The Management of Hydrocarbons in Stormwater Runoff: A Literature Review

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Executive Summary

One of the key questions regarding Auckland stormwater quality is "how does Auckland's stormwater quality compare to elsewhere in relation to hydrocarbons?" This question is important because, if the quality of stormwater in Auckland is similar to stormwater quality elsewhere in relation to hydrocarbons, then best practice to improve stormwater hydrocarbon contamination identified elsewhere can be adopted in Auckland. However, if the quantity or diversity of hydrocarbons in Auckland's stormwater is unique, best practice elsewhere may not necessarily be appropriate.

This review considers the likely occurrence and environmental risk of hydrocarbons in stormwater runoff based on available literature. The intended purpose of this literature review is to present collated research from both national and international sources as to the likely occurrence of hydrocarbons in stormwater and align those data with studies that have been undertaken in Auckland. This review can be used as a resource for managing hydrocarbons in stormwater and the receiving environments but is not intended to provide specific guidance on hydrocarbon reduction practices.

Sources of hydrocarbons identified through this literature review include atmospheric deposition (from fuel combustion in vehicles, fires and evaporation from storage), vehicle losses, retail facility losses (e.g. petrol stations) and industrial facility losses. In general, the polycyclic aromatic hydrocarbons (PAHs) seen in downstream sediments were identified as being derived from water-borne and atmospheric deposition. Studies have shown atmospheric point sources are unlikely to be a significant contributor in Auckland, but that stormwater runoff may contribute to PAH concentrations in some localised Auckland streams. The available data indicate that low concentrations of monocyclic aromatic hydrocarbons (MAHs) may be present in stormwater if local sources, such as motor vehicles and vehicle fuel (which are considered to be the primary source of MAHs) contribute. MAHs may also be present following fuel spillages, but their physical properties mean these compounds are readily lost from surface water and sediment through volatilisation.

Data for New Zealand indicate that the concentrations of MAHs in stormwater (prior to entering receiving environments) are typically below the maximum concentrations given in freshwater quality guidelines to protect aquatic biota. As such, MAHs in typical stormwater runoff are not considered a high risk to freshwater environments, nor are they considered a high risk to estuarine and coastal environments (i.e. they are not the key contaminants of concern driving mitigation option design) and therefore should not require additional targeted mitigation methods. However, generic stormwater treatment devices (for instance, constructed wetlands) are designed to remove a broad range of pollutants, including MAHs. Specific controls are however, crucial at sites where there is potential for major hydrocarbon losses that could result in acute environmental effects (such as car parks and petrol stations).

The available data indicate that most of the PAHs present in stormwater are associated with suspended particles. Consequently, dissolved concentrations of PAHs in stormwater are low. Low molecular weight PAHs, which like MAHs readily volatilise, are often absent from stormwater, and are rarely seen in sediments. The PAHs measured in sediments tend to be high molecular weight PAHs, which are more stable. The concentrations of PAHs in freshwater and marine environments are typically below environmental thresholds. However, in some locations where specific hydrocarbon sources are involved, concentrations in sediment have been found to exceed international or local (e.g. Auckland Council) thresholds.

While the limited local, national and international datasets are not sufficient for a thorough comparison of hydrocarbon concentrations, there is no evidence to suggest Auckland's stormwater pollutant profile is in any way unique. It is therefore assumed that the pollutant profile of stormwater in Auckland's runoff is comparable to other areas.

In addition, there appear to be no downstream environmental data (water or sediment quality or ecotoxicological responses) that identify TPH as a pollutant of concern in Auckland requiring specific upstream controls in relation to specific landuses or general activities (e.g. carparking). Consequently, there is insufficient information and data to conclude that treatment of urban stormwater (from residential and commercial landuse) to specifically remove TPH is required.

THE MANAGEMENT OF HYDROCARBONS IN STORMWATER RUNOFF

Table of Contents

1.0	Introd	Introduction1			
2.0	Hydro	carbons	2		
2.1	Intro	duction	2		
2.2	Alipł	natic hydrocarbons	2		
2.3	Aror	natic hydrocarbons	3		
2.4	Tota	I petroleum hydrocarbons	4		
2.5	Wha	t hydrocarbons are considered in this review?	5		
3.0	Hydro	carbon formation	6		
3.1	Intro	duction	6		
3.2	Phyt	ogenic hydrocarbons	6		
3.3	Petr	ogenic hydrocarbons	7		
3.4	Pyrc	genic hydrocarbons	7		
4.0	Hydro	carbons in stormwater	8		
4.1	Intro	duction	8		
4.2	Sou	rces	8		
4	.2.1	Introduction	8		
4	.2.2	Aliphatic and monocyclic aromatic hydrocarbons	9		
4	.2.3	Polycyclic aromatic hydrocarbons	12		
4	.2.4	Total petroleum hydrocarbons	14		
4.3	Sum	imary	14		
5.0	Compa	arison of hydrocarbon sources	16		
5.1	Intro	duction	16		
5.2	Hyd	rocarbons found in stormwater across Auckland	16		
5	.2.1	Introduction	16		
5	.2.2	Roads	17		
5	.2.3	Service stations and carparks	17		
5	.2.4	Landuse	18		
5	.2.5	Key findings	20		
5.3	Hyd	rocarbons found in stormwater nationally	20		
5	.3.1	Introduction	20		
5	.3.2	Waikato	21		
5	.3.3	Bay of Plenty	21		

5.3.	4 Hawke's Bay		21
5.3.	5 Wellington		21
5.3.	6 Canterbury		22
5.3.	7 Otago		22
5.3.	8 Key findings		22
.4	Hydrocarbons found in s	stormwater internationally	23
5.4.	1 Introduction		23
5.4.	2 Monocyclic aromati	ic hydrocarbons	23
5.4.	3 Polycyclic aromatic	hydrocarbons	24
5.4.	4 Total petroleum hyd	drocarbons	25
.5	Summary		26
5.5.	1 Monocyclic aromati	ic hydrocarbons	26
5.5.	2 Polycyclic aromatic	hydrocarbons	26
5.5.	3 Total petroleum hyd	drocarbons	26
5.5.	4 Key findings		27
H	ydrocarbons in downst	ream environments	28
.1	Introduction		28
.2	Hydrocarbons in stream	waters	28
.3	Hydrocarbons in freshwa	ater sediments	28
6.3.	1 Auckland	;	28
6.3.	2 Elsewhere in New 2	Zealand	31
.4	Hydrocarbons in coastal	l sediments	32
6.4.	1 Auckland		32
6.4.	2 Elsewhere in New 2	Zealand	35
.5	Summary		36
6.5.	1 Freshwater sedime	nts	36
6.5.	2 Coastal sediments		36
R	egulatory guidance		37
.1	Introduction		37
.2	Freshwater, estuarine a	nd coastal waters	37
.3	Sediments		39
.4	Summary		40
P	otential environmental	effects of hydrocarbons in stormwater	41
.1	Introduction		41
.2	Mobility and stability		41
	5.3. 5.3. 5.3. 5.3. 5.3. 5.3. 5.4. 5.4.	5.3.4 Hawke's Bay 5.3.5 Wellington 5.3.6 Canterbury 5.3.7 Otago 5.3.8 Key findings 5.3.8 Key findings 4 Hydrocarbons found in statistics 5.4.1 Introduction 5.4.2 Monocyclic aromatic 5.4.3 Polycyclic aromatic 5.4.4 Total petroleum hydrocarbons in downst 5.5.1 Monocyclic aromatic 5.5.2 Polycyclic aromatic 5.5.4 Key findings 5.5.4 Key findings .1 Introduction .2 Hydrocarbons in downst .1 Introduction .2 Hydrocarbons in stream .3 Hydrocarbons in coastal 6.4.1 Auckland 6.3.2 Elsewhere in New 2 .4 Hydrocarbons in coastal 6.4.1 Auckland .5 Summary .6 Summary .6 Summary .7 Introduction .8 Sediments	53.4 Hawke's Bay 53.5 Wellington 53.6 Canterbury 53.7 Otage 53.8 Key findings 4 Hydrocarbons found in stormwater internationally 54.1 Introduction 54.2 Monocyclic aromatic hydrocarbons 54.3 Polycyclic aromatic hydrocarbons 54.4 Total petroleum hydrocarbons 55.1 Monocyclic aromatic hydrocarbons 55.2 Polycyclic aromatic hydrocarbons 55.3 Total petroleum hydrocarbons 55.4 Key findings Hydrocarbons in downstream environments 1 Introduction 2 Hydrocarbons in stream waters 3 Hydrocarbons in reshwater sediments 63.1 Auckland 63.2 Elsewhere in New Zealand 4 Hydrocarbons in coastal sediments 65.2 Coastal sediments 65.3 Summary 65.4 Freshwater sediments 65.5.2 Coastal sediments 65.4 Freshwater sediments 65.5 Summary

THE MANAGEMENT OF HYDROCARBONS IN STORMWATER RUNOFF

8.3	3	Ecot	oxicity	42
	8.3.	.1	Introduction	42
	8.3.	.2	Toxicity in water	42
	8.3.	.3	Phototoxicity	43
	8.3.	.4	Bioavailability and toxicity in freshwater sediment	43
	8.3.	.5	Bioavailability and toxicity in estuarine and marine sediments	45
8.4	ŀ	Bioa	ccumulation and biomagnification	46
	8.4.	.1	Bioaccumulation	46
	8.4.	2	Biomagnification	47
	8.4.	.3	Hydrocarbon bio-uptake in Auckland	47
	8.4.	.4	Key findings	48
8.5	5	Bioto	oxicity	48
8.6	6	Sum	mary	49
9.0	Tł	he Aı	ckland context	51
9.1		Intro	duction	51
9.2	2	Mon	ocyclic aromatic hydrocarbons	51
9.3	3	Poly	cyclic aromatic hydrocarbons	51
9.4	ŀ	Tota	I petroleum hydrocarbons	53
9.5	5	Sum	mary	54
10.0	S	umm	ary	55
10	.1	Mon	ocyclic aromatic hydrocarbons	55
10	.2	Poly	cyclic aromatic hydrocarbons	55
10	.3	Tota	I petroleum hydrocarbons	56
Biblie	ogra	aphy.		57

List of Figures

Figure 1:	Saturated (top) and unsaturated (bottom) aliphatic hydrocarbons	2
Figure 2:	Monocyclic (top) and polycyclic (bottom) aromatic hydrocarbons	3
Figure 3:	Petroleum fractions by carbon range	5
Figure 4:	The typical progression of hydrocarbons, from living organisms through to combustion	6
Figure 5:	Median TPH concentrations in sediment from Auckland catchments	29
Figure 6:	PAH ratio plot showing source characteristics	30
Figure 7:	PAH fingerprints - concentration profiles for stream sediments in Canterbury streams	31
Figure 8:	Auckland Council sediment sampling locations where PAH data are available	34
Figure 9:	Probability plots for HMWPAHs in Auckland estuarine and marine sediments	35

List of Tables

Table 1:	Key properties of aromatic hydrocarbons	. 4
Table 2:	Emission sources for key MAHs	11
Table 3:	Monocyclic aromatic compounds in stormwater	23
Table 4:	TPH in stormwater from US locations	25
Table 5:	Regulatory guidelines for hydrocarbons in aquatic environments (mg/m ³)	38
Table 6:	Regulatory guidelines for PAHs in sediments (µg/kg)	39
Table 7:	Comparison of ARC (2004) HMWPAH sediment quality thresholds with other guidelines (mg/kg)	40

THE MANAGEMENT OF HYDROCARBONS IN STORMWATER RUNOFF

Abbreviation List

ANZECC	Australian and New Zealand Environment and Conservation Council
API	American Petroleum Institute
ARC	Auckland Regional Council
ATSDR	Agency for Toxic Substances and Disease Registry
BAF	Bioaccumulation factor
BAP	Benzo(a)pyrene
BCF	Bioconcentration factor
BTEX	Benzene, toluene, ethylbenzene and xylene
CCME	Canadian Council of Ministers of the Environment
CSIRO	Commonwealth Scientific and Industrial Research Organisation
ECan	Environment Canterbury Regional Council
EPA	Environmental Protection Authority/Te Mana Rauhi Taiao
ERL	Effects range - low
ERM	Effects range - medium
HBRC	Hawke's Bay Regional Council
HMWPAH	High molecular weight polycyclic aromatic hydrocarbon
HSNO	Hazardous Substances and New Organisms
ISQG-Low	Low interim sediment quality guidelines
ISQG-High	High interim sediment quality guidelines
IUPAC	International Union of Pure and Applied Chemistry
LEL	Lowest effect level - Lowest concentration at which toxic effects have been observed
LPG	Liquefied petroleum gas
LMWPAH	Low molecular weight polycyclic aromatic hydrocarbon
MAH	Monocyclic aromatic hydrocarbons
MPCA	Minnesota Pollution Control Agency
MfE	Ministry for the Environment
MW	Molecular weight
NA	Not applicable
NIWA	National Institute of Water and Atmospheric Research
NOAA	National Oceanic and Atmospheric Administration

NRC	Northland Regional Council
NZWERF	New Zealand Water Environment Research Foundation
OME	Ontario Ministry of the Environment
PAH	Polycyclic aromatic hydrocarbons
PEL	Probable effects level - Concentration above which adverse effects are frequently expected
RDS	Road derived sediments
SEL	Severe effect level - Concentration above which most benthic organisms cannot tolerate
SQGV	Sediment quality guideline value
TEL	Threshold effects level - Concentration below which adverse effects are expected rarely
ТРН	Total petroleum hydrocarbons
TSS	Total suspended solids
USEPA	United States Environmental Protection Agency
VOC	Volatile organic carbon
WRC	Waikato Regional Council

1.0 Introduction

This literature review provides information on the nature of hydrocarbon contamination in urban stormwater in the context of national and international literature. To obtain this information, the following tasks have been undertaken:

- Identifying the range of hydrocarbons that may enter stormwater (e.g. fuel, oil leaks, polycyclic aromatic hydrocarbons (PAH) from combustion) through:
 - An overview of hydrocarbon chemistry (Sections 2 and 3)
 - A review of the sources of hydrocarbons in stormwater (Section 4)
- Identifying the concentrations of hydrocarbons that have been determined in stormwater nationally and internationally (Section 5) and in downstream environments (Section 6)
- Identifying receiving environment toxic levels through the provision of:
 - Water quality criteria/guidance used to protect receiving environments (Section 7)
 - Information on the toxicity of the various key groups of hydrocarbons (Section 8)
- Using available data to determine if the hydrocarbon concentrations measured in Auckland stormwater are of concern (Section 9)
- Summarising the findings of the literature-based review in the context of Auckland (Section 10).

2.0 Hydrocarbons

2.1 Introduction

Hydrocarbons are often considered to be a broad group of organic compounds. However, hydrocarbons, as defined by the International Union of Pure and Applied Chemistry (IUPAC, 2014), are organic compounds that consist only of carbon and hydrogen. Hydrocarbons are divided into two classes:

- Aliphatic hydrocarbons
- Aromatic hydrocarbons.

2.2 Aliphatic hydrocarbons

Aliphatic hydrocarbons have carbon atoms joined in straight chains, branched chains, or non-aromatic rings (in which case they are called alicyclic hydrocarbons). Aliphatic hydrocarbons can be saturated (where carbon atoms are joined by single bonds) or unsaturated (where at least two carbon atoms are joined by a double or triple bond). Saturated hydrocarbons that have a straight or branched structure are referred to as alkanes, while saturated hydrocarbons with a cyclic structure are referred to as cycloalkanes. Hydrocarbons containing a double bond (and which are not aromatic – see Section 2.3) are referred to as alkenes, while those with a triple bond are referred to as alkynes. Some examples of aliphatic hydrocarbons are provided in Figure 1.

Ethane (alkane)



Ethene (alkene)



Cyclohexane (cycloalkane)



Ethyne (alkyne)



Figure 1: Saturated (top) and unsaturated (bottom) aliphatic hydrocarbons Image source: Ben Mills / Wikimedia Commons / Public Domain

2.3 Aromatic hydrocarbons

Aromatic compounds are cyclic hydrocarbons with alternating double and single bonds. Aromatic compounds can be monocyclic or polycyclic. Benzene, ethylbenzene, toluene and xylene are examples of monocyclic aromatic hydrocarbons (MAHs) that are collectively referred to as BTEX compounds. Polycyclic aromatic hydrocarbons (PAHs) with two rings are categorised as low molecular weight PAHs (LMWPAHs) and those with three or more rings are high molecular weight PAHs (HMWPAHs). Some examples of MAHs and PAHs are shown in Figure 2.

Benzene (MAH)



Naphthalene (LMWPAH)





Pyrene (HMWPAH)



Figure 2: Monocyclic (top) and polycyclic (bottom) aromatic hydrocarbons Image source: Ben Mills / Wikimedia Commons / Public Domain

A large number of MAHs and PAHs (both LMWPAHs and HMWPAHs) have been identified in studies on PAHs in the environment. The United States Environmental Protection Agency (USEPA, 2013) identifies the MAHs of benzene, ethylbenzene and toluene as priority pollutants, along with 16 PAHs. The solubility and vapour pressure of some of these hydrocarbons are provided in Table 1 with their molecular weights (MW). Solubility in water and vapour pressure will determine whether the hydrocarbon is seen visually in stormwater, freshwater streams and in downstream freshwater, estuarine and coastal sediments.

Table 1: Key properties of aromatic hydrocarbons

Туре	Compound (no. of rings)	MW (g/mol)	Water solubility (g/m ³)	Vapour pressure (mm Hg 25°C)
	Benzene (1)	78.11	1,780	76
MALL	Toluene (1)	92.13	534	36.7
MAH	Ethylbenzene (1)	106.16	140	9.53
	Xylene* (1)	106.16	178	6.61
	Naphthalene (2)	128.2	32	0.018
LIVIVVPAH	Acenapthylene (2)	152.2	3.9	0.003
	Pyrene (4)	202.1	0.14	6.9 x 10 ⁻⁷
HMWPAH	Benzo[a]pyrene (5)	252.3	0.0038	5.5 x 10 ⁻⁹
	Benzo[ghi]perylene (6)	276.4	0.00026	1 x 10 ⁻¹⁰

Notes: MW = molecular weight; MAH = Monocyclic aromatic hydrocarbons; LMWPAH = low molecular weight polycyclic aromatic hydrocarbons; HMWPAH =high molecular weight polycyclic aromatic hydrocarbons * ortho (o), meta (m) and para (p) isomers and PAH solubilities from Herngren *et al.* (2010).

2.4 Total petroleum hydrocarbons

Total petroleum hydrocarbon (TPH) is defined as the measurable amount of petroleum-based hydrocarbon in an environmental media (Agency for Toxic Substances and Disease Registry [ATSDR], 1999). Therefore, it is dependent on analysis of the medium in which it is found (Gustafson, 1997). TPH results are method-specific as the result is the total concentration extracted and measured by that specific method. Since analytical methods for TPH have changed over time, comparisons over time and between studies may not necessarily be like-for-like.

The amount of TPH found in a sample is useful as a general indicator of petroleum contamination (ATSDR, 1999). In addition, by dividing TPH into hydrocarbon fractions (groups of petroleum hydrocarbons, each with specific carbon ranges), useful information about the likely source of the hydrocarbon can be inferred (refer Figure 3 for examples).

THE MANAGEMENT OF HYDROCARBONS IN STORMWATER RUNOFF



Figure 3: Petroleum fractions by carbon range "Obtaining kerosene from petroleum through fractional distillation" by the Institute of Petroleum is licensed under CC BY-SA 3.0

2.5 What hydrocarbons are considered in this review?

Urban stormwater contains a wide range of organic compounds (many of which are not hydrocarbons) that are released to the environment from residential and industrial premises. These include groups of compounds such as polychlorinated biphenyls, herbicides and pesticides. Moncrieff & Kennedy (2004) and Gadd & Kennedy (2004) provide more information on organic compounds in emission sources associated with motor vehicles in New Zealand.

Given the extensive number of organic compounds present in urban stormwater, this review focuses on:

- Some aliphatic hydrocarbons
- MAHs, and in particular, BTEX
- PAHs.

Although TPH can include organic compounds that may not comprise carbon and hydrogen alone, TPH has also been considered in this review, as it is the most common measure used to assess the presence of hydrocarbons in urban stormwater.

3.0 Hydrocarbon formation

3.1 Introduction

Hydrocarbons are produced through biological, geological and combustion processes that can be natural or anthropogenic (man-made). Hydrocarbons produced via biological processes are referred to as phytogenic hydrocarbons, while hydrocarbons formed by geological processes (e.g. the conversion of plant material to coal) are petrogenic hydrocarbons. Hydrocarbons that are formed by combustion processes are referred to as pyrogenic hydrocarbons, and include those resulting from the combustion of petrogenic hydrocarbons (e.g. PAHs formed by the internal combustion of petrol by vehicles).

3.2 Phytogenic hydrocarbons

Phytogenic hydrocarbons represent chemical compounds formed within organisms, including plants, animals, bacteria and fungi. Phytogenic hydrocarbons can be considered precursors to petrogenic hydrocarbons, which in turn are generally the precursors of pyrogenic hydrocarbons (Figure 4). Because they occur naturally, phytogenic hydrocarbons are not typically considered in assessments of hydrocarbon contamination. However, they can be included in hydrocarbon analytical results and as such, interpreted as being a man-made hydrocarbon contribution. This inclusion may be relevant where industrial production of naturally occurring hydrocarbons has resulted in elevated concentrations above what would naturally be found in the environment.



Figure 4: The typical progression of hydrocarbons, from living organisms through to combustion (Image: Nathaniel Wilson / Public Domain

3.3 Petrogenic hydrocarbons

Petrogenic hydrocarbons are predominantly paraffins (alkanes), naphthenes (alkanes that have formed rings), and PAHs. Common petrogenic hydrocarbons in stormwater include those found in coal, oil, petrol, and grease, and are particularly associated with losses, spills of oil or other petroleum products. Naphthalene and fluorene are examples of petrogenic PAHs.

3.4 Pyrogenic hydrocarbons

Pyrogenic hydrocarbons are formed by the natural or purposeful combustion of fuels (e.g. wood, coal, oil and other combustible materials). The type of hydrocarbon formed depends on a range of factors, including the combustion temperature, whether combustion was complete or not, and the initial material combusted (e.g. coal fires may produce different pyrogenic hydrocarbons than the combustion of petrol in an internal combustion engine). The PAHs produced during combustion tend to be more complex (i.e. heavier) than those found in petrogenic sources, and pyrogenic hydrocarbons, especially pyrogenic PAHs, are less readily biodegradable than phytogenic or petrogenic hydrocarbons. These less biodegradable hydrocarbons are therefore, the hydrocarbons most likely to accumulate in the sediments of receiving environments (such as streams, estuaries, harbours and depositional areas in the coastal environment). Benzo(α)pyrene (BaP) and fluoranthene are examples of pyrogenic PAHs.

4.0 Hydrocarbons in stormwater

4.1 Introduction

Understanding the sources of hydrocarbons observed in stormwater provides important information that, in conjunction with estimates of the hydrocarbon load, assists in determining levels and types of controls required where adverse effects are identified in downstream environments. The aim of this section is to show that some sources are more important sources of hydrocarbons than others. The presence and type of hydrocarbon in any of the primary environmental compartments, i.e. air, soil, sediment and water (freshwater, estuarine and coastal), is a function of how the hydrocarbons were released or formed.

4.2 Sources

4.2.1 Introduction

Phytogenic hydrocarbons

In stormwater, the principal sources of phytogenic hydrocarbons are leaves and other plant material, and decomposing organisms (e.g. invertebrates, fish and birds). Phytogenic hydrocarbons are therefore, most abundant in runoff from forested, rural and suburban catchments, and least abundant in stormwater from industrial catchments.

Petrogenic hydrocarbons

Stormwater generated on roads, at petrol or fuelling stations and industrial sites handling hydrocarbons are likely to be the largest sources of petrogenic hydrocarbons. Other less known sources include tyre abrasion (as rubber also contains aliphatic and aromatic hydrocarbons), and the erosion of bitumen. Coal-derived hydrocarbons are rarely found in urban stormwater, but may be expected where coal is being mined (e.g. the north Waikato mines near Huntly and Maramarua), and transported or used in industries that employ coal-fired burners (e.g. Glenbrook steel mill in Waiuku).

Pyrogenic hydrocarbons

Sources of pyrogenic hydrocarbons in stormwater include soot from fires (both wood and coal fires), coal tars and vehicle exhausts (Depree & Ahrens, 2007a). As a result, petrogenic hydrocarbon concentrations are typically higher in stormwater from urban catchments (including suburban, commercial and industrial sub-catchments) than in rural and forested catchments.

Summary information on the presence of aliphatic hydrocarbons, MAHs and PAHs is presented in the following sections. It should be noted that the literature relating to hydrocarbons in source emissions and in environmental compartments is extensive, and as such this report provides a limited, high level overview of this literature. Selected information is provided to illustrate some source information. It is also noted that international literature presenting hydrocarbon data is location-specific and may not represent what is occurring in New Zealand urban areas, as the nature of industrial activity and other factors, such as fuel composition, may differ.

4.2.2 Aliphatic and monocyclic aromatic hydrocarbons

Urban air contains a wide range of hydrocarbon species. Volatile organic compounds (VOCs) in ambient air are associated with emissions from a range of sources, such as motor vehicle exhaust; motor vehicle fuel evaporative losses; industrial activities; petroleum refining; petroleum storage and dispensing facilities; surface coating and solvent use; domestic wood heaters; biomass burning; environmental tobacco smoke; use of solvents and glues; and cleaners in arts and crafts (Hinwood *et al.*, 2006). The specific VOCs seen in urban environments, and the concentrations present are therefore a function of the sources present in any urban area, coupled with factors such as local climate and meteorology.

Vehicle and tunnel studies

There are a number of sources of BTEX compounds and other VOCs associated with motor vehicles. Moncrieff & Kennedy (2004) provide an overview of organic compounds associated with the various motor vehicle sources that may add to hydrocarbons to the environment. In the absence of specific industrial sources (refer below), it would be expected that motor vehicle emissions would be the dominant source of VOCs in urban air around road corridors. Tunnel and roadside monitoring studies provide direct information on the nature of hydrocarbon emissions from vehicles (refer to inset box below).

Tunnel and roadside monitoring - Volatile organic compounds

Schneidemesser et al. (2010) showed that VOC concentrations in central London declined significantly between 1998 and 2008. The changes were attributed to the implementation of the European Union emissions standards for passenger cars which were implemented in 2000 (Euro III) and 2005 (Euro IV). The regulations affected emissions of non-methane hydrocarbons (VOCs) and particulate matter, with different limits set for petrol and diesel light-duty (passenger) vehicles.

Exhaust and tunnel air studies (e.g. Haszpra & Szilagyi, 1994; Duffy & Nelson, 1996; Lai & Peng, 2011) demonstrate that vehicles generate a range of alkanes, alkenes, naphthalenes and aromatics (especially BTEX). The work of Lai & Peng (2011) showed that tunnel exhaust composition comprised similar proportions of alkanes and aromatics (about 35% each) with a lower proportion of alkenes (about 22%). Ho et al. (2002) examined VOCs in air at a roadside monitoring station in Hong Kong. The key BTEX compounds had mean concentrations ranging from 2.85 μg/m³ for o-xylene to 28.81 μg/m³ for toluene.

Fuel types determine the amount of VOCs entering the environment and, although general fuel formulations are relatively similar world-wide, aspects of fuel composition do change with time. Petrol and diesel contain a significant range of hydrocarbons. Diesel contains saturated and unsaturated aliphatic hydrocarbons, naphthalenes and a range of aromatics. Evaporative losses include most of the compounds in petrol and diesel with an emphasis on compounds with a greater tendency to evaporate. A range of VOCs appear in exhaust emissions. Kennedy *et al.* (2002) provides information on VOC loss rates from engine oils.

Borden *et al.* (2002) examined the aromatic hydrocarbon composition of regular and premium petrol in North Carolina in the United States. Mean composition of samples examined were benzene (1%), toluene (6.1%), ethyl-benzene (1.5%), xylenes (7.8%), total BTEX (16.3%). Concentrations of many aromatic compounds are governed by fuel specifications in New Zealand (refer Kennedy *et al.* 2002). Ministry of Business, Innovation and Employment's Engine Fuel Specifications Regulations 2011 limit benzene concentrations to 1%. Hydrocarbons can be lost from motor vehicles through evaporative emissions.

Batterman *et al.* (2005) examined hydrocarbon emissions from vehicles with missing or faulty fuel caps. It was noted the losses were small, but the losses could be reduced. The authors noted 10% of the vehicle fleet in their study had high losses relative to most of the vehicle fleet due to poorly fitting fuel caps, and they indicated that observed fuel cap failure rates are higher in older vehicles. Losses increase in summer in these vehicles due to warmer temperatures.

Urban wide studies and national inventories

The BTEX group of compounds has wide use in urban areas. Xylene has many sources as an industrial solvent and raw material. End products include architectural coatings, wood coatings, adhesives and sealants used in residential and commercial applications. The inset box below provides background information on VOC sources in urban environments. Although there are no inventories of VOC use in New Zealand, many countries operate national inventories which provide data on emissions by industry.

Urban landuse studies - Emission of VOCs

Chang et al. (2006) considered xylene was predominantly sourced (about 80%) from vehicle emissions. However, for toluene, 55% was identified as being derived from vehicles. Spatial variation in airborne C3-C12 hydrocarbons occurred from rural to residential to industrial to roadside locations in Hong Kong (So & Wang, 2004). Seasonal variation in concentrations was attributed to evaporation of fuel, and the toluene to benzene ratio was dependent on the aromatic hydrocarbon content in unleaded petrol.

Guo et al. (2004) measured non-methane hydrocarbons at two sites: 39% and 48% of the total NMH came from vehicle emissions, 32% and 36.4% of the total non-methane hydrocarbons came from solvent use and 11% and 19.4% were attributed to LPG or natural gas leakage, 5.2% and 9% of the total non-methane hydrocarbon mass concentration was attributed to other industrial, commercial and domestic sources. It was also found that vehicle emissions and LPG or natural gas leakage were the main sources of C3–C5 alkanes and C3–C5 alkenes while aromatics were predominantly released from paints.

Choi et al. (2011) reported that solvent sources account for the largest portion of total nonmethane hydrocarbons at suburban and urban areas in South Korea. Their analysis at three urban locations classified sources into stationary combustion and transport, fugitive emissions from fuel, industrial process, solvents (including coatings) and undefined. They noted:

- A 'coating source' (solvents) was represented by high concentrations of toluene, n-octane, nnonane, n-decane, n-undecane, methylcyclo-hexane, n-heptane and methylheptane.
- One evaporative source with an abundance of C2-C5 alkanes (from natural gas, LPG and gasoline vapour). A second evaporative source had an abundance of C4-C6 alkanes, such as isopentane, n-pentane, isobutane, and n-butane, followed by 2-methylpentane and nhexane.
- A 'petrochemical source' was characterised by ethylene and propylene and a 'refinery' fugitive source by C3-C5 alkanes, n-hexane, 2- and 3- methylpentanes, toluene and benzene. Combustion sources had an abundance of typical combustion products, such as ethylene and acetylene, and fugitive emissions from natural gas and other combustion.

THE MANAGEMENT OF HYDROCARBONS IN STORMWATER RUNOFF

The European Environment Agency (2007) indicates that solvent use is a major contributor to (non-methane) VOC (NMVOC) emissions, accounting for about 25% of the man-made NMVOC emissions. Choi *et al.* (2011) summarised that solvent sources accounted for 58.3% of NMVOC emissions in South Korea, compared to industrial processes (17.3%), transport (15.3%), waste (4.4%), fugitive emissions from fuel (3.3%), and stationary combustion (1.4%). They reported that solvent source contributions in other countries range from 31.7% in France to 74.0% in Japan.

The Australian National Pollutant Inventory provides data relating to a range of sources of hydrocarbons. Table 2 identifies sources of MAH emissions in Australia. The National Pollutant Inventory Database shows that benzene emissions are dominated by emissions to air from vehicles, followed by solid fuels and then other sources such as lawn mowing, boats and service stations. Toluene is dominated by emissions to air, with vehicles being the dominant source. However, architectural coating, domestic and commercial solvent and a number of other sources, deliver an amount similar to vehicles. Xylene emissions follow a pattern similar to toluene.

MAH	Industry	Transport	Diffuse	Consumer
Benzene	Industries producing, using or handling, benzene such as the rubber industry, oil refineries, chemical plants, footwear manufacturing and petrol.	Vehicle exhaust, evaporation of vehicle fuels from motors and vehicle fuel tanks.	Present in crude oil and cigarette smoke. Releases to air from service stations; evaporation of fuels during petrol refilling; releases to groundwater from underground storage tanks that leak.	Glues, adhesives, household cleaning products, paint strippers, some art supplies and petrol. These products may contain benzene as a contaminant rather than a deliberately added component (e.g. Shellite may contain 0.1% benzene by volume).
Toluene	Oil refiners, chemical industry, rubber manufacturers, pharmaceutical industry, metal degreasing, printing, manufacturers of paints, varnishes and lacquers. These emissions are mainly to the air, but are also to soil and water.	Some toluene is found in vehicle exhaust.	Vapours and spilling of petrol, commercial and household painting and paint, varnish and lacquer removal, tobacco smoke, and consumer products containing toluene. These emissions are to the air unless there is a spill.	Adhesives, auto-polish and cleaners, floor polish, hard surface cleaners, paints, inks, paint cleaners, paint and varnish removers and thinners, coatings, particleboard, leather dressings, lubricating oils, fingernail enamels and removers, shoe polish and cleaners, solvent thinned products (e.g. exterior stains and primers), colouring pens and markers, wood office furniture, vinyl flooring.

Table 2: Emission sources for key MAHs

MAH	Industry	Transport	Diffuse	Consumer
Xylene	Chemical and petrol manufacture, polyester manufacture, manufacture of paints, dyes, and lacquers. Most xylene emissions will be to the air, unless there is a spill. Much of spilt xylene will end up as an airborne pollutant due to evaporation.	Motor vehicles give off emissions to the air.	Commercial and household painting, woodburning stoves, and fireplaces. These emissions are to the air.	Xylenes are common in domestic products such as aerosol paints, automobile and machinery paints and primers, caulks, insecticides and fungicides, hard surface cleaners, lubricating oils, markers, automotive chemicals, paints and paint removers and thinners, pet flea and tick products, pesticides, shoe polish, interior clear finishes, undercoats, sealants, resin and rubber adhesives, water proofing and wood office furniture.

Source: Australian National Pollutant Inventory database: http://www.npi.gov.au/substances/fact-sheets.

4.2.3 Polycyclic aromatic hydrocarbons

PAHs are a class of widespread semi-VOCs that are distributed between the vapour and particulate phases in the environment. The properties of the PAHs change as their molecular weight changes. LMWPAHs (i.e. the two ringed compounds - refer Section 2.3) are more common in the vapour phase, while HMWPAHs with five or more rings are predominantly associated with particles. This vapour-particle distribution has a significant influence on the PAHs seen in each environmental compartment and on changes observed in the composition of materials containing PAHs over time.

The ratios of different PAH sources have commonly been used to help identify the sources that contribute to the PAHs (e.g. those that are petrogenic and those of pyrogenic origin) in different environmental media (e.g. soil, sediment, water, air). Tobiszewski & Namiesnik (2012) and Alam *et al.* (2013) both concluded that ratios are affected by different factors in different environments and in particular, ratios derived from low molecular weight PAHs should be used with caution due to their reactivity.

Vehicle sources

Vehicles contribute PAHs to the local and regional atmosphere from fuel combustion. Vehicles contribute PAHs to the road surface from exhaust particle impaction and deposition, condensate loss from exhaust systems and crankcase oil loss where it occurs (PAH concentrations in used oil can be in the order of 1% [Ngabe *et al.*, 2000]). Kennedy *et al.* (2002) and Moncrieff & Kennedy (2004) provide information on PAH emissions from motor vehicles in a New Zealand context.

Other key factors regarding source contributions are the changes that may have occurred over time in the composition and load contributed by a particular source, especially when comparing older and newer data. Kennedy *et al.* (2002) and Moncrieff & Kennedy (2004) summarised PAH concentrations in a range of diesel fuel types (available at that time). Traffic emission composition has changed markedly in recent years. Hesterberg *et al.* (2011) and McClellan *et al.* (2012) reported that more stringent emissions standards for particulate matter in diesel exhaust resulted in significant technological advances in diesel engine technology and diesel fuel/lubricant composition. The exhaust emissions from new technology (refer Hesterberg *et al.*, 2008) are considered by Hesterberg *et al.* (2011) to be similar to particulate emissions from natural gas and

petrol engines. Their review identified an 80% or more reduction in hydrocarbons, such as alkanes, single ring aromatics, and more than 90% reduction in PAHs between 2000-04 and 2007 diesel engines.

New Zealand introduced legislation (the Land Transport Rule: Vehicle Exhaust Emissions 2003) supporting vehicle emission standards in 2003. This resulted in a progressive improvement in emissions such that the standards were updated in 2010 to incorporate the Euro 5 emission standards. The mean hydrocarbon emissions for a vehicle meeting Euro 5 standards are 85% less than a pre-2003 vehicle (refer Kuschel *et al.*, 2012 and inset box). These decreases are similar to the changes identified by Schneidemesser *et al.* (2010) and described in the previous section.

Vehicle hydrocarbon emissions in New Zealand

Kuschel et al. (2012) describes the changes in hydrocarbon emissions from the light vehicle fleet in New Zealand. They conclude that hydrocarbon emissions are significantly higher for pre-2003 age petrol vehicles compared to more modern vehicles. They identified that an average vehicle in the overall light fleet in 2011 now emits 39% less hydrocarbons relative to 2003. The corresponding figure for the diesel light fleet was 67%.

Petrol vehicle emissions declined to 37% of the 2003 value and the new (in New Zealand) petrol vehicle emissions fell to 31% of what they were in 2003. Emissions from Japanese imports did not fall as much. Diesel vehicles decreased to 67% of what they were in 2003 with a lower decline to 48% for Japanese imports. Overall, the improvements identified in the emissions from the diesel fleet come from improvements in New Zealand new vehicles.

Roof runoff and landuse

Roofs and other impervious surfaces in urban areas act to accrue deposited particulates and collect rainfall along with particulates and gases washed out of the atmosphere. As such, roof runoff composition reflects general and regional atmospheric quality (and therefore emissions to air).

Kingett Mitchell & Diffuse Sources (2004) reported that total PAH concentrations ranged from less than 81 μ g/m³ in rural roof runoff to 211 μ g/m³ in residential roof runoff to 476 μ g/m³ in roof runoff from industrial areas of Auckland. The results from the study indicated that the lower molecular weight PAHs (2-3 rings) such as naphthalene were more common in the wet and/or dry deposition occurring in industrial areas. Higher concentrations of some four-ring PAHs (e.g. pyrene and fluoranthene) also occurred in higher concentrations in industrial areas. However, concentrations of many HMWPAHs were lower and less varied between land uses.

Exposure to coal tar based PAHs has been identified as a concern in parts of the US where coal tar based sealcoats are used for roof and parking lots. Witter et al. (2014) reviewed PAH sources and source profiles in an urban area in Pennsylvania. Their study found strong correlations between rural sediments and cokeoven emissions sources and between urban sediments and coal tar based sealcoat "dust", supporting other work in various locations in the US (refer Witter *et al.* 2014) that coal tar based sealcoat is an important urban PAH source. Auckland Regional Council's Technical Publication 378 – *Polycyclic Aromatic Hydrocarbons in Auckland* records that historic coal tar roads are also a significant PAH source in specific localised areas of Auckland, such as Motions Creek (Depree & Ahrens, 2007a).

4.2.4 Total petroleum hydrocarbons

A wide range of hydrocarbons are stored, handled and used throughout urban environments. It is not possible to describe within this review, the large variety of sources and manner of handling hydrocarbons that might result in losses of TPH to the environment that could then result in hydrocarbons entering stormwater. Hydrocarbons are stored and handled in a range of industries and commercial premises. There is no means of identifying what these sources are without a hydrocarbon life-cycle analysis being available.

Some 60 million litres of lubricating oil are sold every year in New Zealand (Auckland Council, 2015) and about 50% of this is recycled, with the remainder considered to be lost through burning or leakage (e.g. refer Norris *et al.*, 2006)¹. EPA (2013) identifies methods of disposal of used oil that are not appropriate (and contravene a variety of regulations). It is likely that there are also intentional losses of hydrocarbons to stormwater through inappropriate wash-down of impervious surfaces and the disposal of used oil, in particular through home vehicle oil changes and maintenance.

Kennedy *et al.* (2002) describes hydrocarbon sources associated with motor vehicles including engine oil, other oils, greases, used oil, lubricants, transmission and hydraulic fluids and engine exhaust emissions. Other non-vehicle sources include compressor oils, electrical insulation and heat transfer oils (EPA, 2013 provides examples of used oil sources) and a large range of oils used in food manufacturing and in commercial and residential food preparation.

Although New Zealand has had guidelines for the management and handling of used oil for more than a decade (MfE, 2000), there appears to be no information available on the extent of losses from this potential source. Likewise, there appears to be no published data on the incidence of industry and commercial sourced hydrocarbon spillages.

4.3 Summary

The broad sources of hydrocarbons in Auckland in terms of landuse are urban, industrial and rural. Each of the identified land uses has its potential point sources, and within each landuse, different sources contribute different proportions of hydrocarbons.

The sources of hydrocarbons contributing to urban stormwater include, but are not limited to, the following:

- Atmospheric deposition of hydrocarbons to impervious sources such as building roofs, pavements, carparks or roads. These hydrocarbons are sourced principally from combustion of fuels in vehicles, heating (wood and coal fires), garden and other fires and a proportion from evaporation from stored and lost hydrocarbons (e.g. spillage and broken hydraulic seals)
- Losses of petrogenic hydrocarbons from motor vehicles and equipment (e.g. broken seals and hoses)
- Losses of petrogenic hydrocarbons from retail facilities (e.g. from petrol stations)
- Losses of petrogenic hydrocarbons from industrial premises (e.g. stored hydrocarbons)

¹ The Environmental Protection Authority/Te Mana Rauhi Taiao (EPA) provides a code of practice for the management and handling of used oil in New Zealand. The code provides guidance to used oil generators, collectors, transporters, processors and end users and regulatory authorities on compliance with regulatory and statutory controls on used oil (EPA, 2013).

- Production of pyrogenic hydrocarbons by vehicles (e.g. petrol, diesel, natural gas and LPG fuelled) • and home heating (e.g. natural gas and LPG burners)
- Emissions of pyrogenic hydrocarbons from industrial facilities with gas and oil-fuelled heaters and • incinerators
- Losses of hydrocarbons from building materials (including roof sealants and shingles containing • hydrocarbons, roading construction materials)
- Losses of petrogenic hydrocarbons through inappropriate disposal of fuels and used oils •
- Losses of petrogenic hydrocarbons through spillage during storage. •

5.0 Comparison of hydrocarbon sources

5.1 Introduction

One of the key questions regarding Auckland stormwater quality is "how does Auckland's stormwater quality compare to elsewhere in relation to hydrocarbons?" This question is important because, if the quality of stormwater in Auckland is similar to stormwater quality elsewhere in relation to hydrocarbons, then best practice to improve stormwater hydrocarbon contamination identified elsewhere can be adopted in Auckland. However, if the quantity or diversity of hydrocarbons in Auckland's stormwater is unique, best practice elsewhere may not necessarily be appropriate.

In the previous section, information was presented that showed that hydrocarbons are derived from a wide range of sources in urban environments. Many of these sources have varying profiles (e.g. transport emissions determined by transport fleet and fuel composition) and the regional profile of many hydrocarbons is determined by the scale of industry within those areas (i.e. the significance of a particular industry).

Hydrocarbon loss on road and parking lot surfaces is evident through visible oil sheens during rain events. Griffiths & Timperley (2005) noted that although the oil observed in sheens or floating in catchpits is only a few molecules thick, "the total amount of oil washed off our streets either floating, dissolved or bound to particulate matter, is quite large". However, the amount was not quantified or compared to other areas.

This section provides a summary of available monitoring information regarding hydrocarbons in stormwater (and in sediment suspended in stormwater) for Auckland, elsewhere in New Zealand, and internationally. In this review of hydrocarbons, it has not been possible to assess how differences in methodology (associated with sampling, sample handling and analysis etc.) have influenced results reported in the literature. It is particularly important that the methods used (especially for volatile hydrocarbons such as the BTEX group) are appropriate and that:

- Individual samples are collected using methods to preserve sample integrity (i.e. prevent loss of volatile hydrocarbons)
- Samples collected are representative of storm events (e.g. only first flush is included in sampling). It is assumed all studies have been conducted appropriately.

5.2 Hydrocarbons found in stormwater across Auckland

5.2.1 Introduction

This section provides an overview of available information on hydrocarbons in stormwater generated within the Auckland region. The information provided encompasses a broad range of studies that have investigated hydrocarbon concentrations in runoff from roads, roofs, service stations and carparks. The results of studies investigating hydrocarbon concentrations in stormwater as a function of landuse are also reviewed.

5.2.2 Roads

There appears to be no data on BTEX and very little data for PAH concentrations in stormwater, specifically from major roads in Auckland.

Moores *et al.* (2009c) found TPH concentrations in untreated road-runoff from SH1 (State Highway1) (at Northcote and Redvale) were below the routine detection limit of 0.7 g/m³. Of 57 samples collected from SH16 at Huapai, a single sample had a TPH concentration of 0.77 g/m³. The remainder had no detectable TPH (below 0.7 g/m³). TPH concentrations in the runoff from SH16 at Westgate were similarly, more often below the detection limit (57 out of 65 samples). In the samples where TPH was detected, concentrations ranged from 0.84 g/m³ to 3.9 g/m³. The occasional detection of TPH in road runoff was attributed to traffic congestion.

Kennedy & Gadd (2003) examined PAH distribution at 32 locations on roads throughout Waitakere City. The median total PAH concentration in road-derived sediments (RDS) was 1.46 mg/kg. Their study reported a median total PAH concentration of 1,462 µg/kg. Davis *et al.* (2010) identified calculated PAH 'yield' data for PAHs based on vehicle traffic numbers and indicated that potential concentrations might range from 0.02 g/m³ for roads with less than 1,000 vehicles per day up to 2.73 mg/m³ for roads with less than 100,000 vehicles per day.

Kennedy *et al.* (2002) identified indicative differences in particulate matter and PAH emissions that were strongly dependent on road level of service and vehicle fleet composition on the road. Hence, it would be expected that observed stormwater PAH concentrations may be determined by a combination of factors.

Depree (2008) demonstrated that RDS from Auckland contained on average, higher concentrations of TPH than RDS collected in Hamilton, Ngaruawahia or Christchurch. No statistically significant difference was noted for PAH concentrations between cities/towns. A cause for this difference in TPH loads was not isolated, but as most of the TPH present were "heavy" (e.g. bitumen), it is possible that the differences were due to differences in road materials used by the cities.

Macaskill and Williamson (1994) estimated that as of 1994, vehicles contributed 40% of the PAHs found in New Zealand stormwater.

5.2.3 Service stations and carparks

URS (2008) reported BTEX, TPH and PAH concentrations measured in stormwater samples collected at five petrol stations in Auckland. Samples were collected at the entry to the American Petroleum Institute (API) separators on-site and in the discharge from the separators during first flush and mid-storm. Samples were also collected from the non-forecourt areas of each service station and from two control sites (a commercial office carpark and the Auckland Museum carpark).

Mid-storm samples were collected from the non-forecourt areas of the service stations and BTEX compounds were not detected with the exception of toluene at one site (6 mg/m³). Benzene was not detected (less than 1 mg/m³) in the first flush and mid-storm samples from the two control carparks. However, the other BTEX compounds were detected in the stormwater from one of the two carparks (1 mg/m³ to 3 mg/m³). No BTEX compounds were detected in the inlet samples of two of the five petrol stations. At the other three, one site had elevated concentrations of ethyl-benzene and xylene in both first flush and mid-flow samples; one site had elevated toluene concentrations in both first flush and mid-flow

samples; and one site had a low concentration of ethyl-benzene in first flush sample only. The API outlet stormwater of one service station contained elevated concentrations of all BTEX compounds at the time of sampling (maximum 205 mg/m³ toluene).

TPH concentrations in the stormwater samples collected from most of the service station sites were below 15 g/m³. At four stations, the API inlet concentrations ranged from less than 0.2 g/m³ to 9.5 g/m³. The corresponding outlet concentrations ranged from less than 2 g/m³ to 11.8 g/m³. At two service stations, the outlet concentration was higher than that measured in the inlet, indicating the inlet and outlet samples were not well matched. TPH was detected in samples of stormwater from non-forecourt areas. A TPH of 15.2 g/m³ was measured in the non-forecourt area sample at one service station and was considered to have arisen due to an inappropriate drainage system. TPH was not detected at the control carparks (less than 0.4 g/m³).

At one service station, low concentrations of PAHs (specifically, anthracene and phenanthrene) were detected in the API inlet samples, but were below the analytical laboratory detection limit in the API outlet sample. The concentration of most PAHs in stormwater at the other four service stations were typically below the detection limit or where detected, were just above the detection limit, in the range of 0.1 mg/m³ to 0.5 mg/m^3 .

The analysis of TPH and PAH concentrations associated with sediment in the API separators in the URS (2008) study identified high concentrations of TPH, with concentrations appearing to reflect the time since maintenance was carried out. It was considered by URS (2008) that the high concentrations reflected the separators' effectiveness at removing sediment with attached TPH. The concentrations may also have reflected the amount of time since the sediment was last removed from the separator (i.e. a longer contact time). Most sample concentrations were similar to concentrations measured in road catchpits and in suspended sediment in urban stormwater (refer Section 5.2.2).

Moores *et al.* (2009a) analysed sediment samples from catchpits receiving stormwater from different industrial landuse activities, including service stations. However as described in the following section, although the TPH concentrations were high in the samples collected from service station catchpits (presumably on site with no other contributing stormwater sources), the number of samples was small and the location of the catchpits in relation to the service station has not been validated.

5.2.4 Landuse

Stormwater studies

In a study of stormwater quality in Auckland City catchments, Griffiths & Timperley (2005) reported the lowest concentrations of TPH and PAH in localised residential catchments (Mission Bay and Cox's Bay) with higher concentrations in the central business district Aotea catchment. The median concentration for the Onehunga catchment was similar to residential catchments. In that case, it was concluded the similarity reflected the activities within the Onehunga catchment.

Moores *et al.* (2009b) measured TPH in samples collected from 15 storm events in a high traffic volume residential/commercial road (Richardson Road). Most samples contained less than 0.7 g/m³ TPH (<0.1 g/m³ to <0.5 g/m³ in the three carbon bands). TPH was detected in 14 samples over nine events, with a tendency for TPH to be detected early in the storm. In all but one of the event series samples collected, the TPH was detected in the C15-C36 band (range 0.41 g/m³ to 1.5 g/m³). As described in Section 5.2.2, Moores *et al.* (2009c) reported few detectable TPH analyses in stormwater from State highways.

Kingett Mitchell (1992) examined TPH and PAHs in stormwater in Pakuranga (residential) and Southdown (industrial) catchments. They reported low, but detectable, concentrations of TPH in stormwater from both catchments (1.9 g/m³ to 8.3 g/m³).

Total PAH concentrations in roof runoff in Auckland were assessed by Kingett Mitchell & Diffuse Sources (2004) as part of a wider study of roof runoff quality. Total PAH concentrations were typically higher in roof runoff from industrial catchments (median 476 μ g/m³) compared to residential catchments (median 211 μ g/m³) and rural roofs (median <81 μ g/m³).

In the absence of any source PAH on the roof (e.g. tar), the primary source of PAH is probably the same for roofs and roads, and the concentration may be similar (for house roofs close to roads). In the presence of other sources (e.g. wood and coal house fires), the contribution of total PAH from roofs probably increases.

Sediment studies

A number of studies have examined hydrocarbon (principally PAH) concentrations in particulate material on road surfaces and sediment catchpits with reference to landuse (refer inset box below).

TPH in catchpit sediments

Moores et al. (2009b) also assessed TPH in Richardson Road catchpits. TPH concentrations in whole samples (total of all carbon chain length ranges) varied from 490 mg/kg to 1,600 mg/kg. About 95% of the TPH was present in the C15-C36 carbon band and hydrocarbons were only detected in two of 10 samples in the C7-9 band.

Gadd et al. (2009) analysed sediment samples from 19 catchpits in industrial sites in the Whau catchment (New Lynn, Te Atatu, Glendene, Kelston, Titirangi, Green Bay Glen Eden, Avondale, Blockhouse Bay and Mt Albert). All of the samples collected in the study contained TPH concentrations more than 1,000 mg/kg and ranged up to 39,500 mg/kg. TPH concentrations were typically highest in catchpits associated with service station sites and lowest in the catchpits of paint manufacturers. Automotive, timber treatment and plastic manufacturing industries were also considered. Hydrocarbons with C15-C36 length chains (i.e. petrogenic hydrocarbons such as diesel and oils) typically comprised more than 88% of the hydrocarbons measured.

Kingett Mitchell (1992) provided information on TPH and PAHs in road gutter dust sediment in the Pakuranga (residential) and Southdown (industrial) catchments. They reported high concentrations of TPH (up to 12,600 mg/kg) in fine suspended solids in stormwater. High TPH concentrations were also measured in stormwater pond sediment (up to 7,700 mg/kg). Overall, TPH was associated primarily with TSS and mostly, with finer particles of sediment. TPH comprised a significant proportion of alkanes in the C12-C30 range. PAH concentrations in both catchments were similar (960 µg/kg and 773 µg/kg). PAH concentrations also increased as particle size became finer. PAHs in the Auckland study were dominated by fluoranthene and pyrene.

Kingett Mitchell & Diffuse Sources (2004) identified that naphthalene (and methylnaphthalene) were important compounds amongst the suite of PAHs with concentrations paralleling the dominant PAH, phenanthrene. Concentrations of a number of LMWPAHs in samples from industrial sites were higher than either residential or rural concentrations. The concentrations of a number of HMWPAHs were higher in industrial sites compared to rural sites (Kingett Mitchell & Diffuse Sources 2004).

Depree & Ahrens (2007a) examined possible sources of PAHs in sediment in Auckland estuaries. They reported that stormwater runoff particulates had PAH compositions of intermediate origins (between petrogenic and pyrogenic sources). The petrogenic traffic-related petroleum discharges include tyre abrasion and oil and lubricant losses. Auckland air particulates have very similar composition to stormwater runoff particulates. The authors' assessment concluded that current sources in stormwater did not appear to be sufficient to account for the PAHs observed in estuarine sediments. This is discussed further in Section 6.

5.2.5 Key findings

Limited data for stormwater quality from a small number of service stations and carparks in Auckland indicate that there is potential for BTEX and PAHs to be discharged to the stormwater system. However, service stations with well-maintained treatment systems will have low discharge hydrocarbon concentrations. There appears to be little published stormwater hydrocarbon data specifically relating to carparks in New Zealand. Stormwater management devices installed in facilities, such as carparks, will treat a number of pollutants including hydrocarbons.

There are a number of indirect studies (roof runoff, RDS and catchpit studies) in the Auckland region providing information on hydrocarbon concentrations in stormwater relating to landuse. Examination of catchpits shows a large variation in TPH concentration in sediment with a suggestion that service station sediments had high TPH compared to sediments in catchpits associated with other industries. However, the dataset in the study contained a low number of samples. Previous studies that showed differences in catchpit sediment TPH concentrations were attributed to the nature of the materials used in road manufacture; however, this was not substantiated. Roof runoff data suggest that PAH concentrations differ significantly between landuse, with higher concentrations in roof runoff in industrial areas. Estimates have been made that attribute significant proportions to motor vehicle emissions.

5.3 Hydrocarbons found in stormwater nationally

5.3.1 Introduction

Generally, most territorial authorities in New Zealand place monitoring requirements on consent holders, rather than undertake independent monitoring of hydrocarbons in stormwater themselves. The onus on consent holders to collect data means that, similar to Auckland, few data are publicly accessible without knowing specific consent numbers. Environment Canterbury Regional Council (ECan) is an exception to this, as data for all consents for the region are available through ECan's website. However, while the number of stormwater consents in the region can therefore be easily identified, monitoring data were generally unavailable except on specific request.

Kennedy (2003) summarised available data on stormwater associated hydrocarbons in New Zealand up to 2004 and determined that, at that time, no data were available for VOCs, such as BTEX in stormwater. The focus of this section is on published studies of stormwater quality throughout New Zealand.

5.3.2 Waikato

O'Riley *et al.* (2002) measured the concentration of four PAHs during six rainfall events in Hamilton. The event mean concentrations ranged from 90 μ g/m³ to 376 μ g/m³ for phenanthrene, 104 μ g/m³ to 665 μ g/m³ for fluoranthene and 211 μ g/m³ to 1,490 μ g/m³ for pyrene. Benzo-[a]pyrene was not detected. Depree (2008) observed no significant difference between TPH or PAH concentrations in the RDS of Hamilton catchpits and street sweepings compared to RDS in Auckland.

5.3.3 Bay of Plenty

As part of a more general stormwater assessment, Macaskill *et al.* (2003), reported that TPH concentrations in Rotorua stormwater were typically below detection limit (0.2 g/m³), with TPH being detected in only a single sample out of seven. The stormwater with measurable (albeit low) TPH (0.5 g/m³) came from an industrial catchment.

5.3.4 Hawke's Bay

Stormwater data for the Hawke's Bay region have been summarised in Aquanet (2011). PAH compounds have been detected in industrial site stormwater discharges. Concentrations have been low in stormwater, but "high" abundances (greater than Australian and New Zealand Environment and Conservation Council [ANZECC] interim sediment guidelines [ANZECC, 2000]) of PAH compounds have been reported in sediments in Napier's harbour, and in the Ahuriri estuary immediately downstream of Hawke's Bay's airport.

5.3.5 Wellington

Sherriff (1998) provided some of the earliest data on TPH and PAH concentrations in New Zealand stormwater, presenting data for motorway runoff in Porirua. TPH concentrations were less than the detection limit of 0.1 g/m³. Total PAH concentrations ranged from 0.0156 mg/m³ to 0.308 mg/m³ (mean 0.057 mg/m³).

Kingett Mitchell (2005) reviewed PAH data in the dissolved and particulate fraction obtained from stormwater samples collected through the Wellington region. Dissolved PAHs were detected in eight of the 11 stormwater samples collected, with the three samples that did not contain any measurable PAHs from residential catchments. For dissolved PAHs there was no apparent relationship between the land use and concentration or PAH compounds detected. The PAHs most often detected across all sites were pyrene and chrysene (high molecular weight 4-ringed PAHs). One residential site had a PAH profile dominated by low molecular weight PAHs, particularly naphthalene (210 μ g/m³). The survey did identify that the highest concentrations of dissolved PAHs (2.11 mg/m³) came from industrial catchments.

In the Wellington stormwater particulate samples, PAH concentrations were highest in larger particles, greater than 59 μ m, compared to size fractions less than 59 μ m. Although HMWPAHs dominated those samples with high PAH concentrations, low molecular weight PAHs were present in elevated concentrations in particulates from a residential site (e.g. 9.2 mg/kg naphthalene in 0.7-59 μ m particles). In general, no relationships were identified between the land use of the catchment and the concentration or type of PAH compounds detected. The PAH profiles of the Wellington stormwater particulate material were variable but did demonstrate a similar dominance of phenanthrene, fluoranthene and pyrene suggesting vehicle-related sources of PAHs. Overall, Kingett Mitchell (2005) concluded that the concentration of PAHs in suspended

particulates exceeded the ANZECC (2000) trigger values for PAHs in a number of samples for most PAHs. The high interim sediment quality guideline (ISQG-High) was exceeded for some PAHs.

In summary, a range of PAH data has been collected in urban stormwater (in the dissolved fraction and in particulates) from the Wellington region. The stormwater particulate data indicates that exceedances of ANZECC (2000) trigger values occur and as such, the potential for contributing to adverse effects in sediments (sediment data are described further in Sections 6.3 and 6.4).

5.3.6 Canterbury

There have been a number of stormwater studies in Christchurch, but little TPH and PAH data have been reported. Pasco (2005) and Brough & Eastman (2005) reported no detectable TPH (less than 0.2 g/m³) in stormwater entering an infiltration basin present in new residential subdivisions in the Upper Heathcote catchment.

Adams *et al.* (2007) conducted stormwater quality monitoring of the Fine Arts carpark at the University of Canterbury. Analysis of PAH concentrations in a stormwater sample from the carpark revealed no detectable PAHs (naphthalene <0.5 mg/m³ and all other PAHs <0.1 mg/m³). Similar low concentrations were noted in an earlier study of the Okeover stream also at the University of Canterbury (Taffs, 2007).

5.3.7 Otago

In Dunedin, Brown & Peake (2006) reported PAH data for RDS and in suspended solids in stormwater. The suspended sediment from a catchment with 20% urbanisation had concentrations similar to the road surface sediment. PAHs were considered to be pyrogenic. The suspended sediment from the Portobello Road catchment contained at least ten times more PAH (105 mg/kg to 503 mg/kg) than in stormwater sediments from a predominantly rural catchment (2.2 mg/kg to 10.8 mg/kg in the Water of Leith catchment). The PAH profiles and isomer ratios for the urban catchment indicated that a disused gasworks was contributing to the PAH concentration in stormwater runoff.

More recently, a range of data has been produced by Dunedin City Council on oil and grease and PAH concentrations in stormwater discharged to Otago Harbour from Dunedin City (as part of Dunedin City stormwater discharge consents). Oil and grease concentrations have been mainly below the detection limit, with the only detectable results of 6.4 g/m³ and 9.5 g/m³ in 2009 and 2010. PAH concentrations were mainly below detection limit, with occasional individual PAHs measured at 0.1 g/m³ to 0.3 mg/m³ for compounds such as fluoranthene and pyrene (DCC 2012; Ryder 2010).

5.3.8 Key findings

Sampling urban stormwater outside the Auckland region has typically shown non-detectable concentrations of TPH. Concentration data for individual PAHs have been obtained for stormwater from residential, commercial and industrial catchments in Rotorua, Wellington and Dunedin. PAH analysis of stormwater particulates in Wellington has shown the importance of suspended particulates in transporting PAHs, and the examination of PAH composition in Dunedin has shown that PAHs have been contributed to by historic gasworks.

5.4 Hydrocarbons found in stormwater internationally

5.4.1 Introduction

This section provides a snapshot of international research from Australian, North American and Asian studies to compare to the results of New Zealand studies. For ease of comparison with New Zealand data, the results of international research are presented by hydrocarbon class (i.e. MAH and PAH).

5.4.2 Monocyclic aromatic hydrocarbons

Kennedy (2003) provided a summary of published MAH data in stormwater. That review noted early United States Geological Survey work (Delzer et al. 1996) that examined VOCs in stormwater in the United States. Table 3 summarises the results for the BTEX group of compounds presented in Delzer et al. (1996) and those reported in Borden et al. (2002), who examined BTEX compounds at sites draining petrol stations and a range of land uses in North Carolina.

Hydrocarbon	Median (mg/m ³⁾	Maximum (mg/m ³)	Detection frequency (%)	Reference
Benzene	0.09	0.15	6.5	Borden <i>et al.</i> (2002)
T 1	0.11	32.84	64.8	Borden <i>et al.</i> (2002)
loluene	0.3	6.6	23.2	Delzer et al. (1996)
	0.07	0.36	16.5	Borden <i>et al.</i> (2002)
Ethylbenzene	0.3	2	5.0	Delzer et al. (1996)
m-,p-xylene	0.09	1.62	68.2	Borden <i>et al.</i> (2002)
o-xylene	0.08	2.37	29.5	Borden <i>et al.</i> (2002)
Total xylene	0.4	6.6	23.2	Delzer <i>et al</i> . (1996)

Table 3: Monocyclic aromatic compounds in stormwater

BTEX compounds were detected in virtually all stormwater draining downstream from commercial and industrial land uses and petrol stations, with a lower frequency of detection from open space and residential. The authors noted there was a correlation between the frequency of detection and the concentration in petrol, i.e. those compounds (such as toluene and xylene) present in higher concentrations in petrol than were commonly found in stormwater.

Analysis of data by landuse showed that percent impervious surface was a good indicator of detection frequency for many of the aromatics. Median BTEX concentrations in runoff from commercial, industrial and mixed small catchments were similar to median concentrations in petrol station runoff (Borden et al. 2002).

5.4.3 Polycyclic aromatic hydrocarbons

Herngren *et al.* (2010) and Rianawati & Balasubramanian (2009) investigated PAH concentrations in urban stormwater in Queensland and Singapore, respectively. Herngren *et al.* (2010) reported the distribution of PAHs in simulated road runoff samples from residential, commercial and industrial sites in Queensland. The study reported PAH concentrations in dissolved phase and in three particle size fractions. Rianawati & Balasubramanian (2009) provided data for dissolved phase PAHs alone. The key points arising were:

- The most common compound found at all sites was naphthalene, both in dissolved and particulate forms. The Singapore stormwater study reported high concentrations of dibenzo[a,h]anthracene compared to the Gold Coast study
- Very low concentrations were reported in the dissolved fraction for all PAHs. However, it was noted that it was possible to see higher dissolved concentrations in the presence of elevated concentrations of dissolved organic carbon
- PAH concentrations in particulates were higher in small particles compared to larger particles. PAHs are predominantly particle-bound due to their solid-water and octanol-water partition coefficients. However, a range of particle size relationships have been reported in the literature. There are a range of site-specific factors relating to organic matter distribution in particle size classes that will influence PAH concentration distribution
- PAH concentrations were higher in samples and particles from the commercial and industrial sites compared to the residential samples. This was considered to be attributable to higher vehicle numbers and a greater range of potential sources
- Regardless of the landuse and particle size fraction characteristics, the presence of organic carbon plays a key role in the distribution of PAHs.

A range of studies have been undertaken on stormwater runoff from parking lots. On-road and off-road parking lots have different characteristics compared to roads. Parking lot studies in the United States have shown significant concentrations of PAHs in stormwater due primarily to the use of coal tar based emulsions in some locations (refer following inset box).

Green (1998) also provided a summary of aliphatic hydrocarbon and PAH concentrations in Australian stormwater. In Sydney, measured PAH concentrations ranged from 0.2 μ g/m³ to 41 μ g/m³ and aliphatic hydrocarbons ranged from 0.6 mg/m³ to 21 mg/m³, compared to stormwater from Hobart, where PAHs were typically lower (0.19 μ g/m³ to 5.35 μ g/m³), but total hydrocarbons were similar (0.26 μ g/m³ to 23 mg/m³).

Hwang & Foster (2006) showed that PAH concentrations in storm flow were higher (1.51 mg/m³ to 12.50 mg/m³) than in base flow samples (0.089 mg/m³ to 0.457 mg/m³) and were significantly enriched in the particle phase, which accounted for 87% (68%-97%) of the total PAHs. Dissolved PAHs dominated base flow concentrations.
Parking lots and sealcote

Steuer et al. (1997) identified that sealed commercial parking lots in Marquette Michigan were a major contributor of PAHs to stormwater. Corsi et al. (1999) provided data for carpark stormwater PAHs showing that the majority of the PAHs were associated with particulate material. Mahler et al. (2004) reviewed the quality of carpark runoff where the carpark had been sealed (coal tar emulsions) and found that particulates contained high concentrations of PAHs. Wash off from carparks contained dissolved PAHs with a mean of 8.6 mg/m³ for coal tar sealed parking areas and a concentration of 0.24 mg/m³ for an unsealed carpark.

Selbig (2009) examined hydrocarbons from streets, roofs, mixed landuse and commercial parking areas. The parking lots included sealed and unsealed surfaces. On average, chrysene, fluoranthene and pyrene were the dominant PAH compounds in all urban stormwater samples. Naphthalene was not detected in this study, but as described in Section 5.4.3, naphthalene can be common in stormwater. Geometric mean concentrations for most individual PAH compounds were significantly greater for a parking lot that was sealed than for lots that were not sealed.

As described for New Zealand, coal tars in the USA have been identified as a significant source of PAHs in stormwater. As part of the Great Lakes PAH reduction project, the use of coal tar based sealcoats are banned in Minnesota from 2014, with prior city bans already in effect in most cities within the state (Minnesota Pollution Control Agency [MPCA] 2013). Parking lots produced the highest concentration for all of the individual PAH compounds (summation equal to 64 mg/m³) with rooftops contributing between 0.61 mg/m³ and 2.06 mg/m³ and low, medium and high traffic streets 1.7 mg/m³, 11.4 mg/m³ and 15.2 mg/m³, respectively (Selbig et al. 2009).

5.4.4 Total petroleum hydrocarbons

Early publications by Hunter *et al.* (1979) and Hoffman *et al.* (1982) provided information about hydrocarbons in stormwater. Hunter *et al.* (1979) provided information on hydrocarbon concentrations in stormwater runoff in Philadelphia showing that average total hydrocarbon concentrations were 3.7 g/m³ with 0.4 g/m³ of the total in the dissolved form. Hoffman (1982) identified that flow-weighted total hydrocarbon concentrations ranged from 0.69 g/m³ to 2.15 g/m³ and that of the hydrocarbons, 83-93% were associated with particulates.

Williamson (1993) provided data for TPH in stormwater in the United States (Table 4). In the 1993 review, it was noted that the likely concentrations varied over an order of magnitude, and therefore predicting "typical" hydrocarbon loads in stormwater was difficult.

Table 4: TPH in stormwater from US locations

Area	Catchment	EMC
North East USA	Commercial	1.4
Philadelphia	General urban	2.5-5.9
Los Angeles	General urban	13.1

Notes: EMC = Event mean concentration of total hydrocarbons (g/m³); data reproduced from Williamson (1993) and references therein.

5.5 Summary

5.5.1 Monocyclic aromatic hydrocarbons

There are very little MAH (and in particular, BTEX) concentration data available on urban stormwater in New Zealand. International monitoring has identified low concentrations of BTEX compounds in stormwater, with the compounds measured being related to the relative abundance of the compound associated with sources (e.g. the concentration in vehicle fuels). Examination of service station stormwater quality in Auckland detected BTEX compounds in the inlets to treatment devices but concentrations were at, or below, the limit of detection at most service stations. Low concentrations of BTEX compounds were detected in stormwater from one Auckland carpark.

5.5.2 Polycyclic aromatic hydrocarbons

International data show that dissolved PAH concentrations are low and that PAHs in stormwater are primarily associated with particulate material with more PAH in smaller particles. These phase distributions reflect PAH physico-chemical properties. Examination of PAH concentrations in stormwater particle size fractions in Wellington showed that higher concentrations can be found in larger sized particles.

Detecting LMWPAHs in stormwater samples is dependent on a range of factors including losses from source occurring within a short time prior to sampling and the weather (effecting evaporation).

PAH concentrations have been measured in a range of studies in Auckland that have included roads, motorways and roof runoff. Concentrations reported have generally reflected international stormwater quality data but as there are a wide range of factors affecting concentrations, direct comparisons of studies have to be made with caution.

5.5.3 Total petroleum hydrocarbons

Recent road data (from key roads and motorways) in New Zealand suggests low concentrations of TPH in road runoff (detection limits of about 0.7 g/m³). Data collected for a range of catchments in Auckland indicates variability between catchments with higher concentrations in key commercial catchments, and that catchment TPH concentrations reflect a range of factors. TPH concentrations recorded in a limited number of carpark samples in Auckland have been measured at below 0.4 g/m³. Median concentrations recorded historically were typically 1 g/m³ to 2 g/m³. It has been suggested that lower concentrations may be a function of improvement in TPH losses from vehicles and other urban sources. However, measurement of TPH in stormwater is also a function of the time since deposition to surfaces, as hydrocarbons will be lost via evaporation.

TPH becomes associated with particles in stormwater (as most hydrocarbons have an affinity for organic matter and fine sediment). Elevated concentrations of TPH can be found in stormwater catchpit sediments. Limited sampling in Auckland suggested higher concentrations in the catchpit sediments of service stations compared to other industries.

The recent New Zealand data suggest lower concentrations than historic international data, however direct comparison is difficult as TPH sources may have changed over this time.

5.5.4 Key findings

MAHs are present in stormwater and international work has shown that BTEX compounds are detected in stormwater from commercial sites, such as petrol stations. Although there are international data for commercial and industrial land uses, there is no comparable information for MAHs present in stormwater generated in New Zealand.

International data show that PAH concentrations are typically low in the dissolved phase and most of the PAH transported in stormwater is associated with particulate matter. International stormwater studies have shown that naphthalene can be common in both dissolved and particulate phases, reflecting its properties.

Higher concentrations of PAHs have been identified in suspended sediment particles from commercial and industrial sites (compared to residential sites). This is reflected in roof runoff PAH concentrations by landuse from Auckland.

International studies have shown that in specific locations, the present use of tar products can introduce significant concentrations of PAHs into stormwater (refer inset box in Section 5.4.3). Although there is little information about such products in New Zealand, historic coal tar residues are locally important in some urban areas of Christchurch and Auckland. This is discussed further in Section 6.3 and elsewhere in this report.

While the limited local, national and international datasets are not sufficient for a thorough comparison of hydrocarbon concentrations, there is no evidence to suggest Auckland's stormwater pollutant profile is in any way unique. It is therefore assumed that the pollutant profile of stormwater in Auckland runoff is comparable to other areas.

6.0 Hydrocarbons in downstream environments

6.1 Introduction

A review of the available data for hydrocarbons in downstream environments shows that there are little data on MAHs (specifically BTEX) in water or sediment in New Zealand and no published data on PAHs in stream or coastal waters. In relation to TPH, data appear to be limited to sediments in urban areas, with very little TPH data for stream water as noted below. What data are available are summarised in the following sections. The lack of environmental data in some areas is potentially a reflection of:

- No formal recommendations to assess TPH or MAHs in stormwater
- No historical identification of aquatic effects relating to TPH or MAH that warranted sampling/monitoring of stormwater
- The cost associated with good quality (low detection limit) PAH analysis.

6.2 Hydrocarbons in stream waters

In 1999, stream quality samples were collected from 30 locations across Waitakere City in 25 catchments (Kingett Mitchell, 2000). Hydrocarbons (C7 through C44) were below the detection limit of 0.2 g/m^3 .

6.3 Hydrocarbons in freshwater sediments

6.3.1 Auckland

Kingett Mitchell (2000) reported TPH data for stream sediments in Waitakere City. No significant differences were found between landuse types, but this was attributable to the variation in concentration at the urban sites. TPH concentrations in reference upper catchment stream sites ranged from less than 5 mg/kg to 18 mg/kg. Of the 30 samples, 23 were less than 20 mg/kg with seven samples having concentrations between 38 mg/kg and 153 mg/kg. Examination of gas chromatography data for the sites where hydrocarbons were detected indicated that the TPH in the sediment was well weathered. No fresh hydrocarbon was detected. Bioresearches (1996) reported TPH data for Waitakere stream sediments (less than 15 mg/kg to 99 mg/kg) and Te Atatu Peninsula (less than 15 mg/kg to 587 mg/kg). Auckland Regional Council (ARC) (1992) reported concentrations of 224 mg/kg to 406 mg/kg in the Pakuranga stream in South Auckland.

Reed *et al.* (2008) reported data on TPH in and below a number of stormwater catchments in Auckland City. In the Motions Creek catchment, concentrations ranged from 210 mg/kg to 670 mg/kg. Reed *et al.* (2008) indicated that TPH concentrations had a different distribution to PAH, suggesting either different sources or fate (as the alkanes will degrade more readily than the HMWPAHs). The Motions Creek and Newmarket catchments had median TPH concentrations between 400 mg/kg and 500 mg/kg, compared to between 60 mg/kg and 100 mg/kg for the other three catchments (refer to Figure 5. Note that µg/g is equivalent to mg/kg). Reed *et al.* (2008) reported a median TPH in road runoff particulates of 1,300 mg/kg.

THE MANAGEMENT OF HYDROCARBONS IN STORMWATER RUNOFF



Figure 5: Median TPH concentrations in sediment from Auckland catchments (from Reed *et al.*, 2008).

Kingett Mitchell (2000) provided results for PAH compounds at eight sites in Waitakere City. Total PAH concentrations averaged 8.2 μ g/kg in sediments from three control locations (in upper Oratia and Opunuku streams) and 17.2 to 71.9 μ g/kg in sediments from four urban stream sites. This compared to 360 μ g/kg in the Pakuranga stream reported by ARC (1992). Concentrations in Waitakere stream sediments were lower than ANZECC ISQG for individual PAHs.

Webster *et al.* (2004) (in Depree & Ahrens, 2007a) reported PAH concentrations of 350 μ g/kg to 31,300 μ g/kg (median concentration 1,500 μ g/kg) in sediment from 16 small streams or drains in the Auckland area. These concentrations compare with the median concentration for PAHs in road surface material in Waitakere City reported by Kennedy & Gadd (2003) of 1,462 μ g/kg, and sediments from the Grafton Gully stormwater system of between 10,000 μ g/kg and 13,000 μ g/kg (Depree & Ahrens, 2007a).

Depree & Ahrens (2007a) reported PAH concentrations in sediments of "suburbanised creeks" of the upper Waitematā Harbour in the range 200 µg/kg to 800 µg/kg. Concentrations in fully-urbanised, industrialised, or high-density catchments, ranged between 1,000 µg/kg to 2,000 µg/kg. HMWPAH concentrations were reported by Depree & Ahrens (2007a) to be mostly below ARC environmental response criteria (1.7 mg/kg). However, they noted some localised waterways in the Auckland region (Meola, Motions and Oakley Creeks and the Whau River and Upper Tamaki Estuary) had concentrations above the ARC red criterion. Ahrens & Depree (2010) reported that pavements in the urban Motions Creek catchment (Point Chevalier) contained up to 10,400 mg/kg PAHs, which were associated with (pyrogenic) coal tars used in paving binders. In Motions Creek itself, 80% of the >15 mg/kg PAH content of stream sediments was attributed to these coal tar binders.

Depree & Ahrens (2007a) used PAH fingerprinting to show that the majority of PAHs in stream sediments with high PAH concentrations (e.g. Motions Creek) were not sourced from vehicle or residential sources, but from coal tar. The presence in downstream sediments indicates contributions from this source are on-going. The presence of PAHs in stream sediments is likely due to a number of factors, including loss of subsurface

materials during maintenance (repairs, services works, road milling) of pavements and roads (Ahrens & Depree, 2010). Coal tar has a range of other uses worldwide (e.g. roof sealant or parking lot sealcote - refer inset box in Section 5.4.3).

Figure 6 (from Depree & Ahrens, 2007a) shows how PAH ratios are used to illustrate the characteristics of sources and environmental materials. Depree & Ahrens (2007a) also noted that PAHs associated with wood and coal soot are absent in Auckland dust samples. The report showed that for stream sediments containing more than 4,000 µg/kg total PAHs, modern runoff particulates contributed only 4-14% of the total PAHs. At these sites, coal tar inputs from historical road construction practices were found to be the major source of sediment PAHs. For sediments containing approximately 1,000 µg/kg PAHs, Depree & Ahrens (2007a) reported that modern runoff typically contributed between 24% and 62% of the PAHs. The actual concentration measured is dependent on the proportion of uncontaminated sediment present (i.e. from erosion) that acts as a dilutent for contaminants (i.e. PAHs). For a given mass of PAH, the amount of sediment present determines the concentration of PAH, so, if uncontaminated sediment concentrations in stormwater decrease and sediment deposition decreases, the concentration of PAH may increase (Depree & Ahrens, 2007a).



Figure 6: PAH ratio plot showing source characteristics

(from Depree & Ahrens, 2007a).

Reed *et al.* (2008) reported data for TPH and PAHs in sediments downstream of a selection of Auckland catchments receiving stormwater from State highways. The highways were SH16 (Motions catchment), SH1 (Newmarket, Onehunga), SH17 (Paremoremo) and SH20 (Puhinui). HMWPAH concentrations exceeding the ANZECC (2000) ISQG-Low guideline were measured downstream of the Motions Creek and Newmarket catchments. However, it was estimated that modern road runoff contributed <5% of the concentrations identified. For the other three catchments, it was estimated that 61-100% (some methods of estimation indicated the contribution was >100%) of the downstream PAH concentration was derived from modern road runoff (all roads).

6.3.2 **Elsewhere in New Zealand**

Milne & Watts (2008) found that PAHs were present in most sediment samples collected from streams throughout the Wellington region in 2005 and 2006. PAHs such as fluoranthene and pyrene were the dominant hydrocarbons in the sediments. Total concentrations of HMWPAHs and total PAHs exceeded ANZECC (2000) guideline values at some sites. Concentrations ranged from "non-detectable" (less than 2 µg/kg) to 263,000 µg/kg (total organic carbon-normalised PAH concentrations of 61,500 µg/kg). Concentrations of LMW PAHs were low in all samples. The PAH composition was dominated by fluoranthene and pyrene (up to nearly 20%), and often also had high abundances of phenanthrene. Overall, the Wellington study concluded that all stream sediments showed a pyrogenic character, and those sites which had higher PAH concentrations exhibited a slightly more petrogenic influence (due to the high phenanthrene concentrations). Likely sources of pyrogenic PAHs identified in that report included soot from coal, diesel, wood or crude oil combustion and creosote/coal tar contamination.

Sediments in many of Christchurch's streams and rivers have also been found to contain high concentrations of PAHs (Depree & Ahrens, 2005; Ahrens et al., 2007). PAH concentration in sediments collected from urban streams in Christchurch and a range of Canterbury streams (Golder, 2012) were highest in waterways in larger, long-established urban areas (i.e. Christchurch). The Avon River/Ōtakāro, Heathcote River/Ōpāwaho, Dudley Creek and Addington Brook all had concentrations elevated above the ANZECC (2000) ISQC-Low values for high and low molecular weight PAHs (Golder, 2012). PAH abundances in other assessed streams elsewhere in the Canterbury region were all below guidance values. Stream sediment concentrations were within the PAH concentration range identified in soils in the Canterbury area (Golder, 2012).

Figure 7 shows the fingerprint pattern for PAHs measured in Christchurch stream sediments. The profile shows that sediments were dominated by phenanthrene, fluoranthene, pyrene, benzo[bj]fluoranthene and benzo[a]pyrene. These four PAHs made up 58.6% of the total PAH at one of the sites (site 10). A further six made up 36.9% of the total. In the Auckland study described above (Depree & Ahrens, 2007a), these four PAHs made up 42.3% of the total PAH (readjusted for those PAH not examined in this study).



Figure 7: PAH fingerprints - concentration profiles for stream sediments in Canterbury streams (from Golder, 2012).

Overall, the PAH fingerprint seen in stream sediment was a relatively common pattern with few LMWPAHs (which have higher solubility and greater potential to volatilise) and more HMWPAHs that are more stable. Golder (2012) suggested that the petrogenic contributions (e.g. oil losses) tended to be short term in nature and may not always be seen in stream sediment samples.

Ahrens *et al.* (2007) reported that PAH sediment concentrations in inner city streams in Christchurch were up to 100 mg/kg. It was considered that the high concentrations found were due to inputs from weathered coal tar (which had been used for paving Christchurch's roads and footpaths (Depree & Ahrens, 2005). As the coal tar contains very high concentrations of PAHs, very little coal tar is required to produce elevated concentrations in stream sediments (Ermens, 2007).

The dominance of three ring PAHs compared to the LMWPAHs (e.g. naphthalene) in the PAH profile is typical as the LMWPAHs, as noted in Section 2, have properties that tend to result in their residing in aquatic environments for only short periods. Those that are typically found in the analysis are more recalcitrant. As a result, the petrogenic contributions (oil losses etc.) tend to be short term in nature and may not be picked up in all samples. As noted earlier, road surface sediments can contain LMWPAHs (e.g. naphthalene) as they are close to source and the source material will have not been on the road surface for long.

In a study of Hamilton's urban streams, PAHs were only detected in sediment samples from seven out of 17 waterways sampled (Clearwater & Valler, 2012) and in all seven cases, abundances of PAHs in the sediments were below ANZECC (2000) guidance values. Sediments in the Clive River have also been assessed as part of Hawke's Bay Regional Council's State of the Environment Programme. TPH results were below detection limit in these sediments (Aquanet, 2011).

6.4 Hydrocarbons in coastal sediments

6.4.1 Auckland

PAHs are detectable in coastal sediments away from direct point sources. Ports of Auckland (POAL, 1990a) reported an average of 51 µg/kg in muddy sediments in the Hauraki Gulf (20 km east of Long Bay). Although the report identified that the PAHs were potentially derived from coal fragments in sediments, the PAHs could have been derived from dispersal of airborne and waterborne PAHs from the Auckland urban area. Higher PAH concentrations have been reported in muddy sediments adjacent to the Whangaparaoa Peninsula (176 µg/kg) and off the East Coast Bays of the north shore of Auckland City (441 µg/kg) (Kingett Mitchell, 2002).

PAHs in Auckland sediments have been measured in a number of environmental monitoring programmes at a range of sites. The Auckland State of the Environment Programme reported data on four occasions (1998, 1999, 2001, and 2005) at 26 sites. In the Upper Waitematā Harbour Programme, 13 sites have had PAHs measured on four occasions (2005, 2006, 2007, and 2009).

Mills *et al.* (2012) examined trends in the concentrations of HMWPAH (defined as the sum of the concentrations of fluoranthene, pyrene, benzo[a]pyrene, benzo[a]anthracene, dibenz[a,h]-anthracene, and chrysene) in Auckland region coastal sediments,. HMWPAH concentrations were generally low, and showed moderate variability. The HMWPAH showed few significant trends with five out of seven sites showing increases and the others, decreases. Mills *et al.* (2012) considered that the changes in HMWPAH measured to date did not "represent any real meaningful trends over time". The three sites where increasing PAH

concentrations were observed were all urban catchments: Anns Creek (Manukau Harbour), Lucas Upper (Upper Waitematā Harbour), and Pakuranga Lower (Tamaki Estuary).

Williamson & Mills (2009a) examined HMWPAH concentration data from the Auckland region as part of ARC's development of sediment quality guidelines (for the regional discharges project, refer ARC, 2004). Although the data were limited to the period 1989 to 1999, it indicated that at seven of 58 sites (12%) concentrations exceeded the ANZECC (2000) ISQG-low of 1.7 mg/kg (Figure 9). Sixteen of the 58 sites had concentrations exceeding the ARC green-amber threshold of 0.66 mg/kg. The authors also noted that 50% of sites could potentially have levels at which "adverse effects on bottom feeding fish might begin to occur".

The commentary provided in Williamson & Mills (2009a) was based on comparing the potential thresholds (230 µg/kg to 2,800 µg/kg) identified by Horness *et al.* (1998) for the onset of liver lesions in English sole, a benthic fish. Although 50% of Auckland sites had HMWPAH concentrations over the lower threshold, less than 5% had concentrations higher than the upper threshold. It should also be noted that the study was a co-occurrence study, in that other contaminants were also present in elevated concentrations and may have played a role in the observed effects.

A more recent review of PAH in sediment data for samples collected from the Waitematā and Manukau Harbours and along the east coast of Auckland indicated elevated concentrations of HMWPAHs are restricted to sites in the central Waitematā and the East Coast Bays (Mills *et al.*, 2012) (Figure 8). Elevated concentrations seen at coastal sites such as the near shore sites adjacent to Motions Creek and Meola Stream, were not considered to represent sites receiving "normal" stormwater, but instead were considered to be unusual as they were probably receiving contributions from road tar and also landfill seepage (refer to the earlier discussion about historic coal tar sources).

Depree & Ahrens (2007a) discussed the sources contributing to PAHs in Auckland estuarine sediments. Used engine oil has been considered a source in overseas studies. However, Depree & Ahrens (2007a) considered that waste oil dumping (or fugitive losses) was considered to be much lower in New Zealand urban areas. In addition, fingerprinting using hopanes (refer Section 2.4) indicated that engine oil is not a significant source of PAHs in stormwater particulates. The authors concluded that the similarity between stormwater and airborne particulates is consistent with them being linked via deposition and re-suspension pathways. The fingerprint indicated road runoff particulates had intermediate PAH petrogenic-pyrogenic composition.

Manukau Harbour sediment cores indicate PAH loads were higher in the early 20th century, and have declined since the use of coal tars ceased in the 1960s (Depree & Ahrens 2007a). A transition from coal to electricity also contributed to a load decrease.



Figure 8: Auckland Council sediment sampling locations where PAH data are available (<500 µm fraction, from Mills *et al.*, 2012).



Figure 9: Probability plots for HMWPAHs in Auckland estuarine and marine sediments

The plot shows the percentage of samples that have concentrations below the red data line. The ISQG-low ANZECC (2000) trigger value is shown assuming the sediment contains 1% total organic carbon (from Williamson & Mills, 2009a).

PAH data for sediments within the Ports of Auckland show that total PAH concentrations in 2011 ranged from 623 µg/kg to 1,996 µg/kg. LMWPAHs, such as naphthalene, were detected in only a few samples (Golder, 2011). Fluoranthrene, pyrene and benzon[b]floranthene were the most abundant PAH compounds in all samples, making up 41-46% of the total PAHs measured.

TPH is not routinely monitored in state-of-the-environment monitoring in the Auckland region or elsewhere in New Zealand. Analysis of TPH in Ports of Auckland sediments (Golder, 2011) provides an indication of TPH concentrations in Waitematā Harbour sediments near Auckland City stormwater outfalls. TPH concentrations were at or below detection limits in all composite samples analysed.

6.4.2 Elsewhere in New Zealand

Milne *et al.* (2008) reported that concentrations of fluorene, phenanthrene, benzo[a]anthracene and HMWPAHs in general were above sediment quality guidelines in samples collected immediately downstream of Wellington's commercial and industrial centres (Evans Bay and Lambton Harbour). These results were linked to stormwater outfalls. However, it was noted that contaminant loads in coastal sediments have decreased since the 1970s.

PAH concentrations have also been measured in coastal sediments off Christchurch (as part of studies for the consenting of the Christchurch City ocean outfall and also the Waimakariri District Council ocean outfall). The concentrations measured in the 2004 survey were low (sediments were predominantly sandy) ranging from 36 µg/kg to 66 µg/kg at New Brighton, 32 µg/kg to 36 µg/kg at a control site near the Ashley River and from 75 µg/kg to 97 µg/kg at a control site near the Waimakariri River (Kingett Mitchell, 2004).

6.5 Summary

6.5.1 Freshwater sediments

There are little recent reported data for TPH and BTEX in freshwater sediments in Auckland and elsewhere in New Zealand. Low concentrations of TPH were reported in stream sediments sampled in a 1999 survey in Waitakere, Auckland and in stream sediments adjacent to stormwater outfalls in Motions Creek and Newmarket stream. Stormwater particulates have been reported to contain higher concentrations of TPH compared to stream sediments.

In Auckland and Christchurch, the use of coal tar in road and pavement construction in the past has had a significant local influence on stream sediment PAH concentrations. Elevated concentrations of HMWPAHs can be found in urban stream sediments across locations such as Auckland and Wellington due to a variety of diffuse and point sources. Where specific sources (e.g. coal tar) are not involved, total PAH and HMWPAH concentrations do not typically exceed ANZECC (2000) sediment quality guidelines.

6.5.2 Coastal sediments

TPH concentrations appear to be low in coastal sediments, but there are very little TPH data for coastal sediments in the Auckland region. Although no detailed fingerprint analysis has been carried out, it is likely that concentrations of PAHs seen in coastal sediments reflect distance from source, both in terms of distance from stream or stormwater discharge and also distance from urban areas (in terms of atmospheric deposition and waterborne particulates contributing PAHs).

LMWPAHs are rarely seen in coastal sediments. PAHs in Auckland coastal sediments are dominated by more stable particulate associated PAHs. PAHs in Wellington Harbour sediments are also dominated by HMWPAHs. Sediments in several estuarine areas in the Waitematā Harbour have elevated PAH concentrations that in some cases are likely attributable to coal tar derived PAHs in adjacent catchments.

7.0 Regulatory guidance

7.1 Introduction

Regulatory guidance is generally provided as a component of overarching environmental management frameworks. Although guidelines may have been developed within a particular framework, they are often utilised and set within other regulatory frameworks, such as within regional or district planning provisions. One such set of regional water quality guidelines (those of ANZECC, 2000) were produced to support the Australian National Water Quality Management Strategy. The guidelines "provide an authoritative guide for setting water guality objectives required to sustain current or likely future environmental values for natural and semi-natural water resources in Australia and New Zealand" (ANZECC, 2000). Water and sediment quality guidelines provide tools to assess environmental guality and to provide assistance in water guality management to meet receiving water management objectives.

A range of regulatory guideline values have been developed for hydrocarbons. Guidelines have been developed for both water and sediments and in most cases, for a limited number of PAHs. There are no ecotoxicological guidelines for TPH in water or sediment. This section provides an overview of key and routinely referenced water quality and sediment quality regulatory guidance around the world.

7.2 Freshwater, estuarine and coastal waters

The most recognised water quality guidance in New Zealand are those from ANZECC, the Canadian Council of Ministers of the Environment (CCME) and USEPA. Buchman (2008) provides a summary of thresholds and guideline values for organic compounds in groundwater and fresh and marine surface waters. The water quality guidelines most commonly used in New Zealand are those of ANZECC (2000). Table 5 provides a summary of available guidelines for MAHs and PAHs in water.

The ANZECC (2000) guidelines do not provide water guality standards in the traditional sense (i.e. fixed standards that should not be exceeded). Rather, ANZECC (2000) states that the uncertainty in the derivation and application of such standards led them to develop trigger values that indicate a potential environmental problem if they are exceeded. Hence, ANZECC (2000) trigger values are not intended to be applied in an absolute fashion. If a trigger value is exceeded, further investigation is required.

ANZECC (2000) trigger values are not all equivalent. Trigger values are classified according to reliability (i.e. high, moderate or low reliability). High reliability trigger values are calculated from chronic 'no observable effect concentration' data, while moderate reliability trigger values (the majority of the triggers) are derived from short-term acute toxicity data (from tests less than 96 hours in duration) by applying acute-to-chronic conversion factors. Low reliability triggers include data derived using quantitative structure-activity relationships.

BTEX trigger values in fresh or marine waters have either low or moderate reliability (refer Table 8.3.14 in ANZECC 2000). Few trigger values have been developed for PAHs. ANZECC (2000) developed moderate reliability trigger values for naphthalene in fresh and marine waters, and low reliability values for anthracene, phenanthrene, fluoranthene and, benzo(a)pyrene in fresh and marine waters. However, the low reliability trigger values are not considered sufficiently robust to be included in Table 5.

Туре	Hydrocarbon	MfE (1997)	CCME (2014) [#]		ANZECC (2000)##		European Union (2008) ^{###}		DEC (2013)###	
		Rec. contact	Freshwater	Marine	Freshwater	Marine	Inland water	Other water	Freshwater	Marine
MAH	Benzene	300	370	110	950/2,000	700/ 1,300	10	8	-	700
	Ethylbenzene	5,000	90	25	ID	ID	-	-	-	-
	Toluene	15,000	2	215	ID	ID	-	-	-	5,000
	O-xylene	8,000*	-	-	350/640	ID	-	-	-	-
	M-xylene	-	-	-	ID	ID	-	-	-	-
	P-xylene	-	-	-	200/340	ID	-	-	-	-
	Anthracene	5,600	0.012	ID	ID	ID	0.1	0.1	-	-
	Acenaphthene	1,800	5.8	ID	-	-	-	-	520	710
	Acenaphthylene	700	ID	ID	-	-	-	-	-	-
	Benz[a] anthracene	-	0.018	ID	-	-	-	-	-	-
	Benzo[a]pyrene	0.03*	0.015	ID	ID	ID	0.05	0.05	-	-
	Fluoranthene	300	0.04	ID	ID	ID	0.1	0.1	-	16
РАН	Fluorene	1,000*	3	ID	-	-	-	-	-	-
	Naphthalene	300	1.1	1.4	16/85	70/120	2.4	1.2	620	-
	Phenanthrene	500	0.4	NA	ID	ID	-	-	-	-
	Pyrene	400	0.025	ID	-	-	-	-	-	-
	Benzo[b&k] fluoranthene	-	-	-	-	-	0.03 (sum)	0.03 (sum)	-	-
	Benzo(ghi) perylene***	-	-	-	-	-	0.002 (sum)	0.002 (sum)	-	-

Table 5: Regulatory guidelines for hydrocarbons in aquatic environments (mg/m³).

Notes: All units mg/m³; # Chronic level of protection; ## 95/80% level of protection; ### Annual averages; #### Chronic guidance values only; * Total xylene concentration; ** Assumes regular contact; *** including the isomer indeno(1,2,3-cd)-pyrene; and ID = Insufficient data to derive a reliable marine guideline or trigger value;.

The guidance values for MAHs in fresh and marine waters are, in most cases, higher than concentrations reported in urban stormwater. The guidance values (e.g. ANZECC (2000)) are instantaneous values.

7.3 Sediments

Internationally, there are a range of sediment quality guidelines. Buchman (2008) provides a summary of sediment quality guidelines for organic compounds. Table 6 summarised the sediment quality guidelines for PAHs developed by CCME (1999) and ANZECC (2000). Although the sediment quality guidelines identified in ANZECC (2000) have recently been revised in Simpson et al. (2013) (with the removal of guidelines for individual PAHs and an increase in the low and high guideline values for total PAH to 10,000 µg/kg dry weight and 50,000 ug/kg dry weight, respectively), the ANZECC (2000) guidelines are shown as they are the most commonly used in New Zealand.

Buchman (2008) also identified target and intervention thresholds for benzene (0.01 mg/kg and 1.0 mg/kg, respectively), ethyl benzene (0.03 mg/kg and 50.0 mg/kg), toluene (0.1 mg/kg and 47.0 mg/kg) and xylene (0.13 mg/kg and 17.0 mg/kg).

РАН		CCME	ANZECC (2000)*			
	Freshwater		Ma	rine	ISQG-Low	ISQG-High
	ISQG	PEL	ISQG	PEL		
Acenaphthene	6.71	88.9	6.71	88.9	16	500
Acenaphthylene	5.87	128	5.87	128	44	640
Anthracene	46.9	245	46.9	245	85	1,100
Benzo[a]anthracene	31.7	385	31.7	385	261	1,600
Benzo[a]pyrene	31.9	782	88.8	763	430	1,600
Benzo[k]fluoranthene	-	-	-	-	-	-
Chrysene	57.1	862	108	846	384	2,800
Dibenz(a,h)anthracene	6.22	135	6.22	135	63	260
Fluoranthene	111	2,355	113	1,494	600	5,100
Fluorene	21.2	144	21.2	144	19	540
2-methylnapthalene	20.2	201	20.2	201	-	-
Naphthalene	34.6	391	34.6	391	160	2,100
Phenanthrene	41.9	515	86.7	545	240	1,500
Pyrene	53	875	153	1,398	665	2,600
Total low-weight PAHs	-	-	-	-	552	3,160
Total high-weight PAHs	-	-	-	-	1,700	9,600
Total PAHs	-	-	-	-	4,000	45,000

Table 6: Regulatory guidelines for PAHs in sediments (µg/kg)

Notes: All units are µg/kg dry weight; ISQG = interim sediment quality guideline; PEL = probable effect level; and * ANZECC (2000) are normalised to 1% carbon.

In ARC guidelines (2004), as with ANZECC (2000) sediment quality guidelines, the trigger values for HMWPAHs are calculated from total organic carbon. ARC (2004) values are for the total sediment in the settling zone and for the mud fraction within the outer zone. Derivation of sediment quality guidelines for use by Auckland Council are described in ARC (2004) and Williamson & Mills (2009a) (Table 7).

Simpson et al. (2013) provides information in relation to the derivation of a SQGV for TPH. They note that the limits of reporting for the carbon bands (between C6 and C36), included by most laboratories detection limits for the determination of TPH, sum to a limit of 275 mg/kg. The Simpson et al. (2013) review refers to a number of earlier TPH toxicity studies, concluding that the limited data makes "setting a SQGV difficult". It was concluded that the chronic effects threshold for some species may be below the reporting limit of 275 mg/kg. Consequently, a detection of TPH would be considered above the trigger value. Simpson et al. (2013) recommended a SQGV of 280 mg/kg to avoid the issue of reporting limits. An arbitrary SQG-High value of 550 mg/kg was identified and at this stage, no account was taken of the binding of TPH to sediment organic carbon.

Application of sediment criteria should consider the analytical technique used as sediment as results can be variable depending on the fraction analysed and the analytical technique. It is important that when comparing results to the quality thresholds, these variables are consistent.

ARC (2004)			MacDonald	<i>et al</i> . (1996)	Long & Mo	rgan (1990)	ANZECC (2000)	
Green	Amber	Red	TEL	PEL	ERL	ERM	ISQG-Low	ISQG-High
<0.66	0.66-1.7	>1.7	0.66	6.7	1.7	9.6	1.7	9.6

Table 7: Comparison of ARC (2004) HMWPAH sediment quality thresholds with other guidelines (mg/kg)

Sources: ARC (2004), MacDonald *et al.* (1996), Long & Morgan (1990), ANZECC (2000). **Note:** Table reproduced from ARC (2004); all data mg/kg; guidelines for organic contaminants are given in concentrations "normalised" to a sediment organic carbon content of 1%.; HMWPAH is the sum of the concentrations of benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene and pyrene (as defined in ANZECC, 2000). TEL = Threshold effects level; ERL = Effects range low; and ERM = Effects range medium.

7.4 Summary

There are few regulatory guidelines for the protection of aquatic biota from the effects of hydrocarbons in fresh or marine waters. ANZECC (2000) provides triggers for benzene in marine and freshwater, but only xylene in freshwater. The only ANZECC (2000) guidance for PAH in fresh and marine water is for naphthalene.

CCME (1999) has developed guidelines for a range of PAHs in sediment, as has ANZECC (2000). Auckland Council (ARC 2004) derived trigger values for PAHs in sediments based on existing sediment quality guidance. The sediment quality guidelines for individual PAHs in ANZECC (2000) have recently been removed following revision in Simpson et al. (2013).

Potential environmental effects of hydrocarbons in 0.8 stormwater

8.1 Introduction

Understanding the effects of hydrocarbons on freshwater, estuarine and marine environments has historically come from understanding the effects arising from spills. Hydrocarbon release through spillage has the potential to result in a range of effects, including:

- Aesthetic effects (e.g. sheens, coatings, tar balls) •
- De-oxygenation of water in confined waterways (through oxygen consumption) •
- De-oxygenation of sediments where TPH is incorporated into sediments •
- Reduction in population numbers or diversity. •

Significant hydrocarbon losses have the potential to result in more acute effects, including fish kill, fish and seafood tainting and adverse effects on wildlife through the coating of bird feathers with oil (e.g. inability to fly).

This section provides an overview of the potential effects of hydrocarbons in stormwater, focussing on hydrocarbon mobility (as this is a key driver of downstream effects), ecotoxicity, bioaccumulation and biotoxicity (changes at the cellular level in individual organisms).

Typically, effects assessments focus on the toxicity of contaminants on individual organisms (acute and chronic effects). However, effects on individuals can have a range of wider effects at the community and ecosystem level. These may include changes in species' diversity due to loss of species or due to increased competition; and changes in trophic dynamics in communities arising from impacts on key species that may have cascading effects through food webs (if diets and/or predator effectiveness change).

8.2 Mobility and stability

Hydrocarbon toxicity depends on its behaviour in water. Highly soluble compounds are easily transported by the hydrologic cycle and tend to have low adsorption coefficients for soils and low bio-concentration factors in aquatic life. Highly soluble compounds also tend to be more readily biodegradable (Nyer et al., 1991). In general, soluble hydrocarbons are more acutely toxic, and insoluble hydrocarbons are acutely toxic to a lesser extent (Williamson, 1993). The behaviour of hydrocarbons in the environment can be assessed using quantitative structure-activity relationship approaches (Environment Canada, 2014). This has been undertaken for organic compounds (including hydrocarbons) emitted by motor vehicles in New Zealand (Moncreiff & Kennedy, 2004).

The solubility of a given hydrocarbon depends upon its structure. Hydrocarbons are non-polar or have a low octanol/water coefficient, so do not dissolve very well in polar solutions, such as water (Rodebush & Masterton, 1954). Furthermore, the larger the molecule, the less likely it is to dissolve in water. As a result, HMW hydrocarbons are typically less soluble than LMW hydrocarbons.

A second aspect to be considered is the volatility of a given hydrocarbon, or its tendency to evaporate. A measure of a compound's ability to partition between the air and water interface is known as the Henry's Law Constant. Volatility is important because if a hydrocarbon becomes gaseous it is in most cases, lost to the atmosphere (and thus no longer present in stormwater). The volatility of hydrocarbons depends on the size of the molecule, with LMW hydrocarbons typically more volatile than HMW hydrocarbons.

A final consideration in assessing the stability of hydrocarbons is how they may be degraded by microorganisms. Bacteria and fungi can use hydrocarbons for energy, by converting hydrocarbons into alcohols, carboxylic acids and other organic by-products (Atlas, 1981). In general, it is easier for bacteria to break down simple hydrocarbons (e.g. LMW aliphatic hydrocarbons with no cyclic groups) than more complex hydrocarbons (e.g. HMW aromatic hydrocarbons with multiple benzene rings).

In summary, the more soluble (and more toxic) LMW hydrocarbons also tend to be more likely to volatilise, and are more easily broken down by microbes. Therefore, the effects associated with more toxic hydrocarbons may be expected to be short-lived and within an area very close to source. Although high-weight hydrocarbons are less toxic, they are more likely to persist in the environment (as solid particles).

The mobility and stability of hydrocarbons explains in part, why the studies discussed in Section 5.0 have typically focused on higher molecular weight hydrocarbons. Lower-weight hydrocarbons associated with stormwater discharges will have already either evaporated, been broken down by microbes, or transported out into the wider environment.

8.3 Ecotoxicity

8.3.1 Introduction

Understanding toxicity effects relating to hydrocarbons in water or sediment requires an understanding of their distribution in the environment and their bioavailability (e.g. refer discussion for PAHs in Burgess *et al.*, 2003). Much of the fundamental understanding of the toxicity of hydrocarbons comes from work undertaken in relation to oil spills (NRC, 2003). However, the responses of biota to spilled oil are complex and change over time following the spill as the oil characteristics change.

The tolerance of aquatic organisms to hydrocarbons depends on the hydrocarbon and the organism. As a rule, smaller organisms at lower trophic levels (benthic invertebrates etc.) are less tolerant than larger organisms (e.g. large fish). As discussed previously, LMW hydrocarbons (shorter carbon chains) tend to be more toxic than HMW hydrocarbons (longer carbon chains), which is reflected in, for example, regulatory guidance for PAHs, where the threshold for LMWPAHs is lower than that for HMWPAHs (refer Section 7.0).

8.3.2 Toxicity in water

At high concentrations, water-soluble MAHs (specifically BTEX) and PAHs can affect the development of fish and invertebrate egg yolks, leading to a range of effects including excess fluid accumulation (edemas), skull abnormalities (craniofacial malformations) and bleeding (haemorrhaging) (McGrath & Di Toro, 2009 and references therein). At higher concentrations, exposure to these hydrocarbons can cause death and other acute effects.

Although the thresholds for effects may vary, recent results indicate the effects of different PAH compounds are similar. In a recent study, Jung *et al.* (2013) exposed zebra fish embryos to two different types of oil (with differing concentrations of individual PAH compounds) and found both caused similar effects (inducing heart defects within 36-48 hours of exposure).

Given the wide range of hydrocarbons that can be present, recent research has focussed on the development of predictive models to assess toxicity. Examples of such models include the Target Lipid Model described in McGrath & Di Toro (2009), (which incorporated toxicity data for MAHs and PAHs from over 140 papers), or PETROTOX, which is built on the Target Lipid Model and allows for better prediction of effects associated with less-soluble compounds (Redman *et al.*, 2012). The advantages of such models is that, in instances such as hydrocarbon contamination of stormwater, there is rarely only a single compound present, and thus individual measures of toxicity may not apply.

8.3.3 Phototoxicity

A wide range of toxicity work has been undertaken in relation to the toxicity of PAHs in aquatic environments (both in water and sediment). Laboratory studies and some *in situ* studies have demonstrated that enhanced toxicity occurs with some PAHs through UV-photoactivation. This process results in the generation of a reactive "singlet-oxygen" which can have adverse effects on cells. In addition, the process may result in by-products. McDonald & Chapman (2002) summarised that the phenomenon is ameliorated by a range of factors and that the ecological relevance of PAH phototoxicity is uncertain as, although a potential hazard has been identified, the ecological relevance has not. However, not all PAHs are phototoxic. Ahrens & Hickey (2002) examined phototoxicity in a number of New Zealand benthic invertebrates exposed to fluoranthene in sediment. They found that as a consequence of phototoxicity, organisms present in shallow intertidal sediments may be more at risk from PAH exposure due to the greater occurrence of UV radiation. Depree & Ahrens (2007b) included an assessment of photoactivation in their assessment of PAH-related toxicity in sediments. This is discussed further in the following section.

8.3.4 Bioavailability and toxicity in freshwater sediment

Toxicity

Pettigrove & Hoffmann (2005) undertook field-based microcosm studies where sediments were spiked with synthetic motor oil (C15 to C36) in the absence and presence of PAHs. Total TPH concentrations ranged from less than the detection limit of 125 mg/kg (control) to 14,266 mg/kg. The authors noted that the lowest treatment concentration (860 mg/kg TPH) resulted in increased numbers of some macro-invertebrates species. At the next treatment concentration (1,858 mg/kg), some invertebrate species declined significantly in numbers and reduced species richness. At 4,632 mg/kg there were fewer taxa. Pettigrove & Hoffmann (2005) also reported that 28% of sediments from water bodies in Melbourne exceeded the concentrations present in their lowest treatment (860 mg/kg), but less than 5% contained more than 4,632 mg/kg.

Anson *et al.* (2008) undertook further work on the effects of TPH on freshwater invertebrates to determine if hydrocarbons found in streams' sediments resembled the synthetic motor oil used in the Pettigrove & Hoffmann (2005) study. TPH concentrations in this series of microcosm experiments ranged from 59 mg/kg to 17,090 mg/kg (mainly C15-C36). A wetland sediment sample assumed to contain naturally elevated TPH (2,740 mg/kg) was found to have no effects on the invertebrates in the microcosm. Sediments contaminated with man-made HMWPAHs (both mineral and synthetic oils) were found to have an effect on aquatic

dipterans (two winged flies). The authors concluded that the cause of the effects was not obvious - whether it was a physical or chemical (toxicity) effect. They also concluded that not all species were affected to the same extent and this supported the results found in the earlier study by Pettigrove & Hoffmann (2005).

Marshall *et al.* (2010) examined the toxicity of sediment in an urban stream in Melbourne using microcosms. Two locations in the stream had high TPH sediment concentrations (1,210 mg/kg and 2,160 mg/kg). The authors noted that the close association of 'heavy metals' and hydrocarbons with microcosm community composition indicated that the key measured contaminants were having a key influence on the microcosm community structure. It was identified that reduced abundance of several invertebrate species had been demonstrated where elevated concentrations of long-chain hydrocarbons were found (Anson *et al.* 2008).

Ahrens *et al.* (2007) conducted short-term sediment toxicity tests with amphipods (Melita sp.) and larval mayflies (Deleatidium sp.) which were exposed in laboratory microcosms to stream sediments collected from Addington Drain, Dudley Creek, Avon River and St Albans Stream in Christchurch (total PAH levels of between 3 mg/kg and 87 mg/kg), and their survival was quantified after four and ten days. In addition, survival of waterfleas (*Daphnia magna*), was determined after two-day exposure to water-leachates of stream sediments, gutter particulates, and coal tar and asphalt pavements. To amplify the response to PAH, the test animals were subjected to solar-strength UV irradiation for 40-90 minutes upon termination of the water-exposure. Significant UV-activated PAH toxicity was observed in waterfleas exposed to leachates from coal-tar pavements, whereas little toxicity resulted from asphalt leachates and stream sediments. Exposure of amphipods and mayfly larvae to stream sediments for 10 days resulted in 15-95% mortality in amphipods, yet little mortality occurred in the mayflies (5-35%). It was found that about 70% of the toxicity response seen in the amphipods correlated with extractable PAH levels.

Bioavailability

Depree & Ahrens (2007b) also assessed sediment PAH bioavailability (in Auckland stream and estuary sediments) using mild extractions that mimic biological uptake as well as seven-day toxicity tests using a benthic crustacean. In general, less than 10% of the PAHs were found to be extractable, and while toxicity tests showed pronounced sediment toxicity, it was probably not attributable to PAHs. Short-term (seven day) toxicity bioassays were conducted using the benthic amphipod Melita sp., to test for evidence of specific PAH-related toxicity, amphipods were exposed to UV radiation for two hours following initial scoring. Only weak correlation was found between amphipod survival and sediment PAH levels. Exposing amphipods to UV radiation for two hours induced virtually no additional mortality.

Results from mild extraction techniques using semi-permeable membrane devices, which are used to estimate the fraction of PAHs available for biological uptake, found that only 3-7% of the sediment PAHs were bio-available. The sediments with the highest concentrations of PAHs (Motions and Meola streams) had the lowest fraction of bioavailable PAHs (ca. 3%). Although significant toxicity was observed for the estuarine sediments, a failure to see enhanced phototoxicity indicates that the toxicity of sediments was probably not attributable to PAHs. It is important to note that the toxicity tests on the sediments used in this study were only acute (or short-term) seven-day tests. The assay did not test for chronic (long-term) effects, which are normally observed at significantly lower contaminant concentrations.

8.3.5 Bioavailability and toxicity in estuarine and marine sediments

Depree & Ahrens (2007a) concluded that the majority of PAH levels in the sediment in Auckland's estuaries (e.g. Waitematā Harbour, Manukau Harbour and Tamaki Estuary) were well below ARC's environmental response criteria (ERC) of 1.7 mg/kg (for high molecular weight PAHs) (refer to Section 7 which summarises regulatory guidance values). Depree & Ahrens (2007a) reported that PAH concentrations have been "more or less stable" between 1998 and 2002. They noted that the analysis of sediment cores from Mangere Inlet suggests that PAH levels were historically higher in the Mangere Inlet (and potentially in the Manukau Harbour and elsewhere) (Wilcock & Northcott, 1995). In most sediments in the Auckland region, sediment PAH concentrations tend to correlate strongly with concentrations of other urban stormwater contaminants, such as zinc and copper. However, there are differences in the sources of PAHs and the metals. The authors noted that the lack of changes seen in sediments may indicate that PAH inputs and losses, to and from the environment, are currently at a steady state.

Williamson & Mills (2009b) discussed PAH concentrations in estuarine sediments in the Auckland region and expected and measured concentrations of PAHs in sediment pore water. They reported that pore water concentrations of PAHs were much lower than predicted by equilibrium portioning modelling. Pore water concentrations of between 15 μ g/m³ and 9 μ g/m³ for fluoranthene were measured for Motions and Meola Creek estuary sediments, which are low compared to USEPA (1993) chronic criteria of 2,960 μ g/m³. It was therefore concluded that toxicity is unlikely to arise from PAHs in pore water.

Mills *et al.* (2012) examined PAH concentrations at sediment monitoring sites in the Auckland region. They concluded that the majority of sites were well below the ERC amber threshold (refer Section 7) and consequently, the PAHs were considered unlikely (on their own) to be causing adverse effects on benthic ecology. It was noted by the authors that PAHs may contribute to cumulative effects that might be associated with the presence of multiple contaminants. An examination of data and trends indicated that "broad-scale changes" in sediment PAH concentrations since 1998 have "generally been small". Few significant trends were observed for PAH. To some extent, the lack of trends is a function of the number of data points and the length of time involved. Williamson *et al.* (2012) also noted that analytical variation was a potential factor contributing to the small observed changes (particularly at the urban sites where possible increases were identified).

Work undertaken in Auckland by the National Institute of Water and Atmospheric Research (NIWA) on the relationship between contaminant concentrations and estuarine benthic community health by Anderson *et al.* (2002, 2006), Hewitt *et al.* (2005, 2009) and Thrush *et al.* (2008) (refer overview in Kelly 2010), has shown that there are relationships between contaminant gradients and the composition of soft-sediment estuarine and harbour communities. The most recent studies identified that zinc and copper explained much of the variance in community composition. In these locations, first-tier risk assessment suggests that observed PAH concentrations (with or without other contaminants that are present) could pose an environmental risk to resident biota.

Simpson *et al.* (2013) reviewed studies of TPH toxicity that included marine sediment studies that produced a range of toxicity indications and toxicity thresholds (e.g., 'no observable effect concentration' of 1,080 mg/kg, observed chronic effects at 50 mg/kg for heavier 21-35 carbon TPHs). The outcome of SQGV development for TPH by Simpson et al. (2013) is discussed earlier in Section 7.3.

8.4 Bioaccumulation and biomagnification

8.4.1 Bioaccumulation

Introduction

Bioaccumulation is a term used to describe the uptake of contaminants (such as hydrocarbons), from water or sediments into plant and animal tissue. Bioaccumulation occurs when the rate of uptake exceeds the excretion rate and/or the contaminant is stored in tissue.

Pathways for such build up include: ingestion, when sediments are eaten or the food eaten has a high sediment content; inhalation (i.e. breathing); absorption through the skin (or through roots in the case of plants); or adsorption (e.g. when contaminants adhere to the roots of a plant, but are not incorporated into the plant). With regards to hydrocarbons, physical ingestion is the dominant pathway, in part because hydrocarbons are insoluble and thus difficult to absorb (Wang & Wang, 2006). Bivalve shellfish, such as mussels or oysters, take up PAHs in water because they are filter-feeders. Animals for which sediments make a large proportion of their diet, such as emergent mayflies, crabs or other invertebrates, can also have the potential to bioaccumulate hydrocarbons if they are present in sediments. These partitioning factors account for some of the differences in bioaccumulation potential seen amongst the range of petroleum hydrocarbons.

It should be noted that bioaccumulation in its own right is a neutral concept. While a contaminant may bioaccumulate, it does not mean that contaminant will adversely affect the organism (or the ecosystem). With regards to effects, it is the amount of bioaccumulation (or biomagnification) that occurs that is important and the specific physiology of the organism involved as different organisms have different strategies to deal with increasing body burdens of unwanted contaminants.

Bioaccumulation is often temporary, i.e. concentrations may build up (accumulate) in a mussel or oyster if their environment has high contaminant concentrations, but such shellfish can filter these contaminants out if their environment improves. However, long-term (chronic) effects may develop if constant exposure occurs (Paasivirta, 2000). Furthermore, recovery from exposure to some contaminants can take time depending on where in the body the contaminant has been stored (e.g. as seen with lead in humans).

Hydrocarbons

Bioaccumulation potential can be expressed as bioconcentration factors (BCF) or bioaccumulation factors (BAF). Any chemical with a BCF exceeding 100 on a wet-weight basis is considered to have a potential to bioaccumulate and is classified as "dangerous to the environment" by the European Union, because it could impair the health of an organism or that of the organisms feeding upon it. Canada considers chemicals with BCF values exceeding 500 as hazardous. BCFs for hydrocarbons range from 50.4 for o-xylene to 69.3 for naphthalene to 583 for benzo[a]pyrene.

Environment Canada (2014) reviewed BAFs for classes of petroleum hydrocarbons, including alkanes and PAHs. The review identified that groups such as C1 to C20 n-alkanes (with some exceptions e.g. n-nonane) are not highly bioaccumulative. The C13 to C15 isoalkanes, C12 to C15 monocycloalkanes and dicycloalkanes, and C14 and C22 polycycloalkanes have the potential for high bioaccumulation.

Bioaccumulation of PAHs in fish and invertebrates is variable (Environment Canada, 2014). Although some PAHs may not be bioaccumulated in fish or invertebrates (e.g. acenaphthylene), the three to six ring PAHs

can bioaccumulate. Excretion rates of higher molecular PAHs (e.g. perylene) are slower than lower molecular weight PAHs (e.g. phenanthrene, fluoranthene and pyrene). Fish (unlike invertebrates) have enzymatic systems that can efficiently detoxify compounds such as PAHs, which is why the BCFs tend to be lower in fish compared to invertebrates.

8.4.2 Biomagnification

Biomagnification is the process whereby contaminants concentrate up the food-web. In large food webs, concentrations of contaminants can be orders of magnitude higher in the top predators (e.g. tuna, sharks, and sometimes, humans) than found at the bottom of the food-web (e.g. shellfish or seaweed). Environment Canada (2014) considered it unlikely biomagnification of PAHs occurs, concluding that:

"biomagnification of parent PAHs and trophic magnification are mitigated by a combination of metabolism, low dietary assimilation efficiency and growth dilution through the food-chain. Field-based TMFs [trophic magnification factor] for PAHs in food webs were mostly <1, with the exception of fluorene and acenaphthene, which are approximately one (Lampi et al. 2010)".

Studies report greater than 10% of bioaccumulated hydrocarbons transfer from one trophic level to another (D'Adamo et al., 1997; Fisk et al., 2001; Wang & Wang, 2006). Environment Canada (2014) reported that biomagnification of alkyl PAHs (e.g. methylated pyrenes) is unlikely but may be possible.

8.4.3 Hydrocarbon bio-uptake in Auckland

PAHs have been measured in a variety of marine biota in the Auckland region. Auckland Council has used shellfish to monitor the effects of discharges (including stormwater) into Auckland's harbours and coasts, to provide an indication of the uptake of contaminants such as hydrocarbons.

Kelly (2007) found that oysters collected annually from the Manukau Harbour, between 1998 and 2005, all contained PAH concentrations above detection limits (0.22 µg/kg to 0.73 µg/kg dry wt), with the highest concentrations measured in Granny's Bay (Mangere inlet, most urbanised site) and Pahurehure (Papakura, adjacent to SH1). PAH concentrations in mussels sampled from sites throughout Auckland between 1998 and 2005 were highest in those sampled from the upper Waitematā Harbour (Hobsonville), upper Tamaki (Mt Wellington) and at the Chelsea sugar factory site (Birkenhead/Northcote). These sites were all close to developing or were already

y highly urbanised areas.

The most recent data for shellfish indicated that generally, concentrations of PAHs in sentinel shellfish had decreased or remained stable compared to historical data (Olsen & Stewart, 2009). However, when normalised to lipid concentrations (as lipids are where PAHs accumulate in shellfish), Olsen & Stewart (2009) noted increases in PAH in mussels from Illiomama (south of Rangitoto), and the Chelsea and Upper Waitematā sites.

Ports of Auckland Limited (POAL, 1990b) reported the results of analysis of PAHs in snapper (Pagurus auratus) muscle tissue from the Waitematā Harbour, Rangitoto Channel and Hauraki Gulf. Little difference was evident in concentrations between the Waitematā Harbour and Hauraki Gulf snapper samples. Mean total PAHs were 1.2 μ g/kg, <0.8 μ g/kg and 1.3 μ g/kg (dry weight), respectively, with only anthracene, fluoranthene, pyrene and chrysene/benzanthracene detected.

Hickey *et al.* (1995) showed that deposit feeding bivalves such as wedge-clams (*Macomona liliana*) contain up to 10 times higher tissue concentrations than suspension-feeding cockles (*Austrovenus stutchburyi*).

Overall, available information on PAHs in estuarine and coastal biota sampled in the Auckland area indicates that PAHs are not strongly bioaccumulated. The degree of uptake is dependent on a range of factors including the ecological niche of the organism. Given that PAHs are predominantly associated with particles, exposure to stormwater-sourced suspended particles or bed-sediment would be expected to result in greater exposure for biota.

8.4.4 Key findings

The extent of bioaccumulation of hydrocarbons is variable both between different aquatic biota (e.g. fish and invertebrates) and between different classes of hydrocarbons. Bio-uptake is most frequently reported for HMPAHs as they are routinely monitored in aquatic biota compared to other classes of hydrocarbons.

Studies report low transfer of hydrocarbons between trophic levels. Although biomagnification is not considered to occur for hydrocarbons, Environment Canada (2014) acknowledges that biomagnification of some hydrocarbons (e.g. methylated PAHs) may be possible.

8.5 Biotoxicity

Williamson & Mills (2009a) summarised that a range of studies have established links between sediment contaminants and health of benthic feeding fish species (such as flounder). Horness *et al.* (1998) identified sediment quality thresholds for PAHs and the onset of lesions in liver of English Sole (*Pleuronectes vetulus*). The thresholds (levels of liver lesions) for total PAH ranged from 230 µg/kg to 2,800 µg/kg. However, as noted by Williamson & Mills (2009a), the evaluation was based on co-varying contaminants so an unknown proportion of the observed effect could have been due to other contaminants.

Diggles *et al.* (2000) examined health of yellowbelly flounder (*Rhombosolea leporina*) in Auckland estuaries. Flounder caught in contaminated areas were found to contain a significantly higher prevalence of neoplastic liver lesions than fish from other areas. No cause-effect conclusions were made but Williamson & Mills (2009a) considered the effects were consistent with adverse effects of compounds such as PAHs and polychlorinated biphenyls.

An investigation into PAH uptake in marine biota using biomarkers indicated flounder have been exposed to PAHs in Hawke's Bay (Ataria *et al.*, 2008). No adverse effects linked to this exposure were reported. Reed *et al.* (2010) examined a number of biomarkers to assess their potential for environmental monitoring in the Auckland region. The biomarkers examined were similar to the range utilised in very recent work by Benedetti *et al.* (2014) (described below).

Reed *et al.* (2010) examined sediments, cockles (*Austrovenus stutchburyi*) and yellowbelly flounder collected from eight estuaries in the Auckland region. Fish liver tissues were analysed for metallothionein (MT) induction, aldehyde dehydrogenase expression, glutathione-S-transferase expression and Cu/Zn superoxide dismutase expression. A micronuclei assay was performed on gill tissues from fish and shellfish. The study documented a range of biochemical and expressed changes which reflected exposure to bioavailable metals and PAHs. Results for the reference site (Te Matuka Bay on Waiheke Island) were 'healthiest' for most biomarkers. The study found induction of micronuclei in tissues at all sites suggesting biochemical and

cellular damage is occurring in the coastal areas sampled. However, the extent and implications of these observations require further evaluation and supporting information.

The gene expression analysis showed increased levels of metallothionein in yellowbelly flounder caught in Cox's Bay, Meola and Shoal Bay compared to sites such as Te Matuku Bay (and others). Metallothionein levels were considered to reflect a biological response to metal bioavailability. Low levels of aldehyde dehydrogenase expression (a known biomarker for PAH exposure) were also observed in flounder caught in the Tamaki Estuary (suggesting lower levels of PAHs at this site) however, expression was notably higher at Shoal, Cox's Bay and Whau than at Tamaki, suggesting PAH contamination.

Information on TPH and PAH toxicity in sediments is available from studies of natural oil and gas seepages. Benedetti *et al.* (2014) carried out a weight-of-evidence investigation in relation to natural seepages in the Adriatic Sea. Concentrations of hydrocarbons and PAHs did not reveal significant differences between sites (reference, oil platform and natural seeps) although volatile hydrocarbons (C6-C10) were higher in the seep sediments. Assessment of bio-uptake in caged mussels (*Mytilus galloprovincialis*) and European eel (*Anguilla anguilla*) showed that aliphatic hydrocarbons (C10-40), naphthalene and a number of high molecular weight PAHs (e.g. pyrene) were present in gills at a higher concentration at the seep site. Mussels accumulated volatile hydrocarbons (C6-C10) at the seep site. Concentrations of HMWPAHs such as pyrene were found at the seep site.

Benedetti *et al.* (2014) reported that the overall bioaccumulation hazard was considered moderate and slight for gills and liver of eel, respectively. Examination of biomarkers revealed higher levels of pyrene type and benzo-pyrene type metabolites in eels at the seep site. Eels revealed a range of physiological changes and variations between the seep and reference sites including decreases in certain enzyme activity (e.g. catalase) and increases in DNA damage (refer detail in Benedetti *et al.*, 2014). Caged mussels revealed fewer changes but the changes indicated a moderate hazard at the seep site compared to the reference site. Overall the weight-of-evidence approach indicated a moderate risk at the seep site compared to the reference site. The results obtained from the battery of biomarkers used by the authors indicated a range of biomarker changes in eel and mussels caged in the seepage area.

8.6 Summary

LMW hydrocarbons are typically more soluble, and as such, more toxic than the HMW hydrocarbons. The smaller LMW hydrocarbons are more likely to volatilise and be broken down by microbes. Therefore, the effects associated with more toxic hydrocarbons may be expected to be short-lived and within an area very close to source. Although HMW hydrocarbons are less toxic, they are more likely to persist in the environment (associated with solid particles).

The extent of bioaccumulation of hydrocarbons is variable both between different aquatic biota (e.g. fish and invertebrates) and between different classes of hydrocarbons. Bio-uptake is most frequently reported for HMPAHs as they are routinely monitored in aquatic biota compared to other classes of hydrocarbons.

Available information on PAHs in Auckland estuarine and coastal biota indicates that PAHs are not strongly bioaccumulated. The degree of uptake is dependent on a range of factors including the ecological niche of the organism. Given that PAHs are predominantly associated with particles, exposure to stormwater-sourced suspended particles or bed-sediment would be expected to result in greater exposure for biota. Studies report low transfer of hydrocarbons between trophic levels. Although biomagnification is not considered to

occur for hydrocarbons, it has been reported (Environment Canada 2014) that some hydrocarbons (e.g. methylated PAHs) may biomagnify.

At high aqueous concentrations, water-soluble MAHs (specifically BTEX) and PAHs can affect the development of fish and invertebrate egg yolks, leading to a range of effects including edemas, skull abnormalities and bleeding. At higher concentrations, exposure to these hydrocarbons can cause death and other acute effects. There is international evidence that hydrocarbons and PAHs can be present in higher concentrations in a range of tissues of biota exposed to these compounds. A number of studies have shown that there are relationships between exposure and a range of cellular biomarkers. Other studies have also indicated relationships between PAH concentrations in sediments and adverse physiological responses to possible exposure to PAHs.

9.0 The Auckland context

9.1 Introduction

To varying degrees, hydrocarbons have the potential to cause toxicity to aquatic biota in both sediments and water, bioaccumulate and taint potential food sources. This section links the available data (presented in Sections 5, 6 and 8) with the likely environmental impact in the Auckland context.

9.2 Monocyclic aromatic hydrocarbons

Detectable concentrations of MAHs (specifically BTEX) are not common in urban stormwater. International data show that low concentrations can be measured in stormwater from a range of land uses (refer Section 5.2.4).

There are very little data for BTEX compounds in New Zealand stormwater and there appears to be no data on BTEX concentrations in urban streams and rivers in New Zealand. Although there is a wide range of sources contributing BTEX compounds to the environment and directly and indirectly to stormwater, the physical properties of these compounds favour loss from water through volatilisation.

No data are available in New Zealand to inform on the contributions from industry to stormwater. BTEX compounds have been reported in a limited set of discharge data from petrol stations and carparks, however the occurrence of detected concentrations is low (Section 5.0). Based on the very limited dataset, concentrations detected of BTEX compounds in stormwater are in nearly all cases, well below guidance to protect freshwater and marine biota from adverse effects of this group of compounds.

The limiting BTEX compound in terms of thresholds for potential adverse effects appears to be toluene, with a CCME (2014) freshwater guideline of 2 mg/m³ (refer Table 5). However, toluene concentrations measured in New Zealand are at the guidance concentration prior to dispersion and dilution within receiving environments. International literature suggests there is the potential for higher concentrations to be present in stormwater (refer Section 5.4.2). There appears to be no data to indicate that BTEX compounds in freshwater or estuarine sediments in the Auckland region, or elsewhere in New Zealand, pose environmental concerns to freshwater biota or estuarine sediment infauna (refer Section 8.0) although further data collection would be required to confirm this.

9.3 Polycyclic aromatic hydrocarbons

PAHs are detectable in stormwater discharged from all urban impervious surfaces (e.g. roofs, roads, and carparks). PAH profiles (the proportions of the typical range of individual PAHs measured in stormwater) change depending on the source and fate of the PAHs. Like the BTEX compounds, LMWPAHs (e.g. naphthalene) tend to evaporate, and the presence of significant concentrations of compounds, such as naphthalene, may reflect how recently the contamination occurred. Higher concentrations of LMWPAHs such as naphthalene have been measured in some New Zealand stormwater samples.

Concentrations of PAHs in stormwater at the point of stormwater discharge are similar to some international guidance for the protection of chronic effects to freshwater biota. However, when assessing the potential for

waterborne effects, the proportion of the PAHs that are in the dissolved or particulate phase should be considered, as the total PAH concentration incorporates the PAH associated with TSS or total organic carbon. For PAHs, ANZECC (2000) only has a trigger value for one PAH – naphthalene (16 mg/m³ for the 95% trigger value for protection of freshwater aquatic biota). Based on this value, roof runoff and urban stormwater would not exceed this trigger. Comparison with other guidance (Table 5) also indicates that it is very unlikely that other regulatory PAH trigger levels in water guidance would be exceeded.

Elevated stream sediment PAH concentrations have been identified in urban streams in major cities including Wellington, Christchurch and Auckland. In these streams, the source of the measured concentrations are considered to be primarily road runoff. PAH concentrations in sediments from fully urbanised and industrialised high-density catchments ranged from 1,000 µg/kg to 2,000 µg/kg, and in newer suburban catchments (e.g. those in the upper Waitematā Harbour), from 200 µg/kg to 800 µg/kg. Some concentrations lie at and above the ANZECC (2000) trigger values for LMWPAHs and HMWPAHs. Exceedance of these trigger values provides an indication that in some situations, additional studies should be undertaken to identify whether adverse effects are present.

Higher concentrations of PAHs (5,000 µg/kg) exceeding ANZECC (2000) trigger values (above those seen in most urban streams) have also been identified in stream sediments in Christchurch and Auckland. In these locations, the source of significantly elevated PAH concentrations has been identified as historic coal tar materials utilised in road and pedestrian pavement construction (Section 6.3). As such, the stream sediments exposed to these historic sources have increasing probability to result in adverse effects in freshwater stream infaunal communities.

Elevated concentrations of PAHs have been identified in estuarine sediments in the Auckland region (Section 6.4). Concentrations over the Auckland Council amber and red HMWPAH threshold have been identified in a limited number of locations (refer Figure 11 and Figure 12). The high concentrations identified in the mid Waitematā Harbour are downstream of Motions and Meola Creeks (known for contributions from coal tar, as well as other significant pollutant sources such as landfills), with elevations also noted in some historical surveys in locations such as the Little Shoal Bay and Panmure Basin (Williamson & Mills, 2009a) (where the PAHs are probably derived from a range of contributory sources). Work undertaken on pore water in Auckland estuaries has indicated that PAH concentrations in pore water may not be high enough to contribute to toxicity.

Available information on bioaccumulation of hydrocarbons indicates that the highest potential for bioaccumulation is for alkylated (e.g. methyl) compounds and for HMWPAHs. There is potential for uptake from media, such as suspended and bed sediment (i.e. by filter feeders, such as mussels, and biota, such as polychaete worms that ingest sediment) and elevated concentrations of compounds such as PAHs have been measured in aquatic biota in the Auckland region.

A number of studies have, however, examined a range of physiological/biochemical/genetic responses (cellular biomarkers) to possible PAH exposure. In studies of flounder and shellfish health, a range of negative responses have been identified that suggest that exposure to PAHs may be responsible, in part or wholly, for the observed responses (Section 8.5). Again, the studies identified foci of observed effects at locations such as Cox's Bay.

9.4 Total petroleum hydrocarbons

The extent that TPH is an environmental issue resulting from the spillage and loss of hydrocarbons from storage and transfer (fuel and oil losses from transfer incidents, valve failures etc.) or accidental loss (e.g. fuel and oil loss from vehicle accidents) is not known. Understanding the extent of issues arising from losses requires information on the number of incidents and their scale.

In Section 5.1, it was noted that the identification of sheens on road surfaces during rainfall events (or in catchpits etc.) provided an indication that TPH loss occurred. However, there appears to be no formal quantification of losses of TPH through urban stormwater in New Zealand (or recent estimations elsewhere). Although the estimated contribution of urban stormwater to global environmental TPH contributions is small (about 10% Yousef *et al.*, 1980; Clark, 1997), in the New Zealand context it is effects to local stream and estuarine environments that requires consideration.

There are no environmental guidelines for TPH in water that provide specific guidance as to the potential for adverse effects on freshwater or estuarine ecological systems. This is not surprising given that TPH is the measurable amount of a complex mixture of petroleum-based hydrocarbons in an environmental media and as such, dependent on analysis of the medium in which it is found (refer Section 2.4). Therefore, the same TPH concentration in two locations may not imply the same potential environmental effect. As such, TPH is typically used as a screening test only and cannot be used to draw specific conclusions.

Although there are very limited data for TPH in stormwater in Auckland, much of the data are below current detection limits and, due to the phase distribution of TPH to particulates, much of the TPH appears to be transported associated with particulates. This report has not presented information on TPH in stormwater discharges from industry due to lack of available published data. Limited petrol station data suggest concentrations in discharges are low (where installed treatment is effective) (refer to Section 5.2.3).

The recently recommended SQGV for TPH by Simpson et al. (2013) of 280 mg/kg provides a threshold to indicate that chronic effects may occur in sediments where TPH is measurable. The SQGV is lower than the sediment threshold (of 860 mg/kg) suggested by Pettigrove et al. (2005).

The limited information on TPH concentrations in freshwater stream sediments in Auckland suggests that most freshwater stream sediments will contain TPH concentrations lower than the SQGV recommended by Simpson et al. (2013). Sediments in localised sections of some urban streams have been reported with concentrations above the SQGV of 280 mg/kg.

9.5 Summary

Although there is little information on MAH compounds (e.g. BTEX) in urban stormwater, the limited data available indicate waterborne toxicity in receiving waters is unlikely. PAH concentrations in stormwater are typically low when compared to receiving water quality guidance. Stream sediment PAH concentrations can however, in Auckland (and in other urban streams), exceed ANZECC (2000) sediment quality trigger values. Exceedance of these trigger values provides an indication that potential adverse effects may arise from elevated concentrations.

Elevated stream sediment PAH concentrations have been identified in urban streams in major cities including Wellington, Christchurch and Auckland urban streams. In streams where the source of PAH is stormwater runoff, concentrations reported in established older urban areas of Auckland ranged from 1,000 μ g/kg to 2,000 μ g/kg. These concentrations lie at, and above, the ANZECC (2000) trigger values for LMWPAHs or HMWPAHs. In some urban stream sediments in Auckland, and also Christchurch, higher concentrations of PAHs have been reported in areas where landuse is a key contributor (including where coal tar has historically been used for pavement and road construction). In stream sediments where higher concentrations have been observed, there is an increased probability of adverse ecological effects.

Studies in some specific Auckland estuaries (e.g. Cox's Bay) have identified a range of negative physiological responses (in flounder and shellfish health). While multiple exposures to a variety of pollutants may be the cause of this, measured PAH concentrations in sediment at those locations may be at levels at which adverse effects on bottom feeding fish might begin to occur.

TPH concentrations in urban stormwater in the Auckland region are typically below laboratory detection limits. The available data for TPH in stream sediments in Auckland indicate that concentrations are predominantly lower than the recently recommended ANZECC TPH threshold. Higher concentrations of TPH have been identified in localised areas of urban streams in Auckland. No frequency or consequence information is available to quantify the extent of environmental issues that might arise from one-off incidents and losses of TPH through spillage from motor vehicles (accidents) and industrial sites (transfer losses, spills, accidents etc.).

10.0 Summary

10.1 Monocyclic aromatic hydrocarbons

There are very limited data for MAHs in urban stormwater in New Zealand. The available data indicate that low concentrations may be present if local sources contribute to stormwater. Motor vehicles and vehicle fuel are considered to be the primary source of MAHs. However, there are a wide range of sources that can potentially contribute these compounds to waterways and the atmosphere (Section 4.0).

The limited New Zealand data (and international data) indicate MAH concentrations in stormwater (prior to entering receiving environments) are typically below freshwater quality guidelines to protect aquatic biota. As such, MAHs in typical stormwater runoff are not considered a significant risk to freshwater, estuarine and coastal environments. Major hydrocarbon loss events can however have acute effects, therefore it is important that controls are in place to mitigate these larger-scale effects.

There are no data for MAHs in freshwater or estuarine sediments. MAHs may be present following spillages of fuel, but their physical properties mean these compounds are readily lost from surface water and sediment through volatilisation.

10.2 **Polycyclic aromatic hydrocarbons**

In general, the PAHs seen in downstream estuarine and intertidal sediments are derived from waterborne (stream and stormwater) and atmospheric deposition. Depree & Ahrens (2007a) concluded marine sources (e.g. boat, ships and lost oil) and atmospheric deposition were not likely to be significant contributors. The authors also concluded that in Auckland, atmospheric point sources were unlikely to be significant contributors, based on the limited dataset reviewed. This left stormwater and catchment runoff as the primary contributor of PAHs to downstream environments, although the typical pyrogenic PAH signature of the sediments sampled indicated petrogenic sources (such as petrol station runoff) were not significant contributors. The exception to this was in catchments where coal tar had historically been used in road and pavement construction (Auckland and Christchurch) and in catchments where gas works' waste might generate PAHs (Dunedin, possibly Auckland).

Dissolved concentrations of PAHs in stormwater are low. The available data confirm that much of the PAH present in stormwater is associated with suspended particles. LMWPAHs, which readily volatilise, are detected in stormwater at times, however are often absent and are similarly rarely seen in sediments. The PAHs in sediments tend to be HMWPAHs, which are more stable.

PAH concentrations in freshwater and marine environments are typically below environmental thresholds. However, in some locations where specific hydrocarbon sources are involved, concentrations in sediment exceed international or local (e.g. Auckland Council) thresholds. Studies in Christchurch and Auckland where stream sediments have been impacted by coal tar sourced PAHs have shown variable responses in a range of toxicity tests. Work on cellular biomarkers in fish and shellfish in Auckland has shown responses which have, in part, been attributable to PAHs. However, the specific ecological significance of the identified biomarker changes has not been identified to the point that it has a direct bearing on management of PAH emissions.

10.3 Total petroleum hydrocarbons

There appear to be very little concentration data for TPH in urban stormwater in Auckland or elsewhere. However, based on the limited data presented in this document, the following points can be made:

- TPH losses from petrol stations are low where treatment systems are well maintained. TPH losses from carparks appear to be similarly low
- TPH concentrations in State highway runoff are low
- Data do not reveal whether there are differences in the concentrations of TPH from different land uses. In particular, the current dataset is not sufficient to determine whether concentrations are elevated in areas of industry where hydrocarbons are stored and handled.

TPH is strongly associated with suspended particulates in stormwater. TPH concentrations can be high in stormwater TSS and RDS, reflecting the affinity of hydrocarbons for particulates. As such, treatment that focuses on removal of TSS will likely provide effective removal of TPH associated with particulates.

Where TPH is present as a free phase (e.g. following a spillage), treatment requires the use of oil-water separators. Effective management of TPH losses to downstream environments requires effective on-site and treatment-device management where losses are identified as a risk.

Like stormwater, there are relatively few published concentration TPH data for Auckland (and New Zealand) stream waters. There are more data for stream sediments than stream waters. Data collected in 1999 in Waitakere, Auckland identified no detectable TPH in stream water and low concentrations in sediments. More recent work in Auckland by Reed *et al.* (2008) also showed relatively low concentrations of TPH in a number of Auckland catchments. Some elevated TPH concentrations have been reported in localised sections of some urban streams (e.g. Motions, Newmarket).

Experimental work with mesocosms in freshwater steams in Victoria, Australia by Pettigrove & Hoffmann (2005) showed that elevated concentrations of hydrocarbon in stream sediments can result in changes in community ecology. A threshold of 860 mg/kg TPH in sediment was identified in that work, although the actual toxicity will be dependent on the mix of parameters which make up the TPH, not simply the total concentration. More recently, Simpson et al. (2013) has recommended a SQGV of 280 mg/kg (the detectable concentration above the limit of reporting of 275 mg/kg) and an arbitrary SQGV-High of 550 mg/kg. Concentrations measured in the Waitakere study in 1999 were lower than the identified threshold. However, that conclusion cannot be extrapolated across the Auckland region. TPH concentrations above the SQGV-Low have been reported for some urban streams in Auckland. TPH concentrations in streams within industrial catchments (where hydrocarbon spillage may have occurred) may be higher than those measured in residential and general urban streams. However, there are insufficient data to reach conclusions in relation to industrial catchments in Auckland.

There appear to be no downstream environmental data (water or sediment quality or ecotoxicological responses) that identifies TPH as a pollutant of concern in Auckland requiring specific upstream controls in relation to specific land uses or general activities (e.g. carparking). Consequently, there is insufficient information and data to conclude treatment of urban stormwater (from residential and commercial landuse) to specifically remove TPH is required.

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THE MANAGEMENT OF HYDROCARBONS IN STORMWATER RUNOFF

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