Urban background	19.2 (% of $PM_{2.8}$)	Traffic: 4% local, 39% remote		–	1 city site	Yue *et al.* (2008)
Prague, Czech Republic	Urban background	8473 (total particle count)	34.2 (% of total count)	37.8 (% of total count)	–	1 city site	Thimmaiah *et al.* (2009)
Several European countries	Urban background	NR	Traffic 12–35		–	48 city sites, 8 countries	Viana *et al.* (2008)
Canary Islands, Spain	Ship emissions	UFP count 35–50 × 10^3/cm	–		65–70	1 near water front	Gonzalez *et al.* (2011)

[a] Values include some two-cycle engine exhausts

NR, not reported; UPF, ultrafine particles

(i) Ships

Kim & Hopke (2008) carried out studies in Seattle, WA, USA, to determine the $PM_{2.5}$ emissions from ships. They had access to a source profile for oil combustion but not for ship emissions, although they knew that ships burn a low-grade residual oil (No. 6 or Bunker C) that contains significant concentrations of vanadium, nickel and sulfur. At three of their sampling sites, analysis of wind patterns back tracked the source locations of vanadium, nickel and sulfate pollutants suggested that 'oil combustion' in the harbour was the source that contributed to ship emissions, and accounted for 4–6% of the $PM_{2.5}$.

Arhami *et al.* (2009) investigated the impact of ship activity in the Port of Los Angeles, CA, USA. Because of the heavy highway traffic in the area of the port, diesel vehicle emissions were elevated. The ship emissions from 'oil combustion' were clearly identified by the vanadium, nickel and sulfate correlations in the quasi-ultrafine particles, but were only a minor source of EC and organic carbon.

Gonzalez *et al.* (2011) conducted a study to determine the contribution of ship emissions to ultrafine particles in the port city of Santa Cruz de Tenerife, Canary Islands, Spain. Changes in the wind direction during the day permitted an assessment of the ship component associated with high levels of sulfur dioxide and ultrafine particles. They estimated that ship exhaust accounted for 65–70% of the ultrafine particles, which was in the range of $35–50 \times 10^3$ particles/cm^3. Because the sampling site was 1 km or more away from the ships, samples taken in closer proximity might demonstrate higher exposures, but few residences were closer.

In summary, the impact of ship emissions on exposures in port areas appears to be small compared with that of diesel vehicles in traffic. However, emissions from ships are a major source of ultrafine particles with significant sulfate nuclei.

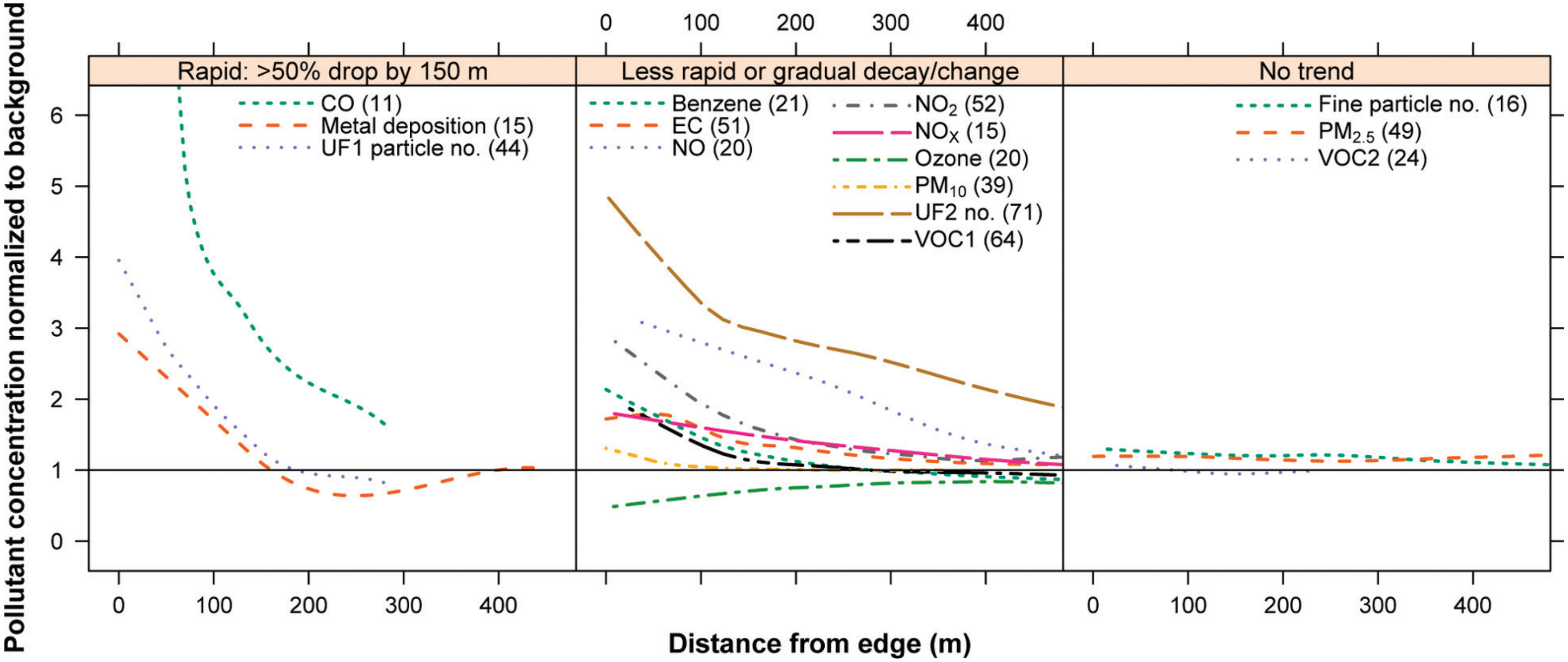
(ii) Diesel generators

In developing countries and locations where electrical supplies are unreliable or lacking, people often rely on small to medium-sized stationary diesel generators to provide electricity. Because these generators have limited emission controls, they can be major sources of exposure to diesel exhaust. In experimental studies, emissions were strongly influenced by engine load, and higher loads produced lower PM emissions. In some areas, waste cooking oil is mixed with diesel fuel (25–75%) and used as a biodiesel for the generators (Betha & Balasubramanian, 2011; Valente *et al.*, 2012). With 50% cooking oil, the emissions of carbon monoxide and hydrocarbons were increased on average by 20.1% and 23.5%, respectively, over a range of engine loads. Although several laboratory tests have been carried out, no reports have been made of exposure concentrations during the home use of generators.

(c) Roadside exposures

Karner *et al.* (2010) summarized 41 studies that assessed the decline in roadside pollutant levels at a distance from roadways. The common markers of traffic were investigated and listed by decreasing number of studies reporting data for EC, $PM_{2.5}$, PM_{10}, number of ultrafine particles, nitrogen dioxide, nitric oxide, nitrogen oxides, carbon monoxide, benzene, sulfur, organic carbon, ozone, volatile organic compounds, number of fine particles, metal deposition, and carbon dioxide. The majority of studies assessed the first eight pollutants, and most investigated emissions from major highways or freeways. Wind speed and direction, and night-time atmospheric stability had considerable effects on the rate of decline in concentrations moving downwind of roadways. During low wind speeds or calm conditions, such as in the evening or at night, emissions accumulated in a wide area surrounding the roadways with little or no

Fig. 1.21 Locally smoothed regression of background-normalized pollutant concentrations at a distance from edge of the road



The horizontal line indicates background concentration. A Loess smoother (α = 0.75; degree = 1) is fitted to each pollutant which is placed into one of three groups. The regression sample size (n) is given in parentheses after each pollutant.

CO, carbon monoxide; EC, elemental carbon; NO, nitric oxide; NO_2, nitric dioxide; No_x, nitric oxides; PM, particulate matter; UF1, UF2, number of particles with data collection beginning at 3 nm and 15 nm, respectively; VOC1, 8 volatile organic compounds whose concentrations varied with distance from road; VOC2, 4 volatile organic compounds whose concentrations did not vary with distance from road

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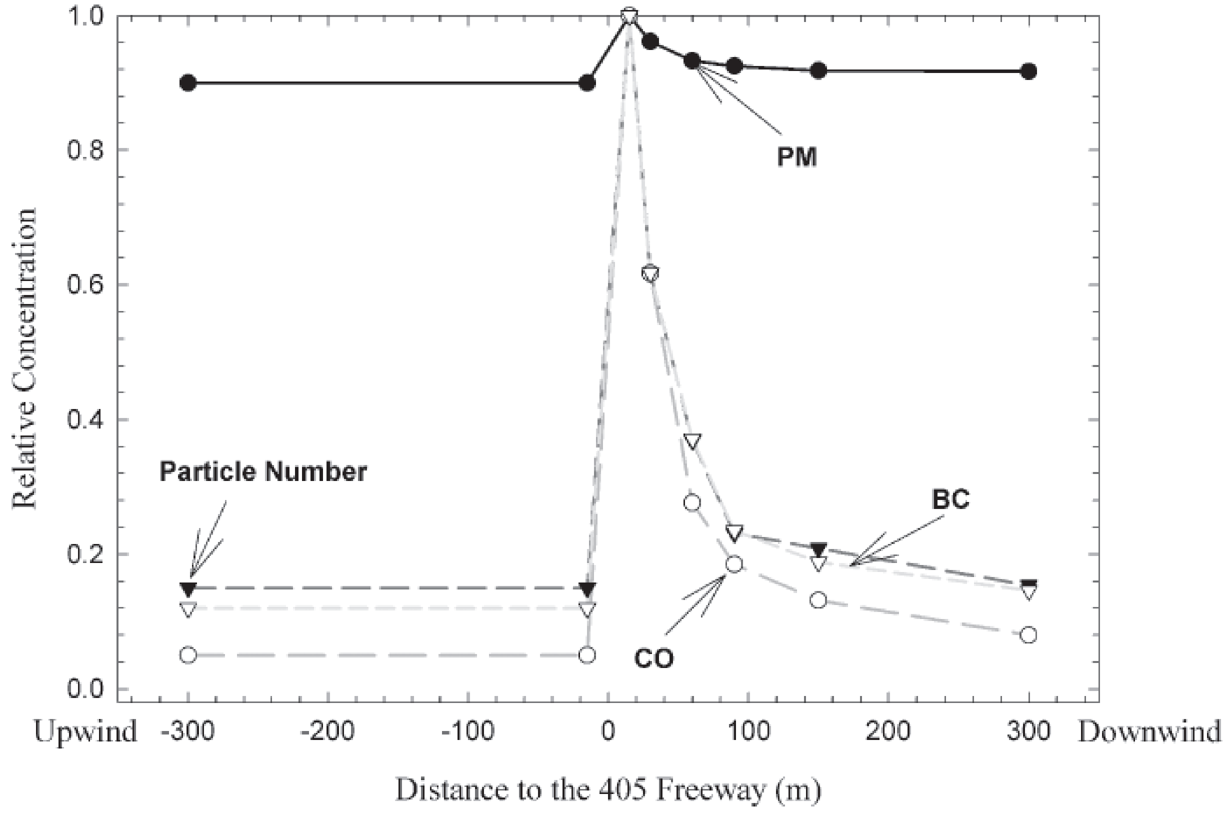
Fig. 1.22 Relative mass and number of ultrafine particles, and black carbon and carbon monoxide concentrations to downwind distance from a freeway



BC, black carbon; CO, carbon monoxide
From Zhu *et al.* (2002). Reprinted by permission of the publisher, Taylor & Francis Ltd, http://www.tandf.co.uk/journals

gradients, and during high wind speeds they were rapidly diluted.

Fig. 1.21 shows smoothed trends of pollutant concentrations with distance from the roadway (Karner *et al.*, 2010). Concentrations of carbon monoxide and metals and the number of ultrafine particles > 3 nm declined sharply to near background levels by about 300 m from the road. The number of ultrafine particles > 15 nm also declined rapidly but did not reach background levels. In contrast, $PM_{2.5}$, EC and most other contaminants showed either moderate declines or no decline with distance.

Zhu *et al.* (2002) studied the decline in $PM_{2.5}$, ultrafine particles, black carbon and carbon monoxide with distance from a freeway. Fig 1.22 shows a rapid exponential decay in the concentrations of ultrafine particles, black carbon and carbon monoxide, but only a slight change in $PM_{2.5}$. Concentrations reached background levels at a shorter distance (within 100 m) compared with the studies reviewed by Karner *et al.* (2010).

A source apportionment study was conducted in Los Angeles, CA, USA, in 2005 to determine how well this approach can distinguish between diesel and gasoline emissions (Phuleria *et al.*, 2007). Samples were collected from one site along a freeway that did not allow HGVs and was assumed to characterize emissions from purely gasoline vehicles, and from one site

Table 1.24 Mean concentrations of the meteorological and bulk-chemical parameters measured near CA-110 and I-710 in Los Angeles, USA

Parameters	CA-110[a]				I-710[b]			
	Freeway		Background		Freeway		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
CO_2 (ppm)	476	39	427	44	430	28	383	10
Temperature (°C)	21.6	3.0	21.3	3.4	18.9	2.9	18.0	2.2
Humidity (%)	50.7	14.2	50.1	15.3	46	11.8	45.3	7.0
$PM_{2.5}$ (µg/m³)	20.0	11.2	15.7	5.6	15.4	5.1	12.0	6.0
EC (µg/m³)	1.8 (9%)	1.2	1.4 (8.9%)	0.9	3.3 (21%)	0.6	0.7 (5.8%)	0.3
OC (µg/m³)	14.9 (74%)	5.2	11.4 (73%)	6.6	6.9 (45%)	1.8	5.4 (45%)	1.6

[a] Only cars are allowed on CA-110.

[b] A combination of cars and trucks travel on I-710, with an average of 17% heavy-duty vehicles.

CO_2, carbon dioxide; EC, elemental carbon; OC, organic carbon; PM, particulate matter; SD, standard deviation

From Phuleria *et al.* (2007)

next to a freeway with HGV traffic (~17% heavy-duty vehicles). Table 1.24 shows that, compared with background, the $PM_{2.5}$ was higher near the freeway with only car traffic, while the percentages of EC and organic carbon were similar. In contrast, the area near HGV traffic had a much higher percentage of EC (21%) than other sites. The percentage of organic carbon was the same at all sites. Fig 1.23 shows a comparison of the two highways for two types of organic tracers, the 15 hopanes and steranes from motor oil and 15 PAHs from combustion with a wide range of molecular weights. The comparison shows clear distinctions between the patterns ('fingerprints') for the two freeways with their different sources. The car traffic was evident from the hopanes–steranes and heavy PAHs, whereas the diesel emissions were evident from the EC and lighter PAHs. It is important to note that tracer patterns were quantitatively related to the amount of vehicle emissions.

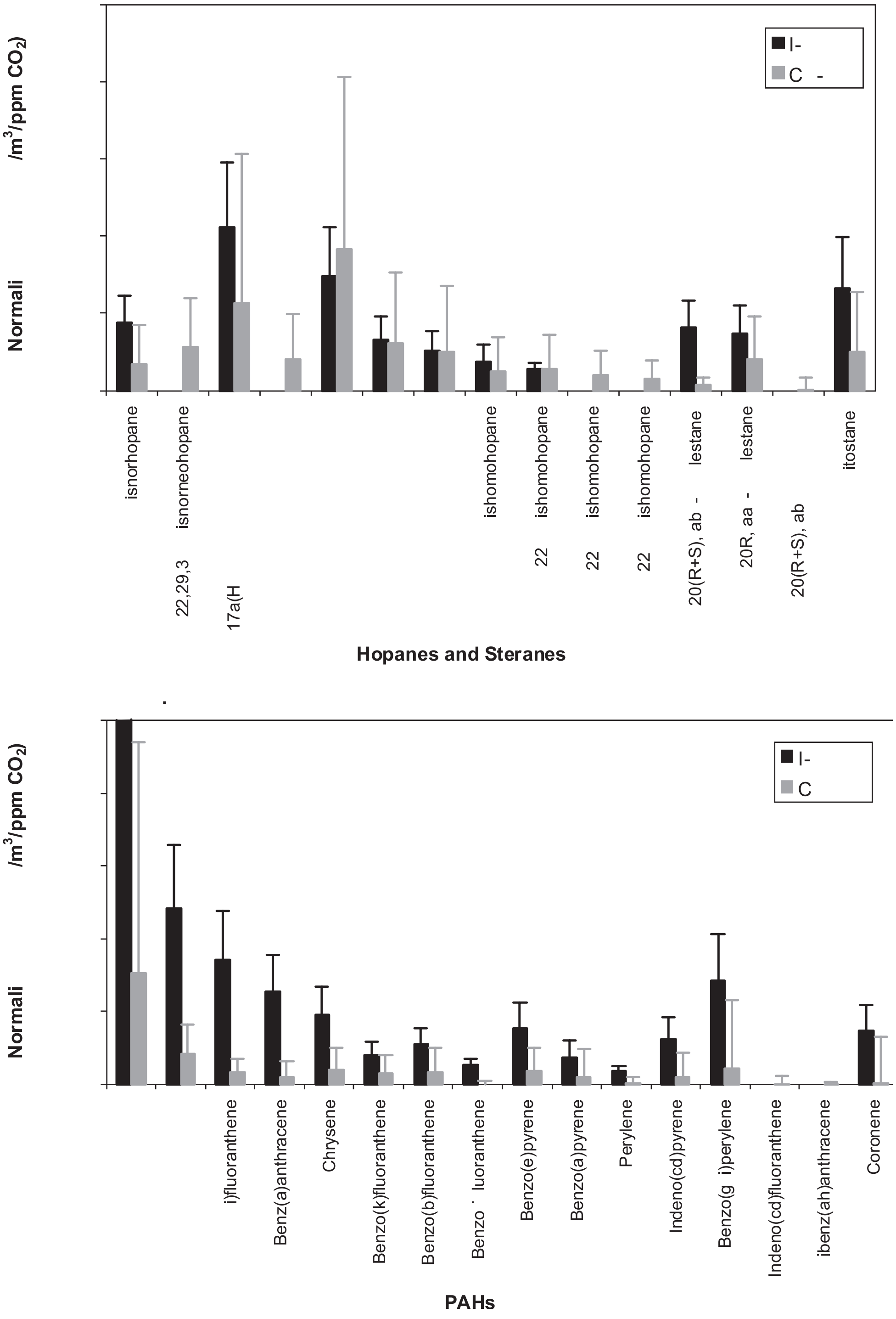
(d) Exposure of children to traffic emissions

Exposures of children to traffic emissions are a strong function of the location of their homes and schools downwind from major highways. Exposure is strongly modified by the prevailing wind directions and speed, distance from the roadways, and the type and density of the traffic. Those who ride school buses are exposed to traffic emissions that depend on the route taken and on the age, engine and fuel type of the bus, and the seal on the engine compartment relative to the passenger compartment. Finally, exposures during walking or cycling are dependent on proximity to heavy traffic and the route taken, with the highest exposures occurring by the roadside.

Several studies have investigated exposures of schoolchildren in large cities (Janssen *et al.*, 2001; Behrentz *et al.*, 2005; Wichmann *et al.*, 2005; Van Roosbroeck *et al.*, 2006; Wu & Batterman, 2006; Weichenthal *et al.*, 2008; Ashmore & Dimitroulopoulou, 2009; Branis *et al.*, 2009; Lin & Peng, 2010; Zhang & Zhu, 2010; Habil & Taneja, 2011).

Van Roosbroeck *et al.* (2007) conducted a study in the Netherlands to validate the use of proximity of a school to heavily travelled roads as a proxy for 'high exposure' situations for epidemiological studies. The investigators carried out personal sampling over a 9-month period to define long-term exposures. Exposures at schools near a very busy freeway were mainly increased, but not those at schools near a ring road.

Fig. 1.23 Comparison of measured (a) hopanes and steranes (normalized to carbon dioxide) and (b) polycyclic aromatic hydrocarbons and elemental carbon (normalized to carbon dioxide) between CA-110 and I-710 in particulate matter ($PM_{2.5}$) size mode



Error bars represent standard error.
CO_2, carbon dioxide; EC, elemental carbon; PAH, polycyclic aromatic hydrocarbon
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Another study (Van Roosbroeck *et al.*, 2006) sought to determine whether a positive answer to 'living near a motorway' on a time activity questionnaire was associated with increased personal exposure of children to black carbon and nitrogen oxides. Children living near a busy motorway had a 35% higher exposure to black carbon ('soot') compared with children living further away from the motorway, even when they attended the same school. The children living near the motorway also had increased exposure to nitric oxide, nitrogen dioxide and nitrogen oxides (14% higher) than children living further away from the motorway. These findings supported the validity of the questionnaire approach.

Janssen *et al.* (2001) reported a study of air contaminants from traffic in 24 schools in the Netherlands as a function of traffic density, distance from a heavily travelled motorway and percentage of time the school was downwind from the motorway. They found that traffic counts for HGVs, but not cars, were related to black carbon. Both indoor and outdoor concentrations of black carbon declined with increasing distance from the road, and the average concentration was about 20% higher indoors compared with outdoors, possibly because indoor samples were only collected when schools were open during the day, whereas outdoor samples were collected around the clock, including low ambient concentrations at night and on weekends. The percentage of time that the school was downwind from the motorway significantly increased the levels of black carbon, nitrogen dioxide and benzene indoors, but not those of benzene and $PM_{2.5}$ outdoors. The level of nitrogen dioxide showed no gradient with distance.

Two studies examined exposures of children while riding school buses in Los Angeles, CA, USA (Behrentz *et al.*, 2005; Sabin *et al.*, 2005). Sabin *et al.* (2005) collected samples and made real-time measurements during 24 morning and afternoon commutes on two bus routes running from South to West Los Angeles, plus seven runs on a rural/suburban route. Mean concentrations of diesel vehicle-related pollutants showed a wide range: 0.9–19 µg/m³ for black carbon, 23–400 ng/m³ for particle-bound PAHs and 64–220 µg/m³ for nitrogen dioxide. These air contaminants were significantly lower inside a compressed natural gas-powered bus compared with conventional diesel buses, although the compressed natural gas bus emitted higher concentrations of formaldehyde. Both studies reported higher concentrations of exhaust-related pollutants when the windows were closed, in part because the exhaust of the bus entered the cabin (Behrentz *et al.*, 2004; Sabin *et al.*, 2005). The levels of black carbon, particle-bound PAHs, benzene and formaldehyde pollutants were also higher on urban bus routes than on the rural/suburban route, and were also substantially higher inside the bus relative to urban background measurements. Driving behind other diesel vehicles contributed to high exposure within the buses. $PM_{2.5}$ showed smaller effects between open/closed window conditions and between bus routes (Sabin *et al.*, 2005).

(e) In-vehicle exposures while driving and commuting

Time spent in vehicles can contribute a large proportion of total exposure to vehicle exhaust (Fruin *et al.*, 2004, 2008). Fruin *et al.* (2008) measured on-road exposures in Los Angeles, CA, USA, extensively. An electric car outfitted with sampling devices was used to minimize the contributions of the sampling platform to the exposures (Westerdahl *et al.*, 2005; Fruin *et al.*, 2008). They used real-time monitors for $PM_{2.5}$, particle counts by size, including ultrafine particles, nitric oxide, nitrogen dioxide, black carbon, particle-bound PAHs, carbon monoxide and carbon dioxide. Sampling frequencies ranged from 2 seconds up to 1 minute. They drove on two routes: a freeway route and an arterial street route. While driving, they videotaped the traffic in and then performed analyses to determine the type of vehicle followed for each 5-minute interval, vehicle speed, acceleration, road type, traffic density, fraction of HGVs among all vehicles and the number of leading and surrounding vehicles during acceleration. In-cabin exposures on Los Angeles freeways were dominated by diesel truck emissions, including ultrafine particles, nitric oxide, black carbon and PAHs bound to ultrafine particles. Table 1.25 summarizes the median concentrations and interquartile ranges for each of the contaminants in different road and traffic settings. In dense traffic on the freeways, the time from emission to entering the passenger compartments of nearby vehicles was very short (Fruin *et al.*, 2008). Exposure concentrations were proportional to the density of HGVs, but not to the total volume of vehicles. Automobiles did not contribute significantly to the variability of freeway pollutants. However, on arterial streets with heavy traffic with mixed vehicles and frequent traffic lights, the emissions were dominated by those from groups of cars accelerating powerfully after having stopped at the lights. Powerful acceleration can overload the catalytic exhaust pollution control, allowing considerably more emissions (Fruin *et al.*, 2008). The close grouping and limited ventilation of the area can lead to brief accumulation of the emissions. High-speed acceleration does not produce the same accumulation because vehicles are more widely spread out and surrounded by high-velocity air flows. Table 1.26 gives the explanatory strength (R^2) for the predictive variables and each of the contaminant measures.

Apte *et al.* (2011) measured in-vehicle concentrations of $PM_{2.5}$, black carbon and ultrafine particles in open-sided auto-rickshaws that carry one to four people in New Delhi, India. They are powered by a 5–6-kW four-stroke engine that burns compressed natural gas. Because of the arrangement of the exhaust system, self-pollution is unlikely. Ambient sampling to measure the urban background was conducted in an affluent area 200–250 m away from the nearest heavily travelled road. Sampling was carried out inside the auto-rickshaw for about 3 h per trip to measure potential exposures of occupants: concentrations for about 60 trips averaged 190 $\mu g/m^3$ for $PM_{2.5}$, 42 $\mu g/m^3$ for black carbon and 280 × 10^3 particles/cm^3 for ultrafine particles; all three pollutants had similar geometric standard deviations of ~1.3. The corresponding geometric mean values for the urban background were 130 $\mu g/m^3$ for $PM_{2.5}$, 12 $\mu g/m^3$ for black carbon and 35 × 10^3 particles/cm^3 for ultrafine particles. The in-vehicle and background levels were much higher than those reported for vehicles in other megacities.

Passenger and driver exposures inside vehicles on heavily travelled roads are consistently higher than community-wide measurements of urban background. Time activity diaries are important to determine the relative contribution of high commuting exposures to the overall exposure of a subject. Fruin *et al.* (2008) estimated daily exposure to ultrafine particles by typical activities in common micro-environments (Table 1.27). On average, while only 1 hour was spent on freeways and arterial roads, it accounted for 36% of the total exposure.

(f) Penetration of traffic emissions into homes and buildings

Children and adults spend a large amount of their time indoors at home or at work. Therefore, the amount of contaminants from traffic that enter indoor spaces is important. Indoor:outdoor ratios of concentrations of ultrafine particles have been measured in Los Angeles (Sarnat *et al.*, 2006) and Boston (Levy *et al.*, 2002), USA. Fruin *et al.* (2008) collected information on indoor:outdoor ratios to estimate indoor exposures in Los Angeles. Gotschi *et al.* (2002) determined the penetration of $PM_{2.5}$ and black carbon in homes in Athens (Greece), Basel (Switzerland), Helsinki (Finland) and Prague (Czech Republic), and found that levels of $PM_{2.5}$ and black carbon

Table 1.25 Average median and interquartile range (P25%, P75%) of pollutant concentrations by road segment or location for four days in Spring, 2003

Location	UFP (1000s/cm^3)	PM$_{2.5}$ (μg/m^3)	NO (ppb)	BC (μg/m^3)	CO (ppm)	CO$_2$ (ppm)	*n*
Long Beach residential	26 (25, 28)	17 (15, 20)	17 (14, 21)	1.5 (1.1, 1.6)	0.13 (0.10, 0.18)	400 (390, 420)	329
Pasadena residential	13 (12, 15)	7.9 (7.3, 8.8)	16 (14, 19)	0.74 (0.39, 0.89)	0.13 (0.10, 0.27)	560 (540, 580)	87
Start of USC	43 (33, 53)	45 (44, 46)	59 (50, 66)	3.3 (2.6, 4.3)	0.54 (0.50, 0.58)	540 (540, 560)	41
End of USC	32 (31, 34)	23 (22, 24)	35 (32, 37)	2.2 (2.0, 2.6)	0.26 (2.4, 3.9)	580 (540, 620)	84
Arterial roads north of USC	33 (24, 53)	23 (20, 26)	79 (45, 120)	1.5 (1.2, 1.8)	1.8 (1.1, 2.5)	710 (690, 750)	117
CA-110N (≈3500 TrPD)	47 (33, 69)	25 (21, 29)	170 (120, 240)	2.4 (1.5, 3.6)	2.3 (1.8, 2.9)	820 (760, 860)	376
I-10E (≈10 000 TrPD)	130 (95, 200)	110 (60, 820)	280 (210, 350)	13 (11, 20)	2.7 (2.3, 4.7)	930 (900, 980)	111
I-710S (≈25 000 TrPD)	190 (150, 240)	54 (44, 60)	390 (330, 470)	12 (10, 16)	1.9 (1.6, 2.3)	850 (790, 910)	500

BC, black carbon; CO, carbon monoxide; CO$_2$, carbon dioxide; *n*, 4-day total number of 10-s average in data set; NO, nitric oxide; PM, particulate matter; TrPD, average number of diesel-powered trucks per day (CalTrans, 2004); UFP, ultrafine particles; USC, University of Southern California

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were lowest in Helsinki, moderate in Basel and higher in Athens and Prague (see Table 1.23). Spearman correlation coefficients for indoor versus outdoor levels were higher for black carbon (range, 0.57–0.86) than for PM$_{2.5}$ (range, 0.05–0.69). In linear regression models, outdoor levels explained clearly the greater variation in indoor black carbon (86%) than in indoor PM$_{2.5}$ (59%), indicating the greater ease with which soot particles penetrate indoors compared with larger particles of PM$_{2.5}$.

Zhao *et al.* (2006) examined the indoor (personal and residential) and outdoor (residential and ambient) concentrations of PM$_{2.5}$ components in low- and moderate-income residences in Raleigh and Chapel Hill, NC, USA, and reported data for PM mass, EC, organic carbon and 19 elements. Traffic emissions were identified as one of the components across all four types of environment: 10.0% of personal exposure; 9.4% of residence indoors; 17.2% of residence outdoors; and 19.4% of ambient outdoors. They found that the relative contribution of indoor and outdoor sources to indoor PM$_{2.5}$ were a strong function of the air exchange rate. When the rate was > 1.1 per hour, the contributions were equal but, when the air-exchange rate was < 0.3 per hour, then only about 25% of particles were from outdoors. Williams *et al.* (2003) studied the PM data for the same population, and reported that the mean personal exposure was 23.0 μg/m^3, while measured indoor, outdoor and ambient (at a central site) levels were 19.1, 19.3 and 19.2 μg/m^3, respectively. Mean personal PM$_{2.5}$ exposures were only weakly correlated with ambient PM$_{2.5}$ concentrations (r = 0.39).

Arhami *et al.* (2010) investigated the penetration of air contaminants into the residences of three retirement communities in the San Gabriel Valley and one in Riverside, CA, USA. During 2005–2007, they looked at the indoor:outdoor values for PM$_{0.25}$, ultrafine particles, EC, organic carbon, selected PAHs, hopanes and steranes, *n*-alkanes, *n*-alkanoic acids, vanadium and nickel. Traffic emissions were found to make up 24–47% of the ultrafine particle mass. Heavy-duty

Table 1.26 Coefficients of determination (R^2) for freeway concentrations by predictive variable[a]

Predictor (No. of labels)	PB-PAH	Ln(UFP)	NO	Ln(BC)	Ln(CO)	CO_2	NO_2
Road + direction (17)	0.65	0.66	0.56	0.69	0.31	0.18	0.16
Truck density (5)	0.67	0.58	0.57	0.64	0.096	0.066	0.14
Hour of the day (wind speed) (9)	0.26	0.26	0.24	0.26	0.11	0.55	0.017 (P = 0.33)
Vehicle followed (6)	0.23	0.20	0.18	0.18	0.24	0.084	0.072
Speed (6)	0.14	0.19	0.23	0.18	0.11	0.053	0.097
Overall congestion (5)	0.21	0.14	0.15	0.14	0.23	0.081	0.051
Day (4)	NA	0.095	0.19	0.09	0.15	0.56	0.072

[a] $P < 0.0001$ unless otherwise noted in parentheses

Road categories: parked (freeway shoulder or residential), arterial, arterial intersection, freeway, freeway entrance, or freeway exit. Direction categories: the relative wind direction to the flow of traffic, and wind speed. Truck density categories: NA, none, 1 or 2 oncoming trucks, ≈5% trucks, > 10% trucks and > 20% trucks. Hour of the day categories: wind speed changes each hour, increasing through the day. Overall congestion: NA, low, medium (many vehicles but free flowing) high (reduced speeds).

BC, black carbon; CO, carbon monoxide; CO_2, carbon dioxide; Ln, Log-normal distribution; NO, nitric oxide; NO_2, nitrogen dioxide; PB-PAH, particle-bound polycyclic aromatic hydrocarbons; UFP, ultrafine particles

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vehicles (large HGVs) comprised 10–15% of all vehicles. [The authors did not distinguish the vehicles by fuel type, but heavy-duty vehicles were predominantly diesel-powered and light-duty vehicles were predominantly gasoline-powered cars.] The air exchange rates for the dwellings were relatively low (0.2–0.4 per hour). The indoor:outdoor ratios for ultrafine particles were 0.63–1.07, and those for PAHs, hopanes and steranes were close to 1, indicating the potential impact of outdoor sources, including motor vehicle emissions. The *n*-alkanes and *n*-alkanoic acids had indoor:outdoor ratios much larger than 1, indicating significant indoor sources, such as cooking, tobacco smoking and candle burning. The finding of a large contribution of ultrafine particles from traffic sources was consistent with the measurements of organic carbon at the same sites (Polidori *et al.*, 2007). [The Working Group noted some uncertainty in the estimates of the vehicular fraction of particles, because light-duty vehicles in the study area may have been older than the average for the area that produced the source profile and might therefore have higher emissions.]

Studies in the Netherlands have shown that black carbon is a better marker of personal or indoor versus outdoor exposures than nitric oxide, nitrogen dioxide or nitrogen oxides (Wichmann *et al.*, 2005; Van Roosbroeck *et al.*, 2006). In addition, the outdoor exposures to black carbon close to busy urban streets compared with those near quiet urban streets were 29% higher for adults (n = 16 days; $P < 0.01$); a similar difference was seen for black carbon in outdoor versus indoor locations (25% higher; n = 25; $P < 0.05$). These differences remained for the indoor values even after adjustment for cooking and unvented heating devices (Wichmann *et al.*, 2005). Wind direction had considerable effects on the personal exposures of children to black carbon: when winds blew > 50% of the time from the busy streets towards their homes, exposure to black carbon increased by 54%. Nitrogen dioxide and nitrogen oxides showed smaller differences of 4% and 21%, respectively, and nitric oxide showed a larger difference (73%), but none of these were statistically significant (Van Roosbroeck *et al.*, 2006). These findings were broadly consistent with several earlier studies using area samplers.

Table 1.27 In-vehicle contributions to total exposures to ultrafine particles based on typical micro-environmental concentrations and activity time

Micro-environment	Time	Duration (h)	UFP concentration (1000s/cm^3)	Source of concentration estimate (low and high conditions)	Fraction of total exposure (%)
Home	7.15 pm–6.45 am	11.5	7.6[a] (7.1[b], 8.9[c])	Outdoor concentration × I/O for seasonal AER[a] (Cyrys *et al.*, 2004) (summer[b], winter[c])	27 (25, 29) [d]
Home, breakfast	6.45–7.15 am	0.5	20 (0, 25)	Average, during operation of tea kettle, toaster oven (Wallace, 2006) (no cooking, frying eggs)	3.1 (0, 3)
Arterial roads	7.15–7.45 am	0.5	58 (41, 76)	Morning measurements from arterial loop, 4/14/03, calm conditions (lower IQR, upper IQR)	8.8 (6, 11)
Freeways	7.45–8.00 am	0.25	204 (126, 253)	9–10 am average, LA, 5% trucks (2.5% trucks, 10% trucks)	16 (10, 19)
Workplace, office	8.00 am–12.00 pm, 1.00–5.00 pm	8	5.3 (1.3, 11)	Average I/O ratio for public places with no cooking times, outdoor annual average (Levy *et al.*, 2002) (lowest I/O value, highest I/O value)	13 (4, 23)
Outdoors	12.00–1.00 pm	1	21 13, 27)	LA annual average, four locations (Singh *et al.*, 2006) (June average, January average)	6.4 (4, 8)
Arterial roads	5.00–5.30 pm	0.5	33 (24, 53)	4-day average, arterial roads North of USC (lower IQR, upper IQR)	5.0 (4, 8)
Freeways	5.30–5.45 pm	0.25	90	4–5 pm average, 5% truck	6.8
Home, dinner	5.45–7.15 pm	1.5	33 (0, 50)	Two gas burners and oven (Wallace, 2006) (no cooking, deep frying)	15 (0, 21)
Average daily exposure		24	14 (8.0, 19) [d]	Time-weighted average (weighted average of low values, weighted average of high values)	
In-vehicle fraction		1.5			36 (45)

[a] Outdoor annual LA average concentration times I/O = 0.42 for an AER = 1.33/h (four evening hours) and outdoor annual average times I/O = 0.33 for an AER = 0.91/h (7.5 night hours) (Cyrys *et al.*, 2004)

[b] January average times I/O = 0.33 for AER = 0.91/h (Cyrys *et al.*, 2004).

[c] June average times I/O = 0.78 for AER = 3.4/h (four evening hours) (open windows) and June average times I/O = 0.42 for AER = 1.3/h (7.5 night hours) (Cyrys *et al.*, 2004; Singh *et al.*, 2006; Wallace, 2006)

[d] Upper and lower estimates given in parentheses

AER, air exchange rate (air changes per hour); I/O, indoor-to-outdoor ratio with no indoor sources; LA, Los Angeles; UFP, ultrafine particles; USC, University of Southern California

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(g) Time trends in exposures to traffic emissions

Air pollution levels have declined over time in the USA and western Europe where major industrial sources, such as coal-fired power plants, steel and other metal production, and chemical manufacturing, have been controlled. Emissions from the large numbers of homes in the cities have also declined, because the heating of homes and buildings has become more efficient and has switched from coal and fuel oil to natural gas and electricity. As a result of these changes and emission controls on vehicles, the nature of air pollution in cities has altered. Although considerable efforts have been made to control and reduce vehicle exhaust from diesel and gasoline engines, the number of vehicles has increased steadily, causing city-wide pollutants to plateau and limiting the effectiveness of individual vehicle reductions. The control activities have also altered the composition of source emissions. For example, reductions in particle mass to meet PM_{10} limitations have tended to reduce the number of larger particles because they contain most of the mass. However, this has not reduced the emissions of smaller particles, which also have much more surface area per gram, to the same extent.

Davis *et al.* (2006) used a historical data set of coefficient of haze measurements covering 1971–2003 for 25 community locations across New Jersey, USA, to determine the time course and determinants of air pollution levels (Davis *et al.*, 2010). Levels of EC were highly correlated with coefficient of haze and both are indicators of diesel vehicle emissions. This data set was analysed with additional annual data on the statewide unemployment and county level markers of activity in the transport industry, which is sensitive to fluctuations in the national economy. Economic indicators of the business activity of the transport industry were used to indicate that local variations in activity affected the community level of coefficient of haze. The analysis showed that 50% of the variability in coefficient of haze was associated with changes in shipping activity. Strengthening Federal regulations also produced a downward trend in the levels of coefficient of haze.

Kirchstetter *et al.* (2008) also examined a long time course of coefficient of haze to determine the historical trends of diesel exposures at 11 locations in the San Francisco Bay Area, USA. The data covered the period from the late 1960s to the early 2000s. The values for coefficient of haze were found to be highly correlated ($R^2 = 0.96$) with the black carbon estimates of the aethalometer. While the use of diesel fuel in the Bay area over this period, as indicated by data on fuel tax, increased by a factor of approximately 6, concentrations of black carbon were seen to decrease by a factor of about 3 over the same period. An analysis indicated that diesel emission factors decreased by a factor of approximately 10 as a result of changes in fuel composition, engine design and emission controls.

Shen *et al.* (2011) performed an analysis of global PAH emissions from motor vehicles. Emissions have declined because of controls applied to vehicles in developed countries. However, since the 1990s, they have begun to increase again because of the increase in vehicles with few controls in the developing world, and especially in China.

Firdaus & Ahmad (2011) reported on trends in air pollution in Delhi, India, where air pollution has steadily worsened due to increased motor vehicle traffic. The number of motor vehicles has increased 19-fold from 1974 to 2005. The number of private cars increased by nearly 10% per year in 1991–97, but the annual growth rate declined to under 5% in 2010. Levels of nitrogen dioxide increased for most years during 1987–2005, and levels of total suspended PM also increased steadily over that period. The level of respirable particles increased from 1998 to 2002, after which it declined until 2006. Pollution controls implemented since 1996 are thought to have mitigated increasing pollution levels (Firdaus & Ahmad, 2011).

Sawyer (2010) reviewed the status of vehicle emissions, their controls and future trends. In the USA, the emissions per vehicle of $PM_{2.5}$ and nitrogen oxides have declined steadily since the 1970s. However, the distance travelled by on-road vehicles has steadily increased, which has partially offset the reduction in emission levels.

References

Adelroth E, Hedlund U, Blomberg A *et al.* (2006). Airway inflammation in iron ore miners exposed to dust and diesel exhaust. *Eur Respir J*, 27: 714–719. doi:10.1183/09031936.06.00034705 PMID:16455836

Alastuey A, Querol X, Plana F *et al.* (2006). Identification and chemical characterization of industrial particulate matter sources in southwest Spain. *J Air Waste Manag Assoc*, 56: 993–1006. doi:10.1080/10473289.2006.10464502 PMID:16878590

Albinet A, Leoz-Garziandia E, Budzinski H, Viilenave E (2006). Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust) and on natural ambient air samples by gas chromatography-mass spectrometry with negative ion chemical ionisation. *J Chromatogr A*, 1121: 106–113. doi:10.1016/j.chroma.2006.04.043 PMID:16682050

Alsberg T, Stenberg U, Westerholm R *et al.* (1985). Chemical and biological characterization of organic material from gasoline exhaust particles. *Environ Sci Technol*, 19: 43–50. doi:10.1021/es00131a003

Amann CA (1990). *Power to burn; a history of the spark-ignition engine*. Mechanical Engineering-CIME.

Ames RG, Attfield MD, Hankinson JL *et al.* (1982). Acute respiratory effects of exposure to diesel emissions in coal miners. *Am Rev Respir Dis*, 125: 39–42. PMID:7065507

Andersen ZJ, Wahlin P, Raaschou-Nielsen O *et al.* (2007). Ambient particle source apportionment and daily hospital admissions among children and elderly in Copenhagen. *J Expo Sci Environ Epidemiol*, 17: 625–636. doi:10.1038/sj.jes.7500546 PMID:17495872

Andersson J, Giechaskiel B, Munoz-Bueno G (2007). *Particle Measurement Programme (PMP) Light-Duty Inter-Laboratory Correlation Exercise (ILCE_LD).* Final Report. European Commission, Directorate General, Joint Research Center (JRC), Institute for Environment and Sustainability, 2007, EUR 22775 EN.

Andersson J, Keenan M, Akerman (2009). *GDI Particles – Legislation, Current Levels and Control.* RD. 09/99801.1. Presented at the 2009 Cambridge particle meeting, 16th March 2009, Engineering Laboratory, University of Cambridge, United Kingdom.

Anttila A, Heikkilä P, Pukkala E *et al.* (1995). Excess lung cancer among workers exposed to lead. *Scand J Work Environ Health*, 21: 460–469. doi:10.5271/sjweh.62 PMID:8824752

Apte JS, Kirchstetter TW, Reich AH *et al.* (2011). Concentrations of fine, ultrafine, and black carbon particles in auto-rickshaws in New Delhi, India. *Atmos Environ*, 45: 4470–4480. doi:10.1016/j.atmosenv.2011.05.028

Arapaki NE, Bakeas G, Karavalakis E *et al.* (2007). *Regulated and Unregulated Emissions Characteristics of a Diesel Vehicle Operating with Diesel/Biodiesel Blends*, SAE paper 2007–01–0071.

Arey J, Zielinska B, Atkinson R, Winer AM (1988). Formation of nitroarenes during ambient high-volume sampling. *Environ Sci Technol*, 22: 457–462. doi:10.1021/es00169a015

Arhami M, Minguillón MC, Polidori A *et al.* (2010). Organic compound characterization and source apportionment of indoor and outdoor quasi-ultrafine particulate matter in retirement homes of the Los Angeles Basin. *Indoor Air*, 20: 17–30. doi:10.1111/j.1600-0668.2009.00620.x PMID:19874400

Arhami M, Sillanpaa M, Hu SH *et al.* (2009). Size-Segregated Inorganic and Organic Components of PM in the Communities of the Los Angeles Harbor. *Aerosol Sci Technol*, 43: 145–160. doi:10.1080/02786820802534757

Ashmore MR & Dimitroulopoulou C (2009). Personal exposure of children to air pollution. *Atmos Environ*, 43: 128–141. doi:10.1016/j.atmosenv.2008.09.024

Attfield MD (1978). *The effect of exposure to silica and diesel exhaust in underground metal and nonmetal miners.* In: *Industrial hygiene for mining and tunneling.* Proceedings of a Topical Symposium, November 6–7, 1978. Denver, CO, USA: The American Conference of Governmental Industrial Hygienists, pp. 129–135.

Ayers GP, Keywood MD, Gras JL (1999). TEOM vs. manual gravimetric methods for determination of PM2.5 aerosol mass concentrations. *Atmos Environ*, 33: 3717–3721.

Ayres SM, Evans R, Licht D *et al.* (1973). Health effects of exposure to high concentrations of automotive emissions. Studies in bridge and tunnel workers in New York City. *Arch Environ Health*, 27: 168–178. PMID:4124690

Bae H, Yang W, Chung M (2004). Indoor and outdoor concentrations of RSP, NO2 and selected volatile organic compounds at 32 shoe stalls located near busy roadways in Seoul, Korea. *Sci Total Environ*, 323: 99–105. doi:10.1016/j.scitotenv.2003.09.033 PMID:15081720

Bakke B, Stewart P, Ulvestad B, Eduard W (2001). Dust and gas exposure in tunnel construction work. *AIHAJ*, 62: 457–465. doi:10.1202/0002-8894(2001)062<0457:DAGEIT>2.0.CO;2 PMID:11549139

Bamford HA & Baker JE (2003). *Nitro-polycyclic aromatic hydrocarbon concentrations and sources in* urban and suburban atmospheres of the Mid-Atlantic region. *Atmos Environ*, 37: 2077–2091. doi:10.1016/S1352-2310(03)00102-X

Bamford HA, Bezabeh DZ, Schantz S *et al.* (2003). Determination and comparison of nitrated-polycyclic aromatic hydrocarbons measured in air and diesel particulate reference materials. *Chemosphere*, 50: 575–587. doi:10.1016/S0045-6535(02)00667-7 PMID:12685733

Behrentz E, Fitz DR, Pankratz DV *et al.* (2004). Measuring self-pollution in school buses using a tracer gas technique. *Atmos Environ*, 38: 3735–3746. doi:10.1016/j.atmosenv.2004.04.007

Behrentz E, Sabin LD, Winer AM *et al.* (2005). Relative importance of school bus-related microenvironments to children's pollutant exposure. *J Air Waste Manag Assoc*, 55: 1418–1430. PMID:16295266

Betha R & Balasubramanian R (2011). Particulate emissions from a stationary engine fueled with ultra-low-sulfur diesel and waste-cooking-oil-derived biodiesel. *J Air Waste Manag Assoc*, 61: 1063–1069. doi:10.1080/10473289.2011.608622 PMID:22070039

Biava PM, Audisio R, Centonze A *et al.* (1992). [An epidemiological study of the health conditions of Milan traffic police with respect to pollution from vehicular traffic] *Med Lav*, 83: 249–258. PMID:1382217

Bionda J (2004). *Investigative Results of NO_X Measurement Bias Due to CO_2 and Moisture Effects*. CleanAir Engineering. Prepared for the 7th Annual Electric Utilities Environmental Conference, Tucson, Arizona, January 19–22, 2004.

Biswas S, Verma V, Schauer JJ *et al.* (2009a). Oxidative potential of semi-volatile and non volatile particulate matter (PM) from heavy-duty vehicles retrofitted with emission control technologies. *Environ Sci Technol*, 43: 3905–3912. doi:10.1021/es9000592 PMID:19544906

Biswas S, Verma V, Schauer JJ, Sioutas C (2009b). Chemical Speciation of PM Emissions from Heavy-Duty Diesel Vehicles Equipped with Diesel Particulate Filter (DPF) and Selective Catalytic Reduction (SCR) Retrofits *Atmos Environ*, 43: 1917–1925. doi:10.1016/j.atmosenv.2008.12.040

Blute NA, Woskie SR, Greenspan CA (1999). Exposure characterization for highway construction. Part I: Cut and cover and tunnel finish stages. *Appl Occup Environ Hyg*, 14: 632–641. doi:10.1080/104732299302440 PMID:10510526

Boffetta P, Cherrie J, Hughson G *et al.* (2002). *Cancer risk from diesel emissions exposure in Central and Eastern Europe: A feasibility study*. In: *HEI special report. Research directions to improve estimates of human exposure and risk from diesel exhaust. A special report of the Institute's diesel epidemiology working group.* McLellan G, editor. Boston, MA: Health Effects Institute, pp. 59–75.

Bonfanti L, Careri M, Mangia A *et al.* (1996). Simultaneous identification of different classes of hydrocarbons and determination of nitro-polycyclic aromatic hydrocarbons by means of particle beam liquid chromatography-mass spectrometry. *J Chromatogr A*, 728: 359–369. doi:10.1016/0021-9673(95)01040-8

Bono R, Piccioni P, Traversi D *et al.* (2007). Urban air quality and carboxyhemoglobin levels in a group of traffic policemen. *Sci Total Environ*, 376: 109–115. doi:10.1016/j.scitotenv.2007.01.086 PMID:17324451

Branis M, Safranek J, Hytychova A (2009). Exposure of children to airborne particulate matter of different size fractions during indoor physical education at school. *Build Environ*, 44: 1246–1252. doi:10.1016/j.buildenv.2008.09.010

Brichac J, Zima J, Barek J (2004). HPLC Determination of Nitrated Polycyclic Aromatic Hydrocarbons after Their Reduction to Amino Derivatives *Anal Lett*, 37: 2379–2392. doi:10.1081/AL-200028178

Brinkman GL, Milford JB, Schauer JJ *et al.* (2009). Source identification of personal exposure to fine particulate matter using organic tracers. *Atmos Environ*, 43: 1972–1981. doi:10.1016/j.atmosenv.2009.01.023

Bukowiecki N, Kittelson DB, Watts WF *et al.* (2002). Real-time characterization of ultrafine and accumulation mode particles in ambient combustion aerosols. *J Aerosol Sci*, 33: 1139–1154. doi:10.1016/S0021-8502(02)00063-0

Bünger J, Bombosch F, Mesecke U, Hallier E (1997). Monitoring and analysis of occupational exposure to chain saw exhausts. *Am Ind Hyg Assoc J*, 58: 747–751. PMID:9342836

Burgess JL, Fleming JE, Mulenga EM *et al.* (2007). Acute changes in sputum IL-10 following underground exposure to diesel exhaust. *Clin Toxicol (Phila)*, 45: 255–260. doi:10.1080/15563650601072142 PMID:17453876

Burgess WA, Diberardinis L, Speizer FE (1977). Health effects of exposure to automobile exhaust–V. exposure of toll booth operators to automobile exhaust. *Am Ind Hyg Assoc J*, 38: 184–191. doi:10.1080/0002889778507935 PMID:68672

Burtscher H (2005). Physical characterization of particulate emissions from diesel engines: a review *Aerosol Science*, 36: 896–932. doi:10.1016/j.jaerosci.2004.12.001

Busch-Sulzer (1913). *The Diesel engine*. Busch-Sulzer Bros.-Diesel Engine Company, St. Louis Busch.

Cadle SH, Mulawa P, Groblicki P *et al.* (2001). In-use light-duty gasoline vehicle particulate matter emissions on three driving cycles. *Environ Sci Technol*, 35: 26–32. doi:10.1021/es0010554 PMID:11352022

CalTrans (2004). *Annual average daily truck traffic*. Sacramento, CA: California Department of Transportation, Truck and Vehicle Data Systems Unit. Available at: http://www.dot.ca.gov/hq/traffops/saferesr/trafdata/

CARB (2011). LEV III PM, Technical Support Document, Development Of Particulate Matter Mass Standards For Future Light-Duty Vehicles, California Air Resources Board, Dec. 2011.

Carey PM (1987). *Air Toxics Emissions from Motor Vehicles (Technical Report)*. Washington DC: US Environmental Protection Agency, No. *EPA-AA-TSSPA- 86–5*.

Castells P, Santos FJ, Galceran MT (2003). Development of a sequential supercritical fluid extraction method for the analysis of nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in urban aerosols. *J Chromatogr A*, 1010: 141–151. doi:10.1016/S0021-9673(03)01121-X PMID:12974286

Chambers D, Farrant GB, Mendham J (1984). Lead levels in exhaust replacement centres. *Sci Total Environ*, 33: 31–36. doi:10.1016/0048-9697(84)90378-4

Chan C-C & Lin S-H (1994). Office worker's exposure to volatile organic compounds while commuting and working in Taipei city. *Atmos Environ*, 28: 2351–2359. doi:10.1016/1352-2310(94)90489-8

Chaspoul F, Barban G, Gallice P (2005). Simultaneous GC/MS analysis of polycyclic aromatic hydrocarbons and their nitrated derivatives in atmospheric particualate matter from workplaces *Polycyclic Aromatic Compounds*, 25: 157–167. doi:10.1080/10406630590922337

Cheng YH (2008). Comparison of the TSI Model 8520 and Grimm Series 1.108 portable aerosol instruments used to monitor particulate matter in an iron foundry. *J Occup Environ Hyg*, 5: 157–168. doi:10.1080/15459620701860867 PMID:18188737

Cheung KL, Polidori A, Ntziachristos L *et al.* (2009). Chemical characteristics and oxidative potential of particulate matter emissions from gasoline, diesel, and biodiesel cars. *Environ Sci Technol*, 43: 6334–6340. doi:10.1021/es900819t PMID:19746734

Chow JC, Watson JG, Crow D *et al.* (2001). Comparison of IMPROVE and NIOSH Carbon Measurements *Aerosol Sci Technol*, 34: 23–34.

Chowdhury Z & Zheng M *et al.* (2007). Speciation of ambient fine organic carbon particles and source apportionment of PM2.5 in Indian cities. *Journal of Geophysical Research-Atmospheres*, 112: D15

Clark N, Gautam M, Wayne W *et al.* (2006). *Regulated Emissions from Heavy Heavy-Duty Diesel Trucks Operating in the South Coast Air Basin*. SAE Technical Paper 2006–01–3395.

Clark NN, Kern JM, Atkinson CM, Nine RD (2002). Factors affecting heavy-duty diesel vehicle emissions. *J Air Waste Manag Assoc*, 52: 84–94. doi:10.1080/10473289.2002.10470755 PMID:15152668

Coble JB, Stewart PA, Vermeulen R *et al.* (2010). The Diesel Exhaust in Miners Study: II. Exposure monitoring surveys and development of exposure groups. *Ann Occup Hyg*, 54: 747–761. doi:10.1093/annhyg/meq024 PMID:20876232

Cohen HJ, Borak J, Hall T *et al.* (2002). Exposure of miners to diesel exhaust particulates in underground nonmetal mines. *AIHA J (Fairfax, Va)*, 63: 651–658. doi:10.1080/15428110208984753 PMID:12529922

Cohen SI, Dorion G, Goldsmith JR, Permutt S (1971). Carbon monoxide uptake by inspectors at a United States-Mexico border station. *Arch Environ Health*, 22: 47–54. PMID:4099772

Colucci JM (2004). *Fuel quality – An essential element in vehicle emission control*. ICEF 2004–982. Proceedings of ICEF 04: ASME Internal Combustion Engine Division 2004 Fall Conference, Long Beach, CA, USA, pp. 1–16.

CONCAWE (2006a). *Motor vehicle emission regulations and fuel specifications, Appendix to Part 1: 2004/2005 update*. Appendix to 5/06. Brussels, Belgium: CONCAWE.

CONCAWE (2006b). *Motor vehicle emission regulations and fuel specifications, Part 1: 2004/2005 update*. Brussels, Belgium: CONCAWE.

CONCAWE (2006c). *Motor vehicle emission regulations and fuel specifications, Part 2: historic review (1996–2005)*. Brussels, Belgium: CONCAWE.

Cooper BJ, McDonald AC, Walker AP, Sanchez M (2003). *The Development and On-Road Performance and Durability of the Four-Way Emission Control SCRT™ System*. Proceedings of DEER: 9th Diesel Engine Emissions Reduction Conference; August 24–25, 2003, Newport, RI, 7 pp.

Cruz Minguillón M, Querol X, Alastuey A *et al.* (2007). PM sources in a highly industrialised area in the process of implementing PM abatement technology. Quantification and evolution. *J Environ Monit*, 9: 1071–1081. doi:10.1039/b705474b PMID:17909641

Cummins CL (1967). *My Days with the Diesel*, The memoirs of Clessie L. Cummins, father of the highway diesel, Chilton.

Cummins CL Jr (1993). *Diesel's Engine. Volume One. From Conception to 1918*. Carnot Press, ISBN 0917308034.

Cyrys J, Pitz M, Bischof W *et al.* (2004). Relationship between indoor and outdoor levels of fine particle mass, particle number concentrations and black smoke under different ventilation conditions. *J Expo Anal Environ Epidemiol*, 14: 275–283. doi:10.1038/sj.jea.7500317 PMID:15254474

Davis ME, Laden F, Hart JE *et al.* (2010). Economic activity and trends in ambient air pollution. *Environ Health Perspect*, 118: 614–619. doi:10.1289/ehp.0901145 PMID:20056563

Davis ME, Smith TJ, Laden F *et al.* (2006). Modeling particle exposure in U.S. trucking terminals. *Environ*

Sci Technol, 40: 4226–4232. doi:10.1021/es052477m PMID:16856739

Davis ME, Smith TJ, Laden F *et al.* (2007). Driver exposure to combustion particles in the U.S. Trucking industry. *J Occup Environ Hyg*, 4: 848–854. doi:10.1080/15459620701643347 PMID:17885912

Department of Energy (2006). *21st Century Truck Partnership*. Roadmap and Technical White Papers. Doc. No. 21CTP-003. Washington, DC: US Department of Energy.

Dyke PH, Sutton M, Wood D, Marshall J (2007). Investigations on the effect of chlorine in lubricating oil and the presence of a diesel oxidation catalyst on PCDD/F releases from an internal combustion engine. *Chemosphere*, 67: 1275–1286. doi:10.1016/j.chemosphere.2006.12.010 PMID:17254630

Echt A, Sheehy J, Blade L (1995). Exposure to diesel exhaust emissions at three fire stations: evaluation and recommended controls. *Appl Occup Environ Hyg*, 10: 431–438. doi:10.1080/1047322X.1995.10387631

Eckerle WA, Lyford-Pike EJ, Stanton DW *et al.* (2008). *Effects of Methyl Ester Biodiesel Blends on NOx Emissions*. SAE Technical report 2008–01–0078.

EPA (2000). *Control of Air Pollution from New Motor Vehicles: Tier 2 Motor Vehicle Emissions Standards and Gasoline Sulfur Control Requirements; Final Rule. 40 CFR*, Parts 80, 85, and 86. *Fed Regist*, 65: 6747–6796.

EPA (2001). Control of Air Pollution from New Motor Vehicles: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements; Final Rule. 40 CFR, Parts 69, 80, and 86. *Fed Regist*, 66: 5002–5193.

EPA (2002a). *Health Assessment Document for Diesel Engine Exhaust*, report EPA/600/8–90/057F, National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, May 2002.

EPA (2002b). *Draft Technical Report, A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions*. (EPA420-P-02–001). Available at: www.epa.gov/OMS/models/biodsl.htm

EPA (2008). *Kansas City PM Characterization Study*, Final Report, EPA420-R-08–009 April 2008.

Firdaus G & Ahmad A (2011). Changing air quality in Delhi, India: determinants, trends, and policy implications. *Reg Environ Change*, 11: 743–752. doi:10.1007/s10113-011-0207-z

Flynn PF, Durrett RP, Hunter GL *et al.* (1999). *Diesel Combustion: an Integrated View Combining Laser Diagnostics, Chemical Kinetics, and Empirical Validation*. SAE paper number 1999–01–0509.

Froines JR, Hinds WC, Duffy RM *et al.* (1987). Exposure of firefighters to diesel emissions in fire stations. *Am Ind Hyg Assoc J*, 48: 202–207. doi:10.1080/15298668791384634 PMID:2437785

Fruin S, Westerdahl D, Sax T *et al.* (2008). Measurements and predictors of on-road ultrafine particle concentrations and associated pollutants in Los Angeles. *Atmos Environ*, 42: 207–219. doi:10.1016/j.atmosenv.2007.09.057

Fruin SA, Winer AM, Rodes CE (2004). Black carbon concentrations in California vehicles and estimation of in-vehicle diesel exhaust particulate matter exposures. *Atmos Environ*, 38: 4123–4133. doi:10.1016/j.atmosenv.2004.04.026

Fujita EM, Zielinska B, Campbell DE *et al.* (2007). Variations in speciated emissions from spark-ignition and compression-ignition motor vehicles in California's south coast air basin. *J Air Waste Manag Assoc*, 57: 705–720. doi:10.3155/1047-3289.57.6.705 PMID:17608006

Fulper CR, Kishan S, Baldauf RW *et al.* (2010). Methods of characterizing the distribution of exhaust emissions from light-duty, gasoline-powered motor vehicles in the U.S. fleet. *J Air Waste Manag Assoc*, 60: 1376–1387. doi:10.3155/1047-3289.60.11.1376 PMID:21141431

Galceran MT & Moyano E (1993). Determination of oxygenated and nitro-substituted polycyclic aromatic hydrocarbons by HPLC and electrochemical detection. *Talanta*, 40: 615–621. doi:10.1016/0039-9140(93)80266-T PMID:18965674

Gamble J, Jones W, Hudak J *et al.* (1978). *Acute changes in pulmonary function in salt miners.* In: *Industrial hygiene for mining and tunneling.* Proceedings of a Topical Symposium, November 6–7, 1978. Kelley WD, editor. Denver, CO, USA: The American Conference of Governmental Industrial Hygienists, pp. 119–128.

Gamble J, Jones W, Minshall S (1987). Epidemiological-environmental study of diesel bus garage workers: acute effects of NO2 and respirable particulate on the respiratory system. *Environ Res*, 42: 201–214. doi:10.1016/S0013-9351(87)80022-1 PMID:2433131

Garshick E, Schenker MB, Muñoz A *et al.* (1988). A retrospective cohort study of lung cancer and diesel exhaust exposure in railroad workers. *Am Rev Respir Dis*, 137: 820–825. PMID:3354987

Garshick E, Smith S, Laden F (2002). *Quantitative assessment of lung cancer risk from diesel exhaust exposure in the US trucking industry: a feasibility study*. In: *HEI special report. Research directions to improve estimates of human exposure and risk from diesel exhaust. A special report of the Institute's diesel epidemiology working group.* McLellan G, editor. Boston, MA: Health Effects Institute, pp. 115–150.

Gekas I, Gabrielsson P, Johansen K *et al.* (2002). *Urea-SCR Catalyst System Selection for Fuel and PM Optimized Engines and a Demonstration of a Novel Urea Injection System*. SAE Technical Paper 2002–01–0289.

Gertler AW, Gillies JA, Pierson WR *et al.* (2002). Real-world particulate matter and gaseous emissions from motor vehicles in a highway tunnel. *Res Rep Health Eff Inst*, 107: 5–56, discussion 79–92. PMID:11954677

Ghittori S, Ferrari M, Maestri L *et al.* (2005). [The significance of enviromental and biological monitoring in workers employed in service stations after the elimitation of tetraethyl lead from gasoline] *G Ital Med Lav Ergon*, 27: 137–153. PMID:16124521

Gibson TL (1983). Sources of direct-acting nitroarene mutagens in airborne particulate matter. *Mutat Res*, 122: 115–121. doi:10.1016/0165-7992(83)90047-7 PMID:6197644

Gonzalez Y, Rodriguez S, Guerra García JC *et al.* (2011). Ultrafine particles pollution in urban coastal air due to ship emissions. *Atmos Environ*, 45: 4907–4914. doi:10.1016/j.atmosenv.2011.06.002

Gotschi T, Oglesby L, Mathys P *et al.* (2002). Comparison of black smoke and PM2.5 levels in indoor and outdoor environments of four European cities. *Environ Sci Technol*, 36: 1191–1197. doi:10.1021/es010079n PMID:11944668

Gourdeau P, Parent M, Soulard A (1995). [Carbon monoxide exposure in automobile garages: evaluation of mechanics] *Can J Public Health*, 86: 414–417. PMID:8932482

Green , Fuller GW, Baker T (2009). Development and validation of the volatile correction model for PM10 – An empirical method for adjusting TEOM measurements for their loss of volatile particulate matter. *Atmos Environ*, 43: 2132–2141. doi:10.1016/j.atmosenv.2009.01.024

Grose M, Sakurai H, Savstrom J *et al.* (2006). Chemical and physical properties of ultrafine diesel exhaust particles sampled downstream of a catalytic trap. *Environ Sci Technol*, 40: 5502–5507. doi:10.1021/es052267+ PMID:16999131

Groves J & Cain JR (2000). A survey of exposure to diesel engine exhaust emissions in the workplace. *Ann Occup Hyg*, 44: 435–447. PMID:10963708

Gupta P, Harger WP, Arey J (1996). The contribution of nitro- and methylnitronaphthalenes to the vapor-phase mutagenicity of ambient air samples. *Atmos Environ*, 30: 3157–3166. doi:10.1016/1352-2310(96)00024-6

Habil M & Taneja A (2011). Children's Exposure to Indoor Particulate Matter in Naturally Ventilated Schools in India. *Indoor Built Environ*, 20: 430–448. doi:10.1177/1420326X11409455

Hagberg M, Kolmodin-Hedman B, Lindahl R *et al.* (1985). Irritative complaints, carboxyhemoglobin increase and minor ventilatory function changes due to exposure to chain-saw exhaust. *Eur J Respir Dis*, 66: 240–247. PMID:4018177

Havenith C, Verbeek RP (1997). *Transient performance of urea deNOx catalyst for low emissions heavy-duty diesel engines*. SAE Technical Paper 970185.

Hayakawa K, Kawaguchi Y, Murahashi T, Miyazaki M (1995). Distribution of nitropyrenes and mutagenicity in airborne particulates collected with an Andersen sampler. *Mutat Res Lett*, 348: 57–61. doi:10.1016/0165-7992(95)00046-1

Hayakawa K, Noji K, Tang N *et al.* (2001). A high-performance liquid chromatographic system equipped with on-line reducer, clean-up and concentrator columns for determination of trace levels of nitropolycyclic aromatic hydrocarbons in airborne particulates. *Anal Chim Acta*, 445: 205–212. doi:10.1016/S0003-2670(01)01279-X

Heeb NV, Schmid P, Kohler M *et al.* (2008). Secondary effects of catalytic diesel particulate filters: conversion of PAHs versus formation of nitro-PAHs. *Environ Sci Technol*, 42: 3773–3779. doi:10.1021/es7026949 PMID:18546721

Heeb NV, Schmid P, Kohler M *et al.* (2010). Impact of low- and high-oxidation diesel particulate filters on genotoxic exhaust constituents. *Environ Sci Technol*, 44: 1078–1084. doi:10.1021/es9019222 PMID:20055402

Heeb NV, Zennegg M, Gujer E *et al.* (2007). Secondary effects of catalytic diesel particulate filters: copper-induced formation of PCDD/Fs. *Environ Sci Technol*, 41: 5789–5794. doi:10.1021/es062962x PMID:17874788

Heitland P & Köster HD (2006). Biomonitoring of 30 trace elements in urine of children and adults by ICP-MS. *Clin Chim Acta*, 365: 310–318. doi:10.1016/j.cca.2005.09.013 PMID:16248993

Herner JD, Hu S, Robertson WH *et al.* (2009). Effect of advanced aftertreatment for PM and NO(x) control on heavy-duty diesel truck emissions. *Environ Sci Technol*, 43: 5928–5933. doi:10.1021/es9008294 PMID:19731699

Herner JD, Hu S, Robertson WH *et al.* (2011). Effect of advanced aftertreatment for PM and NOx reduction on heavy-duty diesel engine ultrafine particle emissions. *Environ Sci Technol*, 45: 2413–2419. doi:10.1021/es102792y PMID:21322629

Hesterberg TW, Long CM, Sax SN *et al.* (2011). Particulate matter in new technology diesel exhaust (NTDE) is quantitatively and qualitatively very different from that found in traditional diesel exhaust (TDE). *J Air Waste Manag Assoc*, 61: 894–913. doi:10.1080/10473289.2011.599277 PMID:22010375

Heywood JB (1989). *Internal Combustion Engine Fundamentals*. McGraw-Hill series in Mechanical Engineering.

Hind CJ (1974). *The Application of the High Speed Diesel Engine as a Light Duty Power Plant in Europe*. In: *Approaches to Automotive Emissions Control*, pp. 159–171.

Hitzenberger R, Jennings SG, Larson SM *et al.* (1999). Intercomparison of measurement methods for black carbon aerosols *Atmos Environ*, 33: 2823–2833. doi:10.1016/S1352-2310(98)00360-4

Hobbs JR, Walter RA, Hard T *et al.* (1977). *Train Generated Air Contaminants in the Train Crew's Working Environment*. National Technical Information Service

Report No. FRA/ORD-77/08: US NTIS PB265–335. Springfield, VA: US Department of Commerce

Holland WD (1978). *Determination of Breathing Zone Concentrations of Contaminants from Emissions from Diesel Powered Vehicles in Underground Mines*. Report No. BuMines OFR 24–80;US NTIS PB80–150766. Washington DC: US Department of the Interior, Bureau of Mines

Hopke PK (2008). The use of source apportionment for air quality management and health assessments. *J Toxicol Environ Health A*, 71: 555–563. doi:10.1080/15287390801997500 PMID:18569626

Hunaiti A, Soud M, Khalil A (1995). Lead concentration and the level of glutathione, glutathione S-transferase, reductase and peroxidase in the blood of some occupational workers from Irbid City, Jordan. *Sci Total Environ*, 170: 95–100. doi:10.1016/0048-9697(95)04606-2 PMID:7569882

Hwang I & Hopke PK (2007). Estimation of source apportionment and potential source locations Of PM2.5 at a west coastal IMPROVE site. *Atmos Environ*, 41: 506–518. doi:10.1016/j.atmosenv.2006.08.043

IARC (1989a). Diesel and gasoline engine exhausts and some nitroarenes. *IARC Monogr Eval Carcinog Risks Hum*, 46: 1–458. PMID:2483415

IARC (1989b). Some organic solvents, resin monomers and related compounds, pigments and occupational exposures in paint manufacture and painting. *IARC Monogr Eval Carcinog Risks Hum*, 47: 1–442. PMID:2636273

IARC (1991). Chlorinated drinking-water; chlorination by-products; some other halogenated compounds; cobalt and cobalt compounds. *IARC Monogr Eval Carcinog Risks Hum*, 52: 1–544. PMID:1683674

IARC (1994). Some industrial chemicals. *IARC Monogr Eval Carcinog Risks Hum*, 60: 1–560. PMID:7869568

IARC (1999). Re-evaluation of some organic chemicals, hydrazine and hydrogen peroxide. *IARC Monogr Eval Carcinog Risks Hum*, 71: 1–315. PMID:10507919

IARC (2000). Some industrial chemicals. *IARC Monogr Eval Carcinog Risks Hum*, 77: 1–529. PMID:11236796

IARC (2002). Some traditional herbal medicines, some mycotoxins, naphthalene and styrene. *IARC Monogr Eval Carcinog Risks Hum*, 82: 1–556. PMID:12687954

IARC (2006). Inorganic and organic lead compounds. *IARC Monogr Eval Carcinog Risks Hum*, 87: 1–471. PMID:17191367

IARC (2010). Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. *IARC Monogr Eval Carcinog Risks Hum*, 92: 1–853. PMID:21141735

IARC (2012d). Radiation. *IARC Monogr Eval Carcinog Risks Hum*, 100D: 1–437. PMID:23189752

IARC (2012a). Arsenic, metals, fibres, and dusts. *IARC Monogr Eval Carcinog Risks Hum*, 100C: 1–499. PMID:23189751

IARC (2012b). Chemical agents and related occupations. *IARC Monogr Eval Carcinog Risks Hum*, 100F: 1–599. PMID:23189753

IARC (2012c). Some chemicals present in industrial and consumer products, food and drinking-water. *IARC Monogr Eval Carcinog Risks Hum*, 101: 1–586.

Iavicoli I, Bocca B, Petrucci F *et al.* (2004). Biomonitoring of traffic police officers exposed to airborne platinum. *Occup Environ Med*, 61: 636–639. doi:10.1136/oem.2003.010744 PMID:15208381

Inazu K, Saito T, Aika K *et al.* (2004) Bioluminescence, Chemiluminescence: progress, perspectives. In: *Proceedings of the 13th International Symposium Pacifico Yokohama* Yokohama: pp. 405–408.

IPCS (2003). *Selected Nitro- and Nitro-oxy-polycyclic Aromatic Hydrocarbons*. Environ Health Criteria No. 229. Geneva, Switzerland: International Programme on Chemical Safety, pp. 1–400.

IRSG (IARC Review Stakeholder Group) (2012a). *A global and historical perspective on the exposure characteristics of traditional and new technology diesel exhaust*. Available at: https://www.concawe.eu/

IRSG (IARC Review Stakeholder Group) (2012b). *A global and historical perspective on traditional and new technology gasoline engines and aftertreatment systems*. Available at: https://www.concawe.eu/

Janssen NAH, van Vliet PHN, Aarts F *et al.* (2001). Assessment of exposure to traffic related air pollution of children attending schools near motorways. *Atmos Environ*, 35: 3875–3884. doi:10.1016/S1352-2310(01)00144-3

Jo WK & Song KB (2001). Exposure to volatile organic compounds for individuals with occupations associated with potential exposure to motor vehicle exhaust and/or gasoline vapor emissions. *Sci Total Environ*, 269: 25–37. doi:10.1016/S0048-9697(00)00774-9 PMID:11305341

Johnson DE, Tillery JB, Prevost RJ (1975). Trace metals in occupationally and nonoccupationally exposed individuals. *Environ Health Perspect*, 10: 151–158. doi:10.1289/ehp.7510151 PMID:1157784

Johnson J (1988). *Automotive emissions*. In: *Air Pollution, the Automobile, and Public Health*. Watson AY, Bates RR, Kennedy D, editors. Washington DC: National Academy Press.

Jones RH, Ellicott MF, Cadigan JB, Gaensler EA (1958). The relationship between alveolar and blood carbon monoxide concentrations during breathholding; simple estimation of COHb saturation. *J Lab Clin Med*, 51: 553–564. PMID:13525831

Jovanović J, Jovanović M, Dordević D (1999). Professional exposure of drivers to carbon monoxide as a possible risk factor for the occurrence of traffic accidents in the road traffic. *Vojnosanit Pregl*, 56: 587–592. PMID:10707607

Kamal A-A, Eldamaty SE, Faris R (1991). Blood lead level of Cairo traffic policemen. *Sci Total Environ*, 105: 165–170. PMID:1925519

Kaplan I (1959). Relationship of noxious gases to carcinoma of the lung in railroad workers. *J Am Med Assoc*, 171: 2039–2043. doi:10.1001/jama.1959.03010330001001 PMID:14404393

Karavalakis G, Bakeas E, Stournas S (2010). *An Experimental Study on the Impact of Biodiesel Origin and Type on the Exhaust Emissions from a Euro 4 Pick-up Truck*. SAE paper 2010–01–2273.

Karavalakis G, Stournas S, Ampatzoglou D *et al.* (2009a). *Regulated and Unregulated Emissions of a Euro 4 SUV Operated with Diesel and Soy-based Biodiesel Blends.* SAE paper 2009–01–2690.

Karavalakis G, Stournas S, Fontaras G *et al.* (2009b). *The Effect of Biodiesel on PAHs, Nitro-PAHs and Oxy-PAHs Emissions from a Light Vehicle Operated Over the European and the Artemis Driving Cycles*. SAE paper 2009–01–1895.

Karnae S & John K (2011). Source apportionment of fine particulate matter measured in an industrialized coastal urban area of South Texas. *Atmos Environ*, 45: 3769–3776. doi:10.1016/j.atmosenv.2011.04.040

Karner AA, Eisinger DS, Niemeier DA (2010). Near-roadway air quality: synthesizing the findings from real-world data. *Environ Sci Technol*, 44: 5334–5344. doi:10.1021/es100008x PMID:20560612

Keskinen J, Pietarinen K, Lehtimaki M (1992). Electrical low pressure impactor. *J Aerosol Sci*, 23: 353–360. doi:10.1016/0021-8502(92)90004-F

Khalek I, Bougher T, Jetter J (2010). *Particle Emissions from a 2009 Gasoline Direct Injection Engine Using Different Commercially Available Fuels*, SAE Technical Paper 2010–01–2117.

Khalek IA, Bougher TL, Merritt PM (2009). *Phase 1 of the Advanced Collaborative Emissions Study*, Final Report; SwRI_Project No. 03.13062, Coordinating Research Council, Inc.: Alpharetta, GA, 2009.

Khalek IA, Bougher TL, Merritt PM, Zielinska B (2011). Regulated and unregulated emissions from highway heavy-duty diesel engines complying with U.S. Environmental Protection Agency 2007 emissions standards. *J Air Waste Manag Assoc*, 61: 427–442. doi:10.3155/1047-3289.61.4.427 PMID:21516938

Khan AB, Clark NN, Gautam M *et al.* (2009). Idle emissions from medium heavy-duty diesel and gasoline trucks. *J Air Waste Manag Assoc*, 59: 354–359. doi:10.3155/1047-3289.59.3.354 PMID:19320273

Khan AB, Clark NN, Thompson GJ *et al.* (2006). Idle emissions from heavy-duty diesel vehicles: review and recent data. *J Air Waste Manag Assoc*, 56: 1404–1419. doi:10.1080/10473289.2006.10464551 PMID:17063863

Khan MH, Khan I, Shah SH, Rashid Q (1995). Lead poisoning–a hazard of traffic and industries in Pakistan. *J Environ Pathol Toxicol Oncol*, 14: 117–120. PMID:9372841

Kim E & Hopke PK (2008). Source characterization of ambient fine particles at multiple sites in the Seattle area. *Atmos Environ*, 42: 6047–6056. doi:10.1016/j.atmosenv.2008.03.032

Kim SR, Dominici F, Buckley TJ (2007). Concentrations of vehicle-related air pollutants in an urban parking garage. *Environ Res*, 105: 291–299. doi:10.1016/j.envres.2007.05.019 PMID:17716646

Kinouchi T, Nishifuji K, Tsutsui H *et al.* (1988). Mutagenicity and nitropyrene concentration of indoor air particulates exhausted from a kerosene heater. *Jpn J Cancer Res*, 79: 32–41. doi:10.1111/j.1349-7006.1988.tb00008.x PMID:3128503

Kirchstetter TW, Aguiar J, Tonse S *et al.* (2008). Black carbon concentrations and diesel vehicle emission factors derived from coefficient of haze measurements in California: 1967â€“2003. *Atmos Environ*, 42: 480–491. doi:10.1016/j.atmosenv.2007.09.063

Kittelson DB (1998). Engines and Nanoparticles: A Review *J Aerosol Sci*, 29: 575–588. doi:10.1016/S0021-8502(97)10037-4

Kittelson DB, Watts WF, Johnson JP (2006). On-road and Laboratory Evaluation of Combustion Aerosols Part 1: Summary of Diesel Engine Results *J Aerosol Sci*, 37: 913–930. doi:10.1016/j.jaerosci.2005.08.005

Kittelson DB, Watts WF, Johnson JP *et al.* (2008). Effect of fuel and lube oil sulfur on the performance of a diesel exhaust gas continuously regenerating trap. *Environ Sci Technol*, 42: 9276–9282. doi:10.1021/es703270j PMID:19174904

Kocasoy G & Yalin H (2004). Determination of carboxyhemoglobin levels and health effects on officers working at the Istanbul Bosphorus Bridge. *J Environ Sci Health A Tox Hazard Subst Environ Eng*, 39: 1129–1139. doi:10.1081/ESE-120028418 PMID:15137724

Kremer J (1999). *Modifications to Heavy-Duty Diesel Emission Rates, Heavy Duty Mileage Accumulation, and Age Distributions in MOBILE5b for Tier 2/Sulfur NPRM.* US Environmental Protection Agency: National Vehicle and Fuel Emissions Laboratory.

Kuo CT, Chen HW, Lin ST (2003). Trace determination of nitrated polycyclic aromatic hydrocarbons using liquid chromatography with on-line electrochemical reduction and fluorescence detection. *Anal Chim Acta*, 482: 219–228. doi:10.1016/S0003-2670(03)00204-6

Kweon C, Okada S, Foster D *et al.* (2003). *Effect of Engine Operating Conditions on Particle-Phase Organic Compounds in Engine Exhaust of a Heavy-Duty Direct-Injection (D.I.) Diesel Engine*. SAE Technical Paper 2003–01–0342. Available at: http://papers.sae.org/2003-01-0342/. Accessed 10 July 2013.

Lavanchy VMH, Gäggeler HW, Nyeki S, Baltensperger U (1999). Elemental carbon (EC) and black carbon (BC) measurements with a thermal method and an aethalometer at the high-alpine research station Jungfraujoch *Atmos Environ*, 33: 2759–2769. doi:10.1016/S1352-2310(98)00328-8

Lawson DR & Hering SV (1990). The Carbonaceous Species Methods Comparison Study––An Overview *Aerosol Sci Technol*, 12: 1–2. doi:10.1080/02786829008959318

Lee PS, Schreck RM, Hare BA, McGrath JJ (1994).) Biomedical applications of tunable diode laser spectrometry: correlation between breath carbon monoxide and low level blood carboxyhemoglobin saturation. *Ann Biomed Eng*, 22: 120–125. PMID:8060021

Lee JH & Hopke PK (2006). Apportioning sources of PM2.5 in St. Louis, MO using speciation trends network data. *Atmos Environ*, 40: S360–S377. doi:10.1016/j.atmosenv.2005.11.074

Leeming JR, Dabill DW (2004). *Measuring exposure to diesel engine exhaust emissions in UK coal and non-coal mines*. In: *Mine Ventilation*. Proceedings of the 10th US/North American mine ventilation symposium. Ganguli R, Bandopadhyay S, editors. Anchorage, AK: AA Balkema Publishers, pp. 135.

Levy JI, Dumyahn T, Spengler JD (2002). Particulate matter and polycyclic aromatic hydrocarbon concentrations in indoor and outdoor microenvironments in Boston, Massachusetts. *J Expo Anal Environ Epidemiol*, 12: 104–114. doi:10.1038/sj.jea.7500203 PMID:11965527

Lewné M, Nise G, Lind ML, Gustavsson P (2006). Exposure to particles and nitrogen dioxide among taxi, bus and lorry drivers. *Int Arch Occup Environ Health*, 79: 220–226. doi:10.1007/s00420-005-0047-6 PMID:16283363

Lewné M, Plato N, Gustavsson P (2007). Exposure to particles, elemental carbon and nitrogen dioxide in workers exposed to motor exhaust. *Ann Occup Hyg*, 51: 693–701. doi:10.1093/annhyg/mem046 PMID:17921238

Lewtas J, Silverman DT (2010). *Diesel exhaust*. In: *Identification of Research Needs to Resolve the Carcinogenicity of High-Priority IARC Carcinogens*. 42nd ed. Lyon, France: International Agency for Research on Cancer, pp. 53 – 62

Li W, Collins JF, Norbeck JM, *et al.* (2006). *Assessment of Particulate Matter Emissions from a Sample of In-Use ULEV and SULEV Vehicles*. SAE Paper No. 2006–01–1076.

Lies K-H, 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*. Ishinishi N, Koizumi A, McClellan RO, Stöber W, editors. Amsterdam: Elsevier, pp. 65–82.

Lin CC & Peng CK (2010). Characterization of Indoor PM(10), PM(2.5), and Ultrafine Particles in Elementary School Classrooms: A Review. *Environ Eng Sci*, 27: 915–922. doi:10.1089/ees.2010.0175

Lippmann M, Cohen BS, Schlesinger RB (2003). *Environmental Health Science. Recognition, Evaluation, and Control of Chemical and Physical Health Hazards*. New York, USA: Oxford University Press, pp. 558. Available at: http://global.oup.com/academic/;jsessionid=07ABB92D64BEB0137989AE3DE7322F86?cc=fr&lang=en&

Liu Z, Berg D, Swor T *et al.* (2009). *A Study on the Emissions of Chemical Species from Heavy-Duty Diesel Engines and the Effects of Modern Aftertreatment*, SAE Paper 2009–01–1084.

Liu ZG, Berg DR, Vasys VN *et al.* (2010). Analysis of C1, C2, and C10 through C33 Particle-Phase and Semi-volatile Organic Compound Emissions from Heavy-Duty Diesel Engines *Atmos Environ*, 44: 1108–1115. doi:10.1016/j.atmosenv.2009.11.036

Liu ZG, Wall JC, Barge P *et al.* (2011). Investigation of PCDD/F emissions from mobile source diesel engines: impact of copper zeolite SCR catalysts and exhaust aftertreatment configurations. *Environ Sci Technol*, 45: 2965–2972. doi:10.1021/es103933e PMID:21446770

Liukonen LR, Grogan JL, Myers W (2002). Diesel particulate matter exposure to railroad train crews. *AIHA J (Fairfax, Va)*, 63: 610–616. doi:10.1080/15428110208984747 PMID:12529916

Lloyd AC & Cackette TA (2001). Diesel engines: environmental impact and control. *J Air Waste Manag Assoc*, 51: 809–847. doi:10.1080/10473289.2001.10464315 PMID:11417675

Lough GC, Schauer JJ, Lawson DR (2006). Day-of-week trends in carbonaceous aerosol composition in the urban atmosphere. *Atmos Environ*, 40: 4137–4149. doi:10.1016/j.atmosenv.2006.03.009

Majewski WA, Khair MK (2006). *Diesel Emissions and Their Control*, SAE International.

Maricq MM, Szente J, Loos M, Vogt R (2011). *Motor Vehicle PM Emissions Measurement at LEV III Levels*. SAE Technical Paper 2011–01–0623.

Mayer A, Czerwinski J, Comte P, Jaussi F (2009). Properties of Partial-Flow and Coarse Pore Deep Bed Filters Proposed to Reduce Particle Emission of Vehicle Engines. SAE Technical Paper Series 2009–01–1087, 15 pp. in SAE Int. *J Fuels Lubr*, 2: 497–511.

Mayer A, Heeb N, Czerwinski J, Wyser M (2003). *Secondary Emissions from Catalytic Active Particle Filter Systems*. Presented at 2003 SAE World Congress, Detroit, MI, March 3–6, 2003; SAE International: Warrendale, PA, 2003; Paper 2003–01–0291.

McDonald JD, Zielinska B, Sagebiel JC, McDaniel MR (2002). Characterization of fine particle material in ambient air and personal samples from an underground mine. *Aerosol Sci Technol*, 36: 1033–1044. doi:10.1080/02786820290092177

McMahon K, Selecman C, Botzem F, Stablein B (2011). *Lean GDI Technology Cost and Adoption Forecast: The Impact of Ultra-Low Sulfur Gasoline Standards*. SAE Technical Paper 2011–01–1226.

Moolenaar RL, Hefflin BJ, Ashley DL *et al.* (1994). Methyl tertiary butyl ether in human blood after exposure to oxygenated fuel in Fairbanks, Alaska. *Arch Environ Health*, 49: 402–409. doi:10.1080/00039896.1994.9954993 PMID:7524452

Morita T, Suzuki N, Satoh N, Wada K, Ohno H (2007). *Study on Low NOx Emission Control Using Newly Developed Lean NOx Catalyst for Diesel Engines*. SAE paper 2007–01–0239.

Murahashi T, Tsuruga F, Sasaki S (2003b). An automatic method for the determination of carcinogenic 1-nitropyrene in extracts from automobile exhaust particulate matter. *Analyst*, 128: 1346–1351. doi:10.1039/b308207e PMID:14700228

Murahashi T, Watanabe T, Otake S *et al.* (2003a). Determination of 3-nitrobenzanthrone in surface soil by normal-phase high-performance liquid chromatography with fluorescence detection. *J Chromatogr A*, 992: 101–107. doi:10.1016/S0021-9673(03)00279-6 PMID:12735466

Naeher LP, Aguilar-Villalobos M, Miller T (2004). Blood lead survey of children, pregnant women, professional drivers, street workers, and office workers in Trujillo, Peru. *Arch Environ Health*, 59: 359–362. doi:10.3200/AEOH.59.7.359-362 PMID:16241040

National Research Council (1983). *Feasibility of Assessment of Health Risks from Vapor-phase Organic Chemicals in Gasoline and Diesel Exhaust*. Washington DC: National Academy of Sciences

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. *Toxicol Lett*, 86: 27–37. doi:10.1016/0378-4274(96)83963-4 PMID:8685917

Nilsson CA, Lindahl R, Norström ÅKE (1987). Occupational exposure to chain saw exhausts in logging operations. *Am Ind Hyg Assoc J*, 48: 99–105. doi:10.1080/15298668791384463 PMID:3565274

NIOSH (1986). *Ryder/pie trucking lines, Cincinnati, OH. NIOSH Preliminary Industrial Hygiene Survey.* Cincinnati, OH: National Institute for Occupational Safety and Health.

NIOSH (1991). *ASARCO New Market/Young mines, Mascot, Tennessee. NIOSH Health Hazard Evaluation Report 88–108–2146.* Cincinnati, OH: National Institute for Occupational Safety and Health.

NIOSH (1992). *International Salt Company, Avery Island, Louisiana. NIOSH Health Hazard Evaluation Report 88–389–2147.* Cincinnati, OH: National Institute for Occupational Safety and Health.

NIOSH (1993). *Morton Salt Company, Weeks Island, Louisiana. NIOSH Health Hazard Evaluation Report 88–391–2156.* Cincinnati, OH: National Institute for Occupational Safety and Health.

NIOSH (1994b). *Ogden Aviation, Newark Airport. NIOSH Health Hazard Evaluation Report 92–0288–2454.* Cincinnati, OH: National Institute for Occupational Safety and Health.

NIOSH (1994a). *Nitric oxide and nitrogen dioxide*. Method No. 6014, Issue 1. In: *NIOSH Manual of Analytical Methods*, Fourth Edition.

NIOSH (1996). *Carbon monoxide*. Method No. 6604, Issue 1. In: NIOSH Manual of Analytical Methods, Fourth Edition.

NIOSH (1998). *Wolfeboro Public Safety Building, Wolfeboro, New Hampshire. NIOSH Health Hazard Evaluation Report 98–0152–2729.* Cincinnati, OH: National Institute for Occupational Safety and Health.

NIOSH (2005). *Air contaminant and noise exposures among transportation security administration baggage screeners at four international airports. NIOSH Health Hazard Evaluation Report 2005–0091–2957.* Cincinnati, OH: National Institute for Occupational Safety and Health.

NIOSH (2006). *Joint pacific marine safety code committee San Francisco, California. NIOSH Health Hazard Evaluation Report 2003–0246–3013.* Cincinnati, OH: National Institute for Occupational Safety and Health.

Niza S & Jamal HH (2007). Carbon monoxide exposure assessment among toll operators in Klang Valley, Kuala Lumpur, Malaysia. *Int J Environ Health Res*, 17: 95–103. doi:10.1080/09603120701219303 PMID:17616865

Nordman CH & Hernberg S (1975). Blood lead levels and erythrocyte delta-amino-levulinic acid dehydratase activity of selected population groups in Helsinki. *Scand J Work Environ Health*, 1: 219–232. doi:10.5271/sjweh.2844 PMID:1228901

Pakbin P, Ning Z, Schauer JJ, Sioutas C (2009). Characterization of particle bound organic carbon from diesel vehicles equipped with advanced emission control technologies. *Environ Sci Technol*, 43: 4679–4686. doi:10.1021/es8030825 PMID:19673251

Pandey SK, Kim KH, Brown RJC (2011). A review of techniques for the determination of polycyclic aromatic hydrocarbons in air. *Trends Analyt Chem*, 30: 1716–1739. doi:10.1016/j.trac.2011.06.017

Parry EM, Ballantine JA, Ellard S *et al.* (1997). Biomonitoring study of a group of workers potentially exposed to traffic fumes. *Environ Mol Mutagen*, 30: 119–130. doi:10.1002/(SICI)1098-2280(1997)30:2<119::AID-EM4>3.0.CO;2-I PMID:9329636

Paschke T, Hawthorne SB, Miller DJ, Wenclawiak B (1992). Supercritical fluid extraction of nitrated polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons from diesel exhaust *particulate matter. J Chromatogr A*, 609: 333–340. doi:10.1016/0021-9673(92)80177-V

Phuleria HC, Sheesley RJ, Schauer JJ *et al.* (2007). Roadside measurements of size-segregated particulate organic compounds near gasoline and diesel-dominated freeways in Los Angeles, CA. *Atmos Environ*, 41: 4653–4671. doi:10.1016/j.atmosenv.2007.03.031

Pio CA, Nunes TV, Borrego CS, Martins JG (1989). Assessment of air pollution sources in an industrial atmosphere using principal component and multilinear regression analysis. *Sci Total Environ*, 80: 279–292. doi:10.1016/0048-9697(89)90082-X PMID:2762806

Polidori A, Arhami M, Sioutas C *et al.* (2007). Indoor/Outdoor relationships, trends, and carbonaceous content of fine particulate matter in retirement homes of the Los Angeles Basin. *J Air Waste Manag Assoc*, 57: 366–379. PMID:17385604

Potula VL & Hu H (1996). Relationship of hemoglobin to occupational exposure to motor vehicle exhaust. *Toxicol Ind Health*, 12: 629–637. PMID:8989843

Pronk A, Coble J, Stewart PA (2009). Occupational exposure to diesel engine exhaust: a literature review. *J Expo Sci Environ Epidemiol*, 19: 443–457. doi:10.1038/jes.2009.21 PMID:19277070

Qin YJ, Kim E, Hopke PK (2006). The concentrations and sources of PM2.5 in metropolitan New York city. *Atmos Environ*, 40: S312–S332. doi:10.1016/j.atmosenv.2006.02.025

Querol X, Viana M, Alastuey A *et al.* (2007a). Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. *Atmos Environ*, 41: 7219–7231. doi:10.1016/j.atmosenv.2007.05.022

Querol X, Minguillon MC, Alastuey A *et al.* (2007b). Impact of the implementation of PM abatement technology on the ambient air levels of metals in a highly industrialised area. *Atmos Environ*, 41: 1026–1040. doi:10.1016/j.atmosenv.2006.09.013

Raja S, Biswas KF, Husain L, Hopke PK (2010). Source Apportionment of the Atmospheric Aerosol in Lahore, Pakistan. *Water Air Soil Pollut*, 208: 43–57. doi:10.1007/s11270-009-0148-z

Ramachandran G, Paulsen D, Watts W, Kittelson D (2005). Mass, surface area and number metrics in diesel occupational exposure assessment. *J Environ Monit*, 7: 728–735. doi:10.1039/b503854e PMID:15986054

Reger R, Hancock J, Hankinson J *et al.* (1982). Coal miners exposed to diesel exhaust emissions. *Ann Occup Hyg*, 26: 799–815. doi:10.1093/annhyg/26.8.799 PMID:7181308

Reisen F, Wheeler S, Arey J (2003). Methyl- and dimethyl-/ethyl-nitronaphthalenes measured in ambient air in Southern California. *Atmos Environ*, 37: 3653–3657. doi:10.1016/S1352-2310(03)00469-2

Ringold A, Goldsmith JR, Helwig HL *et al.* (1962). Estimating recent carbon monoxide exposures. A rapid method. *Arch Environ Health*, 5: 308–318. PMID:14492369

Rodríguez S, Querol X, Alastuey A *et al.* (2004). Comparative PM10–PM2.5 source contribution study at rural, urban and industrial sites during PM episodes in Eastern Spain. *Sci Total Environ*, 328: 95–113. doi:10.1016/S0048-9697(03)00411-X PMID:15207576

Roegner K, Sieber WK, Echt A (2002). Evaluation of diesel exhaust controls. *Appl Occup Environ Hyg*, 17: 1–7. doi:10.1080/104732202753306050 PMID:11800399

Romieu I, Ramirez M, Meneses F *et al.* (1999). Environmental exposure to volatile organic compounds among workers in Mexico City as assessed by personal monitors and blood concentrations. *Environ Health Perspect*, 107: 511–515. doi:10.1289/ehp.99107511 PMID:10378996

Sabin LD, Behrentz E, Winer AM *et al.* (2005). Characterizing the range of children's air pollutant exposure during school bus commutes. *J Expo Anal Environ Epidemiol*, 15: 377–387. doi:10.1038/sj.jea.7500414 PMID:15592444

Sakurai H, Tobias HJ, Park K *et al.* (2003). On-line measurements of diesel nanoparticle composition and volatility. *Atmos Environ*, 37: 1199–1210. doi:10.1016/S1352-2310(02)01017-8

Salvat O, Marez P, Belot G (2000). *Passenger Car Serial Application of a Particulate Filter System on a Common-Rail, Direct-Injection Diesel Engine*. SAE Technical Paper 2000–01–0473.

Samaras Z, Ntziachristos L, Thompson N *et al.* (2005). *Characterisation of Exhaust Particulate Emissions from Road Vehicles*, Final Report, European Commission – DG TrEn, 5th Framework Programme, April 2005.

Sapkota A, Williams D, Buckley TJ (2005). Tollbooth workers and mobile source-related hazardous air pollutants: how protective is the indoor environment? *Environ Sci Technol*, 39: 2936–2943. doi:10.1021/es0489644 PMID:15926536

Sarnat SE, Coull BA, Ruiz PA *et al.* (2006). The influences of ambient particle composition and size on particle infiltration in Los Angeles, CA, residences. *J Air Waste Manag Assoc*, 56: 186–196. PMID:16568802

Sawyer RF (2010). Vehicle emissions: progress and challenges. *J Expo Sci Environ Epidemiol*, 20: 487–488. doi:10.1038/jes.2010.44 PMID:20820162

Schauer C, Niessner R, Pöschl U (2004). Analysis of nitrated polycyclic aromatic hydrocarbons by liquid chromatography with fluorescence and mass spectrometry detection: air particulate matter, soot, and reaction product studies. *Anal Bioanal Chem*, 378: 725–736. doi:10.1007/s00216-003-2449-1 PMID:14704835

Schauer JJ (2003). Evaluation of elemental carbon as a marker for diesel particulate matter. *J Expo Anal Environ Epidemiol*, 13: 443–453. doi:10.1038/sj.jea.7500298 PMID:14603345

Schauer JJ & Cass GR (2000). Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environ Sci Technol*, 34: 1821–1832. doi:10.1021/es981312t

Schauer JJ, Fraser MP, Cass GR, Simoneit BRT (2002). Source reconciliation of atmospheric gas-phase and particle-phase pollutants during a severe photochemical smog episode. *Environ Sci Technol*, 36: 3806–3814. doi:10.1021/es011458j PMID:12322754

Schauer JJ, Rogge WF, Hildemann LM *et al.* (1996). Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos Environ*, 30: 3837–3855. doi:10.1016/1352-2310(96)00085-4

Scheepers PT & Bos RP (1992). Combustion of diesel fuel from a toxicological perspective. I. Origin of incomplete combustion products. *Int Arch Occup Environ Health*, 64: 149–161. doi:10.1007/BF00380904 PMID:1383162

Scheepers PT, Martens MH, Velders DD *et al.* (1995a). 1-Nitropyrene as a marker for the mutagenicity of diesel exhaust-derived particulate matter in workplace atmospheres. *Environ Mol Mutagen*, 25: 134–147. doi:10.1002/em.2850250207 PMID:7535227

Scheepers PT, Theuws JL, Bos RP (1991). Mutagenicity of urine from rats after 1-nitropyrene and 2-nitrofluorene administration using new sensitive Salmonella typhimurium strains YG1012 and YG1024. *Mutat Res*, 260: 393–399. doi:10.1016/0165-1218(91)90025-H PMID:1870628

Scheepers PT, Thuis HJ, Martens MH, Bos RP (1994). Assessment of occupational exposure to diesel exhaust. The use of an immunoassay for the determination of urinary metabolites of nitroarenes and polycyclic aromatic hydrocarbons. *Toxicol Lett*, 72: 191–198. doi:10.1016/0378-4274(94)90028-0 PMID:7515517

Scheepers PTJ, Fijneman PHS, Beenackkers MFM *et al.* (1995b). Immunochemical detection of metabolites of parent and nitro polycyclic aromatic hydrocarbons in urine samples from persons occupationally exposed to diesel exhaust. *Fresenius J Anal Chem*, 351: 660–669. doi:10.1007/BF00323344

Schlatter J (2000) *International round robin test of particle size measuring equipment.* Report No. 2000–230–436. Bern, Switzerland: Swiss Federal Office of Metrology.

Schuetzle D & Frazier JA (1986). Factors influencing the emission of vapor and particulate phase components from diesel engines. *Dev Toxicol Environ Sci*, 13: 41–63. PMID:2435499

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. doi:10.1080/00022470.1983.10465636

Seidel A, Dahmann D, Krekeler H, Jacob J (2002). Biomonitoring of polycyclic aromatic compounds in the urine of mining workers occupationally exposed to diesel exhaust. *Int J Hyg Environ Health*, 204: 333–338. doi:10.1078/1438-4639-00116 PMID:11885357

Servati H, Petreanu S, Marshall S *et al.* (2005). *A NOx Reduction Solution for Retrofit Applications: A Simple Urea SCR Technology.* SAE paper 2005–01–1857.

Seshagiri B (2003). Exposure to diesel exhaust emissions on board locomotives. *AIHA J (Fairfax, Va)*, 64: 678–683. PMID:14521426

Sharp CA, Howell SA, Jobe J (2000). *The Effect of Biodiesel Fuels on Transient Emissions from Modern Diesel Engines, Part II Unregulated Emissions and Chemical Characterization*. SAE paper 2000–01–1968.

Shen HZ, Tao S, Wang R *et al.* (2011). Global time trends in PAH emissions from motor vehicles. *Atmos Environ*, 45: 2067–2073. doi:10.1016/j.atmosenv.2011.01.054

Singh M, Phuleria HC, Bowers K, Sioutas C (2006). Seasonal and spatial trends in particle number concentrations and size distributions at the children's health study sites in Southern California. *J Expo Sci Environ Epidemiol*, 16: 3–18. doi:10.1038/sj.jea.7500432 PMID:16077742

Sloan AP (1964). *My Years with General Motors.* McDonald J, editor. Garden City, NY, USA: Doubleday, LCCN 64011306, OCLC 802024. Republished in 1990 with a new introduction by Peter Drucker (ISBN 978–0385042352).

Stanevich RS, Hintz P, Yereb D *et al.* (1997). Elemental carbon levels at a potash mine. *Appl Occup Environ Hyg*, 12: 1009–1012. doi:10.1080/1047322X.1997.10390641

Stone R (1999). *Introduction to Internal Combustion Engines*, Third Edition, SAE International and Macmillan Press.

Suzuki S (1990). Health effects of lead pollution due to automobile exhaust: findings from field surveys in Japan and Indonesia. *J Hum Ergol (Tokyo)*, 19: 113–122. PMID:1717547

Tejada SB, Zweidinger RB, Sigsby JE Jr (1986). Fluorescence detection and identification of nitro derivatives of polynuclear aromatic hydrocarbons by on-column catalytic reduction to aromatic amines. *Anal Chem*, 58: 1827–1834. doi:10.1021/ac00121a050

ten Brink H, Maenhaut W, Hitzenberger R *et al.* (2004). Europe for measuring the carbon content of aerosol *Atmos Environ*, 38: 6507–6519. doi:10.1016/j.atmosenv.2004.08.027

Thimmaiah D & Hovorka J *et al.* (2009). Source Apportionment of Winter Submicron Prague Aerosols from Combined Particle Number Size Distribution and Gaseous Composition Data. *Aerosol and Air Quality Research*, 9: 209–236.

Tola S, Hernberg S, Vesanto R (1976). Occupational lead exposure in Finland. VI. Final report. *Scand J Work Environ Health*, 2: 115–127. doi:10.5271/sjweh.2818 PMID:959791

Turrio-Baldassarri L, Battistelli CL, Conti L *et al.* (2004). Emission comparison of urban bus engine fueled with diesel oil and 'biodiesel' blend. *Sci Total Environ*, 327: 147–162. doi:10.1016/j.scitotenv.2003.10.033 PMID:15172578

Twigg MV (2005). Controlling automotive exhaust emissions: successes and underlying science. *Philos Transact A Math Phys Eng Sci*, 363: 1013–1033, discussion 1035–1040. doi:10.1098/rsta.2005.1547 PMID:15901550

Twigg MV (2011). Catalytic control of emissions from cars. *Catal Today*, 163: 33–41. doi:10.1016/j.cattod.2010.12.044

Twigg MV, Phillips PR (2009). Cleaning the Air We Breathe – Controlling Diesel Particulate Emissions from Passenger Cars Emission Control. *Platinum Metals Rev*, 53: 27–34 27.

Ulfvarson U, Alexandersson R, Aringer L *et al.* (1987). Effects of exposure to vehicle exhaust on health. *Scand J Work Environ Health*, 13: 505–512. doi:10.5271/sjweh.2012 PMID:2448871

Ulfvarson U, Alexandersson R, Dahlqvist M *et al.* (1991). Pulmonary function in workers exposed to diesel exhausts: the effect of control measures. *Am J Ind Med*, 19: 283–289. doi:10.1002/ajim.4700190303 PMID:1706909

Valente OS, Pasa VM, Belchior CR, Sodre JR (2012). 2–6-2012. Exhaust emissions from a diesel power generator fuelled by waste cooking oil biodiesel. *Sci Total Environ*, 431C: 57–61.

Van Roosbroeck S, Jacobs J, Janssen NAH *et al.* (2007). Long-term personal exposure to PM2.5, soot and NOx in children attending schools located near busy roads, a validation study. *Atmos Environ*, 41: 3381–3394. doi:10.1016/j.atmosenv.2006.12.023

Van Roosbroeck S, Wichmann J, Janssen NAH *et al.* (2006). Long-term personal exposure to traffic-related air pollution among school children, a validation study. *Sci Total Environ*, 368: 565–573. doi:10.1016/j.scitotenv.2006.03.034 PMID:16650461

Verma DK, Finkelstein MM, Kurtz L *et al.* (2003). Diesel exhaust exposure in the Canadian railroad work environment. *Appl Occup Environ Hyg*, 18: 25–34. doi:10.1080/10473220301386 PMID:12650546

Verma DK, Shaw L, Julian J *et al.* (1999). A comparison of sampling and analytical methods for assessing occupational exposure to diesel exhaust in a railroad work environment. *Appl Occup Environ Hyg*, 14: 701–714. doi:10.1080/104732299302332 PMID:10561882

Viana M, Kuhlbusch TAJ, Querol X *et al.* (2008). Source apportionment of particulate matter in Europe: A review of methods and results. *J Aerosol Sci*, 39: 827–849. doi:10.1016/j.jaerosci.2008.05.007

Viana M, Querol X, Alastuey A *et al.* (2006). Identification of PM sources by principal component analysis (PCA) coupled with wind direction data. *Chemosphere*, 65: 2411–2418. doi:10.1016/j.chemosphere.2006.04.060 PMID:16766018

Volkswagen (1989). *Launch of Volkswagen's Umwelt Diesel, Ward's Automotive Reports*, 1989, September 18, 301.

Vouitsis E, Ntziachristos L, Pistikopoulos P *et al.* (2009). An investigation on the physical, chemical and ecotoxicological characteristics of particulate matter emitted from light-duty vehicles. *Environ Pollut*, 157: 2320–2327. doi:10.1016/j.envpol.2009.03.028 PMID:19386405

Wail J, Hoekman S (1984). *Fuel composition effects on heavy Duty Diesel Particulate Emissions*. SAE Technical Paper Series 841364

Wallace L (2006). Indoor sources of ultrafine and accumulation mode particles: size distributions, size-resolved concentrations, and source strengths. *Aerosol Sci Technol*, 40: 348–360. doi:10.1080/02786820600612250

Wang SC & Flagan RC (1990). Scanning electrical mobility spectrometer. *Aerosol Sci Technol*, 13: 230–240. doi:10.1080/02786829008959441

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.

Weichenthal S, Dufresne A, Infante-Rivard C, Joseph L (2008). Characterizing and predicting ultrafine particle counts in Canadian classrooms during the winter months: model development and evaluation. *Environ Res*, 106: 349–360. doi:10.1016/j.envres.2007.08.013 PMID:17919560

Wenger D, Gerecke AC, Heeb NV *et al.* (2008). Secondary effects of catalytic diesel particulate filters: reduced aryl hydrocarbon receptor-mediated activity of the exhaust. *Environ Sci Technol*, 42: 2992–2998. doi:10.1021/es071827x PMID:18497156

Westerdahl D, Fruin S, Sax T *et al.* (2005). Mobile platform measurements of ultrafine particles and associated pollutant concentrations on freeways and residential streets in Los Angeles. *Atmos Environ*, 39: 3597–3610. doi:10.1016/j.atmosenv.2005.02.034

Wheatley AD & Sadhra S (2004). Occupational exposure to diesel exhaust fumes. *Ann Occup Hyg*, 48: 369–376. doi:10.1093/annhyg/meh018 PMID:15148050

Wheeler RW, Hearl FJ, McCawley M (1981). An industrial hygiene characterization of exposure to diesel emissions in an underground coal mine. *Environ Int*, 5: 485–488. doi:10.1016/0160-4120(81)90103-3

White MC, Johnson CA, Ashley DL *et al.* (1995). Exposure to methyl tertiary-butyl ether from oxygenated gasoline in Stamford, Connecticut. *Arch Environ Health*, 50: 183–189. doi:10.1080/00039896.1995.9940385 PMID:7618951

Whittaker LS, MacIntosh DL, Williams PL (1999). Employee exposure to diesel exhaust in the electric utility industry. *Am Ind Hyg Assoc J*, 60: 635–640. doi:10.1080/00028899908984484 PMID:10529994

Wichmann J, Janssen NAH, van der Zee S, Brunekreef B (2005). Traffic-related differences in indoor and personal absorption coefficient measurements in Amsterdam, the Netherlands. *Atmos Environ*, 39: 7384–7392. doi:10.1016/j.atmosenv.2005.09.015

Williams R & Suggs J *et al.* (2003). The Research Triangle Park particulate matter panel study: PM mass concentration relationships. *Atmos Environ*, 37: 5349–5363. doi:10.1016/j.atmosenv.2003.09.019

Woskie SR, Kalil A, Bello D, Virji MA (2002). Exposures to quartz, diesel, dust, and welding fumes during heavy and highway construction. *AIHA J (Fairfax, Va)*, 63: 447–457. doi:10.1080/15428110208984733 PMID:12486778

Woskie SR, Smith TJ, Hammond SK *et al.* (1988). Estimation of the diesel exhaust exposures of railroad workers: II. National and historical exposures. *Am J Ind Med*, 13: 395–404. doi:10.1002/ajim.4700130308 PMID:3281456

Wu J, Houston D, Lurmann F *et al.* (2009). Exposure of PM(2.5) and EC from diesel and gasoline vehicles in communities near the Ports of Los Angeles and Long Beach, California. *Atmos Environ*, 43: 1962–1971. doi:10.1016/j.atmosenv.2009.01.009

Wu YC & Batterman SA (2006). Proximity of schools in Detroit, Michigan to automobile and truck traffic. *J Expo Sci Environ Epidemiol*, 16: 457–470. doi:10.1038/sj.jes.7500484 PMID:16622481

Xu L, McCabe R, Dearth M, Ruona W (2010). *Laboratory and Vehicle Demonstration of "2nd-Generation" LNT + in-situ SCR Diesel NOx Emission Control Systems*. SAE paper 2010–01–0305.

Yezerets A, Currier NW, Stroia BJ *et al.* (2007). *Development of a NOx Adsorber System for Dodge Ram 2007 Heavy Duty Pickup Truck*. Presented at the 2007 Diesel Engine-Efficiency and Emissions Research (DEER) Conference, Detroit.

Yue W, Stölzel M, Cyrys J *et al.* (2008). Source apportionment of ambient fine particle size distribution using positive matrix factorization in Erfurt, Germany. *Sci Total Environ*, 398: 133–144. doi:10.1016/j.scitotenv.2008.02.049 PMID:18433834

Zabalza J, Ogulei D, Hopke PK *et al.* (2006). Concentration and sources of PM10 and its constituents in Alsasua, Spain. *Water Air Soil Pollut*, 174: 385–404. doi:10.1007/s11270-006-9136-8

Zaebst DD, Blade LM, Morris JA *et al.* (1988). *Elemental carbon as a surrogate index of diesel exhaust exposure*. ln: *Proceedings of the American Industrial Hygiene Conference*, 15–20 May 1988, San Francisco, CA, Cincinnati, OH:, National Institute for Occupational Safety and Health, Division of Surveilance, Hazard Evaluation and Field Studies.

Zaebst D, Stern F, Heitbrink W *et al.* (1992). Evaluation of techniques for reducing diesel forklift emissions. *Appl Occup Environ Hyg*, 7: 17–18. doi:10.1080/1047322X.1992.10388008

Zaebst DD, Clapp DE, Blade LM *et al.* (1991). Quantitative determination of trucking industry workers' exposures to diesel exhaust particles. *Am Ind Hyg Assoc J*, 52: 529–541. doi:10.1080/15298669191365162 PMID:1723577

Zhang Q & Zhu Y (2010). Measurements of ultrafine particles and other vehicular pollutants inside school buses in South Texas. *Atmos Environ*, 44: 253–261. doi:10.1016/j.atmosenv.2009.09.044

Zhang S & McMahon W (2012). Particulate Emissions for LEV II Light-Duty Gasoline Direct Injection Vehicles *SAE Int. J. Fuels Lubr.*, 5: 2012

Zhang W, Zhang GG, He H-Z, Bolt HM (1994). Early health effects and biological monitoring in persons occupationally exposed to tetraethyl lead. *Int Arch Occup Environ Health*, 65: 395–399. doi:10.1007/BF00383250 PMID:7518422

Zhao WX, Hopke PK, Norris G *et al.* (2006). Source apportionment and analysis on ambient and personal exposure samples with a combined receptor model and an adaptive blank estimation strategy. *Atmos Environ*, 40: 3788–3801. doi:10.1016/j.atmosenv.2006.02.027

Zhen F, Clark NN, Bedick CR *et al.* (2009). Development of a heavy heavy-duty diesel engine schedule for representative measurement of emissions. *J Air Waste Manag Assoc*, 59: 950–959. doi:10.3155/1047-3289.59.8.950 PMID:19728489

Zheng M, Salmon LG, Schauer JJ *et al.* (2005). Seasonal trends in PM2.5 source contributions in Beijing, China. *Atmos Environ*, 39: 3967–3976. doi:10.1016/j.atmosenv.2005.03.036

Zhou W, Yuan D, Ye S *et al.* (2001). Health effects of occupational exposures to vehicle emissions in Shanghai. *Int J Occup Environ Health*, 7: 23–30. PMID:11210009

Zhu Y, Hinds WC, Kim S, Sioutas C (2002). Concentration and size distribution of ultrafine particles near a major highway. *J Air Waste Manag Assoc*, 52: 1032–1042. doi:10.1080/10473289.2002.10470842 PMID:12269664

Zhu YF, Fanning E, Yu RC *et al.* (2011). Aircraft emissions and local air quality impacts from takeoff activities at a large International Airport. *Atmos Environ*, 45: 6526–6533. doi:10.1016/j.atmosenv.2011.08.062

Zielinska B, Sagebiel J, McDonald JD *et al.* (2004). Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles. *J Air Waste Manag Assoc*, 54: 1138–1150. doi:10.1080/10473289.2004.10470973 PMID:15468666

Zielinska B & Samy S (2006). Analysis of nitrated polycyclic aromatic hydrocarbons. *Anal Bioanal Chem*, 386: 883–890. doi:10.1007/s00216-006-0521-3 PMID:16761124

Zühlke J, Knopp D, Niessner R (1998). Determination of 1-nitropyrene with enzyme-linked immunosorbent assay versus high-performance column switching technique. *J Chromatogr A*, 807: 209–217. doi:10.1016/S0021-9673(98)00081-8 PMID:9646496

Zwirner-Baier I & Neumann HG (1999). Polycyclic nitroarenes (nitro-PAHs) as biomarkers of exposure to diesel exhaust. *Mutat Res*, 441: 135–144. doi:10.1016/S1383-5718(99)00041-8 PMID:10224330