DIESEL AND GASOLINE ENGINE EXHAUSTS

1. Composition of Engine Exhausts

1.1 Introduction

Diesel and gasoline engines are the major power train sources used in vehicles. They are both internal, intermittent combustion engines. In diesel engines, the fuel is self-ignited as it is injected into air that has been heated by compression. In gasoline engines, the fuel is ignited by sparking-plugs. The fuels used in diesel and gasoline engines also differ, with diesel fuel consisting of higher boiling range petroleum fractions (see IARC, 1989). Primarily because of its higher density, a litre of diesel fuel contains approximately 13% more energy than a litre of gasoline.

There are two categories of diesel engine: open-chamber or direct-injection engines are preferred for heavy-duty applications because they offer the best fuel economy; divided-chamber or indirect-injection engines have been preferred for light-duty applications because they are less sensitive to differences in fuels, have a wider range of speeds (and therefore greater power:weight ratio), run more quietly and emit fewer pollutants (National Research Council, 1982).

The major products of the complete combustion of petroleum-based fuels in an internal combustion engine are carbon dioxide (13%) and water (13%), with nitrogen from air comprising most (73%) of the remaining exhaust. A very small portion of the nitrogen is converted to nitrogen oxides and some nitrated hydrocarbons. Some excess oxygen may be emitted, depending on the operating conditions of the engine. Gasoline engines are designed to operate at a nearly stoichiometric ratio (air:fuel ratio, $\simeq$14.6:1); diesel engines operate with excess air (air:fuel ratio, $\simeq$25–30:1; Lassiter & Milby, 1978).

Incomplete combustion results in the emission of carbon monoxide, unburnt fuel and lubricating oil (Yamaki *et al.*, 1986) and of oxidation and nitration products of the fuel and lubricating oil. These incomplete combustion products comprise thousands of chemical components present in the gas and particulate phases (Zaebst *et al.*, 1988); some specific chemical species and classes found in engine exhausts are listed in Table 1. The concentration of a chemical species in vehicle exhaust is a function of several factors, including engine type, engine operating conditions, fuel and lubricating oil composition and emission control system (Johnson, 1988).

Table 1. Some compounds and classes of compounds in vehicle engine exhaust[a]

Gas phase
- Acrolein
- Ammonia
- Benzene
- 1,3-Butadiene
- Formaldehyde
- Formic acid
- Heterocyclics and derivatives[b]
- Hydrocarbons (C_1–C_{18}) and derivatives[b]
- Hydrogen cyanide
- Hydrogen sulfide
- Methane
- Methanol
- Nitric acid
- Nitrous acid
- Oxides of nitrogen
- Polycyclic aromatic hydrocarbons and derivatives[b]
- Sulfur dioxide
- Toluene

Particulate phase
- Heterocyclics and derivatives[b]
- Hydrocarbons (C_{14}–C_{35}) and derivatives[b]
- Inorganic sulfates and nitrates
- Metals (e.g., lead and platinum)
- Polycyclic aromatic hydrocarbons and derivatives[b]

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

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

Reports of measurements of polycyclic aromatic hydrocarbons (PAHs) emitted from spark-ignition gasoline engines first appeared in the literature in the 1950s (Kotin *et al.*, 1954) and early 1960s (Begeman & Colucci, 1962; Hoffmann & Wynder, 1962a). More recently, nitrated PAHs (nitroarenes) were detected in vehicle engine emissions. Some nitroarenes that have been identified in exhaust are listed in Table 2. Research has also been undertaken to determine if these compounds are formed as a result of the combustion process or subsequently in the exhaust. It has been shown in many studies that PAHs may undergo further reaction during sampling, but that these reactions can be minimized by using proper sampling apparatus and procedures (see section 2.3; Schuetzle, 1983; Schuetzle & Perez, 1983; Lies *et al.*, 1986).

Table 2. Some nitroarenes identified in vehicle exhaust[a]

1,3-Dihydroxynitropyrene
2,5-Dinitrofluorene
2,7-Dinitrofluorene
2,7-Dinitro-9-fluorenone
1,3-Dinitropyrene
1,6-Dinitropyrene
1,8-Dinitropyrene
9-Methylcarbazole
1-Nitro-3-acetoxypyrene
9-Nitroanthracene
2-Nitroanthracene or -phenanthrene
x-Nitroanthracene or -phenanthrene (two isomers)[b]
6-Nitrobenzo[*a*]pyrene
x-Nitrobenzoquinoline[b]
2-Nitrobiphenyl
3-Nitrobiphenyl
4-Nitrobiphenyl
1-Nitrochrysene
x-Nitrodibenzothiophene (two isomers)[b]
x-Nitro-y,z-dimethylanthracene or -phenanthrene (five isomers)[b]
1-Nitrofluoranthene
3-Nitrofluoranthene
7-Nitrofluoranthene
8-Nitrofluoranthene
2-Nitrofluorene
3-Nitro-9-fluorenone
10-Nitro-1-methylanthracene or -phenanthrene
10-Nitro-9-methylanthracene or -phenanthrene
x-Nitro-y-methylanthracene or -phenanthrene[b]
1-Nitro-2-methylnaphthalene
3-Nitro-1-methylpyrene
6-Nitro-1-methylpyrene
8-Nitro-1-methylpyrene
1-Nitronaphthalene
2-Nitronaphthalene
2-Nitrophenanthrene
1-Nitropyrene
5-Nitroquinoline
8-Nitroquinoline
x-Nitroterphenyl[b]
x-Nitro-y,z,z′-trimethylanthracene or -phenanthrene (six isomers)[b]
x-Nitrotrimethylnaphthalene (three isomers)[b]

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[a] From Nishioka *et al.* (1983); Manabe *et al.* (1985); Schuetzle & Jensen (1985); White (1985); Draper (1986)

[b] x, y, z, and z′ imply position is unknown

Considerable effort has been made to identify mutagenic and carcinogenic chemicals in vehicle exhausts, primarily from diesel engines. Most effective has been the use of protocols combining short-term bioassays for genetic and related effects or for tumorigenicity with chemical analysis (Brune *et al.*, 1978; Schuetzle *et al.*, 1982; Grimmer *et al.*, 1983a, 1984, 1987).

The use of the *Salmonella typhimurium* mutagenesis assay to study factors which may alter the emission of mutagens from diesel and gasoline engines has been reviewed (Claxton, 1983). Effects of engine design, fuel composition and operation on mutagenicity in *S. typhimurium* have been reported (Huisingh *et al.*, 1978; Clark *et al.*, 1981; Huisingh *et al.*, 1981; Clark *et al.*, 1982a,b,c; Ohnishi *et al.*, 1982; Zweidinger, 1982; Clark *et al.*, 1984; Schuetzle & Frazier, 1986). The effect of sampling methodology, environment (laboratory, tunnels and ambient urban air) and atmospheric transformation in the *S. typhimurium* mutagenesis assay have also been reported (Ohnishi *et al.*, 1980; Claxton & Barnes, 1981; Pierson *et al.*, 1983; Brooks *et al.*, 1984). Typical factors that affect emissions are shown in Tables 3 and 4. The data on mutagenicity are included for comparative purposes to indicate the quantity of total genotoxic components. The reader is referred to section 3.2 (p. 119) for summaries of studies of the genetic effects of diesel and gasoline engine exhausts.

Table 3. Levels of emissions from various diesel and gasoline engines (1980–85; US Environmental Protection Agency Federal Test Procedure (FTP) cycle only) and their mutagenicity

	Heavy-duty diesel vehicle	Light-duty diesel vehicle	Light-duty gasoline vehicle	
			Without catalytic converter	With catalytic converter
Gas phase in mg/mile (mg/km)				
Benzene	–	24[a] (15)	162[a] (101)	13[a] (8)
Carbon monoxide	10 000[a] (6250)	1270[b] (794)	28 500[b] (17 813)	12 200[b] (7625)
Formaldehyde	–	20[a] (13)	56[a] (35)	4[a] (3)
Nitrogen oxides	28 000[a] (17 500)	1270[b] (794)	3520[b] (2200)	2350[b] (1469)
Propylene	–	–	230[a] (144)	18[a] (11)
Toluene	11[a] (7)	–	215[a] (134)	32[a] (20)
Gas-phase PAHs and PAH derivatives in μg/mile (μg/km)[a]				
Anthracene	8960 (5600)	2100 (1313)	3200 (2000)	60 (38)
Fluoranthene	1240 (775)	300 (188)	450 (281)	7 (4)
	–	910 (569)	300 (188)	–
2-Nitrofluorene	–	90 (56)	–	–
Pyrene	1580 (988)	380 (238)	580 (363)	9 (6)
	1580 (988)	1130 (706)	200 (125)	–
Particulate-phase PAHs and PAH derivatives in μg/mile (μg/km)				
Anthracene	439[a] (274)	105[a] (66)	160[a] (100)	3[a] (2)
Benzo[*a*]pyrene	54[a] (34)	13[a] (8)	20[a] (13)	0.4[a] (0.3)
	–	1[a,c] (0.6)	(1–10)[d]	(0.1–1)[d]

Table 3 (contd)

	Heavy-duty diesel vehicle	Light-duty diesel vehicle	Light-duty gasoline vehicle	
			Without catalytic converter	With catalytic converter
Benzo[*a*]pyrene (contd)		–	3[e] (2)	0.1[e] (0.06)
	–	–	15[f] (9)	3[f] (2)
	142[a] (89)	34[a] (21)	15[b] (9)	2[b] (1)
Benzo[*e*]pyrene	64[a] (40)	15[a] (9)	23[a] (14)	0.4[a] (0.3)
Fluoranthene	933[a] (538)	224[a] (140)	340[a] (213)	5[a] (3)
	–	683[a] (427)	225[a] (141)	–
	–	933[a] (583)	224[a] (140)	–
2-Nitrofluorene	–	97[a] (61)	–	–
1-Nitropyrene	45[a] (28)	11[a] (7)	0.3[a] (0.2)	<0.1[a] (<0.06)
	–	4[c] (3)	0.2[f] (0.1)	0.2[f] (0.1)
		8[b] (5)	0.2[b] (0.1)	0.2[b] (0.1)
Pyrene	1182[a] (739)	284[a] (178)	431[a] (269)	7[a] (4)
	–	848[a] (530)	150[a] (94)	–
	–	284[f] (178)	19[f] (12)	10[f] (6)
	–	39[a,c] (24)	47[a] (29)	26[a] (16)
Total PAH		200–1000[g] (125–625)		
Other emissions				
Total particulate phase				
in mg/km	1036[h]	246[h]	62[h]	11[h]
in mg/mile (mg/km)	–	–	103[f] (64)	32[f] (20)
Total extractable matter				
in mg/km	188[h]	124[h]	10[h]	6[h]
in mg/mile (mg/kg)	–	–	21[f] (13)	14[f] (9)
Mutagenicity				
TA98 (without activation)				
rev/km	226[h]	595 000[h]	61 000[h]	30 000[h]
rev/mile	–	99 000[a,c]	15 000[a]	4000[a]
rev/mile	–	509 000[b]	152 000[b]	41 000[b]
TA98 (with activation)				
rev/mile	–	590[a,c]	260[f]	80[f]
rev/km	40 000–530 000[i]	240 000–320 000	180 000[i]	30 000[i]
rev/mile	–	–	258 000[b]	71 000[b]

[a] From Schuetzle & Frazier (1986); [b] from Zweidinger (1982); [c] see Table 4, 22% fuel aromaticity; [d] from Holmberg & Ahlborg (1983) [assumed to be FTP cycle]; [e] from Williams & Swarin (1979); [f] from Lang *et al.* (1981); [g] from Clark *et al.* (1982b); [h] from Schuetzle (1983); [i] from Lewtas & Williams (1986)

Table 4. Factors affecting rate of emission of polycyclic aromatic hydrocarbons in μg/mile (μg/km) from diesel engine exhausts and mutagenicity[a]

	Vehicle[b]				Fuel aromaticity[c]		Engine conditions[d]		
	A	B	C	D	22%	55%	Retarded timing	Standard timing	Advanced timing
Pyrene	39 ± 16	62 ± 15	29 ± 15	24 ± 11	39 ± 18	125 ± 39	31 ± 20	39 ± 18	35 ± 22
	(24 ± 10)	(39 ± 9)	(18 ± 9)	(15 ± 7)	(24 ± 11)	(78 ± 24)	(19 ± 13)	(24 ± 11)	(22 ± 14)
Benzo[*a*]pyrene	1.3 ± 0.9	1.9 ± 0.1	1.6 ± 0.2	0.6 ± 0.1	1.3 ± 0.5	7.1 ± 3.6	1.7 ± 1.1	1.3 ± 0.5	1.5 ± 0.6
	(0.8 ± 0.6)	(1.2 ± 0.06)	(1 ± 0.1)	(0.4 ± 0.06)	(0.8 ± 0.3)	(4.4 ± 2.3)	(1.1 ± 0.7)	(0.8 ± 0.3)	(0.9 ± 0.4)
Benzo[*e*]pyrene	2.3 ± 1.2	5.1 ± 0.2	3.0 ± 0.4	1.3 ± 0.4	3.0 ± 1.1	10.3 ± 4.1	3.6 ± 2.1	3.0 ± 1.1	4.2 ± 0.5
	(1.4 ± 0.8)	(3 ± 0.1)	(1.9 ± 0.3)	(0.8 ± 0.3)	(1.9 ± 0.7)	(6.4 ± 2.6)	(2.3 ± 1.3)	(1.9 ± 0.7)	(3 ± 0.3)
1-Nitropyrene	3.0 ± 1.0	7.8 ± 2.2	1.8 ± 0.9	3.8 ± 1.4	4.1 ± 1.9	3.7 ± 1.6	2.3 ± 0.5	4.1 ± 1.9	15.5 ± 7.7
	(1.9 ± 0.6)	(4.9 ± 1.4)	(1.1 ± 0.6)	(2.4 ± 0.9)	(2.6 ± 1.2)	(2.3 ± 1)	(1.4 ± 0.3)	(2.6 ± 1.2)	(10 ± 5)
Nitrogen oxides in g/mile (g/km)	–	–	–	–	–	–	0.9 ± 0.02	1.0 ± 0.01	1.3 ± 0.1
							(0.6 ± 0.01)	(0.6 ± 0.006)	(0.8 ± 0.06)
Mutagenicity in 10^6 rev/mile (10^6 rev/km)									
TA98 (without activation)	1.0 ± 0.4	1.3 ± 0.3	0.8 ± 0.3	0.8 ± 0.2	0.99 ± 0.35	2.9 ± 0.80	2.2 ± 1.6	3.4 ± 1.5	6.4 ± 2.7
	(0.6 ± 0.2)	(0.8 ± 0.2)	(0.5 ± 0.2)	(0.5 ± 0.1)	(0.6 ± 0.2)	(1.8 ± 0.5)	(1.4 ± 1.0)	(2.1 ± 0.9)	(4.0 ± 1.7)
TA98 (with activation)	0.5 ± 0.2	0.7 ± 0.2	0.6 ± 0.2	0.5 ± 0.1	0.61 ± 0.18	2.1 ± 0.49	1.0 ± 0.5	1.8 ± 0.7	2.5 ± 1.1
	(0.3 ± 0.1)	(0.4 ± 0.1)	(0.4 ± 0.1)	(0.3 ± 0.06)	(0.4 ± 0.1)	(1.3 ± 0.3)	(0.6 ± 0.3)	(1.1 ± 0.4)	(1.6 ± 0.6)

[a] From Schuetzle & Frazier (1986)

[b] Duplicate tests on each vehicle run on four different fuels of 22% aromatic composition

[c] Duplicate tests on four vehicles run at standard timing on four different fuels

[d] Duplicate tests on two vehicles

In the descriptions below of the chemical and physical characteristics of emissions from diesel and spark-ignition (gasoline) engines, primary emphasis is placed on the identification of PAHs in different engines, with different fuels and under various operating conditions.

1.2 Diesel engine exhaust

In reviewing the data, the reader should recognize that detailed chemical characterization of engine emissions, especially for nitroarenes, was performed mostly in the late 1970s and 1980s. During that period, substantial changes occurred in engine and emission control technologies, and additional changes are to be expected in the future. It is also reasonable to expect that the emissions characterized recently may not represent fully emissions in earlier times. The available data refer mainly to light-duty vehicles; quantitative data on emissions from heavy-duty diesel engines are relatively sparse. Because of these limitations, the data presented here should be considered only as illustrative of the emissions of internal combustion engines; they should not be interpreted as representative of either current emissions from the wide range of engines used at present or of those that may have occurred in the past.

Compounds emitted from diesel engines include all of the compounds and compound classes listed in Table 1. Diesel engines produce two to ten times more particulate emissions than gasoline engines (without catalytic converter) of comparable power output and two to 40 times more particulate emissions than gasoline engines equipped with a catalytic converter (Table 3). The particles consist primarily of elemental carbon (Ball, 1987; 60–80%, Zaebst *et al.*, 1988), sulfuric acid (2–7%; Pierson & Brachaczek, 1983) and some metallic species, e.g., iron from the engine and exhaust system (Lang *et al.*, 1981), barium from fuel (Hampton *et al.*, 1983) and zinc from lubricating oil (Hare & Baines, 1979), and adsorbed organic compounds (National Research Council, 1982).

(*a*) *Distribution in particulate and gas phases*

The distribution of emissions between the gas and particulate phases is determined by the vapour pressure, temperature and concentration of the individual species. The partitioning of constituents between the particulate and gas phases has been measured by several investigators (Hampton *et al.*, 1983; Schuetzle, 1983). On the basis of these data, an empirical relationship between the molecular weight and the particulate- to gas-phase partition coefficient (P:G) for several of these compounds was derived, as shown for the PAHs in Table 5 (Schuetzle & Frazier, 1986).

(*b*) *Gas-phase emissions*

Gas-phase emissions from diesel engines comprise C_1–C_{18} hydrocarbons, two- to four-ring PAHs and nitrated and oxygenated derivatives of C_1–C_{12} hydrocarbons and two- to three-ring PAHs. The C_1–C_{10} hydrocarbons result almost entirely from the combustion process, which involves cracking of higher molecular weight materials (National Research Council, 1982). The quantities of some of these gas-phase species in diesel exhaust are given in Table 3.

Table 5. Particulate- to gas-phase partition coefficients for some polycyclic aromatic hydrocarbons in diesel exhaust[a]

Compound	Molecular weight	Partition coefficient
Phenanthrene	178	0.05
Anthracene	178	0.05
Pyrene	202	0.75
Fluoranthene	202	0.75
Benz[*a*]anthracene	228	1.46
Benzo[*a*]pyrene[b]	252	21.00

[a] From Schuetzle & Frazier (1986), unless otherwise specified

[b] From Schuetzle (1983)

(*c*) *Particulate-phase emissions*

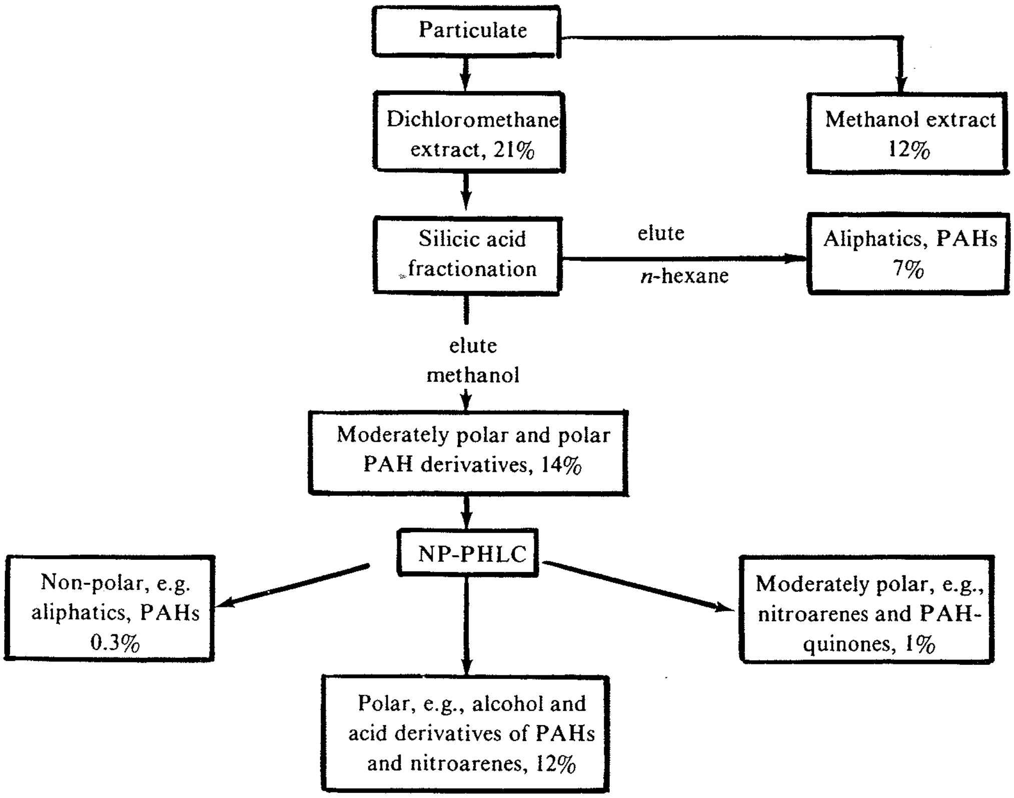
Diesel particles are aggregates of spherical primary particles of 0.1–0.5 μm (National Research Council, 1982). Those generated under laboratory conditions in dilution tunnels have mass or volume median diameters ranging from 0.15 to 0.50 μm, depending on the operating conditions (Cheng *et al.*, 1984). Smaller primary spheres, formed within the combustion cylinder, grow by agglomeration and by acting as nuclei for the condensation of organic compounds (Duleep & Dulla, 1980).

The elemental carbon core of the particles has a large surface area which greatly enhances adsorption of organic compounds. Larger particles (>0.2 μm) tend to be flaky in nature (Moore *et al.*, 1978). If an engine is running under low load, there may be incomplete combustion, leading to a relatively low particle concentration and a higher proportion of organic compounds associated with the core particles (Dutcher *et al.*, 1984).

A variety of solvents has been used to extract organic compounds from diesel particles (Bjørseth, 1983; see p. 80). The soluble organic fraction of diesel particles usually accounts for 15–45% of the total particulate mass. Figure 1 shows the distribution of mass for the various subfractions of a standard heavy-duty diesel particulate extract (Schuetzle *et al.*, 1985).

The nonpolar fractions contain hydrocarbons derived from unburnt fuel and lubricating oil. In addition, many PAHs in the molecular weight range of 178–320 have been identified. Some PAHs and thioarenes identified in diesel engine exhausts are listed in Table 6 (Tong & Karasek, 1984). The alkyl substituted derivatives of at least some PAHs are more abundant than the parent hydrocarbons. If the amount of dimethylanthracenes or dimethylphenanthrenes is taken as 1.00, the relative abundance of anthracene or phenanthrene is 0.27, that of the methyl derivatives, 0.54, and that of the trimethyl derivatives, 0.37 (Schuetzle *et al.*, 1981). Since moderately polar fractions have been found to contribute a significant proportion of the mutagenicity of the total soluble organic fraction, much effort has been expended to characterize them. The distribution of PAH derivatives in one light-duty diesel particulate extract is given in Table 7 (Schuetzle, 1983).

Fig. 1. Analytical scheme for fractionation of heavy-duty diesel particulates (National Bureau of Standards Standard Reference Material (NBS SRM)-1650)[a]



[a] From Schuetzle *et al.* (1985). Recoveries are given as weight percent of total particulate mass. NP-HPLC, normal phase-high-performance liquid chromatography

Table 6. Polycyclic aromatic comounds identified or tentatively identified in three light-duty diesel particulate extracts[a]

Compound	Molecular weight	Concentration[b] (μg/g of extract)
Acenaphthylene	152	30
Fluorene	166	100–168
Trimethylnaphthalene	170	30–50
Anthracene	178	155–356
Phenanthrene	178	2186–4883
Dimethylbiphenyl	182	30–91
Tetramethylnaphthalene	184	50–152
Dibenzothiophene	184	129–246
4*H*-Cyclopenta[*def*]phenanthrene	190	517–1033
2-Methylanthracene	192	517–1522
2-Methylphenanthrene	192	1099–1481
3-Methylphenanthrene	192	929–1287
Trimethylbiphenyl	196	50

Table 6 (contd)

Compound	Molecular weight	Concentration[b] (μg/g of extract)
Methyldibenzothiophene	198	101–323
Benzacenaphthylene	202	791–1643
Fluoranthene	202	3399–7321
Pyrene	202	3532–8002
2-Phenylnaphthalene	204	650–1336
Dimethylphenanthrene	206	443–1046
2- or 9-Ethylphenanthrene	206	388–464
Dimethylphenanthrene or -anthracene	206	86–585
Benzo[*def*]dibenzothiophene	208	254–333
Ethyldibenzothiophene	212	151–179
Benzo[*a*]fluorene	216	541–990
Benzo[*b*]fluorene	216	175–538
Methylfluoranthene or -pyrene	216	224–552
1-Methylpyrene	216	144–443
Ethylmethylphenanthrene or -anthracene	220	286–432
Benzo[*ghi*]fluoranthene	226	217–418
Cyclopenta[*cd*]pyrene	226	869–1671
Benz[*a*]anthracene	228	463–1076
Chrysene or triphenylene	228	657–1529
Benzonaphthothiophene	234	30–126
Benzo[*b*]naphtho[2,1-*d*]thiophene	234	30–53
Methylbenz[*a*]anthracene	242	30–50
3-Methylchrysene	242	50–192
Benzo[*b*]fluoranthene	252	421–1098
Benzo[*j*]fluoranthene	252	492–1367
Benzo[*k*]fluoranthene	252	91–289
Benzo[*e*]pyrene	252	487–946
Benzo[*a*]pyrene	252	208–558
1,2-Binaphthyl	254	30–50
2,2-Binaphthyl	254	89–283
1-Phenylphenanthrene	254	89–163
9-Phenylphenanthrene	254	30–94
Phenylphenanthrene or -anthracene	254	30–116
Benzo[*ghi*]perylene	276	443–1050
Indeno[1,2,3-*cd*]pyrene	276	30–93
Dibenz[*a,h*]anthracene	278	50–96
Coronene	300	301–521
Dibenzopyrene or -[*def,p*]chrysene	302	89–254

[a] From Tong & Karasek (1984)

[b] Concentrations of less than 50 μg/g extract were obtained by approximate calculation

Table 7. Distribution of polycyclic aromatic hydrocarbon (PAH) derivatives in the moderately polar fraction[a] of a light-duty diesel particulate extract[b]

PAH derivative	Fraction (wt %)
PAH ketones	24.7
PAH carboxyaldehydes	20.6
PAH acid anhydrides	9.1
Hydroxy-PAH	19.0
PAH quinones	12.0
Nitro-PAH	0.5
Other oxygenated PAH	14.1

[a] Comprising 9% of the particulate phase by weight

[b] Schuetzle (1983)

The types of nitroarenes identified in diesel vehicle particles are listed in Figure 2. More than 50 nitrated derivatives of PAHs have been identified tentatively and 23 have been identified positively. These compounds occur in very low concentrations in comparison with the other PAH derivatives (Schuetzle & Jensen, 1985). The concentrations of nitroarenes measured in a light-duty diesel particulate extract by a method with a 0.3-ppm (μg/g) limit of detection are given in Table 8. Overall, about 40% of the direct mutagenicity of diesel particulate extracts can be accounted for by 1-nitro-3-acetoxypyrenes, dinitropyrenes and 1-nitropyrene (Manabe *et al.*, 1985). Studies in which biological and other methods were used to estimate the contribution of nitro-PAH to the genetic effects of diesel emissions are discussed in section 3.2.

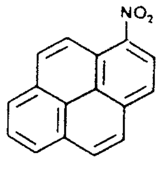
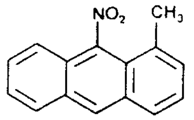
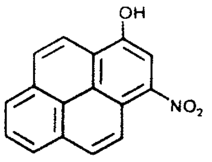
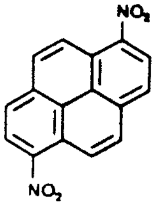
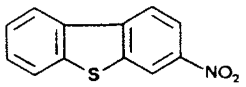
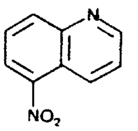
Examples of compounds in the polar soluble organic fraction of diesel vehicle particulate extracts include phenols (1-naphthol, 2-naphthol, cresol), acids (benzoic, naphthoic, phthalic and phenathroic acid), bases (benzacridines, dibenzacridines, pyridine, aniline) and some polar nitroarenes (National Research Council, 1982).

(*d*) *Effect of engine source, fuel and operating conditions on emissions*

In this section, the influence of several factors on the emission of four compounds — pyrene, benzo[*a*]pyrene, benzo[*e*]pyrene and 1-nitropyrene — is summarized (Schuetzle & Frazier, 1986). Particulate samples were collected from four diesel vehicles produced by four major manufacturers, which run on a variety of diesel fuels under various operating conditions (see Table 4). Overall, the emission rates of these compounds varied by no more than a factor of three.

The emission of PAHs was increased by a factor of three to four when the aromaticity of the fuel (content of aromatic hydrocarbons) increased from 22 to 55%, resulting in 2–24 and 2–60 mg/l pyrene, respectively. Exhaust pipe emissions of pyrene were not related to the pyrene content of the fuel, indicating that the primary source of PAHs is their formation

Fig. 2. Types of nitro-polycyclic aromatic hydrocarbons (PAHs) and nitroheterocyclic compounds identified in diesel emission particulates[a]

Compound type	Rings	Examples	Number reported	
			Tentative	Confirmed
NO_2-PAH	2–5	 1-Nitropyrene	10	9
NO_2-alkyl-PAH	2–4	 1-Methyl-9-nitroanthracene	22	5
NO_2-oxy-PAH	3–4	 1-Hydroxy-3-nitropyrene	10	–
Di-NO_2-PAH	2–4	 1,6-Dinitropyrene	3	7
NO_2-S-PAH	2–3	 3-Nitrodibenzothiophene	2	–
NO_2-N-PAH	2–3	 5-Nitroquinoline	4	2

[a] From Schuetzle & Jensen (1985)

during the combustion process and not their presence in unburnt fuel in the exhaust. In contrast, fuel aromaticity had no effect on the emission of 1-nitropyrene, suggesting that nitrogen oxides, and not pyrene, are the limiting factor in the chemical formation of 1-nitropyrene (Schuetzle & Frazier, 1986).

Table 4 also presents data that demonstrate the effect of engine operating conditions on diesel emissions. Changes in engine timing have little effect on PAH emissions, but the 1-nitropyrene content increased by several fold, correlating with the increase in emissions of

Table 8. Concentrations of some nitroarenes (μg/g) in diesel particulate extracts

Compound	Concentration	Reference
1-Nitronaphthalene[a,b]	0.95[c]	Paputa-Peck *et al.* (1983)
2-Nitronaphthalene[a,b]	0.35[c]	Paputa-Peck *et al.* (1983)
2-Nitrofluorene[b]	1.2[c]	Paputa-Peck *et al.* (1983)
1-Nitropyrene[b]	75	Paputa-Peck *et al.* (1983)
3-Nitrofluoranthene	3.5[c]	Paputa-Peck *et al.* (1983)
8-Nitrofluoranthene	1.3[c]	Paputa-Peck *et al.* (1983)
6-Nitrobenzo[*a*]pyrene[b]	4.2[c]	Paputa-Peck *et al.* (1983)
1,3-Dinitropyrene[b]	0.30	Paputa-Peck *et al.* (1983)
1,6-Dinitropyrene[b]	0.40	Paputa-Peck *et al.* (1983)
1,8-Dinitropyrene[b]	0.53	Paputa-Peck *et al.* (1983)
2,7-Dinitrofluorene	4.2, 6.0[d]	Schuetzle (1983)
2,7-Dinitro-9-fluorenone	3.0, 8.6[d]	Schuetzle (1983)
1-Nitro-3-hydroxypyrene	70	Manabe *et al.* (1985)
1-Nitro-3-acetoxypyrene	6.3	Manabe *et al.* (1985)

[a] Tentative identification: confirmed by gas chromatographic retention times of authentic standards, but not by mass spectrometry

[b] Concentration estimated from chromatographic intensity by the Working Group within ± 50% error limits

[c] Considered in a monograph in this volume

[d] Two light-duty diesel particulate extracts

nitrogen oxides. Engine speed and load significantly affect the emission of nitroarenes in engine exhaust, as shown in Table 9. High load and high speed raise engine and exhaust temperatures, enhancing the partial oxidation of nitroarenes. Thus, the emission of nitroarenes, and possibly of other oxygenated PAH species, is highly dependent on source conditions (Schuetzle & Perez, 1983).

1.3 Gasoline engine exhaust

All research to date indicates that emissions from spark-ignition engines run on unleaded gasoline are qualitatively similar to the emissions from diesel engines (Alsberg *et al.*, 1984; see Tables 3, 6 and 10). However, there are significant quantitative differences (see section 1.4). The data reported below relate to four-stroke engines, unless otherwise specified, although the emissions from two-stroke engines are qualitatively similar. Since several PAHs have been shown to be carcinogenic (IARC, 1983, 1987a), much research has been directed to the identification of individual compounds in these emissions (Table 10; Grimmer *et al.*, 1977). As for diesel fuel, the emission of PAHs (measured as benzo[*a*]-pyrene) varies with the aromatic content of the gasoline (Schuetzle & Frazier, 1986).

Table 9. Effects of engine operating conditions on concentration of nitro-polycyclic aromatic hydrocarbons in heavy-duty diesel particles[a]

Compound	Concentration in particles ($\mu g/g$)[b]		
	HDD38, idle	HDD34, high speed, zero load	HDD4, high speed, full load
2-Nitrofluorene	84 (164)	62 (134)	1.9 (15)
3-Nitro-9-fluorenone	18 (35)	7.9 (17)	8 (63)
2-Nitro-9-fluorenone	10 (19)	4.8 (10)	3.7 (29)
9-Nitroanthracene	94 (184)	16 (35)	5.1 (40)
9-Nitro-1-methylanthracene	129 (252)	13 (28)	0.2 (1.6)
3-Nitro-1,8-naphthalic acid anhydride	23 (46)	10 (22)	22 (174)
1-Nitropyrene	14 (28)	3 (6.5)	0.13 (1)
2,7-Dinitrofluorene	15 (30)	18 (39)	3.9 (31)
2,5-Dinitro-9-fluorenone	5.5 (11)	8 (17)	2.1 (17)
2,4,7-Trinitro-9-fluorenone	<1 (<2)	0.4 (0.9)	NR[c]
1,3-Dinitropyrene	<0.8 (<1.6)	0.6 (1.3)	0.4 (3.1)
1,6-Dinitropyrene	<0.8 (<1.6)	1.2 (2.6)	0.8 (6.3)
1,8-Dinitropyrene	<0.8 (<1.6)	1.2 (2.6)	0.8 (6.3)
6-Nitrobenzo[*a*]pyrene	<3.2 (<6.5)	1.6 (3.5)	0.3 (2.4)

[a] From Schuetzle & Perez (1983)

[b] Number in parentheses is concentration in extract in micrograms per gram; extraction of samples HDD38, HDD34 and HDD4 gave 51, 45.9 and 12.7% extractables, respectively.

[c] NR, not sufficiently resolved from several other components

Little detailed information is available on the occurrence of PAH derivatives (e.g., nitroarenes) in gasoline exhaust. Some acridines, including benz[*c*]acridine, dibenz[*a,h*]-acridine and dibenz[*a,j*]acridine, have been identified in gasoline engine exhaust (Sawicki *et al.*, 1965). 1,2-Dichloroethane (38–2900 $\mu g/m^3$) and 1,2-dibromoethane (22–1360 $\mu g/m^3$) have been measured in exhausts from engines run on leaded gasoline (Tsani-Bazaca *et al.*, 1981). Methyl bromide has been found in the exhaust of cars using leaded (71–217 $\mu g/m^3$) and unleaded (<4–5 $\mu g/m^3$) gasoline (Harsch & Rasmussen, 1977).

The particles emitted from gasoline engines run on leaded fuel are physically different from particles emitted from diesel engines. Particles from gasoline engines are discrete, compact and dense. The mass median equivalent diameter of the particles, as measured along roads at steady speed (≃80 km/h) is 0.03–0.04 μm but increases to 0.2–0.4 μm when the vehicle is operated under cyclic conditions. Particulate mass comprises ammonium and lead sulfates, lead bromochloride and lead oxide, which are soluble in water. The proportion of organic solvent-extractable material is much smaller than that typically found in diesel particles (see Table 3). The remaining elemental carbon core of the particle has fewer sites available for adsorption of organic material, but quantitative comparisons with diesel particles are not available (Chamberlain *et al.*, 1978).

Table 10. Polycyclic aromatic hydrocarbons identified in gasoline engine fuel and exhaust (μg/l of original or combusted fuel)[a]

Compound	Molecular weight	Gasoline	Exhaust A[b]	Exhaust B[b]
Naphthalene	128	+	+	+
1-Methylnaphthalene	142	+	+	+
2-Methylnaphthalene	142	+	+	+
Acenaphthylene	152	+	+	+
Diphenylene	152	+	+	+
Acenaphthene	154	+	+	+
Diphenyl	154	+	+	+
1,2-Dimethylnaphthalene	156	+	+	+
1,3-Dimethylnaphthalene	156	+	+	+
1,4-Dimethylnaphthalene	156	+	+	+
1,5-Dimethylnaphthalene	156	+	+	+
1,6-Dimethylnaphthalene	156	+	+	+
1,7-Dimethylnaphthalene	156	+	+	+
1,8-Dimethylnaphthalene	156	+	+	+
2,3-Dimethylnaphthalene	156	+	+	+
2,6-Dimethylnaphthalene	156	+	+	+
2,7-Dimethylnaphthalene	156	+	+	+
1-Ethylnaphthalene	156	+	+	+
2-Ethylnaphthalene	156	+	+	+
Fluorene	166	+	+	+
Methylacenaphthylene*	166	+	+	+
Dibenzo[*b*,*d*]furan	168	–	+	+
Diphenylmethane	168	–	+	+
2-Methyldiphenyl*	168	+	+	+
3-Methyldiphenyl	168	+	+	+
1,3,7-Trimethylnaphthalene	170	–	+	+
1,6,7-Trimethylnaphthalene	170	+	+	+
2,3,6-Trimethylnaphthalene	170	+	+	+
Anthracene	178	1 555	534	642
Phenanthrene	178	15 700	2 930	2 356
Methylfluorene*	180	+	+	+
1-Methylfluorene	180	+	+	+
2-Methylfluorene	180	+	+	+
3,3′-Dimethyldiphenyl (*m*,*m*′-Ditolyl)	182	–	+	+
4,4′-Dimethyldiphenyl (*p*,*p*′-Ditolyl)	182	+	+	+
1,2-Diphenylethane	182	–	+	+
4,5-Methylenephenanthrene	190		473	762
3-Methylphenanthrene	192	6 870	264	510
2-Methylphenanthrene	192	7 730	269	578
2-Methylanthracene	192	739	92	104
4- and 9-Methylphenanthrene	192	1 243	190	330
1-Methylphenanthrene	192	3 180	256	404
Dimethylfluorene*	194	– to 372	– to 161	184–192
Dimethylfluorene* and 1-phenylnaphthalene	194 204	143	37	108

Table 10 (contd)

Compound	Molecular weight	Gasoline	Exhaust A[b]	Exhaust B[b]
Dimethyldiphenylenoxide*	196	+	+	+
Methyldiphenylethane*	196	+	+	+
Fluoranthene	202	1 840	1 060	1 662
Pyrene	202	4 700	2 150	2 884
2-Phenylnaphthalene	204	538	103	186
Dimethylphenanthrene*	206	− to 1128	− to 95	− to 216
Benzo[*a*]fluorene	216	1 500	82	136
Benzo[*b*]fluorene and benzo[*c*]fluorene	216	1 420	65	112
1-Methylpyrene	216	+	+	+
4-Methylpyrene	216	+	+	+
Cyclopento[*cd*]pyrene	226	−	987	750
Benzo[*ghi*]fluoranthene	226	3	244	112
Benz[*a*]anthracene	228	39	83	50
Benzo[*c*]phenanthrene	228	+	+	+
Chrysene	228	52	123	85
Triphenylene	228	30	60	40
3-Methylchrysene	242	−	+	+
2- and 5-Methylchrysene	242	8	5	5
4- and 6-Methylchrysene	242	8	5	5
Benzo[*b*]fluoranthene	252	159	48	19
Benzo[*k*]fluoranthene	252	9	17	7
Benzo[*j*]fluoranthene	252	9	27	11
Benzo[*e*]pyrene	252	307	59	37
Benzo[*a*]pyrene	252	133	81	50
Perylene	252	18	14	7
11*H*-Cyclopenta[*qrs*]benzo[*e*]pyrene (8,9-Methylenebenzo[*e*]pyrene)	264	13	43	17
10*H*-Cyclopenta[*mno*]benzo[*a*]pyrene (10,11-Methylenebenzo[*a*]pyrene)	264	5	18	8
Anthanthrene	276	20	17	26
Benzo[*ghi*]perylene	276	484	333	115
Indeno[1,2,3-*cd*]fluoranthene	276	16	32	12
Indeno[1,2,3-*cd*]pyrene	276	59	86	32
Dibenz[*a,h*]anthracene	278	+	+	+
Dibenz[*a,j*]anthracene	278	+	+	+
Picene (Benzo[*a*]chrysene)	278	1	1	1
Benzo[*ghi*]cyclopenta[*pqr*]perylene (1,12-Methylenebenzo[*ghi*]perylene)	288	−	41	19
Coronene	300	165	271	106
Picene (Benzo[*a*]chrysene) (1,2,6,7-Dibenzopyrene)	302	16	−	−

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[a] From Grimmer *et al.* (1977); compounds that could not be identified are not included in the table.

[b] Exhaust A, vehicle with air-cooled four-cylinder engine (44 PS); Exhaust B, vehicle with water-cooled four-cylinder engine (68 PS)

+, characterized by mass spectrometry; concentrations given when available

−, not detected; limit of detection about 0.2 μg/l combusted fuel

*, isomer uncertain

1.4 Comparison of emissions from different engines

A number of studies have recently been undertaken to determine emissions from a wide variety of engines. Levels of selected gas and particulate species and of total particulate matter from light-duty diesel, heavy-duty diesel and gasoline engines (with and without catalytic converters) in 1980–85 are summarized in Table 3.

The levels of carbon monoxide and nitrogen oxides emitted are similar for light-duty diesel and for gasoline engines with catalytic converters. The particulate emission levels from light-duty and heavy-duty diesels are two to ten and eight to 40 times greater, respectively, than the emission levels from catalyst equipped light-duty gasoline engines (Table 3).

Fuel evaporation (e.g., from fuel lines and carburettors) has become relatively more important as a source of hydrocarbons since emissions from exhaust pipes have been reduced. Currently, fuel evaporation accounts for 30–60% of the total hydrocarbon emissions from passenger gasoline vehicles with catalytic converters. The vapour pressure of most current diesel fuels under ambient conditions is so low that emissions due to evaporation of diesel fuels are not significant (National Research Council, 1982).

The levels of PAHs in emissions from light-duty diesel engines and from gasoline engines without catalytic converters are comparable, although the diesel engines emit at least ten times more nitroarenes than the gasoline engines. Catalytic converters reduce the level of total PAHs by more than ten times (Table 3).

Nitric acid, which can react with PAHs to form nitroarenes, has been measured in diesel exhaust (Harris *et al.*, 1987), and Paputa-Peck *et al.* (1983) measured low-molecular-weight nitroarenes in diesel particles (Table 8). In view of the vapour pressure relationships, these nitroarenes would also be present in the gas phase (Hampton *et al.*, 1983). A value for 2-nitrofluorene is given in Table 3 (Schuetzle & Frazier, 1986). Liberti *et al.* (1984) found several gas-phase nitro-PAHs in diesel exhaust (Table 11).

Table 11. Gas-phase nitro-polycyclic aromatic hydrocarbons identified in diesel exhaust[a]

Species	Relative concentration
x-Nitrofluorene[b]	1.00
1-Nitronaphthalene	0.10
x-Methyl-1-nitronaphthalene[b]	0.20
2-Nitronaphthalene	0.30
2-Nitrofluorene	0.75
9-Nitroanthracene	0.50
Dinitronaphthalene	0.20

[a] From Liberti *et al.* (1984)

[b] x, position unknown

Aliphatic amines are present at very low concentrations in exhausts from cars equipped with catalytic converters. Total emissions were less than 2.2 mg/mile (1.4 mg/km), and average emission rates of monomethylamine and dimethylamine were no more than 0.3 and 0.1 mg/mile (0.2 and 0.06 mg/km), respectively (Cadle & Mulawa, 1980). Levels of 0.1–1.4 μg/m^3 *N*-nitrosomorpholine and 0.5–17.2 μg/m^3 *N*-nitrosodimethylamine were measured in crankcase gases of heavy-duty diesel engines (Goff *et al.*, 1980). In one study in a vehicle tunnel, no *N*-nitrosodimethylamine was detected (detection limit, 0.1 μg/m^3) in the air (Hampton *et al.*, 1983).