



Date

May 12, 2014

Authors

Nikos Pastramas

Christos Samaras

Giorgos Mellios

Leonidas Ntziachristos

Client

European Environment Agency



Draft Report

EMISIA SA Report

No: 14.RE.011.V1

Update of the Air Emissions Inventory Guidebook - Road Transport 2014 Update

Project Title European Topic Centre on Air pollution and Climate change Mitigation (ETC/ACM)	Call for Tender No:
Report Title Update of the Air Emissions Inventory Guidebook - Road Transport 2014 Update	Contract No: EEA/ACC/13/001
Project Manager Dr. Giorgos Mellios	Contractor: EMISIA SA
Author(s) Pastramas, N.; Samaras, Ch.; Mellios, G.; Ntziachristos, L.	
Summary This report summarizes the changes introduced in the 2014 update of the road transport Air Emissions Inventory Guidebook chapter. The final values, together with the literature presented and the synthesis conducted are included in the report. In summary, the changes introduced included new emission factors for Euro 5 & 6 light duty vehicles, new emission factors for Euro V & VI heavy duty vehicles, NH3 and N2O emission factors update, as well as new values for the NO2/NOx ratio and organic species (PCB/HCB/PCDD/PCDF).	
Keywords Vehicle emissions, COPERT, AEIG, non regulated, Euro 5, Euro 6	

Internet reference No internet reference			
Version / Date Draft version / May 12, 2014		Classification statement PUBLIC	
No of Pages 53	No of Figures 9	No of Tables 21	No of References 56
Approved by:  Giorgos Mellios		Emisia is an ISO 9001 certified company 	

Contents

1	Emission factors of regulated pollutants at Euro 5/V and 6/VI levels.....	4
1.1	Introduction	4
1.2	Methodology.....	5
1.3	Results and Observations	6
1.4	References	7
2	Update of PCDD/Fs, HCB and PCB emission factors.....	8
2.1	Introduction	8
2.2	Emission sources and mechanisms	9
2.3	Toxic equivalency.....	10
2.4	Emission factors in COPERT	11
2.5	Literature study	12
2.6	Methodology.....	18
2.7	Emission factors.....	19
2.8	Conclusions.....	24
	References	25
3	Update of NH ₃ emission factors.....	27
3.1	Introduction	27
3.2	Literature research	27
3.3	Methodology.....	31
3.4	Results	32
3.5	Conclusions.....	35
	References	36
4	Update of N ₂ O emission factors.....	37
4.1	Introduction	37
4.2	Literature research	37
4.3	Methodology.....	40
4.4	Results	40
4.5	Conclusions.....	43
	References	44
5	Update of f-NO ₂ emission factors	45
5.1	Introduction	45
5.2	Literature research	45
5.3	Methodology.....	49
5.4	Results	49
5.5	Conclusions.....	50
	References	51
6	Abbreviations	52
7	Annex.....	53



1 Emission factors of regulated pollutants at Euro 5/V and 6/VI levels

1.1 Introduction

In passenger cars and light commercial vehicles, the introduction of the Euro 5 step in 2010 introduced the mandatory implementation of Diesel Particle Filters (DPFs) to all diesel vehicles, due to a particle number specific limit that has been introduced. This decreased the emission levels of PM by as much as 20 times. In parallel, more strict NO_x control significantly reduced NO_x emissions, at least over the statutory driving cycle (NEDC). NO_x control is primarily achieved with the use of exhaust gas recirculation (EGR) which can be tuned for optimum emission performance over a portion of the engine operation map only. Outside of this area, the engine can be tuned for minimum fuel consumption, thus not offering significant benefits in terms of NO_x. Therefore, the control of NO_x over real world operation has not been as effective as was originally designed. For gasoline cars and vans, Euro 5 did not lead to a change in emission limit values, but more strict durability and on-board diagnostic (OBD) control of emissions. Therefore, base emission factors for Euro 5 cars are not expected to fundamentally differ from Euro 4 ones.

The next standard (Euro 6) is basically introduced in two periods. The first step with introduction date Sept. '14 for passenger cars and small vans and one year later for larger vans requires more strict NO_x control (80 µg/km instead of 180 µg/km at Euro 4). This low level is expected to be reached with the use of selective catalytic reduction (SCR) for the majority of diesel vehicles, although a Euro 6 diesel car with no de-NO_x aftertreatment has already made it to the market. Such vehicles are expected to suffer - to a certain degree - from the same lack of NO_x reduction efficiency in operation outside of the statutory cycle. The variability of the technologies implemented for NO_x control makes it therefore difficult to predict emission levels. The next step is Euro 6c with a planned introduction date by 2017/2018. This requires emission control not only over the statutory cycle but also over real drive emissions, i.e. while the vehicle operates in actual conditions on the road. Therefore, this step is expected to bring significant reductions, over actual operation as well. For gasoline cars, Euro 6 did not lead to significant changes over Euro 5. The only exception is direct injection vehicles, for which a strict particle number standard is introduced in 2017 that is deemed to require a Gasoline Particle Filter (GPF) to be reached.

Developments in the heavy duty vehicles world were also fast, with the Euro V step already introduced in 2008 and the Euro VI step in 2013. Euro V introduced SCR to the majority of heavy duty engines while Euro V brings DPFs to reach the strict particle mass and number limits. Other regulatory requirements included emission control over cold starts, development of OBD and durability requirements, etc. Hence, significant reductions to emission factors of these vehicles have been brought.

All these regulatory changes require a new set of emission factors so that representative emission levels are proposed for each vehicle category and technology. These new emission factors are proposed in this chapter.

1.2 Methodology

In order to derive updated emission factors (EF) for Euro 5 and Euro 6 vehicles, the emissions data from the newest version of the Handbook on Emission Factors of Road Transport (HBEFA version 3.2) were used as an input. The new equations were produced by applying regression analysis on the given HBEFA data. New EF equations were derived for passenger cars, light duty vehicles, heavy duty vehicles and buses, including all the subcategories that are fuelled with gasoline and diesel. The equations produced include CO, NO_x, HC and PM exhaust, as well as fuel consumption (FC). Table 1-1 summarizes the vehicle categories, Euro technologies and the corresponding pollutants, for which the new EF equations were derived.

Table 1-1: Vehicle types for which new emission factors are proposed.

Sector	Sub-Sector	Pollutants	Euro Technologies
PC	Gasoline <0,8 l	CO, NO _x , HC, PM	5, 6 and 6c
PC	Gasoline 0,8 - 1,4 l	CO, NO _x , HC, PM	5, 6 and 6c
PC	Gasoline 1,4 - 2,0 l	CO, NO _x , HC, PM	5, 6 and 6c
PC	Gasoline >2,0 l	CO, NO _x , HC, PM	5, 6 and 6c
PC	Diesel <1,4 l	CO, NO _x , HC, PM	5, 6 and 6c
PC	Diesel 1,4 - 2,0 l	CO, NO _x , HC, PM	5, 6 and 6c
PC	Diesel >2,0 l	CO, NO _x , HC, PM	5, 6 and 6c
LDV	Gasoline <3,5t	CO, NO _x , HC, PM, FC	5, 6 and 6c
LDV	Diesel <3,5 t	CO, NO _x , HC, PM, FC	5, 6 and 6c
HDV	Rigid <=7,5 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and VIc
HDV	Rigid 7,5 - 12 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Rigid 12 - 14 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Rigid 14 - 20 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Rigid 20 - 26 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Rigid 26 - 28 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Rigid 28 - 32 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Rigid >32 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Articulated 14 - 20 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Articulated 20 - 28 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Articulated 28 - 34 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Articulated 34 - 40 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Articulated 40 - 50 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
HDV	Articulated 50 - 60 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
BUS	Urban Buses Midi <=15 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
BUS	Urban Buses Standard 15 - 18 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
BUS	Urban Buses Articulated >18 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
BUS	Coaches Standard <=18 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and Vic
BUS	Coaches Articulated >18 t	CO, NO _x , HC, PM, FC	V (EGR & SCR), VI and VIc

The emission factors in HBEFA 3.2 have been worked out by the Technical University of Graz (TUG) and have been introduced in HBEFA 3.2 by INFRAS. The work has been coordinated



within the ERMES group (www.ermes-group.eu). The approach for the values proposed in this chapter are based on experimental measurements on vehicles and generation of engine pollution maps, where emission rates are associated with engine load and speed. Then, a dedicated vehicle model per emission technology is generated in the model PHEM and is allowed to run over a range of driving conditions (Kühlwein et al., 2013). The emission factors in HBEFA are therefore expressed as a function of road type, service level, and road speed limit, hence they are single values, corresponding to ~250 individual driving conditions.

Kühlwein et al. (2013) present a number of limitations regarding the emission factors developed. In particular, the Euro 6 vehicle sample has been limited and the vehicle models tested belong to rather the more expensive classes. Hence, different emission concepts may be used for more economical (and smaller) vehicles that may significantly change the average emission levels proposed at a Euro 6 level. Moreover, practically only one Euro 6 vehicles has been available at time of testing. For Euro 6c, proposed emission factors are based on emission limit equivalence only and no actual measurement.

1.3 Results and Observations

Regression on these values produced the emission functions with speed proposed in this chapter. These functions are given as a separate electronic file (Annex I) to this report. The R^2 value given next to the function parameters shows the goodness of fit of the speed-average functions to the individual HBEFA values. In general the fit is very good and shows that the COPERT and HBEFA emission factors should be at the same levels for the technologies included in this chapter.

The following remarks need to be made to the functions produced:

- For passenger cars, emission factor functions are distinguished only according to vehicle technology and fuel used (diesel, gasoline) but not according to vehicle size. There is no evidence that emission performance differs according to vehicle size. However, this may well change in the future as different emission control technologies may be proposed depending on vehicle size and (price) class.
- Base fuel consumption for Euro 5 and 6 passenger cars are not differentiated over the Euro 4 levels, as fuel consumption is not a function of the emission standard but rather of model year. A separate function in COPERT, based on fleet average characteristics has been proposed already in V10.0 for predicting real world emission levels.
- Similar to the previous vehicle types, different emission factor equations were produced for heavy duty vehicles and buses based on vehicle load (0%, 50% and 100%) and the road slope (-6%, -4%, -2%, 0%, 2%, 4% and 6%); 21 separate equations were derived for each HDV/BUS subcategory and for each pollutant.
- Regulations Light commercial vehicles (N1 vehicles) into three categories, depending on the gross vehicle weight (GVW), namely N1-I, N1-II, and N1-III, with increasing GVW. We have retained for simplicity the distinction only per fuel and not per GVW. However, recent trends show that gasoline LCVs are mostly into the smaller sizes with diesel ones dominating all three classes. In order to reflect the trend of decreasing

average size for gasoline LCVs, we have also corrected the Euro 3 and Euro 4 fuel consumption factors for these technologies.

1.4 References

1. Kühlwein, J., Rexeis, M., Luz, R., Hausberger, S. Update of Emission Fctors for Euro5 and Euro6 passenger cars for the HBEFA Version 3.2 – Final Report. **2013**. Report No. I-25/2013/Rex EM-I 2011/20679, Graz University of Technology, Austria, p.54.



2 Update of PCDD/Fs, HCB and PCB emission factors

2.1 Introduction

Dioxins are a family of several hundreds of toxic chlorinated organic compounds that share a specific chemical formula and several common properties. They are members of three closely related families: the chlorinated dibenzo-p-dioxins (CDDs), the chlorinated dibenzofurans (CDFs) and certain polychlorinated biphenyls (PCBs) [1]. According to the World Health Organization, the polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two families of almost planar tricyclic aromatic compounds with very similar chemical properties. Their volatility is quite low and they are solids at room temperature [2]. Upon exposure, dioxins and furans have been observed to have significant health impacts even at low ambient concentrations, increasing the morbidity and mortality rates of populations. Moreover, they are resistant to environmental degradation and are capable of long-range atmospheric transport [3].

Polychlorinated biphenyls (PCBs) are a group of oily stable chemicals with increased stability and low flammability. Their stability has promoted their use in industry (insulating materials for electrical equipment, plasticizers in plastic products and heavy duty hydraulic oils among others) but also makes them extremely persistent in the environment. Although PCBs are not dioxins, due to the fact that they contain small amounts of dioxin-like PCBs as well as dioxin impurities, especially PCDFs, they are considered to have dioxin-like properties [4].

Hexachlorobenzene (HCB) is also considered a very persistent environmental substance due to its chemical stability and resistance to biodegradation. HCB's long life time, from 2.7 to 6 years in the atmosphere, allows its transboundary transport [5]. It is considered a probable human carcinogen and is toxic by all routes of exposure. HCB bioaccumulates in fish, marine animals, birds, lichens and their predators, the ingestion of which or their products appears to be the most significant source of exposure for the general human population [6]. The same applies for PCDD/Fs and PCBs, with food being the major source of human exposure to them, in particular fatty foods such as dairy products, fish, meat and eggs [4]. However, exposure through inhalation is also a probable route.

With regard to the reporting of PCDD/Fs, PCBs and HCBs, according to the Convention on Long-range Transboundary Air Pollution, the members of the United Nations Economic Commission for Europe are required to provide their total national emissions. These reports are annual and provide the total emissions by NFR source category. However, during the 32nd EMEP Steering Body session, it was decided that reporting for PCB would be included only as a voluntary item, and thus, since 2009 the POPs that need to be reported annually and as per NFR source category are PAHs [Mg], PCDD/Fs [g I-Teq] and HCB [kg].

2.2 Emission sources and mechanisms

Main sources for the production of PCDD/Fs are different combustion processes, primarily in waste incineration and metal processing [4]. HCB can also be found as a by-product in the manufacture of several chlorinated solvents and pesticides or in agriculture if it is still used in the sector. Other sources include sewage sludge incineration, metal smelting, sintering processes, and production of magnesium and cement [5]. Although HCB and PCB have been widely used in agriculture and industry respectively, neither of them is any longer produced in the European Union. Currently, the only human related emission of PCB and HCB is as unintentionally produced pollutant. They are also formed through a similar mechanism to dioxins and furans, and their emission follows the same chemical and thermal processes [1].

Of particular interest to transport are the emissions of POPs from fossil fuel combustion. Engines emit hydrocarbons, which include polycyclic aromatic hydrocarbons (PAHs), nitro-polycyclic aromatic hydrocarbons, and PM with a significant fraction of elemental carbon. These substances, along with the presence of chlorine (Cl) either from the fuel or the ambient air, lead to "the formation of PCDD/Fs via either the precursor or de novo synthesis routes" [8], referring to altering of a preceding substance into PCDD/F or to the synthesis of complex molecules from simple ones.

Persistent organic pollutants are formed in every combustion process, if organic matter and chlorine are present in the combustion environment. The main sources responsible for the presence of POPs in exhaust gases are [4]:

1. The pre-existing POPs either in the fuel or in the ambient air, which did not decompose during combustion.
2. The gas-phase synthesis of chlorinated precursors at temperatures over 500°C.
3. Heterogeneous catalytic chemical reactions on the surface of dust particles containing metals and their oxides such as Cu, Ni, Fe, Al, Zn, including in temperatures below 400°C.
4. The "de novo" synthesis from free radicals, elemental carbon and chlorine, catalysed by heavy metals, occurring in the temperature range of 250-700°C.

The formation of dioxins takes place during the cooling of the exhaust gas, with slow cooling favouring the formation and rapid cooling reducing it [4].

The emission levels of hexachlorobenzene, dioxins and furans have been found to vary during the years in different inventorying studies. Winter *et al.* [7] stated that PCDD/F and HCB emissions have been decreasing in the period 1985-1994 as a result of stringent regulations on industrial and waste incineration. After an initial increase in 1995 and 1996, PCDD/Fs and HCB emissions declined until 2001. In Austria, HCB emissions in particular, have seen a small increase in their levels from 2000 to 2005, but have been dropping ever since 2006, with a significant reduction in 2009, primarily due to the overall reduction in economic activity [7]. Figure 2-1 shows the downward trend in onsite releases from point sources in Canada during the years 2000-2007.

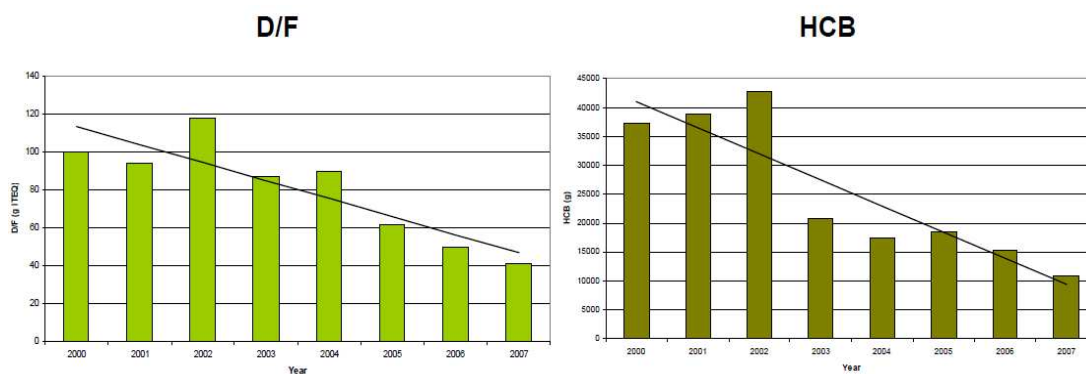


Figure 2-1: Total point source releases of PCDD/F and HCB (2000 to 2007) in Canada [26]

The relative contribution of transport to the total emissions has been overall relatively low. In the US, heavy duty diesel engines in 2000 were responsible for an estimated 4.6% of total PCDD/F emissions, thus rating as the sixth largest source, an estimation based on relevant emission factors [12]. For hexachlorobenzene in Austria's case, the share of transport in emitted HCB was estimated to account for 1% of total emissions, including maritime and air transport [7]. However, as stated by Chuang *et al.* [22] for Taiwan in particular, due to the decrease in the emissions of chlorinated compounds from stationary sources, the relative contribution factor of transport has gradually increased.

Although the initial goal of the report was to determine road transport emission factors of HCB only, all POP substances were examined together for the three following reasons:

- The rather complete lack of data for HCB and limited data for PCB emissions from road vehicles, that made mandatory to collection of all available data to establish an order of magnitude for the emission factors.
- The chemical and thermal processes, from which HCB and PCB emissions are produced, are identical to those for dioxins and furans. The similarities present also in the structure and occurrence for HCB and dioxins and furans often lead to the assumption that those parameters that favour the formation of one, lead also to the formation of the other [7]. Hence, factors that affect the formation of one species are expected also to generally favour the formation of the other, as well.
- A good correlation has been observed between the concentrations of PCDD/Fs and HCB in exhaust gases from industrial installations (r correlation coefficient 0.7-1) [9]. This correlation could also be used for road vehicles as well.

2.3 Toxic equivalency

The most important member of the PCDD/Fs compounds is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), which has the higher toxicity and has been extensively studied. Because of its toxicity, TCDD was also selected as the reference in order to express the toxicity of the remaining dioxins and furans. According to the Toxic Equivalency method, each compound in the PCDD/PCDFs list is assigned a factor, based on the comparison of its toxicity to TCDD, thus

allowing mixtures of compounds to be expressed by a single number, the TEQ (Toxic Equivalency), and facilitating risk assessment. The toxicity equivalent factors of each member are given in Table 2-1

Table 2-1: Toxicity Equivalent Factors

Congener	WHO 1998 TEF	WHO 2005 TEF
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	0.0003
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.03
2,3,4,7,8-PeCDF	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.001	0.0003

2.4 Emission factors in COPERT

The emission factors currently in use in COPERT 4 (i.e. up to V10.0) can be seen in Table 2-2. These values have been collected from a relatively old publication by the Federal Republic of Germany's Environment Agency [10], and correspond to bulk emission factors expressed in pg/km, aggregated to main vehicle categories.

Table 2-2: Emission Factors used in COPERT 4, up to version 10.0 (Nov. '12)

	Toxicity equivalent emission factor [pg/km]		
	PC gasoline conv.	PC diesel IDI	Heavy-duty diesel
Polychlorinated dibenzo dioxins			
TeCDD TOTAL	3.8	0.2	1.4
PeCDD TOTAL	5.2	0.2	0.9
HxCDD TOTAL	1.0	0.1	0.3
HpCDD TOTAL	0.2	0.0	0.2
OCDD	0.1	0.0	0.2
Total Dioxins	10.3	0.5	3.0
Polychlorinated dibenzo furans			
TeCDF TOTAL	3.6	0.1	0.6
PeCDF TOTAL	8.2	0.5	2.8
HxCDF TOTAL	8.1	0.4	3.9
HpCDF TOTAL	1.3	0.0	0.5
OCDF	0.0	0.0	0.1
Total furans	21.2	1.0	7.9



There are no emission factors regarding hexachlorobenzene and polychlorinated biphenyls currently in COPERT. Moreover, those emission factors did not distinguish for vehicle technology.

2.5 Literature study

Due to their toxicity and potential health risks to the public, chlorinated emissions from different anthropogenic sources have been thoroughly investigated. Emission factors from different sources can be found ranging from heavy industrial units to small-scale domestic applications. Such emission factors are given either as part of reports as for example on Persistent Organic Polluters (POPs) [10] or in reports specific for each substance [11].

Since heavy duty diesel vehicles have been considered as the major source of PCDD/Fs emissions, the main focus has been on them and the different exhaust aftertreatment technologies. Laroo *et al.* [12] investigated the PCDD/F, PCB, and PAH exhaust emissions from a model year 2008 diesel engine, with different configurations of aftertreatment devices (diesel oxidation catalyst - DOC, catalytic diesel particle filter - CDPF, and selective catalytic reduction - SCR) included in the testing. Results showed no significant increase in PCDD/F and PCB emissions from the engines with catalytic aftertreatment, in comparison to the engine-out configuration. In a relative study by Laroo *et al.* [13], a legacy on-road heavy duty engine was examined (1993 model year), firstly to determine the PCDD/Fs from a category of vehicles that can still be found in operation, but also to offer a comparison to the modern diesel engines equipped with exhaust aftertreatment. The results showed increased emissions of this older engine when compared to a modern diesel engine, showing that the improvements in the diesel engine combustion technology in order to meet the restrictions imposed on the regulated pollutants, also seem to decrease emissions of non-regulated pollutants.

Similar testing was done by Hsieh *et al.* [14], in which the effect of three different aftertreatment systems (mobile metal filter plus CDPF, DOC+CDPF and partial DPF) were investigated. Lower emissions of PCDD/F and PCB from vehicles with lower mileage were observed, and the partial DPF exhibited the largest reduction. However, the significant differences between the trials reveal that the reduction of PCDD/F and PCB could be more complex than that of the straightforward reduction of particulate matter. Liu *et al.* [15] measured the dioxin and furan emissions from mobile source diesel engines and investigated the impact of copper zeolite SCR and other exhaust aftertreatment configurations with an engine-out measurement as reference. It was found that all configurations with aftertreatment systems reduced PCDD/F below engine-out levels, with the values less than 2 orders of magnitude lower than those used by EPA to estimate total emissions from diesel on-road trucks in the year 2000 and about 1000 times lower than the emission limits per dry standard cubic meter of exhaust from point sources, such as medical waste incinerators and cement kilns. In a different testing by Liu *et al.* [16], the emissions were measured during transient and multi-mode engine operation, with exhaust aftertreatment configurations including combinations of DOC, DPF and either Cu/zeolite or Fe/zeolite SCR. No significant difference in the emissions between the Cu/ and Fe/zeolite SCR was found, with the emissions again being at least three

orders of magnitude lower than those of municipal waste incinerators per dry standard cubic meter of exhaust.

Heeb *et al.* [17] examined the formation of PCDD/Fs induced by DPFs with different metal catalysts. It was concluded that the iron-catalyzed trap had a minor effect on PCDD/F patterns and low influence on total I-TEQ. On the contrary, copper-based DPF shifted PCDD/F patterns towards lower oxygen and chlorine proportions and resulted to an at least 60-fold increase of 2,3,7,8-TCDD emissions. In two reports, dating from 1999 and 2000, Geueke *et al.* [18] and Ryan *et al.* [19] also examined heavy duty diesel engines, without any mention of any exhaust aftertreatment system used. The first study referred to PCDD/F emissions that even in the worst case scenario were estimated to contribute up to 31.5 g I-TEQ/year for all western European countries, making dioxin emissions from diesel engine "appear to be almost irrelevant" [18]. The second report, apart from presenting actual emission factors, highlights the advantages of the on-road measurement technique over tunnel studies, which were at the time the only source for the estimates for US HDDV PCDD/F emissions and came up with a wide range of predictions regarding the significance of HDDVs contribution to the total emissions. The report also calls for the need of "an extensive multi-vehicle, multi-route sampling program" in order to produce higher confidence emission factors for the heavy duty diesel vehicles [19].

With regard to the impact of fuel properties on emissions, a study by Lin *et al.* [20] tested a non-catalyst diesel engine (model year 1994) with a number of different fuels in order to examine the reduction of dioxin and furan emissions when using palm oil derived biodiesel. It was found that biodiesel blends reduced PCDD/F emissions. Ullman *et al.* [3] examined the toxic air contaminants of school buses in an effort to see if emissions from compressed natural gas were less dangerous from low emitting diesel and conventional diesel fuels. From the three different engines tested (8.7, 8.7 and 8.1 L) only the low emitting diesel engine employed a catalysed diesel particulate filter. Low emitting diesel technology was found to have the lowest level of emissions. The emissions of PCDD/F from gasohol and ethanol fuels were measured by Abrantes *et al.* [21] from two light duty vehicles (1.6L, model years 1998 and 2004 respectively) both equipped with a catalytic converters. The emission results were found 150 times lower than that of vehicles without catalysts. The importance of ambient air as a source of chlorine in PCDD/F formation was also acknowledged in this paper, the authors of which suggest more detailed studies in this direction.

Regarding passenger vehicles and motorcycles, even less data from testing has been collected. Chuang *et al.* [22] measured the dioxin and furan emissions from three categories of vehicles, sports utility (SUVs), diesel personal (DPVs) and heavy duty diesel vehicles (HDDVs). Four vehicles were measured from each category and although there is no mention of exhaust aftertreatment in the report, the vehicles used were models existing in the market (model years 2003-2005, 2003-2006 and 2004-2006 for each category respectively), thus, the existing exhaust aftertreatment technologies of the period can be considered. The emissions were found rather higher compared to previous studies, a result that the authors attribute to the effect of cold start tests. Chuang *et al.* [23], taking into account the increasing number of motorcycles especially in metropolitan and suburban areas, measured the PCDD/Fs emissions from three 2-stroke and three 4-stroke motorcycles, all equipped with two-way catalytic



converters. Despite the smaller cylinder size of the motorcycles, their emissions were found comparable to those of larger 4-wheel vehicles. In a different measurement programme, Chang *et al.* [24] estimated the emission factors for PCDD/F by measuring both the air quality inside of a tunnel and at the vehicle exhaust. The results showed increased PCDD/F emissions when the engine was at idle, indicating higher dioxin concentrations during traffic jams and, thus, supporting the need for more investigation on the risk of dioxin emissions in areas with high population and vehicle density. Lastly, two reports containing aggregated information for dioxins were taken into account. In "Dioxins Emissions from Motor Vehicles in Australia" [25] by the Department of the Environment and Heritage of the Australian Government, a number of laboratory and on-road studies were examined and an emission factor range was proposed for different vehicle categories. In a similar manner, the emission factors from a number of studies, dating from 1987 to 1997, were gathered by the US Environmental Protection Agency [8].

All the sources mentioned above were collected and results were synthesized from these values. All values obtained from the literature sources addressing relatively recent vehicle types and technologies are summarized in Table 2-3.

Table 2-3: PCDD/Fs emission levels proposed by different literature sources

Engine/Vehicle Type	Fuel	Exhaust Aftertreatment	Emission Factor [pg I-TEQ/km]	Source according to refs list (year)
PCs, LCVs and Motorcycles	Leaded	Non catalyst	10-280	25 (2004)
PCs, LCVs and Motorcycles	Unleaded	Non catalyst	2-20	
PCs, LCVs and Motorcycles	Unleaded	Catalyst	1-3	
LDVs (PCs, LCVs)	Diesel	None	6-50	
Heavy duty	Diesel	None	15-650	
Buses	Diesel	None	12-530	
Truck	Diesel	Not reported	676-1325	8 (2006)
Passenger car	Unleaded	Catalyst equipped	<13	
Passenger car	Unleaded	Not reported	<20	
Passenger car	Unleaded	No catalyst	0.36-0.39	
Passenger car	Unleaded	Catalyst equipped	0.36	
Truck	Diesel	Not reported	<18	
Passenger car	Unleaded	No catalyst	5.10	
Passenger car	Unleaded	Catalyst equipped	0.70	
Passenger car	Diesel	Not reported	2.10	
Passenger car	Unleaded	No catalyst	9.6-17.7	
Passenger car	Unleaded	Catalyst equipped	1- 2.6	
Passenger car	Diesel	No catalyst	1-13	
Truck	Diesel	No catalyst	13-15	
Truck	Diesel	No catalyst	29	



Engine/Vehicle Type	Fuel	Exhaust Aftertreatment	PCDD/Fs Emission Factor [pg I-TEQ/km]	Source (year)
Modern diesel (2008, 6.7 L)	Diesel	Engine-out	0.62	12 (2011)
		CuZ SCR HT	0.53	
		CuZ SCR LT	0.84	
		FeZ SCR	0.92	
		DOC + CDPF	0.41	
		T DOC+CDPF+CuZSCR+ASC+urea	0.42	
		T DOC+CDPF+FeZ SCR+ASC+urea	0.12	
		T DOC+CDPF	0.07	
		T DOC+CDPF+CuZ SCR+ASC+urea, 10 ppm Cl	0.06	
6.2 J-series 6.2 L (1985)	Diesel	No aftertreatment	4.33	13 (2012)
6V98 9 L (1987)			4.48	
L10 10 L (1993)			2.35	
Heavy duty	Diesel	MMF+CDPF	21.08	14 (2011)
		MMF+CDPF	243.66	
		DOC+CDPF	33.23	
		DOC+CDPF	4.86	
		DOC+CDPF	6.47	
		PDPF	47.66	
HDD Engine (8.9 L, 12.9 L, 2010)	Diesel	Engine Out	4.13	15 (2011)
		DOC+DPF+SCR	1.60	
Transient and multi-mode engine operation (8.9L 2010)	Diesel	DOC+DPF+SCR (SRC: Cu/Z type)	0.31	16 (2011)
		DOC+DPF+SCR (SRC: Fe/Z type)	0.20	

Engine/Vehicle Type	Fuel	Exhaust Aftertreatment	Emission Factor [pg I-TEQ/km]	Source (year)
1991 Freightliner diesel tractor with a 10.3 L	Diesel	Not reported	15.13	18 (2000)
Heavy Duty MAN (12 L)	Diesel	None	116.00	19 (1999)
Heavy duty diesel engine (Liebherr, 6.11 L)	Diesel	Diesel particulate filter (iron- and copper- based fuel additive)	17.49	17 (2007)
Engine Cummins B5.9-160 HDDE	Prem. Diesel	Non catalyst	22.58	20 (2011)
	B20		12.86	
	B100		3.36	
School bus 8.7 L (2001)	Conv. Diesel	None	161.46	3 (2003)
School bus 8.7 L (2001)	Low emit. diesel	Engelhard PDX catalysed diesel particulate filter	161.46	
School bus 8.1 L (2000)	CNG	None	155.25	
Light duty vehicle (1.6 L, 1998)	Gasohol	Catalytic converter	0.0294	21 (2011)
Light duty vehicle (1.6 L, 2004)	Ethanol	Catalytic converter	0.0310	
SUV	Unleaded	Not reported (2003-2005 market vehicle)	123.00	22 (2011)
DPV	Diesel	Not reported (2003-2006 market vehicle)	80.00	
HDDV	Diesel	Not reported (2004-2006 market vehicle)	1690.00	
Motorcycle 2-stroke	Unleaded	Two way catalytic converter	96.60	23 (2010)
Motorcycle 4-stroke	Unleaded	Two way catalytic converter	81.00	
Average vehicle in Taiwan	Gasoline	Tunnel sampling- average vehicle	22.93±4.93	24 (2004)
	Diesel		91.73±19.71	



2.6 Methodology

The focus of the literature study was to collect values in order to obtain emission factors in pg or ng of I-TEQ per kilometre. Averaged values were initially considered and relevant ranges of uncertainty were proposed. Several of the studies were not based on European vehicles and no Euro-standard classification was available. In such cases, the measurements were considered only when the emission control technology was similar to the one used in any of the Euro standards and the fuel used was of similar specifications, to the extent this could be verified. As a general comment, we were mostly looking for order of magnitude emission factors, rather than precise values, hence the exact vehicle emission control tuning was not of importance as long as the general specifications were within the typical European configurations. The size of the engine and the model year were also considered of interest and, thus are also presented when these were available in the literature sources used. Few emission levels that clearly differed from the majority of measured values were left outside of the averaging, considering these were outliers.

Although most of the studies and publications presented the emission factors in units of toxicity equivalence per unit of distance travelled, some studies, namely [14], [15] and [16], provided the results per unit of volume of emissions. In such cases, conversions were conducted using volume to distance factors that were considered relevant for the vehicles and operation considered in each study.

In two studies, [13] and [17], the emission factors were given in pg per litre of fuel. An average fuel consumption was used in order to convert these values to pg per km. Since, as it can be seen in the tables, the variance between the emission levels in the different sources is already very high, the assumptions considered herein are assumed to add a small additional error to the final results.

For heavy duty vehicles, we have considered that engines of Euro 4 and older are of rather similar characteristics. The same emission factor is therefore assigned to all such vehicles. This is a simplification owned to the lack of data to split into individual Euro classes. Euro V trucks are then assumed to be equipped with SCR technology and Euro VI to be equipped with both SCR and DPF and separate emission factors are proposed to those technologies.

Diesel light duty vehicles are also split into Euro 4 and earlier, Euro 5 and Euro 6. This is with consideration that Euro 5 ones are equipped with DPFs, while Euro 6 may also be equipped with SCR.

Two technology groups were distinguished for gasoline vehicles, one considering Euro 2 and older vehicles and one considering Euro 3 and more recent. The basic aftertreatment technology in all gasoline cars is the same, i.e. unleaded fuel and stoichiometric combustion and three way catalyst. Hence, the change in the emission levels mostly reflects the impact of ageing on emissions.

Taking into account the above assumptions, the emission levels and the associated emission factors derived from the literature sources publications are presented in the following tables, along with the main characteristics of the tested vehicles.

2.7 Emission factors

Table 2-4 shows literature average emission levels for the main vehicle categories, Heavy Duty Diesel (HDD), Light Duty Diesel (LDD) and gasoline.

Table 2-4: Aggregate PCDD/Fs emission factors

Vehicle Type	EURO	AVERAGE (pg I-TEQ/km)
Heavy Duty Diesel	EURO IV or older	62.9
	EURO V	0.41
	EURO VI	0.40
Light Duty Diesel		61.0
Light Duty Gasoline	EURO 2 or older	32.5
	EURO 3 or newer	6.8

Average aggregate emission levels for PCDD and PCDF separately can be seen in Table 2-5.

Table 2-5: Aggregate PCDD and PCDF emission levels

Vehicle Type	EURO	PCDD (pg I-TEQ/km)	PCDF (pg I-TEQ/km)
Heavy Duty Diesel	EURO IV or older	25.3	37.6
	EURO V	0.16	0.25
	EURO VI	0.16	0.24
Light Duty Diesel		25.0	36.0
Light Duty Gasoline	EURO 2 or older	13.1	19.4
	EURO 3 or newer	2.7	4.1

Owned to the limited available data, a number of additional assumptions were made to produce emission factors for all Euro vehicle classes. The emission factors for motorcycles and mopeds were considered equal to those of passenger cars. Light duty diesel and diesel passenger cars were also considered to have equal emission factors, and for the calculation of more recent EURO classes, the ratios in the reduction in emissions between EURO IV and EURO V of the Heavy Duty Diesel vehicles were used.

Finally, as mentioned before, the existing data on HCB and PCB emissions from mobile sources is limited. With regard to PCB, three scientific papers were found, containing the results of measurements of PCB and PCDD/F from heavy duty vehicles ([12], [13], and [14]). From these papers the ratio between the PCB and PCDD/Fs was calculated, which was found to range around 0.2 on average.



Regarding HCB, no similar data, linking the PCDD/F to HCB emissions for road vehicles could be found. The next option was to gather the ratios of HCB to PCDD/F from other combustion sources and evaluate their differences and similarities to road vehicles (Table 2-6). The ratios collected exhibit a wide range, from 0.6:1 (stove combustion) to more than 600:1 (marine bunker fuel). The fuel characteristics and the combustion differ between these individual sources and also between these sources and the combustion in the cylinder of a vehicle. Even compared to the most similar source found, a ship's engine, still we cannot but acknowledge the particularities of the road vehicle's combustion in being more efficient and regulated, and also in use of a much "cleaner" fuel. Additional to this is the fact that the ambient air that a ship uses has a much higher concentration of chlorine than that of an average road vehicle, a factor that is connected to the formation of polychlorinated substances [8]. Furthermore, since observing that the PCB:PCDD/F ratio is 0.2 and taking into account that PCDD/F, HCBs and PCB have similar formation mechanisms, it was expected that emissions of HCB would also be of the same magnitude.

Hence, the only assumption we could do is that the maximum HCB emission rate from road vehicles could not exceed these of PCDD/F. This should rather be considered the maximum range. Measurements to support or reject this assumption are necessary. The final proposed emission factors for PCDD/Fs, PCB and HCB are presented in Table 2-7, Table 2-8, Table 2-9.

Table 2-6: Range of HCB:PCDD/F ratio for different combustion sources

Emission source	HCB	PCDD/F	Units	Ratio HCB:PCDD/F	Source
Residential plants Hard/Brown Coal)	0.62	0.8	µg/GJ	0.78	5
Residential plants Biomass	5	0.8	µg/GJ	6.25	
Commercial/institutional Hard/Brown Coal	0.62	0.203	µg/GJ	3.05	
Commercial/institutional Biomass	5	0.1	µg/GJ	50.00	
Residential Plants-Solid fuel (not biomass)	0.62	0.5	µg/GJ	1.24	
Biomass Residential (fireplaces, saunas)	5	0.8	µg/GJ	6.25	
Residential Plants - Wood	5	0.8	µg/GJ	6.25	
Residential Plants - Solid, not biomass Stoves	0.62	1	µg/GJ	0.62	
Residential Solid fuel,not biomass, small boilers	0.62	0.5	µg/GJ	1.24	
Commercial/institutional, Gas Oil	0.22	0.001	µg/GJ	220.00	
Coal	0.46	0.0015	µg/GJ	306.67	7
Fuel Oil	0.08	0.0004	µg/GJ	200.00	
Heavy duty oil in gasworks	0.12	0.009	µg/GJ	13.33	
Other oil products in gasworks	0.14	0.0017	µg/GJ	82.35	
Refinery Gas	0.04	0.0006	µg/GJ	66.67	
Natural Gas	0.04	0.0002	µg/GJ	200.00	
Natural Gas II	0.08	0.0004	µg/GJ	200.00	
Industrial waste/unspecified	14.48	0.024	µg/GJ	603.33	
Biomass >1 MW	2	0.01	µg/GJ	200.00	
Wood <1MW	28	0.14	µg/GJ	200.00	
Wood/straw	24	0.12	µg/GJ	200.00	
Gaseous Biofuels	0.072	0.0006	µg/GJ	120.00	
In exhaust from industrial and hospital waste incinerators	11.5	0.041	ng/Nm ³	280.49	9
Experimental PVC combustion [600 C]	1	47	ratio to PeCB	47.00	11
Back yard burning in open barrel	2	14	ratio to PeCB	7.00	
Ship engine operating conditions: Marine Distillate	20	0.03	ng/kWh	666.67	27
Ship engine operating conditions: Residual Oil	30	0.1	ng/kWh	300.00	
			Average	147.75	

Table 2-7: Emission factors for total PCDD/F

		PCDD/Fs [pg I-Teq/km]	Standard Deviation
Passenger Car Gasoline	EURO 1	32	55
	EURO 2	32	55
	EURO 3	6.8	9.2
	EURO 4	6.8	9.2
	EURO 5	6.8	9.2
	EURO 6	6.8	9.2
Passenger Car Diesel	EURO 1	61	46
	EURO 2	61	46
	EURO 3	61	46
	EURO 4	61	46
	EURO 5	0.74	0.55
	EURO 6	0.74	0.55
Light Duty Gasoline	EURO 1	32	55
	EURO 2	32	55
	EURO 3	6.8	9.2
	EURO 4	6.8	9.2
	EURO 5	6.8	9.2
	EURO 6	6.8	9.2
Light Duty Diesel	EURO 1	61	46
	EURO 2	61	46
	EURO 3	61	46
	EURO 4	61	46
	EURO 5	0.74	0.55
	EURO 6	0.74	0.55
Heavy Duty Diesel	EURO I	63	96
	EURO II	63	96
	EURO III	63	96
	EURO IV	63	96
	EURO V	30	-
	EURO VI	0.4	0.55
Motorcycles	EURO 1	32	55
	EURO 2	32	55
	EURO 3	6.8	9.2
	EURO 4	6.8	9.2
	EURO 5	6.8	9.2
	EURO 6	6.8	9.2
Mopeds	EURO 1	32	55
	EURO 2	32	55
	EURO 3	6.8	9.2
	EURO 4	6.8	9.2
	EURO 5	6.8	9.2
	EURO 6	6.8	9.2



Table 2-8: Emission factors for PCDD and PCDF, with comparison to the existing emission factors in COPERT

		PCDD [pg I-Teq/km]		PCDF [pg I-Teq/km]	
		COPERT 4 v.10	New	COPERT 4 v.10	New
Passenger Car Gasoline	Pre-EURO	10.3	10.3	21.2	21.2
	EURO 1	10.3	13.0	21.2	19.0
	EURO 2	10.3	13.0	21.2	19.0
	EURO 3	10.3	2.7	21.2	4.1
	EURO 4	10.3	2.7	21.2	4.1
	EURO 5	10.3	2.7	21.2	4.1
	EURO 6	10.3	2.7	21.2	4.1
Passenger Car Diesel	Pre-EURO	0.5	24.5	1.00	36.5
	EURO 1	0.5	24.5	1.00	36.5
	EURO 2	0.5	24.5	1.00	36.5
	EURO 3	0.5	24.5	1.00	36.5
	EURO 4	0.5	24.5	1.00	36.5
	EURO 5	0.5	0.3	1.00	0.44
	EURO 6	0.5	0.3	1.00	0.44
Light Duty Gasoline	Pre-EURO	10.3	10.3	21.2	21.2
	EURO 1	10.3	13.0	21.2	19.0
	EURO 2	10.3	13.0	21.2	19.0
	EURO 3	10.3	2.7	21.2	4.1
	EURO 4	10.3	2.7	21.2	4.1
	EURO 5	10.3	2.7	21.2	4.1
	EURO 6	10.3	2.7	21.2	4.1
Light Duty Diesel	Pre-EURO	0.5	24.5	1.00	36.5
	EURO 1	0.5	24.5	1.00	36.5
	EURO 2	0.5	24.5	1.00	36.5
	EURO 3	0.5	24.5	1.00	36.5
	EURO 4	0.5	24.5	1.00	36.5
	EURO 5	0.5	0.3	1.00	0.44
	EURO 6	0.5	0.3	1.00	0.44
Heavy Duty Diesel	Pre-EURO	3.0	25.0	7.9	38.0
	EURO I	3.0	25.0	7.9	38.0
	EURO II	3.0	25.0	7.9	38.0
	EURO III	3.0	25.0	7.9	38.0
	EURO IV	3.0	25.0	7.9	38.0
	EURO V	3.0	13.0	7.9	17.0
	EURO VI	3.0	0.16	7.9	0.24
Motorcycles	Pre-EURO	10.3	10.3	21.2	21.2
	EURO 1	10.3	13.0	21.2	19.0
	EURO 2	10.3	13.0	21.2	19.0
	EURO 3	10.3	2.7	21.2	4.1
	EURO 4	10.3	2.7	21.2	4.1
	EURO 5	10.3	2.7	21.2	4.1
	EURO 6	10.3	2.7	21.2	4.1
Mopeds	Pre-EURO	10.3	10.3	21.2	21.2
	EURO 1	10.3	13.0	21.2	19.0
	EURO 2	10.3	13.0	21.2	19.0
	EURO 3	10.3	2.7	21.2	4.1
	EURO 4	10.3	2.7	21.2	4.1
	EURO 5	10.3	2.7	21.2	4.1
	EURO 6	10.3	2.7	21.2	4.1

Table 2-9: Emission factors for HCB and PCB

		HCB* [pg /km]	PCB [pg /km]
Passenger Car Gasoline	Pre-EURO	31.5	6.4
	EURO 1	32	6.4
	EURO 2	32	6.4
	EURO 3	6.8	1.36
	EURO 4	6.8	1.36
	EURO 5	6.8	1.36
	EURO 6	6.8	1.36
Passenger Car Diesel	Pre-EURO	1.5	1.5
	EURO 1	61	12.2
	EURO 2	61	12.2
	EURO 3	61	12.2
	EURO 4	61	12.2
	EURO 5	0.74	0.15
	EURO 6	0.74	0.15
Light Duty Gasoline	Pre-EURO	31.5	31.5
	EURO 1	32	6.4
	EURO 2	32	6.4
	EURO 3	6.8	1.36
	EURO 4	6.8	1.36
	EURO 5	6.8	1.36
	EURO 6	6.8	1.36
Light Duty Diesel	Pre-EURO	1.5	1.5
	EURO 1	61	12.2
	EURO 2	61	12.2
	EURO 3	61	12.2
	EURO 4	61	12.2
	EURO 5	0.74	0.15
	EURO 6	0.74	0.15
Heavy Duty Diesel	Pre-EURO	10.9	10.9
	EURO I	63	12.6
	EURO II	63	12.6
	EURO III	63	12.6
	EURO IV	63	12.6
	EURO V	0.76	0.15
	EURO VI	0.4	0.08
Motorcycles	Pre-EURO	31.5	31.5
	EURO 1	32	6.4
	EURO 2	32	6.4
	EURO 3	6.8	1.36
	EURO 4	6.8	1.36
	EURO 5	6.8	1.36
	EURO 6	6.8	1.36
Mopeds	Pre-EURO	31.5	31.5
	EURO 1	32	6.4
	EURO 2	32	6.4
	EURO 3	6.8	1.36
	EURO 4	6.8	1.36
	EURO 5	6.8	1.36
	EURO 6	6.8	1.36

* Not based on actual measured data. Rather, this should be the maximum assuming HCB=PCDD/F.



2.8 Conclusions

Use of the new emission factors, when compared to the existing ones in COPERT 4 v.10, will obviously lead to a change of estimated total emissions of dioxins and furans in the EU27, especially from diesel vehicles. Emission factors for PCDD/Fs for diesel passenger cars and light duty vehicles of Euro 4 or earlier classes are increased almost 50 times, followed by a decrease in Euro 5 and Euro 6 classes. The estimated total PCDD/Fs emissions from these categories are expected to significantly increase, since the population of Euro 4 or older vehicles is much greater than that of Euro 5 and newer (79% for EURO 4 or older passenger cars and 86.9% for light duty in 2012 for EU27 according to EC4MACS). An increase but of smaller size is also expected from the heavy duty diesel vehicles, since the effect of the 8 fold increase of Euro IV or earlier is limited by the 10 fold decrease for Euro VI HDD vehicles, which attribute to 23.5% of the total population in the EU27.

The reverse outcome is expected from the new emission factors of PCDD/Fs with regard to the gasoline vehicles. Although changes in EURO 1 and 2 are mixed, increase for dioxins and decrease for furans, the total estimated emissions from gasoline motorcycles, passenger cars and light duty vehicles is expected to decrease due to the 4- and 5-fold decrease in the emission factors of dioxins and furans respectively for Euro 3 and newer vehicles. Mopeds are expected to show an increase in total PCDD and a decrease in PCDF emissions, since the population of EURO 2 or earlier vehicles greatly outnumbers the EURO 3 or newer.

No comparison between old and new PCB and HCB emissions is feasible, since no emission factors for the substances were present in COPERT.

The most important conclusion though is that the values presented in these tables are based on a small sample, often inconsistent measurements and with a limited number of European tests. Differences in the sampling techniques, fuel properties, as well as concentration of species in the ambient air are also important factors to the observed differences. Additionally, the different aftertreatment technologies appear to have a complex effect on the emitting PCDD/PCDF, signifying that these types of pollutants are not targeted by the current exhaust aftertreatment technologies. Although there are existing studies that examine, for example, the effect of iron-catalysed DPF on PCDD/F emissions [17], they are of limited number and more are needed in order to better define their effect.

In particular, we could not locate any single recent study on HCB measurements from road vehicles. This creates huge problems in identifying a reasonable emission range for this pollutant. Thus, a new set of studies, with the aforementioned parameters taken into account is to be considered a priority.

References

1. Anderl M., Kother T., Muik B., Pazdernik K., Schodl B., Poupa S., Wappel D., Wieser M., Austria's Informative Inventory Report (IIR) **2009**, Submission under the UNECE Convention on Long-Range Transboundary Air Pollution, Report REP-0218, Umweltbundesamt GmbH, Wien.
2. World Health Organization, Chapter 5.11 Polychlorinated dibenzodioxins and dibenzofurans, online: http://www.euro.who.int/_data/assets/pdf_file/0017/123065/AQG2ndEd_5_11PCDDPCDF.pdf, WHO Regional Office for Europe, Copenhagen, Denmark, **2000**.
3. Ullman, T.L, Smith L.R., Anthony J.W., Slodowske W.J., Trestrail B., Cook A.L., Bunn W.B., Lapin C.A., Wright K., Clark C.R., Comparison of exhaust emissions, including air contaminants from school buses in compressed natural gas, low emitting diesel and conventional diesel engine configurations, 2003-01-1381, SAE International, **2003**
4. Tuomisto J., Vartiainen T., Tuomisto J.T., Synopsis on Dioxins and PCBs, National Institute of Health and Welfare, Amnnerheimintie 166, FIN-00300 Helsinki, Finland, **2001**.
5. Joint EMEP/CORINAIR Atmospheric Emission Inventory Guidebook- December 2006 UPDATE. Copenhagen: European Environment Agency, **2006**.
6. The USEPA Persistent, Bioaccumulative and Toxic Pollutants (PBT) HCB Workgroup, PBT National Action Plan For Hexachlorobenzene (HCB) for Public Review, Draft, November 9, **2000**.
7. Winter B., Moser G., Bohmer S., Clara M., Deutsch K., Eberhartinger-Tafill S., Freundenschuss A., Frichenschlager H., Gallauer T., Hischenhuber M., Muller D., Nagl C., Kother T., Rauchbuchl A., Storch A., Stranner G., Thanner G., Weiss P., Wiesenberger H., Windhofer G., Zechmeister A., (**2012**). National action plan pursuant to article 5 of the Stockholm Convention on POPs and article 6 of the EU-POP Regulation, First Review, Umweltbundesamt GmbH, Wien.
8. U.S. EPA (Environmental Protection Agency). An inventory of sources and environmental releases of dioxin-like compounds in the United States for the years 1987, 1995, and 2000. (**2006**) 03/002F. Available from: National Technical Information Service, Springfield, VA, and online at <http://epa.gov/ncea>.
9. Węgiel M., Chrzęszcz R., Maślanka A., Grochowalski, A Study on the determination of PCDDs/Fs and HCB in exhaust gas, Chemosphere, Volume 85, Issue 3, October **2011**, pages 481-486.
10. Umweltbundesamt. Determinations of Requirements to Limit Emissions of Dioxins and Furans, Texte 58/95, ISSN 0722-186X. **1996**.
11. Hogendoorn, E.A., Bruinen de Bruin Y., Janssen M.P.M., Inventory emission factors for pentachlorobenzene, RIVM Letter report 601773002, **2009**.
12. Laroo, C.A., Schenk C.R., Sanchez L.J. and McDonald, J., Emission of PCDD/Fs, PCBs, and PAHs from a modern diesel engine equipped with catalyzed emission control systems, Environ. Sci. Technol. **2011**,45,6420-6428.
13. Laroo C.A., Schenk C.R., Sanchez L.J., McDonald J., Smith P.L.,**2012**, Emissions of PCDD/Fs, PCBs, and PAHs from legacy on-road heavy-duty diesel engines, Chemosphere 89 (2012) 1287-1294.
14. Hsieh, L.T., Wu M.Y.E., Wang L.C., Chang-Chien G.P, Yeh Y.F., Reduction of toxic pollutants emitted from heavy-duty diesel vehicles by deploying diesel particulate filters, Aerosol and air quality research, 11:709-715, **2011**.
15. Liu, G.Z., Wall, J.C., Barge, P., Dettman, E.M., Ottinger N.A., Investigation of PCDD/F Emissions from Mobile Source Diesel Engines: Impact of Copper Zeolite SCR Catalysts and exhaust aftertreatment configurations, Environ. Sci. Technol. **2011**,45, 2965-2972.
16. Liu G.Z., Ottinger N.A., Wall J.C. and Barge P., Measurement of Dioxin and furan emissions during transient and multi-mode engine operation, SAE International, 2011-01-1158, **2011**.
17. Heeb N.V., Zennegg M., Gujer E., Honegger P., Zeyer K., Gfeller U., Wichser A., Kohler M., Schmid P., Emmenegger L., Ulrich A., Wenger D., Peterman J.L., Czerwinski J., Mossiman T., Kasper M. and Mayer T., Secondary effects of catalytic diesel particulate filters: copper-induced formation of PCDD/Fs, Environ. Sci. Technol. **2007**,41,5789-5794.
18. Geueke K.-J., Gessner A., Quass U., Broker G., Hiester E., PCDD/F Emissions from heavy duty vehicle diesel engines, Chemosphere, Vol 38, No 12, pp. 2791-2806,**1999**



19. Ryan J.V., Gullet B.K., On-Road Emission Sampling of a Heavy Duty Vehicle for Polychlorinated Dibenzop-dioxins and Polychlorinated Dibenzofurans, *Environ. Sci. Technol.* **2000**, 34, 4483-4489.
20. Lin Y.C, Liu S.H., Chen Y.M., Wu T.Y., A new alternative paraffinic-palmdiesel fuel for reducing polychlorinated dibenzo-p-dioxin/dibenzofuran emissions from heavy-duty diesel engines, *Journal of Hazardous Materials* 185 (**2011**) 1-7.
21. Abrantes R.d., Assuncao, Pesquero, C.R., Nobrega R.P. and Buns R.E (**2011**), Comparison of Emission of Dioxins and Furans from Gasohol- and Ethanol-Powered Vehicles, *Air & Waste Manage. Assoc.* 61:1344-1352.
22. Chuang, S.C., Huang, K.L., Chen, S.J., Wang, L.C., Chang, G.P. Chang-Chien and Jen-Hsiung Tsai, PCDD/F Emissions from gasoline and diesel fueled vehicles, *Sustain.Environ. Res.*, 21(1), 29-36, **2011**.
23. Chuang S.C., Chen S.J., Huang, K.L., Chang-Chien, G.P., Wang, L.C., Huang, Y.C. (2010), Emissions of Plychlorinated dibenzo-p-dioxin and Polychlorinated Dibenzofuran from Motorcycles, *Aerosol and Air Quality Research*, 10: 533-539.2010.
24. Chang M.B., Chang S.H., Chen Y.W., Hsu H.C., Dioxin emission factors for automobiles from tunnel air sampling in Northern Taiwan, *Science of the total environment* 325 (**2004**) 129-138.
25. Smit R, Zeise K, Caffin A, Anyon P, **2004**, Dioxins Emissions from Motor Vehicles in Australia, National, National Dioxins Program Technical Report No. 2, Department of the Environment and Heritage, Canberra.
26. Wong A. (2009), Canada Update on Dioxins/Furans and HCB Emission Inventory, Sources and measurements workshop, CEC North American Strategy for Catalyzing Cooperation on dioxins, furans and HCB, December 10th, 2009, Mexico City, Mexico.
27. Cooper D., HCB, PCB, PCDD and PCDF emissions from ships, IVL Swedish Environmental Research Institute Ltd., report B1620, October, **2004**.



3 Update of NH₃ emission factors

3.1 Introduction

The emissions of air pollutants from road vehicles in the European Union have been in a constant decline over the last two decades. The implementation of consecutive Euro standards has led to significant reductions of regulated pollutants, while the upcoming Euro 6 standard for passenger cars will introduce even more stringent emission limits. This rapid reducing trend in emissions from regulated pollutants (CO, HC, NO_x, PM) is not always accompanied by a similar reduction of unregulated ones (non-NO_x nitrogen species, organic species, individual PM species, etc.). The aftertreatment technology used could in fact lead even to an increase of some unregulated pollutants in certain occasions. SCR technology for example, which is the dominant aftertreatment technology for NO_x control in new diesel vehicles, is known to increase NH₃ emissions, through possible "ammonia slip" events, which refer to ammonia, used to reduce NO_x concentration, exiting the SCR device without reacting. The relevant emission factors were developed in this study in order to quantify the impact of such effects and to be able to predict emissions from different vehicle types. This study is a continuation on the work done in a LAT/AUTh study [1], which provided NH₃ and N₂O emissions for the different vehicle classes and emission standards up to Euro 4. The methodology followed in the present study provides the emission factors for Euro 5 and 6 emission standards, as a function of the total mileage and the different driving conditions.

3.2 Literature research

A general literature research has been performed to assess the COPERT emission factors of older vehicle types, based on the latest measured information. The information collected in this updated research rather led to a validation of the factors used in COPERT for Euro 4/IV and older vehicles, so no revisions were deemed necessary. Only the publications referring to Euro 5/V and 6/VI vehicles and compatible technologies in US are therefore presented in this study.

In a study by Durbin et al. [2], three light duty gasoline vehicles were tested over different driving cycles. The vehicles were certified at the ULEV standard for California and no information regarding their aftertreatment is given. The results showed a dependency of NH₃ emissions on driving cycle, with increased emissions for more aggressive driving. It was also observed that even vehicles on a similar technological level may have much different NH₃ emissions, which is attributed to the fact that NH₃ is not regulated. Livingston et al. [3] tested a representative fleet of 41 light and medium duty gasoline vehicles, ranging from Tier 0 to SULEV LEV II standard without mention of the aftertreatment used, finding a mean ammonia factor of 46 mg/km. Medium-duty vehicles with older emission technologies and mid-range odometer readings had the highest emission rates of ammonia and aggressive driving showed increased emissions. Woodburn et al. [4] provided NH₃ emissions from Euro 3 gasoline vehicles, equipped with three-way catalysts over the New European Driving cycle, with the results showing low but not trivial levels (average of 9.2



mg/km). The study also mentioned the difficulty in achieving accurate and repeatable measurements of ammonia, which introduces uncertainty in the measurements. Bielaczyc et al. [5] compared the ammonia emission from three European passenger cars operating with three different fuels (gasoline, LPG and CNG). Results showed that ammonia emissions from vehicles running on gasoline were quite low (5.5 mg/km on average). The effect of fuel was also examined by Suarez-Bertoa et al. [6] using gasoline and ethanol blends. Great variance was seen in the results between the vehicles (11-27 mg/km for NEDC at 22°C) with the flexi-fuel car also producing fewer emissions when fueled with 85% ethanol. Eight low- (LEV) and ultralow- (SULEV) emission vehicles running on commercial California phase 2 gasoline were tested by Huai et al. [7] with the results varying considerably for the different vehicles and real-time emissions data, showing NH₃ emissions primarily generated during acceleration events.

Less information was available with regard to diesel vehicles. Rahman et al. [8] tested one diesel vehicle (Oxicat+cDPF) along with three gasoline (dual TWC and TWC as aftertreatment) ones. The results showed that diesel vehicles without SCR have rather low NH₃ emissions. Johnson et al. [9] tested a fleet of heavy duty vehicles and buses, finding NH₃ emissions occurring during transient accelerations and a high NH₃ release associated with high CO. Nakatani et al. [10] measured the emissions from a 9.2l HDDV with urea-SCR and a lean burn gasoline car in different cycles. Results showed that the HDDV had lower NH₃ emission levels than the lean-burn gasoline car. The values collected from the different scientific papers can be seen in Table 3-1



Table 3-1: NH₃ emission levels in different literature sources [mg/km]

Vehicle Type	Nb of vehicles	Emission standard	Aftertreatment	Cycle	Fuel	NH ₃ emissions [mg/km]	Source	
Light duty gasoline	3	EURO 5/6	-	FTP	gasoline	15.53	2	
Passenger cars	7	EURO 5/6	-		gasoline	19	3	
	1	EURO 5/6	-			34		
	4	EURO 5/6	-			15		
Passenger car - Vehicle 1	1	EURO 5	-	NEDC	stdr gasoline	17.78	4	
				UDC		17.18		
				EUDC		15.02		
Passenger car - Vehicle 2	1	EURO 5	-	NEDC		3.756		
				UDC		4.708		
				EUDC		2.103		
Passenger car - Vehicle 3	1	EURO 5	-	NEDC		5.709		
				UDC		6.711		
				EUDC		4.407		
Passenger car	1	EURO 5	-	NEDC	gasoline	5.27	5	
				UDC		6.7		
				EUDC		4.46		
Gasoline, 1390cm ³ ,	1	EURO 5	-	UDC	E5	14	6	
				EUDC		10		
				NEDC		11		
Gasoline, 1997 cm ³ ,	1	EURO 5	-	UDC		E5		39
				EUDC				17
				NEDC				27
Flexifuel light duty 1596 cm ³	1	EURO 5	-	UDC	E85, E75 HVP	8		
				EUDC		3.1		
				NEDC		5		
Passenger Car -	2	EURO 5/6 (SULEV)	O.E.	FTP	gasoline	1.5	7	



Average SULEV 2000-2001 vehicles				Hot Running		1	
				NYCC		7	
				US06		11	
				MEC01v7		44	
			aged equipment	FTP		2.5	
				Hot Running		0.5	
				NYCC		6	
				US06		7.5	
				MEC01v7		19.5	
			Passenger car - Average ULEV 2000-2001 vehicles	2		EURO 5/6 (ULEV)	
Hot Running	2						
NYCC	10						
US06	70.5						
MEC01v7	61						
aged equipment	FTP	11.5					
	Hot Running	1					
	NYCC	5.5					
	US06	61					
	MEC01v7	57					
Passenger Car - DI Diesel 2.0L	1	EURO 6	oxicat+cDPF	cold ftp75	diesel	3.11	8
				hot ftp75		0.62	
HDDV (2008)	1	EURO 6	DOC/DPF	-	diesel	5.71	9
HDDV (2004)	1	EURO 5	Urea SCR	JE05	diesel	5.5	10
				JE05-2		6	
				JE05-3		4	
				D13		27	

3.3 Methodology

These studies that were collected from the literature were further analysed to derive emission factors. A database was created with all of the collected values. The averages of these values were used to estimate the EF_{BASE} , which is the emission factor, without taking into account the contribution of the vehicle's age.

Of particular use were those studies, in which the emissions of new and "aged" versions of the same vehicle type were measured. The measurements from these dedicated experiments, where the only changing factor is the mileage of the vehicle, were used in order to define the effect that mileage, i.e. vehicle age, has on emissions. The emission factor in [mg/km], corrected for the average mileage of the specific vehicle fleet, is given by equation (1):

$$EF = [a \times CMileage + b] \times EF_{BASE} \quad (1)$$

In equation (1), the $CMileage$ is the cumulative mileage or the mean odometer reading of a vehicle fleet, which also expresses the age of this particular vehicle fleet. In this way, the aging of the vehicle's engine but also of the exhaust aftertreatment system is also taken into account in determining the unit emissions per kilometre. The coefficients a , b and EF_{BASE} have been derived from the data available in the literature research and differ according to the driving conditions (urban, rural and highway). A main difference to the earlier LAT/AUTH study [1] is that only a single category of (low) fuel sulphur level has been considered in determining the a , b parameters, since the aftertreatment technologies implemented at Euro 5/V or Euro 6/VI levels are not compatible with higher fuel sulphur contents.

A number of assumptions were made in order to develop the emission factors for all vehicle categories. Most of the assumptions refer to converting vehicle technologies of US into equivalent European based emission standards. This was necessary due to the lack of European data, especially in appreciating the impact of mileage on emissions. More relevant testing is required, especially for the different driving conditions (urban, rural and highway) so that better estimations on the emissions can be made.

Table 3-2 shows the vehicle technologies that were considered to be employed in Euro 5/V and 6/VI vehicles and the correspondence between the Euro and California standards used.

Table 3-2: Aftertreatment technology per Euro standard

Category	Vehicle Technology	Euro Class
Light Duty Gasoline	TWC (ULEV)	Euro 5/6
	TWC (SULEV)	Euro 5/6
Light Duty Diesel	DPF	Euro 5
	DPF+DeNOx	Euro 6
Heavy Duty Diesel	SCR	Euro V
	SCR+DPF	Euro VI



3.4 Results

The corrected emission factor is given by equation (1) with the relevant emission factor EF_{BASE} and the coefficients a and b .

Table 3-3: NH₃ EFs for Euro 5/6 Gasoline, CNG, E85 Passenger cars and LDVs

Driving Conditions	EF _{BASE} NH ₃ [mg/km]	a	b	St. Deviation
Urban Cold	13.8	3.23E-06	0.917	12
Urban Hot	4.1	1.73E-06	0.955	3.6
Rural	8	9.04E-07	0.977	6.0
Highway	21.8	5.95E-08	0.999	16.4

Due to lack of relevant data, in order to derive the EF_{BASE} for urban hot and highway, the ratios from the Euro 4 standards were used. The standard deviations for these values were also derived from multiplying the relevant values from Euro 5/6 to the Euro 4 ratios.

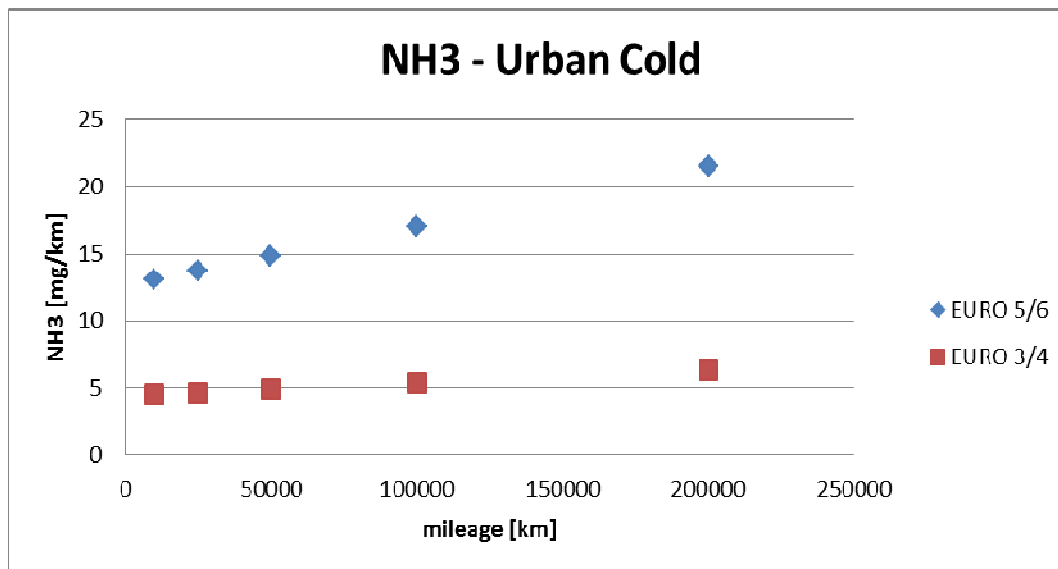


Figure 3-1: Comparison of NH₃ emissions [mg/km] from Euro 3/4 and Euro 5/6 gasoline vehicles in urban-cold driving conditions

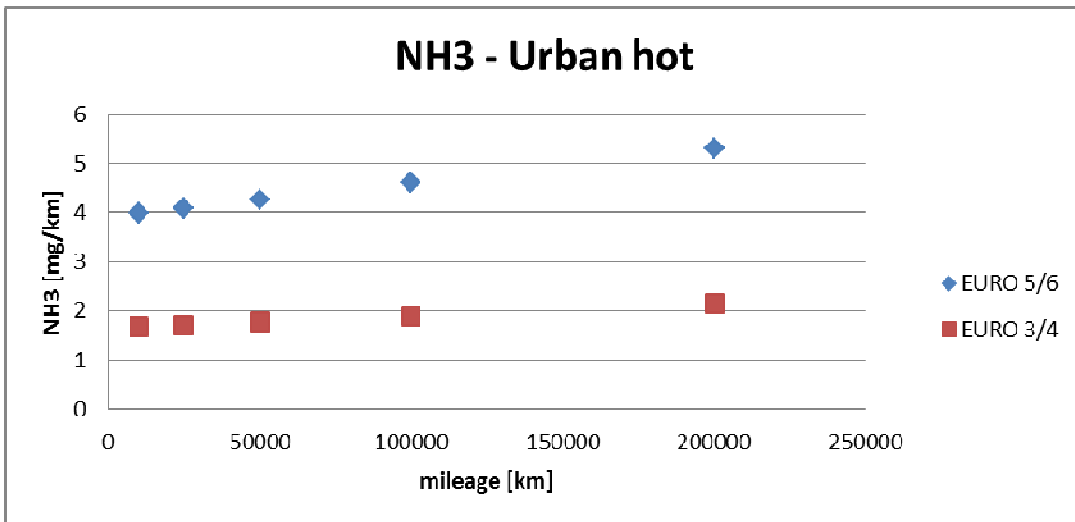


Figure 3-2: Comparison of NH₃ emissions [mg/km] from Euro 3/4 and Euro 5/6 gasoline vehicles in urban-hot driving conditions

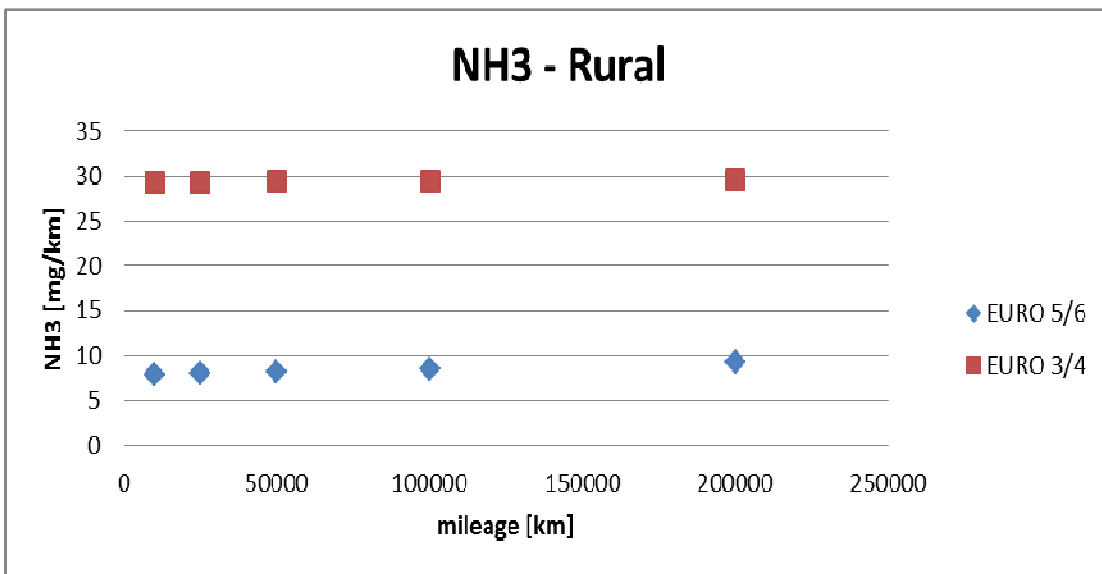


Figure 3-3: Comparison of NH₃ emissions [mg/km] from Euro 3/4 and Euro 5/6 gasoline vehicles in rural driving conditions

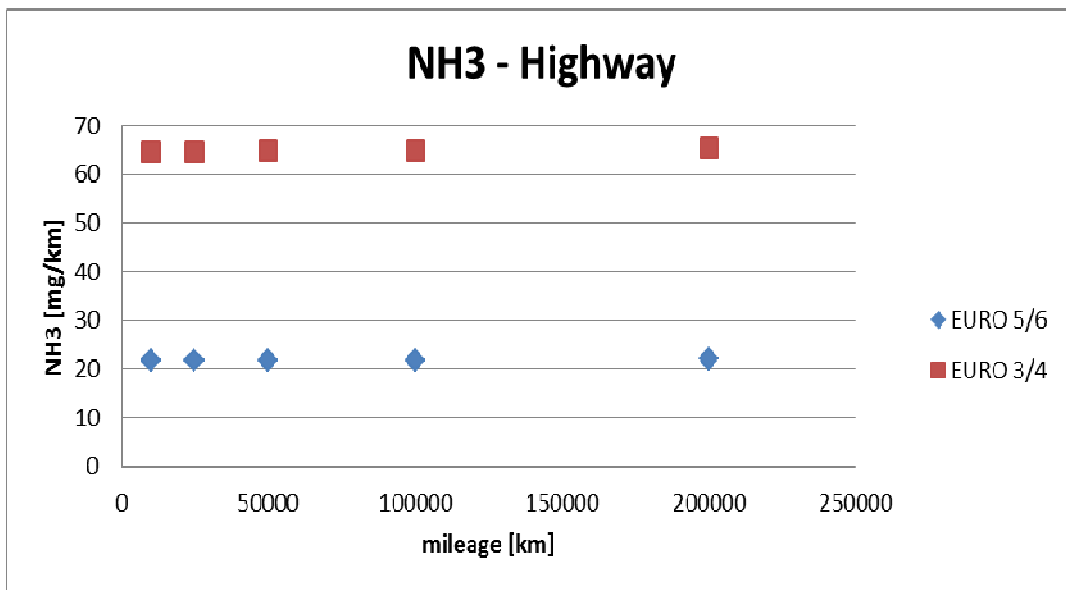


Figure 3-4: Comparison of NH₃ emissions [mg/km] from Euro 3/4 and Euro 5/6 gasoline vehicles in highway driving conditions

Figure 3-1, Figure 3-2, Figure 3-3 and Figure 3-4 offer a comparison between the emission factors between Euro 3/4 vehicles [1] and the current ones, developed for Euro 5/6 over the different driving conditions.

Table 3-4: Euro 5/6 and Euro V/VI NH₃ emission factors [mg/km] for diesel vehicles

Vehicle Category	Urban [mg/km]	Rural [mg/km]	Highway [mg/km]
Diesel PC – Euro 4 or earlier	1	1	1
Diesel PC - Euro 5	1.9	1.9	1.9
Diesel PC – Euro 6	7	7	7
Heavy Duty – Euro IV or	3	3	3
Heavy Duty - Euro V	11	11	11
Heavy Duty - Euro VI	9	9	9

Table 3-4 shows the emission factors for light and heavy duty diesel vehicles. The values for Euro 4 and Euro IV emission standards are the ones already used in the EMEP/EEA air pollutant emission inventory guidebook. The emission factor for Euro 6 diesel passenger car was estimated at 7 [mg/km], according to the relative increase for the heavy duty Euro IV to Euro V, due to the presence of SCR technology also for Euro 6 diesel passenger cars.

3.5 Conclusions

As seen in the results, gasoline fuelled vehicles are the main NH_3 polluters among the Euro 5 and 6 categories. For gasoline cars, urban cold emissions are greatly increased compared to urban hot and the influence of aggressive driving can be seen in the relative increase of the emissions from rural and highway driving cycles. In general, partial efficiency conditions of the three way catalyst are the ones favouring ammonia formation.

In comparison to vehicles of older technology, a mixed behaviour is observed, since Euro 5/6 vehicles have increased emissions over urban-hot and urban-cold driving conditions and reduced for rural and highway.

With regard to diesel, the fact that the NH_3 emissions are not zero is attributed to the presence of SCR in the exhaust aftertreatment. "Ammonia slip" is also the reason for the increase in NH_3 emissions from the Euro V and 6/VI vehicles.



References

1. Papathanasiou, L. and Tzircas, S. (2005). N₂O and NH₃ emission factors from road vehicles. LAT/AUTH report 0507, Thessaloniki, Greece (in Greek).
2. Heeb V.N., Saxer C.J., Forss A.-M., Bruhlmann S., Correlation of hydrogen, ammonia and nitrogen monoxide (nitric oxide), *Atmospheric Environment* 40 (2006) 3750-3763
3. Livingston C., Rieger P., Winer A., Ammonia emissions from a representative in-use fleet of light and medium duty vehicles in the California South Coast Air Basin, *Atmospheric Environment* 43 (2009) 3326-3333
4. Woodburn J., Bielaczyc P., Szczotka A., Chassis dynamometer testing of ammonia emissions from light-duty SI vehicles in the context of emissions of reactive nitrogen compounds, SAE international, 2013-01-1346, Published 04/08/2013
5. Bielaczyc, P., Szczotka, A., Swiatek, A. and Woodburn, J., A Comparison of Light-Duty Vehicles Operating on Gasoline, Liquefied Petroleum Gas (LPG), and Compressed Natural Gas (CNG), *SAE Int. Fuels Lubr.* 5(2):2012, doi: 10.4271/2012-01-1095.
6. Suarez-Bertoa R., Zerdini A. A., Astorga C., Effect of temperature on ammonia emissions from gasoline and ethanol flexi fuel cars, European Commission Joint Research Centre Ispra, Institute for Energy and Transport, Sustainable transport unit, 21027 Ispra (VA), Italy
7. Huai T., Durbin T.D., Miller J.W., Pisano J.T., Sauer C.G., Rhee S.H. and Norbek, Investigation of NH₃ emissions from new technology vehicles as a function of vehicle operating conditions, *Environ Sci. Technol.* 2003,37, 4841-4847
8. Rahman M., Hara K., Natakani S., Tanaka Y., Emission testing of n₂o (bag sampling from diverse vehicles by laser, SAE International, 2011-01-1155, Published 04/12/2011
9. Johnson K., Durbin T., Miller J. W., Emissions from in-use NG, propane and diesel fueled heavy duty vehicles, 2011 Directions in Engine-Efficiency and Emissions Research (DEER)
10. Nakatani S., Yoshimura T., Mori Y., Kihara N., Adachi M., Goto Y. and Suzuki H., Development of a Real-time NH₃ Gas Analyzer utilizing Chemi-luminescence detection for vehicle emission measurement, SAE International, Powertrain & Fluid Systems, Conference and Exhibition, Tampa, Florida, USA, October 25-28,2004

4 Update of N₂O emission factors

4.1 Introduction

For the same reasons as for NH₃, an update of the N₂O emission factors for the newer vehicles was considered necessary. The introduction of the Euro 6 emission standards will lead to new emission technologies implemented in vehicles in an effort to reduce the emissions from the regulated pollutants, having also a mixed effect on the unregulated ones. The calculation of the N₂O emissions factors of such vehicles, performed in this study, will assist in the estimation of the total emissions of this species.

4.2 Literature research

During the literature research, papers covering from pre-Euro to Euro 6/VI standards were examined. Papers referring to up to Euro 4/IV standards led to a validation of the emission factors used currently in COPERT. The papers referring to Euro 5/V and 6/VI and the compatible technologies from the US, were used in order to develop the new emission factors, and are presented here.

Rahman et al. [2], apart from the NH₃ emissions mentioned in the previous chapter, provide also emissions of N₂O from the four examined vehicles, three gasoline-fuelled and a diesel (Oxicat+cDPF). The port injection gasoline vehicle showed the lowest N₂O emissions, with the direct injection diesel slightly higher. The effect of catalyst aging on N₂O emissions is examined in a paper by Ball et al. [3], according to which, seven ultra-low emission gasoline vehicles equipped with close coupled and underfloor catalysts were measured as new (6400 km) and 5 of them also after aging on a dynamometer to the estimated equivalent of 240.000 km. The results show an increase of N₂O emissions with aging, although emissions from all vehicles remained below 10 mg/mile, a regulation set by the EPA and NHTSA to reduce greenhouse gases. Similar results were found from Graham et al. [4] during the measurement of light duty gasoline vehicles. Measurements of N₂O emissions from 467 vehicles were examined and the analysis verifies the increase of N₂O emissions with the mileage. The results show also little influence from the size of the vehicle, with passenger cars and light duty vehicles having small difference in N₂O emissions. The effect of different fuels on N₂O emissions was examined by Willner [5] by measuring 3 vehicles (2 CNG city buses and a diesel dual fuel DDF). The dual fuel vehicle showed less N₂O emissions when fuelled by diesel compared to the DDF mode. The per kilometre emissions, as found in the literature research, are given in Table 4-1.



Table 4-1: N₂O emissions levels in different studies [mg/km]

Vehicle Type	Emission standard	Aftertreatment	Cycle	Fuel	N ₂ O emissions [mg/km]	Source
DI Diesel, 2L.	EURO 5/6 (Year 2005)	Oxicat+cDPF	cold start FTP75 hot start FTP75	diesel	9.32 11.18	2
2.4 PFI	SULEV	close coupled and underfloor catalyst	FTP72+US06	gasoline	0.0621	3
2.5 PFI	SULEV	close coupled and underfloor catalyst	FTP72+US06		0.1863	
2.5 PFI	SULEV	close coupled and underfloor catalyst	FTP		0.0621	
			FTP - cold		1.1178	
			FTP - hot		3.2292	
2.0 PFI	SULEV	close coupled and underfloor catalyst	FTP		0.8073	
			FTP - cold		0.3105	
2.4 PFI	SULEV	close-coupled catalyst	FTP - cold start		0.3105	
			FTP - hot		1.5525	
2.0 GTDI	SULEV	close coupled and underfloor catalyst	FTP -cold		1.242	
			FTP - hot		4.8438	
1.6 GTDI	Bin-8	close-coupled catalyst	FTP -cold		4.347	
			FTP - hot	4.968		
			FTP	4.968		
Passenger Cars	ULEV	catalyst - new	FTP Comp	1.24	4	
		catalyst - old		3.15		
		catalyst - new	FTP phase 1	3.73		
		catalyst - old		8.08		
		catalyst - new	FTP Phase 2	0		
		catalyst - old		0.5		

		catalyst - new	FTP Phase 3		2.49	
		catalyst - old			2.87	
		catalyst - new	US06		0	
		catalyst - old			0.96	
	SULEV	catalyst - new	FTP Comp		0.62	
					catalyst - old	
		catalyst - new	FTP phase 1		2.8	
					catalyst - old	
		catalyst - new	FTP Phase 2		0	
					catalyst - old	
		catalyst - new	FTP Phase 3		0.31	
					catalyst - old	
		catalyst - new	US06		0	
					catalyst - old	
Heavy DV (long haul converted to Diesel dual fuel)	EURO V	DOC, SCR	FIGE (average)	Dual fuel	24	5
				Diesel	19	



4.3 Methodology

The procedure followed for nitrous oxide was identical to that of NH_3 . By examining the available literature on N_2O emissions and calculating the averages, the base emission factors were estimated and with the information from dedicated studies, where the only alternating factor is the mileage of the vehicle, the contribution of the vehicles "age" was also quantified. As for NH_3 , one (low) category for sulphur concentration in the fuel was considered only, since the technologies implemented in Euro 5 and 6 vehicles are not compatible with higher sulphur content.

4.4 Results

Table 4-2 and Table 4-3 show the results for the N_2O emissions. The corrected emission factor is given by equation (1) by using the base emission factor EF_{BASE} and the coefficients a and b for the different driving conditions.

Table 4-2: Euro 5/6 Gasoline, CNG, E85 Passenger cars and LDVs

Driving Conditions	$EF_{BASE} \text{ N}_2\text{O}$ [mg/km]	a	b	St. Deviation
Urban Cold	2.8	2.49E-06	0.559	2.5
Urban Hot	2.4	7.83E-07	0.861	1.8
Rural	0.2	2.61E-06	0.726	0.17
Highway	1	3.30E-06	0.918	0.82

Due to lack of relevant data, in order to derive the EF_{BASE} for rural and highway driving conditions, the ratios from the Euro 4 standards were used. The same ratios were used to derive the standard deviation for the same driving condition categories. The Euro 5/6 a and b coefficients for rural and highway were considered equal to Euro 4.

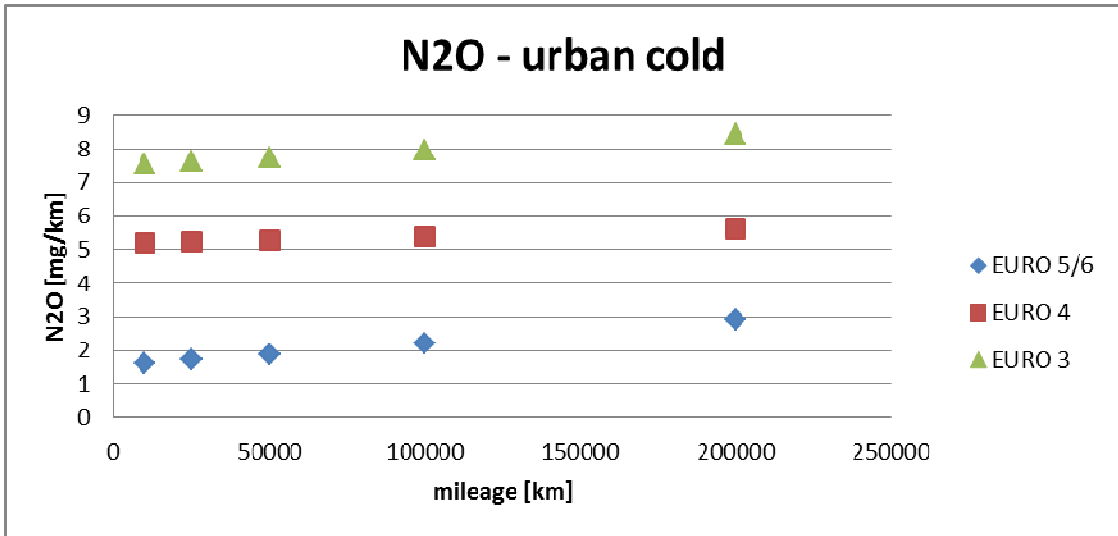


Figure 4-1: Comparison of N₂O emissions [mg/km] from Euro 3, 4 and 5/6 gasoline vehicles under urban-cold driving conditions

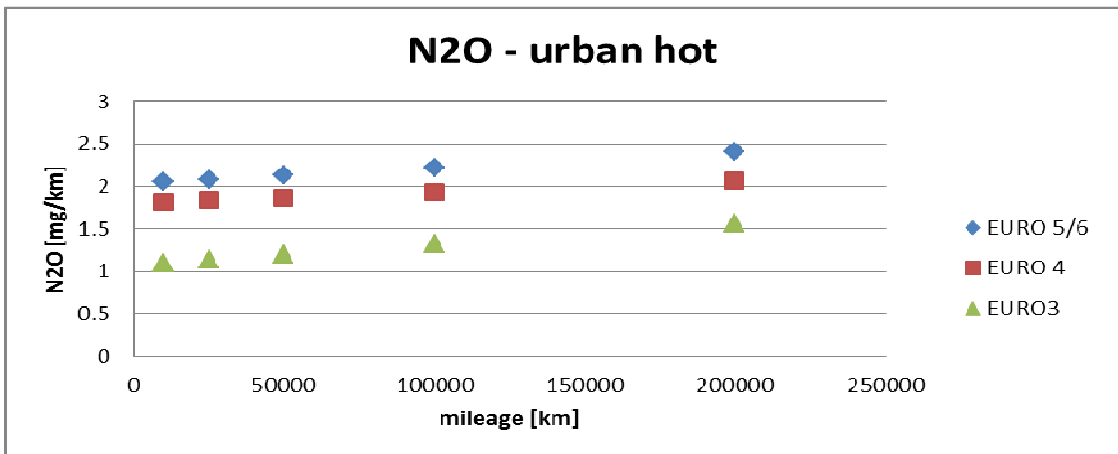


Figure 4-2: Comparison of N₂O emissions [mg/km] from Euro 3, 4 and 5/6 gasoline vehicles under urban-hot driving conditions

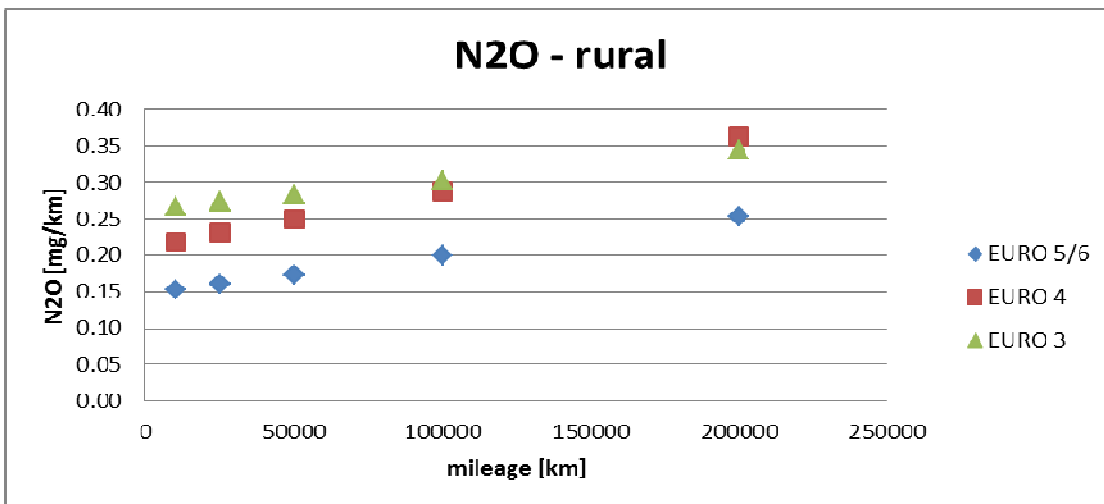


Figure 4-3: Comparison of N₂O emissions [mg/km] from Euro 3, 4 and 5/6 gasoline vehicles under rural driving conditions

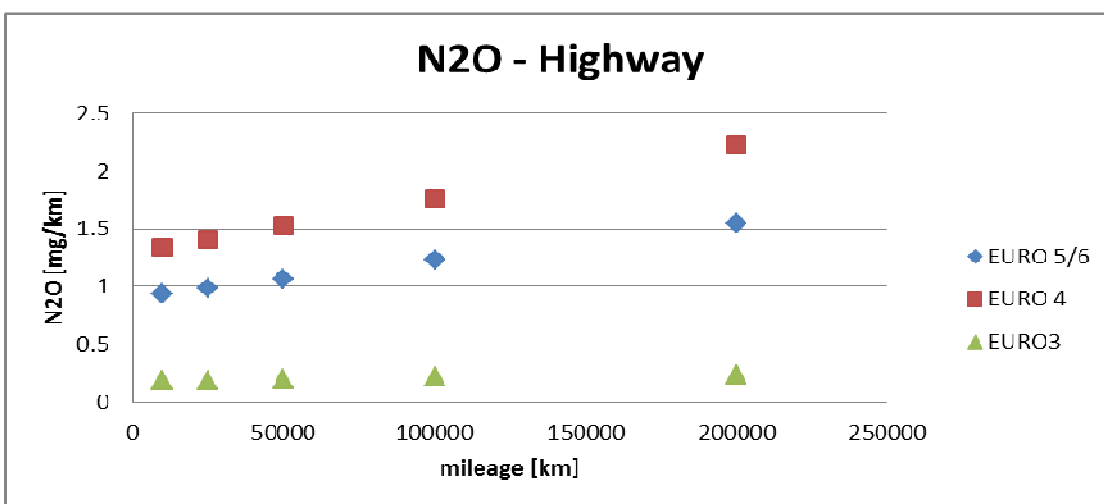


Figure 4-4: Comparison of N₂O emissions [mg/km] from Euro 3, 4 and 5/6 gasoline vehicles under rural driving conditions

Figure 4-1, Figure 4-2, Figure 4-3 and Figure 4-4 show the change between the emission factors for Euro 3/4 vehicles [1] and the current ones, developed for Euro 5/6.

Table 4-3: Diesel Passenger cars and LDVs

	Urban Cold	Urban Hot	Rural	Highway
Conventional	0	0	0	0
Euro 1	0	2	4	4
Euro 2	3	4	6	6
Euro 3/4/5	15	9	4	4
Euro 6	9	11	4	4

Table 4-3 shows the bulk emission factors for diesel passenger cars and LDVs. The values for Euro 5 and earlier emission standards have been obtained from the EMEP/EEA air pollutant emission inventory guidebook. Due to lack of data, the diesel Euro 6 passenger car emission factors for rural and highway driving conditions were considered equal to the Euro 3/4/5

4.5 Conclusions

N₂O emissions from gasoline vehicles under urban-cold driving conditions are relatively increased compared to the other driving conditions. The comparison to Euro 3 and Euro 4 vehicles shows a mixed behaviour, with Euro 5/6 showing increased emissions under urban-hot driving and reduced in the remaining categories. This mixed behaviour signifies the little influence that Euro standards impose on unregulated pollutants, which are not targeted by the necessary aftertreatment technologies, used to achieve the regulation limits. This effect can be seen also in the diesel passenger cars and LDVs, where although there is an average reduction in the emission factors, the emission factors for urban-cold and urban-hot are reduced and increased respectively.



References

1. Papathanasiou, L. and Tzircas, S. (2005). N₂O and NH₃ emission factors from road vehicles. LAT/AUTH report 0507, Thessaloniki, Greece (in Greek).
2. Rahman M., Hara K., Natakani S., Tanaka Y., Emission testing of n₂o (bag sampling from diverse vehicles by laser, SAE International, 2011-01-1155, Published 04/12/2011
3. Ball D., Moser D., Yang Y., and Lewis D., N₂O emissions of low emission vehicles, SAE International, 2013-01-1300, Published 04/08/2013
4. Graham L.A., Belisle S., Rieger P., Nitrous oxide emissions from light duty vehicles, Atmospheric environment 43 (2009) 2031-2044
5. Kristina Willner, Testing of unregulated emissions from heavy duty natural gas vehicles, Svenskt Gasteknisk Center AB, 2013:289



5 Update of f-NO₂ emission factors

5.1 Introduction

NO and NO₂ are usually treated as a single substance regarding emissions. NO_x, which covers the mono-nitrogen oxides, nitric oxide and nitrogen dioxide, is the sum of the emissions from the two substances and a heavily regulated pollutant. Although regulations in vehicles have led to a substantial decrease in the emitted NO_x and in a fall in NO_x concentrations at urban center sites, the decline in NO₂ was much more modest. The increased market penetration of diesel vehicles and the emissions of NO₂ from new technologies such as catalytically regenerative traps, have led in a rise in the NO₂/NO_x ratio [1]. Apart from the literature research in regard to f-NO₂, the growing implementation of such exhaust aftertreatment such as diesel particle filters has been taken into account in the suggested values. Especially for Euro 6 diesel vehicles, where SCR and DPF are almost essential to reach the emission levels, the final estimation of f-NO₂ given here takes into consideration the expected increase in the f-NO₂ that these technologies will introduce.

5.2 Literature research

In a similar manner to NO₂ and NH₃, the literature research for f-NO₂ did not cover only the most recent developments but was extended to previous vehicle technologies, as an effort to assess the relevant emission factors. In this section, only the publications used in order to produce the Euro 5/V and 6/VI emission factors are presented. However, due to the fact that few measurements of f-NO₂ from Euro 6 vehicles have been made and the uncertainty of real world behaviour of such vehicles remains high, the final values are not an average of the found measurements, but include an assumption regarding the aftertreatment technologies that are expected to be used in Euro 6/VI vehicles. This assumption is necessary to estimate NO₂ emissions, since NO₂ emissions are highly depending on the aftertreatment technology.

In a paper that summarises key findings from measurement campaigns in the U.K. during the summer of 2012, Carslaw et al. [2], produced the emission factors for a number of vehicle categories. Among other findings, the authors also observed a mileage related deterioration, a factor that should be looked into, since it is not examined in the current study. Bishop and Stedman [3] address the issue of f-NO₂ emission increase due to diesel particle filters (DPF) and offer values from measurements in Sweden and the U.S. of America. Among the results was also the expected influence of DPF in the f-NO₂ of the NO_x emissions.

Two sets of measurements, by IVECO and TNO [4], provide the f-NO₂ emissions for the different vehicle categories, acknowledging the impact of the aftertreatment technology on tailpipe NO₂ emissions. In a paper by Nylund et al. [5], a fleet of diesel and CNG vehicles were examined in order to provide for unbiased emission data on CNG vehicles, as well as an evaluation of diesel



technology, with results showing CNG vehicles equivalent to CRT filter equipped diesel. Values for NO_2 and NO emissions are given from Rahman et al. [13], for 4 passenger cars, three gasoline and one diesel. The configuration of DPF+SCR was measured by Czerwinski et al. [6]. Significant reductions were observed between the engine-out and DPF-SCR configuration, depending also on the drive cycle used for the measurement. The effect of the combined diesel particle filter-de NO_x on reactive nitrogen compounds was examined by Heeb et al. [7]. Different levels of urea feed factor were used, with results showing DPN technology (combined diesel particle filter – DeNox System) as a valid measure to reduce NO_2 emissions.

An evaluation of DPF+SCR for a heavy duty retrofitting was done by Czerwinski et al. [8]. The three point measurement, P1:engine-out, P2:after DPF and P3: after SCR, showed the increase of f- NO_2 from 4.3% at engine-out to 48.11% after the DPF and down to 3.7% after the SCR. Exhaust emissions from Euro 5 and 6 vehicles were tested [9] in an effort to predict the total reduction in emissions from Euro 6/VI regulations. Although the f- NO_2 emissions from one measured Euro 6 diesel passenger car were low (3.5%), the technology used in the measured vehicle was not considered among the most popular ones, as the authors state that real life emissions from Euro 6 light diesel vehicles may be 30-50% of total NO_x emissions. NO_x emissions from Euro 6 diesel vehicles were also examined by Weiss et al. [10]. The vehicle fleet tested contained one Euro 6 car and six Euro 4-5. Results showed a decrease in NO_x and an increase in f- NO_2 . The authors' concern is also expressed due to the fact that all of the tested vehicles exceeded their NO_x emissions standards by $260 \pm 130\%$. Emission tests for Euro-5 diesel passenger cars were made by TNO [11], in an effort to develop the national Dutch emission models. The results show a significant reduction in f- NO_2 from Euro 4 to Euro 5 but an increase in NO_x emission factors. A second recent publication by TNO that was examined [12], provides the results from the measurements of f- NO_2 and the proposed emission factors for the Dutch emission models for diesel Euro 6 vehicles. Nine diesel Euro 6 vehicles were tested, equipped with EGR+SCR, EGR+LNT and EGR configurations. The relevant values can be found in Table 5-1



Table 5-1: f-NO₂ [%]

Vehicle Type	Emission Standard	Exhaust Aftertreatment	Cycle	Fuel	f-NO ₂ [%]	Source
Passenger Cars	EURO 5	-	-	Diesel	29.65	2
	EURO 5	-	-	Gasoline	3.00	
	EURO 4	-	-	petrol hybrid	3.00	
	EURO 5	-	-		3.00	
Vans	EURO 5	-	-	diesel	27.20	
HGVs	EURO V	-	-	diesel	9.40	
BUSES	Euro V	EGR	-		19.60	
	Euro V	SCR-HYBRID	-		5.10	
	Euro V	SCR	-		18.90	
	Euro V	SCR	-		1.10	
Passenger Cars	Euro 5	SCR	-	diesel	5.88	4
	Euro 5	SCRT	-	diesel	18.75	
Passenger Car	EURO 6	-	-	diesel	22.08	12
DI diesel, 2.0L	EURO 5	oxicat+cDPF	-	diesel	43.55	13
LDDV diesel, 3L	EURO 3	engine out	-	diesel	8.22	7
	EURO 6	DPF -SCR (α=1)	-		13.26	
Toyota Avensis	EURO 5	-	Helsinki city cycle	diesel	31.14	9
Toyota Verso D-Cat	EURO 5	-		diesel	30.62	
Mazda CX-5	EURO 6	(SKYACTIVE - low compression ratio)		diesel	3.47	
Passenger Cars	EURO 5	EGR, OC, DPF	-	diesel	38.00	10
	EURO 5	EGR, OC, DPF	-		54.00	
	EURO 5	EGR, OC, DPF	-		35.64	
	EURO 5	EGR, OC, DPF	-		24.20	
	EURO 6	EGR,OC,DPF,SCR	-		51.25	
Diesel passenger cars	EURO 4	-	average of urban cong. free	diesel	54.98	11
	EURO 5 (old)	-	rural and highway		54.99	
	EURO 5	-	-		30.60	
Buses	EURO IV	Ox. Catalyst	-	diesel	3.41	5



	EURO V	Diesel CRT	-	CNG	8.16	
	-	Ox. Catalyst	-		4.11	
	-	SM CNG	-		2.44	
	EURO VI	DPF	ARB 2002	diesel	33.33	
	EURO VI	DPF	International 2003	diesel	33.33	
IVECO 3L, HDDV	EURO III	engine out	ETC	diesel	8.27	6
			WHTC		9.43	
			NYCC		20.60	
			Braun		21.51	
	EURO VI	DPF+SCR	ETC		6.70	
			WHTC		17.99	
			NYCC		10.84	
			Braun		2.12	
Buses	EURO III	-	-	diesel	29.91	3
	EURO VI	DPF EGR	-		51.74	
	EURO V	-	-		37.71	
		CNG	-		7.94	
		No control	-		14.95	
	EURO IV	DOC	-		12.84	
	EURO VI	DPF	-		26.86	
HDDV	EURO III	engine-out	-	diesel	37.86	8
	EURO III + DPF	DPF	-		10.08	
	EURO VI	DPF+SCR	-		8.19	
Scania 9L	EURO VI	-	city/delivery cycles	diesel	1.85	9
		-	motorway		50.00	

5.3 Methodology

The values from the fore mentioned literature study were evaluated in order to develop the fraction of NO₂ emitted. The data was divided according to vehicle type, fuel used and Euro emission standard and the averages of each category were created. However, the values for Euro 6/VI, seen in Table 5-2, Table 5-3 and Table 5-4 are not always the exact averages. The values proposed take into account which aftertreatment technologies are expected to be mostly employed by manufacturers in order to reach the imposed emission limits. In this particular study, it was considered that 70% of new Euro 6 diesel vehicles will be equipped with an SCR preceding a DPF.

5.4 Results

Table 5-2: Petrol cars and LDVs

Emission	f-NO₂
Pre-EURO	0.07
Euro 1	0.06
Euro 2	0.05
Euro 3	0.04
Euro 4	0.05
Euro 5	0.03
Euro 6	0.03

Table 5-3: Diesel Cars and LDVs

Emission Category	f-NO₂
Pre-EURO	0.15
Euro 1	0.13
Euro 2	0.13
Euro 3	0.27
Euro 3 with DPF	0.51
Euro 4	0.46
Euro 4 with DPF	0.42
Euro 5	0.33
Euro 6	0.30



Table 5-4: HDDVs and Buses

Emission	f-NO₂
Pre-EURO	0.11
Euro I	0.11
Euro II	0.11
Euro III	0.14
Euro IV	0.10
Euro V	0.17
Euro VI	0.08
Euro III+CRT	0.36

5.5 Conclusions

According to current evidence, gasoline cars and light duty vehicles are not expected to show any difference in f-NO₂ emissions. The efficiency of the three-way catalyst has led to a reduction in NO_x emissions over the consecutive Euro level vehicles, and at the same time kept f-NO₂ levels low, at 3%.

Diesel passenger cars, however, show great variation in the f-NO₂. Emissions from Euro 5 and, in particular, Euro 6 diesel passenger cars, are significantly depending on the exact configuration of the exhaust aftertreatment system. Use of an LNT may lead to f-NO₂ values of above 40%, while use of SCR limits f-NO₂ to a moderate 10-20% in real world conditions. However, if a catalysed DPF follows the SCR, then this could increase f-NO₂ to levels to up to 50%. The literature research showed also a Euro 6 diesel passenger car without any deNO_x aftertreatment that has demonstrated f-NO₂ values that are at gasoline car levels (2.5%). This concept, however, is not considered to be really popular between the individual manufacturers. Thus, a wide range of possible values for f-NO₂ exists for diesel Euro 6 cars, and the actual average value will depend on the share of each aftertreatment configuration to the total vehicle fleet. The suggested value in Table 6 assumes SCR to be the dominant deNO_x technology with some 70% of SCRs preceding the DPF and 30% of SCRs following the DPF.

The f-NO₂ values for Euro V and Euro VI trucks are expected to remain relatively low. In all commercial applications, the SCR is installed downstream of the DPF so NO₂ remains well controlled. A special case is also presented in Table 5-4 for those earlier heavy duty vehicles (Euro III) retrofitted with continuous regeneration particle filters (CRT). The DPF installed in this case disproportionally increases the f-NO₂.

References

1. AQEG, Air Quality Expert Group (2005), Trends in Primary Nitrogen Dioxide in the UK, Draft report for comment, August 2006.
2. Carslaw D., Rhys-Tyler G., Remote sensing of NO₂ exhaust emissions from road vehicles, A report to the City of London Corporation and London Borough of Ealing, Version 16th July 2013
3. Bishop G.A., Stedman D.H., Emissions of Nitrogen Dioxide from Modern Diesel Vehicles, WIT Transactions on Ecology and the Environment, Vol 116, 2008 WIT Press
4. Keenan M., Study of costs and impact upon CO₂ and primary NO₂ emissions of a range of limits for emissions of NO_x and PM in the timescale 2014, Ricardo UK Ltd, United Kingdom, 18 July 2008
5. Nylund L.-O., Erkkila K., Lappi M., Ikonen M., Transit bus emission study: Comparison of emissions from diesel and natural gas buses, VTT Processes, Research report, PRO3/P5150/04, 15.10.2004
6. Czerwinski J., Zimmerli Y., Mayer A., Heeb N., D'Urbano G., Diesel emission with DPF+SCR in VERTdePN - Testing & Potentials, SAE International, 2011-01-1139, Published 04/12/2011
7. Heeb N.V., Haag R., Seiler C., Schmid P., Zennegg M., Wichser A., Ulrich A., Honegger P., Zeyer K., Emmenegger L., Zimmerli Y., Czerwinski J., Kasper M. and Mayer A., Effects of a combined diesel particle filter-DeNox system (DPN) on reactive nitrogen compounds emissions: a parameter study, ACS Publications, Environ. Sci. Technol. 2012, 46, 13317-13325
8. Czerwinski J., Zimmerli Y., Mayer A., Heeb N., Lemaine J., D'Urbano G., Bunge R., Testing of combined DPF+SCR systems for HD-retrofitting - VERTdePN, SAE International, 2009, 9-2009-01-0284
9. Hagman R., Amudsen A.H., Exhaust emissions from vehicles with Euro 6/VI Technology, Institute of transport economics, Norwegian Centre for Transport Research, TOI Report 1259/2013, Oslo 2013
10. Weiss M., Bonnel P., Kuhlwein J., Provenza A., Lambrecht U., Alessandrini S., Carriero M., Colombi R., Forni F., Lanappe G., Le Lijour P., Manfredi U., Montigny F., Sculati M., Will Euro 6 reduce the NO_x emissions of new diesel cars? - Insights from on-road tests with portable emissions measurement systems (PEMS), Atmospheric Environment 68 (2012) 657-665, Elsevier 2013
11. Ligterik N.E., Kadijk G., van Mensch P., Determination of Dutch NO_x emission factors for EURO-5 diesel passenger cars, TNO Report, TNO 2012 R11099, 7 December 2012
12. Ligterink N., Kadijk G., van Mensch P., Hausberger S., Rexeis M., Investigations and real world emission performance of Euro 6 light-duty vehicles, TNO Report, TNO 2013 R11891, 5 December 2013
13. Rahman M., Hara K., Natakani S., Tanaka Y., Emission testing of NO₂ (bag sampling from diverse vehicles by laser, SAE International, 2011-01-1155, Published 04/12/2011



6 Abbreviations

ASC: Ammonia Slip Catalyst

CDPF: Catalysed Diesel Particulate Filter

DOC: Diesel Oxidation Catalyst

DPF: Diesel Particulate Filter

DPV: Diesel Personal Vehicle

HCB: Hexachlorobenzene

H_pCDD: Hepta-dioxins

H_xCDD: Hexa-dioxins

H_xCDF: Hexa-furans

H_pCDF: Hepta-dioxins

HDDV: Heavy Duty Diesel Vehicle

I-TEQ: International Toxic Equivalency Factor

LDD: Light Duty Diesel

MMF: Mobile Metal Filter

PAH: Polycyclic Aromatic Hydrocarbons

PCB: Polychlorinated Biphenyl

PDPF: Partial Diesel Particulate Filter

POP: Persistent Organic Polluters

PCDD: Polychlorinated dibenzo-p-dioxins or simply dioxin

PCDF: Polychlorinated dibenzofuran

PeCDD: Penta-dioxins

PeCDF: Penta-furans

SCR: Selective Catalytic Reduction

SUV: Sports Utility Vehicle

TeCDD: Tetra-dioxins

TeCDF: Tetra-furans

TEF: Toxic Equivalent Factor

TEQ: Toxicity Equivalency Quotient

TWC: Three Way Catalyst

WHO: World Health Organization

7 Annex

Excel file containing all emission factor functions for Euro 5/6 and Euro V/Vi vehicles