Subject: Recommended control measures for reducing emissions of persistent organic pollutants from mobile sources

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For purposes of this document "mobile sources" means vehicles driven by engines burning petrol or diesel fuel. Though being relevant sources of air pollutants aviation and seagoing ships are not covered.

1 Emission Control Technology for Vehicles

Due to incomplete combustion of fuel in the engine combustion chamber or due to formation of new chemical compounds exhaust fumes may contain quite a number of hazardous substances. Among those newly formed substances are polynuclear aromatic hydrocarbons (PAH) and chlorinated dioxins and furans (PCDD/Fs) which have been identified as unintentionally produced persistent organic pollutants (POPs) in annex III under the protocol.

An ever increasing number of vehicles entails increasing air pollution problems particularly in urban areas. Concern about impact on human health and the environment sparked development of technical measures to reduce air pollution from traffic in the beginning of the 1970s. Since then emission standards and standards for fuel quality were continuously tightened in developed countries to keep pace with a steadily increasing number of vehicles and to mitigate air pollution problems from these diffusive sources.

The main focus of technological developments was however not on the reduction of POP substances but rather on precursors for ground level ozone formation, i.e. NOx and volatile hydrocarbons (VOC); or carbon monoxide (CO) and particulate matter (PM).

1.1 Petrol (gasoline) cars

In order to reduce the emissions of HC, CO and NOx in vehicle exhaust three-way catalytic converters have widely been implemented in automotive engines (passenger cars, light duty vehicles) during recent years. For proper functioning the converter requires a specific ratio or air/fuel (14.7:1 or lambda = 1). This is accomplished by an electronic control unit in the exhaust manifold which continuously analyses surplus oxygen in the exhaust leaving the combustion chamber. That catalytic device effectively reduces emissions of hydrocarbons, i.a. PAH which may be formed during the combustion process.

Air pollution persists for cold starts of the engine when the converter has not yet reached its operating temperature (imperfect burning). Under certain operating conditions petrol engines with direct injection may produce elevated emissions of particulates as compared to extern
carburation. Properly maintained three-way catalytic converters prevent relevant tailpipe emissions of PAH along with emissions of other organic compound but particulate reduction devices may be required when emission limits are tightened.

Three-way catalytic converters have been fitted mandatorily to passenger cars in the EU since 1990. Similar obligations came into force back then in other UNECE countries (US, Canada) as well.

1.1.1 Halogen containing Fuel Additives

Since 1920s (alkyl) lead was added to petrol to boost octane levels (anti-knock) and to protect exhaust valve seats from excessive wear. But three-way catalytic converters, which are operated together with electronic fuel injection and combustion controlling facilities are vulnerable to lead poisoning\(^1\). To this end unleaded petrol had to be gradually phased out. For removal of lead with the exhaust halogenated scavenger substances were added to leaded petrol fuel. Since halogenated additives became redundant in unleaded petrol, declining market shares of leaded fuels were paralleled by a decline in PCDD/F emissions from automotive engines. According to the European Dioxin Inventory\(^2\) of October of 1999 dioxins and furans attributed to leaded gasoline accounted for 97.8 g [g I-TEQ/a], whilst for unleaded gasoline and diesel these figures were almost negligible (7.8 g/a and 5.5 g/a respectively).

1.1.2 Polynuclear Aromatic Hydrocarbons (PAH)

Although been formed mainly during combustion of diesel fuel PAH are also generated to a minor degree also during incineration of petrol, particularly at cold start conditions.

Properly maintained three-way catalytic converters prevent relevant tailpipe emissions of PAH along with emissions of other organic compounds.

1.2 Emissions from Diesel Engines

Diesel exhaust tends to be high in NO\(_x\) and particulates. Both are significant environmental pollutants. Unlike the exhaust of petrol engines, diesel exhaust contains much less unburned or partially burned hydrocarbons and carbon monoxide since Diesel engines are run under lean conditions (i.e. excess of, lambda > 1). Hence three-way catalytic converters can not be employed. Instead oxi-converters are installed to oxidize carbon monoxide and hydrocarbons (HC) incl. PAH. However, the main components of concern about diesel exhaust, NO\(_x\) and PM, are not - or just insufficiently- affected.

Some of the fuel droplets may never vaporize, and thus, never burn. But the fuel doesn't

\(^1\) Tetraethyl lead (TEL) and tetramethyl lead (TML) have formerly been widely used as additives in petrol (gasoline) to reduce “knock” in combustion engines and to lubricate internal parts of the engine. Along with that compounds brominated and chlorinated alkanes were added to gasoline acting as scavengers for lead radicals in order to avoid deposits of lead oxide on valves and spark plugs. However, beside intended formation of volatile lead halides exhausted from the combustion chamber along with other combustion products various side reactions are also entailed; among those formation of PCDD/Fs. Environmental and human health concern over the emission of lead and PCDD/F was one rationale for phasing-in unleaded gasoline in most industrialized countries.

\(^2\) http://europa.eu.int/comm/environment/dioxin/download.htm
remain unchanged; the high temperatures in the cylinder cause it to decompose. Later, these droplets may be partly or completely burned in the turbulent flame. If they are not completely burned, they will be emitted as droplets of heavy liquid or particles of carbonaceous material. The conversion of fuel to particulates is most likely to occur when the last bit of fuel is injected in a cycle, or when the engine is being operated at high load and high speed. At higher engine speeds and loads, the total amount of fuel injected increases and the time available for combustion decreases. Also, some of the lubricating oil on the cylinder wall is partially burned and contributes to particulate emissions. Finally, a poorly operating or mistimed fuel injection system can substantially increase emissions of particulates.

Beside vapour press of the compounds gas-particle phase distribution of semivolatile PAH depends also on engine loading\(^3\). Diesel fuelled engines produce 20 up to 200 times more particulate matter than petrol driven cars. To this end beside NOx, limits are set for particulate matter (PM). Diesel engines are substantial emitters of particulate matter (PM) particularly in urban areas. The PM fraction contains a large portion of semivolatile PAH found in diesel exhaust associated to the surface of that soot nuclei. Stepwise stricter emission standards and technological progress in control technology were established or are being phased-in for diesel-fuelled passenger cars and light duty vehicles in most UNECE countries.

However, emission control technologies for Diesel exhaust show complex trade-off effects for competing reduction targets (nitric oxides, particulate matter, fuel consumption).

### 1.2.1 Passenger cars and light duty vehicles

Initial progress in diesel emission control can been achieved through engine technologies. Smaller diesel engines can meet Euro 4 (see below) requirements in this way but heavy-duty engines require particulate filter systems.

#### 1.2.1.1 Engine modifications

The most effective engine modifications for cleaner diesel exhaust are

- advanced fuel injection systems
  (higher injection pressure leading to better atomisation and smaller fuel droplets, which vaporize more readily than larger ones)
- combustion chamber modification
  The position and angle of the injector in the cylinder head and the design of the nozzle are optimised to minimize emissions
- charge shaping
  rate of fuel (charge) injection can be controlled (shaped); e.g. pre-injection of a small amount of fuel initiating ignition and subsequent injection of the major amount of fuel into the flame
- increase of air motion
  better mixing of fuel/air

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lower oil consumption
reduction of lubricating oil that seeps past the piston rings into the combustion chamber

1.2.1.2 Particulate filters

For more stringent tailpipe emission reduction requirements particulate filter systems are required. PM are trapped in small channels of the filter. Since the system would become successively blocked during operation deposits have to be removed regularly.

Various techniques can be applied, e.g. burning by heating-up the ceramic matrix to burn the particles (> 500 °C in 500-1000 km intervals). This requires an increase of exhaust temperature (injection of fuel) or reduction of combustion temperature (fuel additives).

Filter traps not just reduce the total mass but also the emitted number of particularly small to medium size particles. While particulate mass reduction rates of about 90 per cent can be achieved the number of small particles (10-500 nm) is reduced by 99 per cent. Various types of particulate traps have already commercially been introduced in the passenger car market.

1.2.2 Diesel Heavy Duty Vehicles

In Europe almost all heavy trucks have Diesel engines. Particulate reduction by means of filter systems is easier to achieve since this category of vehicles have higher exhaust temperatures than passenger cars. This facilitates burning off particles from the filter surface. Particulate filters have been successfully passed testing in municipal bus fleets.

Successfully employed in commercial vehicles (urban bus fleets) is a continuously regenerating trap system (CRT) which combines oxidation catalytic converter (operating temperature of 300 C, electrical heating, pressure and temperature control devices) and particulate filters. This combination also considerably reduces carbon monoxide and gaseous hydrocarbons (e.g. PAH).

2 Emissions Standards

Emission standards set in various regions (US, Europe, Japan) are hardly to compare since test cycles, durability requirements, time lines for phasing-in, etc. do agree on the main lines, but may vary considerably in detail.

2.1 Petrol Driven Cars

Since phasing out of leaded petrol for on-road transport has been completed in almost all UNECE countries there is virtually no further need to add halogenated scavenger substances which in the past were a major source of unintentionally formed chlorinated and brominated dioxins and furans.

Unleaded fuel, along with well maintained catalytic converter systems should have rendered

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4 Combination of catalytic of oxidation and filter trap; the oxidation product NO2 is employed for continuous burning of the soot deposits at comparatively low temperatures of 200-450 °C

5 Progress in phasing out lead in gasoline, UNEP/GC.22/INF/23, 2002
vehicles equipped with internal combustion positive-ignition engines a negligible source of PCDD/F and PAH. Nevertheless some minor emission reductions may be achieved from improvement of e.g. cold start behaviour, etc. and substitutes for leaded aviation fuel.

### 2.2 Diesel Engines

Emission standards in various countries are hardly to compare due to diverging conditions of test cycles, classification of vehicle types, phasing in-periods, transition periods, etc. A comprehensive overview over existing emission standards set out for various types of vehicles in various parts of the world can be found on the Internet at [http://www.dieselnet.com/standards.html](http://www.dieselnet.com/standards.html).

#### 2.2.1 European Union

Legislation within the EU on emission from motor vehicles is driven by two objectives: (i) approximation of the laws of the Member States and (ii) continuous tightening of emission standards in order to improve air quality. A number of directives and consequent amendments and adaptations have been issued pursuing those objectives. A comprehensive compilation of legislation on this issue can be found on the Internet at [http://europa.eu.int/comm/enterprise/automotive/directives/index.htm](http://europa.eu.int/comm/enterprise/automotive/directives/index.htm).

No more than 0.025 g/km PM must be emitted by newly approved passenger cars as from 2005. This limit does not necessarily require particulate filter systems but can be met by specific engine modifications. More efficient separation efficiency (around 0.01 g/km) can be accomplished by means of particulate traps systems. E.g., an emission standard of 0.01 g/km will also apply for passenger cars in the US (Tier II bin 5) or do apply already in some EU member states.

Technologies developed for passenger cars may gradually translate to heavy-duty on-road vehicles and off-road vehicles. A weight-staggered approach is followed in the EU for light duty vehicles. From 2005/2006 onwards PM emissions shall not exceed 0.04 g/km (1305 to 1760 kg) and 0.06 g/km (vehicles > 1760 kg) respectively.

Progressively more stringent emission levels are also foreseen for heavy-duty on-road vehicles. A limit of 0.03 mg/kWh is set from 2008 within the EU for heavy-duty engines. As from 2007 this limit will be further reduced in the US by a factor of about 2 (0.013 g/kWh). As for passenger cars particulate filters may lead to substantial improvement in PM emission performance of heavy-duty vehicles.

In addition legislation has been implemented on the use of on-board diagnostic systems (OBD) indicating that emissions are too high. Finally more realistic test conditions were introduced, taking into account short-trip and cold start conditions.

For off-road machinery (excavators, bulldozers, front loaders, compressors, agricultural and forestal tractors, locomotives, etc.) environmental standards for air pollutants have been tightened as well. Depending on the net power of the machinery limit values are differentiated along with date of entering into force. Existing EU emission standards are summarized in table 1 and 2 below.
Tier | Diesel | Petrol (Gasoline)
---|---|---
Euro 1 (1992-1993) | 140 | -
Euro 2 (1996) | 80/100 | -
Euro 3 (2000) | 50 | -
Euro 4 (2005) | 25 | -
Euro 5 (proposal) | 2.5 | 2.5

1) in direct injection and direct injection

**Table 1 EU emission standards for particulate matter (mg/km) for passenger cars**

Tier | Diesel
---|---
Euro I (1992-1993) | 400
Euro II (1996) | 150
Euro III (2000) | 100/160
Euro IV (2005) | 20/30
Euro V (proposal) | 20/30
Euro VI (proposal) | 2/3

1) ESC and TC test cycle respectively

**Table 2 EU emission standards for particulate matter (mg/kWh) for heavy vehicles**

### 2.2.2 United States

Federal emission standards are set by EPA, California standards by ARB and can be found on the Internet for

- Heavy-Duty Truck and Bus Engines
- Cars and Light-Duty Trucks
- Nonroad Diesel Engines
- Locomotives
- Marine Engines

### 3 Fuel Standards

#### 3.1 Petrol

**3.1.1 European Union**

As mentioned in section 1.1 unleaded petrol is a prerequisite for employing three-way catalytic converters. For this reason the marketing of leaded petrol is banned since 1 January 2000⁶ in the European Community according to Directive 98/70/EC. The maximum content

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⁶ By way of derogation, a Member State may be allowed to request to continue to permit the marketing of
of lead in unleaded petrol is 0.005 g/L. Some MS have set stricter limit of 0.001 mg/L.

3.1.2 LRTAP Protocol on Heavy Metals

The Protocol requires that no later than 6 months after entering into force (29 June 2004) the lead content of marketed petrol shall not exceed 0.013 g/L. By way of derogation Parties may permit to extend this period up to ten years under special conditions. Marketed leaded petrol shall not contain more than 0.15 mg/L of lead. In addition a Party is permitted to market small quantities (= up to 0.5 per cent of its total petrol sales) of leaded petrol with a lead content not exceeding 0.15 g/L to be used for special purposes (e.g. old vehicles).

3.1.3 United States

U.S. phase-out of lead in gasoline began in 1975 and was nearly accomplished by the end of 1986. In 1995 leaded fuel accounted for 0.6 percent of total gasoline sales. Effective 1 January 1996, the Clean Air Act banned the sale of the small amount of leaded fuel for use in on-road vehicles. However, fuel containing lead may continue to be sold for off-road uses, including aircraft, racing cars, farm equipment, and marine engines.

3.1.4 Canada

Sale of leaded gasoline in Canada was halted in 1990. According to the Gasoline Regulation SOR/90-2477 the maximum concentration of lead in gasoline, except for special uses defined in the regulations, is 5 mg/L. Lead gasoline for use by farm equipment, boats or heavy-duty trucks may have a concentration up to 30 mg/L if manufactured in Canada, or up to 26 mg/L if imported. Lead gasoline for use in competition vehicles has special record-keeping requirements. as in other countries gasoline for use in aircraft is exempted.

The federal "Sulphur in Gasoline Regulations" took effect July 2002 and require an average petrol sulphur concentration of 150 mg/kg as of July 2002 and 30 mg/kg as of January 2005.

3.2 Diesel

The feasibility of the emission standards is based on the use of high-efficiency exhaust emission control devices that would be damaged by sulphur in the fuel. To this end sulphur content should be reduced as far as possible.

In addition to after-treatment devices improvement of automotive diesel fuel quality is of utmost importance for further reduction steps of PM emission. Legislation setting mandatory specifications for maximum sulphur content has evolved in most UN/ECE countries. Further information on fuel standards can be found on the internet at http://www.dieselnet.com/standards/fuels/index.html (liable to charge)

leaded petrol until 1 January at the latest. Furthermore MS may continue to permit the marketing of leaded petrol (<= 0.15 g/L) up to a maximum of 0.5 per cent of total domestic sales.

http://www.canlii.org/ca/regu/sor90-247/
3.2.1 European Union

A maximum of 50 mg/L of sulphur will apply in the EU\(^8\) as from 2005 for Diesel (and petrol) and further tightening to 10 mg/L of sulphur is envisaged. Some "countries" do already comply with that specifications ("sulphur free").

3.2.2 Canada

The Sulphur in Diesel Fuel Regulations SOR/2002-254\(^9\) set a maximum limit of 15 mg/kg for sulphur in on-road diesel fuel (starting June 1, 2006) that is produced or imported for use or sale in Canada and for on-road diesel fuel that is sold or offered for sale. (until 2006, the limit is 500 mg/kg.)\(^{10}\).

3.2.3 United States

The Environmental Protection Agency, which has a mandate to assure healthy air quality, has regulated highway diesel fuel quality since 1993 and most recently established low sulfur requirements in diesel fuel starting in 2006. Information about most recent Diesel fuel programmes and regulations for the US can be found at http://www.epa.gov/otaq/regs/fuels/diesel/diesel.htm

In various cases no absolute limit do apply but phase-in of standards are often materialized on a percent-of-sales basis.


\(^{10}\) in the northern supply area for use in on-road vehicles shall not exceed 500 mg/kg until August 31, 2007; and 15 mg/kg after August 31, 2007.