



INFRASTRUCTURE  
AUCKLAND FOR THE  
PUBLIC GOOD



*Emission Factors for Contaminants Released  
by Motor Vehicles in New Zealand*



MINISTRY of TRANSPORT  
TE MANATŪ WAKA





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Prepared for



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&



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**AUCKLAND** FOR THE  
PUBLIC GOOD

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# Abbreviations

Ag	Silver
Al	Aluminium
As	Arsenic
Au	Gold
B	Boron
Ba	Barium
Bi	Bismuth
Ca	Calcium
Cd	Cadmium
Ce	Cerium
Co	Cobalt
COPC	Contaminant of potential concern
Cr	Chromium
Cu	Copper
EC	European Commission
EU	European Union
Fe	Iron
g	gram
HC	Hydrocarbon
HDM	Highway Development Model
HDV	Heavy duty vehicles
Hg	Mercury
In	Indium
K	Potassium
kg	kilogram
km	kilometre
L	litre
La	Lanthanum
LCV	Light commercial vehicle
LDV	Light duty vehicles
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
MoT	Ministry of Transport (New Zealand)
Ni	Nickel
NZ-TER	New Zealand – Traffic Emission Rates
Pb	Lead
PAH	Polyaromatic hydrocarbons
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzofurans
Pd	Palladium
PGE	Platinum group elements
PIARC	The World Road Association
PM	Particulate matter
PM <sub>10</sub>	Particulate matter of less than 10 µm in diameter
PM <sub>2.5</sub>	Particulate matter of less than 2.5 µm in diameter
Pd	Palladium
Pt	Platinum
PULP	Premium unleaded petrol
Rh	Rhodium
Sn	Tin
Se	Selenium
SVOC	Semi-volatile organic compound
Ti	Titanium
USEPA	United States Environmental Protection Agency
VFECs	Vehicle fleet emissions control strategy; MoT programme
VFEM	Vehicle Fleet Emissions Model (New Zealand)

VOC	Volatile organic compound
W	Tungsten
Zn	Zinc
Zr	Zirconium

# 1. INTRODUCTION

## 1.1 Contaminant Emissions

Motor vehicles are an important source of contaminant emissions within urban areas. Four key pieces of information are required to provide information on the amount of those contaminants available to enter aquatic environments. They are:

1. The identification of a contaminant in a particular motor vehicle emission source.
2. The concentration of the contaminant in that emission source.
3. The load being released by the motor vehicle from that source.
4. The proportion of the load from a particular source that ends up on the road surface and is available for entry into the stormwater system.

Moncreiff et al. (2002) provided an overview of how and where motor vehicles generate contaminants. There have been, a wide range of tools, developed for calculating the amount of particular contaminants generated by urban areas and roads. Most assessments of contaminant loadings for roads or within urban areas utilise generic area loadings to obtain information on the contaminant loads generated by land uses within catchments.

In New Zealand, there have been few loading estimates made for specific catchment land-uses. As a result most of the data utilised for making assessments of contaminant loads in New Zealand urban catchments is international data (predominantly US data). Loading assessments have typically been obtained from field studies of runoff quality. Early urban loading assessments include those carried out by Novotny & Goodrich-Mahoney (1978). A range of more recent studies have, examined runoff and loadings from general urban areas, roads and highways (e.g., Wu et al. 2000).

## 1.2 Assessment Tools

There are a variety of modelling tools that can be used to predict the pollutant loads derived from urban impervious areas such as roads (Charbeneau & Barrett 1998, Heany et al. 1999). Zoppou (2001) provides a review of urban stormwater models. The wide variety of modelling tools reflects the understanding of stormwater system engineering and system design. The most well known models used include the Stormwater Management Model (SWMM) and Storage, Treatment, Overflow, Runoff Model (STORM). Table 1.1 provides a summary of some of the key urban runoff quality models. Stormwater pollutant loads can be measured using simple and complex models and both types of models are appropriate under different circumstances (refer Horner 1994). These models use default load information (based upon literature data) or user defined constituent concentrations to generate contaminant loads.

In New Zealand, emissions of key constituents from motor vehicles to air can be assessed using the Vehicle Fleet Emission Model. The user output from a run of this model is currently provided in the form of the user model NZ-TER (refer MoT 1998, MoT 2000, MonCrieff & Irving 2001).

The information presented in this report has two points of focus. Firstly, this report provides background information for the development on behalf of the Ministry of Transport (MoT) of the Vehicle Fleet Emissions Model for Water (VFEM-W). In addition, the report provides background information for professionals undertaking motor vehicle contaminant loading assessments associated with stormwater management or transport/infrastructure projects (e.g., for organisations such as Infrastructure Auckland).

**Table 1.1 - Listing of some urban water quality models.**

<b>Model</b>			<b>Authors</b>	<b>Year</b>
QUAL-2			Hydrologic Engineering Center	1975
SWMM	Storm Water Management Model		Huber et al.(Huber & Dickinson 1988)	1975
STORM	Storage, Treatment, Overflow and Runoff Model		Hydrologic Engineering Center	1977
HSPF	Hydrologic Simulation Program- Fortran		Johanason et al.	1980

Emissions loading factors can be used to obtain relative information on the total load of contaminants that are likely to be emitted within a given road transport corridor by the vehicle fleet within that corridor. These can be compared between roads and between different traffic volumes.

The emission loads calculated can, be used to estimate the amount of contaminant that may be available for transport to the stormwater system and then to a receiving environment. This report provides a very preliminary discussion of this aspect of contaminant emission transport.

### 1.3 Focus of this Emissions Overview

The current work being undertaken for the Ministry of Transport, focuses on the effects of road transport on aquatic ecosystems and by default is concerned with the contaminants and their loads generated by motor vehicles (Moncreiff et al. 2002). All of the stormwater quality models that are commonly in use deal with the overall loads produced by all activities within urban areas. This report focuses on three aspects of the information required by the VFEM-W. These aspects are those that provide the framework for the emissions hub within the model (refer Figure. 1.1). The cells for any given source within the hub contain three key pieces of information that allow emissions of contaminants to be calculated over time within a given section of roadway. These are:

- ❑ The concentration of contaminant present.
- ❑ The rate that the contaminant is released by an individual motor-vehicle.
- ❑ The rate at which the emission from a particular source is deposited to the road surface and is then available for stormwater transport.

A wide range of contaminants are emitted from motor vehicles (Gadd & Kennedy 2000; Kennedy & Gadd 2000; Moncreiff et al. 2002). Typically estimates of emissions are only required for those contaminants whose discharge to the environment is of environmental significance. The focus of this report is for those key sources known to contribute contaminants and those contaminants identified as being of potential environmental concern (COPC) (COPC as defined by Kennedy (2000) and Moncreiff et al. (2002)). Typically the COPC include the USEPA priority inorganic and organic pollutants in addition to a range of motor vehicle specific organic compounds. However where data is available on other significant contaminants in emissions from motor vehicles it is identified in this document.

The report presents information on the emissions from motor vehicles in seven sections following this introduction.

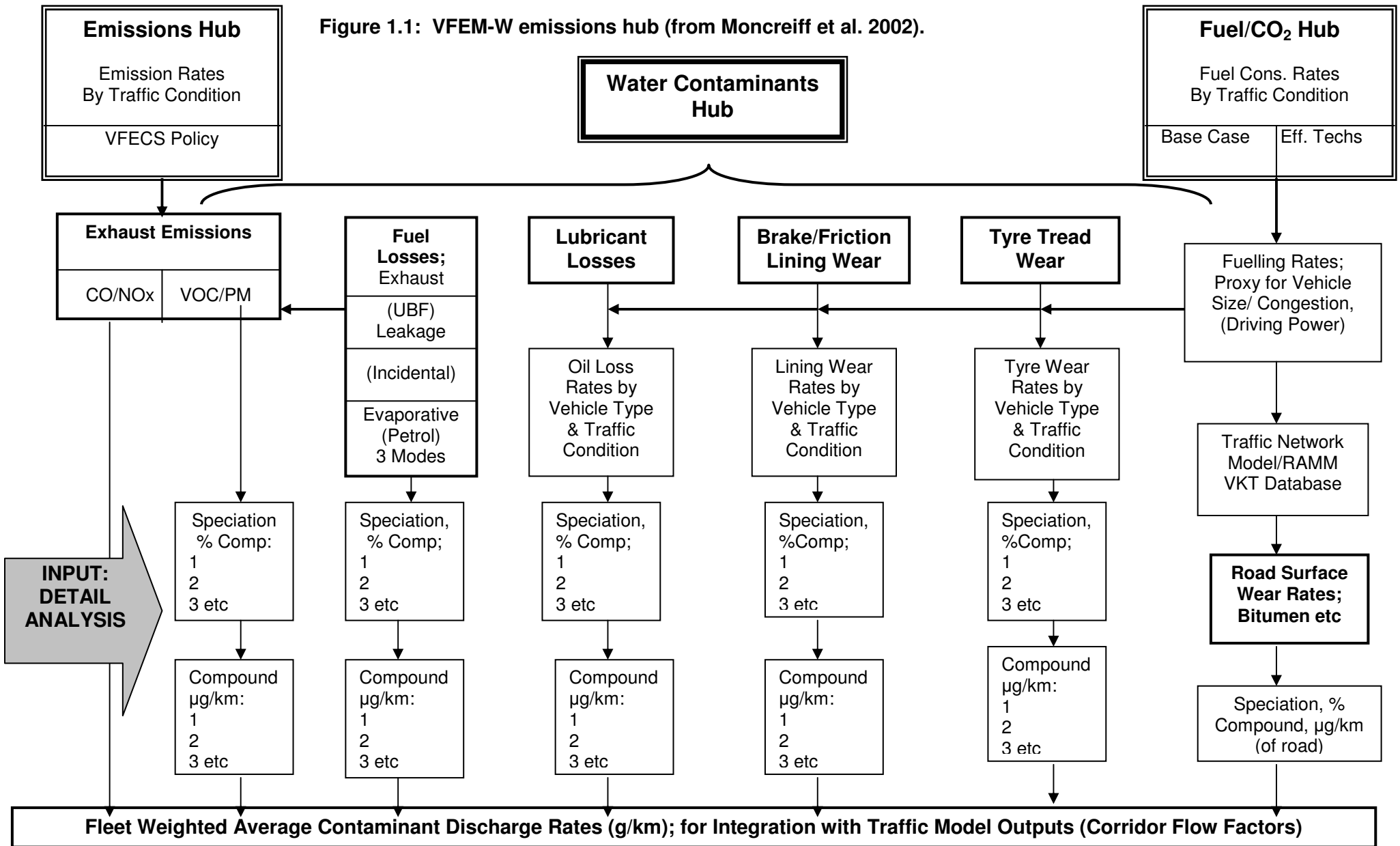
- ❑ Section 2 provides an overview of the vehicle fleet and how it is categorised and how VFEM-W handles vehicle types and some of the core factors that influence emissions.
- ❑ Section 3 provides information about emissions from brake systems.
- ❑ Section 4 presents information about emissions from motor vehicle tyres.
- ❑ Section 5 presents information about emissions of lubricants and greases.
- ❑ Section 6 provides information about emissions of coolants.

- Section 7 provides information about the emissions from vehicle exhaust systems and includes specific discussion on the emission of contaminants from vehicles with catalytic converters.
- Section 8 examines the wear of material from bitumen road surfaces.

In each of these sections information is presented on the contaminants present in that source and the available information on emission rates for that source. Finally in Section 9 information is presented in relation to the pathway from the source to the road surface, as not all of the emitted contaminant is likely to end up on the road surface and then be available for stormwater transport to a fresh or coastal receiving environment. Factors are identified that provide a first estimate of air to road deposition.

It should be noted that at this stage, the emissions information presented in this report (or the VFEM-water) does not deal with evaporative losses vehicles losses from vehicles (other models are available for this, e.g., USEPA EVAP 3.0). . This loss involves volatile organic compounds (e.g., benzene etc.) and under most circumstances do not contribute to the quality of sediments/dust on road surfaces or become immediately involved in stormwater quality except during rainfall (refer section 9 in relation to this matter). In addition, the report does not deal with air-conditioning system losses and materials lost through general wear and tear (chrome and paint flakes, rust flakes etc.) and through accidents (broken head lights, spillages etc.).

Figure 1.1: VFEM-W emissions hub (from Moncreiff et al. 2002).





## 2. VEHICLE FLEET

### 2.1 New Zealand Fleet Profile

The release of materials and contaminants from motor vehicles is described in relation to the composition of the New Zealand vehicle fleet in this report. MoT (1998) describes the composition of the New Zealand vehicle fleet. The New Zealand vehicle fleet profile is summarised in Table 2.1.

**Table 2.1 - New Zealand Vehicle Fleet Numbers (by type, size and fuel type) from transport registry data, mid-1998 (MoT 1998).**

Type		Petrol	Diesel	CNG	LPG	Electric/ Other	Total
Cars	< 1350 cc	285,999	95	30	1	90	286,215
	1350 – 2000 cc	1,099,542	39,609	94	172	281	1,139,698
	> 2000 cc	308,479	53,529	162	466	151	368,787
	Sub-total	1,694,020	99,233	286	639	522	1,794,700
LCVs	< 1350 cc	1,664	6,023	1	49	63	20,405
	1350 – 2000 cc	101,404	13,513	53	86	58	115,114
	> 2000 cc	62,209	98,887	79	91	45	161,311
Sub-total	Sub-total	165,277	118,423	133	226	166	296,830
MCVs	3.5 – 5.0 t	1,627	13,708	55	54	1	15,445
	5.1 – 7.5 t	1,261	13,917	114	98	-	15,390
	7.6 – 10.0 t	688	4,782	52	29	4	5,555
	10.1 – 12.0 t	909	3,924	36	49	-	4,918
Sub-total	Sub-total	4,485	36,331	257	230	5	41,308
HCVs	12.1 – 15.0 t	795	6,809	16	49	-	7,669
	15.1 – 20.0 t	321	6,014	4	36	-	6,375
	20.1 – 30.0 t	75	15,541	-	16	-	15,632
	> 30.0 t	41	2,916	-	-	-	2,957
Sub-total	Sub-total	1,232	31,280	20	101	-	32,633
Buses	< 3.5 t	2,343	2,006	20	80	2	4,451
	3.5 – 5.0 t	101	597	-	9	-	707
	5.1 – 7.5 t	246	778	2	11	-	1,037
	7.6 – 10.0 t	330	714	34	66	1	1,145
	10.1 – 12.0 t	37	984	6	6	2	1,035
	12.1 – 15.0 t	9	1,328	15	-	1	1,353
Sub-total	Sub-total	3,066	6,407	77	172	6	9,728
Total excluding 2-wheelers		1,868,080	291,674	773	1,368	699	2,175,199
Two Wheelers	Mopeds	9,314	11	1	-	36	9,362
	Motorcycles ≤ 60 cc	1,593	-	-	-	-	1,593
	Motorcycles > 60 cc	45,625	20	-	-	13	45,658
	Sub-total	56,532	31	1	-	49	56,613
Total, including 2-wheelers		1,924,612	291,705	774	1,368	748	2,231,812

**Notes:** LCV = Light commercial vehicles; M = medium; H = heavy.

The information in Table 2.1 was derived from data collected from transport registry data during 1998. The vehicle fleet is divided into a number of key categories of vehicles that include cars, commercial vehicles (light, medium and heavy), buses, motorcycles and mopeds. Vehicles are further subdivided by size, either by engine size (e.g., <1350 cc for cars) or by vehicle size (e.g., >3.5 tonnes for commercial vehicles and buses). Note that the vehicle fleet profiling in the VFEM is updated annually, from available Transport Registry data.

Vehicles are also described by fuel type: petrol, diesel, CNG (compressed natural gas), LPG (liquid petroleum gas), electric and other. The transport registry records the main fuel source, so CNG/petrol and LPG/petrol vehicles may not be accurately recorded (they account for a very small proportion of the

fleet, in total numbers). Petrol is the most common fuel for light vehicles, whereas diesel is the most common fuel used by heavy-duty vehicles.

The VFEM which, forms the basis of the VFEM-W model, uses the basic fleet profile in New Zealand.

- ❑ Passenger cars - subdivided into three engine-sized groups (<1350 cc, 1350-2000 cc, >2000 cc).
- ❑ Light commercial vehicles - subdivided into three engine sized groups (<1350 cc, 1350-2000 cc, >2000 cc).
- ❑ Heavy trucks - subdivided into three gross weight groups (3.5-7.5 t, 7.5-12.0 t, >12.0 t).
- ❑ Heavy buses - - subdivided into two gross weight groups (<12.0 t, >12.0 t).
- ❑ Motorcycles and mopeds.
- ❑ Miscellaneous vehicles (e.g., tractors, fire engines etc.,).

The structure of the VFEM can be readily adapted to suit the particular characterisation required of the fleet, in representing it as an emissions source, for particular contaminant relationships and discharge mechanisms.

For the sections that follow, where adequate data exists, the wear rates and emissions will be divided up into the key categories (or aggregates thereof) of vehicle type as defined by the New Zealand vehicle fleet profile.

## 2.2 Other Model Vehicle Categories

The highway development and management model HDM-4 developed by PIARC (Permanent International Association of Road Congresses, or World Road Association) and the World Bank, provides comprehensive tools to examine road user and environmental matters arising from road development and management. The HDM-4 model uses a flexible vehicle input framework but contains 16 basic vehicle types. These are summarised in Table 2.2. There is considerable similarity between the vehicle classes used by HDM-4 and the VFEM and NZ-TER.

The USEPA MOBILE model is referred to on a number of occasions later in this document. The model uses a vehicle classification system similar to that of NZTER. The classes of vehicle used in the latest version of the model (MOBILE 6, Released in January 2001, USEPA 2002) are summarised in Table 2.3.

## 2.3 Road types and driving conditions

Within this report the release of materials and contaminants from motor vehicles is described in relation to the nature of the road environment and driving conditions. The classification used in this report follows that used for the VFEM (MoT 1998).

### Road types

There are four primary road types used in the VFEM. These are:

- ❑ Motorways.
- ❑ Central urban roads.
- ❑ Suburban roads – major and minor arterials and local roads.
- ❑ Rural roads – rural highways and other rural roads.

**Table 2.2 - Summary of vehicle classes used in the World Bank model HDM4 (From Bennett & Greenwood 2001).**

Vehicle Category Code	Vehicle category	Code	Description
1	Motorcycle	MC	P, 2 axles, 2 wheels.
2	Small car	PC-S	P, 2 axles, 4 wheels
3	Medium car	PC-M	P, 2 axles, 4 wheels
4	Large car	PC-L	P, 2 axles, 4 wheels
5	Light delivery vehicle	LDV	P, 2 axles, 4 wheels
6	Light goods vehicle	LGV	P, 2 axles, 4 wheels
7	4 Wheel drive	4WD	P/D, 2 axles, 4 wheels
8	Light truck (<3.5 t)	LT	D, 2 axles, 4 wheels
9	Medium truck (>3.5 t)	MT	D, 2 axles, 4 wheels
10	Heavy truck (multi axle rigid truck)	HT	D, 3 axles, 10 wheels
11	Articulated truck or truck trailer	AT	D, 5 axles, 18 wheels
12	Mini bus	MNB	P, 2 axles, 4 wheels
13	Light bus (<3.5 t)	LB	D, 2 axles, 4 wheels
14	Medium bus (3.5-8 t)	MB	D, 2 axles, 6 wheels
15	Multi axle or large 2 axle bus	HB	D, 3 axles, 10 wheels
16	Large bus (long distance)	COACH	D, 3 axles, 10 wheels

**Table 2.3 - Summary of vehicle classes used in the USEPA model MOBILE6 (From USEPA 2002).**

Number	Code	Fuel	Description
1	LDGV	Petrol	Light duty petrol (passenger cars)
2	LDGT1	Petrol	Light duty trucks 1 Up to 6000 lb gross vehicle weight
3	LDGT2	Petrol	Light duty trucks 2 (0 – 6001 lbs)
4	LDGT3	Petrol	Light duty trucks 3 (6001 - 8000 lbs)
5	LDGT4	Petrol	Light duty trucks 4 (6001 - 8000 lbs)
6	HDGV2b	Petrol	Class 2b HD vehicles (8,501 - 10,000 lbs)
7	HDGV3	Petrol	Class 3 HD vehicles (10,001 - 14,000 lbs)
8	HDGV4	Petrol	Class 4 HD vehicles (14,001 - 16,000 lbs)
9	HDGV5	Petrol	Class 5 HD vehicles (16,001 - 19,500 lbs)
10	HDGV6	Petrol	Class 6 HD vehicles (19,500 – 26,000 lbs)
11	HDGV7	Petrol	Class 7 HD vehicles (26,001 – 33,000 lbs)
12	HDGV8a	Petrol	Class 8a HD vehicles (33,001 – 60,000 lbs)
13	HDGV8b	Petrol	Class 8b HD vehicles (>60,000 lbs)
14	LDDV	Diesel	Light duty diesel vehicles (passenger cars)
15	LDDT12	Diesel	Light duty diesel trucks 1 and 2 (0 – 6,000 lbs)
16	HDDV2b	Diesel	Class 2b HD vehicles (8,501 - 10,000 lbs)
17	HDDV3	Diesel	Class 3 HD vehicles (10,001 - 14,000 lbs)
18	HDDV4	Diesel	Class 4 HD vehicles (14,001 - 16,000 lbs)
19	HDDV5	Diesel	Class 5 HD vehicles (16,001 - 19,500 lbs)
20	HDDV6	Diesel	Class 6 HD vehicles (19,500 – 26,000 lbs)
21	HDDV7	Diesel	Class 7 HD vehicles (26,001 – 33,000 lbs)
22	HDDV8a	Diesel	Class 8a HD vehicles (33,001 – 60,000 lbs)
23	HDDV8b	Diesel	Class 8b HD vehicles (>60,000 lbs)
24	MC	Petrol	Motorcycles
25	HDGB	Petrol	Buses (all)
26	HDDBT	Diesel	Transit and urban buses
27	HDDBS	Diesel	School buses
28	LDDT34	Diesel	LD Trucks 3 and 4 (6,001-8500 lbs)

**Notes:** HD – Heavy Duty

The breakdown of urban roads into central and suburban is not clearly defined but central urban typically refers to those roads located in the central business areas comprising short distances between intersections with a high density of signal and roundabout control. Suburban roads comprise all other roads within the urban area boundary (MoT 1998) other than motorways.

In addition to this primary classification the following road section types are noted as having some influence on vehicle emissions as discussed in this report:

- ❑ Motorway on and off ramps.
- ❑ Roundabout approaches (a sub-set of urban roads).
- ❑ Controlled intersections (lights, stops and give ways – a sub-set of urban roads).

Vehicle movement on motorway on and off-ramps is an area of rapid acceleration and deceleration to and from motorway speeds. MOBILE6 freeway ramp VMT is based on the assumption that freeway ramps are 8% of all VMT assigned to motorways and their on and off ramps.

### Driving conditions

As described by MoT (1998), driving conditions are a function of several key factors. These include:

- ❑ The vehicle fleet composition on the road.
- ❑ The road speed limit and the actual speeds on the road.
- ❑ The effects of other activities such as kerb-side parking and side road 'friction'.
- ❑ The presence of controlled intersections.

The general method of classifying traffic conditions used by the VFEM and NZ-TER is based upon the Level of Service (LoS). The LoS on a given road can be graded from uninterrupted free flow (referred to as level of service A) to a capacity level of service (service level D/E) and then conditions under which traffic jams occur (service level F). In the VFEM the driving conditions are categorised into three bands. These are LoS A/B, C/D and E/F and these correspond to free flow, interrupted and congested driving conditions. These driving conditions are all for warmed up engine conditions. Cold start is considered as a separate category. A 'cold start' running period is considered as a separate category, as part of the drive cycle.

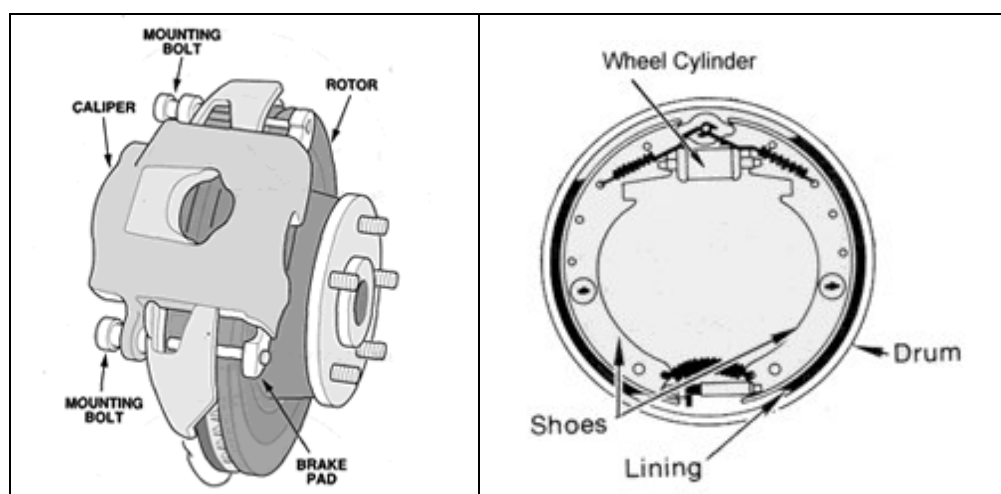
The VFEM then uses an emission factor matrix based upon road type and driving conditions. This produces a basic matrix with 16 cells in it. This matrix is then repeated for factors such as vehicle category (refer previous section), fuel type, model year and country source of emission technology.

This matrix is used in this report as the basis for the development of wear rate factors that require these factors to be taken into account. Within the following sections, key influences on the emission factors are identified and briefly discussed. Depending then upon the available information to develop those factors, the emission factors used to develop the source/emissions inventory may be simple or complex.

## 3. FRICTION LININGS (Brakes)

### 3.1 Introduction

There are two main types of brakes used in vehicles – disc brakes and drum brakes (Figure 3.1). These brakes are both lined with replaceable parts, known as brake pads (used on disc brakes), brake linings, brake-shoes (used on drum brakes) or more generally as friction linings. The composition of friction linings differs depending on application, as cars require different performance from friction linings compared to heavy trucks. The action of braking, results in wear of the friction linings and consequent release of a wide variety of materials (elements and both inorganic and organic compounds) into the environment. The wear rates of the friction linings differ, due to both the differences in composition and the differences in how they are used. These differences result in considerable variation in emission rates from this source.



**Figure 3.1 - Diagram of a disc brake and a drum brake, showing the position of brake pad and friction linings (from about.com – autorepairs.com.)**

Until the late 1960s most motor vehicles used drum brakes on all wheels. Disc brakes came into use in the 1960s and 1970s (Armstrong 1994) and today most light duty vehicles use disc brakes in the front and drum brakes in the rear. More expensive vehicles may use disc brakes on all 4 wheels.

The overall size or mass of the brake pads varies with vehicle type. Typically trucks use larger brakes than passenger vehicles because the mass of vehicle that requires slowing down or stopping is greater. Garg et al. (2000) reported weights of pads ranging from a minimum of 105 g for passenger vehicles up to 380 g for larger trucks. This is not dissimilar to the weights of individual pads used on the New Zealand vehicle fleet.

This section of the report presents information on the general composition and wear of brake linings. Specific information on the inorganic and organic contaminant concentrations present within linings or the products of wear is presented. This information is used to provide an indication of the most appropriate data to use for estimates of contaminant loadings from this source.

## 3.2 Brake Pad Wear

### 3.2.1 General

Disc brakes consist of a rotor (attached to the wheel) and two brake pads. When the brakes are applied, the brake pads squeeze against the moving rotor to slow the wheel. Drum brakes contain brake shoes within a rotating drum. When the brake is applied, these shoes apply an outwards force against the inside of the drum. The rotor may be ventilated to improve cooling.

When brakes are applied, a contact zone is developed between the disc and pad or lining and drum. In this zone, energy is transferred, heat dissipated and a friction film is created (Gudmand-Høyer et al. 1999). The contact zone is very small compared to the total area, due to surface roughness at a microscopic level (Eriksson & Jacobson 2000). The friction film consists of particles worn from the surface and volatile compounds from the pads and disc or drum (Gudmand-Høyer et al. 1999).

As the brake wears, the less wear resistant constituents such as resins and fillers are removed leaving the mechanically stable and wear resistant components on the pad (Eriksson & Jacobson 2000). These then deteriorate when the brake is re-applied. Debris worn from the brake pad is momentarily retained between the brake pad and the disc or drum as the friction film. This leads to further wear of the brake pad surface. During this process, the worn particles are, further broken up by the motion of the wheel and brake pad (Eriksson & Jacobson 2000). Once the wear particles are fine enough, they either rejoin the brake pad or are released from the contact area. Some of the particulates worn from the brakes are not released into the environment and are retained in the brake housing (Rogge et al. 1993). This is particularly the case for rear drum brakes where a significant amount of debris is retained within the drum brake housing.

The wear rates of brake pads and linings depend on the mode of driving (e.g., heavy use of brakes) and the composition of the brake lining used (e.g., long wearing versus high performance). The key factors that influence the amount of brake pad worn as a result of the use of the brakes is the amount of force applied to the pad during the braking to influence the movement of the vehicle (the inertial weight) and the temperatures attained as a result of braking.

$$\text{Braking power } P = F_t \cdot V$$

Where  $F_t$  = total braking force

Where  $V$  = vehicle speed

### 3.2.2 Wear Rates

Wear rates are typically measured as the mass of particulate matter emitted per kilometre or mile travelled. However unlike many other motor vehicle sources, brake wear does not occur on a constant basis. Wear of the friction linings occurs when the brakes are used to slow down or stop the vehicle. Following the generation of particles from the wear of the brakes and the entry of the particles into the road air corridor, their presence is likely to be more widely distributed than the location of the point of generation. Particles may also be emitted from the wheel housing away from the point where the brakes were used.

Unit distance wear rates are the typical form of presentation for brake pad wear rates when assessing the loads of contaminants generated by motor vehicles.

Todorovic et al. (1995) showed that the wear rate was a linear function of cumulative work done by the brake or the number of brake applications and temperature and that this approach could be used to predict lining life expectancy.



## Brake use

Cha et al. (1983) identified the necessity of defining braking patterns during driving as the brake cycles are a function of initial speed before braking, speed reduction, duration of the braking cycle and brake pressure. The authors concluded overall, that brake pressure was the most important factor. Cha et al. (1983) then classified braking cycles by initial speed, speed reduction and braking cycle interval into a series of braking cycle classes.

Todorovic et al. (1995) identified that the total work done by the brake per kilometre was necessary to assess brake wear. The authors identified that the definition of typical roads may be a means of defining brake wear better. This is discussed further below.

## MOBILE factors

Wear rates have been measured for a range of vehicles from passenger cars to heavy trucks and the results reported by a number of authors. The primary model used in the United States for the assessment of particulate emissions from motor vehicles is the USEPA PART5 model (USEPA 1995). The PART5 model uses a particulate emission rate of 12.8 mg/mile (20.6 mg/km) for the emissions from light duty petrol vehicles. The rate used was derived in work carried out by EPA (1985). As noted by Garg et al. (2000), the rate was derived from tests using asbestos brakes and as such may not represent the wear rates from current brakes used on the US vehicle fleet (in the year 2000).

## Other studies

A number of other studies have identified brake pad wear rates. These have in nearly all cases been estimated based upon wear rates over the life of the pad.

Legret & Pagotto (1999) identified wear rates of 20, 29 and 47 mg/vehicle/km for passenger cars, light goods vehicles and heavy lorries respectively.

Cha et al. (1983) determined that the weighted average particle emissions from a front disc brake were 2.43 mg/brake application. Earlier work by Williams & Muhlbaier (1980) (cited in Cha et al. (1983)) reported 3.3 mg/stop. Cha et al. (1983) then calculated the wear rate per mile travelled by multiplying their average wear rate by the average number of brake applications per mile. This produced an average wear rate of 11.8 mg/mile (7.3 mg/km). The differences between the Cha et al. (1983) and Williams & Muhlbaier (1980) work are attributable to the amount of work performed during the braking. The number of braking applications per distance, was higher in the Cha et al. (1983) study but the Williams & Muhlbaier (1980) braking applications were complete stops.

Garg et al. (2000) tested 7 brake pads in high use on the American market for wear rates under a range of temperatures. Wear rates were calculated on the basis of the mass lost per stop (with time and kilometres travelled varying) as the material lost occurs as a result of the use of the brake on individual occasions. The amount of material lost over the seven brake pads tested ranged from 0.27 mg/stop to 131.0 mg/stop (median 5.0 mg/stop, 10%ile 1.4 mg/stop and 90%ile 28 mg/stop). Garg et al. (2000) also measured airborne emissions separately during this testing and calculated an emission loss that ranged from 5.1 to 14.1 mg/mi (8.2 to 22.7 mg/km) for emissions from small cars to large pick-up trucks. All of the brake pads contained fibres of some type and the composition of the pads used by Garg et al. (2000) in their testing is described further in the following sections.

Garg et al. (2000) noted that front brakes on US motor vehicles are expected to last about 35,000 miles (56,000 km) under normal use and rear brakes about 70,000 miles (113,000 km). During this life about 80% of the brake pad lining material is worn away. Garg et al. (2000) estimated that this corresponded to a loss rate of about 18 mg/mile (11 mg/km) for a small car, about 28 mg/mile (17 mg/km) for a large car and about 47 mg/mile (29 mg/km) for a pick-up truck.

Westerlund (2001) calculated brake lining wear for vehicles in Stockholm. Front brake linings (weighing 0.13-0.15 kg) in passenger cars used in city driving conditions were replaced after 30,000 - 40,000 km and rear brake linings (weight 0.9-0.11 kg) after 60,000 - 80,000 km. The authors estimated that with linings replaced after 70% of their life and front linings replaced every 40,000 km (four linings) this corresponded to a wear rate per km per front pad of 2.625 mg/km. For rear linings replaced every 60,000 km (four linings) this corresponded to a wear rate of 1.28 mg/km for rear pads. This corresponded to a total wear rate of 15.62 mg/km. The authors also reported wear rates for goods vehicles and buses. For four-wheel goods vehicles wear rates were estimated as 84 mg/km (average life 100,000 km, front linings (number vary with model) weigh 2.4 kg in the front and 3.5 kg in the rear). For buses, the corresponding wear rate was 110 mg/km travelled.

These two studies and the earlier work of Cha et al. (1983) indicate the considerable range in emission rates that have been estimated for motor vehicles. It is evident that general wear rates can be estimated based upon the total wear rates of brake pads over the life of the material worn. Such estimates are however likely to over-estimate the amount of brake pad materials worn and entering the environment in areas of low brake usage and under-estimate the brake pad derived particulate emissions in areas of high intensity brake use.

Examination of general brake pad wear rates in New Zealand, has indicated that OEM practice for truck tractor units is from a loss before replacement (typically at 400,000 to 500,000 km) of up to 12-13 mm (from an initial pad thickness of 16 mm). For a 6 x 4 tractor unit, with pads 410 mm x 150 mm on each wheel, the total brake pad area is 9,800 cm<sup>2</sup>. For an 8 x 4 tractor unit, with pads 410 mm x 220 mm on each wheel, the total brake pad area is 12,300 cm<sup>2</sup>. A loss of 12-13 mm before replacement corresponds to a total material loss of around 1,200 cm<sup>3</sup>. Averaging the two truck tractor types provides a loss of around 25 mm<sup>3</sup>/km. At a density of 2.2, this corresponds to a loss of about 54 mg/km over the life of the linings.

### Release of particles and size of worn particles

Cha et al. (1983) examined particles produced by the wear of brakes used under controlled laboratory conditions. They examined the ratio of airborne particulate matter to deposited particles (material deposited on the sampling box and within the brake system). They noted that airborne debris also deposit on the ground as a function of time. Examination of the particle size of worn particles indicated that the particle diameters of initial wear dust, airborne and deposited dust were generally similar. Peak particle size distribution is in the range 2.1-3.3 µm and about 10% of particles in the sub-micron size range.

The authors calculated the total wear per brake application and the percentage of airborne particles. The percentage airborne particles increased with vehicle speed.

As part of their study, Cha et al. (1983) examined the proportion of particles that were considered to become airborne. Of the weighted average particle emissions from a front disc brake (2.43 mg/brake application) some 0.75 mg of that material was considered airborne (69% deposited). Earlier work by Williams & Muhlbaier (1980) reported 3.3 mg/stop and 1.6 mg of that being airborne (51.5% deposited). Cha et al. (1983) also identified an average wear rate of 11.84 mg/mile (7.36 mg/km) of which 3.78 mg/mile (2.35 mg/km) were airborne and 8.06 mg/mile (5.01 mg/km) were deposited (68% deposited). The differences between the Cha et al. (1983) and Williams & Muhlbaier (1980) work are attributable to the amount of work performed during the braking.

Cha et al. (1983) also determined that there were differences in the proportion of airborne particulates released by disc brakes as compared to drum brakes. They identified an emissions ratio of 69% between drum and disc brakes based upon the earlier work of Williams & Muhlbaier (1980).

Garg et al. (2000) examined the particle size of particles generated in a number of the brake pad wear tests they conducted. Although some differences in particle size distribution were noted between the test pads under different braking temperature conditions, the differences do not appear to be significant. Garg et al. (2000) reported average mass median diameters ranging from 0.62 to 2.49 µm with an overall

average of 1.49  $\mu\text{m}$ . Typically averages of 86% of the particles were  $<10 \mu\text{m}$  in diameter; 63% were  $<2.5 \mu\text{m}$  in size and 33% were  $<0.1 \mu\text{m}$  in diameter. Garg et al. (2000) discussed the possible causes of the large fraction of particles smaller than  $0.1 \mu\text{m}$  in size in their data (e.g., compared to earlier studies - refer above). However, the authors considered that the high temperatures at the brake/rotor interface are likely to volatilise some of the brake pad components, which may then condense when leaving the brake environment. With an estimated 30% of the wear being airborne particulate material this corresponded to loss rates of 5.1 to 14.1 mg/mile (3.2 to 8.8 mg/km) for the small car and pickup truck identified earlier in relation to their work. Rauterberg-Wulff (1998) (cited in Weckwerth 2001) noted that the dominant size of particles analysed in their study lie between 2.5-10  $\mu\text{m}$ .

### Overall wear rate information

The available published information provides data on both the average wear rate per stop and the average wear rates based upon the wear over the life expectancy of the friction lining. The data for average wear rates per stop is mostly derived from passenger cars. Data is available for a number of vehicle types for average wear rates and these are summarised in Table 3.1.

Based upon the information presented in the previous section, it is evident that:

- ❑ Average brake wear does not adequately represent the wear rates on roads with significantly different driving conditions. As the amount worn is related to the total brake use then the primary factor to be considered is the number of brake applications made and the force of the applications (i.e., the load and speed reduction over the required distance). The number of brake applications made is dependent upon the route geometry and the driving conditions.
- ❑ Use of car brake wear rates does not appear to adequately describe the average fleet wear rates due to the larger wear losses from heavy duty vehicles.
- ❑ The amount of material worn during braking is then dependent upon the speed of the vehicle prior to braking, the speed that the vehicle is reduced to as a result of braking (i.e., the difference), the mass of the vehicle and the temperatures attained as a result of braking.

**Table 3.1 - Summary of average wear rates for motor vehicles (mg vehicle/km).**

Vehicle type	Average wear rates	Vehicle type	Source
Passenger car	11-17	Small to large cars	Garg et al. (2000)
	15.62	Cars	Westerlund (2001)
	20	Cars	Legrat & Pagotto (1999)
	20.6	Cars	USEPA PART5
	24.7	Cars	Cha et al. (1983)*
	29	Pick-up-truck	Garg et al. (2000)
Light duty vehicle	29	Light duty vehicle	Legrat & Pagotto (1999)
	84	4 wheeled goods vehicles	Westerlund (2001)
Heavy duty vehicle	47	Heavy duty vehicle	Legrat & Pagotto (1999)
	54	trucks	Estimate – this study
Buses	110		Westerlund (2001)

**Note:** \* assumes 2 disc and 2 drum brakes with 69% ratio between wear rates.

### 3.3 Discs and Rotors

Before discussing the composition of friction linings it must be remembered that the brake system works by pressing the friction lining against a rotor or disc. The pressure of the friction lining against the rotor or

disc produces the stopping power. The pressure of the friction lining against these surfaces results in their contact and interaction under both pressure and heat.

Brake discs are usually cast iron but can be made of reinforced aluminium. The two types of materials work completely differently with the aluminium discs requiring the formation of a thick 'transfer film' on the disc surface. The cast iron discs however, require some wear to remove iron oxide coatings that develop (Eriksson & Jacobsen 2000). Eriksson & Jacobsen (2000) reported on the composition of a cast iron disc used in a Volvo 850. The disc contained a small amount of manganese (0.6 wt%) and chromium (0.15 wt%). Howell & Ball (1995) reported that some aluminium rotor material contained a small amount of copper (0.12 wt%).

## 3.4 Composition of Friction Linings

### 3.4.1 Introduction

Vehicle manufacturers internationally and in New Zealand know what materials and products they use to manufacture linings but they typically do not know the chemical composition of the friction linings that they use. In New Zealand it is estimated that there are more than 400 different types of brake pads and linings in use and over 1,000 are available in the United States (Armstrong 1994). Information on the composition is generally limited to the materials present in the pad and there is little quantitative analytical information on their composition.

### 3.4.2 General

Brake linings are typically grouped into three key categories: semi-metallic, organic and non-asbestos organic. In addition, there is a range of specialised brake pads on the market for race and luxury cars (e.g., using paper, carbon, and resin-bonded graphite or ceramic particles in metal matrices). Table 3.2 provides a summary of the main structural materials used in brake linings. Typically brake pads contain a binder of some type, fillers and fibres. The inset box on the following page provides additional information on the general composition of friction linings.

**Table 3.2 - General composition of brake pads.**

Main element	Use	Example compound
Fibres	Provide mechanical strength	Organic (aramid). Inorganic (copper, steel, brass, carbon, glass, kevlar, asbestos)
Abrasives	Increase friction coefficient and disc wear	Silica, e.g., zirconium silicate or aluminium oxide
Binders	Hold the components together, form thermally stable matrix	Rubber, phenolic resins
Fillers	Assist in manufacturing, reduce wear, reduce cost	Barytes, vermiculite, friction dust
Solid lubricants	Stabilise the friction coefficient at high temperatures	Graphite or metal sulphides (Cu <sub>2</sub> S, MoS <sub>2</sub> , PbS, ZnS or Sb <sub>2</sub> S <sub>3</sub> )

### Binders

A variety of different modified phenol-formaldehyde resins are used as binders in friction linings and more than one resin type may be used in a pad (Filip et al. 1997). The binder may be modified in a number of ways depending upon the brake pad specifications. To stop resins from becoming brittle, a softer resin (e.g., polyvinylbutyral) may be added (Verma et al. 1996). Birch et al. (1991), reported on the use of

binding 'plastics' composed of acrylic denatured phenol in a new Honda brake pad. The same pad contained butadiene-styrene rubber.

### **Summary of friction lining composition (from Filip et al. 1997)**

#### **Yellow Group**

The yellow group of brake pads contain either or brass chips or copper powder. The pads also contain barium and or antimony sulphate. The pads also contain glassy phase materials which are typically amorphous materials comprising alumina silicates (thought to be from blast furnace slag). The binder is typically phenolic resin. Visual examination of the pads showed the presence of large grains of anthracite, fusinite maceral and white dendritic particles of copper powder.

#### **Brown Group**

The pads with a brown appearance were dominated by aramid fibres, phenolic resin, glassy phase, ground sulphur and a variety of minerals. Kevlar fibres were present and antimony sulphate was also used in the pads. In contrast to the yellow group carbonaceous materials such as coke and anthracite were absent.

#### **Steel Group**

The pads with the steel appearance contained low-carbon steel and or iron powder. Carbonaceous materials were present. The steel pads had complex structure because of the variety of forms of the coke and graphite. Steel particles were found to have oxide coatings. A range of minerals such as limestone and other minerals such as kaolinite were found. The latter substituting for barium sulphate.

#### **Grey Group**

The grey group is moderately complex and Filip et al. (1997) identified three sub-groups based on the range of pads that they examined. The pads typically contained copper and or brass with some containing copper and steel chips. Glassy phase material, carbonaceous materials and phenolic resin were the other key constituents. The red sub-group contained coloured glassy and aramid fibres. The bright gray group contained alumina silicate glasses that contained zirconium and tin particles. The red group also contained antimony sulphates, magnesium and chromium oxides.

### **Fillers**

A range of fillers are used in the manufacture of friction linings. These are typically low cost materials such as inorganic compounds (e.g., barium sulphate), silicates (e.g., clays), various inorganic oxides (e.g., magnesium oxides), ground slag, stone and metal powders. Some of these materials assist in maintaining frictional properties and assist in keeping the surface of the friction lining clean (e.g., from molten metal and plastic).

### **Modifiers and Friction dusts**

Modifiers are added to influence the wear characteristics of the lining. These materials include a range of carbon based materials (e.g., graphite, coke, anthracite etc.), kevlar and sulphur. Some metallic particles may also be used to modify friction properties. Friction dusts are also added (Filip et al. 1997). These materials are wide ranging in nature and can include cashew nut dust.



## Fibres

Fibres are added to the matrix to provide strength and structure to the friction lining. A wide range of fibre types is used including mineral and ceramic fibres, low carbon steel, copper, brass and aramid fibres. Potassium titanate is also used. The glass fibres used are typically low cost materials such as alumina silicates and recycled materials such as blast furnace slag. Asbestos fibres have historically been used for the main fibre content.

Asbestos use is decreasing due to health and safety concerns in manufacturing, however it is still used in brake linings on the New Zealand market. A range of fibre types is now used in brake pads (Table 3.2). Garg et al. (2000) also identify the use of potassium titanate fibres in a number of brake pads on US vehicles.

Table 3.3 provides examples of brake pad composition data presented in two studies. The composition reflects the varied types of brake pads manufactured. The data in Table 3.3 shows that some components such as fillers and lubricants may make up a significant part of the pad matrix. Table 3.4 presents a summary of semi-quantitative analysis of brake pads.

**Table 3.3 - Examples of brake pad composition (all data %).**

Main Component	Name/compound	Howell & Ball (1995)			Eriksson et al. (2001)
		Organic	Semi-metallic	Semi-metallic	Organic
Pad type					
Fibres	Organic (aramid)	20	-	-	3
	Inorganic	0.6	61	20	27
Abrasives	Aluminium oxide	-	-	5	5
Binders	Resin, rubber	45	30	16	9
Fillers	Barytes, vermiculite, friction dust	15	-	52	16
Solid lubricants	Graphite, Cu <sub>2</sub> S, MoS <sub>2</sub> , PbS, ZnS or Sb <sub>2</sub> S <sub>3</sub>	15	7	4	23
Metallic ingredients	Brass, bronze	-	-	-	15
Other		4.4	2	3	2



### 3.4.3 Inorganic Constituents

Semi-metallic friction linings contain a significant amount of inorganic material as they are a mixture of fragments or powdered metal held together with phenolic resins and other binders and fillers. The metal is present for heat transfer and the amount present depends upon the specific heat transfer requirements. In some brake linings, iron, steel (e.g., steel wool and iron sponge) and titanium are used for their high heat transfer coefficients. In situations, which are not so demanding, such as the rear disc brakes of normal passenger vehicles, the pads may contain softer metals such as copper and brass. Organic friction linings and non-asbestos organic linings contain a lower content of metallic material, however the inorganic content can still be high with inorganic fillers etc.

**Table 3.4 - Summary of semiquantitative analysis of brake pad samples (from Filip et al. 1997) (all data %).**

Constituent	Brake pad type					
	Yellow	Brown	Steel	Bright grey	Dark grey	Red & grey
Maceral char	8			4		
Graphite			6	8	18*	18*
Coke & petroleum			34			
Anthracite	13			18	6	6
Sulphur		11				
Copper	11			6	9	9
Brass		8			8	6
Iron powder			23			
Steel chips			8			14
Tin					0.5	
Cr <sub>2</sub> O <sub>3</sub>						3
MgO						4
Glassy phase	22	22		19	16	23
Limestone			2			
Barium sulphate	21			21	28**	16***
Sulphates		6				
Calcium alumina-silicate			3			
Potassium titanate	6				2	
Kevlar fibres		17				
Aramid fibres					3	5
Porosity	9	13	7	9	8	7

**Notes:** \* - coke and graphite, \*\* - BaSO<sub>4</sub> and Sb<sub>2</sub>(SO<sub>4</sub>)<sub>5</sub>. \*\*\* - Antimony sulphate.

Metals that have been identified as used in brake pad linings include aluminium, chromium, copper, iron, lead, nickel, tin and zinc (Shaheen 1975; Jacko et al. 1984; Cooper et al. 1987; Yamaguchi 1991; Armstrong 1994). Barium, calcium, cesium, molybdenum, magnesium, silicon, chloride have also been reported (Cooper et al. 1987). Antimony has been reported at concentrations between 1 – 4% (Helmers 1996, Dietl et al. 1996). Weckwerth (2001) noted a number of German publications that provided additional information on brake lining composition. One of these; Oehl & Paul (1990) identified upper concentrations of antimony (4.3%) and copper (16%) in the samples they examined.

The inorganic composition of brake pads used in New Zealand was, investigated by Kennedy & Gadd (2000) and the results obtained in that study are summarised in Table 3.5 below. The preliminary work carried out in that study demonstrates the extreme variability of the brake pad composition on the New Zealand market. Of all of the elements examined this was most notable for copper (median 35 mg/kg with a range of 11 to 112,000 mg/kg) and antimony (median 6 mg/kg with a range of 0.07 – 29,500 mg/kg). The upper range of antimony reported by Kennedy & Gadd (2000) is similar to the ~2% reported by Weckerth (2001).

The Kennedy & Gadd (2000) study, as with most of the other studies reported in the literature, examined mostly the composition of new brake linings. When brake pads are used they are subject to a range of processes that physically and chemically affect the composition of the materials lost from the pad surface. For inorganic materials, chemical alteration is not a concern as, the composition of elemental materials will not be altered significantly by temperature (apart from the oxidation state of some metals). However, the pads come in contact with discs, rotors and brake drum housings and this contact has the potential to alter the composition of the particles lost through the abrasion of the material the brake pad or disc comes in contact with. Garg et al. (2000) examined the composition of airborne particulate matter and brake pad dust samples. This study found that the brake pad dust samples tended to be lower than the airborne particle results. This was attributed possibly to the volatilisation of more carbon from the airborne particles compared to the dust. Table 3.5 compares the results on analysis of brake lining matrix and brake lining dust samples obtained in New Zealand with information in the literature.

**Table 3.5 - Inorganic constituents in brake linings (all data mg/kg unless stated).**

	Shaheen (1975)	Armstrong (1994)	Legret & Pagotto (1999)	Kenedy & Gadd (2000)	Kennedy & Gadd (2000)	Westerlund (2001)
				PC linings* N=8	PC - brake dust N=6	PC N=24 Front/rear, N=48 All
Fe %	-	-	-	2.02 (1.17-63.7)	17.65 (8.9-46.8)	-
Mn	-	-	-	323.5 (181-1920)	1450 (856-2870)	-
As	-	-	-	<2.5 (<2-18)	3.5 (<2-11)	-
Cd	-	< 2.5	2.7	0.55 (0.1-1.8)	0.4 (<0.06-2.6)	-
Co	-	-	-	26.25 (11.6-45.8)	28.3 (12-42.4)	-
Cr	2,200	30 - 160	-	199 (39-411)	329 (135-1320)	F - 129 (2.3-305) R - 45.8 (5.73-248) All - 93.1
Cu	30,600	<62.5 – 205,000	142,000	41.4 (11-39,000)	219.5 (71-1980)	F - 130,000 (63.9-234,000) R - 123,000 (12.7- 229,000) All - 123,000
Hg	-	-	-	0.2 (<0.1-0.3)	<0.15 (<0.06-0.30)	-
Mo	-	-	-	2.7 (0.4-215)	29.1 (5-98.9)	-
Ni	7,454	60 – 140	-	318 (44-660)	419.5 (80-730)	F - 117 (12.4-382) R - 39.3 (3.6-156) All - 106
Pb	1,050	<100 – 119,000	3,900	8.0 (1.28-873)	38.6 (4-1290)	F - 1480 (21.3-39700) R - 617 (<5.8-56600) All - 1092
Sb	-	-	-	5.2 (0.07-201)	22.4 (4-133)	-
Sn	-	-	-	1.5 (<1-15)	5.25 (4.5-115)	-
Zn	124	100 – 188,000	21,800	882 (25-34500)	1600 (360-9630)	F - 25,500 (125-107,000) R - 11050 (14.5-96100) All - 11850

**Note:** \* 7 passenger cars (PC) and 1 four-wheel drive.

Six brake lining dust samples (recovered during brake lining replacement) were also analysed for the same range of elements as brake pads by Kennedy & Gadd (2000). However, it should be noted that the pad and dust samples were not matched so the comparison should only be taken as a general one. Table 3.5 provides a summary of the brake pad dust data collected by Kennedy & Gadd (2000). Comparison with the whole pad data revealed that the brake dust samples contained higher concentrations of iron and tin when compared to the brake lining analyses. This is likely to be from wear of the brake drum and disc brake rotor which are typically, made of steel and alloys and may have oxide coatings cleaned off by the friction lining contact.

### 3.4.4 Organic Compounds

There is little industry information available on the organic composition of friction linings with regard to particular organic compounds. Early work by Hildemann et al. (1991) and Rogge et al. (1993) investigated the organic composition of brake wear dust compared to other sources of particulate matter.

Hildemann et al. (1991) presents results of analyses demonstrating the presence of n-alkanes and acidic organic compounds. Rogge et al. (1993) analysed particles from brake linings of a light truck and detected 87 organic compounds from a range of chemical groups. Polyethylene glycol ethers dominated the composition. It was considered that these were derived from hydraulic fluids that were lost from the hydraulic brake system and able to contact the dust in the rear brake lining of the vehicle. n-Alkanoic acids were also at high concentrations in the brake lining particles.

Rogge et al. (1993) reported concentrations of n-alkanes of 38.47 mg/kg, with highest concentrations in the range C33 to C40. Hildemann et al. (1991) detected n-alkanes in C12 through to C34 with little present at >C34. Rogge et al. (1993) detected a number of PAHs and substituted PAHs, with a total concentration of 16.16 mg/kg. These were considered to have been formed by the heat generated during braking (600 °C, which would be sufficient to pyrolyse some organic compounds).

A preliminary examination of organic compounds in brake pads used in New Zealand was carried out by Gadd & Kennedy (2000). Table 3.6 provides a simplified summary of the results obtained by Gadd & Kennedy (2000) and compares them with results from Rogge et al. (1993). As Table 3.6 demonstrates, the composition was dominated by phenols, with concentrations of phenol ranging from 6.9 to 1,310 mg/kg.

**Table 3.6 - Concentrations of organic compounds identified in a selection of 6 brake pads available in New Zealand compared with literature (data mg/kg).**

	<b>Gadd &amp; Kennedy (2000)</b> <b>(range of concentrations detected)</b>	<b>Rogge et al. (1993)</b>
Phenol	6.9 - 1310	-
Hydroxyphenylmethylphenol	5.5 - 500	-
Bis(2-ethylhexyl) phthalate	ND - 486	-
Methylene-bis-phenol	4.3 - 462	-
Alkyl phenols	1.5 - 231.9	-
Long chain acids and methyl esters	4.3 - 204.4	91.4
Butoxy ethoxy ethanol	1.1 - 90.8	45.7
Benzodioxin	16 - 34	-
Aromatic amines	1.0 - 27.7	ND
Alkyl amines	ND - 22	ND
Alkyl amides	3.8 - 18.2	ND
Butylated hydroxy anisole	3.3 - 17	-
Benzaldehydes	5.0 - 17	4.7
Benzothiazole	1.5 - 6.9	ND
Other nitrogen containing compounds	1.0 - 5.1	ND
Benzothiazolone	1.3 - 2.0	-
Benzophenone	1.1 - 1.7	-

**Note:** ND = Not detected

## 3.5 Emission Rates

### 3.5.1 Introduction

The composition of the chemicals emitted from brake pads during their use is not necessarily the same as the brake pad composition. Different parts of the brake pads wear at different rates (Eriksson & Jacobson

2000) and chemical changes occur at the high temperatures the brake pads are subjected to. Cha et al (1983) note that organic binders in brake pads start to degrade at about 250°C. It was noted by the authors that at high temperatures, thermal decomposition of the organic binders in the outer layers of the lining occurs. Kim & Jang (2000) also noted that oxidation of metallic ingredients and breakdown of phenolic resins into char also occurs. In addition, the work of Kennedy & Gadd (2000) has shown that the composition of brake pad dust differs to that of brake pads.

A number of average brake pad wear rates have been identified in the literature as presented above. These range from early data used in the USEPA MOBILE5 model to more recent evaluations of wear rates by Garg et al. (2000). There is some data for average brake-wear rates for a number of different vehicle classes. The average wear rate data in Table 3.7 provides initial data that can be used to estimate the total load of particulate matter generated by vehicle brakes. General data is of value in undertaking general catchment wide assessments of contaminants derived from this source.

**Table 3.7 - Summary of estimated particle emissions from wear of friction linings for particulates (mg/km).**

<b>Vehicle class</b>	<b>Average wear rate</b>	<b>Low brake use</b>	<b>Moderate brake use</b>	<b>Intense brake use</b>
Passenger car	<b>21</b>	<b>10.5</b>	<b>31.5</b>	<b>42</b>
Light duty vehicle	<b>30</b>	<b>15</b>	<b>45</b>	<b>60</b>
Heavy duty vehicle	<b>80</b>	<b>40</b>	<b>120</b>	<b>160</b>

However, as noted earlier, the brake pad material wear rates vary significantly depending on brake use. This is dependent upon road and driving conditions. It is considered that calculations of brake pad wear should be undertaken using more appropriate vehicle driving condition information that relates vehicle power to driving conditions. The VFEM-W will eventually include such an approach to assess the contaminant contribution from brake wear.

The VFEM-W utilises the LoS classification as the primary description of driving conditions. To provide a preliminary refinement of the wear rates for different driving conditions, the wear rates have been identified in three classes. These are represented by low wear rates (LoS A/B), moderate wear rates (LoS C/D) and intense use (LoS E/F). The latter category is considered to also correspond to those sections of road leading up to roundabouts and controlled intersections (lights and signs). The rates identified in Table 3.7 have been derived using a ratio from the average wear rates identified in the literature (refer Table 3.1). Although this factor is arbitrary it provides some spread in the wear rates that reflects the known difference in brake pad wear attributable to driving conditions. This can be updated when refined wear rates are available for different driving conditions or a suitable driving condition wear rate model is available. In the absence of any clear data on the wear rates for larger vehicles with heavier and a greater number of linings per vehicle, the rates have been assumed to be as set out under particulate material in Table 3.7. With more specific information for given vehicle classes in the New Zealand vehicle fleet this would be adjusted to take the different vehicle classes into account.

### 3.5.2 Inorganics Contaminants

Overall, the inorganic composition of brake pads is relatively well known. As discussed, the range of different friction linings used in motor vehicles is very large and the range in composition is also extensive. Most studies including those carried out in New Zealand have examined only a limited range of friction lining samples. This results in considerable difficulties in deriving an average composition by vehicle type or for the vehicle fleet. As such, the available data has been used to derive preliminary estimates of average brake pad composition using all of the New Zealand data. The limitations of this dust quality data must be understood when using the data. Table 3.8 provides a summary of the preliminary emission friction lining dust composition data used in this assessment.

**Table 3.8 - Summary of concentrations of selected elements in New Zealand brake pads for use in calculating emission factors (all data mg/kg or ng/mg, n = 12 unless noted).**

	10%ile	Median	90%ile
<b>COPC</b>			
Ag	0.2	0.2	1.19
As	1	1	17.2
Cd (n=13)	0.1	0.6	4.58
Co	11.8	24.75	40.17
Cr (n=13)	41.08	233	435.8
Cu (n=39)	29	280* (5,000 interim value)	116,000
Hg	0.1	0.2	0.29
Mo	0.725	3.6	136.92
Ni (n=13)	44.2	342	652.2
Pb (n=39)	5.626	50	949.2
Sb	0.653	6.09	158.8
Sn	0.5	1.5	5.6
Zn (n=39)	127.2	1630	37,400
<b>Other Elements</b>			
Al	812.35	3100	17140
Fe %	1.17	1.8325	19,024
Mn	143.2	315.5	1087.6
Ti	32	110	988
B	12	47.5	869
Ba	558.2	3195	6144

**Note:** This value may be an underestimate of actual median concentration, – refer text.

The determination of emission rates for inorganic materials e.g., copper) is determined by the accuracy of the combined concentration data and wear rates. As an example, Davis et al. (2001) assessed copper emission rates from brakes based upon copper release from brake abrasion being 1.5 mg/VKT as determined by Malmquist (1983) and a copper in brake pad concentration of 5% as copper particles (based on work of Hewitt & Rashed 1990)). This resulted in an average copper discharge rate of 75 ug Cu/VKT. This rate is based on two general pieces of data and as a result produces an emission rate factor with a high degree of uncertainty. In this review, the median copper concentration is lower at 280 ng/mg (compared to 5%). Examination of the New Zealand data used to derive this number (Kennedy & Gadd 2000) shows that the data is highly skewed. Given the variability of copper in brake pads and then significant differences in the copper content of pads on New Zealand market there is considerable doubt as to what is an appropriate media, copper concentration to use in loading estimates. Until further work is undertaken to revise this figure it is recommended that a concentration of 5,000 mg/kg is used.

**Inorganic contaminant emission losses from brake lining wear can be calculated as:**

$$\text{Brake wear emission within a given section of road (mg)/unit time period} = \text{VKT/unit time period} \times \text{particle emission rate (mg/km) (Table 3.7)} \times \text{median concentration (ng/mg) (Table 3.8)}$$

The final on-road contribution is determined by multiplying the emission load by the factor presented in Section 9.

### 3.5.3 Organic Compounds

The lack of robust quantitative data for organic compounds in brake pads or dust generated by brake pad wear limits the identification of emission factors for most organic compounds, PAHs are however one key group of compounds for which data is available. Table 3.9 provides a summary of those compounds for which there is data to provide information for emissions calculations.

**Table 3.9 - Summary of concentrations of selected organic compounds for calculating emission factors (data mg/kg or ng/mg).**

<b>Compound</b>	<b>Median</b>
<b>COPC</b>	
Phenol	292*
Hydroxyphenylmethylphenol	164*
Methylene-bis-phenol	213*
Alkyl phenols	16*
Polycyclic aromatic hydrocarbons	16.16**
<b>Other Compounds</b>	
n-Alkanes	38.5
n-Alkanoic acids	529.7
Substituted benzaldehydes	19.0**
Benzoic acids	34.5**
Polyalkylene glycol ethers	879.1**
Polycyclic aromatic ketones and quinones	3.0**
Pentacyclic triterpanes	3.1**
Benzaldehydes	19.04**
Natural resins	10.1**

**Note:** \* From Gadd & Kennedy (2000); \*\* from Rogge et al. (1993).

The Gadd & Kennedy (2000) data is based on the examination of six new brake linings. For the other organic compounds the data of Rogge et al. (1993) is used to provide initial data. As with inorganic contaminants, the emitted load of individual organic compounds can be calculated using the same approach as described earlier in this section.

#### 3.5.4 Overview

There is reasonable data available for the wear rates of brake pads that shows that brake pad wear is a logical function of brake pad use. The more intense the use, the more the pad wears. The rate of wear is also dependent upon the amount that the speed has to be reduced by the brake. That is greater wear occurs on sections of road where greater speed reductions occur. As a result roundabouts and traffic lights will be areas of key brake pad wear. There is not however sufficient data to provide wear rates for each of the New Zealand Vehicle fleet. At this stage preliminary values are provided for cars, light goods and heavy vehicles. To produce better data, the wear rate values need to be refined by vehicle class and number of wheels/brake linings involved.

There is data for inorganic and organic composition of brake pads. Given the variation in brake pad composition evident from both international and New Zealand data, fleet averaged composition data is required to produce meaningful contaminant emissions load data. As an example the variation in composition between the 10 and 90%ile data for New Zealand brake linings is about 200 times for a number of environmentally significant elements (e.g., Sb, Mo, Zn) but for copper the factor is even greater at 4,000 times. This significant difference arises from brake pads in use that contain no copper through to pads containing copper fragments.

If brake pad wear varies by a factor of four (as used in this preliminary assessment) and the concentration varies by a factor of 4,000 then the overall variation in calculated copper load contributed by individual sections of road in New Zealand will vary significantly.

A range of environmentally significant organic compounds, are known to occur in brake lining materials. Although there are likely to be some changes in the composition of those compounds arising from the wear process (temperature), emission factors can only be identified for a limited number of compounds and compound groups. Preliminary emission factors for PAHs are provided.



To provide more suitable data to assess emissions of contaminants from this source the following is required.

1. Identify the predominant brake linings used in New Zealand motor-vehicles by vehicle brand.
2. Identify the vehicle fleet composition by vehicle type and brand.
3. Calculate vehicle fleet or fleet average inorganic contaminant concentration data based on selected linings that are representative of the fleet brake pad wear.

The importance of appropriate and current fleet weighted concentration data being used in emission load prediction is demonstrated by the difference between the low median copper concentration data identified by Kennedy & Gadd (2000) and the high median values identified in overseas studies. The overseas data suggest a much higher proportion of high concentration copper containing brake pads on the market. The 90<sup>th</sup> percentile concentration of the New Zealand data is similar to the overseas median values. It is suggested that an interim value of 5,000 mg/kg be used at this stage for the assessment of copper in wear rate particles.

## 4. TYRES

### 4.1 Introduction

Tyres are an essential part of any vehicle and the number and size of tyres increase with the size of the vehicle. Contact between tyres and the road surface causes the tyres to wear, with the rate dependent on tyre composition and driving conditions (i.e., heavy braking and accelerating increases tyre wear). Tyres are composed of rubber with a range of additives, including some trace elements. Concentrations of additives vary depending on the tyre usage. Emission rates of these are dependent on the tyre composition and wear rates. For characterisation purposes, four main vehicle groups can be considered for tyres; passenger cars, light trucks, heavy trucks and the 4WD RVs, as distinct groups. Tyre designs that are representative of the main market in New Zealand are:

- ❑ “Budget” tyre, 82 series, cross/bias ply 520/13 for passenger cars; all these tyres are imported, typically from South East Asia and are old style technology. This type of tyre is not a major part of the market.
- ❑ High performance, low aspect ratio steel belt radial, Z rating 45 series, passenger car. This type of tyre is more typical of the larger part of the light vehicle fleet.
- ❑ Truck tyre; bias ply.
- ❑ Truck tyre; radial; for light trucks, typical is C type radial, 185/R14, 8 ply.
- ❑ Truck tyre heavy; typical is 11R 22.50 radial.
- ❑ Passenger car retread, any.
- ❑ Truck retread, any.

This section of the report presents information on the general composition and wear of tyres. Specific information on the inorganic and organic contaminant concentrations present within tyres or the products of wear is presented. This information is used to provide an indication of the most appropriate data to use for estimates of contaminant loadings from this source.

### 4.2 Tyre Wear

#### 4.2.1 General

Tyre wear occurs through frictional contact between the tyre and the road surface. In addition to frictional processes, tyres are affected by heat and also through their contact with water on the road. Cadle & Williams (1978a) reported on the emission of gases from tyre wear. Gaseous emissions included a number of monomers and dimers of styrene-butadiene co-polymers. Friction causes small and larger particles to wear from tyre, which are then either released as airborne particulates, deposited onto the road surface or retained in the wheel hub temporarily or permanently (until washed off). The rate at which tyres wear depends is dependent upon a number of factors that influence how the tyre interacts with the road surface. Le Maitre et al. (1998) reviewed these factors. They are:

- ❑ The route and style of driving.
- ❑ Road surface.
- ❑ Seasonal influences.
- ❑ Vehicle characteristics.
- ❑ Tyre composition.

## The route and style of driving

The route and style of driving determine the amount of acceleration. The acceleration of the vehicle determines the forces applied to the tire. The wear between the tire/road interface (the contact patch) is determined by and is directly proportional to these forces. Le Maitre et al. (1998) report that the wear caused by different drivers is significant and varies by a factor of six times. However, the range is caused by differences between professional and regular vehicle users (i.e., their method and level of driving skill).

Le Maitre et al. (1998) also report that the 'route' factor (independent of road surface type) results in a wear factor of up to ten times. For example, ~0.5 g/100 km on highway to ~8 g/100 km on windy roads. It is likely that variations in acceleration also contribute to this difference. The authors also note that two different driving scenarios can result in the same overall tyre wear rates (e.g., enhanced longitudinal acceleration or a windy route).

Information provided by Dunlop (South Pacific tyres, Mr Bill Prebble pers comm), indicates that wear rates increase from straight and level driving (representing 100% of tire life) to 96% on straight but slightly hilly roads, to 76% on slightly hilly and curvy roads, to 50% on hilly and curvy roads. The increased wear rates on curvy and hilly roads come from acceleration and braking forces being applied to the tires.

## Road surface

The road surface causes friction and abrasion and therefore the roughness of the surface will affect the wear rate by a factor of 2-3 times.

Information provided by Dunlop (South Pacific tyres, Mr Bill Prebble pers comm), indicates that wear rates deteriorate with increasing friction coefficient and road surface aggressiveness. Total mileage obtained during the life of the tyre therefore reduces on certain surfaces. For example to 95 % on concrete, 85% on tarmac, to 64% on gravel to 50% on dirt roads for average passenger tyre cars (from well maintained asphalt being 100%). Given that this assessment is concerned primarily with urban roads, the relative influence of road surface to tyre wear rates is considered small compared to other sources of wear variation.

## Seasonal influences

The season results in temperature and humidity and water contact variations. The amount of tire wear may vary by a factor of two between seasons and between wet and dry conditions. Wear rates are lower in wet compared to dry conditions. The environmental interaction is also dependent upon the nature of the rubber in the tyre (refer tyre composition below).

## Vehicle characteristics

The vehicle characteristics influence the wear by a factor of two. The key influences are the weight, suspension and steering geometry. Axle geometry changes result in uneven wear (often as much as 1 mm across the tire width).

## Tyre composition

The tyre type influences the wear significantly. In particular, the shape of the tyre (determined by stiffness), the rubber volume (tread pattern) and the characteristic of the tyre (rubber type etc.). As a result, tire size and inflation are key factors in overall wear patterns. As a consequence of different manufacturing specifications, different brands of tires wear at different rates. The U.S. Department of Transportation and NHTSA provide information on tyre characteristics under a uniform tyre quality grading system. This system provides information on heat dissipation, traction and wear for all of the key

tyre construction types and brands produced by all of the manufacturers in the United States (138 manufacturers). Based on controlled tread-wear testing, the wear rates vary between tyre types. Examination of tread-wear grades indicates that the wear grades vary by several factors. Table 4.1 provides some typical information for relative wear rates (based on comparison to a relative wear rate of 100, with 200 being a tyre that wears two times less than one with a rating of 100) several key manufacturers.

The information in Table 4.1 shows that the relative wear rate for passenger car tyres is relatively similar. The relative wear rates vary by a factor of about four times. Other factors that accelerate wear are over- or under-inflation and the overall quality of the road surface.

**Table 4.1 - Examples of relative wear grades for some passenger car tyres (from US DoT).**

<b>Brand</b>	<b>Tyre construction</b>	<b>Relative tyre wear - median</b>	<b>Relative tyre wear – range</b>	<b>Number of tire lines</b>
Dunlop	Radial	300	160-560	29
Falken	Radial	360	140-560	26
Goodyear	Radial	320	20-640	102
Kelly	Radial	390	280-640	20
Kuhmo	Radial	300	200-460	24
Yokohama	Radial	180	40-320	90

Table 4.2 provides a summary of the wear rate factors described above and the range in the wear rate variation identified in the literature.

**Table 4.2 - Summary of relative wear rates under different conditions and by different factors.**

<b>Source of Variation</b>	<b>Typical variation</b>
Route type and driving style	10
Tyre brand	4
Season	2
Vehicle characteristics	2
Urban road surface type (roughness)	1-1.5

Bennett & Greenwood (2001) described tyre ‘consumption’ as it related to the Highway Development and Management model, HDM-4. They summarised the key factors that influence wear of tyres as:

1. Pavement conditions increase tyre wear as the pavement roughness increases. Pavement roughness results in increased vertical loading on tyres.
2. Tyre wear is increased by severity of road alignment especially the horizontal curvature.
3. Traffic conditions cause acceleration and deceleration which affects wear.
4. Tyre wear is proportional to vehicle loading.
5. The tyre properties will influence the tyre wear rate. In particular, whether the tyre is new or a retread, what the properties of the rubber are and what the inflation pressure is in relation to the ideal inflation pressure.

Tyre wear rates can be determined from tyre wear experiments and from individual or fleet tyre wear. Tyre wear rates have been found to vary significantly between a wide range of studies that have been carried out (Bennett & Greenwood 2001). Tyre wear rates or the life of the tyre is considered to follow a

log-normal distribution. That is, the tyre wear life is skewed and typically has a tail of higher distances travelled for part of the on-road tyre population.

Bennet & Greenwood (2001) made note of the proportion of retreads in any given tyre population. Cenek et al. (1993) reported that 20% of New Zealand passenger tyre sales were retreads. A sample of buses in the New Zealand fleet indicated that retreads made up 75% of the tyre tread.

There are three types of tyre wear.

1. Contact of the tyre tread with the road surface results in abrasion of particles. Cenek et al. (1996) report a range of 300-600% in tyre abrasion rates between different road surface textures.
2. Wear as a result of tyre fatigue, which occurs as a result of oxidation and repeated deformation.
3. Thermal decomposition occurs under extreme conditions such as wheel lock during braking and wheel spin during rapid acceleration.

The bulk of the wear occurring on roads is abrasive wear.

Retreads are considered to wear more than new tyres. Wear rate studies on tyre fleets reported in Bennett & Greenwood (2001) indicated that retreads only had about 75% of the tyre tread volume that new tyres had.

Bennett & Greenwood (2001) reviewed literature on tyre read wear. One of the key factors in tyre wear was identified as roughness.

Highway geometry is also a key factor with rise and fall in roads resulting in increased tread wear.

Significant differences in tyre wear occur between tyres used on paved and unpaved roads. Although this is a significant geographic factor on a national basis in New Zealand, it is not a significant factor within urban areas in New Zealand nor is it significant in terms of total vehicle kilometres driven. Studies have also reported greater tyre wear in urban (23% higher) compared to rural areas due to the greater number of stop starts and their effect on tyre wear.

In summary, the key factor influencing wear rates in urban environments is the nature of the road and the driving conditions. Both combine to contribute to wear. Tyre brand (design and composition) is the other significant contributing factor.

The driving conditions have been considered further in the following sections where specific wear rates are considered. Providing for brand influences on wear rates within vehicle classes requires knowledge of the vehicle fleet tyre compositions at any point in time.

#### 4.2.2 Wear Rates

Wear rates for tyres, like brake pads, are typically measured as the mass of particulate matter emitted per kilometre or mile travelled. Tyre wear occurs constantly for moving vehicles, but is significantly higher for cars braking suddenly or accelerating rapidly. Occasionally particles are visibly deposited onto the road surface under these conditions, however in general, particles are smaller in size and more widely distributed.

The rate of wear is essentially linear through the life of a tyre, with material loss measured by tread surface depth, though there is a slightly higher rate when new (as the sharp edges from manufacture wear down).

## Emissions Models

There are several models developed to assess vehicle emissions that include emissions from tyre wear. This includes the USEPA PART 5 model; PART-TX1, developed by the Texas Natural Resources Conservation Commission; and PMFAC, developed for the European Union. Each of these models use the emission factors developed by the USEPA for the PART 5 model.

The MOBILE model uses the emission factors for light duty vehicles (passenger cars) for all vehicle classes as there was no data available for other classes. USEPA (1985) note that the wear rates for other vehicle classes will be different to those predicted for passenger cars. However, the MOBILE/PART5 models provide information only on airborne particulates not the total particulate emissions.

The data utilised in the MOBILE5 and PART5 models cannot be used in this assessment as the model only considers the amount of airborne particulate matter (1.24 mg/km). The identified rate of airborne particulate matter derived from passenger vehicles can be used if required to estimate regional transport and contributions from this motor vehicle emission source.

### HDM-4

The slip energy tyre consumption model was used in the HDM-3 model. The factors used were extended in the HDM-4 model to include the influence of horizontal curvature forces and traffic interaction effects. Cenek & Carpenter (1999) report that most tyre wear occurs as a result of lateral rather than circumferential forces. The inset box on the following page provides some information from the HDM-4 model. At present the required information on the force involved in calculated the wear is not easily obtainable. However, the HD-4 model work has shown that with the appropriate data tyre wear can be modelled and estimates of wear matched to road conditions can be obtained.

Temperature is also an important consideration in tyre wear. 21.25% increase in wear consumption are encountered for temperature changes between 20 and 25°C. It may therefore be necessary to include a seasonal and geographic factor to the tyre wear emissions rates identified.

Speed variation is an important factor. Carpenter & Cenek (1999) have shown that the effect of speed variation is highest at low speeds as a result of inertial effects and effective mass. The effect is therefore directly related to the mass of the vehicle.

Lateral force effects on tyres were examined by Carpenter & Cenek (1999), who assessed tyre wear on routes of different amounts of horizontal curvature, and found that there was little variation in FNL.

Cenek et al. (1993) reported that the results of a pilot study indicated that the appropriate wear coefficient for steel belted car radial tyres being driven on medium sized chipseal was 0.0005 dm<sup>3</sup>/1000 km J/m. This coefficient was similar to others published for radial tyres.

Cenek et al. (1993) reported the results of a tread wear study carried out over two routes in New Zealand. The results showed that the tyre wear of the driven wheel is two to four times that of the non-driven wheel due to slippage when driving or braking forces are applied. The difference in tread wear between the two routes was a factor of 2.5 for the driven wheels and for the un-driven wheels a factor of about 5 times. It was considered that the differences are caused by differences in suspension used. The results are summarised in Table 4.3.

### Notes on the HDM-4 tyre wear model

Abrasion losses are proportional to frictional energy dissipation. Bennett & Greenwood (2001) and Carpenter & Cenek (1999) overviewed the mathematical model for describing tyre wear in terms of the circumferential force (CFT) on the tyre and the lateral force on the tyre (LFT) (both in N). The relationship is non-linear and can be represented by:

$$\text{TWT} = \text{square root of } (CFT^2 + LFT^2)$$

This formula forms the basis of the micro-tread wear model \*Watanabe et al. 1987; Cenek et al. 1993, 1997) which can be expressed as:

$$\text{TWT} = CT \cdot (\text{TFT}^2/\text{NFT}) \quad (1)$$

Where:

TWT = volumetric tyre wear rate ( $\text{dm}^3/1000$  tyre km).

CT = coefficient of tyre tread wear ( $\text{dm}^3/\text{MNm}$ ).

TFT = the total tangential force acting on the tyre (N).

NFT = the load on the tyre normal to the tyre-road contact area.

The equation can only be solved simply if TFT is constant however, during normal driving conditions TFT is a constantly changing force and TFT is required for any given section of road. As noted by Carpenter & Cenek (1999) the variation in TFT due to factors such as cornering, acceleration, braking and gradients are typically unknown. Carpenter & Cenek (1999) examined modifications to the basic equation (1) given above to separate circumferential and lateral forces that act on the tyre.

$$\text{TWT} = CT_c \cdot (CFT^2/\text{NFT}) + CT_L \cdot (LFT^2/\text{NFT}) \quad (2)$$

Where:

CFT = Circumferential force on the tyre (N)

LFT = lateral force on the tyre (N).

$CT_c$  = Circumferential coefficient of tyre tread wear ( $\text{dm}^3/\text{MNm}$ ).

$CT_L$  = Lateral coefficient of tyre tread wear ( $\text{dm}^3/\text{MNm}$ ).

and to add in components to account for the range of independent factors that effect the tyre wear.

$$\text{TWT} = \text{FLV} \cdot (CT_c \cdot (CFT^2/\text{NFT}) + CT_L \cdot (LFT^2/\text{NFT}) + \text{TWT}_0) \quad (3)$$

Where:

FLV = factor for local effects, vehicle type etc.

$\text{TWT}_0$  = tyre tread wear constant ( $\text{dm}^3/1000$  km)

Equation 3 can then be modified to account for the variation along a section of road in CFT and LFT. Carpenter & Cenek (1999) identified the factors FNC and FNL. FNC being the influence of the variation of the circumferential forces and FNL represents the influence of the variation of lateral forces.

#### CT

Motorcycle CT =  $0.0009 \text{ dm}^3/\text{NMm}$

All cars, deliver vehicle and 4 wheel drives CT =  $0.0005 \text{ dm}^3/\text{NMm}$ .

For trucks and buses CT =  $0.0003 \text{ dm}^3/\text{NMm}$ .

#### FNC

For cars, delivery vehicles and 4 wheel drives FNCs for different speeds are set out below:

Mean speed	30 km/hr	50 km/hr	70 km/hr	100 km/hr
Speed variation (acceleration noise)				
Low	1.3	1.2	1.1	1.1
Medium	3.8	2.6	2.0	1.5
High	12.2	7.4	4.7	2.9

For all motorcycles FNC =  $0.5 \text{ FNC}_{\text{cars}} + 0.5$

For all trucks and buses FNC =  $2\text{FNC}_{\text{cars}} - 1$ .

**Table 4.3 - Preliminary tread wear results from New Zealand (Cenek et al. 1993).**

Test Run	Tyre position	Weight loss (g/1000 km)	Weight loss (mg/km)
Low severity - Aotea Quay to Palmerston North	Front Left	5.6 ± 1.5	5.6
	Back right	4.0 ± 1.5	4.0
High severity - Haywards to Featherston	Front left	38.4 ± 0.9	38.4
	Back right	19.9 ± 0.9	19.9

### Tire life

Carpenter & Cenek (1999) calculated tyre life estimates for three classes of motor vehicles in New Zealand. These were:

Motorcycle (CT = 0.0009 dm<sup>3</sup>/NMm), tyre life - 12,000 km.

Medium car (CT = 0.0005 dm<sup>3</sup>/NMm) tyre life - 47,000 km.

Heavy truck (CT = 0.0003 dm<sup>3</sup>/NMm) tyre life - 119,000 km.

### Other Studies

Wear rates for tyres have typically been calculated based on tyre lifetime (in kilometres travelled) initial weight and tread surface depth.

Environment Agency (1998) reports that tyre lifetimes have increased from an average of 24,000 km in 1975 to 48,000 km in 1990, with changes in technology and the introduction of radial tyres.

In New Zealand, an industry rule of thumb is that a personal car tyre (PC) should have a useful service life of 35,000 - 50,000 km. The overall life expectancy of the tire varies depending upon how 'hard' the tires are used (i.e., worn). However, this assessment deals with normal driving conditions and it is assumed that the tyre wear attributable population of drivers on New Zealand roads follows a 'normal distribution'. That is, only a small proportion of drivers cause low wear and extreme wear of their tires. Le Maitre et al. (1998) reported examples of tire life for passenger cars as set out in Table 4.4.

**Table 4.4 - Examples of tires lives at three usage severities (from Le Maitre et al. 1998).**

	D10*	D50	D90*
Tire 1	20,000 km	33,000 km	53,000 km
Tire 2	18,000 km	35,000 km	58,000 km

**Notes:** \* - 10 % of drivers will wear their tires out by these distances.

Tyre wear rates have been measured and estimated for a range of vehicles from passenger cars to light trucks and heavy trucks and results reported by authors as either emission per tyre or per vehicle. These include:

- Environment Agency (1998) summarised passenger car tire wear rate information in the United Kingdom. Using a life of tyre weight loss of 1.5 kg over 50,000 km estimated wear per km corresponds to 30 mg/km/tyre. This corresponds to a wear rate of 120 mg/VKT under average driving conditions.
- Muschak (1990) estimated that motor vehicles lost 0.12 g/VKT in Germany.



- ❑ MOT (1996) estimated that 1,850 g of rubber was lost from a tire during the time that it took to be replaced. This amount to 53 mg/km per tire if a lifetime of 35,000 km is assumed.
- ❑ Legret & Pagotto (1999) identified an average wear rate for a single tyre as 17 mg/km. This was based upon the following information - 50,000 km wear, dimensions 0.54 m in diameter, 0.12 m wide, 6 mm thickness, density of 1, 30% void due to tread depth, total material loss 857 g. The authors assumed that the amount per vehicle was therefore 68 mg/km (i.e., 0.068 g/VKT) and twice this quantity for heavy vehicles (>3.5 t).
- ❑ Le Maitre et al. (1998) reported tyre wear rates for passenger vehicles from tyre/driver surveys of wear rates. They reported wear rates for passenger cars under a range of route/driving conditions. For example:

Highway use	0.5 g/100 km or 5 mg/km.
Urban use	2.8 g/100 km or 28 mg/km.
Medium use	3.3 g/100 km or 33 mg/km.
Severe use	7.8 g/100 km or 78 mg/km.

In New Zealand, emission factors have been identified in association with industry for PCs, light trucks and heavy trucks. Industry has supplied the following measures for material loss indicators over the tyre service life:

PC tyre, 1.1 kg.  
 Light truck tyre, 1.8 kg.  
 Heavy truck tyre, 7.5 kg.

This is assuming that the tyre is replaced at the legal tread depth limit, with the figures being based on average tyre sizes in each category. Taking the minimum service life of 35,000 km, this translates to an “emissions rate” of 0.031 g/km per PC tyre to 0.21 g/km per heavy truck tyre of total tyre compound, assuming that the tyre is replaced at the legal tread depth limit. Another estimate is for a tyre to lose around 10-20% of its total weight through its lifetime use (equivalent to between 30-40% of its tread weight). For car tyres this is around 1.5 kg. Table 4.5 provides a summary of the wear rate information based on average life of tyre wear rates described above.

**Table 4.5 - Summary of average vehicle tyre wear rates under average driving conditions (all data mg/tyre/km).**

Reference	Passenger Car	Light Truck	Heavy Truck
Cadle & Williams (1978)	30		
Rogge et al. (1993)	6 – 90		
Ministry of Transport (1996)	53		
Environment Agency (1998)	35.5		
Le Maitre et al. (1998)	33 (medium use)		
Legret & Pagotto (1999)	17		~136
Cenek et al. (1993)	20 (low severity)		
New Zealand industry estimate	31	51	210

### Wear loss particle size

Tire wear particles are larger than those produced by other sources such as brakes or fuel combustion. As such, a smaller proportion of the particles are in the airborne size range (EPA 1985). Material loss from tires occurs mainly through abrasion in form of particles with minor loss of larger fragments. Some of these particulates will remain on the road and incorporated into stormwater, whereas some will be entrained into the air in the road corridor. The proportion depends on the size distribution of the wear particles. Rogge et al. (1993) reports that 10% (by mass) of tyre tread particles are <3 µm in diameter. Cadle & Williams (1978a) reported that emissions of gases and airborne particles was nearly independent

of wear rate and accounted for up to 20% of the total emissions depending upon the wear severity. The balance was large particles, which would settle close to the road surface. Weckwerth (2001) commented on the influence of tyre particles on airborne particle compositions and commented that most of the particles worn from the tyres probably fall directly onto the street without reaching fall out samplers placed 2 m above the ground (this is discussed further in Section 9).

## 4.3 Tyre Composition

### 4.3.1 General

Like brake pads, tyres are composed mainly according to performance standards (e.g., wet grip, wear rate and drive-by noise), however there is more information available on the composition of tyres and a smaller range of ingredients are used. The ratio of these ingredients is adjusted to produce the performance required.

As noted in Section 4.1, tires are subject to heat during use. Cadle & Williams (1978b) noted that analysis of large particles of rubber worn from tyres showed that chemical degradation has occurred during the wear process. This was identified as devulcanisation of about 30% of the styrene butadiene rubber. In addition to heat effects, some loss of rubber components is likely during contact of tires with water on the road. This arises as some organic compounds (e.g., benzathiozoles) and inorganic constituents (e.g., zinc) are soluble in water. Although solubility of compounds such as benzathiozoles have been examined (e.g., refer Reddy & Quinn 1997) the effects of driving in wet conditions on losses to stormwater do not appear to have been evaluated.

Table 4.6 provide a summary of the general composition of vehicle tyres. Tyre formulations change with anticipated use of the tyre. As such passenger car tyres differ from those tyres used by heavy machinery in off road conditions. As noted earlier, tyre formulation results in considerable variation in wear rates.

**Table 4.6: - General composition of tyres.**

Main element	Use	Example compounds	Content
Polymer base	Structure	Natural rubber (polyisoprene) Synthetic rubber (SBR – styreneised polyisobutylene)	30% (ratio between 60:40 and 70:30 synthetic: natural rubber)
Carbon black	Reinforcement, provides stiffness, strength and hardness.	Carbon black of various particle sizes	30
Hydrocarbon oil	Processing aid/softening agent	Paraffinic, naphthenic or aromatic oil	10-15
Resins	Processing aids	Aromatic hydrocarbon polymer Thermoplastic phenol-novolac resin	0 – 7%
Antidegradants	Anitoxidants and antiozonants	Paraffin wax Quinolines Phenyldiamines	1 – 1.5%
Cure activators	Assist in curing	Zinc oxide/stearic acid mix	2.0 – 2.5%
Cure agent	Assist in curing	Elemental sulphur	1.0 – 1.5%
Accelerators	Promote curing	Complex amines Sulphonamides Thiazoles	1.5%
Retarders	Slow the curing rate	Acids or phthalates	0.1%
Bonding agent	Improve bond strength between tyre and steel/cord belt	Resorcinol resin	
Bracing		Steel (sometimes coated in brass)	

### 4.3.2 Inorganic Constituents

There have been a number of studies investigating the inorganic composition of vehicle tyres, including a major study by Environment Agency in the UK (Environment Agency 1998). This study reports the presence of major elements such as calcium (calcium oxide used as a desiccant), magnesium (magnesium oxide used as an accelerant), silica and phosphates (used in fillers and plasticisers). No other major inorganic elements were detected in the tyres including iron, manganese and phosphorus.

A number of trace elements have been reported as being used in the manufacture of tyres including antimony, cadmium, copper, lead and zinc (Christensen & Guinn 1979; Hewitt & Rashed 1990; MoT 1996; Dietl et al. 1997; Environment Agency 1998; Legret & Pagotto 1999). The reported concentrations are summarised in Table 4.7. Zinc oxide is added as a vulcanisation activator (the ZnO is added as fine particles of precipitated ZnO along with stearic acid to form zinc stearate). The ZnO may also carry some other trace elements with it depending upon the process used to manufacture it (either electrochemical or precipitation). Bayer, report that ZnO additive contains a small amount of lead oxide (about 5 mg/kg). Zinc is also reported, to be used in zinc ethyl and other dithiocarbamates (used as accelerators), in zinc dibenzamide diphenyl disulphide (a peptiser) and zinc metaborate dihydrate (a flame retardant) (Environment Agency 1998).

Weckwerth (2001) noted that a few analysis of different tyres showed that the zinc content (1-2%) was independent of different tyre types. Sorme et al. (2001) used a zinc concentration of 1.6% for tyre wear estimates. Davis et al. (2001) reported mean concentrations of lead (17 mg/kg), copper (5 mg/kg), cadmium (1 mg/kg) and zinc (3,400 mg/kg) following the extraction of fresh worn tyre particles with acidic rainwater.

**Table 4.7 - Comparison of published data for trace elements in vehicle tyres (all data mg/kg).**

Element	Christensen & Guinn (1979)	Hewitt & Rashed (1990)	MoT (1996)	Legret & Pagotto (1999)
Tyre type				
Cadmium	-	0.28-4.96	0.77	2.6
Copper	-	5.5-29.3	-	1.8
Lead	-	-	0.84	6.3
Zinc	7,300	-	5,624 (based on 0.7% ZnO)	10,800

Kennedy & Gadd (2000) examined the elemental composition of a selection of 12 tyres available in New Zealand. The tyres were from passenger cars, 4WD, light utility vehicles and trucks and the elemental composition is summarised in Table 4.8. The data suggests a number of differences in the inorganic composition, with passenger cars containing more calcium than other tyre types. Furthermore, the truck tyres analysed contained considerably more zinc (13,800 – 18,300 mg/kg) than the tyres from passenger cars (range 5,640-9,640 mg/kg), 4WD and light utility vehicles (1,190 – 9,640 mg/kg).

### 4.3.3 Organic Compounds

The composition of tyres is dominated by organic compounds, with a wide variety of compounds used in the manufacture of tyres, as noted above in Section 3.2.1. Information on organic compounds in tyres is available in Hildemann (1991), Rogge et al. (1993), Kumata et al. (1997), Reddy & Quinn (1997), Environment Agency (1998) and Gadd & Kennedy (2000). Table 4.9 presents data from two of those studies.

Gadd & Kennedy (2000) examined organic compounds in six tyres on the New Zealand market, ranging from tyres for small passenger cars to large trucks. These results are presented below in Table 4.9. It should be noted that the data in Table 4.10 represents detected data presented in that report. It is not possible to calculate median data from that data set unless a result was reported for all six tyres examined in that study.

**Table 4.8 - Summary of elemental composition of a selection of 12 tyres available in New Zealand (all data mg/kg, Kennedy & Gadd 2000).**

	Passenger Cars (n = 7)			4WD (n = 1)	Light Utility Vehicle (n = 2)		Truck (n=2)	
	Minimum	Mean	Maximum		Minimum	Maximum	Minimum	Maximum
Ca	100	330	1680	270	60	60	150	230
Mg	<4	12	37	<4	5	37	10	15
Na	120	200	530	70	<20	80	530	590
K	110	255	410	<50	<50	120	200	430
P	10	20	50	<20	<20	<20	120	205
Al	7	20	129	<5	9	13	51	139
Fe	40	80	220	30	100	110	195	210
Mn	0.8	1.45	2.5	<0.5	0.7	1.0	3.2	6.1,5.7
Be	0.05	0.3	0.7	0.2	0.1	0.3	0.3	0.4
Cd	<0.05	0.24	0.34	0.13	<0.05	0.10	0.28	0.56
Co	0.5	1.4	4.1	0.3	0.4	2.4	0.9	1.0
Cr	<1	0.5	2	<1	<1	<1	1	2
Cu	<1	1	2	<1	1	3	1	2.5
Hg	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01
Mo	<0.2	0.3	1.4	<0.2	0.3	0.6	0.65	1.1
Ni	<1	2	3	<1	<1	1	<1	1
Pb	1	2.75	5.7	1.5	0.8	1.5	3.2	9.7
Sb	<0.2	0.1	0.9	<0.2	<0.2	<0.2	<0.2	1.3
Sn	<0.5	0.25	1	<0.5	<0.5	0.6	<0.5	<0.5
Zn	5,650	8,470	9,640	4,180	1,190	3,640	13,800	18,300
Ba	10.4	32.7	166	42.3	8.78	39.8	13.2	13.6
Li	<0.2	<0.2	2.6	<0.2	<0.2	<0.2	<0.2	<0.2
Rb	<0.2	0.3	0.6	<0.2	<0.2	<0.2	0.9	1.5
La	<0.1	<0.1	0.4	0.1	<0.1	<0.1	<0.1	0.2
Sr	<0.5	1.3	2.6	<0.5	<0.5	<0.5	0.7	1.6

**Note:** Not detected Au, Ge, In, Pd, Se.

**Table 4.9 - Comparison of published data for organic compounds in vehicle tyres (all data mg/kg).**

Compound	Rogge et al. (1993)	Reddy & Quinn (1997)
n- Alkanes	18,842	
n-Alkanoic acids	12,197	
n-Alkenoic acids	1279	
Benzoic acids	74.8	
Substituted benzaldehydes	7.8	
Polyalkylene glycol ethers	nd	
Benzothiazole	124.3	171
2-hydroxybenzothiazole		80.9
2-(4-morpholino)benzothiazole		3.76
Total PAHs	226.1	
Phenanthrene	11.8	
Fluoranthene	11.1	
Pyrene	54.1	41.4
Benzo[g,h,i] fluoranthene	6.3	
Chrysene/triphenylene	8.2	
Benzo[e]pyrene	5.2	
Benzo[a]pyrene	3.9	
Polyaromatic ketones and quinones	0.45	
Regular steranes	74.2	
Pentacyclic triterpanes	684.4	
Natural resins	9,513.3	
Amides	12.9	
Chlorinated organics	5.3	
Phenols	17.6	

**Table 4.10 - Concentrations of semi-volatile organic compounds in a selection of 6 tyres available in New Zealand (all data mg/kg).**

	Car minimum	Car maximum	4WD	Truck
<b>Polycyclic aromatic hydrocarbons</b>				
Acenaphthylene	8.2	19.8	<5	<10
Phenanthrene	6.2	6.3	<5	<10
Fluoranthene	9.4	28.5	<5	<10
Pyrene	10.8	69.7	<5	6.3
Benzo[g,h,i]perylene	<10	<10	17	<10
<b>Nitrosamines</b>				
N-Nitrosodiphenyl & diphenylamine	<20	60	18	34
<b>Anilines and Benzidines</b>				
Aniline	<10	217	<5	<10
<b>Long chain acids and methyl esters</b>				
Tetradecanoic acid	9.30	33.2	-	-
Hexadecanoic acid, methyl ester	-	-	-	38.8
Hexadecanoic acid	383	1480	256	266
Octadecanoic acid, methyl ester	-	-	-	17.9
Octadecanoic acid	166	1040	138	-
<b>Aromatic amines</b>				
2-phenylmethylbenzenamine	-	33.4	-	20.5
2-methyl-N-(2-methylphenyl)-benzenamine	-	8.95	-	-
Diphenyl benzenediamine	-	300	150	207
Methyl substituted diphenyl benzenediamine	-	738	364	727
Ethyl substituted diphenyl benzenediamine	-	344	159	366
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine	1170	1790	1050	1190
N-isopropyl-N'-phenyl-p-phenylenediamine	-	44.3	-	-
<b>Benzothiazoles</b>				
Benzothiazole	23.5	70.4	67.9	44.7
Methylthiobenzothiazole	6.30	6.70	-	-
Mercaptobenzothiazole	242	437	-	-
<b>Heterocyclic amines</b>				
Dihydrotrimethylquinoline	14.6	72.5	-	7.5
Substituted quinolines	-	9.20	-	-
Substituted indoles	-	4.45	-	-
Isoindole-dione	4.25	27.9	-	11.4
<b>Phenols</b>				
Propenylphenol	-	-	-	21.7
Di(methylbenzyl)phenols	-	627	-	-
Tri(methylbenzyl)phenols	-	715	-	-
Substituted methoxyphenol	-	22.6	-	-
<b>Misc organic compounds</b>				
Benzothiazolone	-	-	-	14.3
Isothiocyanatocyclohexane	31.4	31.8	-	-
Isocyanatocyclohexane	-	-	5.25	-
Sequiterpenoid compounds	-	17.45	-	-
N,N'-diphenylguanidine	-	135	-	-
1,3-bis(methylethyl)benzene	-	5.45	-	-
1,4-dimethyl-7-(1-methylethyl)azulene	-	110	-	-
bis-1,1'-(3-methyl-1-propene-1,3-diyl)benzene	-	9.60	-	-
tert-Butyl-hydroxyanisole	-	-	146	-
Dibenzothiophene	-	-	4.20	-
Methyldibenzothiophene	-	-	11.4	-

**Note:** From Gadd & Kennedy (2000).

## 4.4 Emission Rates

### 4.4.1 Particulate Material

Based upon the information presented earlier in this section, emission rates for particulate material from tyres can be estimated based upon average wear rates. The total wear rate is dependent upon the number of tyres on the vehicle.

Table 4.11 provides a simple summary of average wear rates for vehicle classes and for the number of tyres that are likely to be present on those vehicles. It can be seen from Table 4.11 that if all other factors that determine tyre wear are ignored then a wear rate per vehicle class (dependent upon the number of tyres) can be generated. With appropriate fleet information, the overall average tyre wear can be estimated.

However, as described earlier, a variety of factors have a significant effect on the amount of tyre wear. A range of factors have been identified as having a significant influence on overall tyre wear rates. The HDM-4 model contains the most technically sound wear rate estimation available. This work was carried out in New Zealand (Cenek et al. 1993).

At this stage however, the tyre wear component in HDM-4 has not been incorporated into the VFEM-W emissions assessment process. Until the incorporation is assessed, the range of wear rates identified by Le Maitre et al. (1998) appear to provide reflect the range or spread in wear rates resulting from:

- Driving conditions (especially road geometry and acceleration/de-acceleration).
- Driven versus non-driven wheels.

However, given the complexity of wear rate physics and the importance of total energy expended to reduce speed (i.e., the vehicle speed reduction amount is important), the range of wear rate factors presented in Table 4.12 can only be considered preliminary or interim. As with brake wear, to provide some interim incorporation of these factors, the wear of tyres has been divided into the three key LoS categories to reflect driving conditions.

**Table 4.11 - Summary of total particle emissions (mg/km) from individual tyre wear and individual motor vehicles.**

Vehicle Class	Wear rate/tyre	Number of tyres/vehicle					
		2	4	6	8	12	18
Two wheelers	30	60	-	-	-	-	-
Passenger cars	30	-	120	-	-	-	-
LCVs	30	-	120	180	-	-	-
MCVs	51	-	204	306	408	-	-
Buses	210	-	-	1260	1680	2520	-
HCVs	210	-	-	1260	1680	2520	3780

Examination of the particle emission rates in Tables 4.11 and 4.12 shows that buses and HCVs produce large amounts of particles compared to light vehicles. This would seem obvious given the number of tyres per vehicle and the mass of the tyres. However, the total mass of particles emitted should be confirmed due to their likely influence on total particle emissions on certain roads.

**Table 4.12 - Summary of vehicle particle emissions (mg/km) from tyre wear under different driving conditions.**

Vehicle Class	LoS	Number of tyres/vehicle					
		2	4	6	8	12	16
Two wheelers	A/B	30					
	C/D	60					
	E/F	120					
Passenger cars	A/B		60				
	C/D		120				
	E/F		240				
LCVs	A/B		60	90			
	C/D		120	180			
	E/F		240	360			
MCVs	A/B		102	153	204		
	C/D		204	306	408		
	E/F		408	712	816		
HCVs	A/B			630	840	1260	
	C/D			1260	1680	2520	
	E/F			2520	3360	5040	
Buses	A/B			630	840	1260	
	C/D			1260	1680	2520	
	E/F			2520	3360	5040	

#### 4.4.2 Inorganic Contaminants

Based upon the available data, Table 4.13 provides a summary of median concentrations for key inorganic contaminants known to be present in tyres. This data should be considered interim only. The inorganic contaminant concentration data for tyre wear can be used along with the estimated wear rates identified earlier to calculate the total wear particle loss from the motor vehicle as follows.

**Inorganic contaminant emission losses from tyre wear can be calculated as:**

Tyre wear emission within a given section of road (mg)/unit time period =

VKT/unit time period x particle emission rate (mg/km) (Table 4.12) x  
median concentration (ng/mg) (Table 4.13)

The final on-road contribution is determined by multiplying the emission load by the factor presented in Section 9.

**Table 4.13 - Summary of concentrations of selected elements in tyres for use in calculating contaminant emission loads (all concentrations mg/kg or ng/mg).**

Element	Median tyre concentration
<b>COPC</b>	
Antimony	<0.2
Cadmium	0.19
Chromium	<1
Copper	1
Lead	2.7
Mercury	<0.01
Molybdenum	1
Nickel	1
Silver	<0.2
Tin	<0.5
Zinc	8310
<b>Others</b>	
Barium	26
Iron	105

#### 4.4.3 Organic Contaminants

Based upon the available data, Table 4.14 provides a summary of median or selected concentration data for key organic compounds in tyres. As with the inorganic components, this data should be considered interim only. To provide more suitable data to assess emissions of organic contaminants from this source additional information and refinement of data is required as identified above in Section 4.4.2 and below in Section 4.4.4.

**Table 4.14 - Summary of concentrations of selected organic compounds in tyres for use in calculating emission loads (all concentrations mg/kg).**

Compound	Median tyre concentration
<b>COPC</b>	
Benothiazole	44.7*
Pyrene	42.6*
Polycyclic aromatic hydrocarbons	226.1**
Chlorinated organics	5.3**
<b>Others</b>	
n-Alkanes	18842**
n-Alkanoic acids	12197**
n-Alkenoic acids	1279**
Substituted benzaldehydes	7.8**
Benzoic acids	74.8**
Polycyclic aromatic ketones and quinones	0.45**
Pentacyclic triterpanes	684**
Benzaldehydes	19.04**
Natural resins	9513**
Regular steranes	74.2**
Amide (4-phenylbenzamine)	12.9**

**Note:** \* From Gadd & Kennedy (2000); \*\* from Rogge et al. (1993).



The Gadd & Kennedy (2000) data is based on the examination of the tread of a limited number of new tyres. For the other organic compounds the data of Rogge et al. (1993) is used to provide initial data. As with inorganic contaminants, the emitted load of individual organic compounds can be calculated using the same approach as described earlier in this section.

#### 4.4.4 Overview

To provide more suitable data to predict contaminant emissions from motor vehicle tyres the following is required.

1. Confirmation of any differences in composition between tyres used by different vehicle classes.
2. Confirm that there are no significant differences between brands of similar tyre types (mainly for passenger car tyres).
3. Calculate vehicle fleet or fleet component average concentration data based on selected tyres that are representative of the fleet tyre use. As discussed in this section of the report this is particularly important for zinc and PAHs.

## 5. OIL, GREASE & LUBRICANTS

### 5.1 Introduction

As described in Moncreiff et al. (2002), there are a variety of oils, greases and lubricants used in motor vehicles. These materials reside in various components of the vehicle power train. An overview of these sources indicates that most are not lost as part of the routine operation of the vehicle. As failure of vehicle components is not considered in the VFEM-W at this stage, loss of material from hoses resulting from hose rupture is not considered.

This section of the report presents information on the general nature and composition of oil, grease and lubricants in vehicles. Specific information on the inorganic and organic contaminant concentrations present is presented where available. This information is used to provide an indication of the most appropriate data to use for estimates of contaminant loadings from these sources where the source is considered to contribute contaminants to the road surface.

### 5.2 Lubricating Oils

#### 5.2.1 Use

Lubricating oils are used in a vehicle engine to lubricate the moving engine parts to reduce friction, minimise wear and tear and maximise performance. Lubricating oils also maintain engine cleanliness, protect against engine rust and corrosion, cool engine parts, seal combustion gases and permit easy starting.

The vehicle user adds lubricating oils to the engine when levels are low, as indicated by the dipstick. Lubricating oils are readily available in service stations, some supermarkets and hardware stores and in automotive parts shops.

#### 5.2.2 Oil Composition

##### 5.2.2.1 General

Lubricating oils comprise a base oil stock with additives. Conventional base stocks are mineral oils, derived from refining crude petroleum. These mineral oils are characterised as paraffinic, naphthenic or intermediate. Semi-synthetic motor oils substitute some of the mineral oil with synthetic base fluids, which are special fluids manufactured with the balanced properties needed to produce a premium motor oil. In a fully synthetic motor oil, the mineral base oils completely replaced with synthetic base fluids such as:

- ❑ Synthesised hydrocarbons – for closer control of compositional ranges.
- ❑ Olefin oligomers – polybutenes, polyalphaolefins (C<sub>10</sub> to C<sub>14</sub> olefins).
- ❑ Alkylated aromatics – mainly alkyl benzenes, with the alkyl chain tetrapropylene.
- ❑ Organic acid esters – e.g., di-esters, phthalate esters, polyol esters such as pentaerythritol, tri-methylol-propane esters.
- ❑ Polyglycols - e.g., polyalkylene-oxides.
- ❑ Silicones, silicate esters and halogenated hydrocarbons

The most widely referred to automotive lubricating oil (sump oil) classification system was introduced by the API, in conjunction with ASTM and SAE (ref. SAE Standard J 183). This is an open ended series of service grades, with the prefix “S” for gasoline engine oils and “C” for diesel, followed by the letter A, B, C etc. indicating improved performance requirements. As newer service grades develop, the earlier grades become obsolete. Oils in current use are typically of SG/SH grades for petrol engines, and CD to CG for

diesels, with a trend towards multi-purpose formulations that conform to the requirements of service grades of both series e.g., SG/CE, SH/CF.

There are many other oil classification systems in force, from manufacturers' own specifications, through military standards, to other global/regional standards (CCMC, ACEA, EELQMS, JASO etc.). Lubricating oils are largely formulated and certified by a complex series of specified engine tests, which makes the process expensive, and makes it difficult to compare the performance of oils across different engine designs, and their consequent approval. Lately, there has been the development of the International Lubricant Standardisation and Approval Committee (ILSAC), led by the MVMA, AAMA and JAMA, in an attempt to set and regulate global lubricant specifications. However, it will be some time before such harmonisation is fully achieved for all service categories. For the time being, the API Engine Service classes provide the best general framework of reference.

Most lubricating oils contain additives, typically designed to affect the properties of viscosity, volatility, stability, cleanliness and cold flow. The specific additives vary from oil to oil, under the blender's proprietary control. Examples of the types of additives in use based upon their function are in Table 5.1. Additive packages in today's oil qualities can account for around 10 to 14% by mass of the oil (Table 5.2).

**Table 5.1 - Examples of additives in oils and their function.**

Class	Function	Example Constituents
Viscosity Improver	Improves viscosity temperature characteristics	olefin copolymers (C <sub>2</sub> to C <sub>4</sub> ), polymethacrylates, styrene-butadiene copolymers, polyisoprene (hydrated)
Pour Point Depressant	Improves low temperature flow properties	polyesters
Anti Oxidant	Helps prevent engine deposits, sludge, high temperature thickening	amines, substituted phenols, copper (low levels, 100 mg/L), zinc, calcium, barium and/or magnesium salts, including carbamates, salicylates, thiophosphates, phenates and sulphonates
Detergents	Helps maintain engine cleanliness	sulfurised metal (sodium, calcium, magnesium) phenates, metal salicylates, thiophosphonates
Dispersants	Helps maintain engine cleanliness	metal soaps (sulfonates), succinimides
Rust inhibitors	Helps prevent engine corrosion	overbased sulfonates, ethoxylated phenols, substituted succinic acids, triazoles, thiodiazoles
Anti wear agents	Helps prevent wear	ZDDPs; (zinc dialkyl/diaryldithiophosphates), sulphur, chlorine and/or phosphorus compounds, lead.
Anti foam agents	Reduces foaming and air in oil	silicon oil, organic co-polymers

**Table 5.2 - Additives in oils (% mass).**

Additive, % mass	SE/CD	API Service Grade	
		SG/CE	SH/CG-4
Ashless Dispersant	5.5	6.0	7.5
Overbased sulfonate	3.0	2.0	2.0
Overbased phenate	2.0	2.0	2.0
Anti-oxidant	-	0.3	0.6
ZDDP*	2.0	1.0	1.3

**Note:** \* ZDDP = zinc dialkyl/diaryldithiophosphates

### 5.2.2.2 Inorganic Constituents

Oil inorganic composition is determined by both the source of the oil (either synthetic or natural) and by design. New motor oils contain a number of metals from additives including calcium, magnesium, barium and zinc (Zięba-Palus 1998; Zięba-Palus & Kościelniak 2000). Used oils contain aluminium, antimony, arsenic, barium, cadmium, calcium, chromium, cobalt, copper, lead, magnesium, manganese, mercury, nickel, phosphorus, silicon, sulphur and zinc (US DOE 1987) (concentration data were not provided by that reference).

Concentrations of metals in 15 unused oil samples ranged from a mean of 630 to 1360 mg/kg of zinc, 1000 - 2140 mg/kg calcium and 14 - 997 mg/kg magnesium (Zięba-Palus & Kościelniak 2000). Concentrations of these and other metals are presented in Tables 5.3 and 5.4 below from a study by Zięba-Palus (1998) where two types of oil were placed into two separate cars and oil samples were drained from the sump after a number of kilometres. This study was conducted in Kraków, Poland. Concentrations of magnesium, cadmium, copper, iron and lead in the oil increased with distance travelled. Barium concentrations did not increase and varied by a factor of three between the oils, due to their composition (amount of barium containing additives). Copper and lead concentrations were initially very similar between the two oils, however after use the concentrations were significantly higher in the Lotos 15W/40 oil. This may be due to differences in materials and corrosion in the car engines used in the test.

**Table 5.3: - Elemental concentrations of fresh and used Lotos 15W/40 motor oil (mg/kg, Zięba-Palus 1998).**

Distance travelled (km)	Ca	Mg	Ba	Cd	Cu	Fe	Pb	Zn
0	5084	16	27.3	0.15	0.46	1.29	2.80	2117
5	3908	179	30.6	0.76	5.7	18.2	424	1939
600	3442	196	34.5	1.13	21.4	36.7	793	1690
1000	3409	199	35.7	1.17	27.0	37.9	905	1648
1550	3399	240	36.9	1.20	33.7	47.7	1077	1627
2000	4065	307	37.1	1.27	34.7	88.0	1522	1945
3000	4120	320	37.6	1.28	34.7	97.7	1775	1971
5000	4132	325	37.9	1.29	34.7	102.9	1799	2011

**Table 5.4: - Elemental concentrations of fresh and used Castrol GTX motor oil (mg/kg, Zięba-Palus 1998).**

Distance travelled (km)	Ca	Ba	Cu	Fe	Pb	Zn
0	1100	90	0.5	1	3.2	1320
1000	1200	80	1.0	10	10.8	1200
4000	1280	95	1.0	31	10.7	1150
6000	1400	98	2.5	48	15.9	1020

Metal concentrations in used car oil were reported in Kingett Mitchell (1994) and are presented in Table 5.5. Cadmium concentrations are slightly lower than the concentrations reported by Zięba-Palus (1998) for oil after at least 600 kilometres travel. Lead concentrations are slightly higher than reported in Lotos 15W/40 and significantly higher than Castrol GTX as reported by Zięba-Palus (1998). The lead concentrations in the New Zealand used oil may be influenced by the leaded petrol used at the time. Mercury and arsenic concentrations were less than 0.5 mg/kg in New Zealand used oils and not analysed by Zięba-Palus (1998).

**Table 5.5: - Metals in used oil in New Zealand (data in mg/kg).**

<b>Metal</b>	<b>Used Oil from Petrol Cars (Kingett Mitchell 1994)</b>	<b>Used Oil (MfE 2000)</b>
Arsenic	<0.5	<0.5
Cadmium	<1	1
Chromium	-	4.6
Copper	-	105
Lead*	2,510-3,160*	71
Mercury	<0.5	1

**Note:** (\*) these analyses were carried out when lead was still added to petrol; all petrol sold at petrol stations is now unleaded in New Zealand.

### 5.2.2.3 Organic Compounds

The organic composition of used motor oil in New Zealand has been described by Kingett Mitchell (1994) and Opus (1997). Both reports present the information in Table 5.6 as an indicator of the composition of used oils in NZ, as analysed from a range of samples. The PAH content of used oil has been reported as 110 mg/kg (Colwill et al. 1984).

USDOE (1987) reports that the principle contaminants in used oil are aromatics (benzene, toluene and xylenes); PAHs (benz(a)anthracene, benzo(a)pyrene, naphthalene and others) and chlorinated organics (dichlorodifluoromethane, trichlorotrifluoroethane, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene and polychlorinated biphenyls).

**Table 5.6: - Summary of used oil composition (all data mg/kg).**

<b>Element/Compound</b>	<b>Petrol Car (Kingett Mitchell 1994)</b>	<b>Mixed Petrol/Diesel Car (Kingett Mitchell 1994)</b>	<b>Used Oil (MfE 2000)</b>
Benzene	171-364	165	-
Toluene	897-2,200	867	-
Ethylbenzene	288-929	283	-
p,m-xylene	605-1,370	617	-
o-xylene	528-1,400	544	-
Naphthalene	122-420	69	125
Acenaphthylene	7	4	-
Acenaphthene	3-4	3	-
Fluorene	25-31	29	-
Phenanthrene	79-129	102	-
Anthracene	14-18	17	-
Fluoranthene	21-23	20	-
Pyrene	50-61	52	-
Benzo[a]anthracene	8-9	8	-
Chrysene	8-9	9	-
Benzo[b +k]fluoranthene	8-10	9	-
Benz[a]pyrene	5-6	4	-
Indeno[1,2,3-cd]pyrene	3-4	3	-
Dibenz[a,h]anthracene	<1	<1	-
Benzo[g,h,i]perylene	15-18	14	-
Total PAHs (sum of above compounds)	369 - 750	344	204
PCBs	-	-	<0.5

### 5.3 Oil Consumption

Oil consumption in motor vehicles occurs through oil contamination and oil loss. Oil becomes contaminated through engine wear and impurities from combustion processes. Over time, the oil becomes more contaminated and needs to be changed. The time between oil changes is recommended by vehicle manufacturers and, ranges from 10,000 to 15,000 km for passenger cars and 5,000 to 20,000 km for heavy duty diesels. Oil loss occurs through carry over into the combustion zone (valve stems, piston rings), as well as through leaks and faulty seals during both vehicle operation and when not in use. Conversely, fuel dilution of the oil, at the piston ring interface, can offset the apparent rate of loss. These will vary with the engine operating conditions.

Oil consumption rates have been economised significantly in recent years, with improved engine design and more sophisticated oil formulations that rely less on top-ups to maintain performance, together with extended drain periods. Oil consumption is usually regarded as a function of fuel consumption, which has typically improved from 0.5% to 0.05% and lower. Typical consumption factors are:

- For light duty petrol vehicles, the sump fill of around 4 to 5 litres will carry a drain period of 10 to 15,000 km, with an oil consumption rate of 0.1 litre/1,000 km (i.e., 0.1 mL/m).
- For heavy duty diesels, sump fill volumes vary greatly, as with the size of engines to be found, from typically 10 to 50 litres, and oil change periods from 5,000 km sometimes up to 20,000 km.

Oil consumption models have been developed based on operating conditions (CRRRI 1982); road conditions (Watanatada et al. 1987, Kadiyali 1991); speed (Schutte 1981) and both operation and oil contamination (Pienaar 1984, Bennett & Greenwood 2001).

CRRRI (1982) related oil consumption to roading conditions, such as gradient, width and roughness. The study found significant effects due to different drivers (i.e., mode of driving).

Watanatada et al. (1987) proposed the model for HDM-III, which relates oil consumption to road roughness (vertical displacement of the car in metres, per kilometre of road travelled).

$$OC = a_0 + a_1.RI$$

where OC is oil consumption in L/1000 km and  $a_0$  and  $a_1$  are coefficients and RI is the adjusted roughness in m/km (adjusted from IRI - international roughness index).

Kadiyali (1991) also included rise and fall of the road and pavement width in his model of oil consumption:

$$OC = a_0 + a_1.RF + a_2.(RI / W)$$

where RF is rise and fall in m/km and W is the pavement width in m.

Schutte (1981) developed findings by Claffey (1971) that travel speed influences oil consumption into the model:

$$OC = a_0 + a_1.S$$

where S is speed.

Peinaar (1984) further developed this relationship by disaggregating oil consumption into those due to contamination and those due to loss. Oil loss is a function of engine speed and is proportional to fuel consumption, with a different rate for petrol and diesel vehicles. This work was adapted for the HDM-4 model, where operational losses are a function of fuel consumption and the contamination is a function of distance between oil changes and oil capacity. The HDM-4 model is:

$$OIL = OILCONT + OILOPER.SFC$$

where OIL is the oil consumption, OILCONT is the oil loss due to contamination, OILOPER is the oil loss due to operation and SFC is the fuel consumption, all measured in L/1000 km. The model parameters used in the HDM-4 model are in Table 5.7.

**Table 5.7 - HDM-4 oil consumption model parameters (Bennett 1996a).**

NZTER Class	HDM-4 Class	Distance between oil changes (km)	Engine oil capacity (L)	Rate of oil contamination (OILCONT) (L/1,000 km)	Oil loss due to operation (OILOPER) (L/1,000 km)
Two wheelers	Motorcycle	5,000	2.0	0.40	0.0014
Car <1350 cc	Small Car	10,000	4.0	0.40	0.0028
Car 1350– 2000 cc	Medium Car	10,000	4.0	0.40	0.0028
Car > 2000 cc	Large Car	10,000	4.0	0.40	0.0028
LCVs <1350cc	Light Delivery Vehicle	7,500	5.0	0.67	0.0028
LCVs 1350 - 2000cc	Light Goods Vehicle	7,500	5.0	0.67	0.0028
	Four Wheel Drive	7,500	5.0	0.67	0.0028
LCVs > 2000 cc	Light Truck	9,000	14.0	1.56	0.0021
All MCvs	Medium Truck	9,000	14.0	1.56	0.0021
HCVs 12.1 – 20.0 t	Heavy Truck	10,000	31.0	3.10	0.0021
HCVs >20.1	Articulated Truck	10,000	31.0	3.10	0.0021
12	Mini Bus	7,500	5.0	0.67	0.0028
Bus < 3.5 t	Light Bus	8,000	14.0	1.75	0.0021
Bus 3.5 – 7.5 t	Medium Bus	8,000	14.0	1.75	0.0021
Bus >7.5 t	Heavy Bus	8,000	20.0	2.50	0.0021
Bus >7.5 t	Coach	8,000	20.0	2.50	0.0021

### 5.3.1 Oil Emission Factors

#### 5.3.1.1 General

The oil's performance deteriorates with service life, through additive depletion as the oil becomes progressively contaminated with engine metal wear materials and the products of the fuel's combustion process. It is this composition that must be considered within the requirements of this study, as the oil is a continuous contributor to the exhaust emission and directly to the road through oil leaks. The main concern over the potential toxicity of used lubricating oil comes from its contamination with the aromatic products from fuel and partially burnt fuel dilution, especially the PAH/particulate loading from combustion. There are also wear metals present (in particular iron, copper, lead and cadmium) and breakdown derivatives of the original additive packages.

#### 5.3.1.2 Loss rates

The loss rate adopted for this assessment of emissions is taken from the oil loss due to operation from the HDM-4 model (OILOPER). This represents the amount of oil that is lost to the road, whereas the total oil consumption includes oil removed during oil changes and disposed of elsewhere.

For cars and most LCVs, HDM-4 suggests an oil loss of 2.8 mL/1,000 km and for the largest LCVs, HCVs and most buses it suggests 2.1 mL/1,000 km.

#### 5.3.1.3 Inorganic Contaminants

The emission factors in Table 5.8 below are calculated from oil loss rates multiplied by metal concentrations in used oil to result in emission factors for barium, cadmium, copper, iron, lead and zinc

(Table 5.8). A specific gravity for motor oil of 0.89 g/mL is used in the calculations, based on the specific gravity of Castrol GTX 20/50 (0.892 g/mL) and other GTX products (0.88 g/mL) (Castrol Oil, pers comm 30/11/2001).

The oil loss rates used were 2.8 mL/1,000 km for cars and LCVs and 2.1 mL/1,000 km for HCVs and buses (taken from the HDM-4 model). The concentration of metals in the oil is taken from Table 5.4 after 4000 km travelled (as this is halfway through the oil change cycle). This data is used in preference to Table 5.3 (Lotos 15W/40 oil), as Castrol GTX is commonly used in New Zealand. Cadmium concentrations were taken from Table 5.3, in the absence of data for oils used in New Zealand. A distance travelled of 5,000 km is used. Arsenic, chromium and mercury concentrations were taken from New Zealand used oil data in the absence of other data. This may over-estimate the emissions as this oil is used, whereas oil leaks occur throughout the lifetime of a vehicle when contamination is expected to be lower.

**Table 5.8 - Emission factors for key inorganic contaminant losses associated with engine oil loss ( $\mu\text{g}/\text{vehicle}/\text{km}$ ).**

<b>Element</b>	<b>Car and LCVs</b>	<b>HCVs and Buses</b>
<b>COPC</b>		
Arsenic	<0.0012	<0.0009
Cadmium	0.0032	0.0024
Copper	0.0025	0.0019
Chromium	0.0011	0.00086
Lead	0.027	0.020
Mercury	<0.0012	<0.0009
Nickel	No data	No data
Zinc	2.9	2.1
<b>Others</b>		
Barium	0.24	0.18
Iron	0.077	0.058

The emission factors above depend on the composition of the oil, in particular the amount of barium and zinc included as additives. Further New Zealand data on used oil composition would be required to increase the confidence in these emission factors. Additional trace elements can be added if required.

**Inorganic contaminant losses associated with engine oil loss can be calculated as:**

Engine oil emission within a given section of road ( $\mu\text{g}$ )/unit time period =

VKT/unit time period x emission rate ( $\mu\text{g}/\text{VKT}$ ) (Table 5.8)

The final on-road contribution is determined by multiplying the emission load by the factor presented in Section 9.

#### 5.3.1.4 Organic Contaminants

The emission factors for organic compounds (Table 5.9) have been calculated as for the metals above, however emission factors have only been calculated for key aromatic compounds and for PAHs, as data is considered insufficient for any other compounds. As above, a specific gravity for motor oil of 0.89 g/mL is used in the calculations and oil loss rates of 2.8 mL/1,000 km for cars and LCVs and 2.1 mL/1,000 km for HCVs and buses.



The concentration of PAHs in car emissions is taken from Table 5.6, for petrol cars. A concentration in the middle of the reported range (369 - 750 mg/kg) is used (560 mg/kg). This is likely to overestimate the PAH emissions from engine oil loss as these analyses were of used oil collected during oil changes (and therefore with maximum contamination), whereas oil leakage occurs through the life of the oil, including when PAH concentrations are lower. The concentrations of PAHs in HCV and bus emissions are taken from Table 5.6, for mixed petrol/diesel cars (344 mg/kg). The other data in Table 5.6 is from a single oil sample and is not used.

**Table 5.9 - Emission factors for key aromatics and PAHs from engine oil loss ( $\mu\text{g}/\text{vehicle}/\text{km}$ ).**

<b>Compound</b>	<b>Car and LCVs</b>	<b>HCVs and Buses</b>
<b>COPC</b>		
Benzene	0.67	0.31
Toluene	3.86	1.62
Ethylbenzene	1.52	0.53
p,m-xylene	2.46	1.15
o-xylene	2.40	1.02
Naphthalene	0.68	0.13
Acenaphthylene	0.017	0.007
Acenaphthene	0.009	0.006
Fluorene	0.070	0.054
Phenanthrene	0.26	0.19
Anthracene	0.04	0.03
Fluoranthene	0.05	0.04
Pyrene	0.14	0.10
Benzo[a]anthracene	0.021	0.015
Chrysene	0.021	0.017
Benzo[b +k]fluoranthene	0.022	0.017
Benz[a]pyrene	0.014	0.007
Indeno[1,2,3-cd]pyrene	0.009	0.006
Dibenz[a,h]anthracene	<0.002	<0.002
Benzo[g,h,i]perylene	0.04	0.03
Total PAHs	1.4	0.64
<b>Others</b>		

PAHs emissions factors for lubricating oils have previously been estimated at  $1.45 \mu\text{g}/\text{vehicle}/\text{km}$  (Westerholm et al. 1988).

**Organic contaminant losses associated with engine oil loss can be calculated as:**

Engine oil emission within a given section of road ( $\mu\text{g}$ )/unit time period =

VKT/unit time period x emission rate ( $\mu\text{g}/\text{VKT}$ ) (Table 5.9)

The final on-road contribution is determined by multiplying the emission load by the factor presented in Section 9.

## 5.4 Greases

### 5.4.1 Use

Grease is used for chassis joint lubrication, bearings (especially wheel bearings) and in the powertrain. They act as a semi-fluid lubricant, such that it stays in place when compared with a liquid lubricating oil. They generally comprise a solid thickener mixed with liquid oil, with modern formulations also containing a number of sophisticated additives to improve their performance. The most common global specification reference is the SAE J310 Recommended Practice, in association with the NLGI and ASTM. This sets out the properties required for the main NLGI grease service classes, of which there are two for chassis service (LA, LB) and three for wheel bearings (GA, GB, GC).

### 5.4.2 Composition

Common soap based greases are a combination of alkali metals; calcium, sodium, lithium or barium with fatty acids (palmitic, stearic and tall oil acids) to form the corresponding metal soap as the thickener, then mixed with a petroleum oil. A widely used base is the lithium salt of 12-hydroxy stearic acid. Complex soaps may use a range of (lower) carbon number carboxylic acids, saponified with the same metal, or inorganic salts such as carbonate, chloride, phosphates, borate. Many additives can be employed to improve the performance of the grease over its base oil plus thickener composition; possible functions include:

- ❑ Anti-corrosion – metal corrosion/rust inhibitors.
- ❑ Metal deactivators.
- ❑ Oxidation inhibitors.
- ❑ Film strength/lubricity/anti-wear/EP.
- ❑ Viscosity modifiers.
- ❑ Water repellents.
- ❑ Dyes, odorants.

Solid inorganic materials are also used as thickeners, such as treated clay (bentonite), silica aerosol and carbon black, in spherulite or platelet form. Substituted ureas and polyureas have become used lately as thickeners in greases for heavy-duty CV joints. Pigments such as phthalocyanines have also been used.

The fluids used are petroleum oil compounds (such as esters), polyolefins, alkylates, polyglycols, polyphenol ethers, polyhalocarbons and silicone fluids are used, usually in association with the solid inorganic thickeners. It is likely that more synthetic based greases will be used in the future, in high performance bearing conjunctions, with petroleum-based greases remaining for general purpose use.

### 5.4.3 Emission Factors

CRRRI (1982) collected data and developed models for grease consumption, however the quantity of these lubricants is so small (consumption per 10,000 km instead of per 1,000 km for engine oil) that it is not considered in other models.

The emissions from this source can be presented in terms of fuel, total hydrocarbons or specific COPCs if required. However, as the loss is considered relatively minor, its inclusion in modelled emission loads is seen as secondary at this stage and could be added to VFEM-W later.

## 5.5 Other Oils

### 5.5.1 Gear Oil

Gear oil is the lubricating oil that is used in a vehicle's gear box to reduce friction and extend the life of the gears. Gear oils are traditionally petroleum derived with synthetic oils becoming more common. Base oil stocks typically contain pour point depressants as necessary, and VI modifiers particularly for multigrade oils. Synthetic stocks are now being used also to formulate wide multigrade gear oils.

The API classification system is the most universal recognised, referred to in the SAE J308 Recommended Practice, originally containing six quality designations relating to the type of gear design. High load carrying ability is required in these conjunctions, requiring special EP compounds to be added to the base mineral oil (which itself conforms to the varying SAE viscosity classifications). Substances that have been used include;

- ❑ Sulphurised fats and fatty esters.
- ❑ Sulphurised olefins and polyolefins.
- ❑ Dialkyl disulfides.
- ❑ Sulfochlorinated olefins.
- ❑ Chlorinated hydrocarbons.
- ❑ Tributylphosphate.
- ❑ Phosphites, phosphonates and phosphoric esters.
- ❑ Phosphorised fats and synthetic fats.
- ❑ ZDDP – zinc dialkyl dithiophosphates.
- ❑ Amine dithiophosphates.
- ❑ Triazoles, thiadiazoles.

As well as EP improvers, additives may also be used for anti-rust, dispersants, friction modifiers and metal deactivators.

### 5.5.2 Automatic Transmission Fluids

Automatic Transmission Fluids (ATFs) are typically formulated to particular manufacturer specifications (e.g., GM – DEXRON, Ford – MERCON etc.). The Society of Automotive Engineers (SAE) provide a reference in the SAE J1285 Recommended Practice. A universal ILSAC ATF standard is under development between the AAMA and JAMA.

ATFs are normally petroleum based, with a complex blend of additives. For example:

- ❑ Oxidation inhibitors – zinc dialkyl dithiophosphates (ZDDPs), hindered phenols, amines and sulfurised compounds.
- ❑ Metal Deactivators – ZDDPs, sulfides and nitrogen compounds.
- ❑ Corrosion inhibitors – ZDDPs, phenates and sulfonates.
- ❑ Rust inhibitors – organic acids, amines, sulfonates.
- ❑ Anti-wear – ZDDPs, organic phosphates, sulfurised/chlorinated compounds, amines.
- ❑ Viscosity modifiers – many different polymers, polyesters.
- ❑ Dispersants – succinimides, thiophosphonates.
- ❑ Friction modifiers – fatty oils, fatty acids and amides, organic phosphorus acids/esters.

### 5.5.3 Hydraulic Oils

Hydraulic fluids fall into two classes:

1. Synthetic chemicals of polyalkylene glycol or borate ester type, such as for braking systems;

2. Inhibited mineral oils for pressurised systems, such as suspension fluids.

Certain formulations also include oil/water emulsions and phosphate esters, polyethers and polyesters.

#### 5.5.4 After Market Oil Additives

After market additives such as Power-Up and MolySlip etc., are usually hydrocarbon carrier for miscibility with the fuel or oil to which it is added, with various mixes of detergents/dispersants and EP lubricating agents. Mo<sub>2</sub>S (molybdenum disulphide) is a common ingredient.

#### 5.5.5 Loss and Emission Factors

CRRRI (1982) also developed models for consumption of gear, differential, brake and steering oils and grease. The quantity of these lubricants is so small (consumption per 10,000 km instead of per 1,000 km for engine oil) that it was not considered in other models.

Lubricant losses to the road from these other oils are not considered a significant factor in the overall assessment of vehicle emission contaminant loads. The emissions from this source can be presented in terms of fuel, total hydrocarbons or specific COPCs if required. However, as the loss is considered relatively minor, its inclusion in modelled emission loads is seen as secondary at this stage and can be included in the VFEM-W model later.

## 6. COOLANTS & RADIATOR LEAKAGE

### 6.1 Introduction

A number of products can be added into a vehicle cooling system including coolants, corrosion inhibitors and stop-leak formulations. The purpose of engine coolant is to maintain engine block temperatures within closely controlled ranges. Whilst water is an effective heat transfer fluid, it has particular shortcomings acting alone as an engine coolant; it freezes at too high a temperature, boils at too low a temperature and causes corrosion of common cooling system materials. For improved operating temperature range, coolants (also known as anti-freeze) are used. Glycols are typically used, comprising 40 to 60% of the coolant mix with water. Ethylene glycol (or monoethylene glycol) is the industry standard (and is considered to be biodegradable); others include diethylene glycol and propylene glycol.

Radiator corrosion inhibitors are designed to protect metal surfaces from corrosion, rust, scale build-up and cavitation erosion. Stop-leak formulations are available in the after-market, for “band-aid” type repair of cooling system leaks. The active components are usually small pieces of natural fibres, vegetable or inorganic, in a carrier fluid.

### 6.2 Composition

The fully formulated coolant also contains corrosion inhibitors, foam suppressor and marking dye. Typical inhibitors may include borates, phosphates, nitrites, nitrates, silicates, mercaptobenzothiazole, tolyltriazole and benzotriazole. A number may be included in a particular balanced formulation to protect the various metals present in the cooling system. For this reason, the recommended coolant formulation is often specified by the engine manufacturer, particularly for heavy-duty diesel vehicles. Engines with extensive use of aluminium may use coolants with elevated levels of silicates. These additives are also designed to keep the coolant in an alkaline condition to neutralise acid products that may form. Anti-foamants are usually higher alcohols or similar surfactant type organics, that affect the surface tension of the liquid and cause any bubbles to break. In addition to the above components, used coolants may contain benzoate, mineral oil, amines, nitrosoamines and heavy metals (Pb, Fe, Cr, Zn, Sn, Cu) (Jehle et al. 1995).

### 6.3 Losses

Losses of coolant into the environment occur through leaks and overflows from the cooling system. Radiator leaks are common in older and badly maintained vehicles, but are rare in new vehicles. No quantitative information appears available in relation to the frequency or volume of radiator overflow.

No information appears available in relation to the amount and frequency of condensation losses from vehicle air-conditioning systems.

### 6.4 Emission Rates

Although, the model has a specific sub-unit to account for radiator coolant losses, these losses to the road are not considered to be a significant factor in the overall assessment of vehicle emission contaminant loads. As the loss is considered relatively minor, its inclusion in modelled emission loads is seen as secondary, but could be included in the VFEM-W model at a later stage.

## 7. EXHAUST SYSTEM EMISSIONS

### 7.1 Introduction

Almost all vehicles currently in the vehicle fleet rely on an internal combustion engine that burns fuel including petrol, diesel, CNG and LPG. The engines operate by burning fuel within the cylinders and converting the expanding force of the combustion or "explosion" into rotary force used to propel the vehicle. Combustion of the fuel produces carbon dioxide, water and pollutants such as carbon monoxide, nitrogen oxides, sulphur oxides and particulate matter (PM). These gases and any un-burnt fuel are then released from the combustion chamber into the exhaust manifold and out through the exhaust system.

Of all the source emissions, exhaust emissions are most extensively investigated with emission controls and emission standards applied in many countries. In most cases, this relates to the emissions of gases (carbon monoxide, nitrogen oxides, sulphur oxides) and particulate matter in relation to air quality. There is less information available that is relevant to stormwater quality issues, such as emissions of trace elements and the more complex organic compounds.

### Estimating emissions

There have been a variety of methods used to estimate the emissions from motor vehicles. As it is not possible to measure the emissions from every vehicle using a section of road, the emissions must be estimated. As described in MoT (1998), all emission models use some of mathematical estimation to attempt to mimic vehicle emission behaviour. Clark et al. (2003) identified a number of approaches that have been used for the estimation of exhaust emissions from heavy-duty vehicles. These included:

1. Use of emission certification data which, provided emissions in grams per brake horse power hour (then converted to g/unit distance). This approach is used in USEPA MOBILE6 and CARB EMFAC7.
2. Use of chassis dynamometer data in g/unit distance.
3. Use of power based emission factors allows emissions to be modelled under a variety of operating conditions.
4. Use of NO<sub>x</sub>/CO<sub>2</sub> ratios.
5. Use of modal approaches (e.g., idling, accelerating etc., in contrast to the use of continuous data) provides a simplified means of modelling emissions.
6. Use of speed- acceleration data (which is similar to modal and modelling approaches). Speed and acceleration are determinands of inertial power demand.

Clark et al. (2003) discuss these approaches in detail and in particular the last approach in relation to emissions of key gases and PM. The VFEM and NZ-TER (MoT 1998, Moncrieff & Irving 2001) uses an approach based upon combining the effect of engine technology (type and fleet structure), road design (four road types) and driving conditions (four key types) to estimate particulate emissions as PM<sub>10</sub> in g/km.

The factors that influence vehicle emissions are complex and have been reviewed extensively elsewhere (e.g., Faiz et al. 1996; Coffey Associates 2000). The inset box on the following page provides an overview of those factors.

## **Factors influencing the emissions from motor vehicle exhausts (from Fiaz et al. 1996)**

### **1. Vehicle/Fuel Characteristics**

- Engine type and technology - two-stroke, four-stroke; Diesel, etc.; fuel injection, turbo-charging, and other engine design features; type of transmission system.
- Exhaust, crankcase, and evaporative emission control systems in place - catalytic converters, exhaust gas re-circulation, air injection etc.,
- Engine mechanical condition and adequacy of maintenance.
- Air conditioning, trailer towing, and other vehicle appurtenances.
- Fuel properties and quality—contamination, deposits, sulfur, distillation characteristics, composition (e.g., aromatics, olefin content) additives (e.g., lead), oxygen content, gasoline octane, diesel cetane.
- Alternative fuels.
- Deterioration characteristics of emission control equipment.
- Deployment and effectiveness of inspection/maintenance (I/M) and anti-tampering (ATP) program.

### **2. Fleet Characteristics**

- Vehicle mix (number and type of vehicles in use).
- Vehicle utilisation (km/vehicle/year) by vehicle type.
- Age profile of the vehicle fleet.
- Traffic mix and choice of mode for passenger/goods movements.
- Emission standards in effect and incentives/disincentives for purchase of cleaner vehicles.
- Adequacy and coverage of fleet maintenance programs.
- Clean fuels program.

### **3. Operating Characteristics**

- Altitude, temperature, humidity (for NO<sub>x</sub> emissions).
- Vehicle use patterns - number and length of trips, number of cold starts, speed, loading, aggressiveness of driving behaviour.
- Degree of traffic congestion, capacity and quality of road infrastructure, and traffic control systems.
- Transport demand management programs.

## **“Exhaust emissions”**

### **Gaseous emissions**

This section of the report does not deal with “evaporative” emissions or crankcase emissions. Faiz et al. (1996) notes that there is no standard procedure for estimating crankcase emissions. Uncontrolled crankcase emissions have been estimated through the measurement of VOC concentrations in blow-by gases. On vehicles with closed crankcase ventilation systems, the crankcase emissions are assumed to be zero (Faiz et al. 1996). Evaporative emissions occur during refuelling and from the carburettor at

times following engine shut-down when the engine is hot. Evaporative emissions involve VOCs. Neither source are included in the estimation of contaminant emissions in this section of the report. As VOCs are the predominant contaminant group involved in evaporative emissions, their exclusion does not have any influence on the emission factors for other semi-volatile or particulate contaminants.

This section of the report presents information on the nature and composition of the primary fuels petrol and diesel. Specific information on the inorganic and organic contaminant concentrations present in both the fuel and the combusted exhaust emission is presented. As discussed later in this section, information on contaminant emissions is available for the exhaust stream and also for contaminants present on particulate matter in the exhaust. In this overview of emission factors, information on the two alternative approaches is presented. The emissions per km travelled are provided to allow comparative calculations with other sources of emission. In addition, information on the concentration of elements or organic compounds associated with particles is also presented as this may allow the emitted mass to be calculated based upon the amount of emitted particulate matter as calculated by models such as NZ-TER. As discussed later in this section this approach requires further evaluation. With other factors such as fuel type and driving conditions affecting contaminant emissions this results in considerable 'complication' of the development of relatively simple emission factors.

Information is also provided on the emissions within the exhaust stream derived from catalytic converters. This information is used to provide an indication of the most appropriate data to use for estimates of contaminant loadings from exhaust sources.

## Liquid losses

One minor source of emissions to the road surface not yet accounted for is the water condensation losses (dripping) that occur to the road surface following engine start up while the exhaust system is still cool. During this time some condensation of water vapour runs from the exhaust system and carried particulate matter from the surface of the exhaust system to the road surface. This loss may amount to 1 mL per vehicle/start-up but no quantitative information has been identified on loss rates through this source of the quality of the water lost.

## 7.2 Fuel Types

At present there are five fuel types/grades specifically available for automotive fuelling in NZ. These are petrol (regular unleaded (RULP) and premium unleaded (PULP)), diesel, natural gas (CNG) and liquefied petroleum gas (LPG). Certain niche uses of other fuels do occur, such as aviation gasoline in classic cars and localised use of biogas, but the following concentrates on the mainstream petroleum fuels for the current baseline.

The generic formulations of petroleum fuels are (currently) essentially the same the world over. In New Zealand, the specifications of the conventional refined petroleum fuels are currently controlled by the Petroleum Products Specifications & Regulations (1998), under the authority of the Ministry of Commerce. The schedules of controls for each fuel grade are based upon conventional practice of a decade or more ago and are due for revision to ensure compatibility with the engine specifications of the developing fleet (refer VFECs, MoT 1999).

The NZRC refinery at Marsden Point produces the large majority of New Zealand's supply of fuel. Table 7.1 summarises the national fuels supply balances for the year 1998. NZRC currently provides virtually all of New Zealand's diesel fuel supply, and 70-80% of the petrol requirements. Finished product and blendstocks are imported for petrol to varying extents, mainly from Australia, but the potential exists for spot market product also to enter the market.



Table 7.1 - NZ Fuels Supply Statistics (Year 1998, 10<sup>3</sup> tonnes).

Fuel Grade	Refinery Production	Imports	Industry Losses/ Own Use	Exports	International Transport	Stock Change	Consumer Energy
RULP	1132.9	462.0	-24.0	0.1	0.0	24.1	1594.7
PULP	457.2	137.5	-9.7	29.5	0.0	2.9	571.9
Diesel	1768.4	59.2	-29.2	62.9	84.6	-21.3	1730.5
LPG/ NGL	181.9 (Net)	-	-	73.6	-	0.2	108.1

**Note:** Source - Energy Data File, Ministry of Commerce.

## 7.3 Petrol Formulation and Composition

### 7.3.1 Introduction

Petrols are low boiling point naphthas, within the C<sub>3</sub> to C<sub>12</sub> range, the main differentiation in type of base and blendstocks being the result of their characterising refinery processing (straight-run, reformat, cat-cracked, alkylate, isomerate etc.). Relative compositions vary with the refining/blending regime used to process a given crude oil feedstock into the required product quality to specification. This is the main form of reference used in the environmental impact classification of gasolines, as this governs the proportions of the main constituent and characterising hydrocarbon groups of alkanes, cycloalkanes, olefins (alkenes) and alkylbenzenes.

### 7.3.2 Formulation

Table 7.2 presents a selection of CONCAWE test petrol (gasoline) formulations and blendstocks. This is only a limited selection as there can be up to one hundred different refinery process streams recognised in the EINECS/CAS classification systems that could be represented in the finished petrol product depending upon the particular refinery source. The petrol product from the NZRC refinery comprises the following blendstocks: Butane; Tops; Platformate; Isomerate; Alkylate; Reformat; Cracked spirit; PULP.

There are likely to be several hundred different chemical species present, as all the potential isomers that could exist within the carbon number range. In addition to the straight hydrocarbons, there will be trace quantities of certain organo-sulphur compounds present, and to a lesser extent, naturally occurring nitrogen, chlorine and oxygen complexes. However, these are minimal in quantity, with only the sulphur being subject to any particular refining control (with forthcoming fuel quality requirements).

**Table 7.2 - Examples of variation in composition and classification of petrols and blendstocks (CONCAWE 95/59).**

Substance	Boiling Range, °C	Composition			
		Alkanes %	Cycloalkanes %	Olefins %	Alkylbenzenes %
Straight-run Light	88-162	45.7	33.9	2.2	17.3
Isomerate 1	34-149	80.3	14.4	2.6	2.6
Cat-cracked Heavy	32-208	33.7	10.0	34.2	18.3
Reformat Light	37-189	32.7	2.5	0.9	63.3
Blend 1	26-180	47.7	5.0	1.1	45.9
Blend 2	26-195	40.3	5.7	11.6	41.4
Reformat Full Range	40-194	30.2	2.7	1.6	63.8
Cat-cracked Light	41-106	38.5	10.9	43.3	6.4
Straight-run Light	24-216	73.2	12.3	1.0	3.3
Isomerate 2	32-103	84.0	15.2	0.2	0.5
Blended Gasoline	39-201	44.9	6.6	12.3	34.4

### 7.3.3 Additives

#### Additives – Initial Formulation

The present specifications allow “oxygenates” to be blended with petrols, primarily to support octane number requirements in the wake of lead removal. The only oxygenate intended is MTBE (methyl-t-butyl ether), at 11% maximum content. However, the domestic oil companies (via NZRC) do not use this, and have a restraint of 1% maximum as a contamination limit (with the shared distribution systems). MTBE would be present in trace amounts in less than 5% of New Zealand’s petrol supply, although the new entrants may be importing finished product with MTBE content.

No lead is added to the current petrols, but the term “unleaded” is used to acknowledge that trace amounts may still be present, as residue in the system from the still relatively recent changeover. This would be negligible in quantity and declining rapidly as the system is being continually flushed through.

Petrols from NZRC normally contain no additives apart from the colouring dyes used to distinguish between the grades, which are usually azo- or anthroquinone formulations. Antioxidants may be used in some imported components used as blendstocks (notably cracked spirit) and finished product from Australia. Imported petrols from Australia may also contain metal deactivator additive (MDA). Both grades of petrol transported to Auckland via the Refinery-to-Auckland pipeline (RAP) are treated with anti-corrosion additive.

#### Additives – Aftermarket

Strictly speaking, there are two forms of after-treatment; the first is by each individual oil marketing company, which may wish to their own additive treatments downstream of the refinery, during distribution to its service stations and the second is by the vehicle owner, direct to the fuel tank during refuelling. The former is an extension of the practices that could be employed at the refinery, in producing a properly balanced, effective and tested finished product, whereas the latter is incidental rather than routine, at the decision of the vehicle owner. The only exception to this, currently, is the use of a replacement for lead for valve seat protection in older cars, as part of the transition towards unleaded petrols.

All four of the main oil companies add detergent additives to their own petrol supplies, for maintaining fuel injectors and inlet systems (back of inlet valves) free of deposits. Such treatments are becoming mandated in fuel specifications overseas, as part of emissions control legislation.

Valve seat protection for older vehicles is provided on the forecourt by all companies in the form of the “Valvemaster” additive, for addition to the tank while refuelling. This is a mixture of petrol-soluble alkylammonium phosphate mono- and diesters, with a polyolefin in a kerosene base. The industry estimates that about 12 to 14% of the car fleet would benefit from its use, but actual usage is much less.

There is also a wide variety of third party fuel additives, added by the vehicle owner, promoted in the marketplace. Some have been established as part of the motoring scene for decades (STP, REDEX, Wynns etc.), others try to take advantage of perceived operational deficiencies in the developing fuel:engine combination (combustion improvers, fuel efficiency promoters, emissions reduction etc.).

There is currently no control over the formulation of these additives, or burden of proof over their effectiveness; their purchase and use is very much a matter of caveat emptor. Without entering the debate over the usefulness of such additives, the concern is that they could interfere with the increasingly sophisticated co-development of fuel and engine specifications, in response to stringent emissions control legislation. Already, changes/ tampering to the engine is becoming forbidden as part of emissions control legislation in USA and Europe, and this could logically extend to additions to a finished fuel product. The use of these additives is not general, nor can be considered routine. To provide an indication of the complexity of additives that can be used in fuels, Table 7.3 and 7.4 provide indications of chemical additives and their concentration in fuels. This information derived from Johnson (1988) is for the US market and represents what was in use at that time.

**Table 7.3 - Summary of chemical additives typically used in petrol and diesel (from Johnson 1988, adapted from Tupa & Doren 1984).**

<b>Additive Group</b>	<b>Petrol Additives</b>	<b>Diesel Additives</b>
Amine detergents	Amines. Alkanol amines. Amides. Amido-amines. Imadazolines.	Same as petrol
Polymeric dispersants	Alkenyl succinimides. Hydrocarbonyl amines. Polyether amine.	Same as petrol
Fluidiser oils	Selected mineral oil. Thermally stable polyolefin (polypropylene) of moderate molecular weight (800-1000) and narrow molecular weight distribution. Ester type synthetic lubricants.	
Combustion modifiers	Methylcyclopentadienyl manganese tricarbonyl.	Cetane Improvers: Alkyl nitrates and nitrites. Nitro and nitroso compounds Peroxides Deposit modifiers: Barium, calcium or manganese.
Flow improvers		Ethylene vinyl acetate polymers. Chlorinated hydrocarbons. Polyolefins.
Anticlers	Alkenyl succinates and amine salts. Monocarboxylic acids and amine salts. Imadazolines and carboxylic acid salts. Amine alkylorthophosphates. Ethoxylated alkyl phenols.	
Corrosion inhibitors	Alkyl succinic acids, esters and amine salts. Dimer acid and other carboxylic acids and amine salts. Mixed alkyl orthophosphoric acids and amine salts. Aryl phosphonic acids and amine salts. Mannich amines. carboxylic acid salts of mannich amines.	Same as petrol
Demulsifiers	Long-chain alkylphenols. Long-chain alcohols. Long-chain carboxylic acids. Long-chain amines.	Same as petrol
Antioxidants	Alkyl- or aryl-substituted phenolenediamines. Alkyl- or aryl-substituted aminophenols. Alkyl- or aryl-substituted phenols.	Tertiary amines. Imadazolines. Tertiary alkyl primary amines.
Metal deactivators	Fuel treated with N,N'-dis-allylidene-1,2-propane. Diamine which produces copper chelate.	Same as petrol
Biocides		Borate esters. Quaternary ammonium salts of salicylic acids. Diamine complexes of nickel. Organo-barium compounds. Glycol ethers.

### 7.3.4 Composition

Published information on petrol composition indicates that there are differences between different petrols sold in the marketplace. Table 7.5 provides an indication of the concentrations of PAHs present in a number of petrol samples. It is evident that both regular and premium petrols are dominated by low molecular weight PAHs. Although there are differences between the petrol samples shown in Table 7.5, there are overall similarities in the concentrations of the different PAHs relative to each other.

**Table 7.4 - General fuel additives and concentration range in fuels (from Johnson 1988 adapted from Tupa & Doren 1984, all data mg/L).**

Additive Group	Additive Use	Petrol	Diesel
Amine detergent	Performance	12 – 120	33 - 200
Polymeric dispersant	Performance	20 – 600	22 - 330
Fluidiser oils	Performance	200 – 1,000	not applicable
Anti-icers	Performance	16 – 60	not applicable
Combustion modifiers	Performance		1300 – 3,300
Corrosion inhibitors	Distribution	4 – 40	3 - 33
Antioxidants	Quality	12 – 20	7 - 26
Metal deactivator	Quality	4 – 16	4 - 16
Demulsifier	Distribution	0.4 – 10	0.3 - 8
Flow improver	Performance	Not applicable	50 - 500

**Table 7.5 – Summary of PAH concentrations in petrol (all data mg/L).**

Compound	Lee et al. (1995)			Marr et al. (1999)	
	Premier gasoline	92 unleaded petrol	95 unleaded petrol	Regular petrol (medium n = 4)	Premium petrol (median n=5)
Naphthalene	1,857	882	1,576	795	2,100
Acenaphthylene	204	219	70	0.24	0.27
Acenaphthene	889	173	125	3.45	6.2
Fluorene	10.2	6.46	15.5	4.75	7.4
Phenanthrene	3.13	11.7	3.83	7.6	14
Anthracene	1.3	8.23	8.63	11.5	19
Fluoranthene	2.18	2.07	3.59	0.95	2.6
Pyrene	1.28	0.78	1.58	4.75	3.1
Cyclopenta[cd]pyrene	0.23	2.05	0.19	-	-
Benz[a]anthracene	0.05	0.92	0.29	0.75	1.8
Chrysene	0.30	0.88	0.15	0.20	0.82
Benzo[b]fluoranthene	0.15	1.10	0.13	0.101	0.28
Benzo[k]fluoranthene	0.31	0.98	0.10	0.038	0.16
Benzo[e]pyrene	0.23	2.34	0.09	-	-
Benzo[a]pyrene	0.32	0.73	0.15	0.23	0.5
Perylene	0.87	1.82	0.16	-	-
Benzo[ghi]perylene	1.05	1.69	0.99	0.16	0.55
Indeno[123-cd]pyrene	2.39	2.80	1.65	0.045	0.14
Dibenz[ah]anthracene	0.81	3.66	0.35	<0.005	<0.005
Sum PAHs*	2,967	1,324	1,809	830	2,157

**Note:** PAH totals do not equal the sum of individual PAHs in the table as other PAHs (e.g., coronene) included in the original publications are not included here.

## 7.4 Diesel Formulation and Composition

### 7.4.1 General

Diesel fuels typically comprise hydrocarbons in the C<sub>10</sub> to C<sub>23</sub> range (at the extremes this can extend to C<sub>6</sub> up to C<sub>30</sub> plus). As the distillation range is so broad, fuel chemical composition is, typically identified by the hydrocarbon families rather than individual hydrocarbon species. Any number of isomers may be potentially present within each of these families. The main groupings are:

- n-Paraffins (saturated straight chain aliphatics).
- i-Paraffins (saturated branch chain aliphatics).
- Olefins (unsaturated aliphatics).
- Naphthenes (saturated cyclo-paraffins).

- Aromatics (unsaturated, benzene ring based structures).

The only significant non-hydrocarbon group is of the organo-sulphur compounds. The latter can be of many different forms; sulfides, disulfides, polysulphides, thiophenes, thiols, and in partially oxidised forms as sulfoxides.

#### 7.4.2 Additives

As with petrol, the NZRC diesel supply to Auckland through the RAP pipeline is dosed with an anti-corrosion additive. All diesel supplies are also treated with conductivity improver (anti-static) that allows the dissipation of electrostatic charge build-up through pumping. During winter seasons, there is increasing use of cold flow improvers, especially in supplies destined for southern regions of New Zealand.

Other additive functions that are contemplated are the use of organo-nitrate cetane improvers, and the use of lubricity improvers for the new high-pressure fuel injection system technology. As with petrols, after-market additives are promoted by third parties, but as an incidental application.

#### 7.4.3 Composition

Contaminant emission loads are dependent upon fuel composition to some extent. Published information on diesel fuel composition indicates that there are differences between diesel types sold in the marketplace. Given that the data utilised in the exhaust emission contaminant characterisation that is presented in the following sections is derived from a variety of diesel fuel sources this information is presented to show that there are trace elements present in the fuel and that the concentration of PAHs as an example can vary considerably between diesel types. Table 7.6 presents a summary of some information on PAH and other organic compound concentrations in diesel fuels.

### 7.5 Exhaust Emissions

#### 7.5.1 General

The chemistry of any combustion exhaust stream is extremely complex, because the potential exists for any permutation to be formed in the intensive but ever-changing combustion conditions, from the compounds and elements present. For a pure hydrocarbon, reacted with air, it can be assumed that exhaust products, apart from oxides of carbon, hydrogen and nitrogen, will be unburnt fuel hydrocarbons and partially oxygenated hydrocarbons (with the potential for nitro-HC derivatives, and ammonia etc.) derivatives from the fuel chemistry.

Both petrol and diesel fuel contains a very wide range of VOC and SVOCs including PAHs. Significant variation in the concentrations of these VOCs and SVOCs has been reported. The information on organic compounds presented in this section focuses on PAHs and the dioxin/furan group for which there is useful data.

The character of diesel exhaust is even more complex than petrol, as a consequence of the greater carbon number variation in the fuel, the heterogeneous nature of the combustion process and the multi-phase composition of the exhaust products that result. The many compounds are distributed between the gaseous and particulate phase. The particulate phase includes contaminants from both fuel and lubricating oil such as traces of metallic components (e.g., Fe, Ca and Zn (mainly from the lubricating oil additives)), sulphates, water and hydrocarbons and PAHs.

Table 7.6 – Summary of PAH concentrations in diesel fuel (all data mg/L).

Compound	Westerholm et al. (2001)		Mi et al. (2000)	Yang et al. (1998)	Lee et al. (1995)	Marr et al. (1999)
	Swedish environmental classified diesel fuel MK1	European program on emissions, fuels and engine technologies reference fuel	Chinese Refining Corporation, diesel, Taiwan			California diesel collected in 1997 (n=5)
Naphthalene	-	-	81.1	17.1	776	280
Acenaphthylene	-	-	81.3	110	1,564	1.4
Acenaphthene	-	-	53.6	207	1,681	28
Fluorene	-	-	53.6	298	973	30
Phenanthrene	1.3	188	11.0	52.2	556	36.0
Anthracene	0.1	5.6	10.3	26.4	499	-
3-methylphenanthrene	0.4	210	-	-	-	-
2-methylphenanthrene	0.5	180	-	-	-	-
2-methylanthracene	0.1	2.8	-	-	-	-
4H-cyclopenta(def)phenanthrene	<0.1	3.0	-	-	-	-
9-methylphenanthrene	0.4	86.2	-	-	-	-
1-methylphenanthrene	0.6	77.9	-	-	-	-
2-phenylphenanthrene	0.1	18.7	-	-	-	-
3,6-dimethylphenanthrene	0.2	74.2	-	-	-	-
3,9-dimethylphenanthrene	0.7	206	-	-	-	-
Fluoranthene	0.1	3.8	5.47	3.8	367	0.089
Pyrene	0.2	287	0.83	0.816	320	15
Cyclopenta[cd]pyrene	-	-	0.19	6.32	60.8	-
Benzo[a]fluorene	0.1	<0.1	-	-	-	-
Benzo[b]fluorene	0.1	<0.1	-	-	-	-
2-methylpyrene	0.2	215	-	-	-	-
4-methylpyrene	0.1	60.3	-	-	-	-
1-methylpyrene	0.1	50.3	-	-	-	-
Benz[a]anthracene	<0.1	0.5	0.63	0.029	-	-
Chrysene	<0.1	3.6	0.43	0.0287	188	<0.01
3-methylchrysene	<0.1	3.3	-	-	-	-
2-methylchrysene	<0.1	1.6	-	-	-	-
1-methylchrysene	<0.1	4.8	-	-	-	-
Benzo[b]fluoranthene	<0.1	0.2	0.97	0.0024	12.8	-
Benzo[k]fluoranthene	<0.1	<0.1	0.16	0.102	115	-
Benzo[e]pyrene	<0.1	0.3	0.05	0.439	17.0	-
Benzo[a]pyrene	<0.1	0.1	1.78	0.0126	3.14	-
Perylene	-	-	0.04	0.0076	5.05	-
Benzo[ghi]perylene	<0.1	0.1	0.40	0.0053	1.82	<0.01
Indeno[123-cd]pyrene	-	-	0.69	0.0062	1.70	-
Dibenz[ah]anthracene	-	-	0.97	1.59	1.97	-
Sum PAHs*	5.8	1,687	285	721	7,341	-

**Note:** PAH totals do not equal the sum of individual PAHs in the table as other PAHs (e.g., coronene) included in the original publications are not included here.

The distribution of emissions between the gas and particle phases in diesel exhaust is determined by the vapour pressure of the individual species, the type and amount of particulate matter present (surface area available for adsorption), and the temperature. Two-ring and smaller compounds exist primarily in the gas phase while five-ring and larger compounds are completely adsorbed on the particles. Three- and four-ring compounds are distributed between the two phases. The contribution from the portion of lubricating oil that is lost through the combustion chamber/exhaust valve tract is also to be considered in the overall exhaust emission. This would comprise partially burnt lubricating oil base hydrocarbons, together with the derivatives of the organo-metallic additives in the oil formulation.

There have been a very large number of studies undertaken over the last 5 - 10 years in relation to the composition of the exhaust streams from petrol and diesel fuelled motor vehicles.

In the following sections, an overview of the particulate emissions from motor vehicles is provided. This is followed by information on the inorganic and organic compound composition of both the exhaust stream and the particulate matter in the exhaust. The latter information is provided as it is the particulate phase that is of greatest interest in terms of deposition in and adjacent to the roadway. Emission rates presented in the following sections are limited to  $\mu\text{g}$ ,  $\text{mg}$  or  $\text{g}/\text{km}$  of particulate emissions or total exhaust emission.

### 7.5.2 Particulates

There is a substantial literature on the emission of particulate matter (PM) from motor vehicles. PM emissions from motor vehicles have been described previously as part of the VFEM preparation and are discussed in detail in MoT (1999). As particle emissions rates from motor vehicles are already included in the VFEM-W database, they are not discussed in detail in this report. Tables 7.7 and 7.8 provide examples of some of the particulate emission rates included in the VFEM and NZTER.

The first significant difference in PM composition between the two fuels is the more complex particulate phase in diesel compared to petrol. The particulate matter is comprised of a carbonaceous soot substrate, typically in the sub-micron size range of 0.02 to 0.5  $\mu\text{m}$ . HD diesel  $\text{PM}_{2.5}$  is composed predominantly of elemental carbon (75%) and organic carbon (19%) with lesser amounts of sulphate and nitrate (1%), metals and other elements (2%) and other materials (3%) (USEPA 2002).

Hydrocarbons emitted in the exhaust are generally condensed or adsorbed onto the particulates and are termed the "soluble organic fraction", in the measurement of particulate composition by mass.

Diesel PM is defined as the mass of material collected on a filter at a temperature of 52°C or less after dilution of the exhaust. As the exhaust is diluted and cooled, nucleation, condensation, and adsorption transform volatile material to solid and liquid PM. Diesel exhaust particles are aggregates of primary spherical particles consisting of solid carbonaceous material and ash, and which contain adsorbed organic and sulfur compounds (sulfate) combined with other condensed material (USEPA 2002).

The organic material includes unburned fuel, lubricating oil, and partial combustion and pyrolysis products. This is termed the soluble organic fraction, or SOF, and can range from less than 10% to more than 90% of the PM mass, with the highest values occurring at light engine load where exhaust temperature is low.

Most of the PM mass is accumulation mode particles ranging in size from 50 - 700 nm and averaging about 200 nm. Aggregated carbonaceous particles and adsorbed organic material are primarily in this mode. The nuclei mode consists of particles in the 5 - 50 nm range, averaging about 20 nm in diameter (USEPA 2002). These are believed to form from exhaust constituents during cooling and to consist of sulphuric acid droplets (from some of the fuel sulphur converted to  $\text{SO}_2$  to  $\text{SO}_3$ , then combining with combustion water), ash particles, condensed organic material, and perhaps primary carbon spherules. The nuclei mode typically contains from 1 - 20% of particle mass and from 50 - 90% of the particle number.

### 7.5.3 Inorganic Contaminant Emissions

#### 7.5.3.1 Petrol

Ondov et al. (1982) reported the concentrations of 27 elements in aerosols collected near a highway and in a highway tunnel in 1974. Although the sampling was not of isolated vehicle exhaust, the results identified that vehicles were a source of a number of elements (summarised in Table 7.9). Ignoring the elevated lead concentration due to the presence of lead in the petrol, the major emitted elements

identified were iron, bromine and aluminium. Zinc was the most significant trace element identified. This was followed by manganese then copper, nickel, chromium and barium in similar amounts. Smaller amounts of cadmium and antimony were identified.

**Table 7.7 - PM emissions from NZTER model for a suburban road (model year is 2001, data in g/km).**

Vehicle Type/LoS	Petrol	Diesel	LPG	CNG
<b>Car</b>				
E/F Congested	0.0267	0.6512	0.0200	0.0179
C/D Interrupted	0.0166	0.3348	0.0125	0.0111
A/B Freeflow	0.0148	0.2560	0.0111	0.0099
<b>LCV</b>				
E/F	0.0350	0.9193	0.0262	0.0234
C/D	0.0212	0.4596	0.0159	0.0142
A/B	0.0189	0.3533	0.0141	0.0126
<b>HCV – Small</b>				
E/F	-	0.9705	0.0485	0.0194
C/D	-	0.8742	0.0437	0.0175
A/B	-	0.6673	0.0334	0.0133
<b>HCV – Medium <sup>1</sup></b>				
E/F	-	1.2368	0.0618	0.0247
C/D	-	0.9894	0.0495	0.0198
A/B	-	0.8481	0.0424	0.0170
<b>HCV – Large <sup>2</sup></b>				
E/F	-	1.8061	0.0903	0.0361
C/D	-	1.6840	0.0842	0.0337
A/B	-	1.5626	0.0781	0.0313
<b>Motorcycle</b>				
E/F	0.0600	-	-	-
C/D	0.0374	-	-	-
A/B	0.0332	-	-	-

**Notes:** <sup>1</sup> Includes medium sized buses. <sup>2</sup> Includes large buses. Order of emissions: central urban >suburban >> rural highway > motorway

**Table 7.8 - PM emissions from NZTER model for different road types for petrol cars (model year is 2001, data in g/km).**

Vehicle Type/ Driving Condition	Motorway	Rural Highway	Suburban	Central Urban
<b>Petrol Car</b>				
Congested	0.0138	0.0138	0.0267	0.0460
Interrupted	0.0080	0.0083	0.0166	0.0225
Freeflow	0.0071	0.0072	0.0148	0.0161



**Table 7.9 - Summary of trace and minor elements in roadway tunnel air (From Ondov et al. 1982; all data mg/m<sup>3</sup>).**

Element	Tunnel intake	Tunnel	Tunnel exhaust
<b>COPC</b>			
Cadmium	0.011	0.077	0.037
Antimony	0.009	0.033	0.033
Copper	0.02	0.11	0.115
Chromium	0.025	0.066	0.045
Cobalt	0.00078	0.0022	0.0022
Lead	0.34	18.0	15.5
Nickel	0.025	0.041	0.0255
Selenium	0.002	0.0024	0.0022
Zinc	0.17	0.52	0.42
<b>Other</b>			
Aluminium	0.4	3.8	2.0
Barium	0.016	0.38	0.325
Bromine	0.083	8.0	6.6
Iron	0.63	5.3	3.0
Manganese	0.037	0.15	0.067

The chemistry of any combustion exhaust stream is extremely complex and includes trace elements from the fuel (ash forming metals, sulphur, chlorides etc.), the engine oil or derived from additives in the petrol. Elemental concentrations in emissions have been investigated by Norbeck et al. (1998) and Cadle et al. (1999) and are summarised in Tables 7.10 and 7.11. The data shows that the exhaust emissions from newer vehicles have lower concentrations of elements.

**Table 7.10 - Inorganic emissions from petrol vehicles (all data µg/km. From Cadle et al. 1999).**

Element	Petrol (91-96)	Petrol (86-90)	Petrol (81-85)	Petrol (71-80)	Petrol (Smoky vehicles)
N	5	9	7	6	7
<b>COPC</b>					
Cu	<1	16	7	7	12
Zn	4	120	67	62	230
Pb	2	17	4	27	22
<b>Other</b>					
Al	<10	25	<10	11	18
Cl	1	7	4	140	240
Ca	2	110	85	44	200
Fe	22	55	40	70	53
Mg	0.006	29	60	18	92
Si	110	80	130	1,600	160
P	3	71	44	58	150
S	12	140	9	320	390

**Notes:** Not detected K.

**Table 7.11 - Inorganic emissions from petrol vehicles (from Norbeck et al. 1998).**

	Median emissions from petrol vehicles ( $\mu\text{g}/\text{km}$ )			
	1991-97	1986-90	1981-85	1965-80
N	8	11	9	11
PM (mg/kg)	3.6	6.6	25.4	25.0
<b>COPC</b>				
Cr	<6	<6	<6	<6
Co	<6	<6	<6	<6
Ni	<6	<6	<6	<6
Cu	3	ND	<6	6
Zn	31	43	37	68
Sn	<6	<6	<6	<6
Sb	<6	<6	<6	<6
V	<6	<6	<6	<6
<b>Other</b>				
Ba	<6	<6	<6	<6
Mn	<6	<6	<6	<6
Fe	84	37	112	93
Al	9	6	12	12
Ti	<6	<6	<6	<6
Pb	<6	<6	6	6

**Note:** \* - <6  $\mu\text{g}/\text{km}$  - based upon a detection limit of 0.00 mg/mile, assumed to be <0.01 mg/mile converted to mg/km. The data has a high degree of uncertainty associated with it.

Based upon the study data shown above, motor vehicle petrol engine exhaust contributes to the presence of a number of trace element COPC in roadway air. The most significant elements present in terms of concentration are lead, copper and zinc (the former when lead is present as an additive in petrol) followed by barium, chromium, nickel, cadmium and antimony (Table 7.12). Exhaust emissions also contribute to the concentration of a number of key crustal elements (e.g., iron, aluminium and manganese). Table 7.13 presents results from Gertler et al. (2002) who measured the inorganic constituents in tunnel exhaust air (from combined diesel, petrol vehicles).

**Table 7.12 – Summary of petrol and diesel PM emission rates for inorganic constituents (from Norbeck et al. 1998, all data  $\mu\text{g}/\text{km}$ ).**

	Petrol	Diesel
<b>COPC</b>		
As, Cd, Co, Hg	<6	<6
Sn, Se, Sb, Pd, V	<6	<6
Cr	<6	6
Cu	6	20
Mo	<6	6
Ni	6	12
Pb	25	2
Zn	110	620
<b>Other</b>		
Ba	6	7
Mn	6	6
Fe	280	830
Al	20	30
Ti	<6	<6

**Note:** \* - <6  $\mu\text{g}/\text{km}$  - based upon a detection limit of 0.00 mg/mile, assumed to be <0.01 mg/mile converted to mg/km. The data has a high degree of uncertainty associated with it.

**Table 7.13 – Summary of emission factors from LD and HD vehicles based upon tunnel air quality data (from Gertler et al. 2002, all data µg/km).**

	LD	HD
<b>COPC</b>		
Cu	14.7	88
Hg	1.7	11.2
Pb	11	37.1
Se	11	NSD
V	7.45	8.8
Zn	45.5	136.6
<b>Other</b>		
Mn	400.2	2,768
Fe	208	1,985
Al	544	NSD
Ti	51.75	250

**Note:** NSD – No suitable data – As the Gertler et al data is derived by regression techniques based on tunnel traffic data and composition, the results produced some negative emission rates. The negative data are reported as NSD.

### 7.5.3.2 Diesel

Table 7.14 provides some information on the emission of some inorganic elements from diesel exhausts. As with petrol, diesel exhaust emissions contribute to the presence of a number of trace element COPC in roadway air. The most significant element present in terms of concentration is zinc. Exhaust emissions also contribute to the concentration of a number of key crustal elements (e.g., iron, manganese).

**Table 7.12 - Diesel vehicle PM inorganic contaminant emission rates (all results µg/km).**

Parameter	Diesel particulates (mg/kg)**	Durbin et al. (1999)	Cadle et al. (1999) PM	Norbeck et al. (1998) PM		
				< 9 years old	10 - 14 years old	> 15 years old
No. samples						
<b>PM (mg/km)</b>				53.8	356	301
<b>COPCs</b>						
Cu	50	<10	1	10	10	10
Cr	62	-	-	10	<6*	<6
Ni	50	-	-	70	10	<6
Pb	23	<10	90	<6	<6	<6
Sb	NR	-	-	<6	<6	<6
Zn	870	6	1,100	90	360	430
<b>Others</b>						
Ba	NR	-	-	40	20	40
Al	<6*	12	190	10	20	<6
Fe	690	<10	2,000	370	110	520
Mn	15	-	-	10	<6	<6
P	740	30	390	-	-	-

**Note:** \* - <6 based upon a detection limit of <0.01 mg/mile converted to mg/km. \*\* From Huggins et al. (2000); ND not detected, NR – not reported.

## 7.5.4 Catalytic Converters

### 7.5.4.1 Use of Precious Metals in Catalysts

The use of the platinum group metals (platinum (Pt), palladium (Pd) and rhodium (Rh)) in vehicle catalysts was the result of a number of unique chemical factors. Pt and Pd were introduced first with Rh being used with the advent of three way catalysts (as this had better activity in relation to NO<sub>x</sub> removal) (Shelef et al. 2000). Coffey Associates (2000) provide further comments on the use of catalytic converters in Australia. The exact proportion of vehicles in New Zealand fitted with catalytic converters is unknown.

The precious metals are dispersed in a 'washcoat' on a ceramic or metal substrate. The substrate is typically Al<sub>2</sub>O<sub>3</sub> modified by the use of oxide stabilisers including oxides of aluminium, zirconium, barium and the rare earths (e.g., cerium (Ce) and lanthanum (La)). Analysis of the washcoat by Palacios et al. (2000) showed that Ce and Zirconium (Zr) were the main catalytic promoters in the washcoat. These were not present in a diesel catalyst washcoat. Currently three-way-catalysts containing Pt/Rh, Pt/Pb/Rh, Pd only and Pd/Rh noble metal combinations are in commercial use. The precious metals are typically present in the catalysts in the form of ammonium/potassium chloro-platinate complex (Bunger et al. 1996).

### 7.5.4.2 Emissions of precious metals in exhaust

There have been a number of studies relating to the emissions of precious metals in exhaust stream of motor vehicles. In an examination of the exhaust emissions from diesel and petrol vehicles with catalysts Moldovan et al. (1999) reported that most of the platinum group elements are emitted in particulate form (>95, >85 and >90% for Pt, Pd and Rh respectively).

Table 7.15 provides a summary of emission factors for petrol vehicles equipped with catalytic converters. Shelef et al (2000) report that the present overall usage in vehicle exhaust treatment of the precious metals is about 2-5 g/vehicle. Hoppstock & Michulitz (1997) found that unleaded and leaded petrols contained low concentrations of platinum (~3 ng/L). Early work reported by Hodge & Stallard (1986) indicated that industry sources reported emission rates of 0.8-1.9 ug/km platinum in the exhaust of vehicles with catalytic converters.

Palacios et al. (2000) showed that the emission rates are much higher for fresh catalyst compared to aged catalysts and that for diesel catalysts (identified as Pt only), the amount of Pt released ranged from 400-800 ng/km and after aging decreased to 107-150 ng/km. Other studies have reported similar concentrations to those of Palacios et al. (2000) presumably for aged catalysts.

**Table 7.15 - Summary of precious metal emission rates from petrol motor vehicles  
(all data ng/km).**

Metal	Palacios et al. (2000)		Konig et al. (1992)	Artlet et al. (1999)
	Fresh catalyst	Aged 30,000 km		
Pt	100	6-8	-	-
Pd	250	12-24	2-60	7-72
Rh	50	3-12	-	-

## 7.5.5 Organic Contaminant Emissions

### 7.5.5.1 Introduction

Particulates in exhaust emissions are much more important than gaseous emissions in the consideration of vehicle associated contaminants in stormwater. Both gaseous and particulate emissions derived from

vehicles are extremely complex containing a very large number of organic compounds. As an example of that complexity, Fraser et al. (1998) provide information on the gas-phase and particulate phase organic compounds emitted from vehicles in the Van Nuys tunnel in Los Angeles. Schauer et al. (1999) reported on the concentration of C1 through C30 organic compounds in emissions from medium diesel trucks. These compound groups include amongst others:

- n-alkanes (e.g., n-butane, n-nonacosane).
- Branched alkanes (e.g., 2-methylpropane, phytane).
- Branches alkenes (e.g., 2-methyl-1-butene)
- Cyclic alkenes (e.g., cyclopentane, pentadecyclohexane).
- n-alkenes (e.g., ethane, isobutene)
- Alkynes (e.g., ethyne).
- Petroleum biomarkers (Steranes, hopanes e.g., 8B,13a-dimethyl-14B-n-butylpodocarpane)
- Aromatic hydrocarbons (e.g., benzene, ).
- Substituted aromatics (e.g., benzaldehyde, dibenzofuran).
- Aliphatic aldehydes (formaldehyde).
- Olefinic aldehydes (e.g., acetone).
- Aromatic aldehydes (e.g., benzaldehyde).
- Dicarbonyls (e.g., methylglyoxal).
- Aromatic acids (e.g., benzoic acid, dehydroabietic acid).
- Other acids (e.g., stearic acid).

Given the complexity of the composition of exhaust emissions, specific information is presented on two key groups of compounds – the polyaromatic hydrocarbons (PAHs) and the dioxins and furans. A comment is provided on VOCs in emissions below.

#### 7.5.5.2 Volatile Organic compounds

Information in the published literature shows that exhaust emissions (Duffy et al. 1999; Schauer et al. 1999; Siegl et al. 1999; Schulz et al. 1999; Schmitz et al. 2000), the ambient air inside motor vehicles and in road or tunnel air (Lawryk & Weasel 1996; Duffy & Nelson 1996; Fraser et al. 1998; Leung & Harrison 1999) contain an extensive range of volatile organic compounds (VOCs). The most well known VOCs are the aromatic hydrocarbons benzene, toluene and xylene. As these gaseous emissions become principally involved with pathways other than the road-stormwater pathway, VOCs are not discussed in detail further in this section and estimates of VOC emission factors are not presented. It is recognised that VOCs are present in stormwater and are able to enter stormwater through rain.

#### 7.5.5.3 PAHs and related compounds

The PAHs appear to be the most significant group of COPC in exhaust emissions. For this group, broad PM emissions may provide a useful surrogate for total PAHs and total PAH may provide good surrogates for individual PAH compounds.

A wide variety of organic compounds are emitted in diesel exhausts as a consequence of the broad spectrum of hydrocarbons included in the diesel fuel. For diesel engine emissions, most of the extracted organic mass is contained in the nonpolar fraction. About 90% of this fraction consists of aliphatic hydrocarbons from approximately C<sub>14</sub> to about C<sub>40</sub>. Polycyclic aromatic hydrocarbons and alkyl-substituted PAHs account for the remainder of the non-polar mass. The moderately polar fraction consists mainly of oxygenated PAHs species, substituted benzaldehydes, and nitrated PAHs. The polar fraction is composed mainly of n-alkanoic acids, carboxylic and dicarboxylic acids, of PAHs, hydroxy-PAHs, hydroxynitro-PAHs, N-containing heterocyclic compounds, etc.

Emissions of PAHs by motor vehicles have been investigated by many authors and some samples of these are summarised in Table 7.16, 7.17 and 7.18. USEPA (2002) report that at least 32 PAHs have been identified in diesel exhaust emissions. As with some other vehicle source characterisation and emission estimates, the range of published emission factors for PAHs appears large. Oxygenated PAH

derivatives such as 9-fluorenone, 9,10-anthracenequinone, phenalene-1-one, naphthalenedicarboxylic acid anhydride, cyclopenta[d,e,f]phenanthrene-4-one, monoaldehydes of phenanthrene and anthracene, mono- and di-ketones of benzanthracenes and benzo[c,d]pyrene and benzofluorenones have been identified in diesel exhaust.

Nitro-substituted PAHs have also been identified as being formed during the combustion process, including amongst others nitrofluorene, dinitrofluorenone, nitroanthracene, nitrofluoranthene, mono- and dinitropyrenes and nitrobenzo[a]pyrene. USEPA (2002) noted that 16 nitro-PAHs have been positively identified in diesel emissions and a larger number of nitro-PAHs have been tentatively identified. These compounds typically occur at much lower rates (typically one to three orders of magnitude less) than for the oxygenated analogues.

USEPA (2002), report that based on the work of Levson (1998) that 1-nitropyrene is the dominant compound present at concentrations of 7-165 µg/g of particles. This was confirmed by Bamford et al. (2003) who reported that 1-Nitropyrene was the dominant nitro-PAH present in diesel particulates. Concentrations of nitro-substituted PAHs in particulates emitted from diesel vehicles are presented in Table 7.19. As noted by USEPA (2002) there is more recent data but the emissions are presented in a variety of formats that are not directly comparable with the concentration data presented in Table 7.19.

**Table 7.16 - PAH emissions from petrol vehicles (µg/km).**

Vehicle Age	Gertler et al. (2002) LD vehicles*	Norbeck et al. (1998) overall average	Norbeck et al. (1998)		
			Median ≤ 8 years old	Median 9 - 14 years old	Median ≥ 15 years old
N		1	1	7	12
FTP Weighted PM			6,960	33,860	26,410
Biphenyl	21	85			
Methylbiphenyls	41	86			
Naphthalene	367	4,396	1,283	2,838	3,798
Methylnaphthalenes	1,299	3,276			
Dimethylnaphthalenes		1,033			
Trimethylnaphthalene	65.4	506			
Acenaphthylene	1.4	199	45	106	156
Acenaphthene	11.4	35	4	9	47
Phenanthrene	NSD	123	29	55	104
Methylphenanthrenes	25	65			
Dimethylphenanthrenes	23	30			
Fluorene	NSD	73	7	37	60
Methylfluorenes	NSD	84			
Anthracene	12.8	6	6	21	34
9-methylanthracene	NSD	1			
Fluoranthene	1.6	43	9	14	32
Pyrene	NSD	10	10	17	40
Methyl pyrene	NSD	19			
Benzonaphthothiophene	NSD	0.6			
Benzo[a]anthracene	2.2	5	1	2	4
7-methylbenz[a]anthracene	NSD	<0.6			
Chrysene	2.4	5	1	2	3
Benzo[b+j+k]fluoranthene	0.9	12	2	4	7
Benzo[e]pyrene	1.4	4			
Benzo[a]pyrene	6.5	5	1	1	2
Indeno[1,2,3-cd]pyrene	0.9	4	1	1	1
Dibenzo[a,h+a,c]anthracene	-	<0.6	0	0	0
Benzo[g,h,i]perylene	0.2	12.4	1	2	5
Coronene	NSD	8.7			
<b>TOTAL</b>	<b>1,883</b>	<b>10,128</b>	<b>2,185</b>	<b>5,856</b>	<b>7,659</b>

**Note:** NSD – No suitable data – \* - As the Gertler et al data is derived by regression techniques based on tunnel traffic data and composition, the results produced some negative emission rates. These are reported as NSD. This data is presented for comparative information; the data should not be used or re-quoted without reference to the original reference and data as the uncertainty factors associated with the data are not presented here.

Duran et al. (2001) examined the emission of PAH in a European diesel PC and using software modelled the changing emissions under different conditions (the authors considered that the results were estimations only). The variables used were fuel consumption parameters (cetane index, aromatic content, gross heat power, nitrogen and sulphur content) and vehicle operation (speed and torque). The study found that torque had only a small effect on emissions but engine speed was the determining factor. Aromatic content greater than 20% was also found to increase emissions markedly at higher engine speed. From an engine speed of 500 rpm the PAH emissions increased by a factor of five to 3,000 rpm.

**Table 7.17 - Summary of PAH emission factors for diesel vehicles (all data µg/km).**

Compound	USEPA (2002)		Westerholm et al. (1988)	Rogge et al. (1993)	Siegel et al. (1999)	Schauer et al. (1999)	Sjögren et al. 1996
	Light duty diesel	Heavy duty diesel	Trucks particulates	Trucks	Passenger vehicles	Medium duty truck	Heavy duty engines (Median)
Naphthalene	3451	1523			1600		
1 & 2-methylnaphthalene					1,130		
2-phenylnaphthalene				3.5			
2-benzyl naphthalene				nd			
Acenaphthene	60	19			190		
Benzacenaphthylene				2.9			
Fluorene	275	41				9.5	
Benzo[a+b]fluorene			2.4	1.9			0.67
Phenanthrene	877	52	29	12.2		47	5.00
Anthracene	153	32	3.3	1.6		10.9	0.71
2-methyl anthracene						22	2.54
Benz[a]anthracene	12.4	41.0		3.6			0.70
Dibenz[a,h]anthracene				nd			
1,2 & 3-methyl phenanthrene	693	77	111	31.3, 56.9*		82.8	4.68
Fluoranthene	132	27	17	13.0		56.6	10.88
Pyrene	152	44	11	22.6		88.5	15.35
Benzo[a]pyrene	8.1	8.1	<0.06	1.3			0.19
Benzo[e]pyrene	11.8	6.2	0.15	2.6			0.36
2 + 1-methyl pyrene	340**	13.7**	2.75				1.84
Perylene			<0.01				0.13
Benzo[ghi]fluoranthene			1.5	6.9		19.8	1.31
Benzo[k]fluoranthene, b,k	34.8#	5.6#	0.29	2.7, 2.9, nd,			0.19
Cyclopenta[cd]pyrene			0.18	1.4		3.5	0.74
Benzo[a]anthracene			0.47			7.76	
Chrysene & triphenylene	18***	5.6***	2.8	9.9		15.6	0.87
Indeno[1,2,3-cd]pyrene	6.2	0.6	<0.04				0.02
Indeno[1,2,3-cd]fluoranthene			<0.09				0.10
Benzo[ghi]perylene	11.2	8.1	<0.13				0.07
Coronene	3.7	0.6	<0.01				0.02
Total	31,648##	13,539##	<230	209.9		364	46.4

**Notes:** \* - all methyl phenanthrenes. \*\* - methyl (pyrenes/fluoranthenes). \*\*\* - chrysene. # - Benz[b+j+k]fluoranthene. ## - Sum of 32 individual or groups of PAHs.

#### 7.5.5.4 Dioxins and furans

Motor vehicle emissions have been recognised as a potential source of PCDDs and PCDFs (Ballschmitter et al. 1986) due to the combustion process. A range of studies has been undertaken examining the PCDD/PCDF emissions and emissions factors from motor vehicles. These studies, which included one New Zealand study (Bingham et al. 1989), ranged from exhaust emission to tunnel air studies. Recent assessments of PCDD and PCDF emissions from vehicles in Europe and Japan have shown that vehicles contribute only a very small proportion of PCDDs and PCDFs in urban air. Overall, Gueke et al. (1998) conducted that "except for vehicles using leaded fuels - emissions from traffic are not likely to be a significant source of PCDD/PCDF". The authors noted that there is some uncertainty as to the emissions from heavy-duty vehicles.

Table 7.18 - Median PAH emissions from diesel vehicles ( $\mu\text{g}/\text{km}$ ).

Vehicle Age	Gertler et al. (2002) HD vehicles*	Norbeck et al. (1998) overall average	Norbeck et al. (1998)		
			$\leq 9$ years old	10 - 18 years old	$\geq 18$ years old
N			1	12	6
FTP weighted PM			53.8	298	505
Naphthalene	2,509	1,277**	310	840	1,490
Methylnaphthalenes	2,377	483			
1 + 2 Ethylnaphthalene	472	-			
Dimethylnaphthalenes	192	608			
Biphenyl	302.4	174			
2-methylbiphenyl	127	196			
Bibenzyl	169	-			
Trimethylnaphthalenes	903.3	521			
Acenaphthylene	339.25	338.6**	43	0.15	410
Acenaphthene	134.7	30**	6	0.016	29
Phenanthrene	448.5	369*8	76	0.23	45
Methylphenanthrene	269.0	149.8			
Di-methylphenanthrene	238	91.3			
Fluorene	310.6	133**	22	0.073	45
Methylfluorenes	198.6	158			
Xanthone	84.8	-			
Acenaphthenequinone	73.9	-			
Anthracene	60.6	63.4**	24	0.043	79
9-methylanthracene	45.2	1.9			
Fluoranthene	35.1	187**	25	0.10	200
Pyrene	40.7	240	34	0.13	270
Methyl-pyrenes	103.0	65.9			
Retene	44.8	<1			
Benzonaphthothiophene	9.4	<1			
Benzo[a]anthracene	1.2	16.8**	1.2	0.008	16
Benzo[a]anthracene-7,12-dione	40.9	-			
Benzo[c]phenanthrene	17.7	-			
Chrysene	0.6	19.9**	1.2	0.007	34
5+6 methyl chrysene	34.2	-			
Benzo[b+j+k]fluoranthene	4.4	54.7**	3.7	0.021	34
Benzo[a]pyrene	6.2	15.5**	0.10	0.005	16
Benzo[e]pyrene	0.38	18.6			
Indeno[1,2,3-cd]pyrene	NSD	7.5**	<0.001	0.0012	8
Dibenzo[a,h+a,c]anthracene	-	<1**	<0.001	0.000	<0.001
Benzo[g,h,i]perylene	2.9	18.6**	1.2	0.005	21
Coronene	27.9	8			
<b>TOTAL</b>			1,300	3,200	7,200

**Note:** NSD – No suitable data – \* - As the Gertler et al data is derived by regression techniques based on tunnel traffic data and composition, the results produced some negative emission rates. These are reported as NSD. This data is presented for comparative information, the data should not be used or re-quoted without reference to the original reference and data as the uncertainty factors associated with the data are not presented here. \*\* - PAH emission rates quoted in USEPA (1999) for estimating Mobile source PAH emissions in the NTI.

Miyabara et al. (1999) examined PCDDs and PCDFs in both petrol and diesel passenger cars. They found total amounts of PCDDs and PCDFs in the suspended matter of 0.21, 0.87 and 26.0 ng/g. The corresponding I-TEQ were 4.2, 11 and 242 pg/g. The congener patterns differed between diesel and petrol and this was considered to be due to the higher chlorine concentration in petrol compared to diesel (14 and 0.6 – 0.9 mg/L respectively). Overall, the total contribution of vehicle exhausts to the PCDD/PCDFs in urban air in Japan was estimated to be 0.3% (Miyabara et al. 1999). Gueke et al. (1999) estimated a contribution of 0.5% in Europe.



A further issue relating to the production of PCDD, PCDFs and PCBs by motor vehicles relating to the type of oil used in the vehicle was discussed by Broz et al. (2000). Broz et al. (2000) noted that the use of halogenated scavengers in leaded petrol has been banned in some countries due to the possible enhancement in the amount of PCDD/PCDF emissions. The authors work indicated that there were a variety of factors that appeared to influence the emitted load of PCDD/PCDFs. Emissions of PCDDs and PCDFs have also been undertaken and are presented in Table 7.20.

**Table 7.19 - Concentrations of Nitro-PAH in light duty diesel PM.**

Compound	Cambell & Lee (1984)	Bamford et al. (2003)	
	ng/g of PM Mass	SRM 2975	SRM 1650a
1-Nitronaphthalene	-	42.1	86.4
2-Nitronaphthalene	-	124	238
2-Nitrobiphenyl	-	<7	15.3
3-Nitrobiphenyl	-	<7	58.1
4-Nitrobiphenyl	2,200*	-	-
5-Nitroacenaphthene	-	<10	37.0
2-Nitrofluorene	~1,800	<2	46.2
2-Nitroanthracene	4,400	2,929	6,080
9-Nitroanthracene	1,200	-	-
9-Nitrophenanthrene	1,000	454	510
4-Nitrophenanthrene	-	25.4	150
3-Nitrophenanthrene	4,100	189	4,350
2-methyl-1-nitroanthracene	8,300	-	-
1-Nitrofluoranthene	1.8	133	274
7-Nitrofluoranthene	700	<2	<2
2-Nitrofluoranthene	-	188	201
3-Nitrofluoranthene	4,400	4,301	65.2
8-Nitrofluoranthene	0.8	656	106
1-Nitropyrene	18,900	39,640	18,330
2-Nitropyrene	-	<4	<4
4-Nitropyrene	-	173	135
7-Nitrobenz[a]anthracene	-	5,300	995
6-Nitrochrysene	-	2,368	44.4
6-Nitrobenzo[a]pyrene	2,500	1,650	1,442
3-Nitrobenzo[e]pyrene	-	1,788	<10
3-Nitrobenzo[e]pyrene	-	6,857	89
1 and 3-Nitrobenzo[a]pyrene	-	<5	<5
1,3-dinitropyrene	300	1,146	44.4
1,6-dinitropyrene	400	2,543	84.5
1,8-dinitropyrene	500	3,580	<9
2,7-dinitrofluorene	4,200	-	-
2,7-dinitro-9-fluorenone	8,600	-	-
3-nitrobenzanthrone	6,600	-	-

**Note:** \* - reported in µg/g in Campbell & Lee (1984). SRM 1650a diesel particulate material; SRM 2975 diesel particulate material (industrial forklift).

**Table 7.20 - Summary of PCDD/PCDF emission factors for motor vehicles.**

Study	Vehicle type	Fuel	Emission factor pg/km (I-TEQ)
Marklund et al. 1987	Passenger car	Unleaded	<13
		Leaded	20 - 220
Bingham et al 1989	Passenger car	Unleaded (1) and leaded (4)	15 - 39
Marklund et al. (1990)	Passenger car	Unleaded	0.36 - 0.39
		Leaded	1.1 - 6.3
Hagenmaser et al. (1990)	Passenger car	Unleaded	0.7 - 5.1
		Diesel	2.4
		LCV	35.0
Gueke et al. 1999	HCV	Diesel	116
Ryan & Gullerd 2000	HCV	Diesel	29 (106)*

**Note:** Calculated factor (upper 95% confidence interval).

## 7.6 Exhaust Emission Factors

### 7.6.1 Introduction

As identified in the introduction to this section, exhaust emission contaminant loads can be estimated on the basis of fuel consumption, on vehicle kms travelled and on the basis of particulate emissions. The use of rates of fuel consumption and particulate emissions has the potential to allow contaminant emissions to be estimated based upon engine power. At this stage, there is insufficient published data to utilise the relationship between concentration in particulates (all particles, PM10 etc.) and the particle mass (e.g., PM10) emitted by the vehicle under different driving conditions. For the purpose of providing emission data, the use of contaminant emission rates/VKT is utilised at this stage. This however should only be regarded as an interim measure as particulate mass can be modelled by VFEM-Water.

### 7.6.2 Inorganic contaminants

Emission data for inorganic contaminants emitted via the exhaust system are extremely variable between studies. The key factors influencing the emission rates are vehicle age, fuel type and vehicle type. Table 7.21 provides a summary of emission factors for a number of key inorganic contaminants in exhaust emissions.

For emissions sourced from exhaust system catalytic converters, rates vary depending upon the age of the catalyst system. Rates for aged systems for Pd emissions are generally similar and a preliminary rate of 50 ng/km is adopted (0.05 µg/km) for the purpose of undertaking a first assessment of emissions. Based on the work of Palacios et al. (2000) a preliminary aged rate of 10 ng/km was identified for both Pd and Rh. Rates of Pt release from diesel catalyst were identified to be about 110 ng/km. It is evident from the available data that emission rates from diesel and petrol powered vehicles are different with diesel vehicles emitting higher amounts of inorganic (metal) contaminants. However until the emission rates can be refined or the use of the particle/contaminant relationship refined further, the interim emission rates are used across vehicle groups and driving/road types.

### 7.6.3 Organic contaminants

As with inorganic contaminants, emission data for inorganic contaminants emitted via the exhaust system are extremely variable between studies. The emission rates being influenced by vehicle age, fuel type and vehicle type. The previous sections have presented a range of PAH data for both petrol and diesel vehicle emissions. Table 7.22 summarises the emission rates per VKT for both petrol and diesel vehicles. The data utilised for emission factors is the average data of Norbeck et al (1998). This data has been used by USEPA for emission inventory assessment.

**Table 7.21 - Summary of concentrations of selected elements in petrol exhaust emissions for use in calculating contaminant emission loads (all data µg/km).**

Element	Emission per VKT - LD vehicles	Emission per VKT - HD vehicles
<b>COPC</b>		
Antimony	<6*	<6*
Cadmium	<6*	<6*
Chromium	<6*	6*
Copper	14.7**	88**
Lead	11**	37.1**
Mercury	1.7**	11.2**
Molybdenum	<6*	6*
Nickel	6*	12*
Platinum	0.01	0.01 (diesel 0.1)
Palladium	0.05	0.05
Rhodium	0.01	0.01
Selenium	11**	NSD**
Silver	NDA	NDA
Tin	<6*	<6*
Zinc	45.5**	136.6** (diesel 620*)
<b>Others</b>		
Barium	6*	7*
Iron	280*	830*

**Table 7.22 - Summary of PAHs in exhaust emissions for use in calculating emission loads (all concentrations µg/km).**

Vehicle Age	Norbeck et al. (1998) overall average Petrol	Norbeck et al. (1998) overall average Diesel
Naphthalene	4,396	1,277
Methylnaphthalenes	3,276	483
Dimethylnaphthalenes	1,033	608
Biphenyl	85	174
Methylbiphenyls	86	196
Trimethylnaphthalenes	506	521
Acenaphthylene	199	338.6
Acenaphthene	35	30
Phenanthrene	123	369*8
Methylphenanthrene	65	149.8
Di-methylphenanthrene	30	91.3
Fluorene	73	133
Methylfluorenes	84	158
Anthracene	6	63.4
9-methylantracene	1	1.9
Fluoranthene	43	187
Pyrene	10	240
Methyl-pyrenes	19	65.9
Retene	-	<1
Benzonaphthothiophene	0.6	<1
Benzo[a]anthracene	5	16.8
Chrysene	5	19.9
Benzo[b+g+k]fluoranthene	12	54.7
Benzo[a]pyrene	5	15.5
Benzo[e]pyrene	4	18.6
Indeno[1,2,3-cd]pyrene	4	7.5
Dibenzo[a,h+a,c]anthracene	<0.6	<1
Benzo[g,h,i]perylene	12.4	18.6
Coronene	8.7	8
<b>TOTAL (no naphthalenes)</b>	<b>10,128 (916)</b>	<b>5,247 (2,358)</b>

## 8. ROAD SURFACE

### 8.1 Introduction

In addition to the contaminant contribution from motor vehicles to the road surface, the road surface contributes to the nature of and amount of material present on the road surface that can be transported to the stormwater system. The road surface contribution arises during the passage of motor vehicles over the road surface and their tyre contact. There is however, a variety of materials present on road surfaces that contribute to the mass of material present on the road surface. Not all of this material is derived from road surface wear. Other sources of material which will have associated contaminants include:

- ❑ Dust deposition from local to regional emissions sources.
- ❑ Deposition of litter from human activities on or adjacent to the roadway.
- ❑ Deposition of materials from motor vehicles including accidents and wear and tear (e.g., plastic and glass fragments).
- ❑ Deposition of plant (e.g., leaves and grass) and animal materials (faecal matter etc.).

None of these arise from the routine emissions sources associated with motor vehicles. In this section of the report, information on road surface types in New Zealand, their composition and wear rates is overviewed.

### 8.2 Road Seal Construction

Roads typically consist of layers of base-course covered by a bituminous protective coating, the exceptions being bridges and motorways where the basecourse is replaced by the bridge structure. The majority of New Zealand's roads utilise the "Double Coat Chip" sealing method. A layer of bitumen binder is spread on the base-course followed by a single layer of uniformly sized stone. Within a short settling period a second application of bitumen and stone is added. Areas such as motorways and bridges are often treated with asphaltic concrete mixes, consisting of bitumen binder and a dense graded aggregate, which is laid as a combined coating. Another form is the "Slurry Seal", produced by screeding a mixture of bitumen binder, cement and stone aggregate directly onto the base-course. The result is a smoother, thinner seal that is applicable to light or medium traffic conditions such as quiet urban streets.

Standard bitumen binder in New Zealand consists of 180/200 penetration grade asphalt cement, an adhesion agent, automotive gas oil and lighting kerosene. The automotive gas oil is a fluxing agent, used to permanently soften the bitumen, with up to 4 parts per hundred incorporated into first coat seals. Lighting kerosene is added to temporarily reduce the viscosity of the bitumen to promote adhesion and wetting of the chips. Once the bitumen is laid the kerosene evaporates and the bitumen returns to its original properties.

### 8.3 Composition

#### 8.3.1 General

Material generated from the road surface typically comprises bitumen and inorganic particulates worn from the aggregate or broken or removed from the seal.

Bitumen is primarily a mixture of high molecular weight hydrocarbons with small quantities of nitrogen (0.1 – 0.7%), sulphur (up to 8%) and trace metals (Boutevin et al. 1989). The exact composition is, dictated by the crude oil source material, however the types of chemical species present are generally consistent

worldwide. Table 8.1 gives the basic elemental composition of New Zealand 180/200 penetration grade Safaniyah bitumen.

**Table 8.1 - New Zealand Safaniyah bitumen (180/200 penetration grade); elemental analysis (Herrington et al. 1993).**

Element	Wt%
Carbon	83.6
Hydrogen	10.7
Nitrogen	0.5
Sulphur	5.9

**Note:** Median of multiple analysis.

The three key bitumen classifications are asphalt, oxidised asphalt and petroleum asphaltenes. The asphaltenes comprise insoluble fractions of bitumen with molar mass greater than 900 (Boutevin et al. 1989). Asphalt contains a relatively high proportion of hydrocarbons having carbon numbers predominantly greater than C<sub>25</sub> with high carbon-to-hydrogen ratios. It also contains small amounts of various metals such as nickel, iron, or vanadium. Oxidised asphalt is complex black solid obtained by blowing air through a heated residuum, or raffinate from a de-asphalting process with or without a catalyst. This increases the molecular weight by oxidative condensation. Asphaltenes (petroleum) are a complex combination of hydrocarbons obtained as a complex solid black product by the separation of petroleum residues by means of a special treatment of a light hydrocarbon cut. The carbon/hydrogen ratio is especially high. This product contains a low quantity of vanadium and nickel.

Herrington (1995) reviewed the use of antioxidants in roading bitumen. Antioxidants are added to bitumen to slow the natural process of oxidation that leads to surface bitumen aging. Two key antioxidants have been used. These are dialkyl dithiocarbamate compounds (including lead or zinc DADC) and hydrated lime. Herrington (1995) also identified preventative oxidants (which include thiols, metal dialkyl dithiophosphates and other compounds), metal deactivators (chelating agents), ultraviolet light absorbers (e.g., benzophenones), chain breaking antioxidants (e.g., phenyl naphthylamines), ketone-amine condensates and alkyl aryl secondary amines (e.g., hindered phenols such as 4-methyl-2,6-di-*t*-butylphenol). Although there are potentially a very wide range of chemicals that could be used as antioxidant agents in bitumen there do not appear to be many in commercial use (Herrington 1995) and they do not appear to be used significantly in New Zealand bitumens.

Traditionally, adhesion agents used in New Zealand bitumen (at typically 0.5-1.5%) contain either, amines, amides, imidazolines, or a combination of these substances. The list below gives an indication of the types and Table 8.2 the commercial names of some common adhesion compounds found in the country's road seal, which incorporate these components singly or in combination.

- Alkyl propylene diamine.
- Alkyl dipropylene triamine.
- Alkyl polypropylene polyamine.
- Alkyl amido-amine.
- Alkyl chain with tertiary amine group.
- Alkyl chain with imidazoline group.

### 8.3.2 Inorganic Constituents

Herrington (1993) and Herrington (2001) report on the concentration of trace elements in Safaniya bitumen. The data in Table 8.3 shows that New Zealand bitumen appears to have relatively high concentrations of vanadium. Vanadium and nickel mainly exist as chelates with various porphyrin species in the bitumen.

**Table 8.2: - Adhesion Agents; Proprietary Additives.**

<b>Adhesion Agent</b>	<b>Recommended Dose Rate (%)</b>
Polyram L200	1.0
Bitran H	1.2
Redicote Z	1.3
Genamin T020	1.0
Wetfix C	1.0
Shell Tenicon A	3.0
Diamin HBG	0.6
Duomeen T	0.7

**Table 8.3 - Trace elements in New Zealand Safaniyah 180/200 penetration grade bitumen (Source, Herrington 1993, Herrington 2001).**

<b>Element</b>	<b>Concentration Detected (<math>\mu\text{g/g}</math>)</b>
Chromium	1.7
Copper	<0.4
Lead	<0.4
Nickel	18
Vanadium	65
Zinc	10

Further inorganic analyses of raw bitumen and bitumen samples collected from roads in New Zealand are reported by Kennedy & Gadd (2000). The analysis of raw bitumen (summarised in Table 8.) shows that the bitumen has a low inorganic content with a few metallic elements such as iron, nickel and zinc present in elevated concentrations. Comparison of bitumen samples containing polymer and those samples not containing polymer demonstrated some differences in the concentration of iron and lithium suggesting that these elements may be either contained in or added along with the polymer. The similar concentration of environmentally significant metals suggests that these elements were not present in the additives in the bitumen samples examined in that study.

Table 8.4 also summarises the data for the analysis of samples of bitumen milled from five roads in North Shore City. A wider range of elements were detected in the road bitumen samples compared with the raw bitumen samples. Concentrations of the major elements (Ca, Mg, Na, K and P) were much higher than in the raw bitumen samples but generally similar between the five road bitumen samples.

The road bitumen samples collected in that study will have included some material that was incorporated into the bitumen surface as a result of vehicles driving on the road surface and some inorganic material that was included with the bitumen when it was milled (as the bitumen often coated very small aggregate particles). A number of priority pollutant elements were detected in the road bitumen samples (14) compared with the raw bitumen (5). Concentrations of cobalt, molybdenum, nickel, tin and zinc (present in raw bitumen) were higher in the road bitumen samples than raw bitumen indicating additional sources of these priority pollutants. Although, the bitumen analysed from the road millings was selected to remove aggregate it is probably more representative of the material worn from old road surfaces. This material contains contaminants derived from road transport driving on the bitumen but also from urban deposition falling onto the road surface.

**Table 8.4 - Summary of elemental composition of a selection of raw bitumen and road bitumen in New Zealand (all data mg/kg).**

Element	Raw bitumen (n = 6)			Road bitumen (n = 5)		
	Minimum	Median	Maximum	Minimum	Median	Maximum
Calcium	<50	<50	<50	6310	8175	9520
Magnesium	<4	<4	<4	15000	26300	29000
Sodium	<20	<20	20	5520	10400	14100
Potassium	<50	<50	<50	1600	2970	3510
Phosphorus	<10	<10	<10	843	1180	1840
Aluminium	<5	<5	7	12400	18200	22100
Iron	<20	<20	100	25100	39800	48100
Manganese	<0.5	<0.5	<0.5	390	543	654
Titanium	-	-	-	2310	3580	3885
Arsenic	<1	<1	<1	0.9	1.5	12.6
Beryllium	<0.1	<0.1	<0.1	0.46	0.65	1.23
Cadmium	<0.05	<0.05	<0.05	0.05	0.07	0.15
Cobalt	<0.2	<0.2	0.2	17.4	28.7	31.6
Chromium	<1	<1	<1	46.3	77.7	102.2
Copper	<1	<1	<1	40.0	46.3	60.1
Mercury	<0.01	<0.01	<0.01	<0.01	<0.01	0.03
Molybdenum	<0.2	0.45	1.5	1.21	1.58	1.97
Nickel	2	16	32	77.1	137	153
Lead	<0.2	<0.2	<0.2	1.89	8.33	146
Antimony	<0.2	<0.2	<0.2	<0.2	<0.2	0.3
Tin	<0.5	~0.6	4.0	0.5	0.7	1.3
Thallium	<0.02	<0.02	<0.02	<0.02	0.03	0.03
Zinc	<2	5.5	99	47.4	53.5	79.9
Barium	<0.2	<0.2	0.2	19.2	24.1	33.0
Cerium	-	-	-	20.1	29.5	46.2
Caesium	<0.1	<0.1	<0.1	0.32	1.56	2.67
Gallium	-	-	-	4.4	6.6	8.3
Lithium	<0.2	<0.2	2.9	3.72	4.31	5.03
Lanthanum	<0.1	<0.1	<0.1	0.56	0.89	9.97
Niobium	-	-	-	2.6	3.0	3.5
Rubidium	<0.2	<0.2	<0.2	7.14	12.4	12.6
Scandium	-	-	-	2.5	3.2	3.6
Strontium	<0.5	<0.5	<0.5	64.8	94.8	119
Uranium	<0.05	<0.05	<0.05	0.32	0.34	0.67
Vanadium	<50	<50	110	60	75	80

**Note:** Not detected Ag, Se, Au, B, Bi, Ge, In, Pd, W: From Kennedy & Gadd (2000).

### 8.3.3 Organic Compounds

Rogge et al. (1993) investigated the organic composition of paved road dust in Los Angeles. The dust was dominated by n-alkanoic acids and n-alkanes. PAHs and pesticides were also present. The road dust fraction includes particulate matter emitted from vehicles, tire wear particles and brake lining particles. The n-alkane profile of the road dust resembled typical profiles of vegetative detritus. The n-alkanals and n-alkanols also present in the road dust samples supported this observation. It was found that exhaust emissions contribute a maximum of 7.6% of the fine road dust, tyre dust contribute up to 1.6% and vegetative detritus (leaves and garden soil) contribute at least 2.2% of the fine road dust mass.

Dust generated from sealed roads will include some proportion of bitumen particles. Bitumen is primarily made of high molecular weight hydrocarbons. Analysis of four raw bitumen samples demonstrated that the composition is dominated by high molecular weight n-alkanes with >C29 comprising 86% (Gadd & Kennedy 2000). N-alkanes of C15-C-28 made up 13% and 1% was present as C10-C14.

Bitumen contains polyaromatic hydrocarbons (PAH); typically, 3-4 condensed aromatic rings with approximately five side chains (aliphatic and alicyclic), with an average of seven carbon atoms. However, only small amounts of individual PAHs are present in bitumen compared to the initial crude oil. The vacuum distillation processing of bitumen removes most PAHs, leaving a total concentration commonly between 0.0012 to 0.0020%.

Table 8.5 presents results for some PAH compounds found in New Zealand bitumen. For comparison some recent data of Brandt & de Groot (2001) is also presented. Although the individual PAH compounds differ slightly in concentration the total PAH concentrations based on the PAHs measured are similar.

Gadd & Kennedy (2000) also analysed a single sample of raw bitumen by SVOC scan. None of the 217 target compounds were present above the detection limit (generally 10 mg/kg).

Sulphur is present in bitumen as aliphatic sulphides and thiophenic rings (approximate ratio of 1:2). Nitrogen is present in bitumen as pyridinic and pyrrolic ring structures. Oxidation of the bitumen over time increases the presence of ketones and converts the sulphides to sulphoxides, nevertheless the oxygen concentration generally does not exceed 1%.

**Table 8.5 - Comparison of polyaromatic hydrocarbon concentrations in New Zealand and overseas bitumen (all results mg/kg).**

Sample*	180/200+P	Safaniya bitumen	Bitumen (Brandt & de Groot		
	(Gadd & Kennedy 2000)	(Herrington et al. 1993).	2001)		
			A	E	G
Acenaphthene	<0.2	NA	0.2	0.7	Bdl
Acenaphthylene	<0.2	NA			
Anthracene	0.2	NA	0.2	0.2	0.1
Benzo(a)anthracene	1.0	det.	0.7	0.2	Bdl
Benzo(a)pyrene	<0.2	0.15	0.7	0.5	Bdl
Benzo(b)fluoranthene	<0.2	12.1	1.0	0.7	0.4
Benzo(g,h,i)perylene	2.2	1.7	2.0	2.0	0.8
Benzo(k)fluoranthene	<0.2	0.10	0.4	0.3	Bdl
Chrysene	1.2	ND	2.4	1.0	0.5
Dibenzo(a,h)anthracene	<0.2	ND	0.5	0.3	Bdl
Fluoranthene	0.4	det.	0.9	0.8	0.3
Fluorene	<0.2	NA	0.3	0.4	0.4
Indeno(1,2,3-c,d)pyrene	<0.2	NA	0.5	0.2	bdl
Naphthalene	0.3	NA	2.7	3.0	2.5
Phenanthrene	0.3	NA	1.8	2.0	1.1
Pyrene	2.1	det.	0.9	1.0	0.3
Total PAH	9.2	det.	15.2	13.3	6.4

**Note:** NA = Not analysed; ND = Not detected. \* - sample identifiers from Brandt & de Groot (2001).

## 8.4 Road Wear Rates

### 8.4.1 Design

Road pavements are designed to be flexible; deformation of both the seal and basecourse occurs with the movement of heavy vehicles for example, a truck tyre can indent into the seal up to 1.6 mm. Oxidation of bitumen leaves it brittle and prone to cracking, and seal cracks can permit the infiltration of water into the base-course. The result is a loss of elasticity and continuing loads lead to pavement damage.



Excess binder coming through to create a smooth surface is referred to as “flushing”. The main causes are surplus binder application and the bleeding of bitumen from the seal. Traffic loads in hot weather force the aggregates through the layers of binder, allowing the bitumen to rise to the top and the surface texture is lost. Hot weather and heavy wheel loads are also responsible for rutting, the formation of surface depressions. Uneven utilisation of the carriageway during periods of softened binder compresses the seal into longitudinal furrows. In an attempt to counter these issues harder bitumen binders are used in warmer climates.

Abrasion by tyres and weathering polishes both the seal and the stone chips. However, in the case of the seal the mechanism is more the deformation of the seal, causing greater or lesser exposure of the embedded stone chip. This leads to a potentially dangerous situation especially when the conditions are wet. The Polished Stone Value (PSV) is a measure of the aggregate’s propensity to smoothing, the higher the value the greater the resistance to this process. Aggregates with high PSVs reduce the probability of skid resistance losses over time. Skid resistance is also decreased by the loss of aggregates from the seal. Softened or brittle bitumen can permit the plucking of chips from the seal via tyre movements.

Deformation of the road is a function of the base-course and there are a variety of causes. Frequently the damage is done, by continuing excess wheel loads, the natural flexibility of the road is surpassed and compression of the carriageway in the longitudinal direction is uneven, giving it a roller-coaster quality when traversed.

When damage to the roadway is relatively minor it is addressed with the application of an additional layer of seal. However, despite the possible lack of damage to a roadway, there is a limit to the number of times a link can be resealed. Resealing increases the height of the road, which reduces stability and poses an obstacle for vehicles travelling from link to link.

Complete failure of the road, through deformation, or of the seal, via excessive binder or mounting layers, requires re-engineering. In some cases restoration is attempted by burning or sand blasting the bitumen component, more often than not the layers of seal are ripped up and dumped, leaving the base-course ready for another round of sealing.

#### 8.4.2 Wear

Road material wear depends on the type of material used on the road and whether the road is sealed or unsealed. Unsealed roads typically release larger quantities of suspended particulate matter from the road surface itself. However, almost all roads in urbanised areas with stormwater systems are sealed. The materials used on roads in New Zealand are asphalt, tar, concrete and occasionally cobblestones. The wear rates for these surfaces depend mainly on the volume of flow (the local traffic model, and RAMM database details on road construction and condition). However, the vehicle size usage is also an influence.

There is effectively no industry information, standards or rules of thumb existing on actual material loss rates from road surfaces; it is something that is not even recognised as a “wear” mechanism by the roading industry. The actual life of a sealed road is not closely related to loss of material from the road but to monitoring and property thresholds including assessments of the seal’s texture, chip retention and overall condition. State Highways are resealed approximately every four years and low demand roads every fifteen to nineteen years. Although the phraseology refers to “pavement wear”, this usually concerns criteria of rutting, deformation, roughness and cracking, rather than actual material loss by surface attrition. The loss of material is not actually recognised as a phenomenon.

Some wear of the road surface does occur. Abrasion by tyres and weathering polishes both the seal and the stone chips. This causes deformation of the seal, causing greater or lesser exposure of the embedded stone chip. Once bitumen is softened or brittle, tyre movements can remove chips from the seal.

In most work looking at tyre/road surface wear interactions, any material loss is dominated by the wear material from the tyre treads. Only in the Scandinavian countries has any work been done on material loss from the road, in the special case of using studded tyres. In this situation the loss mechanism is more by grinding rather than any general abrasive wear. In that situation, the studs tend to wear the aggregate in the seal where the major part of the asphalt is composed of aggregate (95%) (Lindgren 1996).

For a chip seal road, in theory, it is the polishing wear of the stone chips that dictates the service life of the road surface, in maintaining skid resistance. The empirical relationship in the inset box below provides an indicator of road seal life.

### Road Seal life

At application a pavement seal has an estimated life,  $Y_d$ <sup>1</sup>

$$Y_d = 9.417 - 2.435 \log(\text{elv}) + \text{ALD} [1.4 - 0.098 \log(\text{elv})]$$

Where  $Y_d$  = design life in years

$\text{elv}$  = equivalent light vehicles/lane/day

$\text{ALD}$  = average least dimension of the sealing chip in mm on the lot

$$\text{elv} = \frac{\text{AADT}}{\text{Number of Lanes}} \left( 1 + \frac{9}{100} \times \% \text{HCV} \right) \text{ Where } \text{AADT} = \text{annual average daily traffic on the road section}$$

$\% \text{HCV}$  = percentage heavy commercial vehicles

Based on the assessment of seal life shown in the box, a two lane road with an AADT of 2,400 and 10% heavy commercial vehicles, would have an estimated life of just over 11 years ( $Y_{dd} = 4,015$  days) if constructed with grade 3 chip ( $\text{ALD} 8.5$  mm).

As there is no empirical wear data to go on, a first order estimate could be used to assume that mass wear is a function of road life, tyre track width (the affected part of the corridor, say 1 metre total, for a two way road) and instinctive feel for the actual surface layer loss (say, fractions of a millimetre). Based upon the replacement period identified earlier we have assumed for the purposes of assessing bitumen contribution that:

Wear per VKT on a given section of roadway is equivalent to:

$$\text{Wear in g/m of road} = 100 (\text{width of wear in cm}) \times 0.85 (\text{depth worn}) / Y_{dd} \times B\% \times \text{SG of bitumen (assume } 1 \text{ g/cm}^3) \times 100.$$

Where  $B\%$  is the % of the wear depth composed of bitumen (assumed to be 50% in this example).

For this example, the amount of bitumen worn by vehicle movements is of the order of 1.06 g/m length of road. Based upon the base example this would correspond to 0.44 g/VKT. In a situation where the bitumen comprises only 10% of the worn surface then this figure would be lower at 0.09 g/VKT. This assumes that wear rates are similar between chip versus tar-seal road surfaces.

This is a first order wear factor and if used as a single factor does not allow for variation in driving conditions and vehicle composition beyond the HCV component noted in the example. To provide more accurate data on wear a simple model would need to be used to calculate wear based upon a variety of factors including road surface type, driving speed, vehicle fleet composition including number of wheels and proportion of HCVs etc.

<sup>1</sup> Transit New Zealand Specification TNZ P/17:1998 "Performance based specification for bituminous reseals"

## 8.5 Emission Factors

### 8.5.1 Particulate Emissions

The USEPA PART5 model and the EU model PMFAC calculate fugitive dust emission factors (re-entrained road dust) for both unpaved and paved roads. The fugitive dust calculations include tailpipe, brake-wear and tyre-wear particulate matter. However, neither model deals with wear and loss of the bitumen surface or material such as aggregate within the road surface.

### 8.5.2 Inorganic Emissions

Based upon the bitumen data obtained by Kenedy & Gadd (2000), Table 8.6 identifies the concentrations used to assess the contribution of key inorganic contaminants arising from road bitumen wear. The data in Table 8.6 represents the contribution from the bitumen in the road seal not that arising from the wear of the aggregate in the road surface and the combined wear.

**Table 8.6 - Summary of elemental concentrations in raw bitumen and bitumen/aggregate mix that might be used for road surface wear contributions (all data mg/kg) (From Kennedy & Gadd 2000).**

Element	Raw bitumen	Road bitumen
<b>COPC</b>		
Arsenic	<1	1.5
Beryllium	<0.1	0.645
Cadmium	<0.05	0.07
Cobalt	<0.2	28.7
Chromium	<1	77.7
Copper	<1	46.3
Mercury	<0.01	<0.01
Molybdenum	0.45	1.58
Nickel	16	137
Lead	<0.2	8.33
Antimony	<0.2	<0.2
Silver	<	<
Tin	~0.6	0.7
Thallium	<0.02	0.03
Zinc	5.5	53.5
<b>Others</b>		
Barium	<0.2	24.1

### 8.5.3 Organic Emissions

The examination of bitumen by Gadd & Kennedy (2000) and others has shown that bitumen contains low concentrations of organic compounds. PAHs have been identified in bitumen. Although there are likely to be some variation in the concentration of individual PAH compounds in bitumen, the total PAH (estimated based on detected PAHs) measured by Gadd & Kennedy (2000) and in the literature are in reasonable agreement. Based on that data an interim concentration of 10 mg/kg PAH in bitumen has been used to identify the contribution of bitumen wear to PAH loading on road surfaces.

At this stage the emission factors do not account for any other source of contribution such as the losses associated with leaching of the bitumen surface by rainfall. As noted earlier, the wear rate is a function of the vehicle fleet composition on the road, the proportion of heavy commercial vehicles needs to be taken into account when assessing pavement wear. This is calculated by identifying the anticipated pavement life on the section of road and then by assessing the rate of wear per m length of road for the width of the road. As a first estimate of losses associated with road bitumen the loss factor identified earlier was estimated to be 0.44 g/VKT. Based upon a total PAH concentration of 10 mg/kg, the emission factor for road bitumen contribution to PAH loading is estimated to be 4.4 µg/VKT.

## 9. EMISSION RATES TO ROAD SURFACE

### 9.1 Introduction

In the previous sections of this report, the emissions of contaminants released from the various sources associated with motor vehicles have been described. A number of key sources are well recognised as sources of contaminants. The physical behaviour of the released contaminants is important as it determines the amount of contaminant deposited onto the road surface and therefore available for transport in stormwater. Moncreiff et al. (2002) described the processes and pathways that determine the fate of contaminants released from motor vehicles.

Once released, the fate of gaseous and particulate emissions are, controlled by a wide range of physical factors. The nature of the emission (i.e., the amount of gas, small or large particles) plus environmental factors determines what proportion settles to the road surface. Information is required for each of the key contaminant sources to determine what proportion of the discharged contaminants, are deposited on the road surface. This material is however then subject to a variety of processes that determine whether or not it remains on the road surface until it rains.

The key elements of any model that determine the amount of contaminant present and available for transport off-site by stormwater are:

- Atmospheric deposition.
- Wind.
- Particle size distribution.
- Number of vehicles and their speed.
- The source of contaminants and method of estimating the loads generated.

Modelling these processes is relatively difficult as the overall process is not completely predictable (or predictable through a single simple process at different locations). Relatively simple procedures are used to assess the accumulation of contaminants on street surfaces. The Source Loading and Management Model (SLAMM) (Pitt & Voorhees 1995) predicts urban runoff discharge parameters for individual storms. The model uses what Pitt & Voorhees (1995) referred to as small storm hydrology and particle wash-off algorithms to assess runoff within complex catchments. Pitt & Voorhees (1995) discussed accumulation of contaminants on road surfaces. Although the accumulation rates were found to be very similar between two locations, the loadings at any given time were not. This was attributed to the initial loading. Early contaminant loading models assumed that contaminant loads were zero following rain events. In reality, street surfaces may still carry a significant initial loading following a rain event. The amount of this initial loading is dependent on the street surface roughness, adjacent landuse, street cleaning practices, rainfall event intensity etc. Pitt & Voorhees (1995) noted that deposition and accumulation rates were about the same until about 1-2 weeks after rain. The accumulation rates then decreased because of fugitive dust losses to the surrounding area. This occurs as a result of vehicle turbulence or wind. EPA (1979) noted that material accumulation on street surfaces is probably constant in areas where rain events are relatively frequent (at least every 1-2 weeks).

SLAMM includes a number of street dust accumulation and deposition rate relationships that have been derived from numerous studies in the US. Accumulation rates are a function of land-use while the initial loadings are a function of street texture.

### 9.2 Brake linings

Section 3 described the wear of brake linings and the composition of the particles generated. In assessing brake lining contaminant loads entering the environment from road transport, the loads have been assessed for dry conditions. During periods of active rainfall, it is considered that increasing rainfall will result in a greater proportion of the airborne material being washed from the air to the road. In

addition, rain and water falling on the vehicle will wash brake dust particles present on the outside of the wheel rim. This is not accounted for in the VFEM-W model at this stage.

Based on the early work of Cha et al. (1983) and others a deposition figure of 70% of all emissions appears to be representative of particles emitted from brake lining wear. The work undertaken by Cha et al. (1983) and Garg et al. (2000) have shown that about 30% of the particles produced during wear become airborne.

Other authors such as Legrat & Pagatto (1999) have carried out an emissions inventory based upon their assessed wear rates and field data and concluded that they could only account for 2% of the emitted copper in stormwater. However, there are likely to be a number of errors associated with the estimates made. This is not totally surprising given the size of the wear particles (1-4  $\mu\text{m}$ ) and due to the pathways that the copper emitted from this and other sources are involved in.

Rogge et al. (1993) indicated that on average some 11% of the dust was retained in the drum brake housing. Although a proportion of the particles are also retained within and on the surfaces of disc brake and wheel surfaces, this proportion will be much lower. This factor has not been included at this stage in accounting for the overall mass balance of the brake lining wear dust.

The work by Weckworth (2001) on airborne particulate enrichment factors is of interest. Examination of the composition of airborne particulates over roadways has identified very high enrichment factors (compared to crustal abundance) for antimony. It was considered that a brake lining component of 0.1-0.6% would be sufficient to explain the measured antimony enrichment in the coarse immission fraction. Similar copper and molybdenum enrichments were noted and appeared, to be dominated in the coarse fraction by material from the brake linings. The abundance ratio in the particles seemed to be similar to that measured by the authors in the brake linings suggesting that brake linings were the primary contributor of this element.

Based on the early Cha et al (1983) data, a preliminary deposition to road surface factor of 0.7 for brake wear has been identified.

In the assessment of losses of contaminant from brake linings to the road surface a factor of 0.7 has been adopted in the interim to account for losses to the air which are subsequently deposited to soil or water surfaces down-wind of the road.

### 9.3 Tyres

The early work by Cadle & Williams (1978a) reported that emissions of gases and airborne particulates from tyre wear was nearly independent of wear rate and accounted for up to 20% of the total emissions from the wear of tyres. The balance was considered to be large particles that would settle close to the road. The authors identified an exponential decrease in concentration of deposited particles from the pavement edge. In addition, measurement of SBR in airborne particles near the freeway examined in their study indicated that most tyre wear particles are not re-suspendable. It was estimated that <5% of the wear product was re-suspendable.

Weckwerth (2001) reported the results of Heinrichs & Brumsack (1997) who concluded that based on the analysis of airborne particles (< 10  $\mu\text{m}$ ) that up to 25% of the particles could have been derived from tyre wear. However, Weckwerth (2001) considered that when condensation particulates from exhaust emissions were accounted for that the proportion of particles derived from tyre wear was only 3%.

In the assessment of losses of contaminant from tyres to the road surface a preliminary factor of 0.8 has been adopted to account for tyre wear products that are deposited to the road environment. This first estimate is based on the work of Cadle & Williams (1978a).

## 9.4 Oil losses

Given that oil losses occur typically directly to the road surface, a loss to the road factor of 1.0 has been selected for the purpose of calculating the loss to the road surface. However, it is likely that some loss may occur through:

- ❑ Adsorption to particles that are re-suspended and removed from the road.
- ❑ Enter the road surface (adsorption, impregnation) and do not become incorporated into stormwater losses.

In the assessment losses of oil and associated contaminants is considered to be completely to the road surface with little off-site loss. An effective loss factor of 1.0 is used as an interim factor.

## 9.5 Exhaust emissions

Particles emitted from both petrol and diesel vehicles are very fine. A wide range of studies have been undertaken on the size of particles emitted from petrol engines, diesel engines and from vehicles fitted with catalytic converters. Silva & Prather (1997) examined particulate emissions from motor vehicles and found that cold start emissions contained particle sizes, which varied between different vehicles. More recently manufactured vehicles had size distributions centred on smaller particles. Two newer vehicles (1991 and 1994) equipped with catalytic converters emitted particles in the 0.1 to 0.7  $\mu\text{m}$  range. In contrast a 1973 vehicle emitted particles typically in the low micron range. However, other studies such as those of Morawska et al. (1998) did not find any variation between vehicle age and emission particle size.

Diesel particulates are typically sub-micrometer agglomerations of particles ranging from 10-80 nm in size with larger particles comprising many thousand individual particles in clusters up to 30  $\mu\text{m}$  in size (Morawska et al. 1998). Studies undertaken by investigators such as Kerminen et al. (1997) (diesel car with catalytic converter) and Panne et al. (1995) and Kleeman et al. (2000) showed that particles emitted from exhaust systems were typically in the 0.1 to 0.2  $\mu\text{m}$  diameter. The use of oxidative catalytic converters on diesel engines can result in 50% reductions in particulate emissions from diesel engines but results in a shift in the particle size distribution to smaller particles for diesel fuel (Bagley et al. 1998). Suarez et al. (1998) also showed that modal diameters of particles emitted by HDDs are larger than those emitted by LDDs.

When particles are discharged from the exhaust system they rapidly disperse (after one second the plume has increased its cross sectional area by 250 times). Coagulation is not expected to be significant during dispersal and water vapour condensation results in some increase in particle size for diesel exhaust particles (Vignati et al 1999).

Deposition of particles on the road surface during periods on no rain occurs by two key process. The first is dry deposition and the second is by impaction. Dry deposition is strongly dependent on particle size. Particles above 10  $\mu\text{m}$  in size are 'significantly' affected by gravitational processes. Atmospheric processes (turbulence etc.) continually bring particles to the road surface. However, the transport of very fine particles such as those emitted from exhausts is more like gases.

Hewitt & Rashed (1990) examined deposition patterns adjacent to roadways and found that for metals such as lead that only a small proportion of the emitted lead was deposited within the roadway. The authors estimated that overall <5% of the lead and 11 % of the organic lead emission was deposited within 50 m of the road. Their work also demonstrated that at least 95% of the low molecular weight PAHs were lost from the road environment and about 70% of the high molecular PAHs. Examination of the deposition data of Hewitt & Rashed (1990) and other studies indicates that for a 10 m wide road, about 67% of the 30% could be deposited on the road surface (i.e., 20%). This is estimate is very dependent upon a wide variety of factors including topography, vehicle speed, local climate etc., and should only be considered a first order estimate. NIWA (M Timperley pers comm.) are undertaking more

detailed assessments of deposition profiles adjacent to roads. This work should allow a more refined estimate of on-road deposition to be included in any calculations.

The work of Hewitt & Rashed (1990) reinforced the nature of the dispersion processes for contaminants in exhaust emissions. Contaminants in gaseous form (e.g., VOCs, gaseous trace elements such as mercury) are transported away from the road environment and end up in the regional environment. Those contaminants that are associated with particulate phases tend to be removed to the ground in closer proximity to the roadway.

Deposition factors for particle-associated contaminants will be higher than those predominant in gaseous form. On the basis of available information, a single factor of 0.05 is identified as an interim factor to assess deposition of particle associated contaminants to the road surface. This figure should be revised as further information becomes available and two factors used. One for low vapour pressure particle associated contaminants and one for particle associated contaminants with high vapour pressure (e.g., low molecular weight PAHs).

## 9.6 Road surface

For the purposes of assessing the contribution of the road surface to the materials transported by stormwater, it is assumed that all of the wear material is available for waterborne transport. However, wind (local and vehicle generated turbulence) will provide off-site transport of particulate matter generated from the road surface.

An interim factor of 1.0 is recommended for the assessment of, the contribution of surface road wear to the road surface burden of contaminants.

## 10. REFERENCES

- Ahyerre, M.; Chebbo, G.; Tassin, B.; Gaume, E. 1998: Stormwater quality modelling, an ambitious objective? *Water science technology* 37(1): 205-213.
- Armstrong, L. J. 1994: Contribution of heavy metals to stormwater from automotive disc pad wear. Woodward Clyde Consultants, Oakland CA. Submitted to the Santa Clara Valley non-point source pollution control program; 1994.
- Artlet, S.; Creutzenberg, O.; Kock, H.; Levsen, K.; Nachtigall, D.; Heinrich, U.; Ruhle, T.; Schlogl, R.; 1999: Bioavailability of fine dispersed platinum as emitted from automotive catalytic converters: a model study. *The science of the total environment*, 228: 219-242.
- Bagley, S. T.; Gratz, L. D.; Johnson, J. J.; McDonald, J. F. 1998: Effects of an oxidation catalytic converter and a biodiesel fuel on the chemical, mutagenic and particle size characteristics of emissions from a diesel engine. *Environmental science & technology*, 32(9): 1183-1191.
- Ballschmitter, K.; Buchert, H.; Niemczyk, R.; Munder, A.; Swerev, M. 1986: Automobile exhausts versus municipal waste incineration as sources of the PCDD and PCDF found in the environment. *Chemosphere* 15(7): 901-915.
- Bamford, H. A.; Bezabeh, D. Z.; Schantz, M. M.; Wise, S. A.; Baker, J. E. 2003: Determination and comparison of nitrated-polycyclic aromatic hydrocarbons measured in air and diesel particulate reference materials. *Chemosphere* 50: 575-587.
- Bennett, C. R. & Greenwood, I. D. 2001: Volume Seven: Modelling road user and environmental effects in HDM-4. The Highway Development and Management Series. Report to the International Study of Highway Development and Management Tools, University of Birmingham.
- Bingham, A. G.; Edmunds, C. J.; Graham, B. W.; Jones, M. T. 1989: Determination of PCDDs and PCDFs in car exhaust. *Chemosphere*, 19: 669-673.
- Birch, S.; Yamaguehi, J.; Demmler, A.; Jost, K. 1991: Tech Briefs. *Automotive engineering*. December pp 45-48.
- Boutevin, B.; Pietrasanta, Y.; Robin, J-J. 1989: Bitumen-polymer blends for coatings applied to roads and public constructions. *Progress in organic coatings*, 17: 221-249.
- Brandt, H. C. A.; De Groot, P. C. 2001: Aqueous leaching of polycyclic aromatic hydrocarbons from bitumen and asphalt. *Water research* Vol. 35, No. 17: 4200-4207.
- Broz, J.; Grabic, R.; Kilián, J.; Lojkásek, M.; Marklund, S.; Ocelka, T.; Pekárek, V.; Přebyl, J.; Tydlitát, V.; Výška, J. 2000: The effect of oils on PAH, PCDD, PCDF and PCB emissions from a spark engine fuelled with leaded gasoline. *Chemosphere*, 41:1905-1911.
- Bunger, J.; Stork, J.; Stalder, K.; Cyto- and genotoxic effects of co-ordination complexes of platinum, palladium and rhodium in vitro. *International archives of occupational environmental health* 69: 33-38 (referred to in Helmers 1996).
- Cadle, S. H.; Williams, R. L. 1978a: Characterisation of tire emissions using an indoor testing facility. *Rubber chemical technology*, 51: 7.
- Cadle, S. H.; Williams, R. L. 1978b: gas and particulate emissions from automobile tires in laboratory and field studies. *APCA Journal*, 28(5): 502-507.



- Cadle, S. H.; Mulawa, P. A.; Hunsanger, E. C.; Nelson, N.; Ragazzi, R. A.; Barrett, R.; Gallagher, G. L.; Lawson, D. R.; Knapp, K. T.; Snow, R. 1999: Composition of light duty motor vehicle exhaust particulate matter in the Denver, Colorado area. *Environmental science and technology*, 33: 2328-2339.
- Campbell, R. M.; Lee, M. L. 1984: Capillary column gas chromatographic determination of nitro polycyclic aromatic compounds in particulate extracts. *Analytical chemistry*, 56: 1026-1030.
- Carpenter, P.; Cenek, P. 1999: Tyre wear modelling for HDM-4. Report prepared by Opus International Consultants limited, Central Laboratories, Lower Hutt. Central Laboratories Report, 98-529474. Prepared for ISOHDM.
- Cenek, P.D.; Jamieson, N.; Sutherland, A.; Swift, A. 1993: Tyre consumption - research plan. Transit New Zealand Research Report PR3-0042.
- Cenek, P. D.; carpenter, P.; Jamieson, N. J.; Stewart, P. F. 1997: Friction and tyre abrasion characteristics of New Zealand road surfaces. Transfund Research Report No 94.
- Cha, S. Carter, P.; Bradow, R. L. 1983: Simulation of automobile brake wear dynamics and estimation of emissions. SAE technical paper series 831036. Passenger car Meeting, Dearbon, Michigan June 6-9, 1983. Society of Automotive Engineers.
- Charbeneua, R. J.; Barrett, M. E. 1998: Evaluation of methods for estimating stormwater pollutant loads. *Water Environment Research*, Volume 70, No. 7, Nov/Dec 1998.
- Christensen, E. R.; Guinn, V. P. 1979: Zinc from automobile tires in urban runoff. *Journal of environmental engineering decisions*. American Society of Civil Engineers 105, EEI: 165-168.
- Claffey, P. 1971: Running costs of motor vehicles as affected by road design and traffic. NHCRP Report 111, Highway Research Board, Washington D.C.
- Clark, N. N.; Gajendran, N. N.; Kern, J. M. 2003: A predictive tool for emissions from heavy duty diesel vehicles. *Environmental science and technology*, 37:7-15.
- Colwill, D.M.; Peters, C.J.; Perry, R. 1984: Water quality of motorway runoff. Transport and Road Research Laboratory Supplementary Report 823. Department of Transport, UK. 23pp.
- Coffey Associates 2000: Review of fuel quality requirements for Australian Transport. Prepared for Environment Australia, March 2000.
- Cooper, J. A. et al. 1987: PM10 source composition library for the south coast air basin. Prepared for the South Coast Air Quality management District, El Monte, CA July 15 (cited in Armstrong 1994)
- CRRRI 1982: Road user cost study in India. Central Road Research Institute, New Delhi.
- Davis, A. P.; Shokouhian, M.; Ni, S. 2001: Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere*, 44: 997-1009.
- Dietl, C.; Reifenhauer, W.; Peichl, L. 1997: Association of antimony with traffic – occurrence in airborne dust, deposition and accumulation in standardised grass cultures. *The science of the total environment*, 205: 235-244.
- Duffy, B. L.; Nelson, P. F. 1996: Non-methane exhaust composition in the Sydney harbour tunnel: A focus on benzene and 1,3-butadiene. *Atmospheric environment*, 30(15): 2759-2768.
- Duffy, B. L.; Nelson, P. F.; Ye, Y.; weeks, I. A. 1999: Speciated hydrocarbon profiles and calculated reactivities of exhaust and evaporative emissions from 82 in-use light duty Australian vehicles. *Atmospheric environment*, 33: 291-307.

- Duran, A.; de Lucas, A.; Carmona, M.; Ballesteros, R. 2001: Simulation of atmospheric PAH emissions from diesel engines. *Chemosphere*, 44: 921-924.
- Durbin, T. D.; Collins, J. R.; Norbeck, J. M.; Smith, M. R. 1999: Effects of bio-diesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles. *Environmental science & technology*, 34(3): 349-355.
- Environment Agency 1998: Tyres and the environment. United Kingdom Environment Agency.
- Eriksson, M.; Jacobson, S. 2000: Tribological surfaces of organic brake pads. *Tribology international*, 33: 817-827.
- Eriksson, M.; Lord, J.; Jacobson A. 2001: Wear and contact conditions of brake pads: dynamic in situ studies of pad on glass. *Wear*, 249: 272-278.
- Faiz, A.; Weaver, C. S.; Walsh, M. P. 1996: Air pollution from motor vehicles. Standards and technologies for controlling emissions. The World Bank, Washington, DC.
- Filip, P.; Wright, M. A.; Marx, D. T. 1997: On-highway brake characterisation and performance evaluation. *Materially speaking* 11: 2-7. Materials Technology Centre and the Centre for Advanced Friction Studies, Southern Illinois University at Carbondale IL.
- Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T. 1998: Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. *Environmental science & technology*, 32(14): 2051-2060.
- Fuels & Energy Ltd, Kingett Mitchell Ltd, 2002: Road transport effects on aquatic ecosystems – Issues and context for policy development. Report prepared for Ministry of Transport, February 2002.
- Gadd, J.; Kennedy, P. 2000: Preliminary examination of organic compounds present in tyres, brake pads and road bitumen in New Zealand. Prepared by Kingett Mitchell Ltd for Ministry of Transport, November 2000. Revised October 2003.
- Garg, B.; Cadle, S. H.; Groblicki, P. J.; Mulawa, P. A.; Laroo, C.; Parr, G. A. 2000: Brake wear particulate matter emissions. GM research and Development centre. R&D - 9033. March 27, 2000.
- Garg, B. D.; Cadle, S. H.; Mulawa, P. A.; Groblicki, P. J. 2000: Brake wear particulate matter emissions. *Environmental science and technology*, 34(21): 4463 - 4469.
- Gertler, A. W.; Gillies, J. A.; Pierson, W. R.; Rogers, C. F.; Sagabiel, J. C.; Abu-Allaban, M.; Coulombe, W.; Tarnay, L.; Cahill, T. A 2002: Real world particulate matter and gaseous emissions from motor vehicles in a highway tunnel. Health Effects Institute, Research Report Number 107, January 2002.
- Gueke, K.J.; Gessner, A.; Quall, U.; Broker, G.; Hiester, E. 1999: PCDD/F emissions from heavy duty vehicle diesel engines. *Chemosphere*, 38(12): 2791-2806.
- Gudmond-Hoyer, L.; Bach, A.; Nielsen, G. T.; Morgen, P. 1999: Tribological properties of automotive disc brakes with solid lubricants. *Wear*, 232: 168-175.
- Hagenmaser, H.; Dawldowsky, N.; Weberups, U.; Hutzinger, O.; Schwind, K. K.; Thoma, H., Essers, U.; Buhler, U.; Greiner, R. 1990: Emissions of polyhalogenated dibenzodioxins and dibenzofurans from combustion engines. *Organohalogen Compol.* 2: 329-334.
- Heaney, J. P.; Wright, L. Sample, D. 1999: Research needs in urban wet weather flows. *Water environment research*, Vol. 71. No. 2.

- Heaney, J. P.; Pitt, R.; Field, R.; Fan, C. 1999: Innovative urban wet-weather flow management systems. EPA/600/R-99-029. National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268.
- Heinrichs, H.; Brumsack, H. J. 1997: Anreicherung von umweltrelevanten metallen in atmosphärisch transportierten schwebstauben. In: Matschullat, J.; Tobschall, H. J.; Voight, H. J. Eds. *Geochemie and Umwelt*. Springer, Berlin, Heidelberg, New York, pp 25-36.
- Helmers, E. 1996: Elements accompanying platinum emitted from automobile catalysts. *Chemosphere* 33(3): 405-419.
- Herrington, P. R. 1993: Safiniya bitumen – verification of chemical properties. Transit New Zealand research report No. 22. 45pp.
- Herrington, P. R. 1995: Antioxidants for roading bitumen. Transit New Zealand Research Report No. 50. Transit New Zealand, Wellington.
- Herrington, P. R. 2001: The role of hydroaromatic species in the oxidation of petroleum bitumens. *Energy & fuels*, in press.
- Herrington, P. R.; Dravitzki, V. K.; Wood, C. W. B.; Patrick, J. E. 1993: Waste oil distillation bottoms as bitumen extenders. *Road and transport research*, 2(4): 56-67.
- Hewitt, C. N.; Rashed, M. B. 1990: An integrated budget for selected pollutants for a major rural highway. *The science of the total environment*, 93 (1990) 375-384.
- Hildemann, L. M.; Mazurek, M. A.; Cass, G. R. 1991: Quantitative characterisation of urban sources of organic aerosol by high-resolution gas chromatography. *Environmental science & technology*, 25, 1311-1325.
- Hodge, V. F.; Stallard, M. O. 1986: Platinum and palladium in roadside dust. *Environmental science and technology*, 20: 1058-1060.
- Hope, K. P.; Lamb, R. E.; Natusch, F.S. 1980: Multielemental characterisation of urban roadway dust. *Environmental science & technology*, Vol.14. No. 2 February 1980.
- Hoppstock, K.; Michulitz, M. 1997: Voltametric determination of trace platinum in gasoline after Wickbold combustion. *Analytica chimica acta*, 350: 135-140.
- Howell, G. J.; Ball, A. 1995: Dry sliding wear of particulate – reinforced aluminium alloys against automobile friction materials. *Wear* 181-183: 379-390.
- Huber, W. C.; Dickinson, R. E. 1988: Stormwater Management Model, Version 4, User's manual. US Environmental Protection Agency, Athens, Georgia. Report EPA/600/3-88-001a.
- Huggins, F. E.; Huffman, G. P.; Robertson, J. D. 2000: Speciation of elements in NIST particulate matter SRMs 1648 and 1650. *Journal of hazardous materials*, 74: 1-23.
- Jacko, M. G.; Tsang, P. H. S.; Rhee, S. K. 1984: Automotive friction materials evolution during the past decade. *Wear* 100: 503-515.
- Johnson, R. C.; Imhoff, J. C.; Dana, H. 1980: User's manual for hydrological simulation program – Forstran (HSPF). US Environmental Protection Agency. Report EPA/9-80-015. Athens, Georgia.
- Johnson, J. J. 1988: Automotive emissions. pp 39-75. In *air pollution, the automobile and public health* Ed. Watson, A. Y.; Bates, R. B.; Kennedy, D. Eds. National Academy Press, Washington D.C.

- Jehle, W.; Staneff, T.; Wagner, B.; Steinwandel, J. 1995: Separation of glycol and water from coolant liquids by evaporation, reverse osmosis and evaporation. *Journal of membrane science*, 102(1995): 9-19.
- Kadiyali, L. 1991: Updating of road user cost study. Report to the Ministry of Surface Transport, L.R. Kadiyali and Associates Ltd., Delhi.
- Kennedy, P. 2000: Ministry of Transport contaminants database. Support manual. Prepared by Kingett Mitchell Ltd for New Zealand Ministry of Transport.
- Kennedy, P.; Gadd, J. 2000: Preliminary examination of trace elements present in tyres, brake pads and road bitumen in New Zealand. Prepared by Kingett Mitchell Ltd for Ministry of Transport, November 2000. Revised October 2003.
- Kerminen, V.; Makela, T. E.; Ojanen, C. H.; Hillamo, R. E.; Vilhunen, J. K.; Rantanen, L.; Havers, N.; von Bohlen, A.; Klockow, D. 1997: Characterisation of the particulate phase in the exhaust from a diesel car. *Environmental science & technology*, Vol. 31, No. 7, 1997.
- Kim, S. J.; Jang, H. 2000: Friction and wear of friction materials containing two different phenolic resins reinforced with aramid pulp. *Tribology international* 33: 477-487.
- Kingett Mitchell, 1994: Used Oil Management in NZ. Report prepared for the Used Oil Recovery Group.
- Kleeman, M. J.; Schauer, J. J.; Cass, G. R. 2000: Size and composition distribution of fine particulate matter emitted from motor vehicles. *Environmental science & technology*, Vol. 34. No. 7, 2000.
- Konig, H. P.; Hertel, R. F.; Koch, W.; Rosner, G. 1992: Determination of platinum emissions from a three way catalyst-equipped gasoline engine. *Atmospheric environment* 26A(5): 741-745.
- Kumara, H.; Tukada, H.; Ogura, N. 1997: In molecular markers in environmental geochemistry. Eganhouse, R. Ed. ACS symposium series 671. American Chemical Society, Washington, DC, pp 291-305.
- Lawryk, N. J.; Weasel, C. P. 1996: Concentrations of volatile organic compounds in the passenger compartments of automobiles. *Environmental science and technology* 30: 810-816.
- Legret, M.; Pagotto, C. 1999: Evaluation of pollutant loadings in the runoff waters from a major rural highway. *The science of the total environment* 235: 143-150.
- Le Maitre, O.; Süssner, Zarak, C. 1998: Evaluation of tire wear performance. SAE Technical paper series 980256. Reprinted from Developments in tire, wheel, steering and suspension technology (SP-1338). International Congress and Exposition Detroit, Michigan, February 23-26, 1998.
- Lee, W-J.; Wang, Y-F.; Lin, T-C.; Chen, Y-Y.; Lin, W-C.; Ku, C-C.; Cheng, J-T. 1995: PAH characteristics in the ambient air of traffic source. *The science of the total environment* 159: 185-200.
- Leung, P-L.; Harrison, R. M. 1999: Roadside and in-vehicle concentrations of mono-aromatic hydrocarbons. *Atmospheric environment* 33: 191-204.
- Lindgren, A. 1996: Asphalt wear and pollution transport. *The science of the total environment*, 189/190: 281-286.
- Marklund, S.; Rappe, C.; Tysklind, M.; Egeback, K. E. 1987: Identification of polychlorinated dibenzofurans and dioxins in exhaust from cars run on leaded gasoline. *Chemosphere*, 16: 29-36 (1987).

- Marklund, S.; Tysklind, M.; Anderson, R.; Ljung, K.; Rappe, C. 1990: Emissions of PCDDs and PCDFs in gasoline and diesel fuelled cars. *Chemosphere*, 20: 553-561.
- Marr, L. C.; Kirchstetter, T. W.; Harley, R. A.; Miguel, A. H.; Hering, S. V.; Hammond, S. K. 1999: Characterisation of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. *Environmental science and technology*, 33: 3091-1099.
- MfE 2000: Used oil recovery, reuse and disposal in New Zealand: Issues and options. Ministry for the Environment, December 2000.
- Mi, H-M.; Lee, W-J.; Chen, C-B.; Yang, H-H.; Wu, S-J. 2000: Effect of fuel aromatic content on PAH emission from a heavy duty diesel engine. *Chemosphere*, 41: 1783-1790.
- Miyabara, Y.; Hashimoto, S.; Sagai, M.; Masatosbi, M. 1999: PCDDs and PCDFs in vehicle exhaust particles in Japan. *Chemosphere* 39(1): 143-150.
- Moncrieff, I.; Irving, P. 2001: NZ traffic and local air quality. *Planning quarterly*, March 2001.
- Moncreiff, I.; Kennedy, P. 2002: Road Transport Impacts on Aquatic Ecosystems - Issues and Context for Policy Development. Report prepared by Fuels & Energy Management Group and Kingett Mitchell Ltd for Ministry of Transport, December 2002, Updated June 2004.
- MoT 1996: Land Transport pricing study. Environmental externalities Discussion Paper March 1996, Ministry of Transport, Wellington.
- MoT 1998: Vehicle fleet emission model; New Zealand vehicle fleet database and model development. A technical report compiled by the Ministry of Transport in support of the Vehicle Fleet Emission Control Strategy. December 1998.
- MoT 1999: Impacts of rail transport on local air quality. Prepared by the Ministry of Transport with technical assistance from Fuels and Energy Management Limited. July 1999.
- Moldovan, M.; Gomez, M.M.; Palacios, M.A. 1999: *Journal of Analytical Atomic Spectrometry*. Determination of platinum, rhodium and palladium in car exhaust fumes.
- Moncrieff, I.; Irving, P. 2001: NZ traffic and local air quality. *Planning quarterly* March 2001: 29-31.
- Morawska, L.; Bofinger, N. D.; Kocis, L.; Nwankwoala, A. 1998: Submicrometer and supermicrometer particles from diesel vehicle emissions. *Environmental science & technology*, Vol. 32, No. 14, 1998.
- Muschack, W. 1990: Pollution of street run-off by traffic and local conditions. *The science of the total environment*, 93: 419-431.
- Norbeck, J.; Durbin, T.; Truex, T. 1998: Measurement of primary particulate matter emissions from light-duty motor vehicles. CRC Project No. E-24-2. Center for Environmental Research and Technology, University of California.
- Novotny, V.; Goodrich-Mahoney, J. 1978: Comparative assessment of pollution loadings from non-point sources in urban land use. *Water Technology*. 10 (5/6): 775-785.
- Oehl, K. H.; Paul, H. J. 1990: Bremsbelage für Straßenfahrzeuge – Entwicklung und Erprobung. Die Bibliothek der Technik Band 49. Verlag Moderne Industrie AG & Co.
- Ondov, J. M.; Zoller, W. H.; Gordon, G. E. 1982: Trace element emissions on aerosols from motor vehicles. *Environmental science and technology*, 16: 318-328.

- Opus, 1997: Environmental Effects of Used Oil Application to Roads for the Suppression of Dust. Report prepared by Opus International Consultants for New Zealand Ministry for the Environment.
- Palacios, M. A.; Gomez, M. M.; Moldovan, M.; Morrison, G.; Rauch, S.; McLeod, C.; Ma, R.; Laserna, J.; Lucena, P.; Caroli, S.; Alimontie, A.; Petrucci, F.; Bocca, B.; Schramel, P.; Lustig, S.; Zischka, M.; Wass, U.; Stembom, B.; Luna, M.; Saemz, J. C.; Santamaria, J.; Morrens, J. M. 2000: . Platinum-group elements: quantification in collected exhaust fumes and studies of catalyst surfaces. *The science of the total environment*, 257: 1-15.
- Pienaar, W. 1984: *Olieverbruik van Padvoertuie in Suid-Afrika*. NITRR Report RT/5, National Institute of Transport and Road Research, CSIR, Pretoria.
- Pitt, R.; Voorhess, J. 1995: Source loading and management model (SLAMM). pp 225-243. National conference on urban runoff: Enhancing urban watershed management at the local, county and state levels. March 30 to April 2 1993. Chicago, Ill. USEPA/625/R-95/003.
- Rauterberg-Wulff, A. 1998: Beitrag des Reifen- und bremsabriebs zur ruBemission an straben. *Fortschritt – Berichte VDI Reihe 15, Nr 202*. VDI-verlag, Dusseldorf.
- Reddy, C. M.; Quinn, J. G. 1997: Environmental Chemistry of benzothiazoles derived from rubber. *Environmental science and technology*, 31(10): 2847-2853.
- Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Case, G. R.; Simoneit, B. R. T. 1993: Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. *Environmental science and technology*, 27: 636-651.
- Ryan, C. J. V.; Gullet, B. K. 2000: On-road emission sampling of a heavy-duty diesel vehicle for polychlorinated dibenzo-dioxins and polychlorinated dibenzofurans. *Environmental science and technology*, 34(21): 4483-4489.
- Shaheen, D. G. 1975: Contribution of urban roadway usage to water pollution. USEPA Report No. EPA 600/2-75-004.
- Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. 1999: Measurement of emissions from air pollution sources. 2. C1 through C30 organic compounds from medium duty diesel trucks. *Environmental science and technology*, 33(10): 1578-1587.
- Schmitz, T.; Hassal, D.; Weber, F-J. 2000: Determination of VOC-components in the exhaust of gasoline and diesel passenger cars. *Atmospheric environment*, 34: 4639-4647.
- Shelef, M.; McCabe, R.W. 2000: Twenty five years after introduction of automotive catalysts: what next? *Catalysis today*, 62: 35-50.
- Schulz, H.; Bandeira de Melo, G.; Ousmanov, F. 1999: Volatile organic compounds and particulates as components of diesel engine exhaust gas. *Combustion and flame*, 118: 179-190.
- Schutte, I. 1981: *The Transportation Evaluation Process - National Cost Data*. NITRR Report RT/7/81, National Institute of Transport and Road Research, CSIR, Pretoria.
- Siegl, W. O.; Hammerle, R. H.; Herrmann, H. M.; Wenclawiak, B. W.; Luers-Jongen, B. 1999: Organic emissions profile for a light duty diesel vehicle. *Atmospheric environment*, 33: 797-805.
- Sjogren, M.; Li, H.; Rannug U.; Westerholm, R. 1996: Multivariate analysis of exhaust emissions from heavy duty diesels fuels. *Environmental science and technology*, 30: 38-49.
- Suarez, A. E. Caffrey, P. F.; Borgoul, P. V.; Ondov, J. M. 1998: Use of an iridium tracer to determine the size distribution of aerosol emitted from a fleet of diesel sanitation trucks. *Environmental science & technology*, 32(10):

- Todorovic, J.; Duboka, C.; Arsenic, Z. 1995: Operational life expectancy of rubbing elements in automotive brakes. *Tribology international*, 28 (7): 423-432.
- Tupa, R. C.; Doren, C. J. 1984: gasoline and diesel fuel additives for performance, distribution, quality. Society of Automotive Engineers paper 841211. Warrendale Pa. In Johnson 1988.
- USDOE 1987: Waste Oil: Technology, economics and environment, health and safety considerations. US Department of Energy Report.
- USEPA 1985: Size specific total particulate emission factors for mobile sources. EPA 460/3-85-005. August 1985.
- USEPA 1995: Draft user's guide to PART5: a program for calculating particle emissions from motor vehicles. EPA-AA-AQAB-94-2. Office of Mobile Sources, U.S. Environmental Protection Agency.
- USEPA, 1999: Revised methodology and emission factors for estimating mobile source PAH emissions in the National Toxics Inventory. Memorandum from R Cook & J Somers (Office of Transportation and Air Quality USEPA) to L Driver (Office of Air Quality Planning and Standards).
- USEPA 2002: User's guide to MOBILE 6.0. Mobile source emission factor model. ESEPA 420-R-02-001, January 2002.
- USEPA 2002: Health assessment document for diesel engine exhaust. National Centre for Environmental Assessment, Office of Research & Development, USEPA. EPA/600/8-90/057F May 2002.
- Verma, A. P.; Vishwanath, B.; Kameswaro Rao, C. V. S. 1996: Effects of resin modification on friction and wear of glass phenolic composites. *Wear* 193: 193-198.
- Vignati, E.; Berkowicz, R.; Palmgren, F.; Lyck, E.; Hummelshøj 1999: Transformation of size distributions of emitted particles in streets. *The Science of the total environment*, 235: 37-49.
- Watanatada, T.; Harral, C.; Paterson, W.; Dhareshwar, A.; Bhandari, A.; Tsunokawa, K. 1987: The Highway Design and Maintenance Standards Manual, Volume 1 - Description. The World Bank, John Hopkins University Press.
- Weckwerth, G. 2001: verification of traffic emitted aerosol components in the ambient air of Cologne (Germany). *Atmospheric environment*, 35: 5525-5536.
- Westerholm, R.N.; Alsberg, T.E.; Frommelin, A.B.; Strandell, M.E.; Rannug, U.; Winqvist, L.; Grigoriadis, V.; Egebäck, K. 1988: Effect of fuel polycyclic aromatic hydrocarbon content on the emissions of polycyclic aromatic hydrocarbons and other mutagenic substances from a gasoline-fueled automobile. *Environmental science and technology*, 22(8): 925-930.
- Westerholm, R.N.; Christensen, A.; Tornqvist, M.; Ehrenberg, L.; Rannug, U.; Sjogren, M.; Rafter, J.; Soontjens.; Almen, J.; Gragg, K. 2001: Comparison of exhaust emissions from Swedish Environmental Classified Fuel (MK1) and European Program on Emissions, Fuels and Engine Technologies (EPEFE) Reference Fuel: A chemical and biological characterisation, with viewpoints on cancer risk. *Environmental science and technology*, 35:1748-1754.
- Westerlund, K. G. 2001: Metal emissions from Stockholm traffic – wear of brake linings. Reports from SLB analys No. 3: 2001. Prepared on behalf of Stockholm Environment and Health Protection Agency and the Swedish Environmental Protection Agency. April 2001.
- Williams, R. L.; Muhlbaier, J. L. 1980: gas and particulate emission rates from asbestos linings. GMR-3434. Warren, MI, General Motors Research Laboratories (cited in Cha et al. 1983).

- Williams, R. L.; Muhlbaier, J. L. 1982: *Journal of environmental research*, 29: 70-82.
- Wu, J. S.; Allan, C. J.; Saunders, W. L.; Evett, J. B. 2000: Characterisation and pollutant loading estimation for highway runoff. *Journal of environmental engineering*, July 1998 584-592.
- Yamaguchi, J. 1991: Honda's non-asbestos, non-metallic, non-glass brake pad composite. *Automotive engineering*, 99(12): 45-46 (cited in Armstrong 1994).
- Yang, H. H.; Lee, W. J.; Mi, H. H.; Wong, C. H. 1998: PAH emissions influenced by Mn-based additive and turbo charging from a heavy-duty diesel engine. *Environment international*, 24(4): 389-403.
- Zięba-Palus, J. 1998: Examination of used motor oils by flame AAS for criminalistic purposes: a diagnostic study. *Forensic science international*, 91:171-179.
- Zięba-Palus, J. & Kościelniak, P. 2000: An analysis of the similarity of motor oils on the basis of their elemental composition. *Forensic science international*, 112:81-90.
- Zoppu, C. 2000: Review of urban stormwater models. Research School of Information Sciences and Engineering, Computer Sciences Laboratory, The Australian National University, Canberra, ACT 0200, Australia.