Section VI.H.

Guidance by source category: Annex C, Part III Source Categories

Motor vehicles,
particularly those burning leaded gasoline

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Information Document on Motor Vehicles

1 INTRODUCTION

For motor vehicles, the process description is relatively straightforward: The gasoline engine derives its power from the explosion of a mixture of air and gasoline, whereas in the diesel engine the fuel burns rather than explodes. The air-fuel mixture, when ignited, expands rapidly in a cylinder, forcing a piston from the top of the cylinder to the bottom. After its release from a vehicle, the exhaust gas is diluted approximately 1,000-fold in the first few seconds and cooled down very rapidly (Environment Australia 1998).

The major fuels used in transportation are gasoline, Diesel, and liquefied petroleum gas (LPG). Most gasoline powered internal combustion engines used today in cars, light trucks, motorcycles, and other vehicles are 4-stroke engines. These engines follow the thermodynamic combustion cycle invented by Nicolaus Otto, which consists of four strokes, namely the intake stroke, the compression stroke, the ignition and combustion stroke, and the exhaust stroke. These four strokes are completed during two full revolutions of the crankshaft. Like all combustion processes, internal combustion engines produce PCDD/PCDF as an unwanted byproduct. Higher emissions have been associated with the use of chlorinated scavengers used in leaded gasoline. However, when unleaded gasoline is used and a catalytic converter is installed for the removal of NO_x as well as unburned hydrocarbons (Toolkit 2003).

Most small gasoline powered internal combustion engines used today in boats, jet-skis, mopeds, small motorcycles, tuk-tuks, lawnmowers, chain saws, and other vehicles are 2-stroke engines. These engines follow the same thermodynamic combustion cycle as the 4-stroke engine; however, it consists of only two strokes, namely the combined exhaust and intake stroke, and the compression, ignition and combustion stroke. The most striking difference to the 4-stroke engine is the fact that all strokes occur during only one full revolution of the crankshaft. Lubrication is usually by oil added to the fuel. Therefore, higher amounts of pollutants may be released and efficiency may be lower compared to 4-stroke engines. However, the simplicity and low production cost of 2-stroke engines make it an ideal motor especially for small engines.

Diesel engines are used in heavy trucks, light trucks, passenger cars, heavy construction equipment, boats, generators, pumps, and farm equipment including tractors and other large equipment. They usually use Diesel (light oil) and a 4-stroke cycle. Compression is used for ignition rather than a spark. Air is taken into the cylinder and compressed. Diesel fuel is added at high pressure and burned. This results also in a more efficient use of fuel and lower specific emissions. However, particle emissions in form of soot are also associated with the operation of Diesel engines due to incomplete combustion especially during start-up, warming, and load changes. Particulate emissions from Diesel engines are well known to contain high concentrations of polycyclic aromatic hydrocarbons (PAH).

Ballschmiter *et al.* (1986) detected PCDD/PCDF in used motor oil and thus provided the first evidence that PCDD/PCDF might be emitted by the combustion processes in gasoline- and diesel-fueled engines. Incomplete combustion and the presence of a chlorine source in the form of additives in the oil or the fuel were speculated to lead to the formation of

PCDD/PCDF. Like all combustion processes, 4-stroke and 2-stroke engines as well as Diesel engines generate PCDD/PCDF as unwanted byproducts (Marklund *et al.* 1987, 1990, Schwind *et al.* 1990, 1991, Hutzinger *et al.* 1992, Gullett and Ryan 1997). Whereas for the gasoline-powered engines, the only relevant release vector of PCDD/PCDF is to air, Diesel engines generate considerable amounts of deposits (soot). However, no measured data are available for PCDD/PCDF concentrations in Diesel soot (Toolkit 2003).

2 PCDD/PCDF FORMATION AND RELEASE

Several European studies and one U.S. study evaluated PCDD/PCDF emissions from vehicles by measuring the presence of PCDD/PCDFs in tunnel air. This approach has the advantage that it allows random sampling of large numbers of cars, including a range of ages and maintenance levels. The disadvantage of this approach is that it relies on indirect measurements, which may introduce unknown uncertainties and make interpretation of the findings difficult. Concerns have been raised that in tunnel studies resuspended particulates and absorbed PCD/PCDF that have accumulated over time, may lead to overestimates of emissions. We found this approach as not appropriate and therefore, did not consider in detail the results of these studies. For further reading we refer to the following publications by Rappe *et al.* (1988), Larssen *et al.* (1990), Oehme *et al.* (1991), Wevers *et al.* (1992), and Gertler *et al.* (1996, 1998).

The study by Bingham *et al.* (1989) on New Zealand vehicles does not provide emission factors and does not give congeners-specific data and neither reported a TEQ.

The first tail pipe emission study was performed by Marklund *et al.* (1987) on Swedish cars. For this study, an artificial fuel was used consisting of unleaded gasoline to which tetramethyl lead (0.15 g/L) and dichloroethane (0.1 g/L as a scavenger) were added. The fuel used may not have accurately represented commercial fuels at that time, which typically contained a mixture of chlorinated and brominated scavengers. Later, Marklund *et al.* (1990) tested vehicles on a chassis dynamometer according to FPT-72 test cycle using commercially available gasoline (Table 4 in the Annex). The heavy-duty diesel vehicle was also operated on a chassis dynamometer but in a static mode with loads according to the U.S. Federal mode 13 cycle. Two tests were performed on the heavy-duty vehicle one with 10 % load and, one with 100 % load according to U.S. Federal 13-Mode cycle. The samples were taken before the muffler, and the exhaust was cooled down to 150 °C before it entered the filter.

Higher emissions were found for the vehicles run on leaded gasoline, which gave emission factors between 10 and 60 pg I-TEQ/L whereas the cars using unleaded gasoline had emissions of 3.5 pg I-TEQ/L. The individual test results are summarized in the Annex in Table 5.

From 1987 to 1990, the German universities of Stuttgart, Tübingen, and Bayreuth with funding from the Federal Ministry for Research and Technology, the Research Association for Internal Combustion Engines, and the German Association for the Petroleum Industry and Coal Chemistry conducted a study using engine test benches and rolling test benches under representative operating conditions. Tests were performed on leaded gasoline engines, unleaded gasoline engines (with and without catalytic converter present; 2,299 cm^3, 97 kW), diesel car engines (1,588 cm^3, 51 kW), and diesel truck engines (3,972 cm^3, 66 kW).

Commercial gasoline and diesel, respectively, were used in the tests. Fuel characteristics are shown in the Annex in Table 6.

The use of motor oils with low chlorine content (in the Diesel experiments) did not result in lower PCDD/PCDF emissions. The study did not reveal that the age of the motor had an effect on the PCDD/PCDF emissions. Except for "no-load operation" where the emissions were significantly lower (leaded gasoline); no influence could be determined with variation of engine operating point, temperature in motor or muffler, nor shape of the muffler. Individual test results are shown in Table 7 in the Annex and the average PCDD/PCDF emission factors per liter of fuel burned in Table 1. The full detailed report was published in 1992 (Hutzinger *et al.* 1992); the results are also included in Table 1.

Table 1: Average PCDD/PCDF emissions for Otto and diesel engines (ng TEQ/L) (Schwind *et al.* 1990, 1991)

Engine, fuel	Otto, leaded	Otto, unleaded, no catalyst	Otto, unleaded, with catalyst	Diesel, cars	Diesel, trucks
pg I-TEQ/L (1990)	1,083	50.7	7.2	23.6	
pg TEQ/L (1991)	740	90	20	50	
pg I-TEQ/L (1992)	52-1,184	96-177	10-26	10-130	70-81

In 1994, Hagenmaier *et al.* (1995) analyzed the emissions of a Diesel-fuelled bus. PCDD/PCDF concentrations were around 1 pg/L for individual 2,3,7,8-substituted congeners resulting in an I-TEQ of 0,01 ng I-TEQ/L. Thus, the 1994 results were much lower than the results obtained in 1990 (Hagenmaier *et al.* 1990). Whereas in 1990, mixed-halogenated (Br and Cl) PXDD/PXDF could be quantified, the 1994 emissions did not contain detectable PXDD/PXDF. These results indicate that with the ban of the use of halogenated scavengers (in Germany: 19^{th} BImSchV 1992) the main source of PCDD/PCDF (and PXDD/PXDF) was eliminated. The results also showed that cross-contamination did occur since the same containers were used for the transport of Diesel, leaded and unleaded gasolines.

From the United States, only one study on testing of vehicle emissions for PCDD/PCDF is available. In 1987, the California Air Resources Board (CARB) produced a draft report on the testing of the exhausts of four gasoline-powered cars and three diesel fuel-powered vehicles (one truck, one bus, and one car). However, CARB indicated to US-EPA that the draft report should not be cited or quoted to support general conclusions about PCDD/PCDF in motor vehicle exhausts because of the small sample size of the study and because the use of low rather than high resolution mass spectrometry in the study resulted in high detection limits and inadequate selectivity in the presence of interferences. Therefore, results from this study that have been cited elsewhere are not taken into account in this information document.

Gullett and Ryan (1997) determined emission factors from 3.0 to 96.8 pg I-TEQ/km (mean of 29.0 pg I-TEQ/km) for on-road, heavy duty Diesel vehicles based on five experiments where trucks (Freightliner diesel tractor, fully loaded) did run either a "city" or "highway" route to reflect different driving conditions. The city drive was performed at an average speed of 35 km/h and the highway drive at about 90 km/h. Individual test results are summarized in the Annex in Table 8.

Geueke *et al.* (1999) determined an emission factor of 291 pg I-TEQ/kg fuel for a diesel truck.

In 2000, Brož *et al.* (2000) reported concentrations of polycyclic aromatic hydrocarbons (PAH), polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF), and biphenyls (PCB) in emissions from a spark ignition engine was studied on a Škoda Favorit engine (118,000 km) fueled with leaded gasoline (0.13 g Pb/kg, 3.0 mg Cl/kg, 37.2 wt.% AH, and 8 % MTBE) and synthetic motor oils added. The test cycle simulated urban traffic conditions on a chassis dynamometer, in accordance with the ECC 83.00 test. PCDD/PCDF emissions for an unused oil and the oil after 10,000-km operation varied from 1.4 to 11 pg WHO-TEQ/m³ (or 300 to 2,000 fmol/m³), PCB (Cl_4-Cl_{10}) emissions from to 75-178 pmol/m³, and PAH emissions from 150-420 µg/m³. The content of PCB in oils varied from 2 to 920 mg/kg.

Kim *et al.* (2003) investigated PCDD/PCDF emissions from diesel engines in US D-13 mode at load rates between 25 % and 75 % at constant speed (2,4000 rpm). The mass concentrations for the three different loads of 14.4, 6.9. and 6.4 pg I-TEQ/Nm³ convert into the following emissions factors: 2.0, 0.6, and 0.5 pg I-TEQ/L diesel.

Table 2: PCDD/PCDF emissions factors for diesel vehicles (Kim *et al.* 2003)

Load	pg I-TEQ/Nm³	pg I-TEQ/L diesel
25 %	14.5	2.0
50 %	6.9	0.6
75 %	6.4	0.5

Chang *et al.* (2004) determined emission factors from a tunnel study and in addition, performed a tailpipe study on diesel engines, which gave concentrations between 6.7 pg I-TEQ/m³ and 41.9 pg I-TEQ/m³; the authors attribute the higher emissions to slower speeds. Emission factors were not given.

3 COUNTRY SITUATION IN JAPAN

In Japan, special measures law on Dioxins (enforced in 1999) regulates concentrations of PCDDs/DFs emissions from specific sources, of which emission gases from motor vehicles are not covered. With regard to motor vehicle fuel, sales of leaded gasoline were prohibited by law on securing quality of volatile oils (enforced in 1996). While oil refining companies in Japan had made voluntary efforts to develop 100 % lead-free gasoline, which had been achieved in the 1980s, import liberalization of petroleum products in 1996 triggered introduction of quality controls by law on lead, benzene and sulfur.

PCDD/PCDF emissions are examined to target on emission gases from motor vehicles running on unleaded gasoline and light oils for diesel vehicles (Miyabara *et al.* 1999, Noda *et al.* 2003, Yokota *et al.* 2002). Table 3 shows concentrations and emissions of PCDD/PCDF (WHO-TEF 1998) per liter of fuel consumption from motor vehicles surveyed by the Ministry of the Environment, Japan Automobile Manufactures Association, Inc., and the Advanced Technology and Research Institute of Petroleum Energy Center (MOE, Japan, 2003). The average PCDD/PCDF emission factor by diesel vehicles was 32 pg TEQ/L (1.2-170 pg TEQ/L) and the average of gasoline-fueled vehicles was 2.9 pg TEQ/L (0.34-16 pg-TEQ/L). Another study reports Diesel Particulate Filter (DPF) does not only remove particulates, but also reduces PCDD/PCDF in emission gases (Sakamoto *et al.* 2003). When examining the oxidation catalyst (Pt) and continuous regenerative DPF as techniques for reducing PCDD/PCDF from diesel vehicles it was found that mostly hepta- and octachlorinated PCDF derived from combustion were captured on the filter. Although generally, the oxidation catalyst (Pt) was effective to reduce PCDD/PCDF, it turned out that is was necessary to examine the catalyst reactivity, because some of lower chlorinated, less toxic PCDF (2,3,7,8-Cl_4DF and 1,2,3,7,8-Cl_5DF) could be changed to congeners with higher toxicity equivalency factors. In Tokyo metropolitan area, Diesel vehicles have to be equipped with DPF.

Table 3: PCDD/PCDF emissions from motor vehicles in Japan (MOE, Japan, 2003)

Type		Conditions of Measurement	Concentrations of Emissions: ng-TEQ/m3	Emissions per Fuel: pg-TEQ/l
Diesel	Truck	① 13 mode[1]	0.00341	99.63
		② 80km constant rate	0.00015	4.99
		40% revolution/load 2)	0.00208	103.36
		③ 13 mode	0.00012	8.65
		④[3] 13 mode	0.00011	3.48
		80km constant rate	0.00004	1.20
		40% revolution/load	0.00006	1.70
	Automobile	⑤ 80km constant rate	0.00041	4.28
		⑥ 80km constant rate	0.00042	4.63
		⑦ 80km constant rate	0.00020	2.21
		⑧ 80km constant rate	0.00006	1.47
		10・15 mode[4]	0.00017	3.70
		⑨ 80km constant rate	0.0100	121.0
		10・15 mode	0.0145	173.5
		⑩ 80km constant rate	0.00069	6.39
		⑪ 80km constant rate	0.00032	3.6
		10・15 mode	0.00057	6.655
Gasoline	Truck	⑫ 80km constant rate	0.00025	0.99
		Actual run mode[5]	0.00004	0.42
	Automobile	⑬ 80km constant rate	0.00166	16.42
		10・15 mode	0.00044	4.50
		⑭ 80km constant rate	0.00007	0.69
		10・15 mode	0.00013	1.25
		⑮ 80km constant rate	0.00035	3.6
		10・15 mode	0.00003	0.34
		⑯ 80km constant rate	0.00008	0.77
		10・15 mode	0.00004	0.36

– (Principal Elements)

– Trucks running on diesel are all direct-injection style and adapted to emission gas regulation in 1994. ③ is load capacity of 2 tons and the others are 10 tons class.

– In terms of automobiles running on diesel, ⑥⑦⑩ are direct-injection style, ⑨⑪ are auxiliary chamber style and adapted to emission gas regulation in 1998, and ⑤⑧ are auxiliary chamber style and adapted to emission gas regulation in 1997.

– Trucks running on gasoline are adapted to emission gas regulation in 1998.

– With regard to automobiles running on gasoline, ⑯ is adapted to emission gas regulation in 2000. The others are adapted to emission gas regulation in 1978.

– ・They were measured on the condition that truck carried half a load and automobile carried a load of 110 kg.

– ・①⑨⑪⑫⑮⑯ were measured by the Ministry of the Environment, ②⑤⑥⑦⑩⑬ were by Japan Automobile Manufactures Association, Inc. and ③④⑧⑭ were by the Advanced Technology and Research Institute of Petroleum Energy Center respectively.
– （Notes）
– １) "13 mode" means the same running conditions as 13 mode for diesel vehicles, which is a legal measuring method of emission gas from large vehicles.
– ２) "40% revolution/load" means the conditions running with 40 % revolutions of the highest engine power and with 40％ loads of the total.
– ３） Measured data of □ only was not from cars but from test using engine itself. And with regard to measuring conditions of 80 km constant rate, it was implemented by recreating the engine conditions of running at constant speed of 80km.
– ４) "10・15 mode" means the same running conditions as 10・15 mode for automobiles, which is a legal measuring method of emission gas from automobiles.
– ５) "Actual run mode" means a mode running actually at the average velocity of 26.1km/h.

4 CONCLUSIONS

The literature documenting results of European, U.S. and Japanese studies gives evidence that:

- PCDD/PCDF emissions from vehicles burning unleaded fuels are lower than the emissions from vehicles burning leaded gasoline;
- The higher emissions from vehicles run on leaded fuels are due to the presence of chlorinated scavengers added to the fuels.
- Catalyst-equipped cars – running on unleaded gasoline - have lowest emissions.
- Diesel particulate filters are efficient to reduce PCDD/PCDF from diesel-fueled vehicles.
- Diesel-fueled vehicles have lower emissions than leaded-gasoline-fueled vehicles and slightly higher emissions than vehicles running on unleaded gasoline and equipped with catalytic converter.

The situation is not clear as to the influence of the age of the vehicles:
– whereas Marklund *et al. (1990)* found higher emissions in older vehicles,
– the German study (Schwind *et al.* 1991, Hutzinger *et al.* 1992) did not find such dependence.

There are no measured data available for vehicles
– 2-stroke engines
– utilizing LPG
– utilizing alcohol-oil mixtures
– utilizing biofuels (rape, *etc.*)

5 CONTROL MEASURES

Primary measures to reduce PCDD/PCDF emissions from motor vehicles may include the following:

1. Prohibition of halogenated scavengers;
2. Prohibition on the use of leaded gasoline;
3. Installation of diesel particulate filters and/or catalytic converters; and

4. Alternatives to gasoline engine (electricity, solar light, and fuel battery) [However, it should be taken into consideration that the production of the alternative fuels may generate PCDD/PCDF, *e.g.,* electricity generation, production of solar cells, *etc.*].

Best practices may include:

1. Separation of transport containers according to the fuel (*e.g.,* not transport leaded gasoline containing halogenated scavengers in container that also are being used for the transport of diesel or unleaded gasoline;
2. Promotion of vehicles with low fuel consumption;
3. Education to identify driving conditions that have low pollutant's formation and release, and
4. Maintain good maintenance practices of the vehicle.

6 REFERENCES

Ballschmiter K., H. Buchert, R. Niemczyk, A. Munder, and M. Swerev (1986): Automobile exhausts versus municipal waste incineration as sources of the polychlorodibenzodioxins (PCDD) and -furans (PCDF) found in the environment. Chemosphere **15**, 901-915

BImSchV (1992): 19.Verordnung zur Durchführung des Bundesimmissionsschutzgesetzes vom 24.07.1992 (Verordnung über Chlor- und Bromverbindungen als Kraftstoffzusatz - 19. BImSchV). Bundesgesetzblatt Teil 1, Jahrgang 1992, 75 (Ordinance on ban of halogenated scavengers, Germany)

Bingham A.G., C.J. Edmunds, B.W. Graham, and M.T. Jones (1989): Determination for PCDDs and PCDFs in car exhaust. Chemosphere **19**, 669-673

Bröker G., B. Schilling, and P. Kirschmer (1990): Chlorierte und bromierte Dioxine und Furane aus Kraftfahrzeugen. Aus der Tätigkeit der LIS 1989 (Ed.) 31-34

Brož J., R. Grabic, J. Kilián, M. Lojkásek, S. Marklund, T. Ocelka, V. Pekárek, J. Přibyl, V. Tydlitát, and J. Výška (2000): The effect of oils on PAH, PCDD, PCDF, and PCB emissions from a spark engine fueled with leaded gasoline. Chemosphere **41**, 1905-1911

Environment Australia (1998): Sources of Dioxins and Furans in Australia: Air Emissions, pp.55-56, http://www.co-incineracao.online.pt/Dioxins-australia.pdf

Gertler A.W., J.C. Sagebiel, W.A. Dippel, and L.H. Sheetz (1996): A study to quantify onroad emissions of dioxins and furans from mobile sources: phase 2. Reno, NV: Desert Research Institute

Gertler A., J. Sagebiel, W. Dippel, and R. Faring (1998): Measurement of dioxin and furan emissions factors from heavy duty diesel vehicles. J. Air&Waste Manage. Assoc. **48**, 276-278

Geueke K.J., A. Gessner, U. Quass, G. Bröker, and E. Hiester (1999): PCDD/F emission from heavy duty vehicle diesel engines. Chemosphere **38**, 2791–2806.

Gullett B. and J.V. Ryan, (1997): On-Road Sampling of Diesel Engine Emissions of Polychlorinated Dibenzo-*p*-dioxin and Polychlorinated Dibenzofuran. Organohalogen Compd. **32**, 451-456

Hagenmaier H., P. Krauß, J. Vatter, and M. Walczok (1995): Eintrag und Verbleib von PCDD/PCDF - Bedeutung der Einträge durch Automobilabgase und Holzfeuerungen. Organohalogen Compd. **22**, 49-54.

Hagenmaier H. (1994): Contributions of diesel-powered vehicles and wood burning to overall PCDD/PCDF emissions. Organohalogen Compd. **20**, 267-270

Hagenmaier H., N. Dawidowsky, U. Weberuss, O. Hutzinger, K.H. Schwind, H. Thoma, U. Essers, B. Buhler, and R. Greiner (1990): Emission of polyhalogenated dibenzodioxins and dibenzofurans from combustion-engines. Organohalogen Compd. **2**. 329-334

Kim K.-S., K.-H. Hong, Y.-H. Ko, K.-D. Yoon M.-G. Kim (2003): Emission characteristics of PCDD/Fs in diesel engine with variable load rate. Chemosphere **53**, 601-607

Marklund S., R. Andersson, M. Tysklind, C. Rappe, K.E. Egebäck, E. Bjorkman, and V. Grigoriadis (1990): Emissions of PCDDs and PCDFs in gasoline and diesel fueled cars. Chemosphere **20**, 553-561

Marklund S., C. Rappe, M. Tysklind, and K. Egeback (1987): Identification of polychlorinated dibenzofurans and dioxins in exhausts from cars run on leaded gasoline. Chemosphere **16**, 29-36

The Ministry of the Environment: Inventory of PCDDs/DFs Emissions (Emissions Inventory)(2003) http://www.env.go.jp/air/report/h15-05/index.html

Miyabara Y, S. Hashimoto, M. Sagai, and M. Morita (1999): PCDDs and PCDFs in Vehicle Exhaust Particles in Japan. Chemosphere **39**, 143--150

Noda A, T. Sakamoto, T. Yamamoto, S. Hori, S. Sato (2003): Investigation on the Behavior of Automotive Unregulated Pollutants and their Reduction Technology, Reports of funded research of National Traffic Safety and Environment Laboratory, VOL.2001, 5.1-5.25. http://www.ntsel.go.jp/jutaku/13files/investigation.pdf

Sakamoto T., S. Sato, and A. Noda (2003): PCDDs/DFs emitted from Diesel Vehicles and its reduction methods. Proceedings of Research Meeting of National Traffic Safety and Environment Laboratory, VOL.3, 211-214, http://www.ntsel.go.jp/ronbun/happyoukai/15files/postr15.pdf

Schwind K-H., H. Thoma, O. Hutzinger, N. Dawidowsky, U. Weberuss, H. Hagenmaier, U. Buehler, R. Greiner, U. Essers, and E. Bessey (1991): Emission halogenierter Dibenzodioxine (PXDD) und Dibenzofurane (PXDF) aus Verbrennungsmotoren. UWSF - Z. Umweltchem. Oekotox. **3**, 291-298

Toolkit (2003): Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases. UNEP Chemicals, May 2003, http://www.chem.unep.ch/pops/newlayout/repdocs.html

Yokota H., S. Izumisawa, M. Funeshima, S. Tahara, F. Sano, Y. Sasaki, H. Yoshioka, and K. Higashino (2002): Emission of PCDDs/PCDFs in Diesel and Gasoline Fueled Vehicles, Journal of Japan Society for Atmospheric Environment **37**, 35-46

Tunnel and ambient air studies:

Larssen S., E.M. Brevick, and M. Oehme (1990): Emission factors of PCDD and PCDF for road vehicles obtained by a tunnel experiment. Organohalogen Compd. **1**, 453-456.

Oehme M., S. Larssen, and E.M. Brevik (1991): Emission factors of PCDD/CDF for road vehicles obtained by a tunnel experiment. Chemosphere **23**, 1699-1708

Rappe C., L.O. Kjeller, P. Bruckmann, and K.H. Hackhe (1988): Identification and quantification of PCDD/CDFs in urban air. Chemosphere **17**, 3-20

Wevers M., R. De Fre, and T. Rymen (1992): Dioxins and dibenzofurans in tunnel air. Organohalogen Compd. **9**, 321-324.

7 ANNEX

Background information and further details from the various studies are summarized in this Annex.

Table 4: Characteristics of the gasoline fueled light-duty vehicles tested in the Swedish study by Marklund *et al.* (1990

Vehicles run on leadfree gasoline
- 1985 - SAAB 90 – 7,400 km with carburettor
- 1987 - Volvo 760 T – 1,900 km with fuel injection
- 1985 - SAAB 900i – 7,000 km with fuel injection catalytic converter

Vehicles run on leaded gasoline
- 1984 - Volvo 245 GL – 71,600 km with carburettor
- 1986 - Volvo 740 GL – 6,900 km with carburettor

The lead concentration in leaded gasoline was 0.15 g/L, which was the typical concentration for leaded fuel in Sweden. It also contained dichloroethane and dibromoethane as scavengers. The lead-free gasoline was a Blend 5 specified by Volvo and specially made to fit the US-EPA specifications for exhaust certification.

Table 5: PCDD/PCDF in the emissions from light-duty vehicles fueled with leaded and unleaded gasoline (Marklund *et al.* 1990).

Vehicle	Lube oil	Sample point	pg I-TEQ/km	pg I-TEQ/L
Leaded gasoline				
Old	New	Before muffler	6.3	60
Old	New	In tailpipe	1.1	10
New	New	Before muffler	2.4	21
New	New	In tailpipe	2.6	23
Unleadedgasoline				
Carburettor	Old	Before muffler	0.36	3.5
Carburettor	New	Before muffler	0.36	3.5
FI (fuel injection)	New	Before muffler	0.39	3.5
FI Catalyst	New	In tailpipe	0.36	3.5
FI Catalyst	New	In tailpipe *	0.36	3.5

Table 6: Characteristics of fuels used in the German study by Schwind *et al.* 1991, Hutzinger *et al.* 1992

Fuel type	Cl content	Br content
Gasoline, Super leaded	70 mg Cl/kg	76 mg Br/kg
Gasoline, Super unleaded	<1 mg Cl/kg	<1 mg Br/kg
Diesel	<1 mg Cl/kg	<1 mg Br/kg
Motor oil	<170 mg Cl/kg	<1 mg Br/kg
Low-chlorine motor oil	5 mg Cl/kg	<1 mg Br/kg

Table 7: PCDD/PCDF emissions for Otto and diesel engines (ng TEQ/L) (Schwind *et al.* 1991)

Characteristic Engine, fuel	No load operation	Full load[1]	Standard[2]	Nominal operation	FTP-75 cycle	Old motor	Lambda = 1
Otto, leaded	0.07	0.55	1.66	0.69	0.41	1.18	
Otto, unleaded			0.15, 0.09, 0.22		0.11	0.05	0.17
Otto, unleaded with catalyst			0.03 0.02, 0.02				

Characteristic Engine, fuel	No load operation	Standard	120 km/h, flat	120 km/h, full load	Cycle, full	Cycle, diluted	Low Cl motor oil
Passenger car, Diesel	0.103	0.009	0.057	0.141	0.025	0.056	0.041, 0.02

Characteristic Engine, fuel	50 km/h, flat terrain	90 km/h, full load
Truck, Diesel	0.088	0.04

[1] 1,500 rpm, [2] 1,800 rpm, torque = 48 Nm (=63 km/h, 3 % incline)

Table 8: PCDD/PCDF emission factors measured at on-road heavy duty diesel vehicles (Gullett and Ryan 1997)

Drive	pg I-TEQ/m³		pg I-TEQ/L		pg I-TEQ/km	
	range	average	range	average	range	average
Highway (n=3)	1.4-2.0	1.7	29.3-47.7	37.2	11.7-18.7	15.1
City (n=2)	0.2; 6.1	3.2	5.1; 173.6	89.3	3.0; 96.8	49.9
All tests combined		2.3		58.1		29.0