COMBUSTION PARTICLES AND NO_X FROM DIESEL AND PETROL VEHICLES

- A 2008 update including some biofuels and additional exhaust components

Ecotraffic

EXHAUST PARTICLES AND NO_X FROM DIESEL AND PETROL VEHICLES
- A 2008 update including some biofuels and additional exhaust components

A report for StatoilHydro
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Abbreviations, acronyms and glossary

ACEA	European Automobile Manufacturers Association
Al_2O_3	Oxide of alumina. Common material in the washcoat of catalytic converters.
Alkanes	Saturated hydrocarbons
AT	Aluminium titanate, a relatively "new" material for monoliths to diesel particle filters (DPFs)
BC	Black carbon or insoluble carbon
BMEP	Brake Mean Effective Pressure, the calculated average pressure in the cylinder necessary to perform the work put out by the engine. Friction and pumping losses imply that the actual indicated mean effective pressure (IMEP) in the cylinder must be higher than the BMEP.
BS	Black Smoke
BSFC	Brake Specific Fuel Consumption. Usually expressed in g fuel per kW of performed work.
BTL	Biomass To Liquid
CADC	Common Artemis Driving Cycle
CCRT™	Catalyzed Continuously Regenerating Particle filter
CeO_2	Ceria dioxide, a common material in the washcoat of catalytic converters but also as oxygen storage material to reduce the regeneration temperature of diesel particulate filters.
Cetane number	The ability of the fuel to ignite in compression ignition engines.
CIDI	Compression Ignition Direct Injection
CNC	Condensation Nuclei Counter (equivalent to CPC)
CNG	Compressed Natural Gas
CONCAWE	Conservation of Clean Air and Water in Europe, the oil companies' European association for environment, health and safety in refining and distribution
COPERT	Simulation model for vehicle emissions.
Cordierite	A common material for monoliths to automotive catalysts and diesel particle filters (DPFs)
CPC	Condensation Particle Counter (equivalent to CNC)
CRT™	Continuously Regenerating Particle filter
CVS	Constant Volume Sampler/Sampling, a dilution device used for dilution of engine/vehicle exhaust for emission measurements.
Cycloalkanes	Cycloalkanes (also called naphthenes) are saturated hydrocarbons with one or more carbon rings to which hydrogen atoms are attached according to the formula C_nH2_n.
D-CAT™	Toyota trade mark for a combined aftertreatment for particulate and NO_X emissions (see also DPNR)
DEER	Diesel Engine Emission Reduction Conference (USA)
$DeNO_X$	NO_X reducing catalyst for lean exhaust such as, e.g. diesel exhaust. In this type of catalyst, HC is used as NO_X reducing agent (see also HC-SCR)
DI	Direct Injection
DISI	Direct Injection Spark Ignition
DMA	Differential Mobility Analyzer
DME	Dimethyl Ether
DMM	Dekati Mass Monitor, an instrument (by Dekati Ltd. in Finland) for measuring (indirectly) particle mass in real time
DMPS	Differential Mobility Particle Sizer
DOE	U.S. Department of Energy

DPF	Diesel Particle Filter
DPNR	Particulate – NO_X Reduction System, Toyota nomenclature for a combined aftertreatment for particulate and NO_X emissions.
DR	Dilution Ratio
EC	Elemental carbon
EC	European Commission
EC1	Swedish environmental class 1 (EC1) fuel (diesel and petrol)
EC2	Swedish environmental class 2 (EC1) fuel (diesel and petrol)
EC3	Swedish environmental class 3 (EC1) fuel (diesel and petrol)
EEA	European Environment Agency
EEPS	Engine Exhaust Particle Sizer, an instrument (TSI Inc.) that measures particle number and particle size distribution in real time
EEV	Enhanced Environmentally Friendly Vehicle
EGR	Exhaust Gas Recirculation
ELPI	Electrical Low Pressure Impactor, an instrument (Dekati Ltd. in Finland) that measures particle number and particle size distribution in real time
ELR	European Load Response test, a test procedure for determining engine smoke under transient conditions
EPA	Environmental Protection Agency (USA)
ESC	European Stationary Cycle
ETC	European Transient Cycle
EUCAR	European Council for Automotive R&D, the automotive manufacturer's association for research and development in Europe
EUDC	Extra Urban Driving Cycle
EUI	Electronic Unit Injector
FAEE	Fatty Acid Ethyl Esters
FAME	Fatty Acid Methyl Esters
FIE	Fuel Injection Equipment
FT	Fischer-Tropsch
FTP-75	The driving cycle used for light-duty vehicles in the USA
GDI	Gasoline Direct Injection
GTL	Gas To Liquid
GTL	Biomass To Liquid
H_2SO_4	Sulphuric acid
HC-SCR	Selective catalytic NO_X reduction using HC as reducing agent (see also $DeNO_X$)
HD	Heavy-Duty
HIDE	Heavy-Duty Engine
HAD	Heavy-Duty Vehicle
IDA	Indirect injection
ILCE	Interlaboratory Correlation Exercise
IMEP	Indicated Mean Effective Pressure (see also BMEP)
IOF	Insoluble Organic Fraction
IOF	Insoluble Organic Fraction
ISFC	Fuel consumption without taking engine friction into account. Determination of ISFC is made by integrating the work performed by the gases in the combustion chamber (see also

	BSFC).
IUC	In-Use Compliance testing. Testing of vehicles to assess the durability of the emission reducing devices on a vehicle.
JRC	The Joint Research Centre, a research based policy support organisation and an integral part of the European Commission.
KFB	Swedish Transportation Research Board. A Swedish governmental organisation that was closed down a couple of years ago.
LD	Light-duty
LPG	Liquid Petroleum Gas
MPI	Multi Point Injection
mRSO	Modified (with viscosity reducing additives) crude rape seed oil (see also RSO)
MSAT	Mobile Source Air Toxics
Nanoparticle	A particle smaller than 50 nm. Slightly different definitions (of size) are also used.
NEDC	New European Driving Cycle
NExBTL™	Trade mark of the Finnish oil company Neste for a fuel made by hydrogenating vegetable oils and animal fats.
NH_3	Ammonia
NH_3-SCR	Selective catalytic NO_X reduction using ammonia (NH_3) as reducing agent.
NREL	National Renewable Laboratory
OBD	On-Board Diagnostics system
OEM	Original Equipment Manufacturer
PAC	Polycyclic Aromatic Compounds, see also PAH below
PAH	Polycyclic Aromatic Hydrocarbons
PAS	Photoelectric Aerosol Sensor, an instrument for measurement of soot mass in diesel exhaust
PM	Particulate Matter
PM_{10}	Particulate Matter with an aerodynamic diameter smaller than 10 μm
$PM_{2,5}$	Particulate Matter with an aerodynamic diameter smaller than 2,5 μm
PMP	Particulate Measurement Programme (the EU programme for developing new measurement methods for particle mass and number)
Polyaromatics	Aromatic compounds with two or more aromatic rings
ppmv	parts per million by volume
PUF	PolyUrethane Foam. Plugs of PUF are used for PAH sampling.
ROR	A “crude” (raw pressed oil, i.e. not transesterified) rape seed oil
RSO	Crude Rape Seed Oil, i.e. same as ROR (see above)
SAE	Society of Automotive Engineers
SCR	Selective Catalytic Reforming
SCR	Selective Catalytic Reduction, a NO_X reducing catalyst
SHED	Sealed Housing for Evaporative Determination
SI	Spark Ignition
SiC	Silicon Carbide, a common material for monoliths to diesel particle filters (DPFs)
SIF	Soluble Inorganic Fraction
SME	Soy Methyl Ester
SMPS	Scanning Mobility Particle Sizer
SO_2	Sulphur dioxide

SO_3	Sulphur trioxide
SOF	Soluble Organic Fraction
TA100	Strain of the bacteria salmonella typhimurium used in mutagenicity (Ames) test
TA98	Strain of the bacteria salmonella typhimurium used in mutagenicity (Ames) test
TD	Thermodenuder, a device that removes volatile aerosols and volatiles adsorbed on solid particles.
TDI	Turbo Direct Injection, the denotation by VW group for a direct injection diesel engine with a turbocharger.
TEOM	Tapered Element Oscillating Microbalance, an instrument (Rupprecht & Pataschnik) for measuring particle mass in real time
TWC	Three Way Catalyst
UDC	Urban Driving Cycle
UNECE	United Nations Economic Commission for Europe.
US06	A US driving cycle for light-duty vehicles with higher speed and greater accelerations than the normal US driving cycle (see also FTP-75)
VOF	Volatile Organic Fraction
VVT	Variable Valve Timing

EXECUTIVE SUMMARY

Introduction and background

The emissions from motor vehicles contribute considerably to the local air quality in densely populated areas but also have an impact on regional and global emissions. Although there has been a shift in focus from local emissions to global warming, local emissions are nevertheless of great concern. Many areas still have problems in meeting air quality norms for, e.g. particle mass and nitrogen dioxide (NO_2). Diesel vehicles contribute significantly to both these emission components, so these vehicles have been under scrutiny during the last couple of years. In order to reduce the emissions of greenhouse gases, the use of bio-components – as blending components but also as neat fuel – has gained an increasing interest. The impact of biofuels and biofuel blends on exhaust emissions is not yet fully clarified.

The aim of this work has been twofold, i.e. to update a study on particle and NO_X emissions conducted last year and to supplement the study with a couple of new topics such as, e.g. the impact of biocomponents in the fuel. A literature survey has been the major part of the study and also forms the basis for the discussion and the conclusions drawn in the report.

Regarding vehicle category, the main focus has been on diesel passenger cars, but to put the emission levels from these cars in perspective, a comparison with petrol cars and heavy-duty diesels has also been made. The trend of these emissions is also described covering the period from the introduction of the earliest European legislation including projections until year 2015, when the most advanced European emission limit, i.e. Euro 6, will be introduced. Parallel development in fuel qualities and the developments in engine and exhaust after treatment technologies are also covered in the study.

Particle emissions

The nature of particulate pollutants may be described from the different characteristics of particles including mass, particle number, the size distribution of the particle population, or the chemical composition. Soot is a major component of the particulate material in combustion engine exhaust but other constituents of importance are condensed organic material, ash and sulphur compounds originating from both the fuel as from the lubricating oil. Sulphur in the form of sulphate or sulphuric acid may give rise to early nucleation of particles, which serve as nuclei for hydrocarbon condensation.

The measurement of particulate mass (PM) has been the method used for diesel vehicle certification purposes and from this follows that the units used in the legislation are g/km for passenger cars (as they are measured for whole vehicle testing on chassis dynamometers) and g/kWh for heavy duty vehicles (emissions are measured for engines in engine test benches).

The evolution of gradually lower and lower emission limit values in parallel with a trend of successively improved fuel qualities (i.e. reduced sulphur concentrations) have encouraged and forced technical development of both engine performance and exhaust aftertreatment technologies to gain impressive achievements in regard to reduced exhaust particle emissions. During the recent year, further development of DPF technology has been

noted, as well as the introduction of NO_X reducing catalysts on light-duty vehicles in the USA and Europe. This is a remarkable achievement, since the emission limits in the USA and California are considered the toughest in the World and, in the latter case; also the future Euro 6 emission limits are fulfilled.

For diesel passenger cars, the emission limit values have been reduced from 140 mg/km in the Euro 1 certification that was introduced in year 1992 to 4,5 mg/km with the new Euro 5 certification that will be implemented in the autumn of year 2009. From the Euro 5b limit introduced in the autumn of year 2011, also particle number emissions will be measured in parallel with particle mass. The introduction of this measure is in line with the increasing awareness of the dangers in regard to human health caused by small particles (<100 nm). In this respect there is a fear that a reduction in PM will not necessarily be reflected in reduced particle number emissions since small particles has a low impact on PM. The particle number emission limit values in forthcoming Euro 5b and Euro 6 legislation has been set at $6x10^{11}$ particles/km measured as solid particles (i.e. with the fraction of condensed organic material removed), a level that in practice will make diesel particle filters (DPFs) mandatory.

Solid particle number has been measured in the interlaboratory correlation exercise (ILCE) in accordance with the new legislative measurement method for Euro 5 and is presented in **Figure ES1** for the same vehicle categories.

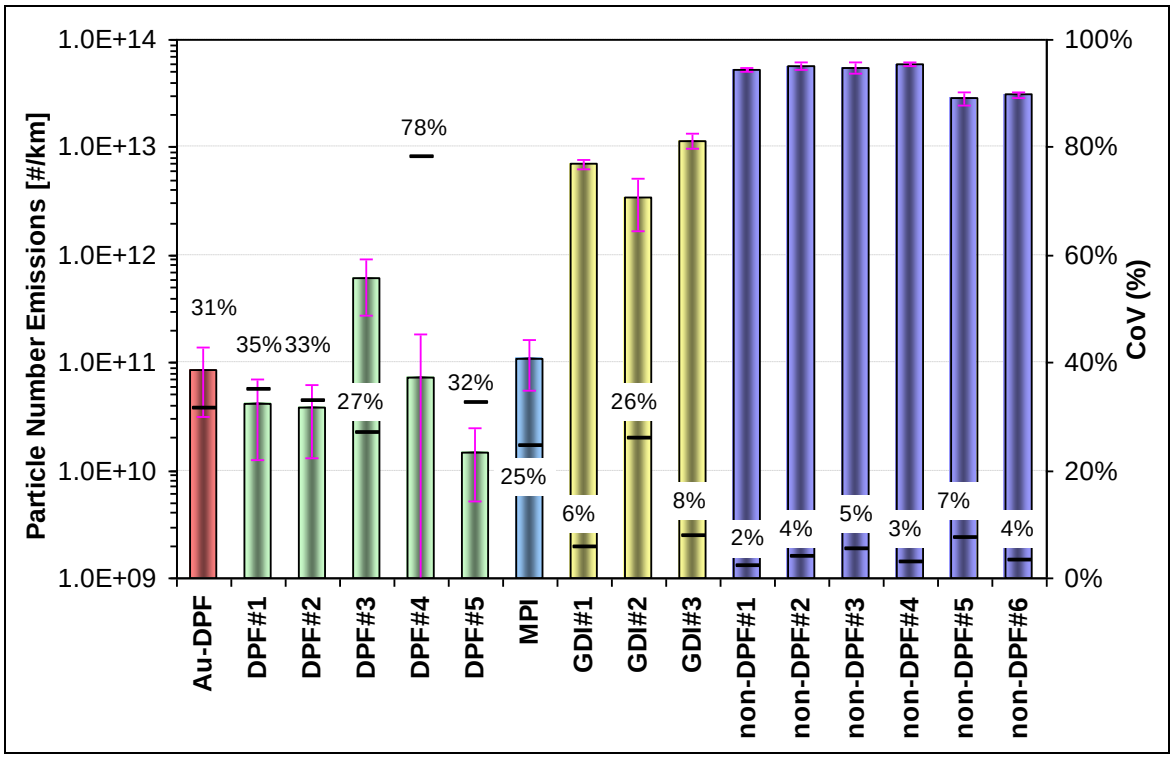

Figure ES1. *Total particle number emissions and repeatability data of all vehicles in the ILCE (Andersson et al., 2007).*

The picture presented in **Figure ES1** is in line with that of PM measurements with the highest emissions for diesel cars without DPF in great contrast to the diesel cars with DPF. The particle number emissions for DPF cars are in the same order as for the conventional multiport injection (MPI) petrol-fuelled cars. The cars with direct injection of petrol (or

gasoline direct injection, GDI) show considerably higher emissions as compared to the MPI.

Projections of the trendlines for PM emissions from petrol and diesel cars determined in the present study are shown in **Figure ES2**. This projection is not limited to the conditions for certification but also takes into account factors such as yearly average temperature and the deterioration of emission control devices (i.e. DPF) anticipated on a certain percentage of the vehicle population.

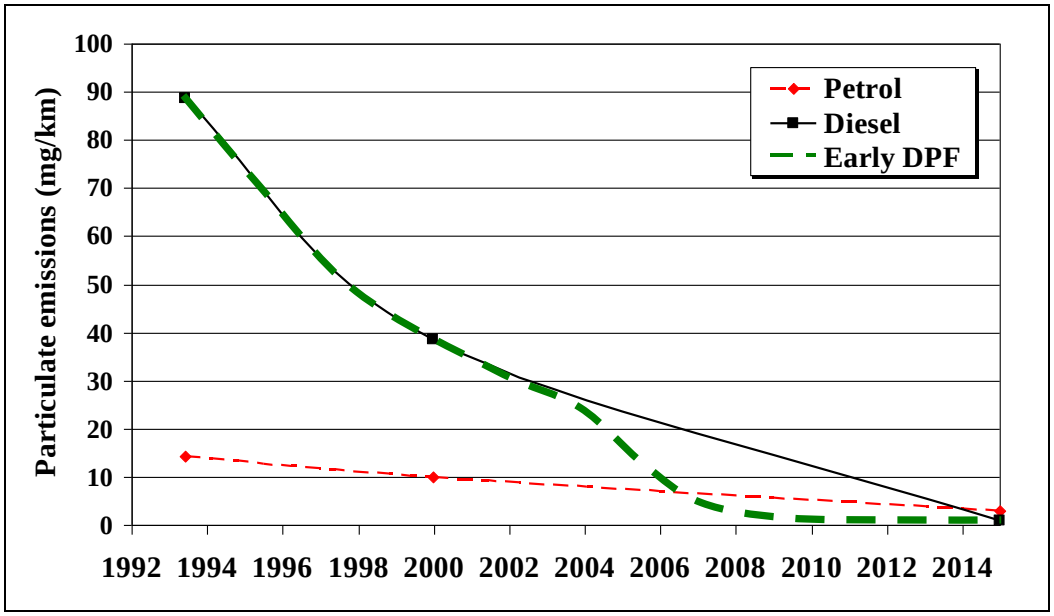

Figure ES2. *Ecotraffic's projection of PM emissions from petrol and diesel cars.*

Today, we see an ever increasing use of DPFs on diesel cars – approaching a 100 % market penetration in many European countries this year – although the Euro 4 emission limits for PM can be met without a DPF. This has been reflected by the green dotted line in **Figure ES2** indicating the impact of early introduction of DPFs. In order to meet Euro 5 and 6 certification levels, it is likely that all diesel cars must be equipped with a DPF. Furthermore, it has been shown that the limits for particle number are stricter than for particle mass on a relative basis. Thus, the DPFs used will have to have very high filtration efficiency commonly showing PM levels of 0,3 to 0,5 mg/km. The trend for a reduction of PM emissions for petrol-fuelled cars can be questioned against the background that the GDI technology that is gaining increased market penetration has higher PM emissions that the conventional MPI technology.

The cold start effect for petrol cars at low ambient temperatures is very pronounced and will increase the averaged life cycle emissions considerably. Test results at higher ambient temperatures (e.g. +25°C) have shown results mostly far below 1 mg/km. For the first generation of GDI cars, it is apparent that practically no car tested so far would meet the 4,5 mg/km limit set by the Euro 5 at a reliable margin. For the second generation GDI cars, it is likely that an "engineering target" of 1,5 to 2 mg/km could be met at the prescribed test temperature (+20°C to +30°C). At a yearly average temperature of +7°C, this level would probably increase more than twofold. Our estimate is that the average real-life particle emission level for petrol cars (as an average for GDI and conventional) taking the

mentioned effects into account will be about 3 mg/km. Thus, real-life particle emissions from diesel cars could be as low – or lower – than from petrol cars already in the very near future.

Another possible scenario is that the limit on particle number under discussion for cars with positive ignition engines – if the limit is set as though as for diesel cars – could also drive down the particle mass from this category of cars (by certain technical measures such as, e.g. inproved injection systems and/or particle filtration systems) to about the same level as for diesel cars, i.e. about one mg/km. That is under the anticipation that the limit for particle number emissions would be much tougher to meet than the limit for particle mass; as for diesel cars. The line for petrol in **Figure ES2** could then be adjusted accordingly to yield approximately the same level for both petrol and diesel cars.

NO_X emissions

Similar calculated results for NO_X emissions as for particle mass are shown in **Figure ES3.**

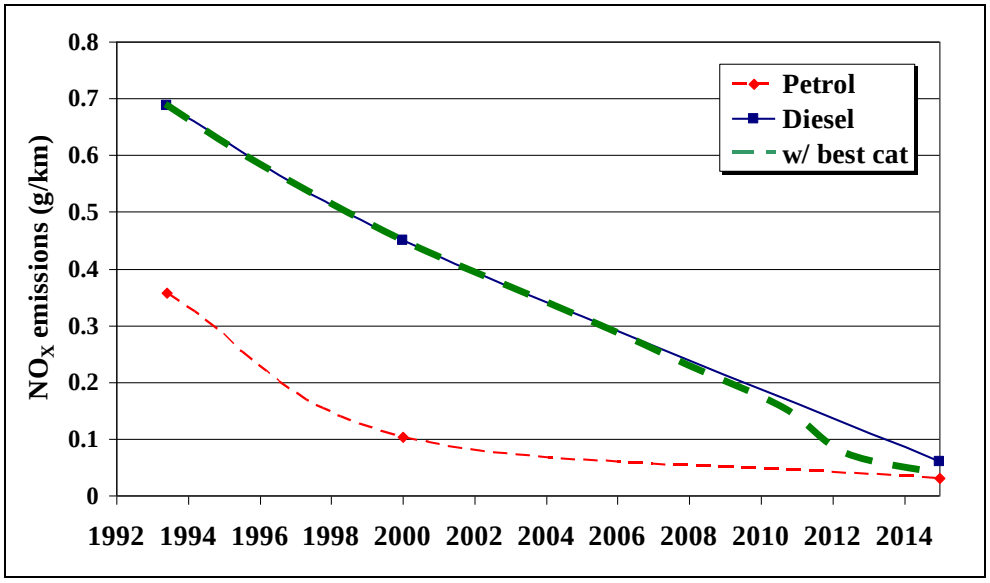

Figure ES3. *Ecotraffic's projection of NO_X emissions from petrol and diesel cars.*

Up till now, the NO_X emissions have been about a factor of 3 higher – during some periods even higher – for diesel cars in comparison to petrol cars. With Euro 6 that sets almost similar limits for both types of vehicles, the relative difference will diminish. Our estimate is that the petrol cars will still have a somewhat lower NO_X level. The uncertainty is about the impact of NO_X aftertreatment for diesel cars. It is likely that Euro 6 will be met using a variety of technologies. NO_X aftertreatment has been introduced already in 2008 in the USA and a few car models are also currently introduced in Europe. The uncertainty here is as to what extent this technology will be introduced well in advance of Euro 6. When this report was written in October 2008, three car models from BMW, Mercedes and VW respectively that are using NO_X aftertreatment for meeting Euro 6 have been introduced in Europe. The impact of an early introduction of such catalysts is also shown in **Figure ES3.** The impact of this technology might diminish the small difference between petrol and diesel cars within a few years.

One particular problem with some aftertreatment technology for diesel vehicles is that NO is oxidised to NO_2. NO_2 is the compound of the two that is more harmful to human health. In ambient air, NO is rapidly oxidised to NO_2 through the reaction with ozone or peroxy-radicals but a higher share of NO_2 in the tailpipe could increase human exposure, for example in environments with low ventilation, such as, e.g. tunnels, mines and parking houses. The best source of data for the ratio of NO_2/NO_X in modern diesel and petrol car exhaust has been the Swedish in-use compliance testing of emission durability. This programme has been conducted by TÜV Nord (Germany) and Ecotraffic for the Swedish Road administration. The results on, in total, 79 vehicles, showed an average NO_2/NO_X ratio of 47 % for the diesel cars and 16 % for the petrol cars. The ratio was highly variable for petrol cars ranging from less than 10 % to 40 %. Since also the total level of NO_X emissions are higher for diesel cars than for petrol cars, the total NO_2 emissions are considerably higher.

Biocomponents in the fuel

There are a number of biofuels available on short and long term horizon. In the present study, the focus has been on biodiesel, synthetic diesel fuels and hydrogenated bio-oils to be used in diesel engines and ethanol (E85) for otto engines. Biofuel alternatives that would require a dedicated diesel engine such as, e.g. alcohols, dimethyl ether and gaseous fuels are not covered here.

The denotation “biodiesel” is mostly used for fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE). Biodiesel is often used in blends with conventional diesel fuel but can also be utilized as a neat fuel in adapted vehicles. The current blending limit in European diesel fuel is 5 % but an increase to 7 % or maybe 10 % has been discussed for future diesel specifications.

An alternative treatment to enable the use of vegetable oils and animal fats as diesel fuel is hydrotreatment, such as the NExBTL fuel produced by the Finnish oil company Neste. The end product in this case is a straight-chain hydrocarbon fuel that contains no oxygen. Its chemical structure is very similar to synthetic diesel (Fischer-Tropsch) fuel produced via synthesis gas (GTL and BTL) and the emissions are comparable. Since biodiesel is regarded as a first generation of biofuel and synthetic diesel the second generation, hydrotreated bio-oils could be considered as generation 1,5.

Most results on biodiesel shows decreasing levels of CO, HC and PM with increasing biodiesel content. However, NO_X emissions tend to increase with biodiesel content up to about 10 % for neat biodiesel. Part of that increase is due to a shift of injection timing giving earlier injection and thus, higher temperatures and increased NO_X formation. With modern injection systems, there will be no shift in injection timing but there still seems to be a remaining small increase in NO_X emissions at some operating conditions (i.e. high engine load). It is likely that this increase could be avoided by optimizing the engine using sensors (physical or virtual) for the fuel content. For example, since less soot is formed with biodiesel, the rate of exhaust gas recirculation (EGR) could be increased to reduce NO_X emissions while still retaining a lower soot level than diesel fuel. One particular problem with biodiesel in light-duty vehicles is that it cannot be used in combination with DPFs, due to the oil dilution by biodiesel during the active regeneration. Currently; this problem does not exist with the DPF technology used on heavy-duty engines.

In contrast to biodiesel, synthetic diesel fuels and hydrotreated bio-oils and fats show reductions of practically all regulated emission components and in most cases also of unregulated emission components. In contrast to biodiesel, the blending levels can be much higher. The problem with some DPF technology experienced with biodiesel is not present for synthetic diesel fuel.

As noted previously, NO_X and PM emissions are the two most difficult emission components to reduce on diesel engines. Although any reduction here is mostly welcome, neither biodiesel nor synthetic diesel fuels can overcome the need for aftertreatment devices, such as e.g. DPF and NO_X catalysts, if very low NO_X and PM emissions are strived for. There could be some scope for substantial improvement in the utilisation of advanced combustion concepts, such as homogenous charge compression ignition (HCCI) engines, with synthetic diesel fuels.

E85 is a popular fuel in Brazil and the USA in light-duty fuel flexible vehicles (FFV). In Europe, the largest market penetration of FFVs has been achieved in Sweden. Some recent results from a Swedish test programme on two FFV cars and one gaseous-fuelled car (biogas and natural gas) are discussed in the present report and some findings have been highlighted. The project was funded by the Swedish Road Administration and carried out by Stockholm University, AVL MTC and Ecotraffic.

PM emissions for the two FFVs fuelled by E85 were low at "normal" (i.e. between +20ºC and +30ºC) ambient temperatures during emission testing, but increased at low ambient temperatures and were slightly higher than for the same cars fuelled with petrol. Also particle number emissions increased at low ambient temperatures.

Emissions of aldehydes were higher for FFV cars on ethanol fuel. Acetaldehyde emissions were much higher than formaldehyde emissions. The results for formaldehyde were on a similar level as for modern diesel cars but higher than for petrol cars. Regarding health effects, formaldehyde is more potent than acetaldehyde.

The most surprising finding in the study of FFVs was the high levels of polycyclic aromatic hydrocarbons (PAH) with ethanol fuel at low ambient temperatures. PAH emissions increased by increasing ethanol content in the fuel. In contrast, the PAH emissions for modern diesel cars with DPF are very low at low ambient temperatures.

Conclusions

Conclusions from this study may be summarized as presented below:

- Particle emissions are influenced by operational factors such as speed, engine load, or ambient temperature for which petrol cars shows a greater dependence. In some operational modes particle number emissions may reach the same range as those found for non-DPF diesel cars.
- Driving conditions shows different effects on solid particle number emissions for passenger car diesels in respect to heavy duty engines (HDE). At urban conditions, the number emissions scale with engine/vehicle size whereas at highway conditions HDE emits more or less as many solid particles as a passenger car per distance travelled or up to one order of magnitude lower emissions per unit of fuel consumed. This illustrates different diesel engine tuning depending on the vehicle application.

- The fraction of condensed organic components is highly variable (depends on, for example, engine technology, driving conditions, or sampling procedures) normally composes 20 to 50% of the particulate mass collected on filters. Diesel PM has a considerable higher fraction of elemental carbon than organic carbon as compared to petrol vehicles.
- Strong indications point to the importance of lubrication oil to the emission of nucleation mode particles and the portion of the particle emission from lubricating oil may very well increase as the fuel sulphur content is reduced.
- Nucleation-mode particles (<100 nm diameter) are to a large extent composed by condensed material of which lubricating oil is a major component whereas particles in the accumulation mode (100 nm-1 000 nm) are normally composed by a higher fraction of elemental carbon.
- Despite the reductions of NO_x emissions that have been achieved for diesel cars their emissions are still considerably higher as compared with those of petrol cars. However, the introduction of low sulphur diesel fuel allows the use of NO_x-reduction catalysts that eventually will reduce the emissions to the same levels as for petrol cars.
- The share of NO_2 emissions of the total NO_X emissions is considerably higher for diesel cars in comparison to petrol cars. This – in combination with higher total NO_X emissions – gives much higher absolute levels of NO_2 for the diesel cars. Although NO is relatively rapidly oxidised to NO_2 in ambient air, higher tailpipe NO_2 emissions can be of importance in environments with low ventilation, such as, e.g. tunnels, mines and parking houses.
- The emissions of NO_X increase for biodiesel compared to conventional diesel fuel, while most other emission components decrease. A shift in injection timing cause most of NO_X increase but modern injection systems do not show this behaviour. Still there is a small increase in NO_X emissions at some operating points even with modern fuel injection (common rail). With future development, it is anticipated that this increase could be eliminated.
- The increase in PN emissions with biodiesel seen in some studies is due to inadequate sampling. The smallest particles are not solid but volatile and will be reduced by the new sampling method in the PMP measurement protocol.
- Currently, there is a problem to use biodiesel in combination with DPFs on light-duty vehicles. Synthetic diesel fuels and hydrogenated bio-oils are not plagued with this problem.
- Synthetic diesel fuels, such as GTL and BTL, but also hydrogenated bio-oils have lower emissions than conventional diesel fuel. This conclusion is valid for most emission components and in contrast to biodiesel, the NO_X emissions are also lower in most studies.
- The use of ethanol fuel (E85 and E70) in fuel-flexible vehicles (FFVs) gives much higher emissions of acetaldehyde than petrol-fuelled cars and about similar level of formaldehyde as diesel-fuelled cars. There was also an increase of PM and PN for ethanol in comparison to petrol at low ambient temperatures.

- Somewhat surprisingly, the emissions of polycyclic aromatic hydrocarbons (PAH) from the FFVs were much higher for ethanol fuel than for petrol at low ambient temperatures. In contrast, the PAH emissions for modern diesel cars with DPF are very low at low ambient temperatures.

1 SCOPE AND OBJECTIVE

Air quality in densely populated areas has been largely associated with the impact from road traffic for the last couple of decades. Although many other sectors also contribute to this problem and great reductions in emissions from vehicles have been made, the focus on motor vehicles still remain. In many of the member states in the EU and other European countries, stricter emission legislation for passenger cars that, in practice, foresee the use of catalytic aftertreatment was introduced the late 1980's or early 1990's. Successive reductions of the emission limits have been made in the EU until today and even stricter limits will be enforced in the future, or are proposed for future introduction.

Besides the impact on air quality, the reduction of greenhouse gases and fuel consumption has gained more interest during the last couple of years. Voluntary commitments by the auto industry on the CO_2 emissions from passenger cars in the late 1990's will shortly be followed by legislative measures in this area (currently under discussion in the EU). Similar measures for light-duty commercial vehicles are also debated, while heavy-duty vehicles are less in focus due to the strong customer demand for low fuel consumption for competitive reasons already today. Diesel engines have the potential for up to 20 % reduction in CO_2 emissions per km driven compared to petrol-fuelled cars and have gained more interest in view of this development. Exhaust emissions from diesel cars are different than from petrol cars, in that respect that the levels of some emission components are lower, while others are higher. In particular, the emissions of oxides of nitrogen (NO_X) and particulates are problematic for diesel engines in comparison to petrol engines. Striving to reduce CO_2 emissions and energy use, the car industry has developed diesel engines and has been promoting them also in other ways.

Due to the different "fingerprint" in exhaust emissions of diesel cars compared to petrol cars, the current trend with increasing market penetration has been challenged in the debate by e.g. environmental organisations. In particular, the debate about particulate emissions has been fierce. Even the introduction of particle filters on diesel vehicles has not always been appreciated. Concern about that the emissions of particle mass and particle number when using particle filters would not decrease to the same extent has been stated. Thus, also the health effects of particle filters have been questioned.

Due to the issues listed above, there has been a need for collecting and compiling updated information about emissions from diesel cars and comparing these results with similar results from petrol cars. The report compiled for StatoilHydro that was published in 2007, aimed at highlighting some of these issues.

In addition to an update of the 2007 study in some of the areas mentioned above, new areas or an increased focus on some of them are made in this study. The following topics have been of interest to penetrate further:

- The concern that new engine technology and/or aftertreatment devices might create a larger number of small particles in comparison to older engine/aftertreatment technology
- Assessment of the emission results on PMP testing conducted by the German testing institute TÜV in the project from 2006 to 2008 commissioned by the Swedish Road Administration.

- Addition of PM results for E85 and biogas
- A highlight of some unregulated emission components will be made, such as NO/NO_2, polycyclic aromatic hydrocarbons (PAH) and aldehydes
- More thorough investigation on the impact of biodiesel (FAME (Fatty Acid Methyl Ester)) of both generation 1 (i.e. conventional biodiesel) and 1,5 (FAME based on hydrogenated bio-oils) and it's blending in diesel fuel on PM emissions and the use of aftertreatment systems.

2 INTRODUCTION AND BACKGROUND

Particulate pollutants is today of high interest since epidemiological and medical findings indicate adverse health effects caused by aerosol particles. The concept of "aerosol" is defined as a gas and the particles suspended therein. Several studies have shown a possible connection between hospital admissions and ambient air particulate concentrations in cities (Dockery *et al*., 1993; Katsouyanni *et al*., 2001). However, the evidence is not conclusive and there are contradicting studies (Wong *et al*., 2002). Particles may be described by different characteristics such as number concentration, size distribution, surface area, and chemical composition of which all are important toxicological parameters. For example, it has been shown by Pope *et al.* (1995) that particles smaller than 2,5 μm ($PM_{2,5}$) show a better correlation between mortality and ambient air concentrations than particles larger than 10 μm (PM_{10}). It has also been shown that PM composed of small inert particles (not associated with toxic compounds) may induce cancer in rats when large numbers are inhaled (Heinrich *et al.*, 1995).

Several studies (e.g. Shi *et al.*, 1999) point out traffic and combustion engines as a main source of fine particles in the urban environment. The formation of soot (often also referred to as "elemental carbon" (EC), "black carbon" (BC), or "insoluble carbon") in a flame is a highly complex process in which fuel molecules produce particles within a few microseconds. As a result of different combustion strategies, diesel engines are associated with higher particle emissions as compared to petrol engines. Even though the diesel engine operates with an overall air surplus, the stratified combustion creates regions in the combustion chamber and in the closest vicinity to individual fuel droplets where the air/fuel ratio is lower than stoichiometric. This favours soot and particle formation. In comparison to the diesel engine, the homogenous stoichiometric fuel/air mixture in normal petrol engine is associated with considerably lower soot formation.

The introduction of the direct injected diesel engines and more recently more advanced injection techniques such as the common rail and unit injectors has greatly reduced the emission of particulates as measured on a mass basis. This is a consequence of higher fuel injection pressures generating smaller fuel drops in combination with improved fuel injection control and operation. This does not necessarily mean that particle number emissions are reduced since the reduction in mass could be due to a reduction in particle size. However, there is no conclusive evidence for higher number of smaller particles from modern diesels as compared to older ones. Other factors that affect combustion engine particle formation include fuel quality, combustion chamber design, and exhaust after-treatment. Specifically, one type of aftertreatment devices, i.e. diesel particle filters (DPF), has a great influence on both particle number and mass, often achieving reductions as high – or higher – than 99 % (number) and 90 % (mass) respectively. In rare cases, the reduction is smaller than just mentioned, and those cases are of special importance to discuss.

2.1 The evolution of the exhaust particle

After formation of particles in the combustion chamber, size and composition of the particles changes as they travel through the exhaust system. New particles may also be formed through homogeneous nucleation in which gas-phase molecules sticks to each other to

form clusters and eventually particles. By "homogeneous nucleation" is meant the process whereby new particles, i.e. solid or liquid condensed matter form randomly from the gas phase by one or several supersaturated components. Homogeneous nucleation starts when two molecules in the gas phase collide and stays together long enough to allow further molecules to adhere and eventually a short lived cluster will form. The driving force behind formation of clusters is the gas phase concentration, the higher the concentration the greater the probability is that large clusters will be formed. The nucleation rate has a strong non-linear dependence of the vapour phase saturation pressure and a small change in saturation may cause a change of several orders of magnitude in nucleation (Hinds, 1982; Seinfeld and Pandis, 1998). Nucleation is therefore often an on-off process, which is substantially affected by ambient conditions (e.g. temperature, humidity, dispersion ratio and rate).

Surface growth by condensation (equivalent to "heterogeneous nucleation") is a process in which gas-phase molecules attach to existing particles by adsorption. Both surface growth and particle formation through homogenous nucleation are dependent on vapour pressure of the gaseous compounds and thus temperature. However, smaller gas phase saturation values are required to have condensation onto already present particles as compared to particle formation from homogeneous nucleation.

Coagulation affects the particle concentration. Particles collide with each other to generate fewer but larger particles with an unaffected mass concentration, a process strongly dependent of the particle concentration. The coagulation rate is dependent on the square of the particle number concentration. In practice, small particles coagulate faster than large particles at the same concentration since the diffusion of small particles is enhanced by "slip" between gas molecules. Aerosols having a distribution of different particle sizes coagulate faster than monodisperse aerosols (having particles with only one diameter). This phenomenon may be thought of as large particles providing the target area and small particles providing a high rate of diffusion that will bring them to the target.

2.2 The appearance of the exhaust particle

Individual particles from engine exhaust are typically made up by a core of carbonaceous spherules agglomerated to build up highly branched 3-dimensional structures with various hydrocarbons, ash, and sulphur compounds associated.

Ash (e.g. inorganic salts and metal oxides) originates either from the fuel or from the lubricating oil. It may be in the vapour phase in the combustion chamber due to high temperatures but supersaturates as exhaust temperatures decreases on exit from the cylinder.

Sulphur in the exhaust originates from the fuel and from the lubrication oil. When burning a sulphur-containing fuel, the sulphur will be found in the gaseous phase after combustion in the form of sulphur dioxide (SO_2) or sulphur trioxide (SO_3) that eventually will react with water vapour to form sulphuric acid. Sulphuric acid (H_2SO_4) has a boiling point of around 350°C and may therefore nucleate or condense when the temperature drops. Water vapour and traces of ammonia facilitates nucleation considerably (Marti et al., 1997).

Another group of potentially nucleating substances is made up of uncombusted fuel residues and vaporized lubrication oil. Petrol normally consists of a complex mixture of hydrocarbons, ranging from C4 to C10 in carbon number and has a final boiling point (the temperature at which the bulk of a sample has boiled off) of less than 220°C. The carbon

number range for diesel fuel varies depending on blend but a distribution starting at C8, peaking at C16 and with little mass beyond C24 is often seen. Typical diesel fuels show a final boiling point between 280°C and 360°C. Lubrication oil contains hydrocarbons with carbon numbers beginning at around C20, peaking between C30 and C35 and with a considerable mass having numbers above C40 (Ziemann et al., 2002). In addition, lubricating oil may contain sulphur concentrations of thousands ppm and high concentrations of metal additives such as calcium and zinc. Lubricating oils most often have final boiling points between 400°C and 550°C. Thus, oil vapours and possibly also a fraction of diesel fuel may have properties that allow homogenous nucleation and condensation when cooled.

Soluble components partly originating from incomplete combustion of fuel and lubricating oil may be extracted from filter samples and typically represents 20 to 40% of the mass.

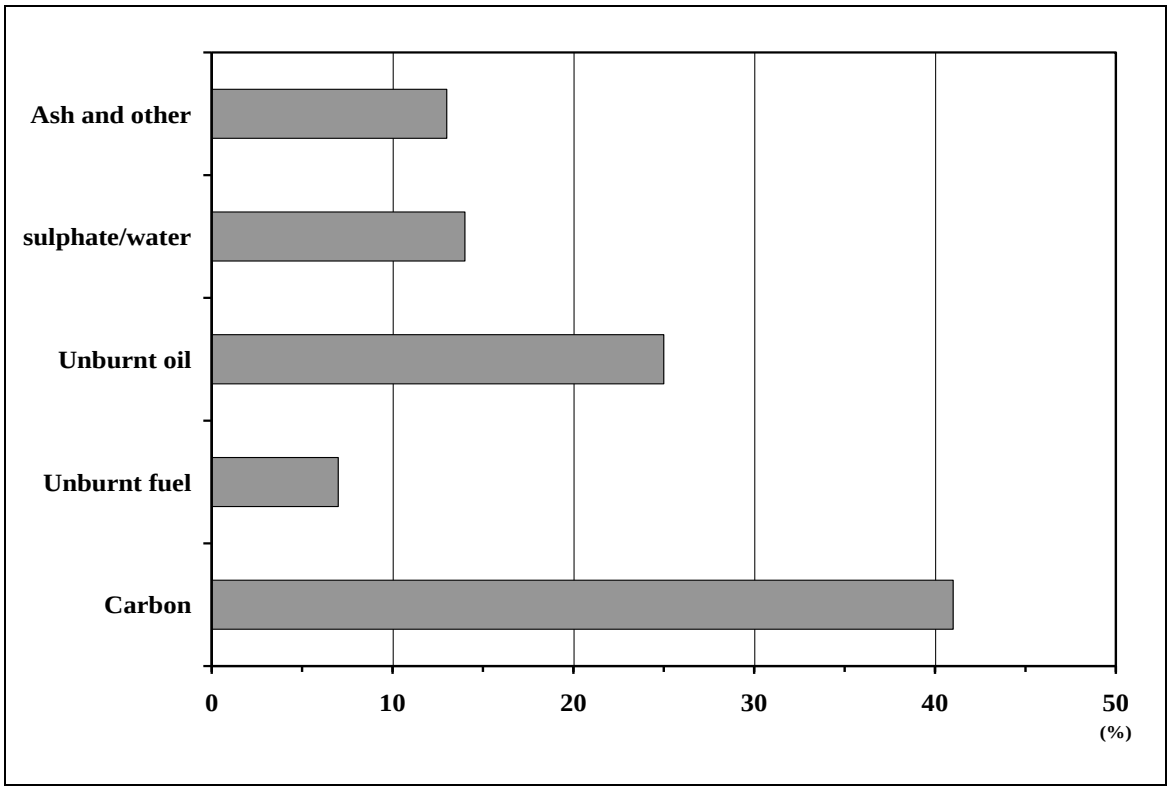

Figure 1. *An example of composition of particles from a heavy-duty diesel engine (Kittelson, 1998).*

The physical size of the particle may be given by one parameter only if the particle is spherical, e.g. a liquid droplet. However, since particles often have irregular shape, it is common to describe the particle size as the "aerodynamic diameter" which is the diameter of a sphere of unit density that has the same settling velocity as the particle in question. Thus, the aerodynamic diameter tells more about the aerodynamic behaviour of the particle than about its actual, physical size. Most measurement instruments dealing with particle size relate to the aerodynamic diameter. An idealized diesel particle distribution is shown in **Figure 1**, which illustrates the difference between mass distribution and number distribution. If the particles are spherical with a known density, it is possible to calculate e.g. the number- or surface concentration distribution from the mass concentration distribution or vice versa. Aerosol particles from combustion or in the ambient air often follow a log-

normal, trimodal size distribution as shown in **Figure 2**, where each peak represents a "mode". The concentration in any size range is proportional to the area under the corresponding curve in that range.

Since the position of a "mode" is dependent on the aerosol history, the phenomenological definitions, "nucleation-", "accumulation-" and "coarse" mode particles are usually used.

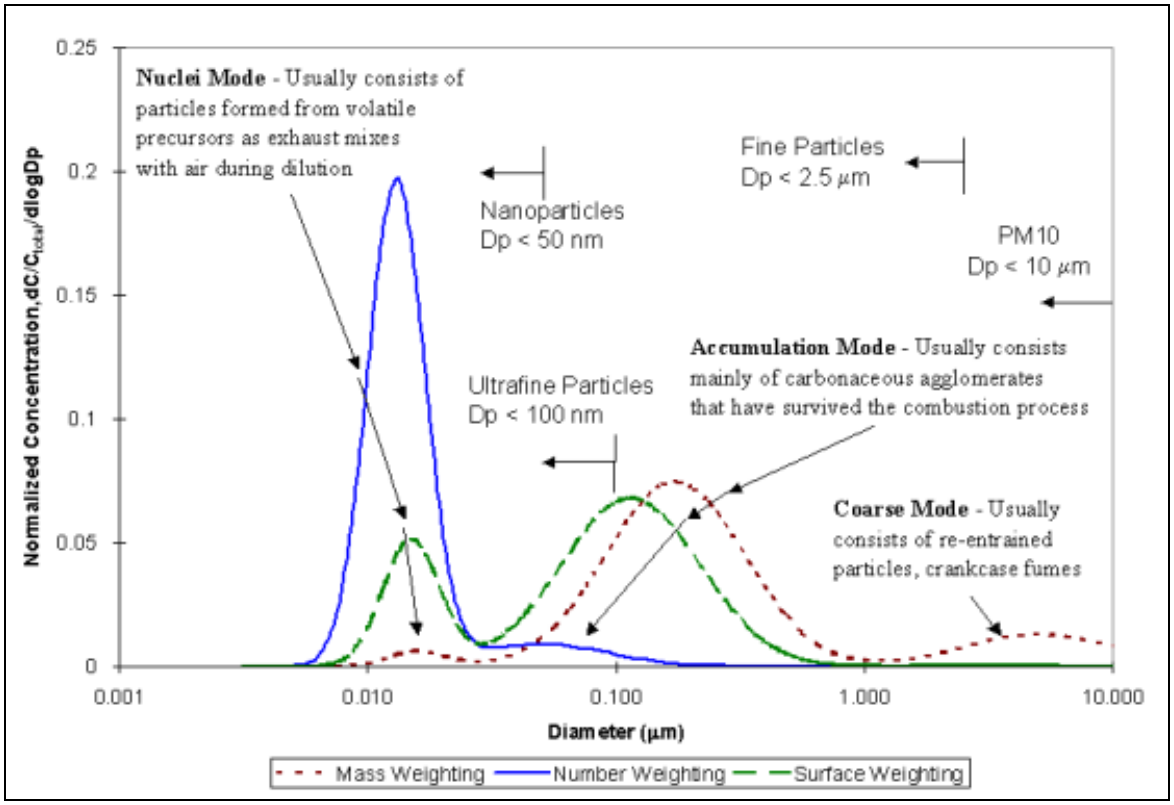

Figure 2. *Typical particle mass and number size distribution of engine exhaust (Kittelson et al., 2002a).*

The highest particle numbers are found in the nucleation mode with particle diameters smaller than 0,1 µm. However, the mass represented by this mode is low (1-20%). Most of the particulate mass is found in the accumulation mode with particle diameters between 0,1 µm and 1,0 µm. The coarse mode with particle sizes lager than 1,0 µm represents 5-20% of the particulate mass while the particle number in this mode are minor.

Nucleation mode particles may grow by coagulation and condensation into the region known as the accumulation mode. Growth by coagulation slows down in this mode because the particle concentration drops and because particles become so large that their diffusion rate becomes low. Small particles may still diffuse to the larger "accumulation" mode particles but their influence on the resulting particle size is small because they bring little mass. Due to the power-of-three dependence of mass on diameter, it takes a rapidly increasing amount of mass to bring about a unit increase of diameter. As an example, the amount of mass needed to increase the particle diameter by one nm from 30 to 31 nm is 75 times the amount necessary to increase size by one nm from 3 to 4 nm. This means that the gas soon runs out of condensable material and the particle growth stops. Further, these particles are quite stable towards gravitational settling, causing them to accumulate in this size

range, the accumulation mode. Homogeneous nucleation, growth by condensation and coagulation are not consecutive processes but occur concurrently e.g. in vehicle exhaust.

The "coarse" mode consists of particles larger than 2,5 μm with an upper limit of around 100 μm. These, relatively large particles are often formed by mechanical processes e.g. re-entrainment of particulate matter, which has been deposited e.g. on exhaust system- or road surfaces. The main removal process for particles in this mode is by sedimentation or by wash out.

As the particles are emitted from the tailpipe into ambient air, the dilution ratio (DR) changes drastically (up to a factor of 1 000 within a few seconds), and thus temperature and the concentration of particles and gaseous exhaust species are reduced. Consequently, the effectiveness of coagulation and nucleation processes is to a great extent halted. If however, the emissions occur in a normal laboratory dilution tunnel system (Constant Volume Sampler (CVS)), the dilution ratio is typically in the range from 5 to 50. Under these conditions the onset of nucleation may be rapid which drastically changes the number concentration of particles as high numbers of new particles are formed (Kittelson *et al.*, 1998). Shi *et al.* (1999) showed that nucleation is favoured by high dilution ratio and high relative humidity while Abdul-Khalek *et al.* (1999) found that favourable conditions for particle formation are associated with lower temperature, lower dilution ratio, and longer residence times. Matter *et al.* (1999) measured downstream a diesel engine exhaust particle trap and observed that the number of small particles downstream the trap may exceed the number of particles upstream the trap at high engine loads. By use of a thermodenuder (TD) that removes the volatile fraction of particles by heating, they showed that particles smaller than 100 nm to a large extent are composed by volatile matter of which a major fraction was sulphur related (**Figure 3**).

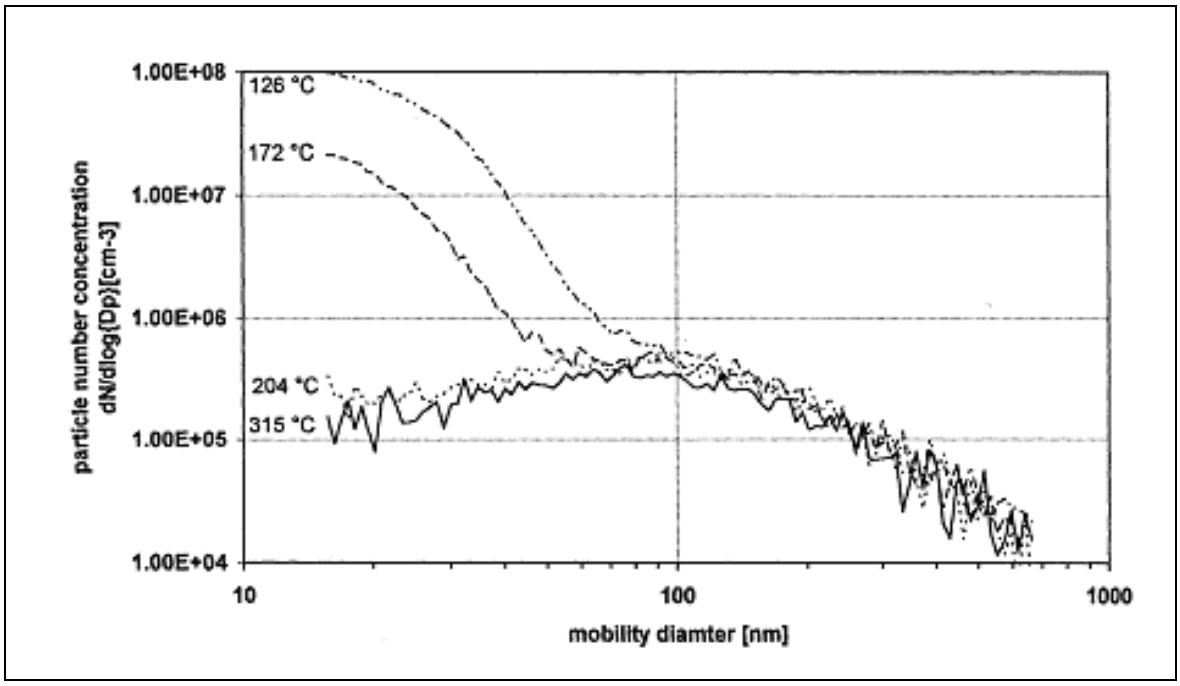

Figure 3. *Size distribution downstream from the particle trap at different temperatures of the thermodenuder (Matter et al., 1999).*

Similar observations have been made by, for example, Lüders *et al.* (1998) and Mayer *et al.* (1998) suggesting that nucleation particles are mainly composed by volatile material as they are completely removed if thermodenuders are used at sufficiently high temperature. Thus, particles from combustion engines have different states: solid, solid with volatile coating, and totally volatile particles, that may be largely altered due to the operation of the vehicle and the conditions at which the particles are measured. Differences in particle number of several decades have been reported (Abdul-Khalek *et al.*, 1999). Thus, it may be troublesome to perform repeatable and representative measurements of vehicle particle emissions if other particle properties than mass are studied. A correct handling of the volatile fraction is essential since it has been shown that volatile components may alter the measurements through homogenous and heterogeneous nucleation processes. It may therefore be concluded that measurements of only number or mass at a certain thermodynamic state will not be readily connected to any ambient limit values of either mass, surface, number, or chemistry.

It has been shown that external factors such as driving patterns (load and speed of the engine) and environmental conditions as for example ambient temperatures have a large influence on particle emissions (e.g. Maricq *et al.*, 1999). Higher vehicle speeds are normally associated with higher emissions of particles and changes in size distribution. There is also generally a difference in particle size distribution between petrol vehicles and diesel vehicle emissions with the maximum number of particles at larger particle sizes for the diesel.

The legislated emission limits are gradually set at lower and lower values and there are also reasons to expect that a common regulation for particulate matter from diesel and petrol vehicles will be set in the future. Currently, both Europe Union and the United States use particulate filter mass as the regulating parameter. The Environmental Protection Agency in the United States (US EPA) seems to favour keeping particulate mass as the measure for the new tight emission limits for the 2007-2010 on-road heavy-duty diesel requirements. They have imposed tighter control of the dilution and weighing and thus lowered the detection limit of the standard CVS system. These enhancements will also be applied for the light duty vehicles. In the EU, the Euro 5 (effective from September 2009) and the Euro 6 regulation have recently been adopted and include particle number emission limit values for diesel and direct injected petrol cars (Euro 5+, effective from September 2001). Cars with positive ignition system (e.g. petrol-fuelled cars) are *not* subject to limits for particle number in Euro 5 and a decision about potential limits in Euro 6 is to be decided at the latest in 2014. The PM emission limit values are reduced for diesel cars and introduced for lean burn direct injection petrol cars at the same levels as for the diesels. For the diesel cars it is most likely that the only practical way to meet the new particle number emission limit values is to use particulate filters.

2.3 Methods to characterize aerosols

Some methods and equipment to characterize aerosols are briefly described below. A single particle may be fully characterized by giving its size, density and chemical composition. However, describing an aerosol by giving these parameters for each particle is in reality quite impractical and all methods and instruments, in one respect or another is a compromise.

2.4 Mass concentration

The classical way of expressing amount of particles is by "mass concentration". This is a simple metric that requires little equipment and moderate expertise to implement. In its simplest form, particle-containing gas is drawn at a constant, known rate through a filter of suitable material. The filter is weighed before and after exposure. The mass concentration is the weight difference divided by the filtered gas volume. It is common to discriminate particles greater than a certain aerodynamic size e.g. in order to mimic the behaviour of the human respiratory system. This can be done by designing the measurement device inlet properly.

The PM sampling method used for certification purposes for passenger cars uses two 47 mm filters in series at a sampling temperature below 52°C. In this method, sampling could be performed by dividing the certification driving cycle (NEDC) in two phases: the urban (UDC) and the extra urban (EUDC) phases.

The PMP work aims to develop a revised filter method to measure PM emissions at lower levels with an improved limit of detection, higher repeatability, and less artefacts from collected condensed volatile organic species. The PMP method differs from the older certification method by using a single 47 mm diameter high efficiency filter kept at a controlled temperature of 47±5°C mounted downstream a cyclone at the same temperature. The PMP method also requires more careful handling of the collected filters and use of a high performance balance. The PMP method has been evaluated in the interlaboratory correlation exercise (ILCE) (Andersson et al., 2007). Removal of the back-up filter appears to reduce the overall PM by up to 25% per filter on cars with very low PM levels (e.g. diesel with DPFs). The most substantial effect though, is the increase in apparent mass emissions between the 1 filter per NEDC result and the sampling performed for the urban plus the extra urban result. This increase, up to ~50% in these experiments, is probably due to the doubling of any volatile collection artefact related to the filter medium used. The ILCE work measurements of diesel-DPF PM values thus indicates that the combined effect of eliminating backup filters and moving from two filters to a single filter per NEDC will reduce PM levels by 30% to 50% relative to the current filter method. However, the authors of the ILCE report conclude that these results may not represent effects from higher DPF porosity substrates which may leak carbon. These observations are in line with earlier comparisons of the two PM measurement methods when operated in parallel for measurements of diesel-DPF particle emissions in the NEDC showing 50% lower values with the PMP method as compared to the older regulated PM method (Bosteels et al., 2006). The two methods have also been compared in parallel for petrol/ethanol cars in the NEDC showing similar results with about 50% lower PM values for the PMP method (de Serves, 2005). In the ILCE it is thus concluded that these differences should be taken into account when the revised measurement technique is adopted in legislation and a new regulatory limit is determined.

Particle inertia may be used to separate particles into size intervals to obtain a mass size distribution. The particle-containing gas stream is accelerated trough a nozzle and then deflected by a plate close to the nozzle exit. Particles too big to follow the streamlines will impact on the plate and stick. This is the principle behind a device known as a "cascade impactor". By passing the gas through a series of nozzles with decreasing diameter, a division into size intervals may be obtained. This device is known as a "cascade impactor". The result of a measurement may be obtained by weighing the plates before and after ex-

posure. The mass concentration is sensitive to large particles since the mass of one 100 μm particle is the same as the mass of 10^6 particles of 1 μm or 10^{12} particles of 0,01 μm diameter, assuming the same density of all particles.

The mass concentration obtained in this way is an average over the collection time. However, real-time mass measurement instruments exist (e.g. DMM or TEOM).

There is a simple, indirect method to assess mass concentration of "black smoke" (BS) i.e. elemental carbon from the blackness of an exposed filter. The light reflectance of the filter is determined by the elemental carbon mass rather than by total particle mass. Studies have documented a relatively high correlation between light reflectance and elemental carbon and if a standard procedure is followed, it is possible to convert reflectance measurements into mass concentration ($\mu g/m^3$). Another somewhat similar method to the filter paper method is to use opacity meters, i.e. instruments that measure black smoke by light extinction. The advantage over the filter methods is that transient effects can be studied. Both the black smoke measurement techniques have more or less reached their detection limit in measurement resolution on modern diesel vehicles. Engines without particle filters but with low particulate emissions give very low readings and in the exhaust from engines with particulate filters no smoke reading can be detected.

2.5 Number concentrations

2.5.1 Particle counters

It is obvious that mass measurements are insensitive e.g. to very small particles. In order to gain information about aerosols, containing small particles it is necessary to count the particles. This can be done by physical methods in real time. Light scattering is the method of preference. In an "optical particle counter", the aerosol is led through a small, intensely illuminated volume. Each time a particle passes the volume, it scatters light in all directions. Some of it is directed onto a light sensitive device that registers a pulse. Each pulse represents one particle and the intensity is related to the particle size. Typically, particles between 10 and 0,5 μm can be counted in this way and by knowing the flow rate, real time concentrations and size distributions may be obtained. Particles with sizes smaller than about 0,5 μm are difficult to detect since they have very small light scattering power. The common way to detect such small particles is to use their property to be able to serve as condensation nuclei. This is used by a device known as a Condensation Nuclei Counter (CNC) which is equivalent to a Condensation Particle Counter (CPC), see The aerosol that contains the particles which are to be counted is continuously led through a chamber where the gas is saturated with a volatile compound, e.g. n-butanol at a temperature slightly above ambient. The saturated gas then continues to a condenser, where the gas temperature is lowered, the gas becomes supersaturated and condenses on the particles present. The particles are allowed to grow to around 10 μm and are then counted optically as described above. The scattered light intensity is of little interest here, since all particles above a certain size pick up vapour and grow. The lower detection size limit is determined

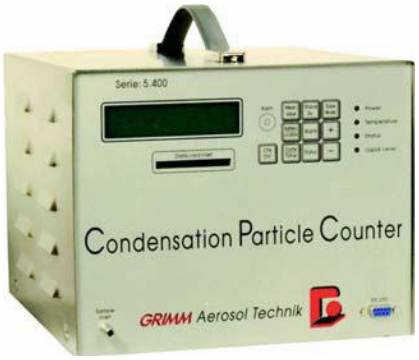

Figure 4. *CPC by Grimm Aerosol*

by the supersaturation that can be achieved in the condenser without causing homogeneous nucleation. A common lower limit is 10 nm but equipment exists that can activate particles as small as 3 nm. Particle number concentration, but no information about particle size, is obtained from the number of counted pulses and the known flow rate..

2.5.2 Particle number measurement systems according to PMP

In the PMP measurement protocol, a CPC is used for particle counting. In contrast to the all-purpose type of CPC, as described in the section above, where as small particles as possible will be detected; the cut-point (50 % detection level) of a PMP CPC is set at 23 nm. To achieve this, temperature settings are generally changed in the CPC. Some other modifications are also prescribed in the PMP protocol. Up to date, there are only two PMP complying CPCs commercially available; i.e. from Grimm Aerosol and TSI.

Besides the specific requirements of the CPC, there sampling and dilution process is also prescribed in the PMP protocol. The PMP system is designed to generate number concentration measurements of aerosol particles from which volatile material is removed from the particulate phase by heating and dilution of the aerosol. In brief, the system may be described as: a sampling probe inside the CVS-tunnel; a unit to remove coarse particles (e.g. a Chinese hat); a dilution unit to provide a dilution factors (DF) in the range of 1:1 to 1:1 000; an evaporation tube (ET) to heat the aerosol; a second dilution stage to provide DF 1-30 and an instrument to measure the particle number concentration (Andersson et al., 2007; GRPE, 2007). A schematic picture of the PMP setup is shown in **Figure 5**.

The measurement system comprises, among other things, a volatile particle remover (VPR). The VPR has a hot stage of dilution (PND1) and a cold stage (PND2) with an evaporation tube (ET) in between. The evaporation tube, which must operate at a fixed temperature level between 300ºC and 400ºC, evaporates the potentially remaining volatiles from the hot stage of dilution.

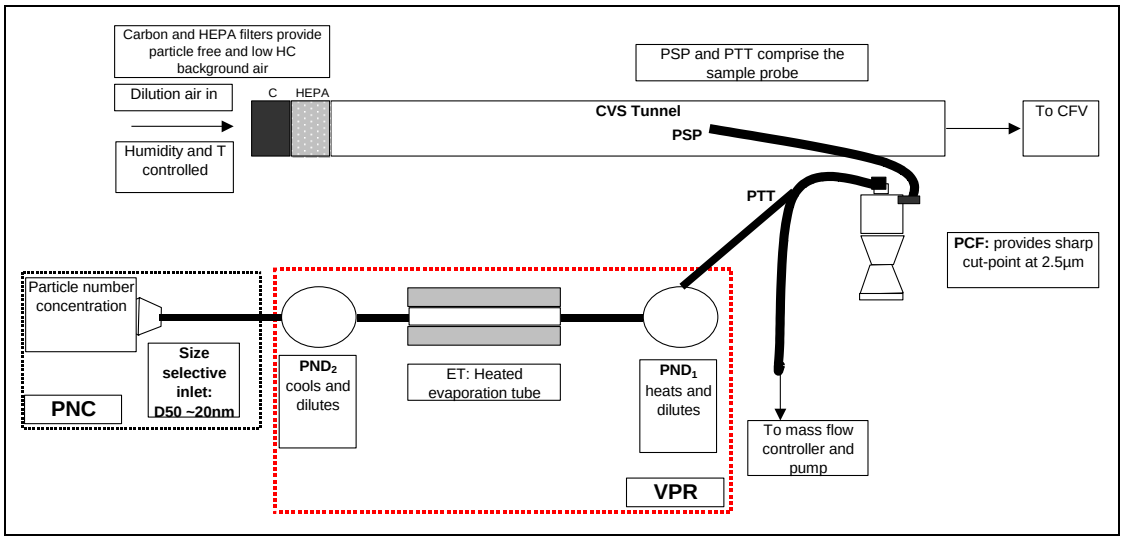

Figure 5. *Schematic of the golden PMS (Andersson et al., 2007).*

Due to the complexity of the measurement system for PMP measurements, it is an advantage if both the dilution system and the CPC can be integrated in a complete measurement system. The first commercially available measurement system of this kind was pre-

sented by the Swiss company Matter Engineering already a couple of years ago. This company was also heavily involved in the development of the measurement methods tested in the PMP projects.

The principle of the Matter Engineering dilution system is based on a rotating disc diluter. The rotating disc was used as the "golden" system in the measurements in the light-duty PMP programme, along with a couple of "alternative" prototype dilution systems from other manufacturers. In the subsequent, and still on-going, similar programme for measurements on heavy-duty engines, a measurement system from Horiba (SPCS) was chosen as the "golden" system. Later, PMP-compliant measurement systems have also been introduced by two other instrument suppliers, i.e. AVL and Ecomesure. The relative complexity of a full PMP measurement system is indicated in **Figure 6** (Rahman et al. 2007).

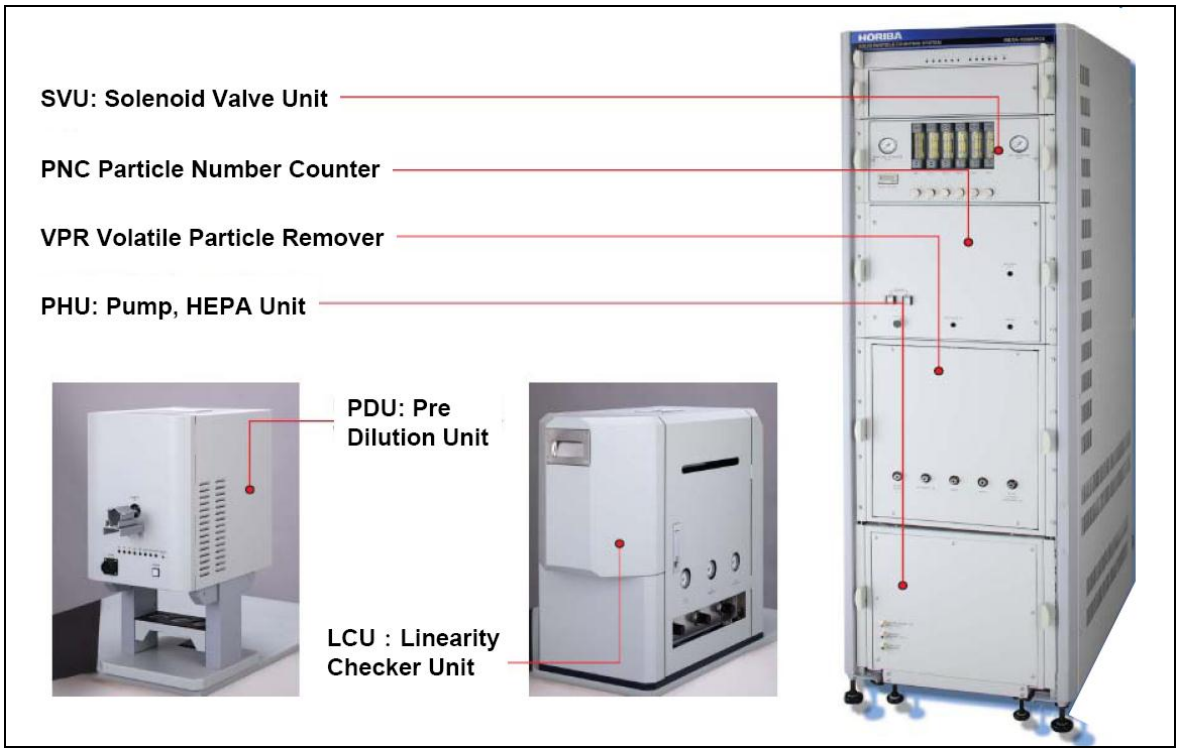

Figure 6. *The PMP measurement system from Horiba*

2.6 Particle size distribution

To obtain information about number-size distributions it is common to use a particle mobility spectrometer known as a Differential Mobility Analyzer (DMA), **Figure 7**. Briefly, the particles of the aerosol to be investigated are made electrically charged. Since a charged particle moves in an electrical field and its velocity depends on its aerodynamic size and the field strength, it is possible to select a certain mobility (i.e. size) range by e.g. selecting the proper field strength. The arrangement is often of cylindrical

Figure 7. *DMA by TSI*

symmetry and then consists of two concentric tube electrodes with the field created in the annular space between the electrodes. The particles in the selected mobility range are led to a CNC for counting while the rest of the aerosol is sent to waste. By sequentially measuring adjoining size intervals it is possible to collect data to allow calculation of a number-size distribution. Depending on the hardware and the measurement strategy, a variety of names have been given to this basic DMA/CNC setup. Differential Mobility Particle Sizer (DMPS) and Scanning Mobility Particle Sizer (SMPS) are names often encountered.

Another size resolving and counting device is the Electrical Low Pressure Impactor (ELPI), **Figure 8**. This is a cascade impactor where the entering particles are given an electrical charge. The number of particles impacting on each stage is quantified in real time by measuring the electrical current draining from the stage. The ELPI covers a size range between 30 nm and 10 µm, but the instrument may perform measurements down to 7 nm if supplied with an additional electrical filter stage downstream the impactor.

Figure 8. *ELPI by Dekati*

One advanced analysis technique has a DMA to select a certain size range of particles from the exhaust, followed by a thermodenuder. A thermodenuder is a device where gas and particles are heated to a selectable temperature and where the compounds evaporated from the particles are removed. The size distribution of the remaining aerosol is then measured by a second DMA/CNC. This so called tandem DMA instrument makes it possible to study the contribution of volatile substances, (in essence, soluble organic fraction, SOF, see chapter below) and non-volatile substances, (in essence, insoluble organic fraction, IOF) to particles over the size spectrum. A similar set-up using a humidifier instead of the thermodenuder makes it possible to study the hygroscopicity of the particles.

2.7 Chemical analysis

From collected particulate samples, analyses of the chemical composition of the particulate phase may be performed. The particulate composition varies with engine and exhaust after-treatment technology, but also with for example engine load and the method and the position used for the collection of the particulate samples. The latter, since volatile material to a higher extent is found in the particulate phase at lower sampling temperatures as a result of condensation, thus affecting both particulate mass and chemical composition.

Filters or impactor plates with enough mass may be subjected to chemical analysis using conventional wet-chemical or other methods to determine composition. Due to the complex chemical composition e.g. of engine exhaust particles, it has been common practice to split filter samples into fractions by extraction. The Soluble Organic Fraction" (SOF) is extracted from the sample by a suitable organic solvent. It typically contains more or less volatile hydrocarbons. It is also termed Organic Carbon (OC). The Soluble Inorganic Fraction (SIF) is a water extract that contains salts and mineral acids, e.g. nitrates, sulphates and sulphuric acid. The Insoluble Organic Fraction (IOF) is mostly soot. Since the particles

collected at the beginning of a measurement will be exposed to the passing gas for extended periods of time they may change composition. They may lose semi volatile substances if the passing gas is sub-saturated or gain substances if gas phase concentration goes up. Thus the result of a mass measurement is sensitive to changing temperature and gas phase concentrations. Adsorption of water is handled by conditioning filters at a controlled humidity before weighing.

Earlier, when lead was used as an octane enhancer, this element was a good tracer for petrol vehicle derived pollution. This possibility does not frequently exist today and new tracer compounds have been sought without much success. Polycyclic aromatic hydrocarbons (PAH) are organic compounds composed of two or more fused aromatic rings. They are formed during combustion of heavy fuels or may be present already in the fuel. The use of PAHs as tracers is limited by their production by other sources, e.g. small scale biofuel burning. There are however, some heavy, organic compounds that originate from solely petroleum that may be analyzed, albeit with some difficulty and used as tracers. Examples are the hopanes and the steranes. These are polycyclic molecules, typically containing between 25 and 35 carbon atoms (Rogge et al., 1993).

3 METHOD

The basis for the data collection in this study has been a literature survey. The authors had already previously much literature readily available from earlier work in this field. In addition, literature searches were made in the database of SAE (Society of Automotive engineers).

3.1 Limitations

Some limitations of the study were made in discussions with StatoilHydro, since the scope of the work is limited. The priorities made can basically also be seen as headings in the study. A couple of these areas that have been covered are listed below.

- Exhaust particle characterisation including parameters in sampling and dilution that affects the measurements
- Diesel market share evolvement
- Test cycles
- Emission legislation
- Fuels and fuel quality
- Instruments and measurement methodology
- Engine and aftertreatment technology
- Results on particle mass, particle number and size distribution due to some of the parameters listed above
- Addendum of new results in respect to the 2007 study, such as e.g. new SAE papers and results from in-use emission testing by TÜV and Ecotraffic commissioned by the Swedish Road Administration.
- Addition of some results on PM for E85 and biogas and a highlight of some unregulated emission components specific for these fuels, such as, PAH and aldehydes in comparison to petrol and diesel
- NO/NO_2 ratio in diesel and petrol exhaust
- More thorough investigation on the impact of biodiesel (FAME (Fatty Acid Methyl Ester)) of both generation 1 (i.e. conventional biodiesel) and 1,5 (FAME based on hydrogenated bio-oils) and it's blending in diesel fuel on PM emissions and the use of aftertreatment systems.

One important issue to consider is the timeframe of interest for the study. Since this issue is not directly discussed in any other section of the report, it is described here.

A technology shift in diesel engines for cars was initiated in 1989 by the introduction of the direct injection technology by Audi[1]. However, not until about 1994, this technology started to spread to other cars brands in the VW group. Some other DI engines entered production a couple of year later but it was not until the common rail injection system was introduced in 1997/1998 that the market penetration of DI diesel cars started to grow. By setting a timeframe limit by mid 1995, the development of the DI technology can be followed as well as the last generation of indirect injection (IDI) engines can be the basis for comparisons. Particle emissions from DI and IDI tend to differ. The other end of the timeframe would be roughly 2015. The new Euro 6 emission limit for light-duty cars will be introduced in September 2014. The technology to be used and emission level could be estimated on this horizon based on the current proposal for Euro 6. To make a forecast beyond that timeframe is very difficult at this stage. It is likely that the focus on a longer timeframe might shift more towards fuel consumption and CO_2 emissions instead of the pollutants under discussion today, since the emission limits proposed for Euro 6 are so stringent.

In view of the discussion above, it was decided to limit the timeframe considered in the study from about mid 1990's to 2015.

3.2 Database search

The main literature database and source of literature has been the SAE Global Mobility Database (GMD). The GMD database contains over 140 000 references and bibliographies starting in 1906. Some specific references or other sources of data were searched in addition to the SAE database. Specific projects of interest were the PMP programme and the EU "Particulates" projects, projects in which one of the authors have been actively participating. These projects were intended to develop new measurement procedures and instrumentation for measurement of particle mass and number in the future. Some selected conference publications, e.g. the DEER (Diesel Engine Emission Reduction Workshop/Conference) were also covered. Publications from a couple of selected emission laboratories in the EU, such as, e.g. AVL MTC, VTT and EMPA were also included. Due to the limited scope of the project, no searches in larger databases than the SAE GMD were conducted. However, due to the limited number of references found on biodiesel and synthetic diesel fuels, search for articles was also carried out in the ACS Journal Energy & Fuels.

3.3 Literature selection

The search carried out in the study in 2007 gave initially more than 2 000 hits. Based on the scope of the project, a selection of some 150 papers and other publications were made based on the information in the abstracts. More than 30 papers that the authors did not already have in their possession were ordered. Specifically, projects from the PMP programme were of interest.

[1] Although Rover and Fiat actually introduced this technology somewhat earlier than Audi, none of these engines was a commercial success so they can be discarded in this discussion.

As a complement to the search carried out in the study in 2007, a search for SAE papers on the same topic was also carried out this year. In addition, more searches in the SAE database was made to cover the new topics on biodiesel, synthetic fuels and NO_2.

Reports and data from the in-use compliance testing programme of light-duty vehicles commissioned by the Swedish Road Administration were also included. Furthermore, a Swedish publication on regulated and unregulated emissions from two fuel-flexible E85 cars and one biogas-fuelled car was added to the list of publications covered in the present report.

In addition to the literature sources above, publications by the authors themselves not covered in the databases mentioned were also included in the study.

Although covered in the literature survey, all papers considered have not been directly discussed in the report. Therefore, the reference list has been limited to the publications discussed in the report.

One specific issue to note is that relatively few publications from the USA has been covered. Although many of those publications were found to be of interest, they often cover other light-duty vehicles than cars (trucks) and the conditions (e.g. driving cycles) are different from those in the Europe. Since Europe was the focus of this study, many publications originating from the USA were omitted.

4 RESULTS

The results chapter covers the main findings of the study.

4.1 Diesel cars and market share development

4.1.1 Traffic development and traffic modes

While rail and public transport were the dominating transport modes in the central and eastern European countries in the early 1990's, road traffic is increasing rapidly (EEA, 2002a; EEA, 2003). The increase of the number of vehicles in the EU-15 Member States in each category of passenger cars, light- and heavy duty vehicles and buses over the period 1981 to 2020 are presented in **Figure 9** (EEA, 2002b). In the last decade, the number of vehicles increased by almost 3% per year. This trend is expected to slow down till 2020 to an annual increase of 1,5 %. Additionally, traffic-related emissions of PM depend strongly on the engine size of vehicles and the type of fuel used (LPG, petrol, diesel). The classification of the passenger car fleet in Europe in accordance to engine size and fuel type is shown in **Figure 9**.

Another important aspect of the relation between road traffic and PM emissions are the annual vehicle-kilometres driven per vehicle category (e.g. passenger cars, light- and heavy duty vehicles and buses) and per driving mode (e.g. urban, rural and highway). This is shown in **Figure 10**.

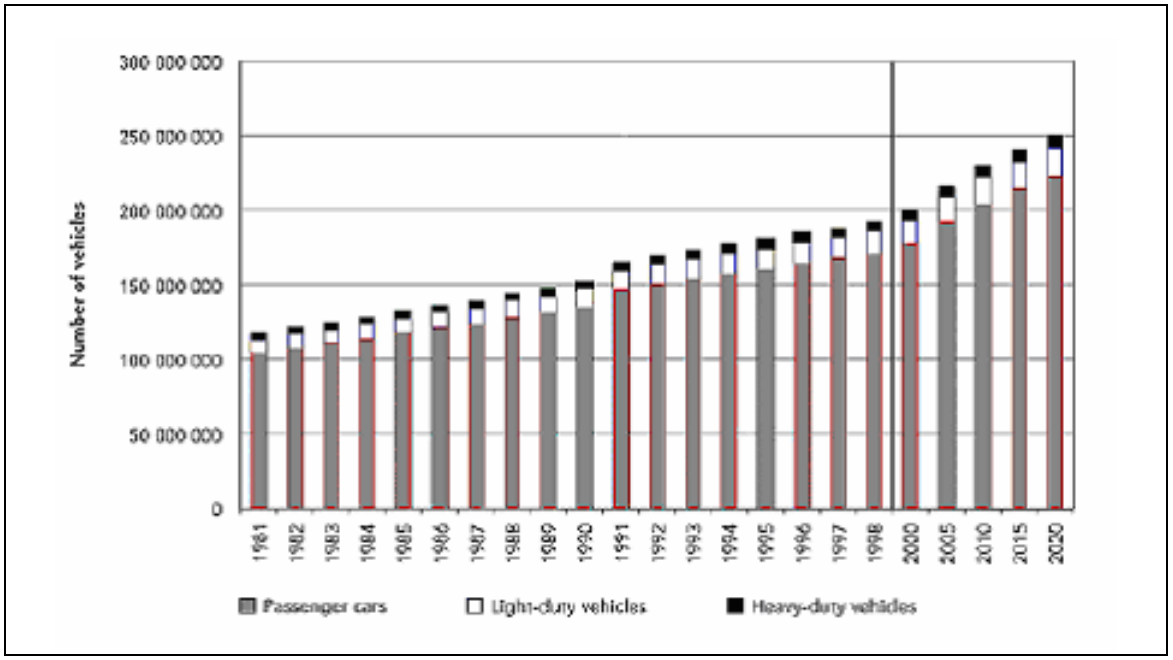

Figure 9. *Number of vehicles in 15 EU Member States from 1981 to 2020 (EEA, 2002b).*

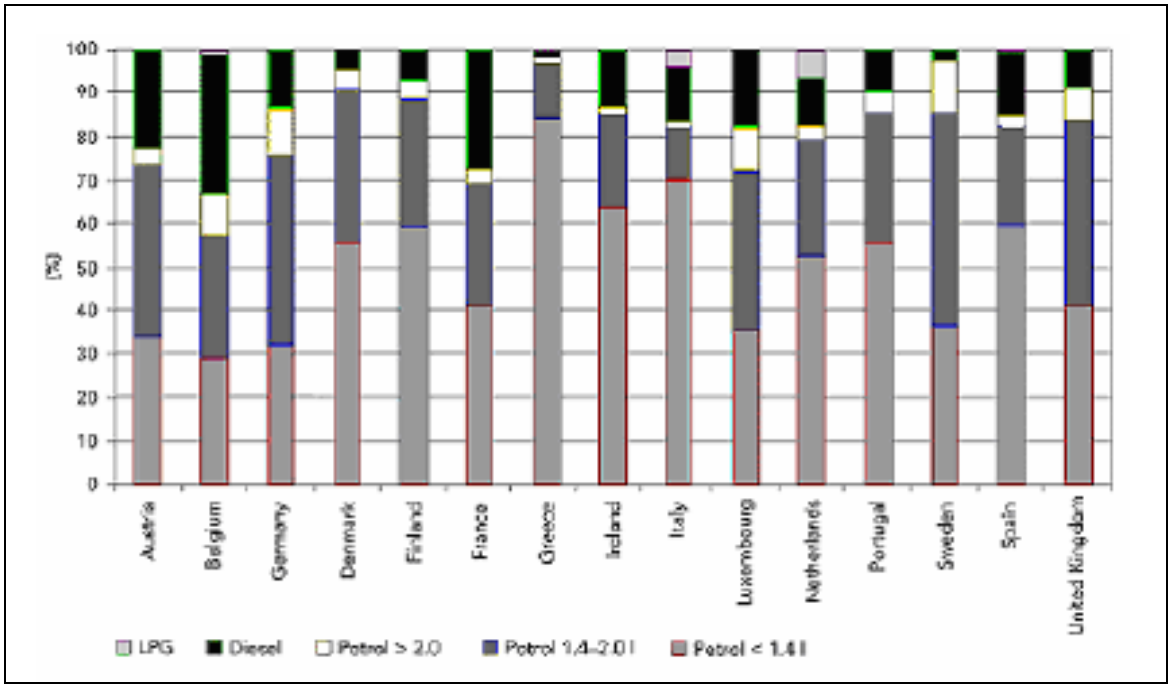

Figure 10. *Classification of car fleet in Europe by engine size and fuel type (EEA, 2002b).*

For example, passenger cars dominate the total number of vehicle-kilometres in Europe, while buses make the smallest contribution. Since diesel engines emit more particles than petrol engines, light duty trucks used for the transport of goods within Europe are expected to have a larger impact on air quality. **Figure 11** provides an example of the average mileage, distinguished by driving mode, for different categories of vehicles in the Netherlands. It is seen that, despite the relatively small number of buses, the average annual mileage of buses in urban areas is about ten times higher than the mileage driven by passenger cars and consequently, the impact of buses on urban air quality may be relatively large. It is logical to assume that a similar situation may apply to other densely populated areas across Europe.

Despite the increase of road traffic, the air quality in urban areas in 2010 is projected to improve by more than 50% for traffic-related pollutants, as compared to 1995. Technological improvements of vehicle engines and fuels – guided by European standards, (1998) – are the main drivers for this development. Nevertheless, it is uncertain if declining emissions by road traffic are sufficient to maintain an adequate air quality in some urban environments. In view of the intensification of space utilization in the urban environment and the growing use of automobiles, it is questionable whether technological improvements alone will be sufficient to meet the air quality standards according to the European legislation.

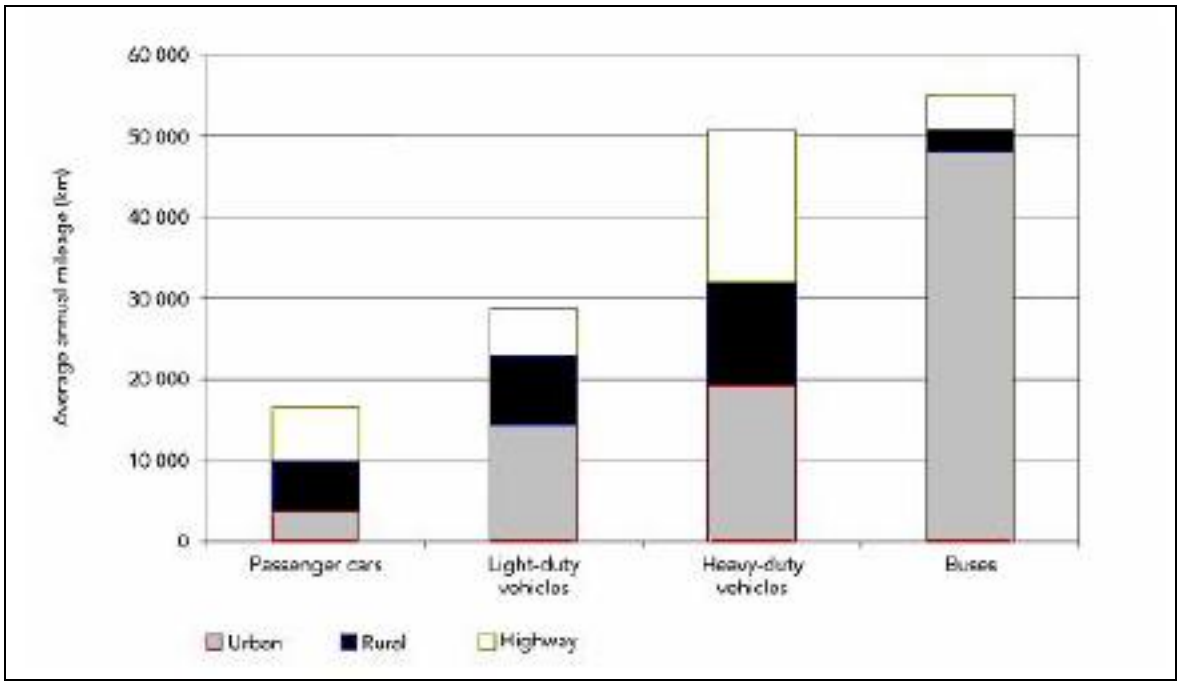

Figure 11. *Average annual mileage for urban, rural, and highway driving modes per vehicle category in the Netherlands in 1995 (EEA, 2002b).*

4.1.2 Development of the market for diesel cars

The increase in sales of diesel cars in Europe during the last decade is evident to anyone. However, it is difficult to find a single reason for this commercial success. Most likely, it is a combination of many different factors that have contributed to this development. Some of these factors have been summarised in a presentation at the 2008 Diesel Engine-Efficiency and Emissions Research Conference (DEER) in the USA (Hiemesch, 2008). One slide from that presentation that summarises some of the most important factors is shown in **Figure 12**.

Since 1983, when BMW introduced their first diesel engine on the market, a continuous increase in performance has reduced – and in many cases also surpassed – the gap to petrol engines for this factor of major importance for customer acceptance. In addition, the fuel consumption has also been reduced significantly, in particular due to the introduction of direct injection in the late 1990's. For a period until a couple of years ago, the gap to petrol cars even increased, while it has remained more or less constant since about 2005. Similarly, the reduction of exhaust emissions has been substantial, although some further reductions of e.g. NO_X emissions will be necessary in the future to keep up with the pace of the development on petrol cars and the emission legislation.

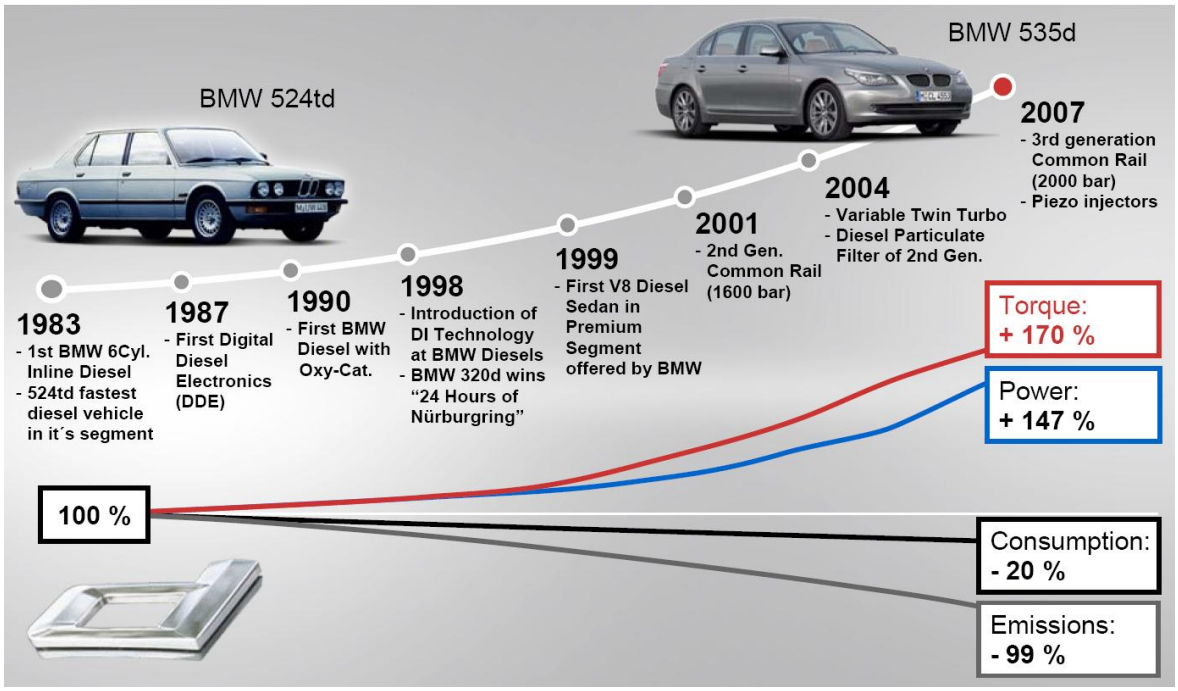

Figure 12. *Evolution of diesel performance (Hiemesch, 2008).*

The market share for diesel cars has increased steadily during the last 20 years and the sales now account for approximately 50% of the market in EU-15. In **Figure 13**, the market share for 2005 in different countries in the Western Europe is shown (Schindler, 2006). It should be noted that the diesel share of some markets with relatively low market penetration has increased considerably during the last couple of years. For example, the market share in Sweden has increased from some 10% in 2005 to about 35% in 2008. Similarly, the market share has increased in Norway and is now about 50%. Thus, both countries have rapidly approached the average in Western Europe.

It is interesting to note that the market development for the diesel share has generally always exceeded the expectations. This is shown **Figure 14** where a couple of prognoses made during the last years have been compiled (Schindler, 2006).

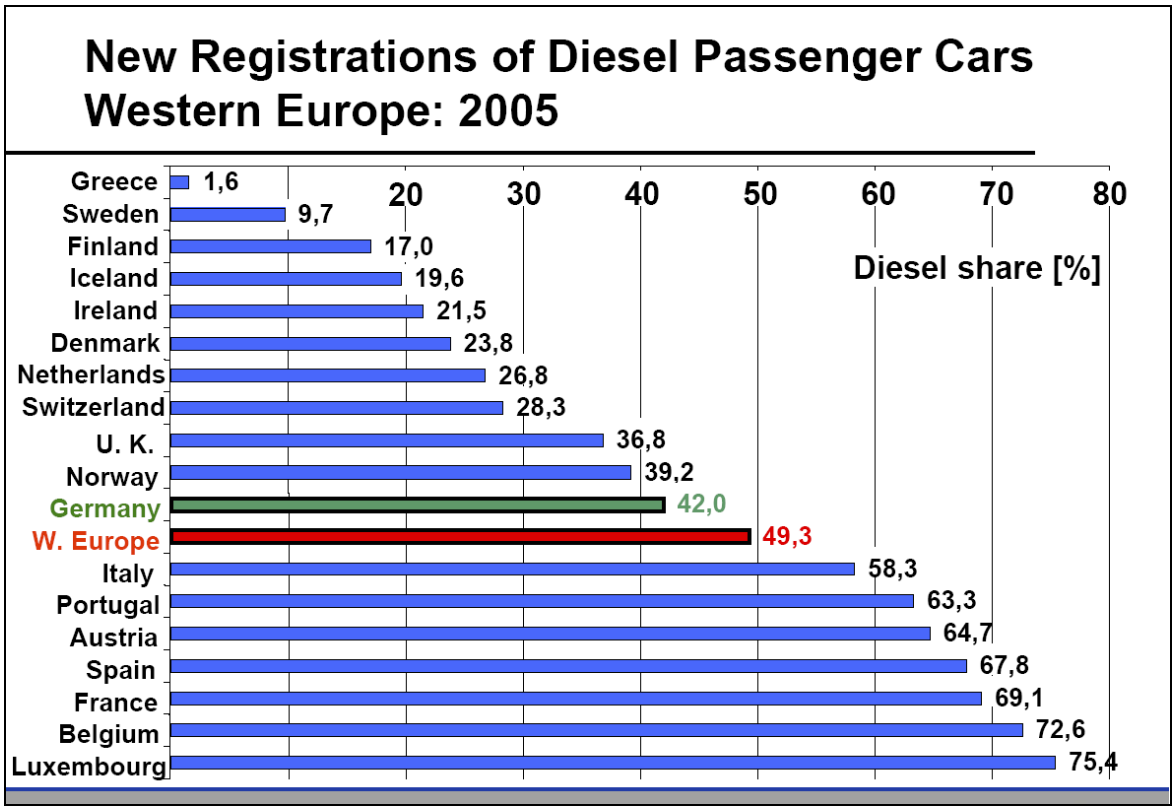

Figure 13. *Market share of diesel cars (Schindler, 2006).*

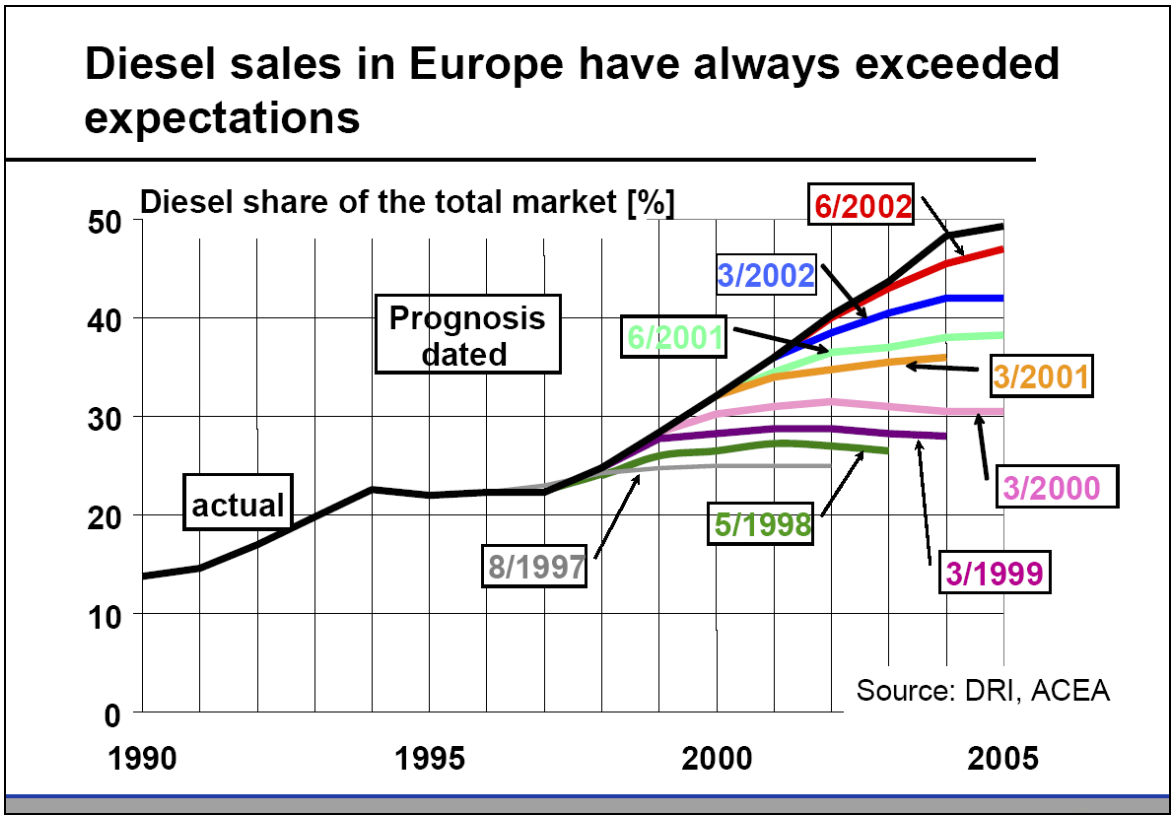

Figure 14. *Prognosis of diesel share (Schindler, 2006).*

Differences in government policies (e.g. taxation) in the EU member states have a great influence on the market penetration of each fuel on a certain market. Therefore, it is easier to estimate the future market penetration for the whole EU, than for individual member states. However, as noted above, this is not easy either. A prognosis about the evolution of the share of diesel cars in Europe was made by Ecotraffic in 2002 (Ahlvik and Brandberg, 2002). These results are shown in **Figure 15**, where the market share of various energy converters (engines) was projected up to 2015.

The technology shift from indirect injection (IDI) to direct injection (DI) for diesel engines is evident from the historical data in **Figure 15**. In the estimate by the authors, the rate of increase of diesel penetration would slow down at the end of the period and then stabilise at a level slightly above 40%. Several reasons for this development were stated. First, the share of diesel fuel from crude oil cannot increase to an arbitrary level with contemporary refinery technology. Second, an increase in the demand for jet fuel and diesel fuel for heavy-duty applications is also likely. Likewise, long-term investments in the refinery business have to pay-off before new commitments are made. Therefore, an increase in the demand for diesel fuel will lead to higher prices and this will stabilise the market penetration for diesel cars at a "natural" level. An increase in fuel trade with countries having a low share of diesel fuel (e.g. the USA) could be one option to offset the anticipated problems in diesel fuel supply. The relevance of these projections has relatively recently become most evident, when prices on diesel fuels have been higher than on petrol in many European countries. In general, it is plausible that the price on diesel fuel will increase even more in the future in comparison to the petrol price.

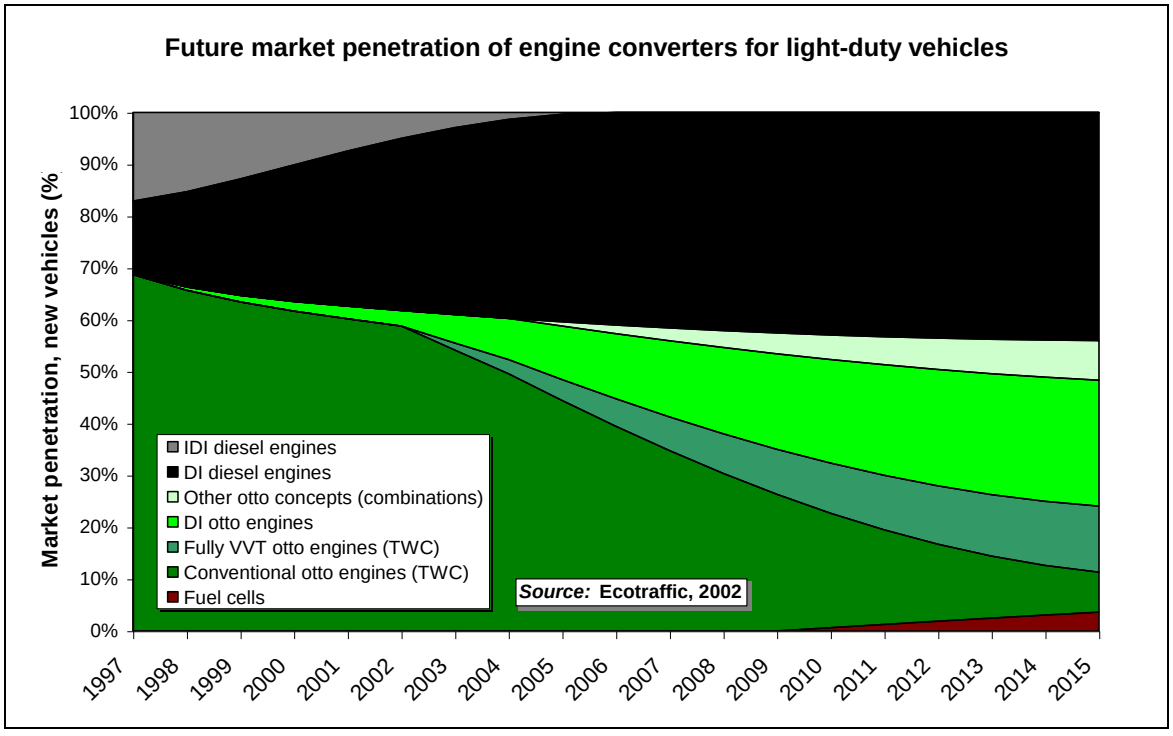

Figure 15. *Future energy converters (Ecotraffic).*

Several representatives from the automotive sector and their suppliers have expressed an opinion that the market share of diesel cars would start to diminish on the time horizon of 2010 to 2020. Besides the reasons stated above, the fuel consumption of petrol-fuelled cars

is anticipated to decrease more than for diesel cars diminishing the fuel consumption advantage for the latter category. Furthermore, the more stringent emission limits are thought to increase the cost for diesel engines. It is also likely that the current tax incentives, that currently favour diesel fuel in most EU member states, will diminish in the future.

A couple of comments on the otto engine options in **Figure 15** can be made. The market penetration of conventional petrol-fuelled otto engines will decrease in favour of direct injection engines and engines with fully variable valve timing, as well as combinations of the two technologies. The denotation "other concepts" in **Figure 15** refers to combinations of fully variable valve timing (VVT) and/or DI with other options, such as e.g. supercharging and/or variable compression. It can be concluded that a metamorphosis of the otto engine will be necessary to fulfil the commitments to reduce fuel consumption and CO_2 in the anticipated timeframe. In general, the technical differences between the engines will also diminish and the synergies regarding the development of components and concepts for each kind of engine will increase.

4.2 Driving cycles

Driving cycles have a significant influence on emissions. Two important categories of driving cycle exist. First, there are driving cycles for whole vehicles. Passenger cars usually use this kind of driving cycles. The emissions are expressed per vehicle km driven, or as g/km. Second, there are driving cycles for engine dynamometers. The emissions in these driving cycles are expressed per work performed by the engine (g/kWh or g/bhp-hr). Driving cycles can be stationary (steady-state) or transient. Usually, most driving cycles for vehicles are transient. For heavy-duty engines a stationary test cycle is still used (ESC).

As an example of a driving cycle for chassis dynamometer, the new European driving cycle (NEDC) is shown in **Figure 16**. The NEDC is used for certification purposes for the European market. The basis for the NEDC driving cycle originates from the 1970's and thus, it has very "sharp edges" with little variation (transients) in between. The NEDC driving cycle comprise two phases; i.e. the "urban" and "highway" phases. The urban part of the cycle begins with a cold engine start (i.e. stabilized at ambient temperature) and therefore cold start emissions are included in the cycle and can be analyzed by, for example, comparing the emissions for the first 400 s with the identical part of the following 400 s of the cycle. The cold start is normally not included in other transient driving cycles such as the Artemis cycles or the US06. A further difference between the NEDC and other driving cycles is the absence of micro transients in the NEDC.

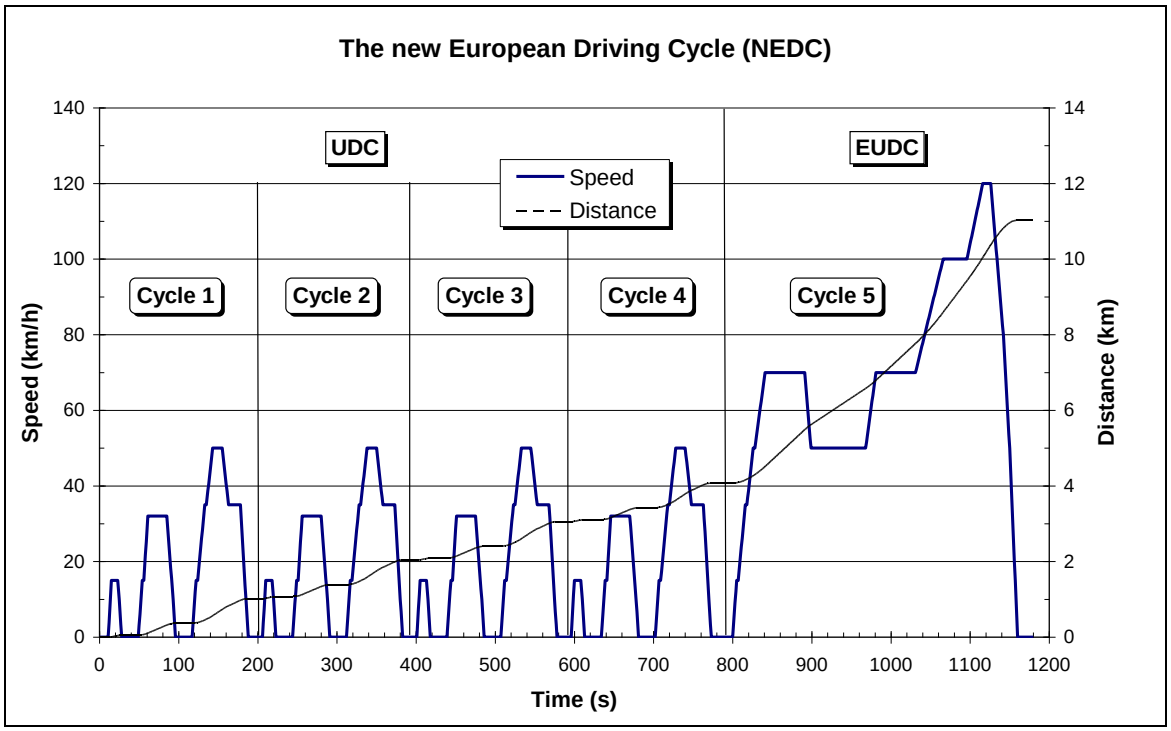

Figure 16. *The NEDC driving cycle*

As a contrast to driving cycles for chassis dynamometers, a driving cycle for an engine dynamometer has set values for both engine speed and torque. An example of a test cycle for and engine dynamometer is the European Transient Cycle (ETC) as shown in **Figure 17**. This test cycle is transient, which is evident by looking at the fast variations of speed and torque.

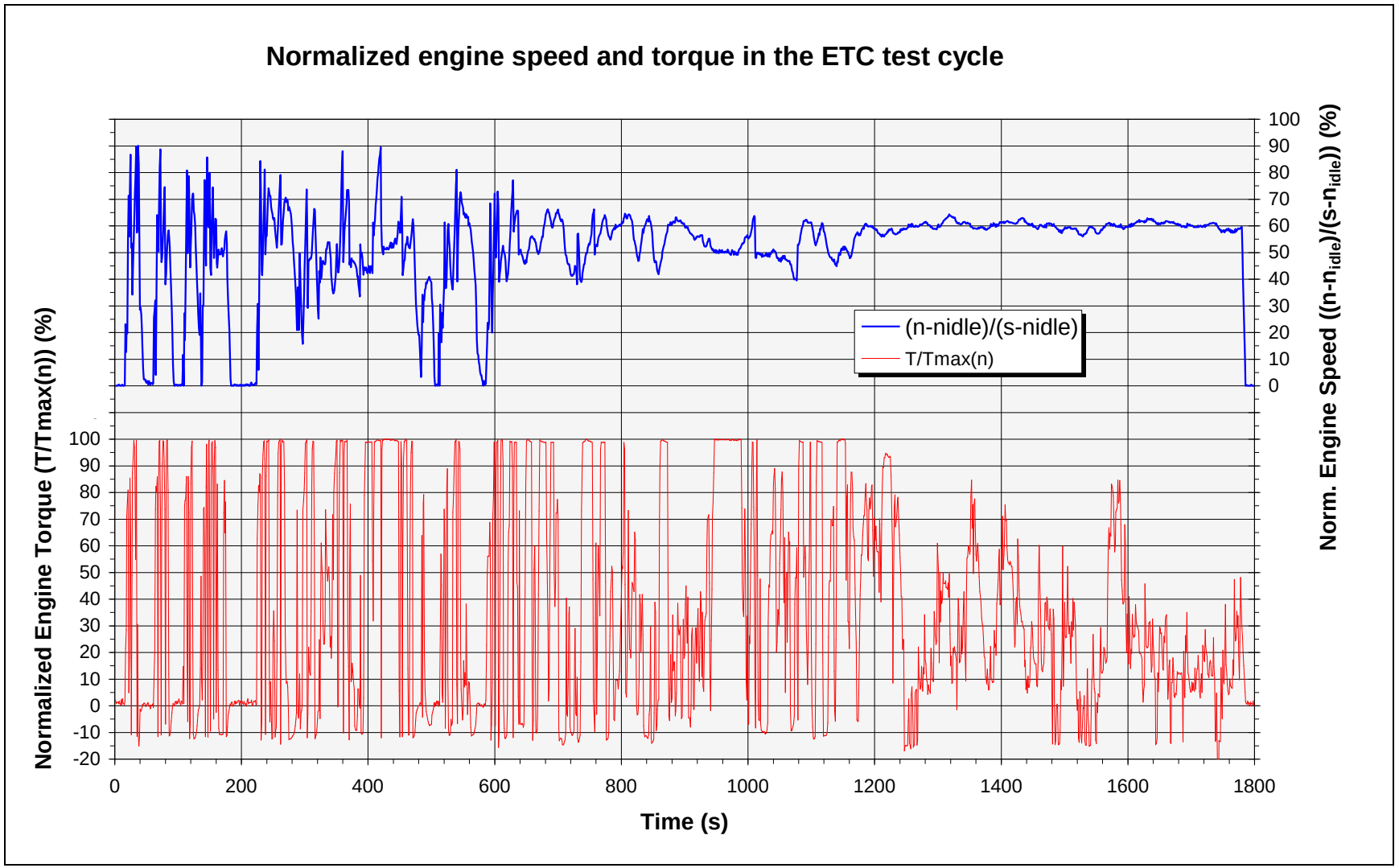

Figure 17. *The ETC driving cycle*

4.3 Emission limit values in the EU, 1993 – 2015

In the literature, both Roman and Arabic numerals are used for European emission limits. In the following, we will use Roman numerals when referencing to European standards for heavy-duty engines (Euro I, II,…), and reserve Arabic numerals for light-duty vehicle standards (Euro 1, 2,…).

4.3.1 Light Duty Vehicles

The emission limit values in the EU are set using the NEDC cycle and by using certified reference fuels. In addition, also evaporative hydrocarbon emissions are measured using a closed chamber (SHED). In Sweden, prior to model year 1995, the FTP75 driving cycle was used and the emission limit values were based on standards in the USA. After the approval of the EES-treaty in 1994 the FTP75 was phased out in order to be fully replaced by the European driving cycle (which was further modified in year 2000 to be the NEDC).

In the year 2002, additional tests were included for petrol vehicles in the European certification procedure in that emissions of CO and HC emissions must meet emission standards set for the NEDC at -7°C. Further requirements include the operation of the On-Board Diagnostics system (OBD) for monitoring error codes in the exhaust after treatment system.

Future changes in the legislation of major importance include emission limit values set for particle number emissions that are presently proposed by the European Commission to be included in the Euro 5 legislation. The proposed number emission limit of 5×10^{11} particles/km would be applicable to all categories of light-duty diesel vehicles at the Euro 5 (in effect September 2009) and Euro 6 (in effect September 2014) stage.

4.3.2 Heavy Duty Vehicles

Emission limit values for heavy duty vehicles are set for engines only in contrast to the light duty vehicles for which the limit values are set for the whole vehicle. It follows that the emissions for the engines are not given for distance but for the work performed by the engine and the unit is accordingly g/kWh. The "driving cycle" for the engines is a set of stationary modes of defined load and engine speeds. This is in contrast to the "real world" in which the engine is subject to transients that affects the emissions. It is thus obvious that the certified emissions from light and heavy duty vehicles are not directly comparable.

Swedish emission limit values for engines are originally, in contrast to the values set for light duty vehicles, based on European methods and limit values. In the directive 1999/96/EG lower emission limit values were set and the term Environmentally Enhanced Vehicles (EEV) was introduced. In 2005, directive 2005/55/EG consolidated the earlier directive and applies to all vehicles above 3500 kg including diesel, petrol, natural gas and LPG. Environmental classes were introduced for model year 1992 in Sweden. Initially environmental class 3 was equivalent with the regulation for 92/93 and the lower emission limit values according to environmental class 1 and 2 were equivalent to the regulation for 95/96. However, as the limit values for the environmental classes have not been adjusted, the environmental class system has lost its importance for heavy duty engines.

4.3.3 Emission limit values for Light Duty Vehicles, EU 1993 – 2015

Today, there are emission limits for most categories of road vehicles in the EU. A more thorough compilation of emission norms for several kinds of vehicles and engines are made in Appendix 1. Here, a concentration is made on the emission limits for passenger cars, since these vehicles was the main focus of this study. On July 18 2008, the Regulation 692/2008 for limiting emissions from light passenger cars and commercial vehicles was adopted (EC, 2008). This was an amendment to the previous Regulation 715/2007 published on 20 June 2007 by the European commission (EC, 2007b). In order to provide some backtrack of the progress since early 1990, emission limits from previous EU directives are also included in the table. The emission limit values in the EU for passenger cars (class M1) are presented in **Table 1**, below. Note that there are similar limits for light commercial vehicles (classes N I, II and III) but to simplify the overview, these limits are not shown here.

Table 1. *Emission limits values in the EU.*

				Emission component and limit						
Directive		**Term**[a]	**Time**[b]	**CO** (g/km)	**HC** (g/km)	**NMHC**[c] (g/km)	**NO_X** (g/km)	**HC+NO_X** (g/km)	**PM**[d] (mg/km)	**PN**[e] (#/km)
91/441/EEG		Euro 1	6/92 1/93	2,72	---	---	---	0,97	140	---
94/12/EC, petrol		Euro 2	1996-01	2,2	---	---	---	0,5	---	---
94/12/EC, diesel IDI[f]				1,0	---	---	---	0,7	80	---
94/12/EC, diesel DIg[f]			1997-01	1,0	---	---	---	0,9	100	---
98/69/EC, row A petrol[h]		Euro 3	2000-01	2,3	0,20	---	0,15	---	---	---
98/69/EC, row A diesel[i]			2001-01	0,64	---	---	0,50	0,56	50	---
98/69/EC, row B petrol[h]		Euro 4	2005-01	1,0	0,10	---	0,08	---	---	---
98/69/EC, row B diesel[i]			2006-01	0,50	---	---	0,25	0,30	25	---
Euro 5 reg. 692/2008[i]	petrol	Euro 5a	2009-09	1,0	0,10	0,068	0,06	---	5,0[j]	---
	diesel		2011-01	0,5	---		0,18	0,23	5,0[j]	---
Euro 5 reg. 692/2008[i]	petrol	Euro 5b	2011-09	1,0	0,10	0,068	0,06	---	5,0/4,5[j]	---
	diesel		2013-01	0,5	---		0,18	0,23	5,0/4,5[jk]	6×10^{11}
Euro 6 reg. 692/2008[i]	petrol	Euro 6	2014-09	1,0	0,10	0,068	0,06	---	5,0/4,5[jk]	---[l]
	diesel		2015-09	0,5	---	---	0,08	0,17	5,0/4,5[jk]	6×10^{11}

Notes:

[a] In this column, the regulations have been denoted with the designations (Euro 1, 2, etc.) commonly used by laymen but lately also very often by both officials and the industry.

[b] The two dates in the table refer to that the implementation is stepwise. The first date is for new type approvals and the latter date is for all type approvals.

[c] NMHC: non-methane hydrocarbons, valid only from Euro 5 and 6 for engines with positive ignition (otto engines).

[d] PM: particle emissions. These limits are from only valid for diesel-fuelled vehicles and, from Euro 5 and 6, for petrol vehicles using direct injection.

[e] P: Particle number emissions. P is regulated only for diesel vehicles in Euro 5 and 6, i.e. no limit is set to petrol-fuelled vehicles although there is a limit for PM emissions (see above) for direct injected petrol cars.

[f] IDI: indirect injection, i.e. injection in a prechamber (or swirl chamber)

[g] DI: direct injection, i.e. injection directly in the cylinder (combustion chamber)

[h] The directive 98/69/EG (2000/2001 and 2005/2006, respectively) are based on the new European driving cycle (NEDC), which uses a modified start procedure (at +20 – +30 °C) compared to the older driving cycle. Therefore, the CO limit (2,3 g/km) in the directive 98/69/EG is actually stricter than the limit in the directive 94/12/EG directive (2,2 g/km) that uses the older European driving cycle (EDC). Since also the HC emissions are higher in the NEDC driving cycle, the reduction in $HC+NO_X$ emissions that can be calculated from the data in the table (from 0,50 till 0,45 g/km) much greater than the levels indicate.

[i] When this report was written, some details of the regulation for Euro 5 and 6 were not finalised.

[j] Particle mass standard only apply to positive injection vehicles with direct injection.

[k] A revised measurement procedure shall be introduced before the application of the 4,5 mg/km standard.

[l] A number standard for vehicles with positive ignition shall be defined before 1 September 2014.

As **Table 1** above is a simplification, the reader should refer to the EU emission regulations for more details. Some further details in **Table 1** needs clarification:

- The Euro 5a emission standard excludes limits for particle number and the revised measurement procedure for particle mass. Furthermore, flexible fuel vehicles are not subject to low-temperature emission testing when tested on biofuel.
- With the introduction of Euro 5b (2011-09-01), a particle number standard is enforced for the first time.
- It is also possible to certify to a Euro 6a standard until the end of 2012, where similar exceptions as for Euro 5a apply for particle mass, number and flexible fuel vehicles tested on biofuel.
- In the "final" Euro 6b standard (not shown in **Table 1**), all the exceptions mentioned above are abolished. Limits on particle mass and number will apply on all vehicle types as well as limits for low temperature on flexible fuel cars.

Interesting to note is that limits for particle mass are only introduced for vehicles with positive ignition that use direct injection. Previously, it was proposed that only direct injection engines that use a lean-burn combustion system should be subject to this limit but this now applies to all vehicles with positive ignition and direct injection. Stoichiometric direct injection engines would then not have had to certify to this limit. A particle number standard for vehicles with positive ignition will not be introduced before Euro 6. No limit has yet been proposed here.

In conjunction with the emission limit values above, durability standards are also set in order not to allow that the emission limit values are exceeded after vehicle operation over a certain driving distance or time:

- Euro 3, 80 000 km or 5 years (of which comes first). The manufacturer may as an option to a deterioration cycle chose determined factors according to: 1,2 for CO, HC, NO_X (petrol), or 1,1 for CO, NO_X, $HC+NO_X$, and 1,2 for PM (diesel).
- Euro 4, 100 000 km or 5 years (of which comes first).
- Euro 5 and 6, 160 000 km or 5 years (of which comes first).

In addition to the requirements above, the 2000/2005 requirements also include:

- The member states in the EU have the right to introduce tax reductions for vehicles introduced prior to 2005 meeting the 2005 requirements.

- Emission limit values for CO and HC for petrol vehicles at -7°C from year 2002.
- Introduction of OBD for monitoring error codes in the exhaust after treatment system.

With the introduction of Euro 3, all vehicles must be equipped with an OBD-system informing the driver if errors in the exhaust after treatment system occur that may lead to exceeding the emission limit values. Limit values for the OBD are higher as compared to the emission limit values. Requirements for durability were introduced from year 2005 and became fully implemented in year 2006. The manufacturer must confirm that the engine meets the emission limit values for the whole period defined as "useful life" for each category of vehicles. In **Table 2**, below, the durability periods for the emissions for each category of vehicle are presented.

Table 2. *Durability periods for emissions.*

Period*	Category of vehicles†
100 000 km or 5 years	N1 and M2
200 000 km or 6 years	N2 N3 ≤ 16 ton M3 Class I, Class II, Class A, and Class B ≤ 7,5 ton
500 000 km or 7 years	N3 > 16 ton M3 Class III, and Class B > 7,5 ton
* km or year period, whichever is the sooner † Mass designations (in tons) are "maximum technically permissible mass"	

4.3.4 Emission limit values for Heavy Duty Vehicles, EU 1992 – 2014

Emission limit values for heave duty vehicles have emerged over a longer period of time and the main steps for this process are presented below:

- Euro 1 was introduced in 1992 and was followed by Euro II in 1996. Both truck engines and city buses were covered by this legislation. However, the certification of bus engines was voluntarily.
- Following the directive 1999/96/EG, Euro III was introduced in year 2000, Euro IV in 2005, and Euro V was introduced in October 2008. This directive also introduces voluntary lower emission limit values for EEV[2] vehicles.
- The directive 2001/27/EG was introduced in year 2001 and prohibits the use of "defeat devices" and "irrational emission control strategies" that potentially reduces the function of the emission control system at normal operation as compared to the function obtained by the emission test procedure given by the certification procedure.
- Durability and OBD requirements were introduced with directive 2005/55/EG and the emission limit values for Euro IV and Euro V were confirmed.
- In addition to reduced anticipated emission limit values in the future (Euro VI and later), it is also likely that emission limit values for presently unregulated pollutants will be introduced as an effect of the introduction of new alternative fuels and the

[2] EEV: Enhanced Environmental friendly Vehicles

use of fuel additives. Furthermore, the requirements for future particle emission limit values are revised in the PMP programme in which also the possibility to introduce emission limit values for particle number emissions are examined.

In **Table 3**, the emission limit values for the different certification levels are presented.

Table 3. *Emission limit values for heavy duty diesel engines, ESC test.*

Level	Date	Test	CO (g/kWh)	HC (g/kWh)	NO_X (g/kWh)	PM (g/kWh)	Smoke (m^{-1})
Euro I	1992, < 85 kW	ECE R-49	4,5	1,1	8,0	0,612	
	1992, > 85 kW		4,5	1,1	8,0	0,36	
Euro II	1996.10		4,0	1,1	7,0	0,25	
	1998.10		4,0	1,1	7,0	0,15	
Euro III	*1999.10, EEVs only*	*ESC & ELR*	*1,5*	*0,25*	*2,0*	*0,02*	*0,15*
	2000,10	ESC & ELR	2,1	0,66	5,0	0,10 0,13*	0,8
Euro IV	2005.10		1,5	0,46	3,5	0,02	0,5
Euro V	2008.10		1,5	0,46	2,0	0,02	0,5
Euro VI[#]	2014.01		1,5	0,13	0,5	0,01	0,5

* For engines of less than 0,75 dm^3 swept volume per cylinder and a rated power speed of more than 3000 min^{-1}
[#] Proposal for Euro VI by the European Parliament's Environment Committee on July 15, 2008. When this report was written (October 2008), the final decision on the Euro VI limits was not made.

In **Table 3**, the contemporary proposal (i.e. when this report was written in October) for Euro VI is listed. This proposal was made by the European Parliament's Environment Committee on July 15, 2008. The changes made to the previous proposal of the Commission were an increase of the NO_X limit from 0,4 to 0,5 g/kWh and an earlier introduction of Euro VI (1/1 2014 instead of 1/10 2014). One proposal of reducing the limit for particle mass from 10 to 5 mg/kWh was rejected.

With the Euro III regulation new driving cycles were introduced and the older ECE R-49 was replaced by the ESC and ETC cycles. In addition the European load response test ELR was also introduced for measurements of opacity (smoke).

For type approval measurements, the following conditions are required for new engines in Euro III (2000).

- Conventional diesel engines are examined in accordance with ESC/ELR.
- Diesel engines with "advanced exhaust aftertreatment systems" (e.g. NO_x reduction systems or DPF) are examined in accordance with ESC/ELR and ETC.
- Gas engines are examined in accordance with ETC.

For type approval of new engines in Euro IV (2005) and later as for EEV, all diesel engines shall be examined in accordance with ESC/ELR and ETC.

In **Table 4**, the emission limit values for all diesel and gas engines examined in accordance with the ETC are presented.

Table 4. *Emission limit values for diesel and gas engines, ETC-test.*

Level	Date	Test	CO (g/kWh)	NMHC (g/kWh)	CH_4[a] (g/kWh)	NO_X (g/kWh)	PM[b] (g/kWh)
Euro III	*1999.10, EEVs only*	*ETC*	*3,0*	*0,40*	*0,65*	*2,0*	*0,02*
	2000.10	ETC	5,45	0,78	1,6	5,0	0,16 0,21
Euro IV	2005.10		4,0	0,55	1,1	3,5	0,03
Euro V	2008.10		4,0	0,55	1,1	2,0	0,03
Euro VI[d]	2014.01		4,0	0,16	0,5	0,5	0,01

a, for natural gas engines only
b, not applicable for gas fueled engines at the year 2000 and 2005 stages
c, for engines of less than 0,75 dm^3 swept volume per cylinder and a rated power speed of more than 3000 min^{-1}
d, Proposal for Euro VI by the European Parliament's Environment Committee on July 15, 2008. When this report was written (October 2008), the final decision on the Euro VI limits was not made.

4.3.5 Comparison of emission limits for light-duty and heavy-duty vehicles

A direct comparison between the emission limits for different applications is more or less impossible. There are a number of factors that affect the comparison that cannot be taken into account. For example, the driving cycles are different. Furthermore, emissions for light-duty vehicles are expressed in g/km while the limits for engines to heavy-duty vehicles are expressed in g/kWh.

In order to obtain some meaningful comparison between emission limits for various kinds of vehicles, the concept of emission index can be used. Here, the emission of each emission component is divided by the fuel consumption. Thus, the emission level in relation to the amount of fuel can be compared. The unit will be dimensionless but for practical reasons, gram emission per kg fuel consumed can be used (g/kg).

In the most recent compilation of the fuel consumption of petrol and diesel fuelled cars in the EU, the average fuel consumption for each category is 7,1 and 5,7 respectively if the ACEA statistics is used (EU, 2006). The official EU statistics shows somewhat higher levels. One could argue that a similar level for fuel consumption could be used in the calculation, since higher fuel consumption will give a lower level for the emission index. The figures for fuel consumption in mass corresponding to the volumetric fuel consumption are 53,5 and 46,5 respectively. This is equal to a 15% higher consumption on mass basis for the petrol cars. Since the energy content per unit mass is only slightly higher for petrol than for diesel fuel (but much lower on volumetric base), it could be argued that using similar fuel consumption on mass basis in both cases would be a fair comparison. However, the fuel consumption data mentioned above have been used anyway.

For engines used in heavy-duty vehicles, the average fuel consumption in the European Transient Cycle (ETC) can be used[3]. A typical figure could be 210 g/kWh for larger engines. By using the numbers cited above, the emission index for the regulated emission components is depicted in the figures below. As indicated before, the data obtained by calculating the emission index should not be compared directly without any further comments. Therefore, only larger general differences should be considered.

In **Figure 18**, the emission index for CO shows that the differences are relatively small. For example, the emission index for CO in Euro 4/IV is approximately the same for petrol-fuelled light-duty vehicles and for diesel-fuelled engines in heavy-duty vehicles. It is interesting to note that the latter level can be achieved without an oxidation catalyst, while a three-way catalyst is needed in the former case. The generally low engine-out level of CO and HC for diesel engines is an advantage here. Also, it should be noted that passenger cars are subject to a cold start while the ETC test cycle is a "hot" test cycle. A lower limit for the diesel cars compared to the petrol-fuelled cars in the emission legislation takes the potential for lower CO emissions into account.

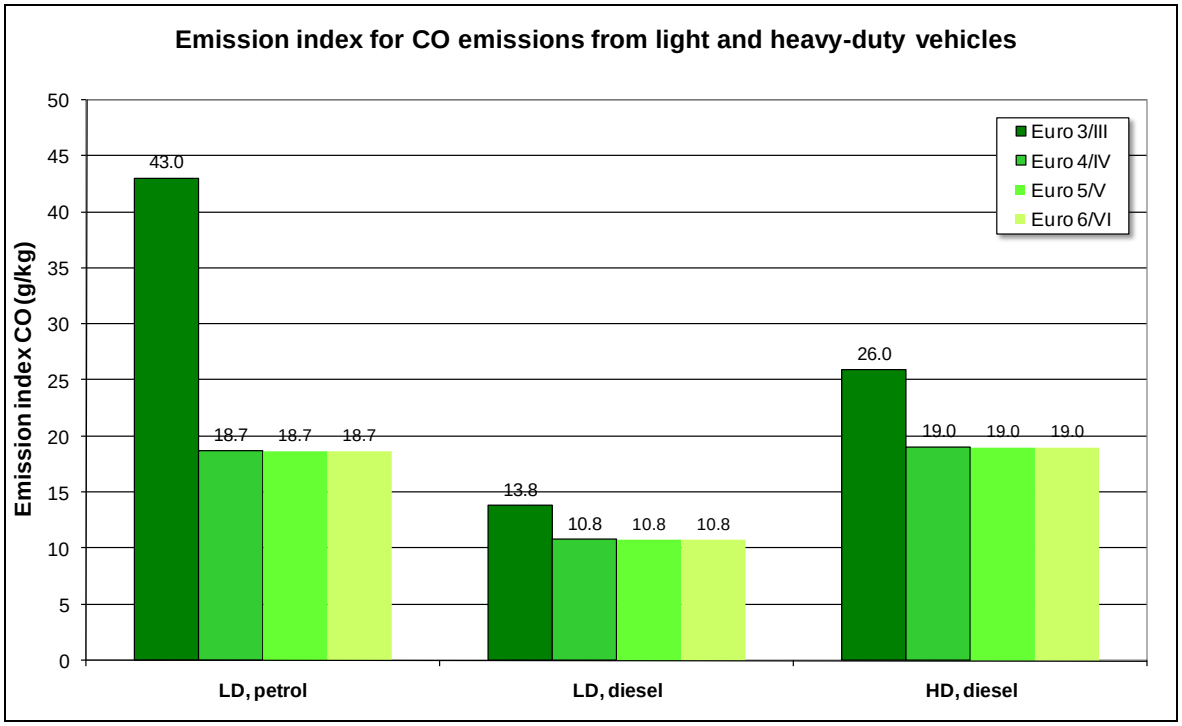

Figure 18. *Emission index for CO (g CO/kg fuel).*

The emission index for HC, as shown in **Figure 19**, indicates a somewhat similar picture as for CO; at least up to Euro 5/V. In Euro 6, the same HC level is set for diesel cars as for petrol cars. In contrast, the level for heavy-duty engines is reduced in Euro VI in comparison to Euro V. This could be that catalytic aftertreatment is anticipated in Euro VI.

[3] There are also emission limits in the European steady-state driving cycle (ESC) for heavy-duty engines that must be met. However, since the driving cycle for passenger cars is transient, the comparison of limits between transient cycles is considered more relevant and no results from the ESC cycle are shown here.

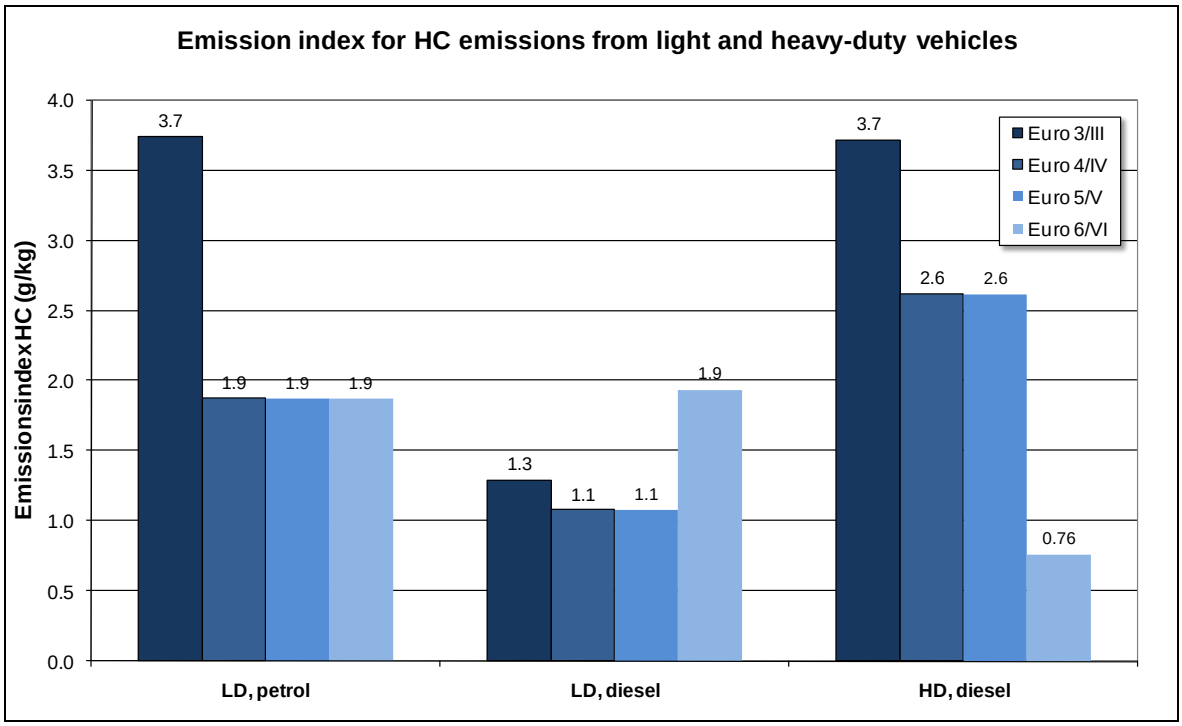

Figure 19. *Emission index for HC (g HC/kg fuel).*

The outcome for NO_V is more dramatic than in the previous cases, as shown in **Figure 20**. The emission limit for NO_X is about one order of magnitude tougher in Euro 4 for light-duty cars in comparison to the corresponding Euro IV level for the engines in heavy-duty vehicles. The relative difference between diesel-fuelled light-duty vehicles and the corresponding engines in heavy-duty vehicles is about a factor of 3. One explanation to this outcome is that the emission legislation for light-duty vehicles in EU has been driven by what can be achieved on petrol-fuelled cars. For NO_X emissions, this implies that the limits for the diesel cars have been lagging behind the petrol cars, albeit that they have been tougher than for heavy-duty vehicles. As a results, exhaust gas recirculation (EGR) was introduced already in the 1980's on diesel cars whereas the same technology was only recently introduced on heavy-duty vehicles. In contrast, exhaust aftertreatment for NO_X reduction such as, e.g. SCR, has already been introduced on heavy-duty vehicles while there is no application yet on passenger cars.

The NO_X emission level for Euro 6 is very similar for petrol (0,06 g/km) and diesel (0,08 g/km) cars. Due to the higher fuel consumption (expressed as g/km this time), the relative level for the NO_X emission index will be higher than for the diesel cars (1,7 vs. 1,1 g/kg), i.e. one kg of diesel fuel is allowed to emit more NO_X than one kg of petrol.

It is likely that the evolution on emission legislation for heavy-duty engines will follow a similar path as in the USA. The proposed emission level for heavy-duty engines corresponding to Euro VI is, when this was written, 0,5 g/kWh, which must be considered somewhat higher although the test cycles are different. However, the relative difference between emission index for heavy-duty engines and the two categories of light-duty vehicles is smaller than for the previous emission norms.

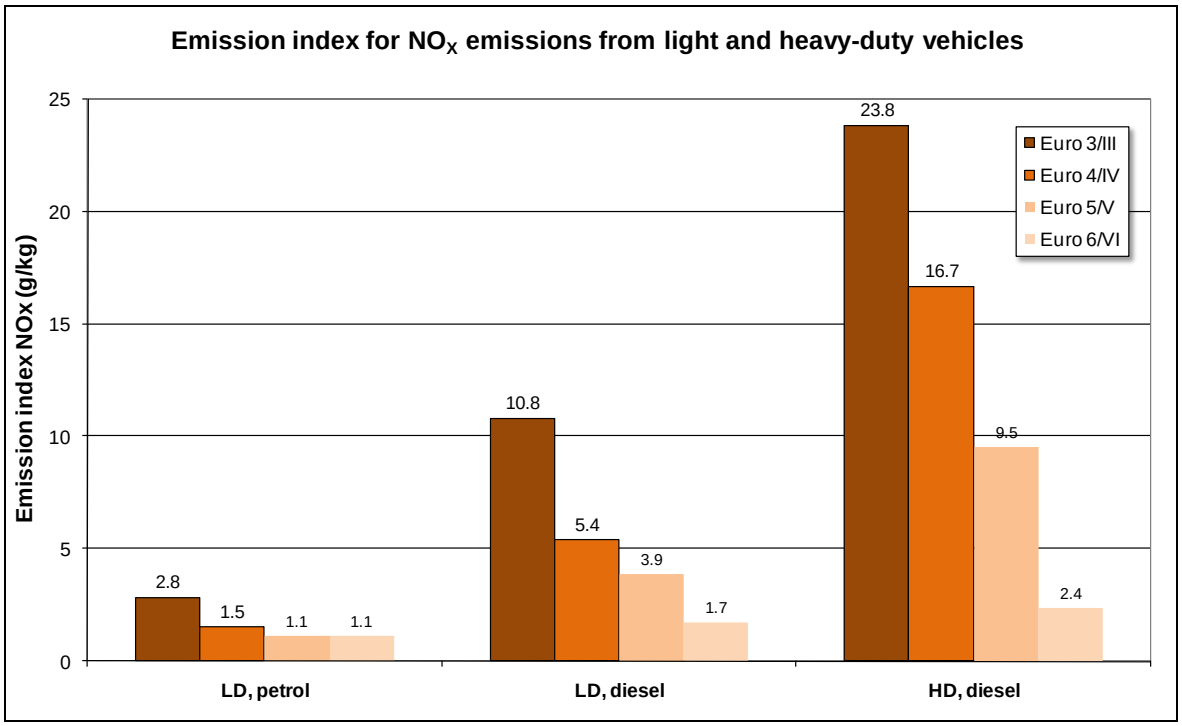

Figure 20. *Emission index for NO_X (g NOx/kg fuel).*

Figure 21 shows the emission index for particulate emissions. In contrast to NO_x emissions, the level for particulate emissions in Euro 3/III and 4/IV is significantly lower for the engines in heavy-duty vehicles compared to the corresponding levels for diesel cars. The level in Euro IV for the heavy-duty engines is almost a factor of 4 higher than for the diesel cars. There are a couple of reasons for this outcome of which the most important are discussed here. First, heavy-duty engines have used much higher injection pressures in the past which reduces the particulate formation. Second, the used of EGR generally increases the particulate formation, while NO_x emissions are reduced, which is a criterion for the development of engines for light-duty vehicles. This is one example of the well-known NO_x/PM trade-off.

The particulate limits in Euro 4/IV can be met on both categories of vehicles/engines without a particulate filter. This is in spite of that the limit is considerably tougher for the heavy-duty engines. In fact, it seems as the particulate emission limit can even be met on heavy-duty engines even if EGR is used. In contrast, particulate filters are used on most new diesel cars. However, in this case the use of aftertreatment technology is most likely driven by market demands and economic incentives and not by stringent emission limits.

In Euro 5 for light-duty vehicles, the particulate limits are much more stringent than the level in Euro 4. For the first time, the level for light-duty vehicles (at 0,10 g/kg) is slightly lower than the corresponding level for heavy-duty vehicles (0,14 g/kg). For Euro VI, the proposed level for heavy-duty engines is again more stringent than for the light-duty vehicles. Supposedly, this limit cannot be met without the use of a particulate filter.

Note that there is no limit for particulate emissions in Euro 3 and 4 for petrol-fuelled cars, as previously described. For comparison, the proposed limit of 4,5 mg/km in Euro 5 and 6 is equal to about 0,08 g/kg, i.e. about half of the Euro IV/V level for heavy-duty vehicles, but about two times higher than the level for Euro VI. It should also be realised that the

apparent tougher level of PM level for petrol-fuelled cars in comparison to diesel-fuelled cars is only due to the anticipated about 20% higher fuel consumption for the petrol-fuelled cars in comparison to diesel cars.

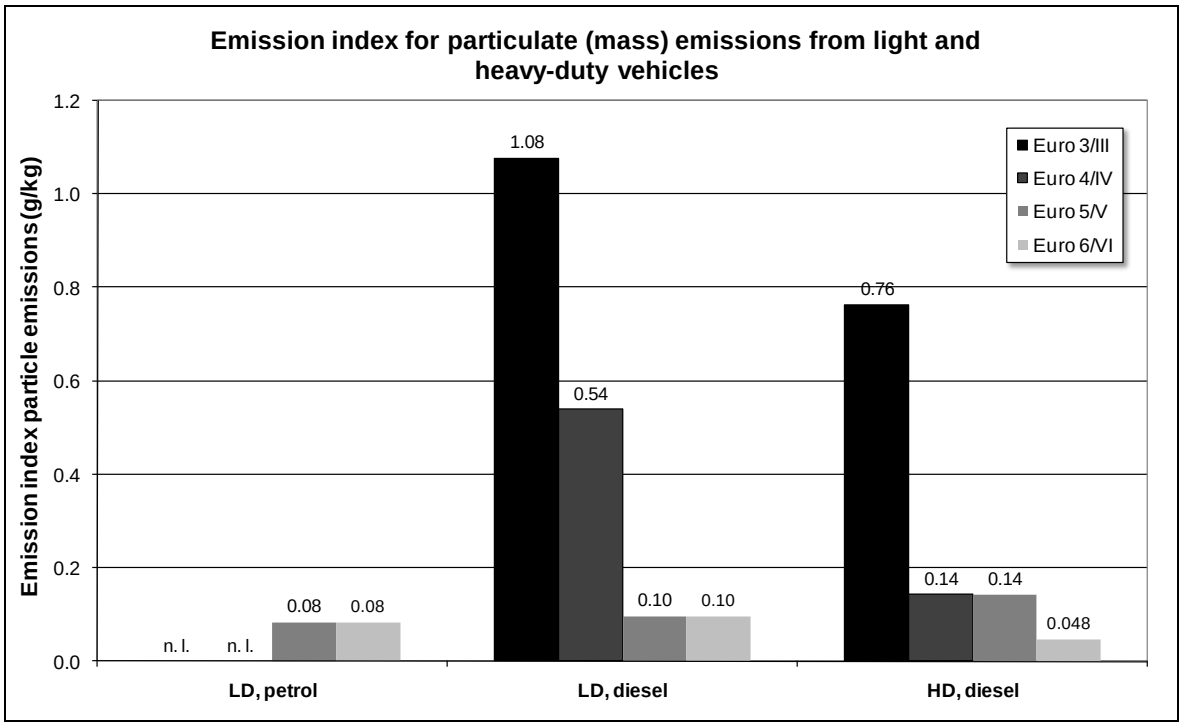

Figure 21. *Emission index for particulate emissions (g PM/kg fuel).*

In summary, the simple comparison of emission limits using emission index shows that the greatest differences can be found for NO_X and particulate emissions. The emission limits for NO_X are tougher for diesel cars than for heavy-duty engines and the situation is the opposite for particulate emissions. In Euro 6/VI the relative differences between emission index will be reduced in comparison to the situation for previous emission norms.

4.4 Fuels and fuel quality development, 1993 - 2015

4.4.1 Diesel fuel

Reference diesel fuel for road vehicles

Since many of the tests discussed in this report have been conducted on reference fuels, it is worthwhile to provide some comments on those fuels. In Appendix 2, tables with these specifications are listed for reference.

A sulphur limit of 300 ppm was introduced year 2000 (Euro 3), and a 50 ppm limit from 2005 (Euro 4). In October 2002, the sulphur specification for Euro 4 type approvals of light-duty vehicles was lowered to 10 ppm in accordance with Directive 2002/80/EC which replaced the earlier specifications.

Automotive diesel fuel for road vehicles

An overview of the diesel fuel specifications is provided in this section. More detailed information is available in Appendix 2. There, also the specific "arctic" grades that are applicable to the Nordic countries during wintertime are listed.

The first EU diesel fuel specification was the EN 590:1993 standard including a sulphur limit of 0,2% in accordance with the Directive 93/12/EEC, which became effective from October 1994 (**Table 5**).

Table 5. *Diesel Fuel Specification (EN 590:1993).*

Fuel Property	Unit	Specification		Test
		Min	Max	
Cetane Number		49	-	ISO 5165
Cetane Index		46	-	ISO 4264
Density at 15°C	kg/m^3	820	860	ISO 3675/ASTM D4052
Sulphur	% (wt.)	-	0,20	EN 24260/ISO 8754
Flash Point	°C	55	-	ISO 2719
Carbon residue (10% btms)	% (wt.)	-	0,30[a]	ISO 10370
Ash	% (wt.)	-	0,01	EN 26245
Water content	mg/kg	-	200	ASTM D1744
Copper strip corrosion, 3h at 50°C		-	Class 1	ISO 2160
Oxidation stability	g/m^3	-	25	ASTM D2247
Viscosity at 40°C	mm^2/s	2,00	4,50	ISO 3104
Distillation (vol. % recovered)	°C			ISO 3405
10% point		report		
50% point		report		
65% point		250	-	
85% point		-	350	
95% point		-	370	
a - limit does not apply if ignition improver additives are used.				

In 1 January 2000, a maximum sulphur limit of 350 ppm and cetane number of 51 was introduced for diesel fuel for road vehicles in the EN 590:1999 in accordance with Directive 98/70/EC (**Table 6**).

Table 6. *Diesel fuel specification ("Euro 3 diesel") (EN 590:1999).*

Fuel Property	Unit	Specification		Test
		Min	Max	
Cetane Number		51	-	EN ISO 5165
Cetane Index		46	-	EN ISO 4264
Density at 15°C	kg/m^3	820	845	EN ISO 3675/EN ISO 12185
Sulphur	mg/kg	-	350	EN ISO 14596/EN

Fuel Property	Unit	Specification		Test
		Min	Max	
				24260/EN ISO 8754
Polycyclic aromatic hydrocarbons	% (wt.)	-	11	IP 391[a]
Flash Point	°C	55	-	EN 22719
Carbon residue (10% btms)	% (wt.)	-	0,30[b]	EN ISO 10370
Ash	% (wt.)	-	0,01	EN ISO 6245
Water content	mg/kg	-	200	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper strip corrosion, 3h at 50°C		-	Class 1	EN ISO 2160
Oxidation stability	g/m^3	-	25	EN ISO 12205
Lubricity, corrected wear scar diameter (wsd 1,4) at 60°C	µm	-	460	ISO 12156-1
Viscosity at 40°C	mm^2/s	2,00	4,50	EN ISO 3104
Distillation (vol. % recovered)[c]				EN ISO 3405
% recovered at 250°C	% v/v	-	65	
% recovered at 350°C	% v/v	85	-	
95% v/v recovered	°C	-	360	

a - to be replaced by EN 12196 when published
b - if ignition improver additives are used, manufacturers must observe the limit prior to the inclusion of additives.
c - for the calculation of cetane index, the 10%, 50%, and 90% recovery points are also needed

The following sulphur limits have been adopted for diesel fuels for road vehicles of the EN 590:2004 standard ("Euro 4") in accordance with the Directive 2003/17/EC (EC, 2003). The new sulphur limit was set at 50 ppm as from 2005. Simultaneously 10 ppm sulphur fuel (both diesel and petrol) shall be available on a balanced geographical basis from 2005. The 10 ppm sulphur limit becomes effective in the year 2009 for all diesel and petrol fuel marketed in the EU member states (**Table 7**).

As can be seen in **Table 7**, the fuel specification for 2009 has not been set yet, besides a few important parameters. When this report was written, the EU was working on the new specifications for diesel and petrol fuels. In a proposal for a new fuel directive by January 31, which has been intensively debated since then, it was proposed to increase the maximum allowable blending level of FAME from 5% to 10% (EU, 2007). It has, however, been claimed later that the proposed 10% level will most likely be replaced by a limit of 7%. In Germany, such a decision has already been taken. In the Swedish environmental class 1 (EC1) diesel fuel, the maximum allowable blending of FAME is limited to 5% today.

Table 7. *Diesel fuel specification, 2005/2009*

Property	Unit	Specification	
		Min	Max
Year 2005			
Cetane Index		51	-
Density at 15°C	kg/m^3	-	845
Distillation			
- 95% v/v recovered at	°C	-	360
Polycyclic Aromatic Hydrocarbons	% wt.	-	11
Sulphur	mg/kg	-	50[1]
Year 2009			
Sulphur	mg/kg	-	10

[1] sulphur-free (max. 10 ppm) fuel must be available in the market.
[2] All diesel fuel and unleaded petrol marketed in the territory of a Member State must have a maximum sulphur content of 10 mg/kg by 1 January 2009.

Diesel fuel for nonroad applications

For mobile nonroad vehicles and machinery (including agricultural and forestry tractors), the same Directive introduces a 1 000 ppm sulphur limit effective 1 January 2008. The Directive also notes that future specifications for road and nonroad diesel should be aligned, calling for the introduction of the 10 ppm sulphur limit in the nonroad sector, provisionally effective 2009. The European Commission must review the future fuel regulations, including the detailed introduction schedule for the 10 ppm diesel, by the end of 2007.

Automotive Swedish diesel fuel

In Sweden, an environmental classification system for fuels was first introduced in 1991. Three Environmental Classes (EC) of diesel fuel qualities have been introduced:

- EC1 with a sulphur content of maximum10 ppm (wt).
- EC2 with a sulphur content of maximum sulphur 50 ppm (wt).
- EC3 equivalent to the EN 590 diesel.

The specifications of the EC1 and the EC2 fuels are listed in **Table 8**, below. The EC1 diesel was at the time of its introduction in 1991 the first ultra low sulphur diesel fuel in the world. The EC3 corresponds to EN 590 and therefore, this specification has changed according to the modifications of EN 590 in the EU. For reference, the current (autumn of 2007) EN 590 specification is listed in **Table 8**.

New environmental driving forces have required an environmental classification also of diesel fuels not fulfilling the specification of EC1. Some examples are biodiesel (FAME) and synthetic diesel fuel. Therefore, a small revision of the environmental classes was introduced on August 1 2006. This decision was based on the results from an investigation in which one of the authors of this report participated in (Swedish Road Administration, 2005a, 2005b). The major difference compared to the old EC1 and EC2 specifications were that the T95 boiling point was raised from 285°C and 295°C respectively to 320°C. According to the new specification it is possible to mix 5% FAME in the EC1 diesel fuel

and thus the same possibility to introduce FAME in the diesel is allowed in Sweden as in the EU. The FAME must comply with the SS-EN 14 214 standard.

Table 8. *Swedish diesel fuel specifications.*

Fuel Property	Unit	EC1	EC2	EC3
				EN 590
Cetane Number		51	51	51
Cetane Index		50	47	
Density at 15°C	kg/m^3	800-820	800-820	-845
Sulphur, max	ppm (wt)	10	50	50*
Aromatics, max	% (v/v)	5	20	-
PAH, tri+, max	% (v/v)	Not measurable	0,1	
PAH, max	% (w/w)			11
Cloud Point, max	°C	0 / -16	0 / -16-	-
CFPP	°C	-10 / -26	-10 / -26	
Viscosity at 40°C	mm^2/s	1,2-4,0	1,2-4,0	2-4,5
IBP, min	°C	180	180	-
T95, max	°C	320	320	360
FAME, max	% (v/v)	5	5	5

* The sulphur limit in EN 590 will be changed to 10 ppm in 2009. This fuel quality has already been introduced on the markets in several EU member states.

The EC1 fuel has been supported by tax incentives as in contrast to the EC3 and thus the EC1 has reached nearly full market penetration in Sweden with only a minor market share for the EC3. The EC2 is virtually phased out from the market in favour of EC1.

4.4.2 Petrol

The current EU directive on fuel quality (Directive 2003/17/EC) was introduced in 2003. The specifications for petrol according to Annex III in the directive is summarised in **Table 9**.

In the proposal for a new fuel directive, which was published in January 31, it was proposed to increase the blending levels of biofuels in petrol (EC, 2007a). In this proposal, two specific fuel qualities could be marked in the national language or in English as: “low biofuel petrol” and “high biofuel petrol”. The first fuel quality would, regarding the content of oxygenates and other environmental properties, correspond to the current limits, while the oxygenate limits of the second quality could be increased. Most importantly, the oxygen content would be increased from 2,7 to 3,7%. The limit for ethanol content would be increased from 5 to 10%, where the latter limits corresponds to an oxygen content of 3,7%. The content for the other oxygenates in **Table 8** would also be increased, except for methanol, where the current limit of 3% would be maintained. After this proposal was made, biofuels have been under debate in the EU and other non-official proposals on blending levels for biofuels have also been made, implying that the current situation is un-

clear. Therefore, we have decided not to go into any detail in this matter or to list the limits proposed for other oxygenates but the 10% limit for ethanol.

Table 9. *Environmental specifications for petrol according to Directive 2003/17/EC*

Parameter(1)	Unit	Limits (2)	
		Minimum	Maximum
Research octane number		95 (3)	—
Motor octane number		85	—
Vapour pressure, summer period (4)	kPa	—	60,0 (5)
Distillation:			
— percentage evaporated at 100 °C	% v/v	46,0	—
— percentage evaporated at 150 °C	% v/v	75,0	—
Hydrocarbon analysis:			
— olefins	% v/v	—	18,0
— aromatics	% v/v	—	35,0
— benzene	% v/v	—	1,0
Oxygen content	% m/m	—	2,7
Oxygenates			
— Methanol (stabilising agents must be added)	% v/v	—	3
— Ethanol (stabilising agents may be necessary)	% v/v	—	5
— Iso-propyl alcohol	% v/v	—	10
— Tert-butyl alcohol	% v/v	—	7
— Iso-butyl alcohol	% v/v	—	10
— Ethers containing five or more carbon atoms per molecule	% v/v	—	15
— Other oxygenates (6)	% v/v	—	10
Sulphur content	mg/kg	—	50
	mg/kg	—	10 (7)
Lead content	g/l	—	0,005

(1) Test methods shall be those specified in EN 228:1999. Member States may adopt the analytical method specified in replacement EN 228:1999 standard if it can be shown to give at least the same accuracy and at least the same level of precision as the analytical method it replaces.
(2) The values quoted in the specification are "true values". In the establishment of their limit values, the terms of ISO 4259 "Petroleum products -Determination and application of precision data in relation to methods of test" have been applied and in fixing a minimum value, a minimum difference of 2R above zero has been taken into account (R = reproducibility). The results of individual measurements shall be interpreted on the basis of the criteria described in ISO 4259 (published in 1995).
(3) Member States may decide to continue to permit the marketing of unleaded regular grade petrol with a minimum motor octane number (MON) of 81 and a minimum research octane number (RON) of 91.
(4) The summer period shall begin no later than 1 May and shall not end before 30 September. For Member States with arctic or severe winter conditions, the summer period shall begin no later than 1 June and shall not end before 31 August.
(5) For Member States with arctic or severe winter conditions the vapour pressure shall not exceed 70 kPa during the summer period.
(6) Other mono-alcohols and ethers with a final boiling point no higher than that stated in EN 228:1999.
(7) In accordance with Article 3(2), by no later than 1 January 2005 unleaded petrol with a maximum sulphur content of 10 mg/kg must be marketed and be available on an appropriately balanced geographical basis within the territory of a Member State. By 1 January 2009 all unleaded petrol marketed in the territory of a Member State must have a maximum sulphur content of 10 mg/kg.

Since it is difficult to meet the limits for vapour pressure with increasing ethanol content, especially in the EU member states that do not have "arctic" climate, where the limit can be higher, the EU proposal mentioned above would allow higher vapour pressure depend-

ing on the blending level of ethanol. To compensate for the higher evaporative emissions that will result from increased vapour pressure due to higher concentrations of ethanol, the Commission has also put forward a proposal for the mandatory introduction of vapour recovery equipment at filling stations.

4.5 Fuel quality and particle emissions

It is well known that the fuel quality is an important factor with respect to the emissions of pollutants. For this reason environmentally more friendly fuels are gradually introduced to the market. Fuel sulphur content has been reduced because of acidification and health concerns, a reduction that is also an important change in regard to particle emissions. Today, the strive for even lower fuel sulphur concentrations is also stimulated in order to avoid sulphur poisoning of catalytic material in exhaust after-treatment systems. Besides sulphur species, also the content of aromatic compounds in the fuel is of importance and especially PAH give rise to particle formation in the combustion process. The change from euro-diesel (**Table 5**; maximum sulphur content of 2000 ppm during that period of time) to Swedish EC1-diesel fuel (**Table 8**; maximum sulphur content of 10 ppm) reduces particle mass emissions with about 15% and particle-associated PAH by 80 to 90% in the light-duty FTP-cycle. Tests with 4-stroke petrol engines in the same driving cycle, using alkylate (i.e. iso-paraffine) petrol reduced the particle mass and PAH emission by 50 to 90% depending on engine oil consumption (Laveskog, 1995; Laveskog, 1998).

Bosteels et al. (2006) sampled PM in the NEDC and CADC (Common Artemis Driving Cycle) driving cycles from four passenger cars meeting the Euro 4 emission standards: one petrol and three diesel cars of which one with DPF. The filter sampling method followed the PMP proposal and the samples were analysed for elemental carbon (EC) and organic carbon (OC). The result presented in **Table 10** shows that diesel particulate matter has a considerable higher fraction of EC as compared to petrol and that the cold start in the NEDC is associated with a higher fraction of condensed material for petrol and to a lesser extent for diesel. The EC-fraction for the diesel-DPF car shows the carbon capture effectiveness of the DPF and that essentially everything captured on the filter is condensed material.

Table 10. *Elemental carbon (EC) as percentage of total PM (Bosteels et al., 2006).*

	NEDC	Artemis		
		Urban	Extra Urban	Highway
Petrol	32,0	12,0	10,0	4,7
Diesel A	85,0	92,0	92,0	88,0
Diesel B	84,6	86,0	81,6	79,2
Diesel DPF	0,8	0,0	1,9	1,5

Carbone et al. (2005) examined in the DG TREN "Particulates" project three HD-engines certified for Euro III, Euro IV (with a CRT-filter), and a Euro V (SCR/urea) for PM emissions and solid particle number emissions using a thermodenuder with the ELPI instrument (TD-ELPI). In addition to this, also 3 diesel and 2 direct injection petrol passenger cars using different exhaust after treatment techniques including oxidation catalyst and DPF for the diesels, and TWC and TWC+NO_x trap for the petrol cars were examined. Five different

diesel fuels were used in both steady-state and transient driving cycles (sulphur content (ppm): 280, 38, 8, <5 (Swedish EC1), and 307), and three petrol fuels (sulphur content (ppm): 143, 45, and 6). The HD-engines with DPF and SCR produced very low PM-emissions. These emissions showed no consistent fuel effect on the dry particle number measurements. The Euro V with SCR/urea produced up to 70% fewer particles as compared to the Euro III but still considerably more than the Euro IV with CRT.

Diesel passenger cars in the NEDC showed no significant PM fuel effect. A fuel effect was however clearly observed in the Artemis Highway cycle with the highest emissions for the highest sulphur fuel for both vehicles while the lowest S-fuel produced the lowest PM-emissions. Sulphate formation was confirmed by analysing the filter deposits for the DPF-car showing 55 and 70% sulphate for the two high sulphur fuels in the Artemis Highway cycle which implies that sulphate together with bounded water accounted for the collected PM. For the diesel-DPF, fuels with less than 50 ppm produced near zero emissions. Steady-state driving at 120 km/h produced similar results as did the Artemis Highway.

Particle number measurements show approximately 10^{14} and 10^{11} particles/km for the cars without and with DPF respectively. No consistent S-fuel effect was observed for any of the driving cycles.

The Petrol cars showed PM emissions far below conventional diesel cars but higher than the DPF-diesel. There was no clear effect of petrol S-content on PM emissions. Fuel differences were not significant in the particle number measurements and did not track increasing sulphur content.

4.5.1 Filter analyses for sulphur effect

An early example of chemical analysis of diesel particles is the work by Schueltze (1983) who sampled and analyzed particulate emissions from several types of vehicles with the intent to characterize mutagenicity. He found the SOF from heavy diesels to be typically around 20% of the total mass. Different solvents were used to split the SOF into three fractions: nonpolar, moderately polar, and polar. Most of the SOF mass (57%) was found in the nonpolar fraction, being mostly (90%) large aliphatic hydrocarbons (C14 and higher). The next largest fraction was polar (32%), containing organic acids and Polycyclic Aromatic Hydrocarbons (PAH) and their derivatives. The remainder (11%) was found in the moderately polar fraction composing e.g. oxygenated- and nitrated-PAH.

Rogge et al. (1993) analyzed samples collected during chassis dynamometer-FTP runs with two heavy diesel trucks. The average emission rate was 400 mg/km with 40,5% IOF and 39,1% SOF and the remaining part unidentified. The authors used organic fractionation, coupled with gas chromatography–mass spectrometric analysis to further investigate the SOF composition. About 90% of the mass was not identified specifically, but was concluded to be large hydrocarbons. Much of the resolved mass was large alkanes and alkanoic acids. Already at this time it was noted that the SOF contained hydrocarbons with a molecular weight resembling those of lubrication oil.

Shi et al. (2000) reported results from bench runs of a model year 1995 turbocharged, intercooled heavy diesel engine using 427 ppm-S diesel fuel. Particle size distribution measurements and bulk analysis of particulate matter collected on filters were performed. Sulphate and IOF were high at high load while the SOF increased with decreased load. The percentage of sulphate and nitrate varied between 11,8 and 1,7, and 4,2 and 1,6, respectively. SOF contributed between 24,4 and 50% and IOF between 51,5 and 33,9% of the mass.

The content of PAH lay between 0,024 and 0,040%. These authors also gave strong evidence for agglomerated elemental carbon particles acting as nuclei for condensation of heavy organic compounds. An interesting observation was that there were indications of a nucleation mode below 10 nm (outside the range of the equipment) for full and half load conditions for some dilution ratios of the exhaust.

The composition of the particles as determined by analysis of the gravimetric filter samples for the transient cycle show that the SOF was between 10 and 20% of the particle mass (ACEA, 2002). The remaining mass was IOF (i.e. soot). The SIF was insignificant when low sulphur fuel was used. The situation changed when a high sulphur fuel (250 ppm) was used. Then a substantial increase both in mass and particle number could be observed.

Kittelson et al (2006) have examined a HDV with a Continuously Regenerating DPF (CR-DPF) system in the ESC cycle using different fuel concentration sulphur levels (Figure 16). The ESC test cycle used is principally a high temperature cycle with CR-DPF temperatures of between 300°C and 500°C throughout the test.

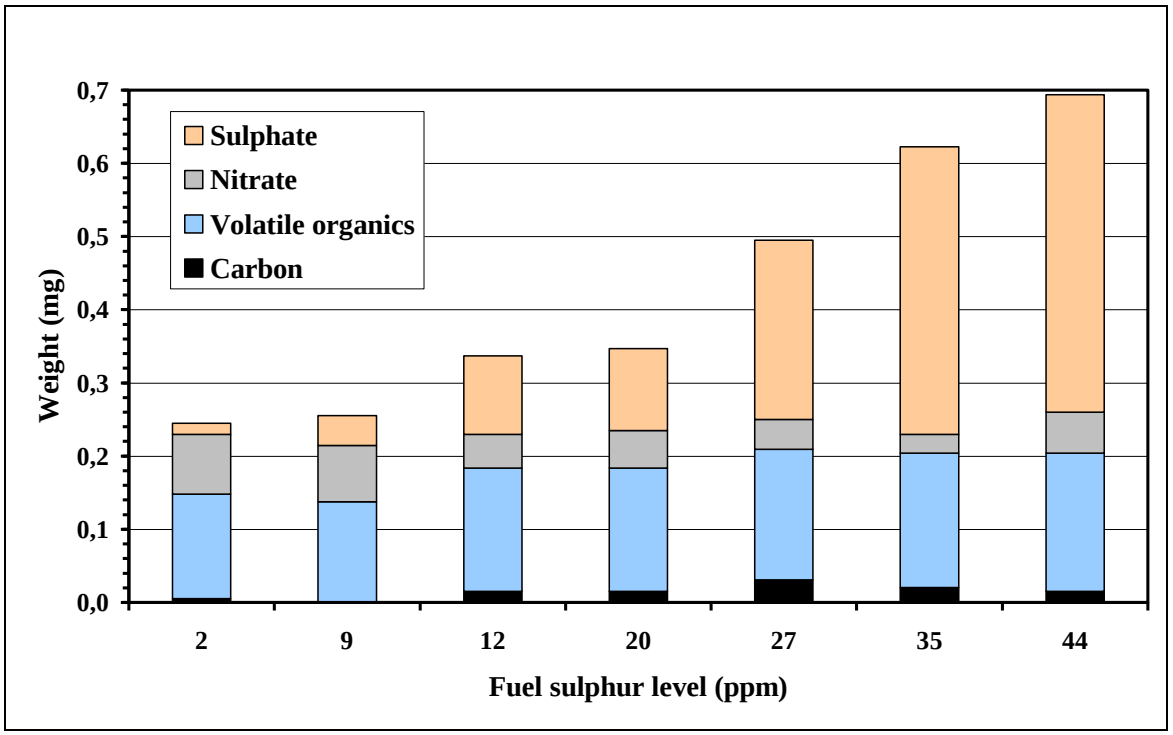

***Figure 22**. Measured chemical specification of PM-emissions from a HDV CR-DPF system as a function of fuel sulphur level (data from Kittelson et al., 2006).*

As a result of the high temperatures in the DPF, SO_2 oxidation is promoted. The carbon, VOF and nitrate emissions were virtually independent of the fuel sulphur level while the PM emissions increased as the fuel sulphur level increased. Thus, even though a CR-DPF system can provide very high conversion rates of CO, HC and PM, the system can convert sulphur compounds from the diesel fuel into sulphates leading to increased PM emissions under some circumstances. Approximately 50% of the fuel sulphur in these tests was converted into sulphate.

4.5.2 Fuel effect

Hall et al. (2000a) measured particle emissions from two heavy-duty diesel engines representing Euro 2 and Euro 3 technology in the ECE R49 test cycle. The measurements were performed using a DDMPS (Dual Differential Mobility Particle Spectrometer) from the CVS-tunnel. Three diesel fuels with different sulphur contents were used: D1 was 498 ppm, D2 was 418 ppm, and D3 was below 1 ppm. The two engines showed a similar bimodal distribution with a split between the nucleation mode and the accumulation mode at around 30 nm (**Figure 23**). When the low-sulphur D3-fuel was used, the number emission was drastically reduced by suppression of the nucleation mode while the accumulation mode was insensitive to fuel changes. PM emission for the Euro 2 was 0,158 and 0,110 g/kWh for the D1 and the D3 fuel, respectively, while no data were reported for the Euro 3 engine.

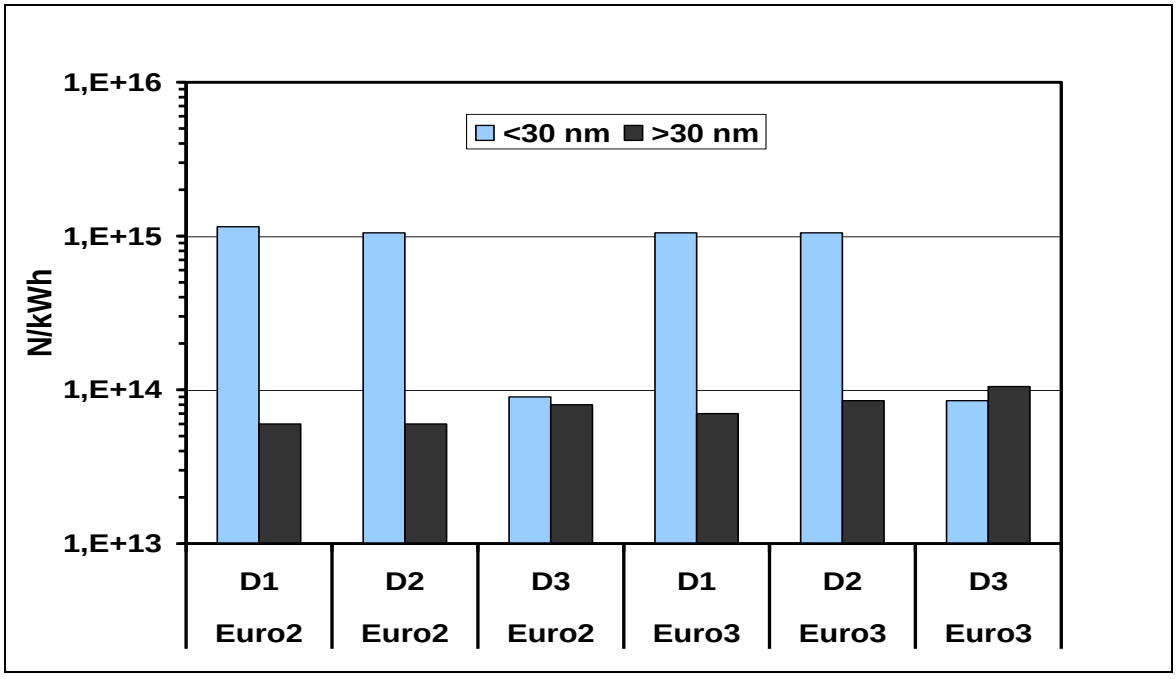

Figure 23. *The weighted total number of particles emitted from the two engines and three fuels during their respective R49 cycle (data from Hall et al., 2000a).*

Similar results were found in a study by Wedekind et al. (2000), using three heavy-duty engines representing Euro 1, Euro 2, and Euro 3 certification levels and three fuels with sulphur contents of 10, 53, and 300 ppm in the ETC. The SMPS measurements were performed from the CVS-tunnel showing a clear trend in the emission of nucleation mode particle number (10 nm) with the highest emission from the high sulphur fuel and the lowest from the low sulphur fuel. It was found that the fuel effect is more important than engine technology in regard to emission of nucleation mode particles. For particles in the accumulation mode (250 nm), the lowest emissions were still found for the 10 ppm-S fuel but engine technology was more important in reducing particle emissions than fuel quality. This was also seen in the filter mass measurements in the ETC, showing at least 15% lower emissions from the Euro3 (0,07 g/kWh) as compared to the Euro 2 (0,09 g/kWh) engine for all fuels.

A comprehensive piece of work concerning analysis of particulate matter from heavy truck diesels was made as part of the E-43 project. Ziemann et al. (2002) made tests on a Deere 4045, a Caterpillar C12, and a Cummins ISM engine (engines that were also used in other parts of the E-43 program) at intermediate speed at light and medium loads. A thermodenuder system and a humidifier system were used to characterize the aerosols. Another set-up allowed selection of a particle size fraction followed by collection on a trap inside a mass spectrometer. The trap was then heated in a controlled way, allowing mass spectrometric analysis of the evaporating substances.

The analyses showed that the organic component of total diesel particles and of nuclei mode particles appears to be comprised predominantly of unburned lubricating oil, whereas the fuel contribution to the total organic component appeared to be relatively small, not more than 20% and likely much less. Low volatility oxidation products such as organic acids and PAH did not appear to be a major portion of the organic mass. Alkanes, cycloalkanes, and aromatics were distributed fairly uniformly across the volatility spectrum.

It was found that the nucleation mode particles were the most hygroscopic, suggesting that they were relatively enriched with sulphuric acid. Such particles were formed when 410 ppm-S was used while no sulphuric acid could be detected in nucleation mode particles when using fuel with 96 ppm-S fuel. A conclusion drawn in the report is that high-sulphur fuels may give rise to early nucleation of sulphuric acid particles which later serve as nuclei for hydrocarbon condensation.

The report gives detailed information for particles from the Cummings diesel, running on a 50 ppm-S fuel and at 20% load using a tandem DMA system. Here, about half of the number of 70 nm particles shrunk to about 65 nm when heated to 300°C, while the other half disappeared (**Figure 24**). The accumulation mode particles was composed by a part of the population consisting only of heavy hydrocarbons, and the other being soot with heavy hydrocarbons condensed onto them.

In the European Community 5th framework project "Particulates", vehicles of different certification levels were examined for particle emissions. The vehicles represented different engine and exhaust after-treatment technologies and were operated using different fuels, diving cycles, and test cell temperatures. Tailpipe sampling was performed followed by simultaneous measurements of solid particles using a thermodenuder-ELPI configuration, and total particles (including VOF) using an aging chamber-CPC configuration in order to examine the "nucleation potential" of the sampled aerosol.

In **Figure 25**, data from Ntziachristos et al. (2004) has been used in order to compare particle emissions from two different diesel exhaust after-treatment technologies with and without DPF (a Peugeot 607 HDi-DPF, and a WV Golf TDI (both Euro 3)). The two cars were operated in the NEDC and in the Artemis Motorway (AMw) driving cycles using Euro2000 (D2), and Swedish EC1 (D5) diesel fuels (**Table 14**).

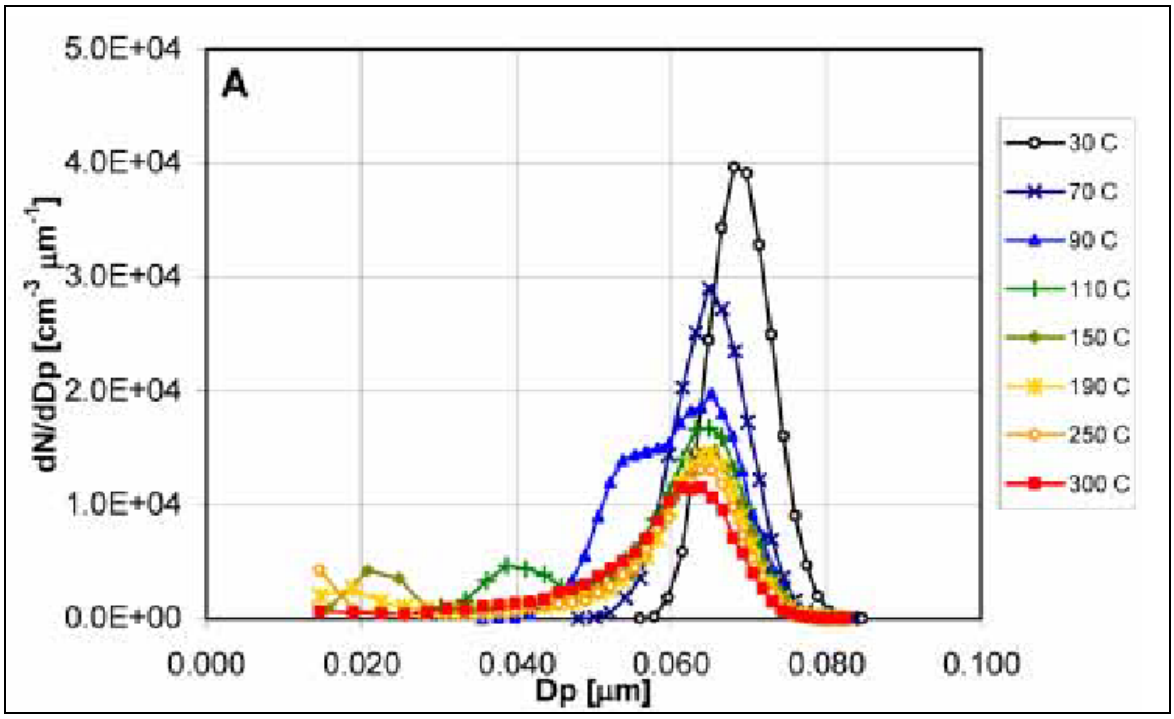

Figure 24. *70 nm diesel particles from the Cummins engine with CA-fuel at 20% load. Tailpipe using TDMA (Ziemann et al., 2002).*

There is an obvious difference between the two technologies. The car without DPF shows higher particle emissions for the D2-fuel as compared to the D5-fuel. The heavier AMw-cycle for this car shows higher emissions than the NEDC with a higher fraction of volatile particles (as the difference between total and solid particles). The car with DPF shows more than 100 times lower solid particle emissions as compared to the one without DPF. However, the volatile particle emission increases drastically for the AMw-cycle when using the D2-fuel as compared to D5, an effect that is not seen in the solid particle emission. Higher emissions of total particles for D2 than D5 are also observed in the NEDC with, again, a larger fraction of volatile particles. These effects are attributed to sulphur-mediated nucleation processes. Filter mass emissions for the DPF in the AMw increased from 0,003 to 0,138 g/km for D5 and D2 respectively but the drastic effect as seen in the number emissions are not observed. Hence, it may be concluded that the high particle number observed by the CPC is mainly due to formation of nucleation mode particles with only a small effect to particle mass.

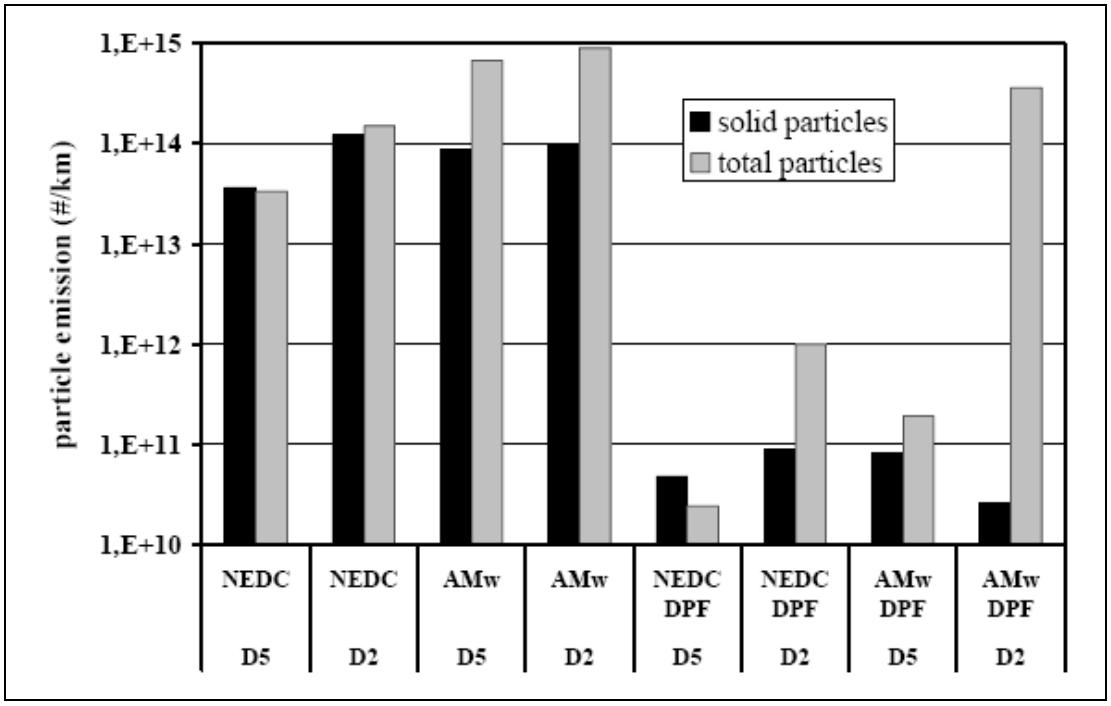

Figure 25. *Solid and total particle emissions for two diesel vehicles, with and without DPF (averages from duplicate tests). Two fuel qualities were used (D2 (Euro2000 diesel) and D5 (Swedish EC1) in two driving cycles (NEDC and Artemis Motorway-AMw) (data from Ntziachristos et al., 2004).*

4.5.3 Biodiesel, synthetic fuels and blends

Introduction to alternative diesel fuels

In the foreseeable future, most alternative diesel fuels with properties somewhat similar to conventional diesel fuel will be of most interest as blending components. Some of those alternatives are discussed here. Alternatives that would require a dedicated diesel engine such as, e.g. alcohols, dimethyl ether and gaseous fuels are not covered here. In the following, the denotation "biodiesel" is used for fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE). We are aware of that wider definitions of biodiesel are used – e.g. blends of FAME and conventional diesel fuel, synthetic fuels (GTL, BTL) and others – but the narrow definition is used here.

To put things into perspective, comparisons between diesel-fuelled vehicles and other fuels, primarily petrol, should also be made. In comparison to the study in 2007, more focus has now be made on biodiesel (FAME), including low blending in diesel fuel. The current production method for biodiesel is transesterification of fatty bio-oils. An alternative route is to hydrogenate these oils. The end product in this case is a straight-chain hydrocarbon fuel that contains no oxygen. Its chemical structure is very similar to synthetic diesel (Fischer-Tropsch) fuel produced via synthesis gas (GTL and BTL). Hydrotreated bio-oils seem to have several advantages for diesel engines regarding exhaust emissions and other properties and need to be discussed in more detail. If conventional biodiesel (FAME) is considered a first generation of biofuel and synthetic diesel fuel from biomass (BTL) the second generation biofuel, hydrotreated bio-oils could be considered generation 1,5. This fuel option could also bridge the gap between the two generations of biofuels. *It should be*

noted that the limit of biodiesel blending in diesel fuel, as discussed below, does not apply for this fuel.

Until now biodiesel (FAME) has been the only alternative diesel fuel on the market. Synthetic diesel fuel or gas-to-liquid (GTL) produced from natural gas is available from a few plants around the world. The production capacity of GTL is expanding and the first commercial pilot plant for the biomass-to-liquid (BTL) option is scheduled to start operation in less than two years. A "new" option is to hydrogenate vegetable oils and animal fats. The Finnish oil company Neste is a pioneer in this field with the so-called NExBTL™ fuel. The first plant (170 000 m^3/year) is about to start production this fall. At least one or two more plants are at the planning stage. In **Table 11**, some typical properties of those fuels are listed in comparison with EN 590 and EC1 diesel fuels.

Table 11. *Some typical properties of alternative diesel fuels in comparison to EN 590 and EC1 (compiled from several sources, among them: Scania).*

Fuel Property	Unit	Biodiesel (FAME)	NExBTL	GTL BTL	EN 590	EC1
Cetane Number	-	51	84-99	73-81	53	>51
Density at 15°C	kg/m^3	~885	775-785	770-785	~835	800-820
Sulphur content	ppm (wt)	<10	<10	<10	<10	<10
PAH, di+	% (w/w)	0	0	0	11%	~0
Cloud Point, max	°C	~-5	~-5…-30	~-0…-25	~-5	0 / -16
Viscosity at 40°C	mm^2/s		-2,9…3,5	-3,2…4,5	~4,5	1,2-4,0
Heating value	MJ/liter	~34	~34	~34	~36	~35
Oxygen content	% (w/w)	~11	0	0	0	0

Biodiesel

Pure vegetable oil can be used as a diesel fuel but requires substantial modifications of the engine. Transesterification of vegetable oils and animal fats to fatty oil methyl esters (FAME) or fatty oil ethyl esters (FAEE) is an option to improve the properties of the fuel, in respect of reduced viscosity and increased stability, and make it more compatible with current diesel engines. These fuel options are usually denoted "biodiesel". The maximum blending allowed today in European diesel fuel is 5% but this might be changed to 7 % or possibly 10 % in the new fuel directive under discussion. In some countries (e.g. France) blending up to 30% is made but then the fuel has to be specifically marked at the fuel station.

The impact of biodiesel and biodiesel blends has been investigated in numerous publications; most of them not referred to here. An excellent overview of the impact on emissions from biodiesel has been compiled by US EPA based on a literature survey mostly on heavy-duty on-highway engines (EPA, 2002). Approximately 98% of the data was collected on 1997 or earlier model year engines. No engine in the database was equipped with EGR, NO_X catalyst or DPF. The most common percentage of biodiesel in the data was 20 % and 100 %. The graph in **Figure 26**, summarises the impact on CO, HC, NO_X and PM emissions. Note that PM and CO more or less overlap.

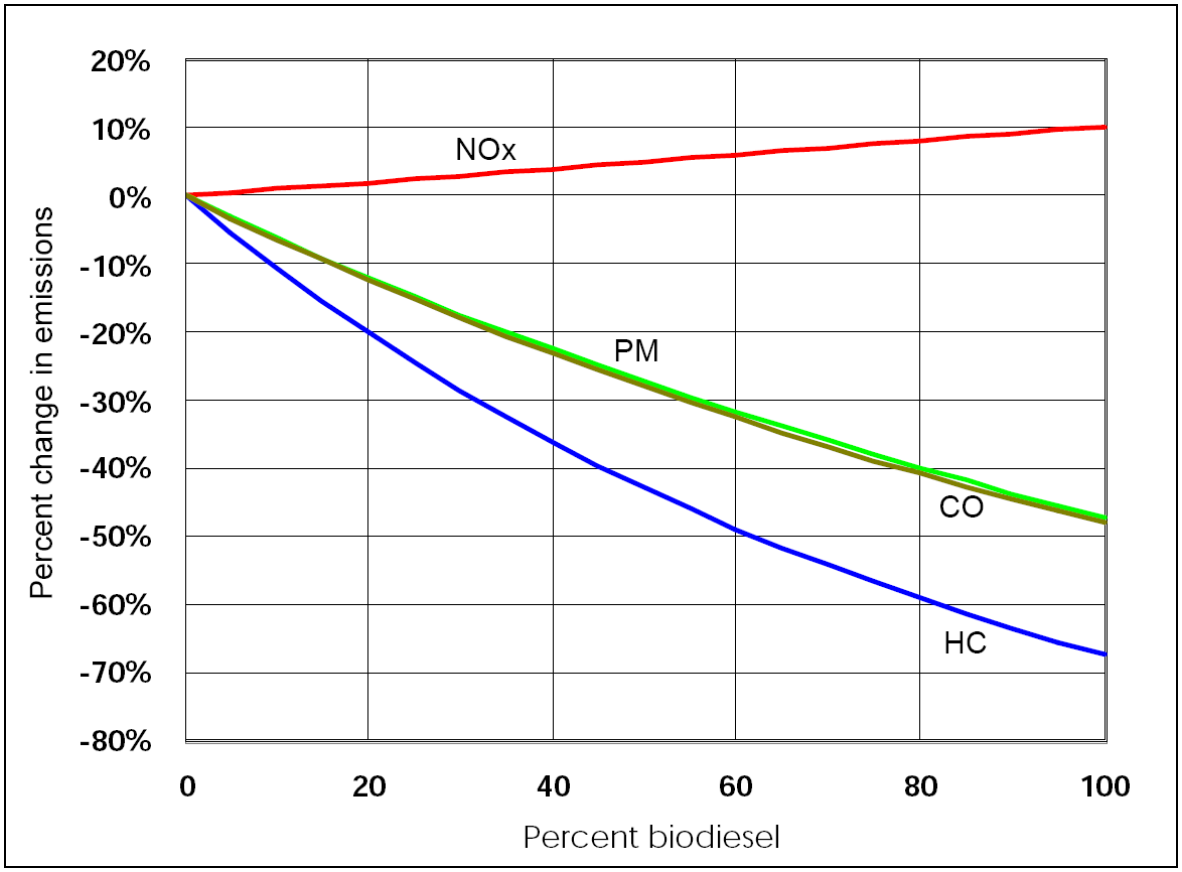

Figure 26. *Average emission impacts of biodiesel for heavy-duty highway engines (adapted from US EPA, 2002)*

As can be noted in **Figure 26**, NO_X emissions increase while all other emission components decrease by increasing biodiesel content. With 100 % biodiesel, the NO_X increase is about 10 %. The trend for NO_X appears to be linear. The increase in NO_X emissions was dependent on the feedstock of the biodiesel fuel. The highest increase, at about 15 % for pure biodiesel, was seen for soybean-based biodiesel while rapeseed-based biodiesel had a lower decrease at about 12 %. The lowest increase, at about 2% was seen for animal-based biodiesel. EPA compared their results with three other similar studies and found reasonable agreement between them.

Some comments to the EPA results could be added by the authors of the present report. The most substantial decrease in the EPA database is for HC emissions but one could note here that some of these emissions are probably trapped in the high-temperature filter (+190ºC) before the HC instrument which is not the case for diesel fuel, which leads to lower levels of HC. Similarly, PM emissions from biodiesel are subject to a high contribution from these volatile compounds. Consequently, the relative difference in soot emissions with biodiesel might be greater than for PM emissions. It should be noted the EPA study was mostly based on emission results from engines of model year 1997 or earlier. Very little data on light-duty was available. In summary, due to the mentioned shortcomings, the validity of the EPA results and conclusions on modern vehicles could be discussed.

The degree of unsaturation of FAME affects its physical and chemical properties. A Lapuerta et al. (2008) note that increasing unsaturation of the fuel improves cold flow properties, worsen oxidation stability, increases density, and reduces both viscosity and the

cetane number. Polymerisation and deposits formation also increases with a higher degree of unsaturation.

The relative proportions of saturated, monosaturated, and polysaturated fatty acids in PME (palm oil methyl ester) are 50%, 40%, and 10% respectively, while corresponding proportions in RME are 8%, 60%, and 32% (Ochoterena et al., 2008). The high content of saturated fatty acids in PME results in it having an elevated cetane number which in combination with the low aromatic content yields low levels of PM, NO_X, CO, and HC. Lapuerta et al. (2008) concludes that a higher degree of unsaturated biofuels shows more retarded start of combustion, higher NO_X emissions and combustion velocities, and lower smoke opacity, particulate emissions and smaller mean diameters of particulate size distributions.

One problem with biodiesel today is that modern passenger cars with DPFs cannot use the fuel without problems. This is due to the lubrication oil dilution that happens during DPF regeneration. In the regeneration process, fuel is injected late during the combustion stroke to increase exhaust temperature and some of the fuel ends up on combustion chamber surfaces and cylinder walls. With the lubrication oil, the fuel is transported to the oil sump. The high boiling range of biodiesel makes the oil dilution problem more severe. Thus, no car manufacturer allows the use of pure biodiesel in their diesel cars with DPF today. One exception is PSA (Peugeot-Citroën) who allow blending of up to 30% biodiesel. In this context, it should be noted that PSA is using a different regeneration strategy for the DPF than most other car manufacturers. With the cerium additive, the exhaust temperature does not have to be raised as much as for a DPF with catalytic coating only and presumably, this is the advantage that enables the used of a higher blending level.

In contrast to conventional diesel fuel, biodiesel contains oxygen (about 11%). This and the other differences in fuel properties also affect the emission level. The oxygen content reduces soot formation. On the other hand, the shift in boiling range produces more volatile particles, as measured by the conventional gravimetric mass measurement method. If an oxidation catalyst is used (as on all modern diesel cars) but no DPF, the particle mass emissions will be significantly lower than for conventional diesel fuel. Regarding particle number emissions on a non-DPF car, we have seen some results with lower levels for biodiesel but there is not sufficient number of studies to draw a firm conclusion.

As mentioned above, biodiesel has a problem with DPF regeneration. Therefore, there has been little interest from researchers to investigate the impact of biodiesel on DPF equipped cars. However, on heavy-duty vehicles, which are using a different regeneration strategy than passenger cars today (passive and continuous regeneration), there are a couple of publications available. The most comprehensive study has been conducted by the National Renewable Laboratory (NREL) in the USA (Willams, 2007). A Cummins ISB 5,9 litre diesel engine with a catalyzed continuously regenerating particle filter (CCRT™) was tested on Soy Methyl Ester (SME) and ultra-low sulphur diesel fuel. A significantly lower balance temperature (the temperature where soot generation equals soot burning in the DPF) was found both for B20 diesel-biodiesel blend and for neat biodiesel. Without the DPF, particulate (mass) emissions were reduced by some 25%. With the DPF, the reduction was as high as 67%. However, it should be noted that the particulate level was very low with the DPF anyway, so it was a very small reduction from an already very clean engine. No results on particulate emissions on neat biodiesel were published in the report but will follow at a later stage.

In regard to particle number and size distribution measurements, there are presently very few studies reported in the literature performed on ”dry” particle emissions from FAME (RME) and to the authors knowledge non has been presented using the PMP-method for particle number concentration measurements. For this reason, below is a number of studies presented that includes both “wet” and “dry” particle measurements in order to expose the nature of particulate appearance for RME and RME/diesel blends.

Mayer et al. (2005) examined a Liebherr D914T bus engine in a standardized steady-state test cycle for gaseous and particulate emissions when using RME blended in diesel (EN590 (<50 ppm-S)). The blending proportions of RME were 0, 15, 30, and 100%. Particle size distribution measurements as performed down-stream a thermodenuder (i.e. “dry particles) revealed that particle number were reduced as 100% RME was used. At the same time all RME blends tend to increase the number of fine particles (**Figure 27**).

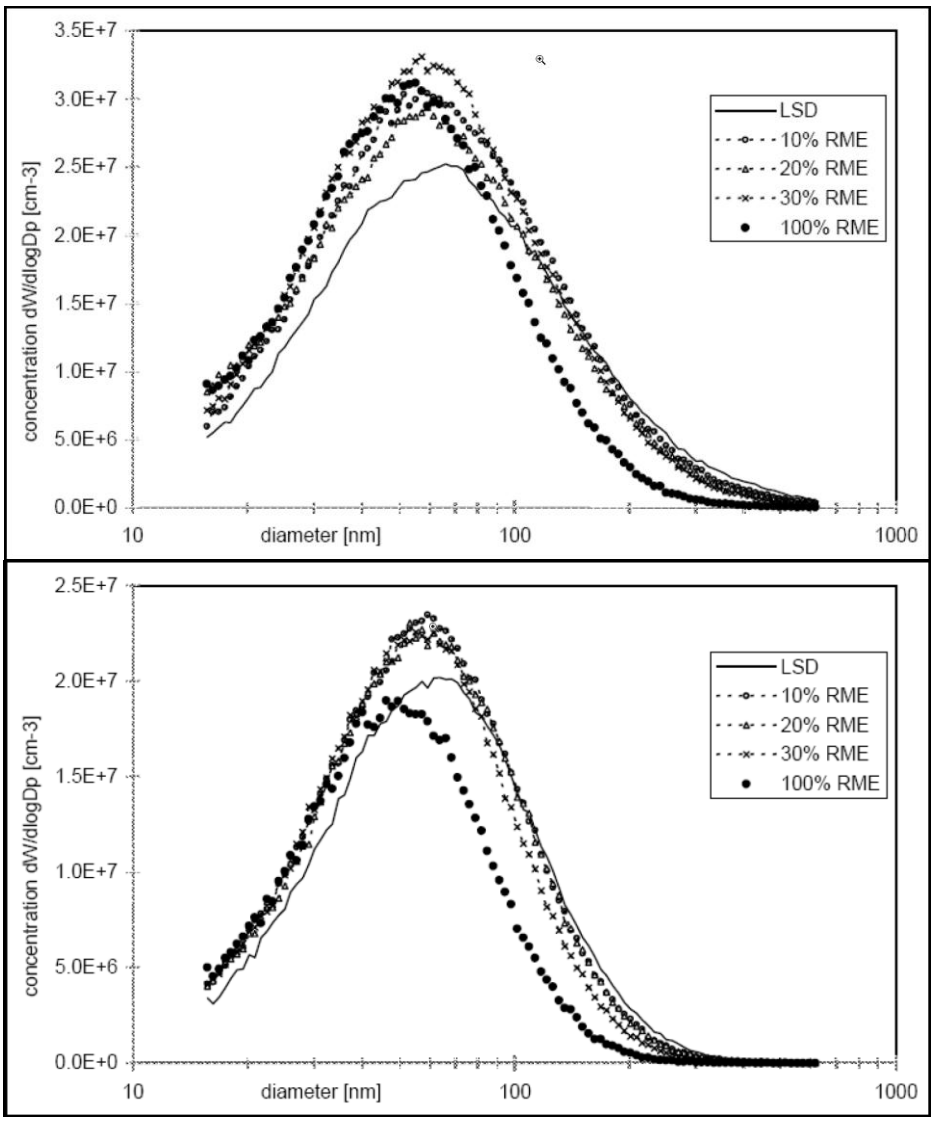

Figure 27. *Particle size distribution at 1400 rpm. The top figure shows at full load and the lower figure shows at 25% load (LSD is Low Sulphur Diesel) (Mayer et al., 2005).*

The authors explains that the lower particle emissions for the RME is due to the high oxygen content of RME promoting internal particle oxidation with a lower overall number of primary particles.

The study also presents particulate break-through studies for a DPF-filter when using the 20% RME blend. There was a slight increase of larger particles (>300 nm) but the finer particles remained unaffected as compared to the diesel-fuel with an interception higher than 99%.

In the resent study by Czerwinski et al. (2007), the PMP-PM method was used and dry particle concentration measurements were performed using PAS (photoelectric aerosol sensor) and DC (diffusion charging sensor) detectors. In parallel to the "dry" particle measurements, number concentration and size distributions measurements were also performed using an SMPS-system. The sampling was performed from a partial flow dilution tunnel. Tests were performed using a 2005 model Liebherr Heavy Duty DI engine operated at different steady-state speeds and loads. Four different fuels were used including low sulphur (<10 ppm) diesel and neat RME.

In **Figure 28**, the particle number concentration measurements as performed with the SMPS are presented at 10 and 80% engine load. In the lower bar diagrams, the "dry" particle DC measurements are also presented roughly correlating with the integrated SMPS measurements. For RME, the nuclei mode is considerably more pronounced as compared to diesel which is attributed to spontaneous formation of small particles from condensates. This is clearly illustrated in **Figure 29**, showing the OC (organic carbon) EC (elemental carbon) analysis results for these operational modes. The OC for RME is at 80% load largely removed reducing the PM emissions. This explains the differences in PM-emissions for diesel and RME as presented in **Figure 28**. Note that the increase in nuclei mode seen for RME would most likely disappear if PMP type sampling and dilution would have been used. In **Figure 28**, results for "crude" rape seed oil (ROR) are also shown but not commented here since this option was not included in the study.

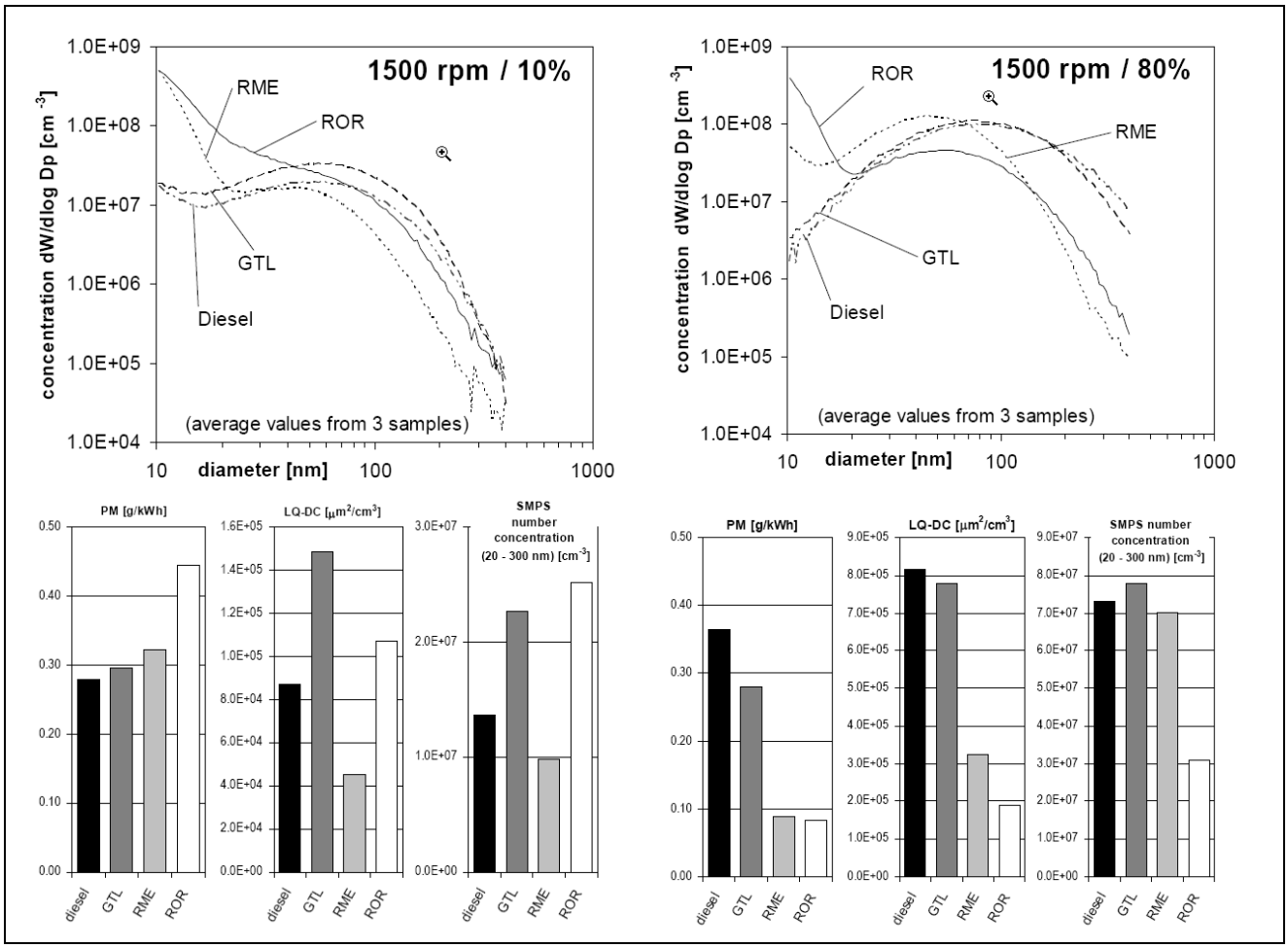

Figure 28. *Particle size distribution (SMPS) and mass emissions of the different fuels at low engine load (left) and high engine load (right) (Czerwinski et al., 2007).*

The particle size distribution measurements in this study may be compared with **Figure 27**, above only including "dry" particles resulting in decreasing number of the finest particles.

For the gaseous emissions it was observed that RME lowers CO and HC emissions and increases NOx emissions at all operating points.

When using RME, quicker increase of injection pressure and faster opening of the injector as compared to diesel was observed.

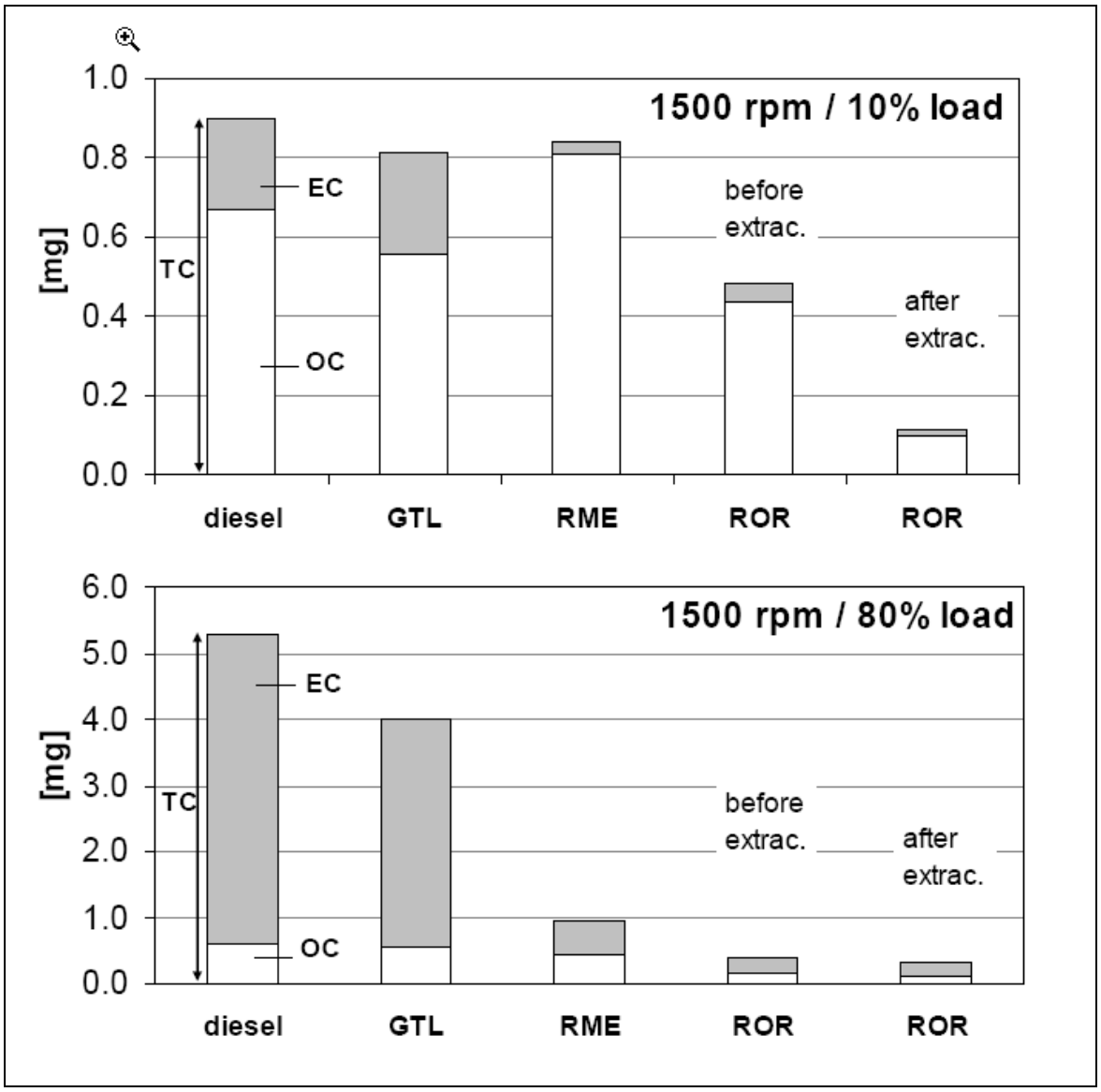

Figure 29. *Absolute values of OC, EC, and TC for the examined fuels (Czerwinski et al., 2007).*

In a study by Aakko and Nylund (2003), emissions from a medium-duty engine was examined in steady state operational modes at +23°C, +5°C, and at -7°C when using a 30 % RME blend in EU2000 diesel or in Swedish EC1 diesel fuel. Particle measurements were performed using a low pressure impactor for gravimetric measurements with sampling from a dilution tunnel. The results, as presented in **Figure 30**, clearly shows increasing PM-emissions at lower test-cell temperatures. It can also be seen that this effect is larger for the EU2000 diesel fuel as compared to the EC1 fuel and its blends with RME. The relatively high sulphur content of over 300 ppm for the EU2000 fuel was probably the main cause of the difference between this fuel and the EC1 fuel.

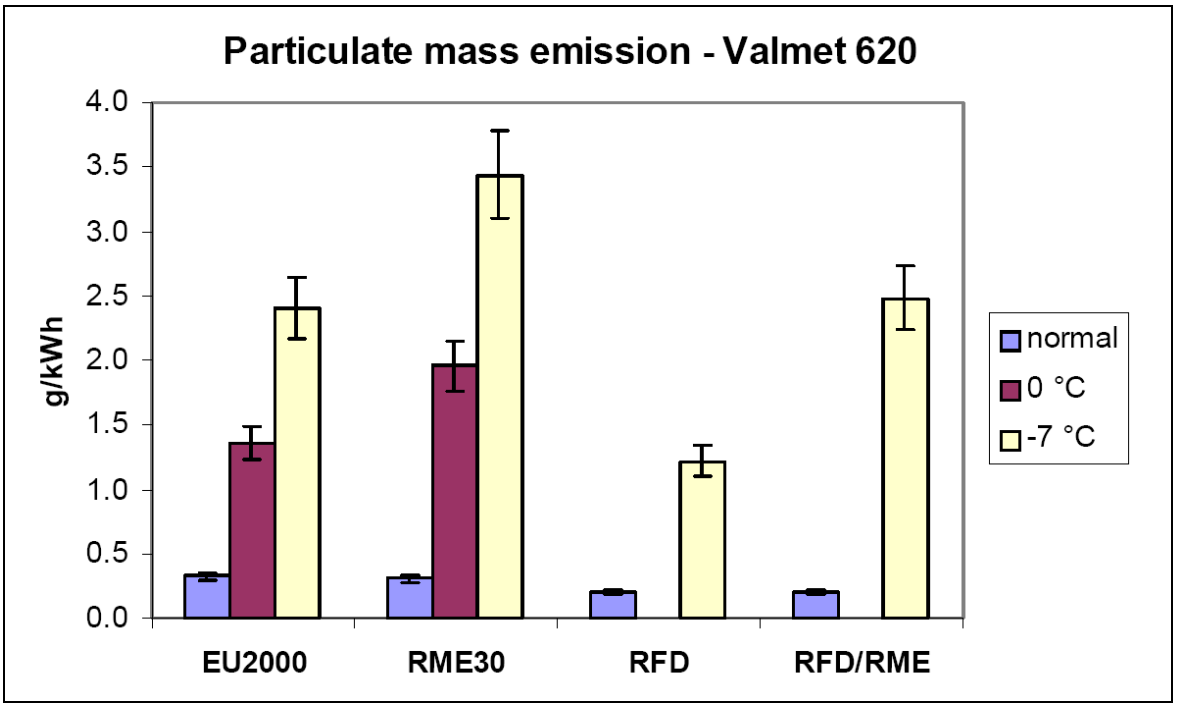

Figure 30. *Particle mass emissions over a steady-state engine test cycle as measured with a low pressure impactor (RFD=Swedish EC1-diesel, RFD/RME is 30% RME in RFD) (Aakko and Nylund, 2003).*

Furthermore, the authors also reports that the deposited material on the impactor stages by visual observations was soot at +23°C whereas at -7°C it was composes by a higher degree of condensed matter.

In a study by Krahl et al. (2003) Swedish EC1-diesel and RME has been compared using a 4 cylinder 5 L Mercedes-Benz OM 904LA engine in the ECE R49 steady-state test cycle. Measurements performed included SMPS and PM from a dilution tunnel. As reported in many publications higher NOx emissions are observed for RME as compared to that of diesel (6,5 and 5,3 g/kWh respectively). The particle size distribution measurements showed more particles as compared to EC1 in the 10-40 nm range but lower emissions for the larger particle fractions. The PM-emissions for EC1 and RME were almost identical but the analysis of SOF showed considerably less solid material (mainly soot/carbon) and a higher fraction of SOF for RME.

The study by Ochoterena et al. (2008) includes some interesting observations concerning the formation of soot and NOx. A one-cylinder HD laboratory engine operated at 25% load and 25% EGR at different fuel injection timings was used. The fuels used in the study included Swedish EC1-diesel, Fischer-Tropsch, and RME and the soot was measured using an AVL soot meter.

Figure 31, below, shows that the diesel fuel has the highest soot emissions whereas RME has the lowest soot emissions. The low emissions of RME are explained by the combined effect of the absence of aromatics and the presence of oxygen in the fuel.

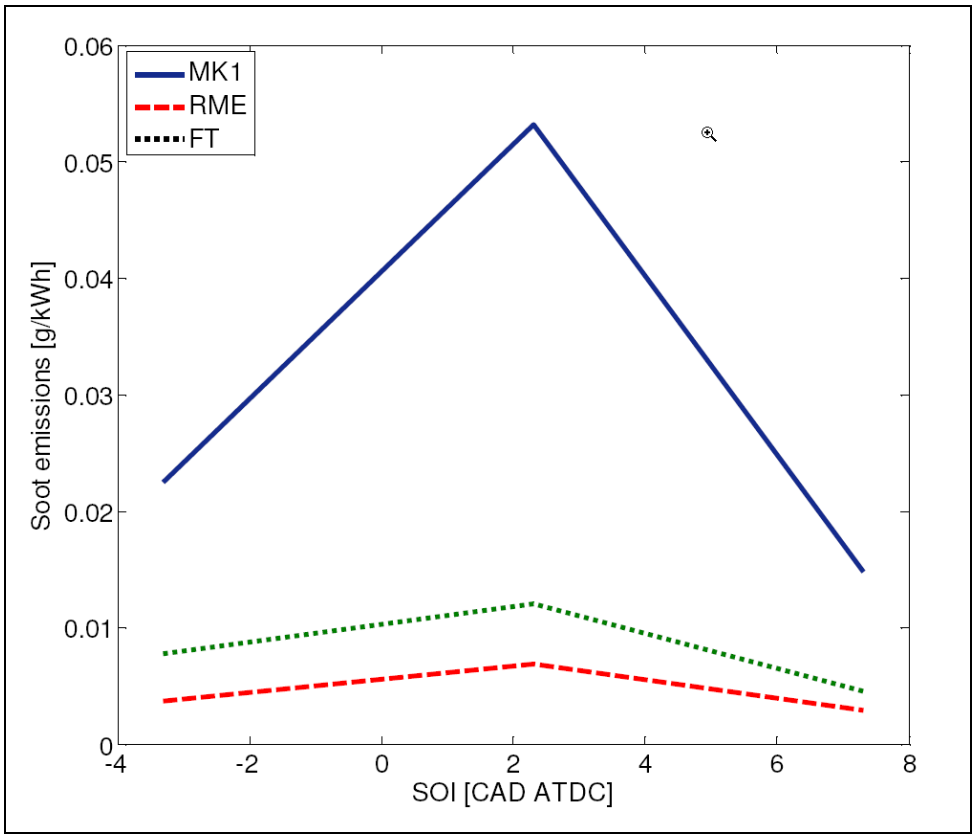

Figure 31. *Soot emission levels at different injection timings for the examined fuels (25% load and 25% EGR) (MK1=Swedish EC1-diesel fuel, FT=Fischer-Tropsch) (Ochoterena et al., 2008).*

Figure 31 also shows that soot emissions increases as the injection timing is retarded from -3,3 to 2,3 CAD ATDC, a phenomenon the authors explains by lower in-cylinder temperature and accordingly lower rates of soot oxidation. At even later injection timings (up to 7,3 CAD ATDC), the soot emissions decreases as a result of longer ignition delays due to lower temperature and hence a higher fraction of the fuel burning under premixed conditions.

For the NOx emissions, late fuel injection results in reduced NOx-emissions (**Figure 32**) as a result of the lower in-cylinder temperatures. However, the highest NOx emissions are found for RME as a result of high flame temperature and a high burning velocity as compared to that of EC1-diesel.

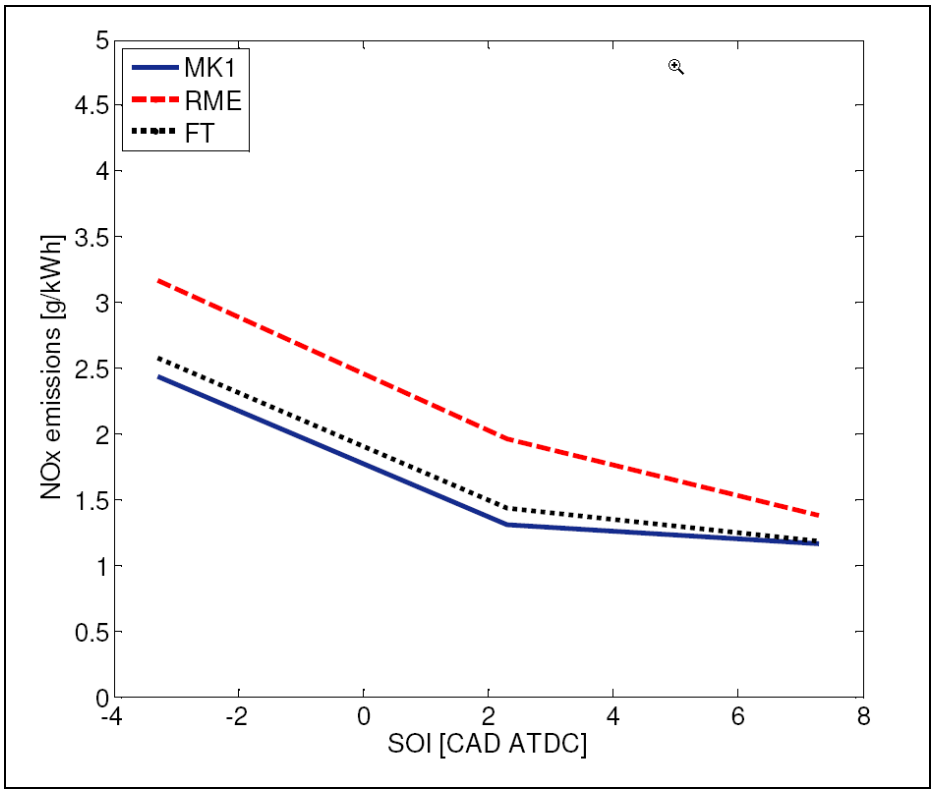

Figure 32. *NOx emission levels at different injection timings for the examined fuels (25% load and 25% EGR) (MK1=Swedish EC1-diesel fuel, FT=Fischer-Tropsch) (Ochoterena et al., 2008).*

As previously discussed, the increased NO_X formation in comparison to conventional diesel fuel is a general problem for this fuel option. No comprehensive and detailed explanation for this problem has been found, although many researchers have tried to solve or alleviate the problem. The NO_X problem is discussed in some more detail below. The basis for the conclusions drawn by the authors of this report has been the information collected from several of the publications studies here. Some of the discussion can be found in a paper by Zhang and Boehman (2007). The three main mechanisms that could explain the increased NO_X formation are:

- Injection timing shift
- Soot radiation
- Prompt NO_X formation

Biodiesel has a much higher bulk modulus, i.e. it is less compressible, compared to conventional diesel fuel. This also gives a higher speed of sound in the fuel. In "older" types of injection system, i.e. pump-line-nozzle fuel systems, the fuel is compressed in the long fuel lines (generally from about 30 cm in light-duty engines to up to 1 m, or more, in heavy-duty engines) and pressure waves travel back and forth between the pump and the nozzle. Consequently, a higher bulk modulus results in advanced injection timing and thus, an increase in NO_X generation, due to the higher temperatures in the cylinder associated with earlier combustion. This effect is clearly illustrated in a paper by Szybist et al. (2005). **Figure 33** shows the needle lift and fuel line pressure for conventional diesel fuel (BP325),

the biodiesel blends (B20, etc.) and Fischer-Tropsch blends (FT20, etc.). In **Figure 34**, the corresponding results for heat release are shown.

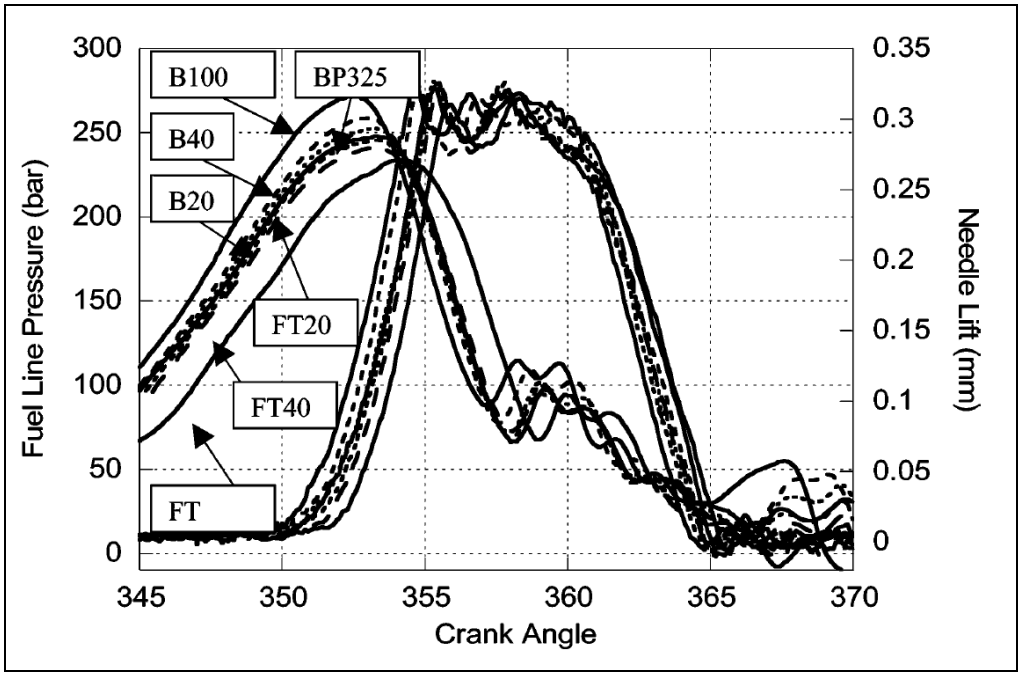

Figure 33. *Needle lift and fuel line pressure at high load (3600 rpm and 75% maximum output)*

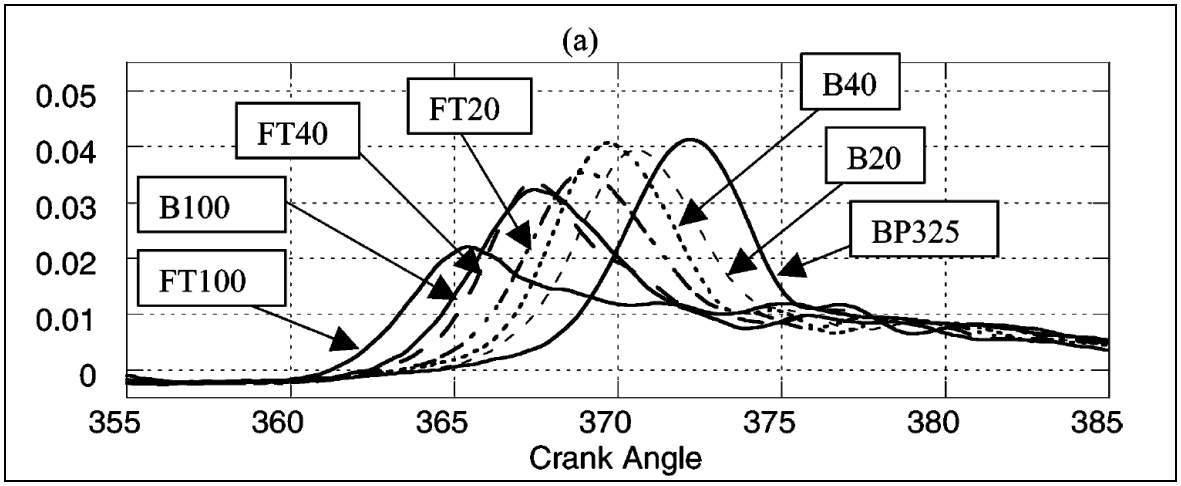

Figure 34. *Heat release (kJ/deg) at high load (3600 rpm and 75% maximum output)*

As can be seen in Figure 33, neat biodiesel (B100) has the earliest injection and the highest fuel pressure, followed by the biodiesel blends (B20 and B40). In contrast, the Fischer-Tropsch diesel fuel and blends have later injection and lower injection pressures. The corresponding heat release rate traces in Figure 34 show earlier combustion for biodiesel and biodiesel blends compared to conventional diesel fuel. The high cetane number of the neat Fischer-Tropsch fuel gives the earliest start of ignition although it was injected latest. The maximum heat release is also significantly lower than for all other fuels. A lower rate of heat release also indicates that less fuel is burned as premixed, which often can be associ-

ated with lower NO_X formation, in spite of the shift in ignition timing. With the substantial differences in injection timing and rate of heat release it is not surprising to find that also the NO_X emissions are different for the fuels investigated. By plotting NO_X emissions versus fuel injection timing for the different fuels, Szybist et al. found that shift in injection timing was largely responsible for the increase in NO_X emissions at high engine loads for biodiesel on this engine (Szybist et al., 2005). However, Fischer-Tropsch fuel and blends with Fischer-Tropsch fuel did not follow this trend but exhibited lower NO_X emissions at the same injection timing.

Besides the shift of injection timing, the higher bulk modulus and the lower energy content of biodiesel compared to conventional diesel fuel also implies that the injection pressure (as discussed above) and presumably also the rate shape of the injection event might change when biodiesel is used. However, one should note that *many of these findings do not necessary apply on new diesel engines equipped with modern injection systems*. This is somewhat unfortunate, since we still find that most of the test results reported even to date have been generated on old types of engines. Some examples of results on modern engines will be shown and discussed below but first some comments on the impact of biodiesel on new injection systems, e.g. unit injector and common rail systems, might be appropriate to add. In contrast to a pump-line-nozzle injection system, a unit injector system has a very short distance from the plunger to the nozzle (only a couple of cm) since both are built in a common unit. Thus, the bulk modulus has little influence on the injection timing. Common rail injection systems do have a long distance from the pump to the injector but in this case, the whole system is pressurised at the desired injection pressure and therefore, the fuel is already compressed. The distance from the valve to the nozzle is in the order of a few cm down to a few mm for the most modern common rail systems. The consistency of injection timing is clearly seen in a paper by Zhang and Boehman (Zhang and Boehman, 2007), where a modern automotive engine for light-duty applications was used (2,5-litre engine by VM Motori). The rate of heat release is shown in **Figure 35** for three tested fuels, where BP15 is conventional diesel fuel and B20 and B40 are biodiesel blends. It is evident that both injection timing and rate of heat release are almost identical for the three fuels.

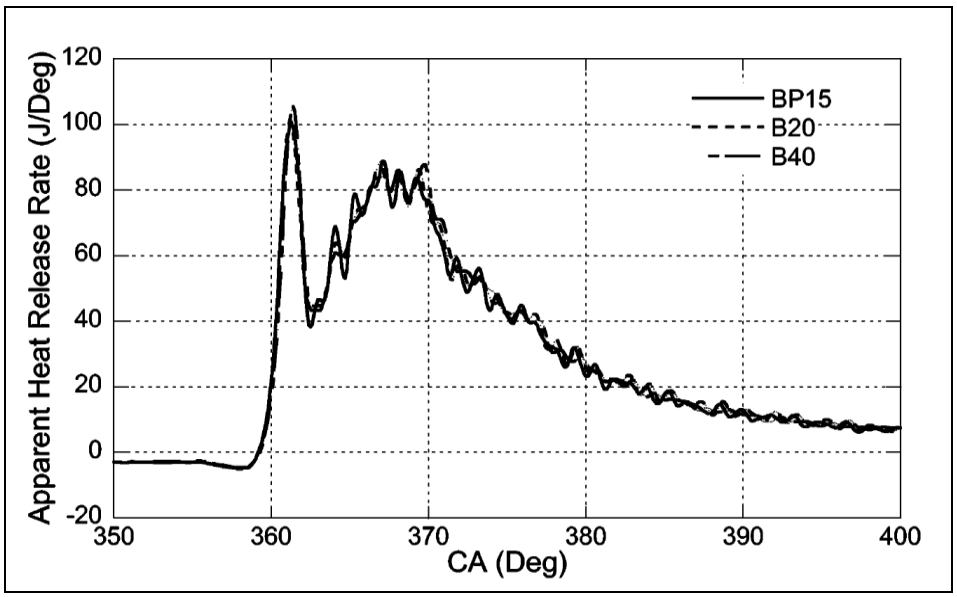

Figure 35. *Apparent heat release rate profiles for the three test fuels*

Although the injection timing and rate of heat release were very similar in the case for the common rail engine above, the NO_X emissions were still higher for biodiesel than for conventional diesel fuel at high engine loads, implying that the two other mechanisms that affect NO_X formation also were important in this case. However, at light engine load, the NO_X emissions were approximately similar. This is shown in **Figure 36**, where also the impact of different strategies for pilot injection is shown (pilot injection timing).

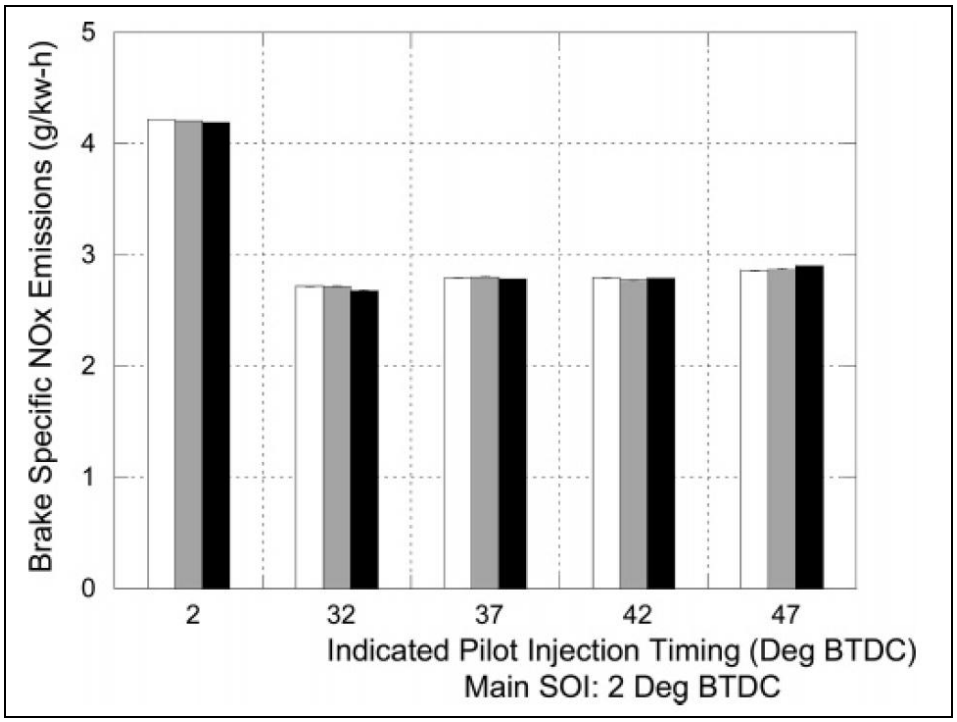

Figure 36. *NOx emissions under double injection conditions compared to the single injection condition for (white bars) BP15, (gray bars) B20, and (black bars) B40.*

Figure 36 also show the importance of pilot injection that reduces the NO_X emissions by up to 35 % compared to single injection (far left in the graph). No clear trend can be seen for the three fuel types with different injection strategies. The NO_X emissions are about equal for all three fuels.

While most of the discussion above has been about the impact of injection timing, injection rate and associated rate of heat release, it is obvious that not all impact on NO_X emissions can be explained by the influence of the injection event. As noted above, even a modern engine with common rail injection system has higher NO_X emissions at full load on biodiesel, although the NO_X emissions at low load seem to be about equal. The two other mechanisms for NO_X increase are, as discussed above, soot radiation and prompt NO_X could possibly explain the difference seen at high load.

Biodiesel contain oxygen and burns with less soot formation than conventional diesel fuel. This is in line with the findings in many studies about the fundamental combustion properties of oxygenated fuels under diffusion combustion, i.e. the type of combustion used in diesel engines. One example cited in the present report is a paper by Hallgren and Heywood (Hallgren and Heywood, 2001) but many other reports confirm a similar trend. Soot formation decreases with increasing oxygen content up to an oxygen content of about 30 % where no soot is formed at all. Other examples underlining this behaviour are that the light

alcohols ethanol and methanol, as well as dimethyl ether (DME), can be used in diesel engines practically without soot formation. In biodiesel, the oxygen content is not high enough to avoid soot formation but a reduction can generally be found. The lower soot formation with biodiesel compared to conventional diesel fuel also means that there will be less radiation and consequently, higher flame temperature that could lead to increased NO_X production. Not all NO_X formed in an engine originate from the thermal NO_X formation (i.e. the Zeldowich mechanism). There is also a contribution from the so-called prompt NO_X. Hydrocarbon radicals form nitrogen containing compounds that can oxidise to NO (and later to NO_2). As the denotation suggests, the formation of prompt NO_X is very fast, whereas thermal NO_X formation is slower. It has been proposed that the double bonds in biodiesel can increase the formation of these radicals, and therefore, could increase the level of prompt NO_X. The different level of double bonds found in biodiesel produced from various feedstocks could also explain differences in NO_X formation.

As mentioned previously, EGR is a very efficient method of reducing NO_X emissions in diesel engines. Since soot formation with biodiesel is reduced compared to conventional diesel fuel, it could be possible to reduce the NO_X emissions by increasing the EGR rate.

Tsolakis investigated the effect of EGR on a small single-cylinder air-cooled diesel engine (Tsolakis, 2006). Since this engine does not represent modern diesel engine technology, the relative NO_X reductions may not be similar on modern engines. However, some of the results are of more fundamental nature and are of interest to comment. When EGR is used with diesel fuel, the ignition delay is increased as EGR is increased. Likewise, the rate of heat release is also affected. Tsolakis found that EGR with biodiesel had a very small impact on ignition delay and rate of heat release. Thus, biodiesel is more tolerant to higher EGR rates. It was found that the relative decrease in NO_X emissions with increasing EGR rate was higher for biodiesel than for conventional diesel fuel and the negative impact on fuel consumption and energy efficiency was lower for biodiesel. Tsolakis also conducted measurements on particle number and particle mass. However, no PMP-type "hot" dilution was used, implying that volatiles might totally dominate the number of nanoparticles. The higher levels of nanoparticles generally found by Tsolakis with biodiesel compared to conventional diesel fuel could presumably be attributed to higher levels of volatile nanoparticles and the results by using PMP sampling could have been totally different. Results on particle number without PMP sampling should be used with caution.

Zhang and Boehman also investigated the use of EGR on the modern common rail engine discussed above (Zhang and Boehman, 2007). B40 biodiesel was used as fuel in this case and comparisons were made with conventional diesel fuel. There was an indication for slightly lower combustion deterioration with biodiesel compared to conventional diesel fuel with high EGR levels. The use of advanced single injection (no pilot injection) with EGR and biodiesel helped to recover the thermal efficiency of the engine, while still keeping the NO_X level low. The results reported by Zhang and Boehman, as well as other researchers, indicate that there is a potential to optimise an engine running on biodiesel to achieve similar – or lower – levels of NO_X emissions as with conventional diesel fuel.

Although health effects of various emission components was not the scope of this study, one set of results should be mentioned, due to the substantial differences seen in comparison to conventional diesel fuel. Krahl et al, 2007 investigated the impact of biodiesel (RME), vegetable oil, GTL and diesel fuel on emissions and mutagenicity (Krahl et al, 2007). The vegetable oil was crude rape seed oil (RSO) and modified rape seed oil with

reduced viscosity (mRSO). For the regulated emission components, most of the results were in line with others already mentioned in this section and the next about synthetic diesel fuels. RME had substantially lower CO and PM emissions compared to conventional diesel fuel. PM emissions were also lower for GTL but this fuel had slightly higher CO emissions. NO_X emissions were lower for GTL but higher for RME. The real surprising results were found in the mutagenicity tests, where the Ames test using TA98 and TA100 strains with (+S9) and without metabolism (-S9) were used on particulate and semivolatile extracts. The results for conventional diesel fuel, GTL and RME were quite similar – and low – in most cases, except for slightly higher levels in PM associated extracts for RME with TA98 and metabolism and TA100 without metabolism. In contrast, RSO and mRSO had mutagenic levels in the particle extract by factors of 9,7 up to 59 (TA98) and 5,4 up to 22 (TA100) respectively. The impact of higher viscosity on mutagenicity by RSO was investigated by reducing the viscosity by preheating the fuel up to 70ºC and using an additive (mRSO). This modification resulted in even higher mutagenicity of the mRSO compared to the RSO. In the view of the authors of the present report, results like these really question the use of crude vegetable oils as motor fuels, particularly in view of that these oils can be relatively easily transesterified or hydrogenated, with improved properties in many other areas as well.

Synthetic diesel fuels

As mentioned above, GTL and BTL fuels have basically similar combustion properties in the engine; i.e. it does not matter which of these fuels is used. Furthermore, whenever differences are between these fuels are claimed, it might as well be due to differences in the production process and/or fuel formulation and not the feedstock per se. The advantage regarding climate change is obvious for BTL over GTL. BTL is generally considered a 2^{nd} generation biofuel in contrast to conventional biodiesel, which belongs to the 1^{st} generation. By hydrogenating vegetable oils and animal fats, a fuel with relatively similar properties as GTL and BTL can be produced. This biofuel is considered here as a generation 1,5 biofuel. The feedstock base (oil and fat) are similar to the 1^{st} generation but the fuel properties are similar to the 2^{nd} generation.

Today, a European specification for FAME has been established. A similar specification for GTL, BTL or NExBTL does not exist so far and these fuels do not fulfil the EN 590 diesel fuel specification. Thus, these fuels cannot be directly used in neat form at public filling stations. Instead, they can be used in dedicated fleets, i.e. fleets where the vehicle manufacturer accepts the used of these fuels without loss of warranties. GTL/BTL and NExBTL are better blending components in diesel fuel than conventional biodiesel. Depending on the properties of the base diesel fuel, a much higher blending level can be achieved than with biodiesel, possibly up to 30 % or maybe even higher (up to 65 to 70 % is indicated for NExBTL by Rothe et al., 2005). In Sweden, the oil company OKQ8 announced the introduction a diesel fuel with 20% blending of NExBTL this spring (OKQ8, 2007). This fuel was about to be launched on the market in October 2007 but was cancelled after a massive campaign from non-governmental organisations (NGO). One feedstock for NExBTL is palm oil and, although the palm oil used by Neste was certified, the fear for that rain forest would be cut down to be replaced by palm oil plantations was the driving force behind this criticism. In general, it has to be noted that environmental organisations and other NGOs are much more critical to the use of biofuels today than one year ago. The blending properties of the NExBTL fuel are shown in **Table 12** for reference.

Table 12. *NExBLT blending properties in Swedish EC1 diesel fuel (source: Neste Oil)*

Property / Blending	EC1	NExBTL 5 %	NExBTL 10 %	NExBTL 15 %
Density @+15°C (kg/m^3)	814	813	811	810
Aromatics vol-%	4,9	4,6	-	4,1
Sulfur content (mg/kg)	1	1	1	1
Cetane index **Cetane number**	53,6 55,0	55,3 55,7	56,7 -	58,3 59,6
5 % distillation (°C)	203	206	205	207
50 % distillation (C°)	236	239	242	245
95 % distillation (°C)	283	288	290	293
Cloud point (°C)	-36	372	-32	370
CFPP	-35	-34	-32	-31
Viscosity at +40°C (mm^2/s)	2,0	-34	-	-32
Lubricity HFRR@ 60°C, with additive in basefuel	391	372	-	370

It is interesting to note that GTL, BTL and NExBTL fuels do not have the same problems with DPF use in light-duty vehicles as (conventional) biodiesel do have. Since the distillation range is roughly similar to conventional diesel fuel, no apparent increase in oil dilution during late fuel injection used for DPF regeneration is expected for the fuels mentioned. Furthermore, since the fuels are basically sulphur-free, continuous DPF regeneration using the "CRT effect" is not negatively affected either. Generally, a positive effect is that the soot loading will be reduced, which is also a positive influence on any type of DPF.

As in the case for biodiesel above, it is of interest to first show an overview of emission results in several different studies on GTL/BTL fuels. Steinbach et al. has compiled such an overview (Steinbach et al., 2006) for GTL fuels tested at four different laboratories (Bosch, DaimlerChrysler, Shell and VW). The results for regulated exhaust emissions, CO_2 and fuel consumption are shown in **Figure 37** and **Figure 38**. The reference level in all graphs is for conventional diesel fuel.

In general, GTL fuels have lower CO_2 emissions than conventional diesel fuel. This is plausible, since GTL fuels have a higher H/C than conventional diesel fuel. However, due to the lower density, the volumetric fuel consumption is higher for GTL fuels. Substantial reductions are generally seen for CO, HC and PM emissions. Great variations in reductions can be seen for CO and HC emissions. In all but one case (Bosch) reductions are also seen NO_X emissions.

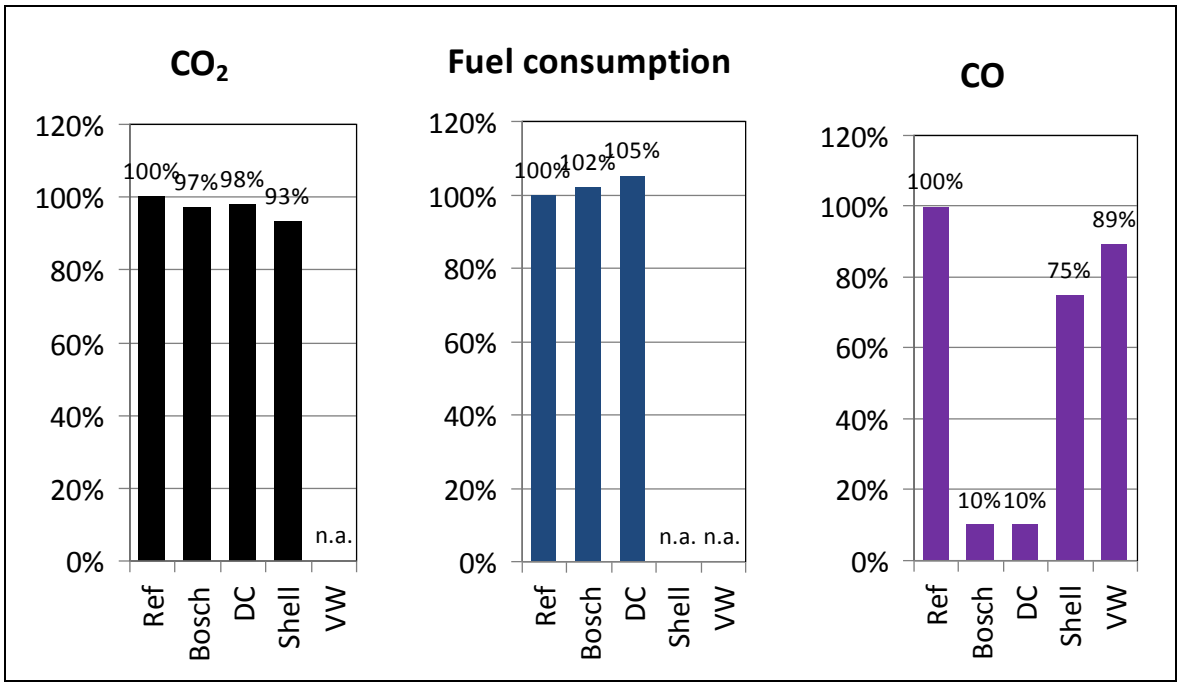

Figure 37. *Comparison of NEDC results on CO_2, fuel consumption and CO emissions (adapted from Steinbach et al, 2006).*

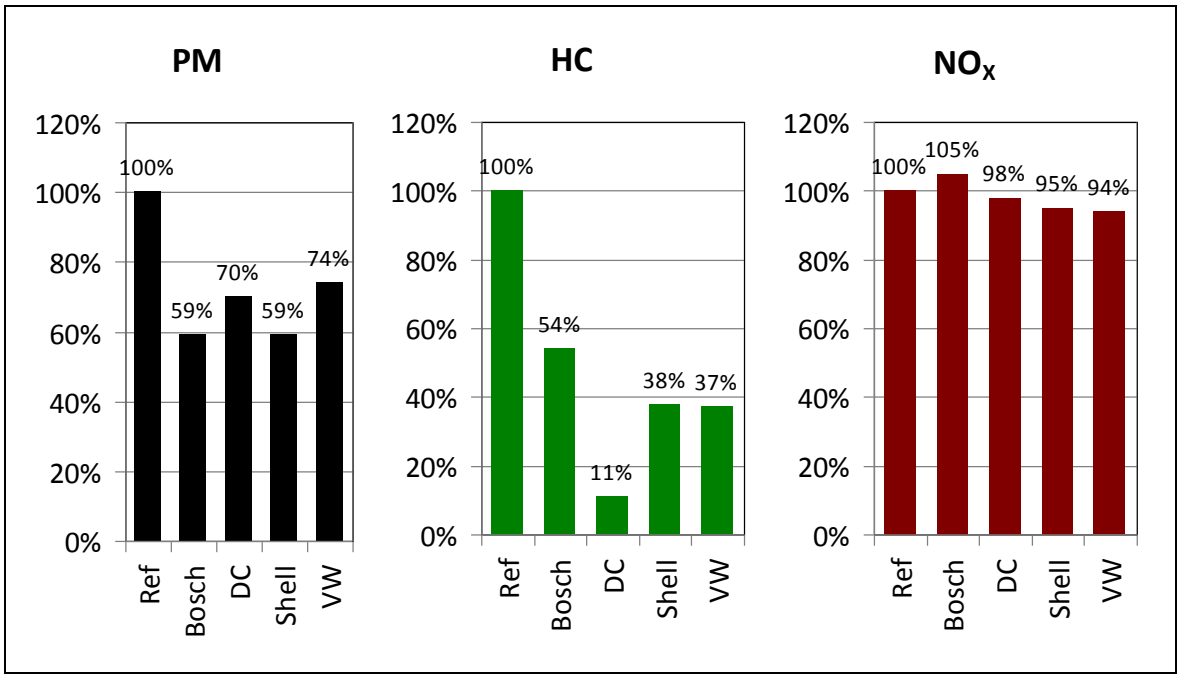

Figure 38. *Comparison of NEDC results on PM, HC and NO_X emissions (adapted from Steinbach et al, 2006).*

The results in the figures above have been more or less corroborated by studies of many other researchers, e.g. Fanick et al. and Schubert et al. (Fanick et al., 2001. and Schubert et al., 2002). The only exception in those two cases was for a slight increase of NO_X in the study by Schubert.

In **Figure 28**, data by Czerwinski et al., 2007 was already shown for GTL fuel. PM emissions was approximately similar to those for conventional diesel fuel at the low engine load (1500 r/min and 10 % load) but lower at the high engine load (1500 r/min and 80 % load). The size distribution, as measured by a SMPS instrument, was relatively similar at the high load but higher at the medium sized for the lower load. Note that PMP sampling was not used in this study, which indicates that the results could change if such sampling would have been used.

Schaberg et al., investigated the impact of particle number and size distribution with Fischer-Tropsch fuel compared to conventional US D2 diesel fuel (Schaberg et al., 2002). One heavy-duty engine and a passenger car engine were studied. Both engines showed similar reductions of gaseous emission components and particle mass for the Fischer-Tropsch fuel in comparison to conventional diesel fuel as discussed previously. Notable is that particle mass was reduced by up to 58 %. A micro-dilution tunnel and a two-stage ejector diluter were used for sampling and dilution. No volatile particle remover as in the PMP regulation was used to remove nucleation particles. Particle size distribution was characterised using a SMPS instrument at a couple of steady-state test modes. The number of particles found in the nucleation mode was substantially reduced (by between 16 % and 96 %) with the Fischer-Tropsch fuel. It was suggested by the authors that the negligible sulphur content of the Fischer-Tropsch fuel that dramatically reduce the sulphates available for nucleation was the primary cause of the observed reduction of nucleation mode particles.

The impact of GTL fuel and a catalysed particle filter has been studied by Alleman et al. in two SAE papers (Alleman et al., 2004 and Alleman et al., 2005). Six US Class 6 heavy-duty trucks from a field test participated in the study, where measurements were conducted on a chassis dynamometer in two separate test rounds. CSHVR and NYBC test cycles were used. In the first test round in the CSHVR cycle, CO and HC were reduced by 11 % and 58 % respectively, while the corresponding reductions in the NYBC cycle were 0 % and 69 %.

Two interesting studies on the used of NExBTL and GTL fuels in modern heavy-duty diesel engines have been prepared by Kleinschek at Scania and Rothe et al, at MAN (Kleinchek, 2005 and Rothe et al., 2005). Both engines use EGR for NO_X reduction.

Rothe et al. found HC, PM and NO_X reductions with NExBTL by 48 %, 28 % and 10 % respectively compared to the base diesel fuel in a Euro IV diesel engine with common rail injection system and no aftertreatment. The reduced aromatic content in the NExBTL fuel was claimed to be the reason for the PM reduction. A reduction in ignition delay by 1º crank angle was seen for NExBTL. Rothe et al. also measured particle size distribution by using a SMPS instrument. However, no PMP sampling was used and consequently, a high peak of presumably volatile nanoparticles was seen at 10 nm size for all fuels. Although a reduction of the level of all particle sizes was seen for neat NExBTL, this was not the case for the lower blends (10% NExBTL). Rothe et al. anticipated that the nanoparticles could be removed completely by using an "open" PM catalyst.

Kleinschek investigated the impact of NExBTL and two GTL fuels with different specifications on exhaust emissions and combustion properties on a modern Euro IV engine with EGR and no aftertreatment. The fuels properties are shown in **Table 13**. Kleinschek used the denotation "BTL" for NExBTL (Sw Class 1 stands for Swedish Class 1 diesel fuel). The very high cetane number for the GTL 2 and BTL fuels are notable.

Table 13. *Reference and test fuel specifications (adapted from Kleinschek, 2005)*

Property / unit	RF Euro IV	Sw Class 1	GTL 1	GTL 2	BTL
Cetane index	52	51	50	92	98
Density @+15°C (kg/m^3)	836	818	795	785	784
Sulfur content (mg/kg)	10	<1	<2	<5	<1
Viscosity at +40°C (mm^2/s)	3	2	3	4	3
IBP (°C)	203	186	-	211	216
95 % distillation (°C)	345	283	360	349	306
Flash point (°C)	75	69	70	91	85
CFPP or LTFT or CP (°C)	-18	-37	-32	0	-16
Lubricity HFRR@ 60°C, with additive in base fuel	375	375	400	280	405

In **Figure 39**, a graph adapted from Oja at Neste Oil from the tests by Kleinschek, shows the impact of the tested fuels on NO_X and PM emissions (Oja, 2006). The two GTL fuels and the BTL fuel reduced NO_X emissions in the range from about 15 to 19 %. Similarly, PM emissions were reduced in the range from 20 to almost 30 %.

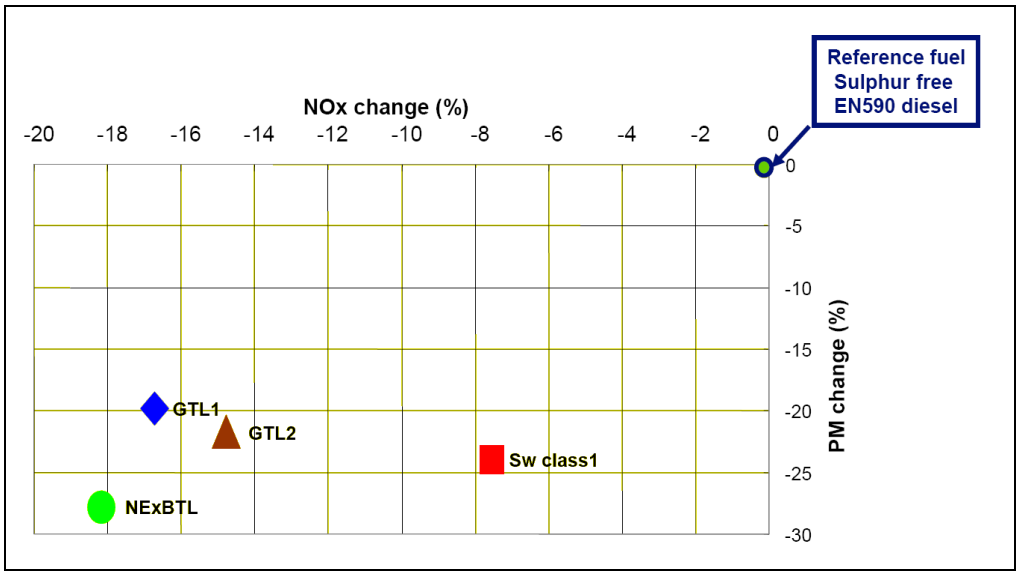

Figure 39. *Relative NO_X and PM emissions with NExBTL, GTL fuel and Swedish Class 1 (EC1) diesel fuels (adapted from Oja, 2006)*

The loss in power ranged from 3 % (GTL 1) to 6 % (BTL). The specific fuel consumption (measured in g/kWh) was reduced in the range of 1,5 to 2,5 % with the GTL and BTL fuels. Further reduction could be achieved by optimizing the engine towards lower fuel consumption (and similar NO_X level as base diesel fuel). Kleinschek did not note any significant change in ignition delay or crank angle for 50 % heat release, i.e. the combustion properties of the fuels were virtually unchanged.

Although emission compounds causing health effects other than the regulated gaseous emission components and particles were not the scope of this study, it could be noted that significant improvements in this area has been seen by many researchers on synthetic diesel fuel and hydrogenated vegetable oils. For example, Neste Oil has cited the following improvements for the NExBTL fuel:

- 30...40 % less formaldehyde and acetaldehyde
- ~ 40 % less benzene
- 30... 40 % less 1,3-butadiene
- up to 80 % less particulate bound hazardous polycyclic aromatic hydrocarbons (US MSAT[4] 7 PAHs)
- up to 80 % less particulate mutagenic activity (Salmonella typhimurium strain TA98-S9) in Ames test

In comparison with most similar results on biodiesel, these results are at least on pair with biodiesel but mostly significantly better.

Concluding remarks for the use of biocomponents in diesel engines

The results discussed above have showed favourable results for all regulated and basically all unregulated emission components (although not discussed in detail in the latter case) for synthetic diesel fuels of generations 1,5 and 2. The emission levels for biodiesel are also favourable in most cases, except for NO_X emissions where an increase in comparison to conventional diesel fuel by approximately 10 % can be seen. With modern engine technology (i.e. injection systems) this increase is reduced but a somewhat increased levels still seems to remain at some operating conditions. It is likely that this increase could be avoided by optimizing the engine using sensors (physical or virtual) for the fuel content. For example, since less soot is formed with biodiesel, the EGR rate could be increased to reduce NO_X emissions while still not increasing the soot level in comparison to diesel fuel. Likewise, new injection systems that have no impact on injection timing and less impact on injection rate, could improve the NO_X level for biodiesel.

As noted previously, NO_X and PM emissions are the two most difficult emission components to reduce on diesel engines. Although any reduction here is mostly welcome, neither biodiesel nor synthetic diesel fuels can overcome the need for aftertreatment devices, such as e.g. DPF and NO_X catalysts, if very low NO_X and PM emissions are strived for. There could be some scope for substantial improvement in the utilisation of advanced combustion concepts, such as homogenous charge compression ignition (HCCI) engines, with synthetic diesel fuels. However, an analysis of these combustion systems have been beyond the scope of this study and are not discussed further here.

Current EU directives and strategy tend to focus on the use of biocomponents in low-level blending. Currently, biodiesel can be blended in diesel fuel up to 5 %, with a possible increase to 7 % or maybe 10 % in the future. The practical blending limit for synthetic diesel fuels is not known but could be as high as 30 % and perhaps even higher for tailored fuels. To be able to use neat synthetic fuel in a widespread fuel distribution, a fuel specification for these fuels would be necessary. It is not practical to try to comply with the current diesel fuel specification for neat synthetic fuels, since the limits for a couple of parameters,

[4] MSAT, mobile source air toxics.

such as e.g. fuel density and/or cold filter plugging point cannot be met without considerable modification of the fuel (e.g. isomerisation) and with a corresponding limitation of the yield. In the latter case, lower boiling components would have to be removed by distillation. To fully utilise the properties of biocomponents as neat fuels, some kind of fuel-flexible engine technology would have to be used.

4.5.4 Lubrication oil and particle emissions

In addition to fuel quality, also lubricating oil affects the particle formation as a source of organic compounds with high boiling temperatures, inorganic ash components, and high contents of sulphur species.

In a yearly review of advances in emission control for 2002, Johnson, (2003) concludes that strong indications point to the importance of lubrication oil to the emission of nucleation mode particles. Also, the fact that vehicles using natural gas emit nucleation mode particles supports the conclusion that lubricating oil may be a large contributor to nucleation mode particle formation. It is suggested that a change to synthetic oil may reduce formation of nucleation mode particles by 50%, presumably due to the higher volatilization temperature.

The specific organic component composition in particles from a diesel engine measured using a tandem-DMA and a thermal desorption particle beam mass spectrometer (TDPBMS) has been determined by Sakurai et al. (2003). It was indicated that 95% of the organic fraction of diesel nucleation mode particles was comprised of unburned lubricating oil, by compounds with carbon numbers in the C24-C32 range. The tests were performed using a heavy-duty diesel engine operated at light and medium steady-state mode using a synthetic Fischer-Tropsch fuel, and the samples were taken at a dilution of 20:1.

Holmén and Ayala (2002) examined steady-state particle emissions at 55 mph from a bus operated with Compressed Natural Gas (CNG) and a conventional bus using diesel fuel with a sulphur content of 11 ppm. The measurements were performed from the CVS-tunnel by use of SMPS. The particle number emission was lower for the CNG as compared to the conventional bus but for particles smaller than 20 nm relatively high emissions were observed and the nucleation mode particle emissions from the two buses were comparable. However, sampling was also performed at tailpipe position using dilution ratios of 18 and 64 as compared to 8 in the CVS-tunnel. The tailpipe sampling system gave total particle number emissions about 30 times lower for CNG as compared for the conventional bus. It was suggested that the low emissions of soot from the CNG combined with release of volatile species from the lubricating oil may promote high numbers of nucleation mode particles for measurements performed in the CVS. Alternatively (or additionally), sulphur species from the lubricating oil may contribute to the formation of nucleation species. It was clear from this study that the higher dilution ratios suppress the formation of nucleation mode particles significantly.

In a study by Kytö et al. (2002), the effect of 2% lubricating oil of four different qualities (both fresh and used) mixed in a diesel fuel was studied in respect to particle mass and number emissions for two heavy-duty diesel engines operated in the ECE R49 test cycle. The measurements were performed with an ELPI (range: 15 nm to 6 μm) and showed that all fuels containing lubricating oil had increased number of small particles, 13 to 20 times higher numbers for the smallest size class, as compared to diesel fuel without added lubricating oil. For the particulate mass measurements, there was a clear difference between the

different lubrication oil qualities with highest addition of particulate emissions associated with the oils with high ash and sulphur concentrations. However, these differences could only partly be explained by the ash content and therefore it was argued that also the base oil characteristics are of importance in respect to droplet formation in the fuel spray and combustion.

4.6 Driving cycles and particle emissions

It is well known that driving pattern is an important factor in regard to exhaust emissions and it appears that exhaust particles, to a great extent, are produced during transient operation. The emissions change, depending on the driving cycle, even though the same distance was driven (**Figure 40**). The average load and acceleration rates of the NEDC driving cycle are considered to be relatively low and the cycle also includes large portions of idle or constant speeds. In comparison, the US06 comprises heavier accelerations and a number of micro-transients but not a cold start as the NEDC does.

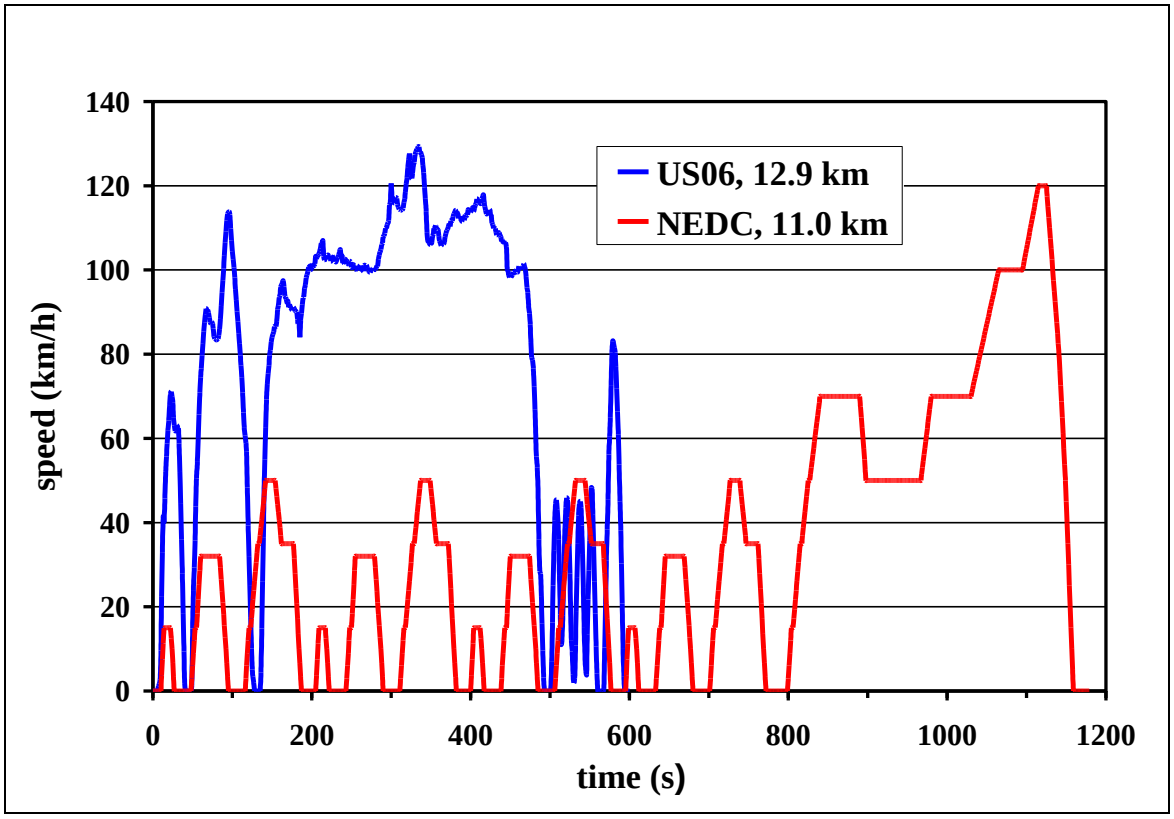

Figure 40. *The NEDC and the US06 driving cycles.*

Hall et al. (1998) examined particle emissions from a number of passenger cars, 4 with diesel engines and 3 with petrol engines, by use of SMPS (16-750 nm) from the CVS tunnel. Different steady-state speeds were used and the result from 50 and 120 km/h are presented in **Figure 40**. The diesel cars showed significantly higher particle emissions at 50 km/h as compared to the petrol cars, a difference that disappeared at 120 km/h as the emissions from the petrol cars increased drastically while the emissions from the diesel remained more or less unaffected. This effect was attributed to the rich air-fuel mixture for

the petrol engines at the high speed. However, in a later publication by Hall et al. (2000b), it was explained that the drastic increase in particle number emissions observed for the petrol cars is not representative to engine exhaust. According to the authors, the high emissions were caused by material deposited in the exhaust system and possibly also in the CVS-tunnel. This material is subsequently released as the temperatures increase during high speed driving. Repeated testing at 120 km/h indicates a diluting effect, showing successively lower particle emissions. The authors supported this hypothesis by observations from on-road driving showing high particle emissions at high speeds that successively fades away after a few minutes to again reach low levels. Thus, the exhaust system may act as a reservoir for particulate precursors released at higher temperatures. Therefore, particle emissions from petrol cars at different conditions should be treated with caution as the "true" particle emission is most likely somewhere in between the fully eluted emission and the emission obtained after a period of precursor deposition. The authors concluded that the history of the car's operation is essential and should be taken into consideration.

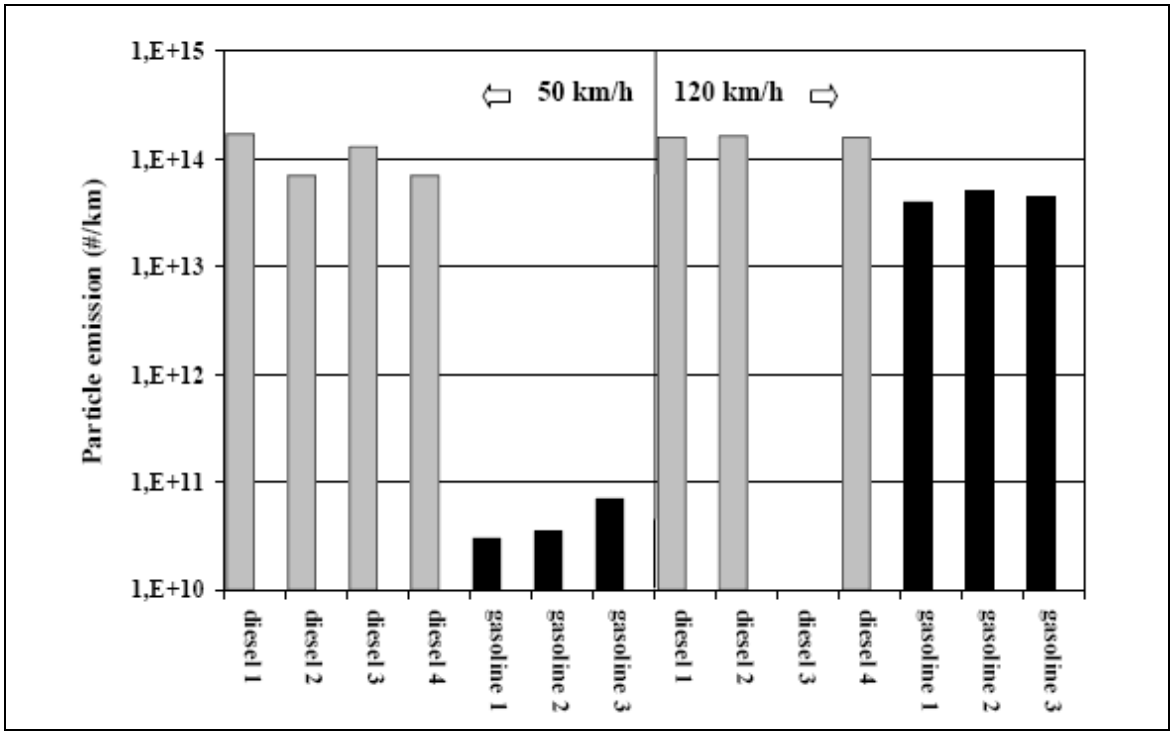

Figure 41. *Total particle number emission for diesel and petrol passenger cars at 50 and 120 km/h. SMPS measurements from CVS-tunnel (data from Hall et al., 1998).*

Similar observations by SMPS measurements from a medium-duty diesel engine were made by Kittelson and Abdul-Khalek (1999). Particle number emissions immediately increased as engine load increased to full load and speed from idling to reach 10 times higher emissions as compared to the emissions after 20 minutes of stabilization. The change was, however, only observed for nucleation mode particles (<30 nm) whereas accumulation mode particles were unaffected. The authors argues that this stabilization effect may be due to two reasons: storage of volatile particle precursors on surfaces during idling and subsequent release at the high temperatures of full power, or it may take a period of time for lubricating oil consumption to stabilize as a temporary increase in oil consumption may contribute to nucleation mode particles formation.

Ahlvik (2002) compared emissions from 4 modern passenger cars in the NEDC and US06 cycles. Two of the cars were petrol fuelled and two were diesel cars, one of which was supplied with a DPF. The average particulate mass emission for the two petrol cars was 1 and 2,6 mg/km for the two cycles respectively. The emissions from the diesel car without particle filter were 22,1 and 33 mg/km and for the car with DPF 0,3 and 0,9 mg/km. The effect of driving pattern is thus more pronounced for the petrol vehicles but the absolute increase in emission from the diesel car is still larger. The same study also includes size resolved particle number emission data as measured by ELPI (range 7 nm-6 μm) from the CVS-tunnel as is shown in **Figure 42**. The particle number emission is drastically higher for the petrol cars in the US06 as compared to the NEDC whereas the two diesel cars showed lower emissions. In the US06, the emissions from the petrol cars approached or even exceeded the emission from the diesel car without particle filter. The size resolved particle emission data reveal that the increase occurs in the smallest particle size measured. Furthermore, the real-time data shows that the highest particle emissions are associated with the cold-start and high speed parts of the cycles. The most significant increase for the petrol cars occurred in the high speed part of the US06.

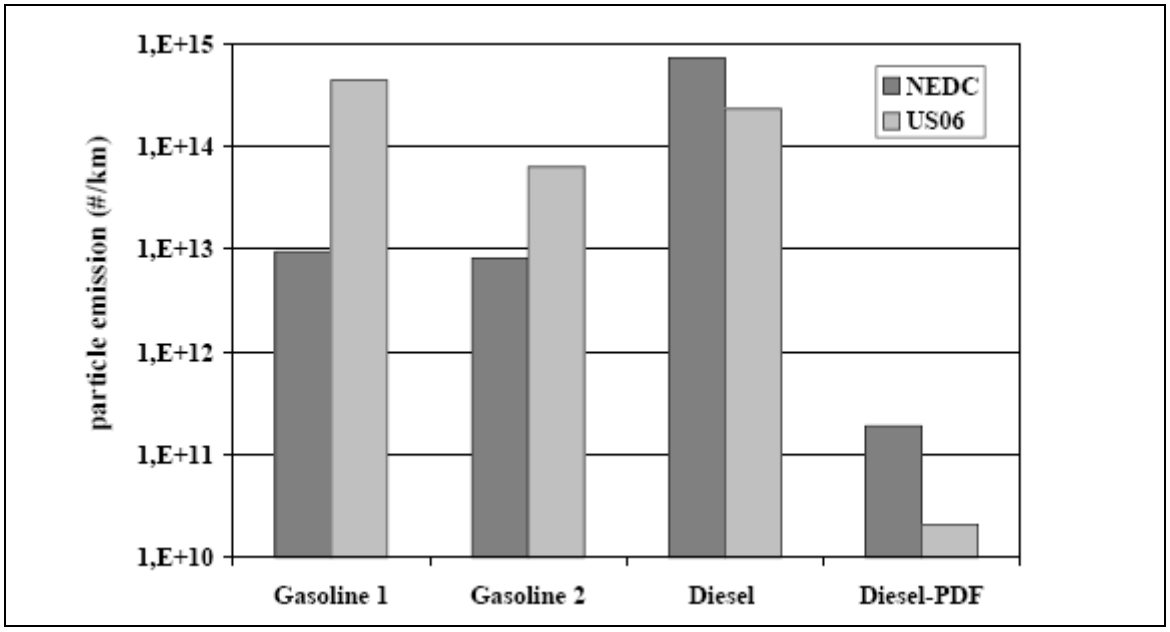

Figure 42. *Total particle emission in the NEDC and US06 for two petrol and two diesel cars respectively (data from Ahlvik, 2002).*

In a study by Färnlund et al. (2001), 45 diesel and petrol cars were studied for effects by engine load and driving pattern to the particle number emission. The particle emissions for the diesels were relatively unaffected by engine load and driving pattern whereas the petrol cars were much more sensitive ultimately reaching the same emissions as the diesel cars. This observation is in line with the study by Ntziachristos et al. (2004) in which it was concluded that petrol cars operated in high power driving may lead to diesel-like particle number emissions.

Mohr et al. (2000) measured particle emissions from two conventional, homogeneous charge petrol cars (engine size 1,4L and 1,8L) in steady-state driving at 50, 80, and 120 km/h. The SMPS measurements were performed from tail-pipe at dilution ratio between 40 and 110. Both cars showed the lowest emissions at 80 km/h and the highest at

120 km/h when operated at normal load with a flat peak size distribution at particle sizes smaller than 100 nm. At the higher speed, the car with the larger engine showed approximately 5 times higher emissions, while the emissions for the small engine car increased by approximately 100 times. When the vehicles were operated at 80 km/h, full load, the particle number emission increased by 50 times for the larger car compared to normal load. The small car particle number emission increased by two orders of magnitude with a significant production of nucleation mode particles. As the nucleation mode particles were fully removed by use of a thermodenuder it was concluded that these particles were composed by volatile material.

It has been shown in several studies that factors such as load and speed of the engine and environmental conditions have a large influence on particle emissions. Maricq et al. (1999) performed a study with one diesel and a number of petrol cars (model year 1995-1998) operated at different steady-state speeds. Particle size distributions were measured with a SMPS from the CVS-tunnel. **Figure 43** shows that particle size distributions change with vehicle speed and that higher emission are associated with higher speeds with the maximum number of particles for the petrol vehicle at about 30 nm. For the examined diesel car, the particle number peak emission was found at around 100 nm.

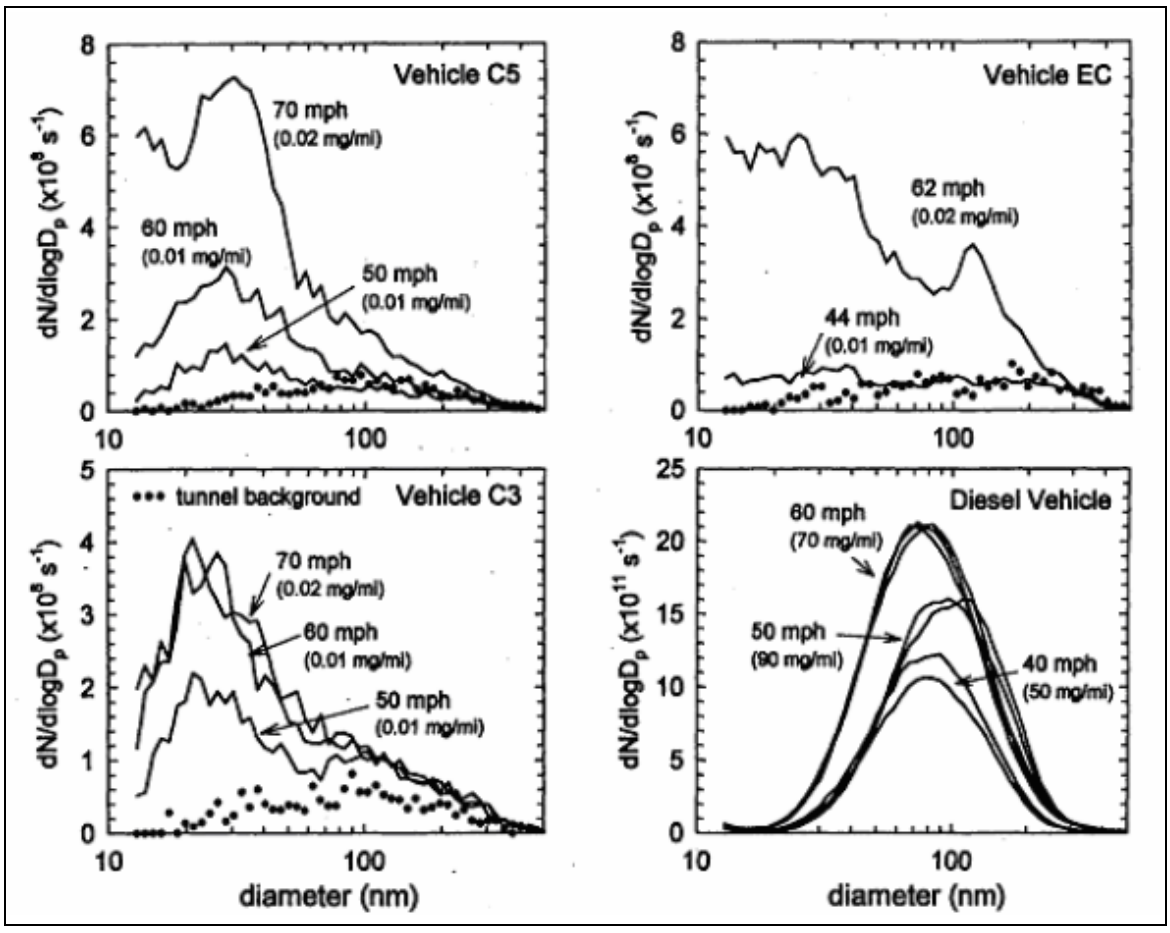

Figure 43. *Dependence of particle emissions on vehicle speed for three petrol cars and one diesel car. Dilution air particle size distributions are given as dotted lines. Exhaust flows for vehicle C5 are 0,010, 0,014, and 0,020 m^3/s at 50, 60, and 70 mph, respectively. For vehicle C3 they are 0,014; 0,019 and 0,026 m^3/s (Maricq et al. 1999).*

In the ACEA programme, (1999), CVS particle measurements using a DMPS were performed from a number of different vehicles representing different diesel and petrol technologies. The results from steady-state runs at 100 km/h are shown in **Figure 44**. The similar size distributions are attributed to the uniform residence times and agglomeration processes in the sampling system with only the initial particle concentration differing. These size distributions were reproduced in the second ACEA program (ACEA, 2002) and, according to the authors, the result indicates that there were not a significant number of nucleation mode particles measured for any of the seven vehicles examined: three diesel (of which one DPF) and four petrol.

Comparing steady state runs at different speed, differences were found between 120, 100 and 50 km/h. The highest loading was found at 120 km/h with the additional mass present as SIF, in particular sulphate and SOF. This could be interpreted in terms of sulphur dioxide oxidation to sulphuric acid. Oxidation would be efficient at the comparably high temperatures following high load. Sulphuric acid would then either nucleate new particles or condense on already existing soot particles. They would then attract water vapour and provide a suitable medium for some soluble organic matter.

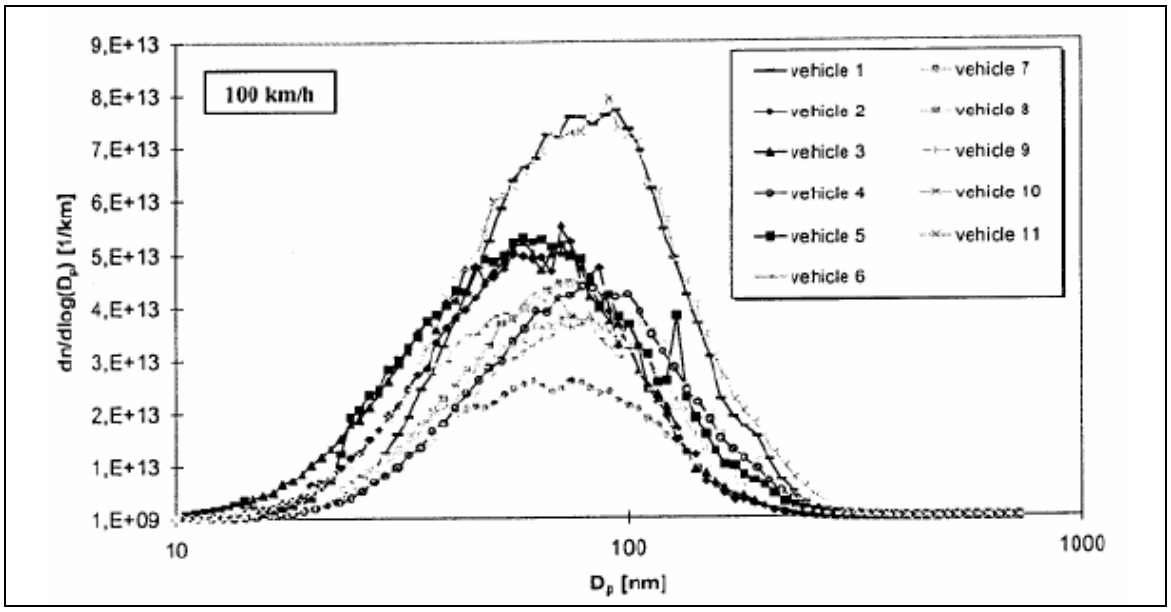

Figure 44. *Particle size distributions for diesel vehicles at 100 km/h steady-state speed (ACEA, 1999).*

Karlsson (2005) examined 4 diesel Euro 4 passenger cars of which 2 were equipped with DPF. The cars were examined in the NEDC driving cycle at 22°C and -7°C and the Artemis driving cycles at 22°C for regulated emissions and particle mass and number emissions according to the PMP-proposal.

In both the particle mass and number measurements, considerably lower emissions were observed for the cars equipped with DPF. In the NEDC cycle, the DPF-cars emitted somewhat less than 10^{10} particle/km as compared to the non-DPF cars with emissions of more than a factor 1 000 higher (**Figure 45**). For the non-DPF cars, the emissions are quite stable for the different driving cycles while the DPF-cars shows higher emissions in the

NEDC which is observed to be a phenomenon during the cold start of the cycle. The NEDC at -7°C did not show any significant changes in particle number emissions.

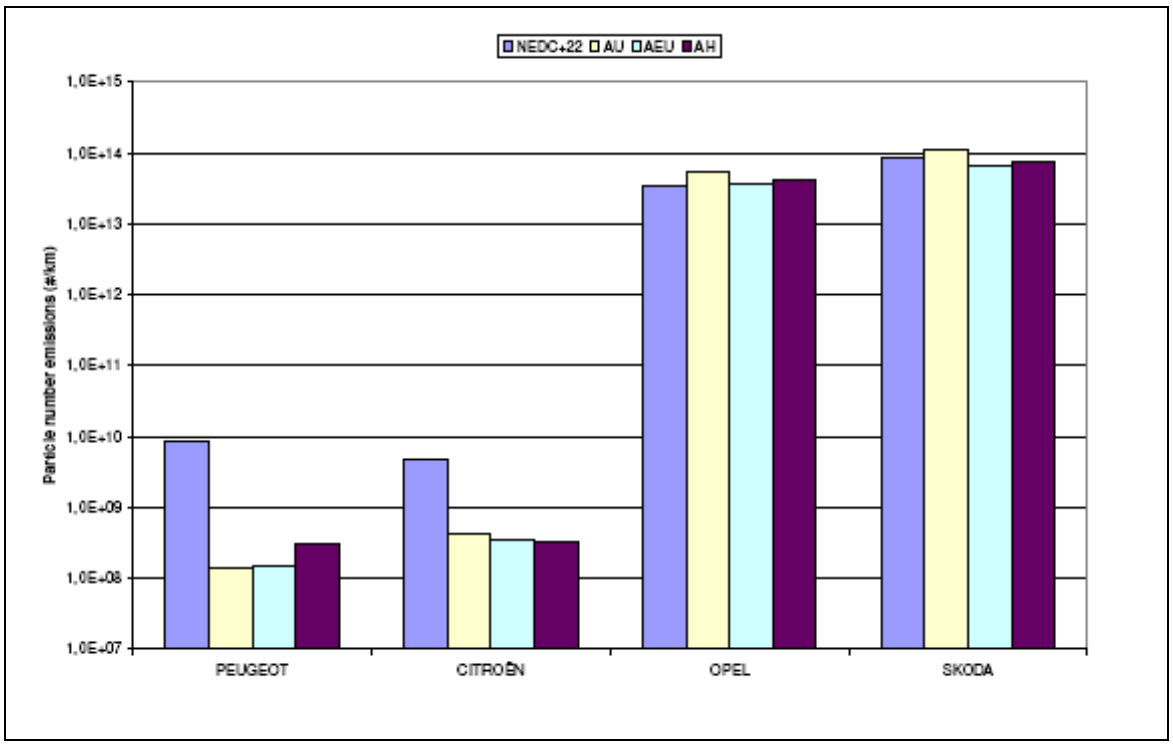

Figure 45. *Particle number emissions from NEDC and Artemis driving cycles at 22 °C. Peugeot and Citroën have DPFs and Opel and Skoda do not (Karlsson, 2005).*

Bosteels et al. (2006) examined particle number emissions from four Euro 4 passenger cars according to the PMP-proposal in the NEDC and the Artemis cycles. The cars included one petrol and three diesel cars of which one with DPF. The results are presented in **Figure 46** and clearly illustrate the effect of the DPF-filter. The difference between the diesel cars without and with DPF is more than a factor of 10^4. Furthermore, the particles is of possibly different solid particle composition since the EC-fraction data presented in Table 10 from the same study shows a very low EC-fraction for the diesel with DPF. The emissions from the petrol car are lower by a factor 100-1000 as compared to the diesels but roughly 100 times higher as compared to the diesel-DPF car.

Mohr et al. (2003) examined passenger cars using low sulphur fuels (<10 ppm) in the NEDC and in steady-state driving modes (50, 100, and 120 km/h) for PM and particle size distribution. The vehicles included diesel-DI with and without DPF, petrol multi-point injection (MPI) and direct injected (both stoichiometric and lean burn). The PM emissions from the DPF car were observed to be 30-40 times lower as compared to the non-DPF diesels and in respect to particle number emissions the emissions were 2 to 3 orders of magnitude lower. The Petrol MPI car emitted significantly less particles as compared to the direct injected petrol cars.

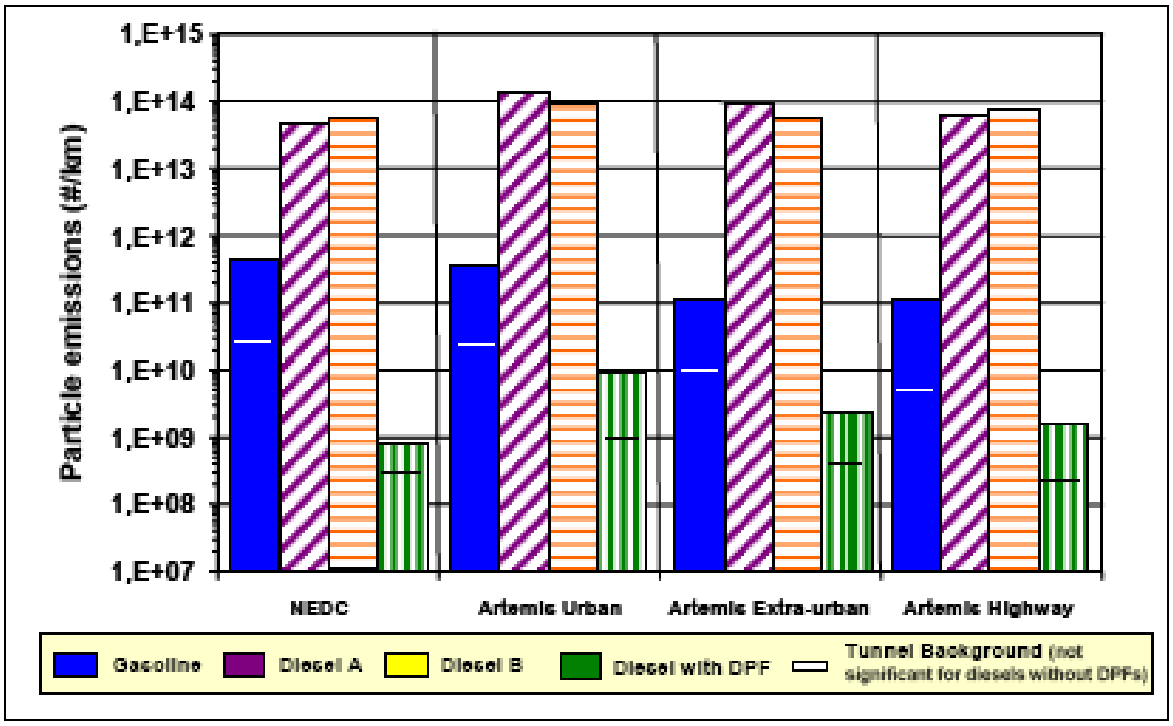

Figure 46. *Particle number emissions in the NEDC and Artemis cycles according to the PMP-proposal (Bosteels et al., 2006).*

In a report by Ntziachristos et al. (2006), non-volatile particles were measured using a thermodenuder-ELPI set-up. Two LDV and three HDE diesels (all Euro 3) were examined and compared using low sulphur fuels (<10 ppm-S) in different operational modes. In order to compare, the results were expressed both per unit of fuel and per unit of distance driven. In **Figure 47**, exhaust particle number concentrations and particle active surface, measured with the same sampling system and conditions, are presented.

It was observed that the particle number emissions scale with engine/vehicle size at urban conditions. However, at highway conditions the HDEs emits more or less as many solid particles as a passenger car per distance travelled. The HDEs exhibit up to one order of magnitude lower solid particle emissions (and up to three times higher NO_x emissions) than corresponding technology passenger cars; per unit of fuel consumed (often expressed as EI, emission index). This indicates different diesel engine tuning, depending on the application. Note that this is also somewhat in line with the difference in PM levels that can be seen in emission index for the two categories of vehicles, as discussed in the previous section 4.3.5 (page 32) on comparison of emission limits.

The shifting from urban to highway driving leads to a narrower speed range and rather lower loads for HDEs while a higher frequency of high loads and speeds is met for LDVs. Since the fuel-to-air ratio is directly proportional to the load for a diesel engine, a higher load leads to a higher fuel-to-air ratio and, generally, a higher particle production.

Parameters that reduce formation of soot include leaner initial fuel-air mixing and early combustion relative to the expansion stroke. These conditions can more easily be met in a larger engine due to the larger available volume for the fuel jet development and the longer time available for combustion due to lower operation speed. Both the available volume and time for the development of the diffusion flame (as a result of a higher operating speed) are

smaller in a light diesel engine than for a heavy duty one. Additionally, wall effects may further increase the tendency of particle formation in a smaller engine.

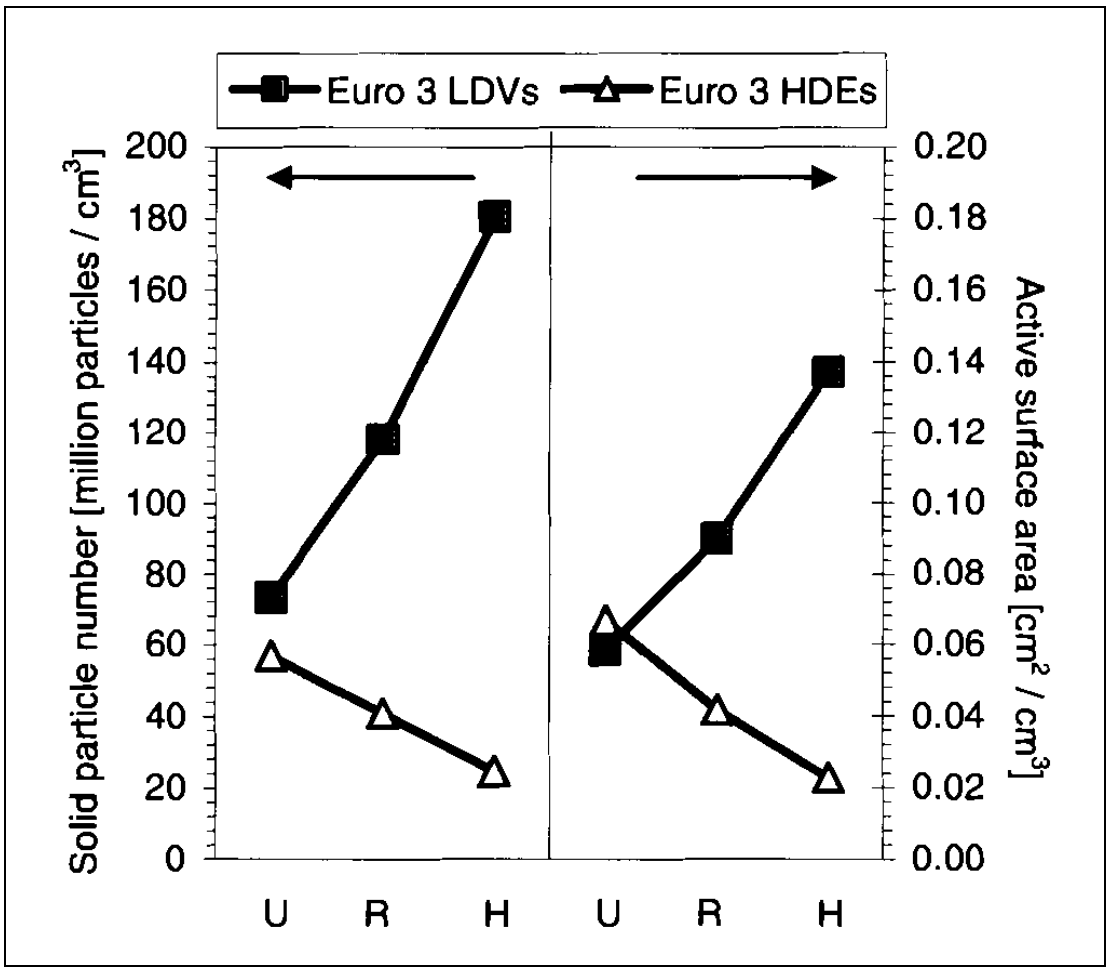

Figure 47. *Solid particle number concentration and active surface as a function of driving mode (U=urban, R=rural, H=highway) for LDVs and HDEs (Ntziachristos et al., 2006).*

A comprehensive source of data regarding the impact of different driving cycles originates from the Swedish in-use compliance (IUC) testing of light-duty vehicles. This programme is commissioned by the Swedish Road Administration and it is carried out by TÜV Nord in Germany and Ecotraffic in Sweden. Vehicle testing is conducted by TÜV in Essen. A more thorough description of the programme is made in chapter 4.8.2 at page 115. Below, only results on particle mass and particle number are covered.

The tests depicted in **Figure 48** shows that the particle mass emissions are generally higher in the Artemis test cycle compared with the NEDC cycle. For particle number emissions (**Figure 49**) there is no clear trend between the two test cycles. Interesting to note is that for diesel cars without DPF, the difference in particle mass emissions between the test cycles is relatively high whereas, in contrast, the particle number emissions is relatively constant for the two cycles. This phenomenon indicates that the average size of emitted particles is larger in the Artemis test cycle compared to the NEDC test cycle. This behaviour is well known – if load increase – also the size of particles may increase.

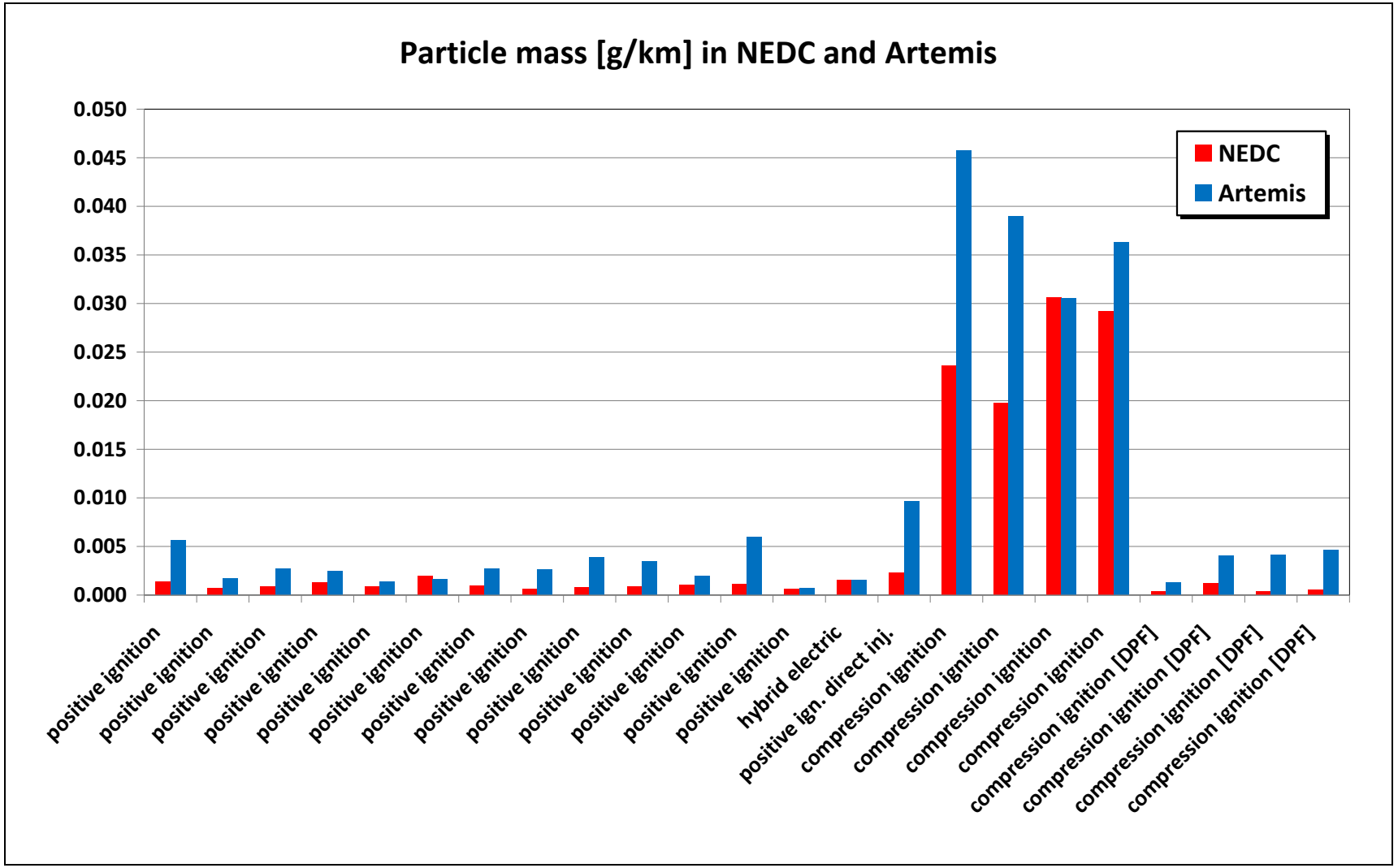

Figure 48. *Particle mass emissions during Artemis and NEDC. Based on average results from Swedish IUC program year 2006 and 2007.*

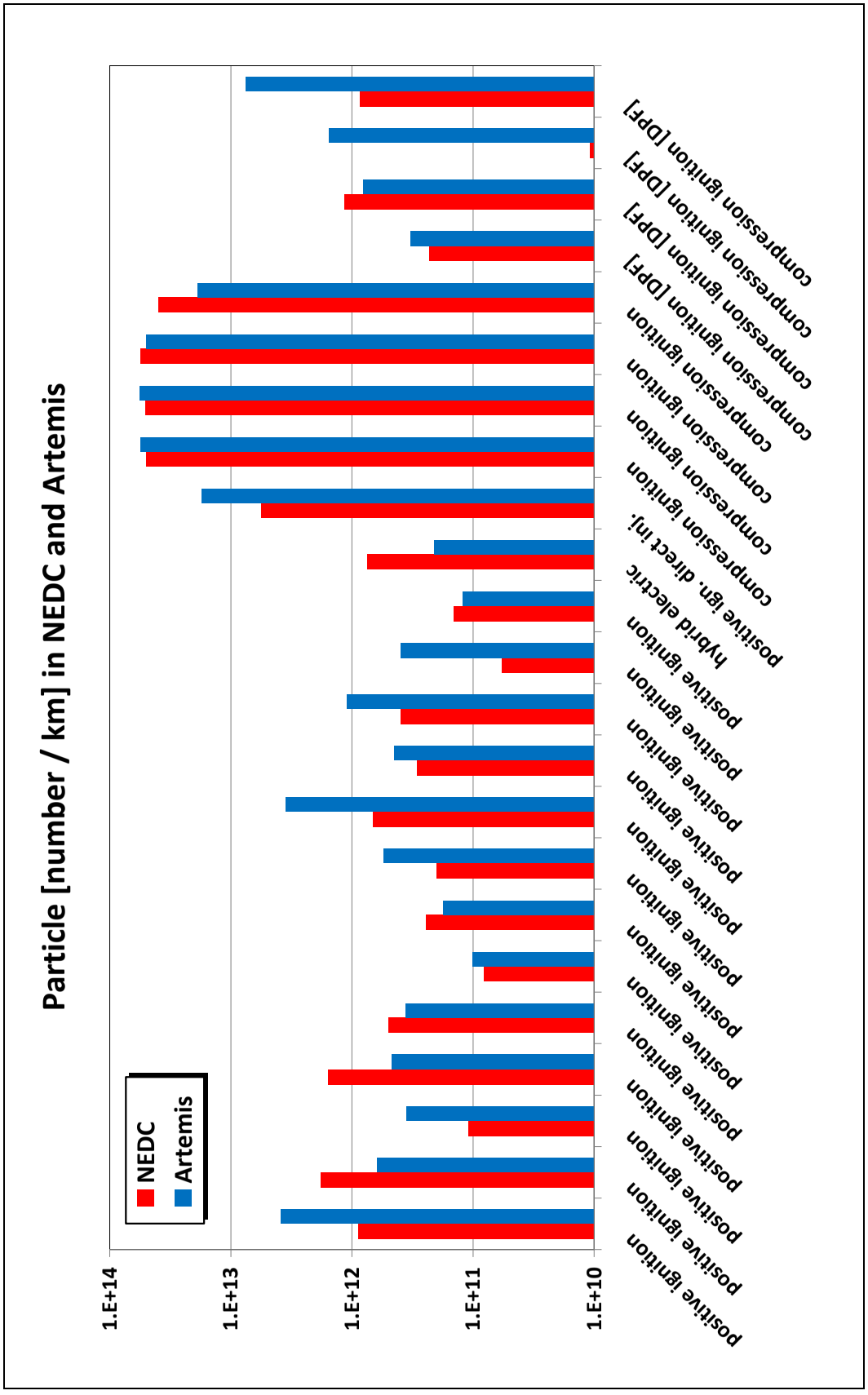

Figure 49. *Particle number emissions during Artemis and NEDC. Average results from Swedish IUC program year 2006 and 2007.*

In **Figure 50**, NO_X emissions in the different phases of the NEDC and Artemis test cycles are shown.

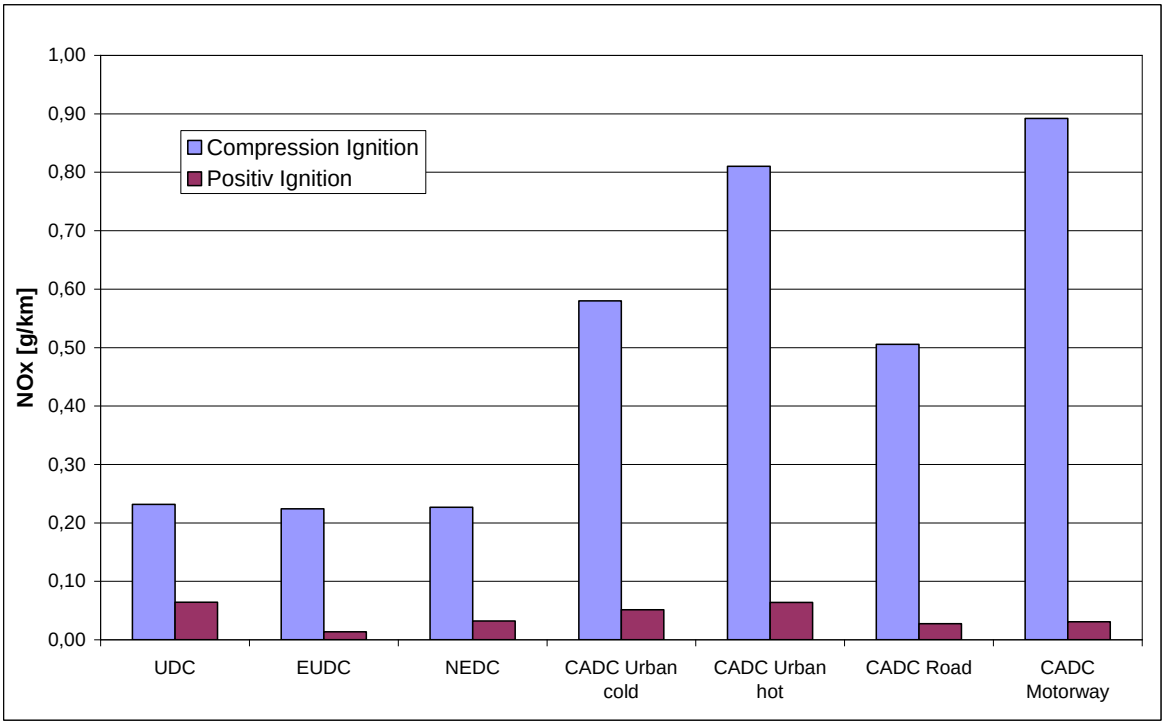

Figure 50. *NO_X emissions during Artemis and NEDC test cycles. Based on average results from the Swedish IUC program year 2006 and 2007*

The NO_X emission does not change much with driving cycle (in absolute terms) for petrol cars although there can be great relative differences (**Figure 50**). For diesel cars, the impact of engine load on NO_X emission is high in absolute terms. A change from NEDC to a "higher load" driving cycle, as the Artemis test cycle, results in much higher NO_X emissions. Since Artemis cycle may be more similar to "real word driving condition" – NO_X emission from diesel cars may generally be underestimated since NEDC is used as "certification cycle". The cars tested in this study are described more thoroughly in section 4.8.2, starting at page 115.

4.7 Engine and aftertreatment development

Particle mass emission data, compiled from NEDC filter measurements performed at AVL MTC are presented in **Figure 51** and illustrates differences between engines and exhaust after-treatment technologies. The Turbo charged Direct Injection (TDI) diesel cars, representing the "normal" diesel, show about 30 times higher emissions than Multi Point Injection (MPI) petrol cars which is representing the "normal" petrol car. The common-rail diesel engine operates with high fuel injection pressure and a high degree of injection control and shows significantly lower particle emissions as compared to the TDI. The lowest particle emissions among the diesels, resembling those of low emitting petrol cars, were found for a vehicle equipped with a DPF. The technology of direct injection of petrol (gasoline direct injection, GDI), designed for improved fuel economy, shows significantly

higher particle emissions as compared with the MPI and approaches the levels of diesel cars.

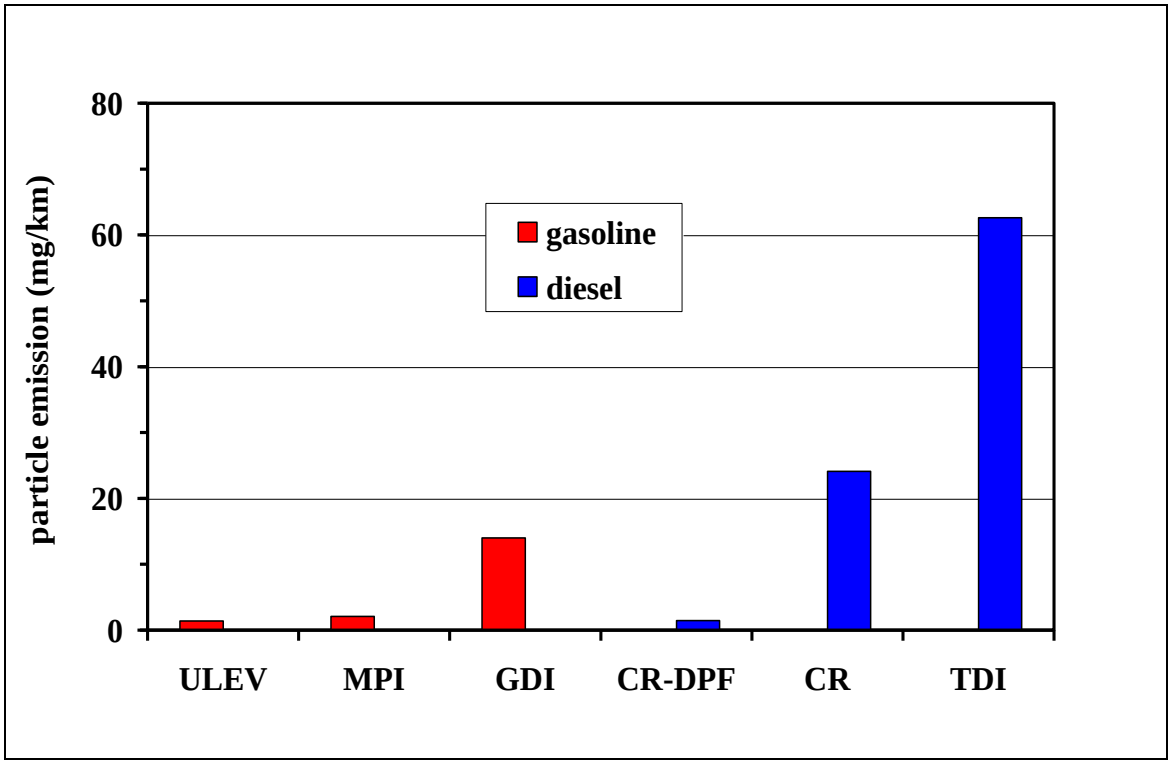

Figure 51. *Particle emissions from different petrol and diesel engine technologies in the NEDC (the number of vehicles for the calculated average is given in brackets: TDI - Turbo Direct Injection(3), CR - Common-Rail(1), DPF - Diesel particle filter(1), GDI – direct injected petrol(1), MPI - Multi Point Injection(5), ULEV - Ultra Low Emission Vehicle(1)). Measurement data compiled at AVL MTC (2002).*

The observations above are in line with those from the more recent study by (Ntziachristos et al. 2004) in which different diesel and petrol vehicles were examined for particle emissions in the NEDC. Eight Euro 2 and Euro 3 diesel passenger cars without DPF showed PM-emissions lower than 50 mg/km for five different diesel fuels (with an additional 10-25% reduction when using Swedish EC1 diesel fuel at 3 ppm-S as compared to Euro2000 fuel at 280 ppm-S (see **Table 8** for fuel specifications). Emissions from vehicles equipped with DPF were generally found below 3 mg/km. The emission level on these vehicles was so low that no significant impact of fuel properties was observed in this case. Normal petrol vehicles showed emissions below 2,5 mg/km, while vehicles using direct injection petrol technology showed considerably higher emissions in the range of 4-11 mg/km.

Measures to reduce particle emissions from LDV include electronic engine control, high pressure injection systems, combustion chamber design, and exhaust after-treatment systems such as DPF and/or catalytic converters. Emission control is driven by the successively tighter exhaust emission regulations applied in the EU and the USA. Future legislation will either make DPF mandatory or set emission limits so that DPF is the only practical way to reach these limits. A more subtle driving force is the marketing value of good and efficient technology to reduce environmental impact of vehicles as environmental concern is growing among consumers.

4.7.1 In-cylinder emission reduction technology

During the first decade after the introduction of the DI diesel engine in passenger cars in the late 1980's, most of the emission reduction was made by in-cylinder methods. The only aftertreatment technology introduced was the oxidation catalyst. Although effective on CO and HC emissions it has little effect on NO_x and particle emissions. Thus, most of the reductions of the latter emission components so far have been accomplished by in-cylinder methods. It is of interest to highlight some of this development and to look for further improvements in this area. In a later section, exhaust aftertreatment, i.e. particulate filters and NO_x catalysts are discussed.

Injection system

The development of the fuel injection equipment for direct injection diesel engines has been basically focussed on reducing the droplet size and the air entrainment in the spray. This has mainly been achieved by the following measures: increasing the injection pressure; reducing the nozzle hole size and thus, the total hole area; and, finally to increasing the number of nozzle holes. A corresponding development of combustion chambers has been to increase the diameter and make it shallower. These measures have decreased the soot formation in the engine, while other methods of modifying the combustion have decreased NO_X formation.

When the DI diesel was first introduced in the late 1980's, the only fuel injection equipment (FIE) available was rotary pumps. The maximum injection pressure attainable at that time was little over 1 100 bar at the injection nozzle[5]. A new generation of rotary pumps was introduced by Bosch in the mid 1990's. Initially, the pressure level was about 1 500 bar but later versions achieved increased levels and the latest versions just after the millennium shift actually approached 2 000 bar.

Another major step in injection system development was taken in 1998 when the so-called common rail injection system was introduced. The first generation of the Bosch common rail system had a pressure level of 1 350 bar. The second generation that was introduced about four years later could manage 1 600 bar. The third generation introduced two year ago facilitated the use of piezo servo valves instead of solenoid valves at the same pressure level. Piezo actuators are some 3 to 5 times faster than solenoid valves. Just recently, the pressure level was raised to 1 800 bar by Bosch and later this year, or early next year, 2 000 bar will be reached. Future generations will be capable of even higher pressure levels.

An injection system competing with common rail, which was introduced almost at the same time as the first common rail, was the electronic unit injector (EUI) system. This injection system was favoured by Volkswagen due to its greater pressure capabilities. A pressure level of 2 050 bar was achieved already at the launch of this system. The system was manufactured by Bosch. Today, a pressure level of about 2 400 bar is used. Similarly, the latest unit injector version supplied by Siemens VDO (currently part of the Continental group) uses piezo actuators instead of solenoid valves.

[5] Due to a superposition of pressure waves travelling from the nozzle to the pump and back again, the injection pressure at the nozzle will be higher than at the injection pump. This paradox is made possible without breaking the laws of energy conversion by the fact that the volumetric flow delivered by the pump is far larger than the injected volume.

In **Figure 52**, the pressure level as a function of engine speed is depicted for a couple of injection systems. This graph has been compiled by using published information and some assumptions. Rotary pumps (exemplified by the Bosch VP44) and unit injectors show a steep rising rate with increased speed. At the highest speed, the achievable injection pressure is higher than for common rail of the same model year. At lower speeds the situation is different. In fact, common rail systems would be capable of attaining the maximum pressure at all speed. To date, this is not feasible due to the extremely short injection period that would be the result and the increase in engine noise that would be the consequence of that. Possibly, the use of multiple injections (up to 7, 8 or more, are discussed in the future) could facilitate the utilisation of higher pressure levels at low speed as well. It should also be noted that the maximum pressure levels are not quite comparable at high speeds between various injection systems due to that the injection pressure is not constant during the whole injection event. As a rule of thumb, a common rail system is equal to a unit injector system regarding it emission performance at a pressure level at least 300 bar lower than for the unit injector. Similarly, the difference between common rail and rotary pumps is some 200 bar.

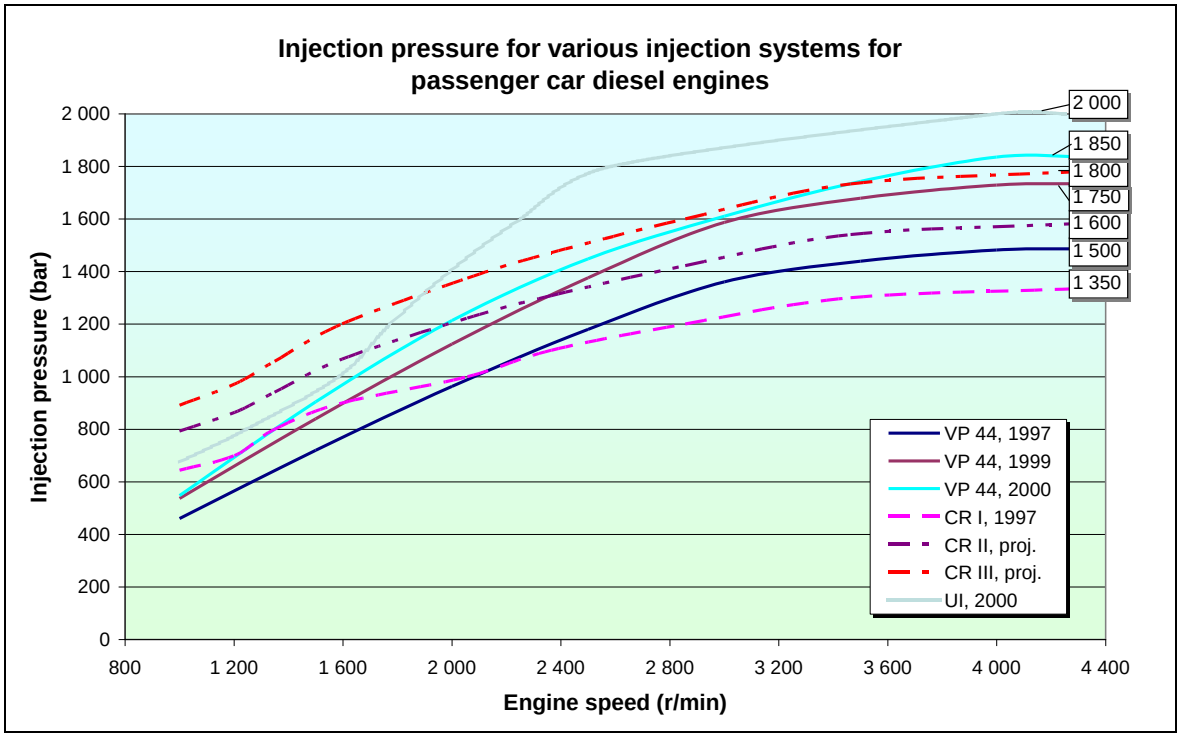

***Figure 52**. Injection pressure for various injection systems.*

The discussion above has summarised a continuous and rather rapid development regarding injection pressure capabilities. Although the first generation of common rail systems was lagging behind the competing systems at that time, they have now cached up. Common rail systems have also other advantages such as reduced engine noise and therefore, they are favoured over other systems today. The rotary pumps are still in use in some developing countries with less severe emission limits or in applications other than passenger cars.

Another important factor besides the maximum injection pressure is the so-called rate shaping of the injection event. This can be achieved in two principally different ways.

First, the injection pressure can be varied during the injection event (used by unit injectors). The injection period for the main injection is usually some 30 degrees crank angle at rated speed and full load. Although relatively short, an increasing injection pressure during this event has some advantages for emissions and noise. The second option (used by common rail systems) is to use multiple injections. While the first generations used only one pilot injection, systems today use up to 5 injections. An example as to how the injection event can be optimised is shown in **Figure 53** (Bauer, 2007).

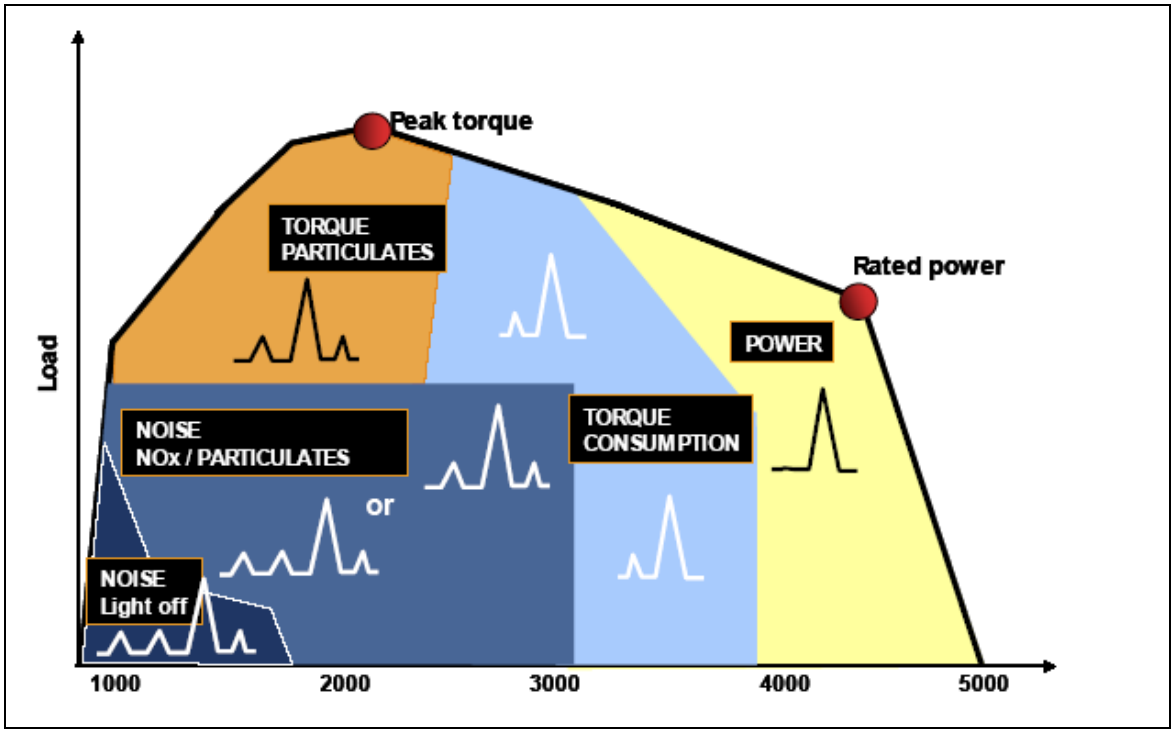

***Figure 53**. Injection strategies.*

As mentioned above, rotary pumps are phasing out of production today. Volkswagen who, together with Land Rover, have been the only proponents of unit injectors announced last year that they would gradually (with a timeframe of a couple of year) phase our these systems in favour of new common rail systems. Thus, the only remaining injection systems in the future will be common rail systems. This does not imply that the development will be stopped there. New generations of common rail systems will have increased pressure levels beyond 2 000 bar. Two stage systems with pressure capabilities beyond 2 500 bar are in an early development phase.

In addition to the features of injection systems mentioned above, many other improvements have also been made in this area. For example, the nozzle hole sizes have decreased considerably, while the number of holes have increased (from 5 to 8). In spite of the increased number of holes, the total hole area has been reduced by more than a factor of 2. The corresponding increase in injection pressure has been made so as not to prolong the injection event.

An important part of the injection system is the electronic control system. Today, this is an integral part of the development of the whole combustion system. Using multiple injections, rate shaping, varying pressure levels and many other parameters, the degrees of free-

dom have increased tremendously. Thus, an optimisation of the engine is now more time consuming.

One interesting feature of new injection systems is the direct actuation recently developed by two of the suppliers of diesel injection systems, i.e. Delphi and Continental, formerly Siemens Automotive (Dober et al., 2008; Shöppe et al., 2008 and Bauer et al., 2008). A schematic comparison between the new injection system with direct acting needle and the current servo actuator (solenoid or piezo) is shown in **Figure 54**.

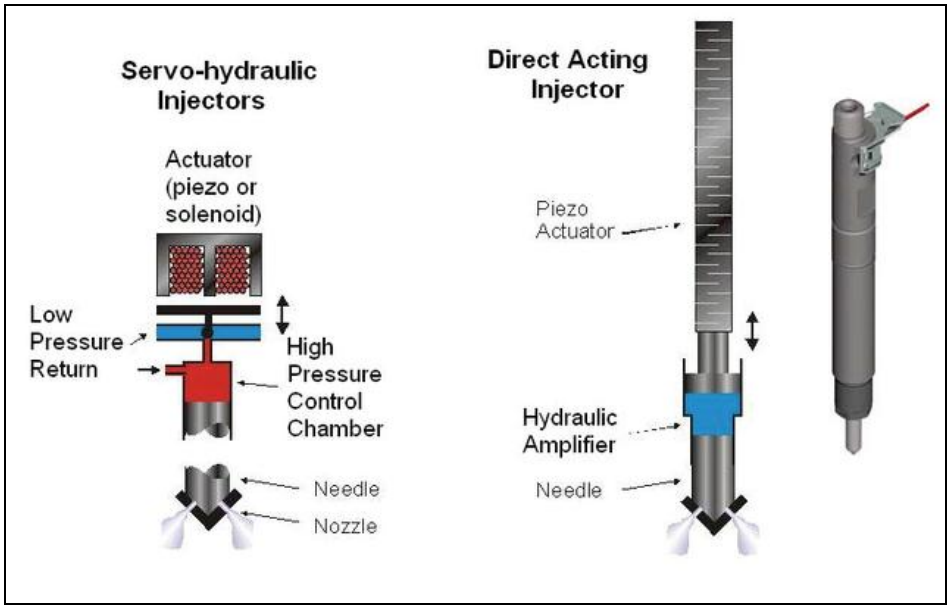

Figure 54. *Delphi direct acting injector, schematic operation (Adapted from Dober et al., 2008).*

By using direct actuation, the needle movement can be much faster and the distance between multiple injections can be shorter. Lower emissions and reduced engine noise are some of the benefits. An additional advantage of the two new injection systems from Delphi and Continental is that the injection pressure is increased from 1 800 to 2 000 bar. The main competitor, Bosch introduced a common rail injection system with 2 000 bar about one year ago but does not yet use direct actuation of the needle.

An illustration of the potential to reduce NO_X emissions with the new injection technology described above was shown by Shöppe et al (2008). In **Figure 55**, Soot, air/fuel ratio (lambda) and indicated fuel consumption (ISFC[6]) is plotted against NO_X emissions. The variation of parameters along the lines is made by changing the EGR rate. In comparison to the baseline engine calibration, a 30 % improvement in NO_X can be achieved with the new injection system at a similar level of soot emissions as the baseline. However, by increasing injection pressure and boost pressure, significantly lower NO_X levels can be achieved. The relative improvement is as great as up to about 75 %. Although it is hardly likely that

[6] ISFC is the fuel consumption without taking the engine friction into account. The determination of ISFC is made by integrating the work perfomed by the gases in the combustion chamber by using high-speed data acquisition of the cylinder pressure measured by a fast pressure transducer. A time resolution down to 0,1° crank angle is usually necessary for the calculation of ISFC. ISFC is often measured on single-cylinder research engines where the mechanical friction is significantly higher than for multi-cylinder engines.

such an improvement can be achieved at all speeds and loads, this improvement could be a great step towards meeting future very stringent emission limits *without any NO_X after-treatment*.

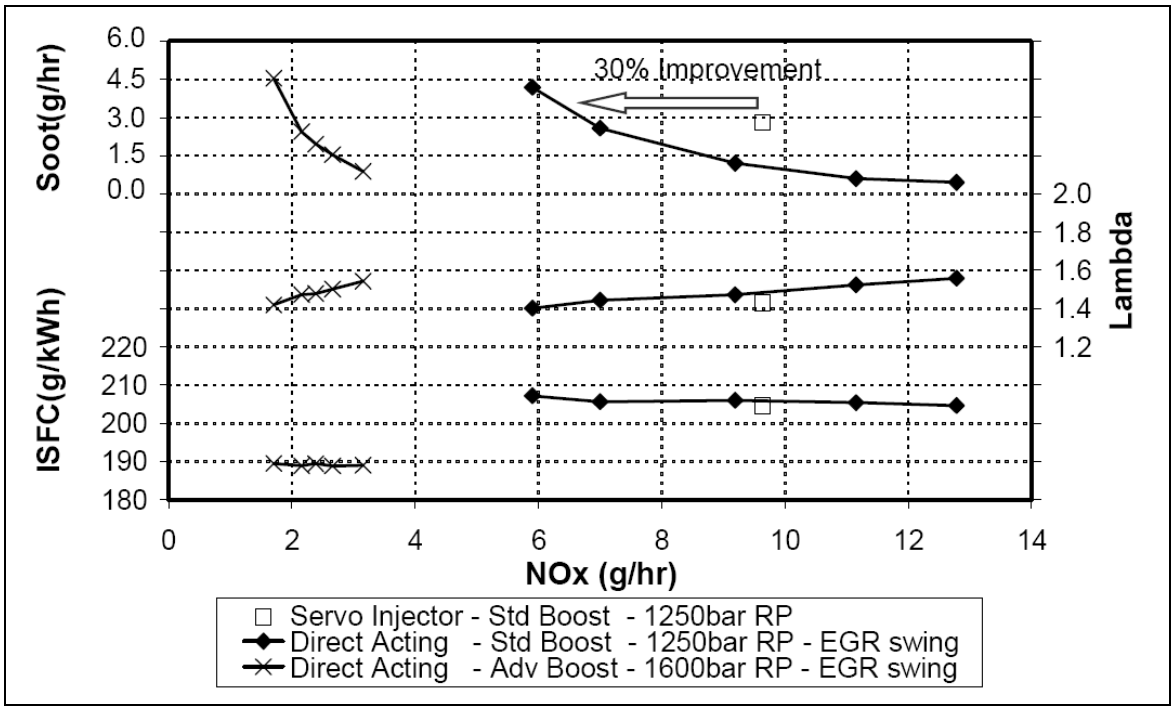

***Figure 55**. Potential for ultra-low NOX (Adapted from Schöppe et al., 2008).*

The spray development at low engine load and particularly during engine cold start for low compression ratios can be improved. Reducing the compression ratio is of interest for increasing the power density of the engine, thus enabling engine downsizing. The recent development of increasing the number of nozzle holes from 5 to the range of 7 to 9 has provided considerable improvement in this area along with improvements of the injection process in general (e.g. multiple injections with common rail injection systems) and improvement of the glow plugs. When direct injection engines were first introduced in the late 1980's, compression ratios were as high as 21:1 to 22:1. During the time period from then until now, the compression ratio has been reduced to the range of about 16:1. Together with other improvements (i.e. increased cylinder pressure capability), this has enabled an increase in brake mean effective pressure (BMEP) and power density by almost a factor of 2 (i.e. from 13 to 25 bar in BMEP).

Although much of the improvement of the specific power of diesel engines has been achieved by decreasing compression ratio, further improvement of the air/fuel preparation process would be necessary if the compression ratio is to be reduced even more, without increase in HC emissions. One possible route could be a drastic increase in the number of nozzle holes, i.e. from the state-of-the-art level of 7-8 today to 18-20. This was demonstrated by Sakata et al. (2008) at Toyota, as can be seen in **Figure 56**. The practical problems of producing such large number of nozzle holes and such small dimensions will probably be a great hurdle for introducing this technology in the near future.

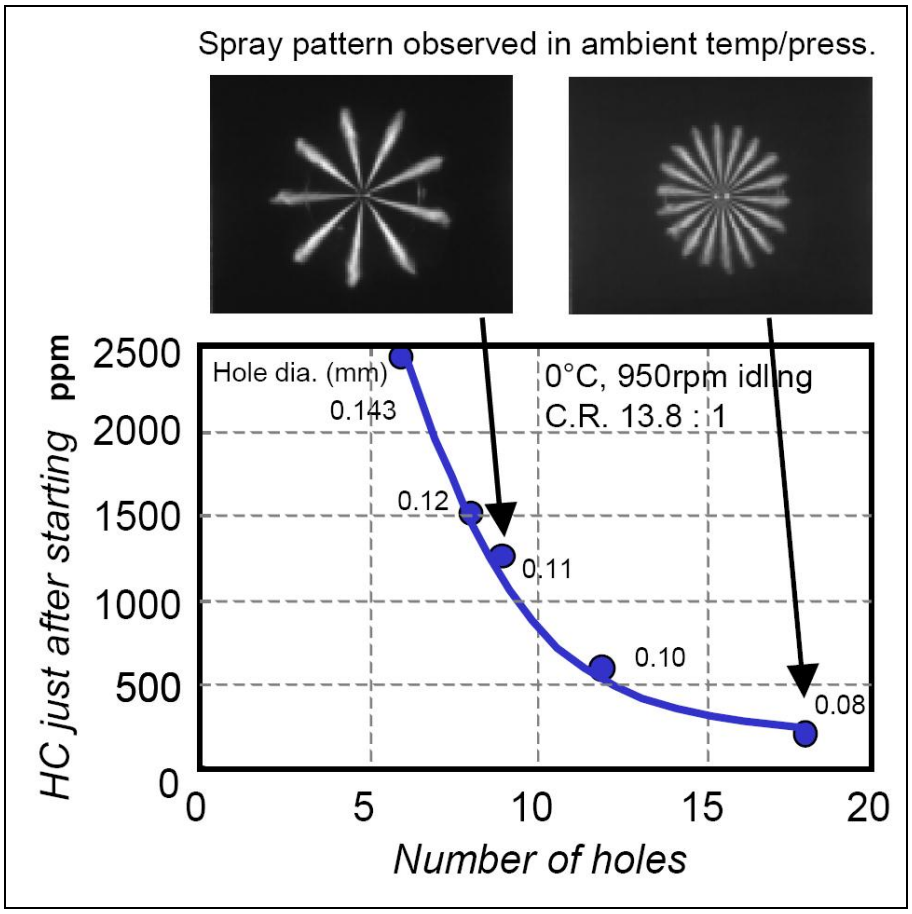

Figure 56. *HC reduction with large number of holes (adapted from Sakata et al., 2008).*

Exhaust gas recirculation (EGR)

The injection system design has been important in order to reduce in-cylinder particle emissions. Similarly, exhaust gas recirculation (EGR) has been the most important parameter to reduce NO_X emissions.

EGR reduces the oxygen concentration and in combination with being an inert gas, it reduces the *local* flame temperatures and thus, the formation of NO. The negative side effect is that particulate emissions increase by increasing EGR. However, a compromise that can reduce both NO_V and particulate emissions can be found by varying both parameters. In **Figure 57**, data from Mercedes (Weber, 2007) have been compiled by Ecotraffic to show the impact of injection pressure and EGR. Note that the emission levels have been expressed in the unit g/kWh.

As can be seen in **Figure 57**, increasing EGR and injection pressure can facilitate a decrease of both NO_x and particulate emissions. These tests were carried out on a first generation common rail system with a maximum pressure level of 1 350 bar. However, at this operating point, representing about 30% of maximum load and a speed of 2000 r/min, the maximum pressure level of the injection system cannot be fully utilised. To give an idea of the development status at the end of the 1990's, NO_x emissions of about 3 g/kWh and particulate emissions of some 0,2 g/kWh were achievable. This corresponds to 20% EGR and an injection pressure of 800 bar. As mentioned above, further improvements will be possible in the future.

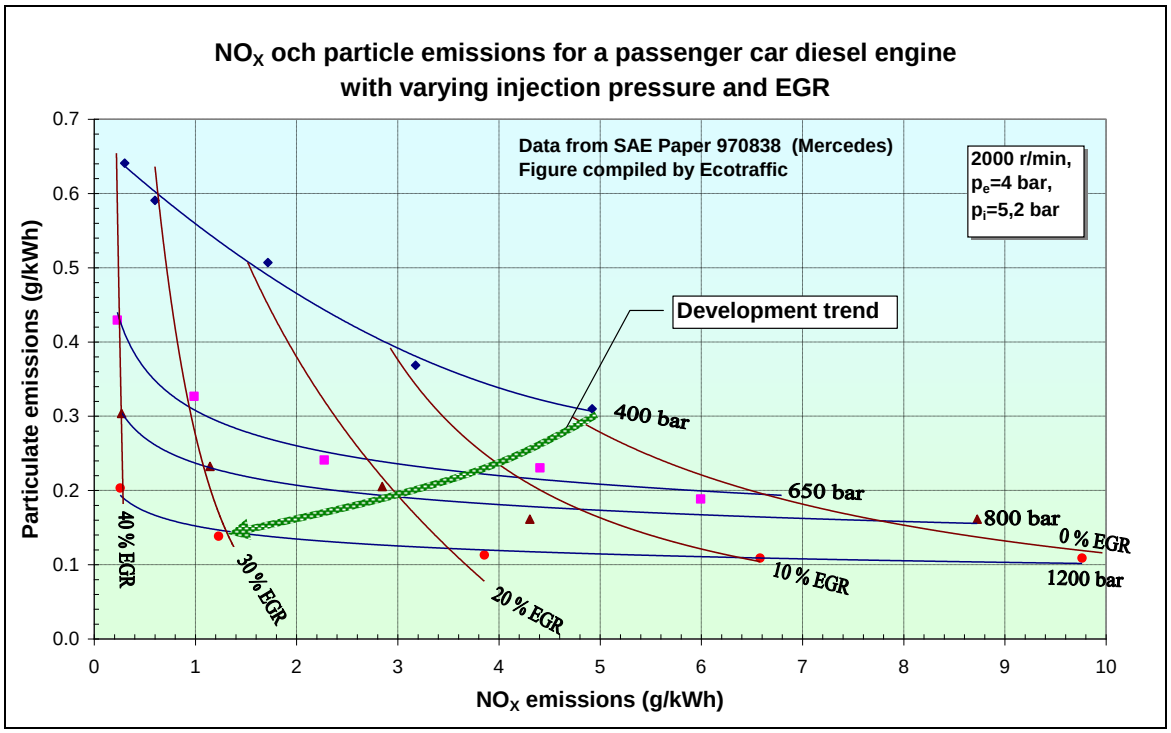

Figure 57*. Impact of EGR and injection pressure*

Although the EGR technology has been in production on passenger cars for more than two decades, there is still potential for further improvement of this technology. Today, all applications of this technology on light-duty engines are of the so-called "high-pressure" or "short-route" type. The other alternative is called "low-pressure" or "long-route", which was first pioneered in production by the Swedish development company STT Emtec as an aftermarket solution (e.g. Andersson et al., 2002). The two EGR alternatives are shown schematically in **Figure 58** below.

In the high-pressure system (**Figure 58**), exhaust is led from the exhaust manifold before the turbine of the turbocharger to the inlet manifold after the intercooler and the compressor of the turbocharger. In the low-pressure system, EGR is led from after the turbine of the turbocharger to before the compressor of the turbocharger. Since diesel exhaust contain soot particles, the risk of fouling or damaging the compressor necessitates that a DPF is used and that the EGR connection is after the DPF. In both systems, an EGR cooler can be used to reduce the EGR temperature. In the low-pressure EGR system, this is more or less a prerequisite since too high inlet temperature to the compressor of the turbocharger

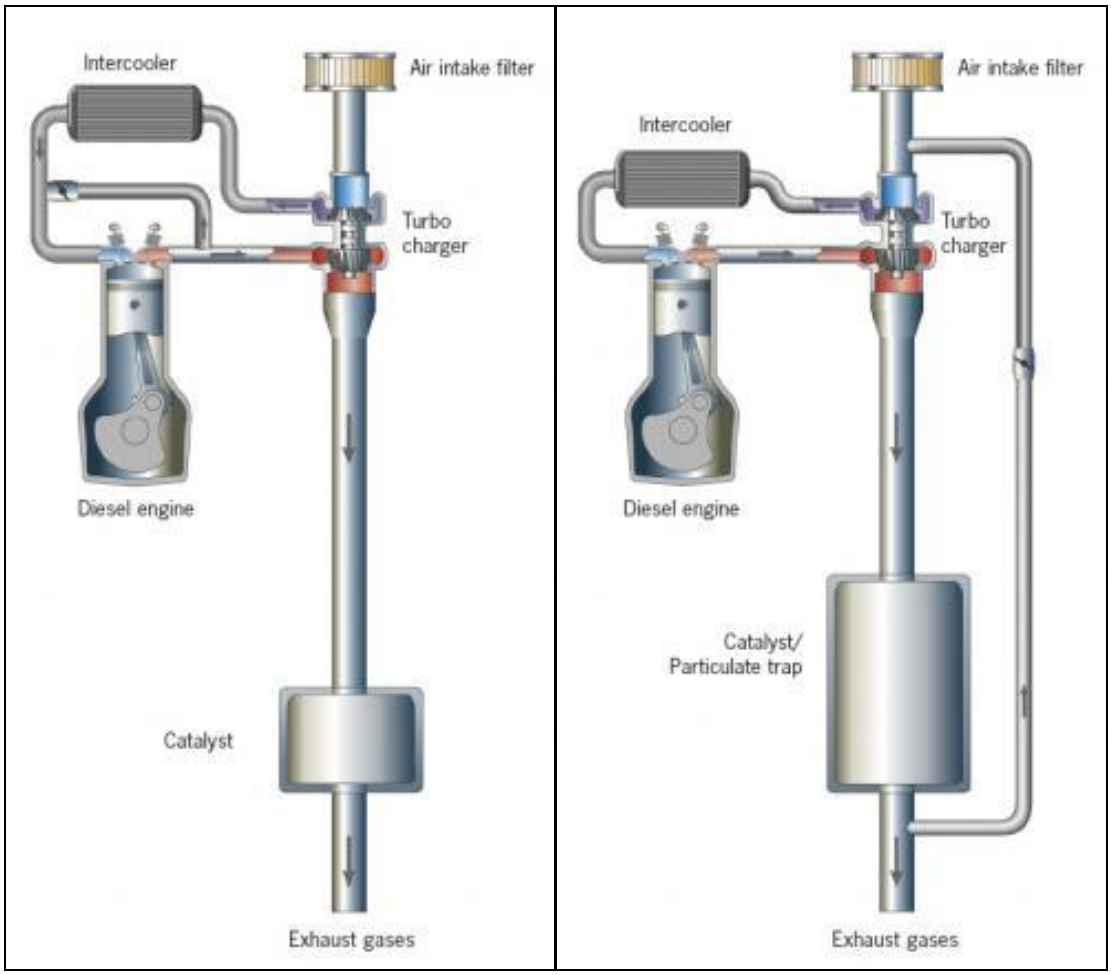

Figure 58. High-pressure or short-route (left) and low-pressure or long-route (right) EGR systems (Andersson et al., 2002).

One problem with high-pressure EGR systems is that the pressure drop is not always in the "right" direction to drive the EGR flow. The use of throttling and/or venturis can be used to maintain sufficient pressure drop, but with a negative influence on fuel consumption. For very high EGR rates this problem is magnified. The low-pressure EGR system avoids this problem. As always, there are also drawbacks for this solution. The compressor inlet flow is affected, and could lead to damage of the compressor wheel if not enough care is taken to avoid this problem. Failure of the DPF could then lead to a breakdown of the compressor. In **Figure 59**, a "real" system for low-pressure EGR on a passenger car size of engine can be seen (Rinaldo, 2008). Since new DPFs are mostly mounted directly after the exhaust turbine, the "long-route" does not necessarily have to be so long after all, which is illustrated in **Figure 59**.

The ideal solution for lowest emissions and fuel consumption could be a combination of both EGR types, the so-called "hybrid" EGR system. This option has now also gained interest by car manufacturers lately, as described by Rinaldo (Rinaldo, 2008) and Hadler et al. (Hadler et al. 2008). In the latter case, this technology is now introduced in production on a VW 2-litre engine, as a solution to meet the US and Californian 2010 emission limits.

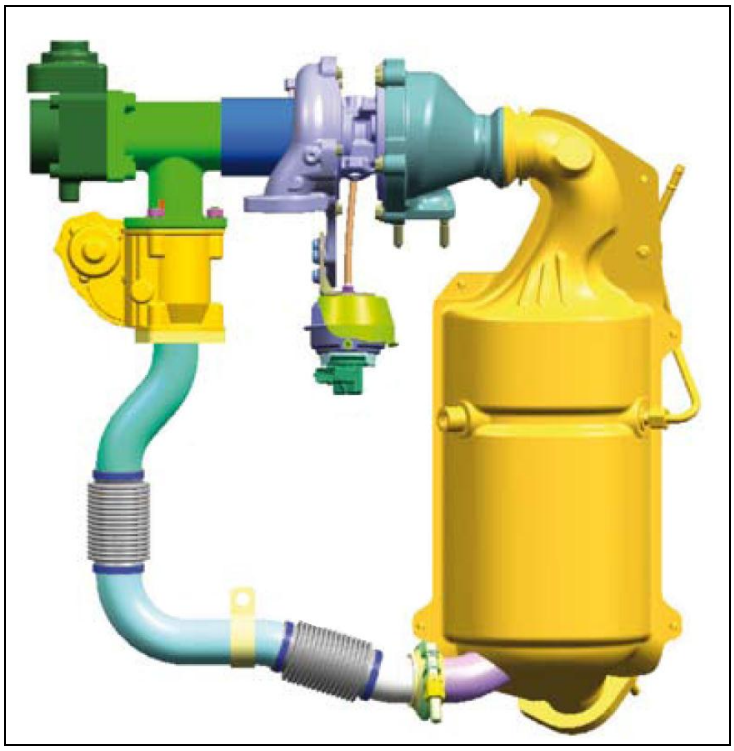

Figure 59. *Low-pressure EGR*

Strategies to meet Euro 6 emission limits

The improvements in the past regarding in-cylinder methods to decrease emissions leads to the question whether it will be possible to meet future emission limits without aftertreatment devices. First, it can be concluded that a particulate filter will be needed to meet the limits in Euro 5 and 6 for this emission component. Second, we can conclude that there are already cars on the market that have NO_x emissions below the Euro 5 limit of 0,18 g/km. Thus it seems very likely that this limit will be met without any NO_x reducing catalyst and with only relatively small improvements on the engine. The Euro 6 limit at 0,08 g/km seems to be much tougher to meet using in-cylinder methods only. However, in view of the development indicated above, our opinion is that this could be possible, at least for smaller engines.

A possible technology mix for various strategies of meeting the NO_x limit in Euro 6 is shown in **Figure 60**. For smaller engines, possibly up to 1,8 or 2,0 litre, Euro 6 could be met without any NO_X aftertreatment. For larger engines, there are several options under development that has the potential to meet the limit. For engines up to 3 litres, NO_x adsorbing catalysts are of great interest, while the largest engines might use an SCR catalyst with dosing of urea as a reducing agent. This is similar to the technology used on heavy-duty vehicles in Europe. A more thorough discussion about aftertreatment technologies can be found in a later section of this report.

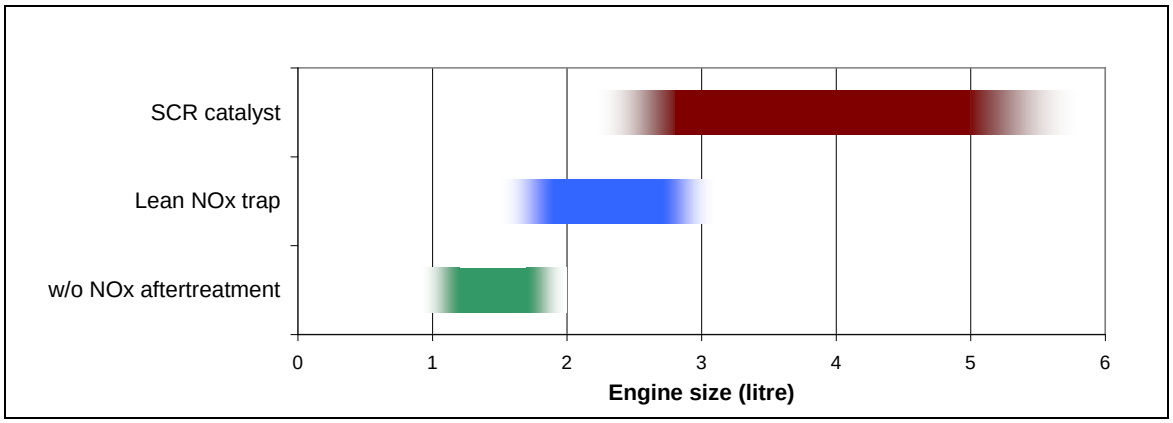

***Figure 60**. Potential strategies to meet Euro 6.*

There has already been published several papers showing the potential of meeting Euro 6 without NO_x aftertreatment. One such recent example is from the 28th Vienna Motor Symposium. By improvements of the injection system (1 800 bar CR), the turbocharging and the EGR systems (improved EGR cooler), Euro 6 could be met on 2-litre engine in a vehicle weighing 1 600 kg (Bauer, 2007). This is illustrated in **Figure 61**. Although there was no margin to the limit in this case, it is plausible that Euro 6 will be met with reasonable margin with further improvements and optimisation. After all, there is also considerable time left for development until Euro 6 is enforced in 2014.

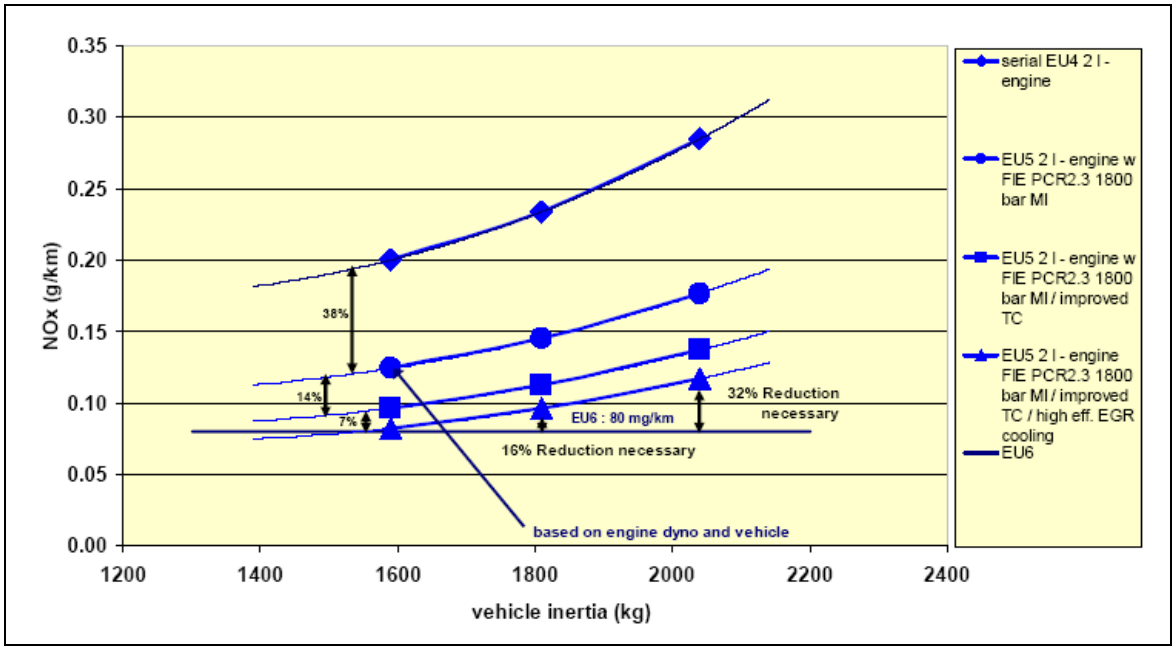

***Figure 61.** Engine-out NO_x emission potential.*

Although the section above was written for the report in 2007, it is clear that considerable improvements have been made in just one year. For example, SCR and NO_X storage catalyst have been introduced in production for both the US market and in Europe. A number of cars fulfilling the Euro 5 limits have been introduced on the European market and many others will follow this autumn and in 2009. To date, no car that fulfil the Euro 6 emission level has yet been introduced, as projected in **Figure 60**. On the other hand, improvements

in injection and combustion systems have to be introduced first to facilitate the reduction in engine-out NO_X levels. However, prototype engines have already demonstrated these levels, so it is only a matter of time before the first car that will meet Euro 6 without NO_X aftertreatment will be introduced on the market.

4.7.2 Diesel Particulate Filters

First, it should be noted that the focus in this section has been on "*closed"* diesel particulate filters (DPFs), i.e. where the channels of a monolith are closed in either end so as to force the flow through the filter material. Various types of "open" filtration devices that can reduce the particulate level to some extent (but not as much as closed DPFs) are not covered here. An example of an open filtration device, or partial filter as it is sometimes denoted, is the so-called PM-KAT® by Emitec, where the structure of a metallic monolith is made with flow devices ("shovels") to cause impaction of particles on the surfaces of the monolith (e.g. Jacobs et al., 2006). There are also devices of the latter type in use on vehicles, primarily on heavy-duty engines, and in some rare applications also on light-duty vehicles (e.g. the Smart cdi diesel car). However, in most cases, these types of filtration devices are used for retrofits on both light-duty and heavy-duty vehicles.

Retrofits of particle filters (open or closed) on light-duty vehicles is another area not covered here. The reason is that it is only in one EU member state, i.e. Germany, where retrofit applications have gained any significant market penetration. Economic incentives have spurred this development in Germany. Problems for some of these retrofit devices have been reported by various sources but since this technology has little in common with the technology used in diesel particle filters fitted by car manufacturers, it has also been omitted from the present study. For those interested in these matters, an excellent overview in Norwegian is provided in a study by Hagman (Hagman, 2008).

Early development

The first light-duty vehicle equipped with a DPF was a Mercedes 300D intended for the California market in 1985. Volkswagen also introduced a car with DPF on the market for a short period shortly after Mercedes. These early utilisations of the particle filter technology were soon abandoned, mainly due to problems associated with regeneration of the filter (DieselNet, 2003).

As soot is collected in a DPF, exhaust flow resistance increases and, ultimately soot has to be removed in the so called regeneration which is technically the most troublesome part in the particle filter technology. In May 2000, a Peugeot 607 equipped with a DPF in combination with an oxidizing catalyst mounted upstream the filter was introduced to the market. The car used a DPF and a cerium-based fuel additive that lowers the temperature for soot combustion from 550°C to 450°C. The system includes active regeneration strategies in order to increase the exhaust temperature to the level of soot combustion such as post injection of fuel and increased engine load. The post injection of fuel increase exhaust HC to be oxidized in order to further increase the exhaust temperature and at the same time NO is converted to NO_2 which further contributes to the combustion of soot accumulated in the DPF. Today, almost every diesel car sold in Europe is equipped with a DPF and the full utilisation of the technology is expected very soon. For example, a commitment has been in Germany by the auto manufacturers and importers to have a DPF on every car by 2008.

Some results on first commercial particle filters

The DPF is designed to retain solid or liquid particles and has a low efficiency to hold volatile compounds of which diesel exhaust particles are partly composed. It has been shown that volatiles may form nucleation mode particles downstream the DPF. Matter et al. (1999) observed higher number of particles smaller than 100 nm downstream a DPF than upstream at high engine loads. By use of a thermodenuder it was shown that these particles were, to a large extent, composed of volatile matter and sulphur related species as is shown in **Figure 62**.

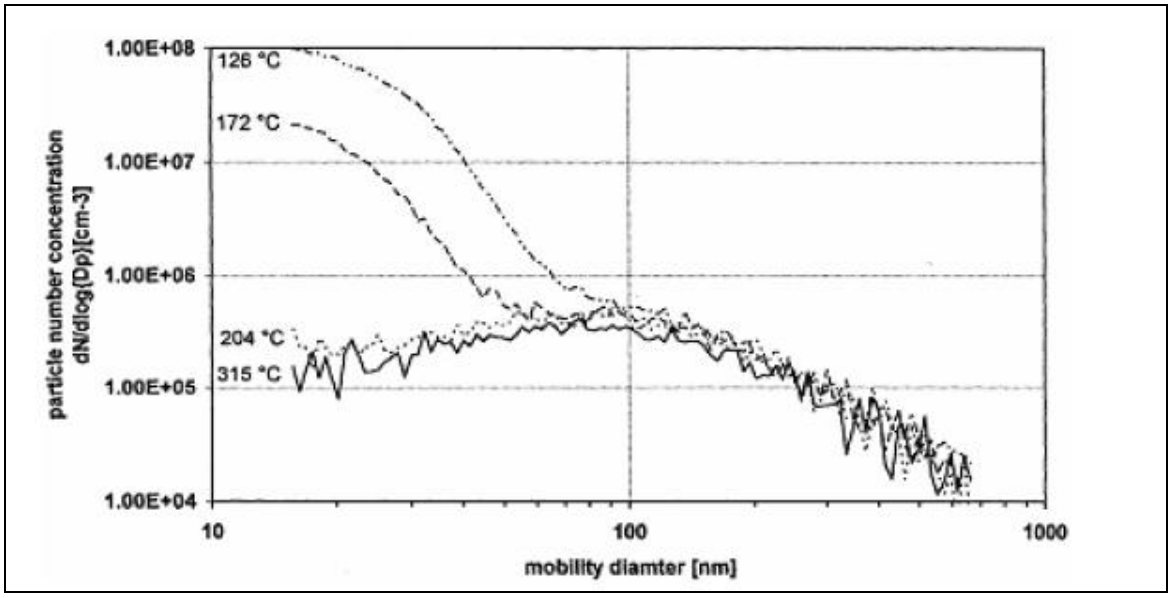

Figure 62. *Size distributions downstream from the particle trap at different temperatures of the thermodenuder (Matter et al. 1999).*

The *relative* contribution to particle emissions from lubrication oil increases as the soot fraction is reduced by the DPF. Ash formation from lubricating oil and ash build-up within the DPF has not shown itself to be a problem in regard to pressure drop over the filter. However, ash components may be released from the DPF at certain modes of operation. In order to reduce particle formation downstream the DPF, ash formation within the DPF, and emission of sulphur, it is desirable to reduce the consumption of lubricating oil. The largest losses of oil have been found from the turbocharger, at low speeds, and from the cylinder, at high speed (Johnson, 2003).

In a study by Liu et al. (2003), nucleation mode particles from particle traps were not observed when using a <10 ppm-S diesel fuel. The authors concluded that besides reducing the number of sulphur related nucleation mode particles, the low sulphur content prevents nucleation and condensation of those volatile organic compounds that typically use sulphur compounds as nuclei downstream the DPF.

Very low particle emissions was observed from a Peugeot 607 equipped with a DPF operated with a 48 ppm-S diesel (de Serves and Westerholm, 2001). Filter measurements from the NEDC cycle showed 1,2 mg/km which is about the same as from a low emitting petrol car, and more than 50 times lower as compared to a conventional diesel car. However, during the regeneration of the DPF, emissions reaching about 7 mg/km were found which render a pooled emission from normal operation and regeneration events lower than 2 mg/km

(pooled: 41 NEDC normal operation and 1 NEDC regeneration). The pooled total number emission of particles was 2 x 10^{12} particles/km. At regeneration, the particle emissions increases sharply in the last part of the NEDC associated with the highest speed of the vehicle and high filter temperatures indicating that regeneration is not effective during the urban mode of the cycle.

Ahlvik, (2002) made observations in line with the study above showing 0,3 mg/km for a newer diesel car with DPF (Peugeot 307) in the NEDC as compared to a modern diesel car with particle emissions of 22 mg/km. The particle number emission was $2x10^{12}$ particles/km for the car with the DPF as compared to $7x10^{14}$ particles/km for the diesel car without a DPF, and a $9x10^{12}$ particles/km average for two modern petrol cars. In the US06 driving cycle (comprising warm start, heavier accelerations and less constant driving as compared to the NEDC) the emissions were lower and the relationship between the two diesels is the same. Drastically increased emissions were, however, encountered for the two petrol cars in the study reaching the same levels as for the diesel car without DPF.

Karlsson (2005) examined the particle number emissions according to the PMP-proposal from a Euro 4 diesel passenger car with DPF in the Artemis highway cycle with and without regeneration. The results are presented in **Table 14**, below, and shows increased particle mass and number emissions during the regeneration. These results are in line with earlier observations but the increased particle number emissions are obviously of "dry" particle origin.

Table 14. *Emissions of two Artemis Highway tests of a Euro 4 diesel-DPF passenger car with and without regeneration (Karlsson, 2005).*

Reg / g/km	CO	HC	NO_X	NO_2	NO_2/NO_X	CO_2	PM	P (#/km)
CAH regeneration	0,45	0,01	0,85	0,33	0,38	0,173	0,0054	1,39E+11
CAH-non-regeneration	0,01	0,00	0,76	0,39	0,51	0,132	0,0012	2,28E+08

Cold start effects were observed for the golden vehicle (diesel DPF) in the ILCE (Andersson et al., 2007) with increased particle number emissions in the first 200 s of the NEDC that is not observed for the same cycle with a hot engine start (**Figure 63**). This observation is in line with Rahman et al. (2007) investigating five different passenger cars for particle number emissions in the NEDC performed in accordance with the PMP method. It was found that all the tested DI diesel DPF vehicles (of which two Euro 4) emitted about 90% of the total particle number emissions within the initial 200 s of the NEDC. Particle emissions decreased drastically once the vehicle and the DPF system attained operating temperature.

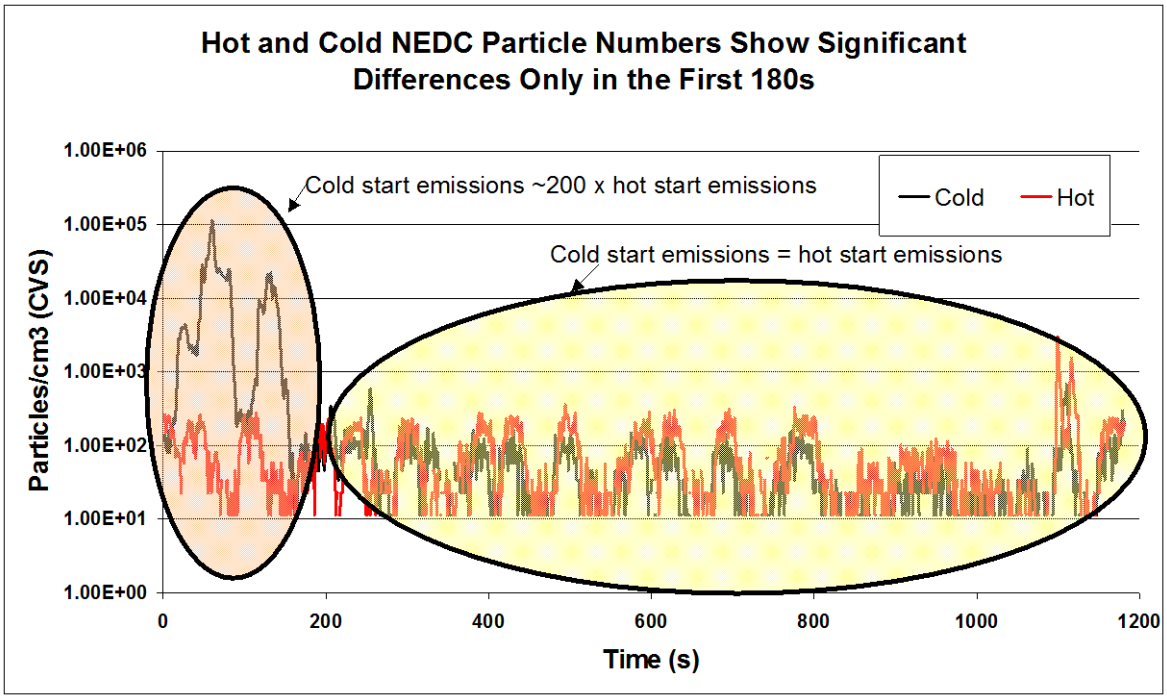

Figure 63. *Particle number emission cold start effect in the NEDC for the ILCE golden vehicle (diesel DPF) (Andersson et al., 2007).*

Similar observations as those reported above have also been reported by Mohr et al. (2003) that measured total particle number emissions from a diesel DPF car with a CPC thermodenuder (TD) set-up in the NEDC using a low sulphur fuel (<10 ppm-S). Increased cold start particle number emissions of possibly "solid" particles were observed since measurements using the TD did not show a significant difference.

In the PMP-interlaboratory correlation exercise (ILCE) (Andersson et al., 2007) different participating laboratories performed measurements of a common diesel DPF car, the "golden vehicle", for particle number and PM. In addition to the golden vehicle the laboratories performed measurements of different cars of there own choice including diesel-DPF, diesel non-DPF, direct injected petrol cars and one MPI-petrol. The results of the ILCE PM measurements are presented in **Figure 64**, below.

From **Figure 64**, the trend previously observed showing comparable PM emissions from petrol and DPF-equipped diesel cars, considerably lower as compared to diesel cars without DPF is confirmed. The direct injected petrol cars show emissions between the diesels with and without DPF.

In **Figure 65**, the total particle number measurements for the same tests as for **Figure 64** using the PMP-method are presented (the proposed Euro 5 emission limit value for diesel cars is $6x10^{11}$ particles/km). A comparison between these two figures shows that the PM measurements differs by approximately 18 times between the non-DPF diesels and the diesel cars with DPF, while the same comparison for the particle number measurement shows a difference of >300 times. Thus, the difference in discriminating power is approximately 20 times greater for the number method as compared to the mass method.

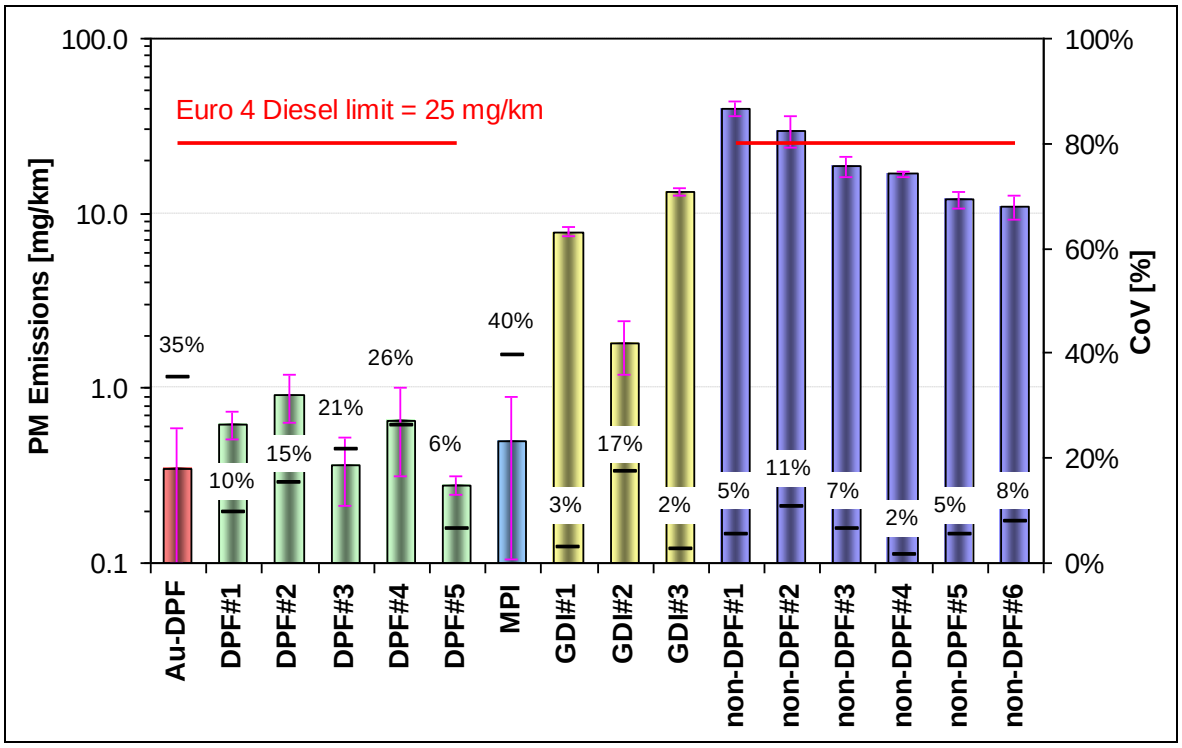

Figure 64. *Particulate mass NEDC emissions and repeatability of all vehicles in the ILCE (Andersson et al., 2007).*

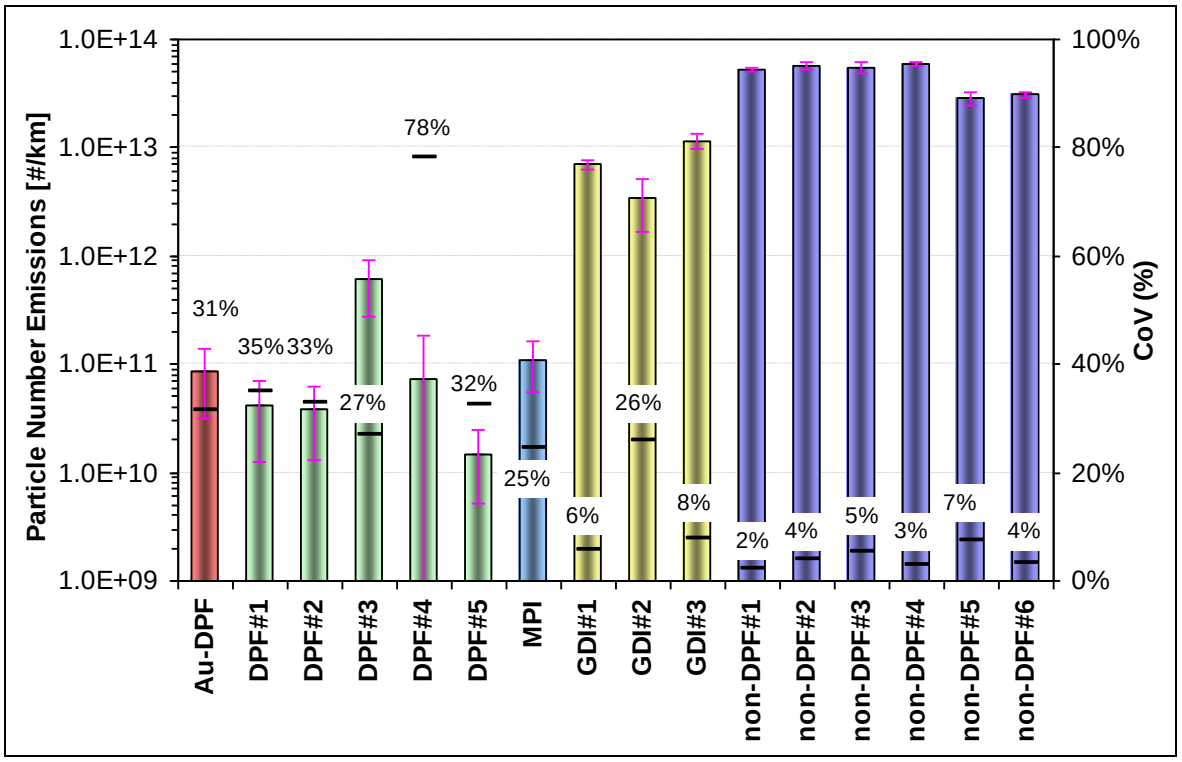

Figure 65. *Total particle number emissions and repeatability data of all vehicles in the ILCE (Andersson et al., 2007).*

As the mean PM and the mean number emissions from all vehicles in the ILCE are compared, a correlation is apparent as reductions in PM are also reflected in the particle number emissions (**Figure 66**). (Note that the unit on the x-axis in **Figure 66** should be mg/km and not g/km.) This correlation holds true for the non-DPF diesels, the direct injected petrol cars, and for a diesel DPF with a high porosity particle filter. However, the correlation is not observed for the low emission vehicles (diesel DPF and the MPI vehicle (petrol)) with carbon emissions virtually eliminated or occurring only at certain events. The emissions for the latter vehicles are very low (<1 mg/km) and are included in the right hand figure of **Figure 66**. From these and similar observations the authors (Ahlvik and de Serves) concluded that parallel measurements of PM and particle number emissions for certification purposes are practically unnecessary since the PM values at the particle number emissions of $5x10^{11}$ particles/km are less than a third of the certification level for Euro 5. Furthermore, the PM measurements at these levels are in a region without any correlation with particle number measurements. The absence of correlation between PM and particle number measurements for low particle emission vehicles such as for diesel DPF has also been shown in other studies (e.g. Bosteels et al., 2006b). For these reasons, only particle number measurements would be needed in the future.

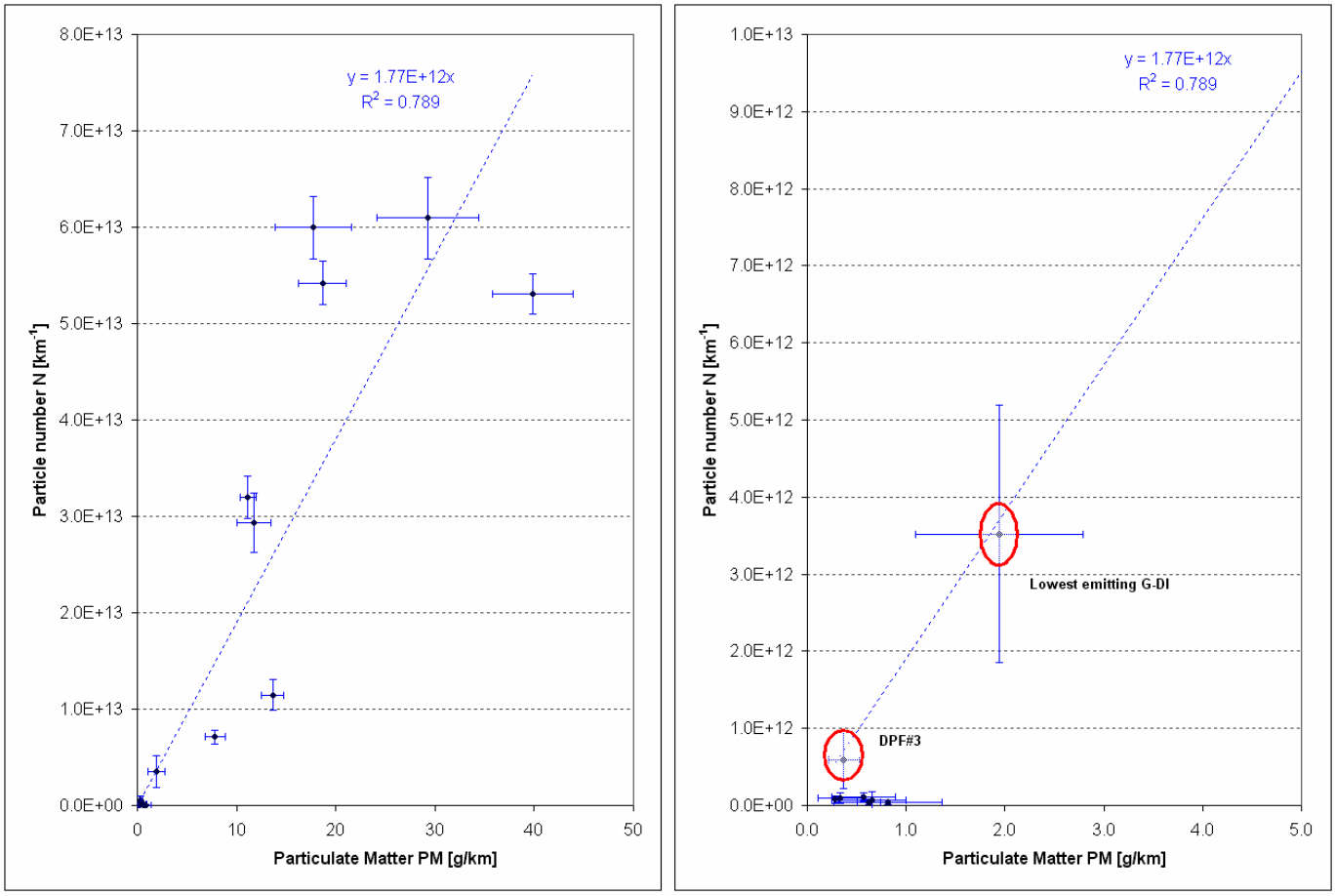

Figure 66. *Correlation of article PM and number emission measurement for all cars in the ILCE presented with different scaling of the axis. Note that the unit on the x-axis should be mg/km and not g/km. (Andersson et al., 2007).*

Bosteels et al. (2006b) examined a diesel-DPF Euro 4 passenger car in the NEDC and the Artemis driving cycles at every 40 000 km up to 160 000 km for emission stability showing good results. Average NEDC PM emissions at 4 000 km were 0,3 mg/km, compared to the Euro 4 PM limit of 25 mg/km, and the total particle number emissions as measured according to the PMP-proposal was 10^9 particles/km. At 160 000 km, the PM emissions were 0,4 mg/km which is within the error bar for the results at 4 000 km. The total particle number emissions were at 160 000 km 10^{10} particles/km. The PM data and the particle number emission data did not show any correlation to each other. The NO_x emissions were 0,167 and 0,204 g/km at 4 000 and 160 000 km respectively and thus below the Euro 4 emission standards.

Bosteels et al. (2006a) concluded that a further benefit of the DPF was seen from particulate and gas phase PAH emissions measurements performed from consecutive filter and PUF (PolyUrethane Foam) sampling. Diesel vehicles without DPF showed PAH emissions of up to 30 μg/km in the particulate phase over the Artemis Extra-Urban cycle; whereas the vehicle with DPF produced particulate-phase PAH emissions of less than 1μg/km over all test cycles. Gas phase PAH emissions were below 10 μg/km for all vehicles. Those for the diesel with DPF were the lowest of the four for all cycles.

A paper that has created significant debate about health effects from diesel engines should be discussed here, although this topic has not been the main focus of this study. The interesting claim by the authors of that study was that the soot emissions from a Euro IV engine exhibit a much higher toxic and inflammatory potential than particles from an old diesel engine operating under black smoke conditions (Sheng Su et al., 2008). The relatively limited information in the paper about the test conditions prompted that the authors were consulted on these issues. Although both the main author and one of the co-authors were contacted, no answer was received. Since the MAN engine used in testing is cited in other publications in the reference list of the paper, another of the co-authors of these papers from the truck manufacturer MAN was contacted (Rothe, 2008). It appears that the soot from the engines was sampled already in 2001. The "Euro IV" engine was a research engine with considerable differences in specification from the later production engines. PM emission in the European ESC cycle was stated to be 50 mg/kWh for this engine, i.e. 2,5 times higher than the limit in the Euro IV regulation. Whereas the production engines used an open type of particle filter (denoted PM-KAT® by MAN) for PM reduction, this engine did not use any form of aftertreatment. The "black smoke condition" (BS) referred to a manipulation of another engine by reducing injection pressure and throttling the air supply to significantly increase the soot production. The soot level of this engine was 200-600 mg/kWh. Compared to a "real" Euro IV engine, which would have to be certified at a PM level as low as 10 mg/kWh to fulfil the limit of 20 mg/kW with some engineering margin, the relative difference in soot level could be up to a factor of 60 higher for the BS engine. Further differences in test conditions were that the Euro IV engine was run in endless ETC tests for 24 hours to collect soot, whereas the BS engine was run at steady-state at part load (400 Nm) at 1125 r/min. It is the opinion of the authors of the present report that none of the engines could be representative of a production engine. Furthermore, there is a considerable difference in testing conditions (steady-state vs. transient test cycles).

In some of the biological tests discussed in the mentioned paper, the relative cytotoxicity of the soot from the Euro IV engine was up to a factor of two more "potent" than the soot from the BS engine on mass basis. However, in an evaluation of the total toxicity one should also consider the difference in mass emissions between the two engines. Consider-

ing that the difference in mass emissions between the BS engine and a range of two fictive engines comprising the prototype Euro IV engines and a "real" Euro IV engine would be in the order of 10 to 60, one could argue that the BS engine has a total toxicity some 5 to 30 times higher than the "modern" engine. With this background, conclusions quite different from those of the authors of the paper might be drawn. However, the conclusion of the authors of the paper that the development of particle filter technology must be directed toward the removal of ultrasmall particles might be more generally accepted.

The Continuous Regeneration Trap

The Continuous Regeneration Trap (CRT) has, so far, mostly been used as retrofit device on heavy-duty vehicles. Thus, it has not been integrated to the electronic control system but rather used as a system with passive filter regeneration. When used in OEM (original equipment manufacturer) applications, it is likely that the CRT will be integrated in the control system and presumably, some active regeneration will be applied as well.

The CRT comprises a ceramic particle trap mounted downstream an oxidation catalyst in which NO is converted to NO_2. Nitrogen dioxide oxidizes soot in the particle trap at temperatures as low as 250°C which is sufficient for HDV applications. However, the CRT system requires diesel fuel with sulphur concentrations lower than 50 ppm. A second drawback of the system is a higher exhaust NO_2 to NO ratio. The "CRT effect" is also used to some extent on other particle trap systems that mainly rely on active regeneration, for example those used on passenger cars.

Holmén and Ayala (2002) operated a bus equipped with a CRT filter and measured particle emissions with a SMPS (range 6-237 nm) from both a CVS tunnel and by use of a minidiluter system. They observed emissions reduced by a factor of about 30 using the CRT as compared to emissions without CRT filter ($2{,}2x10^5$ and $6{,}2x10^6$ particles/km in the CVS). Sudden nucleation events with particles smaller than 10 nm were however observed in the CVS even exceeding the emissions encountered without CRT filter. These nucleation events were attributed to dilution tunnel effects promoting nucleation since they were not observed at higher dilution ratios when using the minidiluter system.

In a study by Thompson et al. (2004), different heavy-duty engines of different certification levels in different combinations of fuels and particulate traps were examined for particle emissions. It was found that diesel engines equipped with particulate traps produced very low particulate mass emissions, low numbers of carbonaceous particles and low total numbers of particles when operating on low sulphur fuels. In short, the regulated filter method in the ETC showed PM-emissions in the 0,07-0,12 g/kWh range for Euro2 and Euro3 engines operating on different fuels while the engines equipped with CRT filters showed PM-emissions in the 0,005-0,030 g/kWh range for the same fuels.

Ahlvik and Smedler (2000) examined particle emissions from a HDV Volvo FL611 (model year 1996: Euro 2) either without exhaust after-treatment, with an oxidation catalyst, or with a CRT filter. The FIGE-cycle, which is a time versus speed cycle for chassis HDV-test resembling the ETC engine test cycle, was used. **Figure 67** shows that the oxidation catalyst has a low impact on particle number emissions since particles smaller than 100 nm are largely unaffected. The CRT filter shows a reduction in particle number emissions by approximately 99% over all particle sizes measured. Results in good agreement with this study have been presented by Eastlake (Eastlake, 2000) showing a minor reduction in particle number using a catalyst while particle mass was reduced by 25 to 30% as organic

compounds are removed. The CRT filter showed a reduction by more than 95% reduction in particle number over the size range measured.

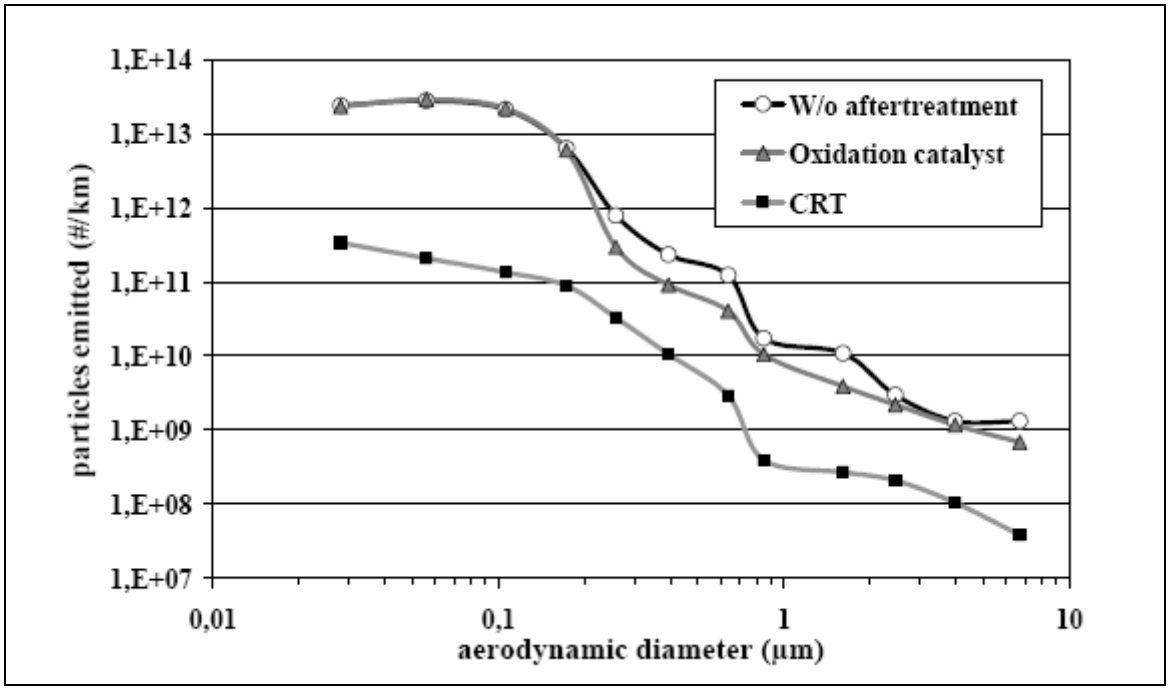

Figure 67. *A heavy-duty diesel vehicle in the FIGE cycle using different exhaust after-treatment (data from Ahlvik and Smedler (2000)).*

However, the operation of the vehicle affects the emissions as was observed in the ECE R49 test (Ahlvik and Smedler, 2000). Extremely low particle number emissions were observed when using the CRT filter as compared to the emissions encountered without after-treatment or with an oxidation catalyst for most of the modes in the cycle. However, during the full load modes 6 and 8, a drastic increase in the emissions from the CRT filter was observed largely exceeding the emissions with catalyst or without after-treatment. A plausible explanation to this observation is release of accumulated matter such as sulphate and ash due to the high filter temperatures associated with these modes. This effect could be enhanced if the washcoat of the catalyst is storing sulphates for a long period of time, which appears to be the case on the CRT filter.

Future development of the particle filter technology

An excellent yearly overview of the progress in the area of DPF and NO_x catalyst is made by Johnson at Corning (Johnson, 2003, 2006, 2007 and 2008). Initially, silicon carbide (SiC) was the only filter material used on passenger cars, while most of the filters used on heavy-duty trucks have been made from cordierite. SiC is more expensive than cordierite, which is also used in oxidation catalysts, and has such high expansion coefficient that it must be sectioned to many smaller monoliths and "glued" together using ceramic cement. Instead, cordierite can be extruded in one single monolith. On the other hand, the physical properties of SiC should provide conditions for better durability than cordierite. So far, Toyota is the only car manufacturer that has used cordierite in production. This also has a NO_x reducing catalyst integrated in the DPF (see also the section on NO_x catalysts below). Limited production of this system started already in 2003 and ramped up the year after.

By the end of 2005, VW introduced a DPF with a monolith made of aluminium titanate (AT) manufactured by Corning as a new filter material on the market (Volkswagen, 2005). As cordierite, this material can be extruded in one monolith and does not have to be built up by sections with ceramic "cement" in between. Aluminium titanate appears to have several advantages such as, e.g. lower back pressure, higher ash capacity and apparently, also lower cost than SiC monoliths.

Johnson (2006) describes aluminium titanate (AT) as a new filter material besides SiC that is since then being used in a high volume series production application. The back pressure advantage of AT DPFs is lower due to tight pore size distribution and cell geometry, specifically, using an asymmetric cell structure (inlet cells larger than exit) and minor changes in cell density and wall thickness. Even though the filter has low thermal conductivity, the high heat capacity and physical properties enable an unsegmented design with maximum soot loadings of about 8 g/L. This compares with cordierite in the 4 g/L range and SiC in the 10-15 g/L range.

An interesting feature of AT filters is that the initial filtration rate is higher than for comparable SiC filters (Ingram-Ogunwum, 2007). This is shown in **Figure 68** – not with the sole purpose of demonstrating the favourable performance of AT filters – but also to show how the so-called filter cake, i.e. the soot collected on the particle filter affects the filtration efficiency.

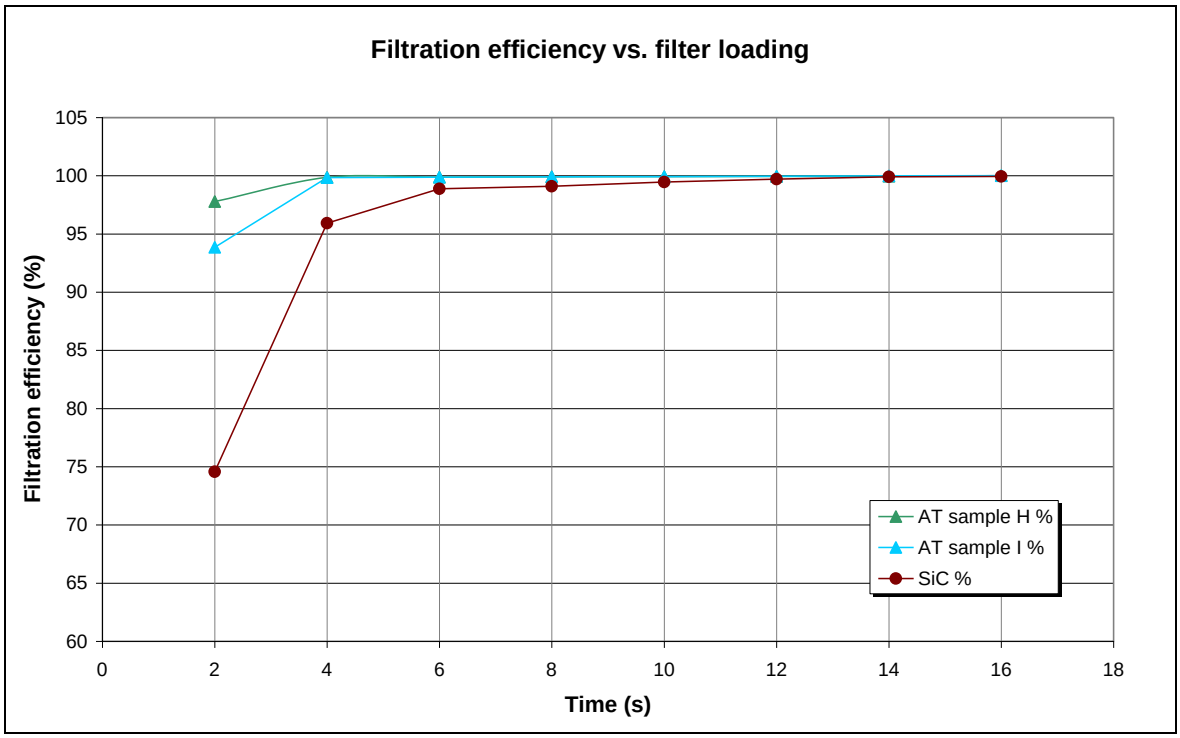

Figure 68. *Initial filtration efficiency for AT DPFs compared to SiC (Adapted from Ingram-Ogunwumi, 2007).*

The filter efficiency has been calculated from filter smoke number measurements (FSN). The measurement time for this method is 2 minutes. As can be seen in **Figure 68**, the initial filtration efficiency of a SiC filter is about 75 % but it increases rapidly in a couple of minutes to reach almost 100 % within less than 15 minutes. In comparison to SiC, the two

samples of AT filters exhibit much higher initial filtration efficiency and also reach close to 100 % much faster. The larger porosity and larger pore size of SiC is the explanation for the observed differences in filtration efficiency.

As indicated above, porosity and pore size are two important factors that affect the filtration efficiency. To illustrate that phenomenon, a diagram from a study by Mizutani T., et al., is shown in **Figure 69** (Mizutani T., et al., 2007).

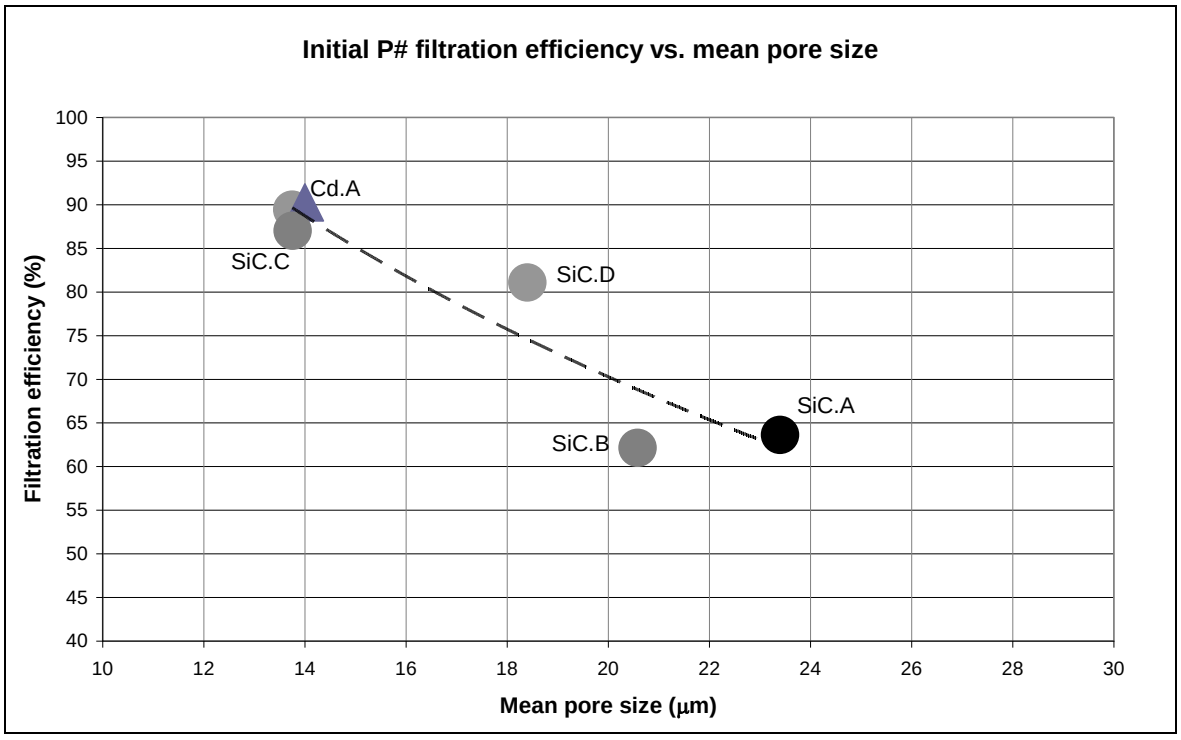

Figure 69. *Initial filtration efficiency for total particle number vs. mean pore size (adapted from Mizutani et al, 2007)*

The results in **Figure 69** were generated by testing both SiC (denotations SiC.X) and cordierite (denotation Cd.A.) type of filters. With increasing mean pore size, the initial filtration efficiency (for total particle number this time) drops. Since there is always a trade-off between initial filtration efficiency and back pressure, the challenge is to find filter types with *both* high filtration efficiency and low back pressure.

Due to the improvements in material properties and manufacture of cordierite monoliths and, in particular, the better control of the regeneration event, it now appears likely that cordierite soon will be commercialised also as a filter material for DPFs in passenger cars. The volume of a DPF is roughly 50% more than the cylinder volume of the engine. For a 2 litre engine that would give a DPF of 3 litres, or about the size of a three-way catalyst (TWC) for a petrol car. The manufacturing cost of a DPF monolith is approximately the same as for a TWC monolith if the material is the same (cordierite). The precious metal loading will also be similar, i.e. implying that the total cost of the aftertreatment would be similar. Thus, the often cited – and more or less generally accepted – cost penalty for diesel engine aftertreatment in comparison to petrol engine aftertreatment could be challenged. The remaining issue would be to integrate NO_x aftertreatment in the DPF. If that could be done, no incremental cost would be associated with NO_x reduction either. In practice, that

is what Toyota has been claiming to be a feature of their D-CAT combined NO_X catalyst and DPF aftertreatment solution.

The discussion and conclusions above were made in the report in 2007 and by looking at the results during the last year all these statements can be corroborated. For example, the first application of cordierite DPFs on light-duty vehicles, besides the combined particulate and NO_X (DPNR) filter already deployed by Toyota in their D-Cat models, has just recently been announced by Bosch (Becker et al., 2008). The key technology does not appear to be advancements in DPF technology per se, but the regeneration control strategy. The Advanced Control regeneration strategy (DPF-AC) has limited the temperature peaks inside the monolith to levels that can be tolerated by cordierite. The control of air/fuel ratio, accomplished by the lambda sensor in the system enables this regeneration strategy.

In summary, improvements of filter materials and filter types will improve both performance and cost of DPFs in the future. Therefore, it appears that the cost penalty for a diesel aftertreatment system with a DPF will diminish in the future. This conclusion would be in conflict with many statements in the literature.

4.7.3 NO_X reducing catalyst

Although NO_x emissions were was a topic of somewhat less focus than particle emissions in this study, it is of interest to discuss the options to fulfil Euro 6 emission limits and the even tougher emission limits enforced in 2010 in the USA and in California. In 2002, the first publication by EPA reported from testing on the European field test version of the Toyota Avensis equipped with the so-called DPNR (Diesel Particulate NO_x Reduction system) catalyst (Bunker et al., 2007). The production version of this combined NO_x catalyst and particle filter was later denoted D-CAT.

In 2004, a new study included four other cars besides the Toyota Avensis (McDonald, 2004). All the other cars were prototypes at different state of development and, in some cases; EPA did not disclose much information about the technology used due to propriety issues. In **Figure 70**, the most interesting graph showing data in the US FTP-75 driving cycle from the cited paper has been digitized by these authors and converted to SI units (from g/mile to g/km). All the cars were equipped with NO_x reducing catalysts and DPFs.

According to the US federal emission legislation, a car can be certified according to several "bins". The fleet average for cars sold must be equal to bin 5. Thus, bin 5 is the emission target in vehicle development. As can be seen in **Figure 70**, some of the test points are well within the bin 5 limit or at the limit. The problem of ageing of the NO_x catalyst is visible for the Mercedes prototype car after 60 000 miles (almost 100 000 km). However, one of the cars (vehicle "E") had much lower NO_x level after 50 000 miles (80 000). This was the most significant finding in the study.

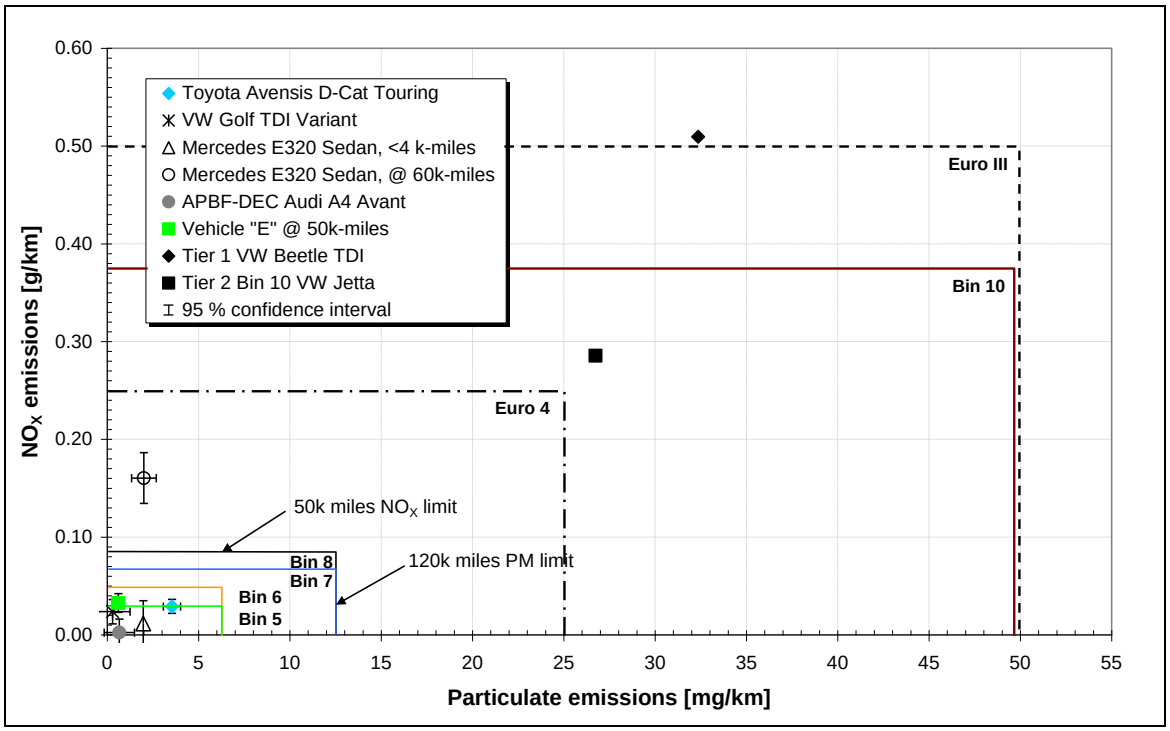

***Figure 70**. PM and NO_X emissions in the US FTP-75 driving cycle.*

One of the latest publications in this field looks at combinations of NO_x reducing catalysts and particle filters (Pischinger, 2007). Lean NO_x traps (adsorbers), SCR catalysts and particle filters have been investigated, partly through simulations of several combinations of these technologies. Both technologies have their pros and cons. The authors concluded that SCR is the preferred solution for heavier light-duty vehicle applications (e.g. SUV) targeting the US bin 5 emission level. The lean NO_x trap is an alternative option for lighter vehicles. Long-term stability remains a challenge for the NO_x trap, while packaging and low temperature activity are issues for the SCR technology.

The emission limits in the USA (federal) and California are the toughest emission limits regarding NO_x control. These limits are introduced gradually during the period from 2007 to 2010. In view of these challenges and that the Euro 6 limits are considered strict by the auto manufacturers, it seems striking that several auto manufacturers have introduced or announced that they will introduce diesel cars on the US market in 2008 or early 2009. These cars should fulfil the US bin 5 emission limits. These manufacturers include (at least) BMW, Mercedes-Benz, Honda and Volkswagen. Until 2008, Mercedes and Volkswagen were the only manufacturers who were represented with diesel cars on the US market but a couple of other manufacturers have now (October 2008) announced the introduction of more cars models. When this report was written in October 2008, three car models from BMW, Mercedes and VW respectively that are using NO_X aftertreatment for meeting Euro 6 have been introduced in Europe. One remaining issue that has to be handled is the availability of ultra-low sulphur diesel fuel on the European market. This hurdle was overcome (15 ppm-S diesel) by mid 2006 in the USA and it could be hypothesised that the car manufacturers have hesitated somewhat before they could introduce the NO_x reducing catalysts that depend on the availability of practically sulphur free diesel fuel (10 ppm-S diesel). By January 1, 2005, lower than 10 ppm-S fuel had to be made available on balanced geographical basis in the member states. By 2009, all diesel fuel must meet this sul-

phur limit. The apparent risk of misfuelling with higher sulphur fuel during the period when both fuel qualities are marketed in parallel could be one reason for the hesitation in introducing NO_x reducing catalysts on the market. This illustrates that the sulphur content in diesel fuel is the most important fuel parameter for the introduction of NO_X reducing catalytic technology in diesel vehicles.

Further development of NO_X reducing catalyst during the last year

In the presence of excess oxygen, i.e. in lean exhaust ($\lambda \geq 1$), the *reduction* of NO and NO_2 to N_2 is a very slow process, although the equilibrium for the temperatures in the catalyst would favour such a reaction. The excess oxygen does not facilitate the reduction of NO_X in a similar way as in the co-called three-way catalyst (TWC) as used in petrol cars. So far, catalyst development of direct reduction of NO_X has not been successful. Today, there are basically three different NO_X aftertreatment technologies under development for diesel engines. These are:

- Selective reduction catalyst with hydrocarbons as reducing agent (HC-SCR). This type of catalyst is also often denoted a "lean-NO_X" catalyst or "DeNO_X" catalyst.
- Selective reduction catalyst with ammonia (or, for practical reasons, urea from which ammonia is produced by hydrolysis) as reducing agent (urea-SCR)
- NO_X storage catalyst

Oxidation catalysts for diesel engines often incorporate some of the properties of the HC-SCR catalyst and can reduce NO_X emissions by a moderate level of some 10 %. By using an "active" system with increased HC levels and potentially, a pre-catalyst (before the HC-SCR catalyst) that can create more "active" species than pure fuel hydrocarbons, the conversion rate can be increased. The use of plasma assist (non-thermal plasma) can also improve the NO_X conversion. Progress has also been made of the formulation of the HC-SCR catalyst. Nevertheless, it seems to be difficult to achieve the high conversion rates of 70 to 90 % desired for meeting the US 2010 and Euro 6 emission limits with this type of catalyst. The development still continues but it seems as the focus have shifted towards other alternatives. It should also be noted that several unwanted, and presently unregulated, emission compounds can be produced in a HC-SCR catalyst, such as, e.g. nitrous oxide (N_2O), which is a very potent climate gas. In addition, an elevated level of HC emissions is a problem often associated with these types of catalysts.

Probably the most interesting catalyst for the moment is the urea-SCR, or ammonia-SCR (NH_3-SCR) catalyst. By using ammonia, preferably produced from a urea/water solution by hydrolysis, much higher conversion rates of NO_X can be achieved than with the HC-SCR catalyst. This type of catalyst has been used in production on heavy-duty vehicles for a couple of years now. The urea solution is distributed under the trade name Adblue®. Urea-SCR is also an option for passenger car diesel engines and has been introduced in production recently, mainly on cars sold in the USA but also in Europe. The objective is to meet US 2010 and Euro 6 NO_X levels.

The second most interesting type of catalyst, after the urea-SCR catalyst, is the NO_X storage catalyst. It is sometimes also referred to as a NO_X trap. In this catalyst, NO_X is stored in alkaline oxides such as, e.g. barium oxide (BaO). In this process, NO is first oxidised to NO_2 for better and greater NO_X storage. The stored NO_X is converted to N_2 during short pulses of fuel enrichment when the air/fuel ratio is slightly below stoichiometric. This re-

duction is similar to the working principle of the so-called three-way catalyst for otto engines. NO_X storage catalysts were first introduced on petrol-fuelled cars and the catalyst technology is very similar to the one used for diesel engines. One car manufacturer who is extensively using this technology on new petrol-fuelled cars is BMW; i.e. practically all 4 and 6-cylinder petrol engines sold in Europe by BMW are equipped with this technology. These engines also use *direct injection* of petrol utilising a second generation direct injection system. On diesel engines, Toyota was the first manufacturer to introduce the NO_X storage catalyst. During last year, Mercedes introduced this technology in their come-back of diesel cars on the US market with the model E 320. Other manufacturers, such as, e.g. Audi, BMW, Honda and VW have also announced the introduction of this technology during 2008 or 2009. The NO_X storage catalyst is sensitive to poisoning by sulphur – the NO_X storage materials also store SO_X – and the lack of virtually sulphur-free diesel fuel (<10 ppm) on the European and US markets until recently has probably hampered the introduction. Even with very low sulphur content, the NO_X catalyst has to be regenerated from time to time to avoid sulphur poisoning. Another problem with the NO_X storage catalyst has been the limited durability, a problem that is also linked to sulphur poisoning and sulphur regeneration, which require high temperatures. In both the mentioned problem areas, considerable improvements have been made in recent years.

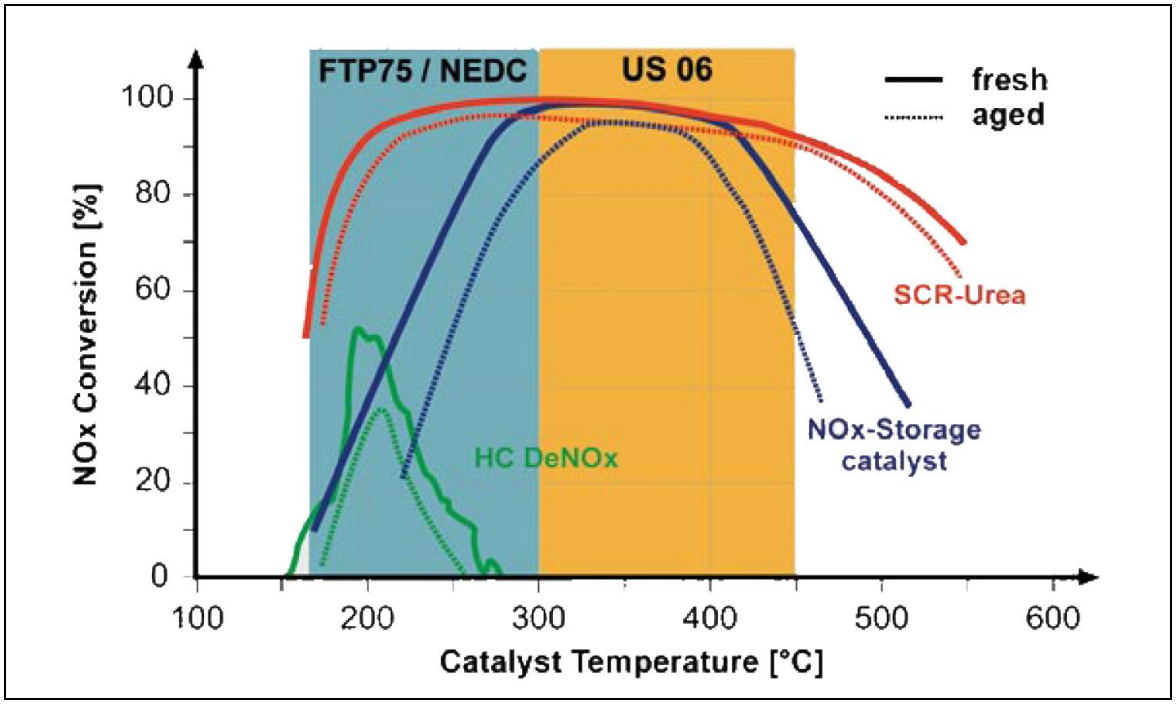

Figure 71. *Conversion rate of various NO_X aftertreatment catalysts (adapted from Shommers et al., 2008).*

Since both SCR and NO_X storage catalysts are viable options for meeting future emission limits, it is of interest to compare both solutions. Various such comparisons have been made in the past. In **Figure 71**, the NO_X reducing efficiency for both these technologies and, in addition, the HC based $DeNO_X$ catalyst (HC-SCR) have been compared by Shommers et al. (2008) at Daimler. Two interesting features can be seen. First, the temperature window is much greater for urea SCR in comparison to the NO_X storage catalyst. Second, the durability (comparing fresh and aged results) of the urea SCR catalyst is also much

better. In addition, it could be noted that the $DeNO_X$ catalyst has its peak efficiency at relatively low temperatures but the maximum conversion efficiency is much lower than for the two other technologies. This also explains why the focus on this technology has been lower than the focus on the two other options.

Since the long-term durability has been a problem for the NO_X storage catalyst, it is of interest to note that there has been considerable improvement in this area during the last couple of years. A recent paper from Rohr et al. (2008) from Umicore shows the improvement in catalyst durability due to decreased temperature requirement for catalyst regeneration **Figure 72** shows that the catalyst "A", which can be regenerated at 650°C instead of 750°C for the two other catalysts ("B" and "C"), has much better durability than the latter ones.

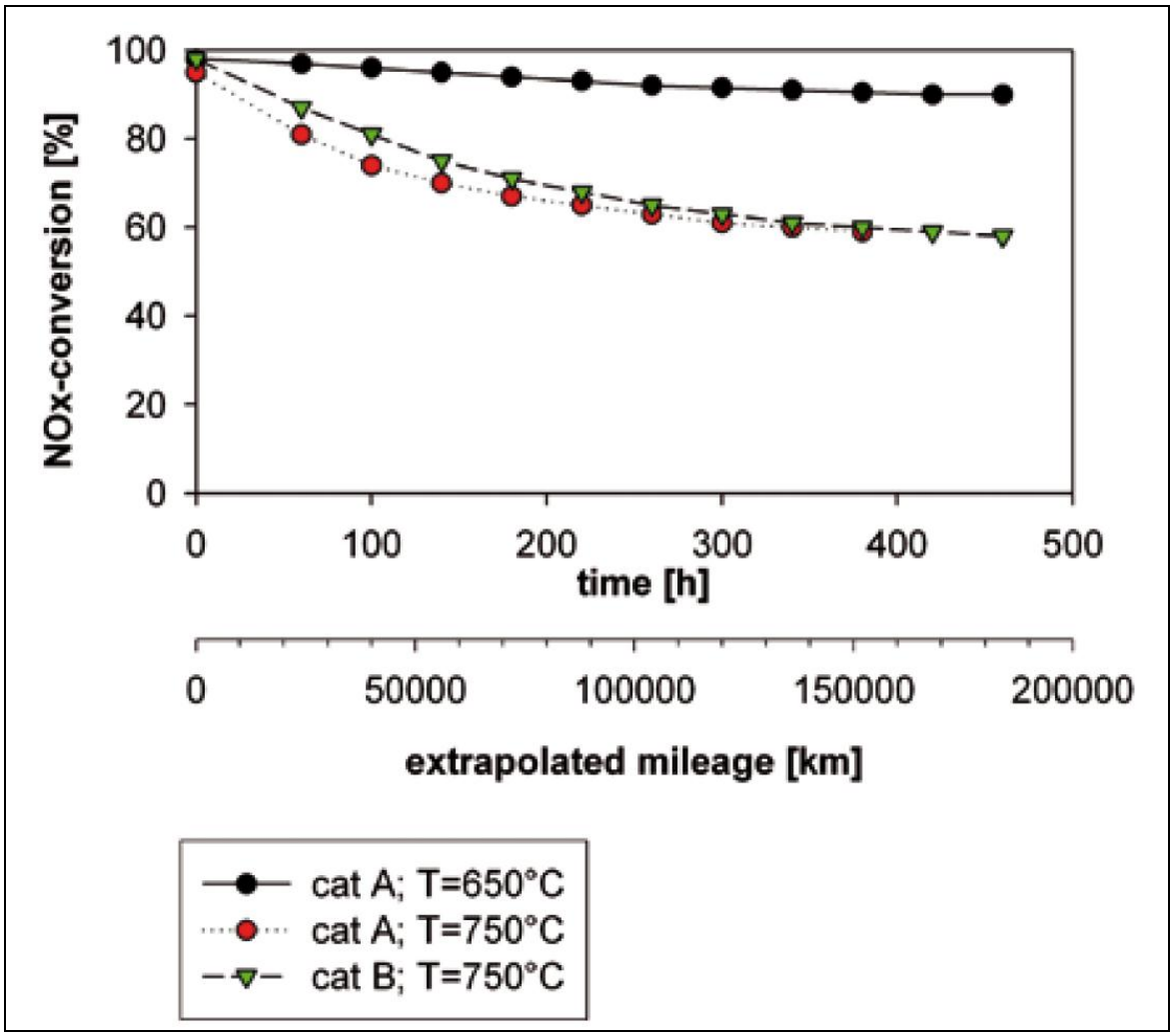

Figure 72. *NO_X conversion vs. mileage (adapted from Rohr et al., 2008).*

As mentioned above, the temperature window for the NO_X adsorber catalyst has been somewhat problematic for the application in light-duty vehicles, where the exhaust temperatures usually are very low. Satoh et al. (2008) from Honda found that a ceria based catalyst had much better low-temperature performance than the conventional alkaline based catalysts. **Figure 73** shows that the exhaust temperature for peak NO_X reduction is at

250°C for the new catalyst whereas the conventional alkaline catalyst has its highest efficiency at 400°C.

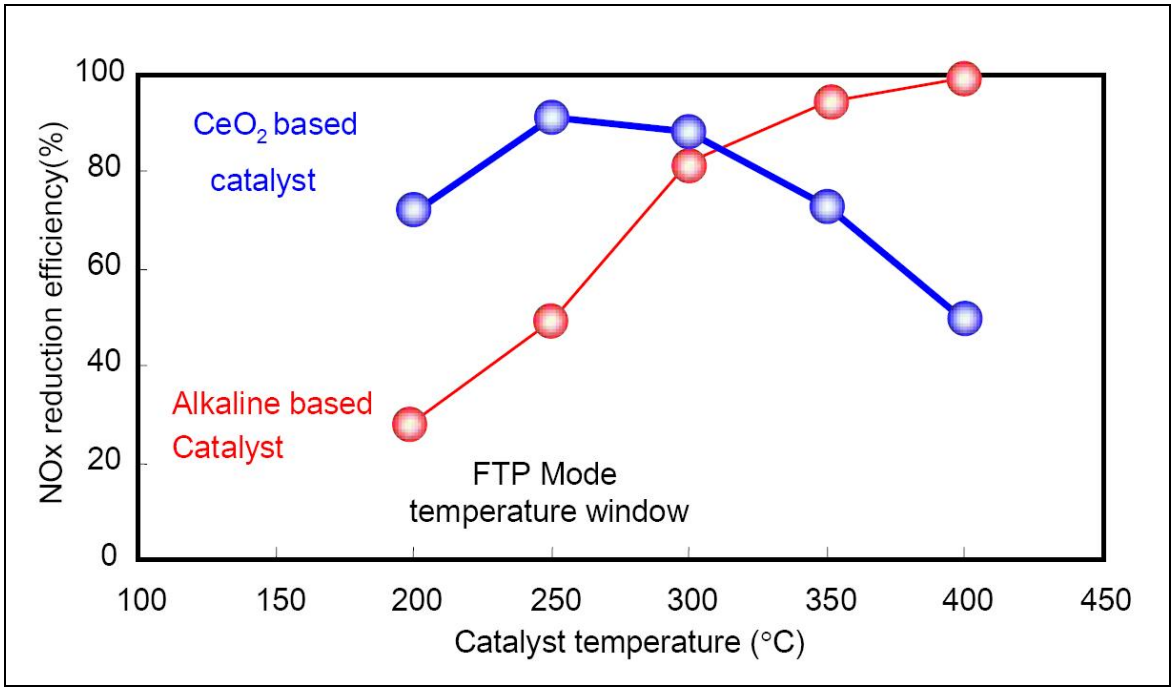

Figure 73. Temperature window for NO_X reduction efficiency (adapted from Satoh et al., 2008).

This catalyst is kind of a combination of both NO_X storage and SCR functions. Three important characteristics for this catalyst can be mentioned:

- High reduction efficiency in a low temperature range
- Sulphur regeneration at lower temperatures than conventional NO_X storage catalysts
- Lower frequency of the rich pulse for regeneration improves the fuel economy.

The catalyst has two layers. In the top layer NH_3 is adsorbed during rich conditions, which provides for a NH_3-SCR reaction function in lean conditions. NO_X adsorption is performed in the bottom layer of the catalyst during lean conditions, and gives NH_3 formation in rich conditions. In the first step, NO_X is adsorbed on ceria-based materials in lean conditions. NO is oxidized to NO_2 on the catalyst, resulting in easy and greater adsorption on the materials. In the second step, the adsorbed NO_X is converted into NH_3 in rich conditions and the NH_3 thus formed is adsorbed on solid acids. Hydrogen (H_2), is necessary for NH_3 formation and is provided from the exhaust gas or is formed in the water gas shift reaction using CO and H_2O in the exhaust gas. In the final step — the subsequent lean operation — the adsorbed NH_3 reacts with gaseous NO_X and oxygen, and NO_X is converted into N_2. In this step, NO_X is adsorbed in parallel.

The NO_X reduction efficiency of the new catalyst was also stable at low temperatures in ten periodic operations, as shown in **Figure 74**, where an alkaline catalyst is the baseline for comparison.

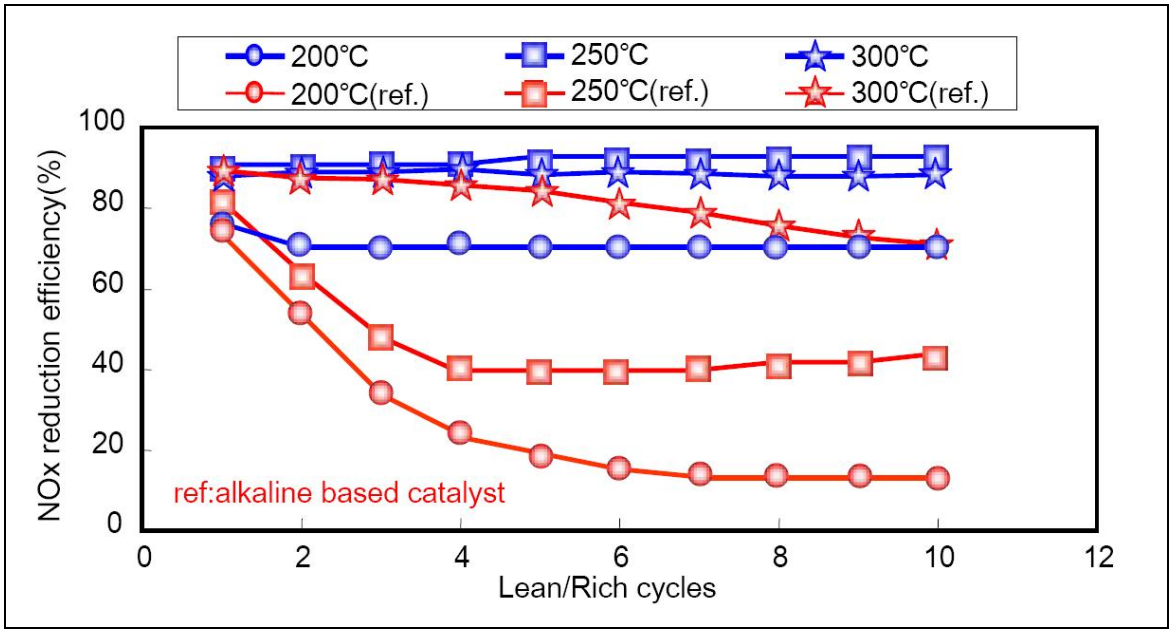

Figure 74. NO_X reduction at different regeneration temperatures (adapted from Satoh et al., 2008).

Additional advantage of the new catalyst was that the sulphur regeneration of the catalyst could be performed at lower temperature than the conventional catalyst, as ***Figure 75*** shows.

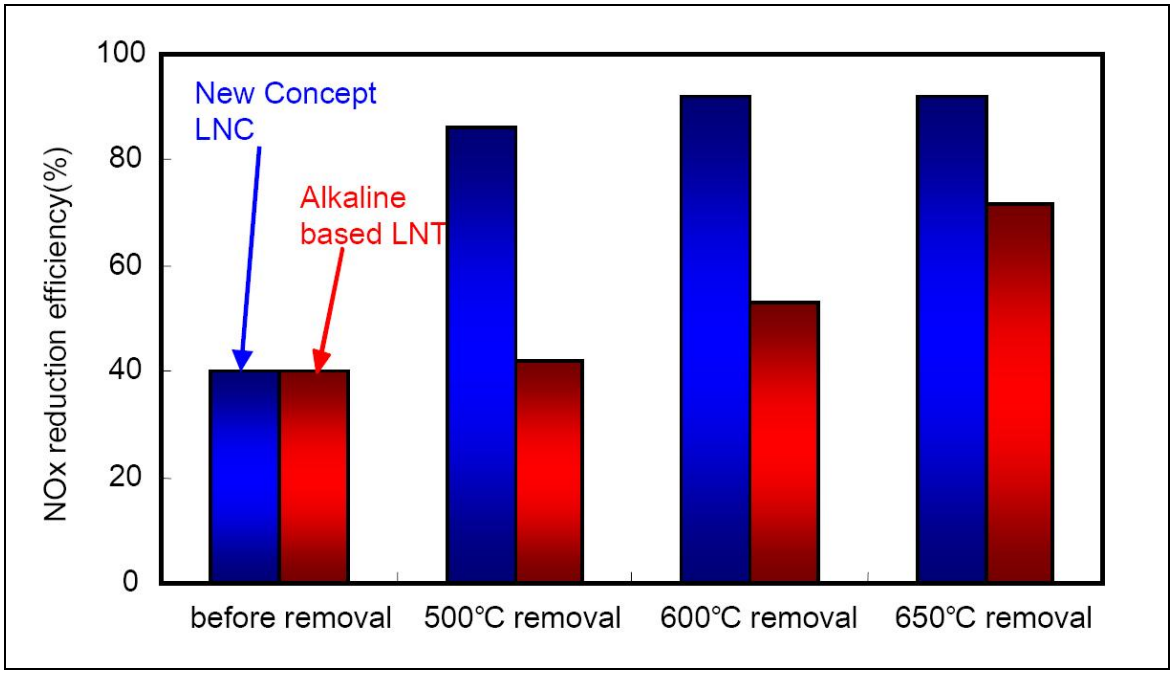

Figure 75. *Regeneration of NO_X catalyst deactivated by SO_X (adapted from Satoh et al., 2008).*

Since Toyota was the first manufacturer to introduce NO_X reducing catalysts for diesel engines, it is appropriate to end this section with a discussion about the recent progress of this type of catalyst. By various improvements, the NO_X reduction of this catalyst has been in-

creased from about 40 % to over 70 % at aged condition in the NEDC test cycle (Ohashi et al., 2008). NO_X storage has been improved by avoiding that small particles of precious (catalytically active) material grow into larger particles, a phenomenon called sintering. Ceria (CeO_2) as catalyst support instead of alumina (Al_2O_3) gives less sintering of platinum (Pt). Improvements in temperature distribution during catalyst desulphurisation have reduced sulphur poisoning. A combination of both in-cylinder injection and injection in the exhaust port (EPI) improves NO_X conversion at low exhaust temperatures without negatively affecting fuel economy, in comparison to EPI only. Better control of multiple injections with advanced common rail injection systems has enabled this improvement.

4.7.4 Direct injection petrol engines

Development of combustion engines with improved fuel efficiency has been stimulated for economical and environmental reasons. Direct injection petrol engines have a potential for significantly lower fuel consumption as compared to conventional petrol engines (numbers of 20 to 28% lower fuel consumption have been mentioned by manufacturers). In contrast to a conventional petrol spark ignited engine, a direct injection petrol engine may be considered as a lean-burn engine since it is possible to run it at higher than stoichiometric air/fuel ratios. The fuel is not homogeneously mixed with air but the fuel is injected in such a way that the mixture is richer in vicinity to the spark plug while the over-all mixture is lean. Thus, the direct injected technique can operate under considerably leaner conditions than is possible with an engine using homogenous air/fuel ratio. At high load, the engine shifts to homogenous charge combustion to maximize air use and to avoid soot formation. The largest gain in fuel economy is thus possible at part load and at idling since the idling speed can be significantly reduced with this technology. However, as in a diesel engine, the stratified combustion results in increased soot formation which is a major drawback of the technique.

The lean and stratified operation at low and moderate load is associated with significantly higher particle emissions whereas the shift to homogenous charged combustion in high load modes is associated with the lowest emissions. Mohr et al. (2000) measured particle emissions from three different petrol passenger cars representing two conventional homogeneous charged and one direct injection engine technology. They found that as the conventional petrol cars increased their particle number emissions at higher speeds the opposite was found for the direct injection petrol car with highest and lowest emissions at 80 and 120 km/h respectively. The particle peak emission was, however, largely unchanged at 70 to 100 nm.

Hall and Dickens (2000b) observed nearly twice as many particles for the stratified mode as compared to the rich mode as higher speeds. A similar observation was made by Graskow et al. (1999) who examined a direct injected model year 1998 Mitsubishi Carisma 1,8L for particle emissions at 5 steady-state speeds from 13 km/h to 90 km/h using a constant dilution ratio at 15. All speeds except the 13 km/h showed a broad monomodal particle distribution with peak emission in between 70 to 100 nm. The highest number particle concentrations were found at 70 km/h ($2{,}8 \times 10^8$ particles/cm^3) and decreasing for lower speeds. The lowest concentrations were found at 90 km/h ($9{,}3 \times 10^7$ particles/cm^3) which reflects the stoichiometric homogeneous charge engine operation at this speed while the lower speeds are operated at lean stratified charge combustion. The 13 km/h speed particle size distribution was different from the others as it was bimodal with high particle concentrations in the nucleation mode but the lowest in the accumulation mode.

Maricq et al. (1999) examined particle emissions from the same type of vehicle as Graskow et al. (1999). In the homogenous mode, particulate number is relatively insensitive to spark timing. However, in stratified mode, the particulate emissions increase 30 to 100 times.

4.8 Particle and NO_X emissions, trends

Early on in this work, it was realised that it would be of great value to show the trend of improvement emission reductions in the past and also to make a forecast for the next coming years. Since the main focus in this study has been on diesel-fuelled passenger cars, NO_X and particle emissions has been of main interest, since these emission components are the main "problem" for these vehicles.

Regarding the task of establishing a trendline for particle mass, it was anticipated that some publication would be available that could show such data. Eventually, this was not the case but some interesting findings from the literature have been included anyway. Simulation models (e.g. COPERT and ARTEMIS) for calculating real-life emissions from car fleets have been available for considerable time. However, the forecast in these models is either negligible or loosely based on the projection of future emission limits. It was beyond the scope in this project to develop an "own" model to fulfil the goal of compiling such data. However, it was still of interest to be able to present such data. Therefore, a "simpler" model based on previous assessments by the authors was used for historic data and as a base for the projection made for the future (Ahlvik, et al., 1999, Ahlvik et al. 2001).

4.8.1 Findings from the European "Particulates" project

As mentioned above, no study has been found in the literature survey that has established the emission trends exactly as anticipated on the "whish list". This was on the condition that the most recent findings regarding particle mass and number according to the PMP protocol would be taken into account in the measurements and calculations. However, one study from the European Particulates project does provide some interesting results that should be discussed.

The study by Ntziachristos et al. (2004) includes different diesel and petrol vehicles meeting various certification levels. The vehicles were examined for PM and solid particle number emissions in the NEDC. Thus, these results are very relevant also in our study.

In **Figure 76**, the results for particle mass (PM) are shown in the NEDC and Artemis motorway test cycle and in Figure 77, the same is shown for solid particle number. For a more thorough definition of individual vehicles, the reader should refer to the original publication. The various groups of vehicle technologies in the figures are: conventional diesel without particle filters (D), diesel with particle filters (DPF), conventional gasoline (G) and direct injection gasoline (DISI). The vehicles were tested on a number of different fuel qualities. Of the diesel fuel qualities, only D4 and D5 may be considered as representative for the diesel fuel used today and in the future, since these fuels had sulphur content of less than 10 ppm. Similarly, only the G3 petrol had sulphur content below 10 ppm.

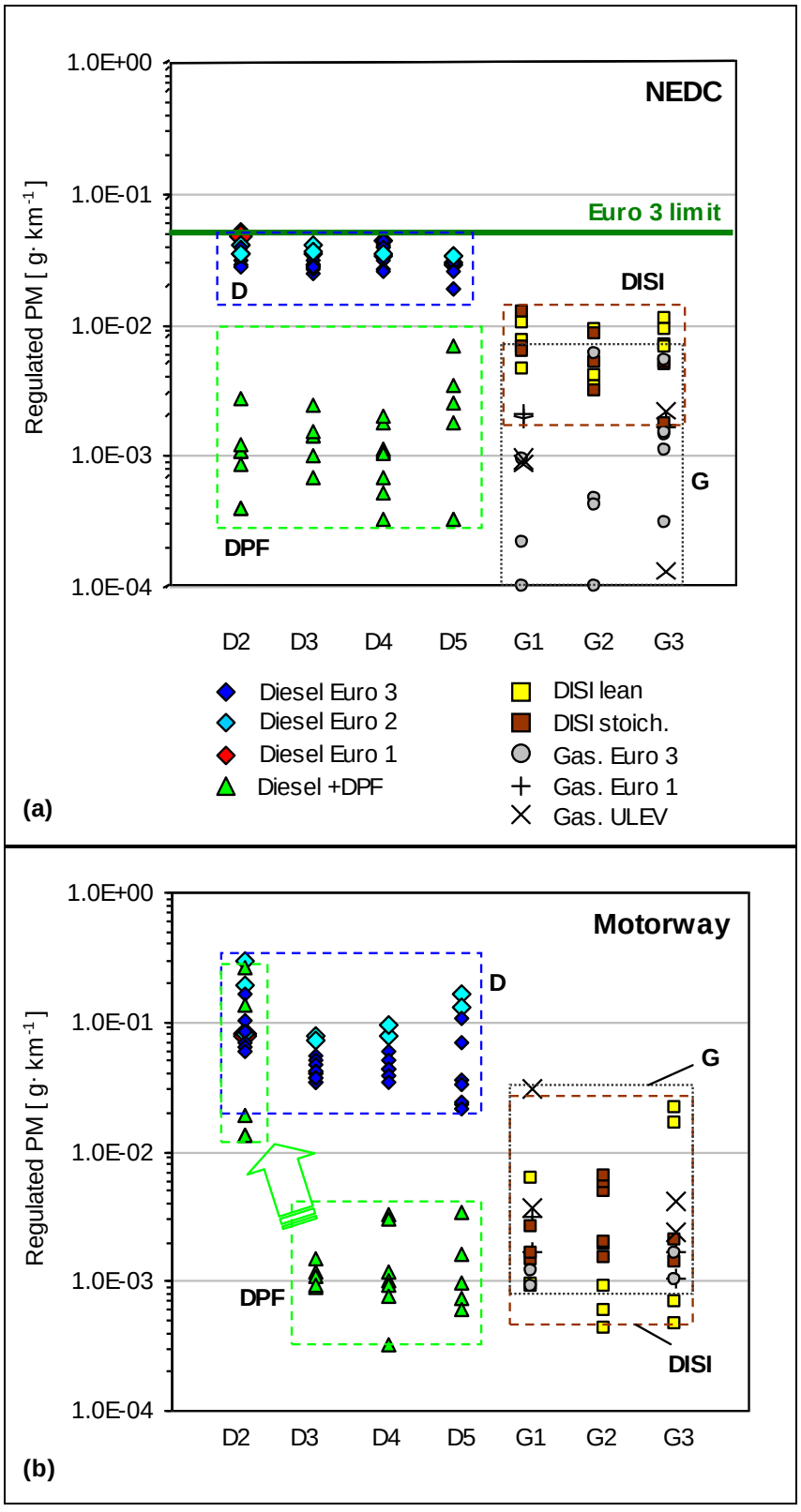

Figure 76. *Regulated PM over (a) NEDC and (b) Artemis Motorway cycles (Ntziachristos et al., 2004).*

As expected, the results in NEDC (**Figure 76**) show that conventional diesel (D) has the highest PM emissions. With one exception, the DPF vehicles had PM levels below 3 mg/km. The scatter for conventional petrol vehicles was somewhat higher but for both DPF and conventional petrol; the level was at or below the detection level of the test method. The DISI vehicles gave PM emissions over the NEDC ranging from 4 to 11 mg/km. These results were above the detection limit and higher than the proposed Euro 5 limit.

The Artemis cycle (**Figure 76**) show increased PM emissions for on high-sulphur fuel for the DPF vehicles. Most of the petrol vehicles (G and DISI) remain at low emission levels (i.e. up to 7 mg/km) for this demanding motorway although both increases and reductions compared to NEDC was observed.

The results for "solid" particles depicted in **Figure 77** were recorded using an ELPI instrument downstream of a thermodenuder and not the CPC type of particle counter recently and the sampling recommended in the PMP protocol. Nevertheless, the results should be representative, since several instrument intercomparisons have showed good correlations between ELPI and CPC instruments. The size range of the ELPI was limited from 30 nm to 1 μm.

The particle number for conventional diesel cars, at about 10^{14} particles per km, is several orders of magnitude higher than for the DPF cars. The range for the DPF cars is about one order of magnitude in the NEDC test cycle. One test result (on D4 fuel) is on a considerably higher level in the Artemis motorway test cycle, while another vehicle is very low. Real-time recordings revealed that solid particles were generated mainly in the cold start part of the NEDC test cycle for the DPF vehicles. Desorption of heavy semivolatile components, which are not removed by the thermodenuder, could be a probable cause.

The DISI vehicles emit 10 to 20 times lower number of solid particles than the conventional diesel vehicles. In comparison to the diesel vehicles with DPFs, the level is considerably higher. Conventional petrol vehicles show the most variable behaviour. Their solid particle emission levels are at equal range with DPF vehicles in the NEDC cycle and, generally, one to two orders of magnitude below DISI. However, in the Artemis highway test cycle, some vehicles approach the level of the diesel vehicles without DPF. Such behaviour is clearly vehicle specific.

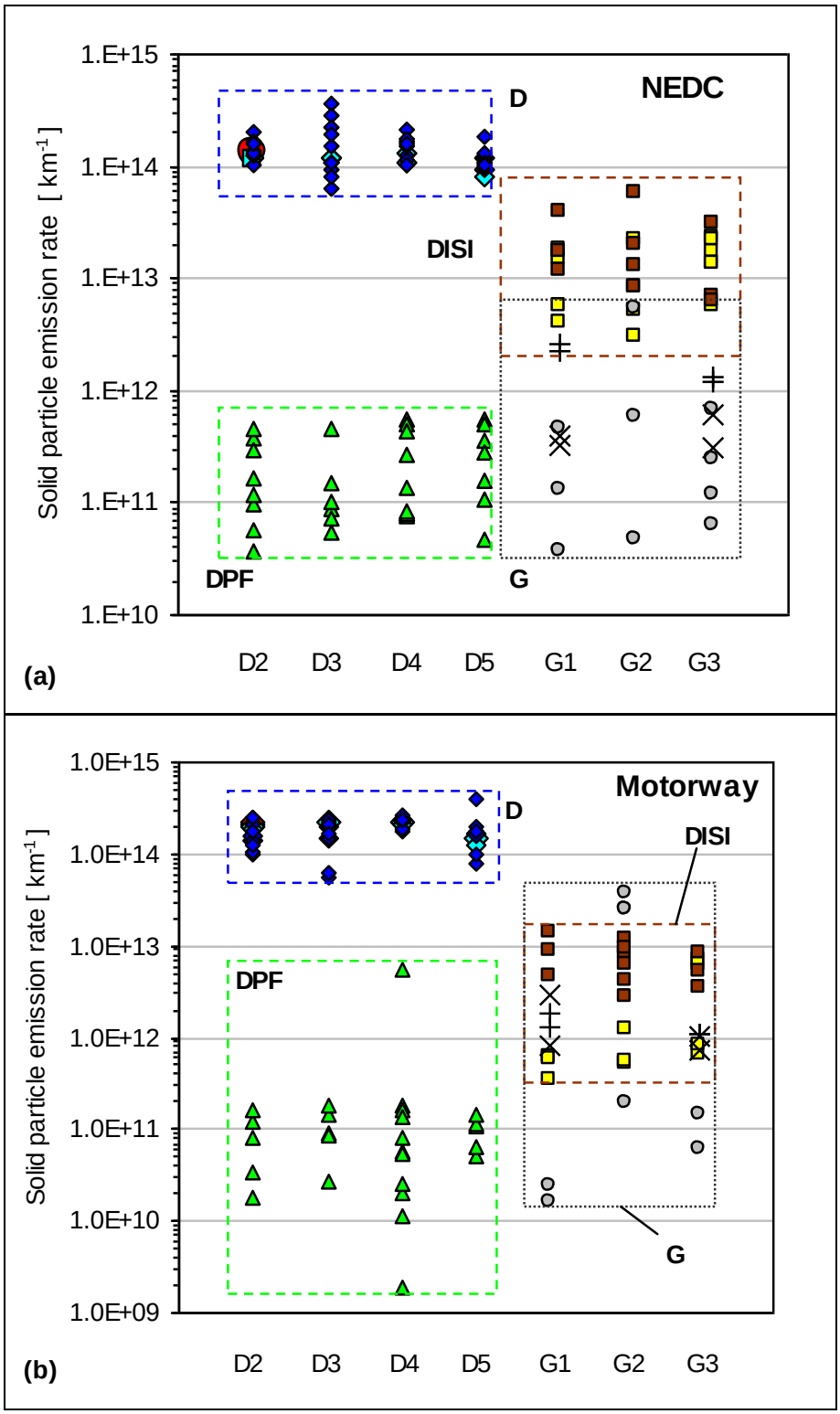

Figure 77*. Integrated solid particle number emission rate over (a) NEDC and (b) Artemis Motorway cycles (symbols as in legend of* ***Figure 76****) (Ntziachristos et al., 2004).*

4.8.2 Findings from the Swedish in-use compliance test programme

This chapter summary interesting results from the Swedish IUC program during year 2006 and 2007. The number of tests and results are great so therefore only a part of all results are presented here.

Background and short summary

In Use Conformity testing of vehicle emissions has a long history in Sweden. In the year 1991, these tests started on regular basis as a national programme at the MTC emission laboratory outside Stockholm. Until 2005, the Swedish EPA (SEPA) was responsible for the programme, but in 2005, the Swedish Road Administration took over the responsibility from SEPA. AVL-MTC continued to perform the tests during 2005 but in early 2006, after a European common procurement, TÜV Nord in Germany in collaboration with Ecotraffic in Sweden was contracted as the new laboratory for the programme.

In October 1998, with the introduction of the Directive 98/69/EC, an In-Use Conformity test of vehicles in operation on the roads in the member states of the EU was introduced. During In-Use Conformity testing emissions of vehicles already in traffic are measured according to type approval conditions. The aim of the program is to determine the influence of the mileage and the age of the vehicle on the exhaust emission behaviour.

The In Use Conformity program is a three year long project, 2006 – 2008. So far (September 2008), only result from the two first years are available.

2006: The In-Use Conformity testing programme included in total 79 vehicles, spread over 10 vehicle types with positive ignition engine, 1 hybrid electric vehicle type with positive ignition engine and additional electric motor and 4 vehicle types with compression ignition engine. These vehicles were tested with respect to the exhaust emissions limited by the corresponding EU directives.

None of the vehicles with positive ignition engine tested exceeded the limits during Type I test. Therefore, all tested vehicle types with positive ignition engine fulfilled the requirements for In-Use testing according to the statistical procedure defined in Directive 98/69/EC. Two of 20 vehicles with compression ignition exceeded at least one Euro 3 limit value during Type I test.

Testing the vehicles in different test cycles showed the influence of driving behaviour and driving conditions on the exhaust emissions. Dynamic driving, high speed, high engine load and cold start conditions cause an increase of CO and HC emissions, especially on vehicles with positive ignition engine. The major environmental exposure caused by compression ignition vehicles is NO_X and particulate emissions. A higher NO_X emission level was emitted by compression ignition vehicles especially during the CADC motorway cycle compared to the other test cycles. This is due to the high temperature inside the combustion chamber at high engine load, combined with a surplus of oxygen within the cylinder, and, presumably, also reduced or no EGR at the highest loads compared to lower loads. High particulate emissions of the compression ignition vehicles were measured, especially at cold start, high speed and high engine load. Note that these diesel vehicles were not equipped with particle filters.

2007: The In-Use Conformity testing program included in total 69 vehicles, spread over 10 vehicle types with positive ignition engine, 1 vehicle type with a petrol direct injection engine and 4 vehicle types with compression ignition engine.

Nine of ten tested petrol vehicle types complied with the Euro 4 limits during Type I test and fulfilled the requirements for In-Use testing according to the statistical procedure defined with Directive 98/69/EC. Two vehicles of one type exceeded the Euro 4 limit for NO_X emissions. The manufacturer is carrying out investigations to identify the reason for the high NO_X emissions on this vehicle type. These investigations are not completed yet. All vehicles with compression ignition complied with the type approved limits during Type I test. Therefore all tested vehicle types with compression ignition engine fulfilled the legal requirements for In-Service testing.

Besides the particle measurement according to the current directive, particle emissions were determined using an advanced method suggested by the PMP group. These measurements included particle mass and number detection on vehicles with compression and positive ignition engines. The particle mass measurement, according to the PMP protocol gave results, which were comparable to the current method with a better repeatability and minor variances for the tested vehicles with compression ignition engine. In contrast to the particulate mass measurement the particle counter (CPC) allows a second by-second recording of particulate emissions. This allowed a more detailed analysis of under which parts of the test cycle, the particulate emissions are generated. The determination of the number of particles showed a good correlation with the results gained during the 'Light-duty Inter-laboratory Correlation Exercise' of the Particle Measurement Program by the United Nations Economic Commission for Europe (UNECE).

Vehicle Selection

It was intended that the vehicles selected should cover as wide a spectrum of manufacturers as possible, while maintaining a representative cross-section of the vehicle types licensed in Sweden. 148 vehicles in total from 16 different manufacturers were investigated in these programs (2006 & 2007). In **Table 15**, the vehicle selection for the year 2006 is listed and in **Table 16**, the same for the year 2007 is listed.

Table 15. *Vehicle selection in the year 2006.*

Vehicle Selection year 2006						
No.	**Fuel**	**Manufacturer**	**Model**	**Emission Approval**	**Swedish Environmental Class**	**Mileage [km]**
1	Petrol	Volvo	S40 / V40	Euro 3	MK 2000	40 625 – 78 344
2	Petrol	Mercedes – Benz	C 180 Komp	Euro 4	MK 2005	23 226 – 58 327
3	Petrol	BMW	525i / 530i	Euro 4	MK 2000	21 000 – 44 195
4	Petrol	Renault	Megane 1.6	Euro 4	MK 2005	18 000 – 47 226
5	Petrol	Saab	9-3	Euro 4	MK 2000	28 864 – 73 069
6	Petrol	Opel	Astra 1.6	Euro 4	MK 2005	29 618 – 78 941
7	Petrol	Volkswagen	Polo 1.4	Euro 4	MK 2000	28 327 – 48 553
8	Petrol	Audi	A4 1.8 T	Euro 4	MK 2005	37 677 – 69 814
9	Petrol	Skoda	Octavia	Euro 4	MK 2000	21 406 – 34 390
10	Petrol / Hybrid	Toyota	Prius	Euro 4	MK 2005	19 417 – 75 240
11	Petrol	Toyota	Yaris 1.0	Euro 4	MK 2005	33 081 – 42 839
12	Diesel	Volvo	V70 D5	Euro 3	MK 2000	24 284 – 78 164
13	Diesel	Renault	Kangoo DCI	Euro 3	MK 2000	16 315 – 33 598
14	Diesel	Volkswagen	Passat TDI	Euro 3	MK 2000	40 794 – 72 322
15	Diesel	Citroen	Berlingo	Euro 3	MK 2000	9 274 – 69 133

***Table 16**. Vehicle selection in the year 2007.*

Vehicle Selection year 2007						
No.	**Fuel**	**Manufacturer**	**Model**	**Emission Approval**	**Swedish Environmental Class**	**Mileage [km]**
1	Petrol	BMW	320 i	Euro 4	MK 2005	34 590 – 61 033
2	Petrol	Ford	Fiesta	Euro 4	MK 2005	20 830 – 34 626
3	Petrol	Hyundai	Getz	Euro 4	MK 2005	32 888 – 77 138
4	Petrol	Mitsubishi	Colt 1.3	Euro 4	MK 2005	42 157 – 59 474
5	Petrol	Nissan	Micra	Euro 4	MK 2005	32 426 – 57 504
6	Petrol	Opel	Vectra	Euro 4	MK 2005	38 549 – 47 121
7	Petrol	Saab	9-5	Euro 3	MK 2005	46 413 – 77 170
8	Petrol	Toyota	Corolla	Euro 4	MK 2005	26 238 – 42 712
9	Petrol	Volkswagen	Passat	Euro 4	MK 2005	21 448 – 40 786
10	Petrol / Hybrid	Volvo	V70	Euro 4	MK 2005	42 604 – 69 350
11	Diesel	Peugeot	407 HDI	Euro 4	MK 2005 PM	7 370 – 53 843
12	Diesel	Saab	9-3 TDI	Euro 4	MK 2005 PM	52 357 – 97 212
13	Diesel	Volkswagen	Caddy	Euro 4	MK 2005 PM	4 894 – 20 482
14	Diesel	Volvo	XC90 D	Euro 4 (class III)	MK 2005 PM	15 229 – 44 018

Test procedures

Before starting the exhaust emission tests on the chassis dynamometer the vehicles were refuelled with reference fuel. For dynamometer setting the same inertia weight and coast down values were chosen as for the type approval test. A deterioration factor was not used for evaluating the Type I test results. The vehicle types were assessed in accordance with Directive 98/69/EC.

The vehicles were tested in a measuring program which not only includes the tests applied for type approval, but also covers other test cycles like Common Artemis Driving Cycle to determine exhaust emission factors. After refuelling the vehicles with reference fuel, the Common Artemis Driving Cycle was driven. This was done to implement an additional conditioning of the vehicles before starting the tests according to the directive. On the afternoon of the day before running the Type I tests, all vehicles were conditioned (NEDC for vehicles with positive ignition, 3 Extra Urban Driving Cycles (EUDC) for vehicles with compression ignition). Type II and III tests on vehicles with positive ignition engine were carried out immediately after the Type I test. The OBD check was done at the end of the test procedure to make sure that the simulation of emission relevant failures could not affect the results of the other tests.

As shown in **Table 18** above the average results for ignition engines complied with the type approval limits during type I tests. In year 2007, all tested diesel cars were fitted with particle filter and all of them already complied with the upcoming 5 mg/km limit for particle mass that will be introduced in the Euro 5 legislation.

***Table 17**. Test / procedure.*

Test / procedure	Positive Ignition	Compression Ignition
Refuelling (reference fuel)	5 vehicles per type	5 vehicles per type
CADC	3 vehicles per type	3 vehicles per type
Conditioning	5 vehicles per type	5 vehicles per type
Type I test	5 vehicles per type	5 vehicles per type
Type II test	5 vehicles per type	Not relevant
Type III test	5 vehicles per type	Not relevant
Type IV test	2 vehicles per type	Not relevant
Type VI test	2 vehicles per type	Not relevant
OBD check	1 vehicles per type	1 vehicles per type

Average exhausts emissions (mass) during type I test

***Table 18**. Average exhaust emissions during Type I test.*

Category	*Directive*	*Cycle*	*CO [g/km]*	*HC [g/km]*	*NOX [g/km]*	*HC+NOX [g/km]*	PM [g/km]
Results year 2006							
Positive Ignition	Euro3	UDC	2,926	0,371	0,124	-	-
		EUDC	0,088	0,013	0,014	-	-
		NEDC	1,136	0,146	0,054	-	-
Limit		NEDC	**2,3**	**0,2**	**0,15**	-	-
Positive Ignition	Euro 4	UDC	0,959	0,133	0,055	-	-
		EUDC	0,037	0,001	0,012	-	-
		NEDC	0,382	0,049	0,025	-	-
Limit		NEDC	**1,00**	**0,10**	**0,080**	-	-
Compression Ignition		EUDC	0,501	0,050	0,426	0,476	0,0297
		NEDC	0,002	0,012	0,370	0,382	0,0236
		NEDC	0,186	0,023	0,391	0,414	0,0256
Limit		NEDC	**0,64**		**0,50**	**0,56**	**0,050**
Results year 2007							
Positive Ignition	Euro 4	UDC	0,886	0,125	0,060	-	-
		EUDC	0,125	0,003	0,011	-	-
		NEDC	0,405	0,048	0,029	-	-
Limit		NEDC	**1,00**	**0,10**	**0,080**	-	-
Compression Ignition	Euro 4	UDC	0,192	0,025	0,215	0,240	0,0007
		EUDC	0,003	0,001	0,179	0,18	0,0004
		NEDC	0,072	0,010	0,192	0,202	0,0005
Limit	Euro 4	NEDC	**0,50**	-	**0,25**	**0,30**	**0,025**
	MK 2005 PM	NEDC	**0,50**	-	**0,25**	**0,30**	**0,005**
Compression Ignition	Euro 4 Class III	UDC	0,219	0,030	0,255	0,285	0,0023
		EUDC	0,000	0,001	0,333	0,334	0,0008
		NEDC	0,080	0,012	0,305	0,317	0,0013
Limit	Euro 4 (III)	NEDC	**0,74**	-	**0,39**	**0,46**	**0,060**
	MK 2005 PM	NEDC	**0,74**	-	**0,39**	**0,46**	**0,005**

The average results in **Figure 78** (particle mass) and **Figure 79** (particle number) are based on 5 vehicles per vehicle models, in total 148 vehicles. By comparing compression ignition vehicles (diesel) with (DPF) and without filter it is obvious that filters have a big positive effect on particle emissions. It is also showed that the numbers of particles are similar for petrol cars and diesel cars equipped with filter. For direct injection petrol cars, the number of emitted particles are below diesel cars without filter – but higher than for diesel cars with filter. The difference in the latter case (direct injection petrol vs. diesel with DPF) is as high as about one order of magnitude if the comparison is made with an average diesel car with DPF. It could be noted that the hybrid-electric car has both particle mass and particle number emissions at a level among the highest of the petrol-fuelled cars.

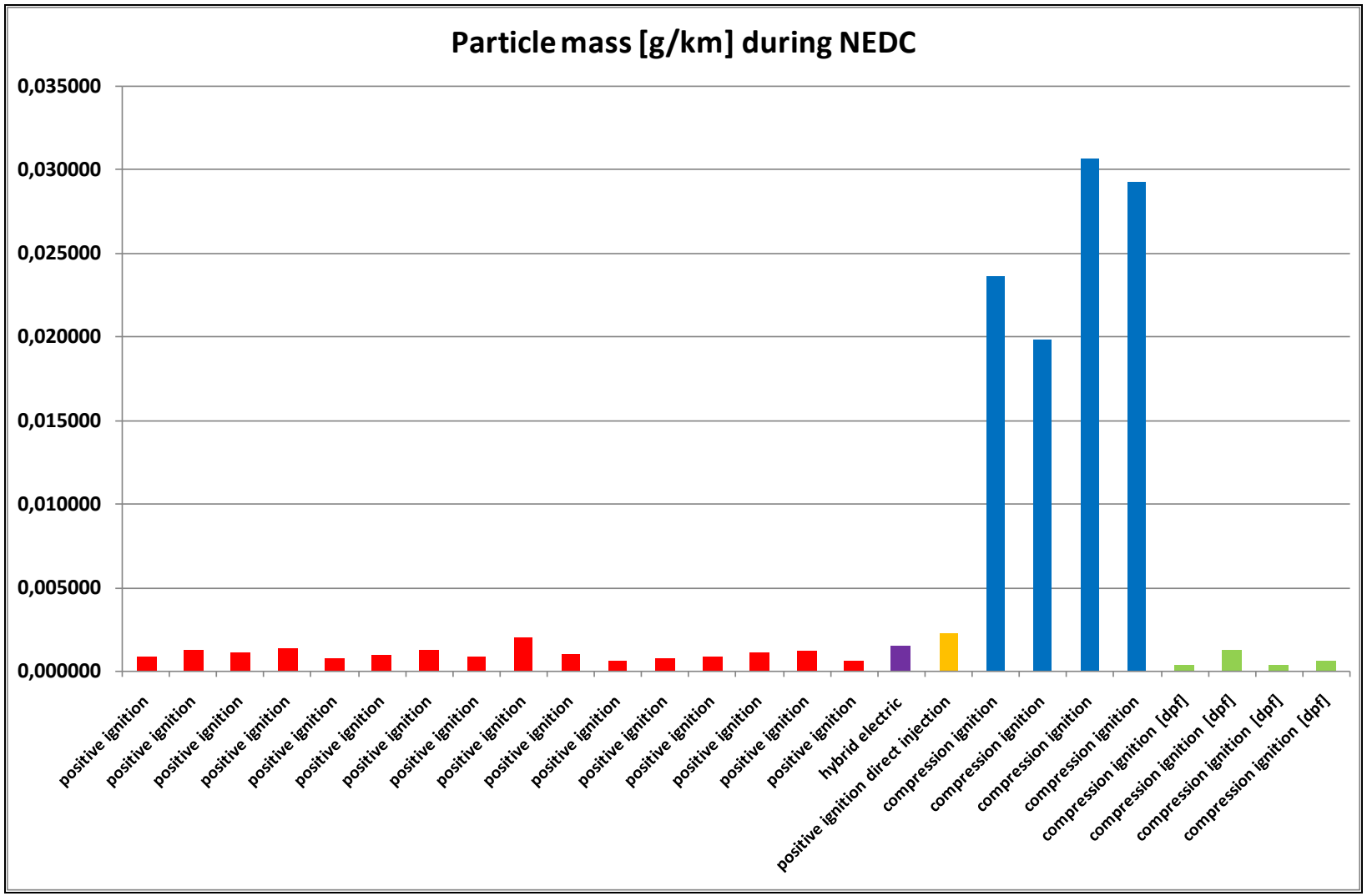

Figure 78. *Particle mass emissions in the NEDC test cycle.*

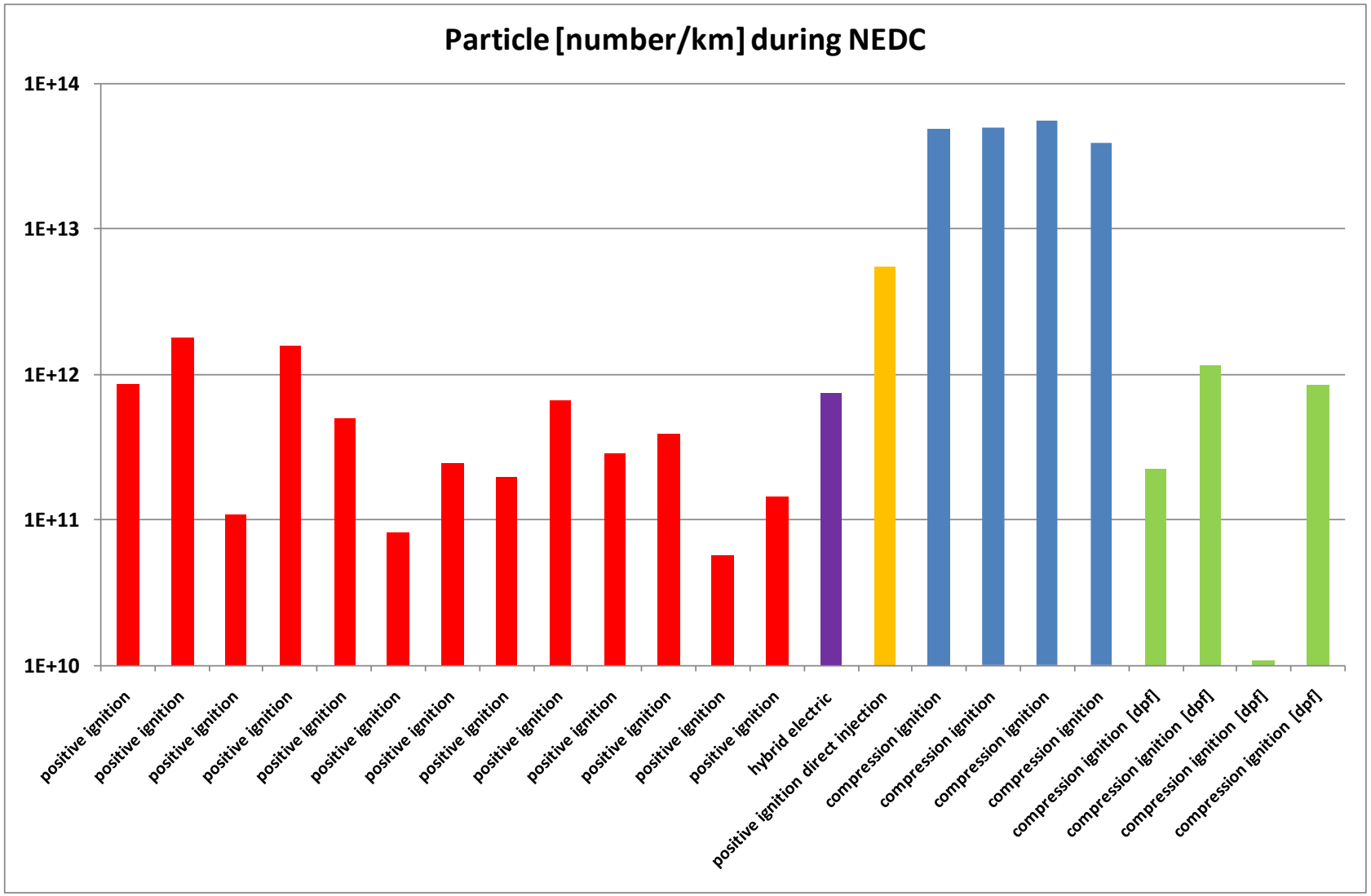

Figure 79. *Particle number emissions in the NEDC test cycle.*

4.8.3 Trendlines

One of the authors has previously compiled information emission trends in two separate projects. The most recent project was carried out in 1999 and 2001 (Ahlvik, et al., 1999, Ahlvik et al. 2001). The timeframe studied in this project was from 1993/1994 to 2010, expressed as model years for the cars. The reason for using a "split" model year of 1993/1994, was that most of the test data in that timeframe originated from these two years and it was considered inappropriate to try to distinguish between these two model years. In addition to 1993/1994 and 2010, a projection for the year 2000 was also included in the mentioned study.

In the new projections reported below, the model years 1993/1994 and 2000 have been kept unchanged from the former study, although a somewhat better estimate could probably have been made today in the latter case. However, by looking at the old results with a "fresh" view, it is not likely that a new calculation would give any significantly different results for the year 2000. However, instead of 2010, 2015 was chosen to better reflect the time horizon of this study. In addition, 2015 is also consistent with the introduction of Euro 6 (September 2014 to September 2015). No direct estimate for 2010 has been made although a discussion about the timeframe for introducing new technology will partly cover this subject.

Corrections

In contrast to the results from emission measurements, we are interested in the "real-life" emission levels for the lifetime of a car in this context. Thus, a number of corrections of emission data should be made. The three most important parameters are:

- Ageing
- Climate
- Driving pattern

Ageing has been a most important parameter for catalyst equipped petrol-fuelled cars. This is both due to catalyst ageing and malfunction of many other parameters in the emission control system (that can be the cause of abnormal catalyst ageing). A significant improvement in this area has been seen since the introduction of the three-way catalyst in the late 1980's. The calculations here take this effect into account based on actual measurements on vehicles in the past and estimates of the ageing for new and future vehicles. Although beyond the scope of this discussion, it could be mentioned that certification data for petrol cars usually are far below the limits in the regulation. By taking into account that the lifetime of the car is significantly longer than the in-use compliance in the emission regulations (previously 5 years or 80 000 km, to be extended in the future), the emission level for real life operation will be approximately at the limit in the regulation.

Diesel cars have historically had a much smaller effect of ageing due to that they have not solely relied on the reduction of emissions in the aftertreatment. However, this has changed somewhat lately due to more complicated in-cylinder emission reduction methods and the use of a DPF. The DPF durability is discussed further below.

Climate is a very important parameter for the emissions, in particular for the Nordic countries. The effect is well-known for CO and HC emissions from petrol cars, where consid-

erably higher levels are seen at low ambient temperatures. Ambient temperature has little effect on NO_X emissions. However, the temperature effect is not at all that much studied for particle emissions. Previous studies by the authors have shown a significant impact of temperature on particle emissions (Ahlvik et al, 1997a and 1997b). In fact, the real-life particle emissions during the life of a petrol-fuelled car are totally dominated by the cold start effect at ambient temperatures. This is illustrated very clearly in the diagram in **Figure 80** below.

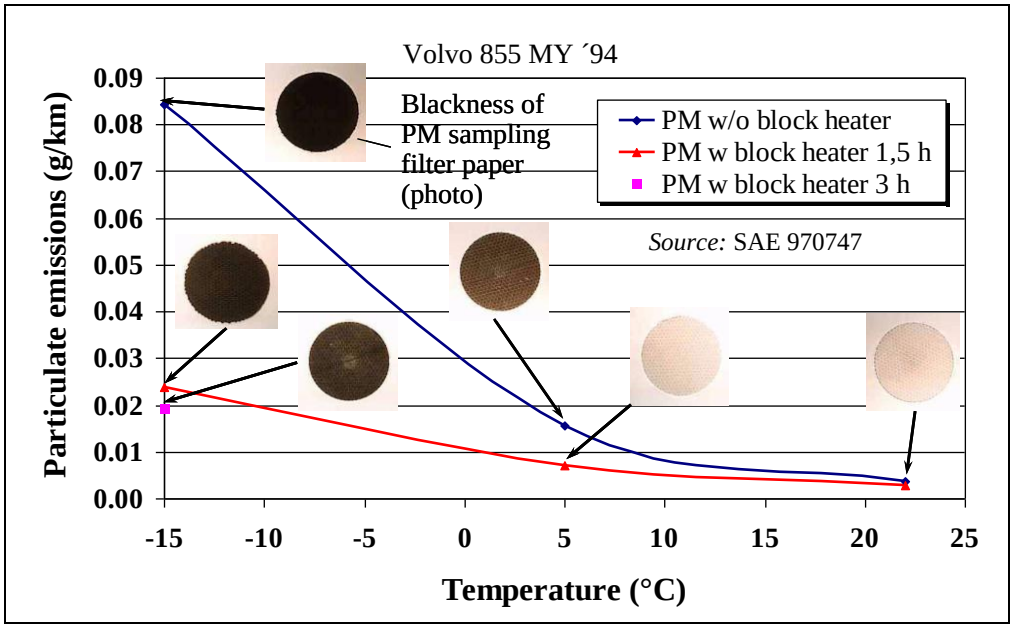

***Figure 80**. PM emissions at low ambient temperatures for one MY'94 car.*

As can be seen in **Figure 80**, the particle emissions increase considerably at lower ambient temperatures. Photos of the sampling filters show an almost white filter at higher temperatures but a more "diesel-like" appearance at the lowest temperatures. Note that the Euro 4 limit for diesel cars at 0,025 g/km is exceeded considerably at the lowest temperature. By using an electric block heater, the particle emissions can be considerably reduced, but the actual use of these heaters is limited to a few per cent of the cold starts. Thus, the practical impact of block heaters is relatively small. In Sweden, the weighted average yearly temperature is about +7°C. It is approximately at the same level also for the other Nordic countries and just a few degrees higher for the rest of Northern Europe. This temperature has been used in the calculations.

The impact of driving cycles has been discussed in other parts of this study. Although it is well-known that the NEDC cycle does not reflect modern driving patterns in Europe, no correction has been made to take this effect into account. Regarding the driving pattern, it is of interest that the driving distance of the cycle is similar as in real-life driving patterns, so that the number of cold starts per driven distance is similar in both cases. In older studies by one of the authors of this report, this effect has been taken into account when the US FTP cycle was used as basis. However, the average driving distance per cold start in Europe is very similar to the 11 km for the NEDC cycle, so no correction has been made in this case (Ahlvik, 1999).

Results

The results calculated for NO_X emissions are shown in **Figure 81**. Up till now, the NO_X emissions have been about a factor of 3 higher – during some periods even higher – for diesel cars in comparison to petrol cars. With Euro 6 that sets almost similar limits for both types of vehicles, the relative difference will diminish. Our estimate is still that the petrol cars will have a somewhat lower level. The uncertainty is about the impact of NO_X aftertreatment for diesel cars. In a previous chapter, this has been discussed in more detail. It is likely that Euro 6 will be met using a variety of technologies ranging from in-cylinder methods for the smallest cars to SCR catalysts for the largest cars. NO_X aftertreatment will be introduced already during next (2008) year in the USA. The uncertainty here is as to what extent this technology will be introduced also in Europe well in advance of the enforcement of the Euro 6 regulation. Several car manufacturers have already shown cars with such catalysts at international fairs in Europe and in some cases (e.g. the new BMW 330d) this technology was introduced in the autumn of 2008. Economic incentives might accelerate this development. The impact of an early introduction of such catalysts is also shown in **Figure 81**. The impact of this technology might diminish the small difference between petrol and diesel cars within a few years.

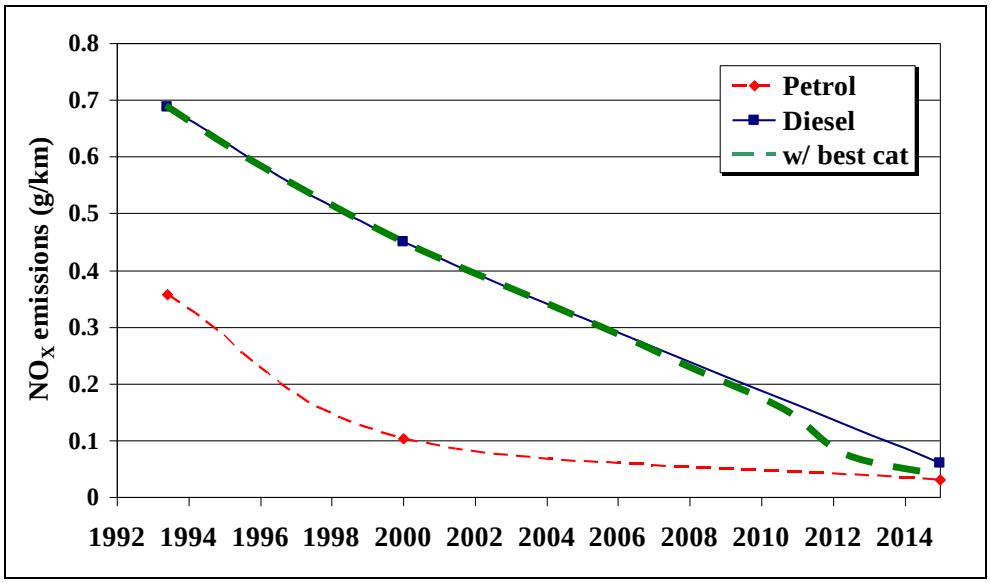

***Figure 81**. Ecotraffic's projection of NO_X emissions from petrol and diesel cars.*

Another variable regarding NO_X emissions to take into account is how fast the introduction of the second generation of direct injected petrol cars will be. These cars will supposedly use a similar technology as one of the options for NO_X aftertreatment for diesel cars, i.e. the NO_X adsorbing catalyst (providing options for future synergies between diesel and petrol). For example, BMW is just now introducing this technology on all their 4 and 6-cylinder engines to be used in Europe. The driving force for DI petrol engines is the demand for reduction of fuel consumption that can be achieved by using this technology. Also Mercedes has introduced one engine (3,5 litre V6) with this technology on the market and other car manufacturers will follow. The first generation of DI petrol cars already in production will most likely, whether using air excess (lean burn) or stoichiometric combustion (with three-way catalyst), be converted to the second generation as well in the near future. The potential for low NO_X levels with DI petrol engines is not as great as for

conventional three-way catalysts but the Euro 6 level can certainly be met. This is also reflected in **Figure 81** above, where three-way catalyst vehicles only could have given a somewhat lower level.

The results for particulate mass emissions are shown in **Figure 82**. As mentioned above, the cold start effect at low ambient temperatures is very pronounced for the real-life emission level for the petrol cars. Although most of the test results at higher ambient temperatures (e.g. +25°C) have shown results, in most cases, far below 1 mg/km, this level will increase considerably for a lower ambient temperature. Furthermore, the DI petrol cars will have a higher level. For the first generation of DI cars, it is apparent that practically no tested car would meet the 3 mg/km limit at a reliable margin. With the anticipated improvements for the second generation DI engines, it is likely that an "engineering target" of 1,5 to 2 mg/km could be met at the prescribed ambient test temperature interval (+20°C to +30). At a yearly average temperature of +7°C, this level would probably increase more than twofold. Our estimate is that the average real-life particle emission level for petrol cars (as an average for DI and conventional engines) taking the mentioned effects into account will be about 3 mg/km.

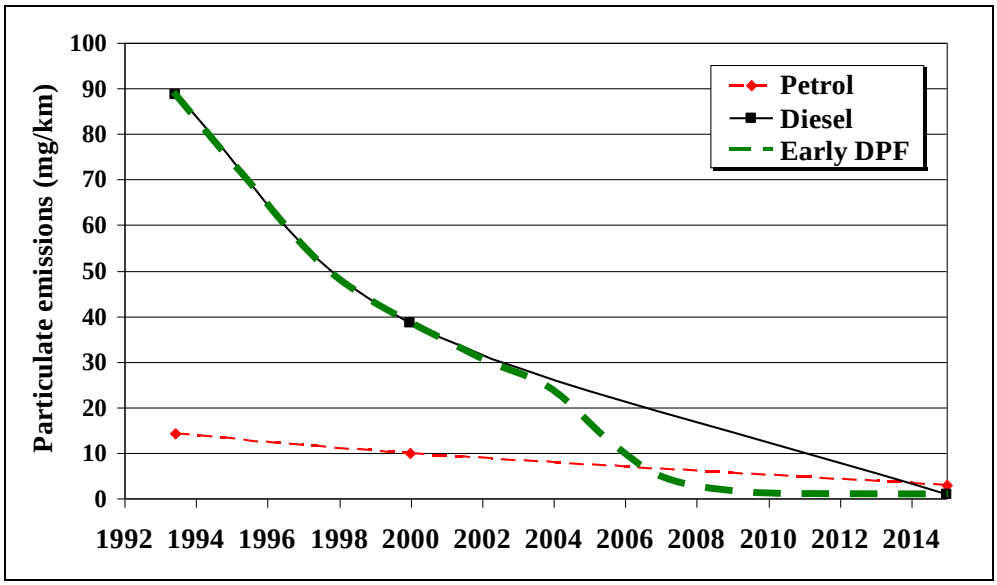

***Figure 82**. Ecotraffic's projection of PM emissions from petrol and diesel cars.*

Regarding the PM emissions from diesel cars, it is likely that all cars must be equipped with a DPF to meet Euro 5 and 6. Furthermore, it has been shown above that the limits for particle number is stricter than for particle mass on a relative basis. Thus, the DPFs used will have to have very high filtration efficiency to meet the particle number limit. Most of the test results in the literature show PM levels far below 1 mg/km for diesel cars with DPFs when a fuel with very low sulphur level is used and when the improved particle mass measurement method according to the PMP protocol is used. A PM level of 0,3 to 0,5 mg/km is common under these conditions. This level is also retained at very low ambient temperatures and in more severe driving cycles, indicating that the correction factors due to these parameters should be negligible. However, there is one very important parameter left, i.e. the durability of the DPF. So far, there are relatively few data available in the literature. Two examples of data on DPF durability has been listed among the references (Jeuland, 2007 and Bostels, 2006b). Basically all published data so far on DPF du-

rability do show a very good durability but this conclusion should be confirmed when new data becomes available. Thus, we have considered that the impact of DPF durability should be reflected in the calculations of real-life PM emissions. A conservative estimate is that the PM level could be that the deterioration would be equivalent to an increase of the PM level by a factor of 2 to 3. That corresponds to a level of 1 mg/km for a Euro 6 diesel car. At that level, a diesel car would have somewhat lower PM level than a petrol car, although it should be admitted that the absolute level for both types of cars would be very low in comparison to old diesel cars without particle filters.

Another possible scenario is that the limit on particle number under discussion for cars with positive ignition engines – if the limit is set as though as for diesel cars – could also drive down the particle mass from this category of cars (by certain technical measures such as, e.g. inproved injection systems and/or particle filtration systems) to about the same level as for diesel cars, i.e. about one mg/km. That is under the anticipation that the limit for particle number emissions would be much tougher to meet than the limit for particle mass; as for diesel cars. The line for petrol in **Figure 82** could then be adjusted accordingly to yield approximately the same level for both petrol and diesel cars.

The impact of deterioration of the DPF can be illustrated in two examples. In both cases we anticipate that the engine-out PM level (before DPF) is 15 mg/km and that the level after the DPF is 0,3 mg/km. In the first example, we presume that 5% of the particle filters would be broken and that the filtration efficiency would be practically zero. This is a rather pessimistic assumption, since it is likely that the on-board diagnostic system and/or the yearly vehicle inspection would detect such a failure. Thus, the car would operate under these conditions only for a fraction of the useful life, indicating that the actual failure rate would have to be several times higher than 5% to generate this effect. With a failure rate corresponding to a total failure of 5%, the fleet average PM emission would be about 1 mg/km. In the second example, we anticipate that 50% of the DPFs would have a crack or similar failure, which would increase the PM level by 10%. Such malfunctions might not be as easy to determine as a total failure but again, this failure is hardly likely to exist during the whole useful life of the car. If we anticipate that this failure would be present for half the useful life, practically 100% of the cars would have to experience this problem to correspond to a failure rate of 50%. This is hardly a likely scenario. The calculation fleet average emissions under these conditions gives a PM level of 0,9 mg/km. These two examples have shown that a certain failure rate might give an increase of the PM level but it is hardly likely that this effect could yield a fleet average PM level above 1 mg/km.

One often discussed factor is whether there is some deterioration effect on particle filters in general. In fact, the trend is the opposite. The accumulation of ash with increasing driving distance actually improves the filtration efficiency. Since most of the published test results have been generated on fairly new cars, the actual average level might be even lower during the lifetime of the car. On the other hand, ash accumulation might result in more frequent filter regenerations. Although the impact of regenerations is generally small on the overall PM emissions, this effect could increase the average PM level to counterbalance the previously mentioned reduction of PM emissions due to improved filtration efficiency due to the accumulaiton of ash.

Today, we see an ever increasing use of DPFs on diesel cars, although the Euro 4 emission limits can be met without a DPF. This trend has been going on for a couple of years now and it is likely that most new diesel cars will have DPFs already during next year. This has

been reflected by the green dotted line in **Figure 82**, indicating the impact of early introduction of DPFs. If this is the case, the real-life particle emissions from diesel cars could be as low – or lower – than from petrol cars already in the very near future.

4.9 Ambient temperatures and particle emissions

4.9.1 Laboratory measurements of cold start emissions

Laboratory measurements are normally performed at +22°C which is also the temperature used for certification measurements. This temperature is, however not, representative for all climatic regions, seasonal behaviour, or diurnal variations. Ambient temperatures are often significantly lower and affect engine operation, exhaust after-treatment, and dilution processes and thus particle emissions.

4.9.2 Some results on petrol-fuelled cars

Normal petrol cars (excluding direct injection engines) show higher particle emissions at lower temperatures. Ahlvik and de Serves (1999) observed 2 to 7 times higher emissions in the NEDC for three petrol passenger cars at -7°C as compared to +22°C. The average emission for the two temperatures was 8,0 and 1,6 mg/km respectively. In a later study performed at the same laboratory, Ahlvik (2002) observed similar results with 3 times higher particle mass emissions for two petrol cars at -7°C as compared to +22°C. The particle number measurements by use of ELPI from the CVS-tunnel were, however, not conclusive since one of the cars increased its particle number emission 3,6 times at the lower temperature while the other two showed reduced emissions by a factor of 2.

Aakko and Nylund (2003) examined one MPI-petrol and one direct injection petrol car at +23°C and -7°C and observed increased particle mass emission in line with those reported above for the MPI-petrol. The direct injection petrol car did not show a significantly higher particle emission for the lower temperature.

Maricq et al. (1999) examined cold start particle number emissions for petrol vehicles as measured from the CVS-tunnel using ELPI by comparing phase 1 and 3 in the FTP cycle (phase 1 and 3 are identical in driving but constitutes cold and warm starts, respectively). They found that the cold start emissions generally outweigh the particle number from hot start by more than a factor of 3. Also, the size distribution was shifted towards larger particles during the cold start. The comparison between phase 1 and 3 for particulate mass showed a ratio in the range 1,2 to 7,4. This leads to the conclusion that warming of the engine and/or catalyst to operating temperature has a significant effect on the rate of particles emitted from the tailpipe.

It is, however, important to keep in mind that even if particulate emissions from petrol cars in general are more sensitive to ambient temperature as compared to diesel cars with DPF, the absolute emissions are still lower even at low temperatures. The relative importance of the cold start effect for petrol cars increases with lower temperatures. Meanwhile, the cold start effect of diesel cars is negligible or small.

4.9.3 Some results on diesel-fuelled cars

Diesel cars show a smaller temperature effect on particle mass and number emissions than petrol cars. For two cars examined for particle mass emissions at +22°C and -7°C in the

NEDC by Ahlvik and de Serves (1999), one showed no effect for the lower temperature while the other showed double the emissions. For the same temperatures, Ahlvik (2002) reports an increase in particle mass emission with the lower temperature by approximately 50% for a modern TDI but no effect for a diesel car equipped with a DPF. Simultaneous measurements of the particle number emission using an ELPI (range 7 nm to 6 μm) showed approximately 15% higher emission for the TDI. For the car with DPF, 3 times higher emissions were observed for the lower temperature which is largely an effect of particles smaller than 0,1 μm.

The NEDC real time ELPI charts as examined by Aakko and Nylund (2003) for two diesel cars do not show higher emissions at lower temperatures but rather decreased except for a somewhat higher particle emissions in the cold start. The authors draw the general conclusion that if a temperature effect occurred, it took place during the cold start and diminished as engine and exhaust after-treatment system were warmed-up.

Karlsson (2005) examined 4 diesel Euro 4 passenger cars of which 2 were equipped with DPF. The cars were examined in the NEDC driving cycle at 22°C and -7°C for regulated emissions and particle mass and number emissions according to the PMP-proposal. The NEDC at -7°C did not show any significant changes in particle number emissions.

4.9.4 Results from the Swedish IUC programme

During 2006 and 2007 of the Swedish IUC programme, particle emissions were not measured in tests at -7 C. The results from testing carried out so far in 2008have not been fully evaluated yet. Since more tests are going on this year, these results will be available at a later stage from this programme.

4.10 Particle emissions and size distribution

Particle size distribution measurements including both solid and condensed particles have been performed by Ntziachristos et al. (2006) at low and medium mode driving conditions for HDV, HDE, and LDV (**Figure 83**).

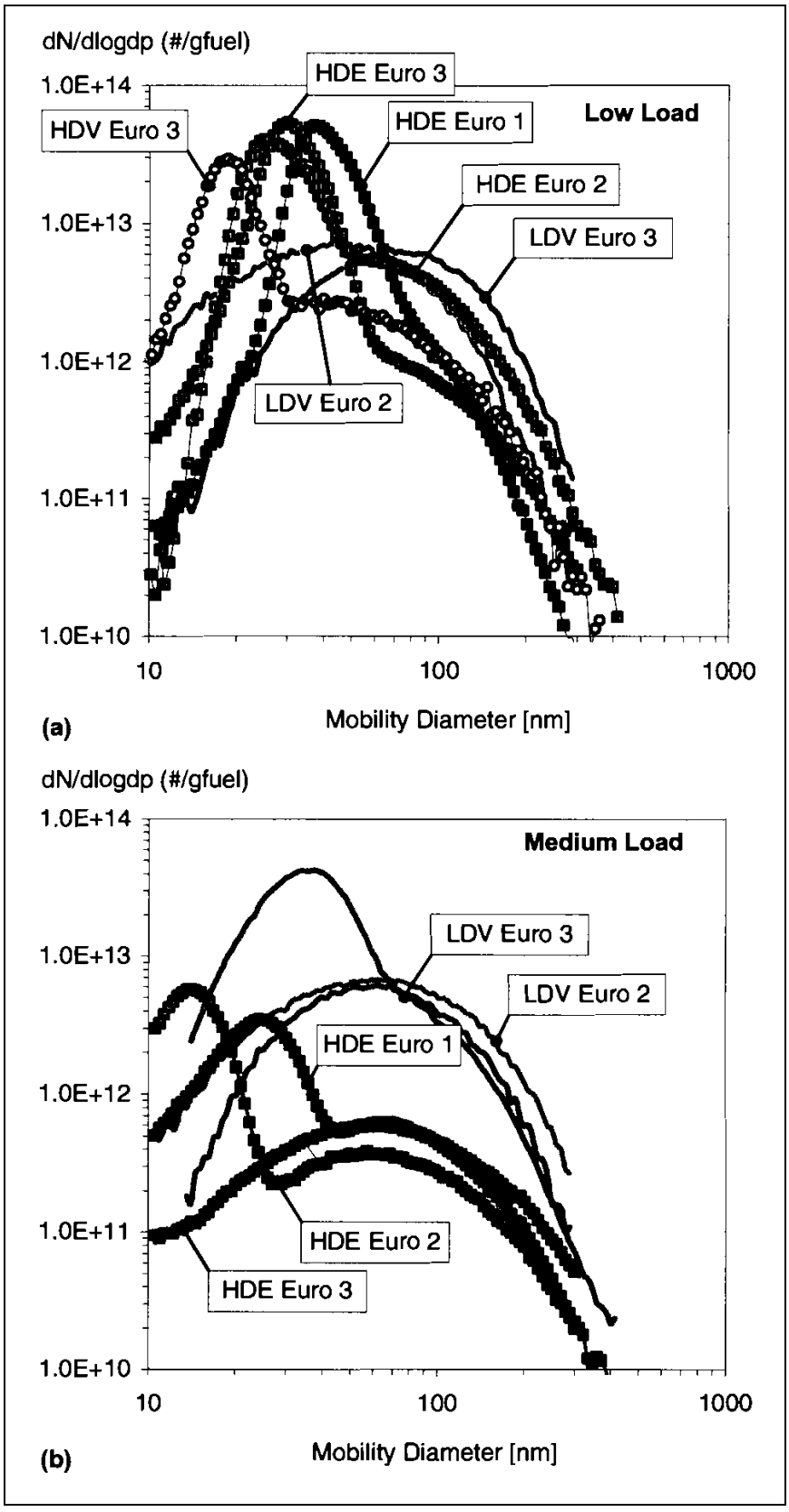

Figure 83*. Particle size distribution measurements using SMPS (both solid and condensed particles) for LDVs, HDEs, and HDVs. Figure a) 50 km/h for LDV, 60 km/h for HDV, and 10% load for HDE. Figure b) 120 km/h for LDVs, and 50% load for HDEs.*

The relatively low solid particle number emissions from HDVs most likely promote the formation of a nucleation mode due to the limited availability of condensation sites for organic material condensation (**Figure 83**). Hence volatile nanoparticles are frequently observed, in particular at low loads, where PM contains a high fraction of soluble organic material. The nucleation mode disappears at high loads for the Euro III engine with the use of a diesel oxidation catalyst. No nucleation mode formation appeared at low loads for light duty vehicles, all equipped with oxidation catalysts. However, the formation of nucleation mode particles is more prone at higher load conditions, where elevated exhaust temperatures (350°C in combination with a Pt-catalyst) promote the formation of sulphates. Nucleation mode particles appeared for one of the Euro 3 passenger cars even though a sub-10 ppm sulphur fuel and a medium sulphur lubricant were used.

Particle size distribution measurements on diesel-DI with and without DPF, petrol MPI, and direct injected petrol (both stoichiometric and lean burn) vehicles have been performed by Mohr et al. (2003). A SMPS-TD set-up was used at different steady state driving modes (50, 100, and 120 km/h). The conventional diesels showed very similar distributions for all speeds with a peak emission at about 70 nm (**Figure 84**). The stoichiometric direct injected petrol car showed a high number of particles smaller than 30 nm at the 120 km/h mode composed by volatile material as they vanished using the TD.

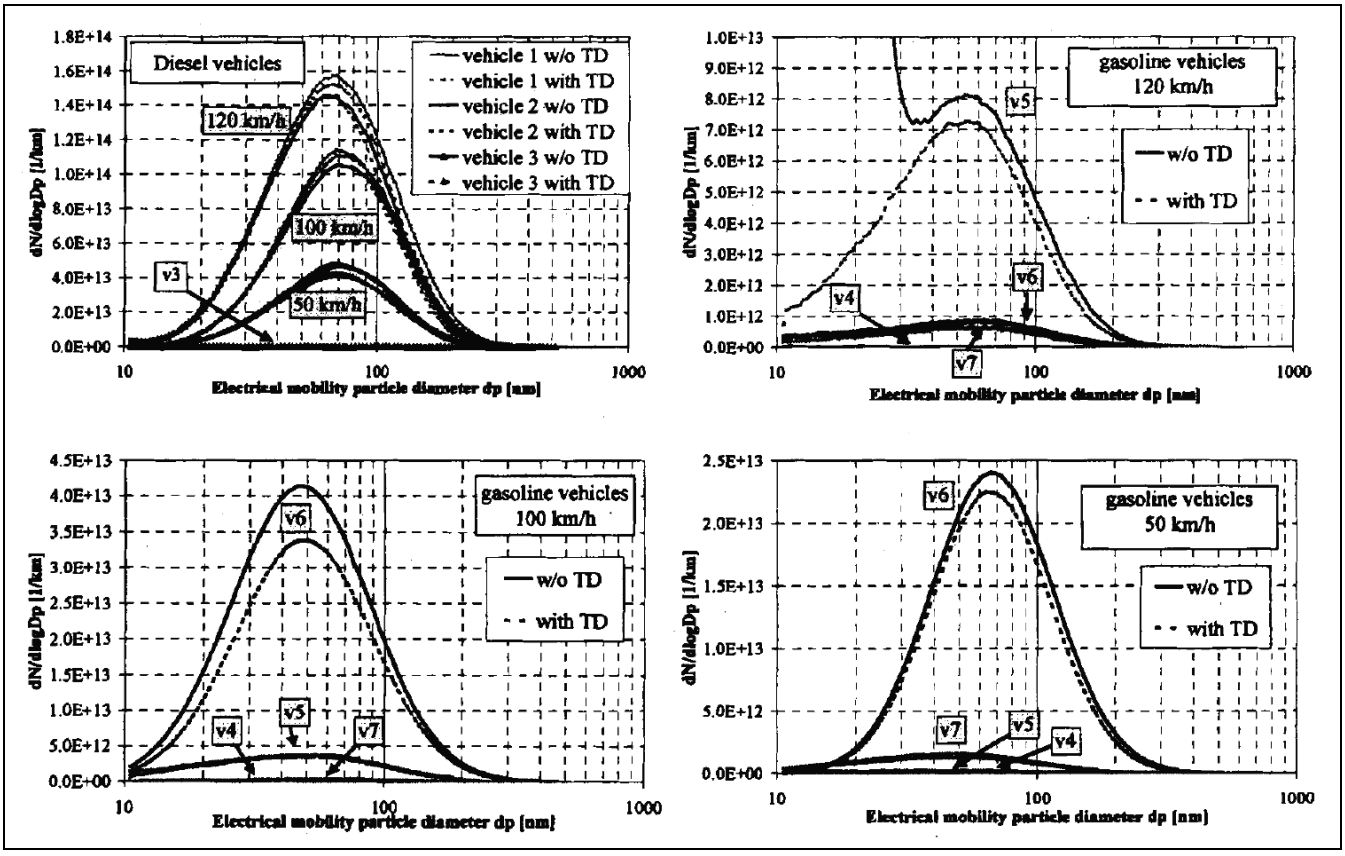

Figure 84. *Particle exhaust size distribution measurements for the three constant speeds. Diesel vehicles all 3 speeds: upper left, petrol vehicles: 120 km/h upper right, 100 km/h lower left, 50 km/h lower right (Mohr et al., 2003).*

Particle size distributions were measured in the PMP ICLE work (Anderson et al., 2007) using an Engine Exhaust Particle Sizer (EEPS; TSI model 3090). The measurements are presented in **Figure 85** for the diesel DPF "golden vehicle" in which the NEDC is divided for urban (ECE) and extra urban (EUDC) emissions. It is obvious that the overall cycle emissions are dominated by the carbonaceous accumulation mode (30-200 nm) from the urban part of the cycle.

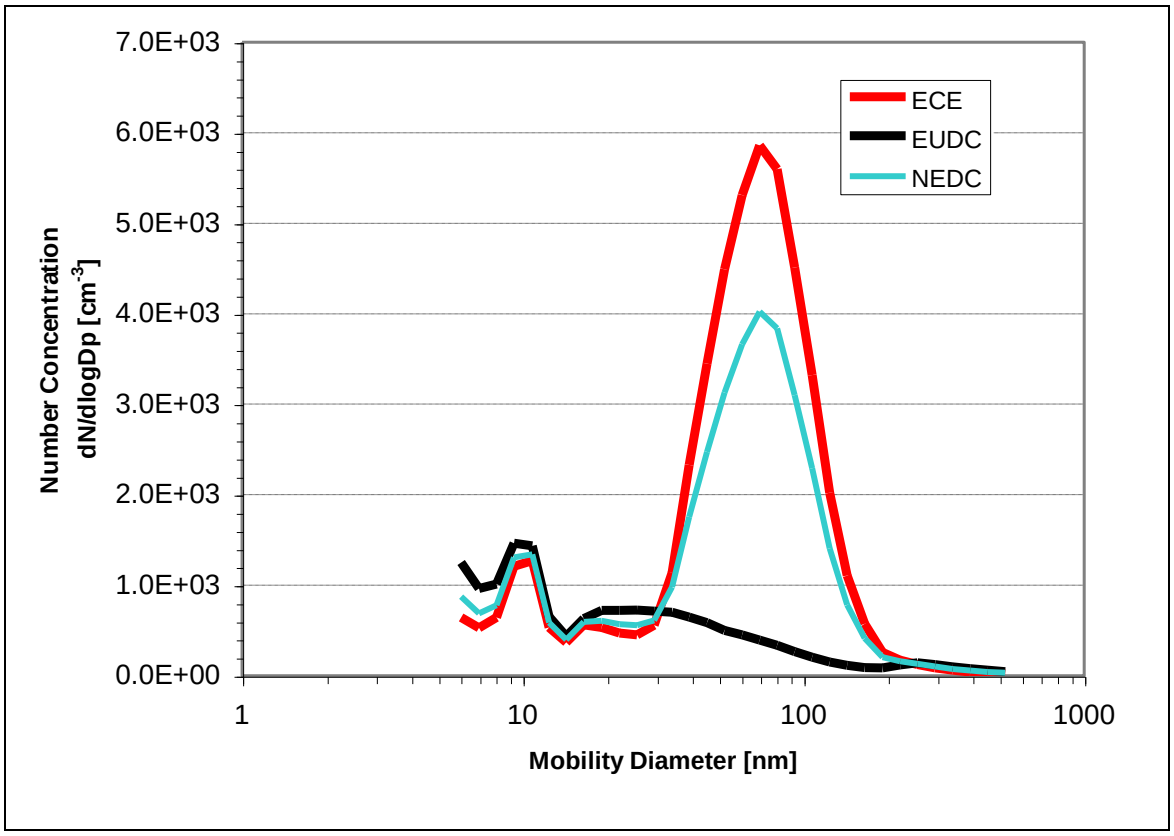

Figure 85. *Particle size distribution for the ICLE golden vehicle in the NEDC as divided for the urban (ECE) and extra urban (EUDC) parts of the cycle (Andersson et al., 2007).*

From the "Particulates" project Ntziachristos et al. (2004) reported particle size distributions as measured by SMPS (including volatile particles) for steady-state operations and by an ELPI-TD set-up for solid particles in transient cycles. Results were compiled from in total 6 different laboratories using identical measurement systems, fuels and lubricating oils. In total, 22 different vehicles were examined including conventional diesels, diesel-DPF, petrol MPI, and direct injected petrol cars (both stoichiometric and lean burn). The vehicles met Euro 1 to Euro 3 certification levels and were operated with 4 diesel and 3 petrol fuels doped with sulphur to different concentrations (D2=280, D3=38, D4=8, and D5=3 ppm-S; G1=143, G2=45, and G3=6 ppm-S). The SMPS measurements for the diesel and the petrol cars are presented in **Figure 86** and **Figure 87**, below.

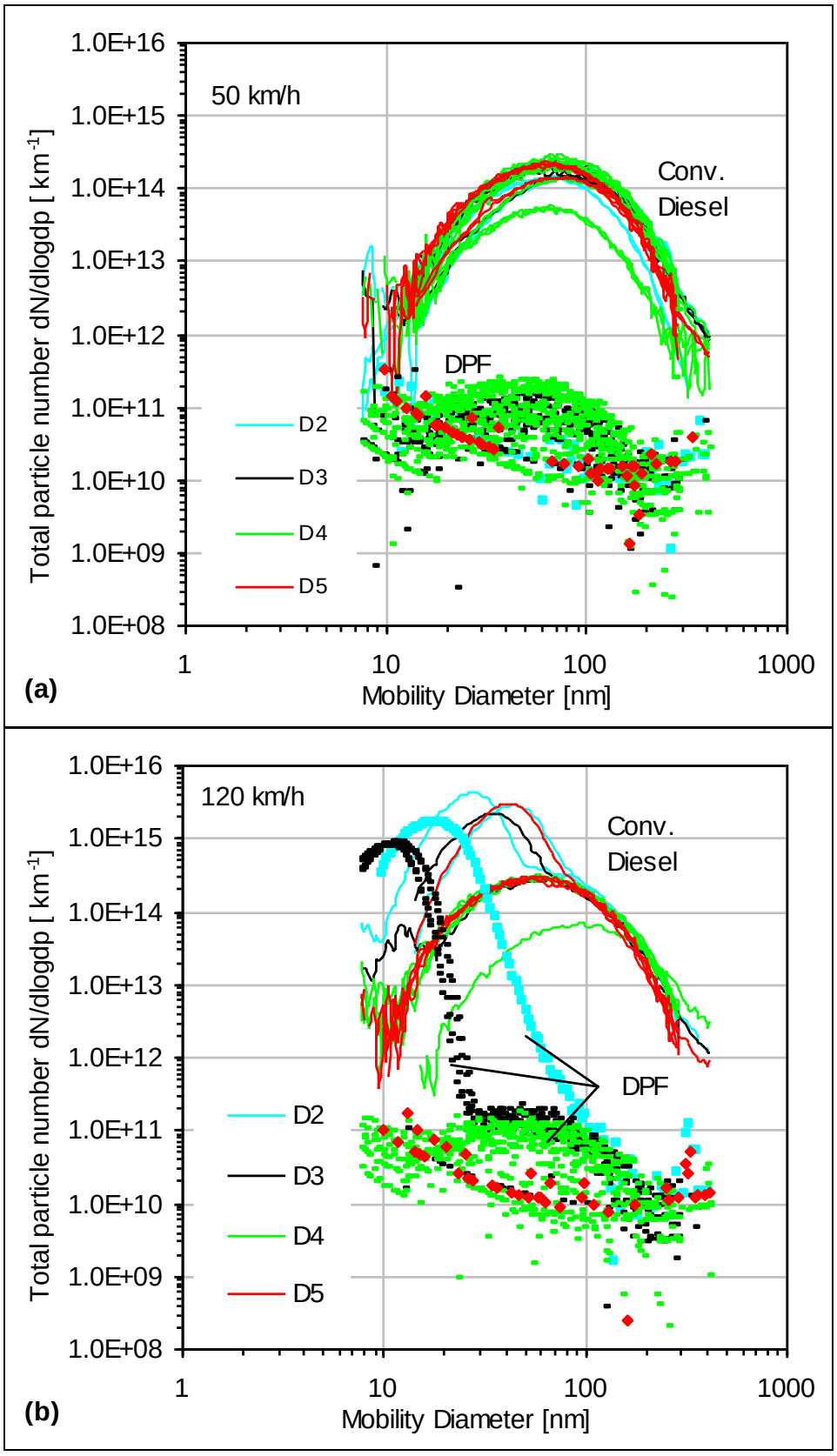

***Figure 86**. SMPS distributions of conventional diesel and DPF vehicles over (a) 50 km/h and (b) 120 km/h (Ntziachristos et al., 2004).*

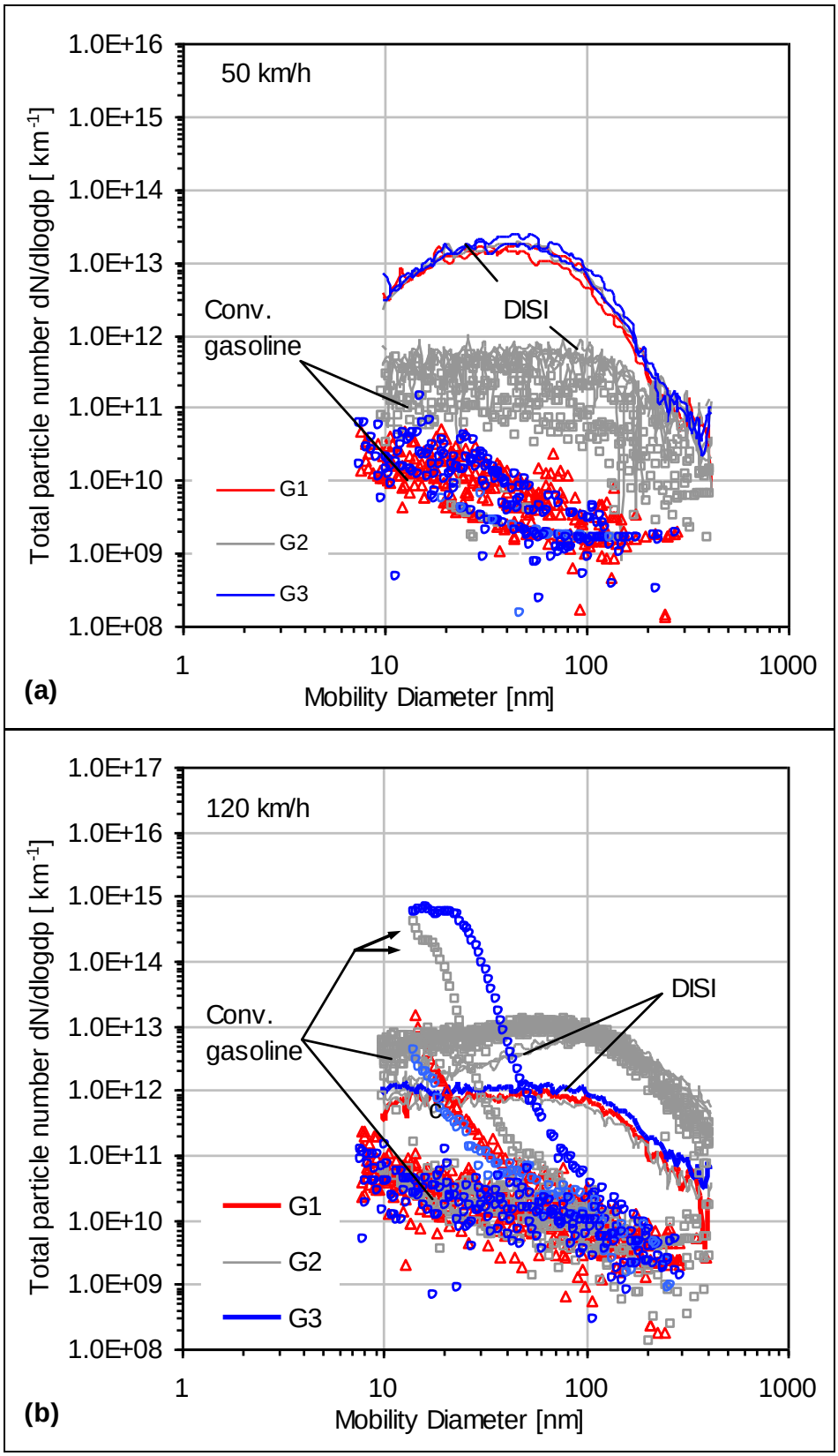

Figure 87*. SPMS distributions of conventional petrol and direct injected petrol Euro 3 cars over (a) 50 km/h and (b) 120 km/h (Ntziachristos et al., 2004).*

From the SMPS particle size distributions, one may observe that the diesel car emissions are affected by driving conditions and fuel sulphur content, with a distinct nucleation mode appearing for the higher speed and the higher sulphur fuel. This picture seems typical for both conventional diesel and DPF diesel cars. For petrol vehicles it is not possible to draw any general conclusions. However, cases have been identified where petrol vehicles may emit significant total number of particles both in the accumulation and in the nucleation mode.

The same vehicles have been examined in the transient NEDC and Artemis Motorway cycles for size distributions of solid particle. These results are presented in **Figure 88** below.

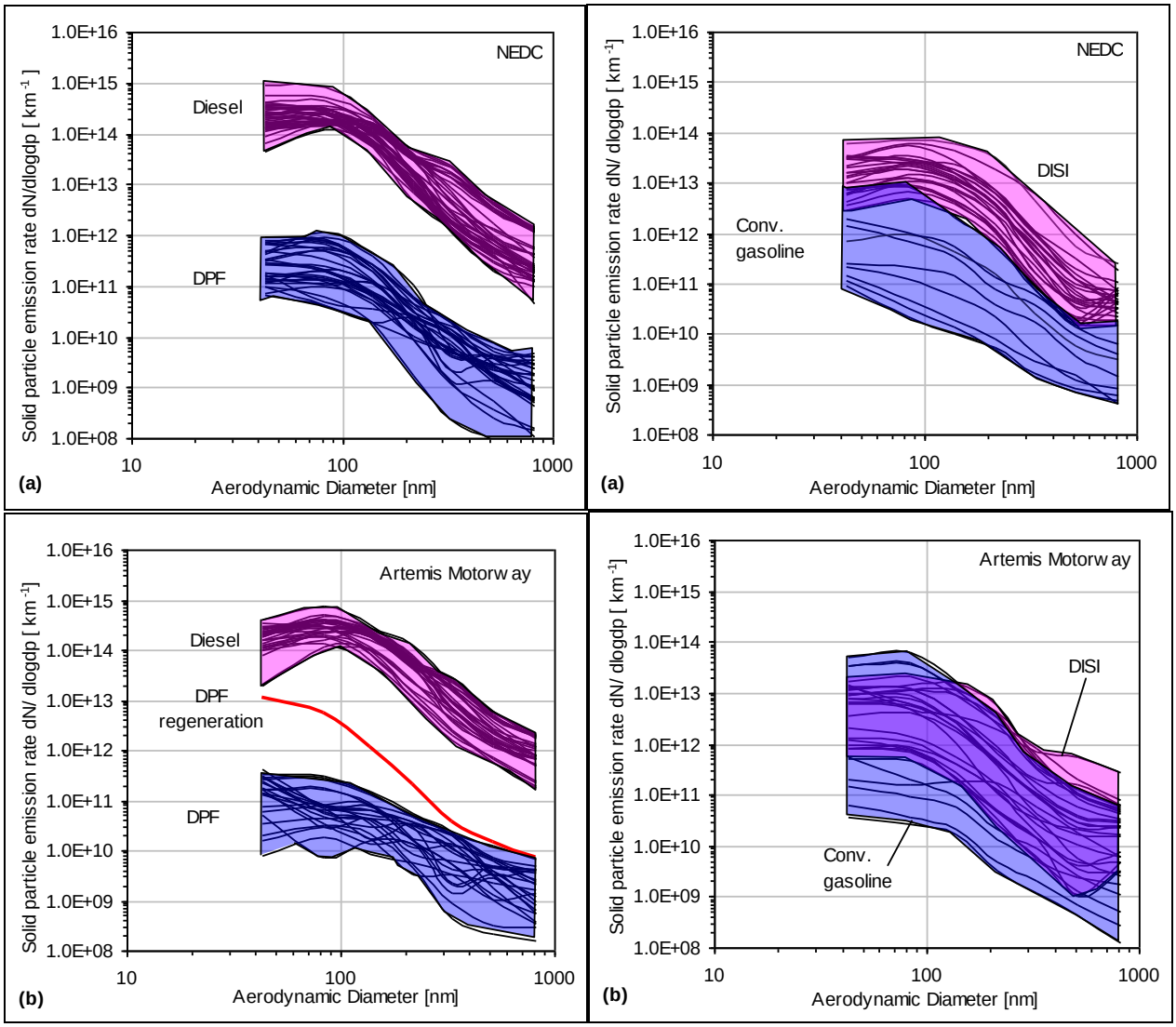

Figure 88. *Solid particle size distributions of conventional diesel Euro 3 and DPF vehicles (left hand figures), and solid particle size distribution of conventional petrol and direct injected petrol Euro 3 cars (right hand figures). (a) NEDC, (b) Artemis Motorway (Ntziachristos et al., 2004).*

The solid particle measurements showed no significant information for either diesel or petrol cars that may be obtained by classifying distributions on a per fuel basis.

Conventional diesel and DPF distributions are very similar in size distribution in the NEDC but the emission levels are 2-3 orders of magnitude lower over the whole size range studied. In the Artemis Motorway, the distributions become more flat due to the absence of a cold-start.

For the petrol vehicles, there is discrimination between the two vehicle technologies over the regulated NEDC, with the particle distribution from the direct injection petrol cars significantly higher and with geometric mean diameters in the order of 72-77 nm. Distributions of normal petrol cars spread over almost three orders of magnitude for the same particle size while mean diameters are found in the 52-66 nm range. In the Artemis Motorway, the picture is partly reversed with normal petrol cars even exceeding the concentration of direct injection petrol cars for small particle sizes but still spreading over several orders of magnitude. Petrol vehicle behaviour is thus largely dependant on driving condition but there is no solid nuclei peak as observed for total particles. However, still significant numbers of small solid particles seem to be emitted under high speed driving.

4.11 NO/NO_2 ratio

Current air quality norms do not regulate the total amount of oxides of nitrogen (NO_X), as in the emission limits in regulations and directives for vehicles and engines. Instead, the NO_2 is regulated in air quality norms. In the vehicle/engine emission measurements, NO is converted to NO_2 via a catalyst, so that the total level for NO_X can be determined. The molecular weight for NO_2 is used in the calculation of NO_X emissions. Some specific emission norms for engines and vehicles used in e.g. mines and tunnel do require the measurement of both NO and NO_2. Parallel measurement of NO and NO_2 often require the use of two instruments, in particular if these measurements are made under transient conditions.

In a study by Sjödin, et al. (2004), the current state of knowledge about the effects of NO_2 was summarised. A literature survey was made in the study as the basis for the conclusions drawn. One general finding in the study was that there is no evidence for that low concentration of NO_2 should have any direct verifiable health effects, at least not in concentrations found in densely populated areas. NO_2 is usually used as an indicator for other air pollution components but other components, such as ultrafine particles are more likely the cause of the observed indications. A paradox in this context is that the ozone levels will increase more rapidly (though from a lower level) in city centres, in comparison to the background regions, due to the decreasing NO_X emissions in densely populated areas. Thus, people in these areas will be exposed to higher ozone levels than before. In contrast to NO_2, there are clear and direct links between ozone exposure and health effects.

Regarding impact from NO_X not related directly to health effects, eutrophication and acidification could be mentioned. These effects are seen on a regional scale rather than locally or globally. NO and NO_2 have approximately similar impact regarding these effects implying that the sum for oxides of nitrogen (NO_X), as in the legislation for vehicles and engines makes sense.

Although perhaps not one of the most noxious emissions components found in vehicle exhaust as stated in the study by Sjödin et al. (2004), NO_2 can sometimes be of significant importance on local scale. This has been recognised for example, in mines where ventilation is based on NO_2 concentrations. Other areas can be tunnels (particularly during con-

struction), parking houses and in areas with very dense traffic. Therefore, aftertreatment devices that favour the formation of NO_2 are not desired. This has been recognised in the so-called VERT project, a joint collaboration between two occupational insurance companies in Austria and Germany and the Swiss EPA (AKPF, 2008)). In the certification regulation for the aftertreatment devices, which was one of the results from this project, limits were set for the NO_2/NO ratio.

In ambient air, NO is rapidly oxidised to NO_2 through the reaction with ozone or peroxy-radicals. In the combustion chamber of an engine, NO reacts with oxygen to form NO_2 ($NO+O_2=NO_2$) but the equilibrium is at the high temperatures that prevails in the engine is shifted to higher concentrations of NO. In general, the average NO_2 share of NO_X in diesel exhaust before any aftertreatment device is, at maximum, in the order of a few per cent. For petrol engines, which do have higher engine-out NO_X (but lower NO_X after the catalyst), the share can be lower than one per cent. As mentioned above, the equilibrium of NO/NO_2 in the combustion chamber of the engine is close to 100 % NO. Since the reaction kinetics of the reactions mentioned is relatively slow in contrast to the time constants for a combustion cycle of an engine. Thus, the fast expansion at the end of the power stroke will "freeze" the concentrations at a very low share of NO_2. With modified combustion system in order to reduce the combustion temperature, e.g. by using EGR, the NO_2 share will increase somewhat. However, the greatest cause of elevated NO_2 share is the impact of the aftertreatment. At the position of the catalyst, exhaust temperatures are far lower than in the combustion chamber and thus, the equilibrium is shifted towards a higher share of NO_2. A catalyst *can* promote oxidation of NO to NO_2 and the extent of this effect is dependant on the catalyst formulation. At very low exhaust temperature, e.g. low load or idle, the exhaust temperature in diesel exhaust will be too low for the catalyst to have any effect on NO oxidation. Therefore, a plot of NO_2 share vs. exhaust temperature will give a "hump" of maximum NO_2 share at a temperature just above when the catalyst activity on NO oxidation has been established. Often, the maximum NO_2 share can be as high, or higher, than 50 %. There must be an excess of oxygen for the oxidation of NO to NO_2. In otto engines, such as petrol engines, the conditions are mostly stoichiometric or understoichiometric, such as at full engine load. Thus, very little oxidation of NO to NO_2 is promoted by the catalyst. Exceptions would be if the engine is using a "lean" combustion system, which gives excess oxygen in the exhaust. This can be found in some modern engines using direct injection. Hypothetically, similar high shares of NO_2 as from diesel engines could be anticipated from these engines. However, in the limited literature survey carried out in this project, no relevant data on NO_2 share from such engines could be found.

For some types of aftertreatment devices, the oxidation of NO to NO_2 is desired, for some not. In conventional diesel oxidation catalyst, there is no additional advantage of converting NO to NO_2. In contrast, catalysts that do have a high activity on this reaction usually also have a high conversion of SO_2 to SO_3, which with water, will be converted to sulphates and be measured as particulate matter on the sample filter in particulate measurements. For particle filters that are continuously regenerating, NO_2 formed in a catalyst before the DPF will strongly promote the oxidation of soot. NO_2 is a much more active species than O_2 in this respect. After the soot has been oxidised, NO_2 is reduced to NO but this reaction does not fully reduce the NO_2 share to pre-catalyst levels. The importance of NO_2 in soot oxidation was shown already in 1989 by Cooper and Thoss at Johnson Matthey (Cooper and Thoss, 1989). Later, this company commercialised a DPF under the

name CRT™ and the soot oxidation effect by NO_2 is often referred to as the "CRT-effect". This regeneration is often referred to as "passive" regeneration. Also "active" regeneration systems for DPFs, such as on passenger cars, use the CRT-effect to a certain extent. Some level of continuous regeneration in these cases can prolong the period before a "forced" regeneration via the active regeneration system is imitated. Another example can be seen in the so-called NO_X storage catalyst, which is used for NO_X abatement on petrol-fuelled direct injection engines that are using the lean-burn combustion system. Similar catalysts are now being introduced on diesel engines. The NO_X storage catalyst relies on the oxidation of NO to NO_2 before NO_X storage. Also in NO_X reduction catalysts of the SCR type, a certain percentage of NO_2 promotes the reaction with ammonia to create N_2 by significantly increasing the reaction rate.

Although the oxidation of NO to NO_2 is desired for many exhaust aftertreatment systems, a high NO_2 share is not desired in the tailpipe exhaust. From time to time, this has been debated in the scientific community. However, relatively few publications are found in the literature where the NO_2 share from modern vehicles has been characterised. In the study by Sjödin et al. (2004) less than 20 interesting papers were found in the SAE database. Although many more papers were found in the literature search in this study, most of them are on fundamental development of catalysts and other aftertreatment devices and not a survey of NO/NO_2 ratio for in-use vehicles.

An interesting summary of the effects of different catalyst formulations in DPF systems has been made by Czerwinski et al. (2006). Some of the results from this study are shown in **Figure 89**. The black line shows the NO_2/NO_X ratio without a DPF. The trend of higher ratio at lower exhaust temperatures is clearly visible here, although the level is low. Different catalyst coatings have varying effects on the NO_2/NO_X ratio. As known from the literature, platinum (Pt) catalysts strongly promote the oxidation of NO to NO_2. The maximum NO_2/NO_X ratio ranges from 20 to over 60 %, with a shift of the peak towards lower temperatures as predicted by the equilibrium. Interesting to note is that other catalyst formulations, such as base metals have little – or negative – effect on the NO_2/NO_X ratio.

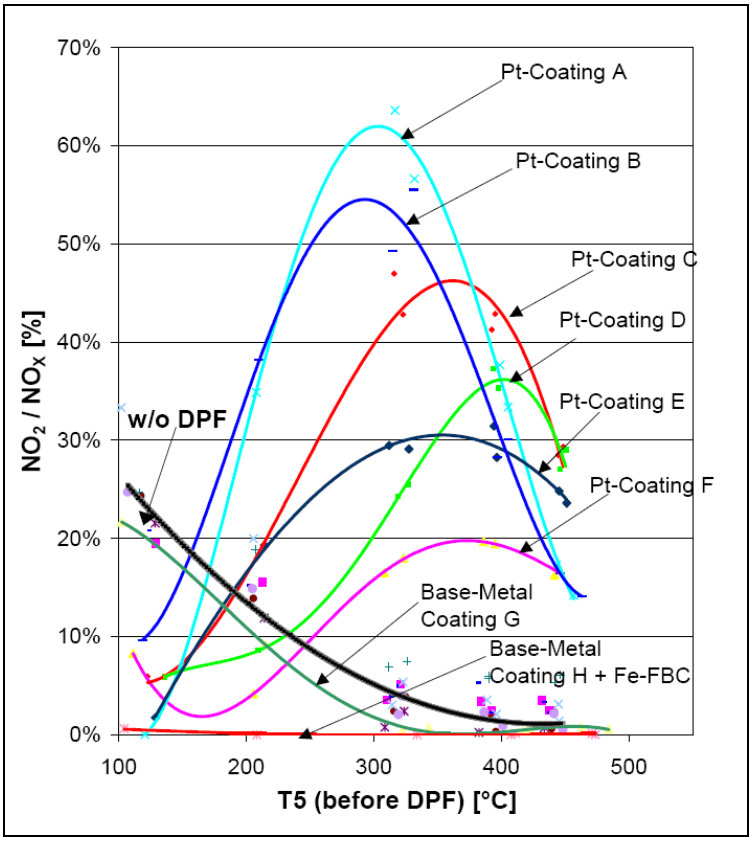

Figure 89. *NO_2/NO_X ratio with different DPF coatings (source: Czerwinski et al., 2006).*

Although not discussed by the authors of the mentioned study, it could be hypothesised that a reduction of NO_2 to NO can only be made in the presence of reducing agents in the exhaust, since the equilibrium for the NO_2/NO_X ratio is very high at 100ºC.

Within the framework of the testing on in-use emissions from light-duty vehicles that was carried out in the Swedish IUC programme during 2007, both NO and NO_2 emissions were measured in parallel. These results are most likely the most comprehensive database on NO and NO_2 emissions from modern cars available to this date. A summary of the results from these tests are shown in **Figure 90**. Each bar in the graph represents the average for all tested cars of the same car model. In total, the graph represents 79 individual cars.

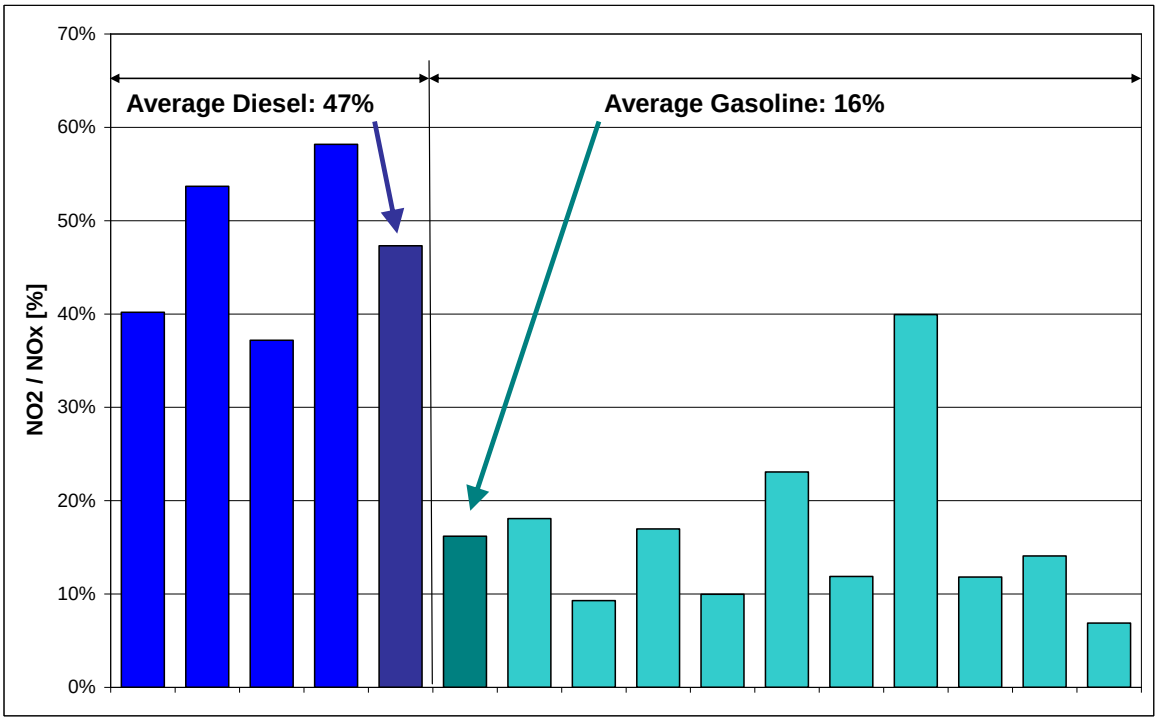

Figure 90. *NO_2 emissions relative to NO_X emissions during Type I test, average values for different vehicle types; based on Swedish IUC tests in 2007. (79 vehicles in total).*

As can be noted in **Figure 90**, the average NO_2/NO_X ratio for diesel cars is about a factor 3 higher than for petrol-fuelled cars. The relative scatter between the test results for different car models are much greater for petrol-fuelled cars ranging from about 7 % to 40 %. The highest level is actually slightly greater than the lowest level for the diesel cars. Since the NO_X emissions are generally much higher for diesel cars, the difference in absolute emissions is much greater.

The fundamentals regarding oxidation of NO to NO_2 for petrol-fuelled cars and diesel-fuelled cars respectively explain the differences between these types of cars noted in **Figure 90**. Diesel cars have lower exhaust temperature and excess oxygen in the exhaust, while these conditions are less frequent in petrol cars.

Since "real world" NO_X emissions (see Chapter 4.8) seems to be much higher than emission levels originating from the NEDC certifications cycle – the in-use "real life" emissions of NO_2 from diesel cars may also be higher than estimated from the use of results from the NEDC test cycle alone.

4.12 Some results on fuel-flexible cars and a biogas-fuelled car

In March 2008, a very comprehensive Swedish project on emissions from alternative fuels in passenger cars was finalised. The project was funded by the Swedish Road Administration and the project partners were Stockholm University (coordinator), AVL MTC and Ecotraffic. Characterisation of emissions was carried out on one bi-fuel vehicle and two fuel-flexible vehicles run on bio-based fuels such as biogas and gasoline/ethanol fuel. The project was focused on the characterisation both regulated and (mainly) on unregulated emission compounds generated under different testing conditions. The testing conditions investigated were two different driving cycles, i.e. the new European driving cycle (NEDC), the Artemis driving cycles. Furthermore, two testing temperatures (+22°C and -7°C) were used in the NEDC. In a subproject the catalyst durability regarding oxidation of methane was studied on ten cars.

Some vehicle parameters of the three test vehicles, in the heading of are provided in **Table 19**. The headings define the denotations (FFV1, FFV2 and BFV) for each vehicle used in the following.

Table 19. *Vehicle specifications.*

Parameter / **Car**	**FFV1**	**FFV2**	**BFV**
Car, model	Saab 9-5 Biopower	Volvo V50 1,8 F	BFV Punto
Model year, month	2005-12	2005-12	2004-12
Certification	Euro 4	Euro 4	Euro 4
Odometer (km)	34 354	11 826	20 696
Inertia mass (kg)	1 670	1 420	1 130
Engine type	L4[b]	L4[b]	L4[b]
Displacement (cm^3)	1 985	1 798	1 242
Power (kW)[c]	110/132	92	44/38
Torque (Nm)[c]	280	165	102/88
Max BMEP[c,d] (bar)	17,7	11,5	10,3/8,9
Compression ratio	8,8:1	10,8:1	9,5:1
Gearbox	M5[f]	M5[f]	M5[f]
Fuel	E5/E85	E5/E85	E5/methane

Notes:

[a] More information on the tested cars can be obtained from the Swedish Road Administration (www.vv.se) or from Bilvision (www.bilvision.se).

[b] In-line 4-cylinder engine (L4)

[a] Higher numbers are for E85 (Saab) or petrol (Fiat); lower for petrol (Saab) or CBG/CNG (Fiat)

[b] Brake mean effective pressure (BMEP)

[c] Fuel consumption: average, city and road.

[d] Manual, five-speed transmission (M5)

Since the cars were tested in the three Artemis test cycles, emission results for each part of the cycle are also presented. These are (with denotations in parenthesis): Artemis Urban (AU), Artemis Rural (AR) and Artemis Motorway (MW).

The fuels tested were: commercial Swedish petrol with 5% ethanol (E5), summer quality of ethanol fuel (E85), winter quality of the ethanol fuel (E70) and compressed biogas (CBG).

It should be noted that data are missing in some cases in the diagrams below due to measurement problems. This is indicated by the denotation m.v. (missing value).

4.12.1 Particle mass emissions

PM emissions of from the three test vehicles are presented in **Figure 91** (FFV1), **Figure 92** (FFV2) and **Figure 93** (BFV). A general conclusion is that the PM emissions were low for all vehicles in the tests at 22°C. In most cases, the PM emissions were below 1 mg/km in these test cycles, i.e. at about the level from diesel-fuelled cars with DPF. The only exception is that higher emissions can be seen in the Artemis motorway test cycle, where PM levels up to 5 mg/km were seen. For comparison with diesel cars with DPF, we should note that also these cars have higher PM emissions in the Artemis test cycle than in the NEDC test cycle, as the results from the Swedish IUC programme shown above (**Figure 49**).

At the low ambient temperature (-7°C) in NEDC, the PM level was higher for all vehicles than at +22°C in the same test cycle. There is a trend for somewhat higher PM emissions with the ethanol fuels (E70 and E85) in comparison to petrol in the fuel-flexible cars. For the BFV car, tests on CBG fuel always give lower PM emissions than the tests running on E5 fuel.

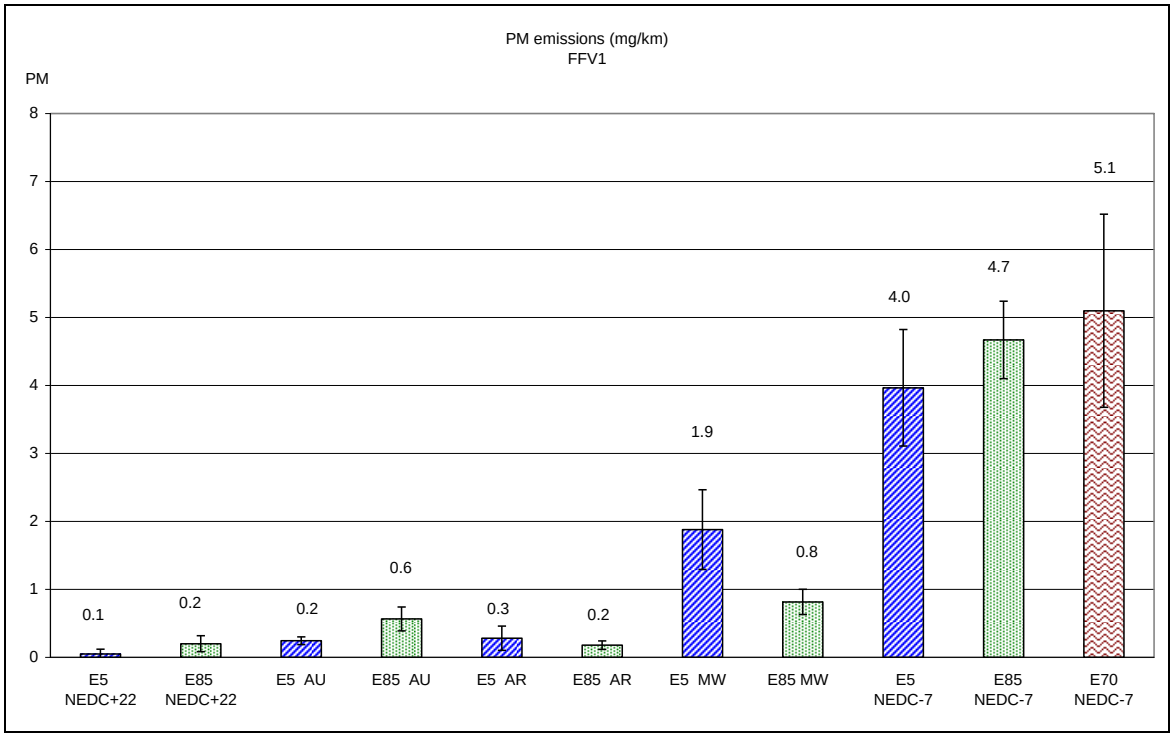

Figure 91. *PM emission from FFV1 (adapted from Westerholm et al., 2008).*

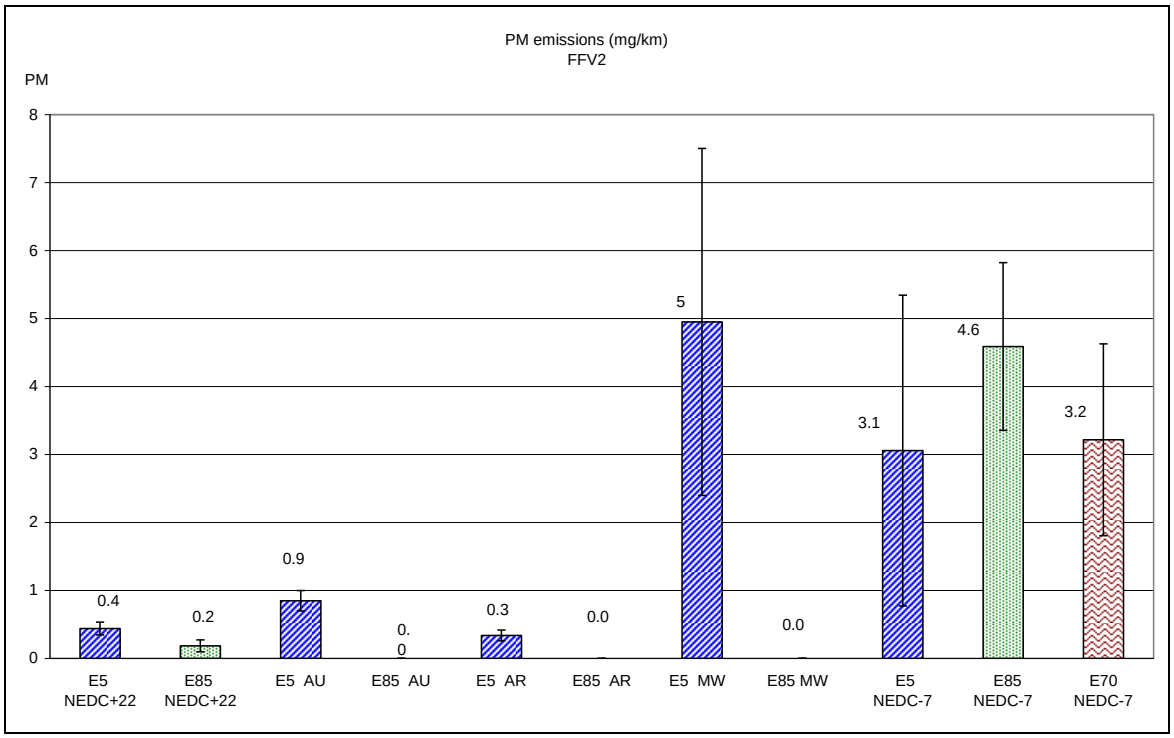

Figure 92. *PM emission from FFV2 (adapted from Westerholm et al., 2008).*

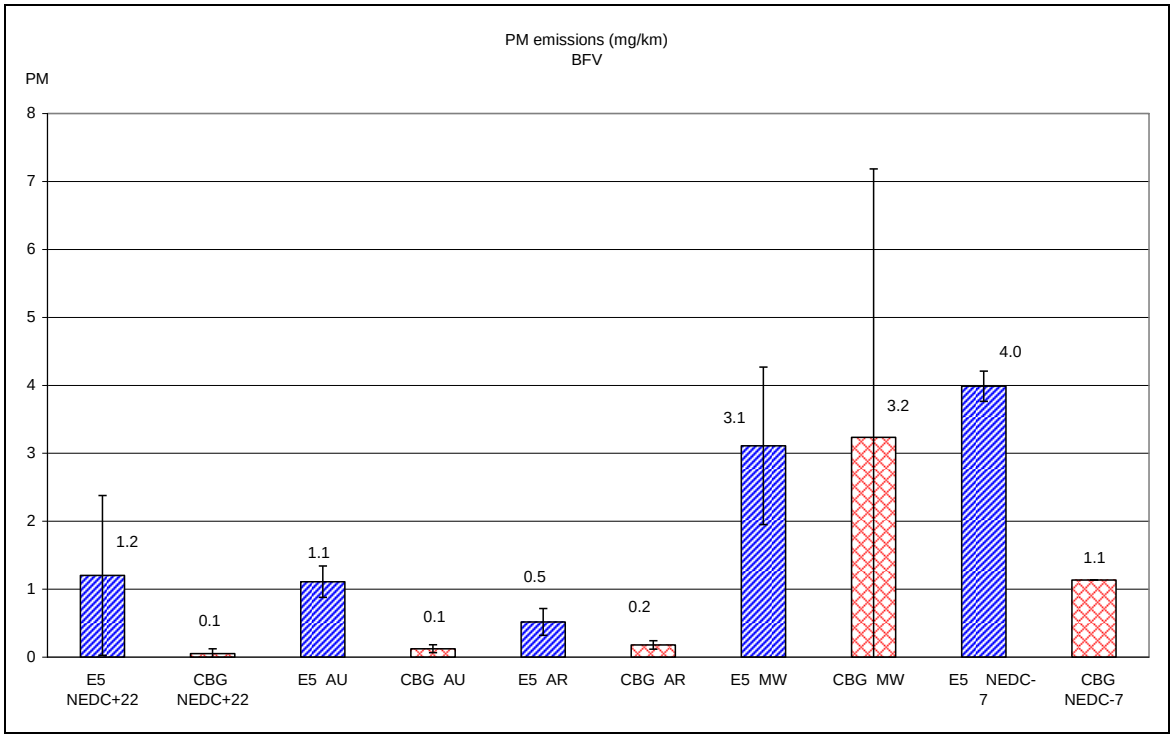

Figure 93. *PM emission from BFV (adapted from Westerholm et al., 2008).*

4.12.2 Particle number emissions

PN emissions were measured using PMP methodology and the ELPI instrument. Good correlations between PN_{PMP} measurement and PN_{ELPI} measurement were seen in most cases, with the PN_{ELPI} emissions somewhat higher than the PN_{PMP} emissions due to that this instrument measures particles down to 7 nm in comparison to the CPC instrument, which has a prescribed cut point of 23 nm. Due to the great number of data, only two examples of results from PN measurements (FFV1 and FFV2) is shown here (**Figure 95** and **Figure 95**). Note that the scale on the y-axis is logarithmic, which is a common procedure for presenting PN emission data.

Most of the results in the various driving cycles are quite similar at +22ºC for the FFV1. In absolute levels, the results are at 5×10^{11} particles/km, i.e. below the limit at 6×10^{11} particles/km set for diesel cars in Euro 5b and Euro 6. As discussed previously, no limit has yet been set for cars with positive injection for Euro 6. This limit will be set, at the latest, by September 1, 2014. At -7 ºC, the PN level is more than one order of magnitude higher than at +22ºC, indicating the great impact of ambient temperature on PN emissions for this car.

The results on the FFV2 car are quite different to those for the FFV1 car. First, the level on E5 in NEDC is at 6×10^{11} particles/km, i.e. the limit for diesel cars in Euro 6. All the levels in the Artemis driving cycles are significantly higher and up to 6×10^{12} particles/km in the most severe Artemis motorway driving cycle. In contrast, the results on E85 are much lower than for E5. All the PN levels are far below 6×10^{11} particles/km, except for the Artemis motorway, where this level is reached. The levels at -7ºC are also elevated for this car on all fuels but slightly lower than for the FFV1 car. The difference between the three fuels is relatively small at -7ºC, but with a tendency for higher level for E85 and E70 in comparison to E5.

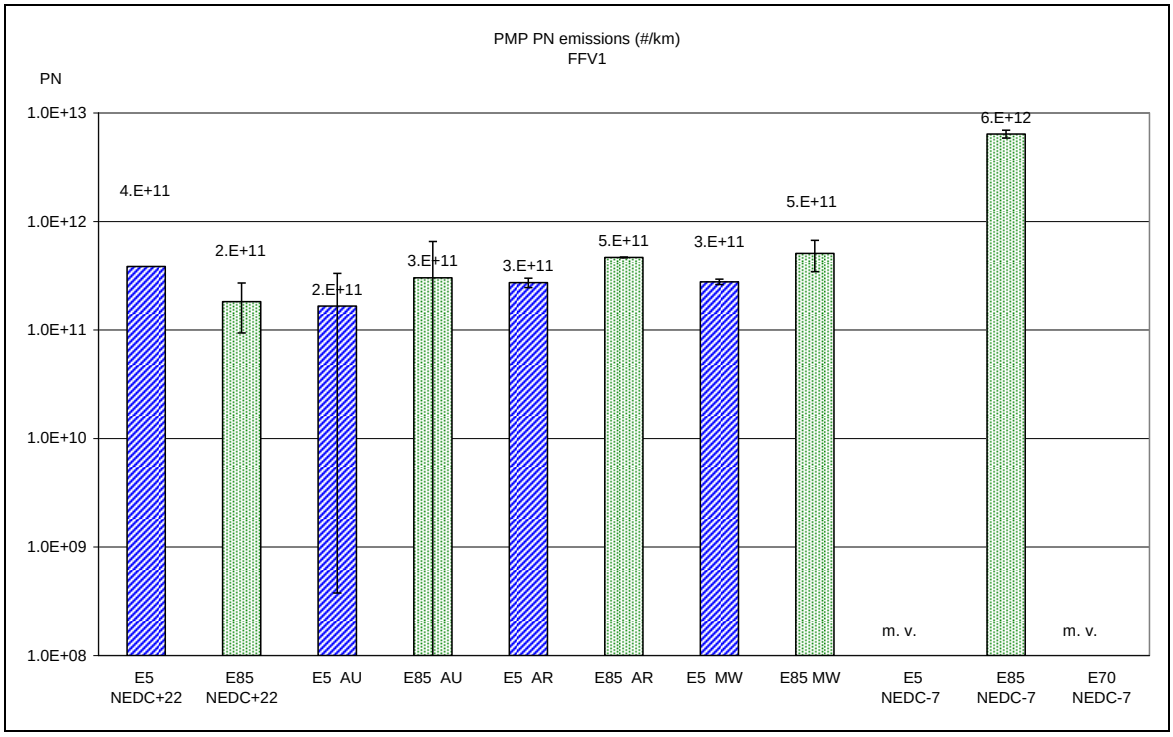

Figure 94. *PMP PN emission from FFV1 (adapted from Westerholm et al., 2008).*

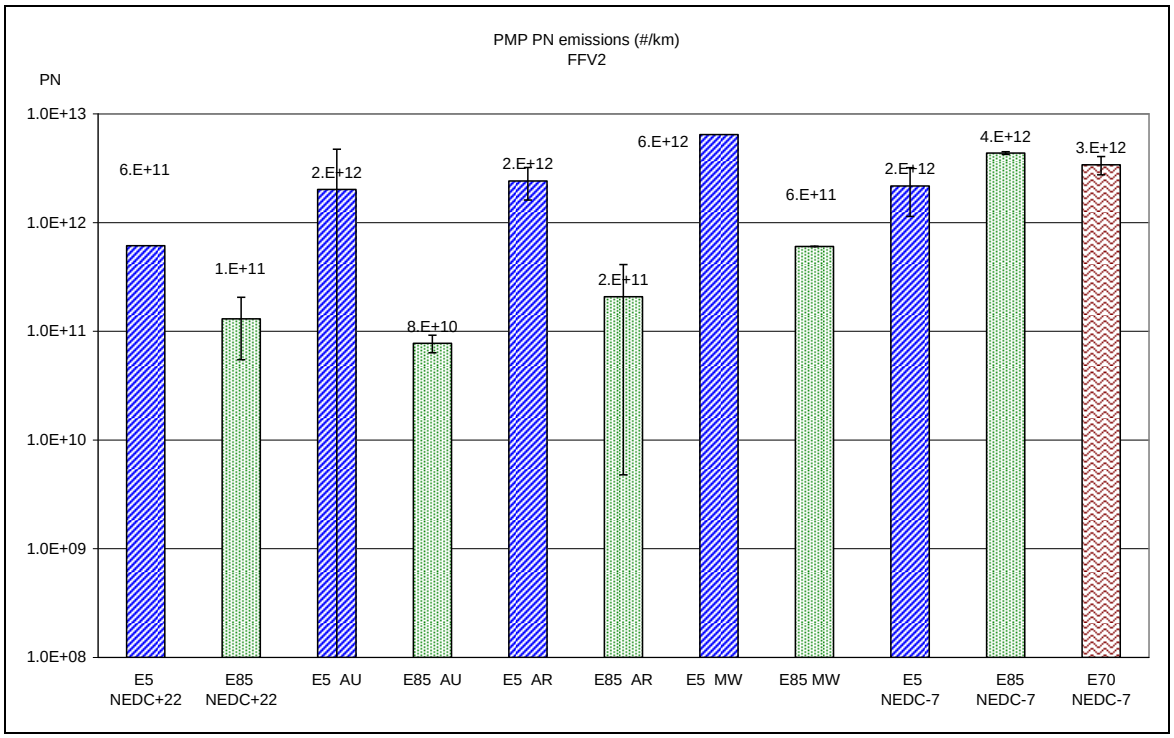

Figure 95. *PMP PN emission from FFV2 (adapted from Westerholm et al., 2008).*

The problem regarding comparison of the levels on the FFV cars above with diesel cars is evident, since there data on diesel cars tested at -7ºC are limited. One study where particle number emissions were measured was a study funded by the Swedish Road Administration, which was carried out by Ecotraffic (Ahlvik, 2002). It should be noted that PN emissions were measured at that time with an ELPI instrument and no PMP sampling was used (this was before the PMP programme was started). Thus, the PN emissions are overestimated in comparison to those that would have been generated by the PMP methodology. Results from this project on PN emissions are shown in **Figure 96**. The two petrol fuelled cars are denoted SI-P and SI-G respectively, the diesel car with DPF is denoted CI-CR/DPF and the diesel car without DPF is denoted CI-UI/HP.

In **Figure 96**, it can be noted that the PN emissions in NEDC at -7ºC are significantly higher than those at +22ºC. Noting that the measurement methodology used in that project overestimates the PN emissions, the level by using a PMP methodology would probably be lower than the limit in Euro 6 and thus, about one order of magnitude lower than the FFV cars discussed above. The results compared here indicate that the PN level for diesel cars with DPF could be significantly lower than for petrol at lower ambient temperatures. However, for the moment, there are no plans in the EU to regulate PN or PM at low ambient conditions.

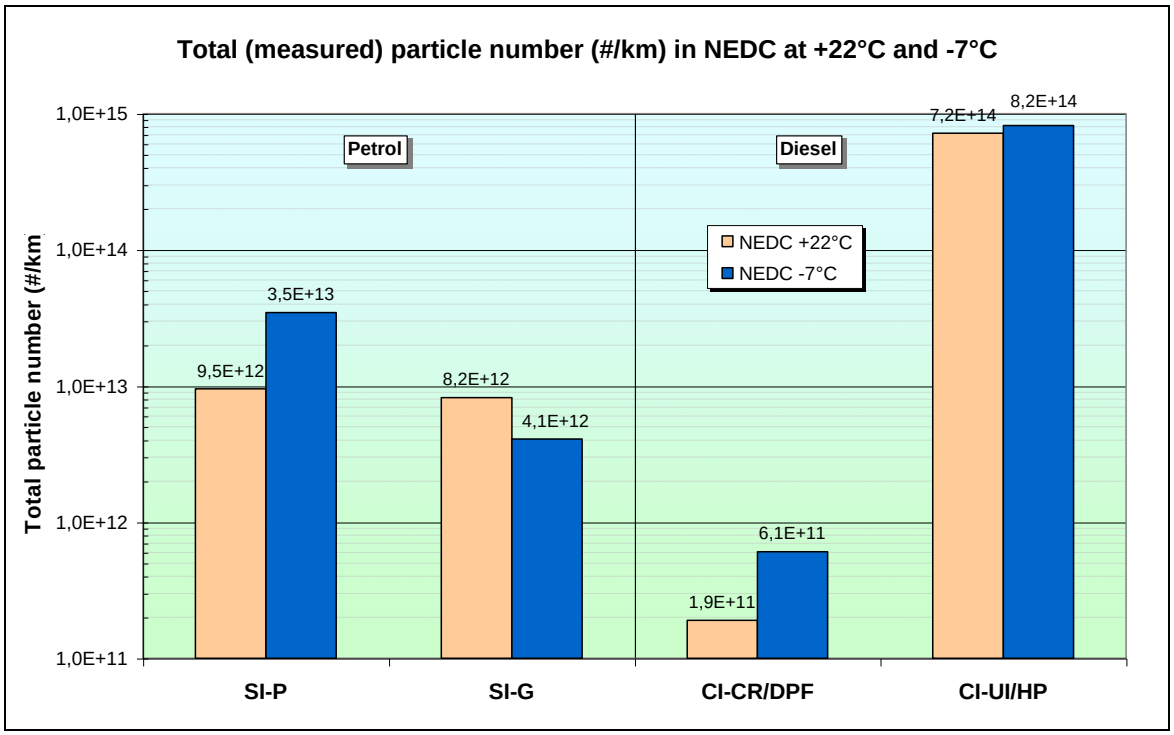

Figure 96. *Total particulate number in NEDC (adapted from Ahlvik, 2002).*

As noted many times previously in the present study, a DPF has a very great impact on PN emissions. In **Figure 96**, the relative difference between the car with and without DPF is in the order of three magnitudes.

The levels for the petrol-fuelled cars in this study were considerably higher than all the other results shown and discussed above. The reason is probably that a high share of these emissions are volatiles, which will be removed by the PMP dilution and conditioning.

4.12.3 Aldehydes

High emissions of aldehydes, e.g. formaldehyde and acetaldehyde, have since long been associated with alcohol-fuelled cars. Acetaldehyde dominates the aldehyde emissions from ethanol-fuelled vehicles, while formaldehyde is the dominating compound for methanol-fuelled cars. Aldehyde emissions have also in the past been associated with diesel engines so a qualitative comparison between these two types of vehicles is of interest.

As an example of the level of aldehydes from E85 cars, **Figure 97** (acetaldehyde) and **Figure 98** (formaldehyde) are shown for the FFV2 car.

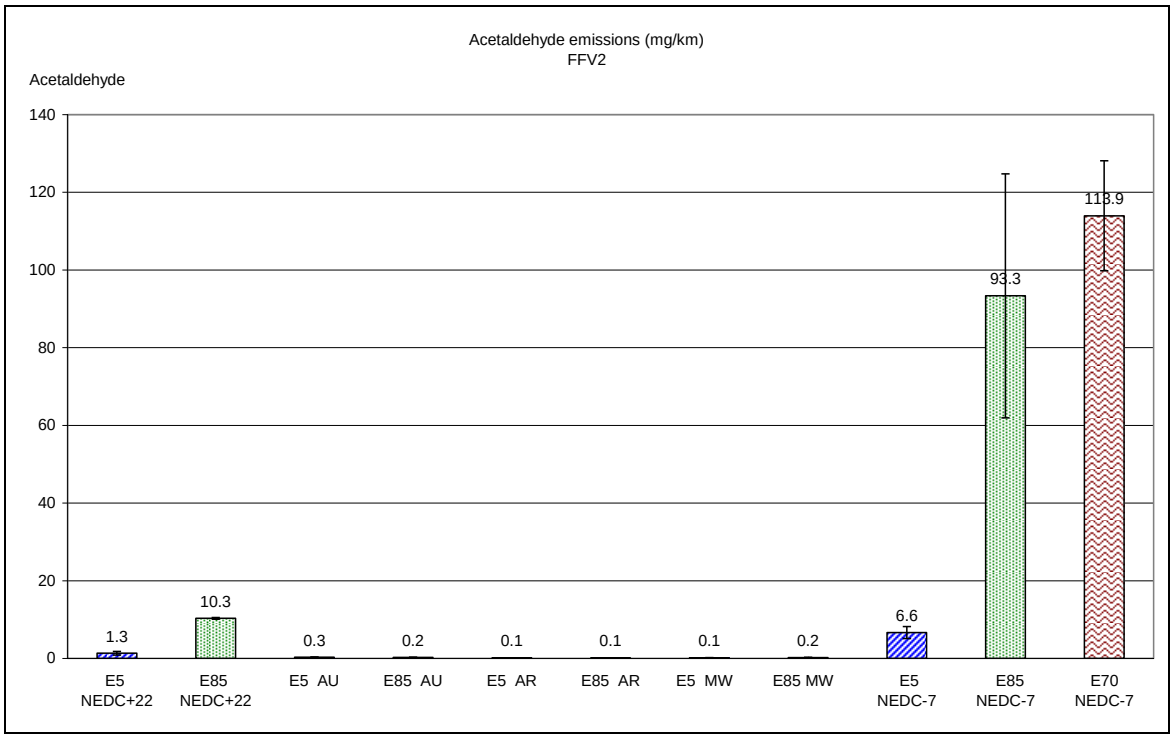

Figure 97. *Acetaldehyde emission from FFV2 (adapted from Westerholm et al., 2008).*

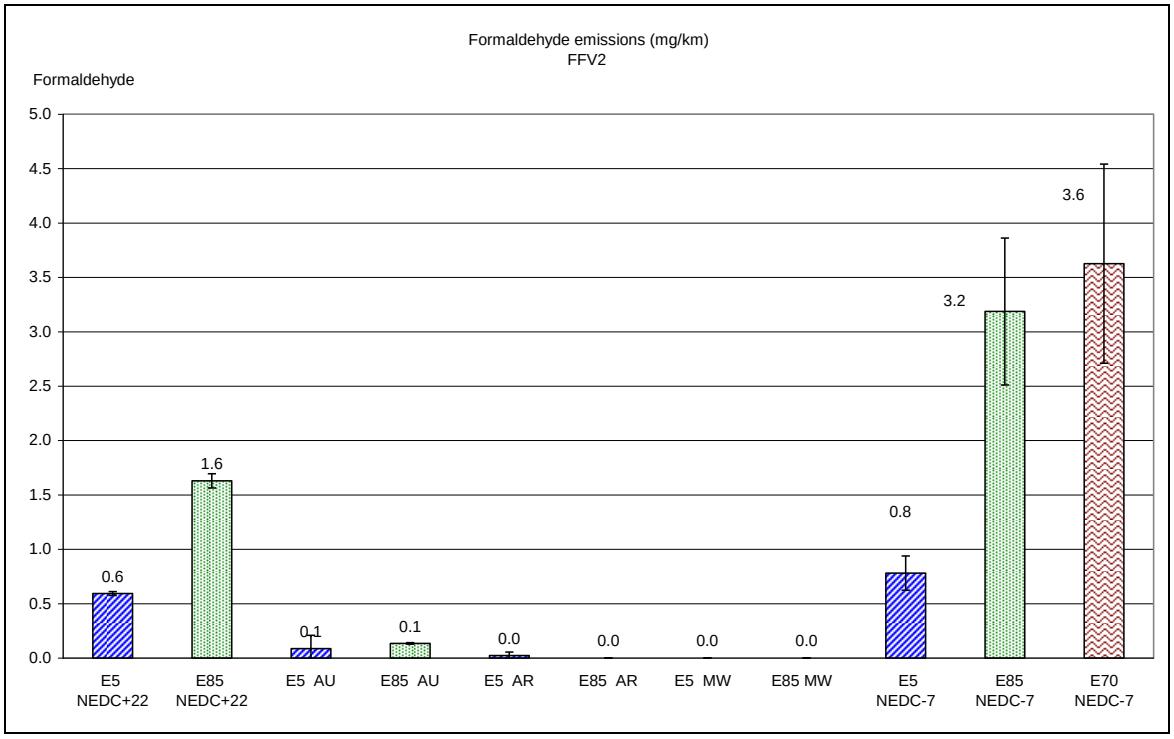

Figure 98. *Formaldehyde emission from FFV2 (adapted from Westerholm et al., 2008).*

The results in the NEDC test cycle at +22°C clearly show that the aldehyde emissions are greater for E85 than for petrol. The aldehyde emissions are far lower in the Artemis test cycles and sometimes below the detection level.

At the lower ambient temperature (-7°C), aldehyde emissions increase significantly for the E85 cars when fuelled with ethanol fuel. This is particularly apparent for acetaldehyde emissions where levels around 100 mg/km are seen. Aldehyde emissions increase with increasing ethanol content (E70 vs. E85) in the fuel. Also the emissions of acetaldehyde are with the E5 fuel are higher at -7°C than at +22°C.

Results on aldehyde emissions from modern diesel cars tested also at low ambient temperatures are relatively few. Also in this case, the previously cited report from Ahlvik (2002) gives a representative level of modern diesel cars with and without DPF. The results are shown in **Figure 99**.

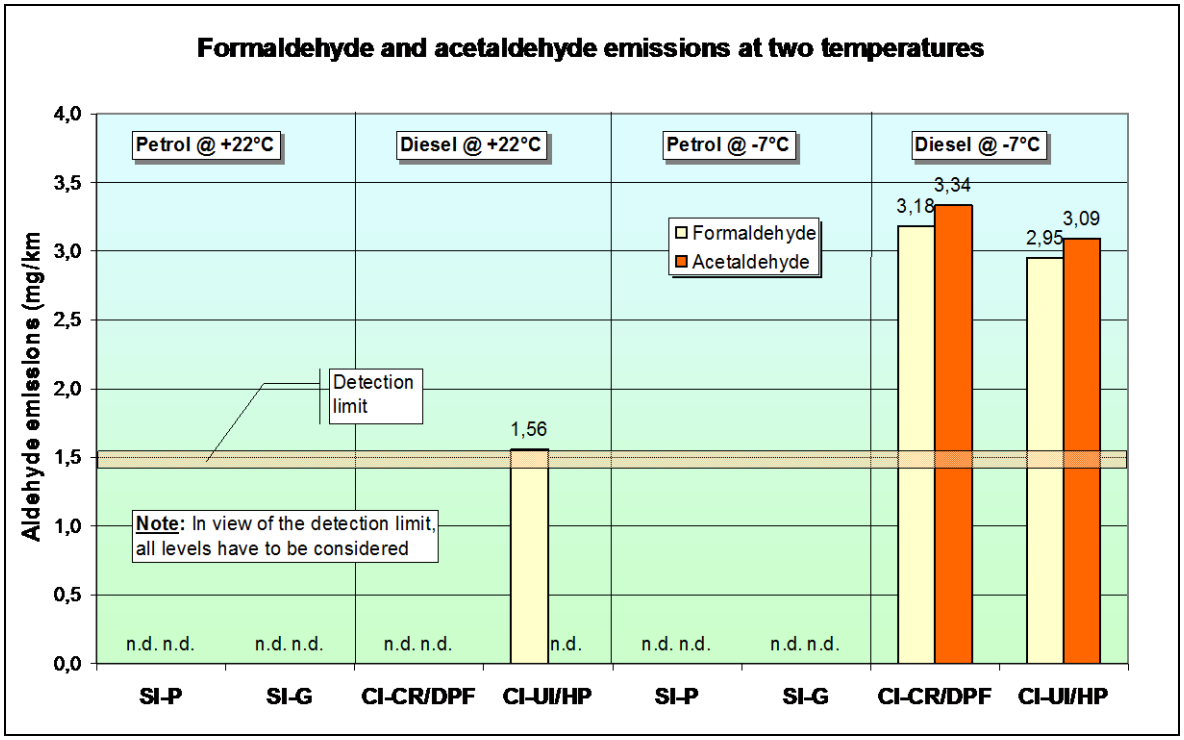

Figure 99. *Aldehyde emissions (Adapted from Ahlvik, 2002)*

As can be noted in **Figure 99**, the aldehyde emissions are very low for both petrol and diesel fuelled cars at +22ºC. Only in one case, i.e. for the diesel car without a particle filter (CI-UI/HP), the measured level reach the detection level of the measurement method used that corresponds to 1,5 mg/km. At -7 ºC, both petrol cars have aldehyde levels below the detection level. This is in line with the observations in the previously discussed data in **Figure 97** (acetaldehyde) and **Figure 98** (formaldehyde). The two diesel cars in shown **Figure 99** have an aldehyde level of about 3 mg/km at -7 ºC, i.e. twice the detection level. For formaldehyde emissions, 3mg/km is on a similar level as for the E85 cars on ethanol fuel. One the other hand, the level for acetaldehyde emissions, at 3 mg/km, were significantly lower for the diesel cars than the level of about 100 mg/km for E85 and E70.

Concluding remarks are that aldehyde emissions are low for both petrol and diesel cars, with a trend for an advantage for petrol cars. E85/E70 gives higher emissions of aldehydes – and acetaldehyde in particular – compared to the formerly mentioned fuels. In the past, aldehyde emissions were considered a major problem area for diesel cars. Apparently, this is not the case any more. Improvements in engine-out levels in combination with the in-

troduction of oxidation catalysts are most likely the reason for the low levels on the two cars tested in the study discussed above. Note that the DPF used on one of the cars did not have a catalytic coating as most of the DPFs today do have. Presumably, the aldehyde levels would be lower for a catalytic DPF but no data are available for such cars at low ambient conditions. Although unregulated gaseous emissions were not the topic of this report, it could be noted that the report by Ahlvik (2002) found that practically all other unregulated gaseous emissions that pose health hazard were lower for the diesel cars than the petrol cars.

4.12.4 PAH emissions

It is important to note that, in the following, only polycyclic aromatic hydrocarbons (PAH) with three and more aromatic rings (tri+ PAH) are summarised as total PAH and not those with two and more rings (di+ PAH), which is often the case. The reason for chosing tri+ PAH only is that it is these heavier PAHs those who are associated with cancer risk, which is not the case for di-aromatic PAH.

The results on PAH emissions from the E85 cars were somewhat unexpected. As for most of the other unregulated emissions, PAH was not the main topic of the present study but, since this was one of the main findings in report by Westerholm et al. (2008) the results should be discussed.

The results on PAH emissions are shown in **Figure 100** (particulate-associated PAH) and **Figure 101** (semivolatile-associated PAH).

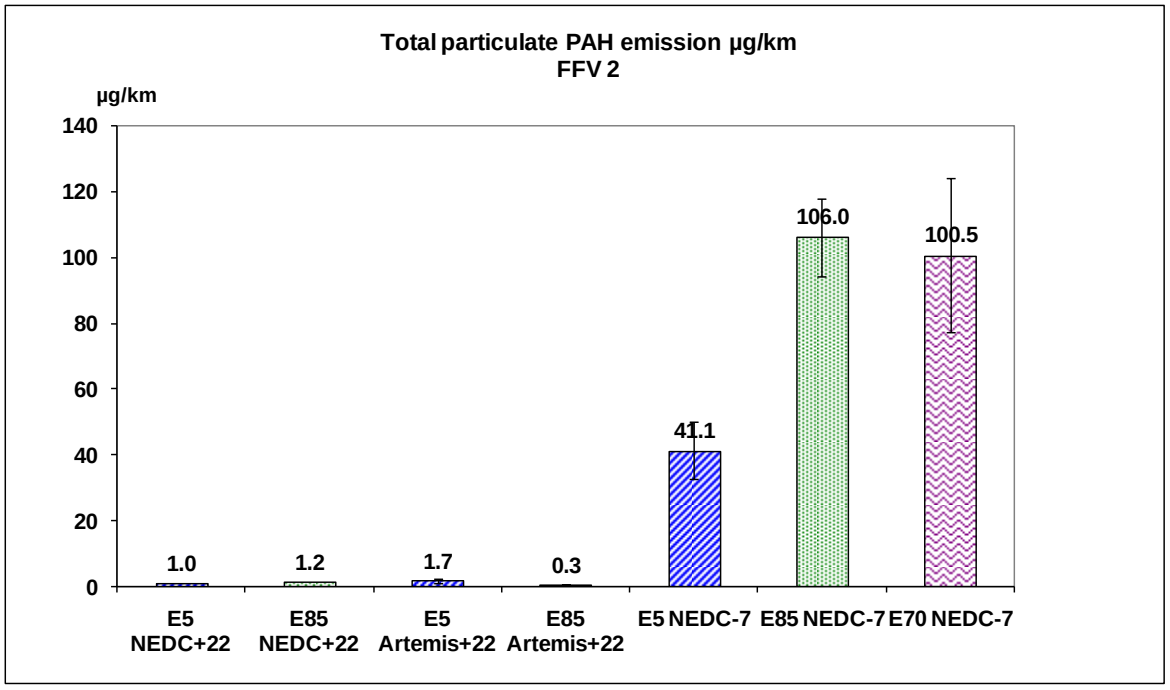

Figure 100. *Total particulate-associated PAH emissions (µg/km), FFV2 (adapted from Westerholm et al., 2008).*

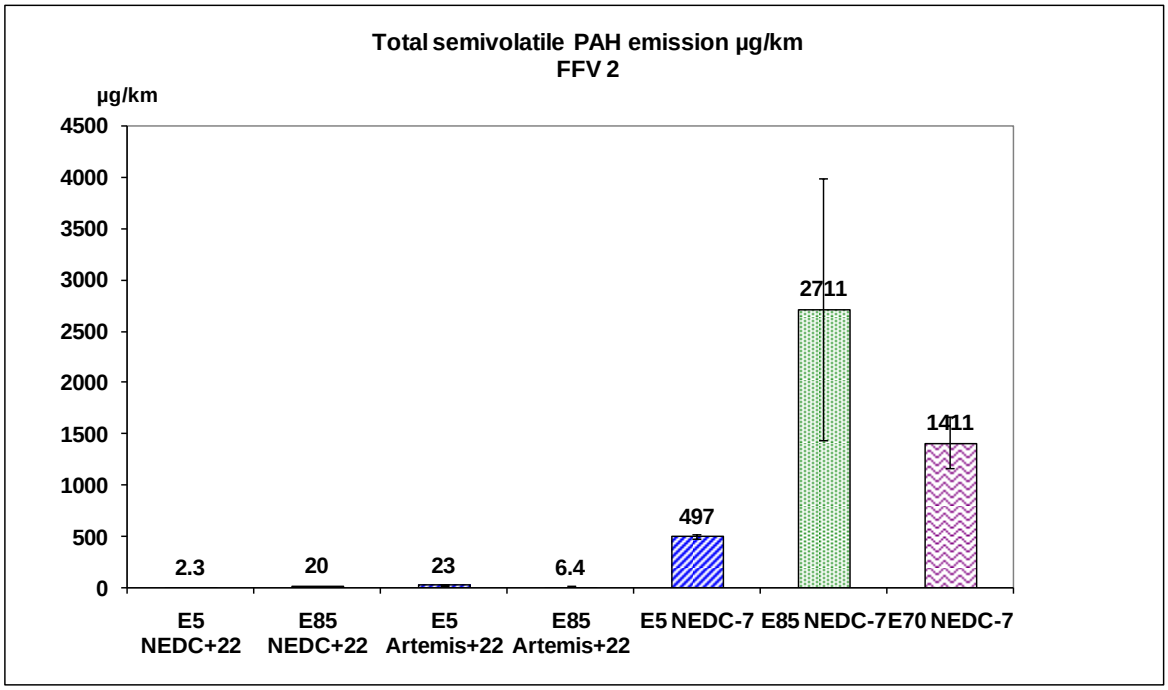

Figure 101. *Total semivolatile-associated PAH emissions (µg/km), FFV2 (adapted from Westerholm et al., 2008).*

At +22ºC, the particulate-associated PAH emissions are very low in all test cycles (**Figure 100**), while the level is higher for the semivolatile-associated PAH emissions in the Artemis test cycle and with E85 in the NEDC test cycle (**Figure 101**). At -7ºC, particulate-associated PAH emissions increase considerably for petrol and even more so for the ethanol fuels, where levels of about 100 µg/km are seen. The increase is even more dramatic for the semivolatile-associated PAH. Here, levels up to 2700 µg/km are seen. The higher ethanol content, the higher PAH emissions.

In the previously cited report by Ahlvik (2002), the emissions were denoted polycyclic aromatic compounds (PAC) emissions to reflect the fact that some of the compounds measured were not pure hydrocarbons. This is in fact true also in the study by Westerholm et al. (2008). Also in study by Ahlvik (2002), most of the PACs are hydrocarbons (PAH). However, the analysed set of PAH/PAC was not exactly the same in both studies. Nevertheless, although the comparison cannot be perfect, the relative difference in results is substantial. This can be seen in **Figure 102**.

Figure 102 shows that the PAC emissions for the diesel car with DPF (CI-CR/DPF) are extremely low at all tested conditions. A level of the sum of particulate-associated and semivolatile-associated PAC at about 1 µg/km in total is barely above the detection limit. In contrast, the PAH/PAC emissions from petrol and E85 cars are several orders of magnitude higher. A simple conclusion would be that the problem of PAH/PAC emissions no longer should be associated with diesel cars with DPF but that the focus rather should be elsewhere.

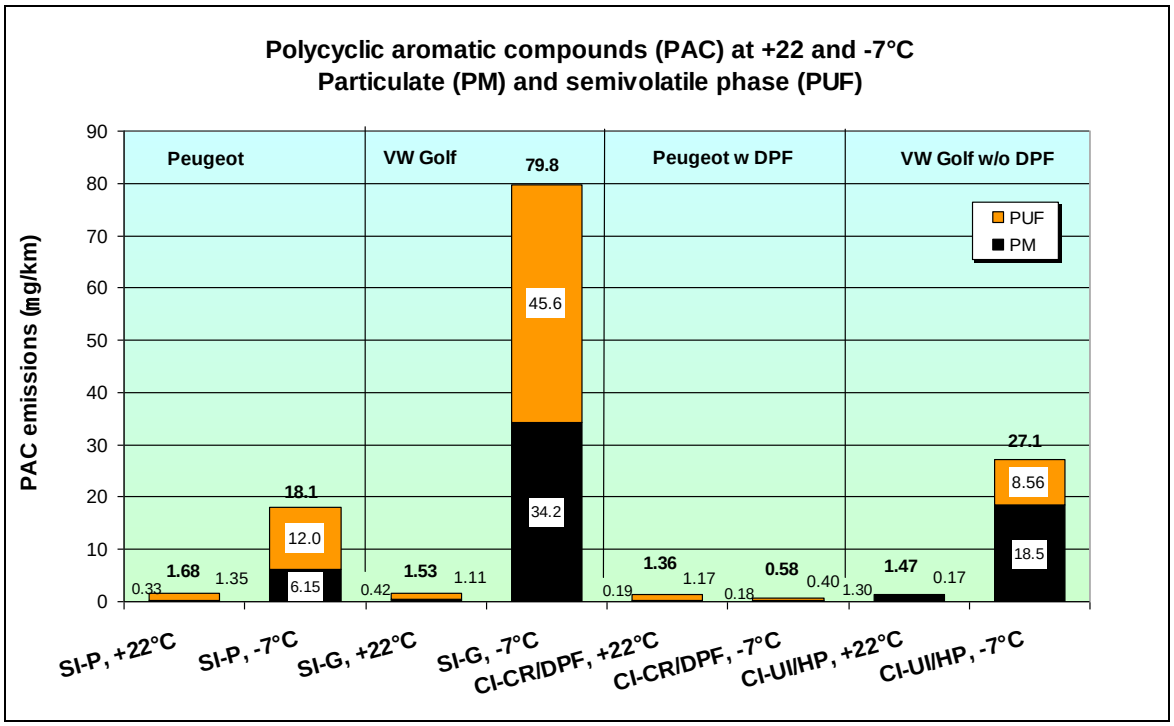

Figure 102. *PAC emissions(Adapted from Ahlvik, 2002).*

4.12.5 Catalyst durability and methane emissions

Methane emissions was not of interest in the present project but it could be noted that all of the, in total nine biogas-fuelled cars, that had high odometer readings also had very high methane emissions when run on biogas, indicating that the catalyst was not working properly. When tested on petrol all these cars had low methane emissions. In contrast to the results on biogas, the only E85 car tested had low emissions on both fuels.

5 CONCLUSIONS

In the present report, a number of, sometimes very different, topics have been addressed. In many cases, these topics are very different and every now and then, it might be quite difficult to follow the main thread in the presentation of the results. Furthermore, most of the discussion is integrated in each section of the report. Therefore, it was chosen not to try to summarise the discussion in a specific chapter such as this but to only list the most important conclusions instead.

Conclusions from this study may be summarized as presented below:

- Particle emissions are influenced by operational factors such as speed, engine load, or ambient temperature for which petrol cars shows a greater dependence. In some operational modes particle number emissions may reach the same range as those found for non-DPF diesel cars.
- Driving conditions shows different effects on solid particle number emissions for passenger car diesels in respect to heavy duty engines (HDE). At urban conditions, the number emissions scale with engine/vehicle size whereas at highway conditions HDE emits more or less as many solid particles as a passenger car per distance travelled or up to one order of magnitude lower emissions per unit of fuel consumed. This illustrates different diesel engine tuning depending on the vehicle application.
- The fraction of condensed organic components is highly variable (depends on, for example, engine technology, driving conditions, or sampling procedures) normally composes 20 to 50% of the particulate mass collected on filters. Diesel PM has a considerable higher fraction of elemental carbon than organic carbon as compared to petrol vehicles.
- Strong indications point to the importance of lubrication oil to the emission of nucleation mode particles and the portion of the particle emission from lubricating oil may very well increase as the fuel sulphur content is reduced.
- Nucleation-mode particles (<100 nm diameter) are to a large extent composed by condensed material of which lubricating oil is a major component whereas particles in the accumulation mode (100 nm-1 000 nm) are normally composed by a higher fraction of elemental carbon.
- Despite the reductions of NO_x emissions that have been achieved for diesel cars their emissions are still considerably higher as compared with those of petrol cars. However, the introduction of low sulphur diesel fuel allows the use of NO_x-reduction catalysts that eventually will reduce the emissions to the same levels as for petrol cars.
- The share of NO_2 emissions of the total NO_X emissions is considerably higher for diesel cars in comparison to petrol cars. This – in combination with higher total NO_X emissions – gives much higher absolute levels of NO_2 for the diesel cars. Although NO is relatively rapidly oxidised to NO_2 in ambient air, higher tailpipe NO_2 emissions can be of importance in environments with low ventilation, such as, e.g. tunnels, mines and parking houses.

- The emissions of NO_X increase for biodiesel compared to conventional diesel fuel, while most other emission components decrease. A shift in injection timing cause most of NO_X increase but modern injection systems do not show this behaviour. Still there is a small increase in NO_X emissions at some operating points even with modern fuel injection (common rail). With future development, it is anticipated that this increase could be eliminated.
- The increase in PN emissions with biodiesel seen in some studies is due to inadequate sampling. The smallest particles are not solid but volatile and will be reduced by the new sampling method in the PMP measurement protocol.
- Currently, there is a problem to use biodiesel in combination with DPFs on light-duty vehicles. Synthetic diesel fuels and hydrogenated bio-oils are not plagued with this problem.
- Synthetic diesel fuels, such as GTL and BTL, but also hydrogenated bio-oils have lower emissions than conventional diesel fuel. This conclusion is valid for most emission components and in contrast to biodiesel, the NO_X emissions are also lower in most studies.
- The use of ethanol fuel (E85 and E70) in fuel-flexible vehicles (FFVs) gives much higher emissions of acetaldehyde than petrol-fuelled cars and about similar level of formaldehyde as diesel-fuelled cars. There was also an increase of PM and PN for ethanol in comparison to petrol at low ambient temperatures.
- Somewhat surprisingly, the emissions of polycyclic aromatic hydrocarbons (PAH) from the FFVs were much higher for ethanol fuel than for petrol at low ambient temperatures. In contrast, the PAH emissions for modern diesel cars with DPF are very low at low ambient temperatures.

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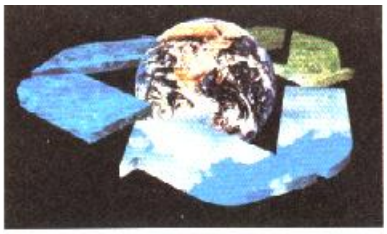

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