



*The Effects of Road Transport on
Freshwater and Marine Ecosystems*



The Effects of Road Transport on Freshwater and Marine Ecosystems

Prepared for



MINISTRY *of* TRANSPORT
TE MANATŪ WAKA

By

Paul Kennedy
Kingett Mitchell Ltd

June 1999

Updated
October 2003

Intentionally Blank

Table of Contents

	Page
1. INTRODUCTION	1
1.1 Transport and the Environment	1
1.2 Report Scope	1
1.3 Report Contents	2
2. TRANSPORT DERIVED CONTAMINANTS IN STORMWATER	3
2.1 Introduction	3
2.2 Sources	3
2.3 Inorganic Contaminants	5
2.3.1 Fuel	5
2.3.2 Oil and Grease	5
2.3.3 Brake Pads	5
2.3.4 Tyres	6
2.3.5 Emission Control Technologies	7
2.3.6 Road Surface	7
2.4 Organic Contaminants	8
2.4.1 Fuel Evaporation and Combustion	8
2.4.2 Oil and Grease	8
2.4.3 Brake Pads	9
2.4.4 Tyres	9
2.4.5 Road surface wear	9
2.5 Summary	9
3. ROAD ENVIRONMENT	11
3.1 Introduction	11
3.2 Street and Gutter Dusts	11
3.2.1 General Composition	11
3.2.2 Particle sizes	12
3.2.3 Metals	14
3.2.4 Organic Compounds	16
3.2.5 Other Constituents	18
3.3 Effects of Traffic	18
3.4 Summary	19
4. STORMWATER RUNOFF	21
4.1 Introduction	21

4.2	Particulates in Urban Runoff and Motorway Runoff	21
4.3	Trace Elements in Stormwater	24
4.3.1	Concentrations in stormwater	24
4.3.2	Dissolved Metals	29
4.3.3	Trace metals in Stormwater Particulates	31
4.4	Organic Compounds in Stormwater	33
4.4.1	Hydrocarbons	33
4.4.2	VOCs	33
4.4.3	PAHs	34
4.4.4	Other SVOCs	36
4.4.5	Dissolved organic compounds	37
4.4.6	TPH and PAHs in stormwater particulate matter	37
4.5	Other Constituents	38
4.6	Effects of Road Surfaces	41
4.7	Catchpits & First Flush	41
4.8	Summary	42
5	PATHWAYS & FATE OF CONTAMINANTS EMITTED FROM TRANSPORT SOURCES	44
5.1	Introduction	44
5.2	Transport and Deposition of Airborne Particulate Matter	44
5.2.1	Introduction	44
5.2.2	Particulate Material	45
5.2.3	Local Deposition	45
5.2.4	Regional and Remote Deposition	46
5.3	Fate on the Street Surface and in the Stormwater System	47
5.3.1	Introduction	47
5.3.2	Street Surfaces	47
5.3.3	Catchpits	52
5.4	Freshwaters	53
5.4.1	Introduction	53
5.4.2	Dispersion	54
5.4.3	Settlement	54
5.4.4	Other Processes	54
5.5	Estuarine and Marine Waters	54
5.5.1	Introduction	54

5.5.2	Settlement	54
5.5.3	Other Processes	55
5.6	Summary	56
6.	ENVIRONMENTAL EFFECTS IN FRESHWATER ENVIRONMENTS	57
6.1	Introduction	57
6.2	Freshwater Ecosystems	58
6.2.1	Introduction	58
6.2.2	In-stream Habitat	59
6.2.3	Aquatic algae	61
6.2.4	Aquatic Invertebrates	62
6.2.5	Fish	65
6.3	Water Quality and Toxicity	68
6.3.1	Introduction	68
6.3.2	General Water Quality	69
6.3.3	Toxic Substances	70
6.3.3.1	Guidelines	70
6.3.3.2	Toxicity data	70
6.3.3.3	Stormwater Quality and Toxicity	72
6.3.4	Toxicity data and Toxicity Tests	76
6.4	Sediment Quality and Toxicity	80
6.4.1	Sediment Quality Guidelines	80
6.4.2	Quality of Detention Pond Sediments	82
6.4.3	Stream, wetlands and Lake Sediments	84
6.4.4	Sediment Toxicity	85
6.5	Bioaccumulation	87
6.5.1	Introduction	87
6.5.2	Bioaccumulation of Trace Elements	88
6.5.2.1	Invertebrates	88
6.5.2.2	Fish	90
6.5.2.3	Other organisms	90
6.5.3	Bioaccumulation of Organic Compounds	92
6.5.3.1	Introduction	92
6.5.3.2	Invertebrates	93
6.5.3.3	Fish	93
6.5.3.4	Other organisms	93
6.6	Summary	93

7. IDENTIFICATION OF ENVIRONMENTAL EFFECTS IN ESTUARINE AND COASTAL ECOSYSTEMS	96
7.1 Introduction	96
7.2 Habitat	96
7.3 Water quality and Toxicity	97
7.4 Sediment Quality	101
7.4.1 Introduction	101
7.4.2 Intertidal	101
7.4.2.1 Intertidal areas and Salt Marsh	101
7.4.2.2 Intertidal soft-shore areas	102
7.4.3 Subtidal	103
7.4.4 Toxicity	105
7.5 Biological Resources	105
7.5.1 Resources	105
7.5.2 Tools	106
7.5.3 Effects	106
7.6 Bioaccumulation	109
7.6.1 Plants	109
7.6.2 Invertebrates	110
7.6.3 Fish	111
7.7 Summary	112
8. OVERVIEW	114
8.1 Vehicles as sources of contaminants	114
8.2 The road environment	114
8.3 Stormwater runoff	115
8.4 Pathways and fate	116
8.5 Freshwater environments	117
8.6 Marine environments	118
9. REFERENCES	121
10. ACKNOWLEDGEMENTS	142

Abbreviations

ACY	Acenaphthylene
AFDW	Ash free dry weight
ANT	Anthracene
ANZECC	Australian and New Zealand Environment and Conservation Council
ARC	Auckland Regional Council
Al	Aluminium
As	Arsenic
B(a)A	Benzo[a]anthracene
B(a)P	Benzo[a]pyrene
B(b)F	Benzo[b]fluoranthene
B(k)F	Benzo[k]fluoranthene
Br	Bromine
BOD	Biochemical Oxygen Demand
BPY	Benzo[g,h,i]perylene
BTEX	Benzene, toluene, ethyl-benzene and total xylene
C	Carbon
Ca	Calcium
Cd	Cadmium
Ce	Cerium
CHY	Chrysene
Cl	Chlorine and the anion chloride (Cl ⁻)
CNG	Compressed natural gas
CO	Carbon monoxide
Co	Cobalt
CO ₂	Carbon dioxide
Cr	Chromium
Cu	Copper
DBA	Dibenz[a,h]anthracene
EIP	Environmental Indicators Programme
EMC	Event Mean Concentration
USEPA	Environmental Protection Agency
EPI	Environmental performance indicators
ER-L	Effects Range Low
ER-M	Effects Range Median
Fe	Iron
FL	Fluorene
FLR	Fluoranthene
GCMS	Gas Chromatography Mass Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
g/m ³	grams per cubic metre = parts per million
HCl	Hydrochloric acid
Hf	Hafnium
Hg	Mercury
HMW	High molecular weight
INP	Indeno[1,2,3-cd]pyrene
K	Potassium
LPG	Liquid petroleum gas
LMW	Low molecular weight
MfE	Ministry for the Environment (New Zealand)
Mg	Magnesium
mg/kg	milligrams per kilogram = parts per million
mg/m ³	milligrams per cubic metre = parts per billion
Mn	Manganese
MoT	Ministry of Transport
MTBE	Methyl tert-butyl ether

MW	Molecular weight
N	Nitrogen
Na	Sodium
NAP	Naphthalene
NEIP	National Environmental Indicators Programme
Ni	Nickel
NIWA	National Institute of Water and Atmospheric Research
NOEL	No observable effects level.
NOx	Nitrogen oxides (nitrogen dioxide etc.,)
NPDES	National Pollution Discharge Elimination System
NASWM	National Agenda for Sustainable Water Management
NWQMN	National Water Quality Monitoring Network
NZ	New Zealand
NZCPS	New Zealand Coastal Policy Statement
OC	Organic carbon
P	Phosphorous
PAH	Polyaromatic hydrocarbons
Pb	Lead
Pd	Paladium
PEL	Probable Effects Level
PGMs	Platinum group metals
PHEN	Phenanthrene
Pt	Platinum
PYR	Pyrene
RBP	Rapid bioassessment protocols
Rh	Rhodium
RMA	Resource Management Act 1991
Sb	Antimony
SEM	Scanning electron microscopy
Sm	Samarium
SO ₄	Sulphate
SO _x	Sulphur oxides (e.g., sulphur dioxide etc.,)
SVOC	Semi-volatile organic compound
TEL	Threshold Effects Levels
TIE	Toxicity identification evaluation
TKN	Total Kjehdahl nitrogen
TLAs	Territorial local authorities
TPH	Total Petroleum Hydrocarbons
VF ECS	Vehicle fleet emissions control strategy
VOC	Volatile organic compound
VPD	Vehicles per day
WRC	Wellington Regional Council
UK	United Kingdom
USGS	United States Geological Survey
USHA	Urban Stream Habitat Assessment method
V	Vanadium
XRF	X-ray fluorescence spectrometry
Y	Yttrium
Zn	Zinc

1. INTRODUCTION

1.1 Transport and the Environment

In 1996, the Ministry of Transport (MoT) released a discussion paper on environmental externalities as part of the Land Transport Pricing Study (MoT 1996). MoT (1996) reported that the contribution of road runoff to the flux of contaminants to freshwater and marine environments was unclear. Road runoff was however, considered to account for 40-50% of urban metal contamination to aquatic ecosystems. It was considered at that time that although effects on water quality and associated aquatic ecosystems was one of the key potential impact areas of road transport, research about the environmental effects of road transport on water quality was not well advanced and that this resulted in an inability to quantify the contribution that road transport made to any specific effects.

MoT (1996) identified effects on water quality and associated aquatic ecosystems as one of the key impact areas of road transport. Work by the Ministry for the Environment (MfE) has subsequently identified motor vehicle emission discharges via stormwater as a key effect issue in relation to freshwater, estuaries and coastal areas. As a result, road transport effects have been identified as a specific matter to be dealt with through the Ministry's Environmental Performance Indicators (EPI) programme. In 1998, MoT released the final report of the Vehicle Fleet Emissions Control Strategy (VF ECS) (MoT 1998). The VF ECS report examined the nature of exhaust emissions from the vehicle fleet and local air quality. Overall, the approach used in the VF ECS was impact-based. Work by the Ministry for the Environment (MfE) has subsequently identified motor vehicle emission discharges via stormwater as a key effect issue in relation to freshwater, estuaries and coastal areas (MfE 2000). As a result, road transport effects have been identified as a specific matter to be dealt with through the Ministry's Environmental Performance Indicators (EPI) programme.

1.2 Report Scope

Internationally there have been a number of reports prepared that have reviewed the effects of road and highway runoff on aquatic ecosystems. These include Folkesson (1994) (Sweden), Peterson & Batley (1992) and Brockbank & Batley (1996) (CSIRO for New South Wales Roads and Traffic Authority). This report examines the effects of contaminants derived from road transport on aquatic ecosystems in a New Zealand context wherever possible. The report aims to provide an overview as to what we know about the effects of the contaminants released by motor vehicles. As such, the assessment is dependent upon what we know about contaminants emitted by motor vehicles to aquatic ecosystems. It should be noted that the report does not deal with:

- ❑ Vehicle maintenance/repair/re-fuelling losses or road repair.
- ❑ The effects of contaminants derived from road transport on terrestrial ecosystems or on groundwater resources.
- ❑ The effects of contaminants derived from road transport on air quality. This was the subject of a separate MoT Study (refer MoT 1996, 1998).
- ❑ The effects of accidental losses of loads from road vehicles.
- ❑ The use of de-icing salts.

As will be described, the stormwater from roads in most locations does not just transport the contaminants generated by motor vehicles. Roads are typically surrounded by other activities that have a significant influence on the nature of runoff from various landuses (refer Heany et al. 1999). This report provides information as part of the overall Ministry of Transport study on the effects of road transport on aquatic ecosystems. Other reports prepared as part of this study include:

1. Moncrieff, I.; Kennedy, P. 2002: Road transport effects on aquatic ecosystems issues and context for policy development. Report prepared for New Zealand Ministry of Transport by Fuels and Energy Ltd and Kingett Mitchell Ltd.
2. Kennedy, P. 2000: Ministry of Transport contaminants database. Support manual. Report prepared for New Zealand Ministry of Transport by Kingett Mitchell Ltd.
3. Kennedy, P.; Gadd, J.; Moncrieff, I. 2002: Emission factors for contaminants released by motor vehicles. Prepared by Kingett Mitchell Limited and Fuels & Energy Limited for New Zealand Ministry of Transport and Infrastructure Auckland.
4. Kennedy, P. 2003: Metals in particulate material on road surfaces. Prepared by Kingett Mitchell Limited for New Zealand Ministry of Transport.
- 5 Kennedy, P.; Gadd, J. 2000: Preliminary examination of trace elements in tyres, brake pads and road bitumen in New Zealand. Report prepared for New Zealand Ministry of Transport by Kingett Mitchell Ltd.
- 6 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.
- 7 Kennedy, P.; Gadd, J. 2002: Evaluation of road surface contaminant loadings in Waitakere City for the development of the vehicle fleet emission model-water. Report prepared for New Zealand Ministry of Transport by Kingett Mitchell Ltd.

1.3 Report Contents

This report is presented in six key sections following this introduction:

Section 2 provides a brief description of transport-derived contaminants. The section identifies the various sources of contaminants and describes how the use of motor vehicles produces contaminants that become incorporated into stormwater. This sets the scene for the environmental quality overview and effects evaluations that follow.

Section 3 provides a short overview of the road environment including information on street dust particulate composition. More detail on metals in road surface particulates is presented in Kennedy (2003).

Section 4 provides information on stormwater quality including data on the measured concentrations of key contaminants emitted by vehicles to the New Zealand environment.

Section 5 describes the pathways and fate of contaminants emitted by motor vehicles. An overview of the fate of airborne contaminants is provided as they contribute through deposition to aquatic systems. Information is provided for each of the key groups of contaminants and a brief summary is provided on the processes that influence their fate in the freshwater and marine environment.

Section 6 examines the effects of stormwater discharge to the freshwater environment. A number of topics are specifically dealt with including effects on habitat; invertebrates and fish in freshwater biological communities; effects on sediment quality and bioaccumulation of contaminants.

Section 7 examines the effects of stormwater discharge to estuarine and marine environments. The matters examined follow those examined for freshwater environments in Section 6.

2. TRANSPORT DERIVED CONTAMINANTS IN STORMWATER

2.1 Introduction

The assessment of actual and potential effects of motor vehicle emissions on aquatic ecosystems, requires an understanding of what contaminants are released by motor vehicles and the nature of those contaminants (contaminants refers to all losses and discharges from vehicles). Effects of contaminants (as discussed later in Sections 6 and 7 of this report) are a function of the concentration and load of a given contaminant entering the environment.

2.2 Sources

The New Zealand road vehicle fleet is dominated by petrol-fuelled vehicles, most of which are cars (about 1.8 million of 2.45 million vehicles). Contributions of transport derived contaminants to aquatic ecosystems occur as a result of direct contributions from road stormwater and from the deposition of material from the air. Moncrieff & Kennedy (2002) described the various sources associated with the motor vehicle that could contribute contaminants to the environment. This was presented as a functional framework. Table 2.1 provides a summary of the key sources and the materials involved in the potential release of contaminants as identified in Moncrieff & Kennedy (2002). However, a limited number of the operational areas within the motor vehicles are involved in most of the release of materials and contaminants to the environment. Fig. 2.1 provides a general illustration of those key sources.

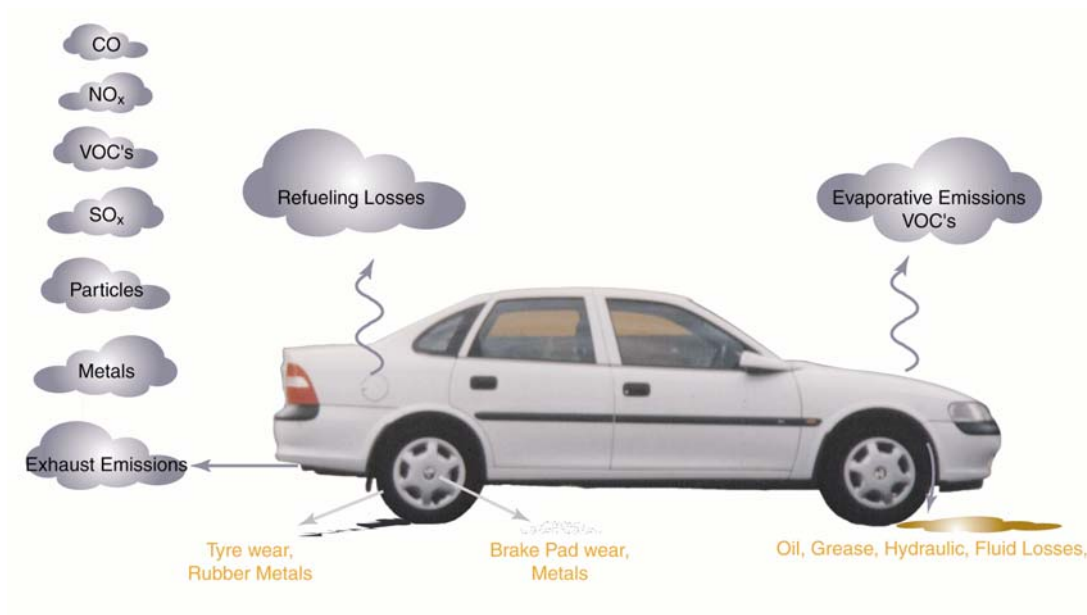


Figure 2.1 - Key sources of contaminants released by motor vehicles.

Table 2.1 - Contaminant Source Classification Framework.

Powertrain Area	Component
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

Kennedy et al. (2002) reviewed available information on the contaminants in key emission sources. Those sources considered in the report were tyres, friction linings (brake pads), exhaust emissions, loss of oil and grease and the wear of bitumen from road surfaces. Some of the information used in the review included analytical data for New Zealand tyres, brake pads and bitumen presented in Kennedy & Gadd (2000) and Gadd & Kennedy (2000).

Both Moncrieff & Kennedy (2002) and Kennedy et al. (2002) present information on the nature of contaminant sources and the nature of contaminants present in and emitted from the key contaminant sources. For further information and detail those reports should be referred to as the following sections provide an overview only of the contaminants in those sources.

2.3 Inorganic Contaminants

2.3.1 Fuel

Fuels contain low concentrations of a range of metals due to their presence in the original unrefined petroleum. Elements known to be present in elevated concentrations in crude oil and therefore possibly present in petrol include cadmium (Cd), chromium (Cr), nickel (Ni), zinc (Zn) and vanadium (V). Following earlier reductions in the lead (Pb) content of New Zealand petrol, it became illegal to sell leaded petrol in September 1996. As leaded petrol is no longer available for motor vehicles in New Zealand, Pb that accumulated in vehicle engines and exhaust systems prior to that date, should have been eliminated from vehicles by now. Although API (1985a,b) identify that there are low concentrations of metals in petrol, no information appears available on the concentration of metals in New Zealand petrol and diesel to confirm the significance of petrol combustion as an emissions source of metals in this country. Metals are not lost through evaporative processes. As such, the evaporative process is not considered to be a significant pathway for inorganic constituents to reach the road environment.

2.3.2 Oil and Grease

Oil contains a range of trace metals, the concentration of which is dependent on the origin of the crude oil utilised to manufacture refined oil. Some oils are synthetic and as such it is assumed that the commercial base product is generally trace element free (no specific elemental analysis of synthetic oils has been sighted). No information has been sighted on the metal content of new oils used in New Zealand motor vehicles. Motor vehicle oil accounts for about 40% of the oil consumed in New Zealand.

Internationally used oils have been shown to contain a wide range of trace element concentrations (refer Vasquez-Duhatt 1989). Low to moderate concentrations of many of the common metals are present in used oil (e.g., iron (Fe), Cd, Cu). The most abundant metal appears to be zinc with concentrations in the 1,000-2,000 mg/kg range. The limited New Zealand data indicates that used motor oil contains low concentrations of arsenic (As), Cd and mercury (Hg) (Moncrieff & Kennedy 2002). Used motor oils historically contained significant concentrations of lead (e.g., >2,000 mg/kg) however with the removal of lead (Pb) from petrol, these concentrations would have reduced significantly

A range of greases and other automotive products are used to maintain and improve the operation of motor vehicles. There are a wide variety of greases used in wheel bearings and other parts of the vehicle. These greases may contain constituents such as molybdenum disulphide which is a common component of grease. Other automotive products used on vehicles to reduce wear and prevent metal components locking contain a range of metal and organic compounds. In addition to molybdenum disulphide which again is a common constituent other metals such as Cu and Pb may also be present.

2.3.3 Brake Pads

Brake pads constitute a relatively complex source of inorganic contaminants due to the large variety of pads/linings on the New Zealand market (Moncrieff & Kennedy 2002). Table 2.2 provides a summary of the relative importance of trace elements in a selection of brake pads. It can be seen from that summary that the key elements in pads and therefore released from pads as they are worn are Fe, barium (Ba), Cu, Cr, Ni and Zn. Other elements such as Pb, antimony (Sb), titanium (Ti), zirconium (Zr) are also contributed by the wear of brake pads.

Kennedy & Gadd (2000) reported on the analysis of a number of brake pads and brake pad dust samples in New Zealand. The key elements present in the pads and dust are manganese (Mn) (181-1920 mg/kg), cobalt (Co) (11.6-45.8 mg/kg), Cr (39-1320), Cu (11-39,000 mg/kg), molybdenum (Mo) (0.4-215 mg/kg), Ni (44-660 mg/kg), Pb (1.28-1,290 mg/kg), Sb (0.07-201 mg/kg), tin (Sn) (<1-115

mg/kg) and Zn (25-34,500 mg/kg). This and international information was reviewed in Kennedy et al. (2002).

Table 2.2 - Summary of sources of elemental contaminants in motor vehicle emission sources.

Element		Environmental Significance	Key Sources		
			Tyre	Brake linings	Road surface
Li	Lithium		-	T	T
Be	Beryllium	EPA	T	T	-
B	Boron		-	P	-
Na	Sodium		P	P	P
Mg	Magnesium		T	AB	-
Al	Aluminium		T	C	-
P	Phosphorus		T	P	C
K	Potassium		P	C	-
Ca	Calcium		P	AB	-
Sc	Scandium		-	T	E
Ti	Titanium		-	P	-
V	Vanadium		-	-	P
Cr	Chromium	EPA	T	AB	-
Mn	Manganese		T	C	-
Fe	Iron		P	AB	-
Co	Cobalt	EPA	T	C	-
Ni	Nickel	EPA	-	AB	P
Cu	Copper	EPA	T	AB	-
Zn	Zinc	EPA	AB	AB	P
Ga	Gallium		-	T	T
Ge	Germanium		-	T	-
As	Arsenic	EPA	-	P	-
Se	Selenium	EPA	-	-	-
Rb	Rubidium		-	P	-
Sr	Strontium		T	C	C
Nb	Niobium		-	T	-
Mo	Molybdenum		T	P	T
Rh	Rhodium			Exhaust	
Pd	Palladium			Exhaust	
Ag	Silver	EPA	-	T	-
Cd	Cadmium	EPA	T	P	-
Sn	Tin		-	P	-
Sb	Antimony	EPA	T	C	-
Cs	Cesium		-	T	T
Ba	Barium		P	AB	AB
La	Lanthanum		-	T	-
W	Tungsten		-	-	-
Pt	Platinum			Exhaust	
Au	Gold		-	-	-
Hg	Mercury	EPA	-	P	-
Tl	Thallium		-	-	-
Pb	Lead	EPA	P	C	-
Bi	Bismuth		-	-	-
Ce	Cerium ^x		T	T	T
U	Uranium ^{xx}		-	-	-

* representing lanthanides elements. ^{xx} representing actinide elements. EPA – US Environmental Protection Agency priority pollutant elements. AB – abundant; C – common; P – present; T – trace.

2.3.4 Tyres

Tyres contain relatively few inorganic contaminants compared to brake pads. Kennedy & Gadd (2000) reported on the analysis of a selection of tyres used in New Zealand. Table 2.2 provides a relative summary of the presence of inorganic elements in tyres. The concentration of most inorganic constituents is low. Zinc is the only trace element present in substantial amounts (1190-13,800 mg/kg). Elements such as Fe (30-220 mg/kg), Pb (0.8-9.7 mg/kg), Ba 8.78-166 mg/kg), Cd

(<0.05-0.56 mg/kg) are also present. Moncrieff & Kennedy (2002) provide an overview of tyre composition and the international literature.

2.3.5 Emission Control Technologies

Emission control technologies are now present on virtually all new and used motor vehicles imported into New Zealand. Metals such as platinum (Pt), palladium (Pd) and rhodium (Rh) (the Platinum Group metals – PGMs) are used as catalysts in catalytic converters that reduce emissions of hydrocarbons, NO_x and CO. Platinum (Pt) (attached to aluminium oxide particles) has been found in the particulate contaminants emitted from vehicles using Pt coated catalytic converters. Emission control technology for diesel engines is discussed in Chapter 3 of MOT (1998). A range of different emission control devices are employed or under study. Of note are trap oxidiser systems that trap solid particulates then burn-off the trapped material. A number of experimental trap systems (not used in New Zealand) utilise rare earth oxides (such as cerium oxide) resulting in their release to the environment as part of the process. Helmers (1996) discussed the use of cerium in catalytic converters and the presence of the elements zirconium (Zr), lanthanum (La) and neodymium (Nd). Kennedy et al. (2002) discuss the composition and contribution of PGMs from exhaust systems to the road environment.

2.3.6 Road Surface

Road surface composition and other highway/roadway features (e.g., presence of walls, or galvanised metal crash barriers and road marking paints) have the potential to influence the composition of road and gutter dusts and stormwater. The possible influences are dependent upon the composition and nature of the road surface materials as described below. The concentration of metals and other elements can be influenced by the higher concentrations in the contributing material and the diluting effects if the concentration of an element is low and the wear particulate contribution from the source. A range of paints are utilised in road markings on New Zealand roads. Most paints are coloured white, yellow or black. The paints used include chlorinated rubber based, alkylal and water based paints. Full composition of paints used on roads has not been assessed. Sullivan et al. (1977) found that 25% of the dust on street surfaces may be associated with the wear of the pavement surface.

Aggregate and other materials

The type of aggregate may influence sediment quality in relation to metal concentration in some instances. However, the use of greywacke aggregate as used in most parts of New Zealand will result in a relatively 'neutral' influence on metal concentrations. Use of basalt chip in an area where greywacke is the geological parent material (forming soils and sediments) may result in an apparent difference due to the presence of some trace elements in basalt at higher concentrations than in greywacke/argillite (e.g., the elements Cr, Ni). The use of re-cycled materials (e.g., blast furnace slag) in road paving may also result in changes in the composition of street dusts and or stormwater transported sediments.

Concrete

Concrete also has the potential to contribute metals to stormwater as the concentration of a number of trace elements are elevated in concrete compared to average crustal abundance. Elements which are elevated in Portland cement compared for example to geological parent materials such as greywacke (which are common within New Zealand) include Ni, Cr, silver (Ag), thallium (Tl) (PCA 1992).

Bitumen

Bitumen is produced in New Zealand at the Marsden Point Refinery and its composition will reflect the source of the crude oil from which it was derived (the source changes over time). The concentration of elements such as Hg, Ni, V and Zn vary considerably between crude oils. Shaheen (1975) reported data on the concentration of metals in bitumen including Cr (350 mg/kg), Cu (50 mg/kg), Ni (up to 1,200 mg/kg), Zn (164 mg/kg). Lindgren (1996) reported lower concentrations of trace elements in a bitumen binder (identified as B180). Nickel, chromium and zinc were present at <35, <17 and <17 mg/kg respectively. Lindgren (1996) cited data from Baekken (1993) that indicated that nickel was detected at 23 mg/kg (range 15-100) and vanadium was present at 340 mg/kg (range 50-600). These examples suggest that the bitumen composition is variable and most likely dependent upon the nature and source of the bitumen.

New Zealand bitumen has been examined for inorganic constituents and organic compounds (Kennedy & Gadd 2000; Kennedy et al. 2002). Concentrations of most elements in raw (synthetic) bitumen are low with Kennedy & Gadd (2000) noting only identifiable concentrations of Ba, Mo, Ni and Zn.

2.4 Organic Contaminants

2.4.1 Fuel Evaporation and Combustion

Fuel evaporation results in the loss of hydrocarbons. Evaporative losses occur during running, during refuelling and when the engine is stopped and is still hot (referred to as hot soak). Evaporative emissions are simpler to identify than combustion sources as they reflect the composition of the original fuel. The key constituents of petrol evaporation are the alkanes butane, pentane and hexane with minor amounts of BTEX. Information on VOCs in vehicle emissions is available from a wide range of studies. Although none of these are New Zealand in origin they provide useful data on the typical composition of the emissions from motor vehicles.

A significant amount of benzene in tailpipe emissions comes from the incomplete combustion of compounds such as toluene. Other tailpipe emission constituents such as formaldehyde, acetaldehyde, 1,3-butadiene are also products of incomplete combustion. A wide range of VOCs are present in urban air from various sources and this confounds the identification of organic compounds in stormwater sourced from motor vehicles.

PAHs are an important component of motor vehicle exhaust emissions. A number of international studies have been conducted to characterise the PAH compounds present in motor vehicle exhausts. Characterisation of tailpipe emissions has shown that there are a large number of different PAH compounds present. Concentrations in particulates may reach high concentrations (for example, 694 mg/kg pyrene).

In New Zealand, Bingham et al. (1990) have shown that although some PCDD and PCDF species may be emitted in car exhaust the concentration of the key compound (2,3,7,8-TCDF) was low compared to published data. It was concluded by Bingham et al. (1990) that vehicles were not a major contributor of dioxins to the New Zealand environment.

2.4.2 Oil and Grease

Dripping of oil from engines represents a direct loss of hydrocarbons to the road surface (Moncrieff & Kennedy 2002). A range of hydrocarbons are present in oils including VOCs such as BTEX and PAHs. Donkelaar (1990) reported that 140 different PAHs have been found in used oil from crankcase lubricated engines. The PAHs may reach high concentrations (e.g., 270-400 mg/L). Kennedy et al. (2002) provide an overview of the composition of oil potentially lost from vehicles to the road surface.

2.4.3 Brake Pads

Brake pads contain a complex range of organic compounds as a result of the inclusion of a range of resins, binders and fillers in the pads. The general composition of pads is provided by Kennedy et al. (2002). Specific information is available on the concentration of some key organic compounds based upon the examination of a limited number of New Zealand brake pad samples (Gadd & Kennedy 2000). Key organic compound groups present include phenols, phthalates, amines and amides and benzothiazoles amongst others.

2.4.4 Tyres

Tyres are composed of synthetic and natural rubbers. Kennedy et al. (2002) provides information on the general composition of tyres and reviews what is known about the composition of tyres in New Zealand and overseas. The New Zealand tyre information comes from analytical data presented in Gadd & Kennedy (2000). That data showed that tyre particulates are dominated by n-alkanes and alkanolic acids and natural resins. PAHs are relatively important constituents with other compound groups such as benzothiazoles, aromatic and heterocyclic amines and phenols also contributing significantly.

2.4.5 Road surface wear

Most road surfaces in New Zealand are composed of bitumen (and aggregate). Kennedy et al. (2002) provide background information on the nature of road surfaces in New Zealand and summarise the results of bitumen analysis presented in Gadd & Kennedy (2000). Bitumen is dominated by n-alkanes with the bulk being $>C_{29}$. Bitumen and asphalt contains a range of biological markers. These compounds include terpanes which comprise cyclic compounds such as hopanes and steranes. Bitumen contains PAHs but typically only at low concentrations. Total PAH concentrations appear to be in the order of 10 mg/kg with concentrations of many individual PAHs being in the range 1-3 mg/kg.

Concentrations of organic compounds are low with a nominal concentration of 10 mg/kg of total PAH identified (Gadd & Kennedy 2000). Takada et al. (1990) found that the PAH concentration of asphalt was found to be lower than that measured in Tokyo street dusts.

2.5 Summary

Motor vehicles are relatively complex emissions sources. Firstly they comprise multiple sources with their own contaminant signatures (tyres; brake pad wear; exhaust emissions; oil, grease and collant losses etc.). Secondly for many of the sources there is considerable variability in the contaminants emitted and the amount emitted as there are a large number of different manufacturers involved in the production of motor vehicles and their parts. For some emission sources there are hundreds of different types of a particular component many of which have different contaminant signatures. This results in potential for considerable variation between countries and over time in contaminant emissions from some sources

For inorganic contaminants (e.g., the trace elements including the heavy metals), there is a reasonable understanding of what elements are present in the sources and in emissions. There is a degree of uncertainty in relation to the variability of some elements that are key constituents of some sources (e.g., Cu in brake pads). This uncertainty arises because of the variation in brake pad specifications between manufacturers. There is less information on the variability in the concentration of some elements for whose presence in emission sources has only relatively recently been confirmed.

For organic compounds there is a less clear picture as to what is emitted from the various emission sources. For exhaust emissions, there is a large body of published research data that examines the

differences between petrol and diesel emissions. The published data provide a good picture of the nature of VOCs in exhaust emissions. There is also good data for some groups of compounds such as the PAHs and their derivatives and also the dioxins and furans. However there are a range of other compounds for which there appears to be less information available. For the solids sources such as tyres and brake pads the amount of information is significantly less. There have been a number of studies that have produced very useful data for the characterisation of these sources. There is considerable variation in the composition of sources such as brake pads leading to uncertainty as to the nature of compounds present (e.g., the occurrence of phthalates in brake pads).

3. ROAD ENVIRONMENT

3.1 Introduction

This section of the report examines the quality of material present on road surfaces that contributes to the particulate material in stormwater. The interpretation of the effect that motor vehicles have on urban stormwater quality is complicated by the influence of other adjacent urban activities. In both general urban stormwater and specific highway runoff, deposition of particulate matter from the atmosphere will contribute material not entirely derived from motor vehicle emissions. Table 3.1 provides a general summary of the sources of material that contribute to general urban stormwater quality. The influence that motor vehicles have on road dust quality is determined by the relative contributions of those contaminants from other urban sources. The material's quality on those roads in rural and urban locations with no significant urban activities adjacent to the road will reflect the contribution from vehicles, the deposition of contaminants from the atmosphere and from wind blown soils etc., from adjacent areas and the contribution from the wear of the road surface.

Table 3.1 - Summary of key sources contributing to general urban stormwater quality (Adapted from ARC 1992).

Source	Comment on Source
Motor Vehicles	Vehicle exhaust emissions, oil and lubricating losses, wear of vehicle body, tyre and brake wear.
Road Surface	Wear and breakdown of road surface including aggregate and other material used in base course and surface, bitumen, concrete and other materials used on road surface (e.g., marking paint).
Litter/Organic Debris	Wide variety of litter and debris of inorganic origin (metal, glass, plastic) and organic (food, paper, plant, litter and animal waste) origin.
Buildings	Corrosion and other weathering products from adjacent buildings including dry and wet losses. Includes losses such as Cu from Cu facings and gutters, roof runoff (paint fragments etc.).
Construction	Building maintenance and construction produces a wide variety of inorganic dust and other debris (e.g., paint waste).
Soil	Wind and rain will transport fines in soils from adjacent areas onto roadways. Materials are typically silts, clays and sands with low organic content.
Rainfall	Atmospheric washout will contribute fine particulate material present in urban air. Sources will be site specific. A portion will be local and vehicle derived.

The quality of the particulate material on the road surface and available for transport by stormwater will influence the quality of sediments in adjacent depositional receiving environments. To ascertain the contribution of contaminants from motor vehicles and understand the contribution they make to any identified adverse effects in the receiving environment requires that the contaminant presence and contribution from the road environment be understood.

3.2 Street and Gutter Dusts

3.2.1 General Composition

Gutters on roadways with kerb and channelling are points that dust and debris accumulate until washed into the stormwater system. Examination of the quality of this material provides information

on the nature of the particulate material transported by stormwater and distributed within the receiving environment. In New Zealand there have been a number of investigations of urban gutter dust quality but few of these studies have examined the general composition of gutter dusts. Overseas, Ellis (1976) provided data on the gross composition of gutter dusts. In New Zealand, ARC (1992) examined the material in gutter dusts in the suburbs of Pakuranga (low and high-density traffic residential) and Southdown (industrial), Ng et al. (2003) in Auckland City and Kennedy & Gadd (2003) in Waitakere City. Composition of the particulate matter in urban street gutters can be summarised as follows:

- ❑ Inorganic matter sourced from road and pavement materials and adjacent soils can make up to 45 to 70% of the mass of material present (Ellis 1976). ARC (1992) estimated that 15 - 60% of the material present in the gutter dust samples collected in that study in Auckland was inorganic.
- ❑ Rubber fragments from tyre wear are common.
- ❑ Metal fragments, rust and other ferromagnetic materials are common (Fergusson et al. 1980).
- ❑ Litter such as paper, glass, plastic and other debris is common (ARC 1992).
- ❑ Organic debris from plants and lawn clippings may be present but the amount tends to be seasonal and varies between areas depending upon landuse (e.g., residential streets, motorway grass verges, median strips etc).

3.2.2 Particle sizes

The particle size distribution on the road surface is a function of a number of factors including the wear and particle size of eroded materials from the road surface, external soil and dust sources and their availability and the particle size of wear and emission products from motor vehicles. On the road surface, sorting by wind and water would be expected to produce a log-normal distribution of particle sizes amongst road surface particulates (Sartor & Boyd 1972, Shaheen 1975, Ellis & Revitt 1982).

ARC (1992) presented data on the grain size distribution of road gutter dust samples from Pakuranga and Southdown in Auckland. Gutter sediments were dominated by particles in the range 0.12 to 1.0 mm (69% and 59% by weight respectively) with only 2.0-3.6% in the <47 µm size range and 6.1-11.2% <0.12 mm. Elsewhere in New Zealand, gutter dusts in Wellington were found to contain 18.7% of particles < 0.15 mm (Kennedy unpublished) and modal size in the range 0.25 - 0.5 mm. Similar grain size distributions have been found in other studies. Table 3.2 provides a summary of the proportion of finer particles in road surface material.

Ng et al. (2003) undertook a comprehensive look at the particle size distribution on road surface material on streets in Remuera (Meadowbank catchment), Hillsborough and Mt Roskill (Oakley catchment) during 2002 and 2003 (vacuum collection from defined road area across road width). 2.4, 4-20% of the total mass of the material collected was >2 mm in size and <5% of the material was <0.045 mm in size. Kennedy & Gadd (2003) reported data for coarse particle size analysis of a range of samples of road surface material collected systematically from roads in Waitakere City (vacuum collection from defined road area across road width). The median % of the material <0.063 µm was 7% and was similar to that identified by Ng et al. (2003) in Auckland City. The Waitakere data identified a median % >2 mm of 29 %. This figure is higher than that observed by Ng et al. (2003) where the maximum % of material >2 mm observed was 20%.

In the study carried out by Ball et al. (1998), the particle distribution for the 10%ile and 90%ile diameters were 16 and 189 µm. Particle size determinations are determined to some extent by the method of sampling (both the equipment used – brush and pan or wet or dry vacuum) and the location of sampling. However, the result of these differences tends to be a relative increase in the proportion of the smaller particles as the removal technique becomes more efficient.

Table 3.2 - Summary of particle size composition data for road surface material.

Location	Particle size	%	Particle size	%	Reference
Auckland	<0.045 mm	<5	<0.106 mm	12	Ng et al. (2003)
Waitakere City	<0.063 mm	7	-	-	Kennedy & Gadd (2002)
Christchurch			<0.11 mm	10-20	Fergusson & Ryan (1984)
Los Angeles	<0.043 mm	5.9	<0.25 mm	39	Lau & Stenstrom (2001)
	<0.074 mm	3.6	-	-	Malmquist (1978)
	<0.043 mm	6	<0.2 mm	16.8	Ball et al. (1998)
	<0.043 mm	5.9	-	-	Sartor & Boyd (1974), Ellis & Revitt (1982)

Table 3.3 provides a comparison between the data obtained by ARC (1992) and Lau & Stenstrom (2001). That data which generally reflects the data found in other studies shows that up to 5% of the material sand size and smaller may be silt and clay sized. The data from those studies also shows that typically about 10% of the material < 2 mm in size is <0.12 mm. A number of authors have commented on the contribution that road surface wear makes to the materials present on the road surface. Such assessments have included 10% (Schaefer & Hay 1983) and 27% (Sullivan et al. 1977). No specific motorway studies have been sighted that specifically deal with particulate material sources on the roadway surface. Some differences might be expected as a consequence of higher vehicle speeds and vehicle generated turbulence resulting in movement and sorting of particulate materials on the road surface.

Table 3.3 - Comparison of grain size fractions in urban road street dusts from Auckland and Los Angeles (all data % dry weight).

Lau & Stenstrom (2001)		ARC (1992)			
Particle size class (mm)	% Total and % of material passing 2 mm	Particle size class (mm)	Pakuranga - residential (low traffic) % < 2mm	Pakuranga - residential (high traffic) % < 2mm	Southdown - industrial % < 2mm
>2.2	11 (0)	>2.0	0	0	0
0.841-2.2	16 (18)	1-2	16.5	15.5	13.4
0.25-0.842	34 (38.2)	0.5-1	23.7	24.6	31.8
		0.25-0.5	28.0	31.1	28.4
0.1-0.25	29 (32.6)	0.12- 0.25-	20.7	22.6	18.4
0.043-0.1	9 (10.1)	0.047-0.12	7.9	4.1	5.5
<0.043	1 (1.1)	0.02-0.047	3.2	2.0	2.6

No specific assessment has been sighted that has specifically identified the contribution that motor vehicles make to the particulate material present on urban street surfaces and in street gutters. An examination of gutter dusts in the general urban environment in New Zealand (e.g., ARC 1992) does not show motor vehicles as a dominant contributor of the visible materials present. Examination of the key motor vehicle emission sources provides information on the nature of the size of particulates emitted by motor vehicles that might reach the road surface. Kennedy et al. (2002) reviewed particle nature information for the key emission sources. The following points can be made:

- ❑ The wear of brake pads results in particles with a size range of 1-3 μm . In one study (Garg et al. 2000) 86% of all particles were <10 μm in size, 63% were <2.5 μm in size and 33% were <0.1 μm .
- ❑ Rogge et al. (1993) reported that 10% (by mass) of tyre tread particles are < 3 μm in diameter.
- ❑ Fuel combustion typically produces small particles in the 0.05-0.7 μm diameter range with an average of around 0.2 μm .

As such, available information indicates that the size of particles produced by the key motor vehicle emission sources is small and as a result they contribute directly to the small particle size composition present on road surfaces and they contribute to the larger size particles through aggregation and attachment to larger particles. Tyres do produce larger particles but there is little data on the actual particle size distribution of fragments worn from tyres. It is evident when comparing the particle size of the key vehicle contaminant sources with the size distribution of particles on road surfaces that the bulk of the material present on road surfaces within urban environments is derived from the road surface and elsewhere.

Overall, particulate matter on road surfaces (in gutters) is dominated by sand sized particles. A range of inorganic (inorganic material derived from the road surface, debris derived from vehicles and litter) and organic particles (e.g., plant leaves) will also be present some of which will have been derived from motor vehicles, their occupants and activities and people on adjacent pavements and land. The contribution from motor vehicles to stormwater particulate concentrations in terms of road wear and vehicle contributions does not appear to have been defined well but the contribution appears to be more important for the smaller particle sizes especially those in the < 63 µm size range.

3.2.3 Metals

A considerable amount of data has been collected on the quality of the dusts and sediments collected in urban street gutters overseas. Examples of studies reporting on the quality of gutter dusts overseas include Pitt & Amy (1973) and Fergusson & Ryan (1984). In New Zealand, there is also a good database of information on the quality of gutter dusts in urban areas. The majority of the published data is from Christchurch (Fergusson et al. 1980, Fergusson & Simmons 1983) and Auckland (ARC 1992, Ng et al. 2003, Kennedy & Gadd 2003) but unpublished data is also available for Wellington (Kennedy unpublished data). This information has been reviewed in Kennedy (2003).

Table 3.4 provides a summary of data for the concentration of key trace elements reported in New Zealand studies of urban gutter dust quality. The lead data presented in Table 3.4 was all obtained after the removal of Pb from New Zealand petrol. In the table, data that exceeds the typical background sediment values and measured concentrations are attributable in part to emissions from motor vehicles are highlighted.

Fergusson & Ryan (1984) examined a total of 26 elements in street dusts in a range of cities that included Christchurch. The analytical parameters examined included common metals (e.g., manganese (Mn), Iron (Fe)), environmentally important metals (e.g., arsenic (As), antimony (Sb)), rare earth elements (e.g., lanthanum (La), cerium (Ce), samarium (Sm), hafnium (Hf) and precious metals (e.g., gold (Au)). Kennedy (unpublished data) examined the distribution of 23 elements in street dusts from Wellington including environmentally important elements such as Hg and uncommon elements such as molybdenum (Mo), niobium (Nb), yttrium (Y), and gallium (Ga). Results for key elements from that dataset are presented in Table 3.2. Specific data and details can be found in Kennedy (2003).

In these studies, variability was encountered in trace element concentrations and in some cases the concentrations were notably elevated (e.g., mercury (Hg) in commercial streets in Wellington, Au in New York streets). However, for most elements, there was insufficient understanding of the variability in the element concentration to determine the magnitude of any increase (e.g., for elements such as vanadium (V)). In addition, although Fergusson & Ryan (1984) discussed the motor vehicles as sources of some of the common elements no assessment of the contribution from motor vehicles was made.

Table 3.4 - Summary of trace element concentrations in New Zealand roadway gutter dusts in (all data mg/kg dry weight unless noted).

Element	Location	Fraction analysed	Median	Minimum	Maximum	N	Ref	Year of sampling
Antimony	Well	<2 mm	11.4*	5.0	43.6	24	1	1978
	ChCh	<0.963 mm	8.9	3.9	22	3	4	1984
Arsenic	Well	<2 mm	6.1	2	10.6	65	1	1978
	ChCh	<0.963 mm	8.25	5.3	11.2	2	4	1984
Barium	Well	<2mm	575	326	3216	93	1	1978
Cadmium	Well	<0.035 mm	2.2*	0.18	8.9	26	1	1978
	Auck	<2mm	0.51	0.51	0.56	3	2	1992
	ChCh	<0.963 mm	1.1	0.8	1.1	3	4	1984
Chromium	Auck	<0.047	0.88	0.68	1.33	3	2	1992
	Well	<2 mm	73	35	703	94	1	1978
	ChCh	<0.963 mm	58	38	76	3	4	1984
Cobalt	Well	<0.035 mm	118	105	121	3	1	1978
	ChCh	<0.963 mm	10.3	9.3	36	3	4	1984
Copper	Well	<2 mm	184	32	1572	94	1	1978
	Auck	<2 mm	318	166	447	3	2	1992
	ChCh	<0.963 mm	106	48	258	3	4	1984
	Auck	<0.047 mm	428	139	432	3	2	1992
	Well	<0.035	488	264	649	3	1	1978
Gold	ChCh	<0.963 mm	0.01	0.01	0.02	3	4	1984
Iron %	Well	<2 mm	3.39	1.64	7.23	92	1	1978
	ChCh	<0.963 mm	2.39	2.36	5.82	3	4	1984
	Well	<0.035 mm	5.02	3.82	5.80	3	1	1978
Lead	Well	<2 mm	1977	207	20,842	94	1	1978
	ChCh	<0.963 mm	1294	887	10,070	3	4	1984
	Well	<0.035 mm	6783	4481	16,609	3	1	1978
	Well	<0.035 mm	2356*	527	5,240	33	1	1978
	Auck	<0.035 mm	1620*	285	10,642	48	3	1988
Manganese	Well	<2 mm	525	251	1,036	92	1	1978
	ChCh	<0.963 mm	399	381	399	3	4	1984
	Well	<0.035 mm	617	558	619	3	1	1978
Mercury	Well	<2 mm	0.68*	0.054	6.48	35	1	1978
	Auck	<2 mm	0.08	0.04	0.09	3	1	1992
	Auck	<0.047	0.13	0.08	0.17	3	2	1992
Nickel	Well	<2 mm	22	12	48	94	1	1978
	Well	<0.035 mm	30	21	41	3	1	1978
Silver	Well	<2 mm	2.3*	<1	10.2	32	1	1978
Tin	Well	<2 mm	11.8*	4	23	15	1	1978
Titanium	Well	<2 mm	2,986	1,726	6,152	94	1	1978
	ChCh	<0.963 mm	2,364	1,854	2,901	3	4	1984
	Well	<0.035 mm	3585	3512	3710	3	1	1978
Vanadium	Well	<2 mm	68	37	92	94	1	1978
	ChCh	<0.963 mm	48	41	68	3	4	1984
	Well	<0.035 mm	84	84	93	3	1	1978
Zinc	Well	<2 mm	689	141	4,377	94	1	1978
	ChCh	<0.963 mm	429	365	850	3	4	1984
	Auck	<2 mm	431	315	504	3	2	1992
	Auck	<0.047 mm	431	315	504	3	2	1992
	Auck	<0.035 mm	420	305	811	3	2	1992
	Well	<0.035 mm	1,593	1,343	3,357	3	1	1978
	Well	<0.035 mm	1,052*	303	2,377	16	1	1978
	Auck	<0.036 mm	-	395	4246	34	3	1983-84

Notes: ¹ Kennedy unpublished. ² ARC (1992). ³ Kennedy et al. (1988). ⁴ Fergusson & Ryan (1984). * - Mean.

The data available within New Zealand is similar to that obtained overseas in a variety of studies (Table 3.5). Brockbank et al. (1999) reported on the concentration of a number of key elements in the <1 mm fraction of material collected from the road surface at two locations in Sydney.

An examination of the international and New Zealand gutter dust chemistry data shows that the three most commonly identified contaminants are copper (Cu), lead (Pb) and zinc (Zn). Increases in the concentration of cadmium (Cd) are also reported. These increases are not unexpected given the available sources of these contaminants on roadways.

A range of other trace and major elements will be present in street and gutter dusts due to the wide range of elements present in the general urban environment and released from motor vehicles (Refer Kennedy 2003). The concentrations of these elements will depend upon the overall contribution from sources on motor vehicles relative to other sources. It is evident from the available data on street dusts that a number of elements are present in road dusts and sediments in higher concentrations than would be expected naturally. A number of these are associated with various motor vehicle emission sources (refer Section 2). Apart from the more common elements such as Fe, Pb, Cr, Ni, Cu, Cd those elements present in higher concentrations than background include antimony and molybdenum.

Table 3.5 - Selected international gutter dust metal concentrations (all data mg/kg dry weight unless noted).

Element	Brockbank et al. (1999)		Lau & Stenstrom (2001)	Li et al. (2001)	Yim & Nau (1987)**
	Mascot, Sydney	Gymnea, Sydney	Los Angeles	Hong Kong	Hong Kong
Cadmium	0.4-1.3	0.2-1.2	1 (5)*	3.77	7.6
Copper	97-280	51-330	236 (221)	173	635
Chromium	-	-	29 (47)	-	-
Iron %	1.6-2.9	2.6-3.4	-	-	-
Lead	230-1600	520-1600	144 (349)	181	1,287
Manganese	220-450	230-340	-	-	-
Nickel	-	-	26 (64)	-	-
Zinc	440-850	300-560	367 (974)	1,450	2,902

Notes: * - whole sample and (<0.047 mm). ** - Cited in Li et al. (2001).

Antimony was identified in moderate concentrations in some brake pads (refer Table 2.1 and also Kennedy & Gadd 2000). Ondov et al. (1982) identified Sb in airborne particulates in highway tunnels. The highest concentrations were observed in particles of 1-4 µm in diameter and typically did not appear to be associated with exhaust particles but rather re-entrained road dust. Helmers (1996) and also Dietl et al. (1996) reported Sb concentrations in deposition and grass (cultures) adjacent to roads in Germany. Their study found a general correlation between traffic intensity and the concentration of Sb in deposition and grass.

The use of metals in emission control systems in motor vehicles, results in changes in the concentration of contaminants in road environments. Platinum (Pt) and other elements used in catalytic converters are found in elevated concentrations in road environments. In Section 2, the possible emission of the lanthanide element Ce from diesel emission control devices was identified. There does not appear to be any published data on Ce in roadway dusts that identifies vehicles as a source of Ce causing elevated concentrations in road dusts.

3.2.4 Organic Compounds

In contrast to metals, there appears to be only limited data for organic compounds in gutter dusts both overseas and in New Zealand. Organic compounds present in gutter dusts will include BTEX and other volatile hydrocarbons, PAHs and a wide range of less common compounds as described for air and emissions earlier in Section 2 (which have become associated with particulate matter). Section 5 provides an overview of the fate of organic compounds as it pertains to effects). Studies on the

organic compound contaminants in gutter dusts encompass a wide range of compounds such as pesticides that are used in urban environments. These compounds may reach roadways via atmospheric deposition and overland runoff.

ARC (1992) reported on the concentration of polycyclic aromatic hydrocarbons (PAHs) and a range of organochlorine compounds in road gutter dusts from Pakuranga and Southdown. The data presented in ARC (1992) comprised information on PAHs in a series of particle size separates. The concentrations measured in the two finest particle size fractions are presented in Table 3.4. PAH concentrations were dominated by fluoranthene, pyrene and chrysene/benz[a]anthracene which made up about 65% of the nine PAHs examined. Table 3.4 provides comparative data on the concentration of PAHs in road edge soil adjacent to a major road in Brisbane with 35,600 VPD (Yang et al. 1991) and PAH concentrations in road dust fractions from Santa Monica, California and Germany (Lau & Strenstrom 2001 and Krein & Schorer 2000). Concentrations were generally similar between the studies.

Table 3.4 - Summary of PAH concentrations in road gutter dust fractions (all data µg/kg, dry weight).

Location	Olwiger Bach Germany ⁴	Santa Monica roads ³		Pakuranga ¹		Southdown ¹		Waitakare City ⁵	Brisbane ² Roadside
Size Fraction (mm)	<2 to 63- 200 µm	<43- 100 µm	<43 µm	47-120 µm	<47 µm	47-120 µm	<47 µm	<63 µm	
Naphthalene	-	-	-	-	-	-	-	<200	-
Acenaphthylene	-	-	-	-	-	-	-	<40	-
Acenaphthene	-	-	-	-	-	-	-	175	-
Phenanthrene	183-1,022	215	515	-	-	715	-	120	715
Anthracene	24 – 147	169	23	22	20	27.8	10	<40	27.8
Fluoranthene	350 – 1,958	224	846	335	545	174	230	208.5	174
Fluorene	-	-	-	-	-	-	-	<40	-
Pyrene	-	444	816	315	560	214	240	275	214
Benz[a]anthracene	-	162	198	-	-	158	-	-	158
Chrysene/benz[a]anthracene	-	263	653 ⁵	290	445	414	120	101.5	414
Benzo[b]fluoranthene	-	-	-	180	270	-	10	135	-
Benzo[k]fluoranthene	-	-	-	70	105	201	40	<50	201
Benzo[e]pyrene	-	820	372	-	-	411	-	-	411
Benzo[a] pyrene	-	541	229	155	210	363	85	70	363
Perylene	-	-	-	-	-	147	-	-	147
Dibenz[a,h] anthracene	11-83	-	-	40	55	-	20	<30	-
Indeno[1,2,3-cd]pyrene	76-402	-	-	-	-	584	-	58	584
Benzo[g,h,i]perylene	217-710	-	-	260	280	598	230	175	598
Coronene	-	-	-	-	-	98.6	-	-	98.6
Total PAH	-	-	-	1,617	2,490	3,346	1085	1,462	3,346

Notes: ¹ ARC (1992); ² Yang et al. (1991). ³ Lau & Stenstrom 2001. ⁴ Krein & Schorer (2000); ⁵ Kennedy & Gadd (2003); ⁶ chrysene/triphenylene.

International studies such as Takada et al. (1990), examined the PAH composition of street dust samples from the Tokyo metropolitan area (36,000 VPD). Total PAH concentrations were in the order of 1,000 µg/kg and higher. The authors examined street dust composition in addition to source materials. Some 64 PAHs were identified in the street dust samples from three ringed phenanthrene (MW 178) to dibenz[a,h]anthracene (MW 278). The street dust PAHs are typically dominated by unsubstituted PAHs and four and five ring PAHs are important. Compositional differences will appear between samples depending upon the contribution from motor vehicles and other combustion sources but generally, the composition of street dusts and emission samples are similar.

Yang et al. (1999) examined the dry deposition of particulates and PAH at two traffic intercessions in Kaohsiung City in southern Taiwan. PAHs are emitted from vehicle exhausts in both gas and particulate phases. The PAHs were identified as contributing only a very small amount of the overall particle deposition. The PAH deposition was considered to be associated with coarse particulates (e.g., >10 µm) through gravitational settling. The contribution of dry-deposition flux from exhausts was more significant for the low MW PAHs than the higher MW PAHs. The relative importance of the individual PAHs to the PAH deposition flux at the two sites were 24.6%, 42.3% for naphthalene; 30.2%, 31.6% for acenaphthylene; 9.99%, 6.81% for phenanthrene; 5.77% for pyrene at one site; 17.6% for fluorine at one site and <5% for the other 17 PAHs. This relative difference arises because the lower MW PAHs have higher gas-phase concentrations in the exhausts of vehicles.

There appears to be relatively little New Zealand data on the presence of vehicle derived organic compounds in roadway dusts and sediments. No data has been sighted on organic compounds in the dusts and sediments on highway or isolated roadways such as bridges in New Zealand. The PAH data reported by ARC (1992) for Pakuranga and Southdown in Auckland is generally similar to the data reported from a number of international studies. Further information is however available in relation to stormwater quality and this is dealt with in Section 3.3.4.

3.2.5 Other Constituents

A range of other constituents is present in roadway gutter dusts. ARC (1992) provides data on a range of other constituents in gutter dusts in Auckland. Organic carbon content of gutter dusts varied depending upon adjacent land uses (e.g., presence of trees and other plants). Concentrations are typically 1- 10% with coarse particulate fractions being an important contributor. Organic matter will be an important contributor to biological oxygen demand. ARC (1992) found concentrations of total Kjeldahl nitrogen of up to 0.5% in residential gutter dusts in Auckland. Variations in concentration were attributed to variations in the availability of plant debris. Phosphorus concentrations in gutter dusts varied but not significantly with up to 153 mg/kg of available phosphorus measured.

Ng et al. (2003) reported results for strong acid extractable phosphorus in particulate material from Auckland City Streets. Their results which included analysis of a range of particle size fractions and showed larger inter-site differences than differences between particle size fractions. Concentrations for most sites and particle fractions were 500-1,500 mg/kg.

Overall, concentrations of N and P in the particulate matter on urban streets reflects the surrounding land use. No specific highway gutter dust data has been sighted where no adjacent land use contribution would confound the assessment of motor vehicle contributions of nitrogen and phosphorus to roadway sediment chemistry.

3.3 Effects of Traffic

Under perfect conditions, given that certain inorganic and organic contaminants have a strong emission signature from motor vehicles, a direct correlation with the number of motor vehicles at the point of sampling would be expected. However, as discussed by Kennedy et al. (2002), the manner of emission of contaminants from vehicles is dependent principally upon the source of the driving conditions. For example:

- ❑ Contaminants sourced from the exhaust system (PAHs) will be influenced by cold start and by stop-go conditions (congestion) and acceleration patterns.
- ❑ Contaminants sourced from tyres (e.g., Zn, Cd, Pb etc.) will be influenced by road surface type, the physical parameters of the road (grade, curves etc.) and acceleration/deceleration patterns (degree of congestion).

- Contaminants derived from brake pad wear (e.g., Cu, Pb, Sb etc.) will be influenced by the nature of the vehicle braking cycle (e.g., degree of congestion, presence of intersections, roundabouts etc.).

If all of these factors were constant and the external factors that affect the build-up of materials on road surfaces and in gutters were similar then the concentration/load of contaminants would probably be well related to the average number of vehicles using a given road. This is however, not the case and these factors result in the nature of many roads with similar traffic numbers having very different contaminant concentrations/loadings. Having said this, there are examples of general correlations between the concentrations of contaminants found in road dusts and sediments with vehicle numbers.

The concentrations of the contaminants Cu, Pb, Mn and Ni were found to have a correlation ($p < 0.05$) with average traffic flow at 12 locations in Wellington and Lower Hutt (commercial, residential and industrial land-uses). Relationships between particulate concentrations and traffic volumes were also identified in Waitakere City (refer Kennedy 2003). Schafer et al. (1998) identified a relationship between the concentration of Pt and Rh in urban-road dusts in Karlsruhe with the concentration of Pt and Rh increasing by a factor of 10 times from 0-10,000 up to 50,000-70,000 vehicles per day.

Drapper et al. (2000) identified a relationship between ADT and median suspended solids and zinc concentration in stormwater generated in the Brisbane area. Traffic volume was considered to explain about 30% of the variance in the data.

Given that many contaminants present in urban road dusts and sediments are derived from sources other than motor vehicles, then some degree of non-correlation might be expected. Those contaminants that have strong signatures from motor vehicles would tend to exhibit stronger vehicle number correlations (e.g., the key metals such as Zn and the PGMs).

ARC (1998) identified the relative contribution that vehicle use makes to urban stormwater contaminant loads. The estimates range from 40% for Zn to 100% for Pb. Accurate estimations of the contributions from vehicles and other specific sources requires information about the direct and measurable contributions from other sources (e.g., building roof runoff, commercial and industrial impervious areas etc.). There is little published information regarding source contaminant loadings within urban areas. Recently however Timperley et al. (2003) have re-assessed the likely contribution of roads to stormwater contaminant loads based upon detailed measurement of contaminant loads from two high volume roads in Auckland City (refer Section 4 following). Their assessment indicated that for Zn the 50thile contribution of roads to the total stormwater Zn load was 16% (20 thile 46%, 80thile 6%) and for Cu the 50thile contribution was 17% (20 th and 80thile, 6 and 77% respectively). The Zn load in this recent estimate is lower than the 1995 estimate. The differences in estimates are in part due to the different approach used by Timperley et al. (2003) but also the more comprehensive data available and obtained by Timperley et al. (2003). The work undertaken by Timperley et al. (2003) also showed that the total load of Pb washing of Auckland City roads was slightly less than that of Cu. Further preliminary estimates of the likely contribution of vehicles to the load present in road surface particulates is provided in Kennedy (2003).

Estimates of source contributions will need to be continually refined as more data becomes available. The ARC (1998) estimate of 100% Pb contribution by motor vehicles is now out of date as the estimate was prepared prior to the removal of Pb from petrol in 1996. The principal uncertainties in any estimate at the present time are the potential contribution from vehicle tyres and the contribution of residual Pb back onto the road surface from areas adjacent to roads.

3.4 Summary

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 is due

to elevated concentrations in tyres and 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).

The particulates on road surfaces in New Zealand also contain elevated concentrations of the elements Cd, Cr, Mo, Ni, and Sb. These are sources 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 no 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.

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. 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. There are still substantial uncertainties associated with these estimates and they will need continued refinement as new data becomes available.

4. STORMWATER RUNOFF

4.1 Introduction

As identified in the previous section, the interpretation of the influence of motor vehicles on urban stormwater quality is complicated by the influence of other adjacent urban activities. In both general urban stormwater and specific road and motorway runoff, deposition of particulate matter from the atmosphere will contribute material not entirely derived from motor vehicle emissions. The chemistry of stormwater is influenced by the chemistry of the sediments washed from roads by stormwater and by aspects of the stormwater system including catchpit water chemistry. A considerable amount of data has been collected on stormwater quality particularly in the United States and the United Kingdom. In the US programmes such as the National Urban Runoff Programme (NURP), have collected an extensive amount of specific highway data and general urban runoff data. In the following sections an overview of stormwater quality is provided in relation to the key constituents of stormwater.

Stormwater constituents chemistry concentrations are expressed typically as g/m^3 or mg/L . Stormwater chemistry is also reported as load or mass/day per unit of contributing stormwater catchment (e.g., kg/day). The event-mean concentration (EMC) is commonly used to describe the concentration of constituents in storm events. The EMC is defined as the total mass discharged during the event divided by the total volume of stormwater discharged during the event. The EMC is therefore a flow weighted average of the constituent concentration. There are several matters that should be taken into account when comparing stormwater data from different sources.

1. The stormwater may be influenced to an unknown extent by off-site non-road related activities.
2. The data may vary from single grab samples to means of grab samples to EMCs and means of EMCs.
3. The stormwater quality will vary depending upon whether the sample was taken from a kerb and channel and piped stormwater system compared to stormwater that has passed overland before it was sampled (e.g., from motorways with no curb and channel).

4.2 Particulates in Urban Runoff and Motorway Runoff

Rainfall will transport particulate and dissolved material on roadway surfaces via the stormwater system to adjacent treatment systems or a receiving environment. Material transported from the street surface and road gutters of urban areas will contain a range of contaminants with some sourced from non-transport related activities. The particulate matter transported from highways, bridges and rural roads will more closely reflect the nature of the road surface and emissions from motor vehicles than general urban roads subject to contributions from other sources.

Suspended Solids

Williamson (1993) provides a review of the concentration of suspended solids in urban stormwater. ARWB (1988) also provides an overview of data on suspended sediment in urban runoff. Williamson (1993) identified a median event mean concentration of 170 g/m^3 for the stormwater data reviewed. Table 4.1 provides a summary of the Williamson (1993) data and some examples of recent motorway runoff data including ARC unpublished data on the S.H.-1 motorway at Otahuhu in Auckland. Data is also presented for a number of US motorway studies.

Urban runoff data shows a high degree of variability as does motorway runoff. The variability amongst the urban runoff data and the motorway data is not surprising given the large number of factors influencing particle sources and contributions of particles to the road surface. The median of the

sample of overseas motorway data reported in Table 4.1 is 90 g/m³. This is similar to the mean concentration of the ARC S.H. -1 motorway data.

Table 4.1 - Suspended solids in urban and motorway runoff (all data g/m³).

Location/Study	Site/Landuse	Concentration	Reference
Urban Runoff			
Review - 10%ile		50	Williamson (1993)
50%ile		170	Williamson (1993)
90%ile		470	Williamson (1993)
Pakuranga, Auckland	R	16.7	ARC (1992)
Pakuranga (median EMC)	R	41.4	ARC (1994)
Glendowie, Auckland	R	151	Worley (2000)
St Heliers, Auckland	R	55.1	Worley (2000)
Rotorua City	R	33	Macaskill et al. (2003)
KaikoraiValley Dunedin	Mainly R	86.9	Mosley & Peake (2001)
Rotorua City	C	20	Macaskill et al. (2003)
Takapuna	C/R	16	Meritec (2000b)
Mt Roskill, Auckland	R/I	97.3	Worley (2000)
Wairau Creek	C/I	79.2	Meritec (2000a)
Waitakere (testing station)	C/I	10	WCC (1997)
Halswell, Christchurch	C/I	102	Elliot (1996)
Southdown, Auckland	I	52.0	ARC (1992)
Tamaki, Auckland	I	253	Worley (2000)
Rotorua City	I	78	Macaskill et al. (2003)
Motorway			
SH1 Auckland	Otahuhu Motorway	91.4	ARC (unpublished)
Charlotte NC	3 Lane Bridge	215	Wu et al. (1998)
	3 Lane Highway	88	
	4 Lane Highway	14	
	Walnut Creek, Dallas Texas	90 (median)	
Austin Texas	Dallas Tollway & Collins Street		Irish et al. (1995)
	MoPac (35 th St)	291	
Austin Texas	MoPac (Convict Hill)	67	Barrett et al. (1995)
		157	
		83	
Austin Texas	35 th Street	131	Barrett et al. (1995)
	Convict Hill Road	118	
United States	Highway	142	
	Highway	41	
Various (median EMC)	Highways	142	Ellis & Revitt (1989)
Netherlands	Highways	194	Berbee et al. (1999)

Particles Size

Urban stormwater contains particulate material ranging in size from clay (<4 µm) to sand (63 – 2,000 µm) and coarser. Particulates are transported in suspension or in 'bedload' along the bottom of the stormwater pipe or channel. The hydraulic conditions and size of particulate material will determine the proportion of each component present. In New Zealand, there has been some work undertaken on the nature of particulate material in road/urban runoff. ARC (1992, 1994) reported on the nature of the particulate matter collected from stormwater samples generated from roads in the residential suburb of Pakuranga in Auckland.

The stormwater samples from Pakuranga and Southdown reported in ARC (1992) contained suspended solids of which particles >500 µm in size contributed 13.5% of the total weight of particles. Particles <63

μm contributed 54.8% of the particle mass (Table 4.2). Brockbank et al. (1999) reported particle size data for single stormwater event samples from Quantas Drive Mascot and Princes Highway, Gymnea (Both in Sydney). That data indicated that 72.4 and 92.7 % of the suspended particles were particles < 63 μm in size (Table 4.2).

Table 4.2 – particle size distribution of urban stormwater suspended solids (all data %).

Particles size category	Mascot	Princes Highway	Bulk Pakuranga (n=3)
	Brockbank et al. (1999)	Brockbank et al. (1999)	ARC (1992)
Coarse			>1000 – 2.8 (1.7-14.8)***
			500-1000 – 4.7 (2.9-10.7)
	>180* – 3.2**	>180 18.3	250-500 – 4.8 (4.6-20.1)
	150-180 – 0.6	150-180 -2.2	120-250 – 15.9 (8.6-19.6)
	75-150 – 2.6	75-150 - 2.6	
	63-75 – 1.0	63-75 - 4.5	63-120 – 13.5 (10.3-28.7)
			20-63 – 24.6 (15.0-28.0)
Fine	0.45-63 – 92.7	0.45-63 - 72.4	<20 – 12.9 (8.5-47.4)

Note: * - particle size in microns. ** - % in particle size fraction. *** - median and range.

Examination of the particle size distribution in a series of samples collected from various stages of the hydrograph in four storm events (ARC 1992) showed that the dominant particle sizes were in the <63 μm particle sizes (Table 4.3). The distribution amongst the various size classes varied between the storms sampled. This is not unexpected as the particle size distribution is dependent upon a variety of factors such as the antecedent period, rainfall intensity and other factors such as the supply of soil from adjacent land.

Table 4.3 – Particle size distribution of stormwater suspended solids from individual storms from the Pakuranga catchment in Auckland (all data %, from ARC 1992).

Particles size category	Pakuranga 1 (n=12)	Pakuranga 2 (n=7)	Pakuranga 3 (n=11)	Pakuranga 4 (n=10)
> 2mm	0	4.2	0	0
1-2 mm	0	3.0	0	0
0.5-1.00 mm	3.65	2.2	0	0
0.25-0.50 mm	4.75	5.8	0	0
0.125-0.25 mm	4.65	18.2	0	0
63-125 μm	15.4	10.9	25.2	0
31-63 μm	6.55	6.2	4.9	8.1
16-31 μm	16.85	16.1	14.1	18.5
8-16 μm	22.05	18.3	23.2	30.0
4-8 μm	15.0	9.3	20.4	27.5
< 4 μm	2.5	1.2	1.8	3.65

Note: Shaded cells are the three significant particle size fractions for each sample.

The data obtained in the ARC (1992) study was similar to that obtained for residential catchments in Hamilton by Williamson (1985) who also found that 50% of particulates were <26 μm in size. Results will be site specific to some extent with the particulate material present being a function of the contribution from surrounding and adjacent sources and the nature of the road surface and traffic density. A range of data is available from overseas studies which show suspended material in urban stormwater contains a higher proportion of smaller particulates than are found in road gutters (ARC 1992).

Roger et al. (1998) examined the physical composition of the material carried by runoff from the A9 motorway in France. Suspended sediments were dominated by particles less than 50 μm in size (86%). Sediment was also collected in a collection channel adjacent to the suspended sediment sampling site. This sample represented all settleable material carried in the runoff from the motorway. In this material, 90% was less than 0.1 mm in size. Overall, when the mass of the sediment transported in the runoff in

suspension and that carried as bed load are considered, Roger et al. (1998) determined that 77.8% of all of the material transported was <50 µm in size. It was noted by those authors, that the results were similar to those of another French study, which showed that 70 – 80% of all particles were less than 50 µm in size (i.e. fall within the clay/silt size particle class). Roger et al. (1998) also showed via a variety of analysis that the particulate matter in the runoff had mineralogical characteristics that reflected the nature of the roadway and the adjacent soils. Clays in particular were derived from adjacent soils.

An earlier study by Patrick (1975) on the characteristics of suspended sediment from the M6 motorway (Lancaster, England) showed that particulate material becomes sorted during transport from the road surface through the stormwater system. Sorting will influence the quality of deposited sediments.

Roadways will contribute particulates transported in suspension and bedload. The particulate matter suspended in the stormwater is typically silt size or smaller. The composition of that material will reflect the composition of the key sources that are road surface wear, the surrounding soils (overland runoff and deposition of wind blown material) and contributions from motor vehicles (e.g., tyre wear particles).

Suspended particles are dominated by particles in the <63 µm size range. Work in Pakuranga by ARC (1992) has shown that on average 51-88% of suspended particles are in this size range.

4.3 Trace Elements in Stormwater

4.3.1 Concentrations in stormwater

General urban-road runoff and roads

ARWB (1988), Williamson (1993), ARC (1992) (in New Zealand) and Makepeace et al. (1995) summarise information on the concentration of metals in urban stormwater. Because of the highly variable nature of urban stormwater chemistry over time, comparisons between studies and samples should be made with some caution. Table 4.4 provides a summary of the concentrations of metals in New Zealand urban stormwater. The data in Table 4.4 shows that the range in the concentration of key contaminants in urban runoff and road runoff is relatively large. Data is also typically limited to the elements Cd, Cu, Pb and Zn.

Some limited data has been collected for Cr and Ni but there is little or no data for other elements. Kingett Mitchell (1989) reported a single arsenic (As) value for stormwater from the Remuera/Meadowbank catchment (11 mg/m³). Mosley & Peake (2001) also reported data for iron (Fe) in urban stormwater from Dunedin. They reported a median concentration of total iron of 1,833 mg/m³ (range 575-17,067 mg/m³). O'Riley et al. (2002) reported EMCs of 7,460 – 50,300 mg/m³ (particulate iron) for six rainfall events at a roundabout on River Rd Hamilton. Although iron is a key contaminant on road surfaces, the concentrations in stormwater are determined by the iron present in the structural matrix and the oxide coatings of inorganic suspended materials in the stormwater. O'Riley et al. (2002) also reported particulate EMC of 328-1,990 mg/m³. Particulate nickel data reported in the same study was very high (8 times the particulate zinc) and although the authors suggested that the source may have been bitumen particles, the results are likely to be erroneous or due to some specific non-road source (or due to some other nickel source in the road surface material).

A substantial amount of work has been undertaken (and is ongoing) in Auckland city by NIWA in recent years in relation to metals and PAHs in road and urban stormwater. Timperley et al. (2003) have reported on metals in runoff from Ash St (about 20,000 VPD) and Richardson Rd (17,000 VPD, no connected roof runoff). Fig. 4.1 from Timperley (2003) illustrates the variation in particulate and dissolved Zn in stormwater from Richardson Rd. The upper figure shows that the particulate Zn concentrations were variable during the event spiking up to 1,000 mg/m³ but declining rapidly following the event. Dissolved Zn concentrations were found in concentrations of 50-200 mg/m³ during rain events but were also found in high concentrations in discharge from the stormwater system during the

tail of the events. There are a number of likely sources for the Zn in the periods of lower flow (e.g., continued release of Zn from sediment within the stormwater system and groundwater infiltration). Studies such as those of Mosley & Peake (2001) in Dunedin provided information on the temporal variation in the concentration of stormwater constituents with a range in concentration of typically five times for most elements which reflected the five times range in the suspended solids concentration. Fig. 4.2 illustrates the variation seen in that study for the three key stormwater elements. Zinc concentrations in that study are similar to those identified by Timperley et al. (2003). Timperley (2002) also noted the high variation in concentration that occurred during first flush during stormwater events for the key contaminants. This is considered further in relation to toxicity.

Table 4.4 - Median concentrations of trace metals in stormwater in New Zealand (all units mg/m³).

Site	Land-use	Cadmium	Chromium	Copper	Lead	Nickel	Zinc	
Mairangi Bay, North Shore City	R	<0.05, 0.09	<0.5, 4.5	7, 7.8	2, 2.5	1.6, <5	61, 80	Opus 2000a
Grey Lynn, Auckland	RI	-	-	20	-	-	900	Worley 2000
Glendowie, Auckland	R	-	-	10	-	-	110	Worley 2000
St Helliers, Auckland	R	-	-	-	-	-	128	Worley 2000
Pakuranga, Manukau City	R	-	-	15 (6-58)	55 (19-212)	-	444 (259-1500)	ARC 1992
Pakuranga, Manukau City	R	0.056 (0.019-0.24)	-	13 (5.1-155)	86 (16-890)	-	330 (170-1,080)	ARC 1992
Pakuranga, Manukau City	R	-	-	10 (3-16)	34 (4-101)	-	285 (63-709)	ARC 1994
Rotorua City	R	0.18 (<0.05-0.44)	1.2 (0.9-1.4)	13.3 (5-15.3)	18.7 (6.2-21.5)	1.2 (<0.5-2.9)	62 (31-96)	Macaskill et al. 2003
Akorangi Drive, North Shore City	R	<0.05	0.7	3.4	1.4	3.1	117	Opus 2000b
Waiatarua stormwater tunnel, Auckland	R	0.6	3	9	29	3	42	Kingett Mitchell 1989)
Rotorua City	C	0.24 (0.15-9.8)	1.6 (1.4-2.2)	8.9 (7.4-12.3)	8 (4.2-11)	11 (1-11)	137 (82-178)	Macaskill et al. 2003
Mairangi Bay, North Shore City	C/I	<0.05	<0.5	2.2	0.8	2.2	93	Opus 2000a
Wairau Creek, North Shore City	C/I	-	-	29 (11-66)	-	8 (<5-20)	383 (180 - 1,600)	Meritec 2000a
Wairau Creek, North Shore City	R	1.0 (0.2-11)	37 (11-82)	22 (6-158)	157 (16-1294)	33 (6-136)	260 (144-900)	Williamson 1986
Wairau Creek	R/I/M	1.8 (0.1-7)	34 (9-150)	50 (14-436)	144 (13-820)	34 (7-101)	378 (118-1,320)	Williamson 1986
Southdown, Auckland	I	-	-	42 (9-303)	82 (<17-491)	-	466 (264-1,880)	ARC 1992
Kaikorai valley, Dunedin	R	-	-	21.9 (4.5-56.4)	34.0 (5.7-94.5)	-	233 (101.0-883.3)	Mosley & Peake 2001
Portobello Rd Dunedin	M	-	-	27 (10-823)	20 (5-4,100)	-	962 (498-18,550)	Brown & Peake 2001
Halswell Junction, Christchurch	C/I	-	-	29	26	-	668	Elliot (1996)
Rotorua City	I	0.23 (<0.05-0.68)	36.9 (30-55)	30.6 (22.1-50)	13.1 (8.3-19.2)	3.3 (3.2-9.8)	252 (229-465)	Macaskill et al. 2003

Notes: Shaded cells represent studies undertaken before lead was removed from petrol in New Zealand.

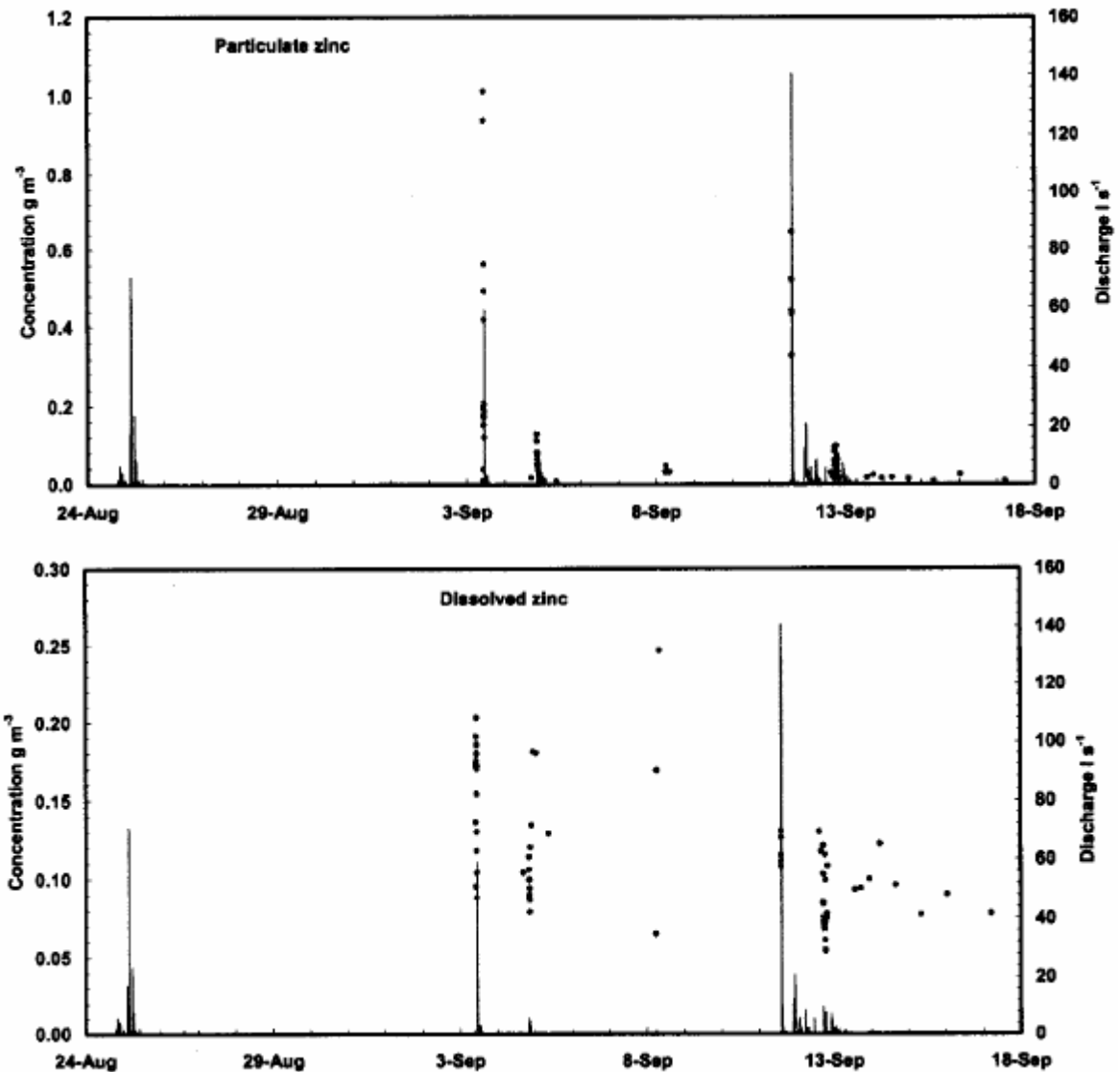


Figure 4.1 - Variation in the concentration of particulate and dissolved Zn in stormwater runoff from Richardson Rd, Auckland City over three storm events (Taken from Timperley et al. 2003).

Motorways

To provide more specific information on the quality of stormwater runoff where motor vehicles are the primary contributor, the chemistry of stormwater from motorways, highways and isolated roads such as bridges needs to be examined. There is very little 'isolated' New Zealand roadway stormwater metals data. Table 4.5 presents data from two studies. One carried out by the ARC in 1996 and a second carried out by the Wellington Regional Council in 1998 (Sherriff 1998). Both studies were limited due to the detection limits employed for the analysis of stormwater being high relative to the actual concentrations. Sampling and analytical method differences between the studies identified in Table 4.5 has not been taken into account.

Table 4.5 - Summary of trace elements in motorway stormwater (all data mg/m³).

Authors	Location	ADT	Cd	Cu	Cr	Pb	Ni	Zn	N
International									
Hares & Ward (1999)	M25 Leatherhead UK	140,000	14.1	274	105	81	93	208	3
	M 25 Oxted UK	120,000	11.9	248	86	70	76	188	3
Berbee et al. (1996)	Netherlands	-	1-5	17-78	3-10	40-195	4-15	200-530	-
Berbee et al. (1999)	Netherlands	53,000	0.8	121	5	93	5	452	3-6
Marsalek et al. (1997)	Skyway Bridge	-	15	136	-	72	69	337	53
Shinya et al. (2000) ⁴	Elevated urban highway, Osaka	75,00	1-3	39-100	2-10	17-39	2-6	427-1191	4
Wu et al. (1995)	3 Lane Bridge	25,000	<5	15.0	6.5	15.0	9.0	-	-
	3 Lane Highway	21,500	<5	12.0	<5	13.0	<5	-	-
	4 Lane Highway	5,500	<5	<5.0	<5	6.0	<5	-	-
Kennedy (1995)	Walnut Creek		-	8	-	7	-	22	-
	Dallas Tollway		-	10	-	11	-	50	-
	Collins Street		-	17	-	11	-	100	-
Irish et al. (1995)	MoPac at West 35 th	60,000	-	22	-	82	-	160	32
				9		23		50	3
				49		123		263	23
	MoPac at Convict Hill			6		16		53	23
Driscoll et al. (1990)	Urban Highway ¹	> 30,000	-	54	-	400	-	329	-
	Rural Highway ¹	< 30,000	-	22	-	80	-	80	-
Barrett et al. (1995c)	35 th Street		-	34	-	50	-	208	-
	Convict Hill Rd		-	7	-	16	-	50	-
Ellis & Revitt (1989)	Various (50%ile EMC)	-	-	54	-	-	-	329	-
New Zealand									
ARC Unpublished ²	Otahuhu	90,000	-	53	-	108	-	159	60
				(12-160)		(20-380)		(44-433)	
Sherriff (1998) ³	Porirua	~50,000	<5	80	<30	<50	-	60	30
				(30 – 350)		(<50-19)	<30	(<30-240)	

Notes: ¹ = Nationwide median EMC. ² = Median EMC, 4 events, range of all samples (n=60). ³ = Median of all data and range of all samples. ⁴ = range of 4 EMC values. ADT = Average daily traffic. N = number of samples.

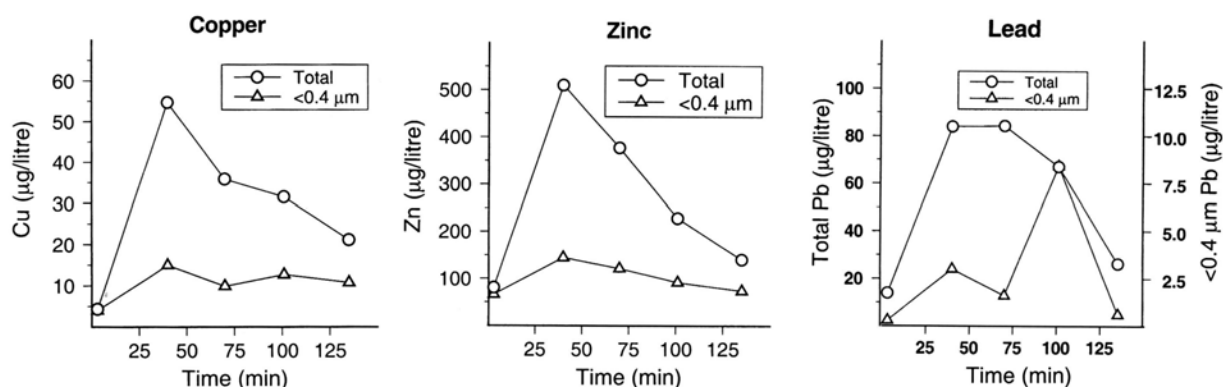


Figure 4.2 - Variation in the concentration of total and dissolved copper, zinc and lead in stormwater from the residential Kaikorai catchment in Dunedin (From Mosley & Peake 2001).

As noted in relation to other aspects of the road environment, the Pb data in Table 4.5 will be a reflection of the concentration of Pb in vehicle fuel at that location at that time). Both sets of data have been collected since Pb was removed from New Zealand petrol. As such, the international data does not necessarily reflect the current concentration of Pb in stormwater at those locations. It is likely that the concentrations of other metals in fuel will have changed over time depending upon methods of refining and the source of the original petroleum. Based on Tables 4.4 and 4.5, the following comments can be made about trace elements in New Zealand urban and roadway stormwater.

There is limited data on Cd in New Zealand motorway stormwater. No published motorway or isolated roadway data appears available in New Zealand. Overseas motorway data appears typically limited by detection limits. Marsalek et al. (1997) reported a concentration of 15 mg/m³ in bridge runoff in Ontario and Hares & Ward (1999) report similar concentrations from the M25 a high traffic volume motorway in the UK (Table 4.3). It should be noted that the 10%ile for the former study was 0.1 mg/m³. Work in the Netherlands by Berbee et al. (1996, 1999) has shown that Cd concentrations were in the range of 0.8 – 0.9 mg/m³ (n=3). This data is similar to the very low results (0.056 mg/m³) reported for the Pakuranga Highway that passes through residential Pakuranga in Auckland (Table 4.2). A number of other urban stormwater studies in Auckland have also reported low Cd concentrations (Table 4.4).

Copper data reported for overseas motorways is generally similar to the urban runoff data reported by ARC (1992). The more recent New Zealand ARC (unpublished) and WRC motorway studies report higher concentrations (Table 4.5). Marsalek et al. (1997) reported a mean EMC for the Skyway Bridge in Burlington, Ontario of 136 mg/m³. Irish et al. (1995) found copper EMCs ranging from 9 mg/m³ for a simulated rainfall event without traffic to 49 mg/m³ for stormwater during natural rainfall. Similar data was reported for highways in the Netherlands. Hares & Ward (1999) reported higher concentrations for runoff from the M25 in the UK (Table 4.5).

There is very little data for Cr and Ni in urban and highway runoff. However, concentrations typically reported for urban areas in New Zealand and for motorways overseas appear low (refer Table 4.5) with the exception of the data for the M25 presented by Hares & Ward (1999). It is likely that local geology (e.g., basalt influence) could influence the concentration of both elements under some circumstances.

The ARC study (unpublished data) indicated that runoff from the SH1 motorway at Otahuhu (conducted in 1995-96) contained a Pb concentration of about 100 mg/m³. In contrast, the more recent WRC study although limited by a high detection limit (50 mg/m³), indicated that concentrations appear to be lower. Two studies undertaken in Dunedin reported median lead concentrations of 20

and 34 mg/m³ in stormwater from a predominantly residential catchment (Mosley & Peake 2001 and Brown et al. 2003).

Overseas study data is variable with some recent data having relatively low concentrations of lead (e.g., Kennedy 1995, Barrett et al. 1995c, Irish et al. 1995, Hares & Ward 1999, Shinya et al. 2000). The ARC motorway data is similar to that of Marsalek et al. (1997) and Berbee et al. (1999). Marsalek (1997) reported EMC 10%ile and 90%ile concentrations of 1 and 166 mg/m³ respectively (from a dataset of 53 events). Marsalek et al. (1997) and Berbee et al. (1999) noted that their data reflected the reductions of lead levels in petrol in Canada and the Netherlands. Lead was removed from petrol in New Zealand in 1996. There does not appear to be any sites that were sampled for stormwater quality prior to and after the removal of lead from petrol. Given that Pb was eliminated a number of years ago the concentrations measured in New Zealand should reflect the decrease in Pb content of fuel and contributions from accumulated Pb in roadside and adjacent soils.

Zinc data are available for urban runoff and motorway runoff in New Zealand. Urban runoff data collected by ARC (1992) and also by Williamson (1985) indicates that New Zealand urban runoff contains elevated concentrations of Zn. International motorway data is variable ranging from average values less than 100 mg/m³ to a 50%ile value of 337 mg/m³ reported by Marsalek et al. (1997). Irish et al. (1995) reported median EMC data ranging from 50 mg/m³ for simulated rainfall without traffic to 263 mg/m³ for a natural event (Table 4.5). Recent ARC motorway stormwater quality data has lower concentrations than residential stormwater reported in ARC (1992).

Hares & Ward (1999) presented data for several elements identified in sections 2 and 3 as being emitted by motor vehicles due to their inclusion in sources such as brake pads. They reported average concentrations of Co of 6.7 and 5.6 mg/m³; Mo of 20 and 19 mg/m³ and Sb concentrations of 8.6 and 5.8 mg/m³ respectively for runoff from the M25 motorway at two locations.

Batley et al. (1994) and Brockbank et al. (1999) reported the findings of extensive studies on two roads in Sydney - Qantas Drive and Princes Highway. The studies examined dissolved and particulate metal concentrations (rather than total concentrations) and the concentration in particulate material. As such, this data is discussed in following sections.

Overall, there is a moderate body of data on total trace metal concentrations in urban and roadway runoff in New Zealand. The available/published data has been reviewed in several publications (e.g., ARC 1992, Williamson 1995). 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.

Specific studies in New Zealand have provided information on the variability in trace element concentrations through storm events. There is insufficient data in New Zealand to provide any comment on the concentration of the elements Cr and Ni in stormwater with certainty.

Currently (2003) extensive stormwater sampling is being undertaken by NIWA in Auckland City as part of stormwater network consents research programmes for Metrowater/Auckland City. As more of this data becomes available it will provide a substantial addition to the available data on stormwater quality in New Zealand. The data will also assist in the determination of source contributions.

4.3.2 Dissolved Metals

Metals are distributed between dissolved (as defined by filtration using a 0.45 µm filter) and particulate phases in stormwater. The proportion dissolved is element specific and generally consistent between studies. Table 4.6 summarises the results of dissolved and acid soluble metal measurements of stormwater samples carried out a number of studies undertaken in New Zealand over the last 10 years. Table 4.7 summarises other data for motorways.

Table 4.6 - Summary of dissolved metal concentrations in urban runoff in New Zealand and overseas (all data mg/m³).

Metal		Pakuranga Auckland	Halswell Junction	Kaikorai Valley Dunedin	Portabello Rd Dunedin	Rotorua City		
		Res	Ind/Comm	Res	Mixed	Res	Comm	Ind
Cu	Acid	13	29	21.9	27	13.3	8.9	30.6
	Dissolved	3.2	9	9.7	9	4.1	5	10.2
	% Dissolved	24.6	31	44.3	33.3	30.8	56.2	33.3
	N	13	3	-	-	5	4	4
Cd	Acid	0.056	-	-	-	0.18	0.24	0.23
	Dissolved	0.018	-	-	-	<0.05	0.13	0.14
	% Dissolved	32.1	-	-	-	<27.8	54.2	60.9
	N	13	-	-	-	5	4	4
Pb	Acid	86	26	34.0	20	18.7	8	13.1
	Dissolved	0.21	<1	2.9	1.2	3.3	1.3	1.4
	% Dissolved	0.2	<3	8.5	6.0	17.6	16.25	10.7
	N	13,7 (Diss)	-	-	-	5	4	4
Zn	Acid	330, 275	668	233	962	62	137	252
	Dissolved	170, 113	435	107	682	33	96	172
	% Dissolved	51.5, 39.6	61	45.9	70.9	53.2	70.1	68.2
	N	13, 5-7	-	-	-	5	4	4
Ref.		ARC (1992, 1994)	Elliot (1996).	Mosley & Peake (2001)	Brown et al. (2003)	Macaskill et al. (2003)		

Note: N = Number of samples

Table 4.7 - Summary of dissolved metal concentrations in motorway runoff in New Zealand and overseas (all data mg/m³).

Metal		Otahuhu Motorway, Auckland	Maitland (US) Interchange	Netherlands
Cu	Acid	35.7	37.5	121
	Dissolved	7.5	26.4	-
	% Dissolved	21.0	70.4	26
	N	3	-	6
Cd	Acid	-	2.5	0.8
	Dissolved	-	1.8	-
	% Dissolved	-	72	24
	N	-	-	3
Pb	Acid	108	163	93
	Dissolved	<20	33.5	-
	% Dissolved	<18.5	20.6	2
	N	3	-	6
Zn	Acid	159	71	452
	Dissolved	68.4	40.4	-
	% Dissolved	43.0	57	24
	N	5	-	6
Ref.		ARC Unpub.	Yousef et al. (1986)	Berbee et al. (1999)

Note: N = Number of samples

Timperley et al. (2003) reported the results of detailed measurements of particulate and dissolved metals in stormwater runoff from Ash St and Richardson Rd in Auckland City. Their measurements showed that for Zn, the dissolved and particulate concentrations were linearly related but not on a 1:1 ratio. The dissolved Zn concentration is relatively constant compared to the particulate concentration.

The authors concluded from their work that 42% of the Zn was in the dissolved phase and 28% of the total Cu was dissolved. Comparing the Timperley et al. (2003) estimates with the New Zealand data in Tables 4.6 and 4.7 shows that for Cu, the results agree very well. The two other Auckland studies reported 24.6 and 21% dissolved and the three South Island studies and the Rotorua study reported 30.8-56.2% dissolved. For Zn the results also agree well. The two other Auckland studies report dissolve percentages that ranged from 39.6-51.5% and the South Island and Rotorua studies 45.9-70.9%. The early work by ARC (1992) (which utilised 'clean' techniques for some of the sampling and analysis undertaken) concluded that, a very low proportion of the lead was dissolved (<1%). Other New Zealand studies have shown that the proportion of Pb in the dissolved phase is low (South island studies <3-8.5%; Rotorua 10.7-17.6%). Recently Timperley et al. (2003) concluded that the percentage dissolved was of the order of 2%.

Macaskill et al. (2003) also reported data for Cr and Ni in stormwater from Rotorua City. Nickel concentrations were low in all three landuses (1.1-3.3 mg/m³ with <0.5-1.7 mg/m³ in the dissolved phase, median dissolved 51.5%). For Cr the concentrations for the residential and commercial catchments were 1.2 and 1.6 total with <0.5 and 0.8 mg/m³ dissolved; for the industrial catchment the median total and dissolved were 36.9 and 12.6% (median dissolved 41.6%). Berbee et al. (1999) also showed that for motorway sites, 20% of the Ni and 15% of the Cr was dissolved. Assessment of the proportion of dissolved metal is determined to some extent by the accuracy of the dissolved metal analysis. Poor detection limits result in an increased estimation of the proportion of metal identified as dissolved.

Analysis of stormwater runoff from parking areas also provides information on runoff quality predominantly from motor vehicles. Tiefenthaler et al. (2001) presented results for the analysis of metals in car park runoff in San Diego. The total metal data obtained for most elements in that study generally reflected that identified in many other urban stormwater studies. The results however indicate higher proportions of dissolved Zn (77%) and Pb (54%) compared to other studies noted above. Insufficient detail was presented by the authors to confirm the validity of the dissolved metal data collected in that study.

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.

4.3.3 Trace metals in Stormwater Particulates

Whole sediment

The concentrations of trace elements associated with stormwater particulate matter would be expected to reflect the composition of the source particulate matter on the impervious surface that the stormwater was derived from. The trace element concentrations of the particulate matter transported in stormwater has been examined in a number of studies. In New Zealand ARC (1992, 1994) measured the concentration of key trace elements in a series of particle size fractions of bulk urban stormwater samples and Hickey et al. (1997) measured trace element concentrations of suspended particulates. Earlier data obtained by Williamson (1985) for stormwater discharging from a residential suburb in Hamilton was similar.

Table 4.8 provides a summary of the data obtained. Data for Cu, Pb and Zn from overseas studies such as Marsalek et al. (1997) and Roger et al. (1998) shows similar concentrations, which reflect the trends and element ratios seen in urban roadway gutter sediments and dusts. The more recent work by Hickey et al. (1997) found lower Cu, Pb and Zn concentrations. The lower Pb concentrations probably reflect the removal of Pb from petrol in New Zealand and the lower Cu and Zn concentrations

probably reflect lower traffic densities in the Mount Albert catchment compared to the stormwater catchments sampled in ARC (1992) and Williamson (1985).

Timperley (2001) presented results of the examination of suspended particles present in storm and stream waters from a variety of sites in Auckland, Hamilton and Christchurch. The results showed that suspended matter could reach high concentrations of copper (e.g., median values of the order of 50-250 mg/kg), lead (e.g., 50-400 mg/kg) and zinc (e.g., 500-2,500 mg/kg) with the concentration typically increasing from residential to commercial to industrial land-uses.

Table 4.8 - Trace elements in urban stormwater suspended particulates (all data mg/kg dry weight).

Parameter	ARC (1992) Residential Stormwater Auckland	Hickey et al. (1997) UNITEC	Brockbank et al. (1999) Sydney	Marsalek et al. (1997) Bridge Stormwater, Ontario	Williamson (1985) Residential Stormwater Hamilton	Roger et al. (1998) A9 Motorway France
Cd	0.89 (0.44-1.7) ^a	1.2	0.1-5.1; 0.2-0.5	-	<10-	-
Cr	61 (29-126)	-	-	-	-	31
Cu	153 (123-187)	5.6	30-770; 42-620	314 (737) ^c	40 – 230 ^b	81
Hg	1.3 (0.95-1.7)	0.227	-	-	-	-
Ni	25 (12-54)	-	-	56 (126)	-	<1
Pb	668 (392-939)	218	66-1,100; 210-1,000	402 (527)	460-4,570	830
Zn	2,221 (2,030-2,480)	514	97-26,000; 250-750	997 (1634)	930-4,370	550

Notes: ^a- Weighted mean and range of particle size fractions. ^b- Range of particle size fractions. ^c - Unsaved sediments and (fine sediments). Brockbank et al. data is EMC concentrations for 6 events from Qantas Drive and Princes Highway in Sydney.

Overall, data for the key urban elements Cu, Pb and Zn shows that they are present in high concentrations in the particulate material transported in stormwater. New Zealand data is only available for urban areas. Overseas motorway data indicates that concentrations would be similar with the possible exception of zinc as New Zealand data suggests higher concentrations of this element are associated with particulate fractions of runoff compared to overseas data.

The Marsalek et al. (1997) data, which is post lead reduction in Canada, still shows the presence of high concentrations of lead in particulate material transported by motorway runoff. Stormwater data obtained post lead in petrol removal in New Zealand indicates that there is still lead in New Zealand stormwater derived from catchment sources and on road (refer Section 3) and roadside sources.

Different particle sizes

ARC (1992, 1994) reported on the analysis of various different particle size samples taken from the Pakuranga stormwater samples described in the preceding section. As with the examination of total whole suspended sediment samples, the concentration present in different particle size fractions would be expected to reflect the concentrations found in the original source materials. The ARC (1992) data did not display significant trends in concentration with decreasing particle size (<20 µm was the smallest particle size examined). The range of concentrations reported for the particle size classes examined are shown as the range in Table 4.8. The data in ARC (1994) showed similar concentration ranges for particles classes 0.5 mm for zinc (2,100-2,400 mg/kg) and lead (about 1,000 mg/kg) but higher concentrations in the particles in the 125-500 µm classes compared to those 20-63, 63-125 µm and >500 µm. The concentrations in the two ARC reports are similar.

Stormwater transports particulate matter containing high concentrations of contaminants. The presence of high concentrations of contaminants is not surprising given the high concentrations present in particulate materials present on road surfaces. 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. This compares with 297 and 723 mg/kg respectively in <0.063 mm particle on road surfaces in Waitakere City.

4.4 Organic Compounds in Stormwater

4.4.1 Hydrocarbons

ARC (1988; 1992) provides an overview of the presence of hydrocarbons in urban stormwater. The review in either study did not specifically deal with the contribution from roads in the absence of other urban sources. Oil and grease has been the traditional measure of hydrocarbons in stormwater. The measurement included non-petroleum hydrocarbons such as plant waxes. More specific analytical measures for petroleum hydrocarbons are now available allowing more definitive information about the nature and type of hydrocarbons present. Most of the hydrocarbons are derived from loss of oil from vehicles and a small proportion from tailpipe emissions. Oil and grease measurements of highway runoff are generally low with:

Wu et al. (1998) reporting median EMCs for three motorway sites of 1.1 to 3.3 g/m³.

Irish et al. (1995) reporting median EMC data for the MoPac Highway in Austin ranging from 0.4 to 5.0 g/m³.

Berbee et al. (1996) reporting oil concentrations of 2-14 g/m³ for three highways in the Netherlands.

Berbee et al. (1999) subsequently reported oil concentrations of 4 g/m³ (3-8 g/m³) for a further highway site.

In New Zealand, ARC (1992) reported 4.3 g/m³ oil and grease in stormwater from the residential catchment of Pakuranga. Sherriff (1998) reported <0.05 - <0.1 g/m³ TPH in samples collected on SH-1 at Tawa just north of Wellington.

Shepp (1998) reported TPH concentrations in stormwater from a range of land uses. EMCs for vehicle dominated land uses included 0.9 g/m³ for all day parking; 2.2 g/m³ for street and 12.4 g/m³ for commercial land use associated with a restaurant. Shepp (1998) suggested a typical range of 0.7 to 6.6 g/m³ for stormwater from vehicle intensive land uses.

Ngabe et al. (2000) commented on the nature of hydrocarbon fractions in urban runoff from Columbia in the United States. The authors noted that GC-FID analysis of total hydrocarbons showed that the aliphatic fraction of the runoff samples was more similar to used crankcase oil than to urban aerosols. Urban runoff will also contain biogenic hydrocarbons (e.g., C₂₉-C₃₁) due to the presence of plant material with associated waxes.

4.4.2 VOCs

A wide range of VOCs are emitted from motor vehicles through evaporation and exhaust emissions (e.g., see Fraser et al. 1998, etc.). VOCs are also present in urban areas as a result of their release from a wide range of daily products and general urban activities. These include solvents, paints, adhesives, deodorants etc., (Lopes & Bender 1998). However, the benzene, toluene, ethylbenzene and xylene (BTEX) group and naphthalene are considered as fuel related VOCs because of their bulk use in vehicle fuels. As a consequence some VOCs would be expected to be present in stormwater especially during periods of rainfall when washout of atmospheric gases occurs. Makepeace et al.

(1995) provide a general review of VOC data in general urban stormwater runoff that was available up to that time.

The United States Geological Survey (USGS) carried out a survey of volatile organic compounds (VOC) in stormwater in 16 US cities required to obtain National Pollution Discharge Elimination system permits (Delzer et al. 1996). It should be noted that detection was influenced by detection limit compared to other VOCs and the seasonality of MTBE emissions in some areas (due to winter use). MTBE detections ranged from 0.2 to 8.7 mg/m³ (median 1.5 mg/m³). The survey conducted from 1991 to 1995 found that the most prevalent VOCs were toluene, total xylenes, chloroform, total trimethylbenzene, tetrachloroethene and naphthalene followed by MTBE. MTBE was detected in 6.9% of the stormwater samples. Table 4.9 provides a summary of the data for selected constituents measured in the USGS survey.

Table 4.9 - VOCs in United States stormwater (all data mg/m³) (From Delzer et al. 1996).

Parameter	Median	Minimum	Maximum	Detection Frequency %
Toluene	0.3	0.02	6.6	23.2
Total xylene	0.4	0.2	15.0	17.5
Total trimethyl-benzene	0.3	0.2	15.0	12.4
Naphthalene	0.3	0.2	5.1	7.4
MTBE	1.5	0.2	8.7	6.9
Ethylbenzene	0.3	0.2	2.0	5.0

Studies on the spatial variability of VOCs in streams on Long Island and New Jersey have been reported by O'Brien et al. (1997). Streams sampled contained urban runoff and other discharges. A range of VOCs were detected of these naphthalene and MTBE were specifically identified as being sourced from motor vehicles. Acetone was detected but has a variety of sources in the urban environment. A range of VOCs were not detected at a detection limit typically of 0.05 – 0.10 mg/m³. No other identified vehicle VOC emission compounds were identified.

Lopes & Dionne (1998) reviewed the occurrence of VOCs in urban stormwater and highway runoff. VOC data for highways is limited. Chloromethane, toluene, xylenes, 1,2,4-trimethylbenzene and 1,2,3-trichloropropene have been detected in highway runoff in Texas.

Fuel related VOCs are present in urban waterways because of their prevalence in the urban environment. Terracciano & O'Brien (1998) reported on VOCs in streams on Long Island, New York. A number of VOCs were commonly detected in samples. These included 1,1,1-trichloroethane (TCA), TTBE, tetrachloroethene, total benzene, toluene, ethylbenzene and xylene. Higher concentrations and frequency of detection was found in winter when volatility was at its lowest. The low level concentrations of MTBE measured in stream waters in the United States has been considered to result from equilibration between atmospheric MTBE and stream water rather than direct discharge.

There appears to be no data on the concentration of VOCs in New Zealand urban and motorway stormwater. Overseas data indicates that the concentration of most VOCs in stormwater are low.

4.4.3 PAHs

Based upon PAH concentrations found in fine particle size fractions of urban gutter dusts, ARC (1992) estimated the PAH concentrations in urban stormwater runoff from residential and industrial roadways in Auckland. Total PAH concentrations were estimated to be 62.2 µg/m³ and 27.1 µg/m³ in the Pakuranga and Southdown catchments respectively. No specific monitoring of PAHs in stormwater in New Zealand was available until recently (Sherriff 1998, Brown et al. 2003, O'Reilly et al. 2002 and Timperley et al. 2003).

Marsalek et al. (1997), examined samples of stormwater from the Skyway Bridge in Burlington Ontario (92,000 VPD) and Shinya et al. (2000) examined stormwater from an elevated urban highway (75,000 VPD) in Osaka, Japan. Table 4.10 provides a summary of the PAH data obtained by the two studies which had similar total PAH concentrations obtained PAH concentrations from. Although, the PAH results of Sherriff (1998) (Table 4.10) were at the low end of the range reported in urban stormwater and motorway stormwater the relative concentrations of the different PAHs are similar between the studies.

Table 4.10 - Summary of PAH concentrations in motorway runoff (all data mg/m³).

PAH	Marsalek et al. (1997) Burlington Skyway Mean (n=29)	Sherriff (1998) Porirua Motorway range (n=30)	O'Riley et al. (2002) EMCs, 6 events	Shinya et al. (2000) EMCs 4 events
Indene	0.0169	-	-	-
2 Methyl-naphthalene	0.0743	-	-	-
1 Methyl-naphthalene	0.0391	-	-	-
Acenaphthylene	0.0147	<0.004 (<0.003-0.007)	-	-
Acenaphthene	0.0248	<0.005 (<0.003-<0.01)	-	-
Fluorene	0.0562	<0.01 (<0.005-<0.01)	-	-
Phenanthrene	0.397	<0.01 (<0.01-0.0547)	0.09-0.376	0.12-0.465
Anthracene	-	<0.002 (<0.002- 0.00825)	-	0.017-0.033
Fluoranthene	0.504	0.014 (<0.005-75.1)	0.104-0.665	0.086-0.419
Pyrene	0.454	0.0163 (<0.005-0.0866)	0.185-1.490	0.090-0.363
Benz(a)anthracene	-	<0.005 (0.002- - 0.0291)	-	0.016-0.081
Chrysene	-	0.014 (<0.003-0.074)	-	0.06-0.175
Perylene	-	-	-	0.005-0.022
Benzo(b)fluoranthene	0.0239	<0.01 (<0.005-0.0349)	-	0.043-0.154
Benzo(k)fluoranthene	0.135	<0.01 (<0.003-37.7)	-	0.02-0.096
Benzo(a)pyrene	0.186	<0.01 (<0.003-0.0247)	-	0.026-0.099
Benzo(e)pyrene	-	-	-	0.032-0.110
Indeno(1,2,3,cd)pyrene	0.143	0.005 (<0.002-0.0302)	-	0.036-0.115
Dibenz(a,h)anthracene	-	<0.002 (<0.001 - <0.010)	-	0.014-0.03
Benzo(g,h,i)perylene	0.222	0.016 (<0.005-0.0657)	-	0.072-0.19
Total PAH	2.291	0.057 (0.0156 – 0.308)	-	0.676-2.351*

Note: EMC – Event mean concentration.* - 0.676, 0.796, 1.281, 2.351 mg/m³.

Brown et al. (2003) found that 67% and 37% of total PAH in the baseflow and stormwater from the Portobello Rd catchment in Dunedin (100% urban) and 71 and 9% respectively in the Waters of Leith which drains a catchment which is 17% urban. The latter storm result is similar to that of Marsalek et al. (1997) who reported that the dissolved phase PAHs represented 11% of the total concentrations measured.

Berbee et al. (1996) reported to be PAH concentration in stormwater from Dutch highways of ~2 mg/m³. Subsequent work (Berbee et al. 1995) reported concentrations of 2.8 and 3.2 mg/m³. Ngabe et al. (2000) reported a geometric mean of 3.05 mg/m³ for total PAH in runoff samples (immediately at entry points from the street to the stormwater system) from Columbia (South Carolina). These are both in the range reported by Marsalek et al. (1997) and Shinya et al. (2000) studies. Pitt et al. (1995) provided PAH data for stormwater from a range of urban land uses including roofs, streets and parking areas. Of 16 parking area samples, most contained no detectable PAHs at a detection limit of 0.5 mg/m³. Ngabe et al. (2000) presented results of PAH monitoring of storm runoff in California. Total PAH concentrations of runoff in Columbia had a geometric mean of 3.05 mg/m³ (range 0.4 – 16.30 mg/m³). In Murrels Inlet (a smaller community) the geometric mean was 0.166 mg/m³ (range 0.035-1.410 mg/m³). In an evaluation of likely sources in the runoff, the authors examined PAH profiles of source materials and concluded that the main source of the PAHs in the runoff was combustion products rather than crankcase oil. A similar conclusion was also reached by Hoffman et al. (1984) and Takada et al. (1990, 1991).

Further data can be found in the Sydney studies of Brockbank et al. (1999) who reported total PAH concentrations of 3.9 mg/m³ in stormwater at Qantas Drive and 8.9 and 9.4 mg/m³ in stormwater from the Princes Drive. It was considered by the authors that the total PAH concentrations may have been affected by aircraft emissions and deposition of material from bush fires which were widespread at the time sampling was undertaken on the Princes Highway.

PAHs are present in urban runoff and in the runoff from motorways and roads uninfluenced by general urban activity. Although, there is limited published data on PAHs in urban runoff in New Zealand, the New Zealand data is within the range of data reported in the international literature. As the New Zealand data is either incomplete or at the lower end of the typical range, it is considered that PAHs are likely to be present in New Zealand motorway runoff at similar concentrations to those reported by Marsalek et al. (1997). Although, the international published PAH concentration data presented here is limited in extent, the median total PAH concentrations are typically around 2.3 mg/m³. (0.676, 0.796, 1.281, 2.351, 2.291, 2.8, 3.05, 3.2 mg/m³).

4.4.4 Other SVOCs

A wide range of SVOCs are present in general urban stormwater (Makepeace et al. 1995). This is not surprising given the large number of SVOCs that are used in urban environments and present in soils within urban areas. As the sediments in street gutters contain a range of SVOCs such as organochlorine pesticides and PCBs, it would be expected that road runoff would contain a range of measurable SVOCs associated with transported particles.

There appears to be little information on the concentration of SVOCs other than PAHs (discussed above) in road runoff that can be attributed to the use of motor vehicles on roads. An indirect approach can be taken to identify whether there are any other SVOCs present that have the potential to have adverse effects when discharged to the environment. There have been a number of studies undertaken that have examined the presence of SVOCs in motor vehicle emissions or indirectly through the examination of source of the emissions. Gadd & Kennedy (2000) examined the SVOCs present in a small selection of tyres and brake pads present used in New Zealand. The organic contaminants identified in that process plus those identified through a review of available literature information allowed the identification of key organic compounds present in those sources that might enter stormwater through emission into the environment. Table 4.10 provides a summary of some examples of the contaminants identified.

Table 4.11 - COPC in tyres and brake pads (from Moncrieff & Kennedy 2002).

Source	Compartment*	Number of COPC	Example of COPC
Brake pad and clutch	Air >90%	1	Diethynybenzene
	Air 50-89%	1	Butylated hydroxytoluene
	Water 50-89%	2	Methylenebis phenol
	Soil-sediment >90%	4	Tetramethy; phenanthrene
	Soil-sediment 50-89%	1	Bis(2-ethylhexyl)phthalate
Tyre	Air 50-89%	1	Butylated hydroxytoluene
	Water 50-89%	4	Mercaptobenzothiazole
	Soil-sediment >90%	4	Diphenyl benzenediamine
	Soil-sediment 50-89%	3	2-methyl-n(2-methylphenyl)-benzenediamine

Notes: * - the compartment (e.g., air, water, sediment) that the compound is distributed within following release into the environment as defined by the modelling.

Tyres and brakepads contain a wide range of SVOCs as the materials used in their manufacture are relatively numerous and variable as they change over time as formulations change. Few data have

appeared in the literature in relation to any of the identified SVOCs. One group of compounds – the benzothiazoles is found present mainly in tyres. Concentrations range from 23.5-70.4 mg/kg for benzothiazole to not-detected to 242-437 mg/kg for mercaptobenzothiazole. Their presence has been confirmed in stormwater. Moncrieff & Kennedy (2002) reviewed the available data for benzothiazole. Concentrations of benzothiazole have been reported at 0.378 and 0.819 mg/m³ in stormwater; 2-hydroxybenzothiazole has been reported at concentrations of 0.721 and 5.640 mg/m³ in river water receiving stormwater (Reddy & Quinn 1997). 2-(4-morpholino)benzothiazole has been reported at concentrations of 0.015-0.384 mg/m³ in river water and highway runoff (Reddy & Quinn 1997, Kumata et al. (2002).

4.4.5 Dissolved organic compounds

The proportion of any organic compound present in stormwater in the dissolved phase is dependent upon the compounds structure and varies significantly between compounds. This variability is illustrated within the PAHs one of the key groups of compounds present in vehicle emissions. Brown et al. (2003) and Brown et al. (2003) reported a good relationship between increasing molecular weight and decreasing solubility with more than 50% of the low MW PAHs naphthalene through fluorine were soluble whereas less than 20% of the high MW compounds such as dibenzanthracene to indeno[1,2,3-cd]pyrene were soluble (Fig. 4.3). Brown et al. (2003) identified that 63% of total PAH (sum of 16 PAHs) were in the particulate phase during storm events. The authors noted that during periods of baseflow a greater proportion of PAHs were associated with the dissolved phase (67%).

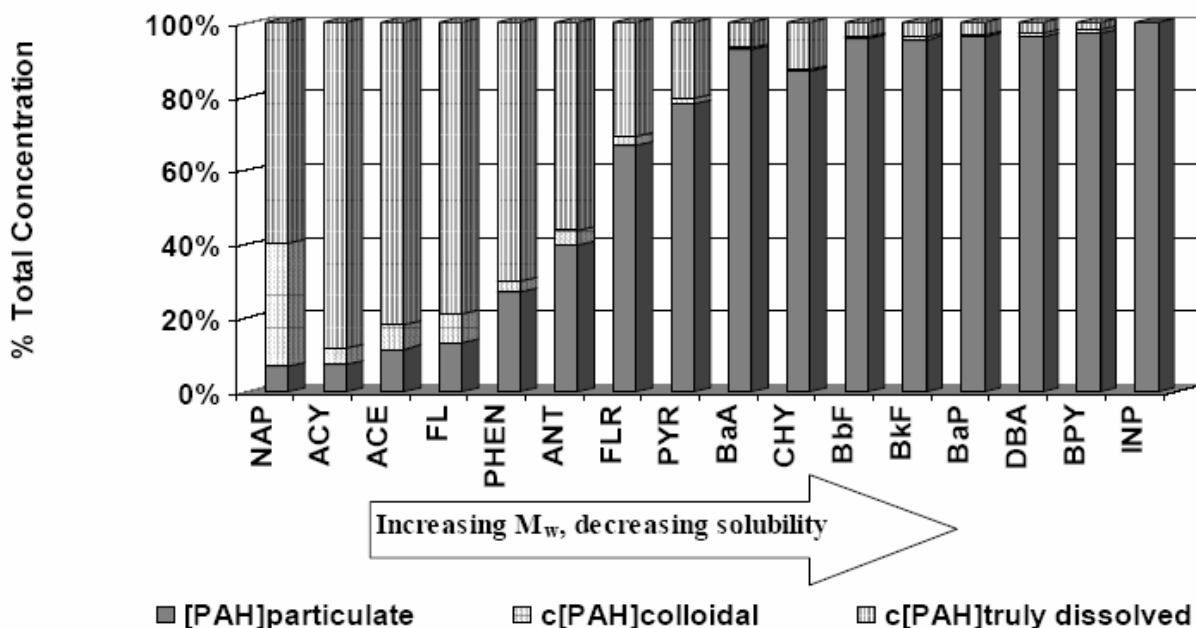


Figure 4.3 - Distribution of key PAHs between the dissolved, colloidal and particulate phases in urban stormwater (Taken from Brown et al. 2003) (For abbreviations refer list of abbreviations).

4.4.6 TPH and PAHs in stormwater particulate matter

ARC (1992) examined the concentration of hydrocarbons and PAHs in settleable suspended sediment in stormwater in Auckland. The suspended sediment in a bulk sample of stormwater from the residential catchment of Pakuranga was found to contain 7,800 mg/kg TPH. Measurements reported

by ARC (1994) indicated that TPH concentrations ranged from 1,000 up to about 4,000 mg/kg in the different particle sizes examined

Williamson (unpublished data in NIWA 1996) measured PAH concentrations in suspended sediment from Hillcrest (Hamilton) of 52 - 2,375 µg/kg. Hickey et al. (1997) examined PAH concentrations in suspended stormwater particulates from Mt Albert in Auckland. The results indicated a total PAH concentration of 972 µg/kg. Data for a total of 24 PAHs was reported ranging from 0.2 µg/kg for naphthalene, to 66 µg/kg for benzo(a)pyrene to 126 µg/kg for pyrene and 148 µg/kg for benzo(ghi)perylene.

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. The PAHs are the most well understood group of SVOCs and have been measured in stormwater.

The amount of any particular organic compound present in the dissolved phase is dependent upon its properties. 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.

4.5 Other Constituents

Other Constituents in Particulate Matter

The particulate matter transported by stormwater carries a range of other constituents other than metals and organic compounds. These other constituents include nutrients and oxygen demanding substances. ARC (1992, 1994) carried out an examination of the concentration of nutrients and their constituents in the particulate matter transported from a residential catchment in Auckland.

Organic carbon concentrations in suspended solids in stormwater were found to be higher than those measured in street gutter dusts (probably due to differential sorting of organic suspended solids). Concentrations of up to 22% organic carbon were measured. Density separation may result in the increase in concentration compared to the source. Increases were also noted in relation to total Kjeldahl nitrogen (TKN) with concentrations of up to 0.09% being measured. In relation to both OC and TKN, no assessment of the relative contribution of road transport to both constituents (from hydrocarbon and NO_x emissions) has been identified. However, although it has been assumed to be low, the relative contribution between road transport and urban landscape and other sources is expected to be highly variable.

ARC (1992) examined the phosphorus content of particulates in stormwater from residential and commercial catchments in Auckland. The results showed that although total phosphorus concentrations were high (typically >2,000 mg/kg), the available fraction was a very small part (typically 2%). Concentrations in that study appeared to be greater than would be expected in local soils (e.g., <1,000 mg/kg). ARC (1994) identified that the concentration of phosphorus was higher in the fine grain size fractions of the Pakuranga stormwater suspended solids.

Roadway runoff carries oxygen-demanding substances (refer ARWB 1988, ARC 1992). The variable nature of organic particulate materials present in stormwater results in variable oxygen demand. It is likely that non-roadway organic materials will have a more rapid five-day Biological Oxygen Demand (BOD₅) demand than materials such as rubber derived from vehicle tyres. No specific assessment of this topic has been sighted.

Urban roadway runoff particulate material is likely to be a source of nitrogen, BOD and possibly phosphorus to stormwater and hence receiving waters. No specific assessment appears to have been carried out identifying the contribution of roadways and vehicles to these primary nutrient

parameters. The oxygen demand processes associated with motor vehicle associated oxygen demanding substances does not appear to have been assessed.

General Stormwater Chemistry

ARWB (1988) and Williamson (1993) provide an overview of the concentration of other constituents in urban stormwater. The other key parameters include oxygen-demanding substances, nitrogen and phosphorus. ARC (1992) has examined the quality of stormwater generated from roads in residential and industrial parts of Auckland. Table 4.12 provides a summary of the concentration of these constituents in urban and motorway runoff. A comment is provided below on the key components and chemistry of stormwater runoff.

Table 4.12 - Summary of the concentration of general constituents in urban motorway stormwater (all data g/m³).

Study		BOD ₅	NO ₃	NH ₄	DRP	TP
Urban						
Williamson (1993)	10%ile	5	0.375	0.025	0.013	0.2
	50%ile	8	0.800	0.100	0.040	0.42
	90%ile	13	1.50	0.25	0.070	1.12
ARC (1992)	Pakuranga Resid.	-	0.606	0.024	0.019	0.098
ARC (1994)	Pakuranga Resid	-	0.626	0.043	0.014	0.101
ARC ((1992)	Southdown Ind	-	0.981	0.038	0.723	0.192
Mosley & Peake (2001)	Kaikorai	-	0.833	-	0.038	0.118
Macaskill et al. (2003)	Rotorua Resid	-	0.0595	0.057	0.036	0.118
	Rotorua Comm	-	0.042	0.062	0.032	0.109
	Rotorua Ind	-	0.034	0.019	0.01	0.179
Motorway						
Wu et. al. (1998)	3 lane bridge	-	0.38	0.66	0.08	0.20
	3 lane highway	-	0.19	0.62	0.26	0.37
	4 lane highway	-	0.08	0.42	0.16	0.26
Kennedy (1995)	Walnut Creek	3.5	0.28	-	-	0.10
	Dallas Tollway	6	0.88	-	-	0.38
	Collins Street	5.2	0.75	-	-	0.19
Irish et al. (1995)	MoPac (at 35 th St)	4.7	0.74	-	-	0.28
		2.1	0.56			0.08
		15.3	1.00			0.41
Barrett et al (1995)	MoPac (Convict Hill)	5.4	0.73			0.08
	35 th Street	12.2	1.03	-	-	0.33
	Convict Hill Rd	5.0	0.73	-	-	0.11
Ellis & Revitt (1989)	Various	-	0.76	-	-	-
Berbee et al. (1999)	Highways	6	0.5-0.9	-	-	-

pH

The pH of urban and highway stormwater runoff is typically around 7.0. Variation about 7.0 is dependent upon the chemistry of contributing land use adjacent to the road, the road surface and the pH of rainfall during the rainfall event. Typically rainfall in New Zealand is acidic (pH <6.0). pH during stormwater runoff events can vary depending upon the volume of accumulated water in catchpits as the pH of catchpit waterways differ to that of the stormwater runoff. pH is an important factor controlling the chemistry of metals in runoff. Macaskill et al. (2003) reported a number of pH results for stormwater in Rotorua with pH typically at about 6.8.

Cations/Anions

Common ionic constituents of stormwater will be derived from the interaction of rainfall with inorganic material on road surfaces and the road surface and from rainfall. Common ionic constituents in stormwater from highways have been measured in a number of studies (Bellinger et al. 1982, Harrison & Wilson 1985). Concentrations of common cations (Ca, Mg, Na, K, Fe, Mn) and anions (Cl, SO₄) are dependent on the geochemistry of soils contributing to particulates on road surfaces and the quality of rainfall. Road surfaces may also contribute and as noted by Mosley & Peake (2001), the changes contributed by surfaces contacted by rainwater will depend upon the time for interaction between the rainwater and the surface. Sadecki et al. (1996) showed that concrete would be expected to produce runoff with higher conductivity, higher (alkaline) pH, higher alkalinity and higher K and Na than asphalt. Environmentally significant changes in runoff chemistry typically only occur as a result of the use of de-icing salts. Although de-icing salts are used in New Zealand, they do not appear to be used in urban areas in New Zealand and as such are not discussed further in this report. Overall, general chemistry of runoff is likely to be site specific and very dependent upon the availability of geochemically reactive surfaces.

Mosley & Peake (1999) examined the ionic composition of stormwater in Dunedin. Their work has shown that the ionic composition of stormwater tends towards that of rainfall during the storm event. pH tended to decrease during the event. The ionic composition of stormwater is important because the toxicity exerted by free ions is influenced by the stormwater hardness. Hardness (calculated from calcium and magnesium concentration) will be greatest during the initial phase of storm events and decrease over time from 80 to 30 g/m³ (as CaCO₃) over the duration of the storm event sampled (Mosley & Peake 1999).

Nitrogen

ARC (1998, 1992) and Williamson (1993) describe the nitrogen content of stormwater. Table 4.12 summarises of nitrate and ammonia nitrogen stormwater data for New Zealand urban and overseas motorway areas. Williamson (1998) reports that total nitrogen is dominated by organic nitrogen and nitrate-nitrogen. Only a small proportion of the dissolved nitrogen is normally present as ammonia (e.g., see Macaskill et al. (2003) for Rotorua stormwater). However, in catchpits, anaerobic conditions can result in a greater proportion being present as ammonia (refer following section). As un-ionised ammonia is toxic, this is discussed further later in this report. The data in Table 4.12 indicates that the concentration of dissolved inorganic nitrogen in motorway and other roadway runoff can be elevated. Given the concentration of nitrogen in rainfall, the actual contribution of motor vehicles to stormwater nitrogen concentrations does not appear to have been identified.

Although motor-vehicles emit nitrogen (e.g., ammonia in exhaust emissions and nitrogen oxides), there is insufficient information to determine whether vehicle emissions are a significant contributor of nitrogen in urban road runoff. It is however, generally acknowledged that vehicles are not an important source of nitrogen in runoff (e.g., Macaskill 2001).

Phosphorus

ARC (1998, 1992) and Williamson (1993) summarise international and New Zealand data for phosphorus in urban stormwater. Some New Zealand data and a range of data for motorways is presented in Table 4.12. Phosphorus has been identified as being present in bitumen. The contribution of bitumen and bitumen wear to dissolved and total phosphorus in urban runoff is not known. It is likely, that the overall contribution is small. Kenedy & Gadd (2000) reported that tyres, brake pads and brake pad dust contained low concentrations of total phosphorus (medians 22.5-172.5 mg/kg). Raw bitumen was found to contain no detectable phosphorus (<20 mg/kg) but on-road bitumen samples from Auckland contained a median total phosphorus concentration of 1180 mg/kg which is at the upper end of concentrations for many rock types in New Zealand. Macaskill et al. (2003) reported moderate DRP concentrations for stormwater in Rotorua (Table 4.12) which were similar to the 50th percentile concentrations reported by Williamson (1993).

Oxygen Demanding Substances and DOC

ARC (1988, 1992) and Williamson (1993) summarise and discuss available data on chemical (COD) and biochemical oxygen demand (BOD) in urban runoff. Data is summarised in Table 4.10. COD is typically higher than BOD. Berbee et al. (1999) reported COD₅ in highway stormwater of 143 - 149 g/m³ compared to BOD₅ concentrations of 6 g/m³. COD is contributed by sediments in addition to biological matter and as such is typically very difficult to interpret. Mosley & Peake (2001) suggested that in Kaikorai in Dunedin, that the majority of the dissolved organic carbon (DOC) present in the stormwater arose from decaying plant material and soil particles (median concentrations 9.7 g/m³). DOC plays an important role in stormwater (and streamwater) chemistry as it complexes a number of key stormwater contaminants.

4.6 Effects of Road Surfaces

A number of studies have examined the effects of road type on the quality of stormwater generated on them (e.g., Kramme & Brosnan 1985).

In New Zealand the composition of road bitumen has been examined in several studies (refer Kennedy & Gadd 2000). Kennedy & Gadd (2000) examined the composition of raw bitumen and bitumen samples collected from roads in New Zealand. Raw bitumen was found to contain few detectable trace elements and few trace elements were identified in on-road bitumen that were present at concentrations similar to typical crustal abundance. Overall most elements were present in low concentrations.

Runoff samples collected following sealing with asphalt did not contain PAHs at a detection limit of 3 µg/m³. Sadecki et al. (1996) assessed the quality of runoff from stockpiles of crushed concrete and bitumen millings from road works. Some differences were observed that could be attributed to the nature of the materials (e.g., higher ionic concentrations in concrete runoff compared to bitumen). Sadecki et al. (1996) examined the runoff from the bitumen for the range of USEPA priority pollutant PAHs. The concentrations were in virtually all cases below detection limits that were in the order of 0.02 to 0.06 mg/m³.

Bitumen also has the potential to contribute hydrocarbons and in particular PAHs to stormwater. The nature of the hydrocarbon is likely to be dependent upon the age of the road surface (i.e., the time since the bitumen was laid down). It would be anticipated that PAH concentrations in runoff from bitumen road surfaces would change rapidly over time following the laying of new bitumen. Measurement of PAH concentrations in runoff from bitumen stockpiles in Minnesota did not find PAHs above detection limits which were typically <0.1 mg/m³ (Sadecki et al. 1996). However more recent work by Brandt & De Groot (2001) who examined the aqueous leaching of PAHs from bitumen and asphalt using static and dynamic leaching tests showed that a range of PAHs were leached from bitumen. The key leachable PAH was naphthalene (0.9-371 µg/m³) with other lighter PAHs (Acenaphthene to benz(a)anthracene) present at lower concentrations (0.1-180 µg/m³). Other heavier PAHs such as benzo(a)pyrene were present at low concentrations (<0.02-0.3 µg/m³).

Takada et al. (1990) considered that asphalt did not contribute a significant portion of the PAH in stormwater as microscopic examination showed that asphalt particles were only a minor component of street dusts in Tokyo. However, Faure et al (2000) considered that asphalt particles were evident in downstream environments from roads.

4.7 Catchpits & First Flush

There are two aspects of stormwater runoff from urban roads that need to be discussed to round of this description of stormwater runoff from roads in urban environments. The first is the influence that catchpits have on stormwater quality and the second is the "first flush" phenomenon that is often discussed.

Catchpits

Between the street surface and the stormwater system are catchpits (often referred to as gully pots or traps). The catchpits of which there are very large numbers in the urban stormwater drainage system 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. Memon & Butler (2002) provide an overview of catchpit water quality dynamics (particularly as it relates to water quality management). 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, BOD₅ (e.g., 13.7 mg/kg), chemical oxygen demand (COD), nitrate (e.g., 9.6 g/m³) and ammonia (e.g., 1.39 g/m³) (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 in the catchpit (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).

First Flush

First flush is a phenomenon that may occur during the early phase of stormwater events when the first passage of water carries material in the “wave” through the stormwater system. The first flush can result in substantial rises in the concentration to a peak in the early phase of the storm event. The peak in concentration is however highly variable between contaminants, between storm events and between catchments as the first flush is dependent upon the availability of materials and the size of the rain fall event (Bertrand et al. 1998, Deletic 1998, Lee & Bang 2000, Lee et al. 2002). First flush characteristics can also be influenced by catchpit contents (that may be flushed from the catchpit) and material accumulated in stormwater pipes (that may be eroded).

The first flush is a characteristic of storm events derived from roadways as the road surface accumulates particulates and contaminants that are subsequently transported through the sewer system. It is a feature of all impervious surfaces. The first flush becomes important to road transport management if vehicles contribute to the presence of contaminants that become an environmental issue in the first flush. This is discussed further in Section 6 of this report.

In summary, 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.

4.8 Summary

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.

Most road surfaces are constructed using bitumen. Some contribution to metal concentrations is likely. PAH concentrations appear low. Little data appears available on the hydrocarbon losses from newly constructed bitumen roads.

Data on gutter dust composition and stormwater sediment composition indicates that copper and zinc are the most abundant metal contaminants present. Most data on the concentration of lead was obtained prior to the removal of lead from petrol in New Zealand.

Although, the data on the composition of stormwater in New Zealand is principally urban in nature, there is data for stormwater chemistry for two New Zealand motorways. That information shows that the New Zealand motorway stormwater chemistry is similar to that from overseas motorways. Confirmation of the lead data should be carried out as lead has been removed from New Zealand petrol.

VOCs are present in stormwater at low concentrations. Their road transport source is 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.

5 PATHWAYS & FATE OF CONTAMINANTS EMITTED FROM TRANSPORT SOURCES

5.1 Introduction

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 the 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. The principle pathways and compartments being:

1. The atmosphere.
2. The road surface, collection and discharge system.
3. The freshwater receiving environment.
4. The estuarine and marine receiving environment.

Within these compartments, the physical and chemical processes that determine fate are complex. The number of different contaminants derived from motor vehicles also means that the contaminants are involved in a range of different physical, chemical and biochemical processes. In this section of the report, these processes are overviewed to provide an introduction to the factors that influence the fate of contaminants and their potential effects within freshwater and marine ecosystems. The key issues and questions examined include:

Transport:

Transport and deposition of airborne particulate matter.
Physico-chemical processes on the street surface.
Physico-chemical effects in stormwater receiving water systems.

Fate:

Fate in freshwater receiving environments.
Fate in estuarine and marine receiving environments.

5.2 Transport and Deposition of Airborne Particulate Matter

5.2.1 Introduction

The emission of particulates (from exhaust, tyres and other sources) to the atmosphere and their subsequent transport away from the point of emission allows road vehicle emissions to potentially have effects within environments adjacent to and remote to the source. As a result vehicle emissions can result in:

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

- Deposition of airborne particulates and gaseous pollutants onto estuarine and coastal waters.

The load or flux of a given contaminant is dependent upon the nature of the contaminant and the distance from source. Transport is dependent upon particle size, chemical and physical stability and climatic conditions. A brief overview of the fate of vehicle emissions is provided to give a context to the off-site effects that may be associated with non-stormwater contributions.

5.2.2 Particulate Material

The size of particles emitted by motor vehicles can range from a few tens of nanometres to millimetres in diameter depending upon engine operating conditions, engine condition, fuel type and other factors (USEPA 1977). Following emission, small particulates will agglomerate to form larger particles. In general, less than 10% of the mass of vehicle emissions particles are < 5 µm in size and 98% are < 11.5 µm in size (Ter Haar & Bayard 1971). 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 also result in particles (e.g., 5-50 µm in size) settling close to the roadway (Habibi 1973).

5.2.3 Local Deposition

A number of studies in New Zealand have shown that there is a 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. 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 close to the road.

Hewitt & Rashed (1990) assessed the examined 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. Ward et al. (1975) identified that 58% of the Pb emitted by motor vehicles on the Desert Road near Waiouru in New Zealand was distributed within 250 m of the roadway.

For PAHs, it was found by Hewitt & Rashed (1990) 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.

The material which would be deposited immediately adjacent to the road 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,

if these environments do occur immediately adjacent to the road.

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. These data are presented in Table 5.1.

Table 5.1 - 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.

5.2.4 Regional and Remote Deposition

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 lead from vehicle emissions.

There has been a very large amount of work undertaken on the distribution of Pb in the environment at a regional and at a global level. This information is widespread in the international literature. For earlier information the reader is referred to significant documents such as USEPA (1986) (Air quality criteria for lead documents).

In New Zealand, Fergusson (1993), showed that the lead dustfall flux decreased westward (inland) from Christchurch with 10-12 µg/cm²/yr being recorded in the inner city, 6-12 µg/cm²/yr in outer

residential areas, 3-5 $\mu\text{g}/\text{cm}^2/\text{yr}$ in rural areas and 1-2 $\mu\text{g}/\text{cm}^2/\text{yr}$ in remote rural areas and 0.1-0.3 $\mu\text{g}/\text{cm}^2/\text{yr}$ 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. Overall, the Fergusson (1993) assessment indicated a factor of 10 between urban and rural deposition and a factor of about 100 between urban and remote deposition in New Zealand.

Since the introduction of catalytic converters to motor vehicles (into the US, Canada and Japan in 1976), PGMs have been emitted from exhausts into the environment. Analysis of ice and snow on Mt Blanc by Van de Velde et al. (2000) demonstrated that Pd and Rh concentrations are higher in the last decades compared to deeper older snow (due to a variety of sources). In a study of PGEs in Greenland snow, Barbante et al. (2001) found that in recent snows dated from 1969-1975, concentrations of Pt, Pd and Rh were already 6, 15 and 45 times higher than observed in pre industrial snow (e.g., 7,000 yrs BP). In the period 1975-1995 following the introduction of catalytic converters, the concentrations had risen to 40, 80 and 120 times higher. The presence of these elements in Greenland snow provides evidence of their tropospheric transport and dispersion in the northern hemisphere.

Given the proportion of nitrogen oxide emissions attributed to motor vehicles (refer section 4), it is likely that motor vehicle emissions contribute nitrogen to fresh waters and coastal waters. It has been estimated that atmospheric nitrogen input to water bodies such as Chesapeake Bay range from 5 to 50% (about 30%). As such, vehicle-derived nitrogen oxides could potentially be an important contribution to the flux of nitrogen in coastal waters (in particular to enclosed harbours adjacent to large urban areas).

Information on the local, regional and global transport of contaminants emitted by motor-vehicles has shown that emissions can be transported to locations removed from the point of origin. The distance of transport and hence deposition is related to whether the contaminant was gaseous or associated with very small particles. Transport away from the source to areas beyond busy roads and urban areas, allows contaminants to be deposited to lake surfaces, intertidal mud-flats and the sea surface. This is discussed further in following sections of this report.

5.3 Fate on the Street Surface and in the Stormwater System

5.3.1 Introduction

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. These processes are important as they influence toxicity, potential bioaccumulation and other interactions with the natural environment.

5.3.2 Street Surfaces

Metals

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, aluminium (Al) (refer Section 2). 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 1977,1986). 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 elemental Pb. 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.

Acidic rainwater (e.g., pH 5-6 in New Zealand) can release metals to solution through two processes. The first is dissolving inorganic compounds, releasing the metal into the dissolved phase. The second occurs through the release of metal species that are attached to the particulate surfaces through the saturation of the surface by hydrogen ions. Typically however, the road surface buffers the pH increasing it towards neutral.

Studies of the chemistry of street surface particulate material have been undertaken using different extractions by a number of authors. The extraction of metals using a sequence of extractants endeavours to distinguish between exchangeable, carbonate, reducible (iron, manganese oxides), oxidisable and residual phases in the material. The oxidisable phase includes organic matter and sulphides. Given the number of emission sources and the different forms that the elements are present in the environmental mobility and the phase distribution will vary between the different sources of the elements. Extraction and speciation approaches are evaluated by authors such as de Mora & Harrison (1984) and Forstner (1986).

A number of studies have examined the geochemical phase distribution of trace elements in road surface particulates (Wilber & Hunter 1979; Harrison 1979; Lau & Wong 1983). Table 5.2 provides a summary of data from Laxen et al. (1981) and two other studies that have used similar extraction schemes (Fergusson & Ryan 1984; Banerjee 2003). Fergusson & Ryan (1984) undertook sequential extraction of the various road surface particulate samples they collected from various cities including Christchurch. The proportion of each element in the five fractions examined was very similar to the results obtained by Banerjee (2003). No significant differences in proportion extracted in the different phases were found between three particle size fractions examined by Fergusson & Ryan (1984). However, 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). The results presented in Table 5.2 are similar to those found using similar extraction schemes in other studies such as Li et al. (2001).

Other studies have utilised 0.5 M HCl extractions to identify a bioavailable fraction in street particulates (e.g., Sutherland & Tolosa 2000). The proportion of element extractable by 0.5 M HCL increased from a low of <20 % for elements such as Ti, V, Cr, Fe to 20-60% for elements such as Ni, As, Co, Mn, Ba, Cu to >80% for Pb and Zn (refer Fig. 5.1).

The key outcomes of the various studies are:

- ❑ The predominance of Cd in exchangeable, carbonate and Fe/Mn oxide phases.
- ❑ The predominance of Cu in organ phases.
- ❑ The predominance of Pb and Zn in carbonate and oxide phases.
- ❑ The predominance of Ni and Cr in more stable forms with most of the Ni in oxide and residual forms and most Cr in residual forms.

Table 5.2 - Sequential extraction data for urban street surface particulate material (all data %).

Extraction fraction	Cadmium		Copper		Lead		Nickel		Chromium		Zinc	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Exchangeable	20 ¹ 17.7 ² 27.16 ³	15-32 8.9-30.4 25.27-29.82	7 1.3 1.68	1.5-11 0-3 0.44-4.11	1.5 1.9 8.3	1-3 0-6.4 1.24-13.18	5.9 ³	1.41-12.47	1.6 ³	0.08-5.53	2 3.4 2.66	1-3 0.6-12.1 1.23-11.22
Carbonate	38 31.4 22.31	22-52 14.9-62.2 19.45-25.87	18 8.6 2.94	5-30 3.7-20.5 0.82-8.2	43 34.1 12	27-62 19.7-52.9 4.83-23.49	5.49	1.86-11.76	0.67	0.07-2.03	44 30.2 20.87	29-68 13.1-44.5 4.3-42.5
Fe-Mn Oxides	28 38.3 8.86	22-38 18.6-59.2 7.54-9.61	4.5 11.3 12.08	2-10 0.7-19.4 1.26-2305	38 44.2 28.26	24-56 26.6-58.5 8.54-54.96	12.31	5.7-19.43	7.47	2.47-13.83	43 50.8 45.64	23-54 42.5-63.5 34.58-60.03
Organic	8 7.8 2.9	2.5-19 1.9-13.9 0.59-5.23	58 53.2 44026	47-68 32.6-74.3 28.32-64.69	7.5 7.1 16.15	4.4-9.5 4.2-9.4 7.67-31.06	5.36	1.97-11.93	2.14	0.66-5.51	7.5 9.1 11.14	4.5-14 4.1-16.9 4.3-18.88
Residual	6 4.7 38.76	4-8 1-18.2 33.18-43.65	12 25.6 39.04	2.5-29 14.9-34.4 14.84-62.15	10 11.2 35.29	7-16 4.4-20.4 5.41-63	70.94	53.92-84.58	88.12	73.09-94.8	4.5 6.6 19.69	1-11 2.2-10.3 7.05-35.58

Note: Highlighted cells are those where the combined extraction is typically >80%. 1 – Harrison et al. (1981); 2 – from Fergusson & Ryan (1984). 3 – From Banerjee (2003)

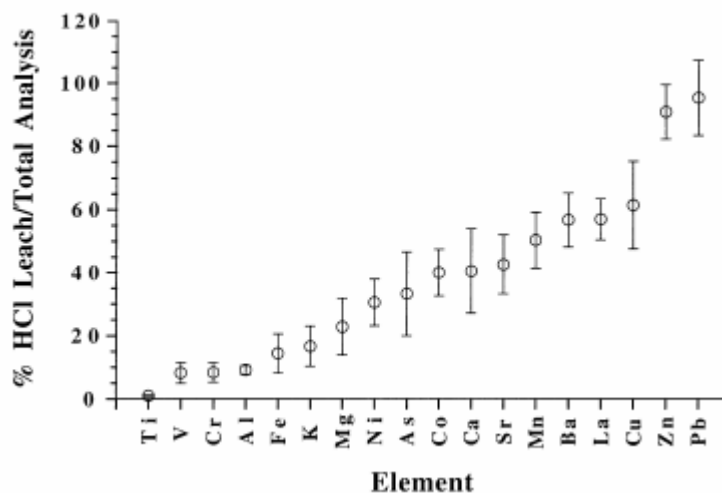


Figure 5.1 - Percentage of 0.5 M HCl extractable elements in road surface sediments from Moana Basin, Hawaii (From Sutherland & Tolosa 2000).

The proportions present in the various phases, provides some information about the environmental mobility under those experimental conditions and probably the broad environmental mobility. The general mobility does not directly relate to the proportion present in the dissolved phase. Examination of the dissolved data presented earlier suggests that for Pb and Cd, the exchangeable fraction may control much of the dissolution process for these elements with some contribution from the carbonate phase. For Zn the exchangeable phase does not contribute much of the Zn seen in storm events and it is likely that this is sourced from carbonate and oxide phases. For Cu, the dissolved copper is likely to come from both organic and oxide phases in street surface particulates. Revitt & Morrison (1987) concluded following an assessment of speciation of key metals through the stormwater system that the proportion considered bioavailable were 59%, 53% 38% and 5% for Cd, Zn, Cu and Pb. The implications of the relative bioavailability, is discussed further in the following sections on effects in freshwaters and marine waters.

Overall, geochemical processes on the road surface affect the behaviour and form of inorganic materials, compounds and metals on the road surface before and during storm events. The key factor is the affect of low pH (acidic) rainwater and the dissolution processes that move metals from solid phase to dissolved phases in stormwater. Although the exact processes are not known for all key metal contaminants, available information indicates that while on the road surface metals undergo phase re-distribution.

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. 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 3.2). 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. BTEX compounds are more biodegradable than MTBE. MTBE is considered relatively re-calcitrant and is not influenced by processes such as hydrolysis and photolysis.

Table 5.2 - 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 (mg/L)	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} = octanol/water partitioning coefficient. Log K_{oc} = octanol/carbon partitioning coefficient. In relation to a number of the key VOCs emitted by vehicles the following comments can be made.

Benzene

Benzene is an aromatic hydrocarbon, it is non-polar and is relatively soluble in water (Table 5.2). Benzene 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 (USEPA 1993). Benzene's low aqueous solubility limits its concentration in rain.

Ethylbenzene

Ethylbenzene has limited solubility in water compared to benzene and xylene (Table 5.2). 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)

Toluene has a moderate solubility in water (Table 5.2). 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

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

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

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., SO₂) in rain and water.

In summary, VOCs present in motor vehicle 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 significant concentrations of VOCs are present in detectable concentrations of stormwater. As noted earlier, this is however very dependent upon the limits of detection used in the analysis of stormwater for VOCs.

Diesel Particulate Matter and PAH

Diesel particulate matter is made up of small (0.1 - 1.0 µm) particles with a carbon core. Below temperatures of about 500°C the particles become coated with adsorbed high molecular weight organic compounds. These compounds comprise open-chained hydrocarbons (14-35 carbons), alkyl substituted benzenes and derivatives of PAHs. The fate of PAHs emitted from motor vehicles is dependent upon the type of PAH as the higher MW PAHs (e.g., benzo[a]pyrene) are more strongly particulate associated than those such as pyrene.

5.3.3 Catchpits

Catchpits (or catchbasins) are the entry points to the piped stormwater system and typically have a 200 mm deep sump at their base to catch larger solid particles that are not caught on the catchpits inlet grate. The sump also acts as an odour seal. Gravel and other objects build up in the sump and are periodically removed as part of maintenance. As the catchpits also contain water and that water may remain in the sump for some time between rain events, the nature of the sump environment may change over time.

A variety of physical and chemical processes occur in catchpits during storm events. Morrison et al. (1988) summarised these as dilution, dispersion, sedimentation, sediment bed build-up and erosion, washout of suspended and dissolved pollutants from the pot liquor and re-aeration of the pot liquor. During stormwater runoff events, the stormwater entering the gullypot can cause changes in pH, ionic strength, dissolved organic carbon and suspended solids concentrations and alterations in these parameters will influence metal speciation (especially bioavailable and toxic forms) (Morrison et al., 1984).

Detailed studies of roadside gullypots have identified their potential as pollutant sources which can contribute significantly to the deterioration of stormwater runoff quality (Fletcher et al., 1978; Mance & Harman, 1978). Fletcher & Pratt (1981) have shown that the liquid in the catchpit sump may contribute up to 22% of the suspended solids in the total outfall runoff for individual storm events. The gullypot contents can undergo significant biogeochemical changes, particularly during prolonged dry periods. The key change that affects geochemical processes in the sump is the generation of anaerobic conditions. Anaerobic conditions in the sump can lead to the release of soluble organic compounds which will influence the distribution of metal species between the dissolved and insoluble phases; changes in the speciation of metals and the conversion of oxidised forms of dissolved inorganic nitrogen to ammoniacal-nitrogen. During this time microbial decomposition of organic matter such as leaves in the sump continues leading to increases in the concentration of dissolved organic compounds in the sump liquid. Morrison et al. (1988), Karunaratne (1992) and others have identified that between storm events, the catchpit sump behaves like a batch reactor. Memon & Butler (2002) examined processes in catchpit sumps. Their examination of catchpit sumps showed that dissolved oxygen dropped within the sump as biochemical/biological processes used up the oxygen such that by about 10 days the DO concentrations in winter were 2-3 g/m³. During summer, concentrations would be expected to fall to zero. Ammoniacal nitrogen concentrations are typically higher in summer compared to winter and rise with time following the cessation of the prior storm event. Concentration differences are greatest for catchpits containing sediment (with organic matter which releases DIN through biological processes) (Memon & Butler 2002).

Morrison et al. (1988) summarised that although, the dissolved metal concentrations increase in the supernatant catchpit sump waters between storms, the pattern of increase can often be irregular due to an increasing tendency as the pH of the sump liquid increases over time for metals to adsorb onto solids in the sump. Morrison et al. (1988) noted that Cd behaviour differs in that dissolved Cd tends to increase to equilibrium over time. Morrison & Revitt (1987) and Revitt & Morrison (1987) discuss speciation and chemical changes in the stormwater and catchpit.

Overall, catchpits play a role in the biogeochemical conversions that street surface particulate material is exposed to. Material trapped in catchpit sumps can be exposed to anaerobic conditions for days between storms. The exposure to anaerobic conditions results in conversion of DIN to ammoniacal nitrogen, release of some metals to dissolved phase. The flushing of catchpit contents during storms results in a pulse of water with different chemical composition entering the downstream stormwater system and entering the receiving environment. The key implication of changes in chemistry from the road to the receiving environment is any potential to transform solid phase non-toxic contaminant phases into dissolved potentially toxic forms. This is discussed further in the following sections.

5.4 Freshwaters

5.4.1 Introduction

Following transport through the stormwater system, the stormwater may be discharged into a freshwater stream, river or lake. Following entry into the freshwater environment, the materials carried in the 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.

5.4.2 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.

5.4.3 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.

5.4.4 Other Processes

Once in the receiving environment other processes influence the fate of contaminants. These include relatively short term processes (noted in Section 3.3) 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).

5.5 Estuarine and Marine Waters

5.5.1 Introduction

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

5.5.2 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 compared to freshwaters (examples of contaminant build-up adjacent to discharge points are provided in Section 6).

5.5.3 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 lead in the sediments of the Manukau Harbour (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/m³ in Long Island stormwater. Wakeham et al. (1983) reviewed the fate of toluene in seawater. The key pathways for removal of toluene were volatilisation and biodegradation (mainly in summer). The authors 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:

Volatilisation accounted for 52% of the flux in winter and 17% in summer.

30% of the toluene remained as dissolved toluene in water in winter and <1% in summer.

16% of the toluene remained in the water as dissolved CO₂ and 2% was lost as gaseous CO₂ in winter. In summer the corresponding figures were 76% and 3% respectively.

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.

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.

5.6 Summary

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

Atmospheric dispersion with consequent wet and dry deposition.

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:

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).

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).

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.

SVOCs such as PAHs will be subject to degradation and other processes (such as biological uptake) which will in the long term result in their loss from the receiving environment. Changes in the receiving environment will be dependent upon the balance achieved between their inward flux and their loss.

Recalcitrant organic compounds such as MTBE will accumulate with the actual concentration depending upon the inward flux to the receiving water and their slow loss (e.g., by bio-degradation).

6. ENVIRONMENTAL EFFECTS IN FRESHWATER ENVIRONMENTS

6.1 Introduction

Freshwater environments in New Zealand include a diverse range of waterbodies from lakes to small lowland streams and large rivers (refer references such as Jolly & Brown 1975, Viner 1987, Collier & Winterbourne 2000). This section of the report discusses the issues and effects associated with the entry of road runoff into freshwater receiving environments. The key issues associated with the discharge of stormwater derived from roads into freshwaters are:

- ❑ Hydrological effects
- ❑ Effects on water quality.
- ❑ Effects on freshwater ecosystem (i.e., the biological community).
- ❑ Effects on sediment quantity and quality.
- ❑ Bioaccumulation (the uptake of contaminants by freshwater organisms).

As noted in the introduction of this report, this reports deals with the non-physical effects of stormwater from roads and as such, hydrological issues associated with imperviousness are not dealt with. Herricks (1995), Burton & Pitt (2002) and Schueler (2003) provide comprehensive reviews of the effects of urban runoff on freshwater environments. Table 6.1 provides an overview of the key impacts (toxic substances, clarity) that may be attributed to roadway runoff. Reviews of the effects of urban runoff on New Zealand streams can be found in Williamson (1993) and Suren (2000). The methods and tools currently used to assess environmental effects within freshwater environments are discussed to identify whether the tools are sufficient to determine the effects of road transport contaminant emissions on the environment.

Table 6.1 - General impacts of urban runoff, which can be partly attributed to road transport.

Input	Effect
Suspended sediment	<ul style="list-style-type: none"> ● Change in bed characteristics ● Blanketing of existing bed
Metals	<ul style="list-style-type: none"> ● Change in organic carbon status and redox status ● Toxicity (acute and chronic effects) ● Bioaccumulation
Organic compounds	<ul style="list-style-type: none"> ● Secondary effects arising from toxicity (elimination of sensitive species) ● Change in sediment quality ● Toxicity (acute and chronic effects) ● Bioaccumulation ● Secondary effects arising from toxicity (elimination of sensitive species)
Hydrocarbons	<ul style="list-style-type: none"> ● Change in sediment quality ● Aesthetics ● Chronic toxicity

6.2 Freshwater Ecosystems

6.2.1 Introduction

Biological monitoring is the use of biological responses to evaluate temporal and spatial changes in the environment, with the intent to use this information as an environmental management tool (for example in a water quality programme). There are a range of different tools available to assess the effects of land use changes and inputs on the biological resources of stream environments. The difficulty in selecting appropriate tools/indicators is knowing what responses can be expected from known environmental stressors. The problem therefore includes the following components:

1. Selecting appropriate response variables.
2. Defining an appropriate variable that relates to the identified contaminant.

Urban runoff has the potential to significantly degrade biological resources within urban freshwater ecosystems (Pitt et al. 1995; Suren 2000, Burton & Pitt 2002, Scheuler 2003). Studies have shown that urban runoff can have deleterious effects on habitat (e.g., Snelder & Trueman 1995), algae (e.g., Winter & Gindley 1980), aquatic invertebrates (e.g., Bascombe 1988, Wilding 1996) and fish (Pitt & Bozemann 1982, Medeiros & Coler 1982). Suren (2000) provides a review of the effects of urbanisation on freshwater ecosystems in New Zealand. Suren et al. (1998) recently described a method for assessing and monitoring in-stream habitat and benthic invertebrates in New Zealand urban streams. Suren's study reflects the growing awareness of the potential effects that urbanisation have on streams amongst policy and regulatory agencies with freshwater management responsibilities in New Zealand. Although there are tools to study the effects of urbanisation on freshwater environments, these tools have been developed to identify effects arising from numerous sources/causal agents that include amongst them the stormwater runoff from roads.

Quantifying the effect of urban runoff on in-stream habitat and biota is complicated by the spatial and temporal variability associated with streams and with discharges. Urban stream water quality and therefore stream biota vary spatially and temporally as a function of stream flow (USEPA 1980). Water quality in urban streams are affected by a range of factors including:

1. Catchment factors (e.g., % impervious area, industrial activity and average daily traffic volume).
2. Hydrological factors (e.g., storm frequency/intensity/duration and antecedent dry period).
3. Transport system (e.g., collection and discharge system and separate or combined sewer).

The potential effects of road transport related pollutant sources on in-stream biota are poorly understood with few 'tools' available to freshwater managers for assessing the specific effects of road runoff. The potential of a range of tools for quantifying the effect that road runoff on in-stream biota has been investigated in a number of overseas studies (e.g., Winter & Gindley 1980, Smith & Kaster 1983, Dupuis et al. 1985, Barrett et al. 1995a,b,c). The potential effects of road runoff will have many components, which are similar to those resulting from the generation of stormwater from non-road impervious areas within urban environments (i.e., general urban runoff).

A range of general biological monitoring tools have been developed to assess and monitor stream biological communities in New Zealand. In general these tools have been developed to assess land use, and point source discharge effects on in-stream habitat and biota. A majority of these tools have focused on addressing pollution problems in rural environments (e.g., QMCI Stark 1993). Many aspects of New Zealand stream environments and the tools for undertaking monitoring are described in Collier & Winterbourn (2000) and in particular in Boothroyd & Stark (2000). The New Zealand Ministry for the Environment has released a number of reports in recent years that provide significant tools for monitoring the health of freshwater streams in New Zealand. These include Stark et al. (2001) (protocols for sampling macroinvertebrates in wadeable streams) and Biggs (2000) (New Zealand periphyton guidelines: detecting, monitoring and managing enrichment of streams).

The following parts of this section of the report aim to:

1. Identify the range of tools available to freshwater managers for assessing and monitoring in-stream biota in New Zealand.
2. Briefly describe the general utility of available tools for assessing and monitoring freshwater biota.
3. Evaluate the applicability of each of the available tools to assessing road transport effects on freshwater ecosystems.
4. Identify gaps in the current range of tools and evaluate additional tools for helping assess road transport effects.

6.2.2 In-stream Habitat

In-stream habitat incorporates all aspects of physical and chemical constituents along with biotic reactions (USEPA 1997). For the purposes of this investigation "habitat" has been defined to include the following elements:

- Stream-bed substrate.
- Organic in-stream debris.
- Stream channel banks.
- Morphological subsections (riffles, runs and pools).
- Riparian vegetation

Effects of road runoff on in-stream and riparian habitat

In-stream habitat plays an important role in determining the health of the biological communities present. Road runoff has the potential to compromise in-stream habitat quality by affecting the habitat elements listed above. The most significant mechanism for these changes is through the input of sediment. As described in Section 2, total suspended sediment is a significant component of road runoff pollution (Barrett et al. 1995). Sediment inputs can result in degraded in-stream habitat quality. Examples of the types of changes in habitat quality that arise from sediment inputs into urban streams include:

- Poorly sorted mobile sediments in runs and riffles.
- Reduced habitat diversity.
- Reduced benthic primary production through smothering of algae.
- Clogging of interstitial spaces.
- Poorly differentiated pools, riffles and runs.

Schueler (1996) identified that stream channel geometry stability can be a good indicator of the effectiveness of stormwater control practices. It was identified in that review that once catchment areas have more than 10 to 15% imperviousness alterations to waterway channel morphology occur. Brookes (1988) also identified stream morphological changes related to urbanisation. These physical changes are primarily responsible for habitat change and loss then has subsequent adverse effects on aquatic communities.

Stormwater from roads will transport gravels and finer particulate material that may cause local changes in substrate conditions near the discharge point. The significance of the change will depend upon the local sediment type and environment. Transport of finer particulate material downstream may contribute changes to particle types in sediment (e.g., particles of asphalt or bitumen – refer Faure et al. 2000) but these changes are not likely to result in significant enough habitat changes which may then induce changes in biological community composition.

General Assessment Tools

Commonly used tools for assessing habitat quality in New Zealand streams include:

1. Rapid Bioassessment Protocols (RBP's) (USEPA 1997).

The RBP's recommends that a wide range of habitat data is collected to help in the interpretation of biological data. The RBP's habitat element list includes:

- Stream width.
- Stream depth.
- Proportion of reach represented by stream morphological types.
- Velocity.
- Channelisation.
- Presence of dams.
- Canopy cover.
- Substrate size classes.
- Sediment deposits.
- Organic substrate components (e.g., woody debris).
- Sediment odours/oils.

2. Modifications of RBP to New Zealand Conditions.

Freshwater researchers and regulatory agencies have modified the RBP's to reflect the unique stream habitat conditions that exist in this country. Included in these changes is the use of invertebrate biological indices such as the macroinvertebrate community index (MCI).

3. Riparian Zone Assessment.

Riparian zones are crucial to determining the water and habitat quality within streams. Assessing riparian zones is therefore an important part of assessing overall stream ecosystem health. Collier et al. (1995) provide a guide to the assessment of riparian zones within New Zealand stream catchments. Roadway runoff has little direct affect if any on riparian vegetation (apart from indirect hydrological effects on stream bank stability in particular circumstances). There are only a small number of studies that have addressed the question of contamination of roadside vegetation (which is related to airborne transport of particulate matter and gaseous and particulate contaminants) and no existing assessment tools have been identified.

4. Urban Stream Habitat Assessment Method (USHA).

USHA (Suren et al. 1998, 1999) is a recent attempt to help freshwater stream managers assess and monitor urban stream habitat quality and benthic invertebrate health. USHA involves the collection of a wide range of habitat data. Benthic invertebrates have been assigned 'tolerance values'. These scores are analogous to the MCI scores developed by Stark (1985) for benthic invertebrates inhabiting stony bottomed streams in Taranaki and which are widely used by regional councils and freshwater biologists in New Zealand. USHA represents the first effort to provide a methodology for assessing urban stream habitat and benthic invertebrates. Its utility for assessing and monitoring the effects of roadway runoff is unclear as it has yet to be incorporated into Regional Council monitoring programmes.

Tools specific to assessing transport effects

Of the biological assessment tools currently available for assessing in-stream habitat none are specifically designed to assess the potential effects of runoff from roads. Assessing substrate

composition and total suspended sediment are likely to provide the most ecologically relevant information for assessing road transport effects on in-stream habitat quality. Sediment sources within urban environments are varied. Quantifying the proportion of suspended and deposited sediment present in urban streams that is derived from roads is therefore complicated. The tools that are currently available are, with some modifications, adequate for quantifying the proportion of road generated sediment inputs to urban stormwater runoff. Modifications to existing sediment assessment tools include:

- ❑ Identifying and quantifying the source of sediment using characteristics of road generated sediment such as rubber, asphalt and specific contaminants.
- ❑ Identifying and quantifying in-stream sediment size composition and comparing this to road surface sediment.

The importance of macroscale factors (geology, temperature etc.,) in affecting macroinvertebrate communities has been emphasised by Suren et al. (1999). Although the USHA assessment programme did not include stormwater quality/significance as a factor in the assessment of variables, it is likely that in some situations, the macroscale factors would have an over-riding effect compared to the potentially toxic effects brought about by short-term stormwater discharges. This requires further evaluation.

Overall, the available biological assessment tools for examining habitat quality can be applied to the assessment of habitat effects on freshwater streams where stormwater from roads is the only influencing factor (i.e., effects are not confounded by other activities, discharges or other contaminants derived from general urban runoff). In those situations where confounding occurs then existing tools do not provide specific information in relation to the effects of road runoff. USHA does provide a systematic process to identify habitat quality and therefore by inference, the likely quality of the biological community that could exist at the site.

Overall, motor vehicles themselves do not have any direct effects on stream and waterway habitat. Any effects are indirect and are related to the effect of the roading infrastructure the vehicles are associated with. Roads form a key component of the overall imperviousness of urban areas. Impervious area is a key factor controlling the nature and quality of aquatic environments within urban areas (Scheuler 2003).

Roads will along with other impervious areas play a role in changing hydrological environments in waterways within urban catchments (through hydrological profiles of storms and changes in base-flows). Roads will also provide particulate materials through wash-off that may result in localised changes in substrate conditions and more diffuse contributions away from the source (e.g., gravel and asphalt particles).

6.2.3 Aquatic algae

Periphyton assemblages (primarily algae) are a useful water quality monitoring tool because of their rapid response time to exposure and recovery. Despite this, algae have not been incorporated widely into monitoring programmes (USEPA 1997). In New Zealand, bio-monitoring programmes have tended to focus on benthic invertebrates ahead of algae. However, Biggs (2000) provides a comprehensive examination of periphyton in New Zealand freshwaters and the effects of human activities on periphyton growth and composition.

Effects of road runoff on aquatic algae

Roadway runoff has the potential to affect aquatic algae in a range of ways including:

1. Altering flow conditions.
2. Increasing water temperature.

3. Increasing sediment inputs.
4. Increasing nutrient inputs.
5. Increasing contaminant loads.

The results of investigations into the effects of highway runoff on algae have to date been somewhat contradictory. Dussart (1984) for example, reported that algal diversity and abundance increased downstream of urban/highway runoff due to an increase in nutrient loadings and a decrease in invertebrate algal grazers. Portele et al. (1982) on the other hand reported that algae biomass decreased with increasing concentrations of highway runoff. Winters & Gindley (1980) concluded that highway runoff has the potential to have an inhibitory or stimulatory effect on algae depending on the chemical composition of the runoff (i.e., the presence of nutrients). Macaskill et al. (2003) identified that stormwater runoff (From Rotorua City in New Zealand) has chronic effects on the growth of the freshwater algae (*Selenastrum capricornutum* 72 hour growth inhibition toxicity test).

General Tools

USEPA (1998) describe a range of periphyton (algae, fungi, bacteria, etc..) metrics currently in use in the United States. Metrics listed include 7 diatom metrics and 6 non-diatom metrics including taxa richness, indicator species, relative abundance, chlorophyll-a and ash free dry weight (AFDW). Methods that use algal indicator organisms are complicated by spatial and temporal variability, naturally rare species and problems associated with identification. However some species, which are known to reflect certain water quality conditions, do provide useful information. In New Zealand biomonitoring programmes have traditionally tended to focus on chlorophyll a, AFDW, and algal abundance. Substantial work has been carried out on periphyton communities in New Zealand waterways as a result of their effect on stream aesthetics and effect on quality of habitat for invertebrates. The reader is referred to MfE (1992) and Biggs (2000) for further information.

Specific Tools for assessing road runoff effects

There are no tools specifically designed to assess the effects of road runoff on algal communities. Stream algal community composition and biomass reflect the nutrient status of the water. Urban streams tend to have relatively high nitrogen and phosphorus inputs and reflect a variety of nutrient sources within the urban environment. Isolating and quantifying the effect that nutrients within road runoff have on algal communities from general urban runoff is therefore likely to be very difficult.

Overall, methods for the measurement and assessment of periphyton communities in waterways are well developed in New Zealand. Use of these tools in localities where urban runoff contains significant contribution from motor vehicles and general urban activities does not allow the specific effects associated with road transport to be identified. However, in locations where stormwater discharges from roads or highways is the sole contributor, the assessment of periphyton quality and composition will provide information on effects of stormwater as it relates to that component of the freshwater biological community.

International work suggests that urban stormwater and road runoff may have both inhibitory and stimulatory effects on in-stream algal communities. The stimulatory effects arise from the nutrients present in road runoff. The inhibitory effects arise from the presence of a variety of contaminants in the runoff. In New Zealand general urban stormwater runoff has been shown to inhibit the growth of freshwater algae.

6.2.4 Aquatic Invertebrates

Invertebrates (aquatic insects, molluscs, oligochaetes etc..) that are ubiquitous in most stream environments are sensitive to water and habitat quality. These features make invertebrates important tools for assessing and monitoring in-stream health. A range of invertebrate monitoring and

assessment tools has been developed. Boothroyd & Stark (2000) review the use of invertebrates in freshwater monitoring. Scheuler (2003) discusses monitoring tools and provides a detailed review of the effects of changing urbanisation through increases in impervious area on freshwater invertebrate communities. The effects of increasing impervious area within catchments has been recognised in a large number of studies. Aquatic invertebrate communities typically respond to increasing imperviousness by a decrease in diversity and richness decreasing and by the loss of pollution sensitive species (e.g., the EPT taxa – refer following section) and a shift towards more pollution tolerant species (e.g., in relation to temperature or other factors).

Effects of road transport on invertebrates

Road runoff has the potential to effect benthic macroinvertebrates through altering a range of water and habitat quality variables. A search of the literature revealed that there has not been any published data describing the specific effects of “road runoff” (in contrast to urban runoff) on benthic invertebrates in New Zealand. Winterbourn (1981) reviewed the use of aquatic invertebrates in studies of water quality in New Zealand and as noted earlier Suren (2000) reviews the effects of urbanisation of macro-invertebrates in New Zealand Streams. These reviews included descriptions of the effects of urbanisation on invertebrate including:

- ❑ Reduced species richness (particularly Plecoptera and Ephemeroptera).
- ❑ Increase in algal and detrital browser abundance.
- ❑ Increase in larval Elimidae (beetles) abundance.
- ❑ Increase in oligochaete, snail, chironomidae and mollusc abundance.

Urbanisation affects aquatic invertebrates by altering biochemical conditions, food resources, respiratory diffusion gradients and habitat space (including filling of substrate interstices).

There are a number of biological monitoring studies from overseas which have investigated the effects of urban/road runoff on benthic invertebrates.

Bascombe (1988) reported on the use biological monitoring of benthic invertebrates for the assessment of heavy metals in urban rivers in the UK. Bascombe observed that it is difficult to relate ecological monitoring observations (e.g., community structure) directly and solely to the impact of heavy metals. However, biological assays (toxicity testing using invertebrates collected from the field) provide a useful tool for establishing cause and effect relationships. Bioassays also have the advantage of been relatively cost effective compared to biological surveys (Barrett et al. 1995).

Dupuis (1985) and Lord (1987) reported finding no relationship between traffic density (12,000-120,000 cars VPD) and effects on in-stream biota. Smith & Kaster (1983) investigated the effects of rural highway runoff on stream benthic invertebrate biomass and abundance and concluded that there was a minimal effect from roadways with 7,000-8,000 VPD. Shutes (1984) investigated the effects of surface runoff on a benthic invertebrate community in an urban stream in London and concluded that urban development resulted in reduced diversity and changes to community composition. Shutes (1984) also observed a decrease in a range of biotic index scores from unimpacted upstream sites compared to sites downstream that were subject to increased levels of urban runoff. Maltby et al. (1995a) determined that in 57% of streams examined, the macro-invertebrate assemblages at sites receiving motorway runoff were less diverse and contained fewer pollution sensitive taxa than at control sites.

A study by Perdikaki & Mason (1999) did not find any major impact of road runoff on macroinvertebrate communities in England. The study results suggested that road run-off might have an effect during low flow conditions but the effect was not considered significant. It was considered possible that other effects were masking the effects of the motorway run-off.

In New Zealand, Suren et al. (1988) reported that in urban streams in nine New Zealand cities, that the invertebrate fauna was dominated by a limited fauna (dominated by oligochaete worms, snails such as Potamopyrgus and chironomids and in low diversity and abundance of EPT taxa. Suren et al. (1998)

considered that taxa richness was relatively high in the New Zealand urban streams they studied. Suren (2000) notes that as urban streams are typically highly modified and water quality is low the overall ecosystem in urban streams is degraded and this is then reflected in the nature of the macro-invertebrate community present (especially when compared with non-urban streams). There have been a number of studies in New Zealand that have examined the biological resources of urban streams. These studies include Kingett Mitchell (2000) who examined stream environments in Waitakere City; Kingett Mitchell (2001), urban streams in North Shore City catchments; Suren (2001), urban streams in Auckland City; Wilding (1996, 1999) urban streams in Auckland; Kingett Mitchell (in prep), Wellington streams and Macaskill et al. (2003), Rotorua City. Table 6.2 summarises the results of the study undertaken in Waitakere City (Kingett Mitchell 2000), which illustrates some of the trends in macroinvertebrate metrics.

Table 6.2 - Invertebrate indices scores for streams in Waitakere City grouped by land use. (taken from Kingett Mitchell 2000).

Land use	Taxa No.	EPT Taxa No.	EPT Ratio	QMCI	QUCI	Margalefs	% Dominant taxon
Native bush	19 ± 2	8.3 ± 3.2	0.5 ± 0.2	5.6 ± 1.1	0.9 ± 0.2	3.5 ± 0.3	34 ± 6
Urban/bush	11 ± 4	3.4 ± 1.3	0.0 ± 0.0	5.0 ± 0.3	1.0 ± 0.4	1.8 ± 0.5	71 ± 9
Rural	17 ± 1	3.6 ± 1.2	0.1 ± 0.1	3.6 ± 0.3	0.4 ± 0.2	2.6 ± 0.2	48 ± 7
Urban/rural	15 ± 3	2.0 ± 1.0	0.0 ± 0.0	2.9 ± 0.2	0.4 ± 0.4	2.3 ± 0.0	52 ± 23
Urban	9 ± 1	0.5 ± 0.2	0.0 ± 0.0	3.2 ± 0.2	0.0 ± 0.0	1.4 ± 0.1	66 ± 5

Note: Values are presented as mean ± 1 standard deviation.

General Tools

Macroinvertebrates are the most commonly used bio-monitoring tool when freshwater bio-monitoring is undertaken (Rosenberg & Resh 1993). In general, benthic invertebrate bio-monitoring focuses on community level characteristics such as taxonomic diversity and the presence/absence of sensitive indicator species. More recently bio-monitoring investigations have assessed the effect of specific environmental stressors on biochemical, genetic, morphological and physiological changes.

Macroinvertebrates assimilate and reflect water quality and habitat conditions over time and are therefore ideal indicators of environmental stress. Advantages of using benthic macroinvertebrates in biomonitoring programmes include:

1. Commonly occurring.
2. Community diversity reflects a wide range of environmental stressors.
3. Relatively sedentary and therefore reflect localised conditions.
4. Bio-accumulate toxic substances.
5. Detectable changes in community structure are obvious to trained biologists.
6. Easily collected and identified.
7. Integrate multiple stressors and therefore reflect overall stream health.

Benthic macroinvertebrates are widely used by freshwater managers in New Zealand to assess and monitor water quality and in-stream health. In New Zealand, benthic invertebrate bio-monitoring has focused on community level data. A range of biological indices has been used to simplify complex species lists into single numbers that are easily understood by non-biologists. The inset box provides a summary of the range of indices and metrics available with which to assess community well-being.

Tools with specific relevance to assessing road transport effects

Tools, which are specific to assessing road runoff effects on macro-invertebrate communities in stream environments, have not been identified in this review. The strength of invertebrate bio-

monitoring is in its ability to assess general effects of land use changes and activities. The inherent spatial and temporal variability of invertebrate communities limits their ability to isolate and quantify specific effects such as those associated with road runoff. It is unlikely therefore that assessing invertebrate community structure will provide meaningful data for isolating/quantifying the effect of road runoff.

A number of the existing invertebrate bio-monitoring tools could be modified to reflect the specific effects associated with road runoff. Invertebrate bio-monitoring tools, which have the potential for development, include:

- Derivations of UQMCI that reflect the sensitivity of invertebrates to road runoff.
- Indicator species approach.

A considerable amount of research would be required to develop these tools to a point that they were able to be used to isolate and quantify the effect of road runoff from general urban stormwater runoff.

Overall, macro-invertebrate monitoring and assessment tools provide information on the overall state of the aquatic environment. In waterways with multiple inflows and other impacts the tools do not allow the effects of road runoff to be isolated.

However, as with other tools, in situations where road runoff is isolated (e.g., in remote locations) or where an upstream-downstream comparison is possible, the tools may isolate effects associated with motor vehicle derived stormwater runoff. The latter assumes no confounding from other urban sources in runoff.

Overall, the various studies that have examined macro-invertebrate communities below road and motorway discharges, have provided variable results with a number of studies not showing any identifiable adverse effect which could be attributable to stormwater runoff specifically associated with roads.

Available information does show however, that urbanisation including changes in the total imperviousness of catchments result in substantial changes in the composition of macro-invertebrate communities in freshwater streams. Those changes are multi-faceted and reflect the various changes that occur as a consequence of urbanisation.

Roads contribute to the changes observed in urban areas as roads constitute a key part of the imperviousness of urban areas. Within urban areas roads are likely to be a contributing factor to the impacted nature of freshwater macro-invertebrate communities observed in New Zealand.

6.2.5 Fish

Effects of road runoff on freshwater fish populations

Jellyman (1987a) characterised the types of water and habitat quality effects that result from various land use changes and activities that effect fishery values in New Zealand. The most significant effects associated with urban stormwater discharges include temperature, nutrients, turbidity, pH, dissolved oxygen. Shueler (2003) examines the effects of urbanisation (as percent imperviousness) of fish communities. Fish community changes are characterised by a shift to more pollution tolerant species and decreased survival of eggs and larvae. Schueler (2003) identifies a considerable number of studies undertaken principally in the US that have examined the impacts of changing impervious cover on freshwater fish communities.

Freshwater macro-invertebrate metrics

1 Richness Measures

Taxonomic richness (number of taxa).
 Number of Ephemeroptera, Trichoptera, Plecoptera (EPT's).
 Number of Chironomidae taxa.

2 Composition Measures

Relative abundance of major taxa.
 % dominant species.

3 Tolerance Measures

Macroinvertebrate Community Index (MCI) (Stark 1985).
 Quantitative Macroinvertebrate Community Index (QMCI) (Stark 1993).
 Semi-Quantitative Macroinvertebrate Community Index (SQMCI) (Stark 1998).
 Urban Macroinvertebrate Community Index (UMCI) (Suren et al. 1998).
 Quantitative Macroinvertebrate Community Index (QUMCI) (Suren et al. 1998).

4 Trophic Measures

Number of predator taxa.
 Number of collector-gather taxa.
 Number of collector-filter taxa.
 Number of scraper taxa.
 Number of shredder taxa.

Of these, taxa number, relative abundances and biotic indices such as the MCI are used most widely by Regional Councils as measures of the relative condition of macro-invertebrate communities in streams (e.g., refer WRC 1998).

5 Multimetric Approach

The simultaneous use of a range of indices can provide a summary of biological conditions targeted at conditions at a particular site. The multimetric approach has not been used widely in New Zealand despite its relevance to the ecosystem health focus of the Resource Management Act 1991.

6 Multivariate Statistics

Multivariate statistical analysis of complex invertebrate, habitat and water quality data is also used in more in-depth investigations of cause and effect relationships between environmental conditions and the invertebrate community. Multi-variate statistical techniques are rarely applied in regular Regional Council bio-monitoring programmes.

7 RIVPAC'S

River Invertebrate Prediction classification system (RIVPACS) has been developed by the Institute of Freshwater Ecology in the U.K. RIVPAC'S is a model that predicts invertebrate communities using a range of environmental variables. RIVPAC'S has been modified and implemented in Australia (Ausriva's) and is currently being trialled for MfE by Environment Waikato.

In New Zealand, there appears to be a shift in fish community composition and diversity with increasing urbanisation. Fish data examined as part of a study of Waitakere City Streams in Auckland (Kingett Mitchell 2000) revealed a decline in the average number of native fish species present with land use from native forest through to urban. There is very little published information that relates the effects of road runoff on fish populations in New Zealand (aside from the effects of culverting on fish passage – refer ARC 2000). There are however a number of overseas studies that have investigated the effects of road runoff toxicity on fish (refer section 6.3.4).

General Tools

Fish are commonly used to assess and monitor water and habitat quality by freshwater managers overseas. Advantages of using fish as biological indicators include:

- ❑ Relatively long-lived and mobile and therefore assimilate a broad range of effects and conditions.
- ❑ Integrate effects from lower trophic levels (algae and invertebrates).
- ❑ Assess human contaminate issues.
- ❑ Easily collected and identified with extensive historic databases.
- ❑ Water quality standards are generally based on fish species.
- ❑ High recreational and conservation values.

The use of fish as a biomonitoring tool is more widespread in the United States. This is in part, due to the greater diversity of the fish fauna which provides greater opportunity to develop indicators for specific water and habitat quality changes. USEPA (1998) for example lists over 30 potential fish metrics (indicators). Fish however, are not widely used in regional council assessment and monitoring programmes in New Zealand. Jellyman (1987a,b) described a range of indicators available for impact assessment using fish populations in New Zealand. Features of fish populations and fisheries which can be studied as indicators of impact assessment are listed in Table 6.3. Fish population data of the type listed in Table 6.3 is often very difficult to interpret due mainly to very high natural variability. It is therefore very difficult to establish cause and effect relationships (Jellyman 1987b). This limits the value of fish as biological monitoring tools when attempting to establish the existence or quantify a known effect (e.g., increased sedimentation from road runoff).

Table 6.3 - Features and indicators of fish population health.

Feature	Indicators
Community composition	Presence/absence of indicator species and species diversity.
Abundance	Density, biomass and catch per unit effort.
Life history	Feeding (diet, growth, condition) Reproduction (fecundity, spawning success and recruitment). Behaviour (habitat utilisation, induced movements, aberrant behaviour, mortality rate)
Habitat availability	Surveys of available/potential habitat.

Note: Modified from Jellyman (1987b).

MfE (1998b) (Environmental Performance Indicators for the terrestrial and freshwater environment) discusses the use of red fin bully and giant kokopu as indicator species for use in monitoring freshwater ecosystem sustainability. The utility of these species in future monitoring programmes has not yet been developed.

Tools with specific relevance to assessing road transport effects

The following tools have relevance to assessing impacts in freshwater and in particular road transport effects.

1. Assessment of community structure.
2. Identification of sensitive or indicator species.
3. Assessment of individual fish health.

Overall, the use of fish as biological indicators is poorly developed in New Zealand and there are no tools currently available for assessing road transport effects on fish populations. A review of overseas literature indicates that assessment of road runoff effects on fish has concentrated on the toxicity of

runoff to fish and not, individual health or population level effects. As noted above, native fish species have been proposed as environmental indicators for freshwaters in New Zealand. As indicators, they will provide information on overall and cumulative impacts on waterways but will not provide transport related cause and effects information.

Although fish health studies have been conducted in New Zealand in relation to the environmental assessment of specific discharges occurring to freshwaters, there do not appear to have been any specific studies where fish health has been monitored (and reported) in urban streams.

Overall, it appears that there is limited potential for developing a biomonitoring tool which uses fish population characteristics as an indicator of specific road runoff effects. However, in situations where road runoff is isolated within a particular receiving water, the use of fish as a biomonitoring tool may provide useful information on the overall quality of the biological environment at that location.

Information on fish community composition with streams in New Zealand indicates that there is typically a decline in the number of native fish species present in urbanised streams compared with non-urbanised streams. A proportion of this effect is likely to be attributable to the increased number of impediments to fish passage (e.g., culverts) that typically arise as a consequence of urbanisation. There is insufficient information to allow the effects of roads (as a component of urban imperviousness) of freshwater fish communities to be identified.

6.3 Water Quality and Toxicity

6.3.1 Introduction

Discharges of stormwater runoff from roads and highways typically result in transitory changes in the water quality of the receiving environment. The changes may last for hours or days depending upon the time of year and the duration of the event or events. Assessment of whether receiving water quality is being adversely impacted by the discharge of road runoff or that the changes in receiving water quality are adversely affecting freshwater biota can be carried out through the assessment of either the stormwater quality, receiving water quality or the toxicity of the discharge or receiving water to freshwater biota.

A range of water quality guidelines/criteria/standards have been developed around the world to assist in the management of water resources. Water quality guidelines relating to aquatic ecosystem protection and the protection of organism quality are relevant to the discharge of contaminants from transport to aquatic ecosystems. In New Zealand, there are no formal water quality criteria. The Resource Management Act 1991 contains in Section 107, a number of narrative standards relating to dissolved oxygen and temperature but no specific standards relating to toxic substances. In the absence of such guidance, Regional Authorities who have the responsibility for the protection of water quality, utilise international water quality guidelines. Regional Councils who have identified standards in their Regional Plans have typically utilised the guidelines developed by ANZECC (1992) and (2000). The New Zealand Ministry for the Environment (MfE) has developed several specific guidance documents that relate to specific water quality guidelines. These include:

MfE (1992): Water Quality Guidelines No. 1: Guidelines for the control of undesirable biological growths in water.

MfE (1994): Water Quality Guidelines No.2: Guidelines for the management of water coloured clarity.

A number of different terms are used to talk about numerical concentration values that are utilised for the protection of water quality values. Three different terms are utilised by regulators to identify these values. The terminology can be confusing in that they tend to be inter-changed. CCME (1991) provides definitions of these terms.

- ❑ Criteria are values that are used to derive guidelines or standards for water uses. Numerical toxicity criteria are the results of toxicity tests.
- ❑ Guidelines are numerical or narrative statements which when applied should protect the particular water use that they were developed for. Numerical guidelines should be based upon criteria.
- ❑ Standards are guidelines that have been translated into statutory form.

The ANZECC water quality guidelines (ANZECC 2000) are the most commonly used water quality guidance values in Australasia. The guidelines are based upon those of CCME (1999).

6.3.2 General Water Quality

Nutrients

As noted above MfE (1992, 1994) has provided guidance in relation to what are considered to be acceptable changes in receiving water quality in relation to nutrients. No specific water quality guidelines were provided by MfE (1992) and subsequent to the release of that document, regional plans have continued the use of narrative statements rather than identifying particular guidelines for dissolved inorganic nitrogen and phosphorus. Specific guidelines were not identified as adverse nutrient related effects are site specific.

Based upon the available data for New Zealand and overseas urban and road stormwater, provides both nitrogen and phosphorus for plant growth at concentrations well above those limiting for plant growth. During the plant growth season, nutrients may become limiting in waterways as a result of uptake by algae and macrophytes. Stormwater from roads provides a source of both nitrogen and phosphorus during storm events. The importance of stormwater as a source of nutrients to freshwater ecosystems is dependent upon the relative contribution of various land uses in the particular catchment.

Overall, as road transport activities release both nitrogen (e.g., through exhaust emissions) and phosphorus (e.g., through wear of asphalt) to the environment. Stormwater from road runoff will contribute to plant growth in freshwater ecosystems. The net contribution of vehicles to nutrient loadings in freshwater systems is not known but will be catchment specific (relative to the proportion of vehicles and road surface area compared to other sources within the catchment).

Clarity

MfE (1994) defined acceptable changes in water clarity in relation to aesthetic properties of water and effects on euphotic depth. The guidelines set out in MfE (1994), have been adopted in various regional plans around New Zealand. In most cases the guidance in those plans is narrative or a 10% change in suspended solids, or clarity (defined by black disc) is set as the guideline. The guidance has been developed to assist managers deal with the potent effects arising from the discharge of particulate matter to freshwater ecosystem. In Section 2 of this report, information was presented that showed that urban stormwater and road/motorway runoff typically has moderate to high concentrations of suspended solids. Data for motorways also indicates that average suspended solids concentrations are such that they would be capable of reducing the clarity of receiving waters close to the point of discharge. The actual change and significance of any effect would be dependent upon:

1. The suspended solids concentration of the stormwater.
2. The upstream in-water suspended concentration.
3. The mixing and dilution that occurred at and downstream from the point of entry.

In general, effects would tend to be more significant in small urban stream and lakes. Although urban and isolated road stormwater contains particulate matter, the proportion of particulate matter sourced from vehicles and road surface wear compared to other non-road sources (e.g., atmospheric

deposition, tracking of material onto road surfaces, litter and debris generation, spillages from vehicles etc.) is not known. As described earlier in this review, vehicles generate particulate matter through tyre and brake pad wear and through combustion of fuel. Most of the particles generated are very small.

6.3.3 Toxic Substances

6.3.3.1 Guidelines

Historically water quality guidelines and criteria developed by USEPA, CCME and ANZECC have received the most use. The number of toxic substances for which guidelines and criteria have been developed is however limited given the complex chemical composition of stormwater runoff. Guidelines are available for the key road transport derived metals, PAHs and selected VOCs.

The ANZECC (2000) guidelines for those parameters that are toxic or able to be bio-accumulated were developed using the methods of CCME (1991). As such, the guidelines were developed to protect all organisms. As with the Canadian approach, application factors were utilised where there was insufficient chronic toxicity data. Where there are no guidelines for a particular substance, a comment is provided on the available data for other key contaminants. Table 6.3 provides a summary of the key water quality guidelines for the key transport related metal contaminants and Table 6.4 provides a summary of guidelines for key transport related volatile contaminants.

Table 6.3 - Summary of water quality guidelines for metals derived from transport emissions discharged to freshwaters (all data mg/m³).

Parameter	ANZECC (2000)		USEPA (2002)		CCME(1999)
	99 ^b	95 ^b	Acute	Chronic	
Cadmium ^a	0.06	0.2	1.16	0.92	0.012
Copper ^a	1.0	1.4	4.3	3.2	2
Lead ^a	1.0	3.4	17	0.66	1
Zinc ^a	2.4	8.0	42	42	30

Notes: a = dependent upon hardness, hardness = 30 g/m³. .

6.3.3.2 Toxicity data

Although there are water quality guidelines for metal toxicant and a large toxicity database in the literature, for many of the VOCs that are present in road transport emissions there is only limited toxicity data. Rowe et al. (1997) reviewed the available toxicity information for VOCs that had been identified in the US NWQAP. Table 6.5 summarises the data presented by Rowe et al. (1997) for the lowest concentration of transport related VOCs that affect aquatic species. When there is insufficient toxicity data to develop water quality criteria, USEPA utilises values that are equal to the LOEC. For the Canadian guidelines, short term toxicity data (96 hour LC50) for the most sensitive species multiplied by application factors (0.05 for non-persistent effects, 0.01 for persistent effects) are used.

Table 6.4 - Summary of water quality guidelines for organic compounds derived from transport emissions discharged to freshwaters (all data mg/m³).

Parameter	ANZECC (2000)	USEPA (2002)		CCME (1999)
	95% level of protection	Acute	Chronic	
Benzene	950	5,300 ^a	-	370 ^c
o-xylene	350			
p-xylene	200			
Ethylbenzene	-	32,000 ^a	-	90 ^c
Methylbenzene ^b	-	17,500 ^a	-	0.8 ^c
Naphthalene	16	2,300 ^a	620 ^a	3.1
Acenaphthene	-	1,700 ^a	520 ^{a,b}	5.8
Anthracene				0.012
Fluoranthene	-	3,980 ^a	-	0.04
Benzo[a]pyrene	-	-	-	0.015
Benz[a]anthracene	-	-	-	0.018
Fluoranthene	-	-	-	0.04
Fluorene	-	-	-	3.0
Phenanthrene	-	-	-	0.4
Pyrene	-	-	-	0.025
Total PAH	3.0	-	-	-

Notes: a = Criteria not derived, LOEL presented. b = Toluene. c = Interim guideline.

Table 6.5 - Summary of lowest effect toxicity data for selected VOCs reported by Rowe et al. (1997) (all data mg/m³).

Parameter	Organism	Lowest Concentration			Effect
		MATC	LOEC	EC50	
Benzene	Fathead minnow	nv	17,200	-	Growth
n-Butylbenzene	Oryzias latipes (fish)	490	-	-	Immobilisation
1,2-dimethyl-benzene	Coho salmon	nv	nv	600	Avoidance
1,3-dimethylbenzene	Selanastrum (green algae)	nv	nv	3,900	Growth
1,3-dimethyl-benzene	Selanastrum	nv	nv	3,200	Growth
Ethylbenzene	Daphnia	nv	nv	1,800	Immobilisation
Methylbenzene	Fathead minnow	nv	6,000	-	Growth
(1-methylethyl)-benzene	Daphnia	nv	nv	601	Immobilisation
Naphthalene	Daphnia	nv	nv	690	Phototactic response
n-Propylbenzene	Selanastrum	nv	nv	1,800	Growth
Tri-methylbenzene	Daphnia	nv	nv	3,600	Immobilisation
1,3,5-Trimethyl-benzene	Daphnia	nv	nv	6,011	Immobilisation

Notes: MATC = Maximum acceptable toxicant concentration. LOEC = Lowest observed effective concentration. EC50 = Median effective concentration. nv = No value.

Kennedy & Gadd (2000) identified toxicity data for organic compounds known to be emitted by motor vehicles and for organic compounds identified as potentially being present in emission sources (e.g., tyres and brake pads) that released particles to the road corridor. Toxicity data was collected generated using the computer programmes ECOSAR and ASTER (derived using molecular weight and kow data and compound structure). The toxicity data was sorted to derive an ENEV (Environmental no-effects value). The ENEV value was calculated from the lowest chronic value where sufficient data was available and an application factor of 10. The toxicity data for the particular compound then allowed it to be ranked into one of three categories (low, medium and high toxicity). The thresholds used were similar but lower than those used by ERMA (1999). The toxicity data was

one factor used to classify organic compounds emitted by vehicles as contaminants of potential concern (COPC) in relation to potential environmental effects.

6.3.3.3 Stormwater Quality and Toxicity

In assessing the potential for adverse effects to arise from the discharge of stormwater to freshwater, resource managers would in the first instance compare available stormwater data with the water guidelines (Table 6.3) identified in the previous sections (e.g., the EMC data in Tables 4.5 to 4.7). There is a relatively significant body of stormwater quality data with which this comparison can be made.

Cadmium

For cadmium, most stormwater data has not been obtained using sufficiently sensitive analytical techniques. Cadmium concentrations in motorway runoff obtained using strong acid digestion are often reported as exceeding USEPA acute criteria and the ANZECC (2000) trigger. Data such as that reported by ARC (1992) are lower than the USEPA chronic criteria of 0.38 mg/m^3 at a hardness of 25 g/m^3 and the ANZECC (2000) trigger of 0.2 mg/m^3 . Although some reported data indicates that Cd concentrations in road runoff might exceed chronic criteria and triggers, work such as that of ARC (1992) suggests that it is likely that most road runoff in New Zealand would not exceed the cadmium criteria.

Copper

Dissolved copper concentrations in motorway and road runoff (in New Zealand and overseas) exceed USEPA acute and chronic criteria and ANZECC (2000) triggers (Tables 4.5-4.7). Comparison of dissolved copper concentrations in New Zealand stormwater runoff and motorway runoff (refer Table 4.7) shows that ANZECC (2000) trigger values are exceeded in urban stormwater runoff. Figure 6.1 from Timperley (2002) illustrates the range in concentration versus the ANZECC (2000) trigger (for 95% protection).

Timperley (2002) has also shown that the concentrations are much higher in the first flush of urban stormwater. Work by NIWA (Webster 2000) examined the influence of DOM on the bioavailability (toxicity) of dissolved metals. The complexing ability of stormwater/stream waters is dependent upon the availability of DOM. In catchments with negligible riparian vegetation there appears to be little complexing ability. Increased inputs of DOM (e.g., humic and fulvic acids) result in greater ability to complex metals such as Cu. In streams with a good supply of DOM, much of the dissolved Cu may be complexed. This may mean that dissolved Cu in stormwater leaving roads entering streams and drains may become complexed by DOM if there is sufficient present. Webster (2000) also noted that the complexing ability is not directly related to the amount of DOC present as the source/composition of the DOC may change. Initial work reported by Webster (2000) also showed that DOM from different plants has different abilities to complex metals. Overall, although concentrations of dissolved Cu in stormwater and urban stream water may exceed ANZECC (2000) triggers, the significance may vary depending upon local water chemistry. Where there is a sufficient supply of DOM, the dissolved copper may be complexed reducing its potential toxicity.

Lead

Initial examination of stormwater Pb data (e.g., the motorway data in Table 4.5) indicates that the concentrations are well above USEPA acute and chronic criteria and ANZECC (2000) triggers. However as described earlier in this report most Pb is present in the particulate phase. The higher concentrations of Pb in the data tables are typically the result of analysis undertaken at times or in locations where Pb was or is still used in petrol. In addition, the Pb presented in some studies may also be the result of poor analytical detection limits. Recent data for stormwater from roads in New

Zealand has shown that the dissolved concentrations are at or 1 mg/m^3. Overall, it is likely that concentrations of dissolved Pb in stormwater are at or below the ANZECC (2000) trigger for the protection of aquatic life. Although Pb was removed from petrol in New Zealand in 1998, there is insufficient data to show whether the concentration of Pb in stormwater has reached equilibrium.

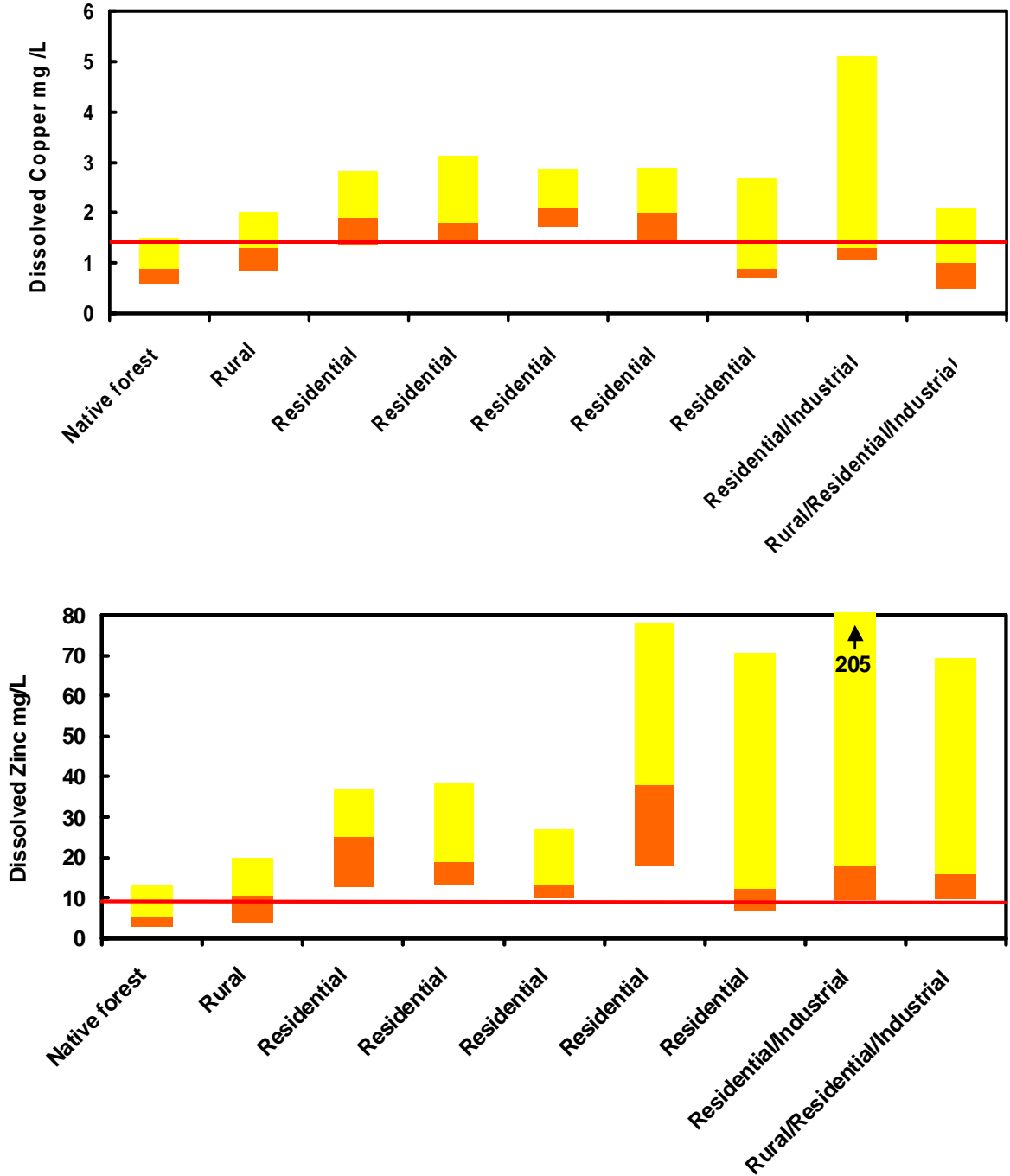


Figure 6.1 - Dissolved copper and zinc in runoff from different land uses. Data boxes are 10, 50 and 90%iles (from bottom to top of boxes). The red lines are the ANZECC (2000) triggers (From Timperley 2002).

Zinc

Measurement of Zn in urban and roadway stormwater in New Zealand and overseas shows that average dissolved concentrations exceed the USEPA acute and chronic criteria and the ANZECC (2000) trigger of 8 mg/m³. Fig. 6.1 (From Timperley 2002) shows that the concentration of dissolved zinc in urban stormwater in New Zealand typically exceed the ANZECC (2000) trigger.

Table 4.7 identified that average dissolved zinc concentrations in motorway stormwater in New Zealand are of the order of 40-70 mg/m³. The ANZECC (2000) triggers for 95 and 99% protection of freshwater biota are 2.4-8.0 mg/m³. Timperley et al. (2003) reported results of monitoring undertaken at two locations in Auckland (Ash St in Avondale and Richardson Rd in Balmoral). The results for Richardson Rd were not dissimilar to the results summarised in Fig. 6.1 and in Tables 4.6 and 4.7. Although variable concentrations were consistently of the order of 100 mg/m³ throughout the period of sampling and well above the criteria and triggers identified above. Unlike Cu, the presence of DOM in stormwater or downstream receiving environments does not reduce the toxicity of Zn. Webster (2000) identified that the concentration of Zn was greater than the Zn complexing capacity. As such very little of the Zn is complexed.

PAHs

For organic compounds such as PAHs a comparison of the motorway concentration data presented in Section 4 with the guideline data in Table 6.4, indicates that the concentrations of specific PAHs in stormwater are considerably lower than the individual USEPA chronic criteria for the protection of aquatic life. The total PAH concentrations are however, in one of the reported data-sets just below the ANZECC (2000) guideline for total PAH.

VOCs

VOC concentrations in stormwater are low (refer Section 2) and typically several orders of magnitude lower than guideline values established by the USEPA and lower than those determined by CCME and ANZECC (2000). There are however, few promulgated guideline values for VOCs. In addition, the VOC data reported for stormwater is limited in some cases by insensitive analytical data. For example, acrolein was not detected in USGS studies at a limit of detection of 2 mg/m³. The ANZECC (2000) guidelines have a no effects level of 0.2 mg/m³. As noted in Section 2, there is no published data for VOCs in stormwater in New Zealand.

Other compounds

A number of organic compounds were identified in tyres that could enter stormwater. They enter stormwater through the production of particles through tyre wear and through the leaching of compounds when the tyre is warm and wet while in contact with the road and water, leaching of skid marks on road surfaces and through the leaching of tyre particles. The leachability of the wide range of compounds present in tyres does not appear to have been comprehensively assessed as it relates to road runoff.

Work has been undertaken in relation to one group of compounds – the benzothiazoles. The inset box on the following page presents an overview of benzothiazole in the stormwater environment. Examination of the theoretical solubility of organic compounds present in tyres and brake pads was assessed by Gadd & Kennedy (2000). In interpreting the comments made above, three matters need to be considered. Firstly, that the comments made need to take into account that any stormwater discharges are subject to the requirements for reasonable mixing.

Benzothiazoles in stormwater and receiving environments

Although benzothiazole was not identified as a COPC by Kennedy & Gadd (2000), it is worth examining what we know about this group of soluble organic compounds and their toxicity. Reddy & Quinn (1997) identified Benzothiazole (BT), 2-hydroxybenzothiazole (HOBT) and 2-(4-morpholino)benzothiazole (24MoBT) in tyres (also identified in New Zealand tyres by Gadd & Kennedy 2000). Reddy & Quinn (1997) identified that following five leaches of tyre crumb particles with deionised water that 50% of the Benzothiazole (BT) compounds was removed. Dissolved BT and other benzothiazolamines have been detected in urban runoff by Reddy & Quinn (1997) and Kumata et al. (2002) (Table 6.6).

Table 6.6 - Summary of mean dissolved concentrations of Benzothiazoles in urban runoff (concentrations ug/m³).

BT	378 –819 (Pawtuxet River, Reddy & Quinn 1997)
HOBT	721 – 5,640 (Pawtuxet River, Reddy & Quinn 1997)
24MoBt	15-383 (Reddy & Quinn 1997 and Kumata et al. (2002) Chuo highway Japan)

The benzothiazoles are strongly water soluble and 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 24MoBT 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. The microbial fate and photolysis of benzothiazoles have recently been evaluated by Kirouani-Harani (2003).

Evans et al. (2000) examined the effects of benzothiazole on sheephead minnows (*Cyprinodon variagatus*). They reported that benzothiazole was lethal and growth inhibitory to sheephead minnow larvae. Lethality occurred after 5 days exposure at 60 g/m³ and significant decrease in growth at concentrations down to the lowest test concentration of 3.75 g/m³. Upper concentration in Table 6.6. of 5.6 mg/m³ are 1,000 times lower than the lower concentration used by Evans et al. (2000) in their toxicity assessment. The data indicates that benzothiazoles are not an acute toxicity risk in receiving environments.

Based upon this simple requirement, copper, lead and zinc concentrations would only require a small amount of dilution to ensure that the potentially chronic effects that could arise from the discharge are avoided. Secondly, there are however, a number of factors that need to be considered when assessing the potential for toxicity. These are:

- a. In many urban streams, stormwater flow may comprise most of the stream flow.
- b. Stormwater metals data is typically reported as total metal. The USEPA guidelines should now be interpreted as dissolved metal concentrations and ANZECC (2000) guidelines for metals are most appropriately compared to dissolved metal concentrations.
- c. The comparison does not take into account the form or the species of metal and therefore the potential toxicity.
- e. There are issues associated with the appropriateness of toxicity tests (see below).

These issues have recently been reviewed by Timperley (1999). Timperley concluded that dissolved concentrations were potentially a poor indicator of aquatic toxicity. This occurs as not all dissolved constituents are bio-available. The proportion of metal in bioavailable form (to exert toxic effect) is dependent upon the pH as the toxicity of the free ion is still dependent upon complexing by major ions

in stormwater and receiving waters (e.g., hydroxide and carbonate). Thirdly, guidelines for the protection of aquatic life are guidelines. USEPA criteria are national guidelines that allow for site specific criteria to be developed. The redrafted ANZECC guidelines have also adopted the approach of site specific guideline development. This contrasts with the approach taken in the 1992 ANZECC guidelines. Overall this approach recognises that a single standard, criteria or guideline is not necessarily appropriate in all situations.

Stormwater quality data from urban areas and from roads and motorways has shown that dissolved concentrations of metals such as Cu and Zn can reach very high concentrations in the first flush of stormwater. Over the duration of storm events, the concentration of dissolved zinc is the most significant in relation to water quality guidelines such as ANZECC (2000). The regular exceedence of dissolved concentrations suggests the likelihood of adverse effects on freshwater biota. Much of the copper in stormwater may be complexed by dissolved organic matter. Only a limited proportion of the dissolved Zn is likely to be complexed leaving most as the dissolved cation.

A wide range of organic compounds are present in urban and road stormwater. There is appears to be little published evidence of organic compounds in roading stormwater (derived from vehicles) being toxic and causing adverse effects on freshwater biological communities.

6.3.4 Toxicity data and Toxicity Tests

Toxicity tests can be used to assess the potential for stormwater discharges to have adverse effects within receiving waters. A number of studies have been conducted that provide information on the toxicity of urban and roadway runoff. Those studies involving isolated roadway or highway runoff provide information without the confounding effects of other sources in the urban environment. These studies are described to illustrate that a variety of studies have identified toxicity in road and highway runoff. As noted in the previous section, exceedence or not of international guidelines for the protection of aquatic life does not imply that there will be, or not be toxicity. The guidelines are simply that, guidance to managers to manage environmental effects.

A number of standard tests are available for assessing the toxicity of discharges and receiving waters. Reviews of toxicity testing and toxicity carried out in New Zealand are provided by Hickey & Roper (1994) and Hickey (2000). Hall (1998a,b) also reviewed the use of toxicity tests and the use of native New Zealand species in toxicity tests. Burton & Pitt (2002) provide an overview of toxicity in stormwater and provide a summary of toxicity testing methods. The authors identified a significant number of issues that influence the evaluation of toxicity test data for stormwater toxicity tests using traditional tests. They identified limitations in many test methods. One of the key conclusions made was that exposure to sporadic pulses of contaminants (such as occur in stormwater) may produce toxicity greater than exposure to constant concentrations. They also noted that “traditional toxicity testing may not produce reliable conclusions when used to detect the adverse effects of: fluctuating stressor exposures, nutrients, suspended solids, temperature, UV light, flow, mutagenicity, carcinogenicity, teratogenicity, endocrine disruption or other sub-cellular responses”. They also concluded that ecologically significant levels of high kow compounds may not produce short-term responses in exposures and this dictates further evaluation of exposure effects in aquatic ecosystems. Crunkilton et al. (1999), Crunkilton & Kron (1999), Hickey (1999) and Brent & Herricks (1999) reviewed and discussed various aspects of stormwater toxicity. A number of key points were made by the authors. These were:

- a) Measured toxicity in US cities using conventional acute and chronic tests typically fails to detect toxic effects.
- b) Longer term toxicity (7-14 days) are required to identify the potential for toxicity to arise from stormwater discharges.
- c) Test design may not be appropriate given the variable nature of storm events.

- d) Causes of toxicity cannot be easily identified.

International work

Winters & Gidley (1980) examined the effects of highway runoff on algae using a five day bioassay. Runoff was at times stimulatory but inhibited growth in the case of heavily used highways. It was concluded that it was nutrients in the runoff that stimulated growth and metals that inhibited it. Evaluation of the effects of highway run-off on the growth rate of the algae *Seanastrum capricornutum* demonstrated that growth was reduced upon exposure to stormwater (Portele et al. 1982).

Rainbow trout exposed to filtered stormwater (to remove particulates) showed no adverse effects as a result of 4 day exposure. Significant mortalities occurred in 50 and 100% dilutions using unfiltered samples (Portele et al. 1982). Differences in toxicity between different sites were also found.

Yousef et al. (1985) found that copper in the water of a highway retention pond was toxic to mosquito fish (*Gambusia affinis*).

Kzos et al. (1990) examined the effect of runoff from a bridge to young bluegill sunfish using 12 day bioassays. The results did not demonstrate significant toxicity apart from runoff containing significant amounts of de-icing salts.

Batley et al. (1994) examined the toxicity of filtered stormwater to green alga. No toxicity was observed even though the concentrations present would have indicated toxicity. In that case it was considered that the Mn and Fe in the waters reduced the potential toxic effect through binding or other process.

Maltby et al. (1995b) examined toxicity in a stream receiving water from the M1 motorway and proposed that PAHs were more toxic to amphipods than metals.

Pitt et al. (1995) reported the results of Microtox testing of stormwater samples from a range of urban impervious surfaces. It was found that filtration significantly reduced the stormwater toxicity. For roads 67% of the samples were considered moderately toxic and none highly toxic. For parking areas 19% of the samples were considered highly toxic and 31% moderately toxic. The authors undertook a series of simple tests and treatments to examine the changes in toxicity. Burton & Pitt (2002) also summarised toxicity testing using freshwater organisms. They identified that 40% of all stormwater samples demonstrated toxicity to *D magna*. No toxicity was observed for a number of other species including *Ceratodaphnia* and *Lemna minor*.

Lopes & Fossum (1995) reported on toxicity testing of urban runoff in Maracopa County, Arizona, identifying that first flush stormwater were generally more toxic than flow weighted composite samples. Toxicity was greater to fathead minnows (*Pimaphales promelas*) compared to *Ceratodaphnia dubia*. The authors reported that 71% of first flush samples were toxic to fathead minnows and 28% to *C dubia*. 36% of flow weighted composite samples were toxic to fathead minnows and 14% to *C dubia*. Toxic samples came mainly from areas of residential and commercial landuse. An influence from recently re-sealed asphalt was identified as a possible cause in the observed toxicity. Examination of the likely causes of toxicity indicated that most of the toxicity was caused by organic compounds but dissolved metals also appeared to contribute. The authors indicated that organophosphate pesticides were not the cause of toxicity in their stormwater samples.

Marsalek et al. (1997) examined the toxicity of urban runoff from a range of urban sites including two large highways (>100,000 VPD). In a comparison of the toxicity of urban stormwater compared to highway runoff, 20% of the highway samples were identified as severely toxic compared to 1% of the urban runoff samples. Table 6.7 provides a summary of the frequency of toxicity detection in a selection of the highway – roadway samples examined by Marsalek et al. (1997). One of the interesting results obtained in the work carried out by Marsalek et al. (1997) was the range of responses obtained. That study utilised a range of toxicity tests (*Daphnia* 48 hour acute; Microtox 15

minute; sub-mitochondrial particle bioassays; SOS-Chromotest). The latter test is utilised to assess genotoxicity. The more severe toxic responses were obtained for the two highway sites. Marsalek et al. (1997) concluded that the results may well have reflected the inherent variation in the quality of stormwater runoff at those locations. To address this issue a further series of samples were collected from the Skyway Bridge during a single storm event. Significant responses were observed in the first 30 minutes but little change was observed subsequently suggesting a first flush effect was present. It should be noted that in the case of the Skyway Bridge site, the most severe toxicity responses were found in winter and involved snow-melt reflecting the presence of salt in the runoff. When winter samples were excluded, 47% of the results were non-toxic, 26% potentially toxic, 14% toxic, and 13% severely toxic.

Table 6.7 - Summary of toxicity data collected by Marsalek et al. (1997) and Marselek et al. (1998) for stormwater samples collected in Ontario Canada from roads and highways.

Site	Type	No of Tests	Not Toxic %	Potential	Toxicity Moderate	Severe
Skyway Bridge Burlington	Highway	125	44.8	11.7	24.2	19.3
401 Scarborough	Highway	14	21.5	35.7	21.4	21.4
Highway 2 Scarborough Bridge	Highway	15	40	33.3	26.7	0
Parking Lot Kingston	Commercial	40	625	12.5	22.5	2.5
Scarborough Pond Inlet	Highway Residential	15	60	26.7	13.3	0

In a further discussion of their stormwater toxicity studies, Marselek et al. (1998) noted that all of the urban stormwater sites are impacted by various and numerous potential sources of toxicants. The authors identified a tentative list of toxicants as including Cu, Zn, Cd, lead, platinum and cyanides along with chlorides and PAHs (Wei & Morrison 1994; Maltby et al. 1995; Mulliss et al. 1996; Boxall & Maltby 1997; Rokosh et al. 1997; Novotny et al. 1998;). Marselek et al. (1998) note that much less is known about the effect that trace organics in stormwater have on toxicity (see also Makepeace et al. 1995).

Schiff et al. (2002) undertook a toxicity characterisation of stormwater draining the Chollas Creek urban catchment in California (16,273 acres, 67% residential, 4% roads). Toxicity was detected with the freshwater test (*C dubia*, 96 hr survival test). The authors undertook toxicant characterisation and found that Phase 1 treatments (particle removal, metal chelation using EDTA, non-polar organic extraction with C-18 columns, chemical reaction using sodium thiosulphate (STS), pH adjustment and assessment of the effects of pesticide metabolic inactivation using peperonyl butoxide (PBO). The organics extraction and the addition of PBO resulted in beneficial improvements in the stormwater toxicity. Variable results were achieved with other treatments but the cause of the variability was not able to be identified. Phase 2 toxicant identification indicated that the toxicity was associated with non-polar organic compounds and the suspected compounds were suspected as being diazinon and chlorpyrifos. The presence of both compounds was confirmed through analysis. These compounds are derived from general catchment use rather than from road transport.

New Zealand

In New Zealand, Nipper et al. (1995) and Hickey et al. (1997), utilised storm and baseflow samples collected from the inlets and outlets of the ponds and sand filter at UNITEC to assess toxicity. Toxicity tests were conducted by Nipper et al. (1995) and Hickey et al. (1997) using:

- 48 hour acute mortality (LC50) and 14 day chronic mortality and reproduction using *Daphnia magna*.

- ❑ 96 hour reproduction inhibition test (IC50) using the alga *Senastrum capricornutum*.
- ❑ 15 minute bioluminescence reduction test (EC50) using Microtox system.

Nipper et al. (1995) noted that few of the baseflow samples collected from the carpark pond inlet and outlet were acutely toxic to Daphnia, algae and bacteria. The inlet and outlet samples caused some enhancement in algal growth and the inlet sample resulted in some enhanced reproduction in Daphnia. When storm flow samples were examined, no acute toxicity was observed in any of the pond inlet and outlet tests. The sand filter inlet sample resulted in acute and chronic toxicity to Daphnia. Moderate chronic toxicity to Daphnia was identified in tests utilising the pond inlet sample and the sand filter outlet sample. Acute responses were observed by Hickey et al. (1997) for Daphnia magna in two of the three storms tested by them. Chronic responses were observed for both algae and Daphnia. No significant differences were observed for filtered and unfiltered samples.

Hickey et al. (1997), found that when the measured toxicity data (UNITEC stormwater ponds) was compared with the toxicity expected based on chemical analyses, toxicity was lower than expected. Hickey et al. (1997) considered that acute toxicity could have been expected for the inflow to the UNITEC ponds on most occasions and on some occasions for the outflow based on total and soluble Cu measurements. It was noted that some toxicity was measured on occasions when no criteria was exceeded suggesting that contaminants other than metals may have contributed to toxicity. Further work by Hickey et al. (1997) in relation to reference toxicants (zinc) indicated that in that case, the overall bioavailability of Zn in the stormwater examined was low.

Macaskill et al. (2003) undertook toxicity testing of stormwater samples collected in April 2002 from Rotorua City. The tests were carried out using algae, water flea and amphipod test organisms. Stormwater from the residential catchment was the least toxic to any of the species tested, with commercial and industrial catchment stormwater comparable but having generally greater toxicity. Samples were most toxic to the freshwater algae followed by minimal toxicity to the water flea and were the least toxic to the freshwater amphipod.

The algae used in the toxicity tests by Macaskill et al. (2003) were found to be the most sensitive of the test species. The authors noted that this, may have in part been due to the short-term chronic test used. Based upon the results some dilution (116, 83 and 5 times) would be required to ensure no adverse effects occurred on algae.

The toxicity test results using the water flea (EC50 values) showed that the no toxic responses were received and only minor dilution was required at the discharge point. EC50 values for amphipods were greater than 100% for stormwater from all catchment landuses. As a result only minimal dilution (about 2 times) would be required to ensure no acute adverse effects occurring on the test species.

The work of Macaskill et al. (2003) showed that of the three test species, algae and at least one of the invertebrate species showed responses to undiluted stormwater samples. The stormwater from the residential catchment was the least toxic to any of the species tested, with commercial and industrial catchment stormwaters generally comparable but having greater toxicity.

Macaskill noted that when comparing the test results with a comparison of stormwater quality with water quality guidelines that the test results were slightly more sensitive than comparing water quality directly with guidelines.

A range of toxicity studies have been undertaken using urban stormwater discharging to freshwater environments. Tests undertaken 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 has chronic effects on growth of freshwater algae (in toxicity tests).

Toxicity tests have undertaken using a range of freshwater organisms and 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 observation reflects data for the concentration of key constituents in first flush stormwater 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

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 severe 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.

6.4 Sediment Quality and Toxicity

6.4.1 Sediment Quality Guidelines

As described in Section 3, a significant proportion of contaminants entering aquatic systems accumulate in the beds of streams, lakes, estuaries and the coastal environment. In contrast to waters, sediments provide a longer-term picture of the nature of the flux of contaminants through that compartment of the environment. Sediments provide a reservoir for contaminants which may depending upon conditions be released back to the overlying water or made available to biota. When measurements are made of the concentration of contaminants in sediments, the question that often arises; when the results need to be interpreted is, how significant are the results?

Sediment quality guidelines have been developed to assist in the interpretation of sediment quality data. The key reason for the development of sediment quality guidelines in both the freshwater and marine environment has been the identification of potential adverse impacts of sediment quality on benthic invertebrate ecological health. Adverse effects may include toxicity and bioaccumulation.

There are currently no promulgated sediment quality guidelines in New Zealand. As noted earlier, ANZECC (2000) have released "Australian Water Quality Guidelines for Fresh and Marine Waters". The guidelines contain a series of recommended sediment quality guideline values (triggers) for both fresh and marine waters. The ANZECC guidelines are based upon overseas guidelines as there is an insufficient database of sediment toxicity information in Australia and New Zealand that can be used to generate a set of guidelines based solely on local data. Sediment screening guidelines have been developed using a number of different methods. Irrespective of the method used, the guidelines have been developed to identify sediment contaminant concentrations at which adverse effects could potentially occur in benthic invertebrate communities. The key sediment screening guidelines used in sediment quality management include:

1. Effects range low (ERL) and effects range median (ERM) developed by Long et al. (1990, 1995) for a range of metals and organic compounds. The effects range values were derived by utilising data from field environmental effects data, laboratory studies, and also equilibrium partitioning data. Long & Morgan (1990) and subsequently Long et al. (1995) derived ERL and ERM values for a range of contaminants. The ERL is the 10th percentile and the ERM the 50th percentile of the data examined by those authors. Effects Range guidelines are available for the key trace elements and PAHs

identified as derived from road transport. The accuracy of the guidelines is however considered to be low for Ni, Cr and Hg. Subsequent to the publication of Long et al. (1995) extensive field verification of the accuracy of prediction has been carried out (Long et al. In USEPA 1997). Toxicity testing of a large number of samples demonstrated that the toxicity increases as the number of chemicals exceeded the ERL or ERM.

2. Threshold effects levels (TELs) and Probable effects levels (PELs) developed by the Florida Department of Environmental Protection (FDEP 1994). These guidelines were developed for the Florida coastal environment using a similar approach to that used by Long et al. (1990). FDEP (1994) should be referred to for further details. The effectiveness of the two guidelines at predicting toxicity was assessed by Long et al. (in USEPA 1997).
3. The Canadian sediment quality guidelines (CCME 1999) (ISQG and PEL) were developed in a similar fashion to those in Florida (Smith et al 1996a,b;). ANZECC (2000) ISQG-low and ISQG-high sediment quality triggers which are based upon the Canadian (CCME) sediment quality guidelines.
4. ANZECC (2000) ISQG-low and ISQG-high sediment quality triggers which are based upon the Canadian (CCME) sediment quality guidelines.

Tables 6.8 provides a summary of sediment quality guidelines for a number of selected contaminants associated with emissions from road transport. Although, the ERL and ERM guidelines of Long et al. (1995) were developed for estuarine and marine sediments, they have been utilised for freshwater sediments.

Table 6.8 - Summary of sediment quality guidelines for road transport derived metals (all data mg/kg).

Parameter	ANZECC 2000		Long et al. (1995)		CCME (1999)	
	ISQG-low	ISQG-high	ER-L	ER-M	ISQG	PEL
Metals						
Antimony	2	25	-	-	-	-
Cadmium	1.5	10	1.2	9.6	0.7	4.2
Chromium	80	370	81	370	52.3	160
Copper	65	270	34	270	18.7	108
Lead	50	220	46.7	218	30.2	112
Nickel	21	52	20.9	51.6	-	-
Zinc	200	410	150	410	124	271
Organics^a						
Acenaphthene	0.016	0.5	0.016	0.50	0.00671	0.0889
Acenaphthylene	0.044	0.64	0.044	0.64	0.00587	0.128
Anthracene	0.085	1.1	0.0853	1.10	0.0469	0.245
Fluorene	0.019	0.54	0.019	0.54	0.0212	0.144
2-methyl naphthalene	-	-	0.070	0.67	0.0202	0.201
Naphthalene	0.16	2.1	0.160	2.10	0.0346	0.391
Phenanthrene	0.24	1.5	0.24	1.50	0.0867	0.544
Low molecular weight PAHs ^b	0.552	3.16	0.552	3.160	-	-
Benzo(a)anthracene	0.261	1.6	0.261	1.60	0.0748	0.693
Benzo(a)pyrene	0.43	1.6	0.43	1.60	0.0888	0.763
Dibenz(ah)anthracene	0.063	0.26	0.0634	0.260	0.00622	0.135
Chrysene	0.384	2.8	0.384	2.80	0.108	0.846
Fluoranthene	0.6	5.1	0.60	5.10	0.113	1.494
Pyrene	0.665	2.6	0.665	2.60	0.153	1.398
High molecular weight PAHs ^b	1.7	9.6	1.70	9.60	-	-
Total PAHs	4.0	45.0	4.022	44.792	-	-

Notes: ^a Normalised to 1% organic carbon. ^b Low Molecular Weight PAHs are the sum of concentrations of acenaphthene, acenaphthalene, anthracene, fluorene, 2-methylnaphthalene, naphthalene and phenanthrene.

High molecular weight PAHs are the sum of concentrations of benzo(a)anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene, chrysene, fluoranthene and pyrene.

All of the guidelines and triggers consist of two concentrations and as a result produce three concentration ranges from low to high concentrations. The lower guideline value or trigger is a concentration threshold below which adverse effects are unlikely. The lower threshold does not necessarily constitute a 'background' concentration. The upper threshold is a probable effects concentration. There is a relatively high probability that adverse effects will occur in a biological community inhabiting sediment containing concentrations of contaminants above this value. Between the two thresholds is a concentration range where the probability of adverse effects arising is lower than would occur when the concentration was above the probable effects threshold.

The Long et al. (1995) sediment quality guidelines have been the most utilised guideline values. The ANZECC (2000) sediment quality triggers are more commonly used in New Zealand since their publication.

6.4.2 Quality of Detention Pond Sediments

A comparison of data for the quality of particulate material on road surfaces (Table 3.4 and Kennedy 2003) and in stormwater (Refer Section 4) indicates that the no-effects guidelines (e.g., the ANZECC ISQG-low) are often exceeded for metals in those materials. For PAHs the guidelines are typically exceeded for some guideline such as the TEL. Median and the high guidelines for PAHs (levels at which effects would be expected) are not exceeded in the data commonly reported in the literature.

A number of studies have examined the quality of sediments in detention ponds that have accumulated stormwater particulates. Cox & Livingstone (1997) carried out a review of the quality of stormwater sediments (ponds and a variety of other stormwater sediments). The study showed that concentrations of Pb and PAHs in pond sediments typically exceeded the Florida Sediment Quality Assessment Guidelines (the TEL = Threshold Effects Level). The quality of sediments in detention ponds is of interest for two reasons. Firstly, ponds are often established as wildlife facilities and secondly similar accumulation processes occur in natural wetlands which stormwater may discharge into.

Sedimentation is the main mechanism for removal of particulate material and the contaminants associated with them in ponds and wetlands. The slow movement of the water in the ponds allows sediment to drop out of the water under gravity. Adsorption of dissolved substances onto suspended particulate matter, bottom sediment, vegetation, plankton or detritus may occur in a pond, reducing phosphate, ammoniacal nitrogen and trace elements (ARC, 1992). Precipitation may result in removal of dissolved species from solution. Some trace elements may form precipitates with sulphides in areas of low or negative redox potential, or form hydroxides under more oxidising conditions (ARC, 1992). Volatilisation of contaminants such as Hg and hydrocarbons, may also occur as a result of evaporation or under windy conditions.

Bottom sediment from stormwater detention ponds are often contaminated with trace metals and man-made organic compounds. There is sediment quality data from a number of stormwater treatment ponds or streams that receive stormwater in the Auckland region. These include the UNITEC detention ponds (Mt Albert), and Link Drive detention ponds (Takapuna) that receive stormwater from a commercial catchment. And the Hugo Johnson Drive ponds (Southdown) receive stormwater from an industrial catchment. No data appears available for stormwater ponds associated solely with road/highway runoff.

Sampled detention pond sediments (in New Zealand) from the industrial stormwater catchments were found to contain elevated concentrations of Cd, Hg, and Zn (Table 6.9). Lower concentrations were found in commercial catchments. High concentrations of Pb were found in detention pond sediments from the commercial and industrial catchments. Copper concentrations were much lower in the Link Drive ponds, receiving stormwater from a commercial catchment, than in other ponds from commercial or industrial catchments.

Table 6.9 - Summary of key trace metals in sediments from stormwater ponds in the Auckland region (all units mg/kg).

Site	Cadmium	Copper	Lead	Zinc
Link Drive Pond ¹	< 0.20	38	127	232
Link Drive Pond ²	0.24	34	78	297
UNITEC upper pond inlet	0.63	3,142	648	727
UNITEC upper pond outlet	0.64	548	151	492
UNITEC lower pond inlet	0.52	376	559	359
UNITEC lower pond outlet	0.12	81	19	48
UNITEC SPM	1.20	56	218	514
Hugo Johnson Drive ^{3*}	2.1	255	371	1089

Notes: *These results are an average of three replicates. All data from Nipper et al. (1995) except, ¹NSC unpublished data, ² ARC (1992). ³ Hickey et al. (1997) SPM = Suspended particulate matter. Red shading indicates exceedence of ANZECC (2000) ISQG-High; Orange shading indicates exceedence of the ANZECC ISQG-Low but not the ISQG-Low.

The trace element concentrations found in the stormwater pond sediments are derived from the sediments transported into the pond. The quality of these sediments reflects the nature of the sediments derived from street surfaces and on properties within the catchment. Concentrations of a number of metals (e.g., Cu, Pb, Zn) in stormwater particulates and in detention pond sediments exceed both lower and upper range sediment quality guidelines indicating that sediments in detention ponds have the potential to adversely effect organisms inhabiting the ponds. It should be noted that all of the detention pond sediment examined have come from ponds receiving general urban runoff. However, given the elevated concentrations of key metals in roadway runoff a similar situation would be expected adjacent to the point of discharge.

A comparison of the metals data for pond sediment quality in Table 6.9 with the sediment quality guidelines in Table 6.7 indicates that guidelines such as the Effects Range-Low (ERL) are exceeded by all metals. The higher guidelines such as the Effects Range-High (ERM) (Long et al. 1995) were exceeded for Cu in pond sediment, Pb in stormwater suspended particulate matter and pond sediment and Zn pond sediment.

Detention pond sediments from urban and industrial stormwater catchments in Auckland have been found to contain high concentrations of polyaromatic hydrocarbons (PAHs). High concentrations of total petroleum hydrocarbons (TPH) have also been measured in detention pond sediments. Table 6.10 provides a summary of the results of testing of detention pond sediments in the Auckland area for organic compounds.

Table 6.10 - Summary of major organic compounds in sediments exposed to stormwater in the Auckland region (all units ng/g unless stated).

Site	TPH (µg/g)	PAH (total) (µg/g)
Link Drive Pond ¹	587	-
Link Drive Pond ²	833	-
UNITEC upper pond inlet	-	3,980
UNITEC upper pond outlet	-	2,730
UNITEC lower pond inlet	-	2,660
UNITEC lower pond outlet	-	930
Hugo Johnson Drive ³	5,203	1,720

Note: Sources refer Table 5.2.

For PAHs in detention pond sediments, the lower sediment quality guidelines are typically exceeded (e.g., the TEL and ER-L).

6.4.3 Stream, wetlands and Lake Sediments

Stormwater within urban areas is typically routed to the closest water body which is typically a stream or channel in heavily urbanised areas. There are a number of New Zealand urban centres which contain urban lakes. In Hamilton, there is Hamilton Lake; in North Shore City, Lake Pupuke and in Auckland City, Western Springs. Several cities are located on the shores of larger lakes such as Taupo on Lake Taupo; Rotorua on Lake Rotorua and Queenstown on Lake Wanaka. Freshwater wetlands on streams in urban areas will act in a similar fashion to a detention pond.

Sediment quality data collected adjacent to an outfall to Hamilton Lake revealed elevated concentrations of Pb and Zn in particular that exceeded ER-L and ER-M sediment quality guidelines (Rajendram 1992 in Snelder & Trueman 1995). There have been a number of studies of sediment quality in urban streams in New Zealand. Data has also been collected on urban stream quality in most large urban areas. There is considerable data for Auckland Streams such as those in Waitakere City (e.g., Kingett Mitchell 2000). The results of that study showed that the common transport related contaminants (Cu, Pb and Zn) exceeded the ER-L in a high proportion of urban catchment samples. Fig. 6.2 illustrates the variation in key trace element concentrations in catchments with varying landuse. The catchments at the top of the figure tend to be rural with the catchments in the lower part of the figure completely urban. Titirangi/Langholm is a bush urban catchment (Kingett Mitchell 2000).

Accumulation of contaminants in lakes is a function of the local physical characteristics of the lake and lake-bed near the discharge. Macaskill et al. (2003) identified low concentrations of key contaminants near stormwater outfalls in Lake Rotorua.

Yousef et al. (1984) assessed the fate of metals discharged from highway bridges in Florida to Lake Ivanhoe (Maitland interchange). Differences in the concentration of a number of elements (Zn, Pb, Cr, Ni, Cu, Fe) were identified below bridge discharge points compared to normal lake concentrations. Gjessing et al. (1984) also examined the effect of highway runoff on Lake Padderudvann in Norway. Concentrations of Pb, Zn and Cd were elevated and exceeded guidelines such as the ER-L and TEL and in the case of lead the PEL.

Given the concentration of Cu, Pb and Zn in the suspended sediments of stormwater draining roads, exceedence of sediment quality guidelines would be expected in areas where stormwater particulates are deposited. Depending upon the ratio of stormwater sediment to uncontaminated stream sediments, elements such as Pb and Zn may exceed guidelines at which adverse effects (on benthic freshwater 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. Trace element concentrations in urban streams are approximately related to the amount of impervious cover and time since urbanisation within the catchment

For lakes, the sediment contaminant 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.

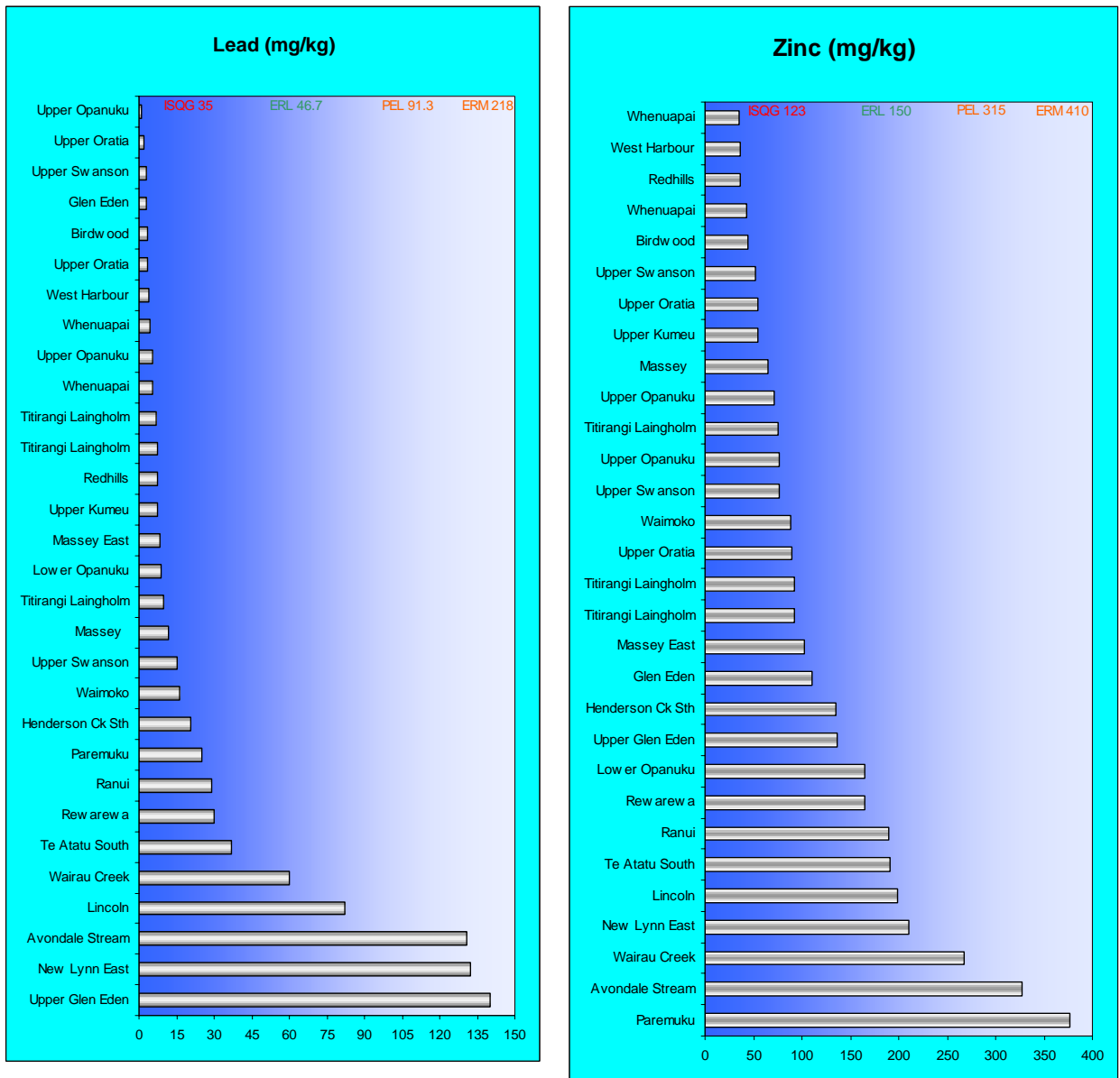


Figure 6.2 – Lead and zinc in Waitakere City Streams. Concentrations mg/kg. The SQGs on the figures are the CCME and Long et al (1995) sediment quality guidance values. The ANZECC (2000) ISQG-low and high are 50/220 mg/kg for Pb and 200/410 mg/kg for Zn (from Kingett Mitchell 2000).

6.4.4 Sediment Toxicity

The accumulation of contaminants in freshwater and marine sediments has the potential to create toxic conditions for invertebrates inhabiting the sediments. Toxicity however results from only a proportion of the contaminant present. As such total contaminant measurements do not provide an accurate reflection of potential toxicity. A number of studies have shown that sediment with the same concentration of metal can have different toxicity. Sediments with significantly differing concentrations of a metal can exhibit similar toxicity (Di Toro et al. 1990).

Although a range of factors influence the toxicity exhibited by a given contaminant, the key factor that controls the toxicity arising from contaminants in sediments is acid volatile sulphide (AVS). AVS is an important controller of toxicity as it influences the amount of a given metal in the pore water of the sediments. It is the pore water that benthic organisms are directly exposed to. AVS is not considered appropriate for the assessment of Hg and Cu that are associated with other phases of sediment. It has been shown that the molar ratio of metals (extracted at the same time as AVS) to AVS is related to toxicity. When lower than one, no acute toxicity (mortality greater than 50%) was found. When the ratio was greater than one, then toxicity was observed. Overall, it is considered that AVS can be utilised to predict whether metal contaminated sediments are acutely toxic (Di Toro et al. 1992). The EPA has utilised the SEM and AVS data to categorise sediments in the US national sediment quality survey into Tier one or two categories.

There are a variety of tests available for the testing of sediment toxicity. These have in many instances been developed as standard tests by regulatory agencies and have been utilised for example for the assessment of the toxicity of dredged sediment to be disposed at sea. Hickey (1998) provides a review of tests utilised in New Zealand to assess the toxicity of freshwater sediments. One of the most commonly tests used is the amphipod *Chaetocorophium cf. lucasi* acute survival and chronic growth test.

Toxicity tests can provide information on the potential toxicity of sediments associated with stormwater discharges from urban and isolated roadways. The results however, do not provide direct information on the cause of the toxicity arising from the contamination. Toxicant identification evaluation (TIE) is an additional method that provides information on the relative toxicity of fractions of complex mixtures of toxicants.

In New Zealand, sediment toxicity tests were performed on sediments collected from the inlet and outlet of the stormwater ponds and the sand filter at the UNITEC carpark in Mt Albert, Auckland (Nipper et al. 1995). Tests conducted included:

- ❑ 10 day acute mortality test using the amphipod *Chaetocorophium cf. lucasi*.
- ❑ 10 day acute mortality test using the clam *Sphaerium novaezelandiae*.
- ❑ 10 day acute mortality test using the worm *Lumbricus variegatus*.
- ❑ 20 day mortality and reproduction test using the worm *Lumbricus variegatus*.
- ❑ Assessment of re-burial ability of the clam *Sphaerium novaezelandiae* following the acute mortality test.

The amphipod survival test results obtained by Nipper et al. (1995) indicated that the sediments that accumulated in the UNITEC carpark pond were toxic with zero to low survival in all tests conducted using sediment samples from both the inlet and outlet. The sand filter test results showed no significant acute toxicity. This reflected the high proportion of original sand in the filter material sample and the relatively low contaminant concentrations in the sediment sample from the filter.

No significant differences were found in the *Sphaerium novaezelandiae* acute survival tests between stormwater pond sediments and reference sediments in the toxicity tests conducted by Nipper et al. (1995) due to the low survival of the clams in the reference sediments. Reburial rates were lower in the sediment from the lower UNITEC carpark pond compared to the reference mud sample but not compared to the reference sand. Worm 10 day survival and reproduction differed between the UNITEC carpark inlet sediments and the reference sediments. In the 20 day test, survival and reproduction differed only between the results for the pond outlets and the reference sediments (Nipper et al. 1995, Hickey 1999).

A number of studies have been carried out internationally that have provided information on the toxicity of sediments contaminated by road runoff (e.g., Maltby et al. 1995a,b). Boxall & Maltby (1995) examined the toxicity of sediment contaminated with road runoff using the TIE process. The sediments examined came from a site adjacent to a stormwater outfall on the M1 motorway (England). The toxicity of the fractions collected were assessed using freshwater amphipod (*Gammarus pulex*, 14 day mortality) and the bacteria *Photobacterium phosphoreum* (Microtox bioassay). Toxicity was demonstrated to both test

organisms. The most significant response (80% mortality) was found in a fraction containing 2 to 5 ring PAHs. Two other fractions one which contained straight and branched chained hydrocarbons and a second which contained substituted phenols and 4 and 5 ringed PAHs did not cause a reduction in mortality.

Lopes & Fossum (1995) examined the toxicity of stream bed and other sediments to the isopod *Hyalella azteca* in Maracopa County Arizona. They attributed high toxicity (77-100%) in some sediment samples to the contaminants accumulated from roads and parking area stormwater and attributed toxicity to cadmium and zinc concentrations.

International studies have shown variable toxicity from receiving water sediment to aquatic biota. The toxicity in one study involving sediments affected by motorway runoff was identified as being caused by PAHs and hydrocarbons. It is likely that the observed toxicity would be limited in extent depending upon the overall quality of sediments.

The New Zealand studies have shown that the particulate matter (from road stormwater) settling in pond systems has the ability to cause adverse toxicity to some test organisms. However only a limited number of toxicity tests have been undertaken.

In urban waterways, road runoff will be responsible for a proportional component of any toxicity to benthic macroinvertebrates that arises as a result of degraded sediment quality.

6.5 Bioaccumulation

6.5.1 Introduction

Bioaccumulation (or bio-uptake) is the uptake of contaminants by biota from their environment. Bioaccumulation can occur through the absorption of contaminants in the dissolved state, through consumption of food and consumption of sediments. Given the strong partitioning of many road runoff contaminants to sediments, increased concentrations of contaminants in sediment in streams, stormwater ponds, adjacent to stormwater outfalls in streams and lakes has the potential to result in the accumulation of those contaminants in exposed organism. Although uptake and bioaccumulation will occur by a number of routes (uptake from water through gill and gut absorption, uptake from food and ingested sediment), those organisms in contact with or ingesting sediment are likely to be the most sensitive to bioaccumulation.

Bioaccumulation of trace elements and organic compounds is a function of several factors. Firstly the ability of the contaminant to be accumulated in terms of its chemistry (e.g., its affinity for lipids), whether there is a nutritional requirement for the contaminant (e.g., Cu and Zn) and whether the organism has a specific mechanism for dealing with increased exposure and uptake (e.g., sequestering the contaminant). All of these factors affect the organisms' response to the contaminant. Bioaccumulated contaminants have the potential to cause chronic toxicity or in extreme circumstances mortality. The potential for adverse effects is dependent upon whether the contaminant is an essential element for the organisms (i.e., it physiologically requires it) or whether it has any ability to biochemically manage any increased body burden of the contaminant. Trace element bioaccumulation is very species specific even within groups such as molluscs. The accumulation of organic compounds such as PAHs appears to be less species specific.

Measurement of bioaccumulation in invertebrates provides a means for assessing the movement of contaminants into biological systems. Bioaccumulation has the potential to have adverse effects on exposed organisms or to result in the storage of the contaminant such that if consumed by a predator (fish, bird, man etc.) it may result in the transfer of the contaminant to the consumer. In New Zealand the quality of food-stuffs and seafood is assessed via the Food Regulations (1984). Limits in regulations such as these provide a mechanism to ensure that food products exposed to runoff are safe to consume.

Bioaccumulation can be assessed through the measurement of contaminants in organisms collected from the field. It can also be assessed through the use of organisms, typically fish or mussels which are placed in cages. Caged organism (such as fish) usually only respond to water borne contaminants. Assessment of the effects of sediment-associated contaminant requires other strategies (in-situ chambers or laboratory studies using sediment). In New Zealand freshwater mussels have been used to monitor metal and organic compound bioaccumulation in the Waikato River (Hickey et al. 1995, 1997; Nipper et al. 1995).

6.5.2 Bioaccumulation of Trace Elements

6.5.2.1 Invertebrates

Bioavailability of metals in aquatic ecosystems is dependent upon the form of the metal within the particular environmental compartment. The key factors that need to be considered in relation to potential uptake include, the chemistry of the metal if in solution (and the nature of the environment), the size and the nature of the particulate the contaminant is associated with.

In New Zealand, Nipper et al. (1995) examined the uptake of contaminants in stormwater by placing caged New Zealand freshwater mussels (*Hyridella menziesi*) in the inlet, outlet and in the stormwater pond at UNITEC (Mt Albert Auckland). The mussels were examined for condition index and uptake of metals after three months and organic contaminants after one month. Mussel condition index showed no significant difference between stormwater pond inlet and outlet mussels. Metal concentrations were found to be lower in the mussels from the outlet compared to the inlet reflecting the removal of bioavailable metals by the treatment pond. Increases in concentration in mussel tissue were observed for Cd, Pb and Zn but not for Cu and Hg.

Macaskill et al. (2003) examined bioaccumulation by whole freshwater mussels near stormwater discharge points from Rotorua City. The study also conducted transplant uptake experiments using mussels (gill tissue analysed) and snails (*Potamopyrgus antipodarum*). The examination of mussel metal concentrations did not reveal any clear trends of concentration of metals with distance from contaminant source. To assist in interpretation, bioaccumulation in mussels was compared using the average Ca normalised concentrations. The concentrations of Cu, Pb and Zn were elevated at the Government Gardens and Utuhina locations compared to the Waiteti location reflecting the influence of stormwater discharges. This was most marked for Pb. The authors note that the strong signal for Pb may be an artefact of its long half-life in biological tissues especially as freshwater mussels are known to have long half-lives. . Therefore the concentrations of Pb measured may reflect its presence in petrol prior to 1995. The concentrations of Cu and Zn were also elevated (but not statistically so) at locations close to stormwater outfalls. Transplanted mussels did not show any bioaccumulation in gill tissue over a 70 day deployment period. No exposure gradient was evident in mussel gill tissue or in the whole snails (soft body). The authors concluded that the results reflected the lack of fine particulate settlement in the areas in proximity to the stormwater discharges.

Goodyear & McNeill (1999) reviewed the bioaccumulation of metals by freshwater macro-invertebrates. Most information in the literature is for the uptake of the key elements Cd, Cu, Pb and Zn. Goodyear & McNeill (1999) found that for Cd, Cu, Pb and Zn displays a unique relationship between metal concentrations in sediments or waters with different feeding guilds that indicates the relative importance of different sources of metals to different feeding groups. The authors concluded that biomagnification did not occur between the guilds. Work by Perdikaki & Mason (1999) did not shown any significant changes in macroinvertebrate Cd, Pb or Zn concentrations that could be attributable to motorway discharges. No relationship between stream sediment concentrations of metals and invertebrate concentrations was identified.

Rauch & Morrison (1999) and Moldovan et al. (2001) examined the uptake of the PGEs by the freshwater isopod (*Asellus aquaticus*) in freshwater rivers, a stormwater detention pond and under experimental exposure. Rauch & Morrison (1999) found that concentrations ranged from 0.04 to 12.4 mg/kg and 0.16-4.5 mg/kg after depuration. Sediments were considered to be the main source of Pt for the isopods. Platinum speciation is very important in relation to uptake. The authors reported 60-90% of the Pt was

present in the exoskeleton. Exposure of isopods to Pt in solution was found to result in a steady exponential accumulation of Pt and it was considered that some storage of the Pt may have occurred to the exoskeleton may have occurred as a biological response to exposure. Higher uptake was found for Pt^{4+} compared to other Pt species. Exposure studies by Moldovan et al. (2001) identified that the bioaccumulation factors for the three PGEs were 150, 85 and 7 for Pd, Pt and Rh respectively. PGE accumulation is also time dependent. When uptake was examined using catalytic converter samples, uptake was similar indicating that environmental transformation was likely to be responsible for the different uptake found in real situations.

Zimmermann et al. (2003) examined the lipid solubility of the PGEs in relation to their uptake when ingested by aquatic organisms. The authors concluded that the formation of PGE complexes with organic compounds in receiving environments influences the uptake of PGEs. Pd was identified as having the highest lipid solubility. The affinity for organic compounds changes the hydrophilic character of the metal ions enhancing the uptake of Pd through cell membranes. A wide range of natural and anthropogenic organic complexing agents are found in surface waters and these may assist in the uptake of PGEs (more so Pd). Zimmermann et al. (2002) examined uptake of PGEs by Zebra mussels (*Dreissena polymorpha*) from road dust finding, that Pd concentrations were 40 times higher than Rh and twice as high as Pt even though the Pt concentration in the dust was eight times higher than the Pd.

Timperley et al. (2001) discussed possible issues associated with the presence of high concentrations of contaminants in the fine particulate material in road runoff. Of particular concern was the fine particulate matter that might become associated with biofilms in streams. Biofilms such as filamentous algae or diatoms are common surfaces in streams and form an important food source for many invertebrate grazers in streams. Concentrations of copper, lead and zinc in these films (sampled in Hamilton, Auckland and Christchurch) can reach concentrations similar to those observed in the suspended sediments present in streams (refer Fig. 6.2). The concentrations are higher than in algal films that do not contain fine particulate material. Timperley (2001) showed that *Potamopyrgus* (a common freshwater grazing snail in New Zealand streams) ingests fine particulate material associated with biofilms when grazing and that 99% of the particles (by number) were $<5 \mu m$ or less in size.

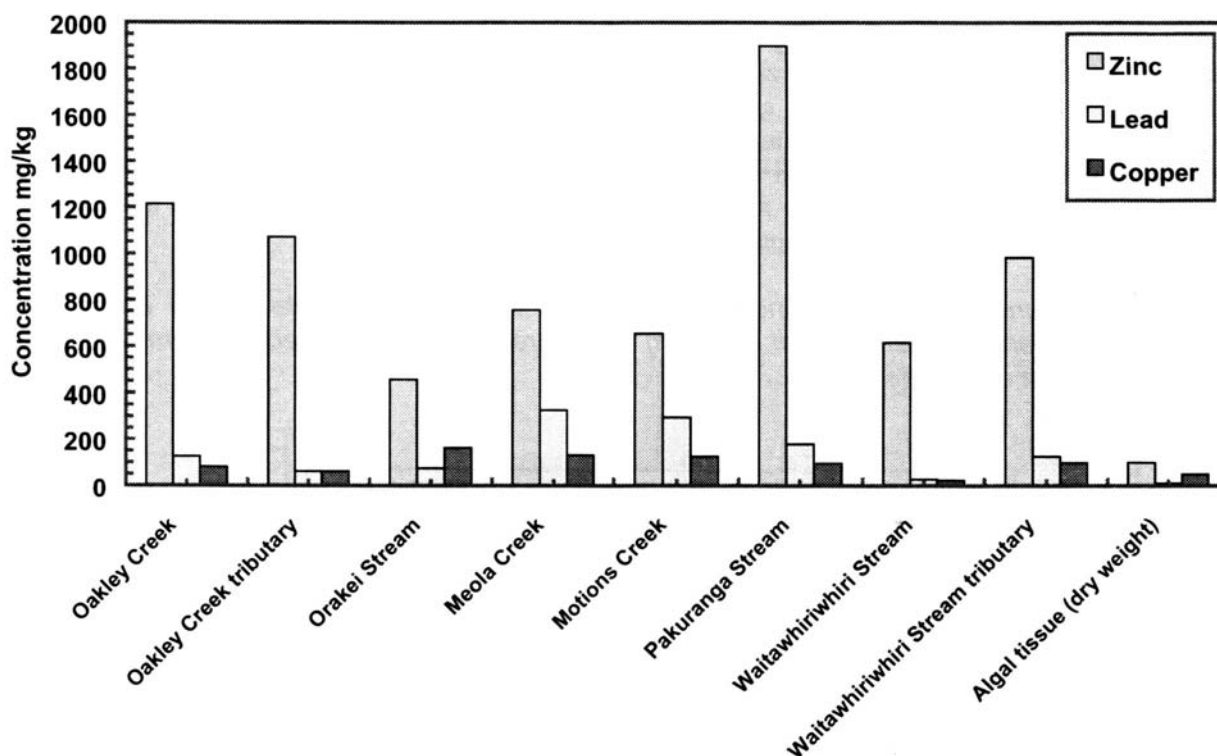


Figure 6.2 - metal concentrations in biofilms (algal tissue and fine particulates) in urban streams (From Timperley et al. 2001).

Karouna-Reiner & Sparling (2001) examined the uptake of metals by invertebrates (molluscs and odonata) in stormwater treatment ponds Maryland. The study found significant effects of landuse for Cu ($p < 0.05$) and Zn ($p < 0.01$) in odonates. The Cu concentrations were higher (twice as high as open-space ponds) in those invertebrates from ponds in commercial catchments compared to motorway and open-space ponds. Zinc concentrations were higher in those organisms from ponds in commercial catchments compared to residential, highways and open-space. The authors noted that the neutral-alkaline nature of the ponds limited the Pb accumulation. Further information can be found in Schueler 1996).

6.5.2.2 Fish

Uptake of metals by fish in freshwater environments has been widely reported in the literature. Studies have focused on particular issues such as the mobilisation of mercury in acidic environments (e.g., Hrabik & Watras 2002).

Campbell (1994) examined the uptake of metals by fish in stormwater ponds in Orlando Florida. The ponds received runoff from shopping centres, apartment complexes and road projects. The study found a number of differences in the concentration of Cd, Ni, Pb, Cu and Zn but the differences varied between the species of fish and the element. Campbell considered that bluegill sunfish (an omnivore) was accumulating Cu; red-ear sunfish (a bottom feeder), was found to accumulate Cu, Ni, Cd, Pb and Zn; large-mouth bass (a carnivore) was found to accumulate Cd and Zn.

Sures et al. (2001) reported on the uptake of Pd by European eels (*Anguilla anguilla*) after being exposed experimentally to road dust. Examination of liver and kidney after four weeks exposure showed uptake of Pd. Palladium was detectable in the eel liver (0.18 ng/g wet wt) but not in the kidney. As reported by Sures et al. (2001) there is little information regarding the kinetics of Pd (or Pt, Rh) uptake by aquatic organisms such as fish.

In New Zealand, Macaskill et al. (2003), reported data for bioaccumulation of metals in common bullies (*Gobiomorphus cotidianus*) in Lake Rotorua adjacent to the city and one location outside of the city. The results suggested an increase in Pb in particular at one urban location with a less significant difference for copper. The concentration of elements such as Cu in tissue were well below concentrations considered deleterious to bully (Macaskill et al. 2003).

6.5.2.3 Other organisms

Although the focus of this report is the potential effects of road transport derived contaminants on aquatic systems, there have been a number of studies on the uptake of metals by other organisms (plants, mammals, earthworms, birds etc.).

A wide range of studies have been undertaken in relation to the uptake of metals by plants growing adjacent to roads. Early studies included work such as that of Cannon & Bowles (1962), Mitchell & Reith (1966), Little (1973) and Chamberlain (1983). More recently further studies have examined the effects of traffic emissions of PGEs on plants. Dietl et al. (1996) and Schafer et al. (1998) examined the presence of metals in plants adjacent to trafficked roads. Dietl et al. (1997) found by using grass cultures that there were positive correlations between deposition of Pb and Sb and concentrations in the grass. A similar profile was not observed for Cd in grass leaves. Schafer et al. (1998) found a measurable uptake of PGEs to vegetables and concluded that the PGEs were immobile to moderately mobile with Pd having greater mobility compared to Pt and Rh.

Dudding & Ward (2002) reported the results of Pt uptake experiments by rye grass (*Lolium perenne*). The study confirmed results of earlier work examining the uptake of Pt from tunnel dust. Very little Pt was

mobilised and taken up into grass leaves. Dongarra et al. (2003) examined the distribution of Pt and Pd in pine needles (as a biomonitor of metal distribution) in urban Palermo. Platinum and Pd concentrations were closely correlated and higher in the centre of the City compared to outside Palermo. The PGE concentrations included elements present on the needle surface as well as within the needle.

In New Zealand and Australia, the uptake of elements such as Pb, Cu, Cd and Zn emitted by motor vehicles by roadside plants (sweet corn, bracken, trees and pasture grasses) has been reported in a number of early studies such as Ward et al. (1974, 1975 and 1977) and by David & Williams (1975).

Jensen et al. (2002) examined PGEs in feathers of sparrowhawks and falcons in Sweden and prey species. The analysis of feathers from 1917 to 1999 revealed a clear trend with significantly higher concentrations in falcon feathers after 1986. Higher Pd concentrations were identified compared to Pt and Rh. PGEs present in feathers are predominantly external being present in nanometre size particles.

Internationally there have been a considerable number of studies that have shown uptake of road-derived contaminants such as Pb by mammals. As with plant studies noted above, many of these studies were undertaken in the 1970s when issues associated with the presence of Pb in petrol were becoming apparent (e.g., Jeffries & French 1972, Welch & Dick 1975, Getz et al. 1977). Ward & Savage (1994) reported the uptake of Pb and Cd by animals grazing near the M25 motorway in London.

There appears to be little information on the uptake of contaminants by aquatic plants associated with wetlands, ponds and waterways below road stormwater discharges. A study by Sriyaraj & Shutes (2001) reported on the concentrations of metals in *Typha latifolia* and *Glyceria maxima* growing in a pond receiving runoff from the M25 outer London motorway. As found elsewhere the concentrations of metals decreased from the root to the leaf. The study showed uptake of metals such as Pb and Zn into roots and rhizomes but the significance of the uptake in relation to plant health wasn't discussed, and no control data was, presented by the authors.

In New Zealand, aquatic plants such as water-cress (*Lepidium sativum*) are collected for food. Uptake of contaminants such as arsenic from water has been demonstrated in the Waikato River (Robinson et al. 2003). Water-cress will grow in drainage channels and streams receiving road runoff and urban stormwater. Uptake of trace elements such as Cu, Pb and Zn from water and from sediment (pore water) may occur. Uptake of elements such as Cu and Zn are not likely to be of public health concern (as both elements are nutritionally important). Uptake of elements such as Pb and Cd, which have limits set to restrict intake through consumption is of greater concern. Although, Pb concentrations have declined since the introduction of lead free petrol into New Zealand, there is still a substantial reservoir of lead within the road and urban environment. Most of the Pb originated from motor vehicles.

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. Information shows 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 differs to that of Pb. Uptake of the PGEs has also been demonstrated to occur in freshwater organisms.

There is little data for bioaccumulation of 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.

There is little information that indicates that any freshwater 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.

6.5.3 Bioaccumulation of Organic Compounds

6.5.3.1 Introduction

Bioaccumulation of organic compounds is a relatively complex phenomenon affected by a variety of factors (refer Carey et al. 1998). Key factors are polarity, hydrophobicity and metabolic rate. Bioaccumulation from water is important as large gradients exist between water and biota for hydrophobic organic compounds. Although bioaccumulation can differ between organisms with differing feeding habits and between freshwater and marine fish (due to differences in their physico-chemical environment), bioaccumulation data can be obtained experimentally and from field data. Even with all of the environmental and biological variables affecting bioaccumulation including both environmental and biological transformation of the contaminant, approximations of bioaccumulation potential are valuable in assessing ecological risk associated with uptake.

Bioaccumulation of a chemical's ability to bioaccumulate has the potential to result in adverse effects on an organism or can result in the transfer of contaminants up food chains as a consequence of consumption of the organism by a predator (biomagnification) or consumption by humans. The degree of bioaccumulation is often expressed as bioconcentration factors (BCFs) or bioaccumulation factors (BAFs). The BCF is usually determined experimentally. The k_{ow} is generally used to estimate the BCF of chemicals and good relationships have been identified between the BCF and the k_{ow} (e.g., Veith et al. 1979, Mackay 1982). However, the relationship is affected by the structure of the chemical.

Kingett Mitchell (2000) examined the BCF (for fish) of all organic compounds identified as being emitted by motor vehicles. The calculations of the BCF, was carried out using information on the K_{ow} and the methodology developed by Meylan et al. (1999). In terms of environmental significance, USEPA (1985) considered that compounds with log k_{ow} values of more than 3.5 (a BCF of 3,162) should be considered further in relation to bioaccumulation. Table 6.11 identifies a range of compounds with BCFs of over 1,000. Most of the compounds identified with elevated BCFs are PAHs or substituted (e.g., nitro) PAHs.

Table 6.11 - BCFs over 1000 for organic compounds emitted from motor vehicles.

Compound	BCF	Source	Compound	BCF	Source
Trimethylnaphthalene	1010	2.1a	Benzo(b)fluorene	5532	2.1a,b
Pyrene	1142	2.1a,b	Benzo(b)fluoranthene	5631	2.1a
1M-anthracene	1167	2.1a	Chrysene	5939	2.1a,b
9M-phenanthrene	1167	2.1a	Benzo(c)phenanthrene	5939	2.1a,b
n-pent-benzene	1183	2.1a	Dibenzo(a,e)pyrene	6875	2.1a
1 tert-1B-3,5-DM-benzene	1405	2.1a	Nitrobenzo(a)pyrene	7304	2.1b
2M-anthracene	1413	2.1a	1,4-dimethyl-7-(1-methylethyl)azulene	7365	8.1
1-nitropyrene	1571	2.1a	Coronene	8574	2.1a
1-M-phenanthrene	1628	2.1a	1-methylbenz(a)anthracene	9388	2.1a
4-M-phenanthrene	1628	2.1a	Benzo(j)fluoranthene	10090	2.1a
2,4-DM octane	1703	2.1a	Benzo(k)fluoranthene	10110	2.1a
1,3,5-triethyl-benzene	1711	2.1a	Benzo(a)pyrene	10470	2.1a,b
1,2,4-triethylbenzene	1711	2.1a	Perylene	12960	2.1a,b
2,2-DM octane	1815	2.1a	1 DME-benz(a)anthracene	14750	2.1a
2M-anthracene	1843	2.1a	3M-cholanthrene	17510	2.1a
l-nonene	1843	2.1a	Benzo@pyrene	18150	2.1a,b
Fluoranthene	1876	2.1b	tetramethylphenanthrene	21450	7.1
Octane	1944	2.1a	Dibenz(a,j)anthracene	21670	2.1a
Benzonaphtho(2,1-d)thiophene	2581	2.1a	Benzo(g,h,i)perylene	25420	2.1a,b
Benzo(a)fluorine	2871	2.1a,b	1M-benzo(a)pyrene	26630	2.1a
3,6-DM-phenanthrene	3080	2.1a	1M-benzo(e)pyrene	26630	2.1a
1-methylpyrene	3310	2.1a,b	Indeno(123-c,d)fluoranthene	28620	2.1a,b
Triphenylene	3367	2.1a,b	Indeno(123-c,d)pyrene	28620	2.1a,b
Benzo(g,h,i)fluoranthene	3558	2.1a,b	Dibenzo(a,h)anthracene	31440	2.1a
Cyclopenta(cd)pyrene	4888	2.1a	Anthracene	56910	2.1a
Benzo(a)anthracene	5435	2.1a,b			

Notes: Sources: 2.1a,b are petrol and diesel exhaust respectively; 7.1 – friction linings; 8.1 – tyres.

6.5.3.2 Invertebrates

In New Zealand, Nipper et al. (1995) examined the uptake of contaminants in stormwater by placing caged freshwater mussels (*Hyridella menziesi*) in the inlet, outlet and in the stormwater pond at UNITEC (Mt Albert Auckland). Organochlorine concentrations (e.g., PCBs, pesticides) in the mussels from the ponds were similar to those measured elsewhere in the Auckland region. Some uptake of PAHs was observed. However, no control samples were examined.

6.5.3.3 Fish

In New Zealand, there have been extensive studies of the concentrations of organochlorine compounds in eel and trout as part of the Ministry for the Environment Organochlorines programme (Buckland et al. 1998). This work does not provide any specific information that related to road runoff.

6.5.3.4 Other organisms

There does not appear to be any specific reports of the assessment of uptake of organic compounds by organisms such as terrestrial or wetland birds that relate to stormwater runoff from roads.

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.

6.6 Summary

In New Zealand there are few specific studies that have assessed the effect 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).

Habitat

Habitat changes in urban streams are one of the major changes that occurs in waterways within urban areas. Vehicles themselves do not contribute materials to stormwater that could result in identified habitat changes. Roads however do contribute coarse particulates such as gravel and asphalt fragments to stormwater. These may become deposited at the point of discharge in the case of larger material resulting in relatively localised physical changes to substrates. In freshwater environments the extent of these changes do not appear to have been assessed.

Water

Stormwater quality data from urban areas and from roads and motorways has shown that dissolved concentrations of metals such as Cu and Zn can reach very high concentrations in the first flush of stormwater. Over the duration of storm events, the concentration of dissolved zinc is the most significant in relation to water quality guidelines such as ANZECC (2000). The regular exceedence of dissolved concentrations suggests the likelihood of adverse effects on freshwater biota. Much of the copper in stormwater may be complexed by dissolved organic matter. Only a limited proportion of the dissolved Zn is likely to be complexed leaving most as the dissolved cation. A range of organic compounds, are present in urban and road stormwater. However, there is little evidence of organic compounds in road stormwater being toxic and causing adverse effects on freshwater biological communities.

Available information indicates that the concentrations of metals in stormwater runoff are typically low compared to water quality guidelines. However it is considered that longer-term exposure may have at present unidentified chronic effects of freshwater organisms present in waterways receiving road and highway runoff.

A range of toxicity studies, have been undertaken using urban stormwater discharging to freshwater environments. Published toxicity test data has shown that first flush stormwater will exhibit greater toxicity than flow weighed samples in some circumstances. Toxicity testing undertaken using Microtox have shown that for runoff parking areas, 50% of samples are toxic and for highways (e.g., isolated bridge runoff), 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 has chronic effects on the growth of freshwater algae.

Tests carried out using a range of freshwater organisms and have not demonstrated consistent toxicity. Work undertaken using general urban runoff has shown toxicity but the toxic agent was considered to be in some studies to be organic compounds (and in some cases in the US to be pesticides used in residential areas). Urban stormwater testing has shown that 40% of all stormwater samples demonstrated toxicity to *D magna* and variable toxicity to species such as *Ceratodaphnia* and no toxicity to others. Given the nature of stormwater runoff and samples collected from roads, there may be limitations in the representativeness of some toxicity tests.

Freshwater organisms below 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.

Sediments

Build-up of sediment discharged from roadways will occur close to the point of discharge (in ponds, wetlands, streams and lakes) if the discharge point does not have sufficient energy to transport the contaminants and sediment away. Based upon the composition of the suspended sediment and measurement of urban stream sediment quality, it is likely that concentrations of contaminants can build-up to concentrations that could have an adverse effect on freshwater benthic organisms.

Given the concentration of Cu, Pb and Zn in the suspended sediments of stormwater draining roads, exceedence of sediment quality guidelines 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 concentration of contaminant in sediment 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 have shown that the particulate matter (from road stormwater) settling in pond systems has the ability to cause adverse toxicity to test organisms.

Bioaccumulation

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. Information shows 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 differs to that of Pb.

There is little data for trace elements such as Mo and Sb emitted by motor vehicles. 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. There is little information that indicates that any freshwater 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.

7. IDENTIFICATION OF ENVIRONMENTAL EFFECTS IN ESTUARINE AND COASTAL ECOSYSTEMS

7.1 Introduction

The New Zealand estuarine and coastal environment is diverse with stormwater discharges occurring into:

- ❑ Estuaries containing saltmarsh (e.g., Pauatahanui Inlet) and mangroves (e.g., the Waitemata Harbour).
- ❑ Large predominantly intertidal inlets and estuaries (e.g., the Avon-Heathcote, Manukau Harbour, Whangarei Harbour).
- ❑ Large predominantly subtidal Harbours (e.g., Wellington).
- ❑ Open coastal waters with rocky shores (e.g., Takapuna to Long Bay Shoreline in Auckland).

This section of the report examines the effect of stormwater discharges from roadways on estuarine and marine ecosystems. The key environmental issues are:

- ❑ Effects on water quality.
- ❑ Effects on sediment quality.
- ❑ Effects on biological resources including toxicity and bioaccumulation.

Since the preparation of the first edition of this report, there have been several specific reviews and reports prepared that provide information in relation to the effects of stormwater discharges on the marine environment. These include Pridmore et al. (2000) and Williamson et al. (2001).

This section reviews the methods and tools currently used to assess environmental effects within estuarine and marine environments with a view to identifying whether they are sufficient to determine the effects of road transport emissions on these environments. This section also examines what we know about the effects of motor vehicles contaminants in isolation or as part of general urban stormwater runoff on the marine environment.

7.2 Habitat

Compared to habitat monitoring in the freshwater environment (refer Section 6.2), there has been little work carried out to identify specific methods for the assessment of habitat quality in the marine environment. Given the diversity of habitat types and the nature of the environment, establishing estuarine and coastal benchmarks is not as straightforward as it is for freshwater. Robertson et al. (2002) represents the most comprehensive assessment of monitoring (including the examination of habitat) in the New Zealand coastal environment. Typical habitat changes in estuarine and coastal marine environments that may be attributable to urban stormwater and other stressors include:

- ❑ Changes in sediment characteristics due to deposition of fine sediments.
- ❑ Changes in sediment characteristics due to the deposition of coarse sediment and debris.
- ❑ Changes in sediment surface micro-flora due to nutrients and the presence of oxygen demanding substances.

- Changes in sediment surface macro-flora (e.g., sea-lettuce, *Gracilaria* due to the presence of nutrients).

As noted in Section 4, sedimentation of particulate material from roads results in the deposition of coarse particulate materials around stormwater outfalls. These deposition areas, which often comprise gritty particulate materials below the outfall (road chips, bitumen and other inorganic material from the road or urban environment such as red brick) are in many cases readily identifiable. The extent of deposition is dependent upon the volume and source of the discharge, and the physical nature of the receiving environment. This zone has been described in studies such as Bolton-Ritchie et al. (1999). The deposition of fine sediments at the point of discharge is not typically a feature of the discharge of stormwater from roads. Discharges capable of resulting in fine sediment deposition are typically associated with earthworks.

No specific tools have been identified for specifically assessing habitat changes that might be attributable to discharges of road stormwater to the marine environment.

Stormwater discharges from roads and urban catchments typically discharge material that settles adjacent to the stormwater outfall. The presence and extent of the distribution of this material is dependent upon the hydrodynamics of the environment at the point of discharge and the characteristics of the material discharged. If the physical environment is depositional in nature then material may accumulate adjacent to the outfall.

7.3 Water quality and Toxicity

7.3.1 Water quality data

As with freshwaters, marine water quality can be monitored for a wide range of specific constituents. This analytical ability allows resource managers to assess the quality of a receiving water in relation to the possible effects of discharges (such as road runoff).

The implications of road runoff discharge to coastal environments (estuaries and near-shore areas) is dependent upon the ratio of stormwater volume to the physical environment at the entry point of the stormwater (e.g., estuary width and length, water depth, tidal currents etc.). In evaluating the effects of motor vehicles on coastal systems, the key constituents of concern are contaminants (metals and organic compounds). Other constituents that are linked mainly to road surface wear and activities on and adjacent to the road (e.g., suspended solids, BOD, bacteria etc.) are not considered further.

The development and dispersal of stormwater plumes in coastal environments has been examined in a number of studies. In each case, the dispersal of stormwater occurs on a site-specific basis. In assessing effects, plume behaviour at the discharge point needs to be considered and is primarily dependent upon whether the discharge point is at the shoreline or offshore, whether the discharge is surface or subsurface and what the volume of the discharge is relative to the receiving environment volume/cross-section. Washburn et al. (2003) describe the formation and dispersal of stormwater plumes from very large urban catchments in California showing that plumes could in that case be detected over kilometres from the discharge point (refer Section 7.5.3).

7.3.2 Toxicity

In New Zealand Hickey et al. (1997) assessed the toxicity of stormwater discharged to the marine environment on the following test organisms:

1. Diatom (*Minutocellus polymorphus*) 48 hour inhibition microplate test.
2. Amphipod (*Chaetocorophium lucasi*) 96 hour acute mortality test.

3. Echinoderm (*Fellaster zelandiae*) 36 hour chronic development.

Toxicity analysis was based upon the use of stormwater collected from the UNITEC stormwater system in Mt Albert, Auckland. As noted earlier for toxicity tests in freshwater, variation was found in the toxicity observed between different storm events tested. Acute responses occurred for marine amphipods in one of three storms while chronic responses were observed for marine diatoms and echinoderms in the tests. Both tests showed that toxic responses were less in unfiltered samples. Hickey et al. (1997) noted that the marine acute criteria for Cu, was exceeded in the UNITEC stormwater pond discharge on several of the sampling occasions. The chronic criteria were exceeded for Cd, Cu and Pb in the UNITEC stormwater.

Tiefenthaler et al. (2001) examined the toxicity of runoff (simulated rainfall) from car park areas in Long Beach California. All samples of simulated runoff were considered toxic but not all species used in the tests responded in a similar manner. The purple sea urchin (*Strongylocentrotus purpuratus*) and marine bacteria were the most sensitive while a mysid shrimp was the least sensitive. Toxicity was related to length of contaminant exposure with toxicity increasing by a factor of 6 after 28 days of exposure. The study also found that a toxic first flush was also present in samples collected in the first 10 minutes of the event with samples twice as toxic as samples taken later in the storm event. These findings follow the pattern of constituent concentrations especially the concentration of dissolved metals (refer comments in Section 4 of this report in relation to dissolved metal concentrations). Tiefenthaler et al. (2001) undertook TIE to elucidate the causal agents for the toxicity. They found that complexation of metals completely removed toxicity, concentrations of dissolved Zn were high enough to elicit a toxic response and variation in the Zn concentration was correlated to the variability in toxicity observed in test organisms.

Bay et al. (2003) examined the toxicity of stormwater from Ballona and Malibu Creeks which discharge into Santa Monica Bay, California. The examination of stormwater samples (using purple sea urchin fertilisation test with exposure for 20 minutes and salinity adjusted using brine) showed that every sample from Ballona Creek was toxic with NOECs ranging from <3-25%. Toxicity was also detected in three of four samples from Malibu Creek. Ballona Creek has a catchment comprising 83% urbanised area compared to 12% for Malibu Creek. Substantial variability was also noted amongst storms suggesting seasonality in toxicity. Purple sea urchin toxicity was also found in the waters of Santa Monica Bay off Ballona Creek during all events examined. Fig. 7.1 summarises the toxicity results from Bay et al. (2003).

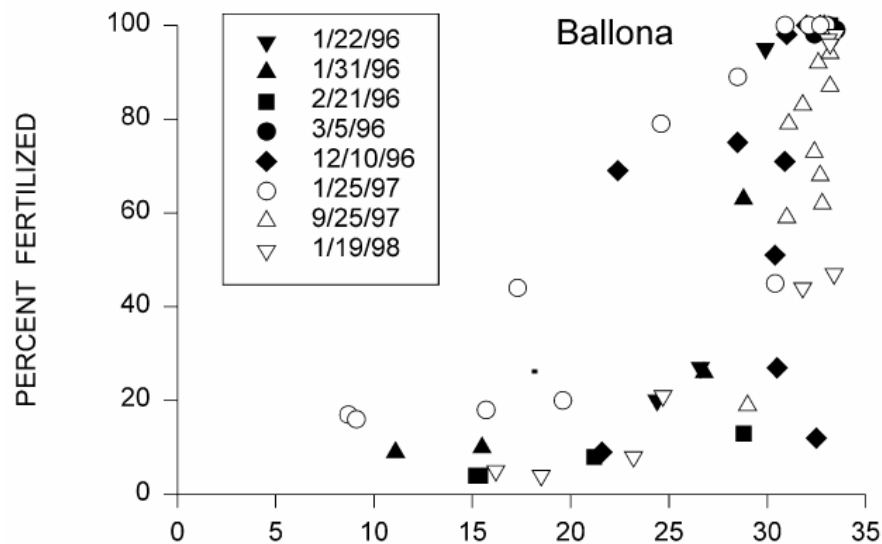


Figure 7.1 - Purple sea-urchin toxicity and plume salinity (at time of collection – x-axis) (taken from Bay et al. 2003) (note that test salinity adjusted to 34 g/kg).

Greater toxicity was present in waters closest to the Creek mouth, while samples collected outside the discharge plume (as defined by salinity) were non-toxic. Toxicity typically extended further off-shore during large events. Toxicity was found to occur within the plume when the diluted plume contained >7% stormwater on one occasion and >10% on another.

Bay et al. (2003) concluded that the toxicity present was related to the amount of diluted stormwater present. As a consequence the authors identified a significant area of coast where toxicity was predicted to occur in seawater based upon the plume dilution. To elucidate the cause of the observed toxicity Bay et al. (2003) undertook TIEs to isolate the likely cause of the toxicity. Addition of EDTA to stormwater samples always removed toxicity; removal of non-polar organic compounds was sometimes effective but removal of particulates or oxidants were not effective. Further work on off-shore water samples produced similar but variable results (refer Fig. 7.2). EDTA was still effective at removing the identified toxicity. Analysis of stormwater samples for dissolved metals identified that dissolved Zn and Cu concentrations averaged 66 and 13 mg/m³ respectively. It was identified that the NOEC values for the two metals were 8 and 17 mg/m³ respectively and the EC₅₀ 29 and 30 mg/m³. It was considered that none of the other elements examined were present in sufficient concentrations to produce a toxic response. However for some elements (e.g., Ag and Hg and Ni) there was not sufficient data put forward by the authors to draw any conclusion.

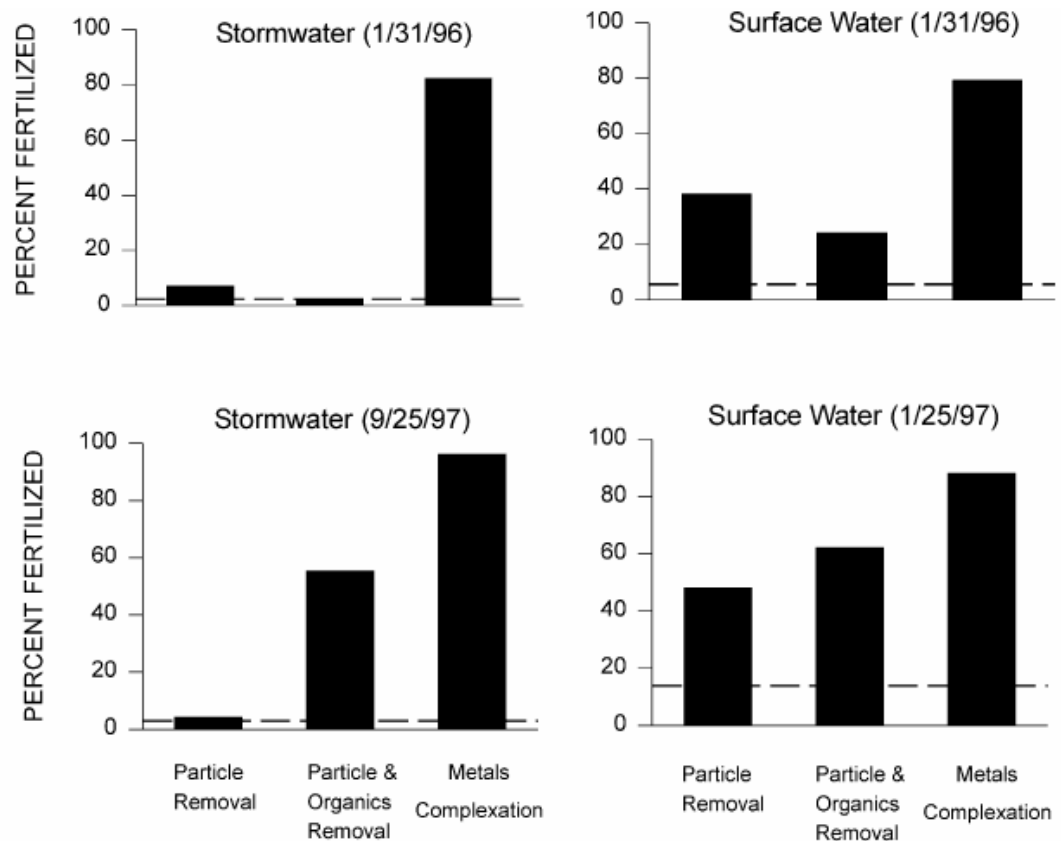


Figure 7.2 - TIE results for Ballona Creek stormwater and offshore water samples (dashed line represents baseline samples) (taken from Bay et al. 2003).

Schiff et al. (2002) also examined stormwater toxicity from Chollas Creek (San Diego, California) which discharges into San Diego Bay. The catchment comprised 67% residential, 12% commercial/industrial and 4% roadways. The purple sea urchin exhibited toxic responses to stormwater at dilutions down to 6-12% stormwater. In contrast, the mysid shrimp (*Mysidopsis bahia*) did not exhibit any toxic response. Tests were also conducted using the freshwater flea (*Ceratodaphnia*) which exhibited intermediate toxic responses. TIEs conducted to identify the constituents contributing the stormwater toxicity revealed that

trace metals (probably Cu and Zn) were responsible for the toxicity to sea urchins. Tests using *Ceriodaphnia* indicated that the toxicity observed arose from organophosphate pesticides present in the stormwater (e.g., diazinon and chlorpyrifos). The findings reflected the known toxicity of these constituents to *Ceriodaphnia*. The authors concluded that the concentrations of Cu and Zn were sufficient to account for between 55 and 95% of the observed toxicity depending upon the storm event. Copper and Zn were also identified as significant toxicants in stormwater by Cooke & Lee (1995, in Schiff et al. 2002).

The examination of the intrusion of stormwater plumes into Santa Monica Bay showed that the plumes were relatively short-lived and plumes unlikely to persist for more than several days depending upon the size of the storm event and the sea-state in the coastal area at the time (Washburn et al. 2003). Bay et al. (2003) note that similar TIE testing undertaken in southern California identified Zn as the primary toxicant.

The comparison of road/motorway stormwater quality with general urban stormwater quality in Section 4 showed that road runoff generally has similar concentrations of Zn and Cu to general urban runoff. Concentrations of dissolved Cu and Zn have been reported in New Zealand at concentrations very similar to those identified above. It is likely therefore that in the case of marine species sensitive to Cu or Zn, toxicity responses may occur in situations where stormwater plumes in the coastal environment occur to dilutions of about 10%.

A summary of relevant water quality guidelines and criteria for the protection of marine aquatic resources that may be used by water quality managers to assess the relative impacts of changes in receiving water quality is presented in Table 7.1. The data identifies both chronic and acute guidelines and criteria for metals and a limited number of organic compounds that have assigned guidelines or criteria. From a comparison of the data presented on the contaminant concentrations present in urban runoff and specific road/highway run-off in Chapter 4 with the data in Table 7.1, it is evident that water-borne toxicity does not appear to be of concern for most metals. Based on average dissolved concentrations of Cu and Zn identified earlier (e.g., 7.5 and 68 mg/m³ respectively) dilutions of about 6 times for Cu and 4.5 times Zn would reduce concentrations below the ANZECC (2000) triggers.

Table 7.1 - Summary of water quality guidelines for potential toxicants derived from transport emissions discharged to marine aquatic ecosystems (all data mg/m³).

Parameter	ANZECC (2000)	USEPA (2002)	
	95% protection	Acute (CMC)	Chronic (CCC)
Cadmium	5.5	40	8.8
Chromium			
Copper	1.3	4.8	3.1
Lead	4.4	210	8.1
Nickel	70		
Zinc	15	90	81
Benzene	700	5100 ^a	700 ^a
Total PAH	-	300 ^a	-
Acenaphthene	-	970 ^a	500 ^a
Fluoranthene	-	40 ^a	16 ^a
Naphthalene	70	2350 ^a	-

Notes: a = criteria not derived, LOEL presented.

However, as Timperley (2003) noted, concentrations of both elements are often much higher during the first flush phase of stormwater discharge from roads (refer Section 4). With concentrations of dissolved Cu and Zn many times the EMCs, moderate dilution would be required to eliminate toxicity due to dissolved Cu and Zn. Toxicity issues are likely to be greater within estuaries with limited mixing compared to open coastal areas. In determining the significance of road stormwater discharges, the key issue is the scale at which toxicity might be evident. Bay et al. (2003) reported that toxicity from Bollana Creek in Santa Monica Bay was evident 2 km alongshore and 1 km off-shore. The Ballona Creek

catchment is large (about 229 km²) compared to many urban catchments in New Zealand. For example the many catchments in Auckland City add up to about 153 km² with catchment areas ranging from 0.6 km² to 15 km². In urban areas such as Waitakere City, there is about 16 km² of catchment draining to the Whau estuary and about 25 km² draining to Henderson Creek (and not all is urban).

It is likely that in New Zealand, the discharge of stormwater to open coastal environments (e.g., as occur along the East Coast Bays of North Shore City) are unlikely to result in toxicity to sensitive marine species. The discharge of roading and urban stormwater to enclosed estuarine environments has the potential to have some toxic effects on sensitive marine species within these environments. At least a 10 fold dilution is required, to ensure that potential toxic effects associated with dissolved Cu and Zn in road runoff are avoided. In most situations in urban areas of New Zealand, road runoff is not isolated from general urban stormwater (e.g., from buildings, commercial and industrial premises and from road surfaces affected by non roading activities). This may in some situations provide dilution prior to discharge but may also provide additional contaminants contributions.

Overall, the toxicity testing carried out in New Zealand by Hickey et al. (1997) has demonstrated that the toxicity of urban stormwater is variable with stormwater from a carpark (Unitec in Auckland) being relatively non-toxic. Hickey et al. (1995) concluded that a dilution of some three times may be required to ensure that there is no water column toxicity after discharge. It was noted in the study that toxicity was lower than expected. Contaminants other than metals were suggested as having a strong involvement in toxicity.

Work undertaken in the United States has shown that toxicity to sensitive marine species can occur in near shore 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. Toxicity is more likely to occur in locations where dilution is poor. Such locations include embayments and estuaries in harbours and estuaries. Given the relatively small size of most New Zealand road and urban catchments, discharge volumes from open coastal stormwater outfalls are typically small with adequate dilution to minimise the risk of acute toxicity.

7.4 Sediment Quality

7.4.1 Introduction

As discussed in Section 4, particulate matter settlement in estuaries and coastal areas is assisted by flocculation. Coarse sediment zones can often be observed adjacent to coastal stormwater discharges. The extent of this zone will be dependent upon site-specific factors. These include the discharge to receiving environment ratio and the local hydrodynamic environment. Increased sediments concentrations have been identified in a number of studies around New Zealand where urban stormwater discharges or vehicle emissions occur adjacent to the marine environment.

7.4.2 Intertidal

7.4.2.1 Intertidal areas and Salt Marsh

As described in Section 4, aerial deposition has the potential to result in the build-up of vehicle emission sourced contaminants. Build-up will be especially pronounced adjacent to bridges, causeways and motorways alongside intertidal areas. In New Zealand, Kennedy (1976 unpublished) examined the distribution of trace elements in sediments in salt marsh adjacent to a road around Pauatahanui Inlet near Wellington carrying 4,900 VPD. Sediment cores taken close to the road showed evidence of enrichment by Cu, Pb, and Zn. Elevated concentrations of the dominant contaminants emitted by motor vehicles (Cu, Pb, Zn) were found adjacent to the road and were detectable to a short distance from the road (15 m). A further study at Pollen Island in Auckland (Kennedy ~1980 unpublished) found that moderate

concentrations of Cu, Pb, Ni, Cr and Zn were present in roadside soils. Elevated concentrations of Cu, Zn, Pb, Ni and possibly V were detected at distances of 20 to 40 m from the motorway edge. Given the nature of the motorway in this location, it was assumed that much of the concentration increases detected in the intertidal mangroves and salt marsh would have been derived from aerial deposition rather than stormwater. The maximum concentrations recorded in the Pauatahanui salt marsh study were Cu (38 mg/kg), Ni (17.8 mg/kg), Zn (157 mg/kg), Pb (78 mg/kg), Cr (54 mg/kg) and in the Pollen Island sediments were Cu (24 mg/kg), Ni (12 mg/kg), Zn (54 mg/kg), Pb (79 mg/kg), Cr (113 mg/kg).

A comparison of the data from these two studies indicated that the concentrations of all elements were below upper threshold sediment guidelines such as the ER-M values of Long et al. (1995). The elements Cu and Zn were measured close to the road at similar concentrations to the ER-L concentration of Long et al. (1995). Only Pb was measured at concentrations above the ER-L and the ANZECC (2000) ISQG-low trigger (close to the road and motorway) in both studies.

Internationally there appears to have been little information published describing the impact of motor vehicles specifically on the build up of contaminant concentrations in inter-tidal environments.

7.4.2.2 Intertidal soft-shore areas

A wide range of investigations, have been carried in the Auckland region on the effects of urbanisation on sediment quality in estuaries from both the Manukau and Waitemata Harbours. The studies have presented information on the overall effects of urbanisation, not specifically on the effects of road transport discharges on such environments. Macaskill (2001) provided an overview of trace element data in sediments adjacent to Auckland City; Williamson & Mills (2002) overviewed sediment quality information for the Auckland region as it related to sediment quality guidelines and Kingett Mitchell (2003c) examined coastal sediment quality around North Shore City as it related to sediment quality management. Recently Timperley et al. (2003) identified best estimates for the relative contributions of vehicles to total loads of contaminants entering coastal areas from Auckland City. The proportional load from roads indicated that roads (and therefore motor vehicles) contributed to the build up of contaminants in coastal depositional environments. A substantial body of information on the distribution of the key transport related elements (Cu, Pb and Zn) in sediments in the Auckland region both spatially and temporally through the examination of sediment cores is also available (e.g., refer Williamson & Mills 2002, Williamson et al. 2003 etc.,).

Webster et al. (2000) examined the distribution of metals from sediments adjacent to a stormwater outfall in the Hatea River within the urban area of Whangarei. The sampling showed that a number of metals were deposited in a halo around the stormwater discharge point (Fig. 7.3). Elevated concentrations of Fe, Mn, Cu, Zn, Pb and As were measured in sediment adjacent to the outfall with highest concentrations closest to the discharge point. No significant accumulation of Cu was found close to the discharge point. The findings were considered to generally reflect the environmental mobility of the elements. For example Cu present in dissolved form was readily leached from sediments while Pb present in particulate form was poorly leached from sediments. Zinc mobility was midway between the two elements. The distribution of elements around the discharge point was influenced by the deposition of Fe-Mn oxides close to the discharge.

Overall, deposition patterns of metals and contaminants such as PAHs near roads would predict that concentration gradients would be found in estuarine intertidal sediments exposed to vehicle emissions. The gradients are however, not as defined as those seen in soils adjacent roadsides, as the sediments are subject to the influence of tidal action that may remove some of the depositing material through hydrodynamic processes. In estuarine and coastal environments of low energy, haloes of contamination by key elements would be expected to be found in sediments. The scale of effects would be very dependent upon the discharge volume, sediment loading and the physical stability of the sediment adjacent to the discharge. Scales of influence for small stormwater discharges are likely to be of the order of 10-20 m depending on the contaminant and its load discharged from the outfall.

7.4.3 Subtidal

The accumulation of contaminants in subtidal sediments adjacent to stormwater discharges has been examined and reported for several locations in New Zealand. For example:

- ❑ Accumulation of metals in sediments adjacent to stormwater outfalls in the central business area of Wellington (Bolton-Ritchie et al. 1999).
- ❑ Accumulation of metals in sediments adjacent to stormwater outfalls draining the central business area of Auckland City (Priestley 1998).

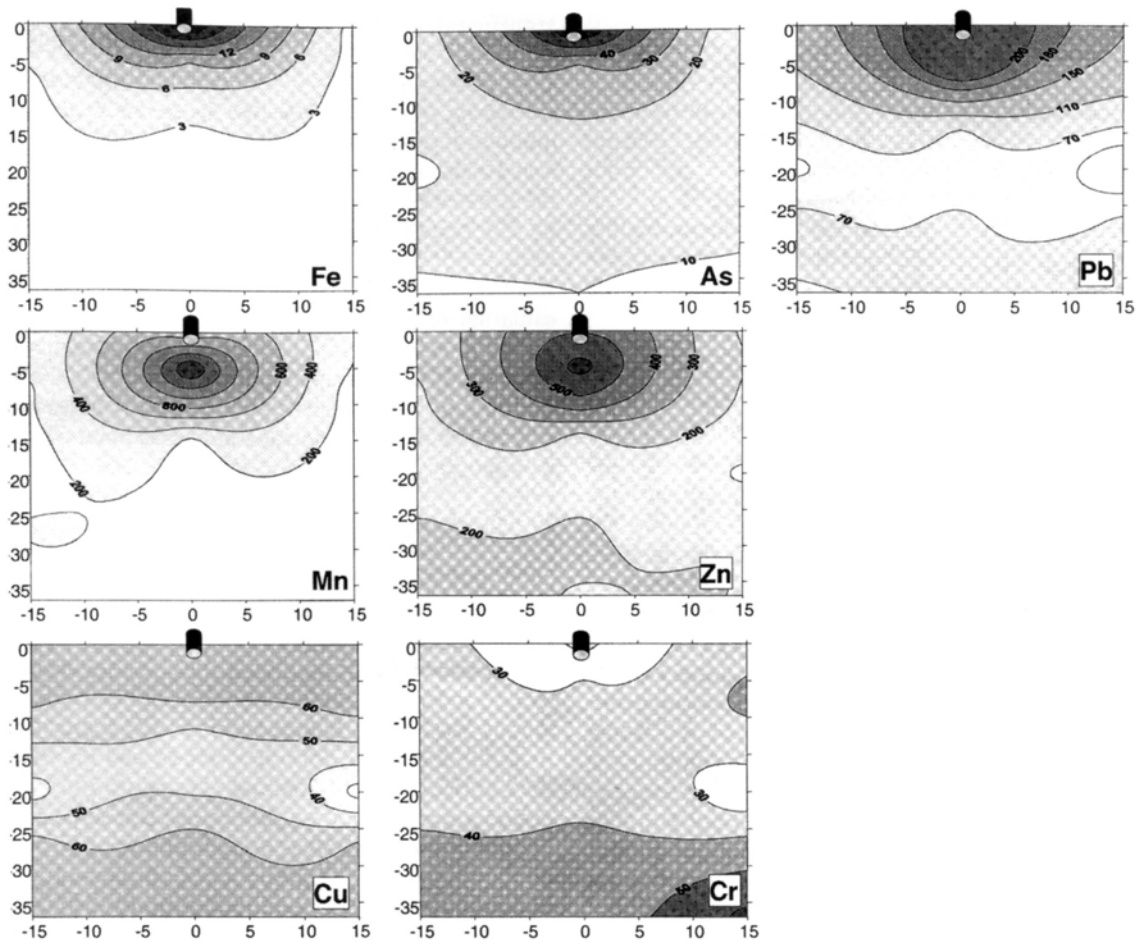


Figure 7.3 - Major and trace element distribution in sediments adjacent to a stormwater drain in the Hatea River estuary (From Webster et al. 2000) (Fe %, all other concentrations mg/kg, axis in metres).

When the concentrations recorded by Bolton-Ritchie and Priestley are compared to sediment quality guidelines such as ANZECC (2000) it is evident that concentrations of key road transport metals exceed sediment quality guidelines.

A considerable amount of work has been carried out on the prediction of effects resulting from the accumulation of contaminants in sediments from urbanised estuaries. Williamson et al. (1999) surmised that concentrations of Cu, Pb and Zn in Auckland estuaries will exceed sediment quality guidelines identifying the level at which biological effects are expected to occur. For example, the work predicted

that “concentrations of Zn in 20-50 years will exceed the sediment quality guidelines at which biological effects are expected to widely occur”.

The predictions, presented in Williamson et al. (1999) and detailed in Vant et al. (1993), Snelder (1995) and Snelder & Trueman (1995) are based upon a series of scenarios. The detailed calculations of which can be found in Appendix 3 of Vant et al. (1993).

The predicted increases in total metal concentrations identified by Williamson et al. (1999) and earlier reports are based upon ‘urban’ stormwater runoff, a proportion of which is contributed by road transport.

The available data has already indicated that contaminant concentrations in urbanised estuaries are at levels with the potential to create adverse effects on biota. However, the direct comparison of concentrations with guidelines such as the ER-L of Long et al. (1995) and the ANZECC sediment quality triggers (refer Section 5), does not confirm that adverse effects have and are occurring as a consequence of the elevated concentrations of the contaminants. In addition, any comparison does not take into account changes in the geochemistry of the contaminant over time (i.e., the potential toxicity may decrease). These factors all add to the difficulty in making such predictions.

Examination of sediment quality adjacent to North Shore City off the East Coast Bays has shown that sediments contain elevated concentrations of elements such as Pb. Concentrations of Pb are about 100% higher than would be expected as a result of historical contributions of Pb from motor vehicle emissions and other sources (Kingett Mitchell 2003c). The concentrations in muddy sediments (about 22 mg/kg) are lower than the ANZECC ISQG-low trigger of 50 mg/kg however.

In New Zealand and internationally there appears to be little data on the distribution of other elements in the marine environment that have been identified as being emitted from motor vehicles (e.g., Mo, Sb etc.,). In relation to the PGEs, Tuit et al. (2000) reported on Pt and Pd in Boston Harbour sediments. The study reported that concentrations had increased about five times above background. Both Pt and Pd are released to the environment from a number of sources. Tuit et al. (2000) described the anthropogenic sources of both elements as being derived from sewage, sewage sludge, medical and dental, chemical and the jewellery industry. The use of Pt in catalytic converters has been the major consumer of Pt (>60%) since 1973. Until 1993 when Pb was phased out of petrol in the US, catalytic converters only accounted for 10% of Pd use. Subsequently Pd use in catalytic converters has increased to about 40% of the demand. The Boston study didn't specifically identify the proportion of Pd and Pt in sediments attributable to vehicle emissions however. It is likely that it will be at least equal to or greater than the amount of those elements used in catalytic converters as the other consumers practise some element recovery.

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 elevated. Concentrations in both intertidal and subtidal sediments can rise above sediment quality guidelines and triggers. For most smaller discharge points haloes of metal concentrations are generally restricted to 10-20 m. In the wider urban and estuary and harbour context it is evident that sediments often contain elevated concentrations of metals and organic contaminants. In locations such as the Waitemata Harbour it is evident that all of the surface sediments in the Harbour are contaminated to some degree. In depositional environments the concentration of elements such as Cu can 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 estuarine 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. This ratio has not been clearly quantified to-date.

7.4.4 Toxicity

Hickey et al. (1997) carried out tests of the toxicity of suspended sediment (from the treatment ponds at UNITEC in Auckland) on the amphipod (*Chaetocorophium lucasi*) and juvenile bivalve (*Macomona liliiana*). The amphipod test was a 10 day acute mortality test and the bivalve test was a 10 day acute mortality test and 28 day chronic survival and growth test. In the tests, suspended sediment was mixed with clean sediment to simulate mixing with uncontaminated sediments. A number of the toxicity tests resulted in low acute survival for amphipods and juvenile shellfish. Another series of tests, resulted in no acute effects. An assessment of the dose response relationship suggested that an EC₅₀ response was obtained at a level of 70% stormwater solids. A threshold response was identified at 10% (EC₁₀) stormwater particulates. The stormwater solids used in the test exceeded the ER-L guideline for most transport related contaminants with Zn (and also dieldrin which is not transport related) exceeding the ER-M. Hickey et al. (1997) suggested that a dilution of 10 times was required to ensure that the elevated concentrations of contaminants in stormwater particulates did not have toxic effects when entering the environment.

One of the difficulties in attributing toxicity to different constituents is that sediment toxicity in muddy sediments can be dominated, by ammonia and sulphides (Stronkhorst et al. 2003; Lahr et al. 2003). TIEs carried out by Stronkhorst et al. (2003) using a number of marine bioassays showed that the predominant toxicity in the sediments they examined using the sea urchin tests and amphipod tests were due to ammonia and in the bacterium test by sulphide. In two of three tests a small reduction in toxicity was observed when persistent organic compounds or metals were removed. The authors were able to isolate a toxic effect from organic compounds even with the toxicity due to ammonia.

Assessment of sediment biology and toxicity by Nipper et al. (1995) and others has resulted in variable results. Although there were clear biological differences, no clear differences between the estuaries studied in relation to toxicity were noted. Morrissey (1999) also noted that sediment transplant experiments indicated that sediment quality did not appear to be the key factor in controlling the quality of infauna. Overall, no clear-cut patterns could be identified that would indicate a specific effect of stormwater at an individual organism level and hence the effects of the road transport stormwater component of urban runoff.

Toxicity testing of stormwater sediments has shown that adverse effects can be obtained in tests. This would suggest that toxicity may occur adjacent to outfalls where deposited sediment may accumulate. 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.

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, are a causal agent in toxicity or changes in benthic biological community composition (refer below).

7.5 Biological Resources

7.5.1 Resources

New Zealand has a diverse coastal ecosystem (refer Morton & Miller 1968) and within this section it is not possible to provide comment on all the different ecological resources found within New Zealand's marine ecological regions. Comment on particular ecosystems is however provided in relation to particular stormwater discharge issues. In this section, the focus of assessment is on the invertebrate biota inhabiting soft shore intertidal and sub-tidal areas of estuaries and nearshore areas. Hard shores are not described and fisheries are not dealt with in this report in relation to ecosystem well-being.

A large amount of detailed research has been carried out in relation to the effects of urban stormwater discharge on the marine biological communities of Auckland estuaries. This work, although providing a great deal of information on the overall effects of urban development on the quality of biological communities, has produced a number of unexpected results.

7.5.2 Tools

The biological resources of intertidal and subtidal benthic environments can be sampled using a variety of semi-quantitative and quantitative techniques (refer Ray 2002). The method of sampling depends upon the nature of the substrate (rocky or soft), environment (intertidal or subtidal) and water depth (hand, diver or grab sampling) and may involve quadrats, cores, dredge or grab samples. In addition, photographic techniques may also be used in particular situations. A wide variety of metrics can be calculated as part of any biological sampling or monitoring programme and may include:

- ❑ Species diversity (i.e., species present).
- ❑ Species abundance.
- ❑ Size (e.g., for molluscs).
- ❑ Condition (especially in relation to edible seafoods).
- ❑ Organism health.

There are however, no established standardised procedures for the collection of information. For metrics such as species diversity a variety of diversity descriptors are used (e.g., Margalef, Shannon-Weiner Index etc. refer Ray 2002).

7.5.3 Effects

Two scales of effects need to be considered in relation to the health of benthic communities adjacent to stormwater discharge points. The first is in the immediate vicinity of the discharge and the second is in the environment downstream of the discharge (i.e., within the main body of an estuary or in the coastal zone in general). A number of studies around New Zealand have included investigations into locations that have been potentially impacted by runoff from road transport. A range of work, has been carried out by the ARC in relation to the effects of urban runoff on the ecosystems. The assessment of environmental effects of urban stormwater runoff (Snelder & Trueman 1995), identified the key factors affecting the ecological health of marine environments in the Auckland area as sedimentation, nutrient enrichment in small lakes and confined water bodies, increases in contaminant concentrations and bioaccumulation (discussed in a following section). The summary provided in Snelder & Trueman (1995) is based upon Vant et al. (1993), Roper et al. (1994) and Snelder (1995). The effects assessment reported in Snelder (1995) and others did not include any specific ecological investigation. Observations reported in Roper et al. (1994) were that the Upper Waitemata Harbour had changed little (ecologically) in the 10 years up to 1994. The most significant changes related to the distribution of Pacific oysters and Asian date mussel. Predictions of contaminant accumulation in sediments on biota, as discussed by the authors is discussed further in Section 7.6 below.

Given the ranges of concentration of contaminants present, it is likely that adverse effects would be expected in areas immediately adjacent to discharge points. Examination of such environments by Bolton-Ritchie et al. (1999) suggested that sediment quality or sediment conditions adjacent to stormwater outfalls in Wellington Harbour, were such that sediment toxicity resulted in a depauperate biological community inhabiting the sediments close to the discharge point. However, the causal factors resulting in the changes seen in the biological community have not been identified and toxicity could potentially be the result of high concentrations of ammonia and or sulphide.

Botherway & Gardner (2002) examined the ecology of sediments adjacent to a stormwater drain discharging into Porirua Inlet. The study found that mean numbers of individuals decreased, mean

number of taxa and the Shannon-Weiner diversity index increased with increasing distance from the discharge point. Examination of temporal changes indicated that the biological communities at distances from the outfall were all variable with trends being seen at certain times of the year (refer Fig. 7.4). The authors could not identify indicator taxa that assisted in explaining any differences in community structure close to the discharge compared to those found outside the immediate receiving environment.

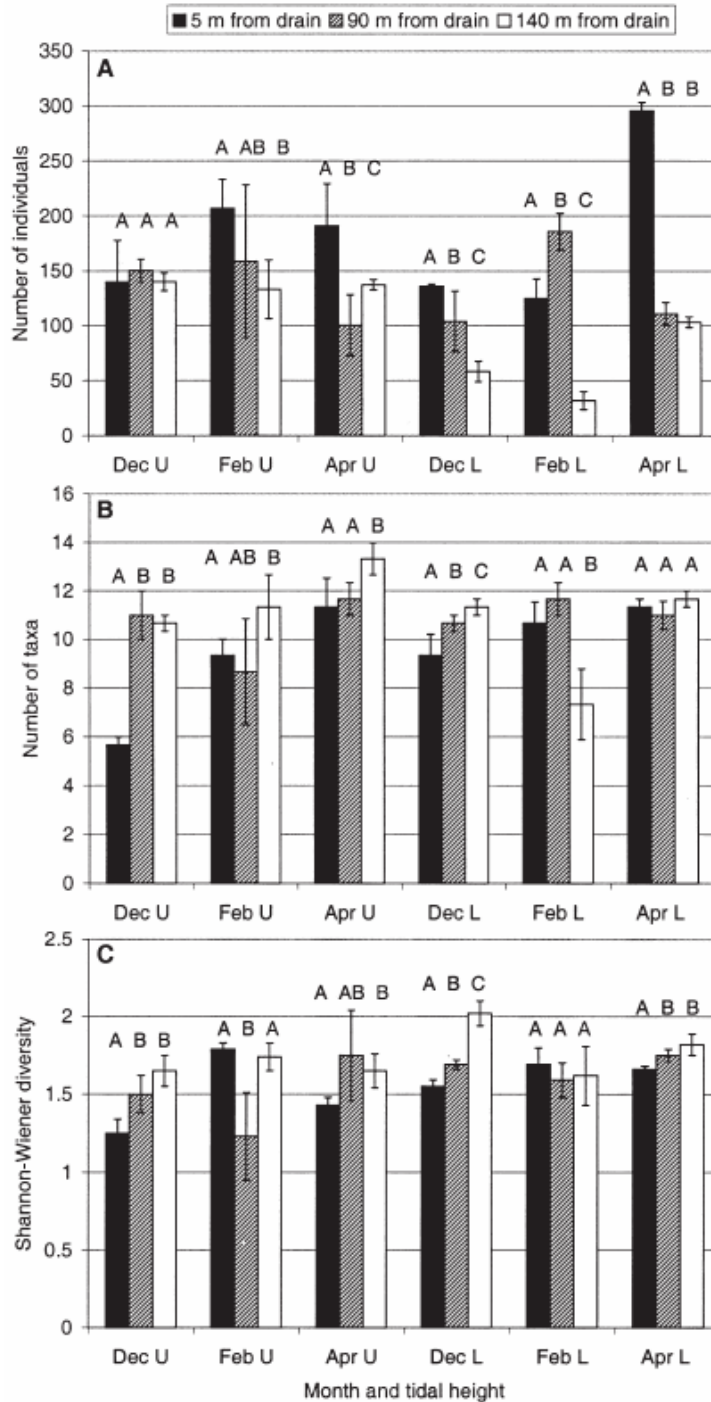


Figure 7.4 - Benthic infaunal indices at sites adjacent to a stormwater drain in Porirua Inlet, Wellington (Taken from Bothway & Gardner 2002).

A review of sediment quality and biological community composition adjacent to stormwater discharge points around Auckland City (Pridmore et al. 2000) indicated that the greatest impacts of stormwater discharges was likely to be in depositional environments (low energy environments). In high energy environments, concentrations of Zn, Cu and Pb were essentially background. In the low energy environments higher concentrations of the three key elements were identified. Examination of the biota at the sites surveyed by Pridmore et al. (2000) indicated that there were faunal assemblage differences between the sites most impacted by sediment metal concentrations (Newmarket and Tohunga) compared to other sites (Fig. 7.5).

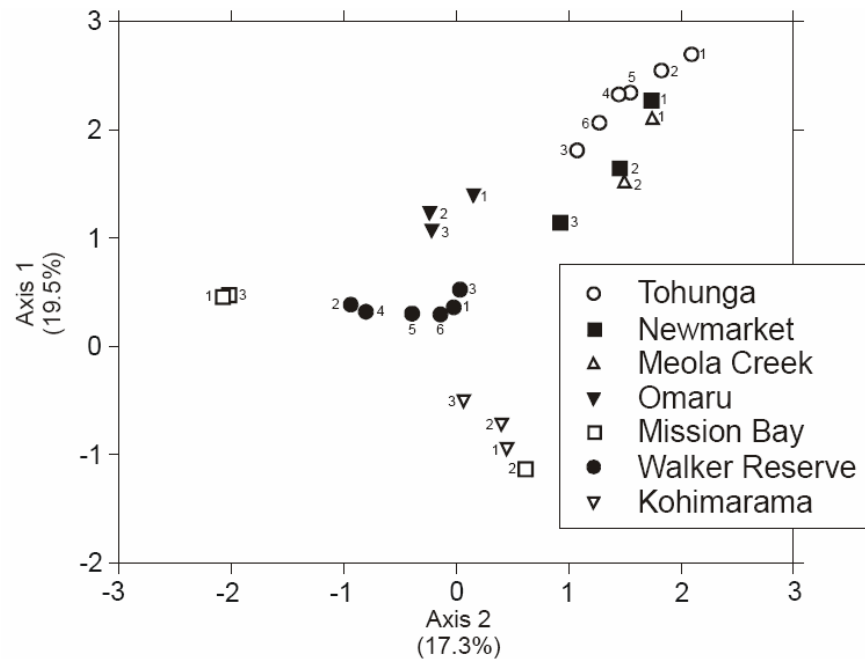


Figure 7.5 - Graphical presentation of results from canonical correspondence analysis conducted on benthic biota from adjacent to stormwater discharge points in Auckland City (Taken from Pridmore et al. 2000).

Roper et al. (1988) examined the concentration of contaminants in sediments of Mangere Inlet in relation to the distribution of invertebrates. The concentrations present were ascribed to surrounding catchment activities but no specific effect of road transport emissions are identified. Invertebrate species abundance and diversity in sediments was found to vary little within sites but significant, between-sites variation was found. Multivariate analysis of biological data indicated correlations with a number of variables including some contaminants. The authors noted the difficulty in detecting runoff effects at the community level in benthic systems.

Morrissey (1999) reviewed the biological effects associated with the build-up of contaminants in estuaries. Based upon earlier and on-going research, Morrissey (1999) concluded that contaminants in urban runoff (including road and highway stormwater) may accumulate at concentrations that, based upon sediment quality guidelines have the potential to have adverse ecological effects. The work carried out by Morrissey (1999) and others has utilised a variety of tools to assess the potential for accumulation of contaminants to produce adverse biological effects. These tools include:

1. Comparing field data to sediment quality guidelines (refer Section 6).
2. Carrying out sediment toxicity tests (e.g., using marine organisms).
3. Carrying out field experiments.

The examination of biological communities in the estuaries of the Manukau Harbour has shown that there appears to be a relationship between the diversity of the community present and the degree of sediment

contamination. However, the assessment dealt with the effects of general urban runoff and did not specifically look at the effect of road or highway runoff.

As part of the ARC programme to investigate the effects of decreasing sediment quality in low energy environments, Anderson et al. (2002) reported on the development of criteria for assessing the health of benthic faunal communities in soft-shore intertidal environments. Following the development of this community health index ARC have been evaluating further the relationship between benthic health and sediment quality through an ongoing benthic environmental quality monitoring program (Kingett Mitchell 2003a,b). This continued evaluation is currently being prepared as an ARC report (Dr Shane Kelly ARC pers comm.).

Overseas, Schiff & Bay (2003) examined the impacts of stormwater discharges on the benthic environment in Santa Monica Bay. Examination of sediments off Ballona Creek indicated increased concentrations of metals up to 2 km and 4 km along-shore in either direction from the Creek. The authors utilised the benthic response index (BRI) (Bergen et al. 2002) to evaluate community composition change. Although the authors identified changes in general physical characteristics of sediments, OM and metal concentrations, they did not observe significant changes in the composition of the benthic community. The authors did not think it was possible that the sampling locations may not have been appropriately positioned in relation to the stormwater plume footprint.

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 effects observed. The proportion of that effect attributable to vehicles 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 necessarily 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.

7.6 Bioaccumulation

7.6.1 Plants

Salt marsh and mangrove are important coastal biological communities in the coastal environment and play an important role in the production of detritus. Salt marsh and mangroves close to roadways are exposed to vehicle exhaust emissions. As described in section 6 of this report, accumulation of trace element contaminants by terrestrial plants (e.g., grass, sweet corn) has been reported in New Zealand. As accumulation occurs through both root uptake and probably through airborne stomatal intake, some uptake by plants growing in intertidal areas would be expected.

Kennedy (unpublished) examined trace element composition of *Juncus* in saltmarsh around Pauatahanui Inlet adjacent to a road carrying relatively low vehicle traffic. The study indicated elevated concentrations of Cu in live and dead tillers and rhizomes, Zn in live tillers and rhizomes and Pb in dead tillers. The elevation occurred close to the roadway.

Samples of mangrove leaves and propagules taken adjacent to the North-western motorway (Pollen Island Marine Reserve) in Auckland (Kennedy unpublished), did not show any significant trends in samples collected at 10, 30, 90 and 120 m from the edge of the motorway. A minor difference was found in the Pb concentration of unwashed and washed leaves (30 % close to motorway and 5% at 120 m). As with the Pauatahanui Inlet *Juncus* samples, a small increase in Pb concentration was found in live and dead tillers close to the motorway (20 m) compared with samples collected 35 - 100 m away.

7.6.2 Invertebrates

Few studies have been carried out in New Zealand that specifically examine the effects of road transport contaminants (stormwater runoff and aerial deposition) on marine organisms. Bioaccumulation in marine organisms is very organism-specific as are the mechanisms involved in the bioaccumulation process. Bioaccumulation would be expected in situations where marine organisms are exposed to stormwater directly and to contaminated sediments. Although no specific published data is available in relation to bioaccumulation in marine invertebrates directly associated with stormwater discharges the following comments can be made.

ARC has assessed uptake of metals and organic contaminants in sentinel organisms such as oysters and mussels and found that there are increased burdens of some metals and organic compounds in urbanised estuaries. Road runoff may contribute part of that burden however the proportion has not been ascertained.

Mussels growing adjacent to stormwater discharge points or alongside urban shorelines have been found to accumulate elevated concentrations of lead (Kennedy unpublished). Table 7.1 provides a general summary to show the range in Pb concentration encountered in two species of mussel. The immediate effects of Pb in stormwater and atmospheric deposition very close to the Wellington commercial centre can be seen and the moderately elevated concentrations at Somes Island in the middle of Wellington Harbour several kms from the city samples. Some examples of comparative New Zealand rural (Taranaki) samples and also remote (subantarctic islands) concentrations are also shown. It should be noted that the wet/dry ration for mussels is typically about 5 resulting in the upper concentrations being in the order of 20 mg/kg on a wet wt basis. New Zealand has a limit of 2 mg/kg (wet wt) for Pb in food-stuffs indicating that these mussels would not have been suitable for human consumption based solely on their Pb content. The uptake of Cu and Zn was shown to be variable and not related to Pb uptake.

Table 7.1 - Trace elements in mussels in Wellington Harbour (pre-lead removal from petrol) (all data mg/kg dry wt, Kennedy unpublished).

Location	Green lipped mussel (<i>Perna canaliculus</i>)	Blue mussels (<i>Mytilus edulis</i>)
Wellington City	13.5 (Freyberg Wharf)	106.4
Kaiwarahara	8.8	24.1
Somes Island	4.2	6.9
Remote	0.4 (Taranaki)	<0.1 (Auckland Islands)

Common intertidal organisms such as the New Zealand mud flat snail (*Amphibola crenata*) have been shown to accumulate metals such as lead from sediment (e.g., van Roon 2000). As such it would be expected that mud flat snails would accumulate Pb where vehicle associated deposition of metals was occurring (from exhaust emissions and from stormwater). As an example, examination of mud flat snails in salt marsh adjacent to roads around Pauatahanui Inlet near Wellington revealed higher Pb concentrations compared to other sites. The concentration of 16 mg/kg (dry wt) would be at or just above the food limit in New Zealand on a wet weight basis.

Table 7.2 - Trace elements in mud flat snails adjacent to roadsides around Pauatahanui Inlet (all data mg/kg dry wt, Kennedy unpublished).

Element	Pauatahanui Inlet roadside	Pauatahanui Inlet roadside	Pauatahanui Inlet away from roadside	Waikanae estuary
Cu	128	162	99	84
Pb	16	13	3	<1
Zn	55	107	53	58

Given the propensity of mud flat snail to accumulate Pb (on about a 1:1 basis over a range up to 1,000 mg/kg dry wt), the maximum concentration of Pb expected in snails that were feeding off sediments impacted by sediments containing a high proportion of stormwater sediments would be equivalent to the sediment Pb concentration. In Section 3.2.3, it was identified that currently particulates on road surfaces in Waitakere City (as an example) contain on average 276 mg/kg Pb in the <0.063 mm sediment fraction. This would result potentially in a Pb concentration in mud flat snails of about 11 mg/kg (on a wet wt basis) in sediments containing 20% stormwater particulates. As such they would not be fit for consumption.

Based upon data discussed earlier, identifiable and significant uptake is only likely to occur in areas close to roads and highways. Based upon the limits set in relation to the quality of foods such as intertidal hard shore filter feeding shellfish, there is little likelihood of stormwater resulting in the accumulation of metals such that they become unfit for human consumption. It is likely that in some locations the Pb still present on roads would result in increased concentrations of Pb in sediment grazing molluscs such as mud flat snails.

7.6.3 Fish

There has been no specific assessment of bioaccumulation of motor vehicle derived contaminants in marine fish in New Zealand. In section 6, the uptake by freshwater fish in locations such as stormwater ponds was noted. As described in Moncrieff & Kennedy (2002), there are a very large range of organic compounds released from motor vehicle emissions. Assessment of BCFs for these compounds (Kennedy & Gadd 2000) indicates that there are a number with the potential for uptake in fish present in estuaries and coastal areas. These are identified in Appendix B of Moncrieff & Kennedy (2002) as those with identifiable partitioning to aquatic biota (through the use of fugacity modelling). These compounds are emitted from all key sources (tyres and brake pad wear, exhaust emissions). However, there is no evidence that any compound emitted from motor vehicles is taken up by fish and accumulated in muscle tissue to the extent that the fish becomes unsuitable for human consumption. Further work on the presence of specific organic compounds in estuarine fish species is required to elucidate the fate of particular groups of organic compounds released by motor vehicles to the estuarine and coastal environment in New Zealand.

Overall, the assessment of the bioaccumulation in marine organisms provides a tool to assess the flux of road transport associated contaminants into marine organisms. Marine organisms have a wide range of 'techniques' for dealing with exposure to metals and organic contaminants. To-date, no specific contaminants have been identified that are unique to road transport that would allow the specific effects of road transport to be isolated in urban areas. Information on the uptake of metals derived from vehicles indicates that many organisms do not accumulate Cu and Zn proportionally to the concentration in the environment and some species (e.g., the mud-flat snail are able to regulate their Cu body burden). Elements such as Pb are able to be accumulated as they do not have any known physiological function. Historical data indicates that prior to the removal of Pb from petrol in New Zealand that the concentration of Pb in filter feeding shellfish and sediment grazing molluscs would have been elevated in some locations such that they would not be fit for human consumption. With Pb removed from petrol it is unlikely that filter feeding shellfish would contain high enough concentrations of Pb such that they would be unfit for consumption. It is possible that in some inter-tidal locations the concentrations in sediment

grazers such as mud flat snails would result in them accumulating sufficient Pb that they should not be consumed.

7.7 Summary

Stormwater discharges from roads and urban catchments typically discharge particulate material that settles adjacent to the stormwater outfall. The presence and extent of the distribution of that material is dependent upon the hydrodynamics of the environment at the point of discharge. If the physical environment is depositional in nature then material may accumulate adjacent to the outfall. 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.

The discharge of urban and roadway stormwater has the potential to cause changes in the quality of the sediment environment immediately adjacent to the point of discharge. The extent of the area is dependent upon the size of the discharge and the nature of the discharge environment (e.g., estuary or open coast). The '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 intertidal and subtidal sediments can rise above sediment quality guidelines and triggers. For most smaller discharge points haloes of metal concentrations are generally restricted to 10-20 m.

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 it appears that all of the surface sediments in harbour are contaminated to some degree. In depositional environments 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 no water column toxicity after discharge. It was noted in that a study that toxicity was lower than expected. Contaminants other than metals were suggested as having a strong involvement in toxicity.

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, discharge volumes from open coastal stormwater outfalls are typically small.

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.

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).

No specific 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 Cu and Zn are not bioaccumulated by many marine organisms. Some shellfish (e.g., oysters) will accumulate Zn. At this point in time there is no information that indicates that road transport contributes to the uptake of contaminants by marine organisms such that they are rendered unsuitable for human consumption.

8. OVERVIEW

8.1 Vehicles as sources of contaminants

Motor vehicles are relatively complex emissions sources. Firstly they comprise multiple sources with their own contaminant signatures (tyres; brake pad wear; exhaust emissions; oil, grease and collant losses etc.). Secondly for many of the sources there is considerable variability in the nature of the contaminants emitted and the amount emitted as there are a large number of different manufacturers involved in the production of motor vehicles and their parts. For some emission sources there are hundreds of different types of a particular component many of which have different contaminant signatures. This results in potential for considerable variation between countries and over time in contaminant emissions from some sources

For inorganic contaminants (e.g., the trace elements including the heavy metals), there is a reasonable understanding of what elements are present in the sources and in emissions. There is a degree of uncertainty in relation to the variability of some elements that are key constituents of some sources (e.g., Cu in brake pads). This uncertainty arises because of the variation in brake pad specifications between manufacturers. There is less information on the variability in the concentration of some elements for whose presence in emission sources has only relatively recently been confirmed.

For organic compounds there is a less clear picture as to what is emitted from the various emission sources. For exhaust emissions, there is a large body of published research data that examines the differences between petrol and diesel emissions. The published data provide a good picture of the nature of VOCs in exhaust emissions. There is also good data for some groups of compounds such as the PAHs and their derivatives and also the dioxins and furans. However there are a range of other compounds for which there appears to be less information available. For the solid sources such as tyres and brake pads the amount of information is significantly less. There have been a number of studies that have produced very useful data for the characterisation of these sources. There is considerable variation in the composition of sources such as brake pads leading to uncertainty as to the nature of compounds present (e.g., the occurrence of phthalates in brake pads).

8.2 The road environment

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 is due to elevated concentrations in tyres and 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).

The particulate matter on road surfaces in New Zealand also contain elevated concentrations of the elements Cd, Cr, Mo, Ni, and Sb. These are sources 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.

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. 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. There are still substantial uncertainties associated with these estimates and they will need continued refinement as new data becomes available.

8.3 Stormwater runoff

There is now a moderate body of data on trace metal concentrations in urban and roadway runoff in New Zealand. 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. Further sampling and assessment of the lead concentration in motorway runoff data should be carried out as lead has been removed from New Zealand petrol.

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.

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. 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.

Most road surfaces are constructed using bitumen. A contribution to some metal concentrations is likely from bitumen. Analysis of PAH in New Zealand bitumen has shown that the PAH concentrations is typically low. Little data appears available on the hydrocarbon losses from newly constructed bitumen roads.

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.

8.4 Pathways and fate

There are two key pathways for road transport-derived material and contaminants. The first is atmospheric dispersion with consequent wet and dry deposition. The second is 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. 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).

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).

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.

SVOCs such as PAHs will be subject to degradation and other processes (such as biological uptake) which will in the long term result in their loss from the receiving environment. Changes in the receiving environment will be dependent upon the balance achieved between their inward flux and their loss.

Recalcitrant organic compounds such as MTBE will accumulate with the actual concentration depending upon the inward flux to the receiving water and their slow loss (e.g., by bio-degradation).

VOCs present in motor vehicle 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 significant concentrations of VOCs are present in detectable concentrations of stormwater. As noted earlier, this is however very dependent upon the limits of detection used in the analysis of stormwater for VOCs.

Catchpits play a role in the biogeochemical conversions that street surface particulate material are exposed to. Material trapped in catchpit sumps can be exposed to anaerobic conditions for days between storms. The exposure to anaerobic conditions results in conversion of DIN to ammoniacal nitrogen, release of some metals to dissolved phase. The flushing of catchpit contents during storms results in a pulse of water with different chemical composition entering the downstream stormwater system and entering the receiving environment. The key implication of changes in chemistry from the road to the receiving environment is any potential to transform solid phase non-toxic contaminant phases into dissolved potentially toxic forms.

8.5 Freshwater environments

In New Zealand there are few specific studies that have assessed the effect 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).

First flush stormwater runoff from roads exposes organisms to very high concentrations of contaminants. A range of toxicity studies have been undertaken using urban stormwater discharging to freshwater environments. Tests undertaken 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 has chronic effects on growth of freshwater algae (in toxicity tests).

Toxicity tests have undertaken using a range of freshwater organisms and 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 observation reflects data for the concentration of key constituents in first flush stormwater 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

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 severe 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.

Build-up of sediment discharged from roadways will occur close to the point of discharge (in ponds, wetlands, streams and lakes) if the discharge point does not have sufficient energy to transport the contaminants and sediment away. Based upon the composition of the suspended sediment and measurement of urban stream sediment quality, it is likely that concentrations of contaminants can build-up to concentrations that could have an adverse effect on freshwater benthic organisms.

It is difficult within urban areas to isolate the effects of road transport (via stormwater) to be identified separately from other urban activities. In remote or rural environments, the tools utilised to assess the condition of the biological community can be applied to assess the effects of road transport. In certain situations an upstream-downstream assessment (of a discharge) may provide sufficient information to assess effects. Given the concentration of Cu, Pb and Zn in the suspended sediments of stormwater draining roads, exceedence of sediment quality guidelines 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.

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. Information shows 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 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.

There is little information that indicates that any freshwater 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).

8.6 Marine environments

Stormwater discharges from roads and urban catchments typically discharge particulate material that settles adjacent to the stormwater outfall. The presence and extent of the distribution of that material is dependent upon the hydrodynamics of the environment at the point of discharge. If the physical environment is depositional in nature then material may accumulate adjacent to the outfall. 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.

The discharge of urban and roadway stormwater has the potential to cause changes in the quality of the sediment environment immediately adjacent to the point of discharge. The extent of the area is dependent upon the size of the discharge and the nature of the discharge environment (e.g., estuary or open coast). The '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 intertidal and subtidal

sediments can rise above sediment quality guidelines and triggers. For most smaller discharge points haloes of metal concentrations are generally restricted to 10-20 m.

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 it appears that all of the surface sediments in harbour are contaminated to some degree. In depositional environments 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.

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. 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.

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.

The assessment of bioaccumulation in marine organisms provides a tool to assess the flux of road transport associated contaminants. 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 Cu and Zn are not typically bioaccumulated by many marine organisms. Some shellfish (e.g., oysters) will accumulate Zn. 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.

9. REFERENCES

- Anderson, M.; Hewitt, J.; Thrush, S. 2002: The development of criteria for assessing community health of urban intertidal flats. Report prepared by NIWA for Auckland Regional Council. NIWA Client report HAM2002-048. October 2002.
- ANZECC 1992: Australian and New Zealand water quality guidelines for fresh and marine waters. Australian and New Zealand Environment and Conservation Council Report.
- ANZECC 2000: Australian and New Zealand guidelines for fresh and marine water quality 2000. Australian and New Zealand Environment and Conservation Council.
- API 1985a: Vanadium: Environmental and community health impact. Report prepared by EA Engineering, Science and Technology Inc for American Petroleum Institute, Washington.
- API 1985b: Cadmium: Environmental and community health impact. Report prepared by EA Engineering, Science and Technology Inc for American Petroleum Institute, Washington.
- ARC, 1992: An Assessment of stormwater quality and the implications for the treatment of stormwater in the Auckland Region. Report prepared by Kingett Mitchell & Associates Limited. Environmental Planning Division Technical Publication No. 5. April 1992. Auckland Regional Council.
- ARC, 1994: Urban stormwater quality, Pakuranga, Auckland 1994. Environmental Planning Division Technical Publication No. 49. Auckland Regional Council.
- ARC, 1998: Auckland region urban stormwater management project - strategy statement. Report prepared by the Territorial Authorities – Auckland Regional Council Stormwater Liaison Group. July 1998.
- ARC, 2000: Fish passage guidelines for the Auckland region. Auckland Regional Council Technical Publication 131. June 2000.
- ARWB: 1988: Assessment of urban and industrial stormwater inflows to the Manukau Harbour. Prepared by Kingett Mitchell & associates Ltd. ARWB Technical Publication No 75.
- Baekken, T. 1993: Environmental effects of asphalt and tyre wear by road traffic. Nordisk Seminar-og Arbejdsrapporter 1993/628, Copenhagen, Denmark 1993 (In Norwegian) (cited in Lindgren 1996)
- Ball, J. E.; Jenks, R.; Aubourg, D. 1998: An assessment of the availability of pollutant constituents on road surfaces. *The science of the total environment* 209: 243-254.
- Banerjee, A. D. K. 2003: heavy metal levels and solid phase speciation in street dusts of Delhi India. *Environmental pollution* 123: 95-105.
- Barbante, C.; Veysseyre, A.; Ferrari, C.; Van de Velde, K.; Morel, C.; Capodaglio, G.; cescon, P.; Scarponi, G.; Boutron, C. 2001: Greenland snow evidence of large scale atmospheric contamination for platinum, palladium, and rhodium. *Environmental science and technology* 35: 835-839.
- Barefoot, R. R. 1997: Determination of platinum at trace levels in environmental and biological materials. *Environmental Science and Technology*, Vol. 31, No. 2, 1997.
- Barefoot, R. R. 1999: Distribution and speciation of platinum group elements in environmental matrices. *Trends in Analytical Chemistry*, Vol. 18, No. 11, 1999.
- Barrett, M. E.; Zuber, R. D.; Collins, E. R.; Malina, J. F.; Charbeneau, P. E.; Ward, G. H. 1995a: A review and evaluation of literature pertaining to the quantity and control of pollution from highway runoff and

construction. Center for Research in Water Resources, University of Texas at Austin, CRWR Online Report 95-5. April 1995.

Barrett, M. E.; Malina, J. F.; Charbeneau, P. E.; Ward, G. H. 1995b: Effects of highway construction and operation on water quality and quantity in an ephemeral stream in the Austin, Texas area. Center for Research in Water Resources, University of Texas at Austin, Report CRWR 262. September 1995.

Barrett, M. E.; Malina, J. F.; Charbeneau, P. E.; Ward, G. H. 1995c: Characterisation of highway runoff in the Austin, Texas area. Center for Research in Water Resources, University of Texas at Austin, Report CRWR 263. October 1995.

Bascombe, A. 1988: Urban Pollution Research Report 11: Biological monitoring of benthic invertebrates for the assessment of heavy metal pollution in urban rivers. Report prepared by the Urban Pollution centre, Middlesex Polytechnic, Queensway Middlesex.

Bascombe, et al. 1988: The role of invertebrate monitoring for water quality management within urban catchments. In, Hooghart, J. C. Ed. Hydrological processes and water management in urban areas. IHP/UNESCO, the Netherlands.

Batley, G. E.; Brockbank, C. I.; Hogan, P.; Ball, J. E. 1994: The chemical composition of stormwater runoff from roads. CSIRO Division of Coal and Energy Technology, Centre for Advanced Analytical Chemistry. Investigation Report CET/IR263. Prepared for the Roads and Traffic Authority of New South Wales, May 1994.

Batley, G. E.; Brockbank, C. I.; Hogan, P.; Ball, J. E. 1994: The chemical composition of stormwater runoff from roads. Prepared for the Roads and Traffic Authority of NSW, May 1994. CSIRO Division of Coal and Energy Technology, Centre for Advanced Analytical Chemistry. Investigation report CET/IR263.

Bay, S.; Jones, B. H.; Schiff, K.; Washburn, L. 2003: Water quality impacts of stormwater discharges to Santa Monica Bay. *Marine environmental research* 56: 205-223.

Bellinger, E. G.; Jones, A. D.; Tinker, J. 1982: The character and dispersal of motorway runoff water. *Water pollution control*, 81(3): 372-390.

Berbee, R. P. M.; Rijs, G. B. J.; Brouwer, M. W. 1996: Treatment of runoff from highways. Rep. 96.017 (Dutch), Institute Inland Water Management Waste Water Treatment, Lelystad, Neth (In Berbee et al. 1999).

Berbee, R.; Rijs, G.; de Brouwer, R.; van Velzen, L. 1999: Characterisation and treatment of runoff from highways in the Netherlands paved with impervious and pervious asphalt. *Water environment research* 71: 183-190.

Bergen, M.; Weisberg, S.; Smith, R.; Cadien, D.; Dalkey, A.; Montagne, D.; Stull, J.; Velarde, R.; & Ranasinghe, J. A. 2001: Relationship between depth, sediment, latitude, and the structure of benthic infaunal assemblages on the mainland shelf of southern California. *Marine biology*, 138: 637-647.

Bertrand, J. L.; Chebbo, G.; Saget, A. 1998: Distribution of pollutant mass vs volume in stormwater discharges and the first flush phenomenon. *Water Research* 1998: 32:2341-2356.

Biggs, B. J. F. 2000: New Zealand periphyton guidelines: Detecting, monitoring and managing enrichment of streams. Ministry for the Environment, Wellington. June 2000.

Bingham, A. G.; Edmunds, C. J.; Graham, B. W. C.; Jones, M. T.; Young, H. 1990: PCDD and PCDF emissions in car exhaust and their impact on the environment. Chemistry Division Report No. CD 9397. DSIR.

Bolton-Ritchie, L.; Chague-Goff, C.; Gardner, C.; Goff, J. 1999: A preliminary investigation into the effects of point source stormwater discharge on the marine benthic environment of inner Wellington Harbour. Poster in comprehensive stormwater and aquatic ecosystem management. First South Pacific Conference. 22-26 February 1999. Auckland.

Bolton-Ritchie, L.; Chague-Goff, C.; Gardner, J. P. A.; Goff, J. 1999: Wellington's storm drain sediments-spreading it around. Proceedings of the New Zealand Water and Wastes Conference, Christchurch, 22–24 September 1999. pp. 137–144.

Boothroyd, I.; Stark, J. 2000: Use of invertebrates in monitoring. In Collier, K. J. & Winterbourn, M. J. Eds. New Zealand stream invertebrates: Ecology and implications for management. New Zealand Limnological Society. Caxton Press, Christchurch. pp 344-373.

Botherway, K. J.; Gardner, J. P. A. 2002: Effect of storm drain discharge on the soft shore ecology of Porirua Inlet, New Zealand. New Zealand journal of marine and freshwater research 36: 241-255.

Boxall, A. B. A.; Maltby, L. 1995: The characterisation and toxicity of sediment contaminated with road runoff. Water research 29 (9): 2043-2050.

Brandt, H. C. A.; De Groot, O. C. 2001: Aqueous leaching of polycyclic aromatic hydrocarbons from bitumen and asphalt. Water Research, Vol. 35, No. 17, pp. 4200-4207, 2001.

Brent, R. N.; Herricks, E. E. 1999: A method for the toxicity assessment of wet weather events. Water research 33 (10): 2255-2264.

Brockbank, C. I.; Batley, G. E. 1996: Road runoff and its impact on the aquatic environment – Literature review update. CSIRO Division of Energy Technology, Centre for Advanced Analytical Chemistry Investigation Report CET/LH/IR522. Prepared for the Roads and Traffic Authority of New South Wales, December 1996.

Brockbank, C. I.; Batley, G. E.; Ball, J. E.; Tilley, J. H. 1999: Metals and hydrocarbons in stormwater runoff from urban roads. CSIRO Division of Energy Technology, Centre for Advanced Analytical Chemistry Investigation Report ET/IR98R. Prepared for the Roads and Traffic Authority of New South Wales, January 1999.

Brookes, A. 1988: Channelised Rivers: Perspectives for Environmental Management. John Wiley & Sons, New York.

Brown, J. N.; Peake, B. M. 2001: Chemical Contamination of New Zealand Urban Stormwater: Levels, Partitioning and Implications for Treatment. In Proceedings of the CWRA BC Branch 2001 Conference – Changing Water Environments: Research and Practice, Whistler, B.C., Canada, 8-11 May, 2001.

Brown, J.; Peake, B.; Robinson, D; Schmid, O. 2003: Partitioning of chemical contaminants in urban stormwater. Third South Pacific Stormwater Conference, Auckland, May 2003.

Buckland, S. J.; Jones, P. D.; Ellis, H. K. 1998. Organochlorines in New Zealand: ambient concentrations of selected organochlorines in rivers. Wellington, New Zealand Ministry for the environment.

Burton, G. A.; Pitt, R. E. 2002: Stormwater effects handbook. A toolbox for watershed managers, Scientists, and engineers. Lewis Publishers. Boca Raton.

Campbell, K. R. 1994: Concentrations of heavy metals associated with urban runoff in fish living in stormwater treatment ponds. Archives of environmental. Contamination and toxicology. 27: 352-356.

Cannon, H. L.; Bowles, J. M. 1962: Contamination of vegetation by tetraethyl lead. Science 137: 765-766.

Carey, J.; Cook, P.; Ciesy, J.; Hodson, P.; Muir, D.; Owens, J. W.; Solomon, K. 1998: Ecotoxicological risk assessment of the chlorinated organic chemicals. Proceedings from the Pellston Workshop on environmental risk assessment for organochlorine compounds 24-29 July 1994. Aliston, Ontario, Canada. SETAC Special Publication Series.

CCME 1999: Canadian water quality guidelines for the protection of aquatic life. In Canadian environmental quality guidelines, 1999. Canadian Council of Ministers of the Environment, Winnipeg.

Chamberlain, A. C. 1983: Fallout of lead and uptake by crops. *Atmospheric environment* 17(4): 693-706.

Collier, K. J.; Cooper, A. B.; Davies-Colley, R. J.; Rutherford, J. C.; Smith, C. M.; Williamson, R. B; 1995: Managing Riparian Zones. Department of Conservation, Wellington.

Collier, K. J.; Winterbourn, M. J. 2000: New Zealand stream invertebrates: Ecology and implications for management. New Zealand Limnological Society, Hamilton, New Zealand.

Collins, J. A. 1984: Roadside lead in New Zealand and its significance for human and animal health. *New Zealand journal of science* 27: 93-99.

Cooke, T. D.; Lee, C. C. 1995: Toxicity identification evaluations (TIE) in San Francisco Bay area urban storm water runoff. Presented at 16th annual meeting of the Society of environmental toxicology and chemistry (SETAC), Vancouver, British Columbia.

Cox, J. H.; Livingstone, E. H. 1997: Stormwater sediments: hazardous waste or dirty dirt: an update. Fifth biennial stormwater research conference, November 5-7, 1997.

Cretney, J. R.; Lee, K. L.; Wright, G. J.; Swallow, W. H.; Taylor, M. C. 1985: Analysis of polycyclic aromatic hydrocarbons in air particulate matter from a lightly industrialised area. *Environmental science and technology* 19 (5): 397-404.

Crunkilton, R.; Kleist, J.; Bierman, D.; Ramcheck, J.; DeVita, W. G. 1999: Importance of toxicity as a factor controlling the distribution of aquatic organism in an urban stream. In comprehensive stormwater and aquatic ecosystem management. First South Pacific Conference. 22-26 February 1999. Auckland. Pp 187-194.

Crunkilton, R.; Kron, D. 1999: Assessing the effectiveness of a pilot scale wet detention basin in reducing toxicity of urban runoff. In comprehensive stormwater and aquatic ecosystem management. First South Pacific Conference. 22-26 February 1999. Auckland. Pp 187-194.

David, D. J.; Williams, C. H. 1975: Heavy metal contents of soils and plants adjacent to the Hume highway near Marulan, New South Wales. *Australian journal of experimental agriculture and animal husbandry* 15: 414-417.

Deletic, A. 1998: The first flush load of urban surface runoff. *Water Research* 1998, 32:2462-2470.

Delzer, G. C.; Zogoroki, J. S.; Lopes, T. J.; Bosshart, R. L. 1996: Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban stormwater in the United States, 1991-1995. United States Geological Survey, Water Resources Investigation Report, 96: 4145.

De Mora, S. J.; Demeke, G. 1990: Chemical fractionation of lead in intertidal sediments from Manukau Harbour, Auckland, New Zealand. *New Zealand journal of marine and freshwater research* 24: 569-575.

DeMora, S. J.; Harrison, R. M. 1984: Physicochemical speciation of inorganic compounds in environmental media. Hazard assessment of chemicals: Current developments Volume 3. Academic press.

Dietl, C.; Wäber, M.; Peichl, L.; Vierle, O. 1996: Monitoring of airborne metals in grass and depositions. *Chemosphere*, Vol. 33, No. 11, pp. 2101-2111, 1996.

- Dietl, C.; Reifenhauer, W.; Peichl, L. 1997: Association of antimony with traffic – occurrence in airborne dust, deposition and accumulation in standardised grass cultures. *The science of the total environment* 205: 235-244.
- Di Toro, D. J.; Mahony, J. D.; Hansen, D. J.; Scott, K. J.; Hicks, M. B.; Mays, S. M.; Redmond, M. S. 1990: Toxicity of cadmium in sediments: the role of acid volatile sulfide. *Environmental toxicology and chemistry* 9: 1487-1502.
- Di Toro, D. J.; Mahony, J. D.; Hansen, D. J.; Scott, K. J.; Carlson, A. A.; Ankley, G. T. 1992: Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environmental science and technology* 26: 96-101.
- Di Toro, D. J.; Mahony, J. D.; Hansen, D. J.; Scott, K. J.; Carlson, A. A.; Ankley, G. T. 1992: Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environmental science and technology* 26: 96-101.
- Dongarra, G.; Varrica, D.; Sabatino, G. 2003: Occurrence of platinum, palladium and gold in needles of *Pinus pinea* L. from the City of Palermo (Italy). *Applied geochemistry* 18: 109-116.
- Donkelaar, P. Van. 1990: Environmental effects of crankcase and mixed lubrication. *The science of the total environment* 92: 165-179.
- Drapper, D.; Tomlinson, R.; Williams, P. 2000: Pollutant concentrations in road runoff: Southeast Queensland case study. *Journal of environmental engineering* April 2000: 313-320.
- Driscoll, E. D.; Shelley, P. E.; Strecker, E. W. 1990: Pollutant loadings and impacts from highway stormwater runoff. Vol. 1 Design Procedure, Technical Report FHWA-RD-88-07, prepared for the Federal Highway Administration, Washington, D.C.
- Driscoll, E. D.; Shelley, P. E.; Strecker, E. W. 1990: Pollutant loadings and impacts from highway stormwater runoff. Vol. 3 Analytical investigation and research report. Technical Report FHWA-RD-88-08, prepared for the Federal Highway Administration, Washington, D.C.
- Dudding, L. M.; Ward, N. I. 2002: Uptake of platinum from catalytic converter material by *Lolium perenne* (Common rye grass). The seventh international highway and urban pollution symposium, Barcelona, Spain. 20-23 May 2002.
- Dudding, L. M.; Ward, N. I. 2002: Platinum in motorway (M25 London Orbital) dust samples. The seventh international highway and urban pollution symposium, Barcelona, Spain. 20-23 May 2002.
- Dupuis, T. V.; Kreutzberger, W.; Kaster, J.; Harris, T. 1985: Effects of highway runoff on receiving waters, Volume V; Resource document for environmental assessments. FHWA/RD-84/066, 228p.
- Dussart, G. B. T. 1984: Effects of motorway runoff on the ecology of stream algae. *Water pollution control*, 83(3): 409-415.
- Elliot, A. H. 1996: Monitoring of stormwater quality at the Halswell Junction Road stormwater treatment pond. Report prepared by Department of Natural Resource Engineering, Lincoln University for Christchurch City Council. August 1996.
- Ellis, J. B. 1976: Sediments and water quality of urban storm water. *Water services* 80(970): 730-734.
- Ellis, J. B.; Revitt, D. M. 1982: Incidence of heavy metals in street surface sediments: solubility and grain size studies. *Water air and soil pollution* 17: 87-100.
- Ellis, J. B.; Harrop, D. O. 1984: Variations in solids loadings to roadside gullypots. *Science of the total environment* 33: 203-211.

- Ellis, J. B. 1986: Pollutational aspects of urban runoff. In Torno, H. C.; Marselek, J.; Desbordes, M. eds. Urban runoff pollution. NATO ASI Series Bol g10, p1-37.
- Ellis, J. B.; Revitt, D. M. 1989: Traffic related pollution on highway surfaces. Research Report 18. Urban pollution. Middlesex Polytechnic, research and consultancy. July 1989.
- ERMA, 1999: Interim guide to the specifications for hazardous substances under the HSNO Act. Draft document under review. ERMA January 1999.
- Evans, J. J.; Shoemaker, C. A.; Klesius, P. H. 2000: In vivo and in-vitro effects of benzothiazole on sheepshead minnow (*Cyprinodon variegates*). Marine environmental research 50: 257-261.
- Faure, P.; Landais, P.; Schlepp, L.; Michels, R. 2000. Evidence for diffuse contamination of river sediments by road asphalt particles. Environmental Science and Technology, 2000, 34, 1174-1181.
- FDEP, 1994: Approach to the assessment of sediment quality in Florida coastal waters, Vol. 1. Development and evaluation of sediment quality assessment guidelines. Prepared for Florida Department of Environmental Protection, Office of Water Policy, Tallahassee, Fl, by MacDonald Environmental Sciences Ltd., Ladysmith, British Columbia.
- Fergusson, J. E. 1993: Sources, pathways and sinks of lead in the natural and modified environment. In Hay, J. E.; de Mora, S. J. Eds. Lead in the New Zealand Environment. pp 4-25. Proceedings of a conference organised by Environmental Source at the University of Auckland. August 1-2, 1988.
- Fergusson, J. E.; R. W.; Tan, S. Y.; Sin, H. T. 1980: Heavy metal pollution by traffic in Christchurch, New Zealand: lead and cadmium content of dust, soil and plant samples. New Zealand journal of science, 23: 292-310.
- Fergusson, J. E.; Simmonds, P. R. 1983: Heavy metal pollution at an intersection involving a busy urban road in Christchurch, New Zealand. 1. Levels of Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb in street dust. New Zealand journal of science 26: 219-228.
- Fergusson, J. E.; Ryan, D. E. 1984: The elemental composition of street dust from large and small urban areas related to city type source and particle size. The science of the total environment 34: 101-116.
- Fletcher, I. J.; Pratt, C. J.; Elliott, G. E. P. 1978: An assessment of the importance of roadside gully pots in determining the quality of stormwater runoff. In Helliwell, P. R. Ed. Urban storm drainage: Proceedings of the International Conference held at the University of Southampton, April, 1978, pp 586-602. Pentech Press, London.
- Fletcher, I. J.; Pratt, C. J. 1981: Mathematical simulation of pollutant contributions to urban runoff from roadside gullypots. In Urban Stormwater Quality, Management and Planning (Edited by Yen B. C.), pp. 116-124. Water Resources Publications, Colo.
- Folkesson, L. 1994: Environmental effects of highway runoff water – a literature review. Swedish National Road and Transport Research Institute. VTI Report No 391A.
- Forstner, U. 1986: Metal speciation in solid wastes – factors affecting mobility. In Landers, L. Ed Speciation of metals in water, sediment and soil systems. pp 13-41. Proceedings of an international workshop, Sunne October 15-16, 1986. Lecture notes in Earth Sciences 11. Springer Verlag, Berlin.
- Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T. 1998: Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. Environmental science & technology 32(14): 2051-2060.

Gadd, J.; Kennedy, P. 2000: Preliminary examination of organic compounds present in tyres, brake pads and road bitumen in New Zealand. Prepared by Kingett Mitchell Ltd for Ministry of Transport, November 2000. Revised October 2003.

Garg, B. D.; Cadle, S. H.; Mulawa, P. A.; Groblicki, P. J. 2000: Brake wear particulate matter emissions. *Environmental science and technology* 34(21): 4463 – 4469.

Getz, L. L.; Verner, L.; Prather, M. 1977: Lead concentrations in small mammals living near highways. *Environmental pollution* 13: 151-156.

Gjessing, E.; Lygren, E.; Berglund, L.; Gulbrandsen, T.; Skaane, R. 1984: Effect of highway runoff on lake water quality. *The science of the total environment* 33: 245-257.

Goodyear, K. L.; McNeill, S. 1999: Bioaccumulation of heavy metals by aquatic macro-invertebrates of different feeding guilds: a review. *The science of the total environment* 229: 1-19.

Gromaire-Mertz, M. C.; Garnaud, S.; Gonzalez, A.; Chebbo, G. 1999: Characterisation of urban runoff pollution in Paris. *Water science technology* 39(2): 1-8.

Gulson, B. L.; Tiller, K. G.; Mizon, X. J.; Merry, R. H. 1981: Use of lead isotopes in soils to identify the source of lead contamination near Adelaide, South Australia. *Environmental science and technology* 15: 691-696

Habibi, K. 1973: Characterisation of particulate matter in vehicle exhaust. *Environmental science and technology* 7: 223-234.

Hall, J. H. 1998: Whole effluent toxicity tests with native New Zealand species. Presentation at a workshop on contaminant toxicity in aquatic ecosystem tools and approaches for New Zealand. 21-22 May 1998. Wellington.

Hall, J. H. 1998: Toxicity tests; what are they and how can we use them. Presentation at a workshop on contaminant toxicity in aquatic ecosystem tools and approaches for New Zealand. 21-22 May 1998. Wellington.

Harrison, R. M. 1979: Toxic metals in street and household dusts. *The science of the total environment* 11: 89-97.

Harrison R. M. 1983: The determination of concentrations and physico-chemical speciation of environmental pollutants. In *Pollution: Causes, Effects and Control*, pp. 67-86. Royal Society of Chemistry Special Publication No. 44.

Harrison, R. M.; Laxen, D. P. H.; Wilson, S. J. 1981: Chemical associations of lead, cadmium, copper, and zinc in street dusts and roadside soils. *Environmental science and technology* 15(11): 1378-1383.

Harrison R. M.; Wilson S. J. 1983 Heavy metal pollution of road drainage water. In *Proceedings of International Conference on Heavy Metals in the Environment* (Edited by Perry R., Muller G. and Forstner R.), pp. 684--687. CEP Consultants Ltd, Edinburgh.

Harrison, R. M.; Wilson, S. J. 1985: The chemical composition of highway drainage waters 1 – major ions and selected trace metals. *The science of the total environment*. 43: 63-77.

Harrison, R. M.; Laxen, D. P. H.; Wilson, S. J. 1985: Chemical associations of lead, cadmium, copper, and zinc in street dusts and roadside soils. *Environmental science and technology* 15: 1378-1383.

Hares. R. J.; Ward, N. I. 1999: Comparison of the heavy metal content of motorway stormwater following discharge into wet biofiltration and dry detention ponds along the London Orbital (M25) motorway. *The science of the total environment* 235 (1999): 169-178.

- Harrop D. O. 1984: Stormwater runoff and water quality in urban sediments. Ph.D thesis, Urban Pollution Research Centre, Middlesex Polytechnic, London.
- Heaney, J. P.; Huber, W. C.; Nix, S. J. 1976: Stormwater management model. Level 1 Preliminary screening procedures. EPA Report No. 66/2-76-275.
- Heaney, J. P.; Pitt, R.; Field, R. 1999: Innovative urban wet-weather flow management systems. EPA Report No. 600/R-99/029.
- Helmets, E. 1996: Elements accompanying platinum emitted from automobile catalysis. *Chemosphere*, 33(3): 405-419.
- Herricks, E. E. 1995: Section 2 (Impacts) Summary. In Herricks, E. E. Ed Stormwater runoff and receiving systems. Impact, monitoring and assessment. pp 23-40. CRC Lewis Publishers. Boca Raton.
- Hewitt, C. N.; Rashed, M. B. 1990: An integrated budget for selected pollutants for a major rural highway. *The science of the total environment*. 93: 375-384.
- Hickey, C.; Roper, D. 1994: Water quality – testing for toxicity in our aquatic environment. *Water & atmosphere* 2(4): 11-14.
- Hickey, C. 1998: Sediment toxicity tests. Presentation at a workshop on contaminant toxicity in aquatic ecosystems tools and approaches for New Zealand. 21-22 May 1998. NIWA.
- Hickey, C. W. 1999: Multispecies assessment of water and sediment toxicity associated with urban and industrial stormwater treatment ponds. How effective are ponds as a toxicity reduction system. In comprehensive stormwater and aquatic ecosystem management. First South Pacific Conference. 22-26 February 1999. Auckland. pp 195-204.
- Hickey, C. W. 2000: Ecotoxicology: laboratory and field approaches. In Collier, K. J. & Winterbourn, M. J. Eds. *New Zealand stream invertebrates: Ecology and implications for management*. New Zealand Limnological Society. Caxton Press, Christchurch. Pp 313-343.
- Hickey, C. W.; Roper, D. S.; Buckland, S. 1995: metal concentrations of resident and transplanted freshwater mussels *Hyridella menziesi* (Unionacea: Hyriidae) and sediments in the Waikato River, New Zealand. *The science of the total environment* 175: 163-177.
- Hickey, C. W.; Buckland, S. J.; Hannah, D. J.; Roper, D. S.; Stuben, K. 1997: Polychlorinated biphenyls and organochlorine pesticides in the freshwater mussel *Hyridella menziesi* from the Waikato River, New Zealand. *Bulletin of environmental contamination and toxicology* 59: 106-112.
- Hickey, C. W.; Golding, L. A.; Martin, M. C. 1997: Assessment of water and suspended sediment toxicity to freshwater and marine species associated with stormwater treatment facilities. Report prepared by NIWA for Auckland Regional Council July 1997. Report ARC 70219.
- Higney, E.; Olive, V.; MacKenzie, A. B.; Pulford, I. D. 2002: Isotope dilution ICP-MS analysis of platinum in road dusts from west central Scotland. *Applied Geochemistry*, 17(8): 1123-1129.
- Hodge, V. F.; Stallard, M. O. 1986: Platinum and palladium in roadside dust. *Environmental science and technology*, Vol. 20, No. 10, 1986.
- Hoffman, E. J.; Latimer, J. S.; Hunt, C. D.; Mills, G. L.; Quinn, J. G. 1985: Stormwater runoff from highways. *Water air and soil pollution*, 25 (4): 349-364.
- Hunter, J. V.; Sabatino, T.; Gomperts, R; MacKenzie, M. J. 1979: Contribution of urban runoff to hydrocarbon pollution. *Journal water pollution control federation* 51(8): 2129-2138.

Hrabik, T. R.; Watras, C. J. 2002: Recent declines in mercury concentration in a freshwater fishery: isolating the effects of de-acidification and decreased atmospheric mercury deposition in Little Rock Lake. *The science of the total environment* 297: 229-237.

Hvitved-Jacobsen, T.; Yousef, Y. A. 1991: Highway runoff quality, Environmental impacts and control. In *Highway Pollution*. Vol 44, *Studies in Environmental Science*, Elsevier Science Publishers, Amsterdam, Neth.

Irish, L. B.; Lesso, W. G.; Barrett, M. E.; Malina, J. F.; Charbeneau, R. J.; Ward, R. J. 1995: An evaluation of the factors affecting the quality of highway runoff in the Austin, Texas area. Centre for Research in Water Resources, Technical Report CRWR 264. University of Texas at Austin. September 1995.

Jarvis, K. E.; Parry, S. J.; Piper, J. M. 2001: Temporal and spatial studies of autocatalyst-derived platinum, rhodium and palladium and selected vehicle-derived trace elements in the environment. *Environmental Science and Technology*, 2001, 35, 1031-1036.

Jellyman, D. 1987(a): Freshwater fisheries and impact assessment. *Freshwater catch* 32: 22-24.

Jellyman, D. 1987b: The use of fish in impact assessment. *Freshwater catch* 33: 13-15.

Jefferies, D. J.; French, M. C. 1972: Lead concentrations in small mammals trapped in roadside verges and field sites. *Environmental pollution*, 3: 147-156.

Jensen, K. H.; Rauch, S.; Morrison, G. M.; Linndberg, P. 2002: Platinum group elements in the feathers of raptors and their prey. The seventh international highway and urban pollution symposium, Barcelona, Spain. 20-23 May 2002.

Jolly, V. H.; Brown, J. M. A. eds 1975: *New Zealand lakes*. Auckland University Press, Oxford University Press.

Karouna-Reiner, N. K.; Sparling, D. W. 2001: Relationships between ambient geochemistry, watershed land-use and trace metal concentrations in aquatic invertebrates living in stormwater treatment ponds. *Environmental pollution*, 112: 183-192.

Kennedy, K. 1995: A statistical analysis of TxDOT highway storm water runoff: Comparisons with the existing north central Texas municipal storm water database. North Central Texas Council of Governments November 1995.

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

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

Kennedy, P.; Gadd, J. 2000: Preliminary examination of inorganic compounds present in tyres, brake pads and road bitumen in New Zealand. Prepared by Kingett Mitchell Ltd for Ministry of Transport, November 2000. Revised October 2003.

Kennedy, P.; Gadd, J. 2002: Evaluation of road surface contaminant loadings in Waitakere City for the development of the vehicle emission model water. Prepared by Kingett Mitchell Ltd for Ministry of Transport, December 2002. Revised October 2003.

Kennedy, P.; Gadd, J.; Moncrieff, I. 2002: Emission factors for contaminants released by motor vehicles. Report prepared by Kingett Mitchell Ltd for Ministry of Transport and Infrastructure Auckland. August 2002.

Kennedy, P. C.; Kjellstrom, T. K.; Farrell, J. 1988: Environmental lead and lead in primary and pre-school children's blood in Auckland, New Zealand. New Zealand Energy Research and Development Committee, Report No. 169. February 1988.

Kingett Mitchell, 2000: Comprehensive Urban Stormwater Management Action Strategy - Preliminary Receiving Environment Study. Report prepared for Waitakere City Council, March 2000.

Kingett Mitchell 2001: Ecological characteristics and ecosystem objectives for North Shore City streams. Report prepared by Kingett Mitchell for North Shore City.

Kingett Mitchell, 2003a: Marine sediment monitoring programme 2002 results. Report prepared for the Auckland Regional Council, March 2003.

Kingett Mitchell, 2003b: Auckland regional benthic ecology monitoring 2002. Report prepared for the Auckland Regional Council, March 2003.

Kingett Mitchell, 2003c: Sediment quality and benthic health in the North Shore coastal marine area. Report prepared for the North Shore City Council, June 2003.

Kingett Mitchell, ESR 1998: Review of performance indicators for Toxic Contaminants in the environment. Report prepared by Kingett Mitchell & Associates Limited and ESR Limited for the Ministry for the Environment.

Kirouani-Harani, H. 2003: Microbial and photolytic degradation of benzothiazoles in water and wastewater. PhD thesis, Fakultät III der Technischen Universität Berlin. June 2003.

Krein, A.; Schorer, M. 2000: Road runoff pollution by polycyclic aromatic hydrocarbons and its contribution to river sediments. *Water research* 34(16): 4110-4115.

Kramme, A. D.; Brosnan, T. M. 1985: Investigations of impacts of selected highway maintenance practices on water quality. Vol 2, FHWA/RD-85/058, Federal Highway Administration, Washington DC.

Kumata, H.; Yamada, J.; Masuda, K.; Takada, H.; Sato, Y.; Sakurai, T.; Fujiwara, K.; 2002: Benzothiazolamines as Tire-Derived Molecular Markers: Sorptive Behaviour in Street Runoff and Application to Source Apportioning. *Environmental science and technology*, 36(4): 702-708.

Kurunaratne, S. H. P. G. 1992: The influence of gully pot performance on the entry of runoff sediment into sewers. London: South bank University 1992. PhD Thesis.

Kzos, K. A.; Winter, J. D.; Storch, T. A. 1990: Toxicity of Chautaugua Lake bridge runoff to young-of-the-year sunfish (*Lepomis macrochirus*). *Bulletin of environmental contamination and toxicology*, 45(6): 923-930.

Lahr, J.; Maas-Diepeveen, J. L.; Stuijzand, S. C.; Leonards, P. E. G.; Druke, J. M.; Lucker, S.; Espeldoorn, A.; Kerkum, L. C. M.; van Stee, L. L. P.; Hendriks, A. J. 2003: Responses in sediment bioassays used in the Netherlands: can observed toxicity be explained by routinely monitored priority pollutants. *Water research*, 37(8): 1691-1710.

Lau, W. M.; Wong, H. M. 1982: An ecological survey of lead contents in roadside dusts and soils in Hong Kong. *Environmental research*, 28: 39-52.

Lau, S. L.; Stenstrom, M. K. 2001: Metals and PAHs adsorbed to street particles, pp 122-134. In Rain – the forgotten resource. Second South Pacific stormwater conference, 27-29 June 2001, Auckland.

Laxen, D.; Harrison, R. 1977: *Water research* 11: 1-11.

Lee, J. H.; Bang, K. W. 2000: Characterisation of urban stormwater runoff. *Water Research*, 34:1773-1780.

- Lee, J. H.; Bang, K. W.; Ketchum, L. H.; Choe, J. S.; Yu, N. J. 2002: First flush analysis of urban storm runoff. *The Science of the Total Environment*, 293 (1-3): 163-175
- Li, X.; Poon, C-S.; Liu, P. S. 2001: Heavy metal contamination of urban soils and street dusts in Hong Kong. *Applied geochemistry* 16: 1361-1368.
- Lindgren, A. 1996: Asphalt wear and pollution transport. *The science of the total environment* 189/190: 281-286.
- Little, P. 1973: A study of heavy metal contamination of leaf surfaces. *Environmental pollution* 5: 159-172.
- Long, E. R.; Morgan, L. G. 1990: The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA technical memorandum NOS OMA 52. National Oceanographic and Atmospheric Administration, Seattle, Washington.
- Long, E. R.; Macdonald, D. D.; Smith, S. L.; Calder, F. D. 1995: Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental management* 19: 81-97.
- Lopes, T. J.; Bender, D. A. 1998: Nonpoint sources of volatile organic compounds in urban areas - relative importance of land surfaces and air. *Environmental Pollution*, 101(2): 221-230.
- Lopes, T. J.; Dionne, S. G. 1998: A review of semi-volatile and volatile organic compounds in highway runoff and urban stormwater. United States Geological Survey Open-File Report 98-409.
- Lopes, T. J.; Fossum, K. D. 1995: Selected chemical characteristics and acute toxicity of urban stormwater, streamflow, and bed material, Maricopa County, Arizona. United States Geological Survey Open-File Report 95-4074.
- Lord, B. N. 1987: Non point source pollution from highway stormwater runoff. *The science of the total environment*, 59: 437-446.
- Mackay, D.; Leinonen, P. J. 1975: Rate of evaporation of low solubility contaminants from water bodies to the atmosphere. *Environmental science and technology* 9:1178-1180.
- Macaskill, J. B. 2001: Stormwater quality in the Auckland City region: a chemical assessment of impacts on the receiving water environments. Report prepared by NIWA for Metrowater Ltd. NIWA Client Report: MWR01105/2 February 2001
- Macaskill, B.; Bowman, E.; Golding, L.; Horrox, J.; Phillips, N. 2003: Rotorua City urban stormwater quality and prediction of environmental impacts: Technical addendum. Report prepared by NIWA for Rotorua District Council. NIWA Client Report HAM2002-020, January 2003.
- Mackay, D. 1982: Correlation of bioconcentration factors. *Environmental science and technology* 16: 274-278.
- Makepeace, D. K.; Smith, D. W.; Stanley, S. J. 1995: Urban stormwater quality: Summary of contaminant data. *Critical reviews in environmental science and technology* 25(2): 93-139.
- Malmquist, P. A. 1978: Atmospheric fallout and street cleaning – effects on urban stormwater and snow. *Progress water technology* 10 (5/6): 495-505.
- Maltby, L. A.; Forrow, P.; Boxall, D. M.; Calow, P.; Betton, C. 1995a: The effects of motorway runoff on freshwater ecosystems: 1 Field study. *Environmental toxicology and chemistry* 14: 1079-1092

Maltby, L. A.; Boxall, D. M.; Forrow, P.; Calow, P.; Betton, C. 1995b: The effects of motorway runoff on freshwater ecosystems: 2 Identifying major toxicants. *Environmental toxicology and chemistry* 14: 1093-1101.

Mance, G.; Harman, M. M. I. 1978: The quality of urban storm-water run-off. In Helliwell, P. R. Ed. *Urban storm drainage: Proceedings of the International Conference held at the University of Southampton, April, 1978*, pp 603-616. Pentech Press London.

Marsalek, J.; Brownlee, B.; Mayer, T.; Lawal, S.; Larkin, G.A. 1997: Heavy metals and PAHs in stormwater runoff from the Skyway Bridge, Burlington, Ontario. *Water quality research journal of Canada*, 32 (4): 815-827.

Macaskill, J. B. 2001: Stormwater quality in the Auckland City region : a chemical assessment of impacts on the receiving water environments. Report prepared by NIWA for Metrowater Ltd. NIWA Client Report: MWR01105/2 February 2001

Medeiros, C.; Coler, R. A. 1982: A laboratory/field investigation into the biological effects of urban runoff. Water Resources Research Centre, University of Massachusetts.

Memon, F. A.; Butler, D. 2002: Identification and modelling of dry weather processes in gully pots. *Water research* 36: 1351-1359.

Meritec, 2000a: Project Care: 1999/2000 North Shore stream and stormwater quality study. Project Care Technical Report 3.05, prepared for North Shore City Council, October 2000.

Meritec, 2000b: Project Care: Mairangi Bay monitoring volume 1 - results. Report prepared for the North Shore City Council. Technical report 3.06, November 2000.

Meylan, W. N.; Howard, P. H.; Boethling, R. S.; et al. 1999: Improved method for estimating bioconcentration/bioaccumulation factors from octanol/water coefficient. *Environmental toxicology and chemistry* 18(4): 664-672.

MfE, 1992: Water quality guidelines No 1: Guidelines for the control of undesirable biological growths in water. Ministry for the Environment. Wellington.

MfE, 1994: Water quality guidelines No 2.: Guidelines for the control of colour and clarity of water. Ministry for the Environment. Wellington.

MfE, 1998a: Environmental performance indicators: Proposals for the marine environment. Ministry for the Environment. December 1998. Wellington.

MfE, 1998b: Environmental performance indicators: Proposals for the terrestrial and freshwater biodiversity. Ministry for the Environment. December 1998. Wellington.

MfE, 2000: Making every drop count. The national agenda for sustainable water management action plan. Ministry for the Environment, Wellington.

Mitchell, R. L.; Reith, J. W. S. 1966: The lead content of pasture herbage. *Journal of science food agriculture*, 17: 437-440.

Moldovan, M.; Rauch, S.; Gomez, M.; Palacios, M. A.; Morrison, G. M. 2001: Bioaccumulation of palladium, platinum and rhodium from urban particulates and sediments by the freshwater isopod *Asellus Aquaticus*. *Water Research* Vol. 35, No. 17, pp, 4175-4183, 2001.

Moldovan, M.; Rauch, S.; Gomez, M.; Palacios, M. A.; Morrison, G. 2001: Bioaccumulation of palladium, platinum and rhodium from urban particulates and sediments by the freshwater isopod *Asellus aquaticus*. *Water research* 35(17): 4175-4183.

Moncrieff, I.; Kennedy, P. 2002: Road transport effects on aquatic ecosystems issues and context for policy development. Report prepared for New Zealand Ministry of Transport by Fuels and Energy Ltd and Kingett Mitchell Ltd. December 2002, Updated June 2004.

Morrison, G. M.; Revitt, D. M.; Ellis, J. B.; Svensson, G.; Balmer, P. 1984: Variations of dissolved and suspended solid heavy metals through an urban hydrograph. *Environmental technology letters* 7: 313-318.

Morrison G. M.; Revitt, D. M. 1987: Assessment of metal species bioavailability and geochemical mobility in polluted waters. *Environmental technology letters* 8: 361-372.

Morrison G. M.; Revitt, D. M.; Ellis, J. B.; Svensson, G.; Balmer, P. 1988: Transport mechanism and process for metal species in gully pot system. *Water research* 22: 1417-1427.

Morrisey, D. J. 1999: Biological effects of contaminant build-up in estuaries. In comprehensive stormwater and aquatic ecosystem management. First South Pacific Conference. 22-26 February 1999. Auckland. Pp 121-127.

Morton, J.; Miller, M. 1968: *The New Zealand sea shore*. Collins, London. 653 pp.

Mosley, L.; Peake, B. 1999: Trace metal partitioning in urban runoff. Poster at first South Pacific's Conference on Comprehensive stormwater and aquatic ecosystem management. 22-26 February 1999, Auckland, New Zealand.

Mosley, L. M.; Peake, B. M. 2001: Partitioning of metals in urban run-off from the Kaikorai Valley, Dunedin, New Zealand. *New Zealand journal of marine and freshwater research*, 35: 615-624.

MoT 1996: Land Transport pricing study. Environmental externalities Discussion Paper March 1996, Ministry of Transport, Wellington.

MoT 1998: Local air quality management – impacts from the road transport sector. Vehicle fleet emissions control strategy. Final report.

Mulliss, R.; Revitt, D. M.; Shutes, R. B. E. 1996: A statistical approach for the assessment of the toxic influences on *Gammarus pulex* (Amphipoda) and *Asellus aquaticus* (Isopoda) exposed to urban aquatic discharges. *Water research* 30(5): 1237-1243.

Ng, W. H.; Buckeridge J. S.; Ockelton, G. 2003: Distribution of heavy metals in road sediments. Third South Pacific Stormwater Conference, Auckland, May 2003.

Ngabe, B.; Bidleman, T. F.; Scott, G. I. 2000: Polycyclic aromatic hydrocarbons in storm runoff from urban and coastal South Carolina. *The science of the total environment*, 255: 1-9.

Nipper, M. G.; Hickey, C. W.; Martin, M. L. 1995: Assessment of water and sediment toxicity associated with stormwater treatment facilities. Report prepared for Auckland regional Council, Environment and Planning Division. NIWA Consultancy Report ARC 242. National Institute of Water and Atmospheric Research, Hamilton.

Nipper, M. G.; Roper, D. S.; Williams, D. S.; Martin, M. L.; Van Dam, L. F.; Mills, G. N. 1998: Sediment toxicity and benthic communities in mildly contaminated mudflats. *Environmental toxicology and chemistry*, 17: 502-510.

NIWA, 1996: Land transport externalities: Water Pollution. Section 3 of Part 2 Detailed Scientific and Economic Reports. Environmental Externalities from Land Transport. Report prepared for Ministry of Transport.

Novotny, V.; Muehring, D.; Zitomer, D.; Smith, D.; Facey, R. 1998: Cyanide and metal pollution by urban snow-melt: impact of de-icing compounds. *Water quality international 1998*: 219-226. Conference pre-print Book 8, IAWQ, London (cited in Marsalek et al. 1999).

O'Brien, A. K.; Reiser, R. G.; Gylling, H. 197: Spatial variability of volatile organic compounds in streams on Long island, NY, and in New Jersey. U.S. Geological Survey, U.S. Department of the Interior, fact Sheet FS-194-97.

Ondov, J. M.; Zoller, W. H.; Gordon, G. E. 1982: Trace element emissions on aerosols from motor vehicles. *Environmental science and technology* 16: 318-328.

Opus International Consultants, 2000a: Mairangi Bay stormwater quality ponds feasibility report. April 2000. Report prepared for North Shore City Council. April 2000.

Opus International Consultants, 2000b: Akoranga Drive stormwater quality pond feasibility report. Report prepared for North Shore City Council. April 2000.

O'Reilly, A.; Pandey, S.; Langdon, A.; Wilkins, A. 2002: Characterisation of runoff contaminants from New Zealand roads, and effects of rainfall events. Transfund New Zealand research report No 228.

Pankow, J. F.; Rathburn, R. E.; Zogorski, J. S. 1996: Calculated volatilisation rates of fuel oxygenate compounds and other gasoline-related compounds from rivers and streams. *Chemosphere* 33(5): 921-937.

Patrick, C. 1975: The nature of significance of sediments derived from roads. Ninth international conference on sedimentology. Nice, France, theme 10, p 94-104.

PCA, 1992: An analysis of selected trace metals in cement and kiln dust. Portland Cement Association 1992.

Perdikaki, K.; Mason, C. F. 1999: Impact of road run-off on receiving streams in Eastern England. *Water research* 33 (7): 1627-1999.

Peterson, S. M.; Batley, G. E. 1992: Road runoff and its impact on aquatic environment: A review. Prepared for the Roads and Traffic Authority of NSW, July 1992. CSIRO Division of Coal and Energy Technology, Centre for Advanced Analytical Chemistry. Investigation report CET/LH/IR076.

Pitt, R. E.; Amy, G. 1973: Toxic materials analysis of street surface contaminants. EPAR2-73-283. August 1973.

Pitt, R.; Bozemann, M. 1982: Sources of urban runoff pollution and its effects on an urban creek. USEPA 600/52-82-090, Ohio.

Pitt, R.; Field, R.; Lator, M.; Brown, M. 1995: Urban stormwater toxic pollutants, assessments, sources and treatability. *Water environment research* 67(3): 260-275.

Portele, G. J.; Mar, B. W.; Horner, R. R.; Welch, E. B. 1982: Effects of Seattle area highway stormwater runoff on aquatic biota WA-RD-39.11, Washington State Department of Transportation, Olympia, WA.

Preistley, S. 1998: Submission presented before the Auckland Regional Council in relation to Chapter 14 Dredging in the Regional Plan: Coastal. Evidence presented on behalf of Ports of Auckland Ltd.

Pridmore, R.; Cummings, V.; Norkko, A. 2000: Ecology of harbour and estuarine environments potentially affected by stormwater discharges from Auckland City. Prepared for by NIWA for Metro Water Ltd. NIWA Client Report: MWR01105. February 2000.

Rajendram, G. 1992: Study of selected chemical constituents in water, sediments, plants and fish in Lake Rotorua, Hamilton, and their possible effects on the Lake ecosystem. Unpublished MSc thesis, University of Waikato.

Ray, D (ed), 2002: New Zealand municipal wastewater monitoring guidelines. New Zealand Water Environment Research Foundation. October 2002.

Rauch, S.; Morrison, G. M. 1999: Platinum uptake by the freshwater isopod *Asellus Aquaticus* in urban rivers. *The Science of the Total Environment* 235 (1999) 261-268.

Rauch, S.; Morrison, G. M. 1999: Platinum uptake by the freshwater isopod *Asellus aquaticus* in urban rivers. *The science of the total environment* 235: 261-168.

Rauch, S.; Lu, M.; Morrison, G. M. 2001. Heterogeneity of Platinum Group Metals in Airborne Particles. *Environmental Science and Technology*, 2001, Vol. 35, 595-599.

Ray, D (ed), 2002: New Zealand municipal wastewater monitoring guidelines. New Zealand Water Environment Research Foundation. October 2002.

Reddy, C. M.; Quinn, J. G. 1997: Environmental Chemistry of benzothiazoles derived from rubber. *Environmental science and technology*, 31(10): 2847-2853.

Revitt, D. M.; Morrison G. M. 1987: Metal speciation variations within separate stormwater systems. *Environmental technology letters* 8: 373-380.

Robertson, B.; Gillespie, P.; Asher, R.; Frisk, S.; Keeley, N.; Hopkins, G.; Thompson, S.; Tuckey, B 2002: Estuarine environmental assessment and monitoring: A national protocol. prepared for Supporting Councils and the Ministry for the Environment. Sustainable Management Fund Contract No. 5096, December 2002.

Robinson, B.; Duwig, C.; Bolan, N.; Kannathasan, M.; Saravanan, A. 2003: Uptake of arsenic by New Zealand watercress (*Lepidium sativum*). *The science of the total environment* 301:67-73.

Roger, S.; Montrejaud-Vignoles, M.; Andral, M. C.; Herremans, L.; Fortune, J. P. 1998: Mineral, physical and chemical analysis of the solid matter carried by motorway runoff water. *Water research* 32(4): 1119-1125.

Rogge, W. F.; Hildemann, L. M; Mazurek, M. A.; Case, G. R.; Simoneit, B. R. T. 1993: Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. *Environmental science and technology*, 27: 636-651.

Rokosh, D.; Chong-Kitt, R.; Lee, J.; Mueller, M.; Pender, J.; Poirer, D.; Westlake, G. 1997: Toxicity of free-way stormwater. In Goudey, S.; Swanson, S.; Treissman, M.; Niimi, A. Proceedings of the 23rd annual toxicity workshop, October 7-9 Calgary, Alberta, 1996 (cited in Marsalek et al. 1999).

Roper, D. S.; Thrush, S. F.; Smith, D. G. 1988: The influence of runoff on intertidal mudflat benthic communities. *Marine environmental research*, 26: 1-18.

Roper, D. S.; Williamson, R. B.; Weatherhead, M. A.; Pridmore, R. D. 1994: Effects of future urbanisation in the catchment of the Upper Waitemata Harbour. *Ecological Impacts*. Report prepared by NIWA for Auckland Regional Council Report ARC100.

Rosenberg, D. M.; Resh, V. H. 1993: Freshwater biomonitoring and benthic macroinvertebrates, New York, Chapman & Hall 488p.

Rowe, B. L.; Landrigan, S. L.; Lopes, T. J. 1997: Summary of published aquatic toxicity information and water quality criteria for selected volatile organic compounds. U.S. geological Survey. Open File Report 97-563.

- Ruck, J. 1998: Evaluation of commercially available toolkits. Presentation at a workshop on contaminant toxicity in aquatic ecosystems tools and approaches for New Zealand. 21-22 May 1998. NIWA.
- Sadecki, R. W.; Busacker, G. P.; Moxness, K. L.; Faruq, K. C. 1996: An investigation of water quality in runoff from stockpiles of salvaged concrete and bituminous paving. Minnesota Department of Transportation. Local Road Research Board. Report Number MN/Pr-96-31. St Paul Minnesota.
- Sartor, J. B.; Boyd, G. B. 1972: Water pollution aspects of street surface contaminants. Environmental Protection Agency Report No. R2-72-081. U.S. Government Printing Office, Washington, D.C.
- Schafer, J.; Hannker, D.; Eckhardt, J-D.; Stuben, D. 1998: Uptake of traffic related heavy metals and platinum group elements (PGE) by plants. *The science of the total environment* 215: 59-67.
- Schäfer, J.; Puchelt, H. 1998: Platinum-Group-Metals (PGM) emitted from automobile catalytic converters and their distribution in roadside soils. *Journal of Geochemical Exploration* 64 (1998) 307-314.
- Shaheen, D. G. 1975: Construction of urban roadway usage to water pollution. USEPA Report No. EPA 600/2-75-004.
- Schiff, K.; Bay, S.; Stransky, C. 2002: Characterization of stormwater toxicants from an urban watershed to freshwater and marine organisms. *Urban Water* 4: 215-227
- Schiff, K.; Bay, S. 2003: Impacts of stormwater discharges on the nearshore benthic environment of Santa Monica Bay. *Marine environmental research* 56: 225-243.
- Schueler, T. (Ed.) 1996: Stream channel geometry used to assess land use impacts in the Pacific Northwest. *Watershed protection techniques*, 2(2): 345-348. Spring 1996.
- Schueler, T. (Ed.) 1996: Trace metal bioaccumulation in the aquatic community of stormwater ponds. *Watershed protection techniques*, 2(3): 450-452 (Article 85).
- Schueler, T. 2003: Impacts of impervious cover on aquatic systems. *Watershed Protection Research Monograph No 1*. Center for Watershed Protection. Ellicott City, MD, March 2003.
- SGC, 1983: Motor vehicles and cleaner air. Report of the Swedish Government Committee on automotive air pollution. Report SOU 1983: 27.
- Shepp, D. L. 1998: Petroleum hydrocarbon concentrations observed in runoff from discrete, urbanised automotive - Intensive land uses:<http://www.epu.gov/owow/watershed/proceed/shepp.html>, 24.11.98.
- Sherriff, J. 1998: An investigation into water quality effects of transport. Resource Investigations Department, Wellington Regional Council.
- Shinya, M.; Tsuchinaga, T.; Yamada, Y.; Ishikawa, M. 2000: Characterisation of heavy metals and polycyclic aromatic hydrocarbons in urban highway runoff. *Water science and technology*, 42(7-8): 201-208.
- Shutes, R. B. E. 1984: The influence of surface runoff on the macroinvertebrate fauna of an urban stream. *The science of the total environment*, 33: 271-282.
- Smith, D. 1986: Heavy metals in the New Zealand aquatic environment. A review. *Water and Soil miscellaneous publication No. 100*. National Water and Soil Conservation Authority, Wellington.
- Smith, M. E., Kaster, J. L. 1983: Effect of Rural Highway runoff on stream benthic macroinvertebrates. *Environmental Pollution (series A)* 321: 57-170.

- Snelder, T. 1995: Comparison of runoff quality from roads versus other urban land uses. Report prepared by NIWA for Auckland Regional Council October 1995. Report ARC 60501.
- Snelder, T. 1995: The effects of urbanisation in the catchment of the Upper Waitemata Harbour: Summary report. Report prepared by NIWA for Auckland Regional Council. Report ARC902.
- Snelder, T.; Trueman, S. 1995: The environmental impacts of urban stormwater runoff. ARC Technical Publication No. 53, May 1995.
- Snelder, T.; Biggs, B. J. F.; Shankar, U.; McDowall, U.; Stephens, R.; Boothroyd, I. 1998: Development of a system of physically based habitat classification for water resources management of New Zealand Rivers. NIWA Client Report: CHC98/96.
- Sriyaraj, K.; Shutes, R. B. E. 2001: An assessment of the impact of motorway runoff on a pond, wetland and stream. *Environment international*, 26: 433-439.
- Stark, J. D. 1985: A macroinvertebrate community index of water quality for stony streams. Water and Soil miscellaneous publication No. 87. National Water and Soil Conservation Authority, Wellington.
- Stark, J. D. 1993: Performance of the Macroinvertebrate Community Index: effects of sampling methods, sample replication, water depth, current velocity and substratum on index values. *New Zealand journal of marine and freshwater research*, 27: 463-478.
- Stark, J. D.; Boothroyd, I. K. G.; Harding, J. S.; Maxted, J. R.; Scarsbrook, M. R. 2001: Protocols for sampling macroinvertebrates in wadeable streams. New Zealand Macroinvertebrate working group report No. 1. Prepared for the Ministry for the Environment. Sustainable Management Fund Contract 5103.
- Stronkhorst, J.; Schot, M. E.; Dubbeldam, M. C.; Ho, K. T. 2003: A toxicity identification evaluation of silty marine harbour sediments to characterise persistent and non-persistent constituents. *Marine pollution bulletin*, 46(1): 56-64.
- Suren, A.; Snelder, T.; Scarsbrook, M.; 1998: Urban Stream Habitat Assessment Method (USHA) NIWA client report No. CHC98/60.
- Suren, A. M.; Snelder, T.; Scarsbrook, R. 1999: Urban stream habitat assessment method: A management tool for resource managers. In comprehensive stormwater and aquatic ecosystem management. First South Pacific Conference. 22-26 February 1999. Auckland. Pp 129-137.
- Suren, A. M. 2000: Effects of urbanisation. Chapter 11 in Collier, K. J.; Winterbourn, M. J. *New Zealand stream invertebrates: Ecology and implications for management*. pp 260-288. New Zealand Limnological Society, Hamilton, New Zealand.
- Sures, B.; Zimmermann, S.; Messerschmidt, J.; von Bohlen, A.; Alt, F. 2001: First report on the uptake of automobile catalyst emitted palladium by European eels (*Anguilla anguilla*) following experimental exposure to road dust. *Environmental Pollution* 113: 341-345.
- Sutherland, R. A.; Tolosa, C. A 2000: Multi-element analysis of road-deposited sediment in an urban drainage basin, Honolulu, Hawaii. *Environmental pollution*, 111: 483-495.
- Takada, H.; Onda, T.; Ogura, N. 1990. Determination of polycyclic aromatic hydrocarbons in urban street dusts and their source materials by capillary chromatography. *Environmental science and technology*, 24(8): 1179-1186.
- Tatsumoto, M.; Patterson, C. C. 1963: Concentrations of common lead in some Atlantic and Mediterranean waters and in snow. *Nature*, 99: 350-352.
- Ter Haar, G. L.; Bayard, M. A. 1971: Composition of airborne lead particles. *Nature*, 232: 553-554.

Terracciano, S. A.; O'Brien, A. K. 1998: Occurrence of volatile organic compounds in streams on Long Island, New York, in New Jersey – Overview of available data and reconnaissance sampling. National Water Quality Assessment Program - Long Island - New Jersey - (LINJ) Coastal Drainages Study Unit.

Tiefenthaler, L. L.; Schiff, K. C.; Bay, S. M. 2001: Characteristics of parking lot runoff produced by simulated rainfall. Southern California Coastal Research Project. SCCWRP Technical Report 343. July 2001.

Timperley, M. 1999: Contaminant bioavailability in urban stormwater. In comprehensive stormwater and aquatic ecosystem management. First South Pacific Conference. 22-26 February 1999. Auckland. Pp 67-74.

Timperley, M. 2000: Chemical contamination of urban streams: how serious is it for stream animals? Presentation at a NIWA seminar "Aquatic habitats in human settlements" held at NIWA Hamilton, July 2000.

Timperley, M. H.; Golding, L. A.; Webster, K. S. 2001: Fine particulate matter in urban streams. Is it a hazard to aquatic life? pp. 135-141. In Rain – the forgotten resource. Second South Pacific stormwater conference, 27-29 June 2001, Auckland.

Timperley, 2002: Urban contaminants research: Transport-Streams-Estuarines. Roading and stormwater Technical Workshop. 6-7 May 2002 Wellington. Workshop jointly presented by the Road Controlling Authorities' Forum, Ministry of Transport, New Zealand Water & Wastes Association.

Timperley, M.; Bailey, G.; Pattinson, P.; Kuschel, G. 2003: Zinc copper and lead in road runoff. 26th Australasian transport research forum. Wellington 1-3 October 2003.

Tuit, C. B.; Ravizza, G. E.; Bothner, M. H. 2000: Anthropogenic platinum and palladium in the sediments of Boston harbour. Environmental science and technology, 34(6): 927-932.

USEPA, 1977: Air quality criteria for lead. US Environmental Protection Agency, EPA-600/8-77-107.

USEPA, 1980: Characteristics of nonpoint source and urban runoff and its effects on stream ecosystems. USEPA 600/3-80-032. Utah.

USEPA, 1985: Technical support document for water-quality-based toxics control. US Environmental Protection Agency, Office of Water Enforcement and Permits, Washington DC. EPA 440/4-35-032.

USEPA 1986: Air quality criteria for lead. USEPA Environmental criteria and assessment office, EPA/600/8-83/028bF, June 1986.

USEPA, 1993: Mobile 5 software and documentation. Office of Air and Radiation. URL-<http://www.epa.gov/omswww>.

USEPA, 1997: The incidence and severity of sediment contamination in surface waters of the United States. EPA 823-R-97-006, September 1997. Office of Science and Technology, Washington.

USEPA, 1997: Revision to rapid bioassessment protocols for use in streams and rivers. Periphyton benthic, macroinvertebrates and fish. EPA 841-D-97-102.

USEPA, 1998: Bioassessment protocols for use in streams and rivers: Algae, benthic invertebrates and fish.

USEPA, 2002: National recommended water quality criteria: 2002 EPA-822-R-02-047. Office of Water, Office of Science and Technology, Washington D.C.

- Veith, G. C.; Defoe, D. L.; Bergstedt, B. V. 1979: Measuring and estimating the bioconcentration factor of chemicals in fish. *Journal of the Fisheries Research Board of Canada* 36 : 1040-1048.
- Van de Velde, K.; Barbante, C.; Cozzi, G.; Moret, I.; Bellomi, T.; Ferrari, C.; Boutron, C. 2000: Changes in the occurrence of silver, gold, platinum, palladium and rhodium in Mount Blanc ice and snow since the 18th century. *Atmospheric environment*, 34: 3117-3127.
- Van Donkelaar, P. 1989: Environmental effects of crankcase and mixed lubrication. *The science of the total environment*, 92:165-179.
- van Roon, M. 2000: The suitability of the gastropod snail *Amphibola crenata* as a bio-monitor of heavy metals in estuaries. Department of Planning, Working paper Series Number 00-3
- Vant, W. N.; Williamson, R. B.; Hume, T. M.; Dolphin, T. T. 1993: Effects of future urbanisation in the catchment of the Upper Waitemata Harbour. Report prepared by NIWA for Auckland Regional Council. Report ARC220R.
- Vasquez-Duhatt, R. 1989: Environmental impact of used motor oil review. *The science of the total environment*, 79: 1-23.
- Viner, A. B. Ed. 1987: Inland waters of New Zealand. DSIR Bulletin 241. Science Information Publishing Centre, Department of Scientific and Industrial Research, Wellington.
- Wakeham, S. G.; Davis, A. C.; Karas, J. L.; 1983: mesocosm experiments to determine the fate and persistence of volatile organic compounds in coastal seawater. *Environmental science and technology*, 17: 611-617.
- Wakeham, S. G.; Canuel, E. A.; Doering, P. H.; Hobbie, J. E.; Helfrich, J. V. K.; Lough, G. R. G. 1985: The biogeochemistry of toluene in coastal seawater: radiotracer experiments in controlled ecosystems. *Biogeochemistry*, 1: 307-328.
- Ward, N. I.; Brooks, R. R.; Reeves, R. D. 1974: Effect of lead from motor-vehicle exhausts on trees along a major thoroughfare in Palmerston North, New Zealand. *Environmental pollution*, 6: 149-158.
- Ward, N. I.; Reeves, R. D.; Brooks, R. R. 1975: Lead in soil and vegetation along a New Zealand State Highway with low traffic volume. *Environmental pollution*, 9: 243-251.
- Ward, N. I.; Reeves, R. D.; Brooks, R. R. 1975: Lead from motor-vehicle exhaust in sweet-corn plants and soils along a highway in Hawke's Bay, New Zealand. *New Zealand journal of science*, 18: 261-267.
- Ward, N. I.; Brooks, R. R.; Roberts, E.; Boswell, C. R. 1977: Heavy metal pollution from automotive emissions and its effect on roadside soils and pasture species in New Zealand. *Environmental science and technology*, 11(9): 917-920.
- Ward, N. I.; Savage, J. M. 1994: Elemental status of grazing animals located adjacent to the London Ornitral (M25) motorway. *The science of the total environment*, 146-147: 185-189.
- Washburn, L.; McClure, K. A.; Jones, B. H.; Bay, S. M. 2003: Spatial scales and evolution of stormwater plumes in Santa Monica Bay. *Marine environmental research*, 56: 103-125.
- WCC 1997: Stormwater quality: Moselle Avenue Subcatchment Henderson. Waitakere City Council, December 1997.
- Webster, K. 2000: Predicting metal bioavailability from metal speciation. Presentation at a NIWA seminar of FRST Research 2000. "Aquatic habitats in human settlements" held at NIWA Hamilton, July 2000.

- Webster, J. G.; Brown, K. L.; Webster, K. S. 2000: Source and transport of trace metals in the Hatea River catchment and estuary, Whangarei, New Zealand. *New Zealand journal of marine and freshwater research*, 34: 187-201.
- Wei, C.; Morrison, G. M 1994: Platinum in road dusts and urban river sediments. *The science of the total environment*, 146-147: 169-174.
- Welch, W. R.; Dick, D. L. 1975: Lead concentrations in tissues of roadside mice. *Environmental pollution* 8: 15-21.
- Wilber, W. G.; Hunter, J. V. 1979: Distribution of metals in street sweepings, stormwater solids, and urban aquatic sediments. *Journal of the Water Control Federation*, 51: 2810-2822.
- Wilding, T. K. 1996: Effects of urban development on small stream ecosystems of Auckland and the influence of riparian vegetation. MSc thesis, University of Auckland 1996.
- Wilding, T. K. 1999: Urban stream ecology and riparian vegetation. *Proceedings of the comprehensive stormwater and aquatic ecosystem management conference*; 22-26 February, Auckland pp 111-121.
- Williamson, R. B. 1985: Urban stormwater quality I. Hillcrest, Hamilton, New Zealand. *New Zealand journal of marine and freshwater research*, 19: 413-427.
- Williamson, R. B. 1986: Urban stormwater quality II. Comparison of three New Zealand catchments. *New Zealand journal of marine and freshwater research*, 20: 315-328.
- Williamson, R. B. 1993: Urban runoff data handbook. Water Quality Centre Publication No. 20.
- Williamson, R. B.; Morrissey, D. J.; Swales, A. 1999: The build-up of contaminants in urbanised estuaries. In *comprehensive stormwater and aquatic ecosystem management*. First South Pacific Conference. 22-26 February 1999. Auckland. Pp 59-66.
- Williamson, B.; Goff, J.; Ray, D.; Mills, G.; Berkenbusch, K. 2001: Effects of urban stormwater in the Wellington region: A synthesis of existing information. Report prepared for Wellington Regional Council, May 2001.
- Williamson, B.; Mills, G. 2002: Sediment quality guidelines for the regional discharges project. Report prepared by Diffuse Sources Ltd for Auckland Regional Council. April 2002.
- Williamson, B.; Kennedy, P.; McCarthy, D.; Mathieson, T.; Kelly, S.; Timperley, M. 2003: Auckland's regional discharge project: The current and future state of Auckland's coastal receiving environment. Third South Pacific Stormwater Conference, Auckland, May 2003
- Winter, G. R., Gindley, J. L. 1980: Effects of roadway runoff on algae. Final Report No. FHWA/CA/TL-80/24. California Department of Transportation. June 1980.
- Winterbourne, M. J. 1981: The use of invertebrates in studies of stream water quality. Water & Soil technical publication No. 22. National Water and Soil Conservation Authority.
- Worley 2000: Metrowater 1999 water quality monitoring programme. Technical report prepared by Worley Consultants Ltd for Metrowater. February 2000.
- WRC 1977: Pollution from urban runoff. Notes on water research No 12, October 1977. Water Research Centre.
- Wu, J. J.; Allan, C. J.; Saunders, C.; Evert, J. B. 1998: Characterisation and pollutant loading estimation for highway runoff. *Journal of environmental engineering*, July 1998. Pp 584-592.

Yang, S. Y. N.; Connell, D. W.; Hawker, D. W.; Kayal, S. I. 1991: Polycyclic aromatic hydrocarbons in air, soil and vegetation in the vicinity of an urban roadway. *The science of the total environment*, 102: 229-240.

Yang, H-H.; Chiang, C-F.; Lee, W-J.; Hwang, K-P.; Wu, E. M-Y. 1999: Size distribution and dry deposition of road dust PAHs. *Environmental international*, 25(5): 585-597.

Yeh, C. K.; Novak, J. T. 1994: Anaerobic biodegradation of gasoline oxygenates in soils. *Water environment research*, 66(5): 744-752.

Yim, W. W. S.; Nau, P. S. 1987: Distribution of lead, zinc, copper and cadmium in dust from selected urban areas of Hong Kong. *Hong Kong engineer*, 7-14.

Yousef, Y. A.; Wanielista, M. P.; Hvitved-Jacobsen, T.; Harper, H. H. 1984: Fate of heavy metals in stormwater run-off from highway bridges. *The science of the total environment*, 33: 233-244.

Zimmermann, S.; Alt, F.; Messerschmidt, J.; von Bohlen, A.; Taraschewski, H.; Sures, B.; 2002: Biological availability of traffic related platinum group elements (Pd, Pt, Rh) and other metals to the zebra mussel (*Dreissena polymorpha*) in water containing road dust. *Environmental toxicology and chemistry*, 21: 2713-2718.

Zimmermann, S.; Menzel, C. M.; Stuben, D.; Taraschewski, H.; Sures, B. 2003: Lipid solubility of the platinum group metals Pt, Pd and Rh in dependence on the presence of complexing agents. *Environ. Environmental pollution*, 124: 1-5.

Zweidlinger, R. B.; Stevens, R.K.; Lewis, C. W. 1990: Identification of volatile hydrocarbons as mobile source trailers for fine-particulate organics. *Environmental science and technology*, 24: 538-542.

10. ACKNOWLEDGEMENTS

Thanks to Richard Montgomerie of Kingett Mitchell who helped write Section 6 of the original 1999 report. Dr Ian Boothroyd and Scott Speed reviewed parts of the report. The writer is also grateful to Dr Mike Timperley for his review of the first version of the report.