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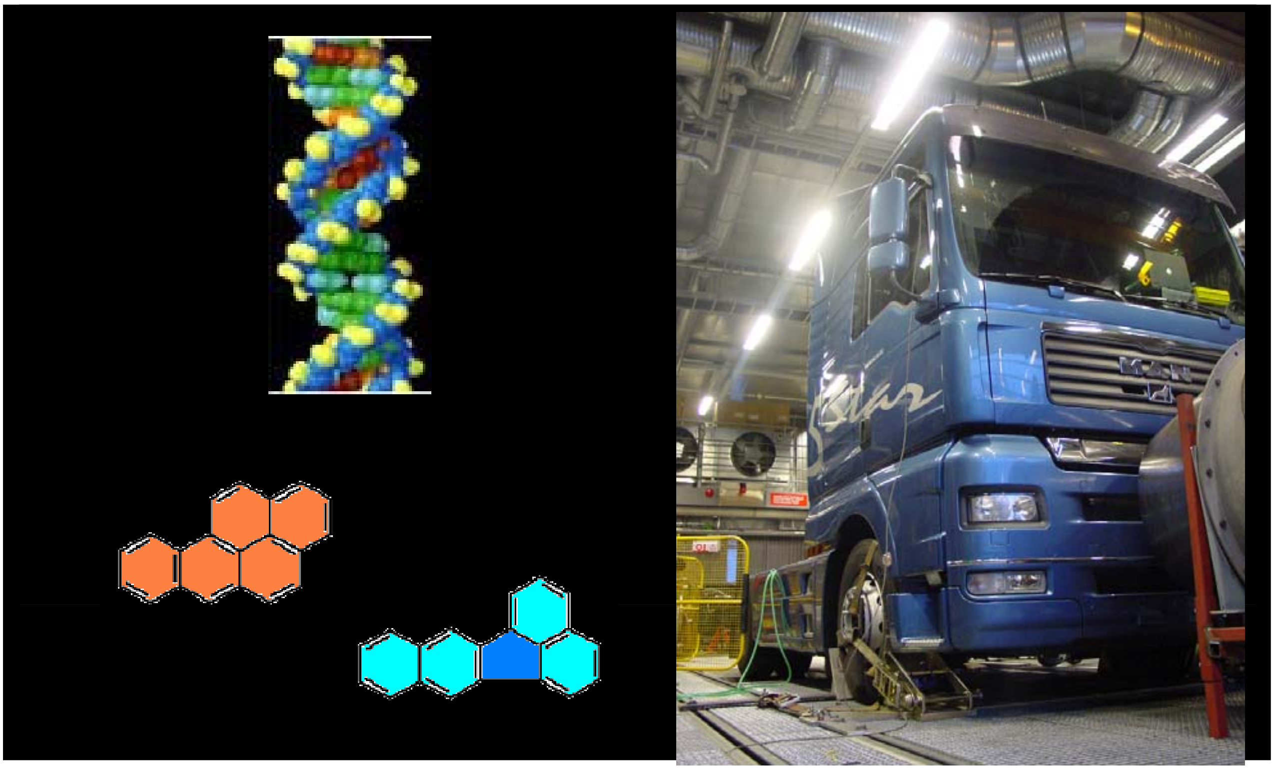

PAH CONTENT OF DIESEL FUEL AND AUTOMOTIVE EMISSIONS

Authors Päivi Aakko, Tiina Harju, Markku Niemi, Leena Rantanen-Kolehmainen

Confidentiality: Public

Abstract

The harmfulness of polyaromatic hydrocarbons (PAH) in diesel fuel has been well evidenced in past. This has lead to limit value of PAH content of diesel fuel in Europe (Directive 2003/17/EC, PAH di+ max. 11 wt%). In Sweden, more stringent limit value is applied for reformulated diesel fuel, and in Finland, before 2004, a tax incentive was given to diesel fuel fulfilling limits for certain properties, i.a. for total aromatics. Recent studies on the effect of fuel aromatics on the PAH emissions have focused on light-duty cars. However, it is important to study the relationship between fuel and exhaust PAHs also with the modern heavy-duty engines/vehicles in real life conditions using transient test cycles. This study on the influence of polyaromatic hydrocarbons of diesel fuel on the PAH emissions was conducted in programme funded by National Technology Agency of Finland (Tekes), Neste Oil, VTT Processes and Ministry of the Environment.

Two diesel fuels were studied, one with polyaromatic content of 1 wt% (di+) and the other with polyaromatic content of 5 wt%. The tests were carried out using six diesel technologies: Euro 2 heavy-duty engine, Euro 3 bus without catalyst, Euro 3 bus with oxidation catalyst, Euro 4 truck equipped with particle oxidation catalyst and two passenger cars (common-rail and TDI). Euro 2 engine was tested using the steady-state cycle, and the heavy-duty and light-duty vehicles using transient cycles on chassis dynamometer. A set of polyaromatic hydrocarbons (PAHs) was analyzed from the soluble organic fraction of particulate matter. Mutagenicity of particulate extracts was studied with Ames-test.

CO and HC emissions were low for the tested diesel applications. No significant difference between the two fuels studied was seen for CO emission. HC emission was lower with fuel containing less aromatics. NO_x emissions from heavy-duty applications were around 5% lower with the fuel containing less aromatics, but no difference was seen for the cars.

PM emission was slightly reduced when aromatic content of fuel was decreasing with the other applications than Euro 3 bus engine. In the tests with catalyst, the particles were rather dry (10-20% SOF), whereas with Euro 3 bus without catalyst wet (40% SOF).

Sum of seven priority PAH compounds showed systematic benefit for lower polyaromatic content of fuel despite of very low PAH emission level. The PAH emissions were 20-80% lower for the fuel containing 1 wt% of PAHs than for the fuel containing 5 wt% of PAHs with major part of diesel applications studied. However, for the Euro 4 truck the PAH emission level was too low to draw conclusions.

Ames test showed same trend as PAH results. Significant benefit of reducing polyaromatic content of fuel was seen with all diesel applications studied. Even with the Euro 4 truck equipped with the particle oxidation catalyst, for which almost no priority PAHs was observed, a substantial benefit of lower polyaromatic content of diesel fuel was evident in the Ames test.

This study showed the significance of polyaromatic content of diesel fuel in reducing harmfulness of the exhaust emissions from modern heavy-duty and light-duty diesel engine/vehicles with or without catalysts. Significant benefit was obtained particularly as concerns PAHs associated with particles, and Ames mutagenicity of particulate extract. However, no exact limit for polyaromatic content can be recommended based on this study. In addition, some open questions remain, like the performance at cold ambient temperatures.

Preface

In Finland, the influence of polyaromatic hydrocarbons in diesel fuel on the PAH emissions from engines and vehicles was studied from June 2005 to January 2006. Research work was divided in two parallel programs. One program was funded by Neste Oil and National Technology Agency of Finland (Tekes) within the research program "FINE Particles - Technology, Environment and Health". Parallel project was funded by VTT Technical Research Centre of Finland and Ministry of the Environment. All participants are acknowledged for funding, which enabled to conduct this interesting task.

The time-frame of the project was challenging when considering the extensive content of task. This required a lot of effort, knowledge and co-operation. Thanks are given to personnel that contributed to the measurements, among these at VTT are Kimmo Erkkilä, Erkki Virtanen, Reijo Mikkola, Timo Murtonen and Päivi Koponen for engine/vehicle emission tests, Marjaana Rättö and Marja-Liisa Jalovaara for Ames tests. In addition, thanks are given to the Nablabs laboratories, who carried out the PAH analyses. Special acknowledgement is given to Ari Juva and Seppo Mikkonen from Neste Oil for their valuable input and comments.

Espoo,

Authors

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1 Abbreviations

AFR	air-to-fuel ratio
CI	compression ignition
CNG	compressed natural gas
CRT	Continuously Regenerating Trap (diesel particle filter)
DI	direct injection
DIR-15	test fuel with total aromatic content of 15 wt-%
DIR-30	test fuel with total aromatic content of 30 wt-%
DPF	diesel particle filter
DPM	diesel particulate matter
EC	elemental carbon (in principle contains only carbon atoms).
EC1	Swedish Environmental Class 1 diesel fuel
HD	heavy-duty
IDI	in-direct injection
LD	light-duty
OC	organic carbon- and hydrogen-containing molecules, unburned diesel fuel and engine lubrication oil.
ox. cat.	oxidation catalyst
PAC	polyaromatic compounds
PAH	polyaromatic hydrocarbons
PM10	particles in the size class below 10 µm
PM-KAT®	particle oxidation catalyst
SCR	selective catalyst reduction
SOF	Soluble organic fraction
TEFs	Toxic Equivalence Factors
TWC	three-way-catalyst
US EPA	U.S. Environmental Protection Agency

2 Introduction

In Finland, the influence of polyaromatic hydrocarbons in diesel fuel on the PAH emissions was studied in a programme funded by National Technology Agency of Finland (Tekes), Neste Oil, VTT Processes and Ministry of the Environment.

The harmfulness of polyaromatic hydrocarbons (PAH) in diesel fuel is a known fact. Thus the amount of polyaromatic hydrocarbons with two or higher number of rings (di+) is limited in the Directive 2003/17/EC. However, the limit for PAHs in the Directive is high: max. 11 wt% (di+). The effect of fuel PAHs on the exhaust emissions have been extensively studied in past. Based on those studies the reformulated class 1 diesel fuel in Sweden has a limit value for PAHs: max. 0.02 vol% of PAHs (tri+). In Finland, before 2004 a tax incentive was given to diesel fuel fulfilling certain properties, i.a. total aromatics max. 20 vol-%.

Regardless of PAH levels or limits in the ambient air, diesel exhaust is known to contain PAHs being harmful for the human health. Exhaust aftertreatment reduce PAH emissions, however, majority of diesel fuel is combusted in heavy duty vehicles of which almost all are today without any exhaust aftertreatment, and it is going to take a long time before the new models with aftertreatment devices replace the old ones in vehicle population. It is also questionable, if aftertreatment devices operate effectively enough e.g. in traffic jams or cold climate, since exhaust temperature of a diesel engine may be low in these traffic conditions compared to the official emission test cycle and temperature required for a proper aftertreatment operation. So, it is foreseen that reduction of fuel polyaromatic content can reduce PAH emissions of the vehicle population today and during the next decade.

Polyaromatic content of diesel fuel in Europe was on average 0-4.5 wt% in 2004 according to EU fuel quality monitoring report (Hill 2005). The maximum content observed was around 10 wt%. This means that a limit of e.g. 6% does not cause any major investments for oil companies, but would be prohibiting sales of some occasional high aromatic fuel batches. According to Dastillung et al. (2005), the annual costs in EU-25 for 6 wt-% limit would be 312 M€ and would increase step-by-step up to 2249 M€ for 1 wt-% limit of polyaromatic content. Net increase of CO_2 emission would be 0.8 Mt/a and 9.2 Mt/a respectively.

The effect of fuel aromatics on the exhaust emissions was studied in the beginning of 90’s especially in Sweden and Finland. Based on these findings, PAH content of Swedish Environmental Class 1 (EC1) diesel fuel has been limited since 1992. In Finland, from 1992 to 2004 a tax incentive was given for “sulphur-free” diesel fuel, for which also total aromatic content was limited. Recently, an extensive study on the effect of fuel aromatics on the PAH emissions from light-duty cars was published (Doel 2005). This study concluded that in older diesel vehicles reducing fuel polyaromatics content gave lower PAH emissions, but the advanced emission control systems, TWC for gasoline cars and oxidation catalysts or particle filters for diesel cars, reduced PAH emissions to very low level, even to the level where no sensitivity to fuel polyaromatic content was observed.

As a summary, there seems to be a gap in knowledge on the relationship between fuel and exhaust PAHs regarding heavy-duty engines/vehicles. Firstly, there in no studies on the effect of fuel PAHs on emissions with modern heavy-duty technologies. Secondly, very little heavy-duty data is available using transient test cycles that describe real-world conditions. In addition, open questions remain on the performance at cold ambient temperatures.

3 Background

3.1 Diesel particles

3.1.1 Diesel exhaust

Diesel exhaust consist of gaseous phase including carbon dioxide, oxygen, nitrogen, water vapor, carbon monoxide, nitrogen compounds, sulphur compounds, numerous hydrocarbons, particles and other compounds. The knowledge on health effects of diesel exhaust is mainly based on data from diesel engines from early 1990’s or older. Even though these studies are still valid due to long service-life of engines, new studies on health effects are needed for new diesel technologies. (US EPA 2002).

Properties and composition of diesel exhaust depend on e.g. engine technology, engine operating conditions and fuel composition. The emissions from engines and vehicles have reduced significantly over the past years. This development has been strongly driven by legislation (Figure 1).

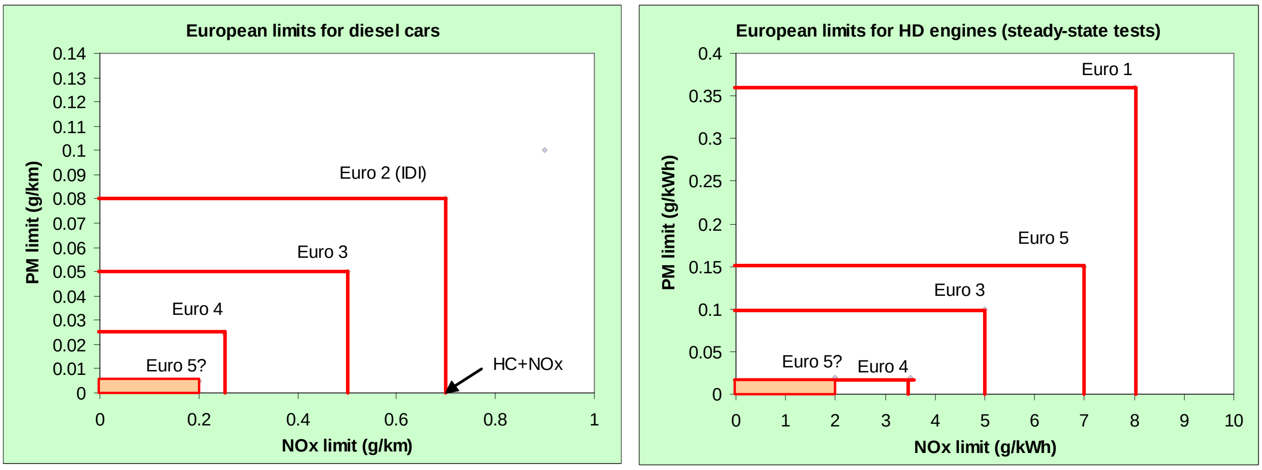

Figure 1. Development of European limit values for NO_x *and PM emissions regarding diesel cars and engines. (EC Directives)*

Many of the compounds found in the exhaust gas from engines or vehicles are harmful for health or environment. Known substances with serious health effects are e.g., benzene, formaldehyde, acetaldehyde, 1,3-butadiene, and polyorganic matter, which contain e.g. aromatic hydrocarbons (PAHs) and nitro-PAHs. These compounds were defined by US EPA as "Air Toxics" that need special attention when exhaust gases from mobile sources are studied. In 2001, US EPA published a revised list of mobile source air toxics (MSAT), meaning compounds emitted from highway vehicles and nonroad equipment, which are known to cause cancer or other serious health and environmental effects (Table 1). It is noticeable that diesel particulate matter and diesel exhaust organic gases as such are mentioned in the US EPA MSAT list.

There health effect studies (e.g. Table 2) so far have found adverse effects of diesel exhaust both on short-term and long-term exposure. Short-term exposure can cause acute irritation (e.g., eye, throat, bronchial), neurophysiological symptoms (e.g., lightheadedness, nausea), and respiratory symptoms (cough, phlegm). Evidence for an increase in responses to known allergens and asthma-like symptoms has been seen also (immunologic effect). Chronic-exposure includes e.g. dose-dependent inflammation and histopathological changes in the lung. An estimate of so called reference concentration (RfC), which does not cause adverse noncancer respiratory effects even if exposed throughout a lifetime, is 5 µg/m3 for diesel PM[1]. (US EPA 2002).

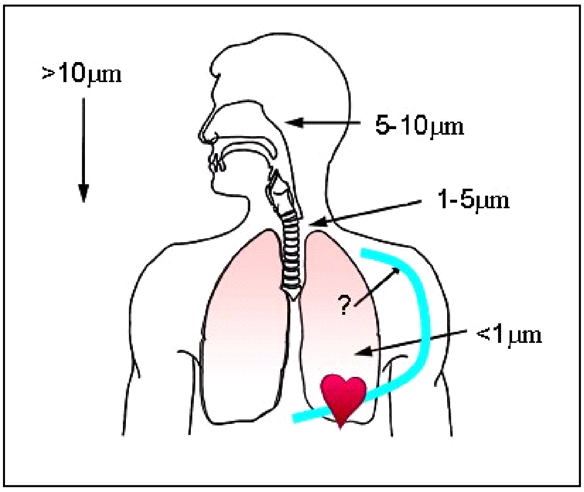

Figure 2. Deposition of particles into human body (Altshuler 2002)

Ambient air particles originate from various sources, and appear in various size classes. Coarse particles are removed e.g. by swallowing or caughing (Figure 2). Smaller particles, especially below 0.1 µm, can reach the surface of the lung. These particles can be removed by scavenging cells (macrophages), but they may also drift into lymphatic vessels, and possibly further into the blood. The smallest, <0.1 µm, particles may play important role as source of the toxicity of ambient particles. (DEFRA 2001). Diesel particles are very small in size, major part of the particle mass emission is well below 1 µm, and more 90% can be ultrafine particles (below 0.1 µm). In some cases, even smaller particles, so called nanoparticles below 50 nm, occur. Diesel particles have a large surface area, which may adsorb various compounds that can be toxic, mutagenic and carcinogenic (e.g., PAHs, nitro-PAHs, oxy-PAHs).

As a summary, the health assessment in USA concludes that diesel exhaust is "likely to be carcinogenic to humans by inhalation" and that this hazard applies to environmental exposures. Diesel exhaust has also potential for "a nonthreshold mutagenic effect". The

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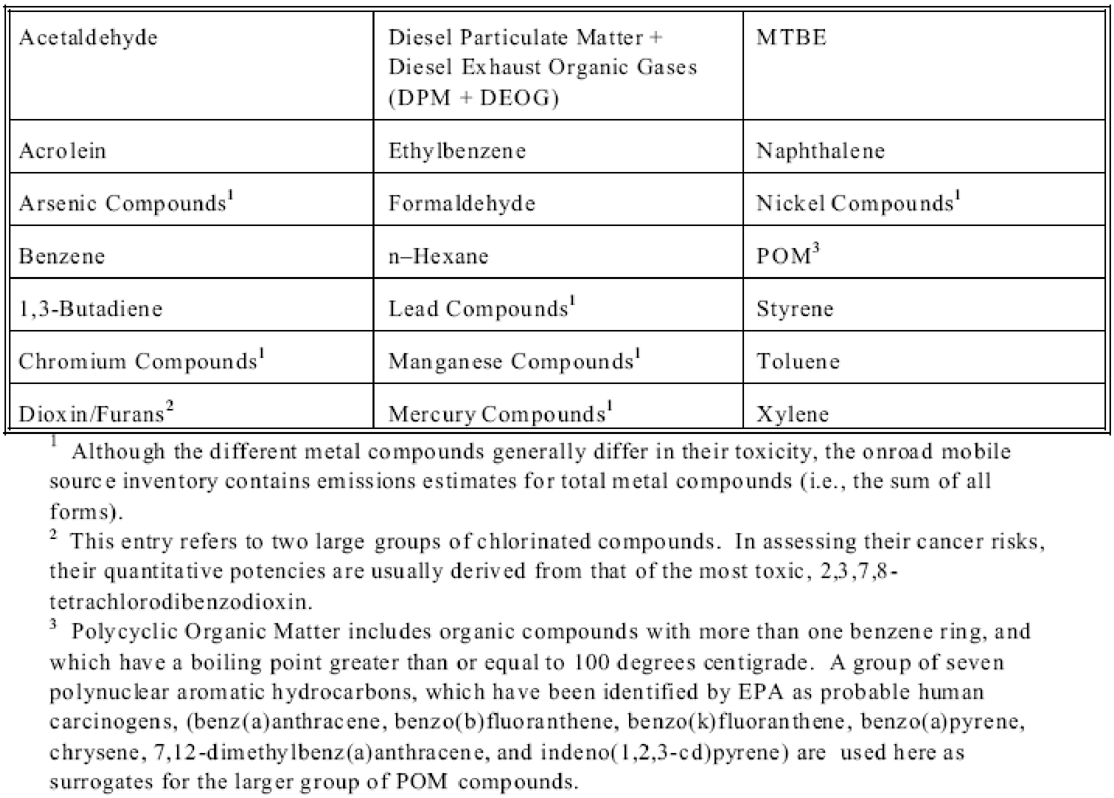
[1] In US, the limit value for ambient PM2.5 is 15 µg/m^3 (annual average concentration) (US EPA 2002). In Europe, the annual limit value for PM10 is 40 µg/m^3 (1999/30/EC).

estimated higher environmental exposure levels are close to, or overlapping, the lower limits of exposures for which lung cancer increases are reported. Alltogether, there is support to deem diesel exhaust as cancer hazard at environmental levels of exposure, even though there is not confidence in understanding the exposure/dose-response relationship. (US EPA 2002).

Table 1. US Mobile Source Air Toxics, MSATs (US EPA 2002).



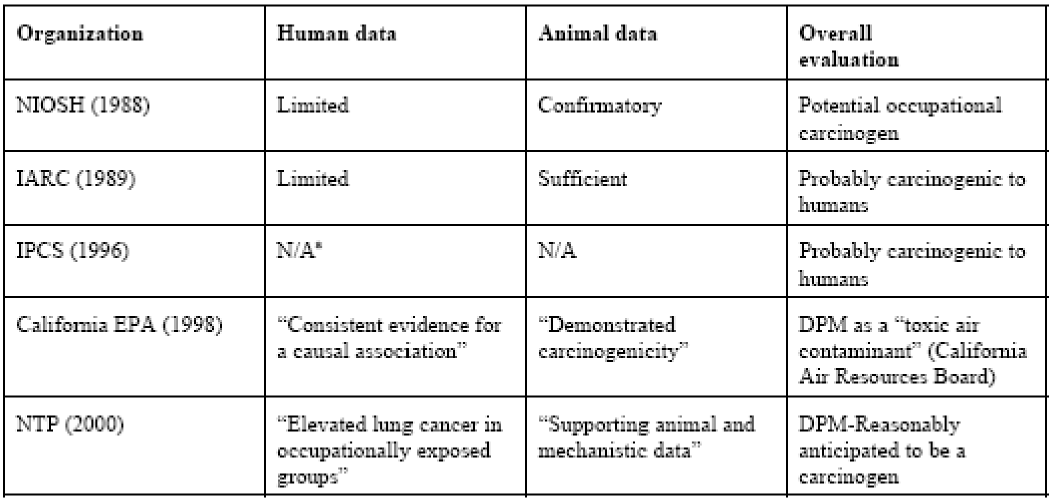
Acetaldehyde	Diesel Particulate Matter + Diesel Exhaust Organic Gases (DPM + DEOG)	MTBE
Acrolein	Ethylbenzene	Naphthalene
Arsenic Compounds[1]	Formaldehyde	Nickel Compounds[1]
Benzene	n–Hexane	POM[3]
1,3-Butadiene	Lead Compounds[1]	Styrene
Chromium Compounds[1]	Manganese Compounds[1]	Toluene
Dioxin/Furans[2]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

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

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

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

Table 2. Evaluations of carcinogenicity of diesel exhaust (US EPA 2002).



Organization	**Human data**	**Animal data**	**Overall evaluation**
NIOSH (1988)	Limited	Confirmatory	Potential occupational carcinogen
IARC (1989)	Limited	Sufficient	Probably carcinogenic to humans
IPCS (1996)	N/A*	N/A	Probably carcinogenic to humans
California EPA (1998)	"Consistent evidence for a causal association"	"Demonstrated carcinogenicity"	DPM as a "toxic air contaminant" (California Air Resources Board)
NTP (2000)	"Elevated lung cancer in occupationally exposed groups"	"Supporting animal and mechanistic data"	DPM-Reasonably anticipated to be a carcinogen

3.1.2 Formation of particles

Compression ignition combustion is nonhomogenous process, which is not easy to control. For instance mixing of fuel and air depends on many parameters, like injection pressure, the properties of the intake ports and piston. A direct-injection technology is predominant in modern diesel engines, whereas in older engines indirect-injection was used to improve mixing (pre-chamber or swirl chamber). Fuel injection varies depending on engine speed and load, and thus also the fuel-to-air ratio varies, however, being in principle always lean. Depending on factors like availability of oxygen, the fuel droplets are either completely or partially oxidized. At temperatures above 1300 K, elemental carbon is formed when the unburned fuel that is not oxidized is pyrolized (stripped of hydrogen) (Dec and Espey, 1995).

After the fuel is injected into the combustion chamber it vaporizes, and burning of the fuel and air mixture starts after the ignition delay period. There is two phases of burning: 1) diffusion-controlled burning when fuel burns as it is injected and diffuses into the cylinder; 2) rate-controlled burning takes place during the expansion stroke, after the end of injection (very small). Carbonaceous particle formation occurs primarily during the diffusion phase of combustion, and is the highest during high load and other conditions consistent with high fuel-air ratios.

Figure 3 shows mixing-controlled direct-injection combustion phase, i.e. diffusion combustion, according to a study of John Dec (Dec 1997). The initial soot formation takes place in a fuel rich regime close to the liquid fuel spray. The diffusion zone surrounds the jet periphery and consumes the unburnt fuel and oxidizes the soot by hydroxyl radicals. It is reported that over 80% of the carbonaceous matter would be oxidized (US EPA 2002 referring to Kittelson et al., 1986 and Foster and Tree, 1994).

Thermal NO formation is taking place in the diffusion flame, but it is a slow process and thus the major part of NO is believed to be produced later, after the end of fuel ignition. According to Dec’s model, most of the fuel is burned twice, first in the fuel-rich premixed combustion zone, and then in the turbulent diffusion-flame zone. The late combustion phase after the end of fuel ignition is not discussed in this model. (Dec 1997, Karila 2004).

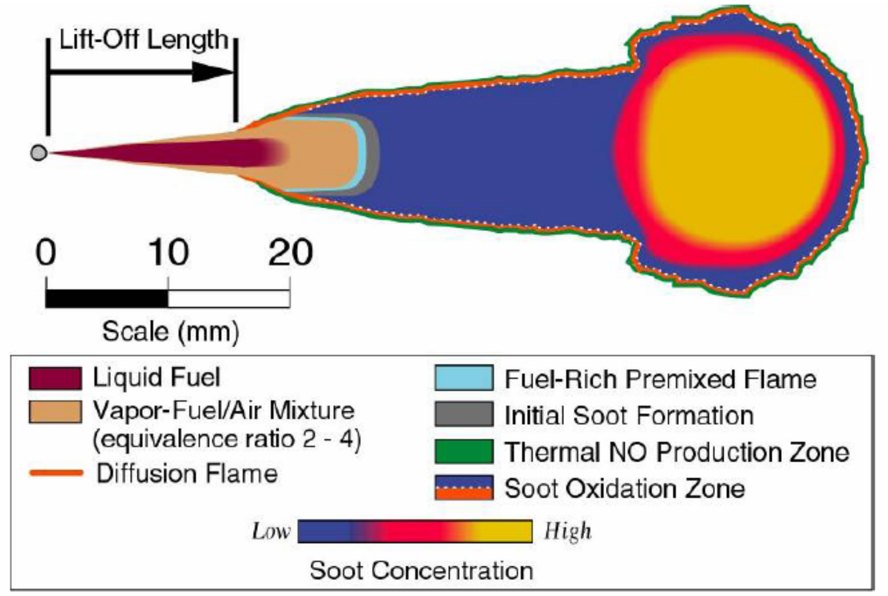


Figure 3. The model of diesel combustion, diffusion combustion phase. (Dec 1997, Musculus et al. 2005).

In flame, hydrocarbon fuels undergo pure or oxidative pyrolysis leading to small hydrocarbon radicals, like acetylene (C_2H_2). Then large molecules like polyynes and PAHs are formed, and these are believed to be soot precursors. The soot particles are believed to form with a homogenous process, either by physical or chemical condensation. Also other theories, like PAH model or polyyne model, have been proposed. (Tao Feng 2003).

After soot formation particle coagulation and surface growth takes place, and leads to larger particles. Surface growth is a heterogeneous process of 1) deposition of gas-phase hydrocarbons on the surfaces of the particles 2) adding carbon atoms on the surfaces 3) desorption reactions from particles. One mechanism proposed for surface growth is based on chemical reactions of large PAHs so that particles begin to stick to each other and agglomerate. (Tao Feng 2003).

Soot oxidation reduces the carbon mass accumulated in the particles. Oxidation is a heterogenous process taking place in the surface of particles. Molecular oxygen as well as O and OH radicals and possibly also H_2O, CO_2, NO, N_2O and NO_2 participate in soot oxidation. (Tao Feng 2003).

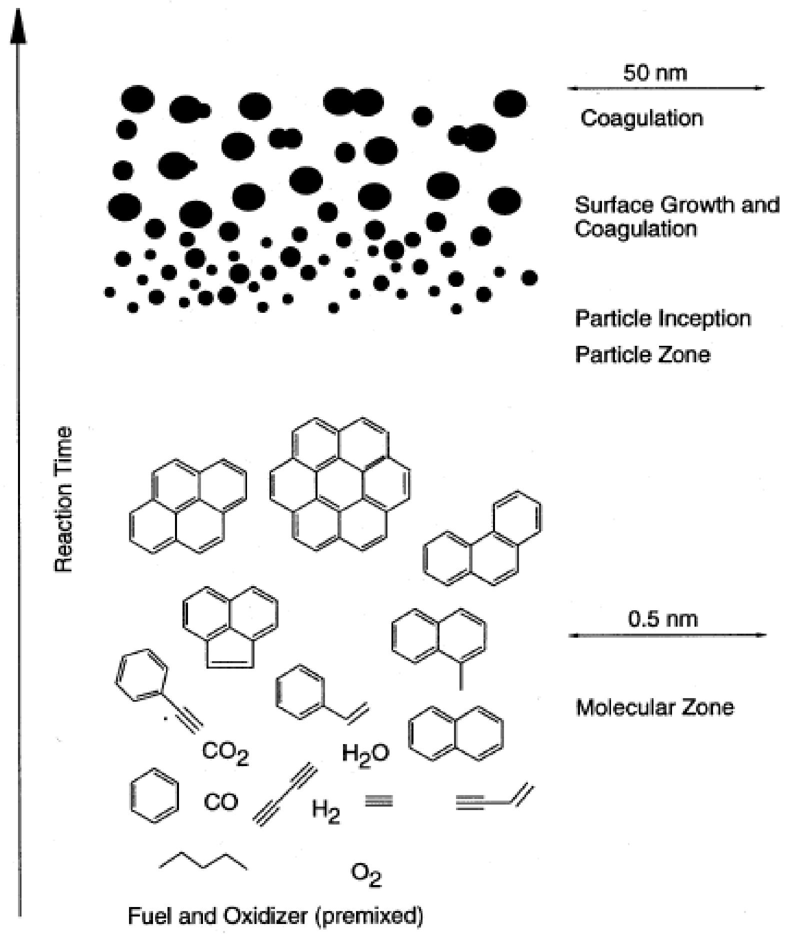


Figure 4. A schematic path leading to soot formation. (Tao Feng 2003; originally in Bockhorn 1994).

3.1.3 Composition of particles

Diesel particles contain elementary carbon, organic carbon, and small amounts of sulfate, nitrate, trace elements, water, and unidentified components (Figure 5). Particles from newer heavy-duty engines tend to be “dry”. Content of elementary carbon can be easily around ~75% (Figure 5). However, composition varies a lot depending on engine and aftertreatment devices, e.g. diesel particle filter can remove particle emissions close to zero. Oxidation catalysts oxidize organic compounds, especially soluble organic fraction, so that particles get dry. On the other hand, oxidation catalysts can generate significant amount of sulphates from sulphur existing in fuel and lubricant. However, the high content of elementary carbon in diesel particulate emission has been used even to distinguish diesel engine sources from other combustion aerosols.

Figure 6 shows a schematic view on of the structure of core particles and combined compounds. Core particles consist of solid carbonaceous material and ash (like trace

metals). Organic and sulfur compounds (sulfate) and other material are added to core particles through coagulation, adsorption, and condensation.
The organic material (SOF) of diesel particles originates from unburned fuel, engine oil, and products of partial combustion and pyrolysis. Major part of SOF is currently classified as unresolvable complex material. SOF is formed when some unburned fuel and lube oil is trapped in crevices or cool spots within the cylinder without possibility to oxidation or pyrolysis. In the high temperatures of exhaust system these compounds are in the gas phase, but upon cooling and dilution, some of the less volatile organic compounds can adsorb to the surfaces of the particles. If sufficient adsorption sites do not exist, the organic compounds may condense on e.g. sulfuric acid nuclei to form nanoparticles. (Johnson and Kittelson, 1996 and Abdul-Khalek et al., 1999 in US EPA 2002). A number of physical reactions take place when the exhaust is cooled and diluted: nucleation, coagulation, condensation, and adsorption. Diesel particulate matter is collected from diluted exhaust gas on a filter on certain conditions, e.g. at a temperature of maximum 52 °C. However, there are large variations permitted for these parameters in measurement protocols affecting directly the composition and mass of particles collected on filters, especially SOF portion of particulate matter.

Composition of diesel particulate matter (DPM) DPM is composed of elemental carbon, adsorbed organic compounds, sulfates, nitrates, and trace elements like metals.

Carbonaceous matter: Organic and elemental carbon - containing compounds in the particle phase.

Elemental carbon (EC): Carbon that has undergone pyrolysis (hydrogen removed). In principle, EC contains only carbon atoms.

Organic carbon (OC): Carbon- and hydrogen-containing molecules, unburned diesel fuel and engine lubrication oil. My contain oxygen, nitrogen, and sulphur containing compounds, and other trace elements.

Soluble organic fraction (SOF): The organic portion of DPM that can be extracted from the particles.

Soot: Agglomerations of EC and OC particles. (in some articles “soot” is used to describe IOF). (US EPA 2002)

The formation of sulfate depends on sulphur content of fuel and lube oil. Most of the sulphur is emitted as gaseous sulfur dioxide (SO_2), only about 2-3% of fuel sulphur is converted to SO_3 in engine. However, effective oxidising aftertreatment devices can convert as much as 70% of the sulphur to SO_3. This means that combination of certain aftertreatment devices and diesel fuel with 5 ppm sulphur content can more than double the sulphate emission when compared to engine without catalyst using diesel fuel with 50 ppm sulphur content. (Rickeard 2000). Sulphur is present in particles mainly as sulphates. Some sulphuric acid and combined water may be present as well.

Metallic compounds originate from engine component wear, and from the fuel and lubricant (e.g. Ca and Zn) (Aakko 2000). Ash from oil combustion may occur as trace amounts. It seems that generally, the low-emission diesel engines produce “dry” particles with lower amount of soluble organic fraction when compared to older generation of engines. The aftertreatment devices influence the composition of particles significantly.

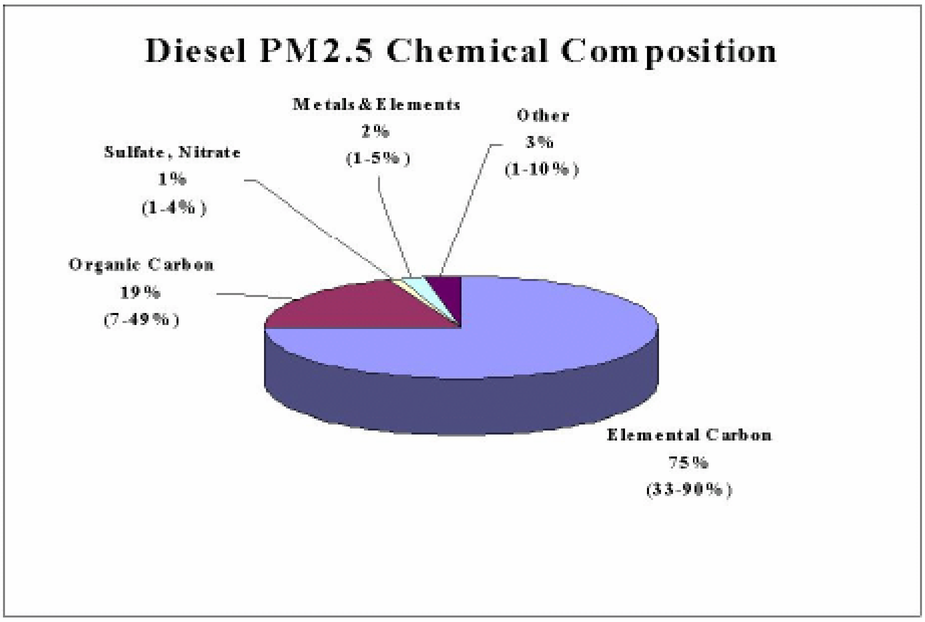


Figure 5. An example of composition of diesel particles (US EPA 2002).

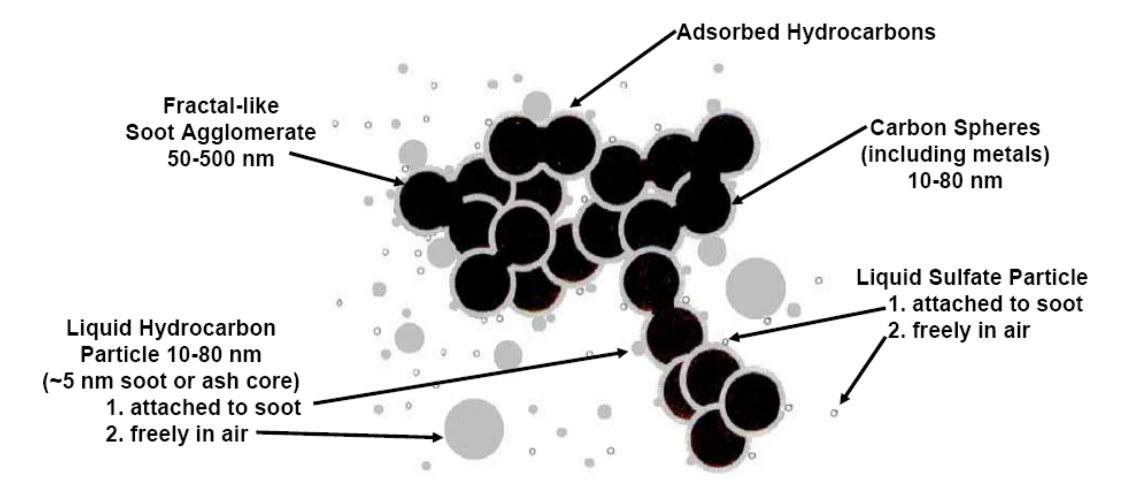


Figure 6. Schematic figure of diesel particles (Kulijk 2002 1998 in Foster 2004).

3.2 Polyaromatic hydrocarbons

Polycyclic aromatic compounds (PAC) consist of pure hydrocarbons or hydrocarbons containing heteroatoms (N, S, O), and contain more than one ring. Polyaromatic hydrocarbons (PAH) consist of two or more aromatic rings, and contain only carbon and hydrogen. Examples of selected PAH compounds are shown in Figure 7.

From automotive exhaust, typically certain set of polyaromatic hydrocarbons (PAHs), “Priority PAHs” are considered. There are several lists of “Priority PAHs” that define the most harmful compounds that should be taken into account for mobile exhaust gases

(Table 3). The US Environment Protection Agency's list included 16 PAHs, whereas US EPA's Mobile Source Air Toxic (MSAT) list from year 2000 includes seven PAH compounds: benzo(a)antracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, 7,12-dimethylbenz(a)anthracene.

There are also national PAH Priority lists, and many differences are found between definitions, e.g. US EPA priority list does not include benzo[e]pyrene, which is included in e.g. NIOSH and VDI 3872 priority PAH lists. IARC defines the group of the 6 most carcinogenic PAHs included in the group of the 12 least volatile PAHs, and classifies also degree of carcinogenicity (groups 1, 2A, 2B, 3 and 4). The low molecular weight PAHs increase the deviation of the results significantly.

PAH compounds are also covered by Persistent Organic Pollutant (POP's) protocol under United Nations Economic Commission for Europe's Convention on Long Range Transboundary Air Pollution (UN ECE CLRTAP). The propocol requires reporting of four PAH compounds annually (Table 3, EU PAH Position Paper 2001).

A recent European directive (2004/107/EC of 15 December 2004), relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, says (art. 4-8): "To assess the contribution of benzo(a)pyrene on ambient air, each Member State shall monitor other relevant polycyclic aromatic hydrocarbons at a limited number of measurement sites. These compounds shall include at least: benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene."

Many studies have been carried out to determine Toxic Equivalence Factors (TEFs) of PAH compounds. EU PAH Position Paper 2001 summarized these studies showing rather significant variation between different authors (Appendix 1).

PAH compounds represent well below 1% of diesel particulate mass emissions, however, they have been useful fingerprints when tracing sources of ambient PM emissions. To identify contribution of diesel engine emissions to ambient PM2.5, especially hopane and sterane (aromatic compounds, >C30) and other PAHs and long-chain alkanes have been useful. (US EPA 2002). Diesel particles contain also more methylated naphthalenes and methylated phenanthrene isomers than other combustion aerosols. Benzo[a]anthracene and benzo[a]pyrene from diesel engines have represented under some conditions a relative contribution of ambient PM. The benzo(g,h,i)perylene (BghiP) is an indicator of the gasoline emissions, with indeno[1,2,3-cd]pyrene (IP). (EPA 2002)

Benzo(a)pyrene is commonly used as a marker for carcinogenic PAHs for air quality management purposes. Many studies have shown a high correlation between BaP and PAH under various conditions. In 1990's typical BaP backround level was below 1 ng/m^3 in rural and below 3 ng/m^3 in urban areas. The levels beside cokery may be up to 30 ng/m^3. In Birmingham, 2-fold PAH level was observed from city center with traffic when compared to background level, 8-fold BaP level in industrial site in Genoa, 14-fold level in city center with traffic in Florence. Summary of PAH concentrations in

Europe based on data newer than 1990 is shown in Table 4 (PAH concentrations in diesel exhaust in Chapter 3.4). European union Directive 2004/107/EC sets for benzo(a)pyrene a target value of 1 ng/m^3 that should not be exceeded starting from 31.12.2012.

The overall PAH emissions in Europe are decreasing due to e.g. reduction in open fires, agricultural burning and cleaner vehicles. Wood burning is the major source of PAH emissions. In EU, PAH emissions from automotive sources are estimated to represent about 8% of atmospheric PAH emissions in 2010 (EU PAH Position Paper 2001).

Table 3. Lists of the PAH[2,3] compounds (EU PAH Position Paper 2001, IARC, 1983 and 1987)

16 EPA PAHs and their IARC classification[4]															
N	Ace	Acy	An	BaA	BaP	BbF	BjF	BkF	Chr	DBahA	F	Flu	IP	P	Phe
2ring	2ring	2ring	3ring	4ring	5ring	5ring	5ring	5ring	4ring	5ring	4ring	3ring	6ring	4ring	3ring
			3	2A	2A	2B	2B	2B	3	2A	3	3	2B	3	3
Directive 2004/107/EC PAHs															
				BaA	**BaP**	**BbF**	BjF	**BkF**		**DBahA**			**IP**		
UNECE persistent organic pollutants (POPs)															
					BaP	BbF		BkF					IP		

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[2] Acenaphthene = Ace, Acenaphtylene = Acy, Anthracene = An, Benzo[a]anthracene = BaA, Benzo[b]fluoranthene = BbF, Benzo[k]fluoranthene = BkF, Benzo[ghi]perylene = BghiP, Benzo[a]pyrene = BaP, Chrysene = Chr, Dibenzo[ah]anthracene = DBahA, Fluoranthene = F, Fluorene = Flu, Indeno[1,2,3-cd]pyrene = IP, Naphtalene = N, Phenanthrene = Phe, Pyrene = P.

[3] Group 1: carcinogenic, 2A: probably carcinogenic, 2B: possibly carcinogenic, 3: not classifiable as to its carcinogenicity, 4: probable non- carcinogenic

[4] US EPA's Mobile Source Air Toxic (MSAT) list from year 2000 includes 7 PAH compounds: BaA, BbF, BkF, Chr, BaP, IP and 7,12-dimethylbenz(a)anthracene.

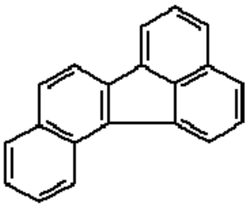
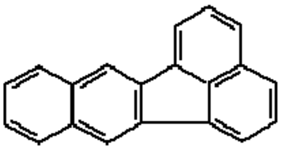
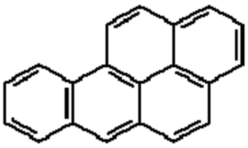
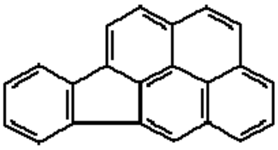
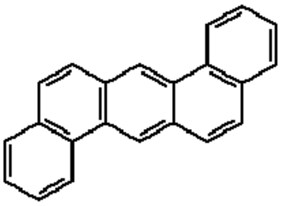
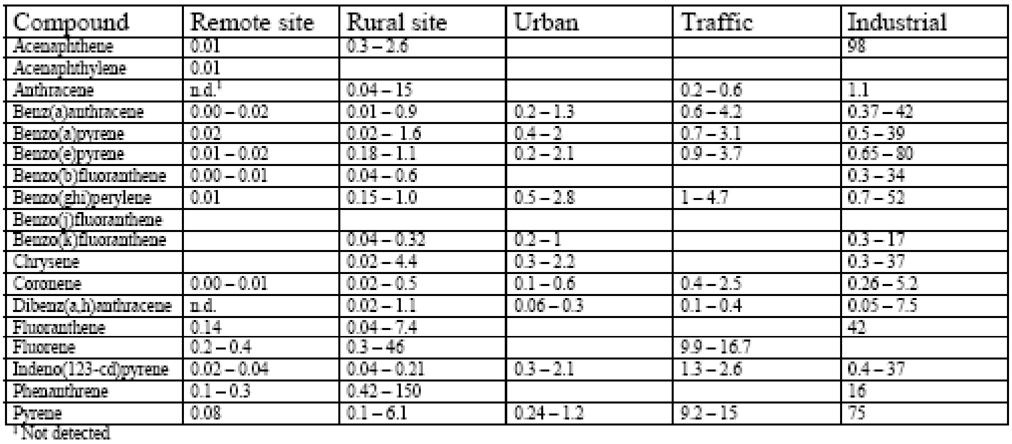
Benzo[j]fluoranthene BjFA 7,8-Benzfluoranthene Benzo[l]fluoranthene 10,11-Benzofluoranthene Dibenzo[a,jk]fluorene **Molecular formula:** $C_{20}H_{12}$ **CAS Registry No.:** 205-82-3 **Boiling point °C:** 480 **Melting point °C:** 165.4 **Vapour Pressure (Pa at 25 °C)** 2.0×10^{-6}	
Benzo[k]fluoranthene BkFA 11,12-Benzofluoranthene 8,9-Benzofluoranthene 2,3:1',8'-Binaphthylene Dibenzo[b,jk]fluorene **Molecular formula:** $C_{20}H_{12}$ **CAS Registry No.:** 207-08-9 **Boiling point °C:** 480 **Melting point °C:** 215.7 **Vapour Pressure (Pa at 20 °C)** 5.2×10^{-8} [1]	
Benzo[a]pyrene BaP Benzo[def]chrysene 3,4-Benzopyrene 6,7-Benzopyrene 1,2-Benzpyrene 4,5-Benzpyrene **Molecular formula:** $C_{20}H_{12}$ **CAS Registry No.:** 50-32-8 **Boiling point °C:** 496 **Melting point °C:** 178.1 **Vapour Pressure (Pa at 25 °C)** 7.0×10^{-7} [1]	
Indeno[1,2,3-cd]pyrene IP 1,10-(1,2-Phenylene)pyrene 1,10-(o-Phenylene)pyrene o-Phenylenepyrene 2,3-(o-Phenylene)pyrene 2,3-Phenylenepyrene **Molecular formula:** $C_{22}H_{12}$ **CAS Registry No.:** 193-39-5 **Boiling point °C:** 536 **Melting point °C:** 163.6 **Vapour Pressure (Pa at 20 °C)** 1.3×10^{-8}	
Dibenz[a,h]anthracene DBAhA 1,2:5,6-Benz[a]anthracene 1,2:5,6-Benzanthracene 1,2,5,6-Dibenzoanthracene **Molecular formula:** $C_{24}H_{14}$ **CAS Registry No.:** 53-70-3 **Boiling point °C:** 524 **Melting point °C:** 266.6 **Vapour Pressure (Pa at 25 °C)** 3.7×10^{-8} [1]	

Figure 7. Examples of selected PAH compounds (EU PAH Position Paper 2001).

Table 4. European PAH- and BaP concentrations after 1990 (EU PAH Position Paper 2001).



Compound	Remote site	Rural site	Urban	Traffic	Industrial
Acenaphthene	0.01	0.3 – 2.6			98
Acenaphthylene	0.01				
Anthracene	n.d.[1]	0.04 – 15		0.2 – 0.6	1.1
Benz(a)anthracene	0.00 – 0.02	0.01 – 0.9	0.2 – 1.3	0.6 – 4.2	0.37 – 42
Benzo(a)pyrene	0.02	0.02 – 1.6	0.4 – 2	0.7 – 3.1	0.5 – 39
Benzo(e)pyrene	0.01 – 0.02	0.18 – 1.1	0.2 – 2.1	0.9 – 3.7	0.65 – 80
Benzo(b)fluoranthene	0.00 – 0.01	0.04 – 0.6			0.3 – 34
Benzo(ghi)perylene	0.01	0.15 – 1.0	0.5 – 2.8	1 – 4.7	0.7 – 52
Benzo(j)fluoranthene					
Benzo(k)fluoranthene		0.04 – 0.32	0.2 – 1		0.3 – 17
Chrysene		0.02 – 4.4	0.3 – 2.2		0.3 – 37
Coronene	0.00 – 0.01	0.02 – 0.5	0.1 – 0.6	0.4 – 2.5	0.26 – 5.2
Dibenz(a,h)anthracene	n.d.	0.02 – 1.1	0.06 – 0.3	0.1 – 0.4	0.05 – 7.5
Fluoranthene	0.14	0.04 – 7.4			42
Fluorene	0.2 – 0.4	0.3 – 46		9.9 – 16.7	
Indeno(123-cd)pyrene	0.02 – 0.04	0.04 – 0.21	0.3 – 2.1	1.3 – 2.6	0.4 – 37
Phenanthrene	0.1 – 0.3	0.42 – 150			16
Pyrene	0.08	0.1 – 6.1	0.24 – 1.2	9.2 – 15	75

[1] Not detected

3.3 Mutagenicity

3.3.1 Definition and determination

Mutagenicity is a term related to genotoxicity and carcinogenesis. Mutagenicity means permanent changes, "mutations", in the cells or organisms involving a single gene or gene segment, or whole chromosomes. Genotoxicity is a broader term meaning potentially harmful effects on genetic material, acting directly or indirectly, and not necessarily associated with mutagenicity. Carcinogenesis means development of cancer with multiphase process; a mutagenic or genotoxic step is needed to start carcinogenesis. (ETAD 1998).

Many PAH compounds are known carcinogens. They can act via genotoxic effect by inducing cancer via mutations in DNA, via epigenetic effect by promoting cancer via increased capacity of affected cells; by triggering an inflammatory response and generating intracellular oxidative stress by free-radical production. Genotoxic effects depend on intracellular conversion of PAH compounds to diol-epoxides. The epigenetic effects involve binding to aryl hydroxylase (Ah) receptor in the cytoplasm. (EU PAH Position Paper 2001)

A large number of mutagenicity tests are available to study genotoxicity with two categories of mutations: gene mutation and chromosomal aberration. The bacterial reverse mutation tests[5], such as Ames test (Salmonella mutagenicity test by Maron & Ames 1983) are in vitro tests that are commonly used as screening tools for genotoxic and mutation inducing activity. Often several bacterial strains or a single strain with multiple markers (e.g. amino acid) are used to enlarge genetic information, which is very narrow for one strain. Enzyme extracts (S9 fraction) enables to study the role of metabolic processes. (ETAD 1998).

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[5] Reversion assays involve bacteria, mutations of which reverse or suppress over the test.

There are several drawbacks of using Ames test to study mutagenicity. The bacterial test does not reflect in vivo mutagenic activity, or show good correlation with the rodent cancer bioassay. The bacterial test is indicating narrow initiation phase mutations, not the whole process of carcinogenesis. Proper testing of genetic and carcinogenic risks should include a) the bacterial test b) in vitro tests using mammalian cells c) in vivo tests. However, bacteria tests can be used as effective first-step screening tool for bacterial mutagenicity. (ETAD 1998).

The bacterial tests are relatively simple and inexpensive. There have been a lot of studies on reliability of these tests, e.g. comparisons with the rodent cancer bioassays. Relatively low correlation has been showed between mutagenicity in bacteria and carcinogenicity in rodents in some studies, e.g. one study with 301 chemicals reported that the bacterial tests detected 56% of the carcinogens and 70% of those that were carcinogenic in both mice and rats. (ETAD 1998).

Generally, one important shortcoming of the bacterial test is lack of detection of non-genotoxic mechanisms. In addition, in vitro bacterial test has a high sensitivity and thus tends to overestimate in vivo activity. The following differences between bacterial tests and in vivo circumstances should be considered:

a) Dose in bacterial tests is “unlimited” (depends only on the solubility and cytotoxicity on tested cells), whereas in the rodent cancer bioassay there as many limitations. Unrealistically high dose may lead to overestimated response, and even impurities may reach levels that show mutagenic response.
b) Tissue-specific: some bacterial mutagens show low in vivo activity. Uptake: Factors specific for in vivo gastro-intestinal, dermal or inhalative absorption. Distribution: If carcinogenicity is specific only in one organ, bacterial tests may not be able to mimic it.
c) Metabolic activation is often needed to convert compounds reactive for DNA. Activation and detoxification systems locate not only in the liver. Conversion into an active metabolite depends on the concentration of enzymes. The liver S9 fraction does not represent the in vivo enzyme network. Ratio of activating and deactivating enzymes may change in production of S9 fractions (usually activating enzymes retained, but deactivating discarded).
d) The test material is added directly to the target cells in vitro, whereas in vivo, the reaction with DNA depend on the stability of the metabolite, the travelling distance and the availability of other trapping groups than DNA.
e) The mutation is a competition between DNA replication (mutation) and DNA repair. Most bacteria tests lack DNA repair systems. Cell proliferation increase the opportunity for DNA adducts to occur, and to reduce time for DNA repair. Bacteria show a high rate of cellular proliferation when compared to in vivo tests. (ETAD 1998).

The development of cancer in humans is even more complicated than the development of cancer in rodents, and situation with humans is “absolutely not comparable to the high dose treatment of bacteria in vitro”. (ETAD 1998).

3.3.2 Mutagenicity of diesel exhaust

A number of mutagenicity studies have been carried out with diesel emissions, volatiles particles, and individual chemicals found in diesel exhaust. Also carbon black particles have been studied for mutagenicity. The studies have been carried out mostly using bioassays, commonly using Ames test. There is not much data on long-term carcinogenicity of diesel exhaust from animal tests. Thus mutagenic potency for diesel emissions is based on semiquantitative mutagenicity data (and in vitro tests) and epidemiology based cancer potency estimations. (US EPA 2002).

The number of chemicals in diesel emissions is very large. Many compounds existing in diesel exhaust have shown mutagenic activity in a variety of assay systems, e.g. ethylene, benzene, 1,3-butadiene, acrolein and several PAHs. Particle associated compounds, PAHs and nitro-PAHs, have been the focus of mutagenic studies both in bacteria and in mammalian cell systems. PAHs ($\geq$4 rings, e.g., pyrene, benzo[a]pyrene) forming nitro-PAHs and nitro-PAH lactones in atmospheric reactions are major contributors of carcinogens in combustion emissions. Many nitro-PAHs ($\geq$3 rings, e.g., nitropyrenes) are potent mutagens and carcinogens and some reaction products (hydroxylated-nitro derivatives) are mutagenic in bacteria (Ames assay). Nitro-PAHs with more than two rings stay in particle phase. (US EPA 2002).

Several reviews show mutagenicity of diesel particle extracts in different strains of *Salmonella typhimurium* e.g. TA1537, TA1538, TA98, and TA100, both with and without rat liver S9 activation. Salmonella strain TA98-S9 has been the most common test strain. Nitrated PACs (e.g. mono- and dinitropyrenes) have been found to contribute on the mutagenicity. One study suggested that i.a. fluoranthene, 1-methylphenanthrene, and 9-methylphenanthrene, would be responsible for activation-dependent mutagenicity. In one study, 94 nitrobenzene derivatives were studied and 61 of those were mutagenic, and 28 of 50 PAHs. Generally, particulate extracts and individual nitropyrenes showed the strongest responses in strain TA98 without activation, whereas benzo[a]pyrene and other unsubstituted PAHs were mutagenic only in the presence of S9. (US EPA 2002).

A number of studies with diesel particle extracts in the mouse assays have shown positive responses, with or without S9 activation, and this has been confirmed in other mammalian cell systems. However, the genetic alterations can be produced by very complex set of routes, hence “no single genotoxicity assay should be expected to either qualitatively or quantitatively predict rodent carcinogenicity”. (US EPA 2002).

3.4 PAH and mutagenicity results from diesel exhaust

3.4.1 PAH and mutagenicity level in diesel exhaust

There are a number of studies reporting the PAH emissions from diesel engines and vehicles, and mutagenicity of diesel particulate extracts. General view on these results was collected in Table 5.

There are some technical problems with collecting PAH results from different reports. Firstly, the set of PAH compounds analysed vary a lot, and many times PAH results are shown as sums based on different "PAH Priority" lists (e.g. Table 1). The set of individual PAH compounds in the sum of PAHs vary between reports, and the results are not comparable with each other. In some cases, the results of individual PAHs are also reported, but not necessary in numerical format. Thus, only benzo(a)pyrene (BaP) is shown in Table 5 to represent PAH compounds in diesel exhaust.

There is in principle a huge amount of PAH data available for older generation of applications. Data on new Euro 3 emission level technologies is more limited, and not much data is available on Euro 4 technologies.

One of the recent extensive projects on emission factors from different light-duty cars was carried out within EU project "ARTEMIS" (Aakko et al. 2005). However, in this study the PAH emissions were studied only limitedly and the levels at different laboratories varied too much to draw definitive conclusions.

De Craeker et al. (2005) studied emissions from prototype Euro 4 heavy-duty engine (DPF) and Euro-5 engines (SCR/urea). According to Doel et al. (2005) this study included limited analyses on particulate phase PAHs showing extremely low PAH emissions when compared to Euro 3 emission level engine (no numerical results, Figure 25 in Doel et al. 2005).

As concerns mutagenicity, the results have been reported typically with Ames test strain TA98, which is shown in Table 5. Some reports included also results with other test strains.

Table 5. Selected BaP and mutagenicity results from exhaust particulates from light-duty and heavy-duty engines and vehicles (references shown in Table).

	Test*	BaP	Ref.	Ames test	Ref
GASOLINE CARS		μg/km		krev/km	
Euro 0	cold-start	<20	Kokko 2000, Perander 2001	*<60 (TA98-S9)*	*Kokko 2000,* Perander 2001
Euro 1	cold-start	<2	Kokko 2000	*<10 (TA98-S9)*	*Kokko 2000*
Euro 2	cold-start	<1	Aakko 1998, Perander 2001	*<1 (TA98±S9)*	Perander 2001
Euro 2	hot-start	0.002 (0.003 μg/m3)	Aakko 1998		
Euro 2 – G-DI	cold-start	<2	Perander 2001	<*20* (TA98±S9)	Perander 2001
Euro 3 MPI	cold-start	~0.3	Doel 2005		
Euro 3 lean-DI	cold-start	~0.2	Doel 2005		
DIESEL CARS		μg/km		krev/km	
Euro 0	cold-start	*<5*	*Rantanen 1996*	*<120 (TA98-S9)*	*Rantanen 1996*
Euro 1	cold-start	*<2*	*Doel 2005*		
Euro 2	cold-start	*<1*	*Doel 2005*		
Euro 3	cold-start	*<0.5*	*Rantanen 2005*	*<10 (TA98-S9)*	*Rantanen 2005*
HEAVY-DUTY ENGINE		μg/kWh		krev/kWh	
Euro 0	hot-start, SS*			~85 (TA98±S9)	Rantanen 1993
Euro 1	hot-start, SS	<0.2	Doel 2005		
EURO-2	hot-start, SS	0.2 (0.025 μg/m3)	Aakko 1998	30-50 (TA98-S9)	Aakko 2002
EURO-2 ox. cat	hot-start, SS	<0.05 (<0.01μg/m3)	*Aakko 1998*	~10 (TA98-S9)	Aakko 2002
Euro 2 DPF	hot-start, SS	below det. limit	*Aakko 2002*	10-20 (TA98-S9)	Aakko 2002
HEAVY-DUTY VEHICLES		μg/km		krev/km	
Euro 3	hot-start, T	<0.5 (PM+VOC)	Nylund 2004	58, 60 (TA98-S9) 52, 55 (TA98+S9)	Nylund 2004
Euro 3 ox. cat	hot-start, T	<0.02 (PM+VOC)	Nylund 2004	85, 86 (TA98±S9)	Nylund 2004
Euro 3 DPF	hot-start, T	<0.03 (PM+VOC)	Nylund 2004	16-30 (TA98-S9)	Nylund 2004
EEV CNG cat.	hot-start, T	~0.03 (PM+VOC)	Nylund 2004	1-5 (TA98-S9)	Nylund 2004

* all tests at normal temperature, SS = steady-state, T=transient

3.4.2 The effect of different parameters

The EU PAH Position Paper (2001), mainly based on Hall et al. (1998), summarises general findings on the effect of fuel properties on PAH emissions from motor vehicles. The following findings are collected from these reports and some studies referred in Tables 5 and 6:

- PAHs from gasoline vehicles depend on AFR, leaner mixture decreases PAH emission

- Aftertreatment devices (TWCs, oxidative catalysts) reduce PAH emissions. TWCs have been reported to decrease PAH emissions more than 80%.

Oxidation catalysts for diesel vehicles are not that effective. Diesel particulate filters remove PAHs very effectively[6].

- Engine temperature, load and speed affect PAH emissions. Urban driving with short distances increase emissions. Age and maintenance of vehicles is also of importance.

- The effect of fuel on PAH emissions have been well evidenced in the studies from 80's and early 90's. Based on these findings PAH content of Swedish Environmental Class 1 (EC1) diesel fuel has been limited to below 0.02 wt% (tri+) since 1992. In Finland, from 1992 to 2004 a tax incentive was given for "sulphur-free" diesel fuel, which contained aromatics maximum 20 vol%.

- There has been studies also in late 90's reporting that fuel with 7-11 wt% diaromatics and 1-3% triaromatics gave significantly higher PAH emissions than fuel containing virtually no di- or triaromatics.

- Sulphur content of fuel has been reported to decrease PAH emissions via more effective operation of aftertreatment devices.

Within the EU, the PAH content (di- and higher aromatics) of diesel fuel is limited to 11 wt% in the Directive 98/70/EC. In 2005, new limit value for total aromatic content of gasoline is 35 vol% (earlier limit was 42 vol%).

The mutagenic response can vary by many orders of magnitude using different fuels in old diesel engines. In 90's relationship between mutagenicity and aromatic content of diesel fuel was reported, especially as concerns di- or triaromatics. A number of individual PAHs and nitroderivatives have been mentioned as possible factors explaining mutagenicity results. Some studies have found effect of sulfur content, but not all studies. Sulphur may affect through catalyst performance (EPA 2002).

CONCAWE has carried out extensive studies on the effect of fuel on PAH emissions from engines and vehicles (Hall et al. 1998, Cuvelier et al. 2002, Doel et al. 2005, De Craecker, R. 2005). Recent report (Doel et al. 2005) included tests with 6 diesel cars model years from 1993-2002) and 3 gasoline cars (2 MPIs 1998, 2002, one lean-DI 2002). In addition, one Euro 1 (1994) HD diesel engine was tested. The PAH samples included both particulate and semivolatile phases. Program was carried out in two phases with different cars and fuels.

Doel et al. (2005) reported that in general, PAH emissions correlate with regulated emissions, especially with total hydrocarbons, showing that both regulated emissions and PAH emissions are lower with new vehicle technologies and aftertreatment devices than with older technologies. Report includes extensive set of data e.g. on 2+ring PAHs

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[6] There has been indications that in some conditions aftertreatment with effective oxidation function may result in increased Ames mutagenicity of particles, possibly due to formation of nitrated PAHs (Aakko 2002).

and 3+ring PAHs (3+ring from EPA 16 PAH list, see Table 1) and BaP. Figure 8 shows the effect of fuel di+ aromatics on BaP with light-duty cars.

In the study of Doel et al. (2005), the effect of fuel PAHs (di+) on exhaust PAHs (2+ and especially 3+) was significant regarding cars representing older technology from 90's one heavy-duty engine tested (Euro 1, 1994). However, using advanced aftertreatment technologies, especially diesel particulate filters (DPF) decreased the effect of fuel PAH to the level where no significant differences between fuels could be observed. For gasoline cars 3+ring PAHs were at low level (~10-20 µg/km), and differences between fuels small.

As a summary, when the data on PAH emissions is evaluated it is clearly seen that a big gap in knowledge exist regarding heavy-duty engines. Firstly, there in no studies on the fuel effect on PAH emissions with modern heavy-duty technologies. Secondly, very little data is available using transient test cycles that describe real-world conditions. In addition, open questions remain on performance at cold ambient temperatures, transient cycles. One must also note that vehicle/engine technology from 90's is in-use for quite long time-period due to high living-age of vehicles.

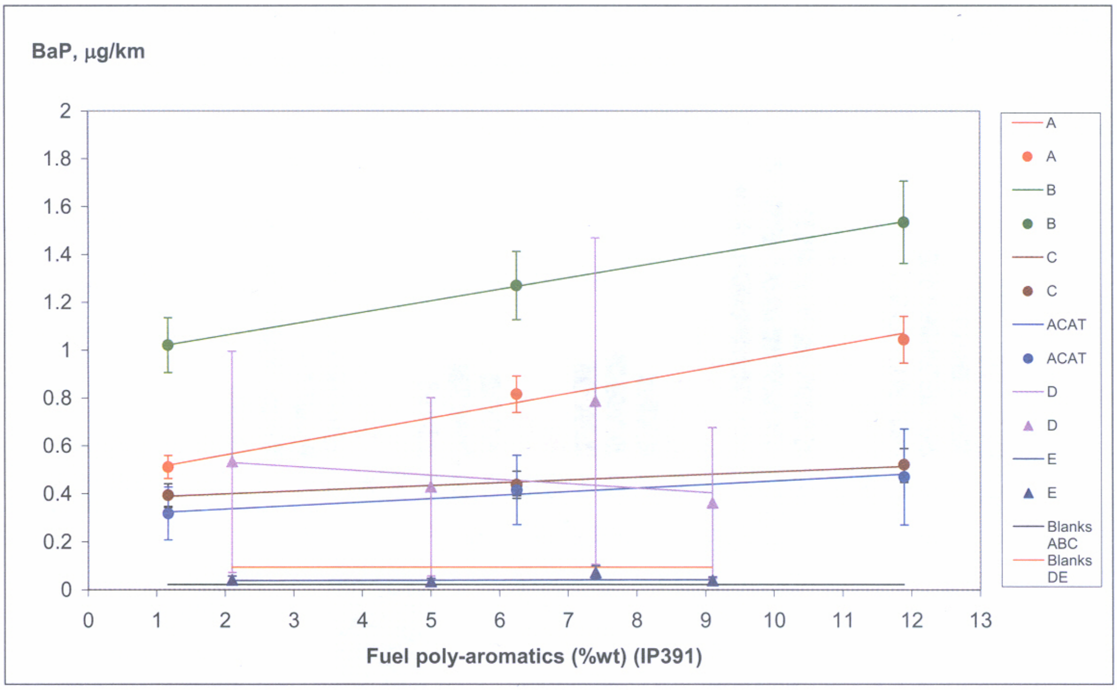


Figure 8. Benzo(a)pyrene emission with light-duty diesel cars using fuels with varying polyaromatics (di+). Cars A (IDI 1997), Acat (IDI,ox. cat. 1997), C (DI ox. cat, 1997), B (IDI ox. cat., 1993), D (DI ox. cat. 2002) E (DI common rail, DPF, 2001) (Doel et al. 2005)

There is limited data on the effect of fuel aromatics on mutagenicity of diesel exhaust gas, especially regarding light-duty cars. In addition, the fuel matrix has not been planned to study fuel aromatics as single parameter, but also other properties of fuels have changes. Mostly, these studies compared reformulated diesel fuels with reference fuel. The mutagenicity results from some of these studies are summarized in Table 6. In these studies, reformulated diesel fuels with e.g. lower aromatic content resulted in significantly lower response in the Ames test for mutagenic activity of particulate matter.

Table 6. Examples of the results of the Ames tests from particulate phase diesel exhaust using different fuels. Fuel aromatic content is not the only variable in these studies.

Engine/car	Fuel	Fuel aromatics, vol-%	Ames test TA98-S9 krev/km	TA98+S9 krev/km	TA98NR krev/km	Reference
Car 1992 (Euro 0)	EN590 - 1997 reformulated	29 17	51 6-14		47 6-13	Rantanen 1996
Van 1991 (Euro 0)	EN590 - 1997 reformulated	29 17	123 8-33		78 9-33	
Car 1988 (Euro 0)	EN590 - 1997 reformulated	29 17	122 85		102 67	
Volvo bus (Euro 0)	D10 D14, D15	20 5	~30 ~10-20	~20 ~10-20		Grägg 1992
Scania bus	EC2 EC1	16 4	22 3	10 1		Grägg 1994
Volvo FH12 truck	EPEFE EC1	30 3.6	70-100 7-15	40-60 0-10	40-50 0-10	Grägg 1995

4 Experimental

4.1 Test fuels, engines/vehicles and test matrix

Neste Oil planned, processed and analysed the test fuels. The fuel matrix included two base fuels: DIR-30 fuel with total aromatic content of 30 wt%, and DIR-15 fuel with total aromatic content of 15 wt%. Polyaromatic content (di+) in DIR-15 fuel was 1 wt% and 5 wt% in DIR-30 fuel. Both fuels are sulfur free (S < 10 mg/kg), and also other fuel properties are as similar as possible for the test fuels (Table 7).

Table 7. Properties of the test fuels.

		DIR-15	DIR-30
Density	kg/m3	836	839
Viscosity at 40°C	mm2/s	3.8	2.7
Sulphur	mg/kg	7	8
Cetane number		59	54
Cloud point/CFPP	°C	-1/<-36	-4/-21
Distillation, 95% recovered at	°C	358	356
Aromatics	wt%		
mono		14.5	25.2
di+		1	5
total		15.5	30.2

One heavy-duty engine (Euro 2), one Euro 3 emission level bus with and without oxidation catalyst, one Euro 4 truck and two passenger cars were tested (Table 8). Euro 3 bus was studied both with and without oxidation catalyst. In the measurements without catalyst the catalytic converter was removed and replaced by muffler. Euro 4 HD truck was equipped with PM-KAT®, which is a new type of aftertreatment device, an alternative to diesel particle filters. PM-KAT® consists of a metal substrate and the “open” channels (not closed like in filters, Figure 9). The MAN PM-KAT® removes particles through turbulence specifically created for this purpose; exhaust is redirected into a trap and forced through a sintered metal fleece. The particulate caught in the fleece is dissolved using the NO_2 from the oxidizing converter ($2NO_2 + C \rightarrow 2NO + CO_2$). This permanent chemical process eliminates the particulate. The regeneration is based on the same principle as in the “CRT” filter. (MAN website)

Table 8. Cars, engine and vehicles tested.

	HEAVY-DUTY ENGINE AND VEHICLES			**Light-duty cars**	
	HD-Euro 2	**HD-Euro 3 bus**	**HD-Euro 4 truck**	**LD-Euro 3**	**LD-Euro 3**
Model Year	1996	2004	2005	2000	2004
Mileage, km		137 500	1 800	176 000	35 000
Displacement, dm3	9.6	8.97	10.5	1.9	1.39
Fuel system & Fuel injection	direct-injection, Bosch in-line pump with EDC	direct-injection electronically controlled fuel injection	direct-injection common-rail	direct-injection unit injection	direct-injection common-rail
Aspiration	turbo-charged water/air cooling	turbocompounding air/air	turbo-charged air/air	turbo-charged	turbo-charged
Emission control	no	ox. catalyst removed in tests w/o cat	particle oxidation catalyst	oxidation catalyst	oxidation catalyst

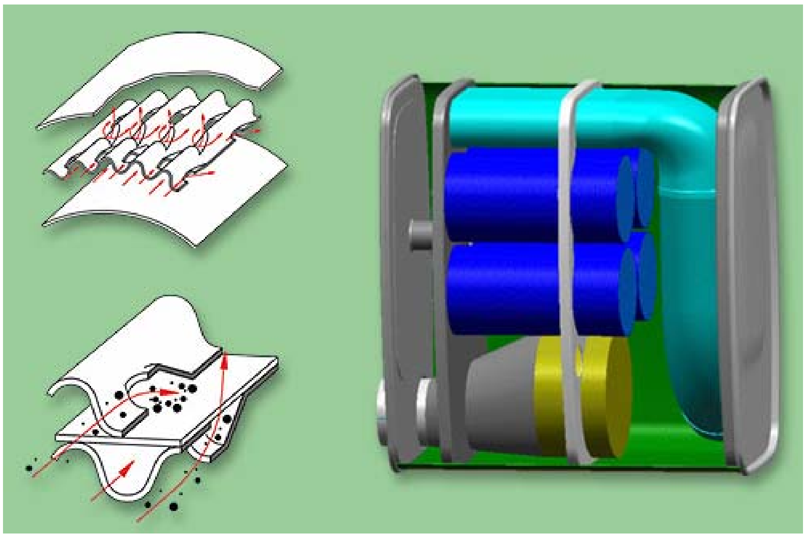


Figure 9. Particle matter separator system, PM KAT ®. (RTA website)

The test matrix is shown in Table 9. Number of tests with each vehicle/fuel/cycle combination varied from 4 to 7 for regulated emissions and from 2 to 4 for unregulated emissions. This gives a reasonable view on the repeatability of these tests.

Table 9. Test matrix.

Engine/ vehicle	Cycle	Fuel	CO, HC, NOx no of tests	PM no of tests	PAH no of tests	Ames-test no of tests
HD-Euro 2	ESC	DIR-15	6	6	2	2
engine w/o cat	ESC	DIR-30	6	6	2	2
HD-Euro 3	Braunschweig	DIR-15	4	4	4	4
bus w/o cat	Braunschweig	DIR-30	4	4	4	4
HD-Euro 3	Braunschweig	DIR-15	4	4	4	4
bus with cat	Braunschweig	DIR-30	4	4	4	4
HD-Euro 4	TR-jakelu	DIR-15	6	6	3	3
truck with cat	TR-jakelu	DIR-30	4	4	3	3
HD-Euro 4	FIGE	DIR-15	4	4	2	3
truck with cat	FIGE	DIR-30	4	4	2	3
LD-Euro 3	European	DIR-15	7	7	4	4
TDI	European	DIR-30	4	4	3	4
LD-Euro 3	European	DIR-15	7	7	4	4
common-rail	European	DIR-30	4	4	3	3

4.2 Regulated emissions

Exhaust emissions and fuel consumption were measured at the Technical Research Centre of Finland (VTT) on an engine dynamometer, on a chassis dynamometer for light-duty cars, and on a chassis dynamometer for heavy-duty vehicles.

Different test cycles were used for different engine/vehicle applications.

4.2.1 Heavy-duty engine

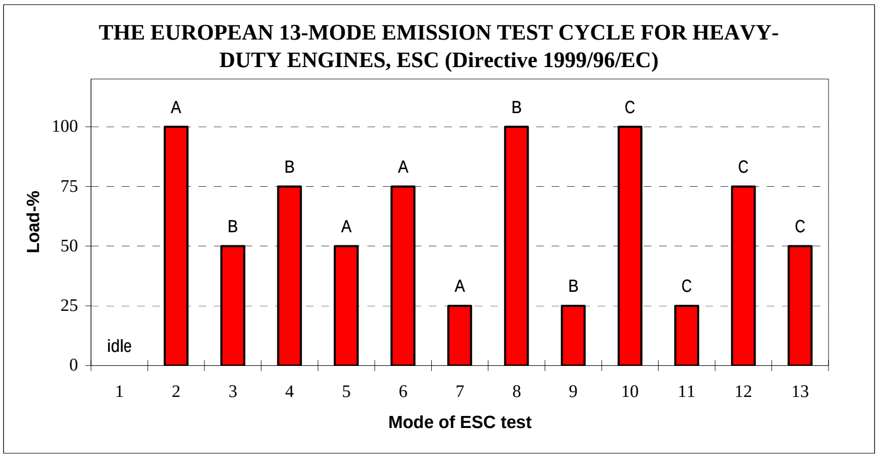
Heavy-duty engine tests were carried out in an engine dynamometer (Figure 10). The main measurement equipment is shown in Table 10. An eddy-current engine dynamometer by Zöllner and a “PUMA Test Assistant” control system by AVL were used for running and controlling the test engine. The gaseous emissions were measured from raw exhaust gas with an analyser system by BOO Instrument AB, which consist of analysers from different manufacturers. Particle mass samples were collected with AVL 474 Mini Dilution Tunnel and with SPC 472 Smart Sampler in parallel. Results with both particle collection systems were around the same level in these tests (Figure 14).

Table 10. The main equipment used in the tests at VTT.

Equipment/function	**Manufacturer/type**
engine dynamometer	Zöllner / B-300 AD
dyno control & data acquisition	AVL / Puma Test Assistant 5
regulated gaseous emissions	BOO Instrument Ab
particle mass emissions	AVL MDT 474 Mini Dilution Tunnel
particle mass emissions, parallel system	AVL SPC 472 Smart Sampler in parallel to MDT 474
particulate filters, Pallflex TX40H12	∅ 70 mm

Figure 10. Euro 2 bus engine on dynamometer.

The ESC test cycle was introduced in Directive 1999/96/EC amending Directive 88/77/EEC, together with the ETC (European Transient Cycle) and the ELR (European Load Response) tests, for emission certification of heavy-duty diesel engines. ESC test cycle comprises of 13 steady-state loads, and the final result is the average calculated with weighting factors (Figures 11 and 12).



Mode	WF
1	0.15
2	0.08
3	0.10
4	0.10
5	0.05
6	0.05
7	0.05
8	0.09
9	0.10
10	0.08
11	0.05
12	0.05
13	0.05

Figure 11. Schematic Figure of 13-mode ESC test cycle.

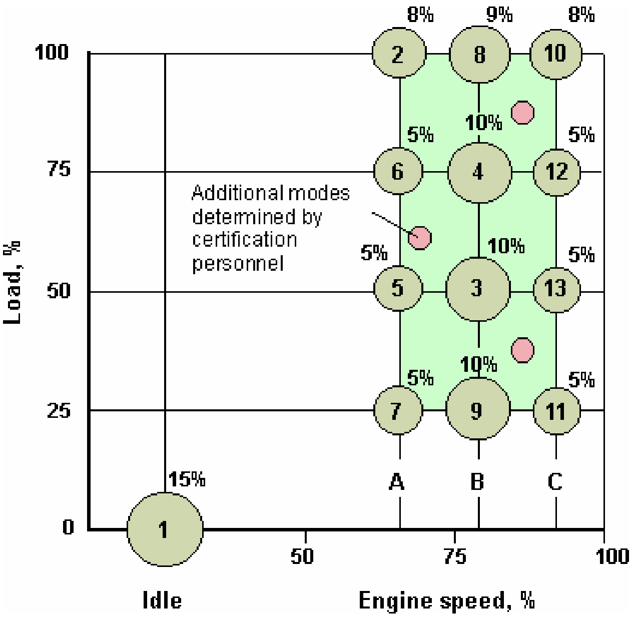


Figure 12. Load and engine speed modes of 13-mode ESC test cycle used in engine tests (DieselNet website).

4.2.2 Heavy-duty vehicles

Heavy-duty vehicles were tested using the heavy-duty transient chassis dynamometer and a full-flow CVS-emission system. VTT’s chassis dynamometer (manufactured by Froude Consine) has a roller diameter of 2.5 metres, and a power absorbtion capacity of 300 kW at the driving wheels (continuous). The dynamometer has a very fast control system and electric inertia simulation making dynamic (transient) testing possible. Inertia can be simulated in the range of 2 500 to 60 000 kg.

Figure 13. Full CVS tunnel for heavy-duty vehicles.

The regulated emissions were measured using a full-flow CVS system (Pierburg CVS-120-WT) and an analyzer set (Pierburg AMA 4000) conforming to the requirements of Directive 1999/96/EC for the measurement of exhaust emissions of heavy-duty on-road engines.

A high-capacity sampling system for particulate mass emission has been developed at VTT for the measurements of low-emission engine/vehicles applications, and this system is useful also for collection of sufficient mass of particles for special analyses like mutagenicity tests from conventional diesel vehicles (Rantanen 1996&2005, Kokko 2000, Perander, 2001, Aakko 2002). The high capacity sampling system was used in parallel with standard sampling system in the heavy-duty vehicle tests. In the high-capacity system, up to 2000 lpm flow of diluted exhaust gas through ∅ 142 mm filter can be used. In these tests, 300 lpm flow with Euro 3 bus and 400 lpm with Euro 4 truck was high enough to obtain appropriate particle masses.

Correlation of the particulate mass emission results (PM) using the two collection systems in the measurements of this project is shown in Figure 14. Correlation was excellent between standard and high-capacity sampling system for Euro 4 truck, but some difference was observed with Euro 3 bus. However, this difference was systematic and thus the results based on concentration in particulate matter were deemed to be representative.

For the measurements on the chassis dynamometer, the specific emissions were calculated per driving distance (g/km), whereas the results for an engine test are calculated per unit of work on the engine crankshaft (g/kWh).

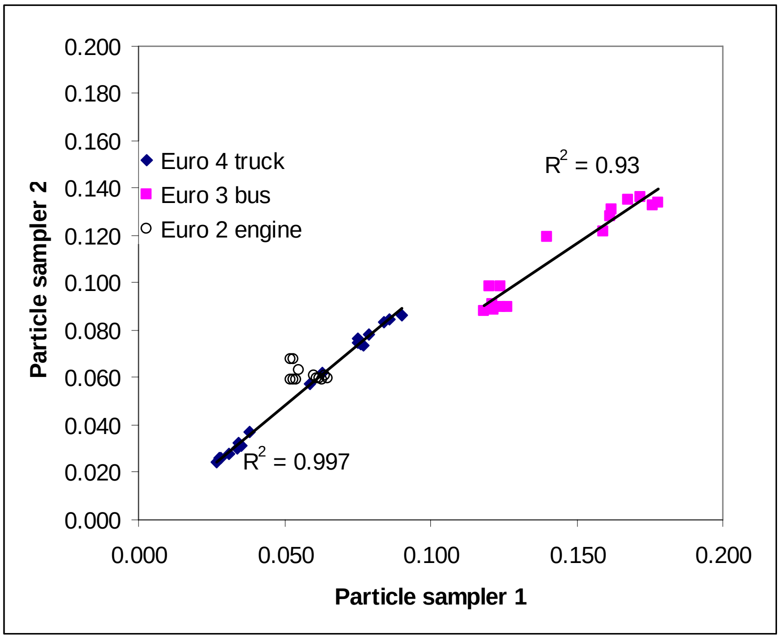


Figure 14. Comparison of the results obtained with two sampling systems.

Emission certification for heavy-duty vehicles is performed by running engines in engine dynamometer, consequently no official chassis dynamometer emission procedures exist. At VTT, chassis dynamometer measurement procedure for heavy-duty vehicles is accredited (T125) with its own in-house method based on existing elements (light-duty certification 70/220/EC, engine certification 1999/96/EC, SAE J2711: Recommended Practice for Measuring Fuel Economy and Emissions of Hybrid-Electric and Conventional Heavy-Duty Vehicles).

The control system of the dynamometer makes it possible to freely simulate the driving resistance of any vehicle. All vehicles were tested simulating the weight of the vehicle itself plus 50% load.

During the test, the driver follows a given speed profile. For Euro 3 bus, so called Braunschweig bus cycle was used (Figure 15). This is a well-known cycle for research work on buses in Europe. Duration of Braunschweig cycle is 1740 seconds, average speed 22.9 km/h and driving distance about 11 km.

Euro 4 truck was tested using two driving cycles. One of the cycles,"TR-jakelu" (Figure 16), has been developed at VTT within a Finnish research program (Nylund 2005). This cycle is specially targeted to represent driving conditions of trucks in delivery duty. "TR-jakelu" cycle has proven to give repeatable results. The duration of the "TR-jakelu" cycle is about 1900 seconds and its length is 19.5 km.

Another cycle that was used for Euro 4 truck on chassis dynamometer was FIGE cycle, which simulates the legislative ETC (European Transient Cycle) cycle of Directive 1999/96/EC that is used for engine certification tests (Figure 17). Transient ETC test cycle is based on the certain torque and speed values, and Figure 17 shows how these values represent the vehicle speed. The cycle was originally developed by FIGE Institute (Germany) as two versions: one for chassis and one for engine dynamometer. ETC test cycle is divided in three sub-parts (urban, rural and motorway). The duration of the cycle is 1800 seconds (each part 600 seconds). (DieselNet website)

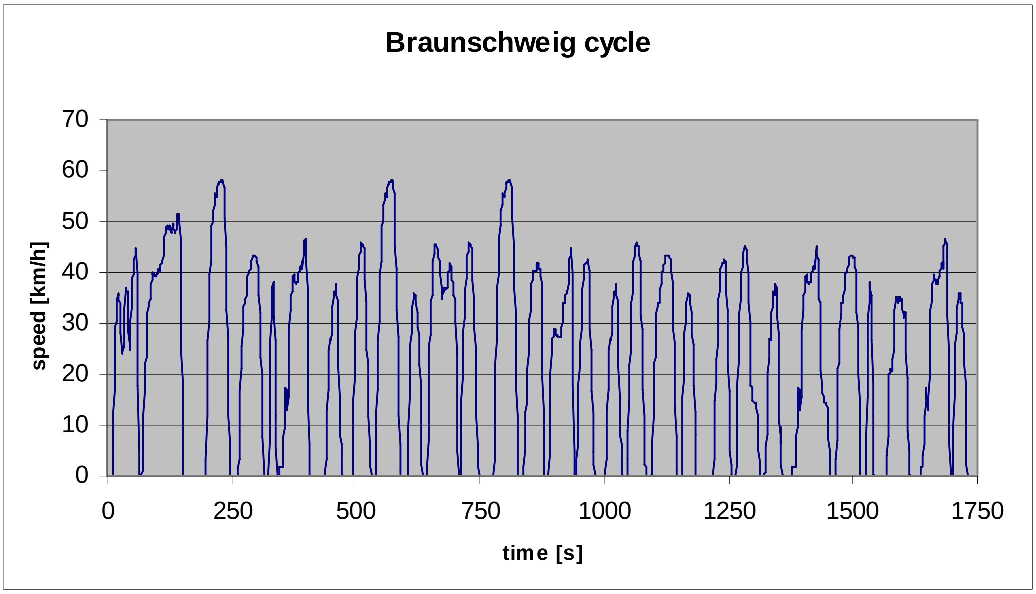


Figure 15. Speed vs. time of the Braunschweig bus cycle.

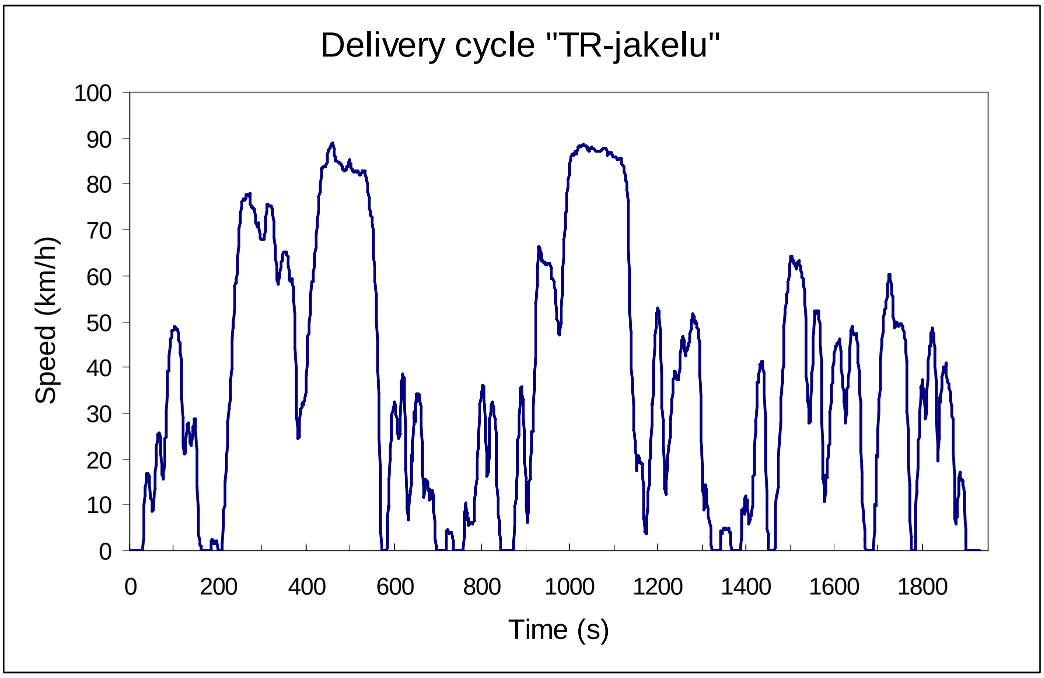


Figure 16. Speed vs. time of the VTT delivery cycle "TR-jakelu".

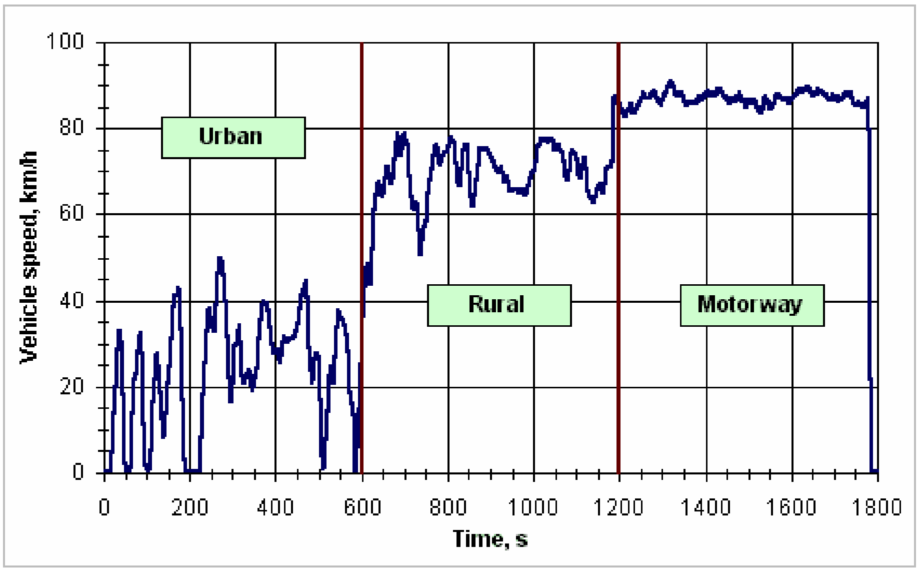


Figure 17. Vehicle speed vs time of FIGE cycle on chassis dynamometer (simulates ETC cycle for engines).

4.2.3 Light-duty tests

Light-duty tests were carried out using the current European test cycle according to 70/220/EEC and its amendments. All equipment used for the measurement of the regulated emissions (exhaust dilution and collection, concentration analysis etc.) conforms to the specifications of the Directive 70/220/EEC and it's amendments (European test). Test equipment is shown in Table 11 and the driving cycle is shown in Figure 18. Measurements were made at a temperature of 23 °C. High-capacity sampler was used to collect enough particle mass for analyses of polyaromatic hydrocarbon compounds and mutagenicity test (200 lpm through 142 mm filters). Before each test one European test cycle was run as a preparation.

Table 11. The basic equipment used in the tests with the light-duty diesel cars.

Equipment	**Manufacturer/type**	**Remarks**
Chassis dynamometer	Froude Consine 1.0 m	DC, 100 kW
Constant volume sampler	Pierburg 12.5 WT	PDP-type with heat exchanger
CO, HC, NO_x, CO_2	Pierburg AMA 2000	regulated gaseous emissions, triple bench
particulate sampling	dilution tunnel with high-capacity sampler	sampler specially developed for low-emission cars
particulate filter*	Pallflex T60A20	∅ 142 mm

* reference runs carried out with standard sampling system showed good correlation with high-capacity system in the light-duty tests.

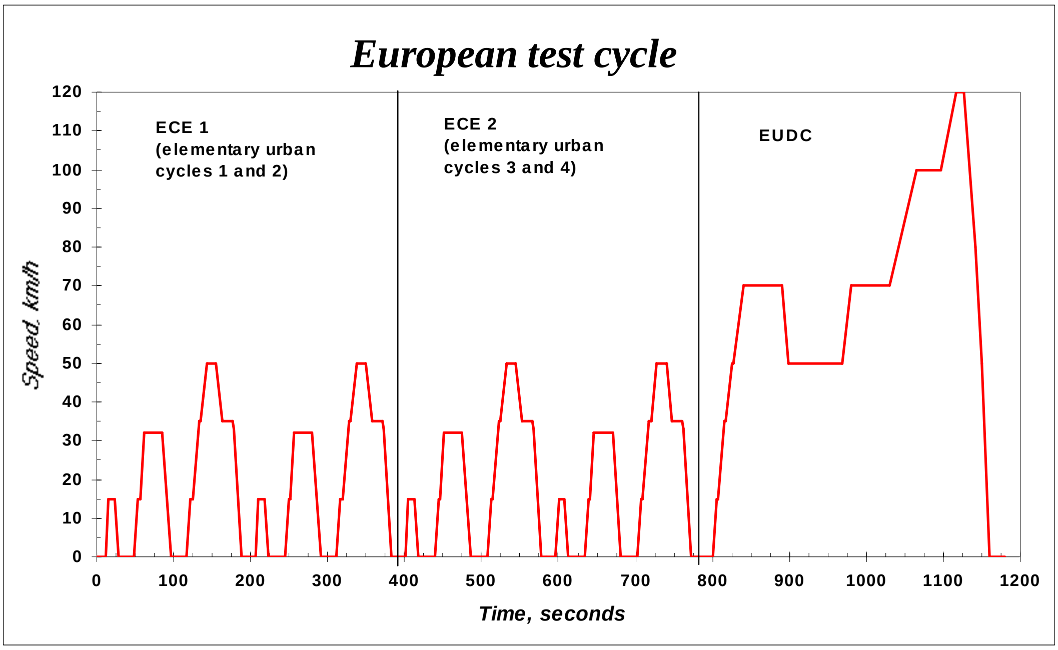


Figure 18. European test cycle.

4.2.4 PAH emissions and Ames tests

A set of polyaromatic hydrocarbons (PAHs) were analyzed from the soluble organic fraction (SOF sample), which was obtained by Soxhlet extraction of particles with dichloromethane. For mutagenicity analyses, the solvent was exchanged to dimethyl sulfoxide (DMSO).

PAH analyses were performed by using GC/SIM-MS after a liquid chromatographic purification of the extract. EPA 610 PAH mixture from Supelco was used as the calibration standard. Detection limits were 0.01 µg component/sample with an accuracy of measurement of ~30%. The extraction procedure and PAH analyses were carried out at Nablabs laboratories. The detection limits as µg/kWh or µg/k varies with application and test cycle. In these tests, detection limit for Euro 2 engine was 0.1 µg/kWh, for Euro 3 bus 0.16 µg/km, for Euro 4 truck 0.15 µg/km using FIGE cycle and 0.35 µg/km using “TR” cycle, and for light-duty cars 0.02 µg/km.

There are also several lists on priority PAHs as is described in Chapter 3.2. In this report, seven PAH compounds based on the European and the US EPA definition is shown in the figures. This sum of seven PAHs in the Figures include the following compounds:

- benzo(a)anthracene (BbA)
- benzo(b)fluoranthene (BbF)
- benzo(k)-fluoranthene (BkF)

- chrysene/triphenylene (ChrT)
- benzo(a)pyrene (BaP)
- indeno(1,2,3-cd)-pyrene (IP)
- 7,12-dimethylbenz(a)anthracene (7,12BaA)

Ames-test using *Salmonella typhimurium* bacteria strains was used to evaluate the mutagenicity of the extracted particulate samples. One strain (TA98) was used without metabolic activation (-S9). The results are calculated in krev/km, which represents the mutagenic activity in emission basis.

With most engine/vehicle/fuel combinations 3-4 samples were analysed. Thus error bars in this report represent the true deviation calculated from these measurements taking into account all sources of uncertainty from engine/vehicle characteristics to analytical methods.

One option to analyse PAHs and mutagenicity of diesel exhaust would be taking semivolatile portion of diesel exhaust into account. Typically, only lighter PAHs are found from semivolatile portion of diesel exhaust. However, a study by Doel (2005) showed that a significant share of heavy PAHs can exist in the semivolatile portion especially with DPF (diesel particle filter) equipped diesel vehicles and gasoline cars.

In principle, it would be reasonable to consider both particulate and semivolatile phase for PAH and mutagenicity analyses. However, this would duplicate the costs of the analytical work due to the fact that the analyses should be carried out separately from particulate and semivolatile phases. Earlier experience at VTT has shown that semivolatile portion of diesel exhaust can be toxic to *Salmonella typhimurium bacteria strains*, and thus it would be too risky to combine particle and semivolatile samples for mutagenicity tests.

5 Results

5.1 Regulated gaseous emissions

The numerical results of the regulated emissions are shown in Appendices 2 and 4.

CO emissions were very low for the tested heavy-duty application, less than 0.4 g/kWh or g/km (Figure 19). One exception to a previous discovery are CO emission from Euro 3 bus without catalyst being around 1.2 g/km. Extremely low CO emission, only 0.13 g/km, was reached for Euro 4 truck with FIGE cycle. For heavy-duty engine and vehicles, CO emissions were only a fraction of the limit values (there is no limit values for HDs chassis dynamometer tests. However, the respective limits were estimated by conversion of ESC test cycle values). The CO emissions with passenger cars were rather close to Euro 3 limit (0.64 g/km).

There was no significant difference in CO emission between DIR-15 and DIR-30 fuels for heavy-duty vehicles or engine. CO emission from Euro 4 truck with FIGE cycle was only third of the HC emission from Euro 4 truck with “TR jakelu” cycle. CO emission for the passenger cars was 20% lower with DIR-15 fuel when compared to DIR-30 fuel.

HC emissions from heavy-duty applications were very low similarly to CO emissions. HC emissions from passenger cars varied from 0.05 to 0.09 g/km, which is very low emission level. HC emissions from both heavy-duty and light-duty vehicles were reduced with DIR-15 fuel when compared to DIR-30 fuel. This reduction in HC emission was 20% for passenger cars and 50% for Euro 4 truck with the delivery cycle “TR jakelu”, while it was around 30% for Euro 3 bus with the catalyst.

NO_x emission was for Euro 2 bus engine around 5.5 g/kWh, for Euro 3 bus around 8-9 g/km with and without the catalyst, while for Euro 4 truck with FIGE cycle around 4.5 g/km. The delivery cycle “TR jakelu” with Euro 4 truck gave 20% higher NO_x emission compared to FIGE cycle. For light-duty cars NO_x emissions were 0.4 g/km. NO_x emissions from all diesel applications were relatively or very close to the limit values, or estimated limit values.

NO_x emissions from Euro 2 engine, Euro 3 bus and Euro 4 truck with FIGE cycle were around 5% lower with DIR-15 fuel when compared to DIR-30 fuel. For passenger cars and Euro 4 truck with delivery cycle, it was not possible to see an evident difference in NO_x emissions between DIR-15 and DIR-30 fuels.

A total aromatic content in fuel had no effect on a measured fuel consumption.

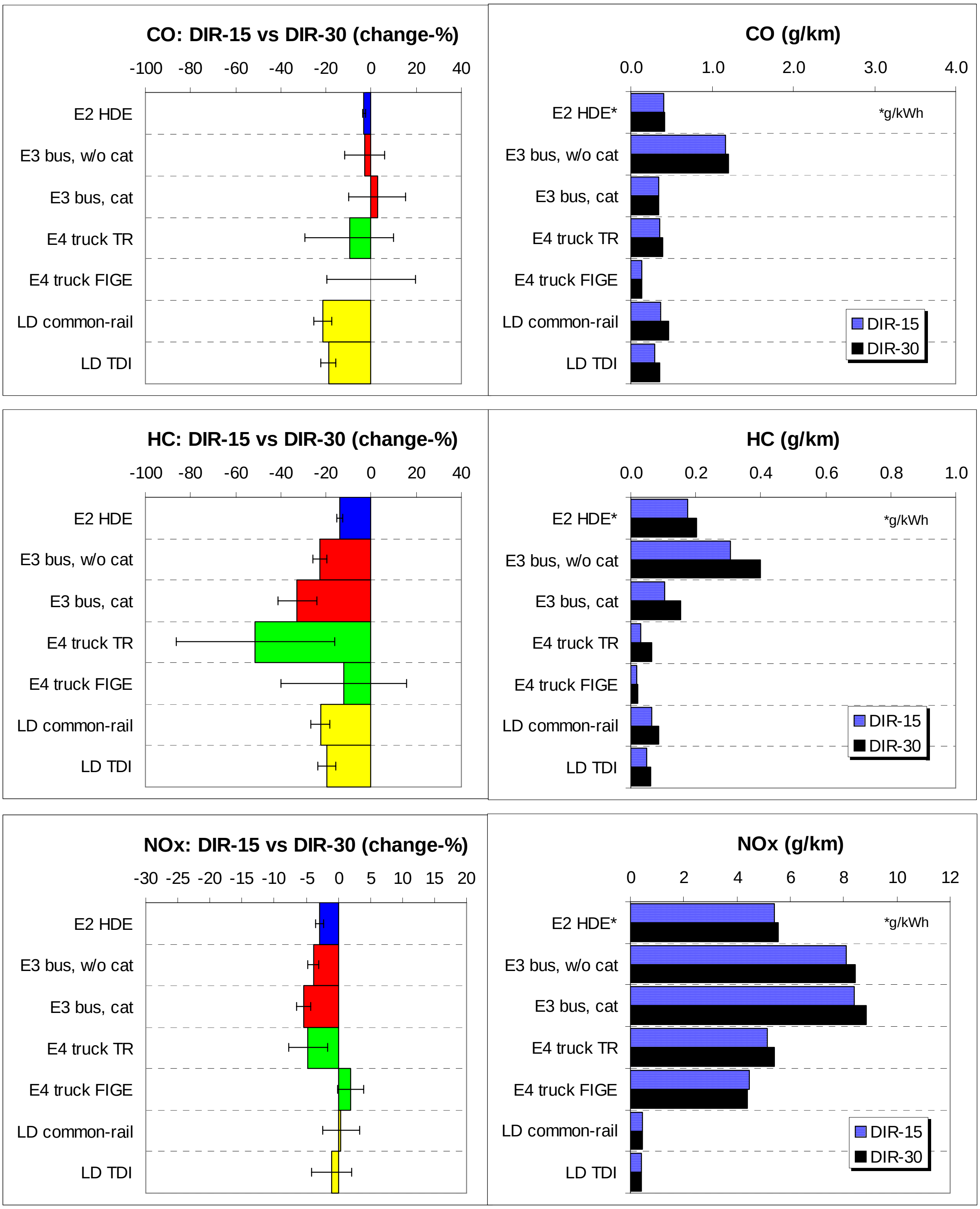


Figure 19. Regulated gaseous emissions. Results with different applications cannot be directly compared with each other due to different test cycles (HD engine- g/kWh [7]).

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[7] *The results for this HDE using ESC test (g/kWh) can be multiplied by factor 1.8 to correspond approximately the results that would be obtained by using Braunschweig cycle (g/km)*

5.2 Particulate matter, PAH and mutagenicity

Particulate matter emission from Euro 2 bus engine was around 0.06 g/kWh, which is low level when compared to respective limit value of 0.15 g/kWh with ECE R49 test cycle (Figure 20). No limit values exist for particulate matter emissions using heavy-duty chassis dynamometer tests. However, it is known that e.g. on average, a two-axle city bus requires about 1.8 kWh of work per km over the Braunschweig cycle. Thus, Euro 3 limit value for PM emission using ESC test cycle (1999/96/EC) would correspond about 0.18 g/km limit-value over Braunschweig test on chassis dynamometer, which was met with Euro 3 bus tested in this study, both with and without oxidation catalyst.

For Euro 4 truck with FIGE cycle, PM emission was a quarter of the emission level of Euro 3 bus equipped with catalyst. This is close to the ratio of Euro 4/Euro 3 limit values for PM emissions for ESC and ETC test cycle (Euro 4 is around fifth of the Euro 3 PM limit). However, the PM emission level was 2.5 times higher when using the delivery cycle “TR-jakelu” than when using the FIGE cycle. The difference between these cycles was not as high for regulated gaseous emissions, and thus it might be concluded that the particle oxidation catalyst is not working as efficiently in the low-speed driving conditions of the delivery cycle than in the FIGE cycle.

Both passenger cars represent Euro 3 emission level, and they also fulfil the PM emission limit of 0.05 g/km with the European test cycle. However, the TDI car was very close to the limit value.

Total particulate matter emission was slightly lower with the DIR-15 fuel than with the DIR-30 fuel for other applications than Euro 3 bus. The most significant change in PM emission was seen for Euro 4 truck when running FIGE test cycle. Total aromatic content of DIR-15 fuel was 15 wt%, whereas DIR-30 fuel contained 30 wt% of aromatics. Polyaromatic content (di+) of DIR-15 fuel was 1 wt%, and of DIR-30 fuel 5 wt%, respectively.

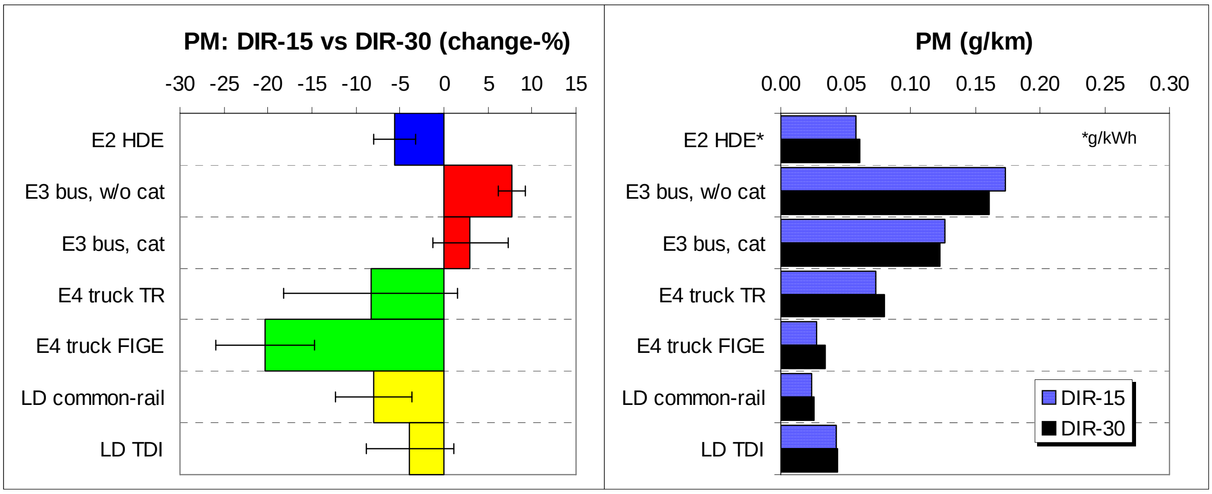

Figure 20. PM emission results with DIR-15 and DIR-30 test fuels (right-hand side) and change-% when comparing DIR-15 fuel to the DIR-30 fuel (left-hand side). Results with different applications cannot be directly compared with each other due to different test cycles (note HD engine- g/kWh [8]).

Table 12 shows the SOF portion of particulate matter from different engine/vehicle applications. The uncertainty of SOF analyses is relatively high. However, it can be seen that particles from Euro 2 bus engine contain around 20% of SOF. Euro 3 bus equipped with oxidation catalyst, Euro 4 truck equipped with particle oxidation catalyst and a TDI car showed SOF level around 10-15%. Particles from Euro 3 bus without catalyst were rather wet showing SOF content around 40%. In this case, a slight influence of fuel was seen indicating a higher SOF portion for lower aromatic fuel, but it is difficult to conclude if this is significant. It seems that particle emissions with diesel applications equipped with catalyst produce rather dry particles. However, engine-out particles can be surprisingly wet especially at low driving speeds.

Table 12. Soluble organic fraction (SOF) of particulate matter.

	Euro 2 HDE	Euro 3 bus		Euro 4 truck		LD cars	
	w/o cat	w/o cat	with cat	TR-cycle	FIGE	common-rail	TDI
	SOF (%)	SOF (%)	SOF (%)	SOF (%)	SOF (%)	SOF (%)	SOF (%)
DIR-15	16-24	40-45	12-15	10-16	11-18	25	13
DIR-30	17-26	32-38	10-15	10-14	8-15	31	13

Figures 21 and 22 show the results from PAH analyses and Ames tests of particulate SOF portion. The numerical results are shown in Appendices 3-4. When these results are compared to other studies, it is noted that BaP emission and Ames mutagenicity with TA98 test strain (-S9) are at similar level as reported elsewhere for diesel applications (see chapter 3.4).

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[8] *The results for this HDE using ESC test (g/kWh) can be multiplied by factor 1.8 to correspond approximately the results that would be obtained by using Braunschweig cycle (g/km)*

BaP emissions were extremely low, below 0.5 µg/kWh or µg/km for heavy-duty applications and for common-rail car. With Euro 4 truck engine equipped with particle oxidation catalyst, the BaP emission did not exceed the detection limit with the FIGE cycle, whereas with the delivery cycle (TR-jakelu), almost similar BaP emission level as with the Euro 3 bus without catalyst was seen. Oxidation catalyst removed BaP from particulate SOF so effectively with Euro 3 bus, that BaP was observed only with the fuel with higher polyaromatic content (DIR-30). The highest BaP level was observed with a TDI car. The average emission level of 7 individual priority PAHs is shown in Figures 24-25.

Sum of seven PAH compounds showed systematic benefit for lower aromatic DIR-15 fuel when compared to DIR-30 fuel despite of very low general PAH emission level. For Euro 4 truck equipped with particle oxidation catalyst, the sum of seven PAHs was below detection limit. With other applications the sum of seven PAHs was 20-80% lower with the DIR-15 fuel containing 1 wt% of polyaromatics (di+) than for DIR-30 fuel containing 5 wt% of polyaromatics. This change was significant for Euro 2 HD engine and Euro 3 bus, but to lesser extent with passenger cars. For Euro 4 truck equipped with particle oxidation catalyst, the PAH emission level was too low to see significant changes.

Ames test showed results well in-line with the PAH results (Figures 22 and 23). Significant benefit was seen of reducing polyaromatic content of fuel for all heavy-duty and light-duty applications studied. With Euro 4 truck, which was equipped with particle oxidation catalyst, a significant response in Ames test was observed even though the PAH emission level was extremely low, below detection limit with FIGE test cycle. In addition, a substantial benefit of reducing polyaromatic content of diesel fuel was observed for this Euro 4 truck with both test cycles used. This indicates that the other exhaust compounds than those classified as the priority PAHs may play a significant role in Ames mutagenicity in this case.

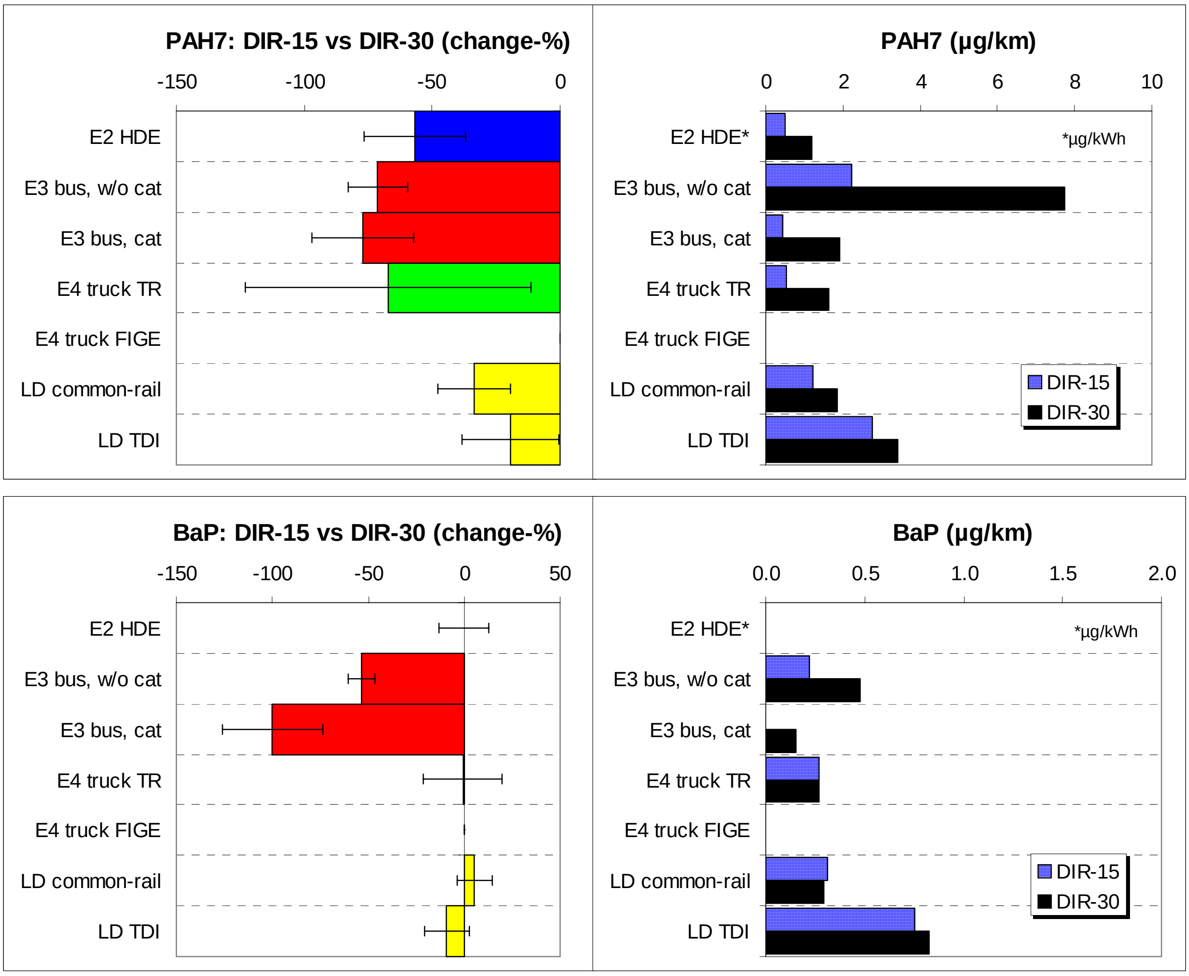

Figure 21. Sum of seven PAHs and benzo(a)pyrene emissions with DIR-15 and DIR-30 test fuels (right-hand side) and change-% when comparing DIR-15 fuel to the DIR-30 fuel (left-hand side). Results with different applications cannot be directly compared with each other due to different test cycles (note HD engine- g/kWh [9]).

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[9] *The results for this HDE using ESC test (g/kWh) can be multiplied by factor 1.8 to correspond approximately the results that would be obtained by using Braunschweig cycle (g/km)*

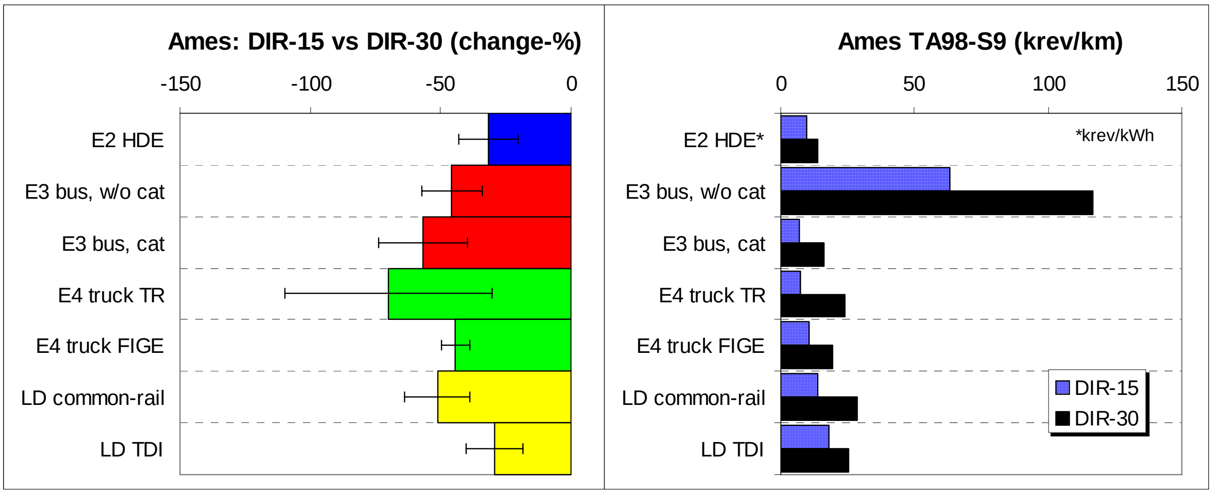

Figure 22. Results from Ames test (TA98-S9) with DIR-15 and DIR-30 test fuels (right-hand side) and change-% when comparing DIR-15 fuel to the DIR-30 fuel (left-hand side). Results with different applications cannot be directly compared with each other due to different test cycles (note HD engine- g/kWh [10]*).*

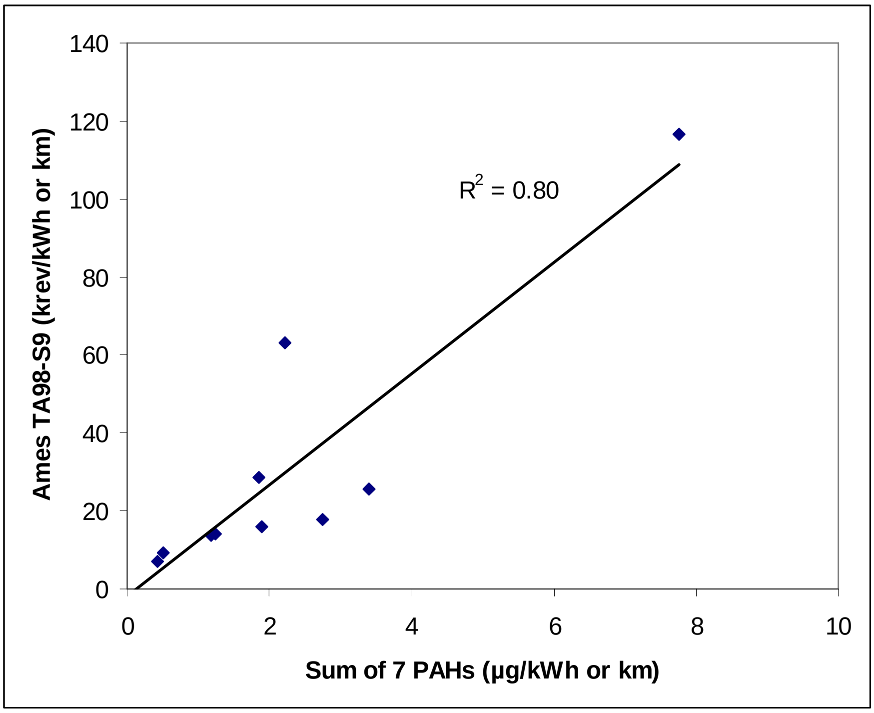

Figure 23. Correlation between the sum of 7 PAHs and Ames mutagenicity from the particulate SOF samples analyzed in this study.

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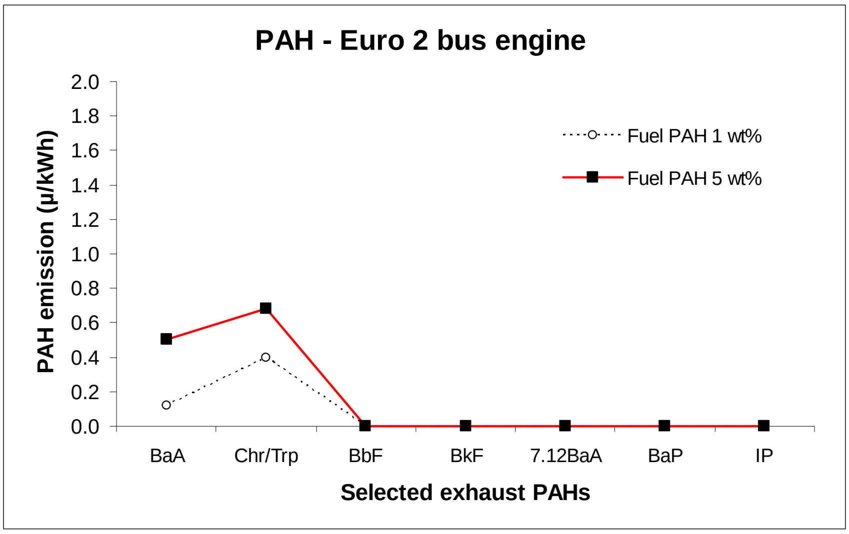
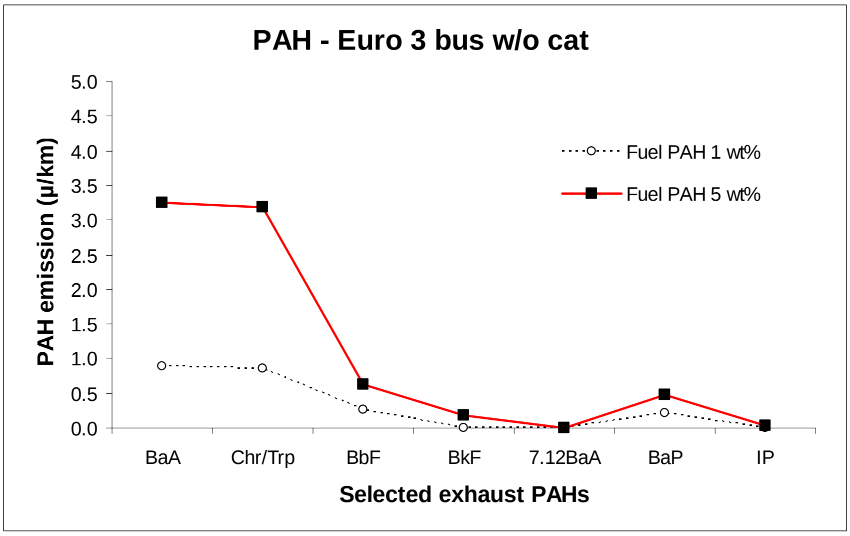
[10] *The results for this HDE using ESC test (g/kWh) can be multiplied by factor 1.8 to correspond approximately the results that would be obtained by using Braunschweig cycle (g/km)*





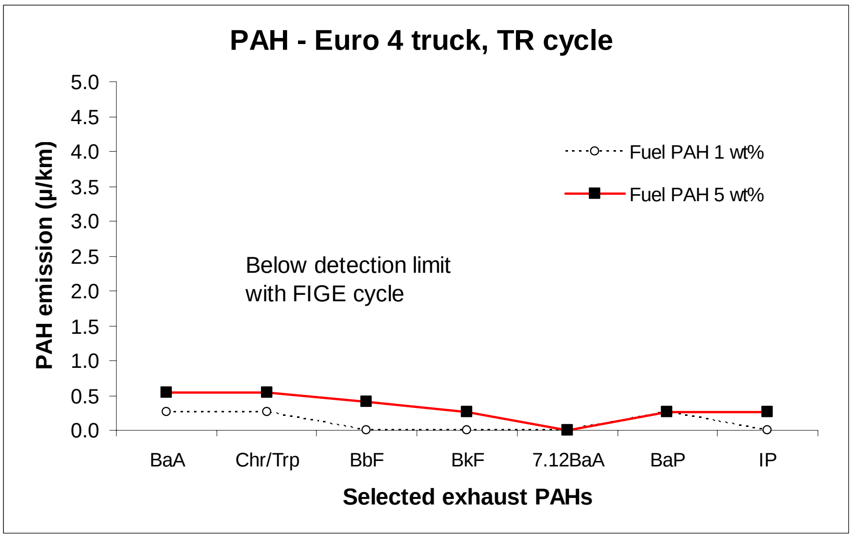
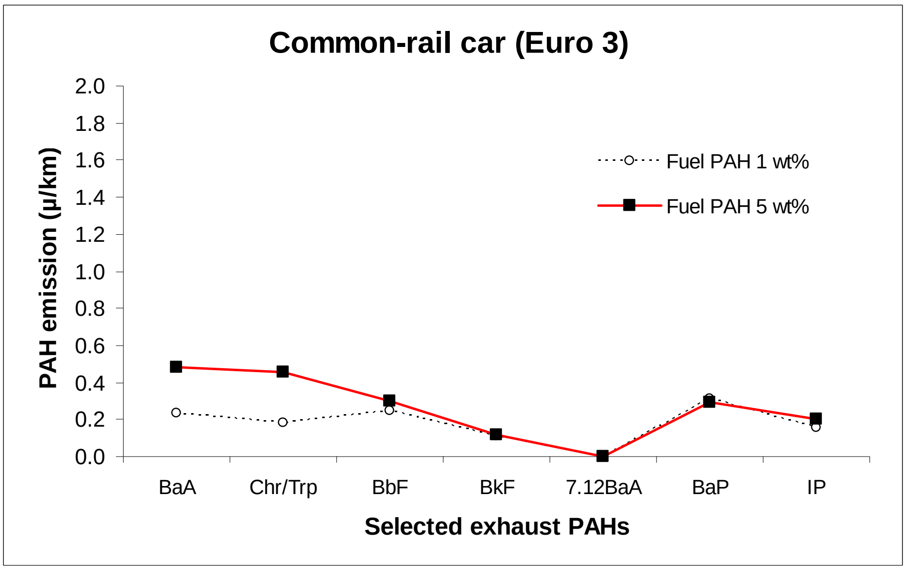


Figure 24. Examples of 7 priority PAHs with Euro 2 enginem Euro 3 bus and Euro 4 truck without catalyst.



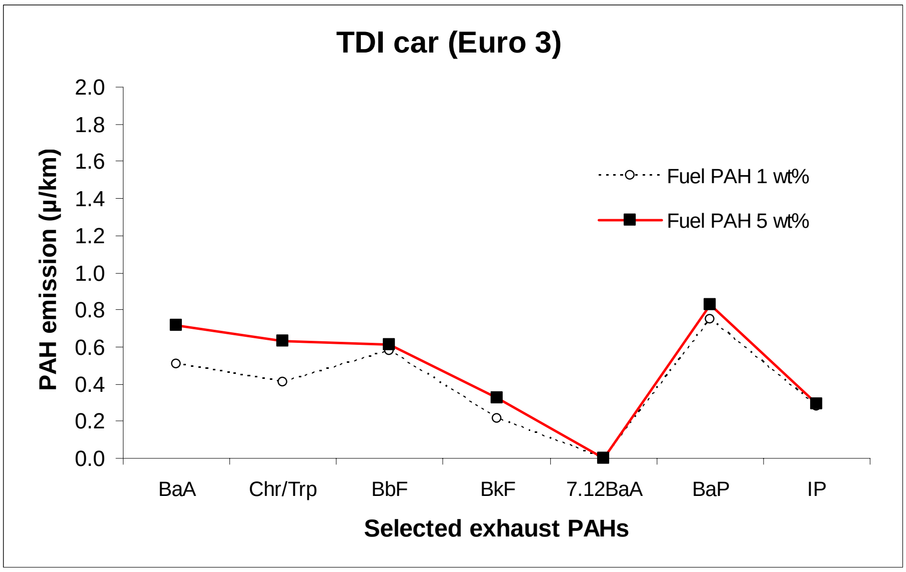


Figure 25. Example of emissions of 7 individual PAHs with passenger cars.

6 Summary

In Finland, the influence of polyaromatic hydrocarbons of diesel fuel on the PAH emissions was studied in programmes funded by National Technology Agency of Finland (Tekes), Neste Oil, VTT Processes and Ministry of the Environment.

The harmfulness of polyaromatic hydrocarbons (PAH) in diesel fuel is a known fact. Thus the amount of polyaromatic hydrocarbons with two or higher number of rings (di+) is limited in the Directive 2003/17/EC. However, the limit for PAHs in the Directive is high: max. 11 wt% (di+). The effect of fuel PAHs on the exhaust emissions have been extensively studied in past. Based on those studies the reformulated class 1 diesel fuel in Sweden has a limit value for PAHs: max. 0.02 vol% of PAHs (tri+), and in Finland, before 2004 a tax incentive was given to diesel fuel fulfilling certain properties, i.a. total aromatics max. 20 vol-%.

Recently studies on the effect of fuel aromatics on the PAH emissions have focused on light-duty cars. Relationship between fuel and exhaust PAHs on the heavy-duty engines/vehicles has not been studied with modern heavy-duty technologies, and very little heavy-duty data is available using transient test cycles that describe real life conditions.

This report includes a review on the diesel exhaust in general, formation of particles in diesel engine, composition of particles. In addition, general aspects on polyaromatic compounds and their harmfulness are discussed, as well as mutagenicity and significance of the different test methods. The results from different studies on PAHs and mutagenicity of automotive exhaust were collected as tables. Also studies on the effect of fuel aromatic content on PAH and mutagenicity results were reviewed. These items are not summarized here, but are found from the report body.

In the experimental task, two diesel fuels were studied, one with polyaromatic content of 1 wt% (di+) and the other with polyaromatic content of 5 wt%. Tests were carried out using six diesel technologies: Euro 2 heavy-duty engine, Euro 3 bus without catalyst, Euro 3 bus with oxidation catalyst, Euro 4 truck equipped with particle oxidation catalyst and two passenger cars (common-rail and TDI). Euro 2 engine was tested using the steady-state ESC test cycle, whereas the heavy-duty (Euro 3 bus, Euro 4 truck) and light-duty vehicles were tested on chassis dynamometer using transient test cycles.

A set of polyaromatic hydrocarbons (PAHs) were analyzed from the soluble organic fraction of particulate matter. Many PAH compounds are known carcinogens. There are also several lists on priority PAHs. In this report, main emphasis was given to the following seven PAH compounds based on the European and the US EPA definitions: benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)-fluoranthene, chrysene/triphenylene, benzo(a)pyrene, indeno(1,2,3-cd)-pyrene and 7,12-dimethylbenz(a)anthracene.

A large number of mutagenicity tests are available, such as Ames test, which us a bacterial reverse mutation test. Ames test is in vitro test commonly used as screening tool for genotoxic and mutation inducing activity. There are several drawbacks of using Ames test to study mutagenicity: the bacterial test does not reflect in vivo mutagenic activity, or show good correlation with the rodent cancer bioassay. However, bacteria tests can be used as effective first-step screening tool, as they are relatively simple and inexpensive. In this study, Ames-test using *Salmonella typhimurium* bacteria strain TA98-S9 was used to evaluate the mutagenicity of the samples. With most engine/vehicle/fuel combinations 3-4 samples were analysed for PAH and Ames.

CO emission and HC emissions were low for the tested heavy-duty and light-duty vehicles. There was no significant difference in CO emission between two fuels studied, but HC emissions were lower with the fuel containing less aromatics. NO_x emissions were around 8-9 g/km for Euro 3 bus when using Braunschweig cycle, while for Euro 4 truck around 4.5 g/km when using FIGE cycle, and some 20% higher when using the delivery cycle “TR jakelu”. NO_x emission level from Euro 3 bus and Euro 4 was around 5% lower with the fuel containing less aromatics, whereas no difference between fuels was seen for passenger cars.

PM emission from Euro 2 bus engine was around 0.06 g/kWh, which is very low level when compared to respective limit value. PM emission from the Euro 3 bus was at the expected level, and PM emission from Euro 4 truck was a quarter of that level, but only when using FIGE cycle. The PM emission from Euro 4 truck was 2.5 times higher with the delivery cycle than with the FIGE cycle, which indicates differences in operation of particle oxidation catalyst in the low-speed driving conditions. Both passenger cars represented Euro 3 emission level, and PM emissions also fulfilled the respective limit value. Total particulate matter emission was slightly lower with fuel with lower aromatic content for the other applications than Euro 3 bus engine. The most significant change in PM emission was seen for Euro 4 truck when running the FIGE test cycle.

The particles from Euro 2 bus engine contained around 20% of soluble organic fraction (SOF). Euro 3 bus equipped with oxidation catalyst, Euro 4 truck equipped with particle oxidation catalyst and a TDI car showed SOF level around 10-15%. Particles from Euro 3 bus without catalyst were rather wet with around 40% SOF content. It seems that particles from diesel applications equipped with catalyst are rather dry, but engine-out particles can be surprisingly wet especially at low loads.

Reducing polyaromatic content of diesel fuel showed systematic benefit in the PAH emissions. The only exception was the Euro 4 truck, for which the PAH emissions were too low to draw conclusions. The PAH emissions were 20-80% lower when polyaromatic content (di+) of fuel was reduced from 5 to 1 wt%. This change was especially significant for the Euro 2 HD engine and Euro 3 bus. For Euro 3 bus, reducing polyaromatics of fuel from 5 to 1 wt% resulted in as high reduction in PAH emissions as oxidation catalyst.

Ames test showed results well in-line with PAH results. Significant benefit of reducing polyaromatic content of fuel was seen for all heavy-duty and light-duty applications studied. Even with Euro 4 truck equipped with particle oxidation catalyst, for which almost no priority PAHs was observed, a substantial benefit of lower polyaromatic content of diesel fuel was evident in the Ames test.

As a summary, this study showed the significance of polyaromatic content of diesel fuel on the exhaust emissions from the Euro 2 to Euro 4 heavy-duty and light-duty diesel engines/vehicles studied. Significant benefit of reducing polyaromatic content of diesel fuel was seen, particularly as concerns polyaromatic hydrocarbons and Ames mutagenicity of particulate extract. However, no exact limit value for fuel polyaromatic content can be recommended based on this study. In addition, open questions remain on the performance at cold ambient temperatures.

7 References

Aakko, P. et al. (2000) Characterization of Engine Exhaust Fingerprints and their contribution on air quality – VTT’s contribution. EC Project PARFIN JOF3-CT97-0040. Research Report VTT ENE5/4/2000.

Aakko, P., Nylund, N.-O., Westerholm, M., Marjamäki, M., Moisio, M., Hillamo, R. & Mäkelä, T. (2002) Emissions from heavy-duty engine with and without aftertreatment using selected biofuels. FISITA Paper F02E195.

Altshuler, S. (2002). Nanoparticle emissions. Presentation to the joint IANGV/NGVC Technical Committee Meeting. Washington DC. In conjunction with NGV 2002.

Cuvelier, D. et al. (2002) Evaluation of diesel fuel cetane and aromatics effects on emissions from Euro-3 engines. CONCAWE report 4/02.

Dastillung, M. et al. (2005) Impact of a potential reduction of the polyaromatics content of diesel fuel on the EU refining industry. CONCAWE report 7/05.

Dec, J.E., (1997) A Conceptual Model of DI DIesel Combustion Based on Laser-Sheet Imaging, SAE Paper 970873 (1997). In Musculus et al. 2005.

De Craecker, et al. (2005) Fuel effects on emissions from advanced diesel engines and vehicles. CONCAWE report 2/05.

DEFRA (2001) Expert Panel on Air Quality Standards Airborne Particles: What is the appropriate measurement on which to base a standard? A Discusson Document Department for Environment, Food & Rural Affairs. 17 May 2001. http://www.defra.gov.uk/environment/airquality/aqs/air_measure/

Dieselnet, http://www.dieselnet.com/standards/cycles/etc.html (restricted website)

Doel et al. (2005) Evaluation of automotive polycyclic aromatic hydrocarbon emissions. CONCAWE report 4/05.

ETAD (1998) Significance of the bacterial reverse mutation test as predictor of rodent and human carcinogenicity. ETAD Information Notice No. 7, March 1998.

EU PAH Position Paper (2001) Ambient air pollution by polycyclic Aromatic Hydrocarbons (PAH). Position Paper. 27 July 2001.

Foster, D. (2004) Some issues that may be important when considering future emission regulations. University of Wisconsin – Madison. International Symposium of the Vehicles Emissions Regulations. Tokyo, Japan. February 3, 2004.

Grägg, K. (1992) Undersökning av tre dieselbränslen främst med avseende på slutkokpunktens betydelse for avgasutsläppet. Report MTC 9109B.

Grägg, K. (1994) Effects of environmentally classified diesel fuels, RME and blends of diesel fuels and RME on exhaust emissions. Report MTC 9209B.

Grägg, K. (1995) Chemical characterization and biological testing of exhaust emissions from truck fuelled with EC1 and EPEFE reference fuel. Report MTC 1995.

Hall. D. et al. (1998) Polycyclic aromatic hydrocarbons in Automotive exhaust emissions and fuels. CONCAWE report 98/55.

Hill, N. (2004) EU Fuel Quality Monitoring – 2004 Summary Report. (AEAT/ED51182/R2)

Karila, K. et al. (2004) Reduction of particulate emissions in compression ignition engines. Publications of the Internal Combustion Engine Laboratory Helsinki University of Technology 78. 2004.

Kokko, J., Rantanen, L., Pentikäinen, J., Honkanen, T., Aakko. P. & Lappi, M. Reduced Particulate Emissions with Reformulated Gasoline. SAE Technical Paper 2000-01-2017.

Lappi M. & Rihko, L. (1996) Moottoriajoneuvojen sääntelemättömät pakokaasupäästöt. Merkitys ja mittaustekniikka. VTT, Espoo. VTT Tiedotteita 1748. 168 s. + liitt. 18 s.

MAN website, Euro 4 with EGR and the MAN PM-KAT® particle filter (http://www.man-mn.com/en/Innovation_%26_Kompetenz/Euro_4_Technology.jsp)

Maron, D. and Ames, B. (1983) Revised methods for the Salmonella mutegenicity test. Mutation Research, 113: 173-212.

Musculus, M. P., Dec, J. E., Pickett, L. M. & Idicheria, C. (2005) In-Cylinder Imaging of Conventional and Advanced, Low-Temperature Diesel Combustion. Diesel Engine Emissions Reduction Conference (DEER), Chicago, USA. August 2005.

Nylund, N.-O., Erkkilä, K., (2005) Heavy-duty truck emissions and fuel comsumption simulating real-world driving in laboratory conditions, Diesel Engine Emissions Reduction Conference (DEER), August 21-25, Chicago, Illinois, USA (http://www.eere.energy.gov/vehiclesandfuels/pdfs/deer_2005/session5/2005_deer_erkkila.pdf)

Nylund, N.-O., Erkkilä, K., Lappi, M. & Ikonen, M. (2004) Transit bus emission study: comparison of emissions from diesel and natural gas buses. VTT report PRO3/P5150/04.

Perander, J., Rantanen, L., Pentikäinen, J., Aakko, P. & Jäntti, A. No major backsliding in air quality when replacing MTBE with isooctane in CARB gasoline. SAE Technical Paper 2001-01-3588.

Rantanen, L., Mikkonen, S., Nylund, L., Kociba, P., Lappi, M. & Nylund, N-O. (1993) Effect of fuel on the regulated, unregulated and mutagenic emissions of DI diesel engines Proc. SAE Technical Paper 932686

Rantanen, L., Juva, A. Niemi, A., Mikkonen, S., Aakko, P. & Lappi, M. (1996) Effect of reformulated diesel fuel on unregulated emissions of light duty vehicles. SAE Technical Paper 961970.

Rantanen, L., Linnaila, R., Aakko, P. & Harju, T. (2005) NExtBTL - biodiesel fuel of the second generation. SAE Technical Paper 2005-01-3771.

Rickeard, D. J. (2000) Particulate Emissions. Presentation for Hart's World Fuels Conference, Brussels, May 2000.

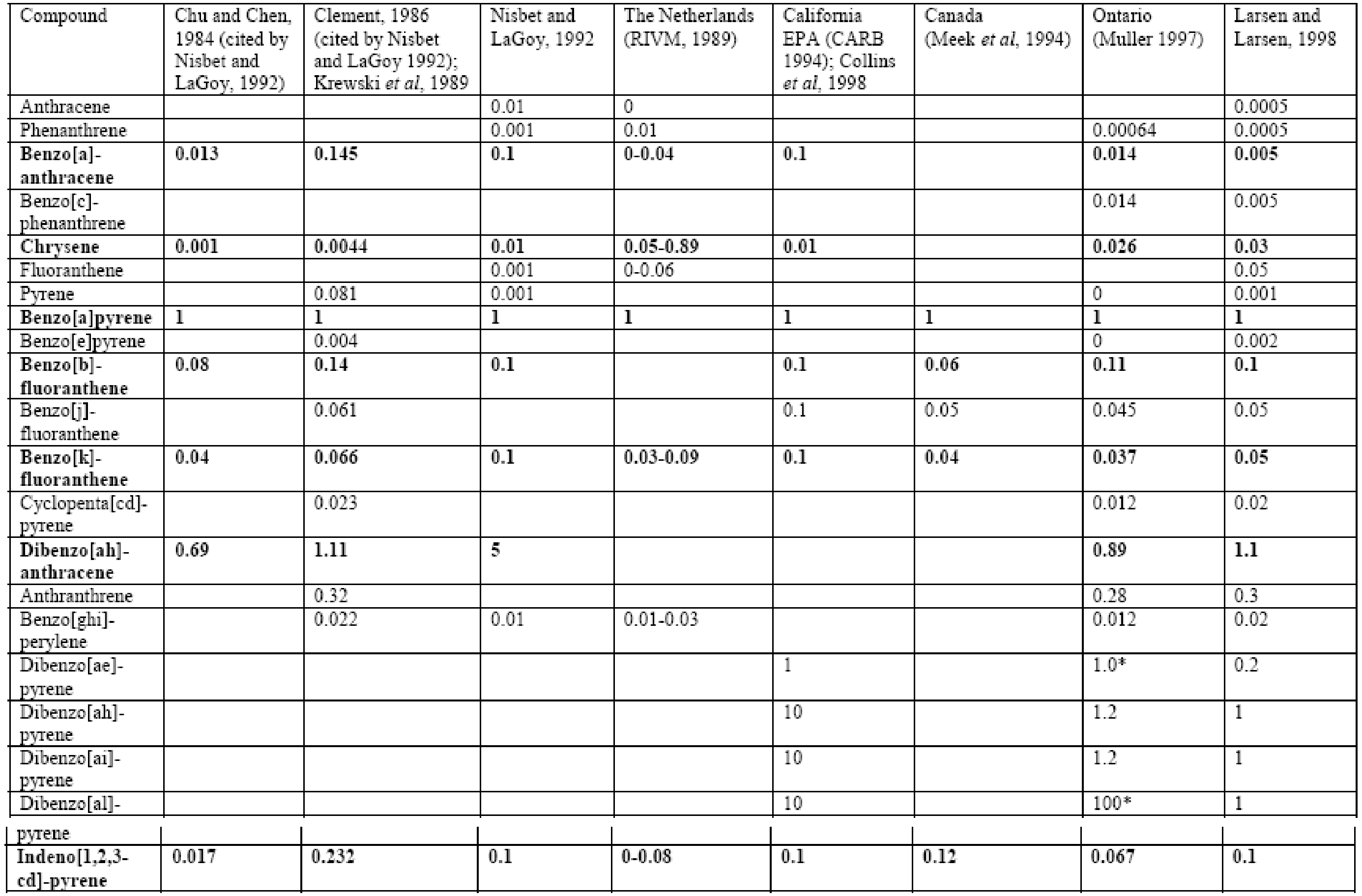
RTA website, Roth-Technik Austria Ges.m.b.H. (http://www.roth-technik-austria.de/english/gointoframe.php?page=content_03_01_03_06.html)

Tao, Feng. (2003) Numerical Modeling of Soot and NOx Formation in Non-Stationary Diesel Flames with Complex Chemistry. Chalmers University of Technology. Doctoral Thesis. 2003.

US EPA (2001) List of Mobile Source Air Toxics (MSATs) http://www.epa.gov/otaq/regs/toxics/msatlist.pdf

US EPA. (2002) Health Assessment Document For Diesel Engine Exhaust. United States Environmental Protection Agency. EPA/600/8-90/057F. May 2002.

Relative potency of individual PAH compared to BaP (TEF-values), according to different authors (from PAH Position Paper 2001)



Compound	Chu and Chen, 1984 (cited by Nisbet and LaGoy, 1992)	Clement, 1986 (cited by Nisbet and LaGoy 1992); Krewski *et al*, 1989	Nisbet and LaGoy, 1992	The Netherlands (RIVM, 1989)	California EPA (CARB 1994); Collins *et al*, 1998	Canada (Meek *et al*, 1994)	Ontario (Muller 1997)	Larsen and Larsen, 1998
Anthracene			0.01	0				0.0005
Phenanthrene			0.001	0.01			0.00064	0.0005
Benzo[a]-anthracene	**0.013**	**0.145**	**0.1**	0-0.04	**0.1**		**0.014**	**0.005**
Benzo[c]-phenanthrene							0.014	0.005
Chrysene	**0.001**	**0.0044**	**0.01**	**0.05-0.89**	**0.01**		**0.026**	**0.03**
Fluoranthene			0.001	0-0.06				0.05
Pyrene		0.081	0.001				0	0.001
Benzo[a]pyrene	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
Benzo[e]pyrene		0.004					0	0.002
Benzo[b]-fluoranthene	**0.08**	**0.14**	**0.1**		**0.1**	**0.06**	**0.11**	**0.1**
Benzo[j]-fluoranthene		0.061			0.1	0.05	0.045	0.05
Benzo[k]-fluoranthene	**0.04**	**0.066**	**0.1**	**0.03-0.09**	**0.1**	**0.04**	**0.037**	**0.05**
Cyclopenta[cd]-pyrene		0.023					0.012	0.02
Dibenzo[ah]-anthracene	**0.69**	**1.11**	**5**				**0.89**	**1.1**
Anthranthrene		0.32					0.28	0.3
Benzo[ghi]-perylene		0.022	0.01	0.01-0.03			0.012	0.02
Dibenzo[ae]-pyrene					1		1.0*	0.2
Dibenzo[ah]-pyrene					10		1.2	1
Dibenzo[ai]-pyrene					10		1.2	1
Dibenzo[al]-pyrene					10		100*	1
Indeno[1,2,3-cd]-pyrene	**0.017**	**0.232**	**0.1**	0-0.08	0.1	0.12	0.067	0.1

Regulated emissions from individual tests.

Engine/ vehicles	Cycle	Fuel	Test id.	CO	HC	NOx	PM	CO2	Fuel Cons. measured	Fuel Cons. theoretical
Euro 2 bus engine w/o cat				g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	
Euro 2, w/o cat	ESC	DIR-15	05090P2	0.41	0.17	5.4	0.060	698	223.4	
Euro 2, w/o cat	ESC	DIR-15	05091P2	0.40	0.18	5.4	0.061	699	224.3	
Euro 2, w/o cat	ESC	DIR-15	05092P2	0.40	0.18	5.4	0.059	699	224.0	
Euro 2, w/o cat	ESC	DIR-15	05093P2	0.40	0.17	5.3	0.056	698	223.4	
Euro 2, w/o cat	ESC	DIR-15	05094P2	0.40	0.18	5.4	0.057	697	223.6	
Euro 2, w/o cat	ESC	DIR-15	05095P2	0.40	0.18	5.4	0.056	699	224.5	
Euro 2, w/o cat	ESC	DIR-30	05096P2	0.42	0.20	5.5	0.061	709	224.3	
Euro 2, w/o cat	ESC	DIR-30	05097P2	0.42	0.20	5.5	0.063	709	224.3	
Euro 2, w/o cat	ESC	DIR-30	05098P2	0.42	0.20	5.6	0.061	710	224.6	
Euro 2, w/o cat	ESC	DIR-30	05099P2	0.41	0.21	5.5	0.061	709	225.0	
Euro 2, w/o cat	ESC	DIR-30	05100P2	0.41	0.21	5.6	0.061	711	224.0	
Euro 2, w/o cat	ESC	DIR-30	05101P2	0.41	0.21	5.6	0.063	712	224.3	
Euro 3 bus w/o cat				g/km	g/km	g/km	g/km	g/km	l/100 km	l/100 km
Euro 3 bus, w/o c	Braunschweig	DIR-15	25R343	1.34	0.30	8.0	0.168	1099	44.1	41.6
Euro 3 bus, w/o c	Braunschweig	DIR-15	25R344	1.34	0.32	8.1	0.172	1096	43.9	41.5
Euro 3 bus, w/o c	Braunschweig	DIR-15	25R345	0.94	0.30	8.2	0.176	1100	44.1	41.6
Euro 3 bus, w/o c	Braunschweig	DIR-15	25R346	1.06	0.30	8.1	0.178	1096	43.9	41.5
Euro 3 bus, w/o c	Braunschweig	DIR-30	25R339	1.16	0.38	8.5	0.162	1106	44.0	41.7
Euro 3 bus, w/o c	Braunschweig	DIR-30	25R340	1.22	0.42	8.5	0.159	1129	44.0	42.6
Euro 3 bus, w/o c	Braunschweig	DIR-30	25R341	1.23	0.40	8.4	0.162	1122	43.9	42.3
Euro 3 bus with cat				g/km	g/km	g/km	g/km	g/km	l/100 km	l/100 km
Euro 3 bus, cat	Braunschweig	DIR-15	25R331	0.40	0.10	8.5	0.140	1125	44.1	42.5
Euro 3 bus, cat	Braunschweig	DIR-15	25R332	0.37	0.09	8.4	0.124	1125	44.0	42.5
Euro 3 bus, cat	Braunschweig	DIR-15	25R333	0.26	0.10	8.3	0.120	1106	43.8	41.8
Euro 3 bus, cat	Braunschweig	DIR-15	25R334	0.36	0.12	8.4	0.121	1132	44.1	42.8
Euro 3 bus, cat	Braunschweig	DIR-30	25R335	0.38	0.14	8.7	0.122	1138	44.2	42.9
Euro 3 bus, cat	Braunschweig	DIR-30	25R336	0.37	0.16	8.9	0.126	1140	44.4	42.9
Euro 3 bus, cat	Braunschweig	DIR-30	25R337	0.30	0.16	8.9	0.118	1137	44.2	42.8
Euro 3 bus, cat	Braunschweig	DIR-30	25R338	0.30	0.16	9.0	0.124	1138	44.3	42.8
Euro 4 truck with particle oxidation catalyst										
Euro 4 truck, cat	TRJAKELU	DIR-15	25R524	0.33	0.05	5.2	0.075	896	36.0	33.8
Euro 4 truck, cat	TRJAKELU	DIR-15	25R525	0.42	0.01	5.2	0.079	898	36.1	33.9
Euro 4 truck, cat	TRJAKELU	DIR-15	25R526	0.50	0.01	4.9	0.088	901	35.9	34.1
Euro 4 truck, cat	TRJAKELU	DIR-15	25R527	0.30	0.04	5.0	0.076	898	36.0	33.9
Euro 4 truck, cat	TRJAKELU	DIR-15	25R540	0.31	0.03	5.1	0.063	894	36.0	33.8
Euro 4 truck, cat	TRJAKELU	DIR-15	25R541	0.25	0.05	5.4	0.058	894	35.7	33.8
Euro 4 truck, cat	TRJAKELU	DIR-30	25R528	0.34	0.08	5.5	0.075	904	36.1	34.0
Euro 4 truck, cat	TRJAKELU	DIR-30	25R529	0.32	0.08	5.4	0.075	909	35.8	34.2
Euro 4 truck, cat	TRJAKELU	DIR-30	25R530	0.46	0.05	5.1	0.085	925	36.2	34.9
Euro 4 truck, cat	TRJAKELU	DIR-30	25R531	0.44	0.05	5.5	0.084	904	36.0	34.0
Euro 4 truck, cat	FIGE	DIR-15	25R536	0.12	0.01	4.4	0.027	678	27.6	25.6
Euro 4 truck, cat	FIGE	DIR-15	25R537	0.18	0.02	4.6	0.029	678	27.4	25.6
Euro 4 truck, cat	FIGE	DIR-15	25R538	0.12	0.02	4.4	0.027	689	27.5	26.0
Euro 4 truck, cat	FIGE	DIR-15	25R539	0.11	0.02	4.5	0.026	679	27.4	25.7
Euro 4 truck, cat	FIGE	DIR-30	25R532	0.11	0.03	4.4	0.034	688	27.7	25.9
Euro 4 truck, cat	FIGE	DIR-30	25R533	0.17	0.03	4.4	0.038	688	27.6	25.9
Euro 4 truck, cat	FIGE	DIR-30	25R534	0.13	0.01	4.3	0.032	686	27.9	25.8
Euro 4 truck, cat	FIGE	DIR-30	25R535	0.12	0.01	4.5	0.033	685	27.7	25.8
Light-duty cars										
LD car, common-	European	DIR15	25111	0.36	0.06	0.47	0.022	124		4.7
LD car, common-	European	DIR15	25114	0.41	0.07	0.44	0.022	117		4.5
LD car, common-	European	DIR15	25115	0.34	0.06	0.44	0.023	120		4.6
LD car, common-	European	DIR15	25118	0.37	0.06	0.43	0.024	120		4.6
LD car, common-	European	DIR-15	25128	0.35	0.06	0.41	0.026	118		4.5
LD car, common-	European	DIR-15	25129	0.38	0.07	0.41	0.026	118		4.5
LD car, common-	European	DIR-15	25132*	0.38	0.07	0.43	0.024	118		4.5
LD car, common-	European	DIR30	25119	0.46	0.08	0.42	0.026	119		4.5
LD car, common-	European	DIR30	25122	0.48	0.09	0.43	0.025	118		4.5
LD car, common-	European	DIR30	25123	0.47	0.08	0.44	0.027	122		4.6
LD car, common-	European	DIR30	25126	0.49	0.09	0.43	0.027	120		4.6
LD car, TDI	European	DIR15	25112	0.30	0.05	0.42	0.047	145		5.5
LD car, TDI	European	DIR15	25113	0.29	0.05	0.41	0.047	143		5.4
LD car, TDI	European	DIR15	25116	0.29	0.05	0.38	0.046	143		5.4
LD car, TDI	European	DIR15	25117	0.27	0.05	0.41	0.042	145		5.5
LD car, TDI	European	DIR-15	25127	0.30	0.05	0.39	0.041	141		5.4
LD car, TDI	European	DIR-15	25130	0.31	0.05	0.39	0.037	143		5.4
LD car, TDI	European	DIR-15	25131*	0.31	0.05	0.39	0.038	143		5.4
LD car, TDI	European	DIR30	25120	0.36	0.06	0.40	0.044	144		5.4
LD car, TDI	European	DIR30	25121	0.38	0.06	0.39	0.044	144		5.4
LD car, TDI	European	DIR30	25124	0.35	0.06	0.40	0.044	144		5.4
LD car, TDI	European	DIR30	25125	0.36	0.06	0.42	0.044	144		5.4
* reference run with different particulate sampling system										

* PM results with Euro 3 bus from standard system, for Euro 2 engine and Euro 4 truck an average of standard and high-capacity systems.

PAH and Ames results from individual tests.

	Cycle	Fuel	Fuel PAH	N	Acy	Ace	Flu	Phe	An	F	P	BaA	Chr/Trp	BbF	BkF	7.12BaA	BaP	IP	DBahA	PAH 7	Ames TA98-S9
Euro 2 bus engine w/o cat				µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	µg/kWh	krev/kWh
Euro 2, w/o cat	ESC	DIR-15		*two samples from combined filters:*																	
Euro 2, w/o cat	ESC	DIR-15		0.07	0.00	0.07	0.07	0.97	0.28	1.38	5.8	0.14	0.21	bd	bd	bd	bd	bd	1.17	0.4	8.0
Euro 2, w/o cat	ESC	DIR-15		bd	0.00	0.10	bd	2.40	0.29	2.89	5.7	0.10	0.58	bd	bd	bd	bd	bd	bd	0.7	10.9
Euro 2, w/o cat	ESC	DIR-30		*two samples from combined filters:*																	
Euro 2, w/o cat	ESC	DIR-30		0.07	0.07	0.07	0.21	3.40	0.42	1.66	3.8	0.55	0.55	bd	bd	bd	bd	bd	0.07	1.1	12.8
Euro 2, w/o cat	ESC	DIR-30		bd	0.00	0.18	0.18	5.75	0.64	2.92	3.6	0.46	0.82	bd	bd	bd	bd	bd	bd	1.3	14.9
Euro 3 bus w/o cat				µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/kr	µg/km	µg/kr	µg/kr	µg/km	µg/kr	µg/kr	µg/km	µg/km	krev/km
Euro 3 bus, w/o cat	Braunschwe	DIR-15	25R343																		
Euro 3 bus, w/o cat	Braunschwe	DIR-15	25R344	0.14	bd	0.58	0.14	4.6	1.01	5.76	31.5	0.86	0.86	0.29	0.00	bd	0.29	0.00	bd	2.3	61.8
Euro 3 bus, w/o cat	Braunschwe	DIR-15	25R345	0.46	bd	0.91	0.30	4.9	1.06	6.23	34.8	0.91	0.91	0.30	0.00	bd	0.15	bd	bd	2.3	66.9
Euro 3 bus, w/o cat	Braunschwe	DIR-15	25R346	0.31	bd	0.77	0.31	4.1	1.07	5.82	32.0	0.92	0.92	0.31	0.00	bd	0.31	bd	bd	2.5	74.2
Euro 3 bus, w/o cat	Braunschwe	DIR-15	344-346 d7	0.29	0.29	0.43	0.43	6.7	1.43	5.71	28.4	0.86	0.71	0.14	0.00	bd	0.14	bd	bd	1.9	50.0
Euro 3 bus, w/o cat	Braunschwe	DIR-30	25R339	0.14	0.00	0.28	0.57	11.4	1.14	8.25	18.4	3.27	2.99	0.43	0.14	bd	0.43	0.00	bd	7.3	112.9
Euro 3 bus, w/o cat	Braunschwe	DIR-30	25R340	0.30	bd	0.15	0.76	13.7	1.83	9.45	21.2	3.81	3.81	0.76	0.30	bd	0.61	0.15	bd	9.4	118.1
Euro 3 bus, w/o cat	Braunschwe	DIR-30	25R341	0.44	0.00	0.29	0.44	10.9	1.31	7.55	18.7	3.05	3.05	0.73	0.15	bd	0.58	0.00	bd	7.6	132.2
Euro 3 bus, w/o cat	Braunschwe	DIR-30	339-341, d	0.43	bd	0.29	0.58	10.8	1.01	7.64	17.9	2.88	2.88	0.58	0.14	bd	0.29	0.00	bd	6.8	103.0
Euro 3 bus with cat				µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	krev/km
Euro 3 bus, cat	Braunschwe	DIR-15	25R331																		
Euro 3 bus, cat	Braunschwe	DIR-15	25R332	0.15	bd	0.00	0.15	4.4	0.87	1.60	5.5	0.29	0.15	0.00	0.00	bd	0.00	bd	0.00	0.4	6.7
Euro 3 bus, cat	Braunschwe	DIR-15	25R333	0.14	bd	0.00	0.00	3.9	0.70	1.41	6.5	0.28	0.14	0.14	0.00	bd	0.00	bd	0.00	0.6	6.9
Euro 3 bus, cat	Braunschwe	DIR-15	25R334	0.92	bd	0.00	0.15	4.0	0.92	1.53	6.4	0.15	0.15	0.15	0.00	bd	0.00	bd	0.00	0.5	8.5
Euro 3 bus, cat	Braunschwe	DIR-15	332-334 d	0.14	bd	0.00	0.00	3.5	0.72	2.60	8.8	0.14	0.14	0.00	bd	bd	bd	bd	0.00	0.3	5.7
Euro 3 bus, cat	Braunschwe	DIR-30	25R335																		
Euro 3 bus, cat	Braunschwe	DIR-30	25R336	0.16	bd	0.00	0.16	10.0	1.13	2.90	5.5	0.97	0.81	0.32	0.00	bd	0.16	bd	bd	2.3	20.9
Euro 3 bus, cat	Braunschwe	DIR-30	25R337	0.15	bd	0.00	0.15	9.1	1.08	2.00	4.2	0.77	0.62	0.31	0.00	bd	0.15	0.00	0.00	1.9	15.1
Euro 3 bus, cat	Braunschwe	DIR-30	25R338	0.00	bd	0.00	0.16	8.4	0.95	2.69	5.1	0.95	0.79	0.16	0.00	bd	0.16	0.00	bd	2.1	16.2
Euro 3 bus, cat	Braunschwe	DIR-30	336-338 d7	0.29	bd	0.14	0.29	10.7	1.43	4.28	8.0	0.57	0.57	0.14	0.00	bd	0.14	bd	bd	1.4	12.0
Euro 4 truck with particle oxidation catalyst				µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/kr	µg/km	µg/kr	µg/kr	µg/km	µg/kr	µg/kr	µg/km	µg/km	krev/km
Euro 4 truck, cat	TRJAKELU	DIR-15	25R524																		
Euro 4 truck, cat	TRJAKELU	DIR-15	25R525*	bd	4.4	bd	2.4	31.3	2.0	7.5	9.5	bd	bd	bd	bd	bd	bd	bd	bd	bd	5.1
Euro 4 truck, cat	TRJAKELU	DIR-15	25R526	2.7	4.9	0.27	3.8	28.5	1.9	7.3	9.8	bd	bd	bd	bd	bd	0.27	bd	bd	0.3	3.2
Euro 4 truck, cat	TRJAKELU	DIR-15	25R527	bd	2.4	bd	1.9	23.6	1.9	7.9	9.8	0.26	0.26	bd	bd	bd	0.26	bd	bd	0.8	11.2
Euro 4 truck, cat	TRJAKELU	DIR-15	25R540																		
Euro 4 truck, cat	TRJAKELU	DIR-15	25R541																		
Euro 4 truck, cat	TRJAKELU	DIR-30	25R528	1.9	4.3	0.27	4.6	69.3	7.1	8.4	8.4	0.82	0.82	0.54	0.27	bd	0.27	0.27	bd	3.0	16.4
Euro 4 truck, cat	TRJAKELU	DIR-30	25R529	2.7	2.4	1.09	3.5	44.8	2.7	6.8	6.8	0.54	0.54	0.27	bd	bd	bd	bd	bd	1.4	29.5
Euro 4 truck, cat	TRJAKELU	DIR-30	25R530	1.9	4.3	0.27	5.1	71.6	3.5	7.6	7.3	0.27	0.27	bd	bd	bd	bd	bd	bd	0.5	25.9
Euro 4 truck, cat	TRJAKELU	DIR-30	25R531																		
Euro 4 truck, cat	FIGE	DIR-15	25R536	bd	0.11	bd	bd	2.9	0.11	0.34	0.69	bd	bd	bd	bd	bd	bd	bd	bd	bd	
Euro 4 truck, cat	FIGE	DIR-15	25R537																		9.4
Euro 4 truck, cat	FIGE	DIR-15	25R538	bd	bd	bd	bd	2.2	0.12	0.46	0.69	bd	bd	bd	bd	bd	bd	bd	bd	bd	11.1
Euro 4 truck, cat	FIGE	DIR-15	25R539																		11.6
Euro 4 truck, cat	FIGE	DIR-30	25R532	bd	0.16	bd	0.2	6.8	0.16	0.64	0.80	bd	bd	bd	bd	bd	bd	bd	bd	bd	18.8
Euro 4 truck, cat	FIGE	DIR-30	25R533*																		6.4
Euro 4 truck, cat	FIGE	DIR-30	25R534	bd	0.11	bd	0.1	7.0	0.23	0.69	0.80	bd	bd	bd	bd	bd	bd	bd	bd	bd	
Euro 4 truck, cat	FIGE	DIR-30	25R535																		19.7
Light-duty cars				µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/km	µg/kr	µg/km	µg/kr	µg/kr	µg/km	µg/kr	µg/kr	µg/km	µg/km	krev/km
LD car, common-rail	European	DIR15	25111	0.056	0.07	0.04	0.20	3.15	0.37	1.06	2.224	0.26	0.17	0.26	0.15	bd	0.35	0.19	bd	1.4	12.3
LD car, common-rail	European	DIR15	25114																		
LD car, common-rail	European	DIR15	25115	0.037	0.06	0.06	0.22	3.53	0.41	1.08	2.233	0.20	0.17	0.15	0.06	bd	0.13	0.17	bd	0.9	13.2
LD car, common-rail	European	DIR15	25118	0.092	0.07	0.09	0.18	3.50	0.40	1.25	2.761	0.24	0.17	0.26	0.11	bd	0.31	0.15	bd	1.2	12.8
LD car, common-rail	European	DIR-15	25128																		
LD car, common-rail	European	DIR-15	25129	0.056	0.08	0.08	0.24	5.83	0.68	1.5	3.007	0.23	0.23	0.32	0.13	bd	0.45	0.11	bd	1.5	17.7
LD car, common-rail	European	DIR-15	25132*																		
LD car, common-rail	European	DIR30	25119																		
LD car, common-rail	European	DIR30	25122	0.019	bd	0.09	0.21	5.79	0.67	1.3	1.4	0.45	0.45	0.22	0.09	bd	0.22	0.15	bd	1.6	25.7
LD car, common-rail	European	DIR30	25123	0.114	bd	0.04	0.21	6.82	0.80	1.4	1.7	0.55	0.47	0.34	0.13	bd	0.3	0.15	bd	2.0	27.9
LD car, common-rail	European	DIR30	25126	0	0.04	0.08	0.19	7.76	0.89	1.5	1.7	0.45	0.45	0.34	0.13	bd	0.36	0.3	bd	2.0	32.4
LD car, TDI	European	DIR15	25112	0.33	0.31	0.09	0.90	5.69	0.66	2.2	3.5	0.46	0.40	0.39	0.15	bd	0.42	0.15	bd	2.0	19.5
LD car, TDI	European	DIR15	25113	0.24	0.29	0.17	0.92	7.19	0.55	2.8	4.6	0.50	0.39	0.66	0.37	bd	1.01	0.31	bd	3.2	19.3
LD car, TDI	European	DIR15	25116	0.351	0.35	0.18	1.00	6.84	0.67	3.1	5.2	0.59	0.50	0.63	0.18	bd	0.7	0.37	bd	3.0	20.8
LD car, TDI	European	DIR15	25117	0.15	0.17	0.13	0.54	5.98	0.56	2.1	3.7	0.49	0.36	0.64	0.17	bd	0.86	0.30	bd	2.8	
LD car, TDI	European	DIR-15	25127																		
LD car, TDI	European	DIR-15	25130																		12.3
LD car, TDI	European	DIR-15	25131**																		
LD car, TDI	European	DIR30	25120																		
LD car, TDI	European	DIR30	25121	0.151	0.19	0.11	1.17	8.67	1.0	2.6	3.4	0.79	0.73	0.72	0.41	bd	1.04	0.41	bd	4.1	25.6
LD car, TDI	European	DIR30	25124	0.244	0.15	0.09	0.79	10.9	1.3	2.4	2.8	0.58	0.51	0.45	0.21	bd	0.58	0.13	bd	2.5	24.6
LD car, TDI	European	DIR30	25125	0.179	0.20	0.16	0.91	10.1	1.2	2.8	3.6	0.78	0.66	0.68	0.36	bd	0.86	0.34	bd	3.7	26.4

* toxicity at highest doses in Ames test, rejected from average

** reference run with different particulate sampling system

Average results of regulated emissions, CO2 and fuel consumption.

Engine/ vehicles	Cycle	Fuel	PAH wt%	CO	HC	NOx	PM	CO2	Fuel Cons. measured	Fuel Cons. theoretical
Euro 2 bus engine, w/o cat				g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	
E2 HDE	ESC	DIR-15	1 wt%	0.40	0.18	5.4	0.058	698	223.9	
E2 HDE	ESC	DIR-30	5 wt%	0.42	0.20	5.6	0.061	710	224.4	
Euro 3 bus with and w/o cat				g/km	g/km	g/km	g/km	g/km	l/100 km	l/100 km
E3 bus w/o cat	Braunschweig	DIR-15	1 wt%	1.17	0.31	8.1	0.173	1098	44.0	41.5
E3 bus, w/o cat	Braunschweig	DIR-30	5 wt%	1.20	0.40	8.4	0.161	1119	44.0	42.2
E3 bus cat	Braunschweig	DIR-15	1 wt%	0.35	0.10	8.4	0.126	1122	44.0	42.4
E3 bus cat	Braunschweig	DIR-30	5 wt%	0.34	0.15	8.9	0.123	1138	44.3	42.9
Euro 4 truck with particle oxidation catalyst										
E4 truck "TR"	TR-jakelu	DIR-15	1 wt%	0.35	0.03	5.1	0.073	897	36.0	33.9
E4 truck "TR"		DIR-30	5 wt%	0.39	0.06	5.4	0.080	910	36.0	34.3
E4 truck FIGE	FIGE	DIR-15	1 wt%	0.13	0.02	4.5	0.027	681	27.5	25.7
E4 truck FIGE	FIGE	DIR-30	5 wt%	0.13	0.02	4.4	0.034	687	27.7	25.9
Light-duty cars										
LD common-ra	European	DIR-15	1 wt%	0.37	0.07	0.43	0.024	119		4.5
LD common-ra	European	DIR-30	5 wt%	0.47	0.08	0.43	0.026	120		4.6
LD TDI	European	DIR-15	1 wt%	0.29	0.05	0.40	0.042	143		5.4
LD TDI	European	DIR-30	5 wt%	0.36	0.06	0.40	0.044	144		5.4

Average results of PAH analyses and Ames tests.

	Cycle	Fuel	Fuel PAH	N	Acy	Ace	Flu	Phe	An	F	P	**BaA**	**Chr/Trp**	**BbF**	**BkF**	**7.12BaA**	**BaP**	**IP**	DBahA	**PAH 7**	**Ames TA98-S9**
Euro 2 bus engine w/o cat				g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	g/kWh	krev/kWh
E2 HDE, w/o cat	ESC	DIR-15	1 wt%	0.07	0.00	0.08	0.07	1.7	0.28	2.1	5.7	**0.12**	**0.40**	**bd**	**bd**	**bd**	**bd**	**bd**	1.17	0.5	9.5
E2 HDE, w/o cat	ESC	DIR-30	5 wt%	0.07	0.04	0.13	0.20	4.6	0.53	2.3	3.7	**0.51**	**0.69**	**bd**	**bd**	**bd**	**bd**	**bd**	0.07	1.2	13.8
Euro 3 bus with and w/o cat				g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km	g/km	krev/km
E3 bus, w/o cat	Braunschwe	DIR-15	1 wt%	0.30	0.29	0.67	0.30	5.1	1.14	5.9	31.7	**0.89**	**0.85**	**0.26**	**0.00**	**bd**	**0.22**	**0.00**	bd	2.2	63.2
E3 bus, w/o cat	Braunschwe	DIR-30	5 wt%	0.33	0.00	0.25	0.59	11.7	1.32	8.2	19.0	**3.3**	**3.2**	**0.63**	**0.18**	**bd**	**0.48**	**0.04**	bd	7.8	116.6
E3 bus, cat	Braunschwe	DIR-15	1 wt%	0.34	bd	0.00	0.08	3.9	0.80	1.8	6.8	**0.22**	**0.15**	**0.07**	**0.00**	**bd**	**0.00**	**bd**	0.00	0.4	6.9
E3 bus, cat	Braunschwe	DIR-30	5 wt%	0.15	bd	0.04	0.19	9.5	1.15	3.0	5.7	**0.82**	**0.70**	**0.23**	**0.00**	**bd**	**0.15**	**0.00**	0.00	1.9	16.0
Euro 4 truck with particle oxidation catalyst																					
E4 truck, cat	TR-jakelu	DIR-15	1 wt%	2.7	3.9	0.27	2.7	27.8	1.9	7.6	9.7	**0.26**	**0.26**	**bd**	**bd**	**bd**	**0.27**	**bd**	bd	0.5	7.2
E4 truck, cat	TR-jakelu	DIR-30	5 wt%	2.2	3.7	0.54	4.4	61.9	4.4	7.6	7.5	**0.54**	**0.54**	**0.41**	**0.27**	**bd**	**0.27**	**0.27**	bd	1.6	23.9
E4 truck, cat	FIGE	DIR-15	1 wt%	bd	0.11	bd	bd	2.5	0.12	0.4	0.7	**bd**	**bd**	**bd**	**bd**	**bd**	**bd**	**bd**	bd	bd	10.7
E4 truck, cat	FIGE	DIR-30	5 wt%	bd	0.14	bd	0.14	6.9	0.20	0.7	0.8	**bd**	**bd**	**bd**	**bd**	**bd**	**bd**	**bd**	bd	bd	19.2
Light-duty cars																					
LD car, common-	European	DIR-15	1 wt%	0.06	0.07	0.07	0.21	4.0	0.47	1.2	2.6	**0.23**	**0.18**	**0.25**	**0.11**	**bd**	**0.31**	**0.15**	bd	1.2	14.0
LD car, common-	European	DIR-30	5 wt%	0.04	0.04	0.07	0.20	6.8	0.79	1.4	1.6	**0.48**	**0.46**	**0.30**	**0.12**	**bd**	**0.30**	**0.20**	bd	1.9	28.7
LD car, TDI	European	DIR-15	1 wt%	0.27	0.28	0.14	0.84	6.4	0.61	2.5	4.3	**0.51**	**0.41**	**0.58**	**0.22**	**bd**	**0.75**	**0.28**	bd	2.7	18.0
LD car, TDI	European	DIR-30	5 wt%	0.19	0.18	0.12	0.96	9.9	1.14	2.6	3.3	**0.72**	**0.63**	**0.61**	**0.33**	**bd**	**0.82**	**0.29**	bd	3.4	25.5