Road Transport Effects on Aquatic Ecosystems
Issues and Context for Policy Development

Ministry of Transport
Te Manatū Waka

Road Transport Impacts on Aquatic Ecosystems

Issues and Context for Policy Development

Prepared For

MINISTRY of TRANSPORT
TE MANATŪ WAKA

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APPENDICES

ABBREVIATIONS

AADT	Average annual daily traffic
AGO	Automotive gas oil (diesel fuel)
Al	Aluminium
AIMSUN2	Advanced Interactive Microscopic Simulator for Urban and Non-Urban Networks
ARC	Auckland Regional Council
As	Arsenic
ASV	Anodic stripping voltametry
Ba	barium
BCF	Bioaccumulation factor
BOD_5	Five day Biological oxygen demand
Br	Bromine
BT	Benzothiazole
BTEX	Benzene, toluene, ethylbenzene, xylene
Cd	Cadmium
Ce	Cerium
Cl	Chlorine
CO	Carbon monoxide
CO_2	Carbon dioxide
COD	Chemical oxygen demand
COPC	Contaminant of potential concern
Cr	Chromium
Cu	Copper
DOM	Dissolved organic matter
ECA	Environmental capacity analysis
ELGO	Emissions loading geographic output
ENEV	Environmental no effects value
EP	Extreme pressure
ERMA	Environmental Risk Management Authority (New Zealand)
EU	European Community
Fe	Iron
g	gram
GDP	Gross domestic product
GIS	Geographic Information System
ha	hectare
HC	Hydrocarbons
HD	Heavy duty
HDV	Heavy duty vehicles
Hg	Mercury
HMW	High molecular weight
HPV	High production volume (chemicals)
HSNO	Hazardous Substances and New Organisms
I-TEQ	International-Toxic Equivalents
K	Potassium
kg	Kilogram
km	Kilometre
L	Litre
LD	Light duty
LDV	Light duty vehicles
LMW	Low molecular weight
LoS	Level of Service
Mg	magnesium
Mn	Manganese
mm	Millimetres
Mo	Molybdenum
MoT	Ministry of Transport (New Zealand)

MTBE	Methyl-t-butyl ether
MW	Molecular weight
NF	Nitro-fluorene
ng	nano-gram
Ni	Nickel
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NOx	Oxides of nitrogen
$N0_2$	Nitrogen dioxide
NP	Nitro-pyrene
N-PAH	Nitro polycyclic aromatic hydrocarbons
NPI	National Pollutant Inventory (Australia)
NZRC	New Zealand Refining Company
NZ-TER	New Zealand traffic emission rates
OH	Hydroxide
OSH	Occupational Safety and Health Service
Pb	Lead
PAH	Polyaromatic hydrocarbons
PC	Passenger cars
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzofurans
Pd	Palladium
PGE	Platinum group elements
PM	Particulate matter
Pt	Platinum
P-ULP	Premium unleaded petrol
QSARS	Quantitative structure activity relationships
RAP	Refinery to Auckland pipeline
Rh	Rhodium
R-ULP	Regular unleaded petrol
Sb	Antimony
SIDS	Screening Information Data Set
SO_2	Sulphur dioxide
SOx	Sulphur oxides
SVOC	Semi volatile organic compound
TBN	Total base number
TCDD	2,3,7,8-tetra chlorinated dibenzo para-dioxin
TEQ	Toxic equivalent
TIE	Toxicity identification evaluation
TSCA	Toxic Substances Control Act (United States)
µg	micro-gram
USEPA	United States Environmental Protection Agency
VFECS	Vehicle fleet emissions control strategy; MoT programme
VFEM	Vehicle Fleet Emissions Model; emissions inventory
VKT	Vehicle kilometer travelled
VOC	Volatile organic compound
VPD	Vehicles per day
Zn	Zinc
ZnO_2	Zinc dioxide
Zr	Zirconium

1. INTRODUCTION

1.1 Background

This work programme addresses the Ministry of Transport's (MoT) requirement to assess the impacts of road transport on the aquatic ecosystems and to determine the need for appropriate forms of policy for their control. The initial priority of this requirement is to develop the analytical framework and general approach, before entering the detailed factors surrounding each potential contaminant. The purpose of this report is to put these general issues into the public domain for wider consideration, to confirm the approach to be pursued. This report to the MoT provides the body of material required for this public discussion document.

Due to the highly complex nature of the subject, the overall work programme comprised a number of stages, and steps. "Stage 1" was a preliminary review of what is known about the potential problems in this regard ("The effects of road transport on freshwater and marine ecosystems"). This report provides the output from "Stage 2" of the project. As additional information on effects became available during "Stage 2", the 'effects' report was updated in 2003 (Kennedy 2003a).

Specific information on the nature of contaminants emitted by motor vehicles is presented in a separate document (Kennedy et al. 2002). That report discusses in some detail the nature of emissions and 'emission factors'. In addition a database of organic compounds emitted by motor vehicles was developed as part of the overall assessment of potential effects of contaminant emissions on aquatic ecosystems (Kennedy 2000). There are seven reports that are referred to in this report:

1. Kennedy, P. 2000: Ministry of Transport contaminants database. Support manual. Prepared for New Zealand Ministry of Transport by Kingett Mitchell Ltd.

2. Kennedy, P.; Gadd, J. 2000: Preliminary examination of trace elements in tyres, brake pads and road bitumen in New Zealand. Prepared for New Zealand Ministry of Transport by Kingett Mitchell Ltd.

3. Gadd, J.; Kennedy, P. 2000: Preliminary examination of organic compounds in tyres, brake pads and road bitumen in New Zealand. Report prepared for New Zealand Ministry of Transport by Kingett Mitchell Ltd.

4. Kennedy, P.; Gadd, J.; Moncrieff, I. 2002: Emission factors for contaminants released by motor vehicles. Prepared New Zealand Ministry of Transport and Infrastructure Auckland by Kingett Mitchell Limited and Fuels & Energy Limited for.

5. Kennedy, P.; Gadd, J. 2002: Evaluation of road surface contaminant loadings in Waitakere City for the development of the vehicle fleet emission model-water. Prepared for New Zealand Ministry of Transport by Kingett Mitchell Ltd.

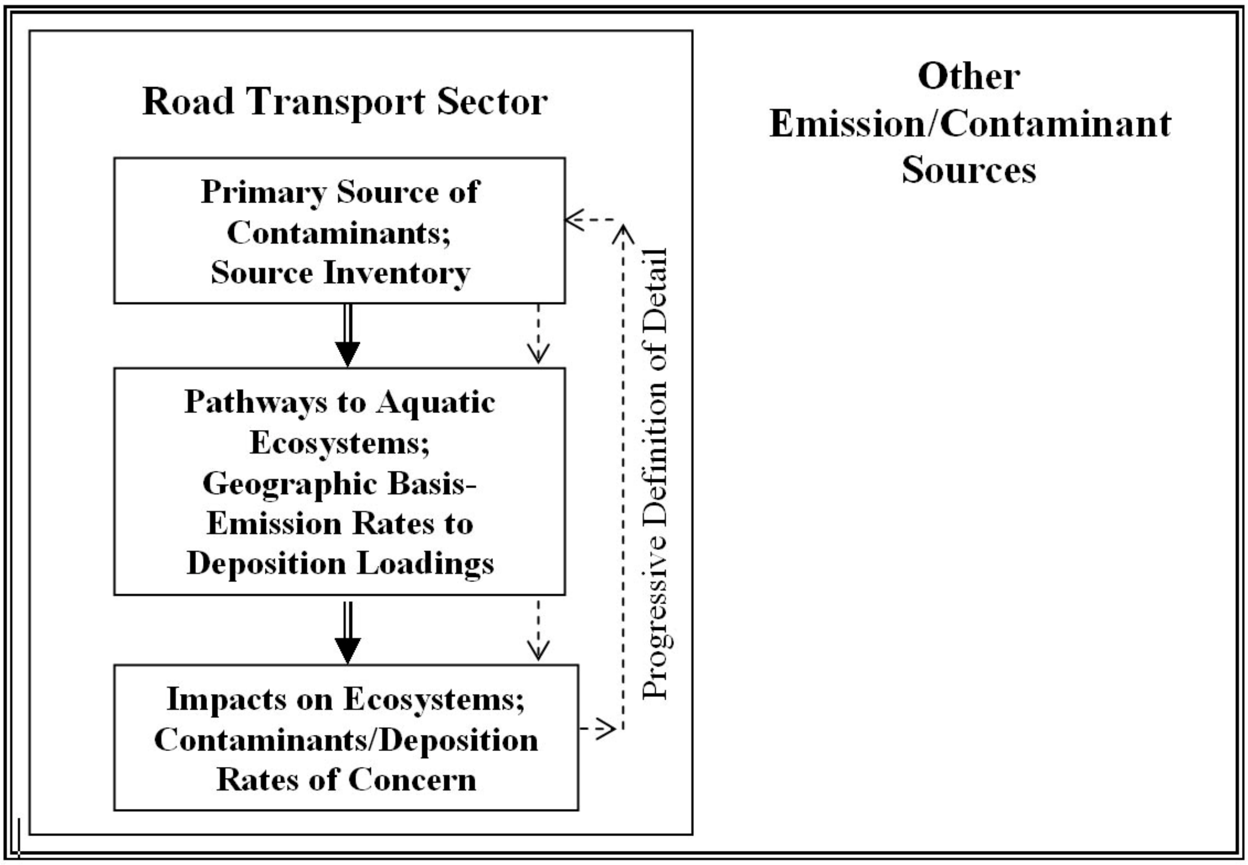
6. Kennedy, P. 2003: Metals in particulate material on road surfaces. Prepared for New Zealand Ministry of Transport by Kingett Mitchell Limited.

7. Kennedy, P. 2003: The effects of road transport on freshwater and marine ecosystems. Prepared for New Zealand Ministry of Transport by Kingett Mitchell Limited.

1.2 Study Logic

This report itself is a product of what has been designated "Stage 2", in which the primary objective was to produce the analytical framework and environmental management approach required to identify the nature of any current or contingent problems, and determine the appropriate policy measures. The basic logic for this Stage 2 is summarised in Figure 1.1 and follows a systematic approach in analysing the subject, through a progressive and interactive work programme that refines the detail to the extent and in the areas necessary. This is itemised in more detail later in Section 3.

Figure 1.1 – The Study Process & Context.



There are direct parallels in this logic with the development of the Vehicle Fleet Emissions Control Strategy (VFECS) programme which examined the impacts of vehicle emissions on air quality. This introduced the Environmental Capacity Analysis (ECA) concept, in recognition of the fact that the information base defining impacts will never be comprehensive, so an iterative process is needed to identify the priorities in some measured way. The same philosophy is called for in the water context, a framework that sets out a consistent impacts driven methodology for managing potentially toxic materials, as they are currently in use, or for screening those that might be introduced through technology evolution in the road transport sector.

Also, as in VFECS, the analysis needs to include two other functions:

- A basis for projecting the effects of change through future time.
- The means to compare the output from the road transport sector against other sources in the same locality, for a given contaminant discharge.

In the Stage 2 programme, the VFECS approach is continued in the development of the source side inventory, in the structure, characterisation, then quantification and profiling of contaminant source factors. This generates output of the primary "emission" rates as functions of vehicle technology and traffic network interaction (road design and driving conditions), for the various modes of uncontrolled material loss.

In the ECA concept, this inventory process is related to a geographic framework of reference, to derive area-defined emission loadings for each contaminant. This is interfaced with the analysis of the:

- Pathways, by which these contaminants end up in an aquatic environment.

- The impacts criteria; the levels and conditions under which the various forms of contamination represent a concern in preserving these ecosystems, and to identify what contaminants pose a threat, where and under what circumstances, and by how much.

1.3 Study Sequence

The main elements of the study are summarised below, these being followed in an iterative manner to give the progressive development of detail.

Step1

- Identify the generic range of compounds/elements that could possibly enter the local environment due to the presence/operation of vehicle traffic, now and through the future developments anticipated in the road transport sector.

- Prepare first approximations of contaminant emission rates, at source (typically at an order of magnitude levels), to give measures of possible maxima to local area (corridor to urban region wide) deposition loads.

- Design a source inventory structure for the appropriate characterisation of contaminant source factors, and to model means for their control. This includes the initial design of the interface required with the geo-spatial frame of reference for the "pathways".

Step 2

- Assess the manner and extent to which these compounds and their possible sub-groups and derivatives, carry any known toxic/environmental threat, actual or potential, at what levels/duration etc; this is to set the criteria and thresholds required for effects based control.

- Focus in more on the precise nature/presence/discharge rate of these compounds (and their precursors) at the source side. Confirm acceptability of using generic measures, or where there is a need for actual material analysis/testing of discharge rates, to better define and calibrate a source side discharge inventory.

Step 3

- Refine definition of pathway factors, linking rates of discharge at source to localised deposition loadings and ecosystem exposure. This will be either local/actual definition (as per ECA process) or by use of representative models, to provide for improved estimation of deposition rates in ecosystems of concern.

- Further investigation of impacts side, to give improved understanding of contaminants/exposure levels that would cause concern; develop targets for impacts based management.

- Develop integrated model that links source ⇒ pathway ⇒ ecosystem impact, on geographic basis, to evaluate management/mitigation options, as may be necessary.

This iteration may require further development in detail, particularly in being able to compare the contaminant loading from road transport against that from other sources in the area. This was an important component of the VFECS programme for managing air emissions.

These steps were refined during the course of the project. Table 1.1 provides a summary of the process set out above and its logical extension, continuing the iteration between source and impact relationships.

Table 1.1 – The Overall Study Process.

Source	Impact
Stage 2 Scope	**Stage 2 Scope**
1. Listing of all contaminant types, potential by source, and typical magnitude of "discharge rates".	**1.** Initial impact assessment of all contaminant types, just by virtue of their possible presence, to highlight those of potential concern, and in what way (characterising the deposition factors).
2. Design source side inventory structure, for appropriate characterisation of source factors.	**2.** Characterisation of "catchment" area/pathway factors, relevant to these deposition factors, to give sense of scale/terrain/intermediates etc.
3. Design inventory geo-spatial framework interface, with pathways. ⇒ Initial Inventory Outputs.	**3.** First calibration of potential impact concerns, under current NZ road transport operations; contaminant types, area/location factors. Indicators of degree of uncertainty in quantifications.
Stage 3	**Stage 3**
4. Assess need for improved source factor calibrations, to improve representation of deposition relationships.	**4.** Develop basis "regulating" control of priority contaminants (Guidelines etc); undertake review of current NZ/global status in setting control parameters, towards establishing targets.
5. Design/conduct of specific "discharge rate" test programmes, for NZ conditions.	**5.** Refine definition of pathway factors, as mechanisms for collection and deposition.
6. Develop inventory as geo-spatial modelling capability (integrated with pathway representation, as for ECA), for evaluating source side control measures.	**6.** Analysis of impacts mitigation as required, by modelling source/pathway control options in integrated source-to-impact process
Stage 4; Other Contaminant Sources - Non Vehicle	

1.4 Stage 2; Scope - Source Inventory

The VFECS programme provides the starting point for the inventory framework, utilising the same vehicle fleet statistical and projections base that features in the Vehicle Fleet Emissions Model for consistency. This also readily provides the basic output measures required for exhaust emissions, as one particular discharge mechanism. These require speciation, for the VOC and PM groups, as it is more the individual component chemistry that is important in the context of aquatic ecosystems.

Added to this are the structures required for characterising other forms of discharge, for wear media and other possible contaminant release that are regular or continuous functions of normal vehicle activity. This does not include sporadic incidents such as "cargo" losses, or the results of a road accident, although it would be possible to apply the process to analysing such events, in a similar manner. The inset box (Inventory restrictions and limitations) provides further detail in relation to the nature of the exclusions in this assessment. The basic approach to the inventory development is described in the following sections.

Item 1; Listing of Contaminant Types

This sets a framework for compiling a reference compendium of all the materials that could in some way emanate from vehicle activity, on the road networks. This "material inventory" addresses;

- Consumables, such as fuel and oil formulations, and other service fluids, and any additives (original specification and after-market) that may be in use.

- Wear media, tyres, brake/clutch linings and other longer term service items.
- Erosion media, such as exhaust catalyst substrates.
- Road wear/erosion materials.

This is based on a system of categorisation that classifies the material's original service function, and then considers the potential derivative compounds arising through their service function and mode of discharge from the vehicle. Refer to section 4 of this report, for the detail.

Inventory Restrictions and Limitations

Restrictions or limitations have been used in a number of national pollutant assessment systems to limit the need for assessments of all substances. NEPC (1999) excluded greenhouse gases and ozone depleting substances in their review of substances for the Australian National Pollutant Inventory (NPI). The basis for exclusion was that these substances had already been the subject of scrutiny. This is also the situation in New Zealand. NEPC (1999) also noted that these substances could be brought back onto the NPI should data such as toxicity come to light that should indicate that inclusion onto the NPI was warranted.

Load limits have been incorporated into various assessment programmes for high volume production chemicals. For example in the United States, some new chemicals are exempt from pre-manufacture notices (under S5 of the Toxic Substances Control Act – TSCA) if the substance is to be manufactured in low volume (10,000 kg/annum); the substance is expected to have low release and low exposure (refer 40 CFR S723.50, March 29, 1995); the substance is a polymer that is not considered chemically active or bioavailable as set out in 40 CFR S723.250.

In New Zealand, the Environmental Risk Management Authority (ERMA) has introduced for the purpose of application types a classification system which in the case of category A applications has some relevance to this assessment (ERMA 1999). Category A applications cover three categories (referred to as A1, A2, A3). Category A1 encompasses substances that have a hazard classification (e.g., falling into ecotoxic categories 9.1D, 9.2D, 9.3D, 9.4C. Category A2 encompasses substances that may be used in a contained way (e.g., in a particular process or on a site). In situations where only restricted volumes of a potential contaminant are produced or imported, volume restrictions are identified as a guide to situations of low risk (for example the volumes range from nil up to <100 kg/year for ecotoxic categories 9.1A, 9.2A, 9.3A, 9.4A and from <100-<1000 kg/annum for ecotoxic categories 9.1B-9.4B). ERMA also specifically identify those substances that are of moderate to high hazard but have limited exposure (e.g., used in small containers).

In identifying the contaminants released from motor vehicles or from their use, a number of criteria were identified that provide some limitation as to what would be incorporated into the assessment at this stage. The criteria included:

1. Contaminants associated with vehicle loads would not be included in the assessment or associated database.
2. Contaminants released as a consequence of accidents would not be included in the assessment or database.
3. Contaminants associated with sealed units in motor vehicles (as a result, no defined release to the environment) would not be included in the assessment or database.
4. Contaminants with estimated annual release to the New Zealand environment of less than 10 kg/annum.
5. Ozone depleting substances and greenhouse gases.
6. 'Inorganic' gases such as NOx, SOx, CO_2.

In the first instance this reference base addresses current fleet technology. The functional classification then follows a systematic review of performance changes required through vehicle/engine technology developments in the future, and the implications on material types and specifications in use as the fleet evolve. Of particular note is the possible introduction of new functional materials, a good example being fuel soluble organo-metallic catalysts for combustion and emissions control.

Excluded from this are specific modes of “purposeful” disposal such as waste oil disposal and leakage from refuelling stations, as other regulatory processes address these.

Item 2; Design of Inventory Structure

As with the VFEM, the primary focus of the inventory is vehicle driving conditions, as these will be a major influence on the rate of discharge for the majority of materials and loss mechanisms involved. This relates to road type and network design factors, and traffic conditions, as well as vehicle life-cycle influences that significantly affect the rate of discharge with vehicle age and service condition.

Item 3; Inventory Geo-Framework

Relating discharge quantities to the local receiving environment is the critical function in this work, to understand the relative loadings imposed and the eco-system response to them. For this to translate to an ECA type analytical tool, it is necessary to develop the geo-spatial interfaces between the road network layout and the catchment and stormwater systems, to understand where the contaminants end up. To this end, this Stage 2 includes a feasibility assessment of the electronic interfacing of catchment GIS data files with traffic modelling procedures (akin to the development of the ELGO concept – “Emissions Loading Geographic Output”- introduced in VFECS). Examples are provided for the Christchurch city situation.

1.5 Stage 2; Scope - Pathways & Impacts

Item 1; Initial Impact Assessment of Contaminants

The impact of any contaminant released as a result of the activity of motor vehicles is dependent upon the physical and chemical properties of each compound and its concentration in the environment. To address the issue of possible impact within aquatic environments it is necessary to have a process to determine the likelihood of impacts.

For contaminants identified as being emitted from motor vehicles, an environmental hazard analysis is carried out using a screening risk assessment process to identify the potential effects of compounds. This process which is developed into a database format assists in the identification of whether a contaminant is a contaminant of potential concern (COPC) based upon the evaluation of four fundamental characteristics of the compound. These are toxicity, degradability, bioaccumulation and persistence. For each of the characteristics a series of properties were identified based upon available and calculated data.

Item 2; Characterisation of “catchment” area/pathway factors

Contaminants enter aquatic environments through a number of different pathways. The pathways differ depending upon the form and properties of the contaminants involved. The contaminants database identifies information on the fate of organic contaminants.

1.6 Stage 3; geo-Spatial model development and emission factor assessment

As set out above, Stage 2 set out the basic inventory structure for correlating the make up of the vehicle fleet with its potential emission of contaminants to the road network (the Vehicle Fleet Emissions Model for Water; "VFEM-W"). Stage 3 carries this through to full integration with general urban contaminant management, by developing a working example for a particular city to demonstrate the concept. This can be used to track contaminant loadings from source through to the receiving environments. This working model will then be subject to a calibration programme in validating the process as a whole. The Stage 3 process was divided into two parts;

Part 3A: Urban Management Framework Development: The first part constructs the interfaces whereby the VFEM-W is linked through the given road network and surrounding urban infrastructure, to establish the pathways between the vehicle traffic and the receiving water systems in the vicinity. It also identifies the links with wider urban planning and development that is, the primary driver for travel demand and vehicle use, and other land use activities that constitute potential emission sources.

Part 3B: Field Validation/Calibration of VFEM-W. The second part involves field sample measurements of contaminants in the road/stormwater environment, to calibrate the emission loading. Following an evaluation of options to undertake this work, it was not considered feasible to undertake a large-scale stormwater sampling programme. To provide some calibration data an assessment of the loads of contaminants on road surfaces was carried out. The Part B scope involved the comparison of output from the VFEM-water model with information on contaminant loadings on road surfaces in Waitakere City with, the intention of comparing the model output with real-time data to assess the relativity of the data.

Both components of the Stage 3 work programme were undertaken in Waitakere City. The main priority is to investigate contamination of aquatic environments but the inventory process will also include the corresponding local air emissions, and have the ability to model the traffic output of CO_2 (in evaluating the effects of local transport management within GHG policy).

2. SOURCE CLASSIFICATION FRAMEWORK

2.1 Introduction

The starting point in setting up the source inventory has been to establish a Classification Framework, as a means of reference throughout the study programme for logically defining the information requirements. This is a system of categorisation based on the material's original service function **-** why it features in the road transport infrastructure in the first place. This then considers the substances and compounds that are likely to be in use for this purpose, and the potential chemical derivatives arising through their mode of use, or mechanism of discharge from the vehicle. The structure is summarised as Table 2.1.

This reference base starts with current fleet technology, then provides for a systematic review of material specification and performance changes that might be required through technology developments in the future, coming in as the fleet evolves. This also allows for the need to consider the retrospective, what has gone before, if certain of the impact problems have been found to be the result of a long term accumulation of contamination.

This classification framework could form the basis for documenting product specification practices in the New Zealand motor industry. It may also provide a reference framework in the convergence of this work with the jurisdiction of ERMA, in applying the HSNO registration system to the same substance groups (which currently has no form of industry type classification; see later).

This framework provides, a first principles “checklist” approach for identifying all those materials potentially introduced to the local ecosystems through the very presence and operation of road vehicles - if this is the function, what materials could be used to provide it? Each of the categories can be progressively subdivided through the analysis, to identify the variants technically available and potentially present in the New Zealand vehicle fleet through the sequence of logic outlined below. In a number of cases there will be interactions between the various classification groups, such as the nature of one component influencing the performance (or performance requirements) of another where they conjoin in operation (e.g., road : tyres, fuel quality : lubricating oil specification).

The progressive review of materials is in accordance with this framework. The main emphasis at this time is placed upon the chemical speciation of materials that are emitted by design, or their loss through wear is essentially uncontrolled.

Examining the characteristic mode of loss also directs the design of the inventory structure, to define the most influential factors in the rate of loss, or primary "emission" to the environment. First approximations of emission rate may provide a parameter for rationalising the number of potential contaminants to be considered in the later impacts analysis.

2.2 Classification

The classification logic is as follows:

Function; the purpose of the material/component in the operation of the vehicle, what it does and therefore why its there.

Mode of Action; how it does what it does, the mechanisms through which it provides its function, at the level of performance required.

Specification; the means by which the performance requirements are specified, and composition controlled, that are relevant to New Zealand and are observed by the industry/regulatory systems.

Table 2.1 - Contaminant Source Classification Framework.

Powertrain Area	Component	Function	Mode of Action	Specification	Formulation	Mode of Loss	Composition of Discharge	Future Influences
Fuel	Base stocks Blendstocks Additives – initial formulation Additives – after-market Evaporative emissions							
Exhaust System	Combustion emissions; gaseous, Combustion emissions; particulate Emissions control system; erosion Emissions control system; control additives							
Lubricants	Engine oil (sump and 2-T) Gear oil Oil additives – after-market Bearing grease Chassis grease							
Coolants	Engine coolant Stop-leak additives Induction intercooler systems Air conditioning refrigerants							
Sealants	Gaskets Jointing compounds Fillers							
Hydraulics	Brake servo systems Clutch servo systems Auto transmission fluid Power transmission Suspension systems Auxiliaries (power transmission)							
Braking (and clutch)	Friction linings							
Tyres	Tread surfaces wear Carcase weathering							
Roads	Pavement surfaces; wear Pavement surfaces; weathering							
Vehicle Body – Sundry	Plasticisers Paintwork Metal corrosion Surface coatings weathering; (paintwork and underbody protection) Windscreen washer additives Vehicle washdown (roadside) Drive belts; engine auxiliaries Battery fluids Cargo losses							

Formulation; the chemical composition of the material in response to the functional performance required of it, and as may be controlled by specifications.

Mode of Loss; the mechanisms by which the material undergoes attrition or change, physically and/or chemically, and/or loss, through to the final mode of discharge from the vehicle.

Composition of Discharge; the chemical form of the final discharge, as a primary contaminant to the local road corridor environment.

Future Influences; the various influences and requirements that, directly or indirectly, could cause change to each and any of the previous aspects through future time, from the present status quo conditions and fleet profile.

2.3 The ERMA HSNO System

This is New Zealand's statutory authority for the control of materials introduced into New Zealand from a hazards point of view. The process is one of declaration, the importer/user etc. being responsible for notifying the authority prior to introduction. The systems are not yet in place to ensure automatic triggering of the process, but it is under consideration e.g., via a link with the Customs coding of materials and substances; currently only dangerous materials such as explosives have links through Customs/OSH. Therefore, for now, compliance with the registration process cannot be assumed to be 100%, but is considered to be relatively comprehensive. However, this is still reliant on the potential applicant being aware of what he must do, which relies for now on education and publicising the process, and advising other authorities such as Customs.

The registration process is currently going through a transition phase, in transferring all that was done before under the old Toxic Substances Act to the new HSNO Act implemented in 1996. This transition process was activated by promulgating that what was not already registered would have to undergo a renewed application when the transition process was over; the number of applications accelerated from just 3,000 on the list from 1983 – 95, to 30,000 more during 1995 – 98, and another 100,000 from 1998 to date. This was for materials already in the country, in use. Therefore, the "register" currently comprises around 130,000 substances/materials, and will represent New Zealand's "Chemical Inventory" when fully established. The oil industry was particularly active in registering all of its materials, in the detail required of the "Notification" format. In theory, every supplier of anything should have gone through the process, even purveyors of after-market additives and the like, but there is no means of checking this at present. This is currently under review by the ERMA compliance authorities, enforcement coming under Part VII section 97 of the act. ERMA should be consulted for further information regarding the current ERMA assessment process (http://www.ermanz.govt.nz/).

There are many obvious areas of convergence in intent between the HSNO process and the policy approach required for controlling environmental impacts in this context. Longer term, the ERMA process will theoretically address the same requirements, in terms of the registration of potential hazard, although at this time there are potential inconsistencies in interpretation (e.g. does "hazardous waste" also cover an exhaust emission, as a by-product of the process/use for which the original material is intended?). There is another question of definition in the HSNO act, between "substance" and a "manufactured article", that concerns the potential for uncontrolled loss.

As is discussed later in this report, the ERMA Hazards assessment is done through six classification steps, three being "physical" three being "biological". As in this analysis, ERMA has to consider the full life cycle from handling, mode of use, losses, discharge and eventual disposal. Waste lubricating oil is a good example. The obvious convergence is with the "Eco-toxicity" hazard group, where a series of benchmark criteria are used to screen for the degree of concern, amount of information required and controls on handling and use. The general approach used is risk-based analysis, in terms of the potential for exposure (amount/concentrations x time). A degree of cost:benefit analysis is also undertaken, i.e., do the benefits outweigh the risks? The registration system does not as yet have any industry based classification method for registering materials.

Decisions are made on the best information available, but with the number of materials in question there is obviously a need for some value judgements. It may be that the approach/criteria used could provide a precedent; it may be sensible for both procedures to be, seen to be harmonised in using the same criteria within an on-going policy process for control. The information required in the "Notification" is mainly an approximation of the chemical composition, rather than the definitive chemical compounds. The CAS number is also requested, if known. Other databases are also consulted such as the Australian Inventory of Chemical Substances (AICS, available in CD-ROM form).

3. PROCESS

3.1 Introduction

The eventual outcome of this work is to define a fully integrated framework that relates measures of the impacts back to source emissions loadings for the individual contaminants of concern. In this way, there will be a measured understanding of the degree to which each contaminant needs to be controlled, to maintain the required environmental protection.

This environmental management approach has been established for air quality, in the control of vehicle exhaust emissions. This programme now seeks to extend the concept to all potential contaminant discharges that could in some way harm the local aquatic environment. However, the degree of complexity this implies is many-fold over the corresponding process for air quality management, in which:

- The number of pollutant types were relatively few, and are formally identified by the air quality management procedures used to define air quality.
- There is more of an immediate "time and space" local correlation between emissions output rates and the corresponding pollution levels, with the local air-shed being the receiving environment in direct contact/surrounding the emissions activity.
- There are essentially no pathway factors that distort this correlation; the emissions enter the air-shed, and the resulting concentrations are measured directly (air movements through meteorology are the main influence on the "dilution" rates, but sensitivity to pollution events is greatest under calm air conditions).

In the water context, each of these is complicated by:

- The impacts problems are not in all cases clearly or systematically defined, in terms of the range of specific chemical contaminants that are of concern, and criteria by which the concern is assessed.
- There is no simple means for defining the spatial correlation, that associates the local area of source activity with the affected receiving environment.
- There are many different pathway factors that influence the relationships between contaminant discharge rates, or source loadings, and the eventual loadings in the receiving environment.

As has been noted, a critical component of this management process is the source inventory of contaminants, to provide first measures of their potential presence. The design of any inventory concerns three main elements;

1. The population of the sources; the number and type of the individual sources of a given contaminant.
2. The activity profiles for each type of source, the mechanisms that cause the discharge of the contaminant.
3. The corresponding emission rates that are characteristic of the type and activity of each source group.

The eventual inventory output is the product of these elements. However, the structural detail and complexity of the inventory is determined by the precision required in the result, in particular in identifying the most influential factors in the final output rates. In effects-based environmental management, this is usually set by measures of the impacts problem to be addressed. From this the process works back to the degree of definition for which the source factors need to be profiled.

This section of the report describes the overall process of contaminant identification and the process used to assess whether contaminants identified to date as being emitted from motor vehicles pose a risk to aquatic environments. The various sources are discussed in relation to the identified contaminants and their key pathways are described.

3.2 Contaminant Listing: Potential Approaches to Screening/Rationalising

The immediate complication in inventory design, is presented by the sheer number of possible contaminants involved. Potentially, thousands (or tens of thousands) of individual chemical compounds could be considered, as introduced to the environment by virtue of road transport. Ideally, all would be individually identified, and ranked by some impacts-based criteria to highlight those of concern. However, working from an established and comprehensive database of chemicals would never be feasible in any policy development sense (as opposed to a specific scientific study) due to:

- The sheer amount of work required in cataloguing the potential impacts of each compound, even assuming the impacts information was already available.
- Keeping track of the potential changes in the compounds used, in proprietary formulations in the road sector, as technology evolves.
- Whether their discharge is incidental, locally specific or routine.
- Whether the cumulative amount of the discharge would be significant.
- Whether it is possible to detect the substance, at what levels of concentration.

The as yet unidentified vagaries of the “pathways” that relates concentrations from discharge to impact, including such as weather, atmospheric reactions, half-lives, urban form etc.

The VFECS precedent had already encountered this for air quality. The resulting ECA concept answered the need for what would be an on-going management process that could deal to individual pollutant issues as they emerged. It was not possible in the air context, nor would it be for water, to undertake an analysis that identified all of the problems and designed all of the solutions in a one-shot process.

In this exercise, where the impacts issues are even more complicated, the first priority is to establish the structural approach to any policy development, rather than a selective focus on what might be out there. For the design of the inventory component of this structure, there needs to be a rational approach to screening and prioritising particular compounds by virtue of their chemistry or potential loading, or any other impacts driven criteria.

Investigating the source side starts off by understanding the nature of the industry; what sorts of materials are in use, and why, what might affect future changes and the way in which such information is available, or could be derived to the level of detail necessary. The nature of the availability of the information itself is a steer on the policy development approach required. With this industry, this mainly starts off with generics. The majority of compounds in use are derivatives of basic classes and their isomers that, provide the characteristic functionality required. The variety of proprietary formulations as particular individual derivatives can be vast, and are usually closely protected trade secrets, so the industry deals with them as generic types. Further, as this is how the industry recognises the materials, so must any structure for policy control, at least in the first instance.

The first question, therefore, is to what extent is it possible to make first approximations of their possible eco-toxicity on the basis of their functional composition? For example, is it necessary to spell out each of the possible 10,000 or so individual hydrocarbon compounds in diesel fuel up to C_{30} before doing the process of elimination, or can a first estimate of possible concentrations allow us to work from classes of compounds? Are there other processes of rationalisation, and what is appropriate to each source group?

Also, how do we need to consider the potential toxicity of each compound/element? For example, if zinc is a concern is it because it is present as:

Zinc (Zn) in its elemental form.

As ZnO_2, as used in tyres.

As ZDDP (zinc dialkyl/diaryldithiophosphates) as used in lubricating oils.

As another resultant product complex, e.g., through the process of combustion, or through reactions that might occur in the receiving environment?

In the following sections, this is discussed further in relation to the Classification Framework for each of the key functional source groups.

3.3 Functional Groups

Fuels

In theory, fuel usage is not an uncontrolled discharge, leakages being incidental – is it a priority at this initial stage of analysis? It would theoretically be possible to list out the great majority of individual compounds (largely done for petrols), but then we are into hundreds/thousands of individual substances for study. The principal form of routine loss would be unburnt/partially burnt fuel as emissions in the exhaust, or as evaporative VOC for petrol. As described in Section 4, the composition of fuel has not been identified as a priority for evaluation in the evaluation process at this stage.

Fuel Additives

As with fuel, this source component is potentially extremely complex, if the chemical detail required is any more than the inorganic element that might feature in formulation that, could emerge in the exhaust stream. After-market additives are used incidentally, rather than routine, so this could be an example of when a material is subject to the inventory/deposition calculation process as part of the actual environmental management process (e.g., as part of its approval for introduction through the ERMA system).

However, if it is necessary to detail all proprietorial substances in existing use, up front, then in theory they should already have been under some form of HASNO control prior to introduction. If so, then it should be feasible to follow up with suppliers under some form of confidentiality agreement (in concert with ERMA).

Overall, it is considered that because the additives are not purposefully lost through motor vehicle use that it is the final emitted products that contribute to the quality of exhaust emissions that require to be addressed. Of primary interest are, the presence of any inorganic elements of environmental concern (e.g., those identified as priority pollutant elements).

Exhaust Emissions

Vehicle exhaust emission is one of the few “intentional” or uncontrolled discharges from the road sector, by design (as opposed to emissions controlled engines, where the pollutant outputs are being minimised).

The potential numbers of individual compounds emitted from this source are extremely large, with the variability of the combustion process adding orders of magnitude to the numbers of compounds involved (e.g., oxy, nitro, sulphur etc., derivatives), as well as derivatives of additives in the initial formulations. Even fully searching the international literature would only indicate what someone has particularly identified within each class of compound; these would be examples but by no means a full speciation, which has never been done, and is not likely to be. Some examples of characterisation are discussed in this report.

The two key issues associated with exhaust emissions related to the significance of this source to aquatic ecosystems are the presence of contaminants associated with particulate matter in the emission and what proportion of those are available to enter aquatic systems. As much of the emissions to air are volatile and subject to further reactions in the atmosphere, the eventual deposition/impacts analysis of this group would be the most influenced by the vagaries of the various "pathway" influences.

Overall, the key focus of the contaminant assessment process, are those contaminants associated with particulate matter. At this stage the VOCs in exhaust emissions are not considered to be a key component of the overall impact assessment process. This is discussed further in Section 4.

Lubricating Oils

This needs to be considered as an uncontrolled discharge, as a small proportion will always escape through the combustion tracts. Leakage loss would be an incidental phenomenon, but is so frequently encountered in vehicles that it could represent a routine discharge in any given traffic corridor.

The two main components are the hydrocarbon base oils and the additive package. The hydrocarbons will be released both as is and also as partial combusted derivatives. This component could then be considered impacts-wise in the same way as the fuel hydrocarbons, the heavier classes found in diesel. The analogy can also extend to identifying the changes and contaminants added to the oil through its service life, in the form of unburnt fuel, acidic combustion products, PAH/PM etc.

For the additives, defining the range of proprietary compounds (beyond basic generic classes) would be extremely difficult, not least due to the strongly protective commercial nature of the industry. It is also an area where some extremely sophisticated formulations are continuing to evolve through the future for both performance and branding purposes. It is theoretically feasible to investigate the precise additive chemistry given some form of HASNO-like authority, but would be an extensive task.

The suggestion is for the policy approach to require notifications, by setting impacts based criteria (the ERMA approach), rather than try to identify/second-guess all that might be in use, in advance. This is an example, with the highly complex organo-metallic additives, of what exactly is the issue of concern; is it the elemental form, or what of the many potential derivative complexes (as formulated, and after use/combustion)?

Coolants/Greases/Transmission, Hydraulic Fluids etc.

None of these represent uncontrolled discharges, with the loss being ideally zero, and not in any way potentially routine in the road corridor as, collectively, lubricating oil leakage might be. Again, if necessary they could be treated as for additives (same basic situation), to the extent required.

Tyres, Brakes

The only other significant “designed loss’ media, as a routine. The formulations of these wear components have, on the one hand, the consistent use of a small group of main compounds, then a wide variety of others that follow little consistency in approach. So, it is easy to identify a main group, but difficult to account for them all in any systematic manner. Also, the New Zealand vehicle industry tends to be a receiver of components from many sources, without an actual knowledge of their composition; in these areas the components are specified solely on the basis of their performance in use, not the mode of manufacture. Chemical analysis of a range of carefully selected examples could be useful, but the ultimately effective approach would be to have some deposition/impacts based sensitivity analysis for setting thresholds for loading (as per the ECA concept).

Road Surfaces

Pavement wear is a term used by the roading industry, but means everything except actual surface wear by attrition (rutting/deformation/cracking). Wear proper is not a recognised phenomenon, so there are no measures of such. The inventory model has been designed to undertake simple sensitivity analysis of hypothetical case studies (in association with the RAMM system), to see if this represents a source of bitumen components of any concern. The same process is applied to the road surface marking compounds.

3.4 Basic Hypothesis; The Equilibrium Situation

The main elements in the equation are as follows:

- The contaminant sources, by type and activity.

- The location and area of the source activity (density of discharge).
- The catchment; the gathering area for the discharges.
- The pathways; that concentrate/dilute/hold-up the amount of gathered discharge, and determine the flow-through to the receiving environment.
- The receiving environment; the particular location/type and ecology that could receive the contaminants.
- The size/volume/flushing of the receiving environment, that determines the rate and concentration of deposition, hence exposure suffered by the ecology.

As a starting point in looking at the impact:source balances, it would be useful (if not misleading) to neutralise the complexities of the pathway factors, and start with an equilibrium situation.

Assume that the primary impact criterion is the cumulative load on the eco-system, in a given location, and that this is long-term time averaged function i.e., over years as opposed to days (this neutralises the variable effects of pathway mechanisms to some extent).

And, that all of the contaminant discharge from source eventually ends up in this receiving environment i.e., the pathway systems are in time averaged equilibrium.

But, still need to determine the area of source activity that relates to the receiving environment location i.e., the catchment.

Also, what is the "area" of the receiving environment-what is the density of the eventual deposition for this cumulative loading, therefore exposure concentration?

3.5 ECA Package Design

The primary aspects of the ECA concept are to relate the emissions/discharges from road transport to the layout and traffic operations of the actual urban road network. The inventory is designed to produce emission outputs rates in g/km by vehicle type and driving condition that can be integrated with traffic models to give corridor emissions loading totals.

In the water context, there is a need to link the corridor layout (and emissions loadings) with their potential receiving environments. This introduces the second aspect of ECA, which correlates geospatially the distribution of source activity (vehicle traffic, in road corridors) to the impacts media. The form of correlation in this case is the water run-off, plus local fall-out etc; the catchment topography, geographically defined. This defines the area of source activity, item 3 above, and leaves the only unquantified factor as the "area" of the deposition (how can this be measured, as this defines the exposure concentrations?). The design of the source side inventory and ECA interface is described in Section 8.

4. ASSESSMENT OF COPC

4.1 Introduction

Processes of assessment have been developed internationally for the identification of chemical hazards. The Organisation for Economic Cooperation and Development (OECD) recognized, the need for hazard data on chemicals in the 1980s, and has developed a comprehensive programme of ensuring that data is available for high production chemicals (HPV). The OECD chemicals evaluation involves a range of countries who carry out evaluations of HPV chemicals at a scale that reflects their GDP. National Pollutant Inventories (e.g., Australia) and assessment programmes such as the USEPA High Production Volume Challenge Program, collect information across the broad definition of human and environmental hazard.

4.2 Hazard Assessment - Endpoints

Internationally, a basic set of data or end-points has been identified in determining the ‘toxicity’ of chemicals. The basic testing information or other data is referred to as the Screening Information Level Data Set (SIDS). SIDS encompasses acute toxicity, chronic toxicity, developmental and reproductive toxicity, mutagenicity, ecotoxicity and environmental fate and also includes information on the nature of the chemical and its properties and the extent of exposures. SIDS Data elements are summarised in Table 4.1.

Table 4.1 - Summary of SIDS elements and identification of those included within the aquatic ecosystems risk assessment.

SIDS Elements			**Inclusion in this Assessment**
Category	**Endpoints**	**OECD Guideline**	
Chemical and physical properties	Melting point	OECD 102	YES
	Boiling point	OECD103	YES
	Vapour pressure	OECD 104	YES
	Partition coefficient (log kow)	OECD 107, 116	YES
	Water solubility	OECD 105	YES
Environmental fate and pathways	Photodegradation	OECD113	No
	Stability in water	OECD 111	YES
	Biodegradation	OECD 301, 302	YES
Ecotoxicity tests	Acute toxicity to fish	OECD 203, 204	YES
	Acute toxicity to aquatic invertebrates	OECD 202	YES
	Toxicity to aquatic plants	OECD 201	YES
	Chronic aquatic invertebrate tests	OECD 202	YES
	Terrestrial toxicity tests	OECD 207, 208	No
Human health effects	Acute toxicity	OECD 401-403	No
	General toxicity (repeated dose)	OECD 407-413, 422	No
	Genetic toxicity (effects on gene and chromosome)	OECD 471-486	No
	Reproductive toxicity	OECD 415, 416, 421, 422	No
	Developmental toxicity	OECD 414, 421, 422	No

4.3 The HSNO Act and ERMA

The HSNO Act (1996) was set up in New Zealand to protect the environment and health and safety of people by preventing or managing the adverse effects of hazardous substances. The requirements of the HSNO Act are managed by ERMA. The HSNO Act requires that assessment covers all aspects of hazard and the process of chemical hazard assessment follows that of the OECD, EU and other agencies (e.g., NICNAS).

ERMA have identified the information processes associated with hazardous substance applications (ERMA 1999a,b). Within the overall assessment process there is one component related to ecotoxicity. As identified by ERMA (1999c), there are five key elements to ecotoxicity. These are aquatic toxicity, effects on the soil environment, effects on terrestrial vertebrates, effects on terrestrial beneficial invertebrates (e.g., bees) and biocidal action. In the context of any assessment of effects on aquatic ecosystems, the ecotoxicity elements that are of direct relevance to this evaluation are primarily aquatic toxicity and secondarily effects on the soil environment (effects on sediment biological communities).

The aquatic ecotoxicity component of the assessment of potentially hazardous substances identified by ERMA follows the approach identified by the OECD (OECD 1998). The OECD system identifies acute toxicity, bioaccumulation, degradation and chronic toxicity as the key elements. In the OECD system, freshwater and marine organism toxicity data are considered equivalent. The system classifies acute and chronic toxicity and bioaccumulation factor and degradability into classes of hazard. These elements have been adopted in New Zealand by ERMA as part of its ecotoxicological hazard classification system (Refer to http://www.ermanz.govt.nz/ for more information).

4.4 Risk to Aquatic Environments

Assessment of the risk of a contaminant to the aquatic environment is a relatively complex task as the assessment involves a number of factors. A variety of processes have been developed by agencies tasked with identifying the risk associated with the release of contaminants to the environment. In this preliminary assessment, the focus is on the potential effects of contaminants on the aquatic environment.

The core premise of the assessment process is that **Risk = Hazard x Exposure**.

As can be seen, the identification of risk requires that the exposure be identified. In this assessment, the exposure is not quantified as the actual rate of exposure is not known for all contaminants. Subsequent identification of component losses and emissions will at a later stage in the assessment allow the environmental contaminant concentrations to be identified and exposure to be quantified.

A second factor also needs to be considered. As described earlier in section 3, contaminants released from motor vehicles may be released in several forms. There are many examples of organic compounds which are released as isomers and trace elements which enter the environment in very different forms and then undergo further transformations. A good example is the occurrence of zinc in a range of forms within several of the motor vehicle sources.

4.5 Assessment Process

4.5.1 Introduction

Following the identification of an element or organic compound as being present in a particular emission source, a particular process was followed. For inorganic constituents, a simple identification that the element is of environmental concern was carried out. That simply required identifying whether the contaminant was identified as a priority pollutant by the USEPA. This is described in the following section. For organic compounds a specific information gathering process was undertaken as described in Section 4.3.

4.5.2 Contaminants

Trace elements

Although, there are a very wide range of elements released in emissions from motor vehicles, only a limited number are categorised as potential contaminants of concern. The primary definition is based on the list of priority pollutants identified by the USEPA.

Table 4.1 lists the USEPA priority metal pollutants. Of the priority pollutant elements most have both chronic and acute water quality criteria for the protection of aquatic life (from the effects of water associated toxicity) and many have sediment quality guidelines reflecting the potential adverse effects associated with their accumulation in both freshwater and marine sediments.

Table 4.1 – USEPA priority pollutant elements.

Symbol	Element
Sb	Antimony
As	Arsenic
Be	Beryllium
Cd	Cadmium
Cu	Copper
Cr	Chromium
Pb	Lead
Hg	Mercury
Ni	Nickel
Se	Selenium
Ag	Silver
Tl	Thallium
Zn	Zinc

Even though all of these elements have been identified as priority pollutants by the USEPA, they only pose a risk to the well-being to aquatic environments if present in sufficient amounts. As noted earlier the identification of a priority pollutant element in a motor vehicle source does not imply effect. It implies potential affect in the absence of data to confirm the environmental concentration.

Organic compounds

The USEPA has identified a considerable number of organic compounds in their list of priority pollutants. Table 4.2 provides a summary of the key groups of organic compounds based upon their structural classes. It should be noted that inclusion in the USEPA priority pollutant list indicates potential adverse effects in any one of a number of environmental compartments or forms of life (including human health).

Of the organic compound priority pollutants, a number have water and sediment quality criteria to assist in the protection of the well-being of aquatic environments.

Based upon the above the presence of any one of these compounds in an emission source would result in it being identified as a COPC. For any compound not in the USEPA priority pollutant list or not having any environmental threshold values (in water or sediment) the identification of that compound as a COPC is made via the assessment process described below.

4.5.3 Assessment Process

The assessment process is described in detail in the supporting manual for the organic contaminant assessment database (Kennedy 2000). The database collates specific information about an organic compound identified as present in a specific emission source. The data entered to the database includes information on bio-availability, persistence, toxicity and bioaccumulation.

Table 4.2 – USEPA priority organic compound pollutants.

Structural Class	No. in class	Example
Phenols	2	Phenol, 2,4-dimethylphenol
Substituted phenols	9	2,4-dichlorophenol, 2-nitrophenol
Organo-nitrogen compounds	9	N-nitrosodimethylamine
Low molecular weight PAHs	6	Naphthalene, phenanthrene
High molecular weight PAHs	10	Benzo[a]pyrene
Chlorinated aromatic hydrocarbons	6	2-chloronaphthalene
Chlorinated aliphatic hydrocarbons	3	Hexachlorocyclopentadiene
Phthalates	6	di-n-butylphthalate
PCBs	7	PCB-1242*
Oxygenated compounds	2	TCDD (dioxin)**
Pesticides	14	
Volatile halogenated alkanes	15	1,2-dichloroethane
Volatile halogenated alkanes	7	Cis-1,3-dichlorpropane
Volatile aromatic compounds	3	Benzene, ethylbenzene, toluene
Volatile chlorinated aromatic hydrocarbons	1	Chlorobenzene
Volatile unsaturated carbonyl compounds	2	Acrolein
Volatile ethers	1	2-chlorethylvinylether

Notes: * - the PCBs are identified as Aroclors in the priority pollutant list. ** TCDD is one of a number of PCDD and PCDF isomers.

Where data exists for any specific property (e.g., the microbial degradation rate or the bioaccumulation factor for fish) these can be entered to the database. However, for most organic contaminants, data of this nature is not readily available. In the assessment process, a theoretical approach was adopted in nearly all cases to obtain the necessary information. This approach was based upon having an understanding of the chemical structure of the identified compound and the relationship of the chemical structure to the chemical properties of the compound (This is referred to as QSARS – Quantitative structure activity relationships). For many properties there is a direct relationship between particular aspects of the chemical structure and a given property of the compound (e.g., melting point, its octanol/water coefficient or the toxicity that it may exert in water). Knowing the structure of the compound allows (through the known relationship between chemical structure and the particular property) the compounds predicted property to be calculated. Further detail can be found in Kennedy (2000).

The following procedure was utilised to identify a contaminant as a COPC.

1. The score for persistence was identified (1-3).

2. The score for bioaccumulation was identified from calculation of the BCF (1-3).

3. The toxicity was assessed through estimation of the ENEV (based upon chronic toxicity) and given a score ranging from 1-3.

4. Bioavailability was assessed by assessing the form and bioavailability in aquatic systems (via presence in water).

The PBT scores are then multiplied together to provide a score in the range 1 (1 x 1 x 1 x 1) to 81 (3 x 3 x 3 x 3). Any contaminant with a score of over 8 is identified as a contaminant of concern. A score of 8 represents at least three of four of the key factors having a moderate P, B or T. Table 4.3 provides a summary of the aquatic risk score calculation matrix. The key question which arises following the identification of a COPC is what does the identification as a COPC mean?

In the context of the screening process, it is a step in the evaluation process. It provides a mechanism to flag the presence of a contaminant for further consideration. It does not mean that the presence constitutes an environmental risk. The output of the screening process is discussed in the following section.

Table 4.3 - Summary of Aquatic Risk Score Calculation.

Category	**Factor**		**Category Score**	**Overall Score**
		Score	$\frac{\textbf{Factor Score}}{\textbf{Number of factors}}$	**1x2x3x4**
1. Bioavailability	1.1 State	√	-	-
	1.2 Solubility	√	-	-
	1.3 Vapour pressure	√	-	-
	1.4 Henry's Law Constant	√	-	-
			√	-
2. Persistence	2.1 Microbial degradation	√	-	-
	2.2 BOD half life	√	-	-
			√	-
3. Toxicity	3.1 ENEV	√	-	-
			√	-
4. Bioaccumulation	4.1 BCF	√	-	-
			√	-
				√

4.6 Summary Points

A process of environmental hazard identification was established for contaminants identified as being emitted from motor vehicles. This process was based upon both OECD and Australian NPI.

The assessment was based upon the identification of key organic compound properties, characteristics and assessment end-points.

Environmental risk equates to hazard and exposure. This assessment process examines the hazard component of the risk assessment.

For trace elements, identification of the element as a priority pollutant (USEPA) was sufficient to identify the element as a COPC.

For organic compounds a hazard assessment process was identified that accounted for the key environmental properties/characteristics of toxicity, bioaccumulation, degradation and persistence. In most cases these are assessed theoretically using QSARS.

5. SOURCE MATERIALS AND CONTAMINANTS OF POTENTIAL CONCERN

5.1 Introduction

This section of the report provides an introduction to the main types of materials, compounds and elements that are typically associated with the road transport sector, as per the structural approach set out in the Classification Framework (Section 2). For each source category, an overview of the contaminants associated with that source is provided and the results of the evaluation of their environmental significance and identification as COPC is provided. This information is based principally upon the information presented in Kennedy & Gadd (2000), Gadd & Kennedy (2000) and Kennedy et al. (2002).

The primary areas of information considered in this section are:

- What contaminants are produced?
- What are the key components or groups of contaminants?
- Which ones are important in terms of the amounts produced and the likely contributions to the road-stormwater pathway?

The pathways are discussed in more detail in the following major section.

5.2 Road Transport Fuels

5.2.1 Fuel Types

At present there are five fuel types/grades specifically available for automotive fuelling in New Zealand. These are:

- Petrol (regular unleaded and premium unleaded).
- Diesel.
- Natural gas
- Liquified petroleum gas.

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 is due for revision to ensure compatibility with the engine specifications of the developing fleet (refer VFECS, MoT 1999).

The generic formulations of petroleum fuels are (currently) essentially the same the world over. The large majority of New Zealand's supplies are produced by the New Zealand Refinery Company (NZRC) at Marsden Point; typically around 75% of petrol and all road diesel. Finished product and blend-stocks are imported for petrol to varying extents, mainly from Australia, and the potential exists for spot market product also to enter the market. There is currently no further supply of synthetic petrol from the SYNGAS plant in Taranaki, this now being devoted to methanol production.

5.2.2 Petrols

Petrols are low boiling point naphthas, within the C_3 to C_{12} range, the main differentiation in type of base and blendstocks being the result of their characterising refinery processing (straight-run, reformate, 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 hydrocarbon groups (e.g., alkanes, cycloalkanes, olefins (alkenes) and alkylbenzenes).

Petrols are however composed of several hundred different chemical species present as a result of all of the potential isomers that could exist within the carbon number range. In addition to the straight hydrocarbons, there will also be trace quantities present of certain organo-sulphur compounds and to a lesser extent, naturally occurring nitrogen, chlorine and oxygen complexes. These groups of compounds are however, minimal in terms of the quantity present, with only the sulphur being subject to any particular refining control.

The present New Zealand fuel specifications allow “oxygenates” to be blended with petrols, primarily to support octane number requirements following the removal of lead from petrol. 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 (suppliers) may be importing finished product with MTBE content.

Additives – Initial Formulation

No lead is added to the current petrols used in New Zealand, 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 and that present in the native petroleum. This would be negligible in quantity, and declining rapidly as the system is being continually flushed through.

R-ULP and P-ULP ex NZRC normally contain no additives (apart from colouring dyes), but antioxidants may be used in some imported components used as blend-stocks (notably cracked spirit) and finished product from Australia. Imported petrols from Australia may also contain metal deactivator additive. Both grades of petrol destined for Auckland via the Refinery-to-Auckland pipeline (RAP) are treated with anticorrosion 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 add their own additive treatments downstream of the refinery, during distribution to its service stations, 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.

Future Influences

Fuel specifications in New Zealand are at the point where a reappraisal of their scope is called for, in response to the modern engine technologies coming into the country from global advances in emissions control. This is one of the main recommendations to emerge from the VFECS study. As the purpose is to ensure proper functioning of the engine and emissions control systems, the evolution of the fuel quality requirements will to some extent follow global trends. For motor gasolines, the immediate emphasis overseas is on the following:

- Closer control of aromatics content, and particularly benzene levels (down to 1%).

- Reduction in olefins (photochemical smog potential).
- Reduction in sulphur content (improve efficiency of exhaust after-treatment systems), down to 150 g/m^3, possibly to 50 g/m^3.
- Use of oxygenates, specifically ethers (although MTBE is currently under scrutiny as a groundwater contaminant in the United States).
- Greater use of special functional additives, for fuel stability and combustion modifiers.

The extent to which these will feature in the New Zealand specification requirements is necessarily the subject of this planned review. However, the potential changes to the chemistry of the fuel can be predicted, and would be tracked in the ongoing application of environmental management policy.

5.2.4 Diesel Fuel

By virtue of their traditional distillation range being so broad, diesel fuels typically comprise hydrocarbons in the C_{10} to C_{23} range (at the extremes this can extend to C_6 up to C_{30} plus). Fuel chemical composition is, typically identified by the hydrocarbon families rather than individual hydrocarbon species. The main groupings are as follows, within which may potentially be present any isomer within the carbon number range above:

- 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.

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 allow 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.

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.

Future Influences

The evolution of diesel fuel property requirements follows the same basic pressures that apply to petrol quality, for emissions control purposes, and similar comments apply. For diesel, the main properties under near-mid term focus are:

- Sulphur content, down to around 350 g/m^3, ultimately (possibly) 50 g/m^3 or less.
- Aromatics reduction, particularly close control of polyaromatics.
- Cetane number improvement.
- Closer limits on density, for injection calibration.
- Reduced boiling range end point (T_{95}).

The future diesel formulations could see an even greater use of additives, beyond those already commonplace. Kennedy et al. (2002) provides further detail with respect of these.

5.2.5 Contaminants

Vehicle fuels contain a range of inorganic elements derived from the native petroleum. Studies undertaken such as those of Yang et al. (1998) have shown that a range of inorganic COPC are present in diesel fuel. This information assists in understanding what elements might be present in the exhaust emission from vehicles. Table 5.1 provides a summary of the inorganic elements of environmental significance in diesel fuel. Yang et al. (1998) also showed that diesel also contained concentration of non-COPC elements such as barium (33.9 g/m^3) at concentrations higher than the COPC. It is also likely that the additions of additives results in increased concentrations of particular elements. However, there appears to be little information on this subject.

Table 5.1 – Concentrations of key inorganic COPC in diesel fuel (From Yang et al. 1998, all data g/m^3).

Element	Concentration
Zinc	8.74
Lead	1.93
Nickel	17.5
Chromium	22.4
Copper	4.22
Cadmium	0.30

Both petrol and diesel fuel contains a very wide range of VOCs and SVOCs. Significant variations in the concentrations of some key components of vehicle fuels (from an environmental perspective) have been reported. For example, Table 5.2 identifies PAH concentrations in petrol and diesel fuels from several sources. Other results such as those of Yang et al. (1998) and Mi et al. (2000) have suggested much lower concentrations of individual PAHs total PAH concentration 285 g/m^3 (Table 5.2). A range of the organic compounds identified as present in fuel were classified as COPC. For information, Appendix A provides a summary of the COPC that were identified in fuel based on industry and literature data.

Table 5.2 - PAH compounds in petrol (from Lee et al. 1995) (all data g/m^3).

PAH	Premium petrol	92 unleaded petrol	95 unleaded petrol	Two stroke petrol
Naphthalene	1857 ± 834	882 ± 22.5	1576 ± 110	378 ± 61.8
Acenaphthylene	204 ± 39.6	219 ± 232	70.0 ± 46.4	123 ± 30.8
Acenaphthene	889 ± 158	173 ± 208	125 ± 54.9	106 ± 115
Fluorene	10.2 ± 8.1	6.46 ± 5.49	15.5 ± 12.5	4.16 ± 0.64
Phenanthrene	3.13 ± 0.06	11.7 ± 17.2	3.83 ± 4.77	5.95 ± 4.81
Anthracene	1.3 ± 0.05	8.23 ± 13.0	8.63 ± 6.88	0.86 ± 1.16
Fluoranthene	2.18 ± 0.56	2.07 ± 2.36	3.59 ± 1.88	6.15 ± 2.92
Pyrene	1.28 ± 0.21	0.78 ± 0.88	1.58 ± 1.87	1.72 ± 1.68
Cyclopenta[c,d]pyrene	0.23 ± 0.15	2.05 ± 1.76	0.19 ± 0.05	3.42 ± 3.68
Benzo[a]anthracene	0.05 ± 0.07	0.92 ± 0.66	0.29 ± 0.25	2.74 ± 0.07
Chrysene	0.30 ± 0.19	0.88 ± 0.86	0.15 ± 0.03	5.08 ± 3.88
Benzo[b]fluoranthene	0.15 ± 0.18	1.10 ± 1.63	0.13 ± 0.07	16.8 ± 2.88
Benzo[k]fluoranthene	0.31 ± 0.31	0.98 ± 0.87	0.10 ± 0.12	21.0 ± 2.01
Benzo[e]pyrene	0.23 ± 0.12	2.34 ± 3.46	0.09 ± 0.01	39.5 ± 9.67
Benzo[a]pyrene	0.32 ± 0.20	0.73 ± 0.38	0.15 ± 0.10	60.6 ± 7.40
Perylene	0.87 ± 1.10	1.82 ± 2.12	0.16 ± 0.04	94.2 ± 39.8
Indeno[1,2,3,-cd]pyrene	2.39 ± 1.43	2.80 ± 2.42	1.65 ± 0.18	371 ± 102
Dibenzo[a,h]anthracene	0.81 ± 0.0	3.66 ± 3.73	0.35 ± 0.12	57.3 ± 50.4
Benzo[b]chrycene	1.09 ± 0.13	2.63 ± 2.34	0.61 ± 0.01	149 ± 107
Benzo[g,h,i]perylene	1.05 ± 0.92	1.69 ± 1.93	0.99 ± 0.13	101 ± 112
Coronene	0.23 ± 0.05	0.19 ± 0.17	0.18 ± 0.24	1.83 ± 2.41
Total	2976 ± 961	1324 ± 770	1809 ± 91.5	1549 ± 460

Overall, the information on fuels provides information on factors that could influence the composition of vehicle exhaust emissions. Although, fuel contains inorganic and organic COPCs, as vehicle evaporative emissions and fuel losses are not considered to be a significant factor in the overall load of contaminants generated by motor vehicles that then enter stormwater, they are not considered at this stage in the assessment of contaminant load from motor vehicles to stormwater.

5.3 Emissions

5.3.1 Evaporative Emissions

The direct emission to atmosphere from the fuel concerns only petrols, due to the volatility of the hydrocarbon constituents. Modern vehicles are equipped with closed fuel systems (fuel injection, rather than carburation), and carbon vapour traps for the venting of the fuel tank. For uncontrolled evaporative loss, the amount of HC emission can be a significant proportion of the total HC emissions from road transport (estimates range up to the level of 30%), in the summer season.

The composition of the discharge reflects the basic chemistry of the fuel (the lighter ends). The majority is of the highly volatile C_3, C_4 and C_5 components, the typical weighting in the emission being in inverse proportion to molecular weight (for non-polar, hydrocarbons). However, potentially every petrol component could be present in the evaporative loss to some extent, including e.g., benzene.

As evaporative emissions involve VOCs in the gas phase, they are not considered to be involved significantly in the direct introduction of contaminants to the road-stormwater system (however, refer Section 6). As such, this source has not been included in the transport contaminant load model at this stage.

Table 5.3 – Examples of PAH compounds in diesel (all data g/m^3).

PAH	Mi et al. (2000)	Yang et al. (1998)	Lee et al. (1995)
Naphthalene	81.1	17.1	776 ± 9.19
Acenaphthylene	81.3	110	1564 ± 685
Acenaphthene	53.6	207	1681 ± 371
Fluorene	35.3	296	973 ± 80.8
Phenanthrene	11.0	52.2	556 ± 65.5
Anthracene	10.3	26.4	499 ± 102
Fluoranthene	5.47	3.8	367 ± 199
Pyrene	0.83	0.816	320 ± 308
Cyclopenta[c,d]pyrene	0.19	6.32	60.8 ± 61.7
Benzo[a]anthracene	0.63	0.029	197 ± 228
Chrysene	0.43	0.0287	188 ± 242
Benzo[b]fluoranthene	0.97	0.0024	12.8 ± 17.4
Benzo[k]fluoranthene	0.16	0.102	115 ± 140
Benzo[e]pyrene	0.05	0.439	17.0 ± 19.8
Benzo[a]pyrene	1.78	0.0126	3.14 ± 3.42
Perylene	0.04	0.0076	5.05 ± 4.16
Indeno[1,2,3,-cd]pyrene	0.69	0.0062	1.70 ± 0.49
Dibenzo[a,h]anthracene	0.97	1.59	1.97 ± 2.62
Benzo[b]chrycene	0.09	0.0053	1.80 ± 2.02
Benzo[g,h,i]perylene	0.40	0.0053	1.82 ± 2.06
Coronene	0.02	0.0059	0.61 ± 0.56
Total	285	721	7341 ± 1491

5.3.2 Petrol Exhaust Emissions

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 un-burnt fuel hydrocarbons and partially oxygenated hydrocarbons (with the potential for nitro-HC derivatives, and ammonia etc.) derivatives from the fuel chemistry. Kennedy et al. (2002) provide further detail.

Also the contribution from the portion of lubricating oil that is lost through the combustion chamber/exhaust valve tract needs to be considered as part of the exhaust emission; this would comprise partially burnt lubricating oil base hydrocarbons, together with the derivatives of the organo-metallic additives in the oil formulation.

Petrol engines also produce particulate matter, albeit of very small amount/size when compared with the diesel combustion process. At this stage, the nature of the PM component from vehicle exhausts is considered below in relation to diesel.

5.3.3 Diesel Exhaust Emissions

The character of diesel exhaust is even more complex than petrol, as a consequence of greater carbon number variation in the fuel, heterogeneous nature of the combustion process and resulting multi-phase composition of the exhaust products. The first significant difference compared to petrol is the more complex particulate phase in diesel (refer to Kennedy et al. (2002) for further information on some of the key compounds present in diesel exhaust). The particulate matter is comprised of a carbonaceous soot substrate, typically in the sub-micron size range of 0.02 to 0.5 µm. Upon this is adsorbed the hydrocarbons discussed above (termed the “soluble organic fraction”, in the measurement of particulate composition by mass) from both fuel and lubricating oil, traces of metallic components such as iron, calcium and zinc (mainly from the lubricating. oil additives) and sulphates/bound water.

Many PAH compounds are also potentially present in diesel exhaust. Appendix B identifies a range of key compounds present in diesel exhaust.

5.3.4 Exhaust Emission Contaminants

Internationally, a wide-range of studies has been carried out on the nature of motor vehicle exhaust emissions. Kennedy et al. (2002) provides an overview of information regarding the composition of exhaust emissions. New Zealand exhaust emission data is limited to key primary pollutants discussed in the VFECs process. In this section, an overview of the emissions from the exhaust train is provided with emphasis on the COPCs that have been identified as part of the assessment process.

Inorganic constituents

1 General

A range of work has been undertaken on the trace element composition of petrol vehicle emissions. It is worth noting the early work carried out by Ondov et al. (1982) on trace elements in emissions from motor vehicles. The authors reported the concentrations of 27 elements in aerosols collected near a highway (Beltsville MD) and in the Baltimore Harbour 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. Table 5.4 provides a summary of that work. The results indicated that the exhaust (or overall emissions) from vehicles released a number of elements some of which are COPC. Ignoring the elevated Pb concentration due to the presence of Pb in the petrol, the major emitted elements identified were Fe then Al. Zinc was the most significant trace element identified. This was followed by Mn then Cu, Ni, Cr and Ba in similar amounts. Smaller amounts of Cd and Sb were identified.

Table 5.4 – Summary of trace and minor elements in air from the Baltimore roadway tunnel (all data g/m^3) (From Ondov et al. 1982).

Element	Tunnel intake	Tunnel	Tunnel exhaust
Lead	0.34	18.0	15.5
Bromine	0.083	8.0	6.6
Iron	0.63	5.3	3.0
Aluminium	0.4	3.8	2.0
Barium	0.016	0.38	0.325
Zinc	0.17	0.52	0.42
Copper	0.02	0.11	0.115
Manganese	0.037	0.15	0.067
Cadmium	0.011	0.077	0.037
Antimony	0.009	0.033	0.033
Nickel	0.025	0.041	0.0255
Cobalt	0.00078	0.0022	0.0022
Selenium	0.002	0.0024	0.022
Chromium	0.025	0.066	0.045

Some work has been undertaken on the emission of elements such as cerium (Ce) derived from fuel additives. HEI (2001) assessed the use (and proposed use) of Ce added to diesel fuel (to enhance soot combustion). The authors predicted Ce concentrations in air and in soils based on predicted use.

2 Exhaust Catalysts

Catalysts are a particular source of one group of metals. Shelef et al. (2000) reviewed the history of automotive catalysts and Farrauto & Heck (1999) and Kaufmann et al. (2000) have reviewed the development and advances in catalysis science. The use of the platinum group metals in vehicle catalysts (platinum (Pt), palladium (Pd) and rhodium (Rh)) 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_x removal) (Shelaf et al. 2000). The precious metals are dispersed in a 'washcoat' on a ceramic or metal substrate. The substrate is typically Al_2O_3 modified by the use of oxide stabilisers including oxides of aluminium, zirconium, barium and the rare earths (e.g., cerium and lanthanum). Analysis of the washcoat by Palacios et al. (2000) showed that Ce and 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).

Shelaf et al. (2000) report that the present overall usage, in vehicle exhaust treatment of the precious metals is about 2-5 g/vehicle. In an examination of the exhaust emissions from diesel and petrol vehicles with catalysts, Moldovan et al. (1998) reported that most of the platinum group elements are emitted in particulate form (>95, >85 and >90% for Pt, Pd and Rh respectively).

A large number of studies have been undertaken on alternative catalysts and promoters in catalytic trains in petrol and diesel motor vehicles. Examples include:

Co/MgO and Co, K/MgO catalysts (Miro et al. 1999, Querini et al. 1998, 1999).
V_2O_5 –WO_3-T_1O_2 catalysts (Finocchi et al. 2000).
Cu-K-V-Cl.
C_5VO_3-KCl; KVO_3-KCl, Cu-K-V-Cl (Badini et al. 1990, Saracco et al. 1999).

Experimentally a wide range of catalyst combinations on different supports have been examined for diesel particulate abatement (these have also included Ag and Mo) (Saracco et al. 2000) and for NO_x control (oxides of Mn, Zr, Ba, Ce, Al -Belton & Taylor 1999). Although, Pt, Pd and Rh are the key environmentally significant elements in catalysts, research into alternative catalysts indicates that there is potential for other elements to be present and therefore emitted via vehicle exhaust systems in the future.

Based upon available information, the emissions from the exhaust train are a source of a number of COPC. These are the elements Zn, Cu, Cr, Cd, Sb and Ni. The exhaust is also a source of a number of key non COPC such as Ba and Fe.

None of the three precious metals used in catalytic converters are identified as COPCs. However, the concentration of Pt, Pd and Rh in the urban environment is reported to be steadily increasing (Schafer et al. 1999). The same study has also indicated that traffic emitted Pt/Pd/Rh has changed over time as the ratio of the elements used has varied. The emission rate will also change as the proportion of catalytic converters on vehicles change and the composition of those catalytic converters changes both with age and replacement.

Organic compounds

1 General

Exhaust emissions contain an extensive range of VOCs. Various studies report on the VOC content of petrol and diesel emissions and identify emission rates for those compounds (Duffy et al. 1999, Siegel et al. 1999, Schmitz et al. 2000). 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 discussed.

Particulates in the exhaust emissions are much more important than gaseous emissions in the consideration of vehicle associated contaminants in stormwater. Although, vehicle exhaust emissions become strongly associated with airborne pathways, the particulates can enter the roadway directly or can enter the stormwater system or receiving environment through a number of secondary pathways. These are described further in the following main section of this report.

Kennedy et al. (2002) provides information on the large number of compounds that are associated with the particulate phase of exhaust emissions (e.g., nitro-PAHs). Johnson et al. (1988) also provided data on the concentration of organic compounds in diesel particulate material. A large number of compounds were identified with concentrations of most compounds being identified as being in the 100s and 1,000s of mg/kg on particulates.

2 SVOCs

For the SVOCs some 101 compounds were identified by the contaminant evaluation process to be COPC. These compounds consisted of a range of compounds with particular emphasis on PAHs and methylated PAHs. The PAHs appear to be the most significant group of COPC in exhaust emissions. The identified COPCs such as the PAHs are strongly associated with particulate matter. For this group, broad PM emissions may provide a useful surrogate for total PAHs and PM and total PAH may provide good surrogates for individual PAH compounds.

3 PCDD/PCDFs

Due to their particular environmental significance, some additional comment on the PCDD and PCDF compounds in the exhaust stream is provided. 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 have 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. As noted earlier, there are difficulties with the tunnel studies as the results include the contradiction from re-entrained dust particles.

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, Geueke et al. (1997) 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 HDVs.

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 g/m^3 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.

The PCDD and PCDFs were not entered to the Contaminant Database for the assessment of COPCs (Kennedy 2000). However, based upon the environmental concerns related to their presence in the environment this group of compounds would be classed as a COPC.

The PCDD and PCDF congeners emitted in motor vehicle exhausts are COPCs. However, there is good evidence that they are emitted in small amounts relative to other organic compounds in the same emissions. It has also been demonstrated in several countries that the PCDD/PCDF emissions from motor vehicle emission sources represent only a small proportion of the overall load of PCDD/PCDFs in the urban environment.

Appendix A provides a summary of the COPC identified through the assessment process. Based upon available information, 104 of the organic compounds in the vehicle emissions source category were identified as COPC.

5.4 Road Transport Lubricants

Lubricating Oils Formulation

Lubricating oils comprise a base oil stock with additives. Conventional base stocks are refinery derived, characterised as paraffinic, naphthenic or intermediate. More recently, the control required over the base stock properties has seen the use of synthetic materials. Kennedy et al. (2002) provides more detail on the nature of lubricants and their formulation.

A number of the performance requirements of the oil are met by the additive packages. The diversity of the chemistry involved is extreme, and under continuous development such that the specifics will vary from oil to oil, under the blender’s proprietary control. Also, a number of the additives are multi-functional, performing a number of duties. Examples of the types of additives in use based upon the functional groups include:

- Pour point depressants.
- Viscosity modifiers.
- Anti-oxidants.
- Anti-wear.
- Anti-corrosion/rust inhibitors.
- Anti-foam.
- Dispersants.
- Detergent/inhibitors.
- Alkaline reserve (TBN).

Additive packages in today’s oil qualities can account for around 10 to 14% by mass of the oil. 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. The oil’s performance obviously deteriorates with service life of the fill, through additive depletion as the oil becomes progressively contaminated with engine metal wear materials, and the products of the fuel’s combustion process. The main environmental concerns arising from used lubricating oil comes from its contamination with the aromatic products from fuel dilution, and especially the PAH/particulate loading from combustion.

Greases

Grease is used for chassis joint lubrication, bearings (especially wheel bearings) and in the power-train. 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 a liquid oil, with modern formulations also containing a number of sophisticated additives to improve their performance. 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. 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 repellants.
- Dyes, odorants.

Coolants

The 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, glycols are typically used, comprising 40 to 60 % of the coolant mix with water. Ethylene glycol is the industry standard (and is considered to be biodegradable). Others include diethylene glycol and propylene glycol.

Contaminants

As described above, the lubricants, greases and coolants used in motor vehicles contain a range of inorganic and organic contaminants. The inorganic contaminants include COPC such as zinc. A range of organic compounds groups are present and little information is available in relation to their specific formulation. The available information was included in the contaminants database and in the COPC assessment process.

One of the organic compounds identified as being present in the coolant source category was identified as a COPC through the assessment process. The compound was mercaptobenzothiaziole.

However, in most cases as identified in Section 3, the sources are contained and therefore not normally a direct, intentional and on-going source of contaminants to the road-stormwater system. Loss rates for overall hydrocarbons from the lubricating system are available, however the lack of specific information regarding the sources and contaminants present precludes their inclusion in the contaminant load calculation/model in any detail.

5.5 Tyres

5.5.1 Introduction

There is a great deal of similarity worldwide in tyre manufacturing practice. In terms of performance the main priorities in tyre development are wet grip versus wear rate, and drive-by noise and these factors to influence tyre composition.

5.5.2 Tyre Composition

Tyre material formulation comprises many ingredients, as compounded rubber. The type of ingredients do not vary much, with tyre design with the main variation being changes in the ratios used in the mix. The main materials in the compound are:

Polymer Base;	this is either natural rubber or a synthetic equivalent, usually a variable mixture of both. Typically the formulations are between 60:40 to 70:30 synthetics:natural rubber, with car tyres typically 40% natural vs. 60% synthetic.
Reinforcement;	this is provided by 'carbon black' of varying particle size grades, when mixed with the heated rubber compounds tangle up the polymer chains to make the rubber stiffer, stronger and harder.
Processing Aid;	the rubber/carbon black mix is too hard to process/mould, thus the added softening agent. This is a mineral hydrocarbon oil, the most often used containing aromatics , including polycyclic aromatic compounds.

These three materials comprise the main bulk of the compounded rubber, typical proportions being 30% polymer, 30% carbon black and 10-15% oil. However, a number of other additives are used in the manufacture of the tyre, which can involve a wide diversity of complex organic compounds, and metals.

- Processing Aids-Flowability.
- Antidegradants – Antioxidants & Anti-ozoneants.
- Cure Activators.
- Cure Agent.
- Accelerators.
- Retarders.
- Bonding Agent.
- Wire bracing/coating

The construction and composition of motor vehicle tyres are considered in more detail in Kennedy et al. (2002).

5.5.3 Contaminants

Kennedy et al. (2002) provides a review of what is known about the composition and contaminants present in tyres. Available information indicates that a range of organic compounds and trace elements would be expected to be present in tyres due to their method of manufacture. Kennedy & Gadd (2000) and Gadd & Kennedy (2000) provide a preliminary evaluation of the inorganic and organic composition of some tyres available in New Zealand.

Trace Elements

The examination of a series of tyres available in New Zealand by Kennedy & Gadd (2000) identified only zinc (median concentration 8,310 mg/kg) as being present in concentrations in tyres that were considered to be present in concentrations that were greater than crustal abundance. As such, the presence of the zinc when emitted would increase local environmental concentrations of the elements.

In general, Kennedy & Gadd (2000) found that the concentration of most inorganic constituents in New Zealand tyres were low when compared to other vehicle sources such as friction linings. The only other trace element COPC that showed consistent presence was cadmium (mean concentration 0.19 mg/kg, range <0.05 – 0.56 mg/kg). As expected, there was a close relationship between the concentration of zinc and cadmium as cadmium is a contaminant in the zinc oxide, which is used in the vulcanisation process (Kenendy et al. 2002).

Dietl et al. (1997) identified that antimony trioxide is used as a flame retardant in the vulcanisation of rubber and speculated that some of the source of antimony found in their environmental samples may have been sourced from tire wear. Of the 12 tyre samples examined by Kennedy & Gadd (2000), 10 tyres contained no detectable antimony (<0.2 mg/kg). One tyre contained 0.9 mg/kg and a further tyre contained 2.4 mg/kg in one duplicate and <0.2 mg/kg in the other. Compared to brake pads, it is unlikely that tyres form a significant source of antimony.

Organic Compounds

A preliminary examination of organic compounds in tyres used in New Zealand (Gadd & Kennedy 2000) revealed the presence of a range of organic compounds. As described in Kennedy et al. (2002), there are a series of specific organic compounds used in the tyre manufacture process. Rogge et al. (1993) also carried out a comprehensive analysis of a single used radial tyre sample (tyre dust generated on a rolling resistance testing machine). Table 5.5 provides a simplified summary of the results obtained by Rogge. et al. (1993) and Gadd & Kennedy (2000). Other data is summarised by Kennedy et al. (2002).

Table 5.5 – Summary of key compound groups and compounds identified in motor vehicle tyres.

Compound Grouping	Rogge et al. (1993)	Gadd & Kennedy (2000)
n- Alkanes	e.g., tetratriacontane (1229.8, total 18842.3)	
n-Alkanoic acids	e.g.,palmitic acid (4818.4, total 12197.3)	e.g., palmitic acid (~650)
n-Alkenoic acids	e.g., oleic ecid (1115.5, total 1279.2)	
Benzoic acids	e.g., benzoic acid (total 74.8)	
Substituted benzaldehydes	e.g., 3-methylbenzaldehyde (total 7.8)	
Polyalkylene glycol ethers	nd	
Thiazole	Benzothiazole (124.3)	Benzothiazole (~5)
PAHs	e.g., pyrene (54.1, total 226.1)	e.g., pyrene (~30)
Polyaromatic ketones and quinones	e.g., 9H-xanthen-9-one (xanthone) (0.45)	e.g., dihydrotrimethylquinoline (~30)
Regular steranes	e.g., cholestanes, ergostanes (total 74.2)	
Pentacyclic triterpanes	e.g., hopanes (total 684.4)	
Natural resins	Dehydroabietic acid (7970.3, total 9513.3)	
Amides	4-phenylbenzenamine (12.9)	e.g., 2-phenylmethylbenzenamine (~30) N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (~1350)
Phenols	p-octylphenol (17.6)	e.g.,Di(methylbenzyl)phenols (~627)

Notes: Data in ( ) concentration in mg/kg for individual compound or total for group.

The work of Rogge et al. (1993) shows that the dominant organic compounds in the tyre wear sample they examined were n-alkanes (C19-C41), n-alkanoic acids (waxes) and natural resins. The n-alkanes include both odd and even number carbon numbers and as such the alkanes generated differ to those produced by plants where there is a tendency for a predominance of odd over even carbon numbers. Other compounds made up only a very small fraction of the compounds identified. The tyre wear particles are composed predominantly of styrene and butadiene polymers. Stearic acid followed by palmitic acid appear to be the predominant n-alkanoic acids in tyres. A number of natural resins are present in the tyres.

The presence of PAHs in the tyres was considered by Rogge et al. (1993) to be possibly due to contamination of the carbon black added to the tyres. Benzathiozole (one of the vulcanisation accelerators) was identified by both Rogge et al. (1993) and Gadd & Kennedy (2000).

The evaluation of the organic compounds identified through information obtained from industry and the literature including the preliminary work carried out in New Zealand (Gadd & Kennedy 2000) has identified 13 specific organic compounds that were rated as COPCs. These are summarised in Appendix A.

In summary, the evaluation of contaminant and COPC in tyres has identified zinc as the key inorganic COPC in tyres. Cadmium another COPC was identified as being present in tyres at low concentrations.

A range of complex organic compounds are present in tyres as part of the manufacturing process. Based upon the compound identification information available, a small number have been identified as being COPC.

5.6 Brake Linings

5.6.1 Formulation

It is very difficult to characterise the typical practices in brake lining (i.e., friction lining) construction, from a chemical composition viewpoint. There are many references for construction standards, in the performance requirements for friction linings, but nothing that either specifies or implies any consistent approach to material composition by manufacturers. This has evolved from almost a century of empirical development. The many manufacturing suppliers in this area use their own formulations, which can vary widely depending upon the nature of the market they aim at. Friction linings are complex composite materials, with five main elements:

- Fibres.
- Abrasives.
- Lubricants.
- Fillers.
- Organics.

Kennedy et al. (2002) provides further details on the general composition of friction linings. The key constituents from an environmental perspective include the metals present and the metallic lubricants that are added to the matrix.

5.6.2 Contaminants

Available information (refer Kennedy et al. 2002) indicates that a range of organic compounds and trace elements would be expected to be present due to their various formulations. Kennedy & Gadd (2000) and Gadd & Kennedy (2000) provide a preliminary evaluation of the inorganic and organic composition of brake pads in use in New Zealand.

Trace Elements

The examination of a series of brake pad samples and brake drum dust samples by Kennedy & Gadd (2000) identified eight elements as being present in concentrations that were greater than crustal abundance (i.e., that present naturally in surrounding soils and rocks) (refer Table 5.6). As such, the presence of these elements when emitted would increase local environmental concentrations of the elements.

The preliminary work carried out by Kennedy & Gadd (2000) in New Zealand demonstrated the extreme variability of the brake pad composition. Of all of the elements examined this was most notable for two of the identified COPCs (Copper, median 35 mg/kg with a range of 11 to 112,000 mg/kg, antimony 6 mg/kg with a range of 0.07 – 29,500 mg/kg. Dietl et al. (1997) examined the distribution of antimony in the environment in relation to traffic. The latter authors identified that they had found 1-4% antimony in some brake linings.

Table 5.6 - Trace elements identified as being present in brake-pads at environmentally elevated* concentrations (From Kennedy & Gadd 2000).

Elements	COPC
Cadmium	Yes
Chromium	Yes
Copper	Yes
Mercury	Yes
Molybdenum	No
Nickel	Yes
Antimony	Yes
Tin	No
Zinc	Yes
Boron	No
Barium	No

Notes: * Compared to crustal abundance.

Deriving valid emission factors for contaminants from motor vehicles can be done for those elements that appear to have relatively constant concentrations because of their common usage. Barium is an example whose median concentration was reported as 2590 mg/kg (range 1800 – 6810 mg/kg, with two lower outliers of 61 and 413 .mg/kg).

Overall, although a number of inorganic COPCs were identified as being present in brake linings, the two most significant were copper and antimony.

Estimates of emission factors for these elements are made difficult as a result of the specific use of these materials by particular manufacturers of brake linings. Precise information on the proportion of friction linings on New Zealand roads that contain high concentrations of copper or antimony is not available. This lack of information arises because of the number of different types of brake linings used in the New Zealand market and the lack of readily available and precise information from distributors and manufacturers

Organic Compounds

The preliminary examination of organic compounds in brake pads used in New Zealand (Gadd & Kennedy 2000) identified the presence of a range of organic compounds. Little industry sourced information regarding the composition of friction linings appears available. This arises for a number of reasons including what may be a lack of awareness of the environmental significance of the nature of materials being used in the manufacture of brake linings. Rogge et al. (1993) also carried out a comprehensive analysis of a single brake pad sample. Table 5.7 provides a simplified summary of the results obtained by Rogge. et al. (1993) and Gadd & Kennedy (2000).

The brake lining dust examined by Rogge et al. (1993) was derived from an organo-metallic pad on a late model light truck. The authors identified small amounts of n-alkanes but reasonable concentrations of n-alkanoic acids. In the latter group, the C6-C9 molecular weight compounds were dominant. Both Rogge et al. (1993) and Gadd & Kennedy (2000) identified some compounds in this group such as palmitic acid at higher concentrations (commercial stearic acid which would be used in tyre manufacture will contain stearic and palmitic acids).

The trace PAHs detected by Rogge et al. (1993) were considered to have been formed by the heat generated during braking (600 °C which would be sufficient to pyrolyse some organic compounds). The polyalkyne glycol ethers identified by Rogge et al. (1993) were considered to be derived from hydraulic fluids. In their case they were considered to be lost from the hydraulic brake system and were able to contact the dust in the rear brake lining of the vehicle.

Table 5.7 – Summary of key compound groups and compounds identified in vehicle brake pads.

Compound Grouping	Rogge et al. (1993)	Gadd & Kennedy (2000)
n- Alkanes	e.g., pentacosane (total 38.47)	
n-Alkanoic acids	e.g., Palmitic acid (83.3, total 529.7)	e.g., palmitic acid (~15)
n-Alkenoic acids	e.g., oleic ecid (total 10.7)	
Benzoic acids	e.g., benzoic acid (total 45.5)	
Substituted benzaldehydes	e.g., 3-methoxybenzaldehyde (total 19.0)	
Polyalkylene glycol ethers	e.g., 2-(2-butoxyethoxy)ethanol (total 879.1)	
Thiazole	nd	Benzothiazole (~5)
PAHs	e.g., benzo[ghi]perylene (total 16.16)	e.g., tetramethyl phenanthrene (~5)
Polyaromatic ketones and quinones	e.g., fluorenone (total 3.0)	
Regular steranes	e.g., cholestane (total 1.55)	
Pentacyclic triterpanes	e.g., hopane (total 3.06)	
Natural resins	Dehydroabietic acid (10)	
Amides	nd	e.g., dimethylamine (~10)
Phenols		e.g., hydroxyphenylmethyphenol (~200)

Notes: Data in ( ) concentration in mg/kg for individual compound or total for group.

Based upon the available information on organic compounds in friction linings a total of nine COPC were identified and these are summarised in Appendix A.

A wide range of organic compounds are present in friction linings. A considerable number are present at low concentrations and some (the key resins and binders) are present at higher concentrations.

As with inorganic materials present, the concentration of these compounds varies significantly between individual brands of friction lining.

5.7 Road Surface Materials

5.7.1 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 base-course 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 basecourse 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, that 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, which is applicable to light or medium traffic conditions such as quiet urban streets.

A standard bitumen binder 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, up to 4 parts per hundred oil is incorporated in first coat seals. As a guideline, if seal cracks occur within eight years of seal application the use of a flux should be considered in future layers. The viscosity of the bitumen is temporarily reduced by a cutter oil, lighting kerosene, to promote adhesion and wetting of the chips, during this process the cutter evaporates and the bitumen returns to its original properties. Alternatively, a quick-breaking anionic or cationic emulsified asphalt is specified. Emulsifying and stabilising agents are employed to create a micro-mix of bitumen and water. Separation of the bitumen from the water to form a continuous film is referred to as "breaking" of the emulsion.

Bitumen is primarily a composite of high molecular weight hydrocarbons with small quantities of nitrogen, sulphur and trace metals. The exact composition is, dictated by the crude oil source material, however world-wide the types of chemical compounds present are generally consistent.

5.7.2 Contaminants

The erosion of bitumen particles from road surfaces has the potential to contribute particulate contaminant to the road-stormwater system. There is little published information on the composition of bitumen on New Zealand roads. Kennedy et al. (2002) provides a summary of available information.

Kennedy & Gadd (2000) and Gadd & Kennedy (2000) recently undertook a preliminary examination of the organic and inorganic composition of a series of samples of new and on-road bitumen. The inorganic analysis (Kennedy & Gadd 2000) demonstrated that the bitumen contains low concentrations of most trace elements and in particular the inorganic COPC. Vanadium (derived from the original petroleum) is one of the trace elements present in moderate concentrations but the concentration is not different to typical crustal abundance in New Zealand.

Analysis of organic compounds in New Zealand bitumen did not identify any significant organic compounds present. Specific measurement of the PAHs which, are known COPC, demonstrated that the PAHs were present at low concentrations with many not detectable (<0.2 mg/kg). It should be noted that the concentration of most individual PAH compounds in New Zealand sediments is <10 µg/kg. As such the low concentration in bitumen will still provide a contribution to receiving waters.

Overall, available information indicates that road bitumen may be a source of base hydrocarbons to the road-stormwater system. The low concentration of PAHs measured on bitumen particles are low compared to the concentration present on other particles derived from other sources. However, their presence is a further contribution to that in receiving waters. Based upon this information, particulate material, total hydrocarbons and total PAH should be included in any load contribution calculations within the road transport contaminant model.

5.8 Summary Points

Vehicle emissions have been identified as coming from six key sources within the road corridor. These are vehicle fuel, vehicle exhaust emissions, vehicle lubricating losses, vehicle tyre wear, vehicle brake lining wear and road surface wear.

Vehicle fuels in most situations represent a contained system. Losses occur from this source. These losses are VOCs and these do not typically directly interact with the road corridor.

Vehicle exhaust emissions are complex and contain a very large number of organic compounds. Both inorganic and organic COPC have been identified in exhaust emissions. In terms of the road corridor, it is the particulate component of the emissions that are of importance. The particulates from diesel fueled vehicles are important contributors of PAHs which constitute a major part of all of the COPCs identified.

Tyres are an important source of zinc to the road catchment. Tyres also contain a range of organic compounds a number of which have been identified as COPC.

Friction linings (brake pads) are an important source of a number of inorganic COPC. Of particular note are copper and antimony. Friction linings also contain a number of organic compounds a number of which have been identified as COPC.

Road surface wear is a source of particulate matter and some organic compounds. Bitumen surfaces contain PAHs in low concentration. These have been identified as a key group of COPC.

6. CONTAMINANTS, PATHWAYS & PROCESSES

6.1 Introduction

Given the number of motor vehicle components, materials and possible sources of emissions to the environment from motor vehicles, it is not surprising that motor vehicles are capable of emitting a wide range of contaminants to the environment. Chapter 3 identified the modes of contaminant loss and it is clear that a variety of processes are involved in the release of contaminants from motor vehicles.

These release processes involve wear and heat (brake linings and tyre wear), combustion (exhaust emissions), exhaust treatment processes (catalytic converters) and physical loss (e.g., oil). Contaminants are released from vehicles in both their native form (i.e., the form that they were used within the vehicle); transformed by processes associated with the operation of the vehicle (for example heating of brake pads, combustion of fuel and heating of oil) and by environmental transformation processes outside the vehicle.

This section of the report provides an introduction to the pathways and processes involved when contaminants are emitted or produced by motor vehicles and are transported to and enter the environment. As will be evident in the following sections, the processes and pathways are complex in nature.

Although the physical pathways are common to many contaminants, the fate and transformation processes are not, and these differ significantly between inorganic elements, inorganic compounds and organic compounds and within these groups. As such rather than present a very lengthy discussion about all of these processes some examples have been presented within this section for key environmental compartments to illustrate the variety of these processes.

In the contaminant evaluation process used as part of this assessment, transformation products of emitted contaminants have not been dealt with. It has been assumed in the assessment that the environmental risk associated with the release of the contaminant from the vehicle will not be increased following environmental transformation. This is a very complex area especially for organic compounds as many compounds will be degraded or stabilised, reducing their environmental significance.

6.2 The road environment

Vehicles contribute contaminants to stormwater through the road stormwater system. There has been a substantial amount of work undertaken to characterise the nature of contaminants on road surfaces to provide information on the contributions derived from both the general urban environment and vehicles to the stormwater system. Recent characterisation of particulate material on road surfaces in New Zealand, has been undertaken by Kennedy & Gadd (2002, 2003) and Ng et al. (2003). Information on metals in particulate material on road surfaces in New Zealand and overseas has been summarised by Kennedy (2003b).

Examination of contaminants in the road environment has shown that motor vehicles contribute a range of trace elements to the road surface and the environment beyond the road (through atmospheric transport and deposition). The key elements are Cu, Zn and Pb. Although Pb has been removed from petrol in New Zealand, Pb is still present on road surfaces. The presence of Pb on road surfaces is due to the presence of Pb in tyres, the re-introduction of Pb to the road surface from areas beside roads where the concentration is elevated (principally because of historic road side deposition from vehicle exhaust emissions) and loaclised point sources (e.g., industrial emissions).

The particulate matter on road surfaces in New Zealand also contain elevated concentrations of the elements Cd, Cr, Mo, Ni, and Sb. These are sourced principally from tyres and brake pads. It is likely that the Sb and Mo are contributed by specific commercial types of brake pads.

A proportion of the New Zealand vehicle fleet uses catalytic converters. As a result, the PGEs (Pt, Rh, Pd) will be emitted to the road environment from the exhaust system. International data shows that there are low concentrations of PGEs on road surfaces. There is currently no published data on the distribution of PGEs in the road environment in New Zealand.

There is limited information on the nature of organic compounds within the road surface environment. Most data that has been collected to characterise organic compounds in the road environment has been on PAHs. Analysis of PAHs in road surface particles in New Zealand has shown that particles on road surfaces have elevated concentrations of a range of PAHs. Based on overseas information, there will be a range of substituted PAHs attached to particles on the road surface.

6.3 Compartments

The fate of contaminants emitted from motor vehicles influences both their concentrations in the receiving environment and the ensuing load entering the environment in the short and long term. Both load and concentration have a role in the possible effects that contaminants may have in freshwater and marine ecosystems. In a simplistic sense, the contaminants can be partitioned into compartments in terms of assessing their fate. Figure 6.1 provides a very simple picture of the key compartments and the processes involved in relation to contaminants discharged from motor vehicles. The primary compartments are:

- The roadway which can be sub-divided into two sub-compartments, the road surface and the air immediately above it.
- The soil environment adjacent to the road, locally and regionally.
- The local air corridor within the immediate urban area or road corridor.
- The regional air corridor (e.g., Auckland metropolitan area) and the offshore (Pacific or global) atmosphere.
- The local receiving water environment (stream, river estuary, harbour or coastal embayment) and the offshore coastal receiving environment.

6.4 Processes and Fate

The compartments shown in Figure 6.1 are inter-connected via a number of physical process. Some compartments are connected by processes that are bi-directional (e.g., dry deposition and entrainment of roadway dust). Within each of the key compartments there are sub-compartments which are involved in partitioning processes that are principally chemical in nature and are influenced by the environment and the properties of the element or organic compound. The properties of the element or compound determine the fate of the constituent. This is overviewed further in this section.

As described in Section 3, there are a number of key properties and characteristics of individual elements and organic compounds emitted by motor vehicles that influence their fate. Table 6.1 provides a summary of the key processes that may influence the fate of a given contaminant within a particular compartment. Of all of the properties, the primary properties that drive their movement between compartments are:

- Vapour pressure (defines the rate of movement to the vapour phase from the material on the roadway or in water or on particles entering the atmosphere).
- Solubility (in water).
- The octanol-water partition coefficient (defines movement from water to lipids – i.e., uptake and bioaccumulation by organisms in the biological compartment).

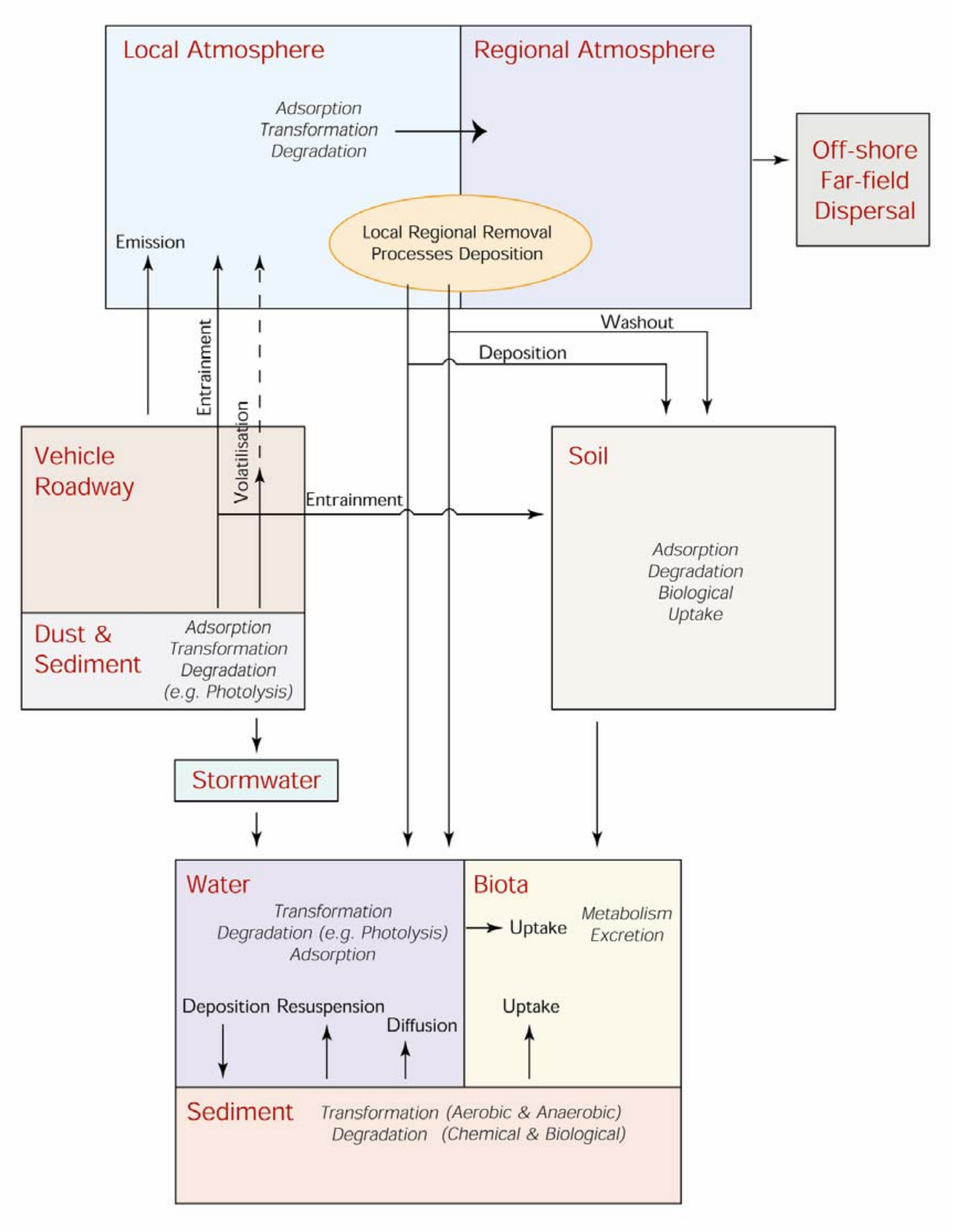


Figure 6.1 - Environmental compartments and key processes.

These properties (and others) were used to assess the distribution of the organic compounds identified as being present in source materials or emitted from motor vehicles (refer Kennedy 2000). Appendix B presents a summary of the simple environmental partitioning information obtained in the contaminant database for the identified COPCs. An examination of the information in Appendix B which is summarised in Table 6.2, shows that a significant number of the COPC identified in fuel and in the exhaust emissions from motor vehicles are volatile and partition significantly to air (88 of 205 identified compounds). These compounds are likely to have little direct and short-term interaction with aquatic ecosystems.

Table 6.1 – Processes that influence contaminant fate.

Compartment		Process	Influencing factors
Roadway	Roadway surface	Solubilisation	Rainfall, water
		Volatilisation	Vapour pressure
		Oxidation	Exposure to air
		Transformation	Interaction with other materials on road surface, pH etc.,
		Degradation	Microbial community
		Wind entrainment	Wind speed, particle size
	Catchpit	Redox equilibria	Anaerobic status of catchpit waters
Soil		Volatilisation	Vapour pressure
		Biological uptake	Organism
		Adsorption etc.,	k_{oc}
		Transformation	Interaction with other materials on road surface, soil pH etc.,
		Degradation	Microbial degradation
		Erosion	Rainfall, earthworks etc.,
Atmosphere	Local, regional	Washout	Rainfall patterns
		Dry deposition	Wind
		Transformations	
		Volatilsation	
		Degradation (e.g., photolysis)	
Aquatic receiving environment	Water	Biological uptake	Organism, k_{ow} of compound.
		Adsorption to suspended particles, plankton	
		Degradation (e.g., photolysis)	Light absorption characteristics
		Diffusion from sediments	Sediment redox state
	Sediment	Adsorption	Organic carbon and particle size
		Poor water chemistry interactions	Redox state and dissolved organic carbon concentration
		Diffusion	Poor water diffusion flux and chemistry
	Biota	Bioaccumulation	Organism, k_{ow} of compound

Few compounds partitioned under equilibrium conditions strongly to water and as such would not result in significant concentrations in a dissolved phase that could have direct toxic effects on aquatic organisms. Of those listed in Appendix B about 5% would fall into that category. A significant number of semi-volatile compounds had strong affinities for particulate matter and sediments/soils. About 50% of the identified COPC fell into this category. Aspects of partitioning are discussed further in following sections.

6.5 Atmospheric Processes and Transport

Atmospheric emissions from motor vehicles are partitioned between the gas phase and particulate matter in the air. Particulate matter is emitted from several sources including the wear of brake linings, wear of tyres and the combustion of fuel. This particulate matter is typically of small size. Size and other processes in the air in and above the road corridor influence both the particle size (via coagulation etc.,) and its dispersion.

Typically roadway air and the deposition in and adjacent to roadways contains much greater amounts of finer particles than in rural areas (Fang et al. 1999). The source of this fine particulate material is vehicle exhausts.

Table 6.2 - Summary of COPC partition categories.

Category	Primary partition compartment	Number of COPC	Example COPC in category
Fuel (101*)	Air >90%	41	1,2,3-trimethyl benzene
	Air 50-89%	2	Anthracene
	Water >90%	1	Phenylene diamine
	Water 50-89%	1	2,7-dinitrofluorene
	Water 25-49%	5	9-nitrophenanthrene
	Soil/Sediment >90%	29	Perylene
	Soil Sediment 50-89%	22	Cyclopenta(cd)pyrene
Exhaust system (104)	Air >90%	42	2,3,5-trimethyl hexane
	Air 50-89%	3	Trimethylnaphthalene
	Water >90%	1	9,10-anthracenedione
	Water 50-89%	1	9-fluorenone
	Water 25-49%	2	Nitrofluorene
	Soil/Sediment >90%	37	Dimethylphenanthrene
	Soil Sediment 50-89%	10	2M-anthracene
Coolants (1)	Water 50-89%	1	Mercaptobenzothiazole
Brake & Clutch (9)	Air >90%	1	Diethenylbenzene
	Air 50-89%	1	Butylated hydroxy toluene
	Water 50-89%	2	Methylenebis phenol
	Soil/Sediment >90%	4	Tetramethyl phenanthrene
	Soil Sediment 50-89%	1	Bis(2-ethylhexyl)phthalate
Tyres (13)	Air >90%	1	Butylated hydroxy toluene
	Water 50-89%	4	Mercaptobenzothiazole
	Soil/Sediment >90%	4	Diphenyl benzendiamine
	Soil Sediment 50-89%	3	2-methyl-N-(2-methylphenyl)-benzenediamine

Notes: * total number of COPC in category. It should be noted that the number of COPC in the partition categories do not add up to the total.

Airborne particulates

The emission of particulate matter to the atmosphere and the subsequent transport of those particles away from the point of emission allow road vehicle emissions to affect environments adjacent to and close to the source. As a result vehicle emissions can result in:

- Deposition onto soils adjacent to or remote from the source.
- Secondary transport of vehicle derived contaminants (deposited to roadway surfaces and soil) to waterways.
- Deposition of airborne particulates and gaseous pollutants onto freshwater, estuarine and coastal waters.

Typically particles > 300 µm in size will settle very close to source as a result of gravitational settling, however, turbulence can distribute large particles away from the source. Turbulent deposition can result in particles (e.g., 5–50 µm in size) settling close to the roadway (Habibi 1973).

Local Deposition

Various studies have examined the deposition of vehicle-emitted contaminants adjacent to roads. The proportion of emitted contaminant deposited on the road and to immediately soil varies between contaminant and between study. Hewitt & Rashid (1990) for example concluded that 14% of the Pb emitted by vehicles was deposited within 50 m of the roadway. This compares with New Zealand estimates such as those of Ward et al. (1975) who found that 58% of the Pb emitted by motor vehicles on the Desert Road near Waiouru was present within 250 m of the roadway.

A number of studies in New Zealand have shown classic depositional pattern of contaminants adjacent to roads. Fergusson et al. (1980) showed that Pb concentrations decreased rapidly in soil adjacent to Riccarton Road (ranging from ~1200 mg/kg at 4 m to <200 mg/kg at 10 m). Collins (1984) found that Pb concentrations decline according to a typical exponential decay pattern with a significant inflection in the concentration gradient being reached by 40 m (roadway traffic 23,000 VPD) and concentrations declining slowly with subsequent distance. Examination of roadside Pb concentrations alongside motorways in Auckland by Kennedy et al*.* (1988), found consistent decline in Pb concentrations out to distances of at least 100 m (Figure 6.2). Even though Pb has been removed from petrol in New Zealand, the fate of Pb is relevant as it provides an indication of the deposition profile adjacent to the road and it demonstrated that a reservoir of Pb still exists in this area, which might provide a source of lead, which can re-enter the road corridor.

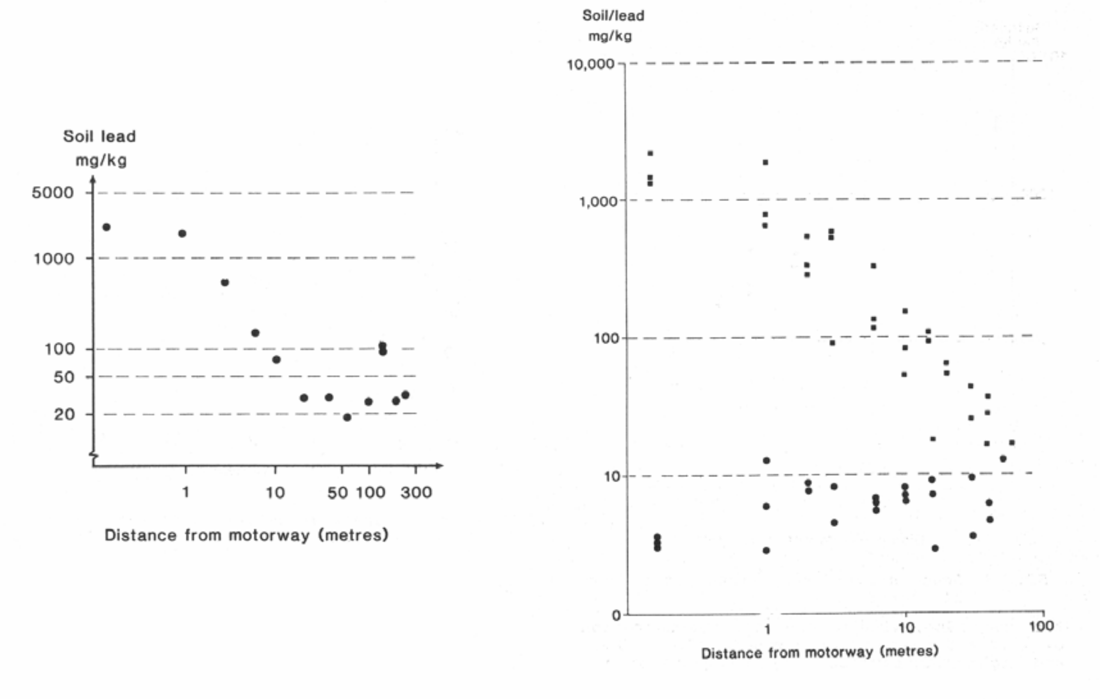


Figure 6.2 - Lead concentrations in soils near motorways in (a) Northcote and (b) at Mangere before (the sequence of horizontal dots typically below 10 mg/kg) and after (the squares) the opening of the motorway (from Kennedy et al. 1988).

Regional and Global Dispersion

Significant work has been carried out to show that vehicle derived contaminants enter both regional and global atmospheric circulation. Scales vary depending upon geographic factors. Samson (1988) identified near-field or local as up to 0.2 km, urban as 0.2-20 km and regional as 20-2000 km. In New Zealand, the scales vary depending upon the scale of the urban area and physical geographic features. Regional scale movements of contaminants occurs as a result of regional scale meteorological processes. Such conditions determine the extent and amount of deposition that might occur to land or to the coastal zone adjacent to the urban centre. Information about the consequence of long distance movement of contaminants has come from several areas of work. The first being a wide range of work that has examined the regional and global dispersion of lead emitted from motor vehicles (and other sources). The second is regional atmospheric dispersion patterns in industrial/urban regions such as Europe.

Gaseous and particulate material remaining airborne following local deposition are available for movement by local and regional climatic processes. The fate of emissions is dependent upon the chemistry of the elements and compounds involved. For example, metals associated with large particles (Fe, Mn) will be preferentially removed by dry deposition and metals associated with smaller particulates or gas phases (Sb, Hg) will travel further.

There is an exhaustive range of studies that have shown that airborne emissions from urban areas, and therefore roadways, can be transported significant distances. Most work that can be related back to motor vehicle emissions has utilised lead as a marker to track the distribution of the emissions. Examples include:

- Hewitt & Rashed (1990) estimated that 86% of the Pb emitted by motor vehicles was available for regional and long-range movement.
- Gulson et al. (1981) utilised Pb isotopes to demonstrate that contamination of soil by lead takes place up to 50 km from Adelaide.
- Tatsumoto & Patterson (1963) found through isotopic composition that the source of Pb in snow 800 km east of Los Angeles was Pb from vehicle emissions. Lead derived from motor vehicles has been identified in all remote locations over the globe.

The PAHs are one of the more important groups of organic compounds emitted from the exhaust system of motor vehicles. Some comments are provided in the inset box on the pathways and processes involved in the regional and global transport of these compounds.

Polyaromatic Hydrocarbons – Atmospheric Fate

PAHs are complex semi-volatile compounds. Their atmospheric pathways are made more complex in that they are capable of re-volatilising from PM surfaces following their emission from motor-vehicle exhausts (both in the air and following deposition) (van Jaarsveld et al. 1997, van Paul et al. 1998). A number of atmospheric removal and degradation processes govern the fate of PAHs when emitted to the atmosphere. These processes are temperature dependent so the importance of the various processes differs between summer and winter.

Nitro-polycyclic aromatic hydrocarbons (N-PAHs) were identified in Section 4 as a key group of COPC. N-PAHs are emitted from incomplete combustion processes which amongst other source include diesel and petrol engines (Cecinato & Zagari 1997). Nitro-PAHs can however also be formed in the atmosphere as a result of reaction between parent PAH molecules and N sources in the air (e.g., N_2O_5 nitration on particle sorbed PAH). The 3-4 ring N-PAHs are almost entirely associated with PM (Fan et al. 1995). Gas phase compounds such as 2-nitropyrene and 2-nitrofluoranthene will condense immediately onto soot PM. Lighter N-PAHs such as nitro-naphthalenes (which have 2 rings) are present almost entirely in the gas phase (Feilberg et al. 1999). The different isomers of the N-PAHs (e.g., 1 or 2-nitropyrene) are produced by different processes.

The dominant degradation route for N-PAHs associated with combustion processes appears to be photolysis (Fan et al. 1995, Fielberg & Nielsen 2000). Feilberg et al. (2001) investigated the distribution of N-PAHs in urban and rural air in Denmark. Concentrations of N-PAHs in air wer relatively low compared to PAHs with Fielberg et al. (2001) identifying concentrations of the order of 100 pg/m^3 (at an urban site in Copenhagen with 60,000 VPD) compared to PAHs which were 10-100 times higher. Traffic at the urban site was estimated to contribute 80-90% of the N-PAH directly (Nielsen et al. 1999). 1NP and 3NF are considered to be emitted directly by diesel vehicles and other combustion processes. On the other hand at both rural and urban sites, 2NF and 2NP are formed by reaction of the parent PAHs in the gas-phase (formed during the day via reactions of PAHs with OH radicals followed by addition of NO_2). These processes influence the proportion of different N-PAHs present in long and short range atmospheric transport.

In New Zealand, Fergusson (1993), showed that the amount of lead in dust-fall decreased westward (inland) from Christchurch with 10-12 µg/cm^2/yr being recorded in the inner city, 6-12 µg/cm^2/yr in outer residential areas, 3-5 µg/cm^2/yr in rural areas and 1-2 µg/cm^2/yr in remote rural areas and 0.1-0.3 µg/cm^2/yr in uninhabited areas. Although Pb has been removed from petrol, the work of Fergusson served to show how far vehicle emissions travelled prior to deposition.

Hewitt & Rashed (1990) examined Pb deposition adjacent to the M6 motorway in England (37,600 VPD with 15% diesel vehicles). The authors found that most of the measurable deposition associated with vehicle emissions occurred close to the motorway with deposition at a distance of 50 m being equivalent to the regional deposition pattern. Hewitt & Rashed (1990), found that 4.8% of the emitted Pb was deposited within 50 m of the motorway, 1% was deposited in the central median strip of the motorway and 8% was removed in the stormwater. Overall 13.8% was deposited on the road or within a short distance of it. For other metals such as Cd and Cu Hewitt & Rashed (1990) were not able to ascertain deposition rates based upon a mass balance evaluation.

For PAHs, it was found that deposition was dependent upon the particular properties of the compound. For LMW PAHs such as phenanthrene and anthracene the deposition was low (1.3 and 1.2% respectively of the total emitted) as these compounds are emitted mainly in the gas phase. For intermediate MW PAHs such as fluoranthene and pyrene, the deposition rates are higher (7.8 and 5.5% of the total respectively). For HMW PAHs such as benzo(a)anthracene/chrysene and benzo(a)pyrene the deposition amounted to 30.8 and 23.3% of the amount emitted.

Two deposition components are important. The first is the immediate deposition on the road surface that can be accounted for in the stormwater discharge. The second is the local deposition close to the road. The local deposition will however include direct deposition and the re-suspension of material deposited on the road surface. These pathways overlap to some degree depending upon the local soil and wind conditions. This material has the potential to:

- Deposit on stream and lake surfaces within a close distance (e.g., 100 m) of the road edge.
- Deposit on estuary and coastal water surfaces within a close distance of the road edge.
- Deposit on inter-tidal sediment surfaces in tidal creeks, embayments and coastal areas.

Calculation of the deposition rates is important to establish the proportion of contaminants entering receiving waters by deposition compared to stormwater discharge. NIWA (1996) estimated contaminant emission and deposition rates adjacent to roadways in New Zealand. These data are presented in Table 6.3. This data is indicative only and has been superceded by recent work (refer Section 9 and Timperley et al. 2003).

Table 6.3 - Contaminant emission and deposition rates adjacent to roadways (from NIWA 1996).

Contaminant	**Total Emission Rate (mg/VKT)**	**Deposition to Roadway (mg/VKT)**	**Deposition to Roadside Margins (ng/m^2/VKT)**		
			0-5 m	**0-15 m**	**0-30 m**
Lead	18	1.8	75	47	32
Zinc	4.0	0.4	17	10	7
Copper	0.16	0.16	0	0	0
Total PAH	0.25	0.015	0.63	0.4	0.27

Note: VKT = Vehicle km travelled.

6.6 Road Corridor

Physical processes within the roadway corridor that determine the fate of contaminants emitted by motor vehicles are relatively complex. The concentration in air adjacent to and above the vehicle (for moving vehicles) is determined by the emission rate, the turbulence induced by the vehicles travelling on the roadway; wind speed and direction, local atmospheric turbulence, local deposition processes (dry deposition and wash-out) and also chemical processes and transformations that occur in the immediate vicinity of the vehicle (Samson 1988). The physical processes are also influenced by, the structures, and buildings adjacent to the roadway. Moving vehicles create turbulent air movement that may influence pollutant dispersion up to a distance of 100 m. Various models of the air and particle movement within the road corridor have been developed to assess the fate of particulate material emitted by motor vehicles (Samson 1988).

Contaminants emitted by motor vehicles reach the road surface as a result of dry deposition and wash-out during rain events. Dry deposition is a continuous process with the balance of on-road contaminant load being determined by deposition and entrainment (due to road vehicle turbulence and wind). Wash-out is an important process as it results in a much greater percentage of contaminants emitted from motor vehicles being transported to the stormwater system compared to non-rain periods.

Wash-out is a very effective process in removing gaseous contaminants above roadways. During rain events, the concentration of gaseous contaminants falls to near zero. This process will remove highly water soluble compounds (this includes a range of VOCs such as toluence and benzene). Each compound will have an individual wash out factor or ratio that is dependent upon their distribution between gas and water during the event (temperature and chemical equilibria constants such as Henry’s Law constant (refer below)).

There are a large number of removal, transformation and degradation processes for gas-phase contaminants. These include amongst other things photolysis (during the day), reactions with common gases and acids (Atkinson 1988). All of these processes result in different compounds emitted from motor-vehicles having different atmospheric residence times. For particulate contaminants their residence times are dependent upon the size of the particle. Very large particles will have short residence times whereas gas-phase contaminants (e.g., Hg) will have very long residence times.

A variety of transformation processes result in the emitted compounds in many cases giving rise to other compounds. This is an extremely complex topic in its own right, for example:

- Discharge of common compounds such as alkanes results in the production of aldehydes, ketones and alkyl nitrates which then undergo further atmospheric transformations.
- As PAHs occur in gas and particulate phases, transformations are phase dependent. Photolysis and reactions with nitrogen are important. Gas phase PAHs include the lower MW compounds fluorene and phenanthrene and solid phase compounds include higher MW compounds such as benzo[a]pyrene. A specific example is discussed in the inset box above.

Organic Compounds

VOCs will be present in rainfall in concentrations that reflect their concentration in air and ambient temperature. VOCs will undergo processes whilst in urban air through reactions with other atmospheric constituents, such as hydroxyl radicals, which result in degradation. Volatilisation of VOCs from street surfaces and particulates is temperature dependent. In a reversal of this physical process, the atmosphere may also contribute VOCs to water, especially in cold weather. BTEX compounds are more biodegradable than MTBE. MTBE is considered relatively re-calcitrant and is not influenced by processes such as hydrolysis and photolysis.

Air/water partitioning of VOCs is described by their Henrys Law constant (H), which identifies the ratio of the partial pressure of the compound in the gas phase to the concentration in the water that is in equilibrium with the atmosphere. A second dimensionless constant (H/RT) is derived using H, gas constant and temperature which provides the ratio of air to water concentrations at equilibrium. A VOC with an H/RT value of 0.05 or larger will be volatile when in water (e.g., BTEX in Table 6.4). Compounds such as MTBE which have lower H/RT values will tend to partition from the gas phase into water. Hence concentrations of MTBE in rain and water tend to be present in relatively constant concentrations.

VOCs such as BTEX and MTBE have low partition coefficients with organic carbon (K_{oc}). Coefficients for benzene (~80) are such that some retention by organic carbon will occur. The coefficient for MTBE is ~11 and little retention by organic carbon will occur.

Table 6.4 - Summary of key physical properties of key VOCs.

Property	Benzene	Toluene	Ethyl-benzene	m,o,p Xylene	MTBE
Molecular weight	78.11	92.13	106.16	106.16	88.15
Specific gravity	0.8765	0.8661	0.867	0.861-0.88	0.744
Water solubility (g/m^3)	1,780	534	140	178	50,000
Vapour pressure (25° C, mm Hg)	76	36.7	9.53	6.61	245-256
Log K_{OW}	2.15	2.69	3.15	3.12	1.2
Log K_{OC}	2.16	2.18	2.94	2.32	1.035-1.091
Henry's Law Constant (H) (atm-m^3)/(g-mole)	5.43x10^{-3}	5.95x10^{-3}	7.89x10^{-3}	6.56x10^{-3}	0.59-3.0x10^{-3}
Dimensionless Henrys Law Constant (H/RT)	0.22	0.243	0.323	0.268	0.02-0.12

Note: Log K_{ow} = octonal/water partitioning coefficient. Log K_{oc} = octonal/carbon partitioning coefficient.

Key Volatile Organic Compounds

Benzene is an aromatic hydrocarbon, it is non-polar and is relatively soluble in water (Table 6.4), it is a stable molecule and is relatively un-reactive in the atmosphere. Slow oxidation of benzene will produce phenols and aldehydes (e.g., glyoxal $[CHO]_2$). Both products are highly reactive and water soluble and will be rapidly removed from the atmosphere by rain. Benzene's low aqueous solubility limits its concentration in rain.

Ethylbenzene has limited solubility in water compared to benzene and xylene (Table 6.4). Volatilisation is probably the key process influencing the fate of ethylbenzene. In water (1 m deep) a half-life of about 5-6 hours has been estimated (Mackay & Leinonen 1975). A half-life for atmospheric oxidation of 15 hours has been estimated. Degradation/breakdown pathways are complex with bacterial oxidation transforming ethylbenzene to compounds such as styrene (ethylbenzene).

Toluene (Methylbenzene) has a moderate solubility in water (Table 6.4). The half-life in water (1 m deep) is estimated to be 5 hours. Some adsorption to organic matter and organic matter such sediments would be predicted from the log K_{ow}. Atmospheric half-life is estimated to be 15 hours.

Formaldehyde is very soluble in water (up to 55%) and reacts in water (hydrates) to form methylene glycol amongst other compounds. Decomposition of formaldehyde can produce a variety of compounds ranging from methanol to formic acid. In the atmosphere, formaldehyde is lost mainly through reaction with hydroxyl radicals and photolysis. The atmospheric residence time is relatively short (e.g., < 1 day). In water, formaldehyde can react with other elements such as sulphur to form compounds such as hydroxymethanesulphonate.

1,3 – Butadiene is produced by the incomplete combustion of fuel. It is an alkene (it has a double bond) and has a short half-life as it reacts with radicals (e.g., hydroxyl) to breakdown to produce acrolein and formaldehyde. Atmospheric residence time is short during the summer but can be 10 times longer in the winter. The water solubility of 1,3-butadiene is low (0.735 g/L at 25°C). As such concentrations in rain and runoff would be expected to be very low.

Acetaldehyde is a saturated aldehyde formed as a result of the incomplete combustion of both diesel and petrol fuels. It is not a component of fuel evaporation. Emissions are reduced through the use of emission control technology. Acetaldehyde has a high vapour pressure and is highly soluble in water (infinite solubility) as such it will be an important component of rainfall and may be present in stormwater. In the atmosphere acetaldehyde degrades through photo-oxidation (e.g., with nitrate radicals to form peroxyacetyl nitrate) and oxidation by hydroxyl radicals to form formaldehyde. Acetaldehyde is also produced by the oxidation of other motor vehicle emissions such as propane and ethanol. Given the reaction times of these processes, acetaldehyde production can vary from hours to days. Acetaldehyde is soluble and as a result of aqueous oxidation, acetic acid can be produced. A range of other products can be produced as a result of reaction with other constituents (e.g., SO_2) in rain and water.

In summary, VOCs present in exhaust emissions have atmospheric retention times that depend upon their solubility and reactivity. Solubility data indicates that atmospheric washout does contribute particular VOCs to receiving water via stormwater. Available stormwater data does not show however that VOCs are present in detectable concentrations of stormwater. This conclusion is however limited by the analytical detection limits utilised in many published studies.

6.7 On-Road Processes

6.7.1 Introduction

Although, the road surface appears relatively un-reactive, there are a variety of physical and chemical processes that occur on the road surface that influence the behaviour of contaminants that enter the road corridor. These processes are numerous as noted in Table 6.1. Some examples of on-road processes that influence the fate of contaminants are discussed below. When contaminants reach the street surface (and adjacent soils) via dry deposition and washout (rain), they undergo a variety of processes that in many cases result in significant changes to the composition, speciation and form of the contaminant. While resident on the street surface, contaminants and particulates are exposed to wind, heat and sunlight. Following rainfall and passage through the stormwater system, they are exposed to water with resultant changes in chemical equilibrium and speciation.

6.7.2 Metals in Road Dust

A variety of elements are added to street dusts in forms ranging from fine aerosol, zinc oxide in rubber, to metal particulates such as Cu, Fe, Cr, Zn, Al (refer Kennedy et al 2003, Kennedy 2003 for more detail). Much of the work that has been carried out on dusts has concentrated on the chemistry of Pb. Lead was emitted from motor vehicles as the mixed halide PbBrCl with minor amounts of lead oxide, sulphate, chlorides and phosphates (Habibi 1973, USEPA 1977). Examination of soils and dusts has shown that lead sulphate is the dominant lead salt present. Fergusson & Simmonds (1983) found that the dominant crystalline species present were sulphates and carbonates along with oxides and Pb.

A number of international studies have assessed the environmental mobility of trace metals in street dusts (Wilber & Hunter 1979, Harrison 1979, Lau & Wong 1983). In New Zealand, Fergusson & Ryan (1984) examined the extractability of metals in Christchurch street dusts. The extractions showed that Cu tended to be associated with organic material while Cd, Pb and Zn were associated with ‘carbonate’ fractions (dilute acid extractable rather than exchangeable). Extractability in dilute acid (0.002 N HCl) tends to increase exponentially with decreasing grain size of the particulates present in street dusts (Kennedy unpublished).

Overall, metals introduced to road surfaces from vehicles will undergo a range of changes including:

- Oxidation due to exposure to air.
- Breakdown due to physical abrasion.
- Chemical reactions due to change in pH and exposure to sulphate, carbonates and other chemical species in the atmosphere or rain.
- De-sorption of adsorbed chemical species.

6.7.3 Tyre Rubber

During normal driving conditions, fine particles of tyre rubber are worn from tyres and are deposited to roadways and dispersed into the local atmosphere (particles range from <100 µm down to smaller than 2 µm). As described earlier, tyre rubber is a complex predominantly organic material. A number of organic compounds were identified in tyres that could enter stormwater. One of the key compounds present in tyres and identified as present in tyres in New Zealand is benzothiazole. The evaluation of the physical and chemical properties of this compound in the Contaminants database did not result in it being identified as a COPC. However, an examination of its fate is of value to illustrate some of the processes involved with particular groups of semi-volatile organic compounds. Reddy & Quinn (1997) identified Benzothiazole (BT), 2-hydroxybenzothiazole (HOBT) and 2-(4-morpholino)benzothiazole (2,4MoBT) in tyres (further information on BT in tyres in New Zealand can be found in Gadd & Kennedy 2000). The authors also identified that following five leaches of tyre crumb particles with deionised water that 50% of the Benzothiazole (BT) compounds was removed. Based upon estimated tyre wear rates the flux of water-soluble BT compounds can be estimated. Dissolved BT and other benzothiazolamines have been detected in urban runoff by Reddy & Quinn (1997) and Kumata et al. (2002) (Table 6.5).

Table 6.5 - Summary of mean dissolved concentrations of Benzothiazoles in urban runoff (concentrations $\mu g/m^3$).

	BT	HOBT	2,4MoBt
February 1995[1]	378	721	198
September 1995[1]	819	5640	154
April 1997[2]	-	-	119 – 384
August 1998[2]	-	-	15 - 93

Notes: [1] Data from Reddy & Quinn (1997), Pawtuxet River. [2] Data from, Kumata et al. (2002), Chuo highway Japan.

The dissolved BTs identified by Reddy & Quinn (1997) were derived from direct leaching of tyres on cars, weathering of worn tire particles, skid marks on road surfaces or possibly from antifreeze. The authors also used the concentration/leaching information to indicate that 0 - 3.4% of the suspended particles in the urban runoff might be tyre particles. Other work reported in Reddy & Quinn (1997) indicated that this figure could be 0.05 – 9.5% of the particles. Relatively low concentrations of these compounds were detected in sediments examined by Reddy & Quinn (1997). The authors considered the environmental fate of this group of compounds. This general picture of fate was reflected in the level one fugacity assessment for benzothiazole provided in the contaminants database. Similar trends in partitioning can be seen for similar compounds such as mercaptobenzothiazole which strongly partition to water. In contrast to the BT compounds, other compounds such as diphenyl benzenediamine (abbreviated to DPPD) which was identified as a COPC in the database, strongly partitions to sediment rather than water (refer Appendix B for fugacity data provided from the contaminants database). Figure 6.3 also presents this partitioning data visually. The data in Figure 6.3 was also obtained using a Mackay Level 1 model (University of Trent) and the results are similar to those presented in Appendix B.

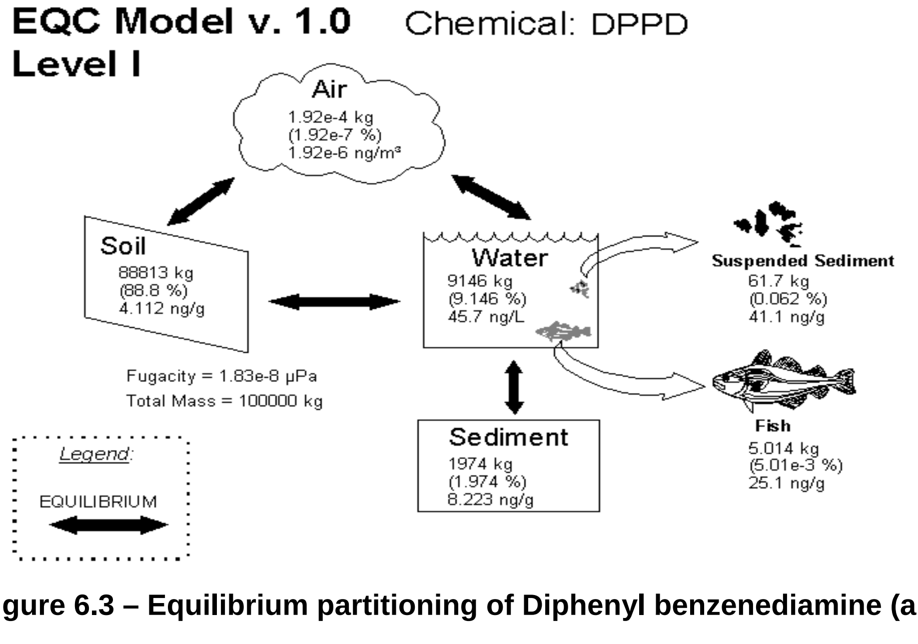


Figure 6.3 – Equilibrium partitioning of Diphenyl benzenediamine (arbitrary mass).

BT and HOBT were considered to absorb sunlight very weakly at wavelengths <290 nm and as such direct photolysis was considered a minor degradation pathway. Indirect photolysis of BT, HOBT and 2,4MoBt was also considered unlikely.

The volatilisation half lives for BT, HOBT and 2,4MoBt were estimated to be 15 days, 235 years and >1,000 years respectively. However, the rates are very dependent upon physical factors and when calculated for shallow water (e.g., 1 mm) such as that present on road surfaces the half lives for BT and HOBT were 33 minutes and 86 days respectively. As such, processes such as volatilisation are strongly influenced by physical conditions at the time.

Reddy & Quinn (1997) examined microbial degradation of the BT group at environmental concentrations and found that the BT and HOBT were found to be degraded in about 30 days. They noted that there was some uncertainty in this information and there may be seasonal and other factors which might influence this process. 2,4MoBt which is more complex and more hydrophobic was considered to be more resistant to microbial degradation.

All three BT compounds were considered to be capable of sorbing to the organic coatings of particles in conditions when particulate concentrations were very high (e.g., 1 g/L).

The k_{ow} values for the BT compounds are small and as such there should be little biological uptake and accumulation of these compounds. Reddy & Quinn (1997) did however point out that there is some information in the literature that indicates some biological uptake. It was also noted that their chemical structures, which do not have hydrolyzable or reactive moieties will restrict abiotic chemical transformations from occurring.

In summary, the BT group of compounds are water soluble. As such they tend to be transported or washed out of the atmosphere in dissolved form. BT is capable of being volatilised and both BT and HOBT can be microbially degraded. With limited biological uptake of this group, the combined environmental processes should see a shift in the concentrations of all three compounds over time. BT and HOBT should decrease and 2,4MoBT increase over time. In estuarine environments and coastal environments there should be a net export of these compounds out of the system in tidal waters.

6.8 Stormwater Runoff

6.8.1 Catchpits

Between the street surface and the stormwater system are catchpits (often referred to as gully pots or traps). The catchpit function is to trap particulate debris and prevent it from entering the stormwater system. The base of the catchpit usually remains filled with water between storm events.

The quality of the catchpit water has the potential to affect stormwater quality. As catchpits retain stormwater between storm events, their chemistry changes over time as a result of changes in the redox chemistry (i.e., the availability of dissolved oxygen) and the biological activity within the catchpit (e.g., decomposition of organic matter). The key changes in catchpit water quality are decreases in dissolved oxygen concentrations, increases in dissolved solids, BOD_5 (e.g., 13.7 mg/kg), chemical oxygen demand (COD), nitrate (e.g., 9.6 g/m^3) and ammonia (e.g., 1.39 g/m^3) (see Fletcher et al*.* 1978, Mance & Harman 1978).

Changes in the concentration of dissolved metals would also be expected. The relative change between particulate and dissolved metals in catchpit waters will depend upon the pH and redox conditions (Fletcher et al*.* 1978). As the catchpit water is replaced by incoming stormwater during the storm event, the quality of the catchpit water has the potential to influence the quality of the initial volume of stormwater discharged to the receiving water. The actual change in stormwater quality is dependent upon the ratio of catchpit water to stormwater. It is likely for a small storm event that the catchpit is an important volume of the overall storm (e.g., 10% or greater).

6.8.2 Copper and Zinc in Runoff

Copper is one of the more common metallic contaminants emitted by motor vehicles (refer Section 3). The predominant source of Cu is the wear of brake linings and as such the primary source is metallic copper (either pure or as brass). When stormwater runoff is examined about 20-25% of the total Cu is found in the dissolved phase (defined by filtration through a 0.45 µm filter). As such, while on the road surface, a proportion of the Cu emitted by vehicles has been transformed to a state allowing it to be dissolved in rainwater.

Sedlak et al. (1997) reported that most of the Cu (and also Ni) in surface runoff are complexed by relatively strong ligands. Hermann et al. (1994) also described the presence of ASV-stable organic complexing agents in stormwater. The speciation of dissolved inorganic Cu (free ionic Cu or complexed Cu) is dependent upon the concentration of other anions (e.g., sulphate, hydroxide and carbonate) and the pH of the water. Timperley (1999) provides further information on the nature of dissolved Cu in New Zealand urban runoff. Webster (2000) also demonstrated in New Zealand that much of the dissolved Cu may be complexed if sufficient DOM is present. This has implications for the toxicity of Cu in stormwater and downstream environments.

As described earlier, the dominant source of Zn in vehicles is the tyres. The Zn is released in particulate form in dry weather and during wet weather in particulate and dissolved forms. A high proportion of zinc in stormwater runoff is in a dissolved form (refer summary of New Zealand data in Kennedy 2003a). The speciation of Zn and other metals in stormwater will be dependent upon the pH and the chemistry of the site specific stormwater runoff. However unlike Cu, Zn is not readily complexed by DOM in freshwaters (Webster 2000) leaving much of the Zn in a form potentially able to exert toxicity to aquatic organisms.

In summary, the quality of catchpit water differs from that of stormwater generated directly from road surfaces. The differences are attributable to processes that occur in the catchpit between storms. These water quality changes have the potential to influence receiving water quality when catchpits are flushed during a storm.

The metals emitted by vehicles to the road surface become distributed between the dissolved and solid phase during storm events. The proportion present in the dissolved phase differs between the metals with some such as Zn having a high proportion in the dissolved state. This difference in distribution affects the fate of particular metals and their potential toxicity in receiving environments.

6.9 Receiving Water Processes

6.9.1 Introduction

The fate of contaminants in stormwater discharged to receiving environments is dependent upon whether the receiving water is fresh, estuarine or coastal. The primary factors that drive the fate of any contaminants are whether the contaminant is associated with particulate matter or is in a dissolved state.

The fate of particulate associated contaminants is driven mainly by hydraulic processes in freshwater (whether the receiving water is a lake or a stream or river with significant flow) and by fresh-salt water interactions when the stormwater reaches the fresh-salt water boundary where physico-chemical processes may result in the coagulation of fine particulate material and physicochemical changes in the speciation of some inorganic constituents.

A significant proportion of the contaminants present in stormwater settle in depositional areas within estuaries, harbours and the nearshore coastal zone. When incorporated into sediment, the contaminant then becomes influenced by two key processes. These are:

- The ingestion of sediment by sediment feeding biota and the bioturbation of sediment by in-fauna.
- The influence of changing redox state of surface sediments.

6.9.2 Freshwater

Following transport through the stormwater system, stormwater may be discharged into a freshwater stream, river or lake. Following entry into the freshwater environment, the materials carried in stormwater are subject to a range of physical, biological and chemical processes. The two key processes which influence stormwater in the receiving water are dispersion (and dilution) and settlement of particulate matter.

Dispersion

Dilution and dispersion results in a decrease in the concentration of constituents in the stormwater present at a concentration greater than in the receiving water. The degree of dilution is a function of the stormwater flow, the size and flow of the receiving water. Dilution and dispersion in stream, river and lake environments can be modelled and assessed. It should be noted however, that in many urban environments, stormwater flow could make up all of the flow in the water body.

Settlement

Settlement occurs in two phases. The first is the deposition of large particles (sand and gravel etc.,) by gravity immediately adjacent to the discharge location. The second is the settlement of finer particles in depositional environments downstream such as wetlands and slow-flowing areas (in the case of streams) to settlement further away from the discharge in the case of lakes. The amount and nature of settlement will depend upon the size distribution of suspended and bed load in the stormwater discharge.

Other Processes

Once in the receiving environment other processes influence the fate of contaminants. These include relatively short-term processes (noted earlier) such as volatilisation across the water-air interface, sorption (a function of sediment type, organic carbon content etc.), hydrolysis (reaction with water) and photolysis (reaction with light) and longer term processes such as bio-degradation (bacterial metabolism and detoxification).

Particulate contaminants which, settle may become re-introduced into the environment via re-suspension and bio-turbation (the disturbance and movement of sediment by biological activity such as burrowing and feeding).

6.9.3 Estuarine and Marine Waters

Stormwater discharged into the estuarine or marine environment is subject to similar processes to those described for freshwater in the preceding section. Dispersion and dilution are site-specific factors that are determined by tides and by coastal geomorphology and oceanography.

Settlement

Settlement processes in estuarine and marine environments comprise:

- Settlement of larger particulate material immediately adjacent to the discharge point.
- Flocculation of aggregated fine particles as a result of the entry of freshwater into saline waters (resulting in a change in the charge associated with fine particles).
- Dispersion of fine particulate matter with tides.

As a consequence of these processes, there tends to be a halo of larger particulate debris on the sediment adjacent to intertidal and sub-tidal stormwater discharge points.

There also tends to be increases in the concentrations of contaminants in estuaries, firstly as a result of the presence of depositional environments (e.g., salt marshes and mangroves) and the location of the fresh-salt water interface. As such, these processes result in a stronger gradient of particulate-associated contaminants (e.g., metals and PAHs) closer to discharge points entering estuarine and marine waters.

Other Processes

Metals

When particulate matter is deposited in estuarine and coastal environments, the particulate matter undergoes two key processes. The first is diagenetic chemical changes in the sediment-water interface that result in the dissolution and precipitation of contaminants with a road transport stormwater origin. Metals are involved in pH/eH sulphide interactions in particular and some metals (e.g., Cu) are involved in processes with dissolved organic carbon.

The chemistry of sediments containing contaminants changes over time. Although influenced by factors such as bioturbation, which may alter sediment chemistry, the phase chemistry of many metals tends towards greater stability over time. This was shown for example in relation to Pb in the sediments of the Manukau Harbour in New Zealand (De Mora & Demeke 1990).

VOCs

In Section 2 it was considered that the concentration of VOCs in stormwater were typically low and few were detected. For example, toluene was found in concentrations with a median of 0.3 mg/m^3 in Long Island stormwater. Wakeham et al. (1985) reviewed the fate of toluene in seawater. The key pathways for removal of toluene were volatilisation and biodegradation (mainly in summer). That study reported a half-life for toluene in a marine experimental mesocosm of 6 days during a storm to 25-35 days during calmer conditions. The mass balance assessments carried out by the authors showed that after 21 days:

1. Volatilisation accounted for 52% of the flux in winter and 17% in summer.
2. 30% of the toluene remained as dissolved toluene in water in winter and <1% in summer.
3. 16% of the toluene remained in the water as dissolved CO_2 and 2% was lost as gaseous CO_2 in winter. In summer the corresponding figures were 76% and 3% respectively.
4. Only small amounts of toluene were associated with particulate matter and non-volatile (polar) pools.

At 56 days, volatilisation accounted for 80% of the toluene loss indicating the importance of the volatilisation pathway in winter. In summer, the dominant process was mineralisation.

In an earlier study, Wakeham et al. (1983) showed that the concentration of toluene in seawater in Narragansett Bay (Rhode Island) was greatest at the head of the Bay with a decreasing gradient further from the coast. Wakeham et al. (1985) concluded that volatilisation probably occurred at rates some 2-6 times faster than measured in the mesocosm. Residence time of any VOC or organic compound is also dependent upon flushing time in estuaries and tidal movement in open coastal areas.

The pathways and processes influencing the concentration of VOCs in estuarine and coastal waters are complex. The residence time of any VOCs in estuarine waters will be dependent upon the seasonal interaction of the physical and biological processes coupled with the flushing characteristics of the estuary. As such, interval between storms will have an important influence on the potential build-up of VOCs such as toluene in estuarine ecosystems.

6.10 Summary Points

The pathways of road transport-derived material and contaminants can be placed into two broad categories:

1. Atmospheric dispersion with consequent wet and dry deposition.

2. Transport via stormwater to freshwater and estuarine/marine environments with subsequent dispersion of material depending upon environmental conditions.

The fate of road transport-derived materials and contaminants is dependent upon the nature of the material and contaminant. The following broad points can be made:

1. Inorganic and recalcitrant particulates will settle close to the discharge point if large enough. Dispersion will be dependent upon physical processes but will typically result in accumulation of particles in the closest depositional environment (pond, lake, river, estuary, coastal shelf).

2. Metals will be transported in dissolved and particulate phases. The proportion is dependent on the element. In the receiving environment, the proportion will change depending upon the environmental conditions that prevail (in terms of pH, eH and other factors).

3. VOCs will be subject to a variety of processes that result in the elimination of the VOC from the receiving waters. The pathway will be dependent upon season and a variety of other factors. The fate of different VOCs will differ depending upon their properties.

7. EFFECTS OF ROAD RUNOFF ON AQUATIC ECOSYSTEMS

7.1 Effects Issues

Environmental effects arising from roadway stormwater are complex and involve physical change (hydraulic changes in receiving environments and changes in physical characteristics) and chemical changes (e.g., changes in metal and other contaminant changes). Kennedy (2003a) reviewed information on the effects of runoff from roads on freshwater, estuarine and coastal environments. There are a number of significant publications about stormwater runoff effects. Most of these discuss the effects of urbanization and stormwater quality. Examples include Burton & Pitt (2002) and Scheuler (2003). In, New Zealand the most significant information of urban stormwater quality was compiled by Williamson (1993). Subsequently further research has been published in the scientific and grey literature increasing our knowledge of both urban stormwater and roadway/motorway runoff quality. This section of the report provides an overview of the effects of stormwater runoff from roads. Kennedy (2003a) discusses the range of environmental issues associated with urban and roadway runoff. In this section the focus is on contaminants and the effects of those contaminants.

7.2 Stormwater runoff

There is now a moderate body of data on trace metal concentrations in urban and roadway runoff in New Zealand (Kennedy 2003a). Motorway stormwater quality data appears available from only two studies in New Zealand and that data is however limited both in extent and in quality. That data however shows that the New Zealand motorway stormwater chemistry is similar to that from overseas motorways.

Specific studies in New Zealand have provided information on the variability in trace element concentrations through storm events. There is only limited data in New Zealand on the concentration of the elements Cr and Ni in stormwater. The available data on dissolved and particulate metal concentrations in urban and roadway stormwater shows that the proportion of Cu Pb and Zn is relatively consistent in New Zealand stormwater. The New Zealand data indicates that as with overseas studies lead is the least soluble of the key elements in stormwater (<10%) with Zn being the most soluble (about 40%). Cd and Cu appear to be moderately soluble with about 30% in the soluble phase. Kennedy (2003a) provided a summary of New Zealand data for the concentration of contaminants in urban and roadway stormwater. Table 7.1 compares a selection of dissolved metal concentrations from recent studies of urban and roadway stormwater concentrations and compares these with USEPA acute criteria and the ANZECC (2000) 95 and 99% effect triggers for the protection of aquatic organisms.

Table 7.1 - Summary of key potential toxicant concentrations in roadway stormwater with ANZECC (2000) triggers.

Constituent	Dissolved concentration*	USEPA acute criteria**	Freshwater ANZECC (2000) 95% effect trigger	Freshwater ANZECC (2000) 99% effect trigger	Marine ANZECC (2000) 95% effect trigger	Marine ANZECC (2000) 99% effect trigger
Cadmium	0.018, <0.05	1.16, 40	0.2	0.06	5.5	0.7
Copper	3.2, 4.1, 7.5, 9.7	4.3, 4.8	1.4	1.0	1.3	0.3
Lead	0.21, 2.9, 3.3	17, 210	3.4	1.0	4.4	2.2
Zinc	33, 68.4, 107, 113, 170	42, 90	8.0	2.4	15.0	7.0

Note: * - Selected data from Tables 4.6, 4.7 in Kennedy (2003a). ** - Freshwater, marine criteria with freshwater criteria for a hardness of 30 g/m^3.

The data in Table 7.1 shows that for cadmium, the dissolved concentrations are unlikely to exceed ANZECC (2000) triggers. For Cu and Zn, dissolved concentrations may exceed USEPA acute criteria and will exceed ANZECC (2000) triggers commonly when discharged into freshwater and marine environments. Moderate dilution is required to bring the concentrations below the respective criteria.

In addition to the information on stormwater quality summarised in Kennedy (2003a), there is significant other data available in the international literature. Table 7.2 summarises the results of extensive monitoring undertaken by California Department of Transportation on highways and ancillary facilities in California (Caltrans 2003)

Table 7.2 – Roadway stormwater quality – from Caltrans (2003) (all data mean and (number of samples), mg/m^3 unless noted).

Constituent	**Highway runoff**	**Park & ride lots**	**Congested highway**	**Free Flowing highway**	**Toll Plaza runoff**	**Weigh Station runoff**
	1998-201	1998-2001	2000-2001	2000-2001	2001	2001
TSS g/m^3	147.3 (1057)	61.8 (179)	86.6 (26)	113.9 (30)	96.2 (16)	67.4 (15)
Nitrate-N g/m^3	1.1 (1042)	0.7 (180)	1.48 (26)	1.3 (30)	1.0 (16)	1.1 (15)
TKN g/m^3	2.3 (1047)	2.6 (179)	3.3 (26)	2.5 (30)	2.8 (16)	3.2 (15)
TP g/m^3	0.4 (992)	0.4 (179)	0.2 (26)	0.3 (30)	0.3 (16)	0.3 (15)
Arsenic-T	1.99 (774)	1.1 (152)	1.73 (26)	1.7 (30)	1.46 (16)	1.57 (15)
Arsenic-D	1.06 (752)	0.66 (152)	1.14 (26)	1.2 (30)	0.79 (16)	1.26 (15)
Cadmium-T	0.84 (941)	0.31 (152)	0.88 (26)	0.73 (30)	1.11 (16)	0.51 (15)
Cadmium-D	0.24 (1005)	0.14 (152)	0.51 (26)	0.31 (30)	0.46 (16)	0.24 (15)
Chromium-T	9.3 (941)	2.8 (152)	8.5 (26)	8.2 (30)	11.4 (16)	8.1 (15)
Chromium-D	2.9 (1006)	0.9 (152)	5.2 (26)	4.3 (30)	4.8 (16)	2.0 (15)
Copper-T	48.1 (998)	16.7 (179)	43.9 (26)	38.3 (30)	60.1 (16)	33.3 (15)
Copper-D	15.2 (941)	9.0 (179)	25.7 (26)	21.7 (30)	31.3 (16)	20.8 (15)
Nickel-T	11.4 (941)	6.0 (152)	9.4 (26)	8.7 (30)	13.4 (16)	9.1 (15)
Nickel-D	4.5 (1006)	3.7 (152)	6.8 (26)	5.5 (30)	6.8 (16)	4.2 (15)
Lead-T	62.6 (998)	9.2 (179)	31.2 (26)	72.5 (30)	23.9 (16)	14.2 (15)
Lead-D	5.4 (1068)	1.2 (179)	6.4 (26)	19.7 (30)	4.0 (16)	3.7 (15)
Zinc-T	208.3 (998)	158.8 (179)	244.3 (26)	222.1 (30)	280 (16)	221.6 (15)
Zinc-D	72.2 (1062)	79.3 (179)	139 (26)	88.4 (30)	136.3 (16)	119 (15)

Notes: detection limits As, Cr, Cu, Pb = 1; Cd = 0.2, Mi = 2; Zn = 5 mg/m^3. T = total; D = dissolved.

A comparison of the data in Table 7.2 with the trace metal data in Table 7.1 shows that the data is generally similar to the roadway and urban stormwater data gathered in New Zealand. If anything the New Zealand data tends to be at the lower end of the concentration range presented from the Caltrans sampling. Earlier Caltrans data up to 2001 which, included medians is presented in Caltrans (2002). The Caltrans data for As, and Ni shows that the dissolved concentrations for those elements are generally below the ANZECC (2000) 99 % trigger values for protection of freshwater organisms (No Cr triggers). The Ni and Cr data are typically below the ANZECC (2000) 99% trigger value for the protection of marine organisms (No As triggers).

Stormwater transports particulate matter containing high concentrations of contaminants. This is not surprising given the high concentrations of metals and organic compounds such as PAHs present in particulate materials present on road surfaces (e.g., refer Kennedy & Gadd 2002). Examination of the concentrations present in different grain size separates obtained from stormwater has shown that concentrations of elements such as Cu and Zn are of the order of 150 and 2,000 mg/kg.

Stormwater from roads contains a wide range of organic compounds. Many contaminants are present as a result of their emission from a number of sources associated with motor vehicles (e.g., tyre and brake pad wear, exhaust emission). Compounds present on road surfaces and in stormwater include volatile organic compounds and a wide range of semi-volatile organic compounds. VOCs are present in stormwater at low concentrations. Their road transport source is principally the evaporation from fuel and loss through the exhaust system. Although there is some international data there does not appear to be any data on the concentrations of VOCs in New Zealand stormwater runoff. The PAHs are the most well understood group of SVOCs and have been measured in stormwater and for which there is data for in New Zealand. A higher proportion of the concentration of low MW PAHs is present in the dissolved phase compared to high MW PAHs which are almost entirely present in the particulate phase.

The quality of catchpit water differs from that of stormwater running off roadways. The differences are attributable to processes that occur in the catchpit between storms. These water quality changes have the potential to influence receiving water quality when catchpits are flushed during a storm.

The quality of stormwater generated in urban areas and motorways is a function of a number of factors the principal influences being rainfall composition, road surface composition, gutter dust accumulation and chemistry.

7.3 Toxicity

7.3.1 Introduction

Our understanding of the toxicity related effects of urban and roadway stormwater has improved markedly in recent years. Toxicity of urban stormwater was reviewed in Kennedy (2003a). In New Zealand there are few specific studies that have assessed the toxicity related effects of stormwater from roads or highways in the absence of the confounding that could arise from other urban stormwater sources (e.g., industrial sites, residential properties, roof runoff).

7.3.2 Water-borne toxicity

Toxicity tests have been undertaken using a range of freshwater organisms but have not demonstrated consistent toxicity. Work undertaken in the United States using general urban runoff has shown toxicity with some studies indicating greater toxicity in the first flush compared to flow weighted stormwater samples. This is not surprising as first flush stormwater runoff from roads exposes organisms to very high concentrations of contaminants compared to whole storm quality. The toxic agent in some US stormwater toxicity studies has been identified to be organic compounds (in some cases pesticides) but it is likely that dissolved metals are a contributor or in some cases the causal agent of toxicity.

Tests undertaken overseas using Microtox have shown that for runoff parking areas, 50% of samples are toxic and for highways (bridge), 20% of samples were severely toxic. Studies involving freshwater algae have shown that nutrients in runoff may stimulate growth but that metals in stormwater may inhibit growth. Work in New Zealand has shown that urban stormwater (e.g., in Auckland and in Rotorua) has chronic effects on growth of freshwater algae and Daphnia (in toxicity tests).

As noted by Grant et al. (2003), few studies have been undertaken that specifically related to stormwater runoff from roadways. There have been several recent pieces of work that have added to the information we have on roadway stormwater toxicity. Caltrans (2003) reported on a significant amount of stormwater toxicity assessment work that they have undertaken up till 2002. Caltrans (2003) identified that they had monitored toxicity at four types of site including, highway drains, maintenance yards, park and ride facilities, and rest areas. In the period 2000-01, 24 highway sites were monitored (278 toxicity tests), four maintenance yards were monitored (65 tests), 8 park and ride facilities (106 tests), and three rest areas (19 tests). Each site was tested from one to four times throughout the season. At least one toxicity test at one sample period (early, mid, and late winter) was significantly different from the control (indicating toxicity) at all but 2 sites. Caltrans reported that 5 sites had dates with no toxicity for any test.

Overall, Caltrans (2003) reported that of the 39 sites monitored, 23 sites indicated significant acute toxicity. Of the 98 tests Caltrans performed using Pimephales (a fish), 82 (83.7%) demonstrated significant toxicity for either one or both tests. Significant reductions in biomass were found in 52 samples, and significant mortality was found in 28 of the samples. Of the 98 tests performed using Ceriodaphnia (water flea), 72 (73.5%) showed acute toxicity. Of the 98 tests performed using Selenastrum (a single cell alga), 46 (46.9%) demonstrated significant toxicity. Of the three types of toxicity test, the Pimephales test resulted in the greatest number of positive test results (significant toxicity) while the Selenastrum (algae) resulted in the least number of positive results.

Caltrans performed thirty TIEs on samples for which acute toxicity was observed (23 sites). The TIEs indicated that no single source of toxicity was common among sites. However, nonpolar organic compounds were suggested as the putative source of toxicity in 5 of the TIEs, metals were suggested as the putative source in 11 TIEs, and surfactants were suggested as the putative cause in 7 cases. In one case, a metabolically active pesticide was implicated, and the remainder had no discernable cause.

The results were consistent across years with the samples collected during the 2001-02 having a slightly higher percentage of toxic samples. In general, the results from the Pimephales tests were almost identical in the overall percentage, and the Ceriodaphnia tests during 2001-02 produced a slightly higher percentage of tests with toxicity. The greatest difference is in the results of the Selenastrum tests performed in both years. Only a small number of samples were determined to be toxic by the Selanastrum test during 2000-01, but almost half of the tests resulted in significant toxicity during 2001-02.

Urban stormwater testing has shown that a moderate proportion of all stormwater samples demonstrate toxicity to a fish or invertebrate species. The degree of toxic effect varies between species with some studies showing toxicity to species such as *Ceratodaphnia dubia* and other not. The degree of variation is not surprising, as toxicity and the degree of toxicity will vary between catchments and locations depending upon a large number of factors. Given the nature of stormwater runoff from roads, there are limitations in the representativeness of toxicity tests arising from the nature of the stormwater sample. However given the results of Microtox testing on parking lot and isolated road runoff some toxicity is likely to be associated with road runoff. Several studies have shown moderate to sever toxicity in 20-50% of samples. Freshwater organisms below road stormwater outfalls are exposed to pulses of contaminants following rainfall events. They may be exposed to a first flush containing significant concentrations of some contaminants. This may be followed by lower level prolonged exposure.

Grant et al. (2003) presented a useful summary of the identified toxicants in urban runoff. Table 7.3 provides a summary of that information classified by contaminant.

Table 7.3 - Summary of identified toxicants in urban runoff (taken and modified from Grant et al. 2003).

Constituent	Source	Test organism	Reference
Copper	Urban roadway runoff	Sea urchin	Bay et al. (1999), SCCWRP (undated)
Zinc	Urban roadway runoff	Sea urchin	Bay et al. (1999), SCCWRP (undated)
Metals	Urban roadway runoff	Water flea	Hall & Anderson (1988), SCCWRP (Undated)
		Microtox	Herricks & Milne (1998)
		Fish	Lopes & Fossum (1995)
PAH	Roadway runoff (sediment)	Water flea	Maltby et al. (1995)
	Urban roadway runoff (in situ)	Water flea	Ireland et al (1996)
Neutral organics	Urban roadway runoff	Fish	Lopes & Fossum (1995)
Pesticides (Diazinon, chlorpyrifos)	Urban roadway runoff	Water flea	SCCWRP (Undated), Lee & Taylor (1997)

In the coastal environment, toxicity testing is carried out using a number of organisms. In the United states these test organisms include the sea urchin (Strongylocentrocus), the mysid shrimp (Americamysis) and bacteria (in the Microtox test). Work undertaken in the United States has shown that toxicity to sensitive marine species can occur in nearshore coastal areas in situations where stormwater discharges are not diluted sufficiently. Studies have determined that a dilution of typically 90% is required to eliminate toxicity to sensitive species. As such, toxicity may occur in locations where dilution is poor. Such locations include embayments and estuaries in harbours and the estuaries of rivers. Given the relatively small size of most New Zealand road and urban catchments road and urban catchments, discharges volumes from open coastal stormwater outfalls are typically small.

7.3.3 Sediment toxicity

Build-up of sediment discharged from roadways will occur close to the point of discharge (in ponds, wetlands, streams and lakes, estuaries and coastal environments) if the discharge point does not have sufficient energy to transport the contaminants and sediment away. There is potential for that material to cause some local change in sediment physical characteristics and hence habitat. The source of the material is principally the wear of road surface material not motor-vehicles.

Given the concentration of Cu, Pb and Zn in the suspended sediments of stormwater draining roads, exceedence of sediment quality guidelines (e.g., such as those of ANZECC 2000) would be expected. Depending upon the ratio of stormwater sediment to uncontaminated stream sediments, elements such as Zn may exceed guidelines at which adverse effects (on benthic organisms) could be expected to occur. In urban areas however, streams may not receive their normal supply of sediments and as a result sediments derived from roadways and other urbanised sources may dominate the sediments in the stream. For lakes, the sediment concentration will depend on the distribution and build-up of contaminants in the lake-bed following stormwater discharge to the lake. Contaminant build-up in small lakes with low natural sediment budgets would be expected. Available data indicates that contaminant concentrations in lake sediment adjacent to stormwater discharges from roads can approach and exceed sediment quality guidelines.

International studies have shown variable toxicity from receiving water sediment to aquatic biota. The New Zealand studies that have been carried out have shown that the particulate matter (from road stormwater) settling in pond systems has the ability to cause adverse toxicity to test organisms.

In estuarine and coastal areas, the contamination ‘halo’ around the discharge location may be such that it results in a depauperate fauna consisting of hardy or opportunistic species. The change in faunal composition appears to be caused by changes in the physical composition of the sediment coupled with changes in the chemistry of the sediments (ammonia, sulphide etc.,). Examination of contaminant concentrations immediately around the discharge points for stormwater runoff from roads and urban areas shows that concentrations of contaminants in sediments are typically elevated. Concentrations in both inter-tidal and sub-tidal sediments can rise above sediment quality guidelines and triggers such as those of ANZECC (2000). For most smaller discharge points readily identifiable haloes of elevated metal concentrations are generally restricted to a distance of 10-20 m from the discharge.

In the wider areas of urban estuaries and harbours, sediments often contain elevated concentrations of metal and organic contaminants. In locations such as the Waitemata Harbour in Auckland it appears that all of the surface sediments in harbour are contaminated to some degree. In depositional environments where sediments are dominated by muds, the concentration of elements such as Cu, exceed sediment quality guidelines. Within New Zealand, such effects are likely to be restricted principally to depositional environments adjacent to urban areas. However, stormwater discharges from roads and smaller urban centres to smaller estuaries will have comparable effects but on a smaller scale. Overall, the contribution that motor vehicles have to sediment contamination is identifiable where the discharge is derived from an isolated road. In urban areas, the contribution from vehicles to sediment contamination adjacent to outfalls and within estuaries and harbours will be dependent upon the ratio of the loads contributed by vehicle sources and other urban sources and activities.

Toxicity testing carried out using stormwater solids and marine organisms in New Zealand has shown that the toxicity of stormwater is variable. The testing indicated that some dilution of stormwater sediments would be required to ensure that no water column toxicity after discharge. It was noted in that study that toxicity was lower than expected. Contaminants other than metals were suggested as having a strong involvement in toxicity.

In depositional areas such as estuaries and harbours in New Zealand, where sediment contaminant concentrations are elevated, there is no direct evidence of sediment related toxicity. There does not appear to be any evidence at the present time that elevated concentrations of key elements (e.g., Zn) that are derived in part from vehicle emissions being a causal agent in toxicity or changes in benthic biological community composition.

There are currently no specific tools for isolating the effects of roadway stormwater discharge on the marine environment. However, in the case of isolated roadway discharges, traditional quantitative sampling and assessment tools that assess abundance, diversity and other metrics are capable of identifying effects of discharges (variability permitting).

Information in New Zealand has shown that build-up of contaminants occurs adjacent to urban stormwater outfalls discharging to the marine environment and in intertidal areas adjacent to roads.

Most studies carried out to-date in New Zealand have dealt with the identification of possible effects of urban run-off on coastal ecosystems. The studies have indicated that urbanisation as a whole results in adverse changes to the diversity of the biological communities present. Further specific research would need to be carried out to isolate the potential effects of road and highway run-off by carrying out effects studies in locations where runoff from roads and highways was isolated from the confounding effects of general urban runoff. If the adverse effects arising from urban runoff are attributable to elements such as Zn, then it is likely that roads and motor vehicles will contribute their proportional share of the adverse effect observed. The proportion of that effect will vary from location to location. At this stage the proportion of any observed effect is not known (even when identified on a contributed load basis).

A number of studies carried out in the Auckland area have shown differences in the quality of sediment benthic invertebrate communities in estuaries with catchments of varying intensities of urban development. Recent work undertaken by ARC has indicated that there are good relationships between macroinvertebrate benthic health in soft muddy sediments and the quality of those sediments (as reflected in the concentrations of Cu, Pb and Zn). However, the observed biological response seen in the field does not reflect urban stormwater contributions from those catchments. At this point in time, the available data indicates that the relationship between sediment quality (contaminants derived from urban runoff) and biological effects is somewhat unclear.

Toxicity testing of stormwater sediments has shown that adverse effects can be obtained in tests. This would suggest that adjacent to outfalls where deposited sediment may accumulate toxicity may occur. The toxicity may arise from the elevated concentrations of key contaminants such as Zn. Adverse effects may also be due to elevated concentrations of sulphide and ammoniacal nitrogen in those sediments or other constituents.

7.4 Bioaccumulation

7.4.1 Freshwater Environments

Available information indicates that elevated concentrations of dissolved or particulate metals in stormwater or stream water have the potential to result in bioaccumulation in freshwater biota. Uptake of contaminants is particularly likely in organisms that graze on biofilms in urban streams. High concentrations of contaminants have been reported in biofilms in urban streams in New Zealand (refer work of Timperley et al. 2001). Studies have shown that concentrations of Cu, Pb and Zn have been reported in a range of species but not consistently between species and feeding groups. Although accumulation has been identified, there is no information as to the potential for any adverse effects arising from that uptake. It has been demonstrated that the response to elements such as Cu and Zn (biological functions) differs to that of Pb (non essential).

There is little information that indicates that any freshwater plant or animal species (e.g., eel, watercress) exposed to those elements derived from road runoff would bioaccumulate those elements to the point that would result in their unsuitability for human consumption.

There is little information in New Zealand on the specific uptake of organic compounds by freshwater macro-invertebrates or fish that relates specifically to road stormwater runoff. Work undertaken on the uptake of PAHs in a car park stormwater pond demonstrated some uptake.

There are a wide range of organic compounds emitted by vehicles and present in stormwater discharged to freshwater environments that have potential for bioaccumulation. The key groups are the PAHs and substituted PAHs. Although uptake of these key groups of contaminants has been identified no adverse effects of bioaccumulation appear to have been identified and bioaccumulation is not likely to occur to a level that would result in adverse effects to the suitability of fish such as eel becoming unsuitable for consumption.

The role, that the uptake of organic compounds play in the health of freshwater organisms at a cellular and whole organism level is not clear. There are, a complex range of organic compounds emitted to freshwaters from a variety of sources. Many compounds are emitted from multiple sources (vehicles and non-vehicle sources).

There is little data available in relation to effects derived from trace elements such as Mo and Sb emitted by motor vehicles. Significant bioaccumulation is however unlikely. For some elements such as Sb and Pd for which there appears to be no nutritional requirement, uptake in a variety of organisms has been demonstrated. The effects of bioaccumulation are however unknown at a cellular and whole organism level.

7.4.2 Marine Environments

No contaminants have been identified that are unique to road transport that would allow the specific effects of road transport on uptake of contaminants by marine organisms to be isolated in urban areas. It is likely that road transport contributes in part to any bio-uptake of contaminants by marine organisms adjacent to roads and urban areas. Two of the key trace element contaminants in road runoff Cu and Zn are not typically bioaccumulated by many marine organisms. Some shellfish in New Zealand (e.g., oysters) will however accumulate Zn to a level that renders them unfit for consumption. The relative contributions, of various sources to the Zn body burden at those locations is not known. At this point in time there is no information that indicates that road transport contributes to uptake of contaminants by marine organisms such that they are rendered unsuitable for human consumption.

7.5 Summary Points

Information on the quality of stormwater runoff from roads in New Zealand shows that the dissolved concentration of Cu and Zn are high enough that dilution is required to prevent toxicity to aquatic organisms. It is likely that dissolved Zn contributes a greater probability of toxicity than Cu as a result of the reduced toxicity imparted by the complexing of Cu by DOM.

Toxicity studies and toxicity evaluations carried out overseas in freshwater and coastal environments has shown that road runoff has the potential to result in toxicity to some freshwater and marine organism. The extent of any toxicity is dependent upon the degree of dilution of road runoff with water in the receiving environment. Toxicity of urban stormwater runoff to freshwater algae and Daphnia has been demonstrated in New Zealand.

Contaminants discharged in stormwater runoff typically accumulate in sediments. In New Zealand, the most significant build-up of contaminants occurs in urbanised estuaries. Measured changes in freshwater and estuarine sediment quality in urban areas within New Zealand have been recorded for Cu, Pb, Zn and PAHs. Vehicle emissions contribute to the increased concentrations of all three contaminants however, the proportion contributed by vehicles is not known with certainty. It was recognised that historic changes in lead concentrations in sediments in New Zealand was contributed by the use leaded fuels (e.g., refer Hay & DeMora, 1988). It is considered that elevated concentrations of contaminants in estuarine sediments are contributing to the poor health of benthic invertebrate communities in some locations in New Zealand.

A range of contaminants (both metals and organic compounds) emitted by vehicles and entering aquatic environments, will be taken up by freshwater and marine organisms. The extent to which this occurs is dependent upon the properties of the individual contaminant. Lead was an example of a vehicle emitted contaminant that was bio-accumulated particularly by some inter-tidal shellfish in New Zealand rendering them unfit for human consumption. There is no information that indicates that any other metals contributed to stormwater by vehicles results in significant bioaccumulation by aquatic organisms. Zinc however is bioaccumulated by oysters in New Zealand and in some locations, stormwater runoff may contribute to the elevated concentrations observed and zinc from vehicle tyres may contribute a proportion of that zinc. There appears to be little information in New Zealand on the bioaccumulation of organic compounds (apart from PAHs) specifically related to emissions from motor vehicles.

8. ECA FRAMEWORK

8.1 Inventory Geo-Framework

The overall work programme has the eventual objective of developing an integrated analysis tool, for use by local authorities in managing the impacts of road run-off contamination, *viz;*

> "Develop integrated model that links source ⇒ pathway ⇒ ecosystem impact, preferably on geographic basis, to evaluate management/mitigation options, as may be necessary (and to the degree….)."

This requires the means to relate vehicle fleet operations to the local geographic framework, to calculate area-based contaminant loading patterns, particularly for the urban environment. The flow diagram in Figure 8.1 summarises the structure and analytical approach to managing the environmental impacts of road transport, as per the ECA process initially introduced for air quality management. In this water context, the aim is to interface the stormwater system layout with the source inventory structure. The run of terrain is the main layer in the interface, in the form of local catchment areas defining surface gradient (topography) effects *(plus other pathway factors as required).*

This section covers the two of the main components involved in the design of the analytical structure:

- The source inventory, for calculating the primary emissions rates for the potential contaminants.
- The catchment interface with the inventory, to determine where the contaminant loadings may be directed downstream of the source activity.

The third component is the way in which the receiving environments are characterised, and the criteria used to define the nature and extent of any ecological issues that might be due to contamination from upstream sources.

8.2 Source Inventory

The design and operation of the "Water" source inventory is best summarised in graphic form, as Figure 8.2.

The main aspects of the inventory design are:

- The profiling and projections of the vehicle fleet should be consistent with that already established as the VFEM, and as used for analysing other environmental issues.
- The inventory structure should allow for extra source groups (functional materials, as per the Classification Framework) to be added as necessary, should any compound concerns be identified or potentially introduced.
- Due to the diverse and changing nature of the range of chemicals involved, the structure should allow for:
    - Analysing the effects of varying compounds and formulations, as routine.
    - Progressively increasing the level of detail, as may be required.

Figure 8.1 - Environmental Impacts of Road Transport; Integrated ECA Management Air, Water, (Noise) & Energy Consumption/GHG

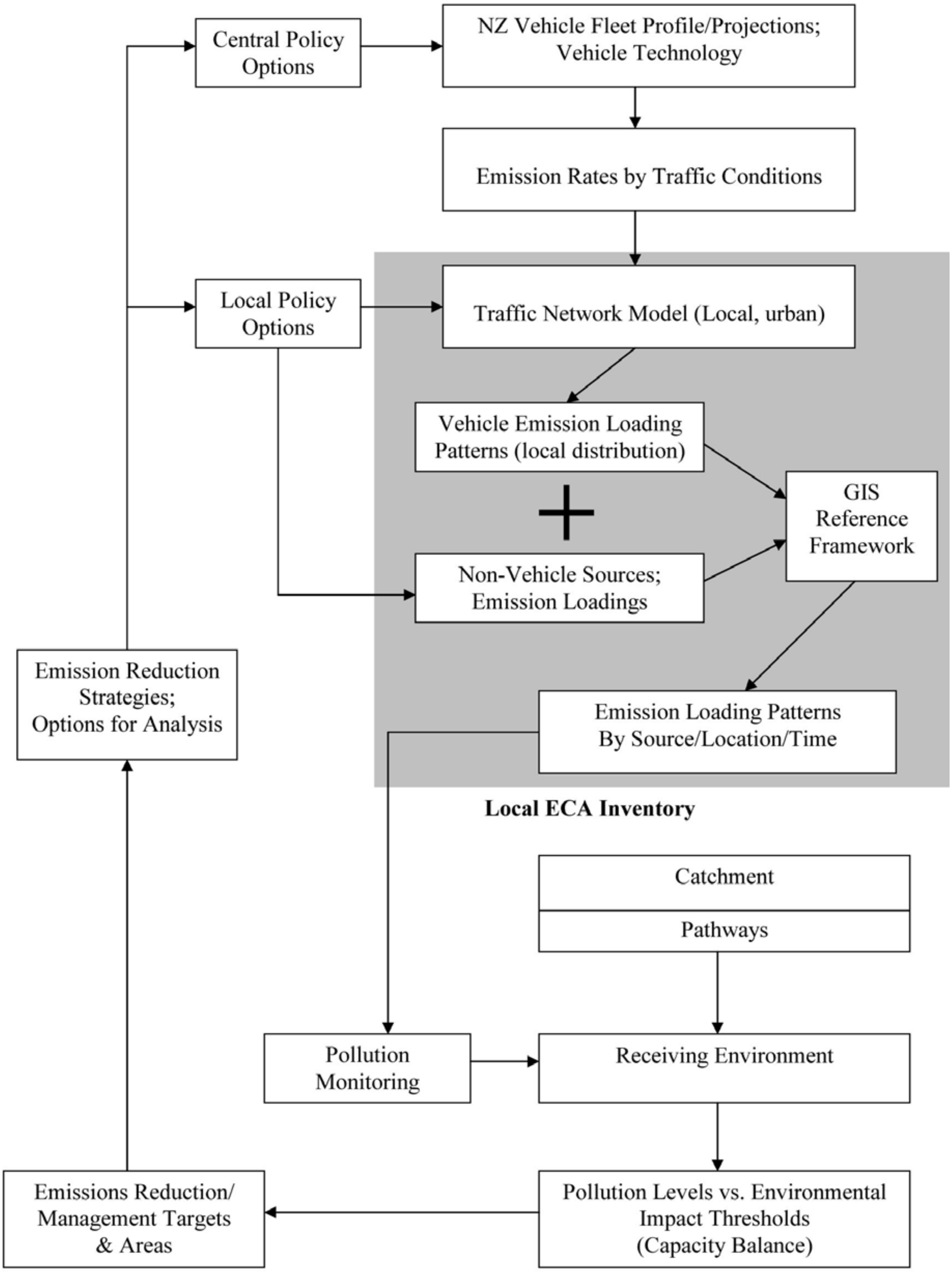


Figure 8.2 - Environmental Impacts of Road Transport; Integrated Emission Source Inventory Analysis.

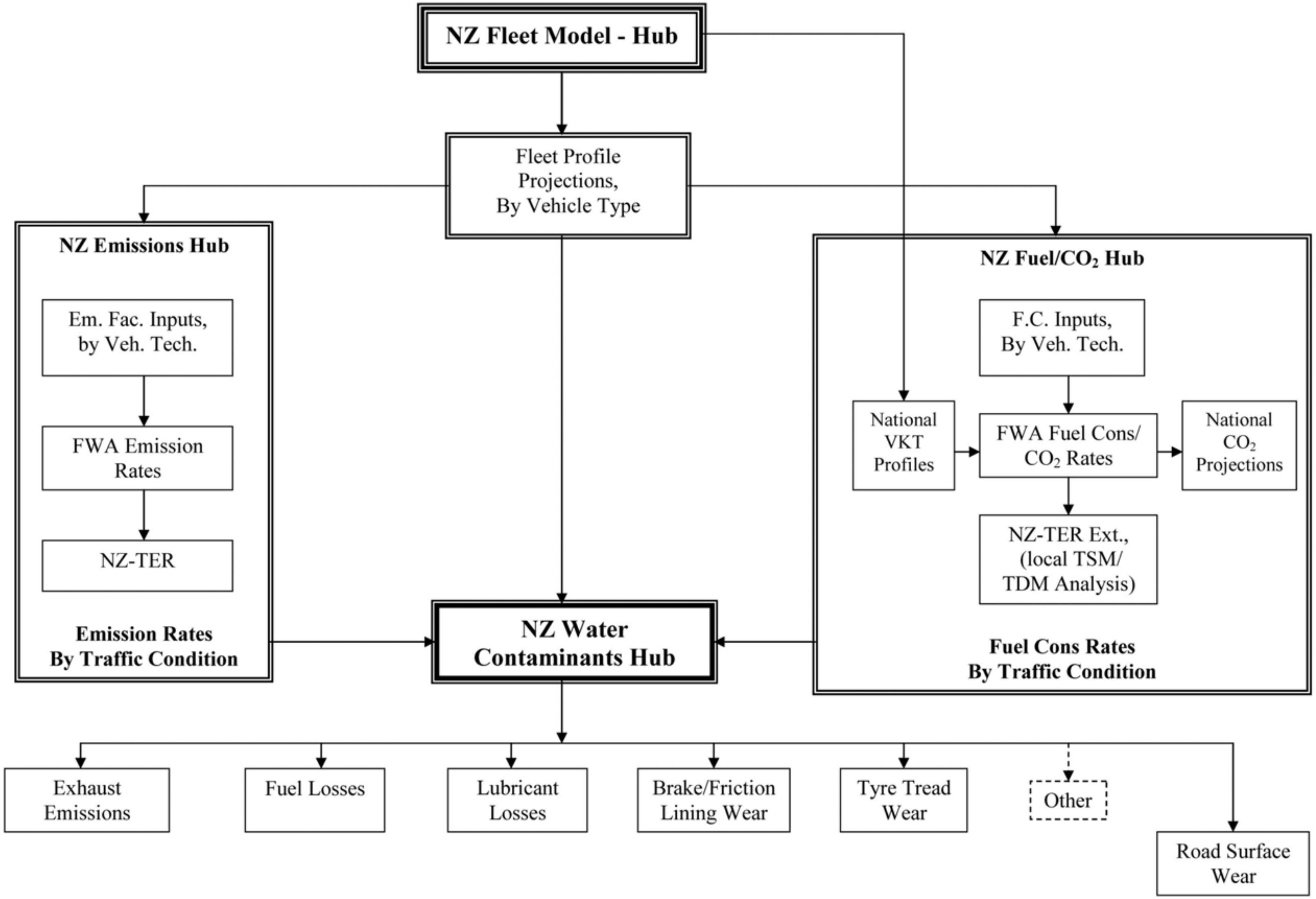
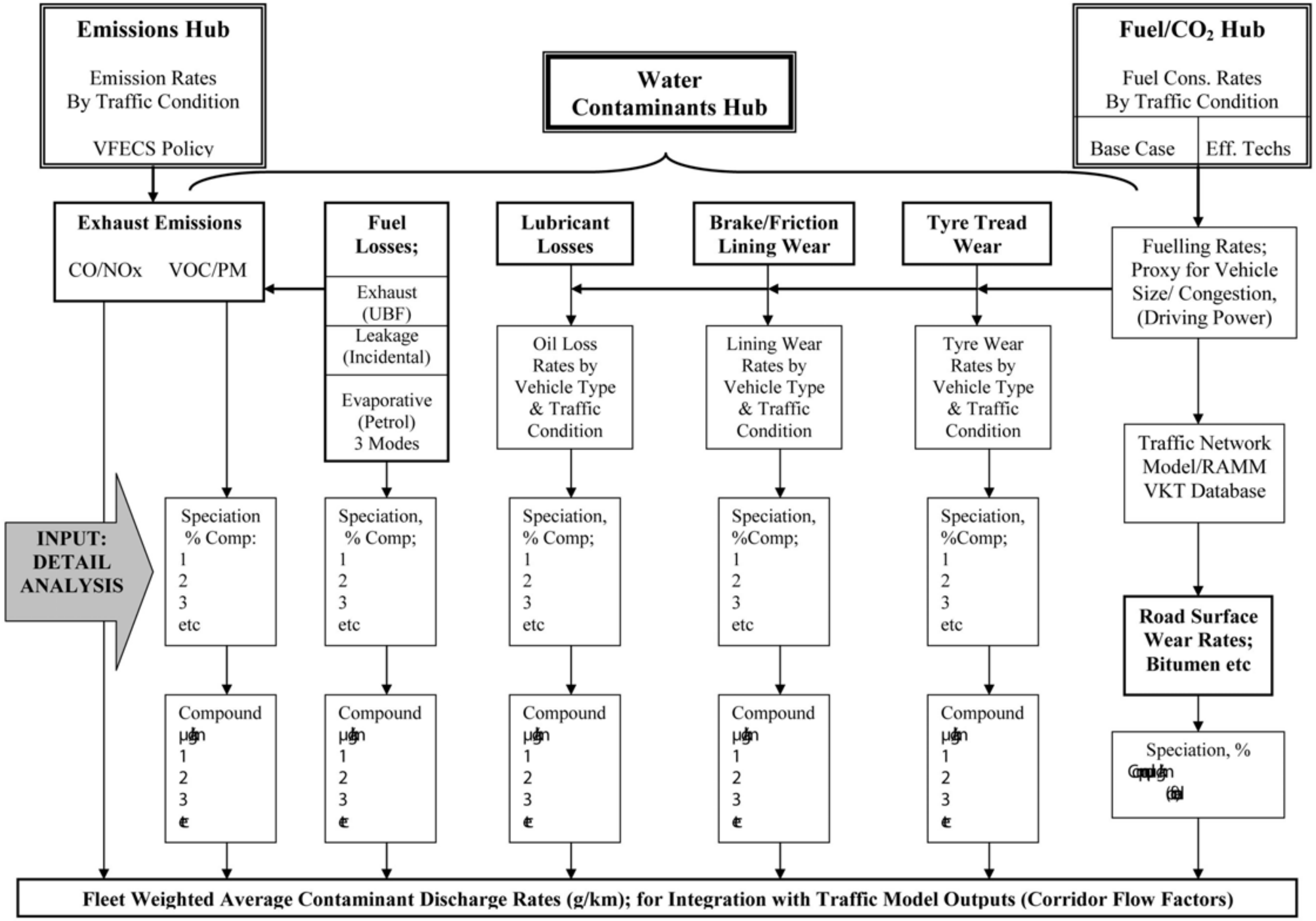


Figure 8.2 – (cont.)



In short, the inventory is designed to be fully responsive to the ways in which impacts problems may be defined, and effects-based solutions analysed as an on-going and developing process.

Referring to the elements in Figure 8.2:

- New Zealand Fleet Model: this is the reference base for the profiling of the fleet, which when run under given preset conditions (as variable inputs) develops the corresponding projections of fleet evolution i.e., fleet profiles by vehicle type and technology. This fleet profile data set then feeds into each of the separate emissions inventory models, for "air", "CO_2/GHG" and now this water contaminant source inventory. A new run/calibration of the Fleet Model automatically updates through into each inventory.
- The New Zealand Emissions and New Zealand Fuel/CO_2 models are designed to produce as output the fleet weighted average emission assigns, for use with local urban traffic network models. The NZ-TER concept is for distributing the results to local authorities, for constructing and maintaining their own dynamic vehicle emissions inventory, in this manner. These outputs also feed into the Water model.
- New Zealand Water Contaminants Model: at present this contains six functional groups of potential materials, this based on the first review of generic road transport practices. These are where there are essentially uncontrolled mechanisms whereby material could be lost to the surrounding environment as routine. Other functional groups can readily be added into the structure, without disruption, should there be the need. The road surface group is slightly offset as the structural linkages required to characterise mode of loss are slightly different from those that emanate from the vehicle itself.
- Exhaust Emissions: the output rates have already been determined by the design and operation of the VFEM. This was initially set up for the four priority indicator pollutants addressed by the VFECS process, but others can readily be added as air quality issues arise. The output rates automatically feed through into the Water inventory, where the VOC and PM groups can then be speciated down to individual chemical compounds.
- Fuel Losses: this provides, for three modes of loss:
    - Unburnt fuel, through the exhaust; therefore covered by the VOC/PM components of the Exhaust Emissions group.
    - Leakage, mainly an incidental event (i.e., not by design, as routine), allowance being included to model as a constant loss rate.
    - Evaporative emissions, refuelling/running/diurnal loss modes as separate calculation processes; note that this applies to petrol vehicles only.
- Lubricant Losses: this concerns sump oil, which has a routine path of loss via the combustion system, and provision is also made for modelling leakage as a routine.
- Brake Wear: lining material loss rates, as a function of vehicle type/size and driving conditions.
- Tyre Wear: tread material loss rates, also as a function of vehicle type and driving condition.
- Road Surface Wear: the material loss is related to the run of actual road corridor, therefore is based more upon the definition of the road network and volume of flow (the local traffic model, and RAMM database details on road construction and condition) than the vehicle technology factors. However, the vehicle size is also an influence.
- Fuel≡Power Proxy: for each of the groups above, other than emissions and fuel losses, the fuelling rates have been used as a proxy for vehicle power use, this being the primary determinant of the rate of material loss by vehicle type (by size) and driving condition. Generally, the larger the engine, and more power developed, especially in transient operation (frequency of acceleration/deceleration), the greater the load on lubricating. oil consumption, brake use and tyre wear. This also applies to the potential wear loading on the road surface, this being generally greater for heavier vehicles, and under interrupted driving. These fuelling rates are drawn from the calibrations and outputs used in the Fuel/CO_2 model.

- Speciation: the outputs from each of the above, is in the form of mg or g/km per vehicle material loss rates, for the primary material in question, by vehicle technology and driving condition. This is then speciated by inputs of the material composition, allowing for as many to be selected as required, or different compositions to be tested. The compounds can be prioritised by virtue of their potential ecotoxicity (e.g., refer Section 5), or any other criteria; if there content is known in the discharge material this step will calculate the corresponding mass emission rate of the compound.
- The final outputs are fleet weighted average emission rates, of individual chemical compounds, by:
    - Vehicle design type.
    - As at the projection year.
    - By road type.
    - Driving condition.

When these are integrated with the local traffic network model, the model will calculate the corridor by corridor loading of contaminants in the network, as primary mass discharge rates (refer back to Figure 8.1). This is directly analogous to the ECA structure for air emissions, in which the surrounding air-shed is both the catchment and receiving environment, and where the emissions loading/pollution level relationships are in more of a short term balance. For the entry of contaminates into waterways, the longer-term balances may be more relevant. If so, it would not be necessary to model traffic flow variables at the same level of detail, such as time of day variations. However, it may be that the area definitions have greater significance, the catchment/pathways that link source to receiving environment (area of capture, concentration, dilution effects etc.

8.3 Catchment Interface

Another objective of the Stage 2 programme has been to examine the feasibility of building a GIS based catchment model that can interact with traffic network models, in a manner akin to the ELGO function developed for the air emissions loading calculations. It should be noted that the ELGO software was originally developed to interact with the AIMSUN2 traffic simulation model, to calculate and display simultaneously the link-wise emissions outputs as vehicles passed through. The same level of functionality is probably not required in this water context, where a pseudo-static average mass discharge rate is probably sufficient output, for the nominated network area (by catchment). However, if useful for demonstration purposes, it would be straightforward to re-assign the ELGO "framework" with the compound discharge rates that result from the Water inventory (albeit, not all of them at once, with the large number involved).

The priority in this case is to correlate area defined systems (traffic network, catchment, stormwater system, water ecosystem) in a geo-spatial reference format. This makes the process relatively simple, the key factor being the availability of such information in electronic GIS format. This appears to be a gradual objective of most urban authorities in New Zealand, to translate the various waterway/stormwater/road system design layouts into a common form of geographic definition. Some are more advanced than others. This is also being considered for the RAMM database system.

Note that the availability of this mapping information in electronic form is not crucial to the viability of the ECA process, its just that it makes the initial construction of the integrated model that much easier, and also ongoing use and updating. Hard copy mapping data can also be used, with a manual assignment of areas etc to a reference system of boundary/grid definitions.

Christchurch was used for this initial appraisal, because of the detailed ECA model developed in the course of VFECS (Fuels & Energy management Group 2000). The GIS transition in Christchurch is currently a work in progress, but there is sufficient detail available to demonstrate the basic feasibility of an integrated model.

The main elements required for this process are as follows:

- The layout of the road network, in electronic format and geographically referenced – this has already been demonstrated in the earlier ECA model.

- The surface topography translated into main and sub catchment zones – these would be the "collection basins"` for the rainfall, hence water run-off from the roads.
- The stormwater collection systems into which the run-off is channeled and directed towards the points of discharge into the water eco-systems
- The water eco-systems themselves, streams/rivers and estuaries that carry and accumulate the final discharge media.

The electronic formats for the last three have been supplied by Christchurch City Council, and presented in a series of three figures presented in Appendix C and illustrate the level of detail available:

- Figures 1a, 1b and 1c in Appendix C: progressively more local examples of the catchment basins, from the greater Christchurch area zooming into the suburban locality used in the ECA model. The pink lines in 1a denote the major catchment zones, of the Styx, Avon and Heathcote Rivers, from north to south respectively. The detail marked form green down to blue shows the local catchments, which in a city as flat as Christchurch is dictated greatly by man made structures such as roads, and with flows directed by the run of pipes.
- The sub-catchments are marked by the green lines, and relate mainly to a connection with a major pipe/open waterway or drain, or tributary of a river. The blue sub-sub catchments mainly relate to road boundaries or smaller pipes.
- Figures 2a, 2b and 2c: this is the corresponding sequence for the stormwater drainage system that, channels the water from the catchment zones. At the time of preparing these figures, this was not yet 100% complete for Christchurch, in this electronic format, hence the gaps. Also, at this stage only pipes of diameter > 300 mm are included.
- Figures 3a and 3b: this gives the run of rivers/tributaries, streams and man made water courses, again down to local level, with the numbers and colours explaining the detail in the legend (not readable in these printouts). This would provide the basis for documenting hydraulic flow levels and variations.

Finally, the stormwater and roadway system can be electronic interfaced on a common geographic reference (as per the ECA Christchurch study, Fuels & energy Management Group 2000). This demonstrates how the activity on a given area of the road network can be related to the catchment/direction of the water run-off to the various discharge points in the surrounding water eco-system. This process essentially provides the definition of the "pathways" as required, but in a geo-framework format that:

- Interfaces with the current local authority information bases, and procedures.
- Provides for quantified analysis of the variables on a spatially defined basis, as is the fundamental intent of the ECA concept.

8.4 Modelling Contaminant Loads

As described in the previous sections, the contaminant hub of the transport model provides information on geo-spatial contaminant loads derived from motor vehicles. This information can be obtained at any geographical scale (intersection, catchment, receiving environment). The transport contaminant load model differs from other model typically used to assess the loads of contaminants in stormwater in that it is in the first instance a direct contribution load model. That is, the source is identified, the emission loads are estimated and the contribution to the stormwater system is therefore available from a specified area.

It is worth briefly over-viewing the modelling of stormwater contaminant loads. Pollutant loads from land-based processes are usually reported as mass/unit area/runoff duration (e.g., kg/ha/year).

A number of authors have reported on the estimation of pollutant loads from roads, highways and urban areas (e.g., Wu et al. 1998, Legret & Pagotto 1999). In these cases, the loads in stormwater runoff are estimated simply from the event mean concentrations (EMC) and the volume of the event. Total loads are then are then estimated by summing the loads per rainfall event for the defined catchment. In many situations, the EMCs are determined and then used for all events. The critical factor is then the determination of the number of events and effective runoff volumes transporting contaminants.

There however a variety of models that are available to assess the loads of contaminants derived from stormwater runoff. The USEPA Stormwater Management Model SWMM 4.4, which is the most well known model is a model for the single event and continuous simulation of urban stormwater runoff quantity and quality (Huber & Dickinson 1992). There are other models available (e.g., MUSIC) but our comments will be limited to SWMM. SWMM simulates real storm events on the basis of rainfall and other meteorological inputs, and system characteristics to predict stormwater output in terms of both quantity and quality. The model can be linked to other receiving water models. Stormwater quality is determined by two key process – build-up and wash-off.

The build-up of contaminants on the road surface may or may not be a function of time and a range of factors including traffic flow, dry deposition, wind and entrainment factors and street sweeping. With the advent of a rainfall event of sufficient magnitude to generate runoff, the contaminants on the surface of the road are washed into the stormwater drain system. The SWMM system also deals with other road compartments such as catchpits whose water also contributes their own particular water quality issues. Rainfall also provides its own contribution of contaminants to stormwater. The quality of rainfall is dependent upon the air quality in the local and regional environment and as such includes a contribution from road transport via wash-out processes.

The model requires the input of contaminant data. Huber (1986) and Huber & Dickinson (1992) describe the build-up process and provides information on the build-up of particular contaminants within different land-uses. SWMM allows the user to choose between various mathematical formulations for the build up and transfer of pollutant loads. The model allows the rainfall event size (mm) and the wash-off characteristics coefficient to be varied allowing the amount of contaminant washed off to vary with site specific characteristics (i.e., first flush or no first flush). The build-up function for particulates is often a function of road condition. Huber & Dickinson (1992) provides informational data on individual pollutant build-up rates, noting that the data provided is no substitute for actual site specific data. Interaction factors between storms need to be considered in the assessment of the build-up process.

The key question that needs to be answered in using a stormwater model as part of stormwater contaminant management is, what are the objectives in using the model? Ahyerre et al. (1998) identified that the mass of pollutant was one of the key impacts that were typically assessed by model users. The authors noted that the efficiency of any of the models used is very dependent upon the quality of the input data. One of the key input data components is the initial pollutant load.

If mass load and not pollutant concentrations is the key information required, then the model needs to focus on the source and contaminant generation and any processes that occur between the source and the discharge point to alter the load of contaminant present. Consequently, the key questions and variables that need to be examined include:
Firstly:

- What are the at source emission characteristics?
- What is the emission rate?
- Have all of the sources been identified?

Secondly:

- What is the source to roadway retention factor?
- What is the on-roadway retention factor?

The retention factors refer to the efficiency by which a given contaminant emitted from a given source becomes available for transport from the road drainage system. The first factor is efficiency of deposition on the roadway and the second is the efficiency of the retention on the roadway. The transport contaminant load model described in this report identifies the at source contributions to the environment. The model allows as many sources within the motor vehicle to be considered and it allows the important variables of driving condition to be considered. This however, still requires emission data for the source or sources being considered. The model can then derive an emitted load for a given length of road or catchment over whatever scale of time is required.

The load in the 'first' output is a total load emitted to the environment. This output is of considerable value as it identifies the contribution to all environmental compartments, both local and regional and on-road and off-road. This first output has an immediate value in that it provides information that can be compared between catchments or locations within a catchment to identify priority areas in terms of contaminant loads. This information does not need to be corrected for losses as the same loss factors can be considered to operate in all areas.

To provide the 'second output' these emitted loads need to be corrected for losses. The emission factors used to produce the first output and the loss adjustment factors required to produce the second outputs are discussed in the following section.

8.5 Summary Points

A traffic contaminant load model has been developed based upon an inventory geo-framework along the lines of that used for the VFECs. The model uses the vehicle fleet profiles as established for the VFEM.

The model utilises information for six key sources. Of these, the emission priorities have been identified as exhaust emissions, tyre wear, friction lining wear (brakes) and road surface wear. Specific emission rates for each given source category are required. The rates are affected by driving conditions and fuel consumption is used as a general proxy for power. Further evaluation of this factor is still required in relation to its precision in relation to sources such as brake use.

Emission factors are available for many materials and contaminants. These can be used to derive 'first output' fleet weighted averaged emission rates. The integration of this information with local traffic network models will allow the calculation of corridor by corridor loadings of contaminant within a catchment, road network or road corridor. This process is analogous to the ECA structure used previously to assess emissions to air from motor vehicles.

The model can be interfaced to other GIS systems to allow the determination of the loads entering particular receiving environment.

9. EMISSION FACTORS

9.1 Introduction

This section of the report summarises the available information in relation to emission factors for the key motor vehicle sources which have been dealt with in detail in Kennedy et al. (2002). Emission factors (e.g., the rate of particle wear per VKT from tyres or the amount of zinc emitted by the exhaust system per VKT) can be used to calculate the on-road contaminants loads and consequently the loads of contaminants potentially available for export via the stormwater system to the receiving environment (as discussed in Section 8).

Although the emission factors for most sources are presented as loss per VKT, the emission factors for exhaust emissions can be presented in two key ways. These are the amount of contaminants generated per VKT or per litre of fuel consumed.

Within each of the sections that follow, each of the source categories (exhaust emissions, brake lining wear, tyre-wear, oil and grease and road surface wear) is considered again following the classification framework set out earlier in the report. As shown in Figure 8.2, the transport contaminants model is set up to provide output for any of the sources within the classification framework. Although, the VFEM described in the previous sections has a specific sub-unit to account for fuel losses, fuel losses to the road are not considered to be a significant factor in the overall assessment of contaminant losses.

9.2 Exhaust Emissions

In section 8.2, it was described that three modes of loss can be dealt with and output presented in terms of emissions/km. The emissions can be presented in terms of fuel, total hydrocarbons or specific COPCs if required. In addition, if a specific contaminant is more closely linked to particulate emissions, the output can be related to the particulate matter output in any model. Each alternative requires different information.

Information is available on the contaminants present in vehicle exhausts and the rate of emission in a number of publications. MoT (2000), describes emissions of key contaminants (including hydrocarbons and particulate matter) from vehicles. Kennedy et al. (2002) provides further background on specific contaminant emissions and typical rates of emission.

In addition to specific vehicle emission studies (on-road and parked), emission quality data has also bee obtained studies through the evaluation of air quality in road tunnels. Tunnel studies are relatively effective in that they allow the examination of an enclosed environment where the principal source is the motor vehicle within the tunnel. However, vehicle source characterisation is compounded by the entrainment of dust within the tunnel. Staehelin et al. (1995) presented the results of the calculation of emission factors for VOCs emitted by all and light duty vehicles using the Gubrist Tunnel in Switzerland. El-Fadel & Hashino (2000) examined air quality in the Salim Slam tunnel in Beirut. Other studies such as Fraser et al. (1998) presented data for gas and particle phase organics emitted in terms of fuel consumption by vehicles in a Los Angeles Roadway tunnel.

Inorganic Contaminants

As described earlier in Section 5, there are a range of metals present in the exhaust emissions from motor vehicles and a number which have been identified as COPC. Kennedy et al. (2002) provided a summary of emission rates for inorganic contaminants (e.g., the trace metals) from vehicle exhaust emissions. It was evident from the examination of literature data that there is a very large range in the available data presented in the literature. For some common elements the range in emission rates (e.g., mg/VKM) varied by a factor of 100 or more. Some of the data is derived from extensive studies involving large numbers of vehicles. The information in Table 9.1 taken from Kennedy et al. (2002) should be seen as an interim summary of data.

Table 9.1 - Summary of concentrations of selected elements in petrol exhaust emissions (all data µg/km).

Element	Emission per VKT - LD vehicles	Emission per VKT - HD vehicles
COPC		
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	NDA
Silver	NDA	NDA
Tin	<6	<6
Zinc	45.5	136.6 (diesel 620*)
Others		
Barium	6*	7
Iron	280*	830*

Notes: NDA – No data available.

There appears to be a general lack of data for some COPC (e.g., antimony, cadmium, mercury, nickel). As an alternative it is possible to calculate metal emission rates from fuel combustion assuming that there is complete emission of the metal in the fuel. Based upon this data, an emission rate dependent upon fuel consumption can be identified. Some examples of such data presented in the literature are shown in Table 9.2. Information on trace elment concentrations in fuels (e.g., Yang et al (1998) provide an indication of what metals may dominate the emission factors for fuel consumption. The data from that particular study suggested that Cr, Ni and Zn would be the key metals present. Comparison of the data in Table 9.2 with that in Table 9.1 shows again that there are large differences between studies and use of any particular data should ensure that it is comparable in terms of fuel use, vehicle fleet type etc. (hence the note of caution regarding the summary in Table 9.1).

Table 9.2 – Emission factors for inorganic COPCs in petrol exhaust emissions based upon fuel consumption (all data mg/km).

Element	(Yang et al. 1998)		Emission rates from Ahlvik et al. (1997)
	Diesel concentration g/m^3	Diesel emission rate (8 L/100 km)	
COPC			
Cadmium	0.301	0.024	0.009
Copper	4.22	0.338	0.016
Chromium	22.4	1.792	0.005
Lead	1.93	0.154	
Nickel	17.5	1.40	0.0066
Zinc	8.74	0.700	0.094
Other			
Barium	33.9	2.712	-
Vanadium	0.549	0.04	-

In addition to metal emissions from fuel consumption, the summary in Table 9.1 contains elements that are contributed by the catalytic converter fitted to the exhaust system. Table 9.3 provides a summary of emission factors for petrol vehicles equipped with catalytic converters. Further information is presented in Section 7.5.4.2 of Kennedy et al. (2002).

Table 9.3 - Summary of precious metal emission rates from petrol motor vehicles (all data ng/km) (from Kennedy et al. (2002).

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	342	-	-

Organic compounds

As described earlier in this report, the range of organic compounds in motor-vehicle exhaust streams is very large. Kennedy et al. (2002) presented an overview of the nature of organic compounds in vehicle exhaust emissions. There is a large amount of published literature about the concentration and emission rates of various volatile and semi-volatile organic compounds in vehicle exhausts. However there is also a great deal of variation within that data. Table 9.4 provides a summary of emission rates for the PAHs in exhaust emissions.

Table 9.4 - 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
Acenapthylene	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-methylanthracene	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+j+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
TOTAL (no naphthalenes)	10,128 (916)	5,247 (2,358)

Kennedy et al. (2002) summarised and presented other data including USEPA (2002) emission factor data for PAHs. The USEPA total emission rates were 31,648 µg/km for light duty diesel and 13,539 µg/km for heavy-duty diesel vehicles.

9.3 Lubricants and Grease

Although, the model has a specific sub-unit to account for lubricant losses, lubricant losses to the road are not considered to be 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.

Kennedy et al. (2002), provide an overview of what is known about this source of contaminants. Published information about the composition of motor vehicle lubricating oils indicates that fresh oil contains low concentrations of many trace elements but may contain high concentrations of zinc. Used oil composition has been evaluated in New Zealand (MfE 2000). Composition degrades over time as a range of inorganic constituents enter through engine wear and fuel combustion.

Oil consumption and oil loss from vehicles has been examined in several studies. Kennedy et al. (2002) presented information from the HDM-4 oil consumption model (Bennett 1996) as an indication of likely loss rates in New Zealand. At this stage, the oil loss rates of 2.1 mL/1000 km for PCs and LCV and 2.8 mL/1000 km for heavier LCVs, HCVs and buses were used in Kennedy et al. (2002) to assess possible losses from this source. Emission factors from this source are restricted to the two broad categories of vehicles and, no allowance has been made for losses under different driving speeds, driving conditions, losses while stationary or vehicle ages.

Table 9.5 presents the summary of assessed emission data from Kennedy et al. (2002) for inorganic emissions associated with oil and grease.

Table 9.5 - Emission factors for key inorganic contaminant losses associated with engine oil loss (µg/vehicle/km).

Element	Car and LCVs	HCVs and Buses
COPC		
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
Others		
Barium	0.24	0.18
Iron	0.077	0.058

Vehicle oil contains a wide range of organic compounds (Kennedy et al. 2002). Of these, the aromatic compounds are the most important. Vehicle oil may contain hundreds to thousands of mg/kg of volatile aromatic compounds and tens to hundreds of mg/kg of less volatile PAHs.

When emission rates are examined, zinc appears to be the most significant inorganic emission (amongst the key COPCs). Total PAH emissions from this source (Table 9.6) are similar to that of zinc (Kennedy et al. 2002).

Table 9.6 - Emission factors for key aromatics and PAHs from engine oil loss (μg/vehicle/km).

Compound	Car and LCVs	HCVs and Buses
COPC		
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

9.4 Friction Linings

Emission rates of particulate matter and contaminants from motor vehicle friction linings are dependent upon a range of factors. These include:

- The mode of driving (i.e., use of brakes during different traffic conditions and different road geometry).
- The concentration of the constituent in the brake lining.

Kennedy et al. (2002) summarise available information about what is known about the wear of friction linings and the contaminants present in vehicle friction linings

In Section 5.6.2 of this report the composition of friction lining was over-viewed. More detail on their composition is presented in Kennedy et al. (2002), including the analysis of some friction linings used in New Zealand vehicles (refer Gadd & Kennedy 2000, Kennedy & Gadd 2000).

Table 9.7 provides a summary of the indicative concentrations of some key inorganic COPC found in linings. Table 9.8 provides corresponding information from Kennedy et al. (2002) in relation to organic COPCs in brake linings.

The overall amount of material emitted by a vehicle to the road is dependent upon the number of linings in-use on the vehicle and the proportion of disc and drum brakes. In most passenger vehicles the number of linings is generally constant but in larger multi axle/wheel vehicles, the number of linings increase. As such, the overall loss of worn particles increases from PCs to HDVs. There does not appear to be any standard brake lining wear model for motor vehicles. Brake use occurs under particular driving conditions. If average wear rates are used to model emissions throughout a road-way or catchment, the emissions will be overestimated in some sections and underestimated in others depending upon the relative wear in those sections of road. Brake use can be modeled if the sections of road where brake use occurs can be identified.

Table 9.7 - Summary of concentrations of selected elements in brake pads for use in calculating emission factors (all data mg/kg).

	Median
COPC	
Ag	0.2
As	1
Cd	0.6
Co	24.75
Cr	233
Cu	280 (5,000 interim value)
Hg	0.2
Mo	3.6
Ni	342
Pb	50
Sb	6.09
Sn	1.5
Zn	1,630
Other Elements	
Al	3,100
Fe	18,325
Mn	315.5
Ti	110
B	47.5
Ba	3,195

Table 9.8 - Summary of concentrations of selected organic compounds for calculating emission factors (data mg/kg or ng/mg).

Compound	Median
COPC	
Phenol	292*
Hydroxyphenylmethylphenol	164*
Methylene-bis-phenol	213*
Alkyl phenols	16*
Polycyclic aromatic hydrocarbons	16.16**
Other Compounds	
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 wear from the linings is a function of the force required to bring the vehicle to rest (which is dependent upon the speed before and after braking and the mass of the vehicle). Until a specific model of brake use/lining wear can be developed for motor vehicles, average (for key vehicle classes) or modified estimates that take account use degrees of use will need to be used. When assessing emission rates, the application of wear rates for different driving conditions will need to be applied to different road sections. For the purposes of this initial evaluation of brake wear, the low, moderate and high brake use categories can be considered to apply to LoS categories A/B, C/D and E/F respectively (for all times or for proportions of the day). Table 9.9 provides a summary of indicative particle wear rates for key vehicle classes under different driving conditions.

Table 9.9 - Summary of emissions from wear of friction linings for particulates (mg/km).

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

9.5 Tyres

Tyre wear is a relatively complex process. Kennedy et al. (2002) summarised available information on tyre composition and tyre wear and in Section 5.5.3 of this report provided an overview of chemical composition. Tyre wear is influenced by a range of factors all of which interact to produce different wear rates for different vehicles under different driving conditions using different types and brands of tyres. Unlike brake linings, tyre composition is less variable as tyres are made to specified safety standards and this limits the variation in composition to a great extent. However, rubber softness and other factors result in the wear rates of tyres differing significantly between brands (Kennedy et al. 2002).

Table 9.10 provides a summary of the concentration of inorganic constituents of tyres. This data taken from Kennedy et al. (2002) is derived from limited information for tyres available in New Zealand. Based upon available information for inorganic constituents in tyre rubber, it is evident that zinc is the dominant inorganic COPC present. However low concentrations of cadmium and lead result in some contributions from this source.

Table 9.10 - Concentrations of selected elements in tyres for use in calculating contaminant emission loads (all concentrations mg/kg).

Element	Median concentration
COPC	
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	8,310
Others	
Barium	26
Iron	105

A range of organic compounds are present in tyres. As tyres are composed of either natural or synthetic rubber they contain a broad range of hydrocarbons most of which are not COPCs. There is only limited data available on the quantitative organic chemical composition of tyres (Kennedy et al. 2002). Table 9.11 provides a summary of the concentration of key organic compounds in tyres. The upper section of the table provides data for some COPCs including total PAHs. Limited data is available for individual PAHs (refer Kennedy et al. 2002).

The wear rates are also likely to be higher during interrupted driving phases such as during acceleration and braking, and also at speed round bends (sideways force). Other service factors that accelerate wear are over/under-inflation, and the quality of the road surface. The key factor influencing the total emissions from this contaminant source are the individual tyre wear rates and the number of tyres on the vehicle. With the number of tyres ranging from two for motor cycles, four for passenger cars, four for light commercial vehicles through to 12-18 for heavy duty vehicles and buses.

Table 9.11 - Concentration of selected organic compounds in tyres for use in calculating emission loads (all concentrations mg/kg).

Compound	Median tyre concentration
COPC	
Benzothiazole	44.7*
Pyrene	42.6*
Polycyclic aromatic hydrocarbons	226.1**
Chlorinated organics	5.3**
Others	
n-Alkanes	18,842**
n-Alkanoic acids	12,197**
n-Alkenoic acids	1,279**
Substituted benzaldehydes	7.8**
Benzoic acids	74.8**
Polycyclic aromatic ketones and quinones	0.45**
Pentacyclic triterpanes	684**
Benzaldehydes	19.04**
Natural resins	9,513**
Regular steranes	74.2**
Amide (4-phenylbenzamine)	12.9**

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

Average wear rates are typically derived from tyre life expectancy data (i.e., rubber worn and total VKT over that time). However, tyre wear varies considerable depending upon road driving conditions. The “physics” of tyre wear has, been considered by a number of authors and for New Zealand driving conditions. Bennett & Greenwood (2001) described tyre consumption in the model HDM-4. The authors identified the key factors influencing wear as pavement condition, road alignment and curvature, traffic conditions (acceleration and deceleration), vehicle loading and tyre properties. The HDM-4 tyre wear model is based upon calculating the abrasive losses using a “slip energy model”. The model requires a number of specific pieces of information including data on circumferential force and lateral force. This road characteristic data is not available in most tyre wear assessment situations but can be obtained with the appropriate measurement equipment (refer to Kennedy et al. 2002 for more information).

Based upon this information, it is evident that a number of factors that influence tyre wear need to be taken into account when assessing tyre wear on specific sections of roads. As this data is not available for most situations, the average wear based upon life expectancy has been identified from literature data. Based upon primary average wear rates for different vehicle categories, and the number of tyres per vehicle, wear rates can be calculated for each vehicle category (Table 9.12).

Table 9.12 - Summary of particle emissions (mg/km) from individual tyre wear and individual motor vehicles (For LoS C/D).

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

Note: For LoS A/B and E/F, divide and multiply the rates in the table by 2.

In the absence of using a tyre wear consumption model such as HDM-4, a simple factor of 2 has been arbitrarily applied to the average wear rates to account for increasing severity of driving conditions. The average wear was assigned to the LoS category C/D and the other modified factors to the LoS A/B and E/F categories. This is likely to account for some of the acceleration/deceleration effects on tyre wear but will not account for the effects of curvature and down-grade on tyre wear. However it provides some degree of variability in wear which needs to be taken into account when considering tyre wear as a source of contaminants. Again as with other estimates, the figures identified should only be considered preliminary in nature.

9.6 Road Surface Wear

In New Zealand most urban roads surfaces are made of aggregate coated in bituminous material. The proportion of aggregate in the surface and the ratio of exposed bitumen and aggregate vary depending upon the wear characteristics of the road surface required. Most road surfaces are made using the "double coat chip" sealing method. Kennedy et al. (2002) reviewed what is known about the composition of asphalt in New Zealand and overseas.

Wear of road surfaces results in materials being worn from the aggregate and from the bitumen on and between the aggregate. Kennedy et al. (2002) reviewed information on the composition of bitumen with and without additives and also bitumen that was in place on roads. That review found that road bitumen contained higher concentrations of many inorganic COPC that raw bitumen. The difference is attributable to the inclusion of material from the aggregate and from motor vehicles emissions. Key differences found were for nickel and zinc. Table 9.13 provides a summary of the concentration of key elements in bitumen.

Table 9.13 - Elemental concentrations in raw bitumen used on New Zealand road surfaces (all data mg/kg).

Element	Raw bitumen
COPC	
Arsenic	<1
Beryllium	<0.1
Cadmiuim	<0.05
Cobalt	<0.2
Chromium	<1
Copper	<1
Mercury	<0.01
Molybdenum	0.45
Nickel	16
Lead	<0.2
Antimony	<0.2
Silver	<
Tin	~0.6
Thallium	<0.02
Zinc	5.5
Others	
Barium	<0.2

Kennedy et al. (2002) discussed the available information on organic compounds present in bitumen. Although a number of organic compounds are present in bitumen, there have been few COPC identified. The review identified that there are low concentrations of PAH in bitumen. Analysis of New Zealand bitumens has shown that they contain about 10 mg/kg total PAH. There are few published results for the concentration of individual PAHs in bitumen. Recent Dutch data reported total PAH in the range 6.4 – 15.2 mg/kg which is similar to the reported New Zealand data. Table 9.14 provides an indication of the PAHs present.

Kennedy et al. (2002) describe wear of bitumen road surfaces. Wear rates used in the assessment of bitumen loss to stormwater are derived from anticipated wear rates based upon the AADT on an example road. An estimation of wear based upon theoretical wear identified a contribution of 0.44 g/VKT for a road surface with only 50% of the bitumen surface available for wear. At 10% this figure would be 0.09 g/VKT.

Table 9.14 - Comparison of polyaromatic hydrocarbon concentrations in New Zealand and overseas bitumen (all results mg/kg) (From Kennedy et al. 2002).

	180/200+P (Gadd & Kennedy 2000)	Safaniya bitumen (Herrington 1993).	Bitumen (Brandt & de Groot 2001)		
Sample*			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.

9.7 Overview – Estimating the contribution to stormwater

Data is available for the concentration of COPC in the key vehicle emission sources. Although data is available it is limited in that it typically comprises variable data or small numbers of data. As such the average or typical concentration data used for COPC in different vehicle emission sources should be regarded as interim only.

Average emission rate information for vehicle emission sources is also available. In most cases it is based upon wear over the life of the source (e.g., tyres or friction linings). For nearly all sources there is sufficient information to show that there are a wide range of factors that influence the emission rate from the individual source. These factors typically relate to the interaction between the vehicle and the road environment. These include speed, road geometry, vehicle mass etc. The influence of these factors varies between the emission sources but given the influence of these factors have to be taken into account when assessing emissions. The only emission source for which specific modeling of wear rates has been undertaken is for tyre wear. However, in that case, the information required to enable the model to calculate wear is not always available.

Estimating the proportion of contaminants in stormwater derived from motor-vehicles is complex as it requires either an accurate estimate of the amount of contaminant emitted from vehicles or an estimate of the amount of contaminant produced by other sources. There have been a number of estimates made of the proportion of contaminants in stormwater generated within urban areas that is emitted by motor-vehicles. Previous estimates have tended to over-estimate the amount of contaminant contributed by vehicles as the estimates were based on only on calculated vehicle emission rates and general information on total stormwater loads. Kennedy et al. (2002) provided some information on the likely proportion of emissions from vehicles that might be deposited on the road surface and become available for transport by stormwater. Those figures vary between the various sources. For example lower proportions of exhaust emission contaminants reach the road surface compared to tyre wear as the exhaust emissions are injected to the road corridor air and are typically of smaller particle size. As a result factors of 0.8 were identified for tyre wear and 0.05 for exhaust emissions.

Given the relative contributions of different sources of COPC in motor vehicles, improvements in COPC data and source emission rates is likely to be continually required to ensure that the errors associated with emissions of COPC are minimised. Table 9.15 provides an indicative summary of the relative sources of emissions for the key inorganic COPC, Cu, Zn and Pb. If the data presented in Kennedy et al. (2002) and above, is used a typical PC (in a road LoS of A/B with average brake use), the vehicle would potentially contribute 0.43 mg Zn/VKT and 0.08 mg Cu/VKT. Timperley et al. (2003) identified stormwater contributions from vehicles for Zn and Cu of 0.447 and 0.06 mg/VKT. For Pb the calculated figure shown in Table 9.15 is very low. Timperley et al. (2003) identified a higher Pb emission rate (similar to Cu). The difference between the two Pb emission rates is not known at this stage.

Table 9.15 – Summary of overall relative emissions of copper and zinc from key motor vehicle emission sources to the road surface (all data mg/km).

Source	Copper	Zinc	Lead
Example is a roadway with all traffic PCs and LoS A/B, average brake use.			
Oil and grease	<0.001	0.003	<0.001
Tyre wear	<0.001	0.398	<0.001
Friction lining wear	0.0735	0.023	<0.001
Exhaust emission	<0.001	0.002	<0.001
Road & bitumen wear	<0.004	<0.005	<0.001
Total based on the above	<0.08	<0.431	~0.001

Comparing some of the calculated data with the modeled and measured data from Timperley et al. (2003) shows that the loadings for the key elements are of the same order. However, the number of factors that affect the actual loads contributed by vehicles to the road surface shows that the contributions at any single location are very site specific.

Specific work undertaken in Auckland City is allowing some refinement of that estimate in New Zealand. The current best estimates identify the 50%ile road contribution for Cu and Zn as 17 and 16% respectively (Timperley et al. 2003). There are still substantial uncertainties associated with these estimates and they will need continued refinement as new data becomes available. A further study undertaken in Auckland (ARC 2004) has also shown the importance of roof surfaces as contributors of contaminants such as Pb and Zn to the stormwater system.

9.8 Summary Points

Contaminant emissions from motor vehicles require information on the mechanism and rate of loss of the contaminant or the material the contaminant is contained in. Contaminants are derived from a number of key sources. The emission of contaminants from these sources is influenced by a range of factors many of which differ from source to source. Information on the nature and concentration of contamination of key contaminants emitted from emission sources.

Information is available on the concentration of key contaminants emitted from emission sources.

There are a range of options for assessing emission rates or factors for each source. The degree of detail is to some extent, dependent upon the use of the contaminant load data.

For exhaust emissions, the existing VFEM can calculate major contaminant emissions. With appropriate COPC data it is feasible to calculate contaminant emission loads under different driving and road conditions.

For tyres, tyre wear and contaminant loss is a relatively complex process. The process has however, been well researched and a working tyre wear model is available. The model however, requires some physical road/tyre information that is not readily available. Average wear data is available.

Friction linings wear and contaminant emissions, is a relatively complex process dependent upon driving conditions. Friction linings also have a high degree of compositional complexity resulting in increased difficulty in developing robust emission factors.

Oil loss models have been developed. Oil loss is also a function of engine power. As such, simple loss factors as identified in this report can be developed further if required. However, given the relatively low overall contaminant contribution, average factors are likely to be sufficient.

Wear of bitumen contributes some contaminants to stormwater. Wear is very dependent upon the vehicle fleet composition and the proportion of exposed bitumen to road aggregate. Average wear contributions based upon life expectancy of the road surface are used in the model to estimate contributions from this source.

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Appendices

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Appendix A

Contaminants of Potential Concern: Overall Risk

Category 1: Fuel

ID Number	Contaminant Name	Road Code	Risk
134	Decane	1.1a; 2.1a	8
250	5M-indan	1.1a	9
238	1,1,4-trimethylcyclohexane	1.1a	9
252	2M-indan	1.1a	9
249	2M-Decane	1.1a	10
247	3E-Nonane	1.1a	10
138	1,2,3-trimethyl-Benzene	1.1a; 2.1a	10
133	1,2,4-trimethyl-Benzene	1.1a; 2.1a	10
153	Undecane	1.1a; 2.1a	10
236	2,6-dimethyl-heptane	1.1a	11.25
89	2,5-DM-Hexane	1.1a; 2.1a	11.25
91	2,4-DM-Hexane	1.1a; 2.1a	11.25
94	2,3,3-trimethyl-Pentane	1.1a; 2.1a	11.25
241	1,2,4-trimethyl-Cychexane	1.1a	11.25
76	2,2,4-trimethyl-Pentane	1.1a; 2.1a	11.25
237	1,1,3-trimethyl-Cychexane	1.1a	11.25
111	2,4-DM-Heptane	1.1a; 2.1a	11.25
234	2,4,4-trimethyl-Hexane	1.1a	11.25
103	2,2,5-trimethyl-Hexane	1.1a; 2.1a	11.25
106	Octane	1.1a; 2.1a	11.25
242	3,4-dimethyl-Heptane	1.1a	11.25
110	2,3,5-trimethyl-Hexane	1.1a; 2.1a	11.25
116	2,3-DM-Heptane	1.1a; 2.1a	11.25
96	2,3,-DM-Hexane	1.1a; 2.1a	11.25
239	2,5-dimethyl-Heptane	1.1a	11.25
244	3,3-dimethyl-Octane	1.1a	12
157	1,2,3,5-Tetramethylbenzene	1.1a; 2.1a	12
155	1,2,4,5-Tetramethylbenzene	1.1a; 2.1a	12
307	3-nitrobenzanthrone	1.1b	12
305	2,7-dinitrofluorene	1.1b	12
208	Nitrofluorene	1.1b; 2.1b	12
245	4M-Nonane	1.1a	12
246	2M-Nonane	1.1a	12
139	1M-4-i-PropBenzene	1.1a; 2.1a	12.5

ID Number	Contaminant Name	Road Code	Risk
137	1M-3-i-PropBenzene	1.1a; 2.1a	12.5
125	i-Propylbenzene	1.1a; 2.1a	12.5
248	1,3-DM-5-ethylbenzene	1.1a	12.5
251	1E-2-n-propylbenzene	1.1a	13.5
160	n-PentBenzene	1.1a; 2.1a	13.5
254	1M-Naphthalene	1.1a; 1.1b; 2.1a	14
253	2M-Naphthalene	1.1a; 1.1b; 2.1a	14
316	Phenylene diamine	1.3	14
154	1,2-DM-3-E-Benzene	1.1a; 2.1a	15
149	1,4-DM-2-E-Benzene	1.1a; 2.1a	15
150	1,3-DM-4-E-Benzene	1.1a; 2.1a	15
151	1,2-DM-4-E-Benzene	1.1a; 2.1a	15
183	Acenaphthene	1.1b; 2.1a; 2.1b	17.5
184	Fluorene	1.1b; 2.1a; 2.1b	17.5
185	2-Methylfluorene	1.1b; 2.1a; 2.1b	17.5
303	1,6-dinitropyrene	1.1b	20
295	9-nitroanthracene	1.1b	20
304	1,8-dinitropyrene	1.1b	20
209	1-Nitroanthracene	1.1b; 2.1b	20
187	Anthracene	1.1a; 1.1b; 2.1a; 2.1b	20
294	2-nitroanthracene	1.1b	20
296	9-nitrophenanthrene	1.1b	20
297	3-nitrophenanthrene	1.1b	20
263	Dibenzothiophene	1.1b; 8.1	24
255	Phenanthrene	1.1a; 1.1b; 2.1a; 2.1b	24
277	1M-fluorene	1.1b	26.25
264	4M-dibenzothiophene	1.1b	30
271	1M-7-isopropylphenanthrene	1.1b	30
299	1-nitrofluranthene	1.1b; 2.1b	30
267	2M-anthracene	1.1b; 2.1a	30
298	2M-1-nitroanthracene	1.1b	30
301	8-nitrofluroanthene	1.1b	30
302	1,3-dinitropyrene	1.1b	30
300	3-nitrofluoranthene	1.1b	30
266	3M-phenanthrene	1.1b; 2.1a	31.5
268	4M-phenanthrene	1.1b; 2.1a	31.5
276	Trimethylnaphthalene	1.1b; 2.1a	31.5
270	1M-phenanthrene	1.1b; 2.1a	31.5
269	9M-phenanthrene	1.1b; 2.1a	31.5

ID Number	Contaminant Name	Road Code	Risk
201	Perylene	1.1b; 2.1a; 2.1b	37.5
210	Nitrobenzo(a)pyrene	1.1b; 2.1b	37.5
262	1-M-benzo(e)pyrene	1.1a; 2.1a	37.5
261	1-M-benzo(a)pyrene	1.1a; 2.1a	37.5
260	1-DME-benz(a)anthracene	1.1a; 2.1a	37.5
259	1-Methylbenz(a)anthracene	1.1a; 2.1a	37.5
258	Coronene	1.1a; 1.1b; 2.1a	37.5
257	Benzo(k)fluoranthene	1.1a; 1.1b; 2.1a	37.5
274	Indeno(1,2,3-cd)fluroanthene	1.1b; 2.1a	37.5
275	Picene	1.1b	37.5
203	Indeno(123-cd)pyrene	1.1a;1.1b; 2.1a; 2.1b	37.5
195	Benzo(a)anthracene	1.1a; 1.1b; 2.1a; 2.1b	37.5
200	Benzo(a)pyrene	1.1a;1.1b; 2.1a; 2.1b	37.5
198	Triphenylene	1.1b; 2.1a; 2.1b	37.5
196	Chrysene	1.1a;1.1b; 2.1a; 2.1b	37.5
188	Pyrene	1.1a; 1.1b; 2.1a; 2.1b	37.5
202	Benzo(ghi)perylene	1.1a; 1.1b; 2.1a; 2.1b	37.5
190	11H-benzo(a)fluorene	1.1b; 2.1a; 2.1b	37.5
194	Benzo(ghi)fluoranthene	1.1a;1.1b; 2.1a; 2.1b	37.5
186	Fluoranthene	1.1a; 1.1b; 2.1a; 2.1b	39.38
265	3M-dibenzothiophene	1.1b	45
189	Benzo(a)fluorene	1.1b; 2.1a; 2.1b	45
193	1-Methylpyrene	1.1b; 2.1a; 2.1b	45
283	1-nitropyrene	1.1b; 2.1a	45
272	2M-Pyrene	1.1b	45
199	Benzo(e)pyrene	1.1a;1.1b; 2.1a; 2.1b	45
256	Benzo(b)fluoranthene	1.1a; 1.1b; 2.1a	45
273	Cyclopenta(cd)pyrene	1.1b; 2.1a	54

Category 2: Exhaust System

ID Number	Contaminant Name	Road Code	Risk
134	Decane	1.1a; 2.1a	8
163	Dodecane	2.1a	10
166	Tridecane	2.1a	10
153	Undecane	1.1a; 2.1a	10
88	2,4,4-trimethyl-2-Pentene	2.1a	10
138	1,2,3-trimethyl-Benzene	1.1a; 2.1a	10
133	1,2,4-trimethyl-Benzene	1.1a; 2.1a	10
290	Biphenylene	2.1a	10.5
289	Biphenyl	2.1a	10.5
94	2,3,3-trimethyl-Pentane	1.1a; 2.1a	11.25
103	2,2,5-trimethyl-Hexane	1.1a; 2.1a	11.25
96	2,3,-DM-Hexane	1.1a; 2.1a	11.25
111	2,4-DM-Heptane	1.1a; 2.1a	11.25
106	Octane	1.1a; 2.1a	11.25
76	2,2,4-trimethyl-Pentane	1.1a; 2.1a	11.25
110	2,3,5-trimethyl-Hexane	1.1a; 2.1a	11.25
91	2,4-DM-Hexane	1.1a; 2.1a	11.25
123	l-Nonene	2.1a	11.25
89	2,5-DM-Hexane	1.1a; 2.1a	11.25
116	2,3-DM-Heptane	1.1a; 2.1a	11.25
114	3,5-DM-Heptane	2.1a	11.25
157	1,2,3,5-Tetramethylbenzene	1.1a; 2.1a	12
205	9,10-anthracenedione	2.1b	12
204	9-fluorenone	2.1b	12
208	Nitrofluorene	1.1b; 2.1b	12
181	2,6-Dimethylnaphthalene	2.1b	12
155	1,2,4,5-Tetramethylbenzene	1.1a; 2.1a	12
126	2,2-DM-Octane	2.1a	12
159	1,2,3,4-Tetramethylbenzene	2.1a	12
127	2,4-DM-Octane	2.1a	12
139	1M-4-i-PropBenzene	1.1a; 2.1a	12.5
136	s-Butylbenzene	2.1a	12.5
125	i-Propylbenzene	1.1a; 2.1a	12.5
141	1M-2-i-PropBenzene	2.1a	12.5
137	1M-3-i-PropBenzene	1.1a; 2.1a	12.5
156	2M-ButylBenzene	2.1a	13.5
160	n-PentBenzene	1.1a; 2.1a	13.5
253	2M-Naphthalene	1.1a; 1.1b; 2.1a	14

ID Number	Contaminant Name	Road Code	Risk
254	1M-Naphthalene	1.1a; 1.1b; 2.1a	14
292	Ethylnaphthalene	2.1a	14
291	Methylbiphenyl	2.1a	14
154	1,2-DM-3-E-Benzene	1.1a; 2.1a	15
149	1,4-DM-2-E-Benzene	1.1a; 2.1a	15
150	1,3-DM-4-E-Benzene	1.1a; 2.1a	15
151	1,2-DM-4-E-Benzene	1.1a; 2.1a	15
152	1,3-DM-2-E-Benzene	2.1a	15
158	1-tert-1B-2M-Benzene	2.1a	15
182	Acenaphthylene	2.1a; 2.1b	17.5
184	Fluorene	1.1b; 2.1a; 2.1b	17.5
183	Acenaphthene	1.1b; 2.1a; 2.1b	17.5
185	2-Methylfluorene	1.1b; 2.1a; 2.1b	17.5
187	Anthracene	1.1a; 1.1b; 2.1a; 2.1b	20
209	1-Nitroanthracene	1.1b; 2.1b	20
255	Phenanthrene	1.1a; 1.1b; 2.1a; 2.1b	24
207	Cyclopenta(def)phenanthrene-4-one	2.1b	26.25
161	1 tert-1B-3,5-DM-Benzene	2.1a	27
299	1-nitrofluranthene	1.1b; 2.1b	30
267	2M-anthracene	1.1b; 2.1a	30
284	3,6-DM-Phenanthrene	2.1a	30
293	Dimethylphenanthrene	2.1a	31.5
288	1M-Anthracene	2.1a	31.5
270	1M-phenanthrene	1.1b; 2.1a	31.5
269	9M-phenanthrene	1.1b; 2.1a	31.5
268	4M-phenanthrene	1.1b; 2.1a	31.5
266	3M-phenanthrene	1.1b; 2.1a	31.5
276	Trimethylnaphthalene	1.1b; 2.1a	31.5
165	1,2,4-Triethyl-Benzene	2.1a	33.75
164	1,3,5-Triethyl-Benzene	2.1a	33.75
197	Benzo(c)phenanthrene	2.1a; 2.1b	37.5
210	Nitrobenzo(a)pyrene	1.1b; 2.1b	37.5
286	Dibenzo(ae)pyrene	2.1a	37.5
285	Dibenz(aj)anthracene	2.1a	37.5
282	Anthanthrene	2.1a	37.5
280	Dibenz(a,h)anthracene	2.1a	37.5
279	Benzo(j)fluoranthene	2.1a	37.5
274	Indeno(1,2,3-cd)fluroanthene	1.1b; 2.1a	37.5
262	1-M-benzo(e)pyrene	1.1a; 2.1a	37.5

ID Number	Contaminant Name	Road Code	Risk
261	1-M-benzo(a)pyrene	1.1a; 2.1a	37.5
260	1-DME-benz(a)anthracene	1.1a; 2.1a	37.5
259	1-Methylbenz(a)anthracene	1.1a; 2.1a	37.5
195	Benzo(a)anthracene	1.1a; 1.1b; 2.1a; 2.1b	37.5
257	Benzo(k)fluoranthene	1.1a; 1.1b; 2.1a	37.5
203	Indeno(123-cd)pyrene	1.1a;1.1b; 2.1a; 2.1b	37.5
202	Benzo(ghi)perylene	1.1a; 1.1b; 2.1a; 2.1b	37.5
201	Perylene	1.1b; 2.1a; 2.1b	37.5
200	Benzo(a)pyrene	1.1a;1.1b; 2.1a; 2.1b	37.5
198	Triphenylene	1.1b; 2.1a; 2.1b	37.5
192	11H-benzo(b)fluorene	2.1a; 2.1b	37.5
196	Chrysene	1.1a;1.1b; 2.1a; 2.1b	37.5
194	Benzo(ghi)fluoranthene	1.1a;1.1b; 2.1a; 2.1b	37.5
190	11H-benzo(a)fluorene	1.1b; 2.1a; 2.1b	37.5
188	Pyrene	1.1a; 1.1b; 2.1a; 2.1b	37.5
258	Coronene	1.1a; 1.1b; 2.1a	37.5
186	Fluoranthene	1.1a; 1.1b; 2.1a; 2.1b	39.38
189	Benzo(a)fluorene	1.1b; 2.1a; 2.1b	45
193	1-Methylpyrene	1.1b; 2.1a; 2.1b	45
199	Benzo(e)pyrene	1.1a;1.1b; 2.1a; 2.1b	45
256	Benzo(b)fluoranthene	1.1a; 1.1b; 2.1a	45
281	Benzonaphtho(2,1-d)thiophene	2.1a	45
283	1-nitropyrene	1.1b; 2.1a	45
287	3M-Cholanthrene	2.1a	45
191	Benzo(b)fluorene	2.1a; 2.1b	45
273	Cyclopenta(cd)pyrene	1.1b; 2.1a	54

Category 4: Coolants

ID Number	Contaminant Name	Road Code	Risk
212	Mercaptobenzothiazole	4.1; 8.1	10.13

Category 7: Braking and Clutch

ID Number	Contaminant Name	Road Code	Risk
325	Hexadecanamide	7.1	8
338	Diethenylbenzene	7.1	9
328	Methylenebis phenol	7.1	9
340	Bis(2-ethylhexyl) phthalate	7.1	10.5
337	Benzophenone	7.1	10.5
326	Hexadecanenitrile	7.1	18
349	Diphenyl benzenediamine	7.1; 8.1	20
331	Butylated hydroxy toluene	7.1; 8.1	26.25
339	Tetramethyl phenanthrene	7.1	31.5

Category 8: Tyres

ID Number	Contaminant Name	Road Code	Risk
343	Hexadecanoic acid, methyl ester	8.1	9
350	N-isopropyl-N'-phenyl-p-phenylenediamine	8.1	10
320	N-cyclohexyl-2-benzothiazolesulphenamide	8.1	10
212	mercaptobenzothiazole	4.1; 8.1	10.13
319	2,2,4-trimethyl-1,2-dihydroquinoline	8.1	10.5
348	2-methyl-N-(2-methylphenyl)-benzenediamine	8.1	12
322	N-cyclohexylthiophthalimide	8.1	12
349	Diphenyl benzenediamine	7.1; 8.1	20
263	Dibenzothiophene	1.1b; 8.1	24
360	Methyldibenzothiophene	8.1	26.25
331	Butylated hydroxy toluene	7.1; 8.1	26.25
318	N-(1,3-dimethylbutyl)-N,-phenyl-p-phenylenediamine	8.1	30
359	1,4-dimethyl-7-(1-methylethyl)azulene	8.1	31.5

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Appendix B: Contaminants of Concern: Environmental Partitioning - Fugacity Model Results

Category 1: Fuel

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
134	Decane	1.1a; 2.1a	8	4.13E-05	99.86	0.07	0	0	0	0.07
250	5M-indan	1.1a	9	4.09E-05	98.71	0.27	0.76	0	0	0.25
238	1,1,4-trimethylcyclohexane	1.1a	9	4.13E-05	99.97	0.02	0	0	0	0.01
252	2M-indan	1.1a	9	4.08E-05	98.76	0.27	0.72	0	0	0.25
249	2M-Decane	1.1a	10	4.13E-05	99.9	0.05	0	0	0	0.05
247	3E-Nonane	1.1a	10	4.13E-05	99.9	0.05	0	0	0	0.05
138	1,2,3-trimethyl-Benzene	1.1a; 2.1a	10	4.1E-05	99.15	0.15	0.55	0	0	0.14
133	1,2,4-trimethyl-Benzene	1.1a; 2.1a	10	4.11E-05	99.43	0.11	0.36	0	0	0.1
153	Undecane	1.1a; 2.1a	10	4.12E-05	99.64	0.18	0	0	0	0.17
236	2,6-dimethyl-heptane	1.1a	11.25	4.13E-05	99.97	0.01	0	0	0	0.01
89	2,5-DM-Hexane	1.1a; 2.1a	11.25	4.13E-05	99.99	0.01	0	0	0	0
91	2,4-DM-Hexane	1.1a; 2.1a	11.25	4.13E-05	99.99	0	0	0	0	0
94	2,3,3-trimethyl-Pentane	1.1a; 2.1a	11.25	4.13E-05	99.99	0.01	0	0	0	0
241	1,2,4-trimethyl-Cychexane	1.1a	11.25	4.13E-05	99.97	0.01	0	0	0	0.01
76	2,2,4-trimethyl-Pentane	1.1a; 2.1a	11.25	4.13E-05	99.99	0	0	0	0	0
237	1,1,3-trimethyl-Cychexane	1.1a	11.25	4.13E-05	99.98	0.01	0	0	0	0.01
111	2,4-DM-Heptane	1.1a; 2.1a	11.25	4.13E-05	99.99	0.01	0	0	0	0
234	2,4,4-trimethyl-Hexane	1.1a	11.25	4.13E-05	99.98	0.01	0	0	0	0.01
103	2,2,5-trimethyl-Hexane	1.1a; 2.1a	11.25	4.13E-05	99.98	0.01	0	0	0	0.01
106	Octane	1.1a; 2.1a	11.25	4.13E-05	99.99	0.01	0	0	0	0.01
242	3,4-dimethyl-Heptane	1.1a	11.25	4.13E-05	99.98	0.01	0	0	0	0.01

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
110	2,3,5-trimethyl-Hexane	1.1a; 2.1a	11.25	4.13E-05	99.98	0.01	0	0	0	0.01
116	2,3-DM-Heptane	1.1a; 2.1a	11.25	4.13E-05	99.98	0.01	0	0	0	0.01
96	2,3,-DM-Hexane	1.1a; 2.1a	11.25	4.13E-05	99.99	0	0	0	0	0
239	2,5-dimethyl-Heptane	1.1a	11.25	4.13E-05	99.99	0.01	0	0	0	0.01
244	3,3-dimethyl-Octane	1.1a	12	4.13E-05	99.97	0.02	0	0	0	0.01
157	1,2,3,5-Tetramethylbenzene	1.1a; 2.1a	12	4.08E-05	98.8	0.39	0.45	0	0	0.36
155	1,2,4,5-Tetramethylbenzene	1.1a; 2.1a	12	4.12E-05	99.71	0.09	0.11	0	0	0.09
307	3-nitrobenzanthrone	1.1b	12	1.6E-12	0	33.7	34.77	0.05	0.02	31.46
305	2,7-dinitrofluorene	1.1b	12	6.64E-12	0	18.51	64.17	0.03	0.01	17.28
208	Nitrofluorene	1.1b; 2.1b	12	2.72E-08	0.07	25.93	49.74	0.04	0.02	24.2
245	4M-Nonane	1.1a	12	4.13E-05	99.91	0.05	0	0	0	0.04
246	2M-Nonane	1.1a	12	4.13E-05	99.91	0.05	0	0	0	0.04
139	1M-4-i-PropBenzene	1.1a; 2.1a	12.5	4.12E-05	99.63	0.12	0.13	0	0	0.11
137	1M-3-i-PropBenzene	1.1a; 2.1a	12.5	4.12E-05	99.66	0.11	0.12	0	0	0.11
125	i-Propylbenzene	1.1a; 2.1a	12.5	4.12E-05	99.7	0.06	0.19	0	0	0.05
248	1,3-DM-5-ethylbenzene	1.1a	12.5	4.11E-05	99.5	0.18	0.15	0	0	0.17
251	1E-2-n-propylbenzene	1.1a	13.5	4.1E-05	99.29	0.32	0.09	0	0	0.3
160	n-PentBenzene	1.1a; 2.1a	13.5	4.09E-05	99.02	0.45	0.1	0	0	0.42
254	1M-Naphthalene	1.1a; 1.1b; 2.1a	14	3.54E-05	85.74	3.69	7.12	0.01	0	3.44
253	2M-Naphthalene	1.1a; 1.1b; 2.1a	14	3.76E-05	91.01	2.33	4.49	0	0	2.17
316	Phenylene diamine	1.3	14	4.179E-07	1.01	0	98.98	0	0	0
154	1,2-DM-3-E-Benzene	1.1a; 2.1a	15	0.00004093	99.06	0.31	0.34	0	0	0.29
149	1,4-DM-2-E-Benzene	1.1a; 2.1a	15	0.00004107	99.41	0.2	0.2	0	0	0.19
150	1,3-DM-4-E-Benzene	1.1a; 2.1a	15	0.00004104	99.34	0.23	0.22	0	0	0.21
151	1,2-DM-4-E-Benzene	1.1a; 2.1a	15	0.00004101	99.26	0.26	0.25	0	0	0.24

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
183	Acenaphthene	1.1b; 2.1a; 2.1b	17.5	0.00001556	37.67	15.29	32.75	0.02	0.01	14.27
184	Fluorene	1.1b; 2.1a; 2.1b	17.5	0.00001141	27.62	24.15	25.63	0.04	0.01	22.54
185	2-Methylfluorene	1.1b; 2.1a; 2.1b	17.5	0.000005322	12.88	38.34	12.9	0.06	0.02	35.79
303	1,6-dinitropyrene	1.1b	20	2.16E-13	0	41.71	19.28	0.06	0.03	38.92
295	9-nitroanthracene	1.1b	20	6.703E-09	0.02	37.4	27.59	0.06	0.06	34.91
304	1,8-dinitropyrene	1.1b	20	2.16E-13	0	41.71	19.28	0.06	0.03	38.92
209	1-Nitroanthracene	1.1b; 2.1b	20	9.261E-10	0	37.41	27.6	0.06	0.02	34.91
187	Anthracene	1.1a; 1.1b; 2.1a; 2.1b	20	0.00003204	77.55	9.58	3.91	0.01	0.01	8.94
294	2-nitroanthracene	1.1b	20	9.261E-10	0	37.41	27.6	0.06	0.02	34.91
296	9-nitrophenanthrene	1.1b	20	9.261E-10	0	37.41	27.6	0.06	0.02	34.91
297	3-nitrophenanthrene	1.1b	20	5.796E-09	0.01	27.67	46.44	0.04	0.02	25.82
263	Dibenzothiophene	1.1b; 8.1	24	1.386E-07	0.34	43.59	15.29	0.07	0.03	40.69
255	Phenanthrene	1.1a; 1.1b; 2.1a; 2.1b	24	0.000000063	0.15	42.6	17.39	0.07	0.03	39.76
277	1M-fluorene	1.1b	26.25	0.00001072	25.94	32.6	10.97	0.05	0.02	30.43
264	4M-dibenzothiophene	1.1b	30	3.946E-08	0.1	48.81	5.43	0.08	0.03	45.56
271	1M-7-isopropylphenanthrene	1.1b	30	4.188E-08	0.1	51.49	0.25	0.08	0.03	48.05
299	1-nitrofluranthene	1.1b; 2.1b	30	4.467E-11	0	45.63	11.67	0.07	0.03	42.59
267	2M-anthracene	1.1b; 2.1a	30	0.00002021	48.91	24.74	3.2	0.04	0.01	23.09
298	2M-1-nitroanthracene	1.1b	30	5.935E-10	0	45.11	12.68	0.07	0.03	42.11
301	8-nitrofluroanthene	1.1b	30	4.467E-11	0	45.63	11.67	0.07	0.03	42.59
302	1,3-dinitropyrene	1.1b	30	2.542E-12	0	44.05	14.75	0.07	0.03	41.11
300	3-nitrofluoranthene	1.1b	30	4.467E-11	0	45.63	11.67	0.07	0.03	42.59
266	3M-phenanthrene	1.1b; 2.1a	31.5	0.000002037	4.93	46.04	5.96	0.07	0.03	42.97
268	4M-phenanthrene	1.1b; 2.1a	31.5	0.000001544	3.74	46.62	6.03	0.07	0.03	43.51
276	Trimethylnaphthalene	1.1b; 2.1a	31.5	0.0000238	57.62	19.9	3.86	0.03	0.01	18.57

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
270	1M-phenanthrene	1.1b; 2.1a	31.5	0.000005026	12.17	42.54	5.5	0.07	0.03	39.7
269	9M-phenanthrene	1.1b; 2.1a	31.5	0.000003504	8.48	44.32	5.74	0.07	0.03	41.37
201	Perylene	1.1b; 2.1a; 2.1b	37.5	8.142E-09	0.02	51.4	0.49	0.08	0.03	47.98
210	Nitrobenzo(a)pyrene	1.1b; 2.1b	37.5	2.792E-13	0	51.21	0.88	0.08	0.03	47.8
262	1-M-benzo(e)pyrene	1.1a; 2.1a	37.5	3.325E-11	0	51.59	0.16	0.08	0.03	48.15
261	1-M-benzo(a)pyrene	1.1a; 2.1a	37.5	3.325E-11	0	51.59	0.16	0.08	0.03	48.15
260	1-DME-benz(a)anthracene	1.1a; 2.1a	37.5	7.026E-11	0	51.66	0.02	0.08	0.03	48.21
259	1-Methylbenz(a)anthracene	1.1a; 2.1a	37.5	6.361E-10	0	51.44	0.45	0.08	0.03	48.01
258	Coronene	1.1a; 1.1b; 2.1a	37.5	1.97E-10	0	51.64	0.06	0.08	0.03	48.19
257	Benzo(k)fluoranthene	1.1a; 1.1b; 2.1a	37.5	4.26E-09	0.01	51.41	0.49	0.08	0.03	47.98
274	Indeno(1,2,3-cd)fluroanthene	1.1b; 2.1a	37.5	2.56E-12	0	51.58	0.17	0.08	0.03	48.14
275	Picene	1.1b	37.5	6.616E-12	0	51.62	0.09	0.08	0.03	48.18
203	Indeno(123-cd)pyrene	1.1a;1.1b; 2.1a; 2.1b	37.5	1.881E-11	0	51.58	0.17	0.08	0.03	48.14
195	Benzo(a)anthracene	1.1a; 1.1b; 2.1a; 2.1b	37.5	7.779E-11	0	50.95	1.39	0.08	0.03	47.55
200	Benzo(a)pyrene	1.1a;1.1b; 2.1a; 2.1b	37.5	3.971E-13	0	51.41	0.49	0.08	0.03	47.99
198	Triphenylene	1.1b; 2.1a; 2.1b	37.5	8.558E-11	0	50.95	1.39	0.08	0.03	47.55
196	Chrysene	1.1a;1.1b; 2.1a; 2.1b	37.5	2.022E-10	0	50.95	1.39	0.08	0.03	47.55
188	Pyrene	1.1a; 1.1b; 2.1a; 2.1b	37.5	8.445E-10	0	48.14	6.82	0.07	0.03	44.93
202	Benzo(ghi)perylene	1.1a; 1.1b; 2.1a; 2.1b	37.5	1.319E-10	0	51.58	0.17	0.08	0.03	48.14
190	11H-benzo(a)fluorene	1.1b; 2.1a; 2.1b	37.5	5.999E-10	0	49.83	3.54	0.08	0.03	46.51
194	Benzo(ghi)fluoranthene	1.1a;1.1b; 2.1a; 2.1b	37.5	4.994E-09	0.01	50.38	2.47	0.08	0.03	47.02
186	Fluoranthene	1.1a; 1.1b; 2.1a; 2.1b	39.38	1.022E-07	0.25	48.03	6.8	0.07	0.03	44.82
265	3M-dibenzothiophene	1.1b	45	2.764E-08	0.07	48.83	5.43	0.08	0.03	45.57
189	Benzo(a)fluorene	1.1b; 2.1a; 2.1b	45	9.843E-09	0.02	49.82	3.54	0.08	0.03	46.5
193	1-Methylpyrene	1.1b; 2.1a; 2.1b	45	1.109E-08	0.03	50.48	2.26	0.08	0.03	47.12

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
283	1-nitropyrene	1.1b; 2.1a	45	4.467E-11	0	45.63	11.67	0.07	0.03	42.59
272	2M-Pyrene	1.1b	45	1.109E-08	0.03	50.48	2.26	0.08	0.03	47.12
199	Benzo(e)pyrene	1.1a;1.1b; 2.1a; 2.1b	45	7.147E-10	0	51.41	0.49	0.08	0.03	47.99
256	Benzo(b)fluoranthene	1.1a; 1.1b; 2.1a	45	8.703E-10	0	51.41	0.49	0.08	0.03	47.99
273	Cyclopenta(cd)pyrene	1.1b; 2.1a	54	1.623E-09	0	49.84	3.54	0.08	0.03	46.52

Category 2: Exhaust System

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
134	Decane	1.1a; 2.1a	8	4.13E-05	99.86	0.07	0	0	0	0.07
163	Dodecane	2.1a	10	4.09E-05	99.05	0.49	0	0	0	0.46
166	Tridecane	2.1a	10	4.03E-05	97.45	1.32	0	0	0	1.23
153	Undecane	1.1a; 2.1a	10	4.12E-05	99.64	0.18	0	0	0	0.17
88	2,4,4-trimethyl-2-Pentene	2.1a	10	4.13E-05	99.98	0.01	0.01	0	0	0
138	1,2,3-trimethyl-Benzene	1.1a; 2.1a	10	4.1E-05	99.15	0.15	0.55	0	0	0.14
133	1,2,4-trimethyl-Benzene	1.1a; 2.1a	10	4.11E-05	99.43	0.11	0.36	0	0	0.1
290	Biphenylene	2.1a	10.5	2.55E-05	61.68	9.47	20	0.01	0.01	8.83
289	Biphenyl	2.1a	10.5	2.43E-05	58.75	13.25	15.6	0.02	0.02	12.37
94	2,3,3-trimethyl-Pentane	1.1a; 2.1a	11.25	4.13E-05	99.99	0.01	0	0	0	0
103	2,2,5-trimethyl-Hexane	1.1a; 2.1a	11.25	4.13E-05	99.98	0.01	0	0	0	0.01
96	2,3,-DM-Hexane	1.1a; 2.1a	11.25	4.13E-05	99.99	0	0	0	0	0
111	2,4-DM-Heptane	1.1a; 2.1a	11.25	4.13E-05	99.99	0.01	0	0	0	0
106	Octane	1.1a; 2.1a	11.25	4.13E-05	99.99	0.01	0	0	0	0.01
76	2,2,4-trimethyl-Pentane	1.1a; 2.1a	11.25	4.13E-05	99.99	0	0	0	0	0
110	2,3,5-trimethyl-Hexane	1.1a; 2.1a	11.25	4.13E-05	99.98	0.01	0	0	0	0.01
91	2,4-DM-Hexane	1.1a; 2.1a	11.25	4.13E-05	99.99	0	0	0	0	0
123	l-Nonene	2.1a	11.25	4.13E-05	99.95	0.03	0	0	0	0.02
89	2,5-DM-Hexane	1.1a; 2.1a	11.25	4.13E-05	99.99	0.01	0	0	0	0
116	2,3-DM-Heptane	1.1a; 2.1a	11.25	4.13E-05	99.98	0.01	0	0	0	0.01
114	3,5-DM-Heptane	2.1a	11.25	4.13E-05	99.99	0.01	0	0	0	0.01
157	1,2,3,5-Tetramethylbenzene	1.1a; 2.1a	12	4.08E-05	98.8	0.39	0.45	0	0	0.36
205	9,10-anthracenedione	2.1b	12	4.72E-08	0.11	3.08	93.93	0	0	2.87
204	9-fluorenone	2.1b	12	2.76E-07	0.67	7.48	84.86	0.01	0	6.98

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
208	Nitrofluorene	1.1b; 2.1b	12	2.72E-08	0.07	25.93	49.74	0.04	0.02	24.2
181	2,6-Dimethylnaphthalene	2.1b	12	0.000041	99.24	0.3	0.18	0	0	0.28
155	1,2,4,5-Tetramethylbenzene	1.1a; 2.1a	12	4.12E-05	99.71	0.09	0.11	0	0	0.09
126	2,2-DM-Octane	2.1a	12	4.13E-05	99.95	0.03	0	0	0	0.02
159	1,2,3,4-Tetramethylbenzene	2.1a	12	4.06E-05	98.38	0.52	0.61	0	0	0.49
127	2,4-DM-Octane	2.1a	12	4.13E-05	99.95	0.03	0	0	0	0.02
139	1M-4-i-PropBenzene	1.1a; 2.1a	12.5	4.12E-05	99.63	0.12	0.13	0	0	0.11
136	s-Butylbenzene	2.1a	12.5	4.12E-05	99.7	0.1	0.1	0	0	0.1
125	i-Propylbenzene	1.1a; 2.1a	12.5	4.12E-05	99.7	0.06	0.19	0	0	0.05
141	1M-2-i-PropBenzene	2.1a	12.5	0.000411	99.58	0.13	0.16	0	0	0.12
137	1M-3-i-PropBenzene	1.1a; 2.1a	12.5	4.12E-05	99.66	0.11	0.12	0	0	0.11
156	2M-ButylBenzene	2.1a	13.5	4.12E-05	99.63	0.17	0.05	0	0	0.15
160	n-PentBenzene	1.1a; 2.1a	13.5	4.09E-05	99.02	0.45	0.1	0	0	0.42
253	2M-Naphthalene	1.1a; 1.1b; 2.1a	14	3.76E-05	91.01	2.33	4.49	0	0	2.17
254	1M-Naphthalene	1.1a; 1.1b; 2.1a	14	3.54E-05	85.74	3.69	7.12	0.01	0	3.44
292	Ethylnaphthalene	2.1a	14	3.02E-05	72.97	10.78	6.16	0.02	0.01	10.06
291	Methylbiphenyl	2.1a	14	1.63E-05	39.54	26.19	9.77	0.04	0.02	24.44
154	1,2-DM-3-E-Benzene	1.1a; 2.1a	15	4.09E-05	99.06	0.31	0.34	0	0	0.29
149	1,4-DM-2-E-Benzene	1.1a; 2.1a	15	4.11E-05	99.41	0.2	0.2	0	0	0.19
150	1,3-DM-4-E-Benzene	1.1a; 2.1a	15	4.1E-05	99.34	0.23	0.22	0	0	0.21
151	1,2-DM-4-E-Benzene	1.1a; 2.1a	15	4.1E-05	99.26	0.26	0.25	0	0	0.24
152	1,3-DM-2-E-Benzene	2.1a	15	0.000041	99.23	0.25	0.27	0	0	0.24
158	1-tert-1B-2M-Benzene	2.1a	15	4.09E-05	99.1	0.37	0.18	0	0	0.35
182	Acenaphthylene	2.1a; 2.1b	17.5	2.71E-05	65.68	6.88	21.01	0	0	6.42
184	Fluorene	1.1b; 2.1a; 2.1b	17.5	1.14E-05	27.62	24.15	25.63	0.04	0.01	22.54

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
183	Acenaphthene	1.1b; 2.1a; 2.1b	17.5	1.56E-05	37.67	15.29	32.75	0.02	0.01	14.27
185	2-Methylfluorene	1.1b; 2.1a; 2.1b	17.5	5.32E-06	12.88	38.34	12.9	0.06	0.02	35.79
187	Anthracene	1.1a; 1.1b; 2.1a; 2.1b	20	3.2E-05	77.55	9.58	3.91	0.01	0.01	8.94
209	1-Nitroanthracene	1.1b; 2.1b	20	9.26E-10	0	37.41	27.6	0.06	0.02	34.91
255	Phenanthrene	1.1a; 1.1b; 2.1a; 2.1b	24	6.3E-08	0.15	42.6	17.39	0.07	0.03	39.76
207	Cyclopenta(def)phenanthrene-4-one	2.1b	26.25	2.58E-06	6.24	40.7	14.98	0.06	0.02	37.99
161	1 tert-1B-3,5-DM-Benzene	2.1a	27	4.11E-05	99.46	0.26	0.04	0	0	0.24
299	1-nitrofluranthene	1.1b; 2.1b	30	4.47E-11	0	45.63	11.67	0.07	0.03	42.59
267	2M-anthracene	1.1b; 2.1a	30	2.02E-05	48.91	24.74	3.2	0.04	0.01	23.09
284	3,6-DM-Phenanthrene	2.1a	30	7.47E-07	1.81	49.68	2.04	0.08	0.03	46.37
293	Dimethylphenanthrene	2.1a	31.5	1.37E-07	0.33	50.43	2.07	0.08	0.03	47.07
288	1M-Anthracene	2.1a	31.5	3.13E-06	7.56	44.77	5.79	0.07	0.03	41.78
270	1M-phenanthrene	1.1b; 2.1a	31.5	5.03E-06	12.17	42.54	5.5	0.07	0.03	39.7
269	9M-phenanthrene	1.1b; 2.1a	31.5	3.5E-06	8.48	44.32	5.74	0.07	0.03	41.37
268	4M-phenanthrene	1.1b; 2.1a	31.5	1.54E-06	3.74	46.62	6.03	0.07	0.03	43.51
266	3M-phenanthrene	1.1b; 2.1a	31.5	2.04E-06	4.93	46.04	5.96	0.07	0.03	42.97
276	Trimethylnaphthalene	1.1b; 2.1a	31.5	2.38E-05	57.62	19.9	3.86	0.03	0.01	18.57
165	1,2,4-Triethyl-Benzene	2.1a	33.75	4.09E-05	98.98	0.51	0.04	0	0	0.47
164	1,3,5-Triethyl-Benzene	2.1a	33.75	4.1E-05	99.23	0.39	0.03	0	0	0.36
197	Benzo(c)phenanthrene	2.1a; 2.1b	37.5	2.39E-09	0.01	50.94	1.39	0.08	0.03	47.55
210	Nitrobenzo(a)pyrene	1.1b; 2.1b	37.5	2.79E-13	0	51.21	0.88	0.08	0.03	47.8
286	Dibenzo(ae)pyrene	2.1a	37.5	2.63E-13	0	51.65	0.03	0.08	0.03	48.21
285	Dibenz(aj)anthracene	2.1a	37.5	6.62E-12	0	51.62	0.09	0.08	0.03	48.18
282	Anthanthrene	2.1a	37.5	2.56E-12	0	51.58	0.17	0.08	0.03	48.14
280	Dibenz(a,h)anthracene	2.1a	37.5	3.37E-14	0	51.62	0.09	0.09	0.03	48.18

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
279	Benzo(j)fluoranthene	2.1a	37.5	1.29E-09	0	51.41	0.49	0.08	0.03	47.99
274	Indeno(1,2,3-cd)fluroanthene	1.1b; 2.1a	37.5	2.56E-12	0	51.58	0.17	0.08	0.03	48.14
262	1-M-benzo(e)pyrene	1.1a; 2.1a	37.5	3.33E-11	0	51.59	0.16	0.08	0.03	48.15
261	1-M-benzo(a)pyrene	1.1a; 2.1a	37.5	3.33E-11	0	51.59	0.16	0.08	0.03	48.15
260	1-DME-benz(a)anthracene	1.1a; 2.1a	37.5	7.03E-11	0	51.66	0.02	0.08	0.03	48.21
259	1-Methylbenz(a)anthracene	1.1a; 2.1a	37.5	6.36E-10	0	51.44	0.45	0.08	0.03	48.01
195	Benzo(a)anthracene	1.1a; 1.1b; 2.1a; 2.1b	37.5	7.78E-11	0	50.95	1.39	0.08	0.03	47.55
257	Benzo(k)fluoranthene	1.1a; 1.1b; 2.1a	37.5	4.26E-09	0.01	51.41	0.49	0.08	0.03	47.98
203	Indeno(123-cd)pyrene	1.1a;1.1b; 2.1a; 2.1b	37.5	1.88E-11	0	51.58	0.17	0.08	0.03	48.14
202	Benzo(ghi)perylene	1.1a; 1.1b; 2.1a; 2.1b	37.5	1.32E-10	0	51.58	0.17	0.08	0.03	48.14
201	Perylene	1.1b; 2.1a; 2.1b	37.5	8.14E-09	0.02	51.4	0.49	0.08	0.03	47.98
200	Benzo(a)pyrene	1.1a;1.1b; 2.1a; 2.1b	37.5	3.97E-13	0	51.41	0.49	0.08	0.03	47.99
198	Triphenylene	1.1b; 2.1a; 2.1b	37.5	8.56E-11	0	50.95	1.39	0.08	0.03	47.55
192	11H-benzo(b)fluorene	2.1a; 2.1b	37.5	6.81E-09	0.02	49.83	3.54	0.08	0.03	46.51
196	Chrysene	1.1a;1.1b; 2.1a; 2.1b	37.5	2.02E-10	0	50.95	1.39	0.08	0.03	47.55
194	Benzo(ghi)fluoranthene	1.1a;1.1b; 2.1a; 2.1b	37.5	4.99E-09	0.01	50.38	2.47	0.08	0.03	47.02
190	11H-benzo(a)fluorene	1.1b; 2.1a; 2.1b	37.5	6E-10	0	49.83	3.54	0.08	0.03	46.51
188	Pyrene	1.1a; 1.1b; 2.1a; 2.1b	37.5	8.45E-10	0	48.14	6.82	0.07	0.03	44.93
258	Coronene	1.1a; 1.1b; 2.1a	37.5	1.97E-10	0	51.64	0.06	0.08	0.03	48.19
186	Fluoranthene	1.1a; 1.1b; 2.1a; 2.1b	39.38	1.02E-07	0.25	48.03	6.8	0.07	0.03	44.82
189	Benzo(a)fluorene	1.1b; 2.1a; 2.1b	45	9.84E-09	0.02	49.82	3.54	0.08	0.03	46.5
193	1-Methylpyrene	1.1b; 2.1a; 2.1b	45	1.11E-08	0.03	50.48	2.26	0.08	0.03	47.12
199	Benzo(e)pyrene	1.1a;1.1b; 2.1a; 2.1b	45	7.15E-10	0	51.41	0.49	0.08	0.03	47.99
256	Benzo(b)fluoranthene	1.1a; 1.1b; 2.1a	45	8.7E-10	0	51.41	0.49	0.08	0.03	47.99

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
281	Benzonaphtho(2,1-d)thiophene	2.1a	45	1.74E-10	0	51.05	1.2	0.08	0.03	47.64
283	1-nitropyrene	1.1b; 2.1a	45	4.47E-11	0	45.63	11.67	0.07	0.03	42.59
287	3M-Cholanthrene	2.1a	45	2.76E-10	0	51.58	0.16	0.08	0.03	48.15
191	Benzo(b)fluorene	2.1a; 2.1b	45	9.84E-09	0.02	49.82	3.54	0.08	0.03	46.5
273	Cyclopenta(cd)pyrene	1.1b; 2.1a	54	1.62E-09	0	49.84	3.54	0.08	0.03	46.52

Category 4: Coolants

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
212	mercaptobenzothiazole	4.1; 8.1	10.13	1.71E-06	4.15	5.99	84.25	0.01	0	5.59

Category 7: Braking and Clutch

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
325	Hexadecanamide	7.1	8	2.29E-06	5.54	48.59	0.41	0.08	0.03	45.35
338	Diethenylbenzene	7.1	9	4.08E-05	98.74	0.24	0.79	0	0	0.23
328	Methylenebis phenol	7.1	9	8.45E-09	0.02	5.33	89.66	0.01	0	4.97
340	Bis(2-ethylhexyl) phthalate	7.1	10.5	3.98E-06	16.9	42.94	0	0.07	0.03	40.07
337	Benzophenone	7.1	10.5	1.47E-05	35.58	6.27	52.28	0.01	2	5.85
326	Hexadecanenitrile	7.1	18	9.01E-08	0.22	51.52	0.06	0.08	0.03	48.09
349	Diphenyl benzenediamine	7.1; 8.1	20	7.8E-10	0	49.11	4.94	0.08	0.3	45.84
331	Butylated hydroxy toluene	7.1; 8.1	26.25	0.000035	84.71	7.78	0.23	0.01	0	7.26
339	Tetramethyl phenanthrene	7.1	31.5	2.06E-08	0.05	51.5	0.27	0.08	0.03	48.07

Category 8: Tyres

ID number	Contaminant Name	Road Cat Code	Overall Risk	Fugacity (Pa)	Air (%)	Soil (%)	Water (%)	Suspended Solids (%)	Aquatic Biota (%)	Sediment (%)
343	Hexadecanoic acid, methyl ester	8.1	9	2.63E-06	6.37	48.37	1.12	0.08	0.03	45.14
350	N-isopropyl-N'-phenyl-p-phenylenediamine	8.1	10	1.97E-08	0.05	30.03	41.83	0.05	0.02	28.03
320	N-cyclohexyl-2-benzothiazolesulphenamide	8.1	10	-	-	-	-	-	-	-
212	mercaptobenzothiazole	4.1; 8.1	10.13	1.71E-06	4.15	5.99	84.25	0.01	0	5.59
319	2,2,4-trimethyl-1,2-dihydroquinoline	8.1	10.5	3.48E-06	8.42	14.01	64.47	0.02	0.01	13.08
348	2-methyl-N-(2-methylphenyl)-benzenediamine	8.1	12	4.01E-07	0.97	16.66	66.78	0.03	0.01	15.55
322	N-cyclohexylthiophthalimide	8.1	12	4.3E-11	0	6.94	86.57	0.01	0	6.48
349	Diphenyl benzenediamine	7.1; 8.1	20	7.8E-10	0	49.11	4.94	0.08	0.3	45.84
263	Dibenzothiophene	1.1b; 8.1	24	1.39E-07	0.34	43.59	15.29	0.07	0.03	40.69
360	Methyldibenzothiophene	8.1	26.25	3.95E-08	0.1	48.81	5.43	0.08	0.03	45.56
331	Butylated hydroxy toluene	7.1; 8.1	26.25	0.000035	84.71	7.78	0.23	0.01	0	7.26
318	N-(1,3-dimethylbutyl)-N,-phenyl-p-phenylenediamine	8.1	30	1.3E-09	0	50.4	2.45	0.08	0.03	47.04
359	1,4-dimethyl-7-(1-methylethyl)azulene	8.1	31.5	5.29E-06	12.81	44.52	1.02	0.07	0.03	41.55

Appendix C

Figure 1a **Christchurch Catchment Basins**

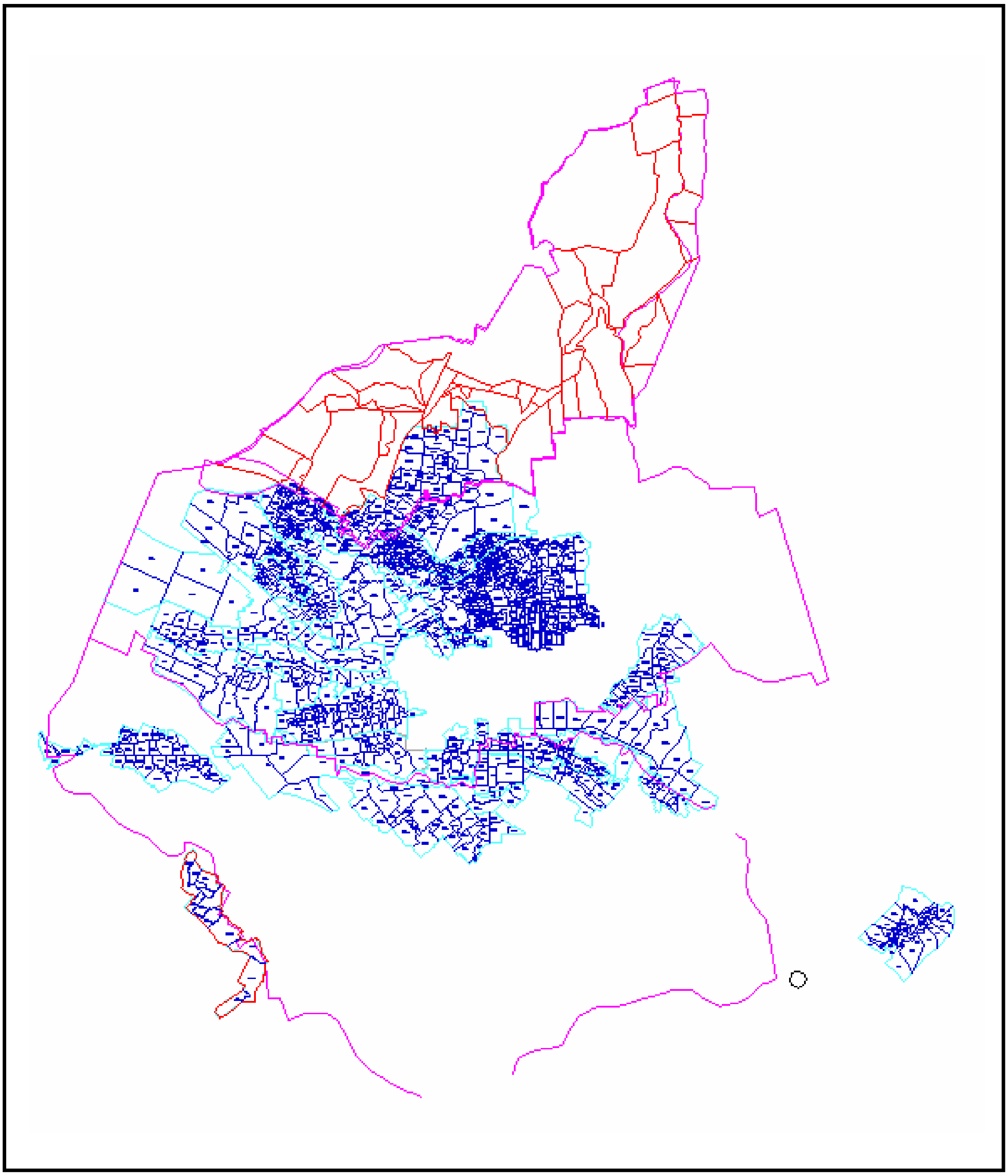

Figure 1b Christchurch Catchment Basins

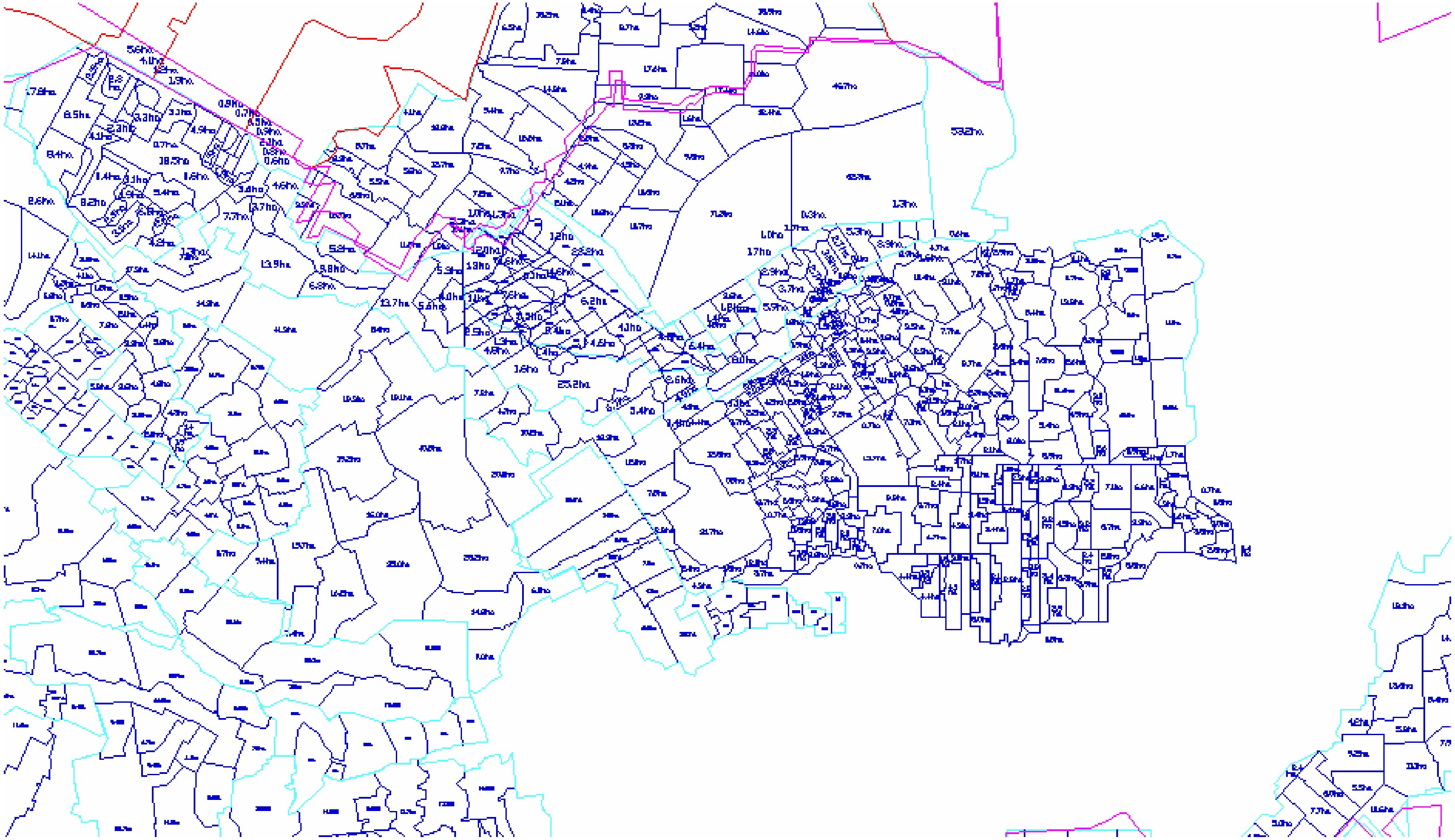

Figure 1c Christchurch Catchment Basins

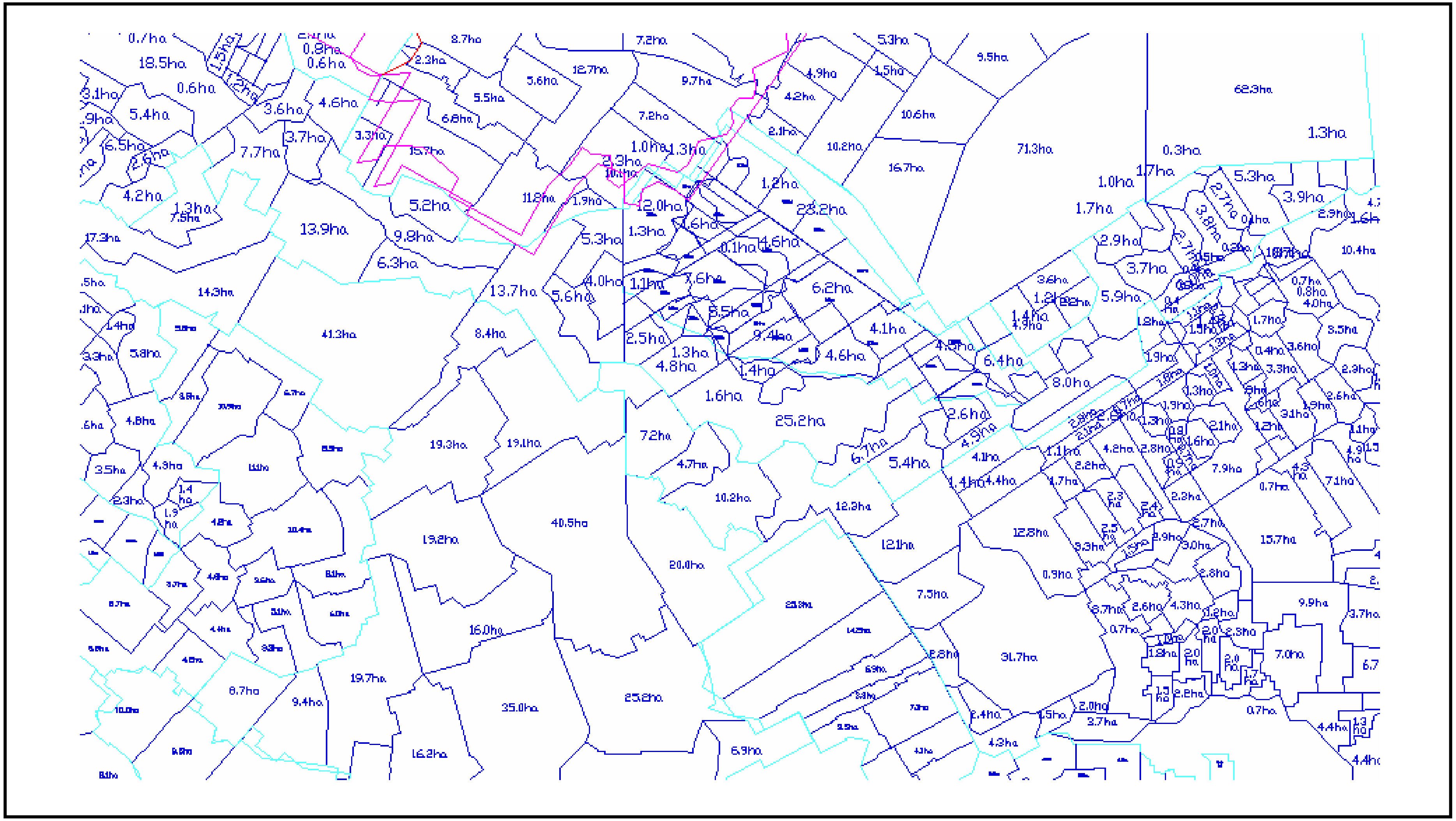

Figure 2a **Christchurch Stormwater System**

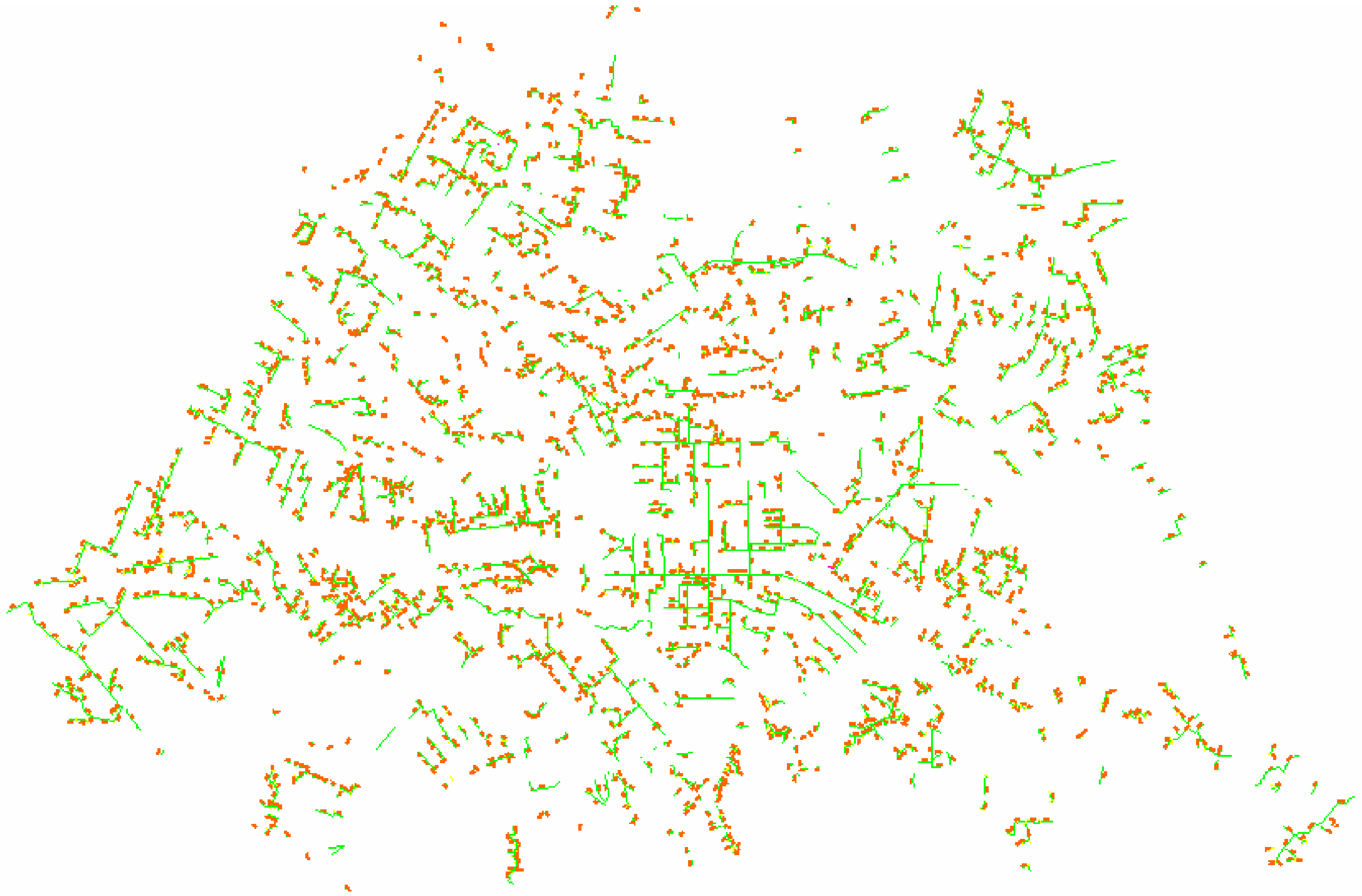

Figure 2b Christchurch Stormwater System

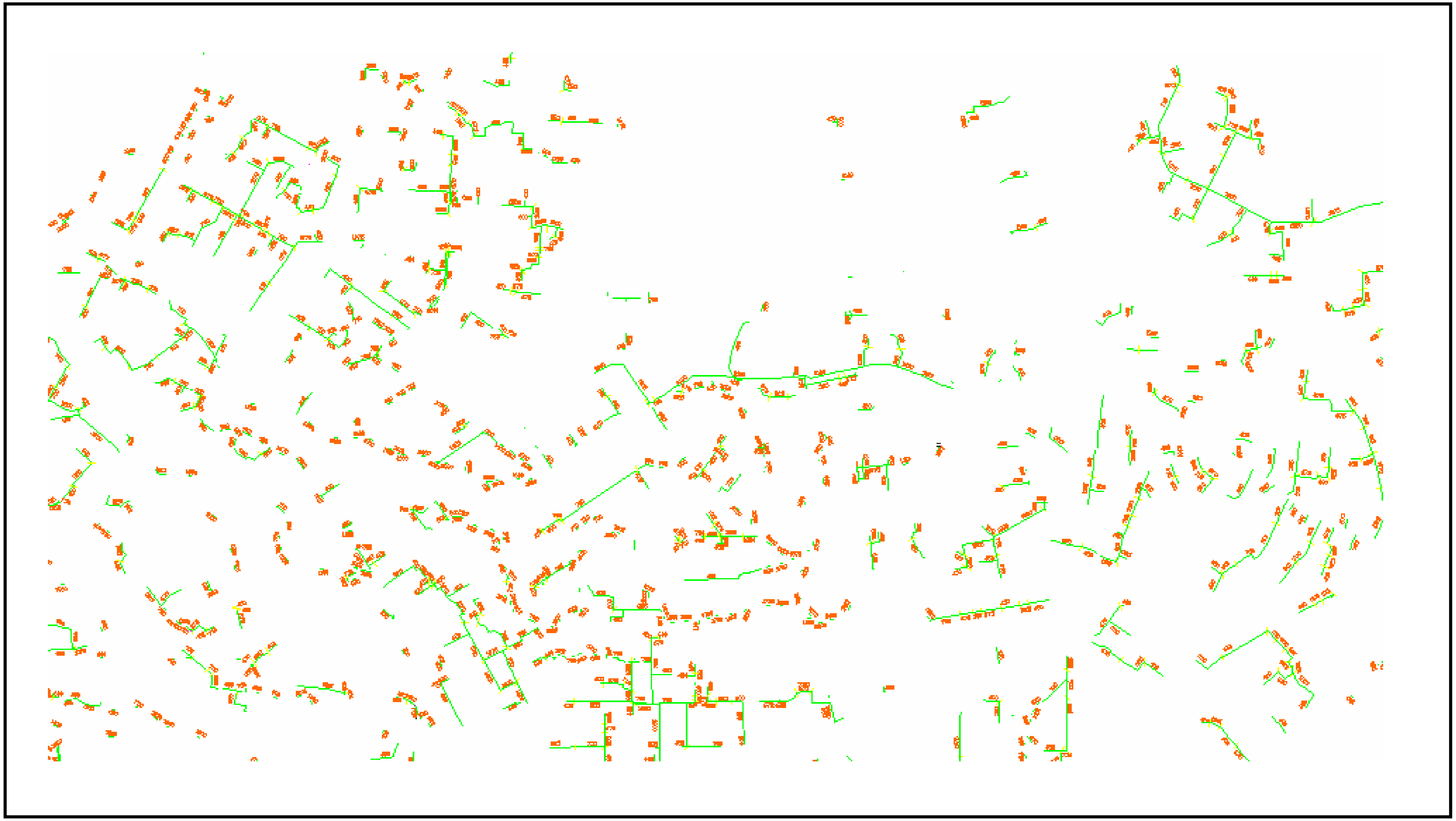

Figure 2c Christchurch Stormwater System

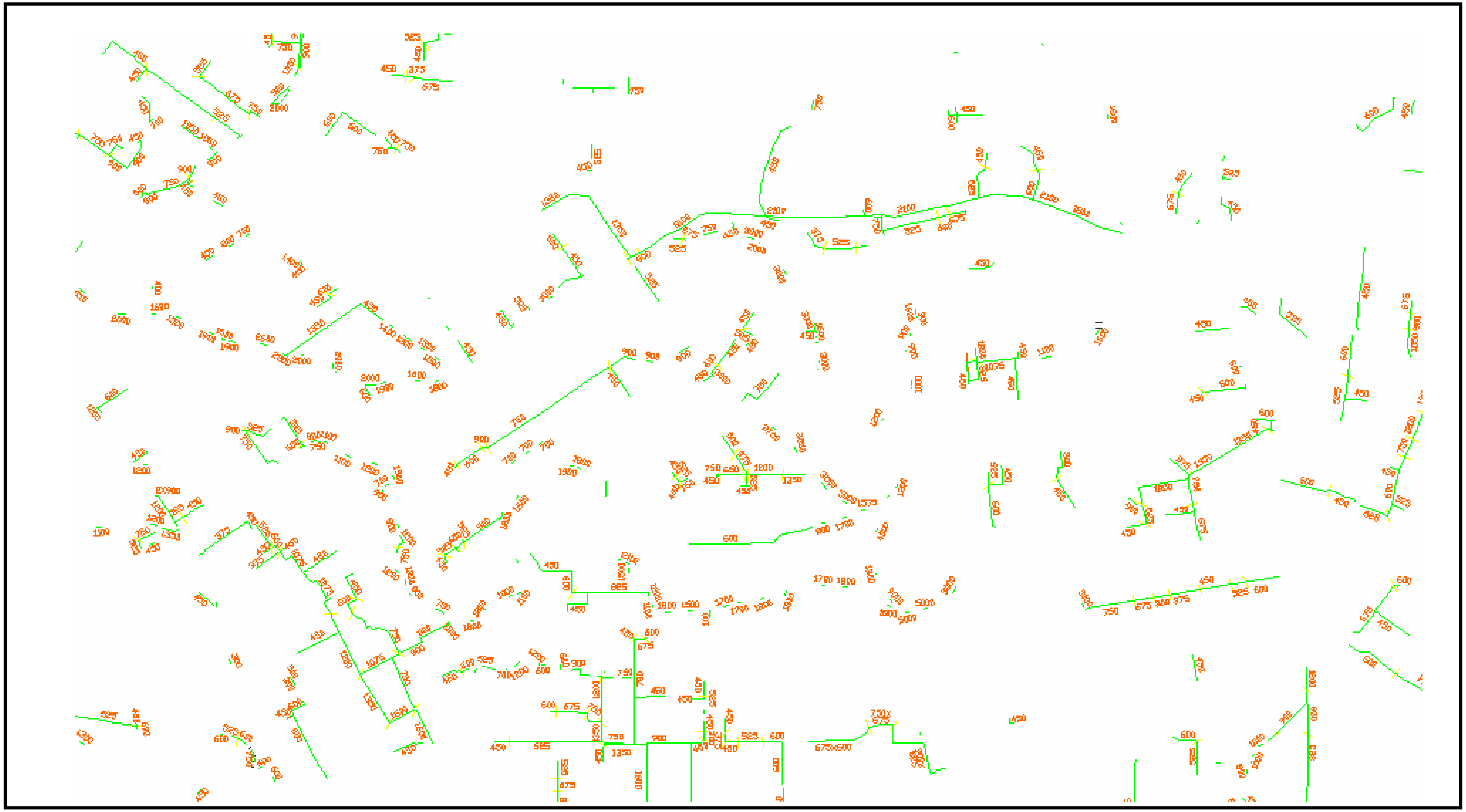

Figure 3a Christchurch Waterways

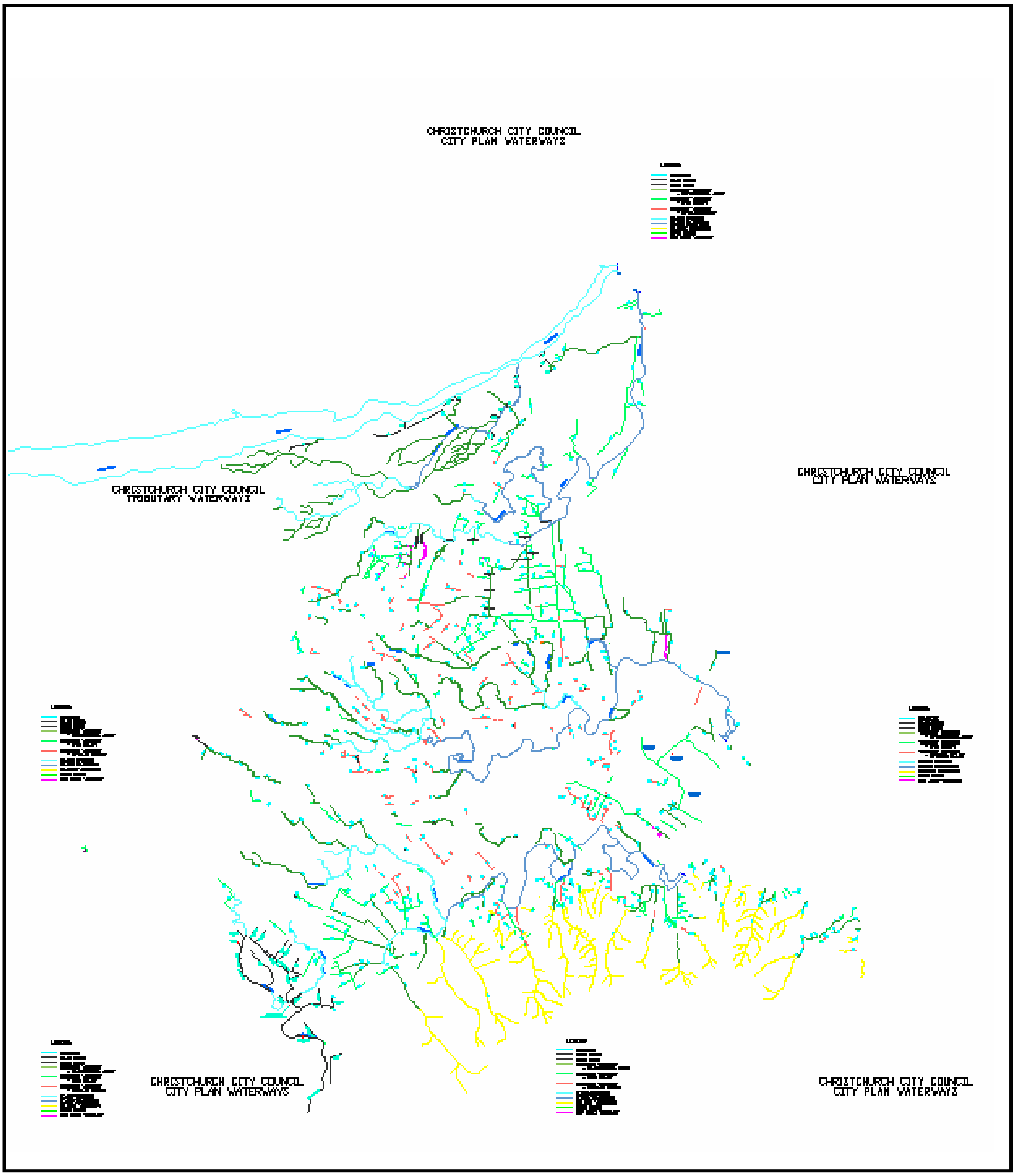

Figure 3b **Christchurch Waterways**

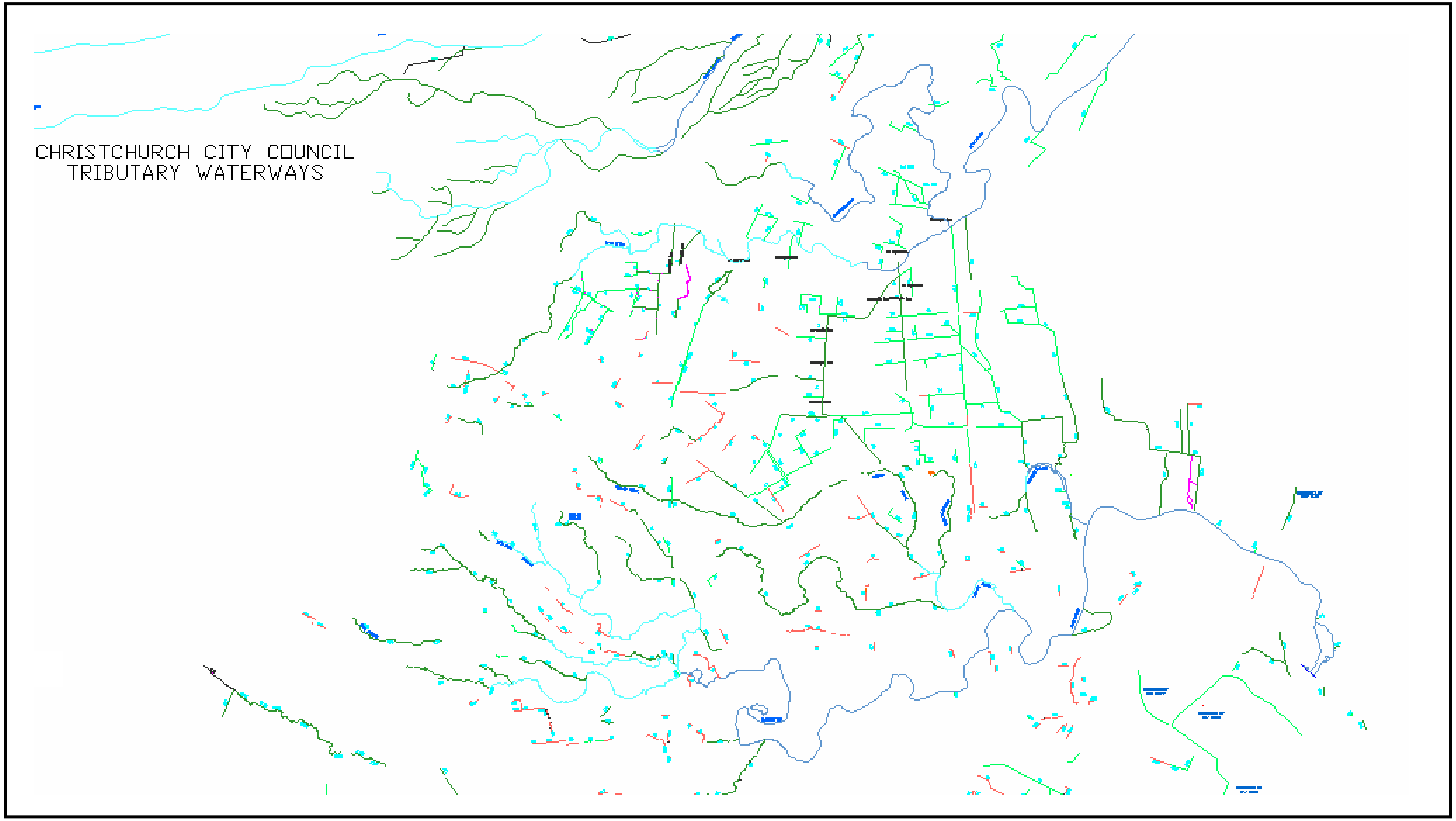

Figure 3c Christchurch Waterways