National Dioxins Program

Technical Report No. 2
Dioxins emissions from Motor Vehicles in Australia

A consultancy funded by the Australian Government
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2. **Dioxins emissions from Motor Vehicles in Australia**
3. Australian Inventory of Dioxins emissions 2004
4. Dioxins in Ambient Air in Australia
5. Dioxins in Soils in Australia
6. Dioxins in Aquatic Environments in Australia
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Foreword

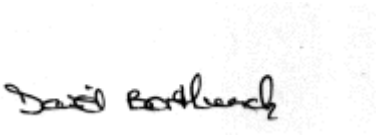
When the Australian Government established the four year National Dioxins Program in 2001, our knowledge about the incidence of dioxins in Australia was very limited.

The aim of the program was to improve this knowledge base so that governments were in a better position to consider appropriate management actions. Starting in mid 2001, a range of studies were undertaken which involved measuring emissions from sources such as bushfires, as well as dioxin levels in the environment, food and population. The findings of these studies were used to shed light on the risk dioxins pose to our health and the environment.

This work has been completed and the findings are now presented in a series of twelve technical reports.

Having good information is essential if there is to be timely and effective action by governments; these studies are a start. Our next step is to foster informed debate on how we should tackle dioxins in Australia, as this is an obligation under the Stockholm Convention on Persistent Organic Pollutants. The Department of the Environment and Heritage will be working closely with other Australian Government, State and Territory agencies to take this step.

Ultimately, the effective management of dioxins will be the shared responsibility of all government jurisdictions with the support of the community and industry.



David Borthwick

Secretary

Department of the Environment and Heritage

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- the Department of Agriculture, Fisheries and Forestry, who assessed the levels of dioxins in agricultural commodities
- Food Standards Australia New Zealand and the Department of Health and Ageing and who assessed the levels of dioxins in foods and assessed the health effects of dioxins
- officers of the Chemical Assessment Section in DEH who assessed the ecological effects of dioxins
- members of the National Dioxins Project Team which included representatives from the State and Territory environment protection agencies, the Australian Health Ministers Conference and the Primary Industries Ministers Council
- members of the National Dioxins Consultative Group which included representatives from industry and agricultural sectors, environment and public health groups and research institutions.

Project Team

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Stephen Lowrie - Australian Bureau of Statistics.

Executive Summary

The presence of dioxins[1] in car exhaust was first reported in 1978. Since 1986, studies have been conducted in the US and Europe to measure polychlorinated dibenzo-p-dioxins (dioxins or PCDD) and polychlorinated dibenzo-furans (furans or PCDF) emissions from vehicles. Although it is clear that motor vehicles are sources of dioxins and furans, the magnitude of their emissions remains uncertain. There are several reasons for this. First of all, there are very few measured data available internationally on dioxins emissions from road traffic. Relatively few tests on dioxins emissions from vehicles are available considering the variety and numbers of vehicles currently in operation and the range of operational, technical and environmental conditions in which they are operated. Secondly, PCDD/PCDF emissions generally show large variability in emission rates and dioxin profiles. Finally, in many cases, published information on dioxins emission factors is contradictory.

As a result, the emission factors developed through desktop analysis in this report remain uncertain and the only way to reduce this uncertainty would be to conduct more measurements. In addition, it became obvious from the international literature review that a considerable amount of potentially useful information is not available. Gaps in data exist which will lead to added uncertainties in the emission factors developed in this study.

The rationale addressed a number of factors that (may) affect dioxins emissions and, therefore, emission factor development. These factors are:

1. vehicle technology type
2. fleet age
3. situations that result in incomplete combustion
4. study type
5. measurement methodology
6. test protocols
7. fuel composition
8. ambient temperature
9. units and calculation methods
10. engine calibration practice.

Consideration of these factors led to a selection of useful data. However, due to the uncertainties associated with dioxins emissions, widely scattered emission factors were derived for the Australian situation. The data did not allow for the development of average emission factors; hence, an emission factor range (minimum to maximum) rather than a point estimate was deemed more appropriate. As a consequence, a range of Australian PCDD/PCDF emission factors have been developed for each vehicle class using Australian fuel economy data.

[1] The term 'dioxins' refer to a large group of polychlorinated dibenzo-para-dioxins (PCDDs) and the closely related furans (PCDFs). The terms 'dioxin', "dioxin/furans', 'PCDDs/PCDFs' are used interchangeably throughout this report.

Total dioxins emissions from Australian road traffic (1998 levels) are estimated to lie between 0.7 and 16.5 g I-TEQ[2] per year, based on VKT[3] data from the Australian Bureau of Statistics (ABS). Vehicles that operated on leaded petrol accounted for about 40-45% of total dioxins emissions. However, leaded petrol was completely removed from sale on 1 January 2002. The phase-out of leaded petrol is, therefore, expected to have already substantially reduced total dioxins emissions. Diesel-fuelled vehicles emit between 35 and 50% of total dioxins emissions, which mainly come from diesel trucks. Despite the fact that vehicles running on unleaded petrol account for 65% of total kilometres travelled, they account for 5 to 20% of total dioxins emissions.

When vehicle activity data are based on fuel consumption data from ABS, similar results are obtained. In this case, total dioxins emissions are estimated to lie between 0.6 and 17.3 g I-TEQ per year. As an independent source of information, fuel consumption data obtained from the Department of Industry, Tourism and Resources (DITR) were used to estimate total dioxins emissions from Australian road traffic. These data resulted in a higher estimate of 0.7-24.3 g I-TEQ per year, but this estimate includes off-road traffic and non-road traffic emissions.

Using total dioxins emission figures for Australia from a previous study (Environment Australia, 1998) as an estimate for 1998 total emission levels, i.e. 150-2,300 g dioxins per annum, road traffic accounts for 0.03 to 16.2% of total dioxins mission levels. These results are in line with emission inventories around the world, ranging from 0.2 to 12% of total annual dioxins emissions. It is noted, however, that these emission inventories are all based on the same limited data that are available from international publications, so these results may not be surprising.

[2] I-TEQ is a unit of measurement. 2,3,7,8-TCDD is considered the most toxic of the dioxins and furan family. By convention it is assigned a toxicity rating (called a Toxic Equivalency Factor, or TEF) of 1.0. The toxicity of a mixture of PCDDs and PCDFs can be expressed by multiplying the concentrations of the congeners present in the mixture by their respective TEFs. The resulting products are called toxicity equivalents (TEQs). TEQs are expressed in the same concentration units as the individual congeners. A number of toxicity rating schemes have been developed (WHO, EADON, NATO/CCMS. Since 1988, the term 'international TEFs' or I-TEFs, which is the sum of the toxicity equivalents for all congeners is the preferred unit.

[3] VKT is an acronym for vehicle kilometres travelled.

Glossary/Abbreviations

ABS	Australian Bureau of Statistics
ADR	Australian Design Rule (i.e. Australian Emission Standards)
AIP	Australian Institute of Petroleum
CARB	California Air Resources Board
CO	Carbon Monoxide
DEH	Department of the Environment and Heritage
DITR	Department of Industry, Tourism and Resources
EDB	Ethylenedibromide
EDC	Ethylenedichloride
EEA	European Environment Agency
Femto (f)	10^{-15}
HC	Hydrocarbons
HDV	Heavy-duty vehicle
I-TEQ	International Toxic Equivalency Factor
LCV	Light-Commercial Vehicle
LDV	Light-duty vehicle
Micro (μ)	10^{-6}
MSW	Municipal Solid Waste
Nano (n)	10^{-9}
NDP	National Dioxins Program
NEPC	National Environment Protection Council
NEPM	National Environment Protection Measure
PAHs	Polycyclic Aromatic Compounds
PBDD	Polybrominated dibenzo-p-dioxins
PBDF	Polybrominated dibenzo-furans
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzo-furans
PHDD	Polyhalogenated dibenzo-para-dioxins
PHDF	Polyhalogenated dibenzo-furans
PC	Passenger Car
Pb	Lead
Pico (p)	10^{-12}
PM	Particulate matter (particles)
PM_{10}	Particulate matter (particles) of aerodynamic diameter less than 10 μm
$PM_{2.5}$	Particulate matter (particles) of aerodynamic diameter less than 2.5 μm

ppm	Parts per million
ppb	Parts per billion
RIVM	The National Institute of Public Health and the Environment
SMVU	Survey of Motor Vehicle Use
TEF	Toxic Equivalency Factors
TEQ	Toxic Equivalent
TNO	Netherlands Organisation for Applied Scientific Research
US EPA	United States Environmental Protection Agency
VKT	Vehicle Kilometres Traveled
WHO	World Health Organization

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1. Introduction

In the 2001-2002 Budget, the Australian Government announced funding of $5 million for a four-year program to assess and manage dioxins in the Australian environment. This program is known as the National Dioxins Program (NDP). In light of the objectives identified under the NDP, Pacific Air & Environment was commissioned by the Department of the Environment and Heritage (DEH) to estimate the total dioxins load from road traffic in Australia on an annual basis. This was to be conducted as a desktop inventory study based on the development of dioxins emission factors from Australian vehicles applied to the Australian motor vehicle fleet.

This information will be used by DEH in the impact assessment phase (Phase Two) of the NDP to evaluate the risks to human health and the environment, from exposure to dioxins. The outcomes of Phase Two will be used to inform the policy development phase (Phase Three) of the program. This will include developing national management strategies to reduce, and, where feasible, eliminate releases of dioxins in Australia.

2. Inventory basis

Various motor vehicle emission estimation models are available for use in a wide range of applications. These include: small-scale traffic planning, 'hot-spot' analysis, environmental impact assessments, air quality modelling, emission inventories, national greenhouse gas emission predictions and evaluation of control strategies through emission forecasting.

Each purpose requires specific spatial and temporal detail and accuracy. No single vehicle emission model is capable of meeting all of the various applications simultaneously. In other words, each methodology has its own range of spatial and temporal application. The availability of emission measurement data and model input data determines the type of model that can be developed and used. Therefore, end-use consideration should dictate the selection of the appropriate modelling approach (i.e. modelling on micro-, meso- (intermediate) or macro-scale), as well as many of the underlying assumptions used to determine emission factors (Smit et al., 2002a).

2.1 Macro-scale approach

For this study, a macro-scale approach is the most appropriate due to the spatial (i.e. country-wide) and temporal (i.e. annual) scale of the project. Moreover, the availability of data on an international scale for dioxins emission factors from road traffic is limited.

Using a macro-scale approach, aggregate emission factors were directly combined with vehicle activity data to provide the dioxins emissions estimates. The total emission calculation is based on a combination of the appropriate emission factors with annual vehicle kilometres travelled (VKTs). Annual VKTs are normally taken from statistics on a national level, according to different vehicle classes and road types.

2.2 Australian-based emission factors

Emission factors are central to the estimation of annual dioxin emissions. In relation to this project, Australian fuel consumption data and vehicle fleet composition will be used.

It should be noted that there is a deficiency in the amount of measurement data available to develop exhaust dioxins emission factors. This project aims to develop basic dioxins emission factors based on information that is (potentially) available from several sources. These include:

- Australian data on dioxins emissions from road traffic
- Database information from overseas agencies such as US EPA (US), CARB (California), EEA (Europe), and RIVM/TNO (The Netherlands), etc.
- Extensive library database search, published papers and reports on the subject
- Established emission model methodologies, presenting the state-of-the-art overseas emission inventory models, e.g. the recent European COPERTIII (released 2000) and US MOBILE 6 (released 2002) vehicle emission models that include condensed American and European data
- Comprehensive Internet searches.

As indicated in the report, the following factors were considered when collecting and investigating information on dioxins emissions:

1. vehicle technology type
2. fleet age
3. situations that result in incomplete combustion
4. study type
5. measurement methodology
6. test protocols
7. fuel composition
8. ambient temperature
9. units and calculation methods
10. engine calibration practice.

2.3 Australian vehicle fleet activity data

There are two methods for estimating VKTs. VKT estimates can be estimated using data from Australian Bureau of Statistics (ABS) derived from annual motor vehicle surveys. VKT data can also be estimated by combining national fuel consumption data with average fuel consumption rates. As indicated in the report, both of these approaches were used to estimate dioxin emission levels from road traffic.

3. Methodology

The table of contents reflect the different steps of the methodology. The first step of the project involved the collection of all relevant information on dioxins emissions available. Several potential sources of information investigated included:

- Extensive library database search (e.g. "Current Contents", "Science Direct" and "Poltox"): published papers and reports on the subject
- Comprehensive Internet search
- Databases/information kept in Australia (State/Territory Environment Protection Agencies, CSIRO, motor vehicle industry)
- Database information from overseas agencies such as US EPA (US), CARB (California), EEA (Europe), and RIVM/TNO (The Netherlands)
- Established emission model methodologies, presenting the state-of-the-art overseas emission inventory models, e.g. the recent European COPERTIII (released 2000) and US MOBILE 6 (released 2002) vehicle emission models that include condensed American and European data.

The results of literature review are discussed in Section 6. In Section 7 an overview of published emission factors is presented. Section 8 presents the development rationale that is used to develop 'Australian' Polychlorinated dibenzo-p-dioxins (PCDD) and Polychlorinated dibenzo-furans (PCDF) emission factors. Section 9 critically reviews the available data and uses the development rationale to arrive at a range of 'Australian' PCDD/PCDF emission factors for each vehicle class. These emission factors are summarised in Section 10. Section 11 summarises vehicle activity data obtained from different sources.

Section 12 presents total annual dioxins emission levels from road traffic in Australia, based on the work presented in the previous Sections. For instance, a specific dioxins emission factor for a petrol passenger car complying with ADR37 ($EF_{petrol, PC, ADR37}$) has been developed in Section 9. The activity data, presented in Section 11, provide the total number of annual VKTs driven in Australia (TAVKT) multiplied by a weighting factor ($W_{f,v}$). This weighting factor breaks down the total VKT figure into fuel (f) and vehicle type (v). The total emissions of dioxins for each specific category ($E_{f,v}$) are then obtained by multiplying EF with W and TAVKT. Summation of all category-specific emissions results then in a total annual dioxins emissions estimate from road traffic in Australia (E). This can be summarised in the following equation:

$$E = \sum^{fv} EF_{f,v} \times W_{f,v} \times TAVKT$$

Section 13 presents the conclusions of this study. Finally, Section 14 discusses the need for Australian measurements and makes some recommendations for future work.

4. Dioxins

Dioxins refer to a large group of chlorinated chemical compounds, polychlorinated dibenzo-para-dioxins (PCDDs) and the closely related polychlorinated dibenzo furans (PCDFs), which share certain similar physical[4], chemical[5] and biological properties, including toxicity. Dioxins and furans are also part of the group of persistent organic pollutants (POPs[6]), which are organic compounds of natural or anthropogenic origin that resist photolytic, chemical, and biological degradation. Dioxins have spread extensively in the environment in the same manner as polychlorinated biphenyls and some chlorinated pesticides (Vainio et al., 1989). For the purpose of the National Dioxins Program the term 'dioxins' is used in the broader sense including co-planar polychlorinated biphenyls (PCBs)[7].

There are 75 different PCDD and 135 different PCDF, called congeners or isomers, which are distinguished by the position and the number of chlorine atoms attached to the benzene ring. A homologue group are PCDD/PCDF isomers having the same number of chlorine atoms. A dioxin is any compound containing the dibenzo-p-dioxin nucleus, while a furan is any compound containing the dibenzofuran nucleus. The general formulae for each of these compounds are presented in

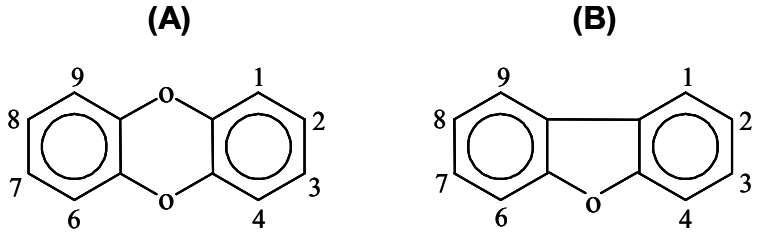

Figure 1.

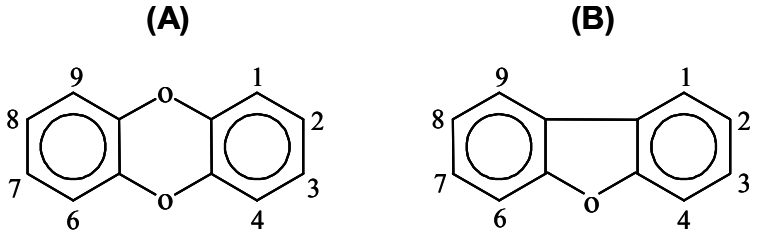

Figure 1 - General formulae of dioxins and furans

[4] Physical properties of the various PCDD/PCDF compounds indicate decreasing volatility with increasing number of chlorine atoms. These compounds have fairly low water solubilities, with furans exhibiting greater solubility than dioxins.

[5] Chlorinated aromatic compounds containing two benzene rings and bonded by one (furan) or two (dioxin) oxygen atoms.

[6] POPs are characterised by low water solubility and high lipid solubility, resulting in bioaccumulation in fatty tissues of living organisms. POPs are semi-volatile and, as a consequence, able to move long distances in the atmosphere. They are also transported in the environment in low concentrations by movement of fresh and marine waters, resulting in widespread distribution across the Earth, including in regions where they have never been used or generated. Thus, both humans and environmental organisms are exposed to POPs around the world, in many cases for extended period of time. POPs are known to produce a wide range of toxic effects in living organisms, even at low exposure levels. Some of these effects include birth defects, cancers, and dysfunctional immune and reproductive system reponses.

[7] PCBs without chlorine atoms in the ortho positions have been found to give similar toxic responses to PCDD/Fs (Haglund *et al*., 1987).

Each of the hydrogen atom positions numbered 1 through 4 and 6 through 9 can be substituted with either a chlorine atom, an-other halogen atom[8] or an organic radical. However, chlorinated species are the compounds of most environmental interest and concern[9]. In fact, only the homologues[10] with four or more chlorine atoms are considered for toxicity purposes and, therefore, normally quoted in the literature. These homologue groups are often abbreviated for convenience as tetra (TCDD/PCDF or D/F4), penta (PCDD/PCDF or D/F5), hexa (HxCDD/PCDF or D/F6), hepta (HpCDD/PCDF or D/F7) and octa (OCDD/PCDF or D/F8). Note the overlap in terminology as PCDD and PCDF can refer to the penta homologue group or to all 210 dioxins and furans.

4.1 Dioxin toxicity

Dioxins have attracted attention since the late 1970s, first in connection with industrial accidents and later as by-products of industrial and traffic emissions (Vainio et al., 1989). PCDD/PCDFs have been considered to be some of the most toxic substances known (Edgerton & Czuczwa, 1989). They are not natural substances in the sense of biogenic formation (Hutzinger & Fiedler, 1989). PCDD and PCDF have been of great public concern because one of the congeners, 2,3,7,8-TCDD, is an extremely potent carcinogen and teratogen in rodents (Vainio et al., 1989).

The toxicity depends on the location and the number of chlorine atoms attached to the benzene rings. Only 29 PCDD/PCDF and PCB congeners are considered by the World Health Organization (WHO) to have significant toxicity[11] (WHO, 1998). The 17 most toxic PCDD/PCDFs are 2,3,7,8-substituted and they belong to the same toxic group denoted as '(dioxin) congener'.

Of these compounds, the most toxic dioxin and most extensively studied is 2,3,7,8-tetrachlorobenzo-p-dioxin or TCDD (WHO, 1998). TCDD is usually resistant to degradation once adsorbed onto soil, with a half-life of 10-12 years and bioaccumulation in fish and mammals (Edgerton & Czuczwa, 1989). 2,3,7,8-TCDD is the most potent animal carcinogen that has been tested (Vainio et al., 1989; Hutzinger & Fiedler, 1989).

4.2 Toxic equivalence schemes

The complex nature of PCDD, PCDF and PCB mixtures complicates the risk evaluation for humans. As a result, the concept of toxic equivalency factors (TEFs) has been developed. It has been introduced to facilitate risk assessment and regulatory control of exposure to these mixtures. The TEF concept is still the most plausible and feasible approach for risk assessment of halogenated aromatic hydrocarbons with dioxin-like properties (Van den Berg et al., 1998).

[8] The halogens are five non-metallic elements found in group 7 of the periodic table. The term "halogen" means "salt-former" and compounds containing halogens are called "salts". The halogens exist, at room temperature, in all three states of matter: solid (iodine, astatine), liquid (bromine) and gas (fluorine, chlorine).
[9] Chlorinated species are those that have a chlorine atom occupying one or more of the eight positions shown in Figure 1 above.
[10] A homologue group is a group of dioxins or furans that have the same number of chlorine atoms.
[11] Observed effects include dermal toxicity, immunotoxicity, endocrine disruption, carcinogenicity, reproductive effects and teratogenicity.

TEF weighting factors are based on available animal-based toxicological data. TEF values for individual congeners in combination with their chemical concentration or mass can be used to calculate the total 2,3,7,8-TCDD toxic equivalents concentrations or mass (TEQs) contributed by all dioxin-like congeners in the mixture using the following equation (WHO, 1998; Van den Berg et al., 1998):

$$TEQ = \sum(PCDD_i \times TEF_i) + \sum(PCDF_i \times TEF_i) + \sum(PCB_i \times TEF_i)$$

This concept allows the toxicity of a complex mixture to be expressed as a single number. The TEQ scheme is a measure of the toxicity of a mixture of PCDDs and PCDFs. However, due to differences in interpretation of experimental animal data, different toxicity equivalence schemes exist. Well-known schemes are Eadon, Nordic and, since 1988, I-TEQ (International Toxic Equivalent[12]).

I-TEQ is the most widely adopted system of TEQs. It only considers the seventeen 2,3,7,8-chlorine substituted dioxins and furans and the entire mixture is assessed as a quantity of 2,3,7,8-TCDD, which has a toxicity rating or TEF of 1.0. Congeners other than the seventeen 2,3,7,8-chlorine substituted dioxins and furans that may be present in a sample are assigned a TEF value of 0.0. As a rule of thumb, I-TEQ values are about 50 times smaller than PCDD/PCDF concentration values.

Sometimes total PCDD/PCDF concentration and the Nordic-equivalence are used, but most emission data after 1988 are generally reported solely as I-TEQ (HMIP, 1995). Nordic TEQs are comparable to I-TEQ and are within 3-6% of I-TEQ (Gullet & Ryan, 1997), but Eadon shows much larger differences.

The TEQ system has recently been updated and expanded by the WHO into a scheme that includes TEF factors for dioxin-like PCBs and uses different TEFs for humans/mammals, fish and birds (WHO, 1998; Dyke & Stratford, 2002). In general, TEQs using the WHO scheme for PCDD/PCDF emissions to air were found to show small increases (in the order of 1-10%) in comparison to I-TEQ. However, in many cases PCBs have not been included in the analysis of samples and emissions, but inclusion can have a significant effect on the overall TEQ (Dyke & Stratford, 2002).

4.3 Dioxin emissions and exposure

Dioxins are predominantly generated as unintended by-products of combustion processes and are most usually discharged into the atmosphere. As a result, the atmosphere represents the primary route of deposition of dioxins to the environment. It is estimated that 96% of dioxins in the environment are emitted to the atmosphere. They can then be deposited on plants, soil, and sediments in water bodies where they can be taken up by animals.

Dioxins concentrate up the food chain so that animals have higher concentrations than plants, water, soil, or sediments. As dioxins tend to accumulate in the body fat of animals, the consumption of animal products with high fat content, such as meat and

[12] ITEQ is proposed by the North Atlantic Treaty Organisation (NATO) and is also denoted as NATO or CCMS for NATO Committee on Challenges of Modern Society.

dairy goods, can increase human exposure to dioxins. Human exposure to PCDD/PCDFs and PCBs occurs primarily through consumption of food.

There is evidence that atmospheric source reductions have been occurring over the past couple of decades or so, with atmospheric concentrations showing significant declines in PCDD/PCDFs. Peak inputs of PCDD/PCDFs to the environment were probably in the late 1960s and early 1970s. The significance of non-industrial PCDD/PCDF sources becomes increasingly important as more stringent emission controls are applied to the industrial sector (Alcock, Sweetman & Jones, 2001).

5. Dioxin emissions from road traffic

This Section forms a general introduction to dioxins emissions from road traffic. First, overseas dioxins emission inventories are briefly reviewed with respect to traffic emission predictions (Section 5.1). Section 5.2 provides background information on dioxins emission formation in internal combustion engines and exhaust systems. Finally, Section 5.3 specifically addresses emissions of brominated dioxins, mixed dioxins and PCBs from road traffic.

5.1 The relevance of road traffic to total dioxin emissions

PCDD/PCDF emissions from road traffic have repeatedly been reported to make up a small fraction of total annual dioxins emissions. A selection of international emission inventories and the proportion of dioxin emissions from road traffic are presented in Table 1.

Table 1 - Dioxin emissions from road traffic in international emission inventories (g I-TEQ/year)

Reference Report/Paper	Year	Country	Dioxins Total [g I-TEQ/year]	Dioxins Traffic [g I-TEQ/year]	Dioxins Traffic [% of Total]
US EPA, 2000	1987	USA	12,331	61.5	0.50
Bremmer et al., 1994	1991	The Netherlands	484	7	1.45
Hagenmaier, 1994	1994	Germany	800-1,200	11-50	1.38-4.17
Eduljee & Dyke, 1996	1992	UK	560-1,100	1-45	0.2-4.1
Miyabara et al., 1999	1994	Japan	5,000	17	0.34
US EPA, 2000	1995	USA	2,888	41	1.41
Bremmer, 1997	1997	The Netherlands	58	0.8	1.38
EC, 1997	1997	EU	3,276	19	0.58
Caserini & Monguzzi, 2002	1997	Italy	33	4	11.71
Environment Canada	1997	Canada	290	9	3.00
Geueke et al., 1999	1999	EU	6,000	31.5	0.53

It is noted that these emission inventories are all based on the same limited data that are available from international publications. Thus, random and systematic errors (bias) in these data sets are propagated into the emission inventories. Some authors have

strongly debated the validity of the estimated small contribution from road traffic (Konheim, 1986; Jones, 1993; Jones, 1995). There are some arguments that may support this opinion.

Firstly, discrepancies have been found between estimated total dioxins emissions from known sources and both human intake and PCDD/PCDF deposition. For example, Jones (1993) noted that aggregate nationwide emissions in the US could not account for more than 2% of the total estimated emissions necessary to explain PCDD/PCDF human intake by all pathways. The most likely explanation for this discrepancy is either incorrect quantitative estimation of PCDD/PCDF emissions from known sources or the existence of still unknown sources of dioxin (Hagenmaier, 1994).

Second, several researchers found that PCDD/PCDF profiles (refer to section 5.5) in the environment closely resemble those of both municipal solid waste incineration (MSW) plants and leaded petrol vehicles (Ballschmitter et al., 1986; Konheim, 1986; Marklund et al., 1987; Rappe et al., 1987; Vainio et al., 1989; Hagenmaier et al., 1990; Jones, 1995). Carvalhaes et al. (2002) collected ambient air samples and suggested that, according to the congener profile, cars running on unleaded petrol and diesel may be the main source of dioxins. In contrast, other workers found that PCDD/PCDF profiles were significantly different from those obtained in ambient samples and in biota and concluded that PCDD/PCDF from petrol vehicles were not considered to be a major environmental pollutant (e.g. Westerholm & Egebäck, 1994).

According to Geueke et al. (1999), a 'typical' PCDD/PCDF profile is still unknown for diesel engine emissions. These workers note that the use of diesel profiles to establish source-sink relationships is rather speculative, particularly if the sinks considered are likely to cause changes of the profile by metabolic processes as is the case for biological systems. Compound-specific reactions, transfer processes and partitioning act to alter the 'blend' of PCDD/PCDFs in emissions to air before they arrive in human tissue (Alcock, Sweetman & Jones, 2001).

Third, it is noted, however, that traffic emissions can be much more important with respect to multipathway exposures than one would expect on the basis of the estimated magnitude of their emissions. This is mainly due to the fact that vehicle emissions are ubiquitous and fairly uniform in densely populated urban areas. In addition, emissions take place close to the recipient, which leads to potentially large exposure from road traffic. There is much less dilution of emissions between the exhaust and the exposed population than between, for example, an MSW incinerator and a downwind community.

Another concern with respect to food chain impacts is that food is transported on roads where highest concentrations occur. For instance, highest PCDD/PCDF concentrations in ambient air have been found in traffic tunnels (Marklund et al., 1990). Increases in concentration levels on pine needle surfaces with reduced distance to a road with dense traffic have also been reported (Marklund et al., 1990).

Again, other researchers arrive at other conclusions. For example, although Bingham et al. (1989) observed a marked decrease in ambient PCDD/PCDF concentrations from motorway and suburban sites to a rural site, the motorway and the suburban sites had essentially similar PCDD/PCDF concentrations, despite the much higher vehicle

activity on the motorway. The authors suggest that this indicates that motor vehicles are not a major source of PCDD/PCDF in these locations.

Finally, traffic can also act as a secondary source, for example through re-suspension of deposited PCDD/PCDF-containing particles by motor vehicles (EC, 1997). At this stage, it is not possible to draw any conclusions on the importance of road traffic with respect to dioxin exposure. Although, emission inventories around the world indicate that traffic is a minor source, the absolute and relative magnitude of vehicle dioxin emissions remains under debate.

5.2 Dioxin formation in vehicle engines and exhaust systems

A basic fundamental understanding of the formation of dioxins is necessary in order to facilitate the development of Australian emission factors and to support the assumptions made in this study.

Dioxins are formed in combustion processes and many studies have been undertaken investigating the mechanisms by which these compounds are formed in combustion processes. However, the specific mechanisms of formation are considered very complex and are neither completely understood nor agreed upon (Environment Australia, 1998) and many questions still remain unanswered (Hutzinger & Fiedler, 1989).

In principle, all production processes in which chlorine and a source of carbon are present at a temperature above 200 °C are potential dioxin sources. Thermal processes typically involve very high temperatures (i.e. 800 °C and above), but with the potential for some parts of the process train to be maintained at lower temperatures. Dioxins are formed when four important process conditions are met: temperature between 200-800 °C (ideal range between 200-400 °C), presence of chlorine, presence of organic (specifically aromatic) matter and presence of oxygen. Furthermore, the residence time of the exhaust gas in the temperature range of 200-800 °C, the quantity of available chlorine and the presence of fly ash and metals (which serve as catalysts) affect the formation of dioxins (Bremmer et al., 1994).

No specific information was found on PCDD/PCDF formation in vehicle engine and exhaust systems from the collection of all relevant information on dioxins emissions available for this study. There are suggestions, however, that the currently known formation processes that occur during combustion also apply to internal combustion engines. This indicates that the chemistry of incomplete combustion in its reaction pathways is little affected by the technical realisation of the combustion process. For example, research has shown that PCDD/PCDFs are formed in the cooler zones of MSW incinerator systems where catalytic surfaces (carbon particles and/or particles with silicate structure), excess oxygen, organic and inorganic chlorine donors and ideal temperatures (~300 °C) are present. Therefore, de novo synthesis theory[13] is directly applicable to diesel (Jones, 1993) and petrol engines (Bacher et al., 1991).

[13] Surface-catalysed PCDD/F formation resulting from combination of carbon, chlorine and oxygen (http://www.ea.gov.au/industry/chemicals/dioxins/pubs/review.pdf).

The following process conditions, which are probably also relevant to vehicle emissions, have been shown to affect dioxin formation:

- High temperatures and long residence times in the furnace leads to *complete combustion*, which results in lower PCDD/PCDF emissions. According to Bumb et al. (1980), combustion processes must be more than 99.9% efficient to ensure reduction of the concentration of dioxin from 1 ppm to 1 ppb. However, vehicle engines are not very efficient, which is illustrated by their substantial emissions of incomplete combustion products such as carbon monoxide (CO) and hydrocarbons (HC). Incomplete combustion in internal combustion engines is likely to increase PCDD/PCDF emissions (refer to Section 8.3)
- Fast cooling of flue gases minimises the time spent in the 200-450 °C temperature region, which results in lower PCDD/PCDF emissions. Temperatures in the combustion chamber and exhaust system and volume flow rates influence PCDD/PCDF formation in vehicle engines. With respect to vehicles, a 'temperature gradient' from in-cylinder combustion to actual exhaust release at the tailpipe-end can be observed. Petrol engine combustion typically occurs at temperatures around 3500 °C at near-stoichiometric oxygen levels. Petrol engine-out exhaust temperatures generally range between 400 and 600 °C. For catalyst cars, catalyst-operating temperatures are typically between 200 and 450 °C and tailpipe exhaust temperatures typically vary between 200 and 300 C. Diesel engines operate at combustion temperatures of about 2000 °C with an excess of oxygen. Diesel engine-out exhaust temperatures range between 200 and 400 °C and tailpipe exhaust temperatures typically are 180 °C. It seems possible that PCDD/PCDFs are formed in both the engine and exhaust system
- High *sulfur concentrations* in the form of sulphur dioxide (SO_2) poison catalytic sites active in dioxin formation, which results in lower PCDD/PCDF emissions. This is interesting because this indicates that lowering the sulphur content of fuels might lead to an increase in dioxins emissions
- Chlorine input concentration and dioxin output concentration are related when concentrations of chlorine in the feed are small (less than 1%) and when poor combustion occurs. Chlorine content of fuel and engine oil is, therefore, important (refer to Section 8.6).

5.3 Emissions of brominated and mixed dioxins

Dioxins can also be formed with bromine and brominated or mixed brominated/chlorinated dioxins and could arise in the same way as chlorinated dioxins. Brominated and mixed halogenated aromatics are of concern because of the potential health effects (Öberg et al., 1987). Brominated and mixed halogenated congeners have not been studied toxicologically, but it seems plausible to assume that they have the same toxicological properties as the chlorinated compounds (Rappe et al., 1987). There

is, however, no toxic equivalence scheme for brominated or mixed brominated/chlorinated congeners of the 2,3,7,8-type. As a result, brominated and mixed dioxins are not included in dioxins emission factors developed in this study, but the information that is available is briefly discussed in this section.

Only a few studies were found that specifically measured poly*halogenated* dibenzo-para-dioxins (PHDD) and poly*halogenated* dibenzo-furans (PHDF) emissions from vehicles. For example, Haglund et al. (1988) found that the highest amounts of poly*brominated* dibenzo-para-dioxins (PBDD) and poly*brominated* dibenzo-furans (PBDF) are emitted from leaded petrol carburetted cars and that much less is emitted from carburetted unleaded petrol cars. The leaded petrol vehicle emitted more TBDFs than TCDFs (0.4-8.1 ng TCDFs/km versus 23 ng TBDFs/km). No PBDD/F emissions were detected in the exhaust from a diesel truck (12 L DI Volvo TD120).

Hagenmaier et al. (1990) investigated polyhalogenated dibenzodioxins and dibenzofurans by testing a spark-ignition engine using different fuels. For leaded petrol they found that under the experimental conditions mainly mixed halogenated and brominated dioxins (PHDD/PHDF and PBDD/PHDF) were detected. The total emission reached several 1,000 ng/m^3 and mainly PHDD/PHDF substituted with 1 to 4 chlorine and/or bromine atoms were detected. The tetra- to octa-CDD/PCDF represented only a relatively small fraction of the total emitted PHDD/F, i.e. 0.1-1%.

For unleaded petrol, the concentration of PHDD/PHDF was substantially lower, i.e. 1-10%. Catalysts further reduce PHDD/PHDF emissions. For the diesel motor mixed PHDDs and PHDFs were detected with concentrations in the same range as found with the unleaded petrol experiment with catalyst. The tetra- to octa-chlorinated compounds comprise only a minor fraction of the total halogenated compounds, particularly for the dibenzofurans.

It is noted that numerous other halogenated hydrocarbons, i.e. 'non-dioxins', have been measured. For instance, Haglund et al. (1987) measured several halogenated PAHs (brominated, bromochlorinated and chlorinated) in particulate matter samples of vehicle exhaust and snow samples near a motorway, which are potentially toxic.

5.4 Emissions of PCBs

Almost no information could be found on PCB emissions from road traffic. One recent study reported on PCB measurements in road dust and it suggested that an industrial source was the main source of PCBs (Irvine & Loganathan, 1998). Broz et al. (2000) recently measured PCB emissions from one spark-ignition vehicle using leaded petrol and found an emission factor of 6-25 ng PCBs/km. PCBs are also absorbed into the oil film on cylinder walls, which leads to increased PCB levels in oil with the time of operation. Measured PCB concentrations in oil vary between 9.9-47 mg/kg (Broz et al., 2000).

5.5 Dioxin profiles

It is generally accepted that the mass fractions of dioxin congeners and homologues (i.e. tetra-CDD/PCDF and above) are specific to a dioxin formation process. Therefore, both the quantity of dioxins emitted and the distribution, expressed as, for example, a

histogram, are important as they may assist in identification of specific combustion sources. However, the relative proportions of the congeners and homologues may alter from the time of discharge to the eventual uptake at the point of exposure, depending on the fate of individual congeners in the environment, so care is needed. The relative concentration of homologues and congeners is usually plotted as a histogram and is called the dioxin profile, signature or fingerprint.

With respect to road traffic emissions, the use of fingerprints in source apportionment of PCDD/PCDF emissions has been reported in a few instances. For example, Edgerton and Czuczwa (1989) used a chemical mass balance model, but at that time no quantitative profiles for vehicles were published. Instead, they used a profile from an ambient monitoring site in an area of high traffic density and known elevated lead concentrations. No direct contribution from road traffic was established, but 'urban background' contribution was apportioned 26-28% in two cases.

The use of dioxin profiles may be preferred over the use of congener or homologue emission factors (picograms per km - pg/km) because of the large variability in dioxin emission factors that have been measured. Smit et al. (2002b) mentioned that normalised hydrocarbon profiles have been reported to be remarkably stable for most hydrocarbons under different conditions. Furthermore, profiles can be directly applied to dioxins emission factors.

This Section discusses dioxin congener and homologue profiles from road traffic. The congener and homologue profiles developed in this Section were developed from published measurement data by calculating the ratio of specific congeners to total congener emissions (congener profile) and by calculating the ratio of specific homologues to total homologue emissions (homologue profile). These profiles for each vehicle class are presented in Appendix A.

In general, the congener and homologue profiles for the different vehicle classes can be quite variable for certain congeners and homologues. For example, 2,3,7,8-TCDF emissions from non-catalyst cars running on leaded petrol can make up between 2 and 43% of the total congener emissions. In contrast, the most toxic 2,3,7,8-TCDD emissions from petrol-fuelled vehicles vary between 0.1 and 1.4%, and are more constant. On the other hand, 2,3,7,8-TCDD emissions from diesel-fuelled heavy-duty vehicles can make up 12% of total congener emissions. The large variability in congener profiles is particularly apparent for diesel heavy-duty vehicles congener emissions, which is illustrated in Figure 2 (note that exact profile data can be found in Appendix A).

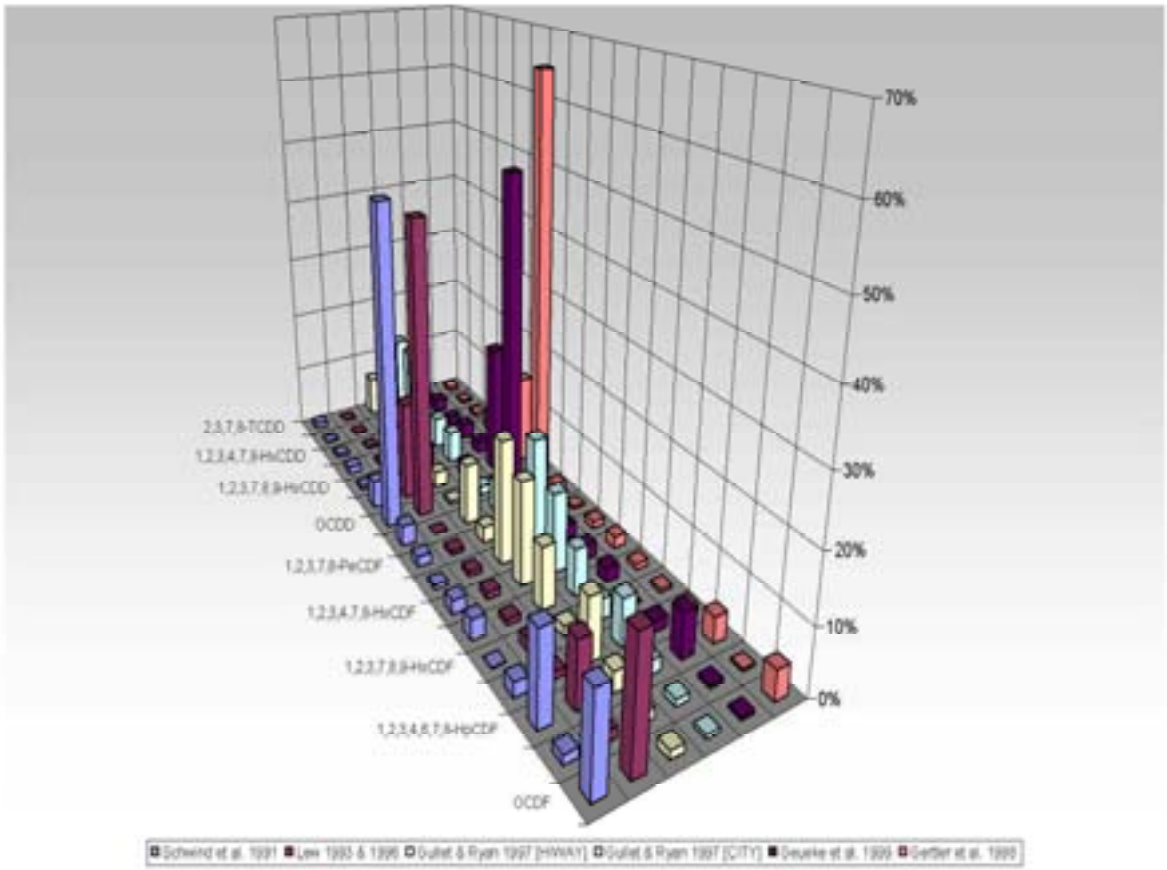

Figure 2 - Congener profile for diesel-fuelled heavy-duty vehicles

This variability in congener profiles has been confirmed by some studies. For example, Gullet & Ryan (1997) observed a large variation in the congener profiles, which were sampled on-board during driving on different routes. Their results suggest a lack of mechanistic constancy, even among similar driving routes. According to Geueke et al. (1999), a 'typical' PCDD/PCDF congener and homologue profile is still unknown for diesel engine emissions. These workers warn that the use of diesel profiles to establish source-sink relationships is, therefore, rather speculative, particularly if the sinks considered are likely to cause changes of the profile by metabolic processes as is the case for biological systems. The reader is referred to the data contained in Appendix A for further information.

6. Literature review

Several data collection techniques have been employed in this study to obtain a complete overview of the available information on dioxins emissions from on-road vehicles, including an extensive library database search, Internet searches and by contacting relevant organisations. As a result, a total of 79 publications were identified that were potentially interesting for this study.

After closer inspection, however, many of these publications did not to contain information that was relevant for the specific purposes of this study. For example, some publications reported on health impacts of (diesel) exhaust, PCDD/PCDF emissions during a vehicle fire in a traffic tunnel or included non-traffic sources only. Some publications were literature reviews themselves based on (a selection of) original studies that were also investigated in this study. An additional library search conducted by DEH did not identify any new publications relevant to this study.

Careful consideration is required when figures are adopted from literature reviews. We have come across cited emission factors that were not correctly adopted from the original source, for example by using wrong units. Therefore, original publications were used in this study as much as possible based on the premise that emission factors directly derived from data measured under known test conditions are most valuable for this study. This approach enables a better assessment of the strengths and weaknesses for application in the Australian situation.

7. Overview of published dioxin emission factors

This Section presents an overview of all known international studies on vehicle dioxins emissions. Study test conditions and results are presented in six different tables (page 14-15). Each table refers to a specific combination of technology type (non-catalyst passenger cars, catalyst passenger cars, light-duty vehicles, heavy-duty vehicles or fleet) and fuel type (leaded petrol, unleaded petrol, diesel or fleet mix). Most of the literature provides emission factors expressed as pg/L of fuel. In order to account for differences in fuel economy between countries, these fuel-based emission factors are combined with Australian fuel economy data for the vehicle type under consideration to arrive at distance-based emission factors expressed as pg/km. This approach uses the following equation:

$$EF_{Distance,\,X} = EF_{Fuel,\,X} \div FE_X$$

In this equation $EF_{Distance}$ is a distance-based emission factor (pg/km) for vehicle type X, EF_{Fuel} is a fuel-based emission factor (pg/L) for vehicle type X and FE is the fuel economy (km/L) for vehicle type X. Fuel economy data for 1998 and each vehicle type have been obtained from the Bureau of Transport Economics.

The six overview tables (Table 2) contain information that is relevant with respect to dioxin emissions:

1. year that the tests were conducted
2. country in which the tests were conducted
3. test conditions (driving pattern, engine load scheme)
4. fuel (commercial or not)
5. operating mode (cold-start, hot-start, hot-stabilised)
6. sampling point (engine-out, before muffler, tailpipe)
7. sampling devices used (filter and/or adsorbent)
8. sampling loss correction
9. vehicle type (passenger car with or without catalyst, light-duty vehicle, heavy-duty vehicle, truck, bus, fleet mix)
10. number of vehicles tested
11. fuel economy expressed as km per litre of fuel
12. emission factors expressed as pg I-TEQ per litre of fuel
13. emission factors expressed as pg I-TEQ per km driven
14. any additional remarks.

These aspects are important with respect to the development of Australian emission factors. In the next sections, the different studies presented in these tables are discussed in much more detail.

Table 2 - Overview tables

LEADED PETROL NON-CATALYST PASSENGER CARS

Reference Report / Paper	Test Year	Country	Test Conditions	Commercial Test Fuel / Lubricant		Operating mode	Sampling Location	Sampling		Loss Correction	Vehicle Type	No. Vehicles Tested	Fuel Economy	Emission Factor (I-TEQ)		Remarks
[-]	[-]	[-]	[-]	Fuel	Oil	[-]	[-]	Filter	Ads.	[-]	[-]	[-]	[km/l]	[pg/l fuel]	[pg/km]	[-]
Marklund et al., 1987	1987	Sweden	A10 method 2 x 12.4 km Cycle	No	Yes		Tailpipe	Yes	Yes	Only For Recovery (Clean-Up)	PCNC	4	-	-	22 - 220	New synthetic oil used + reference petrol, unleaded petrol + 0.15 g/l tetra-ethyllead and 0.1 g/l dichloroethane added, I-TEQ calculated from Eadon.
California Air Resources Board, 1987 Jones, 1993	1987	USA	Engine Test Bench Steady-State @ 50 km/h								PCNC	1	8.3	1 794	216	Congener distribution data used to convert to I-TEQ
Bingham et al., 1989	1989	New Zealand	Chassis Dynamometer A10 Cycle (12.1 km)	Yes			Tailpipe	Yes	Yes	Yes (Before Sampling)	PCNC (CARB)	4	-	-	16 - 40	Petrol (96 octane) contained 0.46 g/l tetra-ethyllead, 0.22 g/l EDC and 0.26 g/l EDB, one new and 3 used cars.
Marklund et al., 1990	1990	Sweden	Chassis Dynamometer FTP72 Cycle	Yes Yes	Yes Yes	CS→HR CS→HR	Tailpipe Tailpipe	Yes Yes	? ?	Sampling, Extraction, Clean-Up, MS-Response	PCNC (CARB) 71600 km PCNC (CARB) 6890 km	1 1	8.3 8.3	10 23 (650)	1.2 2.8 (80)	I-TEQ 88, new semi-synthetic oil, normal commercial petrol with 0.15 g lead/l & EDC/EDB (63 ppm chlorine), no PCDD/F's detected in blank samples. EPA 1987: [illegible] in ng/l Within brackets: Hagenmaier 1994 & 1995.
Hagenmaier et al., 1990	1990	Germany	Engine Test Bench Steady-State @ 1800 rpm, 50 NM (63 km/h, 3% Road Grade)				Engine-Out	Yes	Yes	Extraction, Clean-Up, MS-Response	PC	1	8.3	1 086 (1 083)	130 (130)	DIN 51600, Cl-content 40 mg/kg, Br-content 84 mg/kg, Hagenmaier 1994 & 1995 values reported here, FAE converted values within brackets.
Schwind et al., 1991 Hutzinger et al., 1992	1991	Germany	Engine Test Bench Various Test Conditions	Yes	Yes						PCNC	1	8.3	52 - 1 184	6 - 143	Results reported in units of pg I-TEQ/l
Broz et al., 2000	2000	Czech Republic	Chassis Dynamometer ECE93 Cycle (Urban)	Yes	Yes		Tailpipe	Yes	Yes		PCNC (SO) PCNC (MO) PCNC (MOO)	1 1 1	-	- - -	2.0 - 17 2.4 - 8.2 1.2 - 8.4	Half-value of detection limit used for non-detected PCDD/F

UNLEADED PETROL NON-CATALYST PASSENGER CARS

Reference Report / Paper	Test Year	Country	Test Conditions	Commercial Test Fuel / Lubricant		Operating mode	Sampling Location	Sampling		Loss Correction	Vehicle Type	No. Vehicles Tested	Fuel Economy	Emission Factor (I-TEQ)		Remarks
[-]	[-]	[-]	[-]	Fuel	Oil	[-]	[-]	Filter	Ads.	[-]	[-]	[-]	[km/l]	[pg/l fuel]	[pg/km]	[-]
Bingham et al., 1989	1989	New Zealand	Chassis Dynamometer A10 Cycle (12.1 km)	Yes			Tailpipe	Yes	Yes	Yes (Before Sampling)	PC (F) 3.3 l	1	-	-	10	
Marklund et al., 1990	1990	Sweden	Chassis Dynamometer FTP72 Cycle	No No	Yes Yes	CS→HR CS→HR	Before Muffler Before Muffler	Yes Yes	? ?	Sampling, Extraction, Clean-Up, MS-Response	PCNC (CARB) 7400 km PCNC (F) 1000 km	1 1	8.3 8.3	3.5 (93) 3.5 (93)	0.4 (11) 0.4 (11)	I-TEF 88, new semi-synthetic oil, no PCDD/F's detected in blank samples. Within brackets: Hagenmaier 1994 & 1995.
Hagenmaier et al., 1990	1990	Germany	Engine Test Bench Steady-State @ 1800 rpm, 50 NM (63 km/h, 3% Road Grade)				Engine-Out	Yes	Yes	Extraction, Clean-Up, MS-Response	PCNC	1	8.3	99 (67)	11 (8)	DIN 51607, Cl-content <1 mg/kg, Br-content <1 mg/kg, Hagenmaier 1994 & 1995 values reported here, FAE converted values within brackets.
Schwind et al., 1991 Hutzinger et al., 1992	1991	Germany	Engine Test Bench Various Test Conditions	Yes	Yes						PCNC	1	8.3	96 - 177	12 - 21	Results reported in units of pg I-TEQ/l

UNLEADED PETROL CATALYST PASSENGER CARS

Reference Report / Paper	Test Year	Country	Test Conditions	Commercial Test Fuel / Lubricant		Operating mode	Sampling Location	Sampling		Loss Correction	Vehicle Type	No. Vehicles Tested	Fuel Economy	Emission Factor (I-TEQ)		Remarks
[-]	[-]	[-]	[-]	Fuel	Oil	[-]	[-]	Filter	Ads.	[-]	[-]	[-]	[km/l]	[pg/l fuel]	[pg/km]	[-]
Marklund et al., 1987	1987	Sweden	A10 method 2 x 12.4 km Cycle	No	Yes		Tailpipe	Yes	Yes	Only For Recovery (Clean-Up)	PCC	2		-	ND (~ < 13)	New synthetic oil used + reference petrol.
California Air Resources Board, 1987 Jones, 1993	1987	USA	Engine Test Bench Steady-State @ 50 km/h								PCC	3	8.9	4 322	490	Congener distribution data used to convert to I-TEQ
Marklund et al., 1990	1990	Sweden	Chassis Dynamometer FTP72 Cycle	No No No	Yes Yes Yes	CS→HR CS→HR CS→HR	Before Muffler Before Muffler Tailpipe	Yes Yes Yes	? ? ?	Sampling, Extraction, Clean-Up, MS-Response	PCC (F) 7000 km	1	8.9	3.5 (93)	0.4 (10)	I-TEF 88, new semi-synthetic oil, no PCDD/F's detected in blank samples. Within brackets: Hagenmaier 1994 & 1995.
Hagenmaier et al., 1990	1990	Germany	Engine Test Bench Steady-State @ 1800 rpm, 50 NM (63 km/h, 3% Road Grade)				Engine-Out	Yes	Yes	Extraction, Clean-Up, MS-Response	PCC	1	8.9	20 (7)	2 (0.8)	DIN 51607, Cl-content <1 mg/kg, Br-content <1 mg/kg, Hagenmaier 1994 & 1995 values reported here, FAE converted values within brackets.
Schwind et al., 1991 Hutzinger et al., 1992	1991	Germany	Engine Test Bench Various Test Conditions	Yes	Yes						PCC	1	8.9	10 - 26	1 - 3	Results reported in units of pg I-TEQ/l
Miyabara et al., 1999	1999	Japan	Soot Deposits in Vehicle Exhaust					Yes	No		?	1	-	4.16 *	0.04 - 0.21	* Emission factor expressed as pg I-TEQ/g particulates

Table 2 - Overview tables (continued)

DIESEL LIGHT-DUTY VEHICLES

Reference Report / Paper	Test Year	Country	Test Conditions	Commercial Test Fuel / Lubricant		Operating mode	Sampling Location	Sampling		Loss Correction	Vehicle Type	No. Vehicles Tested	Fuel Economy	Emission Factor (I-TEQ)		Remarks
[-]	[-]	[-]	[-]	Fuel	Oil	[-]	[-]	Filter	Ads	[-]	[-]	[-]	[km/l]	[pg/l fuel]	[pg/km]	[-]
California Air Resources Board, 1987; Jones, 1993	1987	USA	Engine Test Bench Steady-State @ 50 km/h								LDV	1	8.3	1 290	156	Congener distribution data used to convert to I-TEQ
Hagenmaier et al., 1990	1990	Germany	Engine Test Bench Steady-State @ 1800 rpm, 50 NM (60 km/h, 3% Road Grade)				Engine-Out	Yes	Yes	Extraction, Clean-Up, MS-Response	LDV	1	8.3	75 (240)	9 (29)	[illegible]. Hagenmaier 1994 & 1996 values reported here, FhAE converted values within brackets
Bröker et al., 1992	1992	Germany	Engine Test Bench FCT Cycle								PC	1	-	-	50 - 70	Only sum PCDD/Fs reported of 2470 and 3440, with and without PCB [illegible]
Schwind et al., 1991; Hutzinger et al., 1992	1991	Germany	Engine Test Bench Various Test Conditions	Yes	Yes						PC	1	8.4	10 - 130	1 - 16	Results reported in units of pg I-TEQ/l
Bühler & Greiner, 1996	1996	Germany									PC		8.4	48	6	Diesel carrying load
Miyabara et al., 1999	1999	Japan	Engine Test Bench 1000 rpm @ 10 kg.m load & Soot Deposits in Vehicle Exhaust					Yes	No	Clean-Up	LDV	1	-	13.5 *	4*	* Emission factor expressed as pg I-TEQ/g particulates

DIESEL HEAVY-DUTY VEHICLES

Reference Report / Paper	Test Year	Country	Test Conditions	Commercial Test Fuel / Lubricant		Operating mode	Sampling Location	Sampling		Loss Correction	Vehicle Type	No. Vehicles Tested	Fuel Economy	Emission Factor (I-TEQ)		Remarks
[-]	[-]	[-]	[-]	Fuel	Oil	[-]	[-]	Filter	Ads	[-]	[-]	[-]	[km/l]	[pg/l fuel]	[pg/km]	[-]
California Air Resources Board 1987; US EPA, 2000	1987	USA	Engine Test Bench Steady-State @ 50 km/h								HDV (7) HDV (8)	1	2.6	3 718 - 7 288	1 308 - 2 803	Congener distribution data used to convert to I-TEQ
Marklund et al., 1990	1990	Sweden	Chassis Dynamometer US 13-Mode Cycle	No	Yes			Yes	?		HDV (7)	1	-	-	ND	Reference diesel fuel used, not commercial + analytical problems
Schwind et al., 1991; Hutzinger et al., 1992	1991	Germany	Engine Test Bench Various Test Conditions	Yes	Yes						HDV (7)	1	2.6	75 - 81	26 - 29	Results reported in units of pg I-TEQ/l
Hagenmaier, 1994	1994	Germany	Chassis Dynamometer Steady-State & Berlin Cycle								HDV (8)	1	-	ND	-	Brominated and mixed chlorinated-brominated dioxins and furans were also below the detection limit
Bühler & Greiner, 1996	1996	Germany									HDV (7)		2.6	77	28	Diesel carrying load
Clunies-Ross et al., 1996	1996	Queensland	Engine Test Bench Single Cylinder 2.1 DI Steady-State @ Constant Speeds				Engine-out	Yes	Yes	Yes	ENG (NORMAL) @ 1,2,3,3.5 kW ENG (DOPED) @ 1,2,3,3.5 kW	1 1	- -	10 300, 23 000, 60 000, 77 000 60 300, 66 000, 85 000, 107 000	- -	Stock diesel fuel (3.9 ppm chlorine) and doped diesel fuel (+34.4 mg copper/l & tcp)
Gullett & Ryan, 1997	1997	USA	On-Road Sampling 10.3 liter 6 cyl. Caterpillar [illegible] City (28 km/h) & Highway Driving (80 km/h)	Yes			Tailpipe	Yes	Yes	Yes	HDV (7) CITY HDV (7) FREEWAY	1	1.8 2.5	89 37	50 15	Fully loaded truck, no blank corrections (detection limits = 0)
CE-CERT, 1998	1997	California	Engine Test Bench 10 liter 6 cyl. Cummins Turbocharged DI FTP Test (Transient)	Yes		1 CS + 7 HD Cycles	Dilution Tunnel	Yes	Yes	Yes	HDV (7) Pre-93 California Fuel HDV (7) Reformulated Diesel	1 1	2.6 2.6	9.3 15.7	3 6	Three filter changes per 8 cycles, new oil for each fuel, maximum I-TEQ shown here, no blank corrections. Chlorine levels were 10 mg/kg (Pre-1993), 50 mg/kg (REFORM) and 230 mg/kg (Engine Oil)
Geueke et al., 1999	1999	Germany	Engine Test Bench 12 liter 6 cyl. MAN D 2866 LF [illegible] FIGE Cycle (= ETC Cycle)	Yes	Yes	HD	Exhaust Duct	Yes	Yes		HDV (7)	1	2.6	291	104	Modern European diesel engine, worst-case estimate

FLEET

Reference Report / Paper	Test Year	Country	Test Conditions	Commercial Test Fuel / Lubricant		Operating mode	Sampling Location	Sampling		Loss Correction	Vehicle Type	No. Vehicles Tested	Fuel Economy	Emission Factor (I-TEQ)		Remarks
[-]	[-]	[-]	[-]	Fuel	Oil	[-]	[-]	Filter	Ads	[-]	[-]	[-]	[km/l]	[pg/l fuel]	[pg/km]	[-]
Oehme et al., 1991	1988	Norway	Tunnel Study (Vålerenga Tunnel, Oslo) Average Speed 50 (Uphill) & 68 km/h (Downhill) Free-Flowing Traffic 60 km/h Average Fleet Age 9 Years	Yes	Yes	Probably Mainly [illegible]	Tunnel Inlet/Outlet	Yes	Yes	Yes	FLEET LDV (20-30% ULP) HDV (7) (DIESEL) LDV HDV (7)	20 000 - 30 000 - 3.5-10% -	- - - 8.0 2.6	- - - 2 700 10 000	800 - 1 000 / 75 - 160 520 / 38 9 500 / 720 (5 400) 238 (5 429)	Uphill (+3.5%) versus downhill (-3.5%). Nordic TEQ used here (could not be converted). Hagenmaier 1994 & 1996 values within brackets
Wevers et al., 1992	1991	Belgium	Tunnel Study (Craeybeckx Tunnel, Antwerpen)	Yes	Yes	Probably Mainly [illegible]	Background vs. 1/4 from Tunnel Exit	Yes	Yes	Yes	FLEET PCNC (LEAD) PCNC (UNL) PCC (UNL) PC (DIES)		- 8.3 8.3 8.5 8.4	- 1 541 77 77 36	48 186 9 7 4	Vehicle PCDD/F emission concentration estimated to be 42-45 pg I-TEQ/Nm3
Gertler et al., 1996	1995	USA	Tunnel Study (Interstate Traffic) Speed Limit 80 km/h Grade +/- 3.8%	Yes	Yes	Probably Mainly [illegible]	Tunnel Inlet/Outlet	Yes	Yes	Yes (Unspecified)	HDV	< 142 014	-	-	280	Unit is TEQ, not sure if it is equivalent to I-TEQ

8. Development rationale

The tables presented in Section 7 show that relatively few tests on dioxins emissions from vehicles are available considering the variety and numbers of vehicles currently in operation and the range of operational, technical and environmental conditions in which they are operated. As a result the emission factors developed in this report are quite uncertain and the only way to reduce this uncertainty would be to conduct more measurements. In addition, it became obvious from the international literature review that a considerable amount of potentially useful information is not available. Gaps in data exist which will lead to added uncertainties in the emission factors developed in this study.

Nevertheless, thorough analysis and consideration of the available data could optimise the use of these data in the development of 'Australian' dioxins emission factors. For this reason, a 'development rationale' is presented in this Section. This rationale presents certain *selection criteria* and they are used for the development of 'Australian' dioxins emission factors in Section 9. The criteria are summarised in Section 8.10.

Making an estimate of Australian dioxins emissions from road vehicles is complicated by several factors and these factors should be considered when emissions factors are derived from literature and applied to the Australian situation. A number of factors may affect PCDD/PCDF emissions from and emission factor development for road traffic:

1. vehicle technology type
2. fleet age
3. situations that result in incomplete combustion
4. study type
5. measurement methodology
6. test protocols
7. fuel composition
8. ambient temperature
9. units and calculation methods
10. engine calibration practice.

These factors are discussed separately in the following subsections.

8.1 Vehicle technology class

In general, air pollutant emissions vary significantly with vehicle characteristics. Of particular importance are vehicle size, vehicle weight, engine type, type of fuel, emission control technology and the age of the vehicle. These factors basically determine vehicle emissions and a vehicle classification scheme is normally used to take them into account. Usually, the impact of vehicle technology is sufficiently covered by the development of air pollutant emission factors for the different

technology classes. The fleet composition reflects the distribution of the different vehicle classes within the on-road fleet.

Vehicle technology classes are usually defined by the emission standards that were applicable at the time of their production. This is a suitable approach because emission standards are closely linked to the vehicle technology that is needed to achieve the emission standards. The Australian Design Rules (ADRs) represent mandatory national standards for motor vehicle emissions. They apply to all vehicles prior to first registration in Australia.

For this project ADR27, ADR37 and ADR70/00 are important. ADR27 and ADR37 regulate exhaust emissions from light-duty petrol passenger vehicles. ADR27 applies to vehicles manufactured between 1976 and 1985 and represents the non-catalyst petrol cars in the Australian fleet. ADR37 applies to vehicles manufactured between 1986 and 2003 and represents the catalyst petrol cars in the Australian fleet. It should be noted that the ADR37 category contains different catalyst technology. The 1986-1988 model year group generally consists of a two-way catalyst and single point fuel injection, whereas cars manufactured from 1989 onwards predominantly use three-way catalysts and multi-point fuel injection. However, the available data on dioxins emissions do not indicate that such a distinction is significant in terms of dioxin emissions.

ADR70/00 sets emission limits for diesel engines used in heavy-duty vehicles (trucks), which apply to diesel engines manufactured from 1995-1997 onwards. It provides manufacturers with the option of complying with one of three sets of emission standards, i.e. EURO1, US1991 or Japan 1993/1994. This ADR is based on engine dynamometer testing procedures, which are different in each country. For this study, only a small proportion of the diesel vehicles are regulated by ADR70/00 because the base year is 1998. It should be noted that ADR70/00 is being superseded by ADR80/00 (EURO3) over calendar year 2002, and by ADR80/01 (EURO4) over calendar year 2006.

With respect to the development of Australian PCDD/PCDF emission factors, a distinction should be made between different vehicle classes. Vehicles classes are defined by three 'variables':

1. vehicle type (passenger cars, trucks, etc.)
2. fuel type (unleaded petrol, leaded petrol, diesel, etc.)
3. emission control technology type (catalyst or non-catalyst).

Different vehicle types would cover major differences in several vehicle characteristics, such as vehicle size, vehicle weight and engine size. Different fuel types present differences in engine[14] and fuel type. Finally, differences in emission control technologies are captured by the presence of catalyst technology[15].

[14] That is, compression-ignition (CI) and spark-ignition (SI) engines. The petrol or spark-ignition engine derives its power from explosion of the air-fuel mixture, whereas in the diesel or compression-ignition engine the fuel burns rather than explodes.
[15] It is theoretically possible that PCDD/PCDFs are destroyed in the catalytic converter (Marklund et al., 1990; EPA, 1997; EC, 1997).

8.2 Fleet age

In general, air pollutant emissions are influenced by the efficiency of fuel combustion and the efficiency by which engine-out emissions are further reduced by emission control technology[16]. The ages of vehicles in the on-road fleet reflects both the distribution of vehicle technology in the fleet (refer to Section 8.1) and the level of deterioration of engine and emission control systems in time (vehicle mileage). Air pollutant emissions are dependent on the actual state of tuning and the state of the emission control system. Vehicles can be badly tuned or tampered with and can have malfunctioning or partly functioning emission control systems, resulting in high emissions. These vehicles are so-called 'high-emitters' and they can make up a significant fraction of the vehicle fleet. For instance, remote-sensing data showed that about 10% of the vehicles in Melbourne are responsible for half or more of the total CO and HC exhaust emissions (Zhang et al. 1995). As a result, emissions from the entire vehicle fleet are influenced by factors such as the vehicle age distribution and the presence of inspection and maintenance programs (Smit et al., 2002b).

PCDD/PCDF emissions have also been reported to increase significantly with vehicle mileage (Marklund et al., 1990; US EPA, 1997). This is thought to be due to increased oil consumption, increased PCDD/PCDF concentrations in used oil and the formation of deposits in the combustion chamber.

It also seems likely that copper content in oils will increase with increasing mileage due to wear of metallic motor components (Broz et al., 2000). This contributes to the formation of PCDD/PCDFs because certain metals can act as catalysts in the dioxins reformation reactions, with copper being the most potent (Clunies-Ross et al., 1996).

However, it is noted that higher engine-out emissions of PCDD/PCDFs do not necessarily result in higher tailpipe emissions, which is shown by Marklund et al. (1990). These workers found that older vehicles using leaded petrol had higher PCDD/PCDF emissions than newer vehicles sampled before the muffler. However, adsorption of PCDD/PCDFs in the muffler was also observed and this adsorption was found to be higher in older mufflers. This resulted in lower tailpipe emissions of the old vehicle running on leaded petrol. No difference between, before and after muffler dioxins emissions was observed for the new cars running on unleaded petrol.

The international literature is indecisive on the impact of ageing or vehicle mileage on dioxin emission rates. For this study, vehicle mileage is, therefore, not considered to be an important criterion. However, if the information is available, it is preferred to use emission data from used vehicles of similar age and mileage to their Australian counterparts.

[16] Due to increased contamination of the catalyst with age, catalyst conversion efficiency will diminish.

8.3 Situations that result in incomplete combustion

It is important to realize that the combustion process in internal combustion engines varies considerably in time due to several factors such as start-up, driving conditions etc. In general, CO and HC are products of incomplete and inefficient combustion and their emission levels increase when the engine is operated under fuel-rich conditions, for example when:

1. the vehicle is operated at certain driving conditions with high engine load, for example during (strong) accelerations, high speed and driving under positive road grades
2. the engine is cold and is started (cold-start emissions), or
3. the vehicle is not well tuned or not well maintained (the engine and emission control system are in a bad technical state).

As with CO and HC emissions, incomplete combustion is also expected to increase PCDD/PCDF emissions (e.g. Haglund et al., 1988). According to Broz et al. (2000), the formation of PCDD/PCDFs and PCBs correlates well with CO concentrations in the exhaust gas, which is not surprising as high CO emissions are an indication of incomplete combustion.

There is, however, not a lot of information on the impact of incomplete combustion on PCDD/PCDF emissions. International publications seem to indicate that driving conditions with higher engine loads promote PCDD/PCDF emissions. For example, Oehme et al. (1991) found much higher emission factors (about a factor 12) for uphill tunnel driving (increased engine load) than for downhill tunnel driving (basically idling). Similarly, Clunies-Ross et al. (1996) found that PCDD/PCDF emissions, expressed as pg I-TEQ/L of diesel fuel, increase with engine load.

Apart from fixed vehicle characteristics such as vehicle weight, shape and size, the engine load is a direct function of the operating conditions of individual vehicles in terms of speed and speed variation. In turn, speed and speed variation depend on traffic conditions (congested, smooth driving, road grade, etc.) and driving style/behaviour (defensive or aggressive, gear selection, use of auxiliary equipment, etc.). It is not hard to see that the influence of all these factors complicates accurate assessment of emissions. For this study it is important that PCDD/PCDF emission data is based on a ‘mixture of engine loads’, or in other words driving patterns or ‘speed-time’ profiles, that are representative of Australian driving conditions. This issue of representative trips is further discussed in Section 8.4.

There is almost no information on the impact of cold-start conditions on PCDD/PCDF emissions, except for one paper. Marklund et al. (1990) tested one fuel-injected catalyst vehicle running on non-commercial unleaded petrol over the FTP72 test cycle in both cold-start and hot-start mode and they found no difference in PCDD/PCDF emissions. Based on the very limited information on start impacts, they are not considered to be a criterion in the development of PCDD/PCDF emission factors. However, a test that has included (cold) starts would be preferred over a test that has not done so, because possible start impacts would then be included in the emission factor.

There is almost no information on the impact of tuning on PCDD/PCDF emissions. According to Konheim (1986), untuned cars have been reported to have higher PCDD/PCDF emission factors. Because of the very limited information on maintenance impacts, they are not considered to be a criterion in the development of PCDD/PCDF emission factors. However, a test based on used vehicles/engines would be preferred over a test that is solely based on new vehicles/engines. This way, possible maintenance impacts would be included in the emission factor.

8.4 Study type

There are different methods to estimate dioxins emissions, namely laboratory engine test bench studies, laboratory dynamometer studies, on-road studies and tunnel studies. Each type of study has its own strengths and weaknesses and these should be considered when they are used for the development of emission factors.

The literature review revealed that most studies have been directed at laboratory measurements. An advantage of laboratory measurements is that they are conducted under controlled conditions. This enables detailed investigation of certain aspects that could influence emissions, for example, driving pattern, muffler adsorption, ambient temperature etc. However, a major disadvantage is the limited number of vehicles or engines that can be tested due to time and budget constraints. As a result, these few vehicles or engines can never truly represent the average emission from an entire vehicle fleet.

Furthermore, the driving cycle employed during testing may not necessarily represent driving conditions that are encountered on the road. For instance, the ADR or FTP driving cycle, which is used in Australia, Sweden and the USA for emission testing, is not representative of modern urban driving due to low acceleration rates and limited speeds present in the cycle. Watson (1995) found that hydrocarbon emission levels in 'real-world' driving (i.e. AUC or Australian Urban Cycle) are considerably higher than might be expected from the FTP cycle test, i.e. a factor 2.2 for catalyst vehicles and a factor 1.5 for non-catalyst vehicles. DITRs (2001) measured even higher AUC/FTP ratios for individual catalyst vehicles up to a factor 16. It is not improbable that dioxins emissions are similarly underestimated, depending on the test cycle used. For instance, some studies measured dioxins emissions using a steady-state test cycle at 50 km/h. As hydrocarbons are dioxins precursors it is expected that the driving cycle or engine test cycle will substantially impact on dioxins emission rates.

For diesel engines, the situation is not so clear. Prior to the introduction of ADR 80/00 (EURO3), which is being phased in during calendar year 2002, diesel engines were certified using a steady-state test. This test contains 13 "modes" - each being constant load, constant speed operation for five minute periods. The modes include maximum power/speed and maximum torque/speed conditions, which may be conducive to higher dioxin emissions.

The newer EURO3 transient certification test, which more closely replicates "real-world" driving, with constantly varying engine speed and load, does not contain sustained maximum load conditions.

It does, however, contain numerous instances of transient operation, most importantly high-load acceleration, where the combination of relatively high exhaust temperatures and incomplete combustion may promote high levels of dioxin emissions. The Australian-developed Composite Urban Emissions Drive Cycle (CUEDC) is a transient test cycle that shares many characteristics with the EURO transient cycle. It is widely used for inventory testing and for comparative emission studies. No published work has been identified that could differentiate between relative dioxin emission rates on these three diesel drive cycles.

An important criterion for this study is, therefore, that the driving or test cycle employed during the measurements replicates an average Australian trip as closely as possible. A transient driving cycle allows changes in speed and load to occur in time in order to mimic actual road operation. It includes different driving modes such as idling, acceleration, deceleration and cruise and presents a mixture of engine loads. It is, therefore, closer to real world driving conditions than steady-state engine tests where engines are tested under constant load. For laboratory engine testing there is the additional issue of possible PCDD/PCDF formation in the exhaust system, which is not determined because only engine-out emissions are measured.

In summary, test conditions need to be carefully considered when extrapolating laboratory data to emissions from the vehicle population under real-world driving conditions.

On-road measurements have the advantage that real-world driving behaviour is replicated during the measurements. However, a major disadvantage is again the limited number of vehicles that can be tested due to time and budget constraints.

In comparison to laboratory and on-road studies, tunnel studies measure emissions from a large fleet sample, including badly maintained vehicles. This increases the data validity. However, a major disadvantage of tunnel studies is that they represent only a limited range of operating conditions, typically smooth high speed driving, which might not translate to other driving conditions, for example urban driving on arterial roads with several intersections. In addition, tunnel study results rely on indirect measurements, rather than tailpipe measurements, which may introduce unknown errors. Also, concerns have been raised that tunnel monitors are detecting resuspended particulates that have accumulated over time, leading to overestimates of emissions. Finally, average fleet emissions from overseas studies should be used with care, as they reflect the fleet composition, state of maintenance, driving behaviour, road grades etc. for a specific country.

It is not possible to conclude which type of study would be preferred for the development of Australian PCDD/PCDF emissions factors. It is very important, however, to consider the limitations of the different study types as discussed in this section. A major consideration will be which engine test cycle(s), driving cycle(s) or driving conditions have been used in the overseas studies and how representative these are for the Australian situation. In principle, on-road driving tests and laboratory tests using driving cycles are preferred over steady-state laboratory tests and tunnel studies with smooth high speed driving conditions. However, another major consideration is the number and type of engines/vehicles that were tested in the different studies. Tunnel study results should, therefore, be used as validation data for laboratory studies.

8.5 Measurement methodology

Although there is no standard approved protocol for measuring PCDD/PCDFs in vehicle exhausts, researchers have developed and implemented several measurement approaches for collecting and analysing vehicle exhausts. Other researchers have estimated vehicle exhaust emissions of PCDD/PCDFs indirectly from studies of tunnel air (US EPA, 2000). Measurement of PCDD/PCDF emissions are complicated and consist of different steps, namely sampling, recovery and clean up and analysis.

Sampling is the first and very critical step in the whole process of obtaining final results. There are a number of different sampling techniques for PCDD/PCDFs, but they are commonly collected with filters for the particulate phase and adsorption devices or cryotechnique for the more volatile compounds (gas phase) from the raw exhaust gas.

There is not a lot of information on the vapour/particle partitioning for PCDD/PCDFs in traffic emissions. Wevers et al. (1992) conducted a tunnel study using both filter and PUF (polyurethane foam) measurements and concluded that at least 12 of the 'dirty seventeen' PCDD/PCDFs were found on the filter for 100%. The remaining five congeners were collected on the filter for at least 90%. It should be mentioned that the measurements were conducted in the Belgian winter months (comparable to say Tasmanian winter temperatures), so these low temperatures would favour the particulate phase. In contrast, other authors have reported much larger fractions of gaseous PCDD/PCDFs. For example, according to Miyabara et al. (1999), about 50% of PCDD/PCDFs exist in the gaseous phase. Gullet & Ryan (1997) found that less than 2% of total PCDD/PCDF mass was found on the filter associated with PM. This might be due to high exhaust temperatures and insufficient time to adsorb onto particles during the cooling phase when PCDD/PCDF concentrations are sampled.

As the literature is inconclusive on the gaseous and particulate dioxins fractions, it seems important that both are collected and analysed. However, not all studies that were reviewed collected both the particulate- and vapour-phase PCDD/PCDFs. As a result, emission factors derived from these studies might underestimate total PCDD/PCDF emissions. A criterion for this study is that both gaseous and particulate dioxins fractions have been sampled and analysed, prior to the development of dioxins emission factors.

After sampling, the PCDD/PCDF present on the filter and adsorbents samples is extracted, pre-concentrated and subsequently 'cleaned up' or purified using liquid chromatography. For analysis, separation is achieved by means of a gas chromatograph (GC) and identification and quantification takes place using a mass spectrometer (MS). In many studies, some or all measurement steps were 'spiked' with certain ^{13}C-labelled PCDD/PCDF isomers. This enabled the researchers to later compensate for losses of PCDD/PCDFs that occurred during specific steps in the measurement process and to correct for variations in the MS response. This is very important because high losses have been reported of up to 95% or more (Haglund et al., 1988; Rappe et al., 1988; Marklund et al., 1990; Oehme et al., 1991; CE-CERT, 1998). Clearly, it is necessary to validate PCDD/PCDF measurements by the addition of labelled standards, otherwise emission factors derived from the measurement data could substantially underestimate PCDD/PCDF emissions. A criterion for this study is that spiked measurements were

conducted to correct for dioxins losses, prior to the development of dioxins emission factors.

Other aspects may have influenced the measurements as well, for example, the actual handling of the samples. Exposure of the sample to sunlight could lead to photochemical deposition of the dioxins resulting in reduced dioxin concentrations (Sommer, Kamps & Kleinermanns, 1996). This does not lead to a criterion for this study, because there is not enough information to correct for this.

Due to the complexity of the analytical procedure, one could expect substantial differences between different laboratories and possibly for tests conducted within the same laboratory. Hagenmaier et al. (1990) confirmed this. These workers showed that total PHDD/F reported by two laboratories differed by 75%. This might be considered a best-case result because these authors note that the two laboratories were subjected to intensive joint validation studies. This fact might explain in part the large variation in measured dioxins emissions. However, it cannot be used as a selection criterion as there is no way to establish which laboratory would generate more reliable data.

Generally, the use of more recent measurement data will have an advantage over older data in terms of measurement accuracy. During the mid-1980s, significant advances occurred in emission measurement techniques and in the development of high resolution mass spectrometry and gas chromatography necessary for analytical laboratories to achieve low level detection of PCDD/PCDF in environmental samples (UNEP, 1999). However, some studies that were conducted more than ten years ago still used less developed analytical methods (Geueke et al., 1999). The testing year is not a strong criterion but recent data are preferred over old data.

In summary, measured PCDD/PCDF emissions and, therefore, derived emission factors, are very sensitive to the way in which the measurements were conducted. Large differences between laboratories are likely to occur.

8.6 Fuel and oil composition

The composition of fuel (petrol, diesel) and engine oil both impact on dioxin emissions from road traffic. Composition refers to the presence of dioxin precursors, PCDD/PCDFs and catalytic metals in fuel and engine oil.

First of all, there are several dioxin precursors that have been found in both fuel and oil. Chlorine is an important dioxin precursor that is found in petrol, diesel and engine oil. Incomplete combustion and the presence of a chlorine source in the form of additives in the oil or the fuel have been speculated to lead to the formation of PCDD/PCDFs (US EPA, 2000). The chlorine content of fuels and oils varies, leaded petrol may have a chlorine content of 50-300 ppm and unleaded petrol may have a chlorine content of 1-10 ppm. According to Miyabara et al. (1999), unleaded petrol and diesel contain 14 and 0.6-0.9 mg chlorine per litre, respectively.

Several studies have identified strong correlations between chlorinated additives in petrol and engine oil and PCDD/PCDF emissions during combustion tests. It has been suggested that most of the PCDD/PCDF emissions found in exhaust gases of spark-ignition engines are due to the addition of halogenated additives or 'scavengers'[17] to leaded petrol or to engine oil (e.g. Marklund et al., 1987; Hagenmaier et al., 1990; Bacher et al., 1991). These halogenated scavengers are added to leaded petrol, because they clean the engine by conversion of lead deposits into volatile compounds. They are, however, a major source of chlorine (and bromine) for PCDD/PCDF formation. As a result, vehicles running on leaded petrol have been a considerable source of chlorinated (as well as brominated) dioxins and furans.

The use of scavengers has decreased with the reduction in the lead content of petrol and their use has been discontinued in some countries, for example Germany. However, omission of these additives does not lead to exhaust free of PCDD/PCDFs. Haglund et al. (1987) suggested that halogen atoms are derived from organic halides, other than EDB and EDC, present in the fuel that can be either natural constituents of the crude oil or introduced to the fuel during refinement or shipment.

Similarly, diesel fuel and motor oil contain small amounts of chlorine (e.g. Clunies-Ross et al., 1996), but this is still orders of magnitude more Chlorine than necessary to chlorinate measured PCDD/PCDF emissions. There is also Hydrogen Chlorine, Sodium Chlorine and free Chlorine in the atmosphere, which could also act as the chlorine donor given the large mass of combustion air consumed by motor vehicle engines (Jones, 1993). Also, cross-contamination of e.g. diesel fuel with chlorinated scavenger compounds in countries that still use leaded fuel might be possible (Geueke et al., 1999).

Nevertheless, PCDD/PCDF and PCB emissions are reduced when halogens are excluded, especially for chlorine, regardless of whether it is organically or inorganically bonded (Broz et al., 2000).

The Australian Institute of Petroleum (AIP) was contacted to obtain information on the composition of both Australian fuels and engine oils. According to the AIP, the presence of halogenated additives and organic halides in fuels is normally not analysed and no information is available on Australian production. The AIP mentioned that one refiner remarked that there are no halogenated additives and organic halides in fuels. According to this source, it is believed that the chlorine content should be less than 1 ppm. If present, the metal content (copper, lead) of fuels is expected to be very low. Some lead replacement petrols, contain manganese as an additive called methylcyclopentadienyl manganese tricarbonyl (MMT).

Engine oils consist of base oil and an additive pack and, according to the AIP, there may be a risk of halogenated additives and organic halides being in the additive pack. To obtain more specific information, several additive manufacturers were contacted. From the information that was acquired, it became clear that so-called "dispersants"[18] could contain up to 300 ppm chlorine as a by-product of the manufacturing process.

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[17] A mixture of 1,2-dichloroethane (ethylenedichloride - EDC), bromo-ethane, pentachlorophenate and 1,2-dibromoethane (ethylenedibromide - EDB) is most frequently used as scavenger in leaded petrol.

[18] Dispersants are non-metallic cleaning agents that are used to keep suspended any particulate matter in the oil.

The chlorine content of lube oil due to this source would be approximately 20 ppm. No other halogens (iodine, astatine, bromine and fluorine) are used by design in additives for engine oils and no organic halides are present in engine oil. Zinc and magnesium compounds are added, but no average quantities could be provided.

Initially, a criterion for this study would be that the composition of test fuel and engine oil in terms of halogen content is similar to the composition of commercial fuel found in Australia. However, due to the lack of information on either the composition of the test fuels and oils and/or on the composition of Australian commercial fuels and oils, this criterion cannot be used. The information that was provided on Australian fuels and oils is, however, still useful for possible future studies in Australia.

It has been suggested that the concentration of aromatics, chlorobenzenes, phenols, dienes and PCBs in the fuel may contribute to PCDD/PCDF emissions (Broz et al., 2000). There is, however, not enough information to use this as a criterion in this study.

Second, PCDD/PCDF have been detected in engine oil (Ballschmitter et al., 1986; Vainio et al., 1989; Hutzinger & Fiedler, 1989; Lulek, 1998), with lowest levels in new oil and highest levels in 'used' oil (CE-CERT, 1998). In addition, Lulek (1998) found that waste engine oils are a main source of PCBs. PCDD/PCDFs may accumulate in engine oil and be emitted when the oil leaks into the combustion chamber or exhaust system and survives the emission process (EPA, 1997).

Third, catalytic metals such as copper and iron, which can increase the rates of formation of dioxins, have been detected in diesel exhaust (CE-CERT, 1998). This is illustrated by Clunies-Ross et al. (1996) who showed that the use of 'doped' diesel fuel, i.e. the addition of organic metal compounds such as copper, in combination with a ceramic regenerative trap to decrease soot formation by 25 to 50%, showed a significant increase in PCDD/PCDF emissions, especially at low load, when compared to normal diesel fuel.

The second and third points support the criterion in Section 8.2 that a test based on used vehicles/engines is preferred over a test that is solely based on new vehicles/engines.

Although not a lot of information is available, other fuel and oil characteristics might be important with respect to PCDD/PCDF formation. For instance, Broz et al. (2000) found differences in PCDD/PCDF emissions between different oils used although they contained the same mineral components. It was suggested that the changes in emissions were mainly due to different lubricating characteristics. There is, however, not enough information to use this as a criterion in this study.

8.7 Ambient temperature

Ambient temperature impacts on air pollutant emissions. For example, hydrocarbon emissions from vehicle exhaust increase gradually with decreasing temperature from about 25 °C and below about 10 C the emissions increase dramatically in a non-linear fashion (Smit et al., 2002b). However, no information could be found on the impact of ambient temperature on PCDD/PCDF emissions, except for one paper. Bacher et al. (1991) found elevated total PCDD/PCDF levels in floor dust of a public underground parking garage during the colder months. It is not clear whether or not this is caused by an increase in the particulate fraction due to lower temperatures or by an increase in

total PCDD/PCDF emissions. It is, therefore, impossible to draw any conclusions on the impact of temperature on PCDD/PCDF emissions.

8.8 Units and calculation methods

In this study, emission factors are expressed as pg I-TEQ per litre of fuel or pg I-TEQ per km. In some studies, emission factors were expressed using other TEF schemes and conversion to I-TEQ was conducted, provided that congener specific data were available. In some cases different emission factors were obtained when we converted original data into I-TEQ values. This is probably due to a different approach with respect to undetected congeners.

When measurement data are used to develop emission factors it can make a big difference whether analytical detection limits of congeners that were not detected are included in the PCDD/PCDF emission factors or not. These different calculation methods basically show a best-case, i.e. non-detected congeners are not included in the emission factor, and worst-case emission factor, i.e. non-detected congeners are included in the emission factor using the detection limit value. This fact might explain in part the large variation in measured dioxins emissions. However, the calculation method cannot be used as a selection criterion because the method used is often not specified. Studies that present their results in I-TEQ units are, therefore, preferred in this study.

8.9 Engine calibration practice

Engine calibration practice, i.e. the fuel and air management and ignition timing “map” of an engine over its full load/speed range, is country specific and it largely depends on emission regulations. This is because engine management systems are calibrated in such a way that they comply with national emission standards. These emission standards specify the requirements with respect to maximum emission levels, driving cycles, test conditions etc. It could, therefore, be argued that countries with similar emission standards, for example in terms of their test cycles, might have similar engine calibration results. In this study, studies conducted in countries with similar emission standards to Australia, such as the United States and Sweden, are preferred over countries that have different emission standards for light-duty vehicles, such as Germany, Japan and Czech Republic.

For diesel engines, both the USA and Europe used the same “13 mode” test until the end of the 1990’s. Japan also used a modal test. Hence, data from either region would be obtained using engines that were certified on generally similar drive cycles and emission standards.

8.10 Summary of selection criteria

The selection criteria that are used in this study to assess the applicability to Australia of published dioxins emission factors are as follows:

1. A distinction between different vehicle categories in terms of vehicle type, fuel type and type of emission control technology
2. The number of engines/vehicles that were tested in the different studies
3. The engine test cycle, driving cycle or driving conditions that have been used during the measurements
4. The dioxins fractions (gaseous and/or particulate) that have been sampled and analysed
5. Correction for dioxins losses during measurements (spiking).

In addition, there would be certain conditions that would be preferential:

1. Recent emission data
2. Tests including (cold) starts
3. Test results presented in I-TEQ units
4. Emission data from used vehicles/engines
5. Test country with similar emission standards to Australia.

9. Development of Australian dioxins emission factors

Dow Chemicals first reported the presence of PCDDs and PCDFs in car exhaust in 1978. Since 1986, several studies have been conducted to measure PCDD/PCDF emissions from vehicles. These studies are discussed in this Section and PCDD/PCDF emission factors will be developed based on the results of the international literature review (Section 7) and the development rationale (Section 8). The following technology groups are considered:

1. non-catalyst passenger cars running on leaded petrol
2. non-catalyst passenger cars running on unleaded petrol
3. catalyst passenger cars running on unleaded petrol
4. light-duty vehicles running on diesel
5. heavy-duty vehicles running on diesel.

Petrol vehicles are discussed in Section 9.1, diesel vehicles in Section 9.2 and other vehicles in Section 9.3. Before the discussion starts, it is noted that although it is clear that motor vehicles are sources of dioxins and furans, the magnitude of their emissions remains uncertain. There are several reasons for this.

First of all, not a lot of measured data are available internationally on PCDD/PCDF emissions from road traffic. This is illustrated by the fact that the US EPA base their

emission factors on measurement data from published literature. US EPA has indicated that additional research is needed.

Second, PCDD/PCDF emissions generally show tremendous variability in emission rates among the different sources. For example, Edgerton & Czuczwa (1989) noted variability of orders of magnitude in total concentrations in municipal incinerators. Road traffic is no exception and there is a similar large scatter observed in published emission factors, sometimes differing by over a factor of 200 (e.g. Geueke et al., 1999). This is probably due to many factors, including different measurement methods, different operating conditions, problems with high detection limits, dissimilar toxic equivalence schemes and incomplete control of factors such as scavenger content in the test fuel used. It is noted that significant differences in emission factors (up to one order of magnitude) for even the same car under comparable test conditions have been reported (e.g. Broz et al., 2000). This shows that PCDD/PCDF emissions are highly variable by their very nature. Emissions are influenced by combustion conditions, fuel and oil characteristics and their variation, even within the same brand.

Third, published information on dioxins emission factors is contradictory. For instance, US and European data (e.g. Oehme et al. 1991; Jones, 1993; Gertler et al., 1998) show that heavy-duty diesel vehicles exhibit the highest emissions per km, whereas other European data show that leaded petrol vehicles exhibit the highest emissions per km (Hagenmaier et al., 1990).

9.1 Petrol vehicles (spark-ignition)

Section 9.1.1 discusses laboratory studies that investigated PCDD/PCDF emissions from petrol vehicles. Subsequently, the rationale presented in Section 8 is used to develop Australian emission factors for petrol vehicles. Section 9.1.2 then compares these emission factors to PCDD/PCDF emission factors derived from tunnel studies. Section 9.1.3 finally presents the Australian emission factors for petrol vehicles.

9.1.1 Laboratory studies

Marklund et al. (1987) provided the first direct evidence of the presence of PCDD/PCDFs in car emissions. These workers measured PCDD/PCDF emissions from non-catalyst cars using leaded petrol with added chlorinated scavengers (22-223 pg I-TEQ/km), but they could not detect these emissions in the exhaust from unleaded catalyst cars (<13 pg I-TEQ/km). New motor oil was used during the tests and all cars were run under good operating conditions.

In a subsequent study, Marklund et al. (1990) tested different technology classes and used different fuels (normal commercial leaded petrol containing both EDC and EDB, unleaded certification petrol and certification diesel). They observed much lower PCDD/PCDF emissions from non-catalyst leaded petrol cars (1-3 pg I-TEQ/km) using chlorinated and brominated scavengers than PCDD/PCDF emissions from leaded petrol cars using only chlorinated scavengers in their 1987 study. This was probably due to formation of mixed brominated/chlorinated isomers (which are not measured) in the 1990 study. The fuel used in the 1987 study may not have accurately represented commercial fuels at the time, which typically contained a mixture of chlorinated and

brominated scavengers. The 1987 study might, therefore, overestimate PCDD/PCDF emissions.

The tailpipe emission factors reported by Marklund et al. (1990) are very low and other publications have indicated that congener-specific results for this study suggest higher emission factors, for example 7.3 pg I-TEQ/km (US EPA, 2000) and even 66 pg I-TEQ/km (Hagenmaier, 1994) for vehicles running on leaded fuel. For vehicles running on unleaded fuel, an emission factor of 0.4 pg I-TEQ/km was reported, but other calculation methods arrive at higher values of 10-11 pg I-TEQ (Hagenmaier, 1994). It is not clear which values are best to use.

Marklund et al. (1987) and (1990) both used the Swedish A10 cycle, which is equivalent to the transient FTP72 (Federal Test Procedure) or the Australian ADR27 driving cycle. Although it does not contain high engine loads, it does represent urban driving conditions.

In 1987 the California Air Resources Board (CARB) produced a draft report on exhaust emission testing of 4 petrol- and 3 diesel-powered vehicles. However, it must be noted that the CARB data may be somewhat suspect due to the use of a low-resolution mass spectrometer, as well as other analytical issues (Jones, 1993). With respect to unleaded catalyst cars, for example, CARB data seem to include an outlier. Therefore, these data were discarded for petrol vehicles.

Bingham et al. (1989) measured dioxins emissions from four cars using leaded petrol and from one car using unleaded petrol. However, analytical results and detection limits were reported for only five PCDD/PCDF congeners, and those congeners were used to convert the data into I-TEQ units. This might result in underestimated emission factors. Emission factors from Bingham et al. (1989) range from 10 pg I-TEQ/km (unleaded petrol non-catalyst car) to 15-40 pg I-TEQ/km (leaded petrol non-catalyst car).

Hagenmaier et al. (1990) tested 4 light-duty vehicle engines using different fuels over a steady-state test cycle. Emission factors range from 2 pg I-TEQ/km (unleaded petrol catalyst car), to 11 pg I-TEQ/km (unleaded petrol non-catalyst car) and to 130 pg I-TEQ/km (leaded petrol non-catalyst car). However, when congener-specific results (excluding OCDD/PCDF) are converted into I-TEQ values, PAE derived lower emission factors, i.e. 0.8 pg I-TEQ/km (unleaded petrol catalyst car) and 6 pg I-TEQ/km (unleaded petrol non-catalyst car). Again, it is not clear which values are best to use.

Although the authors state that these test conditions are similar to FTP driving cycle conditions, it clearly does not include all driving modes (acceleration, deceleration, idle, cruise) encountered in the real world. Moreover, engine-out emissions were measured and not tailpipe emissions. Hagenmaier (1994) carried out one laboratory measurement in 1993 and, without giving any more details, mentions that scavenger free leaded petrol has similar PCDD/PCDF emissions to unleaded petrol.

A German study (Schwind et al., 1991 and Hutzinger et al., 1992 as cited in US EPA, 2000) conducted several non-steady state engine tests on leaded and unleaded petrol car engines, diesel car engines and diesel truck engines. The emission factors derived from this study ranged from 1-3 pg I-TEQ/km (unleaded petrol catalyst car), to 12-21 pg I-TEQ/km (unleaded petrol non-catalyst car) and to 6-143 pg I-TEQ/km (leaded petrol non-catalyst car).

Miyabara et al. (1999) investigated PCDD/PCDF levels in petrol car exhaust particles. These workers reported an emission factor of 4.2 pg I-TEQ g^{-1} particulates. This translates to a very low dioxins emission factor ranging from 0.04 to 0.21 pg I-TEQ/km, when we assume a PM_{10} emission rate between 10 and 50 mg/km for petrol vehicles. However, the PCDD/PCDF emission factors may be seriously underestimated, as gaseous PCDD/PCDFs were not included in the measurements. Moreover, expressing PCDD/PCDF emission factors as grams PCDD/PCDF per grams particulates may be risky. Wevers et al. (1992) showed that measured PM and dioxin concentrations are not strongly correlated and they are dependent on the actual sampling system used. Therefore, these data are discarded for this study.

Broz et al. (2000) recently investigated the effect of three different engine oils on PCDD/PCDF emissions and reported a range of emission factors for a leaded petrol non-catalyst car of 1-17 pg I-TEQ/km. Their work is based on the ECC83.00 test, which uses the ECE15 driving cycle or European urban driving cycle that has been shown to underestimate emissions compared to those recorded over more representative cycles under the same average speed conditions (e.g. Joumard et al., 2000). Nevertheless, the ECC83.00 test does include all driving modes (acceleration, deceleration, idle, cruise) encountered in the real world and would, therefore, be more representative of urban driving conditions than steady-state engine testing.

Table 3 presents an overview of the selection criteria as described in the rationale of Section 8. In this table each study is assessed against the selection criteria. The last column shows whether the emission factors presented in the study are likely to overestimate (indicated with $\downarrow$), underestimate (indicated with $\uparrow$) or are expected to remain the same (indicated with $\approx$) as a result of test conditions or uncertainties in reported values.

Table 3 - Rationale for petrol vehicles

Reference Report / Paper	Number of Vehicles Tested	Sampling Location Tailpipe	Representative Driving Conditions	Both Particulate & Gaseous	Loss Correction	Similar Emission Standards	Cold-start Included	Flaws in Measurements	Results in I-TEQ	Complete Congener Profile	Used Vehicles/ Engines	EF
Marklund et al., 1987	2-4	Yes	Transient	Yes	Yes	Yes	NR	No	No	No	NR	↓
Jones, 1993	1-3	NR	Steady-State	NR	NR	Yes	NR	Yes	No	NR	NR	Discarded
Bingham et al., 1989	1-4	Yes	Transient	Yes	Yes	New Zealand	NR	No	No	No	Yes	↑
Marklund et al., 1990	1-2	Yes	Transient	NR	Yes	Yes	Yes	No	Unknown	No	Yes	↑
Hagenmaier et al., 1990	1	No	Steady-State	Yes	Yes	No	NR	No	Unknown	No	NR	≈
Schwind et al., 1991 Hutzinger et al., 1992	1	NR	NR	NR	NR	No	NR	NR	Yes	NR	NR	≈
Miyabara et al., 1999	NR	Yes	NR	No	NR	No	NR	No	Yes	NR	NR	Discarded
Broz et al., 2000	3	Yes	Transient	Yes	NR	No	NR	No	Yes	Yes	Yes	≈

NR = Not Reported

Due to the uncertainties associated with PCDD/PCDF emission factors, an emission factor range rather than a point estimate seems most appropriate. Combining the review with information presented in Table 2, the following PCDD/PCDF emission factors are proposed:

1. non-catalyst passenger cars running on leaded petrol: 10-140 pg I-TEQ/km
2. non-catalyst passenger cars running on unleaded petrol: 2-20 pg I-TEQ/km
3. catalyst passenger cars running on unleaded petrol: 1-3 pg I-TEQ/km.

9.1.2 Tunnel studies

Tunnel studies can be regarded as validation studies that test a large number of in-use vehicles under certain operating conditions.

Rappe et al. (1988) measured PCDD/PCDF concentration levels in a traffic tunnel in Hamburg (Germany) that clearly showed that traffic with leaded petrol and halogenated additives is a source of PCDDs and PCDFs in ambient air. They did not develop emission factors from this data.

Oehme et al. (1991) conducted a tunnel study in Norway and they found high emission factors for light-duty vehicles (LDVs) of 38 pg Nordic TEQ/km for 3.5% downhill driving and 520 pg Nordic TEQ/km for 3.5% uphill driving. These values could not be converted into I-TEQ values, but Nordic TEQs are comparable to I-TEQ and within 3-6% of I-TEQ. 25-30% of LDVs used unleaded petrol, so the LDV emission factor largely represents vehicles running on leaded petrol. Using Australian fuel economy figures, an average LDV emission factor of approximately 340 pg I-TEQ/km is calculated. This emission factor is 2.4 times larger than the maximum emission factor for non-catalyst passenger cars running on leaded petrol derived from laboratory measurements. This is surprising as the driving conditions in the tunnel are characterised by smooth free-flowing traffic. Increased load due to driving under grade partly explains the high average LDV emission factor. Oehme et al. (1991) suggested that this is because the tunnel study includes a large car fleet with a mixture of new and old cars that are not always properly maintained.

A tunnel study conducted in Belgium by Wevers, De Fré & Rymen (1992) found lower emission factors than the Norwegian study. Using Australian fuel economy figures, an emission factor of 198 pg I-TEQ/km is calculated for non-catalyst passenger cars running on leaded petrol. This emission factor is still 1.4 times larger than the maximum emission factor derived from laboratory measurements. The emission factors developed for catalyst and non-catalyst vehicles running on unleaded petrol are 1 and 9 pg I-TEQ/km, respectively, and lie in the range of Australian emission factors developed in Section 9.1.1.

More recently, Gertler et al. (1998) conducted a tunnel study in the US, but they could not determine emission factors for light-duty vehicles due to similar tunnel inlet, vent and outlet concentrations. At the time of these measurements more than 99% of the cars ran on (unleaded) petrol. This finding supports the low emission factors for vehicles running on unleaded petrol.

In summary, the limited number of tunnel studies demonstrated that PCDD/PCDF emission factors for vehicles running on *unleaded* petrol correlate with laboratory measurements. In contrast, the maximum emission factor for *leaded* petrol vehicles derived from laboratory measurements seems to underestimate PCDD/PCDF emissions by a factor of 1.4 to 2.4, as was demonstrated by the two tunnel studies discussed in this section. It is, therefore, proposed that the maximum emission factor for leaded petrol vehicles be increased to a value of 280 pg I-TEQ/km.

9.1.3 Australian emission factors for petrol vehicles

Based on the available literature on PCDD/PCDF emissions, the following emission factors are proposed for light-duty vehicles running on petrol:

1. non-catalyst passenger cars running on leaded petrol: 10-280 pg I-TEQ/km
2. non-catalyst passenger cars running on unleaded petrol: 2-20 pg I-TEQ/km
3. catalyst passenger cars running on unleaded petrol: 1-3 pg I-TEQ/km.

9.2 Diesel vehicles (compression-ignition)

Similar to petrol vehicles, PCDD/PCDF emission data from diesel vehicles are scarce. Moreover, data on dioxins emissions from heavy-duty diesel are plagued by some controversy. According to Jones (1995), there is a growing body of evidence that suggest that mobile sources, in particular diesel powered vehicles, may be the predominant direct and indirect source of human dioxin exposure. Jones (1995) is of the opinion that mobile diesel dioxin emissions account for the largest dioxin source category in the US. Jones (1993) estimated that heavy-duty diesel vehicles were the largest source of PCDD/PCDF emissions when road traffic and waste incinerators are considered, i.e. they accounted for 40% of total emissions in 1990 and 54% in 2000.

Other studies also indicate that diesel emissions might be significant. For example, Miyabara et al. (1999) investigated PCCD/PCCF levels in suspended particulate matter (only) obtained from a highway tunnel. The total amount of PCDD/PCDF was found to be a factor 30 and 122 higher compared to levels in LDV diesel and petrol particulates. The authors suggest that this may be due to emissions from heavy-duty engines. However, it was also noted that the congener pattern suggests that non-volatile congeners (hepta- and octa-PCDD/PCDF) from petrol cars had accumulated in the particulates in the electrostatic precipitators, so these findings may be flawed. An Australian study by Clunies-Ross et al. (1996) seems to support the possibility for very high dioxins emission factors from diesel engines.

The reason for the formation of PCDD/PCDF in a diesel engine and the origin of the chlorine are not yet clear. Typically, the Cl-content in diesel fuel is in the order of 1 ppm or lower. PCDD/PCDF have been found in motor oil from diesel engines, indicating that they are actually formed during combustion. The higher combustion temperature of a hydrogen-poorer fuel may favour the formation of PCDD/PCDF in a diesel engine, even from trace amounts of chlorine.

In contrast, some studies did not detect PCDD/PCDF in diesel emissions (Hagenmaier, 1994), but in some cases this was attributed to analytical problems (e.g. Marklund et al., 1990). Other studies reported low emission factors for diesel vehicles (Hagenmaier et al., 1990), but again some studies encountered problems with the measurement methodology (CE-CERT, 1998). It should be noted that heavy-duty diesel engines also tend to have higher rates of engine lubricating oil combustion than light-duty engines, so this may be a contributing factor to higher PCDD/PCDF emission rates in these engines.

Section 9.2.1 discusses laboratory and on-road studies that investigated PCDD/PCDF emissions from diesel vehicles. Subsequently, the rationale presented in Section 8 is used to develop Australian emission factors for diesel vehicles. Section 9.2.2 then compares these emission factors to PCDD/PCDF emission factors derived from tunnel studies. Section 9.2.3 finally presents the Australian emission factors for diesel vehicles.

9.2.1 Laboratory and on-road studies

It was mentioned in Section 9.1.1 that the CARB data might be considered suspect because of the use of a low-resolution mass spectrometer, as well as other analytical issues (Jones, 1993). These data were, therefore, discarded for both petrol vehicles and diesel light-duty vehicles. However, CARB did state that the results of a single sample from the heavy-duty diesel truck could be used, because congeners from most of the homologue groups were present at levels that could be detected by the analytical method. There were also no identified interferences in this sample (US EPA, 2000). Therefore, these data are taken into account. The emission factors presented by CARB for trucks range from 1328-2603 pg I-TEQ/km and are quite large compared to those given in other (mainly European) publications.

In addition to petrol vehicles, Marklund et al. (1990) also analysed PCDD/PCDF emissions from a diesel truck, but none were detected. It was pointed out, however, that the test fuel was a non-commercial reference fuel and that analytical problems occurred with respect to the detection limit. Therefore, these data were discarded.

Hagenmaier et al. (1990) tested one light-duty diesel vehicle engine over a steady-state test cycle and reported an emission factor of 9 pg I-TEQ/km. However, when congener-specific results (excluding OCDD/PCDF) are converted into I-TEQ values, PAE derived lower emission factors, i.e. 3 pg I-TEQ/km. It is not clear which values are best to use.

Bröker et al. (1990, as cited in Geueke et al., 1999) conducted PCDD/PCDF emission measurements on one diesel passenger car using the ECE test cycle. Only total PCDD/PCDF emission factors were reported, which could not be converted. However, as a rule of thumb, I-TEQ values are about 50 times smaller than PCDD/PCDF concentration values. Using this rule, emission factors are estimated to be 50-70 pg I-TEQ/km.

A German study (Schwind et al., 1991 and Hutzinger et al., 1992 as cited in US EPA, 2000) conducted several non-steady state engine tests on diesel car engines and diesel

truck engines. The emission factors derived from this study ranged from 1-16 pg I-TEQ/km (diesel car) to 25-29 pg I-TEQ/km (truck).

Hagenmaier (1994) carried out one laboratory measurement on a diesel bus and was unable to detect PCDD/PCDF (detection limit of 1 pg/L for individual congeners). Hagenmaier argues that this is a strong indication that the main source of halogens for dioxin formation observed previously were scavengers used in leaded petrol, which entered the diesel fuel when the same transport tanks were used for both petrol and diesel transport. However, it is difficult to see how such a small amount of residual petrol could have any significant effect.

Bühler & Greiner (1996, as cited in Gullet & Ryan, 1997) presented an emission factor for a passenger vehicle of 6 pg I-TEQ/km and for trucks of 28 pg I-TEQ/km.

In Australia, Clunies-Ross et al. (1996) tested the effect of different diesel fuels (stock diesel fuel and 'doped' diesel fuel with added copper) on a single-cylinder diesel engine and found very high dioxins emission factors per litre of fuel burned. The test conditions do not easily translate to diesel vehicles on the road, so these data cannot be used in the development of emission factors.

Gullet & Ryan (1997) used on-road sampling to determine PCDD/PCDF emission factors for one fully loaded diesel truck (20.4 tonne) in two driving conditions: city driving and freeway driving. The average emission factor for city driving was a factor 3 higher than for freeway driving.

City driving showed large variability in the emission factors, a difference of a factor of 32 between two tests, but with the same truck and using the same route. This is in contrast with freeway driving, which was more consistent. The emission factors presented by Gullet & Ryan (1997) for diesel trucks range from 15 pg I-TEQ/km (freeway driving) to 50 pg I-TEQ/km (urban driving).

CE-CERT (1998) conducted dioxin measurements on a diesel engine and found that blank levels were a significant part of the emission sample (25-50%). Many of the PCDD/PCDFs with I-TEQ factors were not detected, including the congeners with the highest potency factors (2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF). I-TEQ emission factors were determined by using the detection limit as an estimate of the upper limit for the concentration of these compounds. Despite this, the results are significantly lower compared to other international studies. When the fuel-based emission factors are converted to distance-based emission factors using Australian fuel consumption data, CE-CERT's emission factors for trucks range from 3-6 pg I-TEQ/km depending on the fuel.

These values are quite low. However, in contrast to other studies where exhaust gases are collected directly, the CE-CERT study used a dilution tunnel where exhaust is cooled with filtered ambient air. Investigation of particulate matter taken from the tunnel walls revealed that PCDD/PCDF concentrations were significantly higher than in the dilution samples. This indicates that there may have been PCDD/PCDF losses to the particulates adhering to the tunnel wall. In addition, the engine used during the tests was brand new and the system was in peak operating condition. Furthermore, the engine oil was changed after each week of testing. It seems likely that emissions are underestimated in this study.

Miyabara et al. (1999) investigated PCCD/F levels in both petrol and diesel car exhaust particles and found that I-TEQ levels in diesel exhaust scrapings were 2.5 times higher. These workers reported an emission factor of 10.6 pg I-TEQ g^{-1} particulates. This translates to a dioxins emission factor of 4.2 pg I-TEQ/km, when we assume a PM_{10} emission rate of 400 mg/km for light-duty diesel vehicles. However, the PCDD/PCDF emission factors may be seriously underestimated, as gaseous PCDD/PCDFs were not included in the measurements. Moreover, expressing PCDD/PCDF emission factors as g PCDD/PCDF g^{-1} particulates may be risky. Wevers et al. (1992) showed that measured PM and dioxin concentrations are not strongly correlated and that they are dependent on the actual sampling system used. Therefore, these data are discarded for this study.

Geueke et al. (1999) recently measured (hot-stabilised) dioxins emissions from one modern HDV diesel engine using a 'real-world' driving cycle identical to the transient ETC cycle and found that exhaust PCDD/PCDF concentrations were almost below or close to the overall background concentration level. A worst-case emission factor was reported: 104 pg I-TEQ/km.

Table 4 presents an overview of the selection criteria as described in the rationale of Section 8. In this table each study is assessed against the selection criteria. The last column shows whether the emission factors presented in the study are likely to overestimate (indicated with ↓), underestimate (indicated with ↑), are uncertain or are expected to remain the same (indicated with ≈) as a result of test conditions or uncertainties in reported values.

Table 4 - Rationale for diesel vehicles

Reference Report / Paper	Number of Vehicles Tested	Sampling Location Tailpipe	Representative Driving Conditions	Both Particulate & Gaseous	Loss Correction	Similar Emission Standards	Cold-start Included	Flaws in Measurements	Results in I-TEQ	Complete Congener Profile	Used Vehicles/ Engines	EF
Jones, 1993 & US EPA, 2000	1-1	NR	Steady-State	NR	NR	Yes	NR	Yes	No	NR	NR	Discarded for LDV
Marklund et al., 1990	1-2	Yes	Transient	NR	Yes	Yes	Yes	No	Unknown	No	Yes	↑
Hagenmaier et al., 1990	1	No	Steady-State	Yes	Yes	Yes	NR	No	Unknown	No	NR	≈
Bröker et al., 1990	1	NR	Transient	NR	NR	Yes	NR	NR	No	No	NR	Uncertain
Schwind et al., 1991 Hutzinger et al., 1992	1-1	NR	NR	NR	NR	Yes	NR	NR	Yes	NR	NR	≈
Bühler & Greiner, 1996	NR	NR	NR	NR	NR	Yes	NR	NR	Yes	NR	NR	Uncertain
Clunies-Ross et al., 1996	1	No	Steady-State	Yes	Yes	Yes	NR	NR	Yes	NR	NR	Discarded
Gullet & Ryan, 1997	1	Yes	On-Road	Yes	Yes	Yes	NR	NR	Yes	Yes	Yes	≈
CE-CERT, 1998	1	Dilution Tunnel	Transient	Yes	Yes	Yes	Yes	Possible	Yes	NR	No	↑
Miyabara et al., 1999	NR	Yes	NR	No	NR	Yes	NR	No	Yes	NR	NR	Discarded
Geueke et al., 1999	1	No	Transient	Yes	NR	Yes	No	NR	Yes	NR	NR	↓

NR = Not Reported

Due to the uncertainties associated with PCDD/PCDF emission factors, an emission factor range rather than a point estimate seems most appropriate. Combining the review with information presented in Table 2, the following PCDD/PCDF emission factors are proposed:

1. light-duty vehicles running on diesel (passenger cars, LCVs): 6-50 pg I-TEQ/km
2. heavy-duty vehicles running on diesel (trucks): 15-104 pg I-TEQ/km
3. buses running on diesel: 12-85 pg I-TEQ/km.

The emission factor range for buses is equivalent to the range for diesel trucks (15-104 pg I-TEQ/km), but has been corrected for a different fuel consumption rate using data from ABS (1998). It is noted that a much higher average emission factor of 1965 pg I-TEQ/km for diesel trucks was reported in one laboratory study.

9.2.2 Tunnel studies

Oehme et al. (1991) conducted a tunnel study in Norway and they found diesel HDVs to have PCDD/PCDF emission factors to be a factor 18-19 higher than LDV emission factors. When Australian fuel consumption data are used, these workers reported a very high average emission factor of 6429 pg I-TEQ/km for in-use diesel trucks. Oehme et al. (1991) used an extrapolation methodology by assuming a linear relationship between the diesel HDV percentage and the average emission factor. HDV percentages in the tunnel varied between 4 and 19%, and although this methodology is commonly applied in tunnel studies, extrapolation to 100% may introduce errors in the HDV emission factor.

In contrast, more recently, Gertler et al. (1998) conducted a tunnel study in the US and a much lower emission factor of 280 pg I-TEQ/km was reported for in-use diesel heavy-duty vehicles. The particulate emission rate for heavy-duty vehicles measured in the study was about 70% lower than the particulate emission rate used by EPA (US EPA, 2000). As a consequence, the study may underestimate PCDD/PCDF emissions under different driving conditions. When the emission factor is corrected for PM emission rates, an emission factor of 650 pg I-TEQ/km is calculated.

Another tunnel study by Wevers, De Fré & Rymen (1992) also showed a low average fleet emission factor of 65 pg I-TEQ/km, with PCDD/PCDF emissions coming primarily from leaded petrol vehicles. A low emission factor of 4 pg I-TEQ/km was reported for diesel passenger cars and no emission factor was reported for diesel trucks.

In summary, one tunnel study demonstrated that PCDD/PCDF emission factors for light-duty diesel vehicles running on diesel correlate with the range measured under laboratory conditions. In contrast, the maximum emission factor for heavy-duty diesel vehicles derived from laboratory measurements may underestimate PCDD/PCDF emissions by a factor of up to 62 according to one tunnel study. A more recent tunnel study reported an emission factor that was a factor 2.7 higher than the maximum emission factor proposed in Section 9.2.1.

The large variability in dioxins emissions from trucks was also observed during on-road measurements (Gullet & Ryan, 1997). Thus, this large range in emission factors derived from tunnel study data might reflect differences in driving conditions, as well as diesel technology and vehicle age. It is proposed that the maximum emission factor for diesel trucks be increased to a value of 650 pg I-TEQ/km. It is noted that a much higher average emission factor of 6429 pg I-TEQ/km for diesel trucks was reported in one tunnel study.

9.2.3 Australian emission factors for diesel vehicles

Based on the available literature on PCDD/PCDF emissions, the following emission factors are proposed for diesel vehicles:

1. light-duty vehicles running on diesel (passenger cars, LCVs): 6-50 pg I-TEQ/km
2. heavy-duty vehicles running on diesel (trucks): 15-650 pg I-TEQ/km
3. buses running on diesel: 12-530 pg I-TEQ/km.

However, it is noted that two studies reported much higher emission factor for diesel trucks. The large range of emission factors for heavy-duty vehicles running on diesel reflects the current controversy on the significance of their emissions.

9.3 Other vehicle and fuel types

Not all vehicle types and fuel types present in the Australian on-road fleet are included in international literature on PCDD/PCDF emissions. Therefore, light-commercial vehicles (LCVs) or light-goods vehicles (LGVs), and motorcycles are assumed to have emission factors that are equivalent to emission factors for passenger cars using the same fuels (leaded petrol, unleaded petrol or diesel), but corrected for differences in fuel economy.

In the absence of any data, fuel types other than petrol and diesel such as liquefied petroleum gas (LPG) and compressed natural gas (CNG) are assumed to have emission factors similar to passenger cars running on unleaded petrol, although future test data may show this not to be the case. This may be regarded as a conservative approach as the very simple chemical structure of LPG and CNG result in generally low levels of air toxic emissions, even though CO and HC levels may be comparable to petrol fuelled engines. On the other hand, engine oils, similar to those in petrol engines, are used in engines running on gaseous fuels and many other complicating factors may be of importance (e.g. level of maintenance). It is noted that the overall impact of these vehicle types on total dioxins is limited. This is because LPG/CNG vehicles account for only a small part of total VKT (7%).

Heavy-duty vehicles (trucks and buses) running on fuels other than diesel are assumed to have emission factors that are equivalent to emission factors for passenger cars, using the same fuels (leaded petrol, unleaded petrol or LPG/CNG), but corrected for fuel economy.

10. Australian dioxins emission factors (summary)

Based on the available literature on PCDD/PCDF emissions, the following emission factors are proposed for the different vehicle classes:

1. non-catalyst passenger cars, light-commercial vehicles and motorcycles running on leaded petrol: 10-280 pg I-TEQ/km
2. non-catalyst passenger cars, light-commercial vehicles and motorcycles running on unleaded petrol: 2-20 pg I-TEQ/km
3. catalyst passenger cars, light-commercial vehicles and motorcycles running on unleaded petrol 1-3 pg I-TEQ/km
4. light-duty vehicles running on diesel (passenger cars, LCVs): 6-50 pg I-TEQ/km
5. heavy-duty vehicles running on diesel (trucks): 15-650 pg I-TEQ/km
6. buses running on diesel: 12-530 pg I-TEQ/km.

11. Australian vehicle activity data

In order to estimate the total dioxins emission load from road traffic, vehicle activity data are required. Vehicle activity data reflects vehicle use and can be expressed as total vehicle kilometres travelled (VKTs) or as total fuel consumed.

11.1 Data sources

Different independent data sources were used to obtain an estimate of Australian vehicle activity data. The ABS publish data on average annual VKTs and fuel consumption broken down by vehicle type (passenger vehicles, light-commercial vehicles, rigid trucks, articulated trucks, non-freight-carrying trucks, buses and motor cycles) and fuel type (leaded petrol - LP, unleaded petrol - ULP, diesel and others including LPG, CNG and dual fuel). The data used in this study are obtained from Survey of Motor Vehicle Use (SMVU) for the period 1 August 1997 to 31 July 18. These statistics are the first detailed results produced from an improved sampling methodology. In this methodology, a sample of approximately 20,000 vehicles is selected to report on vehicle use by using questionnaires.

The DITR (Resources Division) maintains a database pertaining to production, refining, exports, imports, stocks and sales of petroleum products. These data are gathered monthly from oil companies and collated to produce the publication Australian Petroleum Statistics. The data used in this study are obtained from this database for the period 1 August 1997 to 31 July 1998.

Finally, the National Environment Protection Council (NEPC) has recently carried out a series of projects prior to developing a Diesel Emissions Environment Protection Measure (NEPM). Part of the Diesel NEPM preparatory work was “Project 1 - Diesel fleet characteristics” (NEPC, 1999), which provides a good overview of activity data for

diesel-fuelled vehicles. The data reflects adjusted ABS data but 1995 was used as a base year. Therefore, this data source is not used for this project.

11.2 Australian VKT data

Table 5 presents information for 1997-1998 on total VKT, broken down by vehicle type and fuel type (ABS, 1998).

Table 5 - Total travel in Australia for August 1997 to July 1998

Type of Vehicle \ Type of Fuel	LP	ULP	Diesel	LPG/CNG/DF	TOTAL*
Passenger vehicles	20,455	101,274	3,833	8,698	134,261
ADR27 (non-catalyst PCs)	*20,455*	*16,064*	-	*2,609*	-
ADR37 (catalyst PCs)	*0*	*85,210*	-	*6,089*	-
Motorcycles	363	987	-	-	1,350
Light commercials	4,685	10,577	6,791	2,905	24,958
Rigid trucks	190	57	5,685	82	6,015
Articulated trucks	1	np	4,914	np	4,921
Non-freight carrying trucks	19	np	91	np	175
Buses	21	107	1,470	40	1,639
Total vehicles	25,734	113,050	22,784	11,749	173,317

LP = Leaded Petrol, ULP = Unleaded Petrol, LPG = Liquefied Petroleum Gas, CNG = Compressed Natural Gas, DF = Dual-Fuel, np = not provided, * million VKT

A breakdown of VKT data into ADR27 (non-catalyst) and ADR37 (catalyst) passenger vehicles was not directly available. Therefore, ABS data for 1996 were used to estimate the percentage of VKT that are driven by ADR27 and ADR37 cars respectively for the year 1998. As a result, ADR37 vehicles accounted for approximately 70% of total VKTs driven by passenger cars and ADR27 vehicles accounted for the remaining 30%. This information has been used to estimate fuel consumption for ADR27 and ADR37 vehicles, which is included in Table 4 (*Italics*).

11.3 Australian fuel consumption data

Table 6 presents information for 1997-1998 on total fuel consumption, broken down by vehicle type and fuel type (ABS, 1998). Total road transport fuel consumption for 1998 was estimated at 23,909 million litres. Passenger vehicles accounted for 66% of this consumption, while trucks consumed 18% and light-commercial vehicles consumed 14%. Eighty percent of all automotive petrol sold in Australia is unleaded. Total fuel consumption has grown at a slower rate than VKTs, due mainly to improved levels of fuel efficiency since 1979. There has been ~6% improvement in fuel efficiency over the 1979-1998 period (Austroads, 2000).

Table 6 - Fuel consumption in Australia for August 1997 to July 1998

Type of Vehicle \ Type of Fuel	LP	ULP	Diesel	LPG/CNG/DF	TOTAL*
Passenger vehicles	2,463	11,427	457	1,478	15,825
ADR27 (non-catalyst PCs)	*2,463*	*1,924*	-	*443*	-
ADR37 (catalyst PCs)	*0*	*9,503*	-	*1,035*	-
Motorcycles	23	56	-	-	79
Light commercials	642	1,348	814	479	3,283
Rigid trucks	52	9	1,606	25	1,693
Articulated trucks	0	3	2,508	0	2,511
Non-freight carrying trucks	5	10	28	9	51
Buses	5	18	427	17	467
Total vehicles	3,191	12,871	5,840	2,007	**23,909**

LP = Leaded Petrol, ULP = Unleaded Petrol, LPG = Liquefied Petroleum Gas, CNG = Compressed Natural Gas, DF = Dual-Fuel, * million litres

Table 7 presents total fuel consumption figures as provided by the DITR and compares them to the ABS data in Table 6.

Table 7 - Fuel consumption in Australia for August 1997 to July 1998

Type of Vehicle \ Type of Fuel	LP	ULP	Diesel	LPG/CNG/DF	TOTAL*
DITR	5,454	12,500	7,016	1,601	**26,571**
ABS	3,191	12,871	5,840	2,007	**23,909**

LP = Leaded Petrol, ULP = Unleaded Petrol, LPG = Liquefied Petroleum Gas, CNG = Compressed Natural Gas, DF = Dual-Fuel, * million litres

The leaded petrol, unleaded petrol and diesel figures from DITR include retail and wholesale fuel sales. Retail sales are basically "at the pump" sales and wholesale includes all deliveries to governments (e.g. car fleets), farms (tractors, pumps, agricultural machinery etc.), other business users, but excludes retail sales. The DITR data, therefore, includes off-road fuel sales, which could not be separated from on-road fuel sales. Nevertheless, these data are still useful as a 'worst-case' and independent source of information.

12. Dioxins emission levels from Australian motor vehicles

The previous sections have laid the foundation for the calculation of total dioxins emissions from road traffic in Australia. Firstly, a range of Australian PCDD/PCDF emission factors (minimum to maximum) was developed for each vehicle class using Australian fuel economy data. Subsequently, two 'types' of vehicle activity data, i.e. total kilometres travelled and total fuel consumption, were estimated for each vehicle class.

In this Section annual PCDD/PCDF emissions from Australian motor vehicles are estimated using national vehicle activity data and PCDD/PCDF emission factors derived from international research studies. The results of combining the minimum and maximum PCDD/PCDF emissions factors with ABS VKT data are depicted in Table 8 and 9.

Table 8 - Minimum total dioxins emissions in Australia expressed as g I-TEQ per year

Type of Vehicle \ Type of Fuel	LP	ULP	Diesel	LPG/CNG/DF	TOTAL
Passenger vehicles	0.20	0.12	0.02	0.01	0.36
ADR27 (non-catalyst PCs)	*0.20*	*0.03*	-	*0.01*	*0.24*
ADR37 (catalyst PCs)	-	*0.09*	-	*0.01*	*0.09*
Motorcycles	0.00	0.00	-	-	0.00
Light commercials	0.05	0.02	0.04	0.01	0.13
Rigid trucks	0.00	0.00	0.09	0.00	0.09
Articulated trucks	0.00	-	0.07	-	0.07
Non-freight carrying trucks	0.00	-	0.00	-	0.00
Buses	0.00	0.00	0.02	0.00	0.02
Total vehicles	0.27	0.14	0.22	0.02	**0.65**

LP = Leaded Petrol, ULP = Unleaded Petrol, LPG = Liquefied Petroleum Gas, CNG = Compressed Natural Gas, DF = Dual-Fuel

Table 9 - Maximum total dioxins emissions in Australia expressed as g I-TEQ per year

Type of Vehicle \ Type of Fuel	LP	ULP	Diesel	LPG/CNG/DF	TOTAL
Passenger vehicles	5.73	0.58	0.19	0.07	6.57
ADR27 (non-catalyst PCs)	*5.73*	*0.32*	-	*0.05*	*6.10*
ADR37 (catalyst PCs)	-	*0.26*	-	*0.02*	*0.27*
Motorcycles	0.05	0.01	-	-	0.06
Light commercials	1.50	0.24	0.34	0.07	2.15
Rigid trucks	0.12	0.00	3.70	0.00	3.82
Articulated trucks	0.00	-	3.19	-	3.20
Non-freight carrying trucks	0.01	-	0.06	-	0.07
Buses	0.01	0.00	0.78	0.00	0.80
Total vehicles	7.42	0.84	8.07	0.14	**16.47**

LP = Leaded Petrol, ULP = Unleaded Petrol, LPG = Liquefied Petroleum Gas, CNG = Compressed Natural Gas, DF = Dual-Fuel

Total dioxins emissions from Australian road traffic are estimated to lie between 0.7 and 16.5 g I-TEQ per year. Vehicles running on leaded petrol account for about 40 to 45% of total dioxins emissions. The phase-out of leaded petrol (completed in January 2002) is, therefore, expected to have substantially reduced total dioxins emissions. Diesel-fuelled vehicles emit between 35 and 50% of total dioxins emissions, which mainly come from diesel trucks. Dioxins emissions from vehicles running on gaseous fuels have a negligible contribution to total PCDD/PCDF emissions from road traffic. Despite the fact that vehicles running on unleaded petrol account for 65% of total kilometres travelled, they account for 5 to 20% of total dioxins emissions. When vehicle activity data are based on fuel consumption data from ABS, similar results are obtained. Total dioxins emissions from Australian road traffic are estimated to lie between 0.6 and 17.3 g I-TEQ per year. For specific data on each vehicle class refer to tables B.1 and B.2 (Appendix B).

For independent validation of this ABS dataset, DITR fuel consumption data were used to estimate total dioxins emissions from Australian road traffic. A higher estimate of 0.7-24.3 g I-TEQ per year was obtained, but this estimate includes off-road traffic and non-road traffic emissions. For specific data on each vehicle class refer to Table B.3 and B.4 (Appendix B).

Using total dioxins emission figures for Australia from a previous study (Environment Australia, 1998) as an estimate for 1998 total emission levels to air, i.e. 150-2300 g dioxins per annum, road traffic accounts for 0.03 to 16.2% of total dioxins emission levels. These results are in line with emission inventories around the world that have calculated a share ranging from 0.2 to 12% of total annual dioxins emissions.

13. Conclusion

This study has developed Australian dioxins emission factors for road traffic based on international literature. When these emission factors are combined with vehicle activity data from the ABS, total dioxins emissions from Australian road traffic are estimated to lie between 0.6 and 17.3 g I-TEQ per year. When these emission factors are combined with independent vehicle activity data from the DITR, a higher estimate of 0.7-24.3 g I-TEQ per year is obtained. However, it should be noted that this estimate also includes off-road traffic and non-road traffic emissions.

The emission factors developed in this report, and, therefore, the estimation of total dioxins emissions from Australian road traffic, are quite uncertain. There are several reasons for this. Firstly, there is not a lot of measured data available internationally on dioxins emissions from road traffic. Relatively few tests on dioxins emissions from vehicles are available considering the variety and numbers of vehicles currently in operation and the range of operational, technical and environmental conditions in which they are operated. Secondly, PCDD/PCDF emissions generally show large variability in emission rates and dioxin profiles. Thirdly, published information on dioxins emission factors is contradictory and the absolute and relative magnitude of vehicle dioxin emissions remains under international debate. In particular there is uncertainty with respect to dioxins emissions from heavy-duty diesel vehicles. The only way to reduce this uncertainty would be to conduct more measurements.

It is noted that dioxins emissions from road traffic are possibly quite important with respect to exposure, due to the fact that vehicle emissions are ubiquitous and fairly uniform in densely populated urban areas. Moreover, emissions take place close to the recipient, which limits the effect of dilution of dioxins emissions.

14. Recommendations for future work

This study has revealed that there are only a limited number of overseas studies that specifically investigate dioxins emissions from road traffic. Moreover, these studies generally consider only a few vehicles. Dioxins emission levels are sensitive to many factors including driving conditions, quality of fuel and engine oil and ambient temperature. These factors led to the development of widely scattered emission factors for the Australian situation. The data did not allow for the development of average emission factors. In particular, there is uncertainty with respect to dioxins emissions from heavy-duty diesel vehicles.

In order to reduce this uncertainty, it might be useful to obtain some Australian data on dioxins emissions from road traffic. As discussed in Section 8, there are different methods to estimate dioxins emissions, namely laboratory engine test bench studies, laboratory dynamometer studies, on-road studies and tunnel studies. Each type of study has its own strengths and weaknesses and these should be considered when they are used for the development of dioxins emission factors in Australia. It is not possible to conclude which type of study would be preferred for the development of Australian PCDD/PCDF emissions factors. However, in the selection process it is very important to consider the limitations of the different study types as discussed in this Section.

14.1 Laboratory measurements

An advantage of laboratory measurements is that they are conducted under controlled conditions. This enables detailed investigation of certain aspects that could influence emissions, for example, driving pattern, muffler adsorption, ambient temperature etc. However, a major disadvantage is the limited number of vehicles or engines that can be tested due to time and budget constraints. As a result, these few vehicles or engines can never truly represent the average emission from an entire vehicle fleet. Furthermore, the driving cycle employed during testing may not necessarily represent driving conditions that are encountered on the road. It is, therefore, important that emission testing is based on a driving pattern that represents ‘real-world’ driving conditions (i.e. an average Australian trip).

14.2 On-road measurements

On-road measurements have the advantage that real-world driving behaviour is replicated during the measurements. However, a major disadvantage is again the limited number of vehicles that can be tested due to time and budget constraints.

14.3 Tunnel studies

Traffic in tunnels gives rise to elevated concentration levels of pollutants, which can be several times higher than in urban streets with similar traffic. Many tunnel studies have been carried out worldwide in order to quantify real-world vehicle emissions or to investigate their composition and establish emission factors.

In comparison to laboratory and on-road studies, tunnel studies measure emissions from a large fleet sample of in-use vehicles, including badly maintained vehicles. This increases the data validity. Tunnel studies measure average fleet emissions, which reflect factors such as fleet composition, state of maintenance and driving behaviour. Relative contributions of light-duty vehicles and heavy-duty vehicles to the total emissions can also be determined using a regression method.

However, a major disadvantage of tunnel studies is that they represent only a limited range of operating conditions, typically smooth high speed driving, which might not translate to other driving conditions, for example urban driving on arterial roads with several intersections. Generally, the vehicles are operating in a hot-stabilised cruise mode with average speed around 40 to 110 km/h and some tunnels have significant grade. If a tunnel study was conducted, it seems appropriate to measure dioxins levels at different levels of congestion, for instance at free-flow conditions (say a traffic density of less than eight cars/km/lane) and at congested conditions (say a traffic density of more than 42 cars/km/lane).

Tunnel study results rely on indirect measurements (rather than tailpipe measurements), which may introduce unknown errors. Also, concerns have been raised that tunnel monitors are detecting resuspended particulates that have accumulated over time, leading to overestimates of emissions. Furthermore, vehicle fleet mix and age can be different in tunnels when compared to other (urban) areas and most tunnels have road grades that will impact on emission levels.

Another major problem, that probably applies to all one-way tunnels, is an air flow (piston flow) in the tunnel tube mainly caused by trucks, which changes the driving resistance of the vehicles and, as a result, the emission behaviour no longer corresponds to that of vehicle operation in free air. However, there are also compensating effects from tunnel walls (wall or blockage effects) and road grade.

Also, tunnel studies allow for a certain ‘aging’ of vehicle emissions before sampling, i.e. changing composition due to (rapid) chemical transformations. However, residence time of air in the tunnel is usually only a few minutes, so the impact of aging on emission composition is likely to be minimal.

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16. Appendices

16.1 Appendix A – dioxin profiles

Table A.1 – Congener profiles

(2,3,7,8) Congener Profiles *Petrol Light-Duty Vehicles [%]*		Leaded Non-Catalyst				Unleaded Non-Catalyst			Unleaded Catalyst		
		Marklund et al. 1990	Hagenmaier et al 1990	Schwind et al. 1991	Briz et al. 2000	Marklund et al. 1990	Hagenmaier et al 1990	Schwind et al. 1991	Marklund et al. 1990	Hagenmaier et al 1990	Schwind et al. 1991
PCDD CONGENER	2,3,7,8-TCDD	1%	1%	0%	1%	1%	0%	1%	1%	1%	1%
	1,2,3,7,8-PeCDD	4%	4%	1%	3%	1%	3%	1%	1%	1%	1%
	1,2,3,4,7,8-HxCDD	2%	2%	0%	2%	3%	2%	1%	3%	1%	1%
	1,2,3,6,7,8-HxCDD	2%	2%	1%	4%	3%	2%	4%	3%	1%	1%
	1,2,3,7,8,9-HxCDD	2%	2%	0%	3%	3%	2%	1%	3%	1%	1%
	1,2,3,4,6,7,8-HpCDD	5%	4%	6%	6%	10%	6%	9%	10%	6%	6%
	OCDD	9%	4%	19%	16%	12%	25%	39%	12%	63%	36%
PCDF CONGENER	2,3,7,8-TCDF	43%	13%	3%	2%	16%	6%	3%	16%	2%	2%
	1,2,3,7,8-PeCDF	2%	9%	3%	4%	2%	6%	2%	2%	1%	2%
	2,3,4,7,8-PeCDF	4%	4%	3%	4%	2%	3%	1%	2%	1%	1%
	1,2,3,4,7,8-HxCDF	1%	7%	5%	5%	2%	6%	3%	2%	2%	2%
	1,2,3,6,7,8-HxCDF	1%	7%	4%	3%	2%	3%	3%	2%	2%	2%
	1,2,3,7,8,9-HxCDF	1%	1%	1%	2%	2%	5%	2%	2%	0%	1%
	2,3,4,6,7,8-HxCDF	1%	2%	12%	5%	2%	8%	2%	2%	2%	4%
	1,2,3,4,6,7,8-HpCDF	5%	35%	27%	12%	10%	4%	12%	10%	6%	11%
	1,2,3,4,7,8,9-HpCDF	5%	1%	1%	4%	10%	2%	0%	10%	0%	1%
	OCDF	9%	2%	13%	22%	17%	17%	17%	17%	10%	8%
TOTAL		100%	100%	100%	100%	100%	100%	100%	100%	100%	100%

(2,3,7,8) Congener Profiles *Diesel Vehicles [%]*		LDV		HDV					
		Hagenmaier et al 1990	Schwind et al. 1991	Schwind et al. 1991	Lew 1993 & 1996	Gullett & Ryan 1997 [HWAY]	Gullett & Ryan 1997 [CITY]	Geueke et al. 1999	Gertler et al 1998
PCDD CONGENER	2,3,7,8-TCDD	1%	1%	1%	0%	6%	12%	0%	1%
	1,2,3,7,8-PeCDD	1%	1%	0%	0%	5%	12%	2%	0%
	1,2,3,4,7,8-HxCDD	1%	0%	1%	0%	3%	4%	1%	1%
	1,2,3,6,7,8-HxCDD	1%	1%	1%	0%	4%	5%	2%	1%
	1,2,3,7,8,9-HxCDD	1%	1%	1%	0%	4%	5%	2%	2%
	1,2,3,4,6,7,8-HpCDD	6%	9%	4%	16%	3%	2%	20%	14%
	OCDD	61%	29%	50%	46%	1%	1%	50%	65%
PCDF CONGENER	2,3,7,8-TCDF	3%	12%	3%	0%	10%	5%	4%	1%
	1,2,3,7,8-PeCDF	1%	6%	2%	1%	3%	1%	1%	1%
	2,3,4,7,8-PeCDF	1%	4%	1%	1%	19%	18%	2%	1%
	1,2,3,4,7,8-HxCDF	1%	4%	2%	1%	16%	12%	2%	2%
	1,2,3,6,7,8-HxCDF	1%	3%	3%	1%	10%	7%	2%	1%
	1,2,3,7,8,9-HxCDF	1%	0%	0%	2%	2%	3%	0%	1%
	2,3,4,6,7,8-HxCDF	1%	2%	2%	1%	10%	7%	2%	1%
	1,2,3,4,6,7,8-HpCDF	6%	11%	14%	10%	3%	2%	7%	4%
	1,2,3,4,7,8,9-HpCDF	1%	0%	1%	2%	2%	1%	1%	0%
	OCDF	12%	16%	15%	19%	1%	1%	1%	4%
TOTAL		100%	100%	100%	100%	100%	100%	100%	100%

(2,3,7,8) Congener Profiles *Fleet [%]*		Tunnel Studies	
		Odhne et al. 1991	Wevers et al. 1992
PCDD CONGENER	2,3,7,8-TCDD	0%	0%
	1,2,3,7,8-PeCDD	2%	1%
	1,2,3,4,7,8-HxCDD	1%	1%
	1,2,3,6,7,8-HxCDD	3%	1%
	1,2,3,7,8,9-HxCDD	2%	1%
	1,2,3,4,6,7,8-HpCDD	14%	11%
	OCDD	1%	53%
PCDF CONGENER	2,3,7,8-TCDF	4%	0%
	1,2,3,7,8-PeCDF	8%	3%
	2,3,4,7,8-PeCDF	6%	1%
	1,2,3,4,7,8-HxCDF	8%	2%
	1,2,3,6,7,8-HxCDF	6%	2%
	1,2,3,7,8,9-HxCDF	0%	3%
	2,3,4,6,7,8-HxCDF	7%	0%
	1,2,3,4,6,7,8-HpCDF	17%	12%
	1,2,3,4,7,8,9-HpCDF	2%	2%
	OCDF	16%	6%
TOTAL		100%	100%

Table A.2 – Homologue profiles

Homologue Profiles *Petrol Light-Duty Vehicles [%]*		Leaded Non-Catalyst			Unleaded Non-Catalyst			Unleaded Catalyst		
		Marklund et al. 1990	Hagenmaier et al 1990	Schwind et al. 1991	Marklund et al. 1990	Hagenmaier et al 1990	Schwind et al. 1991	Marklund et al. 1990	Hagenmaier et al 1990	Schwind et al. 1991
HOMOLOGUE TOTAL	TCDD	21%	5%	5%	4%	11%	8%	4%	6%	5%
	PeCDD	1%	4%	2%	1%	12%	16%	1%	5%	5%
	HxCDD	2%	2%	5%	13%	8%	10%	13%	5%	6%
	HpCDD	0%	1%	5%	3%	2%	8%	3%	8%	5%
	OCDD	0%	1%	8%	2%	4%	17%	2%	35%	30%
	TCDF	61%	59%	22%	54%	14%	14%	54%	11%	16%
	PeCDF	10%	13%	16%	2%	23%	10%	2%	11%	13%
	HxCDF	2%	7%	16%	13%	10%	3%	13%	7%	8%
	HpCDF	1%	7%	15%	6%	12%	5%	6%	6%	7%
	OCDF	0%	0%	6%	2%	3%	7%	2%	6%	4%
TOTAL		100%	100%	100%	100%	100%	100%	100%	100%	100%

Homologue Profiles *Diesel Vehicles [%]*		LDV		HDV			
		Hagenmaier et al 1990	Schwind et al. 1991	Schwind et al. 1991	Lew 1993 & 1996	Geueke et al. 1999	Gertler et al. 1998
HOMOLOGUE TOTAL	TCDD	4%	6%	5%	0%	6%	1%
	PeCDD	2%	3%	1%	0%	11%	1%
	HxCDD	3%	2%	3%	4%	15%	11%
	HpCDD	10%	5%	5%	18%	15%	20%
	OCDD	48%	8%	31%	30%	19%	42%
	TCDF	8%	44%	18%	2%	12%	9%
	PeCDF	4%	17%	5%	4%	12%	5%
	HxCDF	3%	7%	12%	15%	6%	4%
	HpCDF	9%	3%	12%	13%	4%	4%
	OCDF	10%	4%	9%	12%	0%	3%
TOTAL		100%	100%	100%	100%	100%	100%

(2,3,7,8) Congener Profiles *Fleet [%]*		Tunnel Studies
		Oehme et al. 1991
HOMOLOGUE TOTAL	TCDD	1%
	PeCDD	5%
	HxCDD	3%
	HpCDD	3%
	OCDD	0%
	TCDF	34%
	PeCDF	26%
	HxCDF	17%
	HpCDF	7%
	OCDF	4%
TOTAL		100%

16.2 Appendix B – total dioxins emissions

Table B.1 – Minimum total dioxins emissions based on ABS Fuel Consumption Data [g I-TEQ/year]

Type of Vehicle \ Type of Fuel	LP	ULP	Diesel	LPG/CNG/DF	TOTAL
Passenger vehicles	0.13	0.13	0.02	0.02	0.29
ADR27 (non-catalyst PCs)	*0.13*	*0.03*	-	*0.01*	*0.17*
ADR37 (Catalyst PCs)	-	*0.10*	-	*0.01*	*0.11*
Motorcycles	0.00	0.00	-	-	0.00
Light commercials	0.03	0.02	0.04	0.01	0.10
Rigid trucks	0.00	0.00	0.06	0.00	0.06
Articulated trucks	0.00	-	0.09	-	0.09
Non-freight carrying trucks	0.00	-	0.00	-	0.00
Buses	0.00	0.00	0.02	0.00	0.02
Total vehicles	0.17	0.15	0.21	0.03	**0.55**

Table B.2 – Maximum total dioxins emissions based on ABS Fuel Consumption Data [g I-TEQ/year]

Type of Vehicle \ Type of Fuel	LP	ULP	Diesel	LPG/CNG/DF	TOTAL
Passenger vehicles	5.83	0.59	0.19	0.11	6.72
ADR27 (non-catalyst PCs)	*5.83*	*0.34*	-	*0.08*	*6.25*
ADR37 (catalyst PCs)	-	*0.25*	-	*0.03*	*0.27*
Motorcycles	0.05	0.01	-	-	0.06
Light commercials	1.52	0.24	0.34	0.08	2.18
Rigid trucks	0.12	0.00	2.92	0.00	3.05
Articulated trucks	0.00	-	4.56	-	4.56
Non-freight carrying trucks	0.01	-	0.05	-	0.06
Buses	0.01	0.00	0.78	0.00	0.80
Total vehicles	7.55	0.84	8.65	0.20	**17.25**

Table B.3 – Minimum total dioxins emissions based on DITR Fuel Consumption Data [g I-TEQ/year]

Type of Vehicle \ Type of Fuel	LP	ULP	Diesel	LPG/CNG/DF	TOTAL
Passenger vehicles	0.22	0.12	0.03	0.01	0.38
ADR27 (non-catalyst PCs)	*0.22*	*0.03*	-	*0.01*	*0.26*
ADR37 (catalyst PCs)	-	*0.09*	-	*0.01*	*0.10*
Motorcycles	0.00	0.00	-	-	0.00
Light commercials	0.06	0.02	0.05	0.01	0.13
Rigid trucks	0.00	0.00	0.07	0.00	0.08
Articulated trucks	0.00	-	0.11	-	0.11
Non-freight carrying trucks	0.00	-	0.00	-	0.00
Buses	0.00	0.00	0.02	0.00	0.02
Total vehicles	0.28	0.15	0.25	0.02	**0.70**

Table B.4 – Maximum total dioxins emissions based on DITR Fuel Consumption Data [g I-TEQ/year]

Type of Vehicle \ Type of Fuel	LP	ULP	Diesel	LPG/CNG/DF	TOTAL
Passenger vehicles	9.97	0.57	0.23	0.08	10.85
ADR27 (non-catalyst PCs)	*9.97*	*0.33*	-	*0.06*	*10.36*
ADR37 (catalyst PCs)	-	*0.24*	-	*0.02*	*0.26*
Motorcycles	0.09	0.01	-	-	0.10
Light commercials	2.60	0.23	0.41	0.07	3.31
Rigid trucks	0.21	0.00	3.51	0.00	3.73
Articulated trucks	0.00	-	5.48	-	5.48
Non-freight carrying trucks	0.02	-	0.06	-	0.08
Buses	0.02	0.00	0.93	0.00	0.96
Total vehicles	12.91	0.82	10.40	0.16	**24.28**