# Characterisation of Runoff Contaminants from New Zealand Roads, & Effect of Rainfall Events

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# Abbreviations

| | |
|---|---|
| AADT | annual average daily traffic |
| AAS | atomic absorption spectroscopy |
| AR | analytical reagent |
| ARC | Auckland Regional Council |
| BOD | biochemical oxygen demand |
| cm | centimetres |
| conc. | concentrated |
| CV | coefficient of variation |
| DCM | dichloromethane |
| DO | dissolved oxygen |
| EMC | event mean concentration |
| Er | percentage relative error |
| eV | electron volts |
| g | gram |
| GC | gas chromatography |
| GC-FID | gas chromatography-flame ionisation detection |
| GC/MS | gas chromatography/mass spectrometry |
| GV | guideline value |
| h | hour |
| H | highway section |
| $H_{max}$ | height at maximum flow rate |
| $HNO_3$ | nitric acid |
| ICP-MS | inductivity coupled plasma-mass spectroscopy |
| ICP-OES | inductivity coupled plasma-emission spectroscopy |
| K | kelvin |
| kg | kilogram(s) |
| km | kilometre(s) |
| L | litre(s) |
| L/s | litre(s) per second |
| LTPS | Land Transport Pricing Study |
| M/z | mass /charge ratio |
| MAV | maximum acceptable value |
| MFE | Ministry for the Environment |
| mg | milligram(s) |
| min | minute(s) |
| mL | millilitre(s) |
| mm | millimetre(s) |
| MoH | Ministry of Health |
| MoT | Ministry of Transport |
| MS | mass spectrometer |
| MSD | mass selector detector |
| NIWA | National Institute of Water and Atmospheric Research |
| nm | nanometre(s) |
| $NO_x$ | nitrogen oxides |
| NURP | US Nationwide Urban Runoff Program |
| PAHs | polycyclic aromatic hydrocarbons |
| PCBs | polychlorinated biphenyls |
| PCDD/F | polychlorinated dibenzo-p-dioxins and dibenzofurans |
| pers. comm. | personal communication |
| Q | flowrate |
| R | roundabout |
| $R^2$ | regressive coefficient |
| $R_F$ | response factor |
| RMA | Resource Management Act, 1991 |
| SIM | selected ion monitoring |
| stdev | standard deviation |
| SWAT | StormWater and Transport |
| TBRG | tipping bucket range gauge |
| TIC | total ion chromatogram |
| TL | traffic light |
| TSS | total suspended solids |
| UK | United Kingdom |
| US | United States |
| USEPA | United States Environmental Protection Agency |
| μg | microgram(s) |
| μg/L | microgram(s) per litre |
| μL | microlitre(s) |
| μm | micrometre(s) |

# Executive Summary

## Introduction

Vehicular traffic on road asphalt generates a variety of inorganic and organic contaminants. These accumulate on the road surface in quantities that depend on the traffic and road conditions. During rainfall events, they are washed from the road surface and make a major contribution to stormwater pollution.

This road runoff contains suspended and dissolved inorganic and organic contaminants. It is transported from the road surface to the underground drainage system and is then discharged into the receiving waterbodies. Road runoff is recognised as a problem contaminant, particularly in urban areas, because of its potential chronic toxicity for aquatic species in the recipient waterbodies.

The management of polluted discharges requires land use practices to avoid, mitigate and/or remedy potential impacts on the environment. In New Zealand, it is governed by the Resource Management Act, 1991 (RMA).

Increasingly in New Zealand, and elsewhere, the incorporation of treatment technologies to mitigate the negative impacts of road runoff before they are discharged into receiving waterbodies is becoming an integral part of road construction. Also local councils need to be satisfied with the data supplied concerning the nature, quantity and quality of the discharge, and the effectiveness of proposed treatment technologies.

## Objectives

The purpose of this research, carried out in 2001, was to investigate contaminants found in New Zealand road runoff and to characterise the components at source. It was also to determine how the relative concentrations, total load, and characteristics change with the frequency and intensity of rainfall events. The specific objectives to allow this to be achieved include:

(1) Method validation of ICP-OES and SIM GC/MS protocols and confirmation of the presence of heavy metal and PAH species in road runoff.

(2) Sampling and identification of a site suitable for monitoring road runoff during rainfall events. Thus a sampling system consisting of a 6700 ISCO automatic sampler was set up to sample continuously from the drain leading from a road roundabout on the outskirts of Hamilton City.

(3) Documentation of variations of heavy metals and PAHs during rainfall events. Of particular interest is the effect of intensity and frequency of rainfall events. These studies should indicate whether the phenomenon of first flush, reported overseas, occurs under New Zealand conditions. Thus samples from six rainfall events were collected between 26/1/2001 and 28/3/2001 at programmed intervals over the first 2 hours of precipitation

(4) Depending on the results obtained for Objective 3, to suggest cost-effective treatment options to minimise the environmental impact of road runoff.

## Experimental Site & Sampling

Automated bottle samplers were used to sample road runoff throughout rainfall events. This method of sampling allowed for the calculation of event mean concentrations, the total contaminant load. and the identification of the variation in contaminant concentration through the rainfall event.

Conductivity, pH, dissolved oxygen (DO), temperature, flowrate and rainfall intensity were monitored continuously. Analysis of Cd, Cr, Cu, Fe, Ni, Pb, and Zn was performed on each of the 1000mL samples using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The remaining volume (c.900mL) was liquid/liquid extracted and analysed by Selected Ion Monitoring Gas Chromatography/Mass Spectrometry (SIM GC/MS) for pyrene, fluoranthene, phenanthrene and benzo(a)pyrene.

## Contaminants of Concern & their Analysis

The heavy meals Cu, Cd, Cr, Fe, Ni, Pb and Zn, and the PAHs (polycyclic aromatic hydrocarbons) including pyrene, phenanthrene, fluoranthene and benzo(a)pyrene, are the pollutants of most concern. They are known to be toxic to the aquatic environment and, in the case of Fe, cause aesthetic problems.

The following analytical techniques were investigated as the most appropriate for metal element analysis of water samples: Atomic Absorption Spectrometry (AAS) (which includes flame and graphite furnace AAS), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

For the identification and quantification of PAHs in the environment, the widely used techniques reviewed were Gas Chromatography (GC) with Flame Ionisation Detection (FID) or Mass Spectrometry (MS) detection, and high-pressure liquid chromatography, especially for the sensitivity limits required for road runoff samples (typically in their ng/L range). The methodology chosen was SIM GC/MS.

## Treatment Options for Minimising Environment Impact of Road Runoff

The working hypothesis for this investigation was that concentration of pollutants in road runoff would follow the first flush effect previously reported from overseas studies. The results give some support to this hypothesis for particulate-bound Fe and pyrene where the rainfall event was preceded by a prolonged dry spell.

Results showed that approximately 30% of the total load for the 2-h monitoring period was contained within the first 275L of runoff irrespective of rainfall intensity.

Thus the diversion and treatment of the runoff from the early stages of a rainfall event have potential for the removal of a disproportionate fraction of total runoff pollutants. However, the diverted runoff should also be treated by technologies that remove pollutants in both suspended and dissolved forms. These could include clarifying devices or filtration devices.

## Summary

- The principal pollutants present in runoff from a suburban roundabout carrying moderate traffic densities include PAHs (pyrene, phenanthrene, fluoranthene), particle-bound metals (Fe, Ni. Zn), and dissolved metals (Fe, Ni, Zn). Pyrene made up approximately 60% of the PAHs. Event mean concentration (EMC) values ranged from 185–1490ng/L.

- The principal metal constituent was Fe with EMC values ranging from 7240–50 300µg/L, although readily detectable levels of Zn and Ni were present in most samples in both particle-bound and dissolved forms. Generally most of the metals were particle-bound.
- One metal notable for its absence at detectable concentrations was Pb. Although Pb was commonly cited in the stormwater studies of the 1970s, the phasing out of Pb in gasoline in 1996 appears to have been effective in preventing the pollution of road runoff with Pb.
- The patterns of heavy metal and PAH constituents at the River Road suburban roundabout runoff were investigated. Where the rainfall event was preceded by a prolonged dry period, the pollutant wash-off patterns for particulate-bound Fe and PAHs demonstrated a first flush regardless of rainfall conditions. Particulate-bound Ni and Zn followed a similar behaviour. Phenanthrene and fluoranthene patterns resembled those of pyrene. The pollutant wash-off patterns for dissolved metal constituents, however, were variable and inconsistent.
- The trends for pyrene and particulate-bound Fe were similar It was concluded that PAHs were predominantly bound to the suspended solids, and that particulate-bound Fe and particulate-bound PAH behaved similarly.
- Pollutant wash-off behaviour was not affected by the intensity of the rainfall, and the amount of pollutant load washed of the road over a 2-h period did not appear to be related to the number of preceding dry days. Total pollutant load did appear to depend on total runoff volume collected over the 2-h period.
- An important practical outcome from the work is the demonstration of a first flush effect for runoff following periods of dry weather. Treatment technologies designed to treat the first flush offer the possibility of cost-effective improvement of the water quality of road runoff. These data showed that treatment to remove pollutants from the runoff produced during the first 2 hours of rainfall should be effective in removing a significant fraction of the total pollutants. Further research is required to determine effects that occur beyond the first 2 hours of precipitation.

## Recommendations for Further Work

- Need for longer sampling period

A difficulty faced in the interpretation of the data obtained in the current study was the limited duration of the sampling period. Data covering the entire event is needed, rather than the first 2 hours. In addition, sampling needs to continue over at least a complete annual weather cycle In this way, the data necessary to test rigorously the effects of first flush, the number of preceding dry days, and the total volume of runoff, can be obtained.

- Need to determine the causes of trends in conductivity and pH

It is of interest to determine the causes of these trends and whether they are vehicle-related or precipitation-related.

- The use of particulate-bound Fe

Using it has the potential to simplify the analytical processes required to monitor patterns of runoff, since particulate-bound heavy metals and PAHs correlated well with particulate-bound Fe. The advantages of using particulate-bound Fe as a tracer for runoff pollutants are that the determination of Fe is analytically simpler, errors are small because of the large amounts present, and low sample volumes are required.

# Abstract

Vehicular traffic on road asphalt generates a variety of inorganic and organic contaminants. These accumulate on the road surface in quantities that depend on the traffic and road conditions. During rainfall events, they are washed from the road surface and make a major contribution to stormwater pollution. This road runoff contains suspended and dissolved inorganic and organic contaminants, and is a problem, particularly in urban areas, because of its potential chronic toxicity for aquatic species in the recipient waterbodies.

This project, carried out in 2001, was to investigate contaminants found in New Zealanmd road runoff, and to characterise the components at source. It was also to determine how the relative concentrations, total load, and characteristics change with the frequency and intensity of rainfall events. A sampling system consisting of a 6700 ISCO automatic sampler was set up to sample continuously from the drain leading from a road roundabout on the outskirts of Hamilton City. Samples from six rainfall events were collected between 26/1/2001 and 28/3/2001 at programmed intervals over the first 2 hours of precipitation.

Conductivity, pH, dissolved oxygen (DO), temperature, flowrate and rainfall intensity were monitored continuously. Analysis of Cd, Cr, Cu, Fe, Ni, Pb, and Zn was performed on each of the 1000mL samples using inductively coupled plasma optical emission spectroscopy (ICP-OES). The remaining volume (c.900mL) was liquid/liquid extracted and analysed by selected ion monitoring gas chromatography/mass spectrometry (SIM GC/MS) for pyrene, fluoranthene, phenanthrene and benzo(a)pyrene.

# 1. Introduction & Review

## 1.1 Introduction

Vehicular traffic on road asphalt generates a variety of inorganic and organic contaminants. These accumulate on the road surface in quantities that depend on the traffic and road conditions (Stotz 1987; Berbee et al. 1999). During rainfall events, they are washed from the road surface and make a major contribution to stormwater pollution.

Road runoff is the water that drains from a road surface during a rainfall event. It contains suspended and dissolved inorganic and organic contaminants (Sansalone & Buchberger 1997). Particles suspended in the road runoff may settle as sediments. The runoff is transported from the road surface to the underground drainage system and is then discharged into the receiving waterbodies. Road runoff is recognised as a problem contaminant, particularly in urban areas, because of its potential chronic toxicity for aquatic species in the recipient waterbody (Ellis et al. 1987; Stotz 1987).

The management of polluted discharges requires practices to avoid, mitigate and/or remedy potential impacts on the environment. In most countries these strategies are required by acts or statutes in the law of the land. In New Zealand, the appropriate legislation is the Resource Management Act, 1991 (RMA). The purpose of the RMA is to "promote the sustainable management of natural and physical resources". Schedule III, 15 outlines the restriction of discharges where "no person may discharge any contaminant into the water" (Statutes of NZ 1994).

Increasingly in New Zealand, and elsewhere, the incorporation of treatment technologies for road runoff is becoming an integral part of road construction (Andoh 1994). Road runoff treatment technologies function by mitigating the negative impacts of the pollutants before they are discharged into receiving waterbodies. Before adopting the best practicable option to prevent or minimise any actual or likely detrimental effect on the environment, a regional council needs to be satisfied with the data supplied concerning the nature, quantity and quality of the discharge, and the effectiveness of proposed treatment technologies (Statutes of NZ 1994).

The purpose of this research is to investigate contaminants found in New Zealand road runoff and to determine how the relative concentrations, total load and characteristics change with the frequency and intensity of rainfall events. This will help determine the extent to which road runoff is a source of contaminants in New Zealand waterbodies.

This information will contribute to the development of pollution treatment technologies for mitigating road runoff discharges. It will also provide information for local authorities, e.g. for Environment Waikato Regional Council in the achievement of their Operative Regional Land Transport Strategy. The information will also be valuable to Transit New Zealand, the organisation responsible for the highway roading system in New Zealand. Runoff treatment devices, which divert the polluted runoff away from sensitive water resources, can then be constructed.

An example of a treatment technology is the use of treatment walls. According to this method, runoff with high loadings is diverted through a barrier filled with material chosen to remove target pollutants (Lee et al. 2000). Other examples of road management practice that function to remove contaminants from runoff are: pervious asphalt; oil and grease systems; wet ponds; extended detention ponds; flow detention/retention by infiltration; sand filters; treatment walls; wetlands; grassy swales; and vegetative filter strips (Beca Carter Hollings & Ferner Ltd (BCHF) 1992; Wong et al. 2000).

Data on the patterns of road runoff during rainfall events will help in the choice and development of optimum treatment technologies.

## 1.2 Stormwater Runoff

During precipitation, rainwater flows from upland areas to the sea. The water is transported through valleys (small catchments) and follows its natural course, picking up sediments and contaminants along the way. The rainfall runoff process in natural systems is dominated by natural surface detention and infiltration characteristics, which in turn are highly influenced by the surface soil type, the vegetation cover and the topography.

Urbanisation affects these processes primarily through the construction of physical systems, such as those needed to provide drainage and transportation facilities, for instance roadways (Ball et al. 1998). Urbanisation causes the natural ground surface to be replaced by impervious surfaces, giving rise to urban stormwater runoff during wet weather.

Stormwater runoff contains contaminants that have accumulated on surfaces such as cultivated areas, roofs, roads, industrial yards, parking lots, footpaths and driveways during dry weather and have become waterborne during rainfall (Snelder & Trueman 1995). There is increasing public concern that stormwater can cause detrimental ecological disturbance to receiving waters through a decrease in ecological health, which will lead to a loss of habitat diversity (Wong et al. 2000; Davis et al. 2001).

## 1.3 Road Runoff

Roads and other transport-related surfaces can constitute up to 70% of the total impervious areas in an urban catchment (Wong et al. 2000). Because road surfaces are generally impervious, they create a path for road runoff, and as a result road runoff can contribute 40–100% of the loading of contaminants in urban stormwater (MoT 1996). A high-density highway may occupy only 5–8% of the urban catchment area, but the runoff can contribute approximately 50% of the total suspended solid, 16% of total hydrocarbon, and between 35–75% of the total metal inputs to the receiving waterbodies. Therefore, input road-drainage water can occasionally dominate stream chemistry (Ellis et al. 1987).

The importance of road runoff as a constituent of stormwater was further illustrated by several worldwide studies. Researchers in Madison, Wisconsin, United States (US), collected rainfall runoff from streets, parking lots, roofs, driveways and lawns. The results indicated that streets produced large contaminant loads for most pollutants in the commercial, industrial and residential areas (Bannermann et al. 1993). Runoff collected from roofs, courtyards and streets in a residential area in Paris produced results that also confirmed the importance of street runoff pollution (Gromaire-Mertz et al. 1999).

A list of pollutant loads in the runoff derived from various land uses in the US was conducted by Livingston (1997). The results are summarised in Table 1.1 and show freeways and parking lots to be amongst the highest sources of pollutants.

**Table 1.1 Urban land use and typical pollutant loads in the runoff (kg/ha/yr) (Livingston 1997).**

| Land use | TSS | Pb | Zn | Cu | TP | TKN | $NH_4$ | $NO_x$ | BOD | COD |
|---|---|---|---|---|---|---|---|---|---|---|
| Freeway | 986 | 5.0 | 2.4 | 0.41 | 1.0 | 8.8 | 1.7 | 4.7 | - | - |
| Parking lot | 448 | 0.9 | 0.9 | 0.04 | 0.8 | 5.7 | 2.24 | 3.24 | 53 | 302 |
| High-density residential | 470 | 0.9 | 0.8 | 0.03 | 1.1 | 4.7 | 0.9 | 2.2 | 30 | 190 |
| Medium-density residential | 213 | 0.2 | 0.2 | 0.15 | 0.5 | 2.8 | 0.5 | 1.6 | 14 | 80 |
| Low-density residential | 11 | 0.01 | 0.04 | 0.01 | 0.04 | 0.03 | 0.02 | 0.11 | - | - |
| Commercial industrial | 1120 | 3.0 | 2.4 | 0.45 | 1.7 | 7.5 | 2.1 | 3.5 | 69 | 470 |
| Park | 3.3 | 0.005 | - | - | 0.03 | 1.6 | - | 0.33 | - | 2.2 |
| Construction | 67 200 | - | - | - | 90 | - | - | - | - | - |

TSS = total suspended solids,
Pb = lead,
Zn = zinc,
Cu = copper,
TP = total phosphorus,
TKN = total kjeldahl nitrogen,
$NH_4$ = ammonium,
$NO_x$ = nitrogen oxides,
BOD = biochemical oxygen demand,
COD = chemical oxygen demand

A New Zealand study showed that, worldwide, total annual loads per unit area from highways were higher than those for residential areas, commercial areas, roads, streets and freeways (Snelder 1995). A Canadian study demonstrated that the highest occurrence of critical toxic responses in *Daphnia magna* was found for winter multi-lane divided highway runoff, while stormwater from mixed urban land uses was considerably less toxic, and rarely critically toxic (Marsalek et al. 1999).

Overseas investigations of pollutant constituents in bridge highway runoff indicated that pollutant levels were higher than those reported for other sections of the highway due to de-icing salts (Wu et al. 1998). In contrast, research in Queensland, Australia, showed that the presence of higher lead (Pb), zinc (Zn) and copper (Cu) concentrations occurred at the bridge exit lanes. The exit lane was exposed to decelerating vehicles over a short distance. The increased brake wear from exiting vehicles caused higher Cu concentrations at these sites, compared with sites without an exit lane near the sampling point. The rapid deceleration and potential for tyre wear also explained the higher Zn concentrations, since Zn is a component in most tyres (Drapper et al. 2000).

An earlier (1990) German study demonstrated that driving patterns could influence contaminant levels. The results showed that traffic lights on a highway yielded higher values than for freeways, for almost all organic and inorganic constituents studied. Stopping and starting at traffic lights led to a higher number of braking and acceleration activities. Associated with the stopping and starting were an increase in tyre abrasion, higher wear of brake linings, higher automotive exhaust gas emissions, and higher leakages of hydrocarbons (Muschack 1990).

## 1.4 Contaminants in Road Runoff

The characterisation of a variety of road-related materials has been the subject of many previous studies. Such studies investigated contaminants present in road dust (Ball et al. 1998), roadside soil and plant samples (Fergusson et al. 1980), receiving stream water and sediments (Maltby et al. 1995a), and road runoff (Barrett et al. 1998; Wu et al. 1998; Legret & Pagotto 1999; Berbee et al. 1999; Drapper et al. 2000).

Twenty-five years (preceding 1995) of international stormwater research, based on the identification and quantification of contaminants in stormwater, have been collated and reviewed by Makepeace et al. (1995).

Although a wide range of contaminants has been identified in stormwater, only a few distinct groups are present in road runoff water. The principal groups of contaminants (discussed in Sections 1.4.1 to 1.4.7 below) are particulate contaminants, metals, non-metals, polycyclic aromatic hydrocarbons (PAHs), other organics, pesticides and other pollution indicators.

### 1.4.1 Particulate Contaminants

The solid component of road runoff consists of suspended solids and sediments. Suspended solids are particles that are suspended in water and are quantified as total suspended solids (TSS). Sediments are particulates that have settled.

The concentrations and loadings of TSS in the runoff from an urban bridge highway segment situated in North Carolina, were double that of the US Nationwide Urban Runoff Program (NURP) (stormwater data). This was due to the presence of insoluble particles in the de-icing salts used (Wu et al. 1998). Runoff from a rural bridge highway segment situated in France confirmed the high level of suspended solids in the runoff due to road de-icing. The levels exceeded the European concentration limit for urban wastewater treatment plant discharges in over 65% of the events studied (Legret & Pagotto 1999).

Only 5% of sediment material is derived directly from vehicle operation (Sheehan 1975). However, the sediment will carry the majority of the heavy metals, oils and greases and complex organic compound loads generated by vehicles (Snelder 1995).

### 1.4.2 Metals

Review of the literature indicated that cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) were the main metals analysed in road runoff (Stotz 1987; Wust et al. 1994; Mungur et al. 1995; Sansalone & Buchberger 1997; Barrett et al. 1998; Wu et al. 1998; Berbee et al. 1999; Dierkes & Geiger 1999; Gromaire-Mertz et al. 1999; Legret & Pagotto 1999; Drapper et al. 2000; Kuschel 2000). Other metals have also been analysed in road runoff, but to a much lesser extent, i.e. aluminium (Al) (Sansalone & Buchberger 1997), chromium (Cr) (Wu et al. 1998; Stotz 1987), nickel (Ni) (Barrett et al. 1998; Wu et al. 1998) and iron (Fe) (Barrett et al. 1998). Iron, while present in high concentrations, has been of less concern because of its relatively low toxicity. Heavy metal concentrations in road runoff from overseas studies are compared in Table 1.2.

**Table 1.2 Heavy metal concentrations (μg/L) in road runoff from overseas studies.**

| Country | Pb | Cu | Cd | Zn | Reference |
|---|---|---|---|---|---|
| Germany | 140 | 86.7 | 0.88 | 320 | (Wust et al. 1994) |
| Germany | 17 | 140 | 1.4 | 1250 | (Dierkes & Geiger 1999) |
| US | 13 | 13 | 2 | 209 | (Sansalone & Buchburger 1997) |
| US | 13 | 12 | 2.5 | - | (Wu et al. 1998) |
| France | 133 | 61 | 0.6 | 550 | (Gromaire-Mertz et al. 1999) |
| England | 84 | 24 | 6 | 67 | (Mungur et al. 1995) |

The high concentration of Zn in the German and French road runoff samples was attributed to safety fences in the catchment of the sampling site (Dierkes & Geiger 1999; Legret & Pagotto 1999). While different sampling sites were involved in the 1994 and 1999 German studies, the results presented in Table 1.2 illustrate the effect of the removal of Pb from petrol (Dierkes & Geiger 1999). Lead was also found to decrease due to the introduction of unleaded fuel in other studies (Barrett et al. 1998; Legret & Pagotto 1999).

In road runoff, metal elements are partitioned between dissolved and particulate-bound fractions. This partitioning is influenced primarily by the pavement residence time, rainfall pH, the nature and quantity of solids present, and the solubility of the metal element. Runoff from a highway site in urban Cincinnati, Ohio, US, demonstrated that events where rainfall pH was lowest and average pavement residence time was highest, resulted in the largest metal element dissolved fractions (Sansalone & Buchberger 1997).

In lateral pavement sheet flow, the predominant dissolved heavy metals are Zn, Cd and Cu. Lead (Pb) is mainly particulate-bound. The soluble portions of Pb, Cu and Zn in highway runoff have been found to constitute 1–10%, 20–40%, and 30–50% respectively, of the total metal composition. Total Cd concentrations are generally too low to have a significant ecological impact. The majority of the total Cd was found to be in the soluble form (Sansalone & Buchberger, 1997).

The soluble heavy metal constituents in road runoff are of concern due to their immediate bio-availability (Mungur et al. 1995; Sansalone & Buchberger 1997). However, studies show that most of the pollutant load is transported by sediments (Marsalek et al. 1999). Contaminants bound to sediments eventually leach into the waters becoming available for plant uptake.

De-icing salt maintenance practices require the use of soluble salts, e.g. calcium chloride, which generate anions and associated cations. The runoff from an urban bridge highway segment situated in North Carolina (Wu et al. 1998) and from a rural bridge highway segment situated in France (Legret & Pagotto 1999) indicated that conductivity and salinity were higher when these salts were used.

### 1.4.3 Non-metals

In studies of highway runoff, oxides of nitrogen and phosphate were found in low concentrations and were attributed to the rainfall (Montrejaud-Vignoles & Herremans 1996; Legret & Pagotto 1999; Drapper et al. 2000). Generally, levels observed were so low they were not of concern.

### 1.4.4 PAHs

PAHs belong to the semi-volatile organic contaminant class and occur in the atmosphere in gaseous and particulate forms (Ollivon et al. 1999). The major source of PAHs in road runoff is believed to be automobile emissions (Section 1.6.1). Because of the number of PAH compounds emitted by vehicles, different workers have reported different compounds (Hewitt & Rashed 1990).

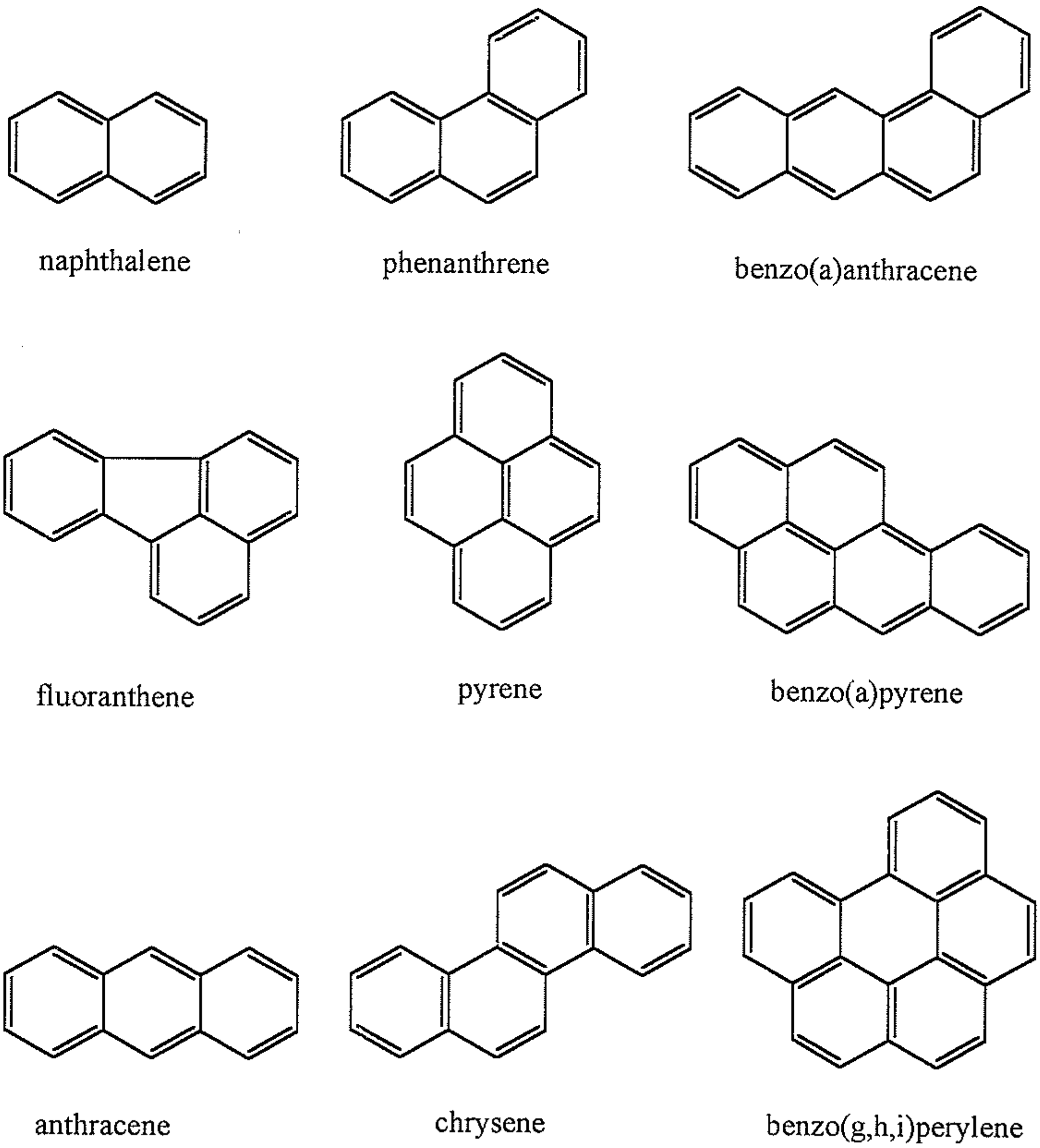
Anthracene and phenanthrene are examples of low molecular PAH compounds. They are emitted mainly in the gas-phase, and have a small impact on the road environment, where as much as 98% is dispersed away from the highway surface. Fluoranthene and pyrene have intermediate molecular weights and are emitted in both gas-phase and particulate forms, where 7% is retained in the road environment, and the remaining 93% is dispersed away from the highway. Benzo(a)anthracene/chrysene and benzo(a)pyrene are high molecular weight PAHs emitted entirely in the form of particulates. The percentage retained in the road environment is approximately 30%, and the remaining c.70% is dispersed away from the highway (Hewitt & Rashed 1990).

The chemical structures of representative PAH compounds are given in Figure 1.1.

Investigations in France demonstrated that the highest PAH level (1430 ng/g) was observed in the sediments along the ditches that line the road, and illustrated the significant contribution of road runoff to the contamination of the Eau Morte river. The results provided evidence for PAH adsorption on particulate matter of ditches and river sediments (Naffrechoux et al. 2000).

Ollivon et al. (1999) found that the main PAHs in car park dusts and rainwater in an urban area were phenanthrene, fluoranthene, pyrene and benzo(g,h,i)perylene. They found that during rainfall events the more volatile PAHs (phenanthrene, fluoranthene and pyrene) equilibrated quickly with rain droplets, while the particulate PAH benzo(g,h,i)perylene was bound to the aerosol phase of rain (Ollivon et al. 1999).

Other research has confirmed the presence of these PAH compounds in United Kingdom (UK) highway runoff (Hewitt & Rashed 1992) and stormwater runoff (Bomboi & Hernandez 1991), except for phenanthrene. However, a nationwide survey of stormwater runoff in the US showed that phenanthrene was detected most frequently along with naphthalene, pyrene and fluoranthene (Maltby et al. 1995a). In addition, urban highway runoff samples collected from four rainfalls in Osaka, Japan, indicated that the predominant PAH compounds were phenanthrene, fluoranthene and pyrene, which comprised about 50% of the 15 quantified PAHs constituents in each sample (Shinya et al. 2000).



naphthalene
phenanthrene
benzo(a)anthracene
fluoranthene
pyrene
benzo(a)pyrene
anthracene
chrysene
benzo(g,h,i)perylene

**Figure 1.1** **Chemical structures of pyrene, phenanthrene, fluoranthene, benzo(a)pyrene, benzo(a)anthracene, naphthalene, anthracene, chrysene and benzo(g,h,i)perylene.**

A New Zealand investigation of pollutants in the Avon/Heathcote rivers and estuary system determined the concentration of hydrocarbon contaminants in cockle (*Austrovenus stutchburyi*) samples. The results indicated the presence of the very toxic carcinogen benzo(a)pyrene, at all sites, but the most abundant PAHs were pyrene, fluoranthene and benzo(a)anthracene/chrysene (Trower & Holland 1992).

### 1.4.5 Other Organic Pollutants

Another organic pollutant that may be a problem in road runoff is phenol. However, data are limited, making it difficult to predict its environmental effect. The presence of pentachlorophenol may be diagnostic of the more dangerous dioxins and furans (Makepeace et al. 1995). It has been suggested that residues from car and truck exhausts contribute to the dioxin/furan load in street runoff (Horstmann & McLachlan 1995). However, stormwater runoff samples collected in the Santa Monica Bay (US) watershed revealed only trace concentrations of polychlorinated dioxins and polychlorinated furans (Fisher et al. 1999).

Nitrophenols are known to originate from car exhaust and atmospheric photochemical reactions, and were studied by Wust et al. (1994). A significant fraction of the nitrophenols was found in precipitation, suggesting that washout from the atmosphere was a major source. The nitrophenols were found in very low concentrations and are not likely to be a problem.

Since the phasing out of Pb in fuel, the presence of alkyl lead has become less of an issue in road runoff. In studies before the phasing out of Pb in England, trimethyl lead was found to be the most predominant alkyl lead compound in the runoff, and the major source of these compounds was from atmospheric deposition (Makepeace et al. 1995).

Total hydrocarbon content originates mainly from oil and grease, though many organic chemicals with different properties and toxicities are involved. Oil and grease have been found in high concentrations on impervious highways (Wu et al. 1998), and high total concentrations of hydrocarbons were found in the runoff (Legret & Pagotto 1999).

### 1.4.6 Pesticides

Pesticides include herbicides, fungicides, insecticides and fumigants. Organic chemicals used in the manufacture of pesticides include: aromatic carboxylic acids; carbamate compounds (e.g. Alicarb); chlorophenoxy compounds (e.g. 2,4-D); organochlorine compounds (e.g. Aldrin, BHC); organophosphorus compounds (e.g. Diazinon); pyridinium compounds (e.g. Paraquat); triazine compounds (e.g. Atrazine); and other compounds (e.g. Acrolein) (Makepeace et al. 1995).

Most of these pesticides have been studied in relation to standards based on drinking water and aquatic life regulations but, apart from organochlorine compounds, most have not been studied in urban stormwater. In a bridge highway runoff study in Queensland, Australia, organochlorine pesticides were not found in detectable levels in pavement runoff, even in the rural bridge areas, which made up 40% of the sites (Drapper et al. 2000).

### 1.4.7 Other Pollution Indicators

Oxygen-demanding wastes are generally organic wastes that can be decomposed by aerobic bacteria. The quantity of oxygen-demanding waste in the water is determined by measuring the biochemical oxygen demand (BOD). BOD measurement is commonly used for stormwater characterisation (Gromaire-Mertz et al. 1999).

Dissolved oxygen (DO) is the molecular oxygen dissolved in the water body, and pollution by degradable organic matter will lead to a lowering of the DO.

The acidity or alkalinity of water is indicated by the pH and is determined as the negative log of the hydrogen ion concentration. In stormwater this varies with the amount of local sulfur dioxide and nitrogen dioxide emissions (Novotny et al. 1985).

## 1.5 Environmental Effects

Effects of road runoff discharges for northern hemisphere sites have generally been reported in four categories: chemical stratification of receiving waterbodies; changes in water quality; toxic effects; and road runoff volume and flowrates.

### 1.5.1 Chemical Stratification of Receiving Waterbodies

Road runoff discharges have been shown to cause chemical stratification of the receiving water by chlorides (the consequence of street de-icing). This had the potential to prevent spring overturn and transportation of oxygen to the bottom strata of a water body, and also to bring about a lack of oxygen, the possible release of metals and high chloride concentrations, and the elimination of some benthic species (Marsalek et al. 1999).

### 1.5.2 Changes in Water Quality

Changes in water quality for small lakes were reported by Gjessing et al. (1984). These changes included increases in conductivity, and deposition of sediments with elevated concentrations of heavy metals and organic compounds such as hydrocarbons (Marsalek et al. 1999).

#### *Heavy Metals*

Lead (Pb) has been identified as the most important contaminant of concern in stormwater research. In the US NURP studies, Pb concentrations exceeded the drinking water quality guidelines in 73% of the samples taken, and was detected in 94% of the NURP Priority Pollutant Study samples. Lead emissions contaminate roadside soils and vegetation, street dust, roadside drainage, and the atmosphere, and it is extracted from these reservoirs with every storm event (Makepeace et al. 1995). However, since the phasing out of leaded petrol in New Zealand in 1996, the levels of Pb in roadside dusts have decreased (Raksasataya et al. 1996).

The reported concentrations for Cu, Zn and Cd in stormwater runoff generally show that they are a concern both for drinking water quality regulations and for aquatic life criteria (Makepeace et al. 1995).

### *Organic Compounds*

Large populations of bacteria decomposing organic compounds can have an effect on the quality of the water by removing the dissolved oxygen from the water, which causes fish and other forms of oxygen demanding aquatic life to die. Organic compounds can also cause acidification, nutrient enrichment, eutrophication and contamination of rivers and groundwaters. Increases in phosphorus also cause eutrophication, ecological degradation and blue green algal blooms (D'Arcy et al. 1998).

## 1.5.3 Toxic Effects

Toxic effects have been reported at some sites, e.g. for *Gammarus pulex* exposed to runoff contaminated sediment (Boxall & Maltby 1995; Maltby et al. 1995b). These effects can be both acute and chronic (Marsalek et al. 1999). The tentatively identified toxicants included the PAHs: pyrene, fluoranthene and phenanthrene; and the heavy metals: Cu and Zn (Maltby et al. 1995a; Boxall & Maltby 1997). Oil and hydrocarbons have also been shown to cause toxicity towards aquatic life (D'Arcy et al. 1998).

### *PAHs*

Extracts of UK stream sediments showed that the toxicity of runoff-contaminated sediment was due to 3-5 ring PAHs. The predominant PAHs present were pyrene, fluoranthene, phenanthrene, anthracene, benzo(a)anthracene, and chrysene. The toxic fraction also contained phthalic acids and furans; however, phenanthrene, fluoranthene and pyrene were shown to account for the major proportion of the toxicity (Boxall & Maltby 1997). Another UK investigation confirmed that the main toxic contaminants were fluoranthene, pyrene and phenanthrene (Maltby et al. 1995a).

The toxicity of contaminated sediments from a heavily urbanised river was investigated by Jones (1995). The results indicated that methylated PAHs derived from lubricating oils contributed to higher mortalities in *Assellus aquaticus* and *Lymnaea peregra* than the more predominant parent PAHs that are produced mainly from combustion sources (Ellis et al. 1997).

PAHs contain numerous known or suspected carcinogenic substances. These are harmful to aquatic life due to their toxicity and mutagenic effects. They are unlikely to cause adverse effects on human health, since, being bound to the sediments in the recipient waterbody, they are unlikely to get into the drinking water (Van Metre et al. 2000).

### *Heavy Metals*

The heavy metals Cd, Cu, Pb and Zn do not generally produce an acute and immediately observable impact. Instead, these contaminants accumulate in living tissues or sediments and consequently have long-term detrimental effects on living organisms (Marsh 1993). The toxic effect of heavy metals on aquatic life has been reviewed recently by Makepeace et al. (1995).

Copper is the major aquatic toxic metal, e.g. to *Daphnia pulex* in stormwater. The NURP studies indicated that Cu is a serious threat to aquatic life in the south-eastern US, and it is quickly accumulated in both plants and animals.

Cadmium bio-accumulates in both aquatic plants and animals, and can have acute and chronic toxicity for rainbow trout and other organisms.

Lead in stormwater runoff is mostly associated with suspended solids. Lead occurs at higher levels in the sediment than in the stormwater, causing concern about acute toxicity for *Daphnia pulex* and chronic toxicity for rainbow trout (*Oncorhynchus mykiss*). Lead is bio-accumulated in aquatic organisms, benthic organisms, plants, invertebrates and fish.

Zinc concentrations exceeded the US Environmental Protection Agency's (USEPA) freshwater chronic criteria in 77% of all NURP samples. Zinc is of less threat to aquatic life than Cu or Pb, but negative impacts can occur at high concentrations or in soft water conditions. Also Zn bio-accumulates easily in plants and animals.

The toxicity of other metals such as Fe and Ni has also been reported. While Fe caused toxicity and aesthetic nuisance (D'Arcy et al. 1998), its addition to Pb, Cu and Zn in synthetic stormwater was found to reduce the overall toxicity for some aquatic organisms such as fish. Makepeace et al. (1995) reported that Ni is toxic for the eggs and adults of rainbow trout.

#### *Oil and Hydrocarbons*

Hydrocarbons have been shown to increase algal abundance either by reducing grazing pressure or by direct stimulation. Oil, a major component of road runoff, has been shown to reduce the decomposition of leaf litter in lakes (Maltby et al. 1995a). Oil and hydrocarbons cause toxicity for aquatic life, as well as contamination of urban stream sediments and groundwater (D'Arcy et al. 1998).

### 1.5.4 Road-runoff Volumes & Flowrates

The hydrological characteristics of road runoff cause detrimental effects to the environment. The increased flows and stream channels provide a poor habitat for aquatic flora and fauna, as faster flood flows destroy the environment in which aquatic life thrives; and also wash away the organisms themselves. Channel modifications reduce the habitat diversity and quality. Reduced base flows can cause increased water temperatures and low dissolved oxygen concentrations, which are unacceptable conditions for most aquatic species (Elliott 1999).

## 1.6 Sources of Road-runoff Contaminants

Most of the literature on the sources of road-runoff contaminants has originated from overseas studies. Very little data comes from New Zealand studies. Contaminants can originate from vehicles, spillages, pavement degradation and residues from activities on or adjacent to the road, e.g. roadway maintenance (Sansalone & Buchberger 1997; Dierkes & Geiger 1999).

### 1.6.1 Vehicular Traffic

Vehicular traffic is considered to be a main source of contaminants on highway surfaces (Stotz 1987; Marsalek et al. 1999). Factors that influence contaminant release from vehicles include traffic density, driving habits and vehicle condition. Vehicles emit tyre particles, fuel combustion emissions, motor and transmissions oil leakages, fuel and other vehicle-specific fluids, fragments from brake linings and rust, onto the road in differing quantities, depending on the traffic and road situations (Stotz 1987; Berbee et al. 1999).

Contaminants may be emitted into the air, e.g. carbon monoxide (CO), nitrogen oxides ($NO_x$), and volatile organic compounds, or be dry-deposited onto the road and surrounding surfaces. These deposited contaminants are joined by oil from engine leaks, material from brake linings, and rubber particles from tyre wear (Kuschel 2000).

Manufacturer information in a French study indicated that the quantity of matter released by tyre wear for light vehicles was 68mg/vehicle/km, and for heavy vehicles (>3.5 tonnes) was 138mg/vehicle/km. It also indicated that the quantity of matter from brake lining wear was 20mg/vehicle/km for tourist vehicles, 29mg/vehicle/km for light goods vehicles, and 47mg/vehicle/km for heavy lorries. The mean gasoline consumption had been assessed to be 58g/vehicle/km for gasoline-powered tourist vehicles, and 61g/ vehicle/km for light goods vehicles (Legret & Pagotto 1999).

Only 5–20% of the total pollution coming from vehicular traffic is deposited on the highway and discharged with the runoff. The remaining percentage is dispersed away from the highway surface and into the atmosphere. It then accumulates on surrounding surfaces through wet or dry deposition (Stotz 1987).

The removal of pollutants from the road surface in drainage waters is more important than wet and dry deposition adjacent to the road, for all pollutants. Results have indicated that drainage waters very efficiently remove pollutants from the highway (Hewitt & Rashed 1990). During storm events, rainwater first washes out atmospheric pollutants and, on surface impact, picks up roadway deposits, before running off into the stormwater system and receiving waterbodies.

It is difficult to quantify the proportion of urban stormwater contaminants originating from vehicular traffic. This is because measuring stormwater composition from road surfaces does not provide an accurate assessment of the proportion of contaminants caused by road vehicle activities. Nevertheless, the emission rates of contaminants from vehicles were estimated in past studies, and these assess the proportion of vehicle-derived contaminants in urban stormwater (Snelder 1995).

#### *Heavy Metals*

Heavy metal concentrations in fuel and automobile components were measured in a French study by Legret & Pagotto (1999) and are listed in Table 1.3.

**Table 1.3 Heavy metal contents in fuel and automobile components (mg/kg) (Legret & Pagotto 1999).**

| Sources | Pb | Cu | Cd | Zn |
|---|---|---|---|---|
| Leaded gasoline | 200 | - | - | - |
| Unleaded gasoline | 17 | - | - | - |
| Brake linings | 3900 | 142 000 | 2.7 | 21 800 |
| Tyre rubber | 6.3 | 1.8 | 2.6 | 10 250 |

Cadmium is a by-product of vehicle use, and its source, though not absolutely determined, has often been suggested as wear of tyres and brake pads, combustion of lubricating oils and corrosion of galvanized metals (Walker et al. 1999).

Typical sources of Cu are from wear of tyres and asphalt, combustion of lubricating oils, wear of moving parts in engines (Walker et al. 1999), wear of vehicle brake linings (Timperley et al. 1999), and metal plating and bearing and brushing wear (Ball et al. 1998).

The sources of Pb are fuel-derived emissions from leaded gasoline-powered vehicles (Walker et al. 1999), tyre wear (Butler et al. 1996), lubricating oil and grease, and bearing wear (Ball et al. 1998).

The significant sources of Zn in road runoff are wear from tyres (Timperley & Kuschel 1999), brake pads, combustion of lubrication oils, corrosion of metal objects, automobile exhausts, atmospheric fallout and pavement wear (Walker et al. 1999).

Typical sources of Ni are the corrosion of welded metal plating, wear of moving parts in engines (Walker et al. 1999), diesel fuel and petrol exhaust, lubricating oil, brushing wear, and wear of brake linings (Ball et al. 1998) and bearings (Makepeace et al. 1995).

Primary sources of Fe are auto rust and moving engine parts (Ball et al. 1998).

Chromium originates from metal plating, moving engine parts and wear of brake linings, (Ball et al. 1998) bearings and bushings (Makepeace et al. 1995).

Measuring the mass fluxes of particles and metals on a regular basis for 10 months assessed the contribution of air deposition. Both the wet and dry depositions were collected in a broad container (Legret & Pagotto 1999). Results calculated from these data for emission values for 1 km of road are presented in Table 1.4.

The study documented in Legret & Pagotto (1999) measured the heavy metal content of solids emitted from various vicinities close to a road. The emission fluxes from each source for each contaminant were added to give the total amount of contaminant emitted. Road runoff samples were then collected and analysed to give the concentrations of heavy metals actually present in the drainage water. The result is expressed as a percentage of the total calculated value, and gives the percentage of the vehicle component found in the drainage water (see Table 1.4).

**Table 1.4 Emission fluxes and percentage estimated to be removed in drainage waters (kg/km/year) (Legret & Pagotto 1999).**

| Sources | Solids | Pb | Cu | Cd | Zn |
|---|---|---|---|---|---|
| *Vehicles* | | | | | |
| Tyre wear | 314 | 0.002 | 0.0006 | 0.0008 | 3.22 |
| Brake linings | 100 | 0.39 | 14.2 | 0.0003 | 2.17 |
| Gasoline | – | 13 | – | – | – |
| *Road* | | | | | |
| Safety fence | – | 0.002 | 0.0002 | 0.0002 | 0.95 |
| De-icing agent | 130 | 0.015 | 0.002 | 0.0007 | 0.002 |
| *Air deposition* | 86 | 0.014 | 0.015 | 0.0009 | 0.21 |
| Total | 630 | 13.4 | 14.2 | 0.003 | 6.55 |
| Drainage water % | 235 | 5 | 2 | 313 | 37 |

Solids originating from sources other than vehicles, e.g. pavement wear and mud clinging to vehicles, were not taken into account in the calculations.

The results showed that most of the Pb was dispersed into the atmosphere. Meanwhile a small percentage of Cu was related to the low traffic density and road geometry, while Cd sources were under-estimated and Cd fluxes were very low compared with the other heavy metals (Legret & Pagotto 1999).

### PAHs

PAHs originate mainly from the abrasion of tyres (Wust et al. 1994) and dry deposition (Walker et al. 1999; Yang & Chiang 1999) from the combustion of fossil fuels, such as diesel and petrol (Rogge et al. 1993; Bomboi et al. 1999; Ollivon et al. 1999). PAHs are also present in automotive oils and lubricants (Ollivon et al. 1999; Timperley & Kuschel 1999), and originate either from dissolved fuel or are produced by incomplete fuel combustion.

A major contributor to the PAH content of stormwater runoff is the leakage of crankcase oil onto the road. Crankcase oil makes up 88% of total hydrocarbon load and accounts for 74% of PAHs. Traffic is a major source of PAHs, with statistics showing that motor vehicles in the US account for approximately 36% of the yearly total PAHs in the runoff (Maltby et al 1995a).

## 1.6.2 Non-vehicular Sources

### Spillages

Spillages can occur from stock trucks (effluent from animals) and vehicular road accidents.

### Pavement Degradation

Roading materials, e.g. asphalt, are important sources of contaminants such as PAHs (Wust et al. 1994) and Ni (Ball et al. 1998). Although solids are generated by dust, soil particles (Butler et al. 1996) and tyre and vehicular part abrasion (Sansalone &

Buchberger 1997), they are also produced from road grit. Depending on the road condition, surfaces will emit pavement particles onto the road in differing quantities (Stotz 1987). Solids can be present in various forms from rapidly soluble, submicron particles to insoluble gravel-size composites (Sansalone & Buchberger 1997).

#### *Residues from Activities on or Adjacent to the Road*

Residues from activities on or adjacent to the road can emit contaminants into the atmosphere or directly onto the road. Fertilisers and airborne dust can become deposited on the road surface from surrounding agricultural or industrial land uses. Roadway activities such as road marking and painting signs may release metals such as Cd onto the road. In addition to roadway activities, de-icing salt maintenance practices used on roads during winter can also generate ions such as cyanide (Novotny et al. 1998).

## 1.7 Effect of Traffic Density, Land Use & Rainfall Events

International literature has characterised road runoff contaminants for traffic density, surrounding land use, and rainfall events.

### 1.7.1 Traffic Density

There is a continuing controversy concerning traffic density and the quality of receiving waters. Early work has shown that deposition of contaminants on highway surfaces is directly related to traffic volume. However, these deposited contaminants did not accumulate at a linear rate. Turbulence generated from vehicular traffic dispersed the deposited contaminants away from the highway surface. The equilibrium between the rate of deposition and dispersal was expected to be reached fairly soon after a rainfall event (Colwill et al. 1984).

Several years later, research by Stotz (1987) calculated the annual pollution load of contaminants in highway surface runoff. Results showed that the amount of contaminants actually discharged with the surface runoff was not directly dependent on traffic density, but varied with wind conditions, rainfall frequency, number of preceding dry days, rainfall intensity, and runoff volume.

However, less than a decade later, Snelder (1995) illustrated that the total annual loads per unit area from high-density roads were greater than those for most other land uses. Confirming this, Ball et al. (1998) suggested that average daily traffic is significant only on a broad scale, with site-by-site variations related to other factors, predominantly the number of preceding dry days. Therefore, the relationship between the quality of road runoff and traffic density is still to be established (Ball et al. 1998).

A recent study by Drapper et al. (2000), on the relationship between traffic density and runoff quality in Queensland, Australia, demonstrated that contaminant concentrations in the runoff for several highway sites, where annual average daily traffic (AADT) was below 30 000, were similar to those reported for US sites with greater than 30 000 AADT.

In contrast, a less recent study suggested that highway runoff pollution became of concern for highways with more than 30 000 AADT (Ellis et al. 1987). This value was used as a benchmark in the US to determine whether the runoff required treatment. However, correlations between traffic density and runoff quality in Drapper et al. (2000) were weakly positive and were not statistically strong enough to propose traffic volume as the best selection indicator for roads requiring runoff treatment. Drapper et al. (2000) suggested this was due to the variability in rainfall intensity and preceding dry days in Queensland, and therefore proposed that a better measure would be to consider the quality of the receiving waters.

### 1.7.2 Surrounding Land Use

Results obtained from an USEPA NURP showed there was no truly discernable and consistent effect of land use on the quality of stormwater runoff (USEPA 1983). However, concentrations of constituents in rural highway runoff differed from urban highway runoff. Concentrations of Pb and Cu were higher in urban highway runoff, while Cd showed no difference. These values are shown in Table 1.5.

**Table 1.5 Metal concentrations (μg/L) for urban and rural highways in the US (USEPA 1983).**

| Contaminant | Urban Highway | Rural Highway |
|---|---|---|
| Lead | 400 | 80 |
| Copper | 54 | 22 |
| Cadmium | 10-30 | 10-30 |
| Zinc | - | - |

Research in Kentucky, US, confirmed the variable results within the urban land uses, where the toxicity of runoff between different land uses gave inconsistent results (Marsh 1993). Land-use category was of little general use to aid in the prediction of stormwater runoff quality at unmonitored sites, or in the explaining of differences between monitored sites. However, the Kentucky study concluded that season, rainfall amount and frequency were the important factors in the toxicity of the runoff.

### 1.7.3 Rainfall Events

The concept of a first flush of road runoff is that much of the material that has accumulated on the road surface during dry weather, will be washed from the road surface during the early stages of a rainfall event. In overseas research, the first flush phenomenon has been studied for rain water, roof runoff, road runoff, discharge of separate stormwater/sewer systems, discharge of combined stormwater/sewer systems and flow-rates of receiving waters (Deletic 1998).

High variations in runoff composition during individual events (Sansalone & Buchberger 1997), and between the events (Marsalek et al. 1997) have been observed.

A highway runoff study of the first flush phenomenon in Texas, US, showed that the overall effect of the first flush was small or negligible but was most evident on a highway receiving storms of short duration and relatively constant rainfall intensity (Barrett et al. 1998). The TSS wash-off pattern for all events is shown in Figure 1.2

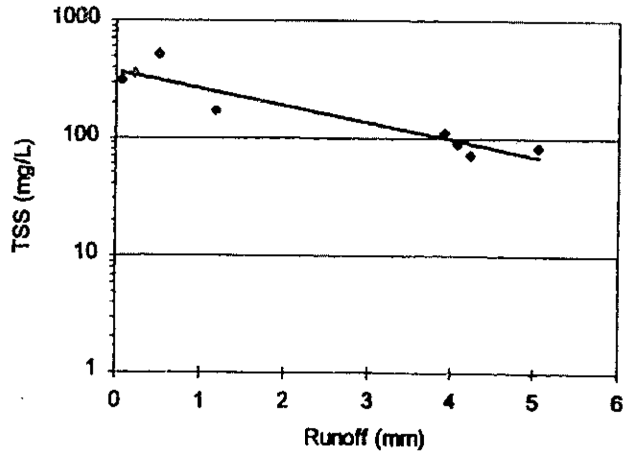


**Figure 1.2 TSS wash-off from a Texas highway (Barrett et al. 1998).**

The graph indicates that TSS concentrations decrease during the first 5mm of runoff. Complete wash-off did not occur during the storm event due to vehicles being a continuous source of pollutants to the road. Changes in traffic volume, rainfall intensity and other variables, decreased the magnitude of the first flush for longer events.

For persistent pollutants present in highway runoff, such as the heavy metals Pb, Zn and Cu, the first flush behaviour varied depending on whether the metal element fraction was dissolved or particulate-bound. Results have indicated that a pronounced first flush for pavement sheet flow occurs for all events for dissolved Zn and Cu, but not for Pb, and the first flush for the particulate-bound fractions of these metals was not well defined (Sansalone & Buchberger 1997).

Another study of the first flush phenomenon examined polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in Bayreuth, Germany. Samples were collected at the beginning and end of two rain events. One rain event had an intensity that was relatively constant over the period of the event, resulting in the PCDD/F concentrations in the runoff being approximately constant in both the first flush and last flush samples. The other event was a thunderstorm where the intensity was very high at the beginning of the storm and decreased rapidly to zero after 30 min. This resulted in PCDD/F levels decreasing by a factor of 5 to 12 from the first flush through to the last flush. This was attributed to changes in the rain intensity and its effect on the cleansing of the street surface (Horstmann & McLachlan 1995).

Marsh (1993) demonstrated that dilution of toxins and nutrients occurred from the first flush runoff to the storm end. Also, the season, rainfall volume and rainfall frequency were important factors in determining the toxicity of the runoff.

Water quality models have been developed by Seager & Maltby (1989) to predict the effects of rainfall intensity and runoff characteristics. Prolonged storms with high intensity rainfall are of concern for flood protection. Conversely, small, frequent storms chronically impact on water quality.

The idea of the first flush phenomenon has been used in the establishment of treatment technologies. Several stormwater treatment structures have been designed to capture the initial runoff from rain events, and thus remove and treat the runoff containing the highest concentrations of contaminants (Barrett et al. 1998).

## 1.8 New Zealand Studies

The contaminants in New Zealand stormwater runoff have been documented (Williamson 1985, 1986, 1993; ARC 1992, 1995), and it has been shown that road-induced runoff is a significant source of. contaminants (Williamson 1993; TADG 1996). Treatment technologies for road runoff are increasingly incorporated into New Zealand road design and management (BCHF 1992).

### 1.8.1 Road-related Research

Several road-related studies have been carried out over the last two decades, with the earliest research by Fergusson et al. (1980) focusing on road dusts. The results demonstrated Pb levels in road dusts were more concentrated at traffic lights than roundabouts. It had been established that Pb emissions from cars increase significantly during the accelerating phase. This was clarified when relatively loose material (dust) inside the car mufflers and exhausts was analysed for Pb. Sudden acceleration can loosen and then emit this dust with normal car emissions. In addition, acceleration of vehicles on highways where speed limits changed from 50 to 80 km/h showed increases in Pb (Fergusson et al. 1980).

Fergusson et al. (1980) also showed that heavy rainfall removed the Pb fraction from the road surface and carried it into the receiving waterbodies, where the level decreased dramatically after the event, consistent with the first flush phenomenon.

More recently, Snelder (1995) estimated the loading rates of vehicle-derived contaminants to New Zealand impervious surfaces and then into urban waterbodies (Table 1.6).

**Table 1.6 Estimated loading rates of vehicle derived contaminants to New Zealand urban waterbodies (Snelder 1995).**

| Contaminant | Loading Rate to Urban Water Ways (g/veh/km) |
|---|---|
| Lead | 6.0 mg |
| Zinc | 0.7 mg |
| Copper | 0.16 mg |
| Cadmium | 17.6 μg |
| Nickel | 0.045 mg |
| Chromium | 0.1 mg |
| PAH | 15.0 μg |

Before the phasing out of Pb additives, the emission rate for Pb was found to be 34mg/vehicle/km for vehicles using leaded petrol, and 75% of this lead was expelled into the environment (Snelder 1995). A similar loss into the atmosphere was assumed in a UK study (Hewitt & Rashed 1990). Therefore, the runoff loading rates for New Zealand urban waterbodies were estimated to be 6mg/vehicle/km for leaded petrol vehicles (Snelder 1995).

The loads in New Zealand urban stormwater attributable to vehicle use are summarised in Table 1.7.

**Table 1.7 Estimated contribution (proportion as %) of vehicle use to New Zealand urban stormwater contaminant levels (Williamson & Macaskill 1994).**

| Contaminant | Proportion Attributable to Vehicle Use (%) |
|---|---|
| Suspended solids | 50 |
| Lead | 100 |
| Zinc | 40 |
| Copper | 50 |
| PAH | 40 |

The mitigation of road-induced pollution was studied in New Zealand by Butler et al. (1996). A probabilistic model has been developed to analyse the impact of highway runoff, as part of the total catchment, on the receiving environment. The modelling made use of the US highway monitoring data and was applied to five highway sites in New Zealand. The results of the water-quality modelling indicated that, while the highway runoff contaminant loading was greater than that of the surrounding catchment, the relative volume of catchment runoff appeared to be a major source of contaminants to the receiving waterbodies. The results were used as a management tool to identify potential problem sites (Butler et al. 1996).

The Land Transport Pricing Study (LTPS, TADG 1996) raised an awareness of the great potential for transport-related, environmental problems. As part of the LTPS, the Ministry of Transport (MoT 1966) released an Environmental Externalities Discussion Paper, the aim of which was to establish the environmental costs associated with road transport. The estimated costs were significant and propelled consideration of the impacts of road transport into the public arena (Kuschel 2000).

Following on from the LTPS, the MoT commissioned the Vehicle Fleet Emissions Control Strategy 1997/1998. Its aim was to formulate policy for the management of local air quality impacts of traffic emissions. As well as concern for transport-related air quality, parallel concerns for water quality, particularly the impact of vehicles on urban waterbodies, were expressed. The MoT (1996) reported that road runoff accounted for up to half the metal contamination in the receiving waterbodies. In response to these concerns, current and continuing work by the National Institute of Water and Atmospheric Research (NIWA) StormWater And Transport (SWAT) programme, aimed to produce a model to predict the fate of transport-generated contaminants in the environment, so that the transport industry and local authorities can develop effective environmental policy (Kuschel 2000).

SWAT's experimental site is a high-density urban highway on Ash Street in Avondale, Auckland. A weir, flow recorder, and an automatic water sampler were installed to collect road runoff samples on a flow proportional basis. Instruments were used to monitor meteorological conditions, vehicle density, vehicle speed, ambient air and deposition. Analyses were conducted for Cu, Zn, Cd, Pb, CO, TSS, total petroleum hydrocarbons, and PAHs. The results indicated that the potential load of various contaminants to urban waterways was significant (Kuschel 2000).

Currently, Transit New Zealand has also collected samples of road runoff from State Highway 1 near Wairakei, Taupo, New Zealand. The collection was by a subsoil drain inside the road basecourse layer. The samples were collected at approximately one-month intervals, with rainfall figures collected at a point 50m away. The fine solid particles were settled out and are currently being tested. The aim of the project is to assess the alteration of the structures' load capacity (A. Grey, pers.comm. 2001).

### 1.8.2 Treatment Technologies

The usual control and treatment of highway runoff is through kerbside catchpits, followed by drainage to a piped or ditched system that may have oil-interceptor and silt-trap controls at the outlet before eventual discharge from the site (Ellis 1999). Other techniques include pervious asphalt, oil and grease systems, coagulation/flocculation, wet ponds, extended detention ponds, flow detention/retention by infiltration, sand filters, treatment walls, wetlands, grassy swales and vegetative filter strips.

Pervious asphalt, oil and grease systems and coagulation/flocculation have been shown to be inadequate as road runoff treatment technologies. Pervious asphalt has poor treatment efficiencies, requires regular maintenance of asphalt permeability, and demands high costs (BCHF 1992; Berbee et al. 1999; Wong et al. 2000). Oil and grease systems do not provide a high level of performance and are not commonly used (Wong et al. 2000). Coagulation and flocculation is expensive and can cause its own toxic effects. However, new technologies are currently being investigated where the amount of coagulant released to the road runoff can be triggered by rainfall.

Flow retention by infiltration trenches has been used for over 10 years in the US, but their long-term performance is still questionable. Infiltration trenches are likely to have limited applicability in Auckland because they need high soil permeability (areas with well-drained soils have been already developed for other land uses), and have potential groundwater and soil pollution and maintenance considerations (BCHF 1992).

Although the use of constructed wetlands is increasingly being seen as a viable solution to the treatment of highway runoff (Mungur et al. 1995), the efficiency of wetland systems in pollutant removal is highly varied. Through poor design, urban wetlands are becoming a long-term liability to the community. Nevertheless, current design guidelines for wetland systems are significantly improving their multi-functional potential to remove fine graded sediments (Wong et al. 2000). However, because of the space required, it is not an economically viable option for urban environments (Shaver 1999).

Wet ponds and extended detention ponds have considerable application in Auckland (Mitchell & Associates Ltd 1992; McKergow 1994a). However, a detention pond (with oil trap at the outlet) receiving highway runoff from the high traffic density M25 in the UK has demonstrated an absence of, or limited success in, oil interception and grit/silt settlement facilities. Current research is establishing more efficient treatment at this site (Ellis 1999).

Sand filters were assessed to be the most appropriate and effective treatment device for runoff from urban intersections (i.e. Great South Road and Station Road intersection in Auckland) and highways (Shaver 1999). They are a compact unit suitable for fully developed urbanised areas, and use only a small amount of space when compared with a more conventional treatment technology such as a detention pond. They function best for smaller catchments with high percentages of impervious surfaces. The advantage of sand filters is their performance in reducing pollutants other than just sediments. Sand filters are effective at reducing the amount of floatable material, oils, grease, and metals from stormwater runoff to a level that meets Auckland Regional Council (ARC) requirements (McLeod 1999).

However, the operation of these filter systems depends on good design, construction, and most importantly, on regular maintenance, especially of the filter media (Shaver 1999). The use of other filter media such as fly ash, lime, wool felt, woodwaste and *Sphagnum* moss in treatment wall technologies provides significant reductions in soluble metals and PAHs in laboratory experiments. They are ideal for localised "hot spots" and are currently being tested by Landcare Research at a roundabout site in Hamilton City (Lee et al. 2001).

For the most adequate treatment of New Zealand road runoff, control and treatment alternatives must resort to much more passive techniques that combine retention/ detention facilities with bio-filtration contact treatment (Wong et al. 2000). This is because impermeable road and highway surfaces generate variable runoff volumes, flowrates (Ellis 1999) and fine particulates containing a significant proportion of heavy metals (Wong et al. 2000). These techniques involve soil infiltration and vegetative filtration by passing flow through grassy swales, filter strips, and constructed wetlands (Ellis 1999; USEPA 1999; Wong et al. 2000).

Swales, as a form of management, seem attractive for runoff from linear catchments such as roads and highways. They are best suited to sites with permeable volcanic soils, but can, however, provide benefits even on poorly draining clay soils in Auckland, provided good vegetation growth can be achieved (BCHF 1992; Barrett et al. 1998). Swales significantly reduce the concentrations of most runoff constituents (Schueler 1995; Barrett et al. 1998).

## 1.9 Concerns Regarding Road Runoff

Motor vehicles contaminate the environment via a number of pathways including exhausts, oil leaks, brake linings, tyre wear and road deposition. Motor vehicles are the single biggest man-made source of air pollution. Air quality guidelines are already being exceeded in major New Zealand cities. In Auckland and Christchurch, health guidelines for CO, and more recently $NO_2$, have been exceeded, especially during May to September when atmospheric conditions are unfavourable for dispersion (e.g. periods of calm). In addition to air quality problems, the concern for water quality, particularly the impact of vehicles on the receiving aquatic environment, is on the rise (Kuschel 2000). This is a concern to New Zealand regional authorities (Leach 2001; Shaver 2001).

### 1.9.1 Experimental Site & Sampling

Worldwide studies indicated that contaminant loads from highways were higher than those for other roads and land uses (Snelder 1995). Further recent investigations of road runoff in Queensland indicated that exit lanes from highway bridge sites produced higher levels of contaminants due to driving patterns (Drapper et al. 2000).

National and overseas road runoff studies have used automated bottle samplers to enable the sampling of road runoff throughout rainfall events. This method of sampling allowed for the calculation of event mean concentrations, the total contaminant load, and the identification of the variation in contaminant concentration through the rainfall event (McKergow 1994b; Sansalone & Buchberger 1997; Barrett et al. 1998; Wu et al. 1998; Legret & Pagotto 1999).

### 1.9.2 Contaminants of Concern & their Analysis

From overseas data it is clear that the constituents of most concern are the heavy metals Cu, Cd, Cr, Fe, Ni, Pb and Zn, and the PAHs including pyrene, phenanthrene, fluoranthene and benzo(a)pyrene. These pollutants are known to be toxic to the aquatic environment and, in the case of Fe, cause aesthetic problems.

In the field of analytical chemistry the following techniques are most appropriate for metal element analysis of water samples: Atomic Absorption Spectrometry (AAS) (which includes flame and graphite furnace AAS), Inductively Coupled Plasma Mass Spectroscopy, and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

Comparison of ICP-OES with other techniques shows that there has been rapid growth and acceptance of ICP-OES analytical analysis in a large number of analytical fields. This has been due primarily to its multi-element (thus, more efficient) capabilities, relative freedom from matrix interferences, low detection limits, a linear dynamic range of 4 to 5 orders of magnitude, and precision of measurement giving 0.5 to 2% Coefficient of Variation (CV) (GBC Scientific 1997).

Many analytical techniques have been developed for the identification and quantification of PAHs in the environment. Two widely used techniques are Gas Chromatography (GC) with Flame Ionisation Detection (FID) or Mass Spectrometry (MS) detection, and High-pressure Liquid Chromatography. Having reviewed available resources in the Chemistry Department, University of Waikato, Hamilton, and the sensitivity limits required for road runoff samples (typically in their ng/L range), the methodology of choice was Selected Ion Monitoring (SIM) GC/MS

### 1.9.3 Contaminant Patterns in Road Runoff during Rainfall Events

A major purpose of the present study was to determine whether road runoff generated under New Zealand conditions was similar to that reported in overseas research. Factors that might contribute to differences include:

(1) New Zealand has the second highest vehicle ownership rate in the world with 2.76 million vehicles for a population of 3.92 million.

(2) No mandatory vehicle emission controls/standards are set despite petrol going fully unleaded in 1996.

(3) The imported vehicle fleet contains a high proportion of used vehicles from Japan, usually 3 to 7 years old at arrival in New Zealand.

(4) New Zealand has a large amount of roading per capita.

(5) New Zealand has a unique temperate island climate with relatively high annual rainfall distributed throughout the year.

## 1.10 Objectives

The stated purpose of this research is to investigate contaminants found in New Zealand road runoff and to determine how the relative concentrations, total load, and characteristics change with the frequency and intensity of rainfall events. The specific objectives to allow this to be achieved include:

(1) Method validation of ICP-OES and SIM GC/MS protocols and confirmation of the presence of heavy metal and PAH species in road runoff.

(2) Sampling and identification of a site suitable for monitoring road runoff during rainfall events. The site needed to be close to Hamilton, secure and easily accessible.

(3) Documentation of variations of heavy metals and PAHs during rainfall events. Of particular interest is the effect of intensity and frequency of rainfall events. These studies should indicate whether the phenomenon of first flush, reported overseas, occurs under New Zealand conditions.

(4) Depending on the results obtained for Objective 3, to suggest cost-effective treatment options to minimise the environmental impact of road runoff.

# 2. Materials & Methods

## 2.1 Sampling & Flow Measurement

The sampling and monitoring equipment included an ISCO 6700 automatic water sampler, YSI 600 Sonde (capable of continuously monitoring conductivity, pH, DO and temperature), 730 bubbler module in conjunction with 45° V-notch weir (to allow the measurement of the flowrate), and a RAIN-O-MATIC tipping bucket rain gauge (TBRG) (used to monitor rainfall intensity).

ISCO Inc., Lincoln, US, provided the sampler, sonde and bubbler module. The rain gauge was manufactured by PRONAMIC, Denmark. The rain gauge funnel and weir were constructed manually.

### 2.1.1 Automatic Water Sampling

The sampler (Figure 2.1) retrieves a sample by drawing the liquid through the strainer and suction line to the pump tube. The liquid flows through the pump tube, past the liquid detector, which senses the liquid. From the detector, the liquid follows the pump tube through the peristaltic pump to the bulkhead fitting and then through the discharge tube to the 500-mL sample bottle (ISCO Inc. 1996).

a. Controller.
b. Center Section.
c. Peristaltic Pump.
d. Liquid Detector.
e. Strainer.
f. Suction Line.
g. Stainless Steel Coupling.
h. A pump tube routed from the liquid detector's intake port through the pump, out the detector's discharge port, and over the side of the controller to a bulkhead fitting at the top of the center section.
i. Bulkhead Fitting.
j. Discharge tube running from the bulkhead fitting on the inside of the center section through the spring and distributor arm.
k. Distributor arm and spring.

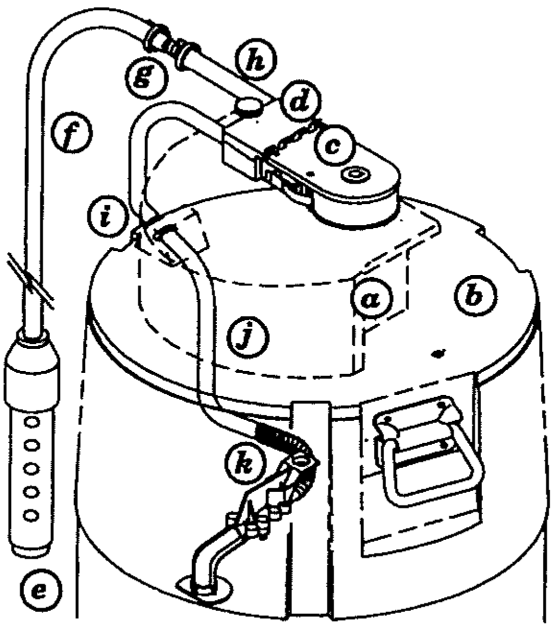


Figure 2.1 Method of sampling (ISCO Inc. 1996).

A typical sampling cycle consists of:

(1) The sampler moves the distributor arm over the bottle that is to receive the sample.

(2) The pump reverses for the pre-sample purge.

(3) The pump direction changes, filling the suction line.

(4) When the detector senses liquid, the sampler begins measuring the sample volume (amount of liquid delivered into a bottle).

(5) After discharging the sample, the pump again reverses for the post-sample purge.

#### *Autosampler Battery*

When the sampler was disabled (without pump action), the ISCO 934 nickel-cadmium battery lasted only about 3 days. The battery power would have been lost even more quickly when the sampler was enabled, thus the battery was unsuitable for the experiment envisaged.

A battery with a greater capacity was required to drive the sampling system and the sampler's peristaltic pump. A deep cycle marine lead-acid battery was chosen for the project. This allowed repetitive discharge and recharge, and about 3–4 weeks' use for each charge cycle.

#### *Downloading Data from the Sampler*

Readings and reports were retrieved and downloaded from the sampler using ISCO's Flowlink software that processes the data on a personal computer.

### 2.1.2 Measurement of pH, Conductivity, Dissolved Oxygen & Temperature

Quick determination of contaminant trends during a rainfall event was obtained by monitoring pH, conductivity, DO and temperature during sampling. This was achieved by connecting a YSI 600 Sonde capable of monitoring the desired parameters to the sampler. The sampler and sonde were programmed as a single unit so that parameter monitoring was combined with the sampling programme. The sonde required an initial and periodic calibration. The calibration procedures were outlined in the YSI Inc. (1999) 600 Sonde Manual.

The calibration procedure for pH required a three-point calibration using pH4, pH7 and pH10 buffer solutions. The sonde was inserted into each buffer solution, and a reading taken when a stable output was obtained.

DO was calibrated by inserting the sonde into an airtight container containing a wet sponge to provide an oxygen-saturated environment. A temperature reading was obtained after about 10 min. when equilibrium between the water and air was established. The temperature reading was cross-referenced to give the solubility of oxygen (mg/L) in water exposed to water-saturated air at 760 mm Hg pressure. This DO concentration was programmed into the sampler.

The conductivity was calibrated by placing the sonde into a 0.01 mol/L potassium chloride standard solution made according to APHA et al. (1992). The specific conductance of 1.412mS/cm was simultaneously entered into the sampler, pressing enter when the sampler reading was stable.

No calibration was required for temperature.

### 2.1.3 Measurement of Flowrates

The theory, design and calibration of V-notch weirs have been described by Grant & Dawson (1997). A V-notch weir of known dimensions was built across the open channel. It consisted of a 45°-angle notch cut into a bulkhead in the flow channel. The apex of the notch was at the bottom, and the sides of the notch were set equally on either side of a vertical line from the apex.

The V-notch weir was used to measure the flowrate (Q) of liquid through the weir. Liquid flows through the notch, where the edge or surface over which the liquid passes is called the crest of the weir.

The equation for determining the flowrate through the weir is based on measuring the vertical distance from the crest of the weir to the liquid surface in the pool upstream from the crest. This liquid depth is defined to be the head (H), and once this is known, the flowrate can be determined using the known head-flowrate relationship of the weir (Grant & Dawson 1997).

The formula used to calculate the flowrate is:

$$Q = K\,H^{2.5}$$

where: Q = flowrate (L/s)
K = a constant, dependent on angle of notch and units of measurement
H = head height (m)

The bay on the sampler's side can accept ISCOs 730 Bubbler Module pressure transducer, which was used to measure the head. The module combined sampling and monitoring of the stream's flowrate. It contained microprocessor-controlled circuitry to calculate level from the signals produced by its pressure transducer, and the data were logged by the sampler.

#### *Optimum Angle for V-notch Weir*

The V-notch weir is an accurate flow-measuring device particularly suited for low flows. This is the best weir profile to measure discharges less than 28L/s, and has a reasonable accuracy for flows up to 280L/s (Grant & Dawson 1997). It is important to measure low flows accurately to enable sampling to be triggered by low runoff flowrates during a storm event, and thus the collection of the first flush.

The construction of a V-notch weir suitable to take into the field, required a preliminary experiment to assess the optimum angle of the V-notch for this purpose.

A preliminary weir was constructed by cutting a 45° V-notch into the sidewall of a 50-L square polyethylene container. After taking flow measurements, the V-notch was cut to 90° for further measurements.

After the sampler, module, weir and bubble line had been installed inside the laboratory, the module was calibrated. Water of varying flowrates was passed through each V-notch angle, and the calibration involved an offset adjustment of the height until the flowrate of water discharging from the weir was 0L/s. The flowrate measured by the sampler was compared with the flowrate measured manually using a stopwatch. The results are presented in Table 2.1.

**Table 2.1. Flowrate (Q) (L/s) measured by autosampler compared to flowrate measured manually.**

| Angle | Q Autosampler | Q Manual | % Error |
|---|---|---|---|
| 22.5° | 0.077 | 0.097 | 21 |
| 45° | 0.18 | 0.16 | 10 |
| | 1.2 | 1.0 | 17 |
| | 0.94 | 0.78 | 17 |
| | 0.59 | 0.45 | 23 |
| | 1.3 | 1.1 | 21 |
| | 1.2 | 1.0 | 17 |
| 90° | 2.7 | 1.9 | 28 |
| | 0.94 | 0.54 | 43 |

The V-notch weir had no crest length. Therefore, smaller flows through the V-notch would have a greater head than most other shaped weirs. The advantage of a V-notch weir when monitoring small flows of an open channel is that the greater head produced reduces associated errors. If the angle size is decreased, the head will further increase reducing error. However, the disadvantage of a small angle is that larger debris carried with the flow can lodge in the weir and cause flow restriction. The results in Table 2.1 illustrate that the 45° V-notch weir produced less error than the 90° angle.

### *Design and Construction of Field Weir*

A more robust weir was constructed for field use following the accepted guidelines outlined by Grant & Dawson (1997). The dimensions of the weir were based on the height of the expected maximum flow ($H_{max}$), where the minimum distance of the sides of the weir from the channel banks should be at least twice the maximum expected head on the weir. The minimum distance from the crest to the pool bottom should also be at least twice the maximum expected head. The bubbler flow module tube, which measures the head, should be placed upstream at a distance of at least three times the maximum expected head on the weir.

It is generally recommended that the minimum head on a V-notch weir be at least 0.06m to prevent the nappe (stream of water leaving the weir crest) from clinging to the crest. It is also recommended that the maximum head be limited to 0.6m, to ensure accuracy of the device head/flow relationship. Based on these lower- and upper-head restrictions, the minimum recommended flowrate for the 45° V-notch weir at a head of 0.06m is 0.504L/s, and the maximum recommended flowrates at a head of 0.6m is 159L/s (Grant & Dawson 1997).

The discharge equation for the 45° V-notch weir with the head in metres is:

$$Q = 571.4\ H_{max}^{\ 2.5}$$

where: $Q$ = expected max flowrate (L/s)
$H_{max}$ = height at max flowrate (m)

The weir dimensions based on $H_{max}$ were calculated as follows.

During an expected high intensity rainfall event the maximum volumetric flowrate, $Q_{max}$ is given by:

$$Q_{max} = A(\text{catchment}) \times I(\text{rain intensity})$$

where: A(catchment) $= 500\text{m}^2$
I(rain intensity) $= 6.94 \times 10^{-6}$ m/s

$$\begin{aligned} Q_{max} &= 500\ \text{m}^2 \times 6.94 \times 10^{-6}\ \text{m/s} \\ &= 3.47 \times 10^{-3}\ \text{m}^3/\text{s} \\ &= 3.47\ \text{m/s} \end{aligned}$$

$$\begin{aligned} H_{max} &= (Q/571.4)^{1/2.5} \\ &= (3.47/571.4)^{1/2.5} \\ &= 0.13\ \text{m} \end{aligned}$$

The dimensions of the weir are shown in Figure 2.2, with $H_{max}$ being 0.14m to allow for extreme rain conditions i.e. flooding.

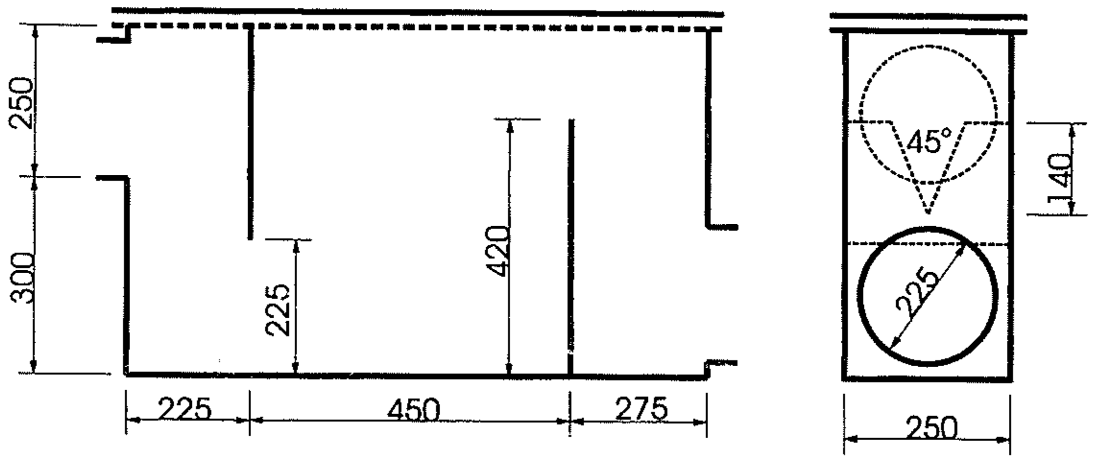


**Figure 2.2 Dimensions of the 45° V-notch weir.**

The weir was installed in the laboratory with the sampler, bubbler and an inflow of water. To check whether the sampler was accurately recording flowrates, three replicates of flowrate measurements at low, medium-low, medium and high flows were performed manually and automatically, and compared. The results for the various flowrates with the measured and theoretical heights are presented in Table 2.2.

Table 2.2. Comparison of flowrates (Q) (L/s) measured manually and automatically.

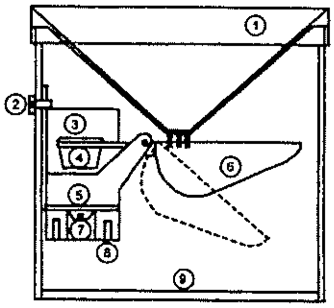
| Flowrate | Manual Flowrate | Autosampler Flowrate | Error (%) | Measured Height (m) | Theoretical Height (m) | Error (%) |
|---|---|---|---|---|---|---|
| Low Q | 0.031 | 0.026 | 17 | 0.021 | 0.020 | 5.0 |
| Med-low Q | 0.154 | 0.186 | 17 | 0.040 | 0.037 | 8.1 |
| Medium Q | 0.415 | 0.423 | 1.9 | 0.055 | 0.056 | 1.8 |
| High Q | 0.769 | 0.772 | 0.39 | 0.070 | 0.071 | 0.9 |

The percentage error for the low flowrates was 17%, which was to be expected due to the higher percentage error in the measurement of the head. The error in the head can be associated with a 3-mm meniscus at the bottom of the V resulting from surface tension, laboratory disturbances and fluctuations in height. The flowrate percentage error decreased as the head increased because fluctuations in the head height become less significant.

The maximum flowrate that would be expected in a typical heavy rain event is c.4L/s. Therefore, the experimental flowrates encompass the first quartile of this rain event and parallel that of smaller more likely events. Thus, the average typical rain event would be more likely c.0.7L/s, at which flow data to within 0.39% can be expected. Therefore, the results indicate that the weir system is suitable for field use.

### 2.1.4 Measurement of Rainfall Intensity

The measurement of rainfall intensity was obtained using a TBRG. This device measures the height of rain per time (intensity), and the data are subsequently stored into an instrument connected to the rain gauge. The data can also be analysed to obtain the rainfall duration and frequency.



| | |
|---|---|
| 1 | Funnel with grille |
| 2 | Screw for whole measurement unit |
| 3 | PCB With on/off switch |
| 4 | Magnet |
| 5 | Bracket fitting |
| 6 | Self-emptying measuring "spoon" |
| 7 | Adjustment screw |
| 8 | Male pin |
| 9 | Base |

Figure 2.3 Diagram of the PRONAMIC RAIN-O-MATIC tipping bucket rain gauge (TBRG).

The principle and layout of the rain gauge was adapted from the PRONAMIC RAIN-O-MATIC Instructions Manual. The rain gauge (Figure 2.3) consisted of three parts: funnel with grille and drip-catcher; box with self-emptying "spoon"; and base used for mounting rain gauge in the desired position. A lead connects the rain gauge and the liquid crystal display (LCD)-counter.

Rain is collected in the funnel and runs through the grille down into a self-emptying "spoon" held by a magnet. The spoon is connected to a reed switch that is normally open; when the magnet comes in contact with the switch, the switch becomes closed. Each time the spoon registers 5g of water, it tips automatically and empties, then returns to its normal position ready to collect rainwater again. Rainfall intensity is measured by counting the number of tips, (each of 0.1mm of precipitation) per min. The gauge registers the recorded amount of precipitation on the LCD-counter.

### *Construction of the TBRG*

The purchase of a TBRG was not part of the project budget. Therefore, the rain gauge was constructed locally.

The aim was to enable the rain gauge to connect to the ISCO automatic water sampler rather than the LCD-counter, because the sampler had the capacity to operate as a complete, self-contained storm water monitoring system when used in conjunction with the rain gauge. This system provided data for detailed daily reports of average rainfall, total volume and intensity (ISCO Inc. 1996).

The lead for the rain gauge was connected to the sampler. The accumulated number of tips was stored in the memory of the ISCO automatic water sampler.

The funnel system was constructed locally. Before construction, initial experimental work was carried out to find the appropriate diameter of the funnel. An electronic alarm was connected to the rain gauge. Water was directed into the box from a 50-mL burette. When the spoon filled, it tipped to raise the alarm. The volume of the water required to tip the spoon was measured three times and found to be 5mL. The measured volume of water and the spoon height estimated the spoon surface area. The area was substituted into the area (circle) equation to obtain the funnel diameter. The calculations are shown as follows:

Surface area = vol (water to fill spoon) /height (of spoon)

Area (circle) = $\pi r^2$

The internal diameter of the funnel required to tip at a height of 0.1mm was calculated to be 252mm. This funnel was constructed out of plastic and glued to fit firmly in an uncapped pipe of an internal diameter of 200mm. This funnel system enclosed the gauge, which was aligned directly under the spout. To enable the maintenance of the gauge, bolts attached the funnel system to the board. The TBRG is illustrated in Figure 2.4.

**Figure 2.4 The TBRG in position.**

### *Testing the TBRG*

The ability of the sampler to record rainfall intensity accurately was tested. The TBRG was connected to the sampler, and a continuous flow of water dripped into the gauge using a burette. The number of tips was counted per min for 60 min. to give the accumulated number of tips within an hour (h). The results were compared with those recorded by the sampler. ISCO Samplink software installed on a Toshiba T2130CS 486 DOS laptop was used to retrieve sampler data, which could then be printed or analysed using Excel spreadsheet software. The results for the total number of tips for both manual and sampler counting are shown in Table 2.3.

**Table 2.3 Total depth of water (mm) measured manually and by the autosampler, during three 1-h sampling periods.**

| Time | Manual Depth | Autosampler Depth |
|---|---|---|
| 10:00–11:00 | 8.0 | 8.0 |
| 13:00–14:00 | 7.7 | 7.7 |
| 16:00–17:00 | 8.3 | 8.3 |

The results indicate that the sampler is accurately recording the number of tips per minute.

### 2.1.5 Installation of V-Notch Weir and Bubbler Module

The 225-mm external diameter polyvinyl chloride V-notch weir was connected to the 225-mm internal diameter saw-cut edge of a concrete drainpipe. The 40-L weir dead volume allowed for the measurement of the water level down to the actual "zero" level of the weir. The bubble line outlet was placed at least 2.5 to 5.1 cm below the weir zero level (ISCO Inc. 1996).

### 2.1.6 Installation of Automatic Water Sampler

The sampler was placed on a relatively flat, horizontal surface, to prevent the sample from missing the bottle mouth. The suction line was directed continuously downhill from the sampler to the weir to help drain the line during pre-sample and post-sample purges. The vertical distance between the liquid level in the weir and the pump was as small as possible to save battery power. The strainer end of the suction line was installed in the upstream compartment of the weir. The weir dead volume allowed for enough water to immerse the sampler probe for sampling and also to prevent it from drying out. Representative samples were obtained by placing the intake in the main current of the flow stream, that is, not in an eddy or at the edge of the flow.

### 2.1.7 Installation of Parameter Sonde and TBRG

A YSI 600/Rain Gauge Y-connect cable was used to connect the rain gauge and parameter module to the sampler via the nine-pin Rain Gauge Connector. Installation of the parameter sonde involved placing it in the upstream compartment of the weir with the strainer. The rain gauge was placed 10m from the sampling site and in an open clearance.

### 2.1.8 Monitoring Programme

The sampler was programmed to collect twelve 1000-mL composite uniform-time paced samples of runoff to allow for the collection of runoff through a rain hydrograph. Samples were collected at regular preset time increments of 2-min intervals for the first flush (Sansalone & Buchberger 1997) and 5-min intervals for the remaining event. This was to ensure the collection of at least 6–8 samples from a storm event (Wu et al. 1998). The sampler was programmed to collect the first 2 h of rainfall and, was enabled when a set flowrate of 0.028L/s was exceeded, to ensure that the rainfall event had at least 0.2mm/h intensity.

When sampling was complete, data were downloaded onto a Toshiba 320CDT laptop, and the samples were transported to the laboratory to be analysed. ICP-OES analysis for Fe, Cu, Cd, Zn, Ni, Cr and Pb was performed using 100mL of the 1000mL collected samples. The remaining volume (approximately 900mL) was liquid/liquid extracted using dichloromethane (DCM), and the concentrated DCM extract was analysed by SIM GC/MS for selected PAHs, namely pyrene, phenanthrene, fluoranthene and benzo(a)pyrene. The runoff hydrographs and profiles of the contaminant concentrations were plotted as a function of time.

## 2.2 ICP-OES Metal Analysis

The ICP-OES instrument was optimised by correcting for interferences, selecting the optimum spectral line for the element being analysed, and making background corrections. Standards were prepared, calibration curves determined, and precision, detection limits and accuracy were assessed. Preliminary samples were then prepared according to the standard methods for the examination of water and wastewater (APHA et al. 1992). Where appropriate, the original methods were modified to improve reliability and convenience.

### 2.2.1 Principle of ICP-OES

The inductively coupled plasma (excitation source) is a unique feature of an ICP-OES instrument. Power is transferred into the plasma gas by inductive heating. The gas passes through the plasma torch, which is located in an induction coil carrying very high frequency alternating current. The electrically conducting ionised gas acts as the secondary coil of a transformer and this heats the gas to temperatures in the vicinity of 10 000 K. The combination of high temperatures and long residence times (approximately 2–3 msec) produces complete vaporisation of the sample solvent and total breakdown of the analyte into free atoms, which are then available for excitation. The nature of the plasma causes nearly every species resident in the plasma to show spectral emission (GBC Scientific 1997). A diagram of an ICP-OES instrument is given in Figure 2.5.

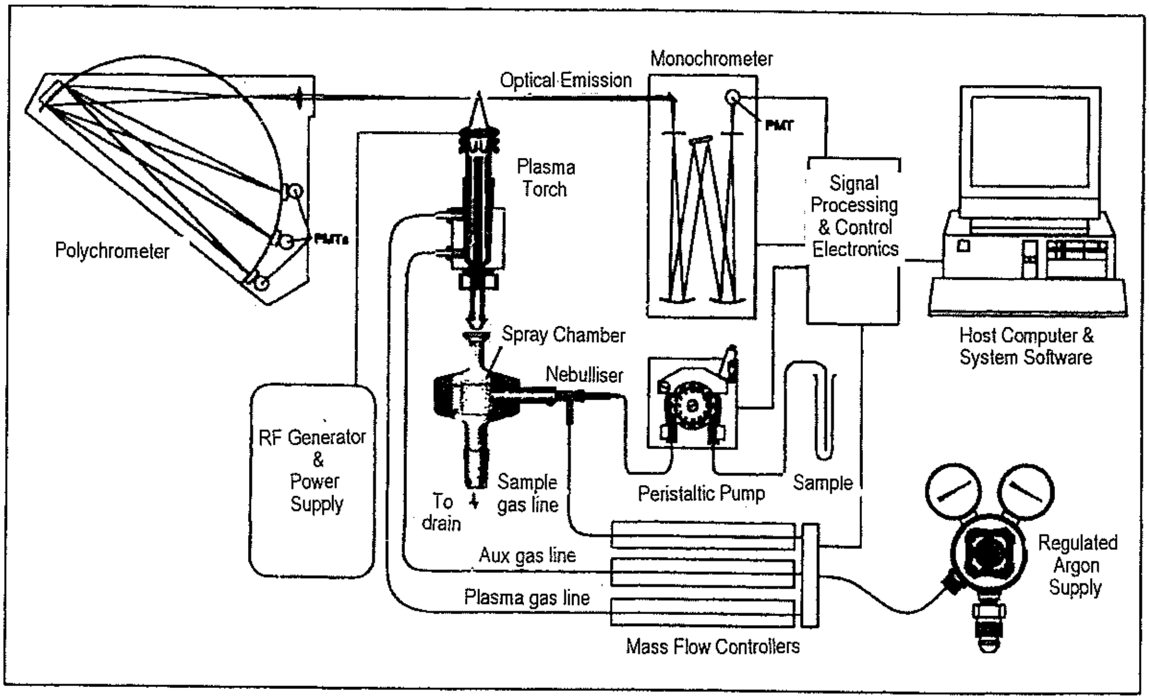


**Figure 2.5 A diagram of an ICP-OES instrument (GBC Scientific 1997).**

The method development for ICP-OES analysis of a given trace-metal requires selecting the analytical lines, testing for inter-element or background interferences, determining the optimum operating conditions and establishing a calibration curve to cover an appropriate concentration range.

### 2.2.2 Calibration Curves

The concentration of a metal in solution is determined by measuring the intensity of the metal and then comparing this with the measured intensity of the same metal in a solution of known concentration. The ICP-OES is a relative method of analysis, therefore a calibration routine is required. This establishes a mathematical relationship between concentration and measured intensity for each metal from a series of standards of known concentrations.

In order to measure low values accurately, it is better to use a calibration curve of the "same order of magnitude", rather than a wide linear dynamic range curve. Using a wide range curve for low-level samples will produce a large error around zero, due to the influence of the far-from-zero points in the least-squares line of best fit. A small range curve will give more weight to the blank reading, thus reducing the error at low concentrations.

It was envisaged that water samples would be much more dilute than extracted sediment samples (see Section 1.4.1). Accordingly, two calibration ranges and the corresponding instrument settings were chosen.

For water samples, standard solutions in the range 0–500 $\mu$g/L (0, 10, 100, 250 and 500$\mu$g/L) were prepared. For sediment samples, standard solutions in the range 0–20 000$\mu$g/L (0, 500, 1000, 10 000 and 20 000) were prepared. In the special case of iron, three further solutions of 250 000, 500 000 and 750 000$\mu$g/L were prepared.

### 2.2.3 Spectral Interferences

Spectral interferences may arise from emissions from elements in the plasma itself, the materials present in the reagent blank, or from other elements in the sample. In most analyses, spectral interferences will most likely arise from elements present in the sample itself. Interference correction was automatically applied by the software during the regular calibration procedure, once the affected and interfering elements had been selected.

Potential spectral interferences were identified by the use of the library spectral lines. To confirm whether the selected analytical line is appropriate for the proposed analysis, a pure solution of the metal element was prepared with a concentration comparable to that expected in the sample for analysis (see Section 1.4.2). Under optimised conditions, the proposed analytical line was examined while aspirating this solution. This established whether the chosen line was sufficiently sensitive for the analysis.

The background component of the analyte emission intensity needs to be subtracted from the total emission signal. The background component of the signal consists of a combination of continuous radiation, stray light, molecular bands, argon spectra and wing overlap from other elements in the sample. In the simplest case, the background is of constant intensity across the wavelength range of interest for all samples. This may be measured by running a sample blank at the analytical wavelength.

### 2.2.4 Non-spectral Interferences

Non-spectral interferences can be caused by physical factors, i.e. the effects associated with the sample nebulisation and transport processes and chemical interferences, i.e. problems related to molecular compound formation, ionisation effects and solute vaporisation effects.

Physical interferences (matrix effects) may arise due to changes in viscosity or surface tension between the calibration solutions and the sample solutions. This causes a difference in the rate of generation and transport of appropriately sized aerosol droplets to the plasma leading to inaccurate analytical results. Transport interferences are more likely to occur in samples that contain high dissolved solids, high acid concentrations and organic samples. There are several approaches to overcome this sort of interference, such as: dilution of sample, standard addition and internal standardisation.

Changes in viscosity between sample and standard solutions can be minimised by preparing standards with a similar matrix to that of the samples.

### 2.2.5 Instrument Control

The observed emission intensities of the spectral lines of an element depend on a number of operating parameters. The predominant parameters include the power of the plasma, the viewing or observation height, and the sample gas flow. The remaining parameters such as auxiliary and plasma gas flows all play a secondary role (GBC Scientific 1997). Table 2.4 indicates the operating parameters and wavelengths selected for the current work.

**Table 2.4 Optimised operating parameters and wavelengths (nm) for each calibration (GBC Scientific 1997).**

| Operating Parameters | Element | Wavelength (0 – 500 $\mu$g/L) | Wavelength (0 – 20 000 $\mu$g/L) |
|---|---|---|---|
| Power: 1000 W | Cd | 228.802 | 228.802 |
| Nebuliser type: Concentric | Cr | 283.563 | 283.563 |
| Plasma gas flow: 10 L/min | Cu | 324.754 | 224.700 |
| Auxiliary gas flow: 0.54 L/min | Fe | 259.940 | 232.739 |
| Sample gas flow: 0.4 L/min | Ni | 221.647 | 221.647 |
| Viewing height: 8 mm | Pb | 220.353 | 220.353 |
| Pump speed: 9 rpm | Zn | 213.856 | 213.856 |
| Pump tubing: Yellow-Yellow | | | |

W = watt, rpm = revolutions per minute, L/min = litres per minute.

### 2.2.6 Precision, Detection Limits & Accuracy

In order to assess the reliability of the ICP-OES analytical method for samples within the expected concentration range, a series of replicate analyses of samples of appropriate concentrations were obtained. The results are tabulated in Appendix 1, Tables A1.1.1 to A1.1.7, and are summarised in Table 2.5.

The detection limit is the minimum concentration of analyte that produces a signal significantly different from the background signal.

Ambiguity over what the term "significantly different" means in this context has lead to various definitions for the detection limit. A widely accepted definition is that the detection limit is equal to three times the standard deviation of the blank, where at least 10 readings of the blank are taken (N. Kim, pers.comm. 2000).

**Table 2.5 Mean (+ standard deviation) for the six replicates of heavy metal standards (summarised from Appendix A1).**

| Known Conc. ($\mu$g/L) | n | Fe | Cd | Cr | Cu | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| *Cal. (water)* | | | | | | | | |
| 0 | 12 | 25 (8.3)† | 0.3 (0.51) | 32 (1.8) | 2 (4.3) | 3 (1.5) | 34 (6.6) | 4 (2.7) |
| 10 | 6 | 25 (2.6) | 10.2 (0.39) | 37 (1.6) | 11.9 (0.67) | 9 (5.2) | 39(5.6) | 13 (2.6) |
| 100 | 6 | 97 (3.6) | 96 (1.0) | 96 (2.2) | 100 (1.1) | 97 (2.7) | 119 (6.9) | 96 (2.7) |
| 250 | 6 | 240 (13) | 251 (2.1) | 254 (4.2) | 254 (3.5) | 251 (4.4) | 260 (6.7) | 248 (2.5) |
| 500 | 6 | 430 (6.5) | 500 (1.7) | 501 (4.7) | 482 (7.9) | 482 (7.9) | 480 (13) | 494 (2.6) |
| *Cal. (sed)* | | | | | | | | |
| 0 | 6 | | 22 (0.39) | 101 (4.1) | 67 (1.5) | 22 (1.2) | 0 (8.2) | 6 (3.9) |
| 500 | 6 | | 560 (2.8) | 590 (16) | 470 (4.9) | 509 (4.0) | 520 (11) | 502 (6.3) |
| 1000 | 6 | | 1080 (15) | 1110 (36) | 990 (11) | 1020 (19) | 1040 (18) | 1030 (22) |
| 10 000 | 6 | | 10 580 (63) | 10 400 (260) | 10 440 (80) | 10 300 (100) | 10 200 (120) | 10 200 (120) |
| 20 000 | 6 | | 21 000 (205) | 20 000 (2200) | 20 600 (230) | 20 400 (350) | 20 200 (200) | 20 200 (120) |
| *Cal. (sed)* | | | | | | | | |
| 0 | 6 | 8790 (20) | | | | | | |
| 250 000 | 6 | 261 000 (7800) | | | | | | |
| 500 000 | 6 | 536 000 (9900) | | | | | | |
| 750 000 | 6 | 800 000 (21 000) | | | | | | |

*Calibration (water) and (sediment) in $\mu$g/L
† 6 replicates only for Fe; n – number of replicates

Random fluctuations of blank readings would give rise to a normal distribution. Thus, 99.7% of all values should fall within 3 standard deviations of the mean (zero). In other words, there is only a 0.3% probability that a value beyond 3 standard deviations of the mean can result from statistical fluctuations. The quantification limit has been determined to be 5 times the standard deviation of the 10 blank replicates (N. Kim, pers.comm. 2000).

Using the data of Table 2.5 for 0$\mu$g/L (0–500$\mu$g/L), the detection and quantification limits for the metals, Cd, Cr, Cu, Fe, Ni, Pb and Zn, have been estimated. The rounded values are presented in Table 2.6.

**Table 2.6 ICP-OES detection and quantification limits (µg/L) for heavy metals, using "low" calibration curves.**

| Metal | Detection Limit | Quantification Limit |
|---|---|---|
| Cd | 2 | 3 |
| Cr | 5 | 9 |
| Cu | 10 | 20 |
| Fe | 20 | 40 |
| Ni | 5 | 8 |
| Pb | 20 | 30 |
| Zn | 8 | 10 |

It is clear that, by using the most sensitive wavelengths, all the metals are detectable at concentrations above 100µg/L and some, in particular Cd, Cu, Ni and Zn, are detectable at 10µg/L.

The CV (coefficient of variation) was calculated for these standard solutions. The results are tabulated in Appendix 1 Tables A1.1.1 to A1.1.7. The overall average of the CV values of the metals above 100µg/L is 2%, which is regarded as acceptable. The high CV values for the 10µg/L standards are consistent with the expectation that CVs will increase as concentration decreases.

The accuracy of the determination was estimated by comparing the determined mean values with the known concentrations analysed. The percentage relative error (Er) for the mean of the data was calculated by the expression:

$$Er = [(x_i - x_t)/ x_t] \times 100\%$$

where: $x_i$ = mean measurement of a quantity
$x_t$ = true or accepted value of the quantity
$x_i - x_t$ = mean absolute error

Tables A1.1.1 to A1.1.7 shows the calculated mean relative errors. The results indicated that the Er for all elements present in the sediment standards was determined to within 6% for the whole concentration range. The mean overall relative error for all metals in the 100µg/L and above water standards was an acceptable 4%. However, the elements Cr, Cu, Pb, Fe and Zn were determined to within 290% at the 10µg/L level, which was to be expected since the ICP cannot detect these metals reliably at this low-level.

### 2.2.7 Sample Storage & Stabilisation

Water samples were stored in clean borosilicate glass and high density or polypropylene containers. Samples were filtered, stabilised by acidifying the filtrate with 6mL of concentrated (conc) analytical reagent (AR) nitric acid ($HNO_3$) to avoid the possibility of adsorption on to vessel surfaces and hydrolysis and precipitation reactions, tightly stoppered, and stored in a refrigerator at 4°C. Liquid samples with metal concentrations in the µg/L range were analysed as soon as possible after sample collection. Dry sifted sediment samples were stored in plastic bags at room temperature and did not require preservation.

### 2.2.8 Cleaning Regime

Initial cleaning of laboratory ware involved washing with metal-free non-ionic detergent solution, rinsing with tap water, soaking in 4 mol/L $HNO_3$ for 24 h and a final rinsing with deionised water. Subsequent washings for the remaining experiment involved three rinses with tap water, overnight in 4 mol/L $HNO_3$ and three rinses with deionised water.

### 2.2.9 Reagents

Reagent water was purified using an E-pure Barnstead system by reverse osmosis, treatment with activated carbon to remove organics and finally deionised with a mixed bed cation/anion exchange resin. A solution of 4 mol/L $HNO_3$ was prepared by a dilution of 25% from conc. (16 mol/L) AR $HNO_3$ that was commercially available from BDH Laboratory Supplies, England.

### 2.2.10 Standards

Stock solutions for each metal were prepared by weighing out a portion of the appropriate metal salt (AnalaR, BDH Ltd, Poole, England) that was required to give one gram of metal (Table 2.7). This was dissolved in 100mL $HNO_3$ and diluted to 1L with deionised water to give a concentration of 1000mg/L. A composite stock standard of 100mg/L of each metal was prepared by adding 10mL from the individual stock solutions into one 100mL volumetric flask which was subsequently made up to the mark with deionised water.

Deionised water was used to dilute the composite to the required concentrations for construction of appropriate calibration curves. The procedure involved adding 0, 0.01, 0.1, 0.25, 0.5, 1, 10 and 20mL of 100mg/L solution to separate 100-mL volumetric flasks containing 6mL of concentrated AR $HNO_3$, and making up to the mark with deionised water. Final concentrations of all metals in the standards were 0, 10, 100, 250, 500, 1000, 10 000 and 20 000$\mu$g/L respectively. Stock solutions of Fe, a special case, were made from diluting a 5000mg/L stock solution to give the concentrations of 250, 500 and 750mg/L. These were prepared to match the sample matrix.

**Table 2.7 Weight of metal salt that is required to give one gram of metal.**

| Element | Weight (g) | Metal Salts |
|---|---|---|
| Cd | 2.7442 | $Cd(NO_3)_2 \cdot 4H_2O$ |
| Cr | 3.7347 | $K_2CrO_4$ |
| Cu | 3.6602 | $Cu(NO_3)_2 \cdot 2.5H_2O$ |
| Fe | 7.2340 | $Fe(NO_3)_3 \cdot 9H_2O$ |
| Ni | 4.9545 | $Ni(NO_3)_2 \cdot 6H_2O$ |
| Pb | 1.5985 | $Pb(NO_3)_2$ |
| Zn | 4.5495 | $Zn(NO_3)_2 \cdot 6H_2O$ |

### 2.2.11 Sample Pre-treatment

Samples were processed to give dissolved metal, suspended metal and total metal of the analytes Cd, Cr, Cu, Fe, Ni, Pb and Zn in runoff water and total metals in the runoff sediment.

Metal element fractionation for runoff water involved separating the water component into suspended solids ($0.45\mu m$ to $400\mu m$) and dissolved ($<0.45\mu m$) fractions. Immediately after each sampling run, samples were transported to the laboratory and pre-filtered through a $400\mu m$ nylon mesh vacuum filter into a 1-L flask. Filtrates were then poured into 1-L reagent glass bottles, labelled and thoroughly homogenised using a magnetic stirrer. A 50-mL sample of the homogenised filtrate was withdrawn from the 1-L flask using a 50-mL glass pipette and passed through a 0.45-$\mu m$ mixed cellulose ester membrane filter paper (ADVANTEC MFS, Inc.) seated on a membrane vacuum filtering device. The filtrate was discarded, and a second 50-mL portion of the homogenised filtrate was passed through the saturated filter paper, and the filtrate was placed in a 100-mL plastic container. Filtrates were acidified with 6mL of conc $HNO_3$ and stored at 4°C until they were used for dissolved metal analysis.

The suspended solid fraction retained on the membrane filter was rinsed with 3mL of deionised water to remove any dissolved material remaining. The residues and associated filter papers were placed in separate 100-mL beakers, and 25mL of 4 mol/L $HNO_3$ was added. The beakers were covered with watchglasses, and the acidified solutions were simmered gently for 35 min. Deionised water was added when needed, to prevent the sample from drying during digestion. After digestion, the samples were cooled and filtered into a 100-mL volumetric flask using a pre-washed filter paper (Whatman No. 1). The beaker was then rinsed with two 5-mL portions of deionised water and the rinsings were passed through the filter paper into the volumetric flask. The resulting solutions were diluted to the mark, mixed thoroughly and stored in 100-mL plastic containers until they were used for suspended solid metal analysis.

The protocol for total metals in runoff waters involved the use of a wide-bore pipette to obtain a 50-mL sample. The sample was transferred to a 100-mL beaker and spiked with 6mL of conc $HNO_3$. The beakers were covered with watchglasses and the acidified solutions were simmered gently for 35 min. Deionised water was added when needed, to prevent the sample from drying during digestion. After digestion, the samples were cooled and filtered into a 100-mL volumetric flask using a pre-washed filter paper (Whatman No. 1). The beaker was then rinsed with two 5-mL portions of deionised water and the rinsings were passed through the filter paper into the volumetric flask. The resulting solutions were diluted to the mark, mixed thoroughly and stored in 100-mL plastic containers until they were used for total metal analysis.

The protocol for total metals in runoff sediment involved drying the wet sediment sample at room temperature for several days. Total metals were obtained by sieving the sediment through a 0.5-mm grating and discarding the larger particles.

The dry sediment was mixed and 1–2g were weighed into separate 100-mL beakers containing 25mL of 4 mol/L $HNO_3$. The beakers were covered with watchglasses and the acidified solutions were simmered gently for 45 min. Deionised water was added when needed, to prevent the sample from drying during digestion. After digestion, the samples were cooled and filtered into a 100-mL volumetric flask using a pre-washed filter paper (Whatman No. 1). The beaker was then rinsed with two 5-mL portions of deionised water and the rinsings were passed through the filter paper into the volumetric flask. The resulting solutions were diluted to the mark, mixed thoroughly and stored in 100-mL plastic containers until they were used for total metal analysis.

A method blank was prepared for each sample batch to ensure appropriate corrections were made to contributions from the reagents used for each batch.

## 2.3 SIM GC/MS PAH Analysis

The methodology for the analysis of PAHs involved the use of SIM GC/MS (see Section 1.9.2). Before sample analyses the performance of the GC/MS system was evaluated by assessing the linearity of detector response and instrument reproducibility for replicate sample injections. The efficiency of sample spike recovery during liquid/liquid extraction was also assessed. Standards were prepared, calibration curves determined, and detection limits established. Samples were prepared for analysis by the continuous liquid/liquid extraction method.

### 2.3.1 Principle of the SIM GC/MS Method

Gas chromatography separates molecules on the basis of their volatility and/or polarity. Separation is achieved by passing vaporised molecules through a column, which temporarily retains less volatile (or more polar) molecules to a greater extent than is the case for more volatile (or less polar) molecules. Since many organic molecules are not sufficiently volatile at room temperature, a GC system incorporates a column oven that can be heated from room temperature to c.300°C. PAHs are thermally stable molecules that can be readily analysed using oven temperatures in the range 150–300°C.

In the present study, the target PAHs were pyrene, phenanthrene, fluoranthene and benzo(a)pyrene, all of which are low to high molecular weight PAHs and amendable to GC analyses.

In GC/MS systems, the column eluent is bombarded with electrons as it exits from the column. The molecule is fragmented to give a collection of "fragment ions" that are pushed out of the ionisation chamber, focussed into a beam and passed through a magnetic field. Ions are detected by an electron multiplier, and the signal can be presented as a total ion chromatogram (TIC) and a mass spectral fragmentation pattern. Each component eluting from the column can be identified by both its retention time, and by its mass spectrum.

The sum of all the detected ions detected in a GC/MS analysis give the TIC of the sample whose profile is generally similar to its GC-FID chromatogram. Approximately 1/360th of the available time is used per ion (dwell time), thus TIC has moderate sensitivity, cannot quantify overlapping peaks, and MS of overlapped peaks are superimposed.

The sensitivity of GC/MS analyses can be greatly increased by using SIM mode. The SIM technique differs from the TIC technique in that only a few pre-selected ions are focused on the detector, e.g. 3 ions – 1/3 of the available time per ion. This can result in a 120-fold increase in sensitivity, compared with TIC GC/MS analysis, largely because a large amount of the time is spent monitoring high intensity fragment ions. This results in a substantial gain in the signal to noise ratio of the detected ions, and in an improvement in the detection limits of the SIM GC/MS protocol.

It was preferable to use SIM GC/MS for the routine quantification of PAHs rather than GC-FID or TIC GC/MS, because of its superior selectivity, sensitivity, ability to quantify overlapping peaks using unique ions. It has the added advantage of having more accurate peak areas since no peak threshold trimming was applied.

### 2.3.2 TIC & SIM GC/MS Analyses

GC/MS analysis of PAHs was performed using a 0.22-mm internal diameter x 25-m HP-1 (Hewlett Packard) methylsilicone capillary column installed in a HP-5980 gas chromatography instrument, fitted with an HP-7673A auto-injector and interfaced to an HP-5970B mass selective detector (MSD). The GC/MS instrument was operated with an electron impact ionisation of 70eV, and the column head pressure was typically set at 15kPa. The GC/MS system was controlled by Hewlett Packard ChemStation software.

The analytical protocol is described in Section 2.3.11. This procedure involved the extraction of c.900mL of sample with DCM, and concentration of the extract to c.1 mL. Using this approach, a detection limit of 0.5$\mu$g/L of PAH (in the original 900mL sample) was obtained.

The GC/MS operation parameters were typically adjusted using response factor mixtures (see Section 2.3.8) until peaks corresponding to concentrations in the range 0.5 to 20$\mu$g/L (based on the original water sample volume) could be quantified.

Initially TIC GC/MS, with M/z 40 to 400 ion detection, was used to identify all compounds that were present in extracts. Typical TIC GC/MS acquisition parameters are given in Table 2.8.

For maximum sensitivity, the SIM GC/MS ion detection was used for routine analysis. The ions used in SIM GC/MS analyses are given in Table 2.9. These ions were used for quantification. Extracted ion chromatograms of each quantification ion were plotted and integrated to determine the peak area contributions of individual PAH compounds.

Table 2.8 Typical TIC GC/MS parameters.

| Injection Parameters | Temperature Programme | TIC Acquisition |
|---|---|---|
| Injector mechanism = Auto | Initial temperature = 75°C | Solvent delay = 3 min |
| Solvent A washes = 3 (DCM) | Initial time = 0.5 min | EM volts = 2400 eV |
| Solvent B washes = 3 (DCM) | 35°C/min to 150°C | Carrier gas = helium |
| Sample washes = 1 | 10°C/min to 285°C | |
| Sample pumps = 3 | Final time = 1 min | |
| Sample volume = 2 $\mu$L | Run time = 16.14 min | |
| Sample viscosity = 1 | | |
| Splitless time = 0.33 min | | |

Table 2.9 Ions used for SIM GC/MS analyses.

| Compound | Quantification Ion Used (M/z) |
|---|---|
| *Target Compounds* | |
| Pyrene | 202 |
| Phenanthrene | 178 |
| Fluoranthene | 202 |
| benzo(a)pyrene | 252 |
| *Primary Standard* | |
| benzo(a)anthracene | 228 |
| *Surrogate Standard* | |
| Naphthalene | 128 |

In SIM GC/MS mode, the injection volume and electron multiplier voltage were adjusted to detect all peaks within the 0.5–20$\mu$g/mL range without column overload or detector saturation.

The capillary columns used in GC/MS analyses are typically 25 to 50m in length, and have an internal diameter in the range 0.22 to 0.53mm for standard and mega-bore types respectively. The performance of the multi-user GC column used in this investigation was monitored before the analyses of PAH containing extracts. When necessary the injector liner was cleaned up, or replaced, and the column was shortened to remove the front section of the column, which tended to accumulate residues that contributed to the degradation of the peak shape of PAHs. Typical SIM GC/MS acquisition parameters are given in Table 2.10.

Table 2.10 SIM GC/MS conditions.

| Injection Parameters | Temperature Programme | SIM Acquisition |
|---|---|---|
| Injector mechanism = Auto | Initial temperature = 50°C | Solvent delay = 3 min |
| Solvent A washes = 3 (DCM) | Initial time = 0.3 min | EM volts = 2000 eV |
| Solvent B washes = 3 (DCM) | 35°C/min to 125°C | Carrier gas = helium |
| Sample washes = 1 | 10°C/min to 285°C | Time windows: |
| Sample pumps = 3 | Final time = 5 min | Time = 3.00 - 18.00 min |
| Sample volume = 2 $\mu$L | Run time = 23.44 min | M/z = 128, 178, 202, |
| Sample viscosity = 1 | | 202, 228, 252. |
| Splitless time = 0.5 min | | |

### 2.3.3 Linearity & Reproducibility of Detector Response in SIM GC/MS

Linearity of the detector response in SIM GC/MS mode was demonstrated using the response factor solutions. The curves are produced by plotting the ratio of the target peak area divided by the primary standard peak area against the amount ($\mu$g) of target injected. The slope of the least squared fitted plots defines the response factor of the target compound relative to the primary standard.

The response curves for pyrene, phenanthrene, fluoranthene and benzo(a)pyrene are presented in Figure 2.6. The linear range for each of these compounds was demonstrated by injecting 2$\mu$L of the response factor solutions generated by mixing 10.02$\mu$g of benzo(a)anthracene and 0.5 to 20$\mu$g of each of the target compounds (see Section 2.3.8). The regression coefficients ($R^2$) are all in the vicinity of 0.99.

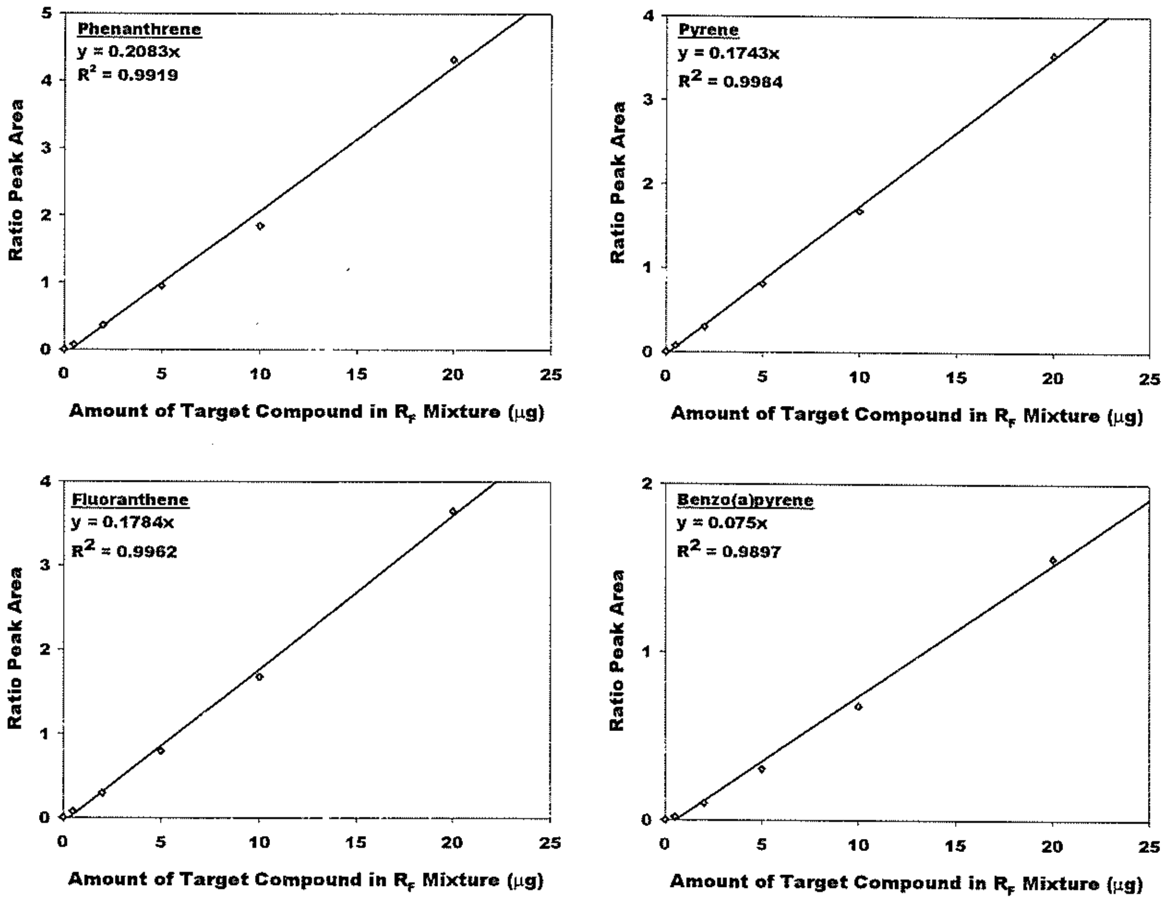


**Figure 2.6 Response curves determined for 2$\mu$L injections for $R_F$ mixtures containing 10$\mu$g of benzo(a)anthracene and 0–20$\mu$g of target compounds, pyrene, phenanthrene, fluoranthene, and benzo(a)pyrene.**

The reproducibility of the SIM GC/MS injection system was also demonstrated using the response factor solutions. In this experiment, 2$\mu$L of the $R_F$ mixture, containing

10$\mu$g of each compound, were injected four times. The integrated areas of each compound are presented in Table 2.11.

**Table 2.11 Peak areas determined for four replicate 2$\mu$L injections of the 10g/mL response factor mix.**

| Injection | Pyrene | Phenanthrene | Fluoranthene | Benzo(a)pyrene | Benzo(a)anthracene |
|---|---|---|---|---|---|
| 1 | 10 014 618 | 10 692 658 | 10 067 317 | 5 040 346 | 6 214 820 |
| 2 | 9 300 847 | 10 940 219 | 9 743 482 | 5 081 372 | 6 360 418 |
| 3 | 10 088 022 | 11 650 310 | 10 088 519 | 4 711 287 | 6 021 679 |
| 4 | 9 831 453 | 11 548 834 | 9 722 216 | 4 621 857 | 6 014 796 |
| Mean (n = 4) | 9 808 735 | 11 208 005 | 9 905 384 | 4 863 716 | 6 152 928 |
| Stdev | 355 366 | 465 149 | 199 603 | 231 158 | 166 523 |
| CV (%) | 3.6 | 4.2 | 2.0 | 4.8 | 2.7 |

The results represented in Table 2.11 show that instrument reproducibility (which includes injector volume precision and detector response) was excellent, with CV values being less than 5%.

### 2.3.4 Reproducibility of Analytical Protocol & Recoverability

The overall reproducibility and standard deviation of the extraction and analytical protocol was evaluated by multiple extractions of a selected sample. The results determined for four extractions of a well-mixed 20-L bulk road runoff sample, collected on 9/8/2000, are presented in Table 2.12.

Sample recoverability was assessed by preparing a reference 1:1 ratio of naphthalene and benzo(a)anthracene. This was achieved by adding 100$\mu$L of benzo(a)anthracene and 100$\mu$L of naphthalene from each of the 100.2mg/L stock solutions into a vial. The percentage recoverability could be determined by comparing the experimental ratio against that determined for the reference mixture (see Section 2.3.8). Poor recovery could be identified by this method and, where appropriate, results were rejected.

**Table 2.12 PAH levels (ng/L), mean, stdev and CV for four replicate analyses determined for a road-runoff sample collected on 9/8/2000.**

| Replicate | Phenanthrene | Fluoranthene | Pyrene | % Recovery |
|---|---|---|---|---|
| 1 | 160 | 62 | 121 | 84 |
| 2 | 230 | 100 | 190 | 103 |
| 3 | 150 | 70 | 130 | 118 |
| 4 | 200 | 80 | 140 | 118 |
| Mean (n = 4) | 185 | 78 | 145 | 106 |
| Stdev | 37 | 16 | 31 | |
| CV (%) | 20 | 21 | 21 | |

The CV values are all in the vicinity of 20%, which indicates that reasonable precision could be obtained for PAH compounds present in very low levels (ng/L) in the runoff. The results showed good recoverability, i.e. within the region of 80–120%.

### 2.3.5 Sample Storage & Stablisation

Samples were transported to the laboratory immediately after the sampling run had been completed. Samples were pre-filtered through a 400-$\mu$m nylon mesh, transferred into clean 1-L glass bottles and stored at 4°C from the time of collection to extraction. Samples were extracted within 7 days of collection and analysed completely within 40 days of extraction. If the samples were not extracted within 7 days, they were preserved with 0.1% sodium azide (Ali Kanber et al. 2000).

### 2.3.6 Cleaning Regime

Cleaning of laboratory ware involved the rinsing of glassware with the last solvent used in it, followed by washing with detergent and hot water, rinsing in tap water, rinsing twice in distilled water, rinsing with acetone, and draining the glassware dry. After drying, the glassware was sealed and stored in a clean environment to prevent accumulation of dust and other contaminants.

### 2.3.7 Reagents

Reagent water was purified using an E-pure Barnstead system by reverse osmosis, treated with activated carbon to remove organics, and finally deionised with a mixed bed cation/anion exchange resin.

Commercially available industrial crude solvent dichloromethane was purchased then distilled at its boiling point of 40°C for analysis.

Authentic specimens of phenanthrene (>96% purity), fluoranthene (98% purity), pyrene (99% purity), benzo(a)pyrene (97% purity), benzo(a)anthracene (99% purity), and naphthalene (99% purity) were obtained from Aldrich Chemical Company, Inc. Milwaukee, Wisconsin, US.

### 2.3.8 PAH Standards

The analytical protocol for the PAH analysis involved the preparation and characterisation of standards. The preparation of the primary, surrogate and target compound standards were made according to the expected PAH concentrations found in road runoff, which were typically found in the literature to be less than 20$\mu$g/L. Six PAH compounds, commonly cited in the literature were obtained: pyrene; phenanthrene; fluoranthene; benzo(a)pyrene; benzo(a)anthracene; and naphthalene. It is important to note the safety considerations necessary when working with PAHs.

#### *Safety Considerations*

Some PAHs, i.e. benzo(a)pyrene, are classified as known or suspected, human or mammalian carcinogens, so care was required when handling solids, solvent extracts or solutions of standard PAHs to ensure no bodily contact. Solid PAHs also give rise to dust hazards, so protective apparatus, such as fume hoods, disposable gloves and dust masks, were used when preparing standards.

### Primary and Surrogate Standards

The primary standard was used for quantification purposes. Benzo(a)anthracene was chosen as the primary standard since it possessed the properties described by Poole & Schuette (1984) outlined in Corban (1994), and refer to Appendix 2 Table A2.1.1. Benzo(a)anthracene (typically 100μL of a 100.2mg/L solution in dichloromethane) was added to the dichloromethane extractive solution as the primary (quantification) standard.

The surrogate standard was used to help quality assurance by analysing the sample recoverability in conjunction with the primary standard throughout the study. Naphthalene (typically 100μL of a 100.2mg/L solution in dichloromethane) was added to the water phase as surrogate (recovery) standard immediately before extraction started and quantified in the same way as the target compounds.

### Response Factor Solutions

A series of response factor solutions was made by adding a fixed amount (100μL of a 100.2mg/L solution of benzo(a)anthracene in dichloromethane) to a series of vials. Different amounts (0, 10, 40, 100, 200 and 400μL) of a "soup" solution containing 50.0, 51.8, 51.3 and 50.0mg/L of phenanthrene, pyrene, fluoranthene and benzo(a)pyrene respectively, were added sequentially to the series of vials. This afforded six different "soup" response factor solutions containing 0, 0.5, 2, 5, 10, and 20μg of the target species. The volume of these $R_F$ mixtures was made up to approximately 1mL. The ratio of target to standard species was 0, 0.05, 0.2, 0.5, 1 and 2 respectively.

Standard solutions were frequently checked for stability, degradation and evaporation, and replaced if there was a problem. Before a quantity of solution was taken for analysis, the level of solution was initially marked at room temperature. The sample was refrigerated (so volume decreased), and after refrigeration, the sample was warmed until the volume returned to the mark.

## 2.3.9 Quantification

In this investigation response factors ($R_F$) were calculated relative to benzo(a)-anthracene. Because authentic specimens for target compounds were available, the response factors were determined using the response factor solutions containing known amounts of compounds. The mathematical expression used to drive SIM GC/MS response factors for authentic specimens is given below:

$$R_F\ (\text{target compound}) = \frac{(\text{peak area of the target compound}) \times (\text{concentration of benzo(a)anthracene})}{(\text{peak area of benzo(a)anthracene}) \times (\text{concentration of the target compound})}$$

The concentrations of PAHs are calculated from peak areas determined for appropriate ion chromatograms (usually high intensity ion), acquired using SIM GC/MS detection and benzo(a)anthracene as the primary standard. The mathematical expression used to calculate the concentration of target compounds is given below:

Concentration (target compound $\mu$g/L) =

$$\frac{(\text{Peak area of the target compound}) \text{ x } (\text{concentration of benzo(a)anthracene})}{(\text{Peak area of benzo(a)anthracene}) \text{ x}(R_F \text{ of target compound})}$$

All calculations were performed using purpose written Microsoft Excel™ spreadsheets.

Quantification results were accepted if the recovery of naphthalene was in the range 80–120%.

### 2.3.10 Sample Pre-treatment & Extraction

Sample pre-treatment can influence the recovery of organic species from water samples. For example, filtration before extraction can remove particle-bound organic species (pollutants) and lead to the recovery of only free (soluble) species. A detailed study of resin acid and resin neutral speciation in Tarawera River samples has shown that 0.45-$\mu$m filtration before extraction typically removes 60% of the resin compounds (Ali Kanber et al. 2000).

PAHs are likely to behave similarly to resin neutrals as they have similar chemical structures and properties. There is little literature on the distribution of PAHs over the different particle sizes found in road runoff. An investigation of this, while of interest, was beyond the scope of the present project.

The continuous liquid/liquid extraction method requires a purpose-built apparatus designed to achieve exhaustive extraction, because hundreds of droplets are produced per hour, each one being a mini-extraction. Experimental work has shown that many small volume extractions are more effective than a single large volume extraction such as the separating funnel method.

Liquid/liquid extraction initially recovers low solubility organics in the aqueous phase, and after a long extraction will recover high solubility organics in the aqueous phase. Therefore, it achieves a complete recovery of about 99.5% with longer extraction times. Typically, 4–8 h is required, but in the present study overnight extraction for 16–24 h ensured complete extraction.

Comparison with the separating funnel extraction method shows that although ideally, a single extraction would recover all (or at least >95–99%) of an organic species from an aqueous phase, this is not always the case. The recovery is dependent on the partitioning of the organic species from the aqueous phase, and the volume of both the extracting solvent and aqueous phase.

### 2.3.11 Methodology applied in Present Study

Water samples (c.900mL) were pre-filtered through a 400-$\mu$m mesh filter, and then liquid/liquid extracted for 16–24 h with redistilled dichloromethane (c.200mL). Naphthalene (typically 100$\mu$L of a 100.2mg/L solution in dichloromethane) was added to the water phase as a surrogate (recovery) standard immediately before the extraction began. After extraction, benzo(a)anthracene (typically 100$\mu$L of a

100.2mg/L solution in dichloromethane) was added to the dichloromethane extractive solution as primary (quantification) standard, and the extraction solvent was removed until a concentrated extract of 1mL remained using a rotary evaporator. Concentrated extract was transferred to a GC/MS vial, which was capped and stored at 4°C before GC/MS analysis. A schematic outline of the SIM GC/MS analytical protocol used to identify the levels of PAHs in the runoff samples is presented in Figure 2.7.

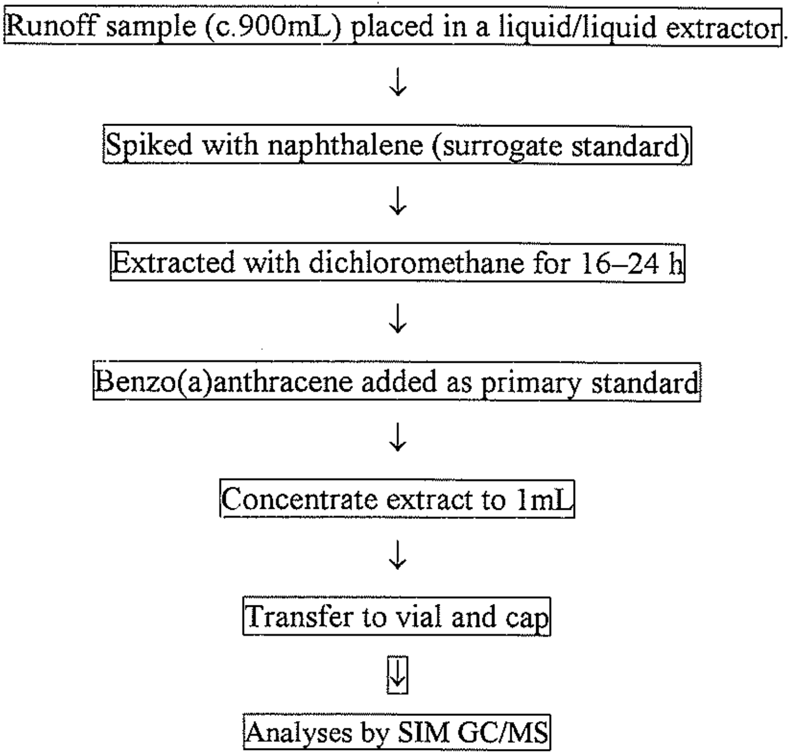


**Figure 2.7** **Flow diagram for the analysis of PAHs.**

### 2.3.12 Summary

Response curves for the PAH standards revealed that linear ranges varied from 0.5 to 20$\mu$g for injected PAHs. Regression coefficients for all target compounds were in the vicinity of 0.99. A reproducibility experiment found that instrument precision was excellent with the CV being less than 5% for all compounds. The recoverability of the organic compounds from the aqueous medium was shown to be within 80 and 120%. Sample results indicated reasonable precision for the extraction and analytical protocol with CV values in the vicinity of 20%.

# 3. Method Validation & Site Selection

## 3.1 Assessment of Analytical Reliability

In order to determine the analytical reliability of the protocols for metals present in actual field samples, a preliminary analysis of a composite sample of road runoff was performed.

### 3.1.1 Sampling

Composite samples of water and sediment were obtained by combining samples collected from the 8 catchpits of 4 urban intersections (see Section 3.2.1) in Hamilton on 9/8/2000, after a rainfall event.

At each site, grab samples of water were obtained by lowering a 500mL plastic sampling cup attached to a 2m rod into the open catchpit. Approximately 100mL of sample was collected from each catchpit. Grab samples of approximately 100g of sediment were obtained by essentially the same procedure.

Liquid samples were filtered through a 0.45$\mu$m membrane filter to obtain the dissolved fraction. Suspended solids were taken as the residue on the filter paper. Dissolved solids, suspended solids and sediments were analysed according to the protocols described in Section 2.2.11.

In the case of the water samples, the effects of pre-filtration by glass fibre, pre-filtration by nylon mesh and pre-saturation of the 0.45$\mu$m filter paper were investigated. In the case of the sediment samples, the effect of sieving the solids through various sieve sizes was determined.

### 3.1.2 Filtration of Water Samples through a 0.45$\mu$m Filter

Six replicate analyses of water samples were performed for total metals (unfiltered), dissolved metal solids (0.45$\mu$m filtered) and particulate-bound metals associated with the suspended solids (retained on the filter paper). Data are presented in Table 3.1.

The data indicate that for most metal elements at levels above the reliable detection limit values (all metals except Cd and Cr), mass balance for the dissolved and suspended components was obtained. However, in the case of Cu and Ni, significantly less metal was determined in the suspended solid and dissolved solid fractions than was obtained for the unfiltered samples. It appears that some metal is lost during filtration. In addition, the analytical variability obtained for these metals was well above the 5% CV expected.

**Table 3.1 Metal concentration ($\mu$g/L) in water samples for total metals (un-filtered), dissolved solids (0.45$\mu$m filtered) and suspended solids (retained on the filter paper).**

| Metals | n | Mean | Stdev | CV (%) |
|---|---|---|---|---|
| Dissolved Cd | 6 | nd | - | - |
| Suspended Cd | 6 | nd | - | - |
| Diss Cd + Susp Cd | | - | | |
| Total Cd | 6 | nd | - | - |
| % Recovery | | - | | |
| | | | | |
| Dissolved Cr | 6 | nd | - | - |
| Suspended Cr | 6 | nd | - | - |
| Diss Cr + Susp Cr | | - | | |
| Total Cr | 6 | nd | - | - |
| % Recovery | | - | | |
| | | | | |
| Dissolved Cu | 6 | 25 | 7.5 | 30 |
| Suspended Cu | 6 | 10.3 | 0.86 | 8.3 |
| Diss Cu + Susp Cu | | 35.3 | - | - |
| Total Cu | 6 | 45 | 8.8 | 20 |
| % Recovery | | 78% | - | - |
| | | | | |
| Dissolved Fe | 6 | 2690 | 92 | 3.4 |
| Suspended Fe | 6 | 2700 | 170 | 6.3 |
| Diss Fe + Susp Fe | | 5390 | - | - |
| Total Fe | 6 | 5600 | 300 | 5.4 |
| % Recovery | | 96% | | |
| | | | | |
| Dissolved Ni | 6 | 16 | 6.1 | 38 |
| Suspended Ni | 6 | 13 | 1.5 | 12 |
| Diss Ni + Susp Ni | | 29 | - | - |
| Total Ni | 6 | 60 | 50 | 84 |
| % Recovery | | 48% | - | - |
| | | | | |
| Dissolved Pb | 6 | 69 | 5.8 | 8.4 |
| Suspended Pb | 6 | 70 | 16 | 24 |
| Diss Pb + Susp Pb | | 139 | - | - |
| Total Pb | 6 | 120 | 30 | 24 |
| % Recovery | | 116% | - | - |
| | | | | |
| Dissolved Zn | 6 | 900 | 310 | 34 |
| Suspended Zn | 6 | 120 | 47 | 41 |
| Diss Zn + Susp Zn | | 1020 | - | - |
| Total Zn | 6 | 1000 | 160 | 16 |
| % Recovery | | 102% | - | - |

nd = not detected

### 3.1.3 Pre-saturation of Membrane Filter & Pre-filtration through Glass Fibre

To remove gross particulate matter and prevent the clogging of the 0.45$\mu$m filter, water samples were pre-filtered through a 9–15$\mu$m glass-fibre filter before filtration through the 0.45$\mu$m filter. In addition, the 0.45$\mu$m filter was pre-saturated with

50mL of water sample to prevent loss of sample in the liquid required to saturate the filter.

The suspended solids were taken as the solids that passed through the glass fibre but were retained by the 0.45$\mu$m filter. This fraction was rinsed with 3mL of deionised water to remove any dissolved material remaining. The results obtained using the modified procedure are presented in Table 3.2.

**Table 3.2 The effect of pre-saturation of the 0.45$\mu$m filter and pre-filtration through the glass fibre filter. Mean concentrations ($\mu$g/L) of metals as dissolved and suspended solids.**

| Contaminant | n | Mean | Stdev | CV (%) |
|---|---|---|---|---|
| Dissolved Cu | 3 | 58 | 6.5 | 11 |
| Suspended Cu | 3 | -3 | 4.9 | 150 |
| Dissolved Fe | 3 | 2870 | 25 | 0.88 |
| Suspended Fe | 3 | 25 | 7.7 | 30 |
| Dissolved Ni | 3 | 1020 | 7.5 | 0.73 |
| Suspended Ni | 3 | 70 | 38 | 57 |
| Dissolved Pb | 3 | 62 | 3.9 | 6.3 |
| Suspended Pb | 3 | 32 | 3.1 | 9.7 |
| Dissolved Zn | 3 | 470 | 11 | 2.4 |
| Suspended Zn | 3 | 9 | 3.2 | 36 |

The improvement in precision obtained by modifying the filtration procedure is apparent from the data presented in Table 3.3 where the ratios of the CVs for the experiments of Section 3.1.2 and 3.1.3 are compared.

**Table 3.3 The effect of pre-saturation and pre-filtration on CVs for dissolved and suspended solid determination.**

| Metal | Dissolved Solid | Suspended Solid |
|---|---|---|
| Cu | 2.7 | 0.055 |
| Fe | 3.9 | 0.21 |
| Ni | 52 | 0.21 |
| Pb | 1.3 | 2.5 |
| Zn | 14 | 1.1 |

Significant improvement in the precision of the data for the dissolved solids is evident. However, results for concentrations of the suspended solids were dramatically lower (see Table 3.2) and overall no improvement in reproducibility was obtained. It was concluded that pre-saturation of the 0.45$\mu$m filter improved the method but that pre-filtration with the glass fibre resulted in major losses of suspended solids.

### 3.1.4 Pre-saturation of 0.45 $\mu$m Filter & Pre-filtration Through Nylon Mesh

It was concluded that pre-filtration through glass fibre while removing gross particulate matter also removed most of the suspended solids. Thus a coarser filtration step was required. A 400$\mu$m nylon mesh, giving a suspended solids fraction of 0.45$\mu$m to 400$\mu$m, was chosen. The pre-filtered sample contained some macroscopic suspended matter, but appeared homogeneous.

The dissolved component, pre-filtered though nylon mesh followed by filtration through 0.45$\mu$m, was analysed. The results are presented in Table 3.4 for both the dissolved and suspended solid fractions.

**Table 3.4 Effect of pre-saturation of the 0.45$\mu$m filter and pre-filtration through the nylon mesh. Mean concentrations ($\mu$g/L) of metals as dissolved and suspended solids.**

| Contaminant | n | Mean | Stdev | CV (%) |
|---|---|---|---|---|
| Dissolved Cu | 3 | 31 | 2.1 | 6.8 |
| Suspended Cu | 3 | 2.3 | 0.27 | 12 |
| Dissolved Fe | 3 | 4010 | 37 | 0.92 |
| Suspended Fe | 3 | 770 | 18 | 2.3 |
| Dissolved Ni | 2 | 1250 | 25 | 2 |
| Suspended Ni | 3 | 470 | 21 | 4.4 |
| Dissolved Pb | 3 | 39 | 1.7 | 4.3 |
| Suspended Pb | 3 | 30 | 3.2 | 11 |
| Dissolved Zn | 3 | 484 | 5.5 | 1.1 |
| Suspended Zn | 3 | 21 | 4.1 | 19 |

Table 3.4 shows generally good reproducibility for dissolved solids and adequate reproducibility for the suspended solids.

### 3.1.5 Effect of Sieving on Precision of Sediment Analysis

Dry sediments were sieved through a 1000$\mu$m diameter sieve and were digested in 4 mol/L $HNO_3$ (see Section 2.2.11). Results are summarised in Table 3.5.

**Table 3.5 Mean metal concentrations (µg/g) in sediment samples sieved through 1000µm diameter sieve.**

| Metal | n | Mean | Stdev | CV (%) |
|---|---|---|---|---|
| Cd | 6 | 1.3 | 0.38 | 30 |
| Cr | 6 | 50 | 11 | 24 |
| Cu | 6 | 80 | 30 | 36 |
| Fe | 6 | 16 400 | 570 | 3.5 |
| Ni | 6 | 26 | 3.7 | 14 |
| Pb | 6 | 180 | 35 | 19 |
| Zn | 6 | 390 | 27 | 6.9 |

Data for sediment samples sieved to a 1000µm particle diameter, showed relatively poor precision even for those metals determined in quantities well above their quantification limit.

The protocol was modified to improve sample homogeneity by sieving sediments to the finer fraction of 63µm particle diameter. Data are presented in Table 3.6.

**Table 3.6 Effect of sieving sediments to a 63µm particle diameter. Mean concentrations (µg/g) of metals as sediments.**

| Contaminant | n | Mean | Stdev | CV (%) |
|---|---|---|---|---|
| Cd | 3 | 5.3 | 0.19 | 3.6 |
| Cr | 3 | 50 | 7.5 | 15 |
| Cu | 3 | 189 | 8.7 | 4.6 |
| Fe | 3 | 21 700 | 780 | 3.6 |
| Ni | 3 | 40 | 1 | 2.5 |
| Pb | 3 | 212 | 2 | 0.95 |
| Zn | 3 | 850 | 19 | 2.2 |

The improvement in precision obtained by modifying the sieving procedure is apparent from the overall lower standard deviation and CVs present in Table 3.6. Table 3.7 also demonstrates this improvement by showing the ratios of the CVs for the two sieving procedures.

**Table 3.7 Effect of sieving sediments from 1000µm to 63µm on CVs for metal sediment determination.**

| Metal | Sediment |
|---|---|
| Cd | 8.3 |
| Cr | 1.6 |
| Cu | 7.8 |
| Fe | 0.97 |
| Ni | 5.6 |
| Pb | 20 |
| Zn | 3.1 |

The concentrations of the metals in the <63$\mu$m sediments were greater than the <1000$\mu$m sediments, indicating that the finer sediments contained higher concentrations of the metals.

## 3.2 Preliminary Survey of Runoff Water & Sediment Concentrations

In a preliminary survey, samples were collected from two roundabouts, two traffic lights (intersections), and one section of highway.

### 3.2.1 Survey of Road Runoff Collected from Five Road Sites

Water and sediment samples were collected (see Section 3.1.1) from two roundabouts situated on Killarney Road and Cobham Drive, two traffic lights situated on Lincoln Street and Bridge Street, and from one highway segment of Cambridge Road, near Newells Road (where only water was collected), in Hamilton City.

The samples were analysed for Cd, Cr, Cu, Fe, Ni, Pb and Zn for total metal concentrations in the water phase and in the sediment. The protocol described in Section 2.2.11, which includes the modifications developed in Section 3.1, was used. Reliable results were obtained for Cu, Fe and Zn in the water samples, and for Pb and Zn in the sediment samples.

The general trend in the water samples showed that concentrations for metals were highest at the roundabouts, followed by the traffic lights, and lastly by the highway. A typical example of this is shown in Figure 3.1 for Fe in the water.

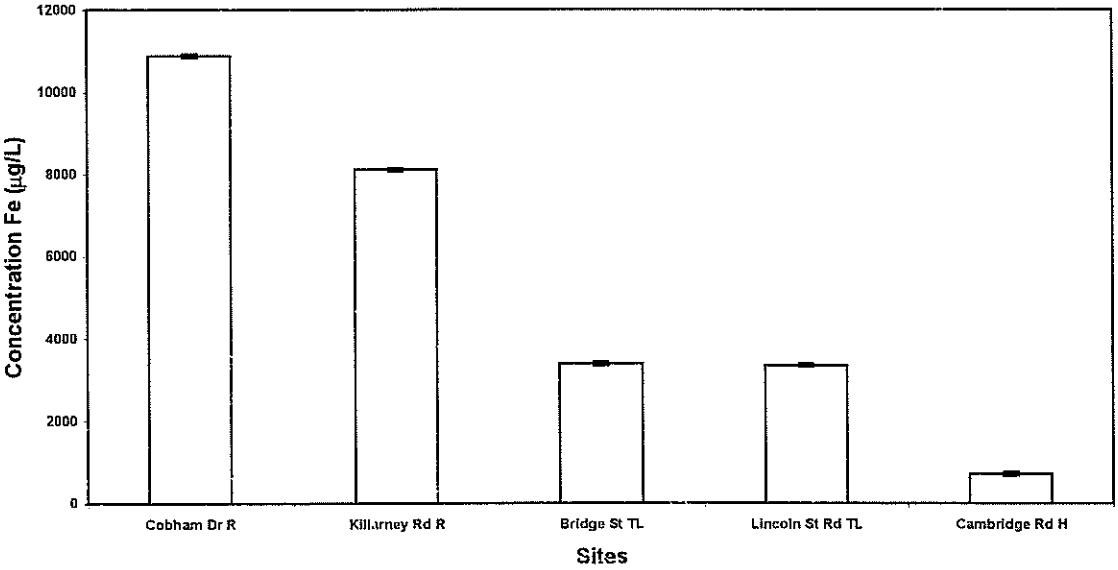


**Figure 3.1 Concentration ($\mu$g/L) of Fe present in catchpit water, obtained from two roundabouts (R), two traffic lights (TL), and a highway section (H).**

The general trend in the sediment samples showed that concentrations for metals were highest from sediment collected from the roundabout compared with that of the traffic lights. A typical example of this is shown in Figure 3.2 for the concentration of Zn in the sediment.

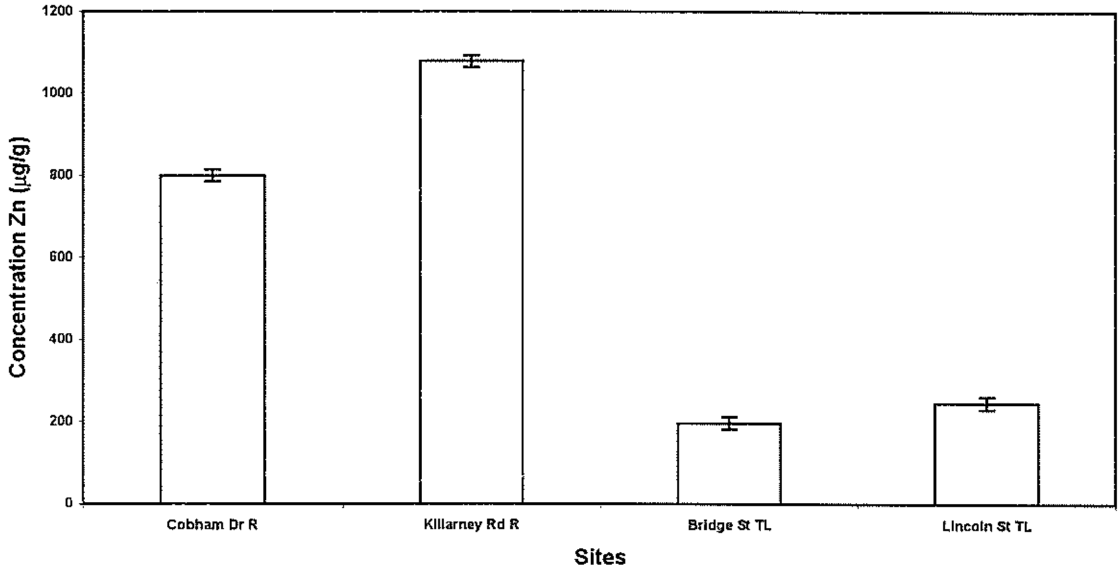


**Figure 3.2 Concentration ($\mu$g/g) of Zn present in catchpit sediment obtained from two roundabouts (R) and two traffic lights (TL).**

The preliminary work showed that the water and sediment samples collected from roundabouts contained the highest concentrations of metals. Based on these conclusions, and on discussion with Hamilton City Council, Landcare Research and Waikato University staff, a suburban roundabout was selected as the experimental site.

### 3.2.2 Experimental Site

The selected experimental site (Figure 3.3) was the roundabout at the corner of River Road and Wairere Drive. This roundabout is situated in a residential, semi-urbanised area, in the northeast part of Hamilton City. The suburban intersection was selected as the experimental site primarily for its ease of operation and for the following factors:

(1) High vehicle numbers to maximise chemical concentrations in the runoff;

(2) Section of roundabout with a clearly defined drainage catchment to a stormwater collection system;

(3) Access to the stormwater system for installation of a weir, flow recorder and automatic water sampler;

(4) A level, secure surface adjacent to the road for parking;

(5) Unused surrounding land;

(6) Minimal potential for damage by vandalising;

(7) Relatively new surface (constructed in 1996, although replaced during the study).

The catchment area was estimated to be 450 $m^2$ (calculated by dividing the total catchment runoff flowrate by the average rainfall intensity) of impervious asphalt, and made up about 25% of the intersection. The average daily traffic counts were c.14 000 vehicles/day. Vehicle speed ranged from 0km/h to 50km/h and above, because of acceleration/deceleration driving phases during exiting and accessing the roundabout.

**Figure 3.3 The roundabout site at River Road and Wairere Drive selected for road runoff analysis.**

The runoff from the trial segment of the roundabout entered a catchpit located along the guttering of the northbound lane of the roundabout (Figure 3.4). The roundabout drainage system was modified by bypassing the drainage from the catchpit away from the main stormwater collection drain. In this way only runoff from the portion of roundabout was collected, and runoff from areas without traffic was excluded.

The runoff flowed from the catchpit into a pipe that delivered it into the installed V-notch weir (see Section 2.1.3), where collection and monitoring of runoff occurred (Figure 3.5).

Figure 3.4 The catchpit that received the roundabout runoff.

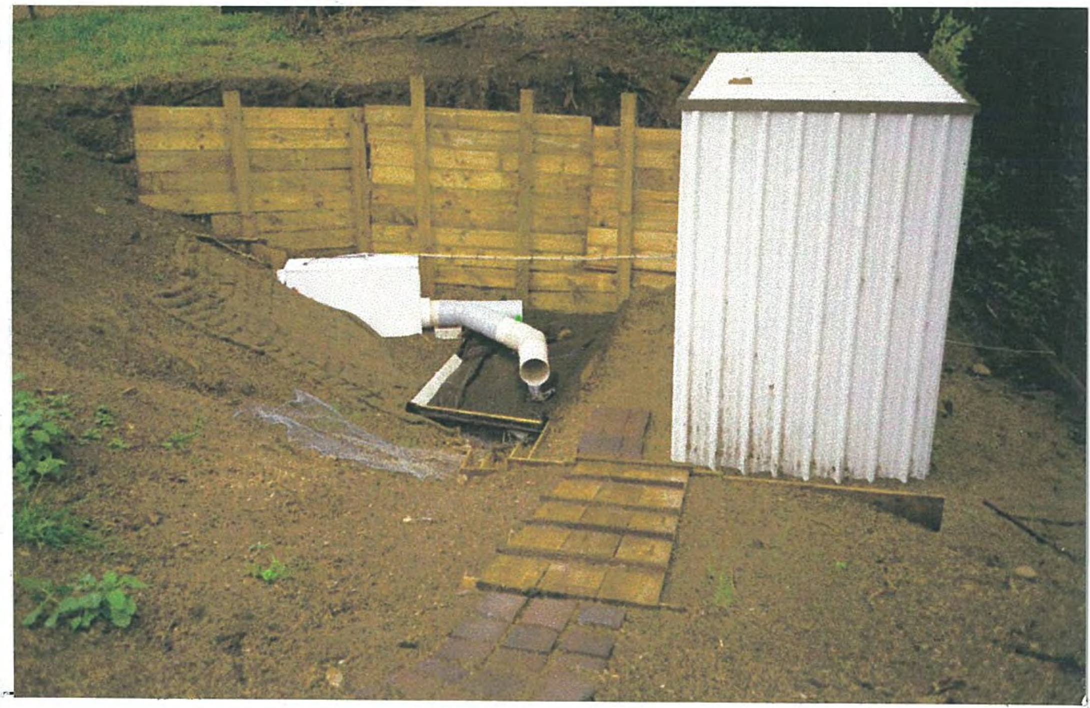


Figure 3.5 The experimental site with the installed equipment.

Exiting runoff from the weir (Figure 3.6) would rejoin the normal flow path for the road runoff to the receiving stream (Figure 3.7).

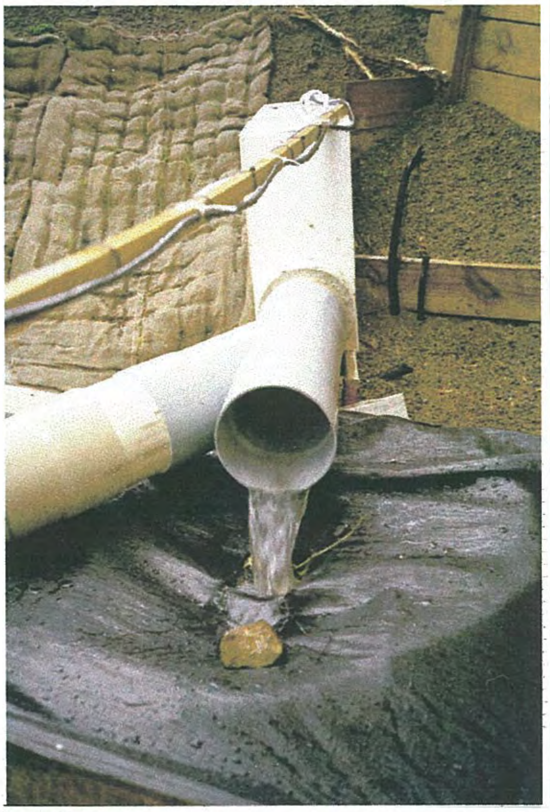


**Figure 3.6. Weir with exiting road runoff.**

**Figure 3.7 Road runoff being piped into receiving stream.**

### 3.2.3 Operation of the System

The installation system was completed early in January 2001. Observations after the installation, and the first rainfall event, showed that the construction of the site led to the efficient collection of runoff from the catchpit to the V-notch weir, and that all the diversions worked as anticipated.

# 4. Contaminant Profiles in Road Runoff for Six Rainfall Events

## 4.1 Introduction

In this chapter data for rainfall intensity and pollutant masses for the first 2 h of six rainfall events are presented. The data were plotted as functions of time and accumulated volume in order to assess the patterns of pollutant mass variation during the initial stages of the rainfall events. A comprehensive set of data is included as Appendix 3, Tables A3.1.1 to A3.1.6 and Figures A3.1.1 to A3.1.3.

Selected data that illustrate principal trends are given in Figures 4.2 to 4.9. Conductivity measurements are summarised in Figure 4.2, particulate-bound metal results are shown in Figures 4.4, 4.6, 4.8, 4.9, and PAH results are summarised in Figures 4.5, 4.7, 4.8, and 4.9.

## 4.2 Rainfall Hydrographs for Six Rainfall Events occurring over the Period 26/1/2001 to 28/3/2001

A total of 72 samples of road runoff were collected from six consecutive rainfall events during the 2-month period from 26/1/2001 to 28/3/2001. The rainfall characteristics are listed in Table 4.1, and the rainfall hydrographs are presented in Figure 4.1.

**Table 4.1 Rainfall characteristics for the six events studied.**

| Event | Date | Preceding Dry Period | Runoff Volume | Intensity | Comment |
|---|---|---|---|---|---|
| E1 | 26/1/2001 | 10 days | 257 L | 0.29 mm/h | Light rain with a heavy shower after c.30 min |
| E2 | 7/2/2001 | 12 days | 178 L | 0.20 mm/h | Light rain with a heavy shower after c.30 min |
| E3 | 11/2/2001 | 3 days | 3060 L | 3.4 mm/h | Initial heavy rain, light rain, final heavy rain |
| E4 | 17/2/2001 | 4 days | 1622 L | 1.8 mm/h | Heavy rain over the period with light pauses. |
| E5 | 9/3/2001 | 13 days | 1792 L | 2.0 mm/h | c.90 min light rain followed by heavy rain |
| E6 | 28/3/2001 | 19 days | 1088 L | 1.2 mm/h | Intensity increased over the period |

Rainfall events over the sampling period were typical of Hamilton weather in late summer. In Figure 4.1, rainfall runoff during events E1 and E2 are very similar. These events, which started with light rainfall followed by a heavy shower after about 30 min, are grouped as low intensity, low runoff volume events. E3 had an initial downpour, followed by a period of light rainfall and another heavy shower; whereas, event E4 had heavy periods of rain, with periods of light rainfall between them. E5 showed a pattern of light rainfall for the first 90 min followed by a heavy downpour. E6 showed an increase in rainfall intensity over the period.

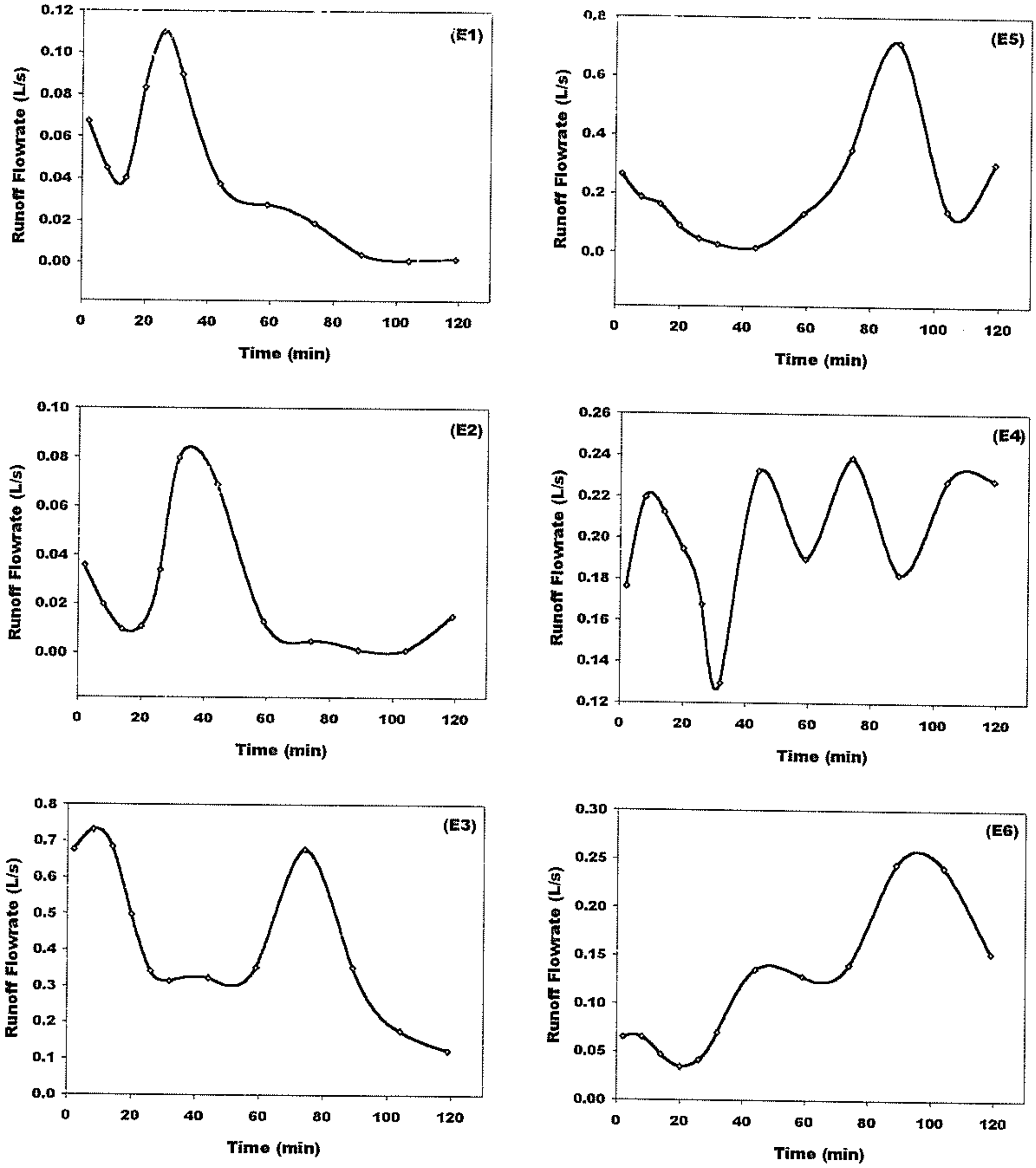


Figure 4.1 Rainfall hydrographs for the first 2 h of precipitation during six rainfall events (E1 to E6) between 26/1/2001 and 28/3/2001.

## 4.3 Variation of Physical Parameters during Rainfall Events

Conductivity, temperature, DO, and pH were continuously recorded throughout each rainfall event. Conductivity data are presented in Figure 4.2. Other parameters are given in Appendix 3, Figures A3.1.1 to A3.1.3. It is clear from the conductivity data that the first flush of runoff has elevated conductivity, indicating high initial levels of electrolyte species. Conductivity levels typically decreased to between 30% and 80% of levels recorded initially.

The typical pattern for pH change during a rainfall event (see Appendix 3, Figure A3.1.2) was a rapid rise by about 0.3, followed by a plateau region or slow decline.

The general pattern for DO and temperature (see Appendix 3, Figure A3.1.1 and A3.1.3) during the runoff event was an initial increase that levelled off during the remaining event period.

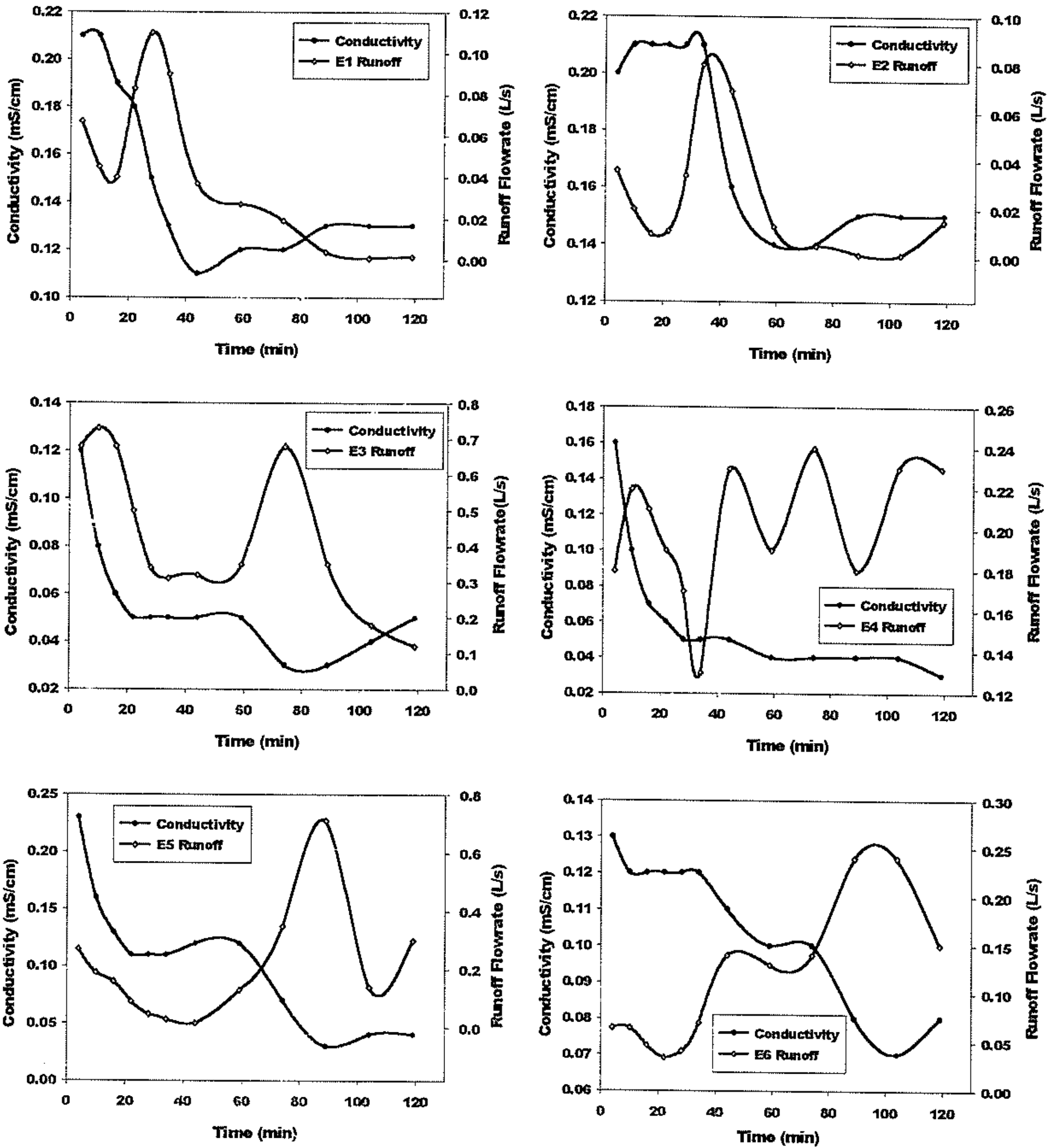


Figure 4.2. Patterns of conductivity (mS/cm) compared with the runoff flowrates (L/s) during the 2 h sampling period for rainfall runoff E1 to E6.

The dissolution of electrolyte deposited on the road surface, and weathered from it, controls the concentration of conducting species (Wust et al. 1994). In overseas studies, conductivity was greater for highway bridge runoff when de-icing salts were used (Wu et al. 1998; Legret & Pagotto 1999). However, this practice is not relevant to the current studies.

The cause of conductivity changes remains unclear. It is possible that it is associated with pH changes in the rainfall itself. For example, leaching of oxides of nitrogen from the air (air quality guidelines for $NO_2$ are exceeded in major New Zealand cities with vehicular traffic being the source of air pollution (Kuschel 2000)) could contribute. It is important to note, however, that oxides of nitrogen were reported to be low in highway runoff from overseas studies (Montrejaud-Vignoles & Herremans 1996; Legret & Pagotto 1999; Drapper et al. 2000). It is uncertain if this is the case for New Zealand conditions.

The possibility that $NO_x$ contributes to elevated conductivity levels is consistent with the trend found in the pH. A fixed reservoir of $NO_x$ present in the air could convert to $HNO_3$, acidifying the initial runoff. It is also noted that the pH of stormwater varies with the amount of local sulfur dioxide and nitrogen dioxide emissions (Novotny et al. 1985).

The temperature generally increased during a rainfall event. This is consistent with the road surface being cooler than the air temperature during rainfall but the explanation is not apparent.

DO generally increased slightly. Initial oxygen depletion caused by microbial activity on the road surface or in the collection system is likely to have been the cause of these trends.

## 4.4 Identification of Chemical Pollutants in Runoff from River Road Sampling Site

A representative SIM GC/MS trace for the PAH contaminants in a typical sample collected from the midpoint of a rainfall event at the River Road site is given in Figure 4.2. The trace shows readily detected and quantifiable levels of phenanthrene, fluoranthene and pyrene, but no benzo(a)pyrene.

The data from ICP-OES analysis (traces not shown) of the same sample indicated that of the elements of interest (Cd, Cr, Cu, Fe, Ni, Pb, and Zn), only Fe, Ni, and Zn were present in amounts detectable by the protocol employed.

## 4.5 Quantification of Inorganic & Organic Contaminants

Target compounds were quantified using the procedures described in Sections 2.2.11 and 2.3.11.

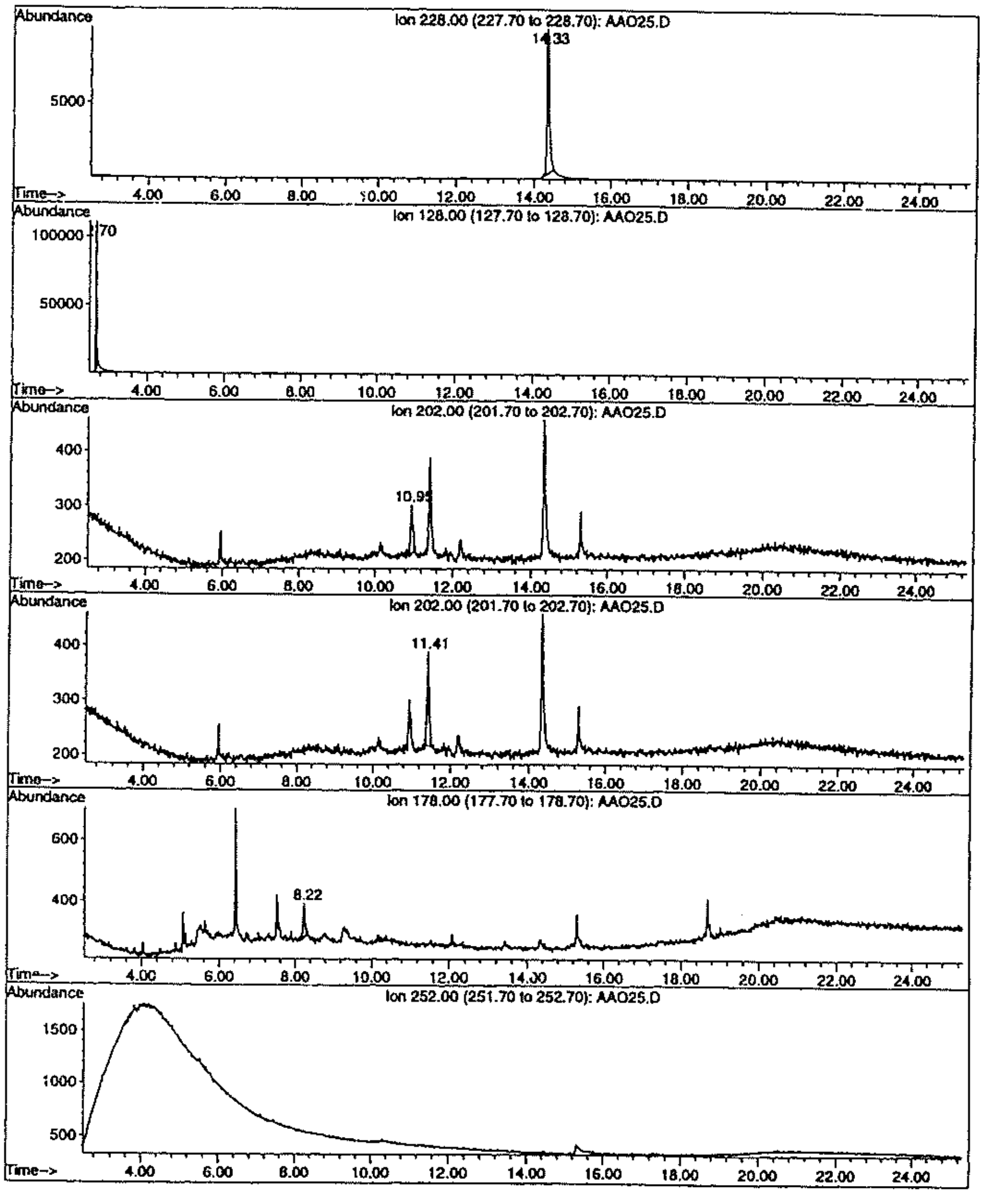


**Figure 4.3. Typical SIM GC/MS ion profiles determined for a road-runoff water sample collected 28/03/01. M/z 128 (naphthalene), 178 (phenanthrene), 202 (fluoranthene), 202 (pyrene), 228 (benzo(a)anthracene) and 252 (benzo(a)pyrene). Benzo(a)pyrene would have appeared at around 17 min.**

Of all contaminants present in the runoff samples, pyrene, phenanthrene, fluoranthene and particulate-bound Fe were all present in large amounts compared with the standard deviations determined for the method. Thus they could be reliably determined in every rainfall event. In some events reliable determinations were also possible for dissolved Fe (E2), dissolved Zn (E1, E2, E3, E5, E6), dissolved Ni (E5, E6), particulate-bound Zn (E1, E2, E5, E6), and particulate-bound Ni (E5, E6). The remaining contaminants, Cu, Pb, Cr and Cd, were below the threshold of detection for all events

## 4.6 Variation of Mass of Metals & PAHs with Time & Runoff Flowrate

The variation of the mass of dissolved metals (Zn, Fe and Ni), particulate-bound metals (Zn, Fe and Ni), and PAHs (phenanthrene, fluoranthene and pyrene) with time and runoff flowrate is discussed in Sections 4.6.1 to 4.6.3.

### 4.6.1 Runoff Time Profiles for Dissolved Metals

The dissolved metal constituents, Zn, Fe, and Ni, were all at very low levels and were not observed in all six rainfall events studied. A complete set of data for dissolved metal constituents is presented in Appendix 3, Tables A3.1.1 to A3.1.6. Where detectable, the trends in soluble metals were varied and inconsistent, e.g. dissolved Zn levels during E5 varied with rainfall intensity, but dissolved Ni remained constant, while no dissolved Fe was detected. In E6, the levels of all dissolved metals followed the pattern of rainfall intensity.

Where detected, the behaviour of dissolved metals during a rainfall event was not as expected. It was anticipated that a first flush would be evident for dissolved metal constituents in every event correlating with the conductivity results, but this was not observed to be the case.

### 4.6.2 Runoff Time Profiles for Particulate-bound Metals

Data for particulate-bound metals are summarised in Appendix 3, Tables A3.3.1 to A3.3.6. Iron was the principal metal determined, with >97% being particulate bound. This is similar to the result found in the highway runoff studied in Japan (Shinya et al. 2000) and in the US (Sansalone & Buchberger 1997). Zinc and Ni, when detected in our study, were also found mainly in the particulate fraction, i.e. 70% and 80% respectively. However, this result contrasts with that of Sansalone & Buchberger (1997) who found Zn and Ni to be present mainly in the dissolved form.

Particulate-bound Fe was present in high concentrations, with low error (1.5%) in all the six rainfall events studied. Particulate-bound Ni and Zn were only present in some of the rainfall events studied but, for the events where these metals were detected, they followed the same behaviour as particulate-bound Fe. Particulate-bound Fe might thus be used to represent all metal constituents in road runoff. Data for particle-bound Fe are summarised in Figure 4.4. The data have been presented in bar diagram format where each bar represents the mass of particulate Fe leached from the trial area of road surface during the relevant time interval. The flowrate (a measure of rainfall intensity) is shown as a continuous curve on the same plot. Error bars have not been shown on the plots because the CVs were all less than 1.5% and were negligible relative to the trends displayed.

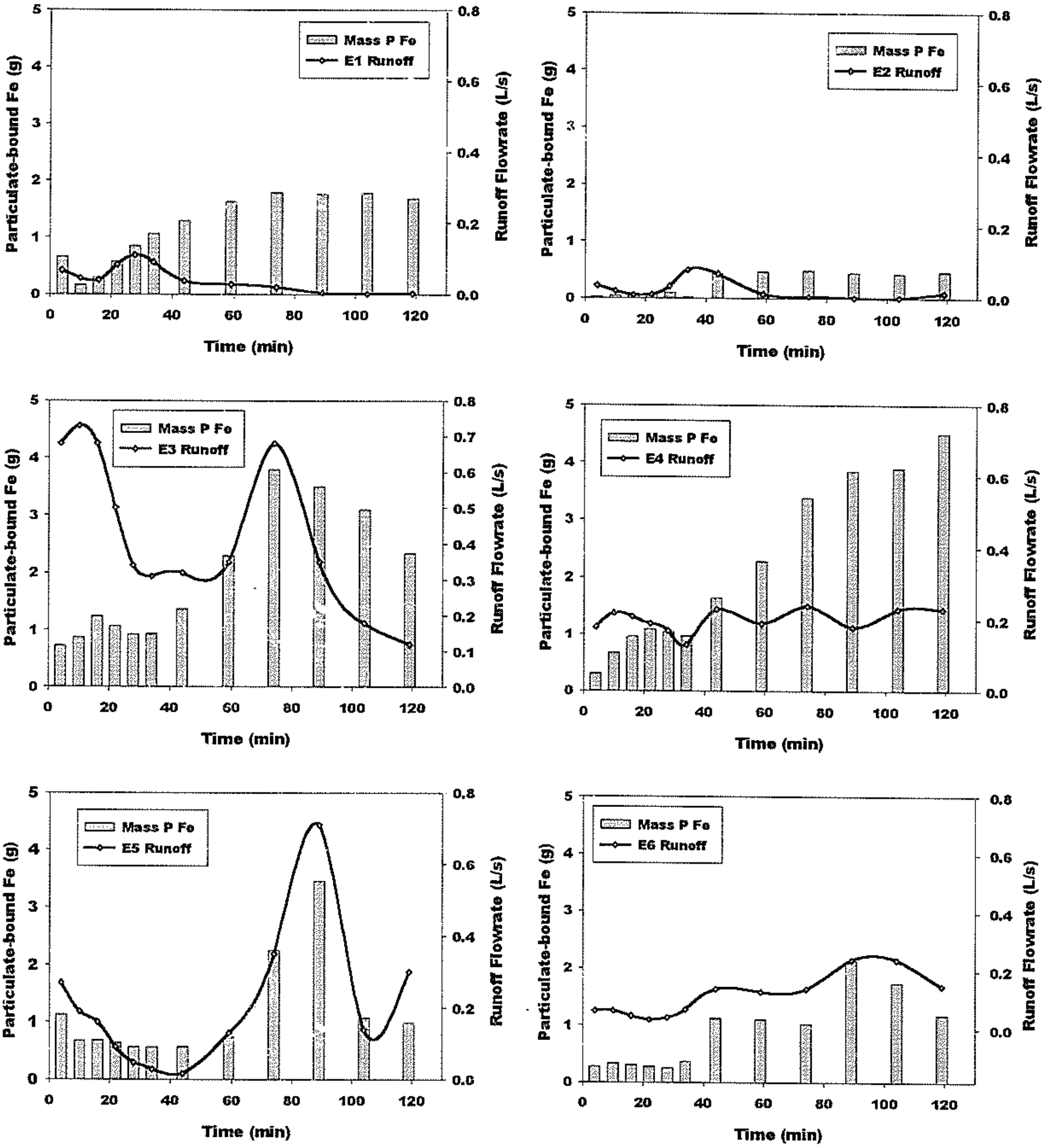


Figure 4.4 **Runoff time profiles for masses (g) of particulate-bound Fe (P Fe) and runoff flowrates (L/s) during rainfall runoff E1 to E6.**

It is clear from the data that the runoff time profile was generally not determined by rainfall intensity. While there appears to be some correlation with rainfall intensity in the data for E5 and E6, this is probably fortuitous in that the rainfall intensity pattern for these two events was light rainfall followed by heavier rainfall. This is similar to the generally observed pattern of a lag between the onset of rain and the highest amounts of particulate-bound iron in the runoff. The clearest indication that rainfall intensity is not a factor is provided by the data for E3, where a heavy initial shower did not result in high initial particulate-bound Fe in the runoff.

### 4.6.3 Runoff Time Profiles for PAHs

The data in Appendix 3, Tables A3.1.1 to A3.1.6, for the PAHs, phenanthrene, fluoranthene, pyrene and benzo(a)pyrene, indicate that pyrene comprised approximately 60% of the PAHs detected (phenanthrene, fluoranthene and pyrene), while carcinogenic benzo(a)pyrene was not detected. This compares to recent results obtained from highway runoff in Japan, where pyrene was one of the predominant PAHs and benzo(a)pyrene only constituted only 3–5% (Shinya et al. 2000).

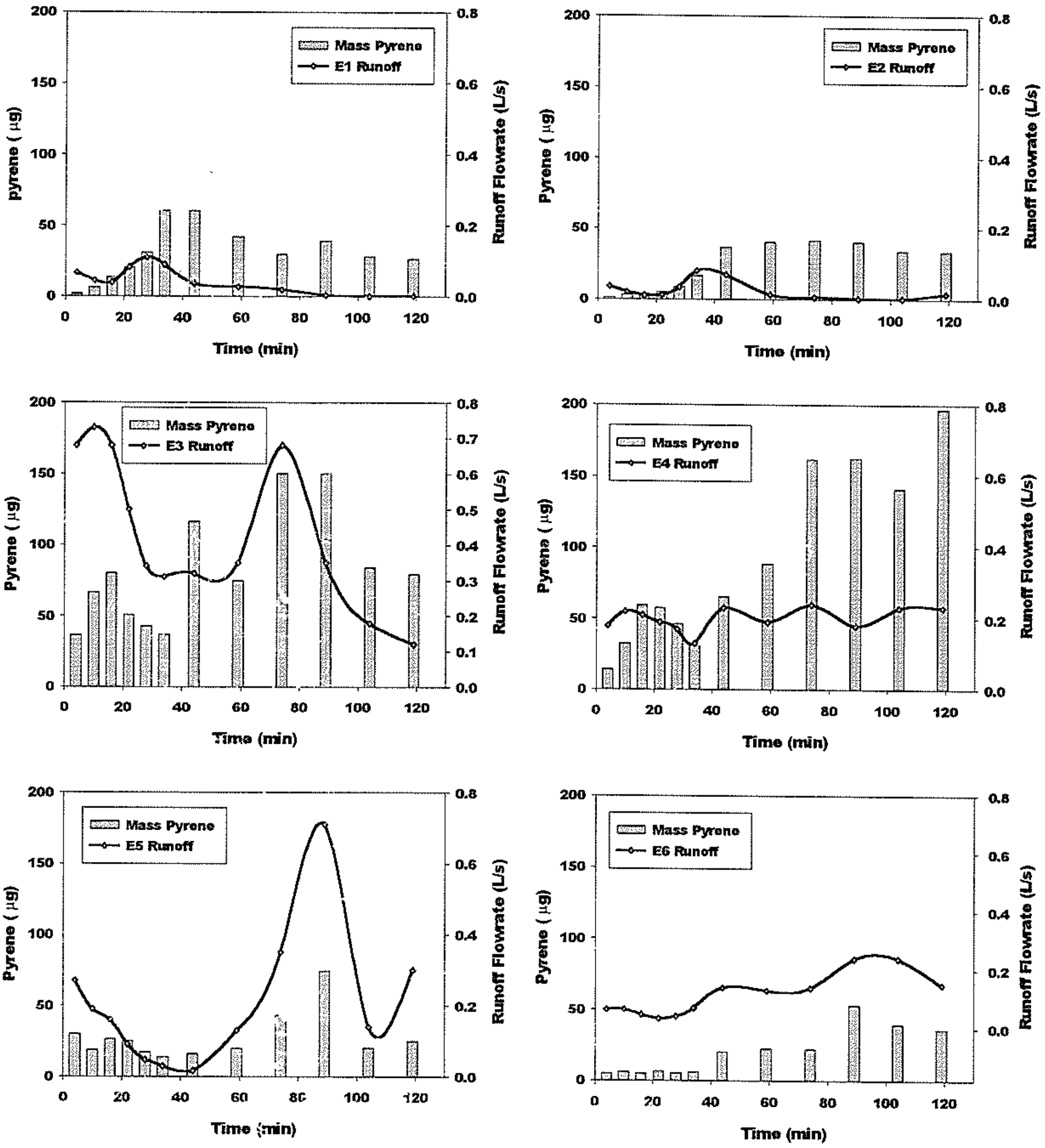


Figure 4.5 Runoff time profiles for masses (μg) of pyrene and runoff flowrates (L/s) for rainfall runoff E1 to E6.

The three detected PAH compounds present in the road runoff behaved similarly during each runoff event, giving very similar profiles. Pyrene, the major constituent, was selected to represent the three PAHs known to be present.

Pyrene data for representative rainfall events are summarised in Figure 4.5. Error bars have not been shown on the plots because the CVs were all less than 4% and were negligible relative to the trends displayed.

Comparison of Figures 4.4 and 4.5 indicate that the behaviour of pyrene consistently followed the trends observed for the particulate-bound Fe. This correlates strongly with a recent New Zealand study of highway runoff that demonstrated that the particulate Zn followed the same behaviour as the particulate PAHs during the storm hydrograph (Kuschel 2000). Overseas data also confirmed this, where the specific load of the particulate-bound Zn and fluoranthene were found to be relatively constant, as their pollutographs resembled the graph of the suspended solids (Wust et al. 1994). Thus, it can be concluded that PAH compounds are predominantly particulate-bound.

## 4.7 Variation of Particulate-bound Fe & Pyrene with accumulated Runoff Volume

The data for accumulated particulate-bound Fe and pyrene are plotted against accumulated volume in Figures 4.6 and 4.7.

From Figure 4.6 it is apparent that different accumulation patterns were followed. The curves for the rainfall runoff E1 and E2 indicated a steep rise in the accumulated pollutant at low accumulated volumes of runoff. This is essentially a first flush effect. Unfortunately, the accumulated volumes for both events were relatively low.

A contrasting behaviour is shown in the Figures for E3 and E4. Here the accumulated pollutant increased much less rapidly and roughly linearly with accumulated runoff volume.

A third type of behaviour is indicated by the plots for E5 and E6. For these events an initial rapid increase in accumulated pollutant amounts with accumulated volume was followed by a period of slower increase in accumulated pollutant. Significantly, the change in slope in these plots occurred after the accumulated volume was greater than the total accumulated volume of approximately 250L recorded for events E1 and E2. It could be that the period of steep increase in accumulated pollutant for E1 and E2 would have been followed by a slower rate of increase, had the accumulated volume been larger. It may also be significant that the events E1, E2, E5 and E6 were preceded by much longer dry spells than was the case for events E3 and E4.

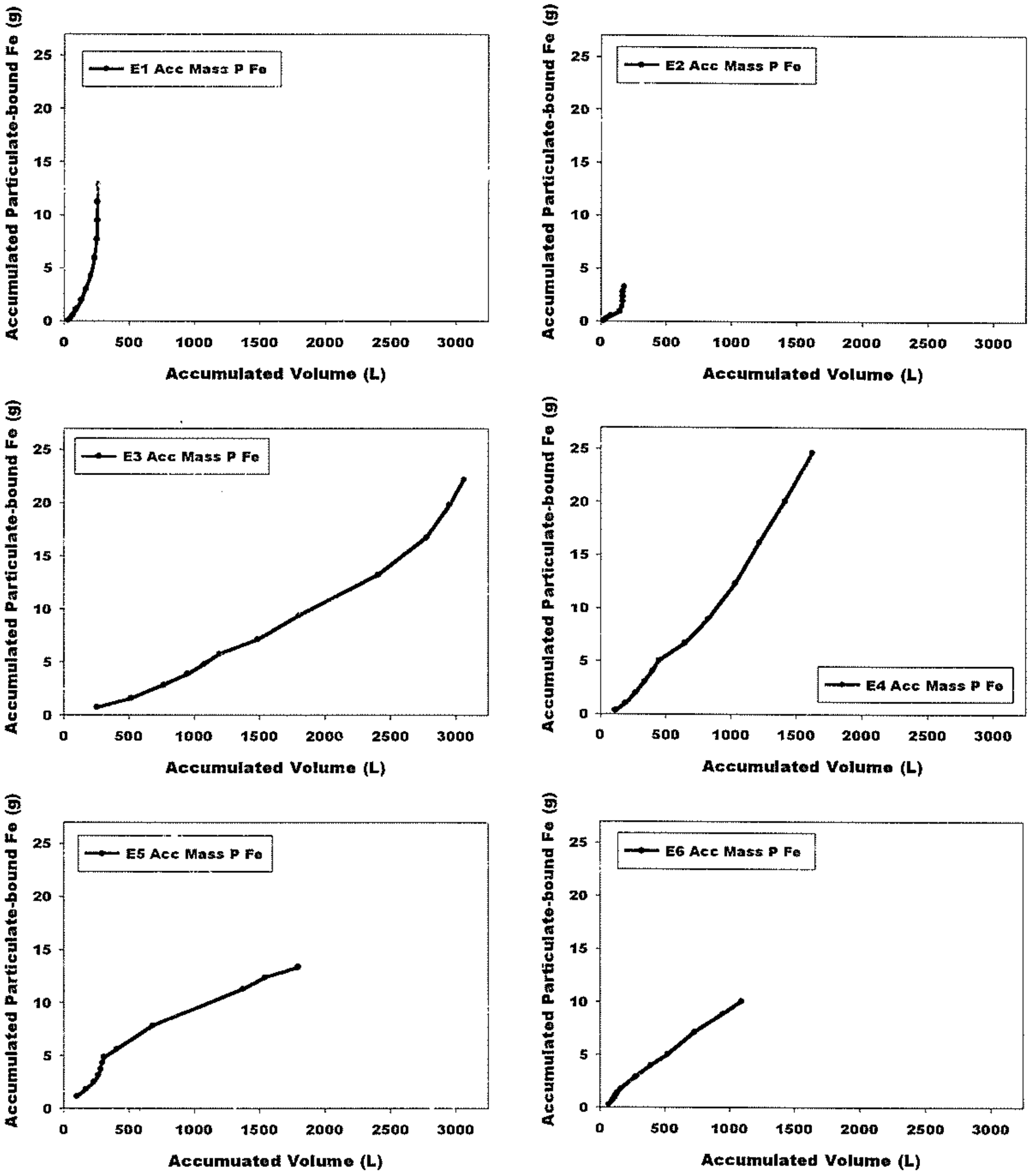


**Figure 4.6 Variation of accumulated mass (g) of particulate-bound Fe (P Fe) with the accumulated volume (L) during the 2-h sampling period for rainfall runoff E1 to E6.**

The nature of a preceding rainfall event is also likely to be important. For example, the road surface will not have been completely clean if the preceding event was of low rainfall intensity and short duration. There is the suggestion of such an effect in the data for particulate-bound Fe. Rainfall for E1 and E2 was of low intensity and did not appear to have cleaned the road surface completely (the amount of pollutant removed was still rising steeply with the volume of runoff). The high intensity and closely spaced events E3 and E4 might be regarded as a continuation of E2, and the lesser concentrations removed reflect the cleaning effect of the previous events. The events E5 and E6 occurred after the road surface had been replaced. The total amounts removed are lower because the accumulation time had been less. The change in the slope of both curves could have been related due to the first flush effect (see E1 and E2) followed by lower amounts of removal similar to those observed in E3 and E4. In the events E5 and E6, the rainfall intensity was sufficient to ensure the transition from first flush to lower pollution release was passed.

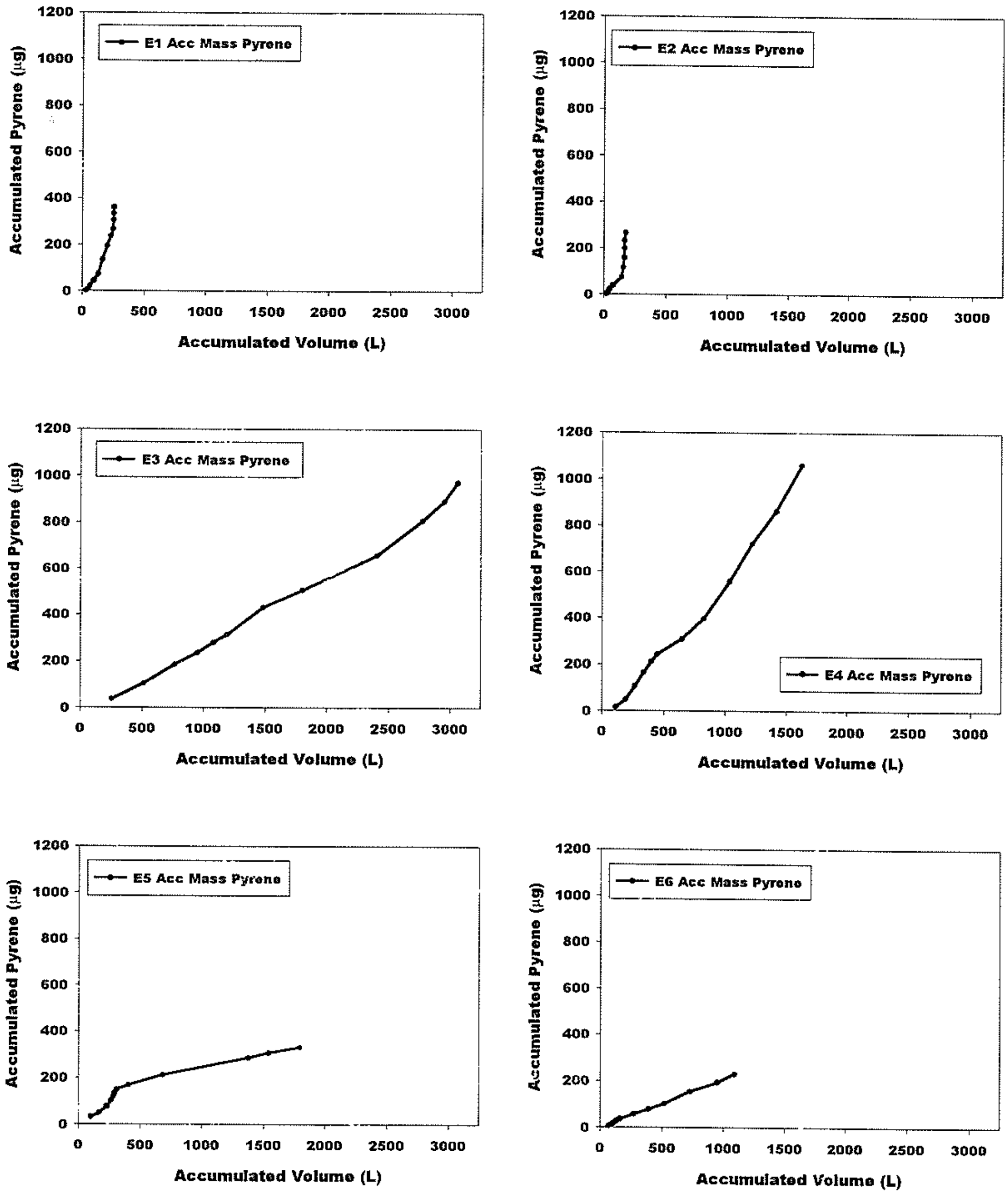


Figure 4.7 Patterns of accumulated mass ($\mu$g) of pyrene compared with the runoff flowrates (L/s) during the 2-h sampling period for rainfall runoff E1 to E6.

Figure 4.7 is the analogous plot obtained from the PAH data. The similarity between the plots obtained for the Fe and PAH data adds weight to the conclusions determined above. A first flush phenomenon was apparent for pyrene during the rainfall events E1, E2 and E5. The first flush did not occur for PAHs during rainfall events E3 and E4, and was less apparent for E6. However, in the latter case the total amount of accumulated pollutant was low and the trends are less well pronounced.

## 4.8 Effect of Number of Preceding Dry Days on Release of Particulate-bound Fe & Pyrene

In order to investigate the effect of the number of preceding dry days on the release particulate-bound Fe and pyrene, the runoff data were plotted to show how, after the 2-h recording period, the accumulated mass varied with the number of preceding dry days (Figure 4.8)

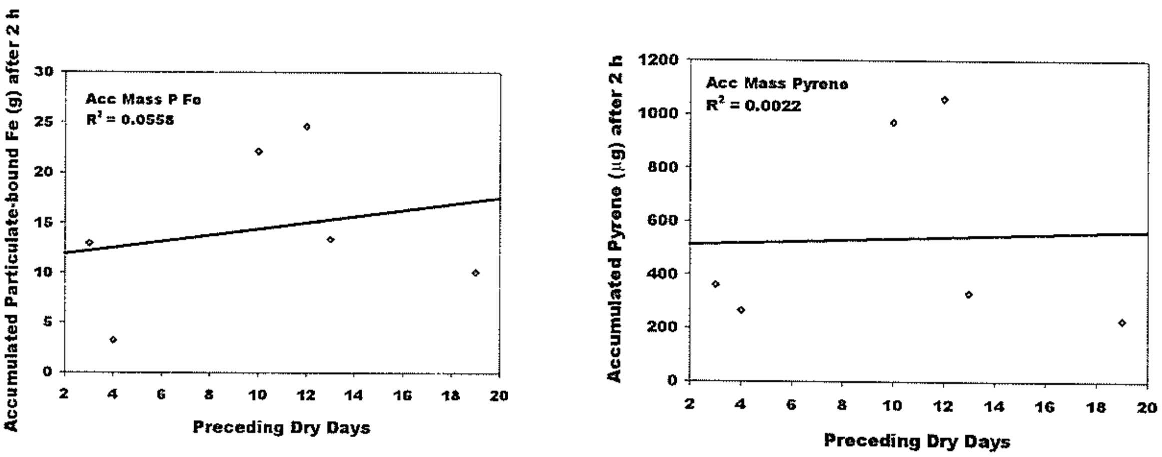


**Figure 4.8. Plots of accumulated mass (g) of particulate-bound Fe (P Fe) and accumulated mass ($\mu$g) of pyrene against the number of proceeding dry days. The amount of pollutant was the total amount collected over the 2 h sampling period.**

There is no correlation between the number of days of dry weather preceding a rainfall event and the total amount of pyrene and particulate-bound Fe washed off the road surface during the first 2-h of each event.

## 4.9 Effect of Accumulated Volume on Release of Particulate-bound Fe & Pyrene

To determine whether there was any correlation of the accumulated mass of pollutant and the accumulated volume of runoff, the accumulated mass after the 2-h period was plotted against the accumulated volume after 2 h (Figure 4.9).

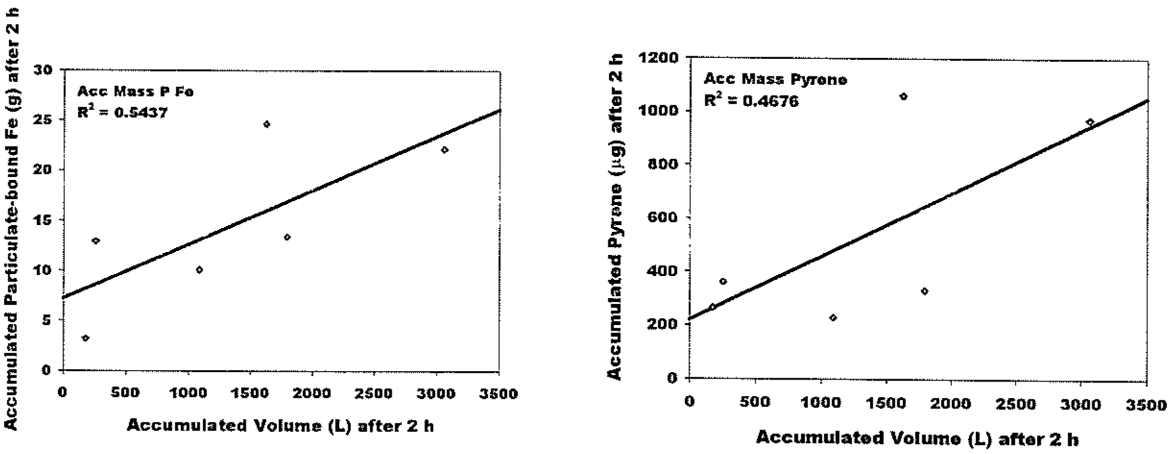


**Figure 4.9 Plots of accumulated mass (g) of particulate-bound Fe (P Fe) and accumulated mass ($\mu$g) of pyrene against the accumulated volume. The amount of pollutant was the total amount collected over the 2-h sampling period.**

The correlation between total pollutant and total volume in the case of particulate Fe ($R^2 = 0.54$) is reasonable, but it is much poorer in the case of the accumulated pyrene ($R^2 = 0.47$). It is interesting to note that the two points which contribute much to the poor correlation were both obtained after the road had been resurfaced. When these points were excluded from the graphs, the $R^2$ values were 0.74 for pyrene and 0.61 for particulate-bound Fe.

# 5. Discussion & Summary

## 5.1 Introduction

The stated purpose of this research was to develop appropriate methodology, to use this methodology to investigate contaminants found in runoff from New Zealand roads, and to determine how the relative concentrations, total load and characteristics change with the intensity and frequency of rainfall events. It was of particular interest to determine the extent to which runoff was affected by a first flush phenomenon.

## 5.2 Validation of ICP-OES Method & Analysis of Heavy Metal Species in Road Runoff

Validation of the ICP-OES method was required for road runoff samples since they typically contained only trace levels of metals. The method validation required the correction of background, spectral and non-spectral interferences and the careful selection of element spectral lines. Good precision and accuracy were demonstrated by the use of metal element standards. Detection limits in $\mu$g/L for the ICP-OES method were 2 (Cd), 5 (Cr), 10 (Cu), 20 (Fe), 5 (Ni), 20 (Pb) and 8 (Zn).

The precision of the field samples required attention. The original methods of APHA et al. (1992) for metal preparation for analysis on the ICP-OES were modified to improve reliability and convenience. In the case of the water samples, the effect of pre-filtration by nylon mesh and pre-saturation of the 0.45$\mu$m filter paper improved the precision of dissolved and suspended solid data. In the case of the sediment samples, the effect of sieving the solids to the size range from 1000$\mu$m to 63$\mu$m improved the precision. It was noted that the concentrations of the metals in the <63$\mu$m sediments were greater than the >1000$\mu$m sediments. This indicated that the finer sediments contained higher concentrations of the metals, and confirmed results of Williamson (1985) who reported a general increase in the concentration of contaminants with decreasing particle size for samples of stormwater from an urban residential catchment. This was attributed to the corresponding increase in specific surface area and has been observed for heavy metals in sediments in general urban drainage.

The only metals present in amounts detectable by the protocol employed included Fe, Ni and Zn. Other elements of interest, Cd, Cr, Cu and Pb, were not detected.

## 5.3 Validation of SIM GC/MS Method & Analysis of PAH Species in Road Runoff

Validation of the SIM GC/MS method was required for road runoff samples since they typically contained only trace levels of PAHs. The SIM technique was chosen for its high sensitivity and selectivity, and therefore, has good detection limits. The

GC/MS system provided a high level of performance, successfully detecting pyrene, phenanthrene and fluoranthene, but not benzo(a)pyrene, to approximately 90ng/L levels with a CV of 4%.

## 5.4 Sampling & Site Selection

Development of the sampling and monitoring equipment was required to enable sampling of road runoff throughout a rainfall event, calculation of event mean concentrations, determination of total contaminant load, and variation of contaminant concentrations throughout the event (McKergow 1994b).

An automated bottle sampler was chosen for this purpose (McKergow 1994b; Sansalone & Buchberger 1997; Barrett et al. 1998; Wu et al. 1998; Legret & Pagotto 1999). The 6700 ISCO automatic water sampler operated as a self-contained road runoff monitoring system. A 45°C V-notch weir (designed according to Grant & Dawson 1997) enabled the accurate measurement of low flows and accurate contaminant loads. Using the 730 bubbler module, the sampler could be programmed to capture the first flush of a rainfall event. Also, attachment of the YSI 600 Sonde allowed the quick determination of contaminant trends for physical parameters during a rainfall event. Attachment of the tipping bucket rain gauge allowed for the accurate measurement of rainfall intensity.

Once the sampling and monitoring equipment was optimised for effective sampling, the site for road runoff analyses was chosen. Results from water and sediment samples collected from two roundabouts, two traffic lights and one section of highway in Hamilton City, demonstrated that roundabout intersections contained the highest concentrations of metals. This was attributed to the accelerating and decelerating driving patterns associated with exiting and accessing the roundabouts. Accordingly, a roundabout at the intersection of River Road and Wairere Drive was selected as meeting the factors outlined in Section 3.2.2. The equipment developed for the project was installed at this site.

## 5.5 Variations of Heavy Metals & PAHs during Rainfall Events

Evaluations of the rainfall intensity and first flush were performed for heavy metal fractions and the total PAH fraction for the six rainfall events studied.

### 5.5.1 Effect of Rainfall Intensity

To assess the contaminant variation with intensity, the rainfall intensity and the mass increment of a contaminant were plotted as a function of the time elapsed since the beginning of the event (see Section 4.6).

In the case of the River Road study, it was evident from the data that the runoff time profile could not be reliably predicted from rainfall intensity. This contrasts with an earlier study by Sansalone et al. (1996) who reported that all particulate-bound metal elements exhibited a behaviour that was a function of rainfall intensity. However, the present work gave patterns similar to the patterns for particulate-bound trace pollutant runoff found for a busy intersection in Germany (Wust et al. 1994).

### 5.5.2 First Flush Effects

To evaluate the first flush phenomenon, the accumulated mass of contaminant was plotted as a function of accumulated volume for the 2-h runoff period of each event. A first flush effect was judged to have occurred when the accumulated pollutant exhibited a steep rise at low accumulated volume of runoff.

The particulate-bound metals and PAHs showed a first flush for some of the events studied, namely those where the number of preceding dry days was greater than 10, for both low and high intensity runoff events. This correlates well with pollutant wash-off patterns from highway runoff in Osaka, Japan, where it was demonstrated that a first flush pattern for both lead and total PAHs occurred for both initially high or low intensity events (Shinya et al. 2000). In the current study, for those events where there were only a few preceding dry days, a contrasting behaviour was observed. The accumulated pollutant increased in a way similar to that typically observed towards the end of high rainfall events. The implication of this result is that the road surface had been largely depleted of readily removed material. A third type of behaviour was exhibited for high intensity events that followed prolonged dry spells. The initial first flush effect was followed by a period of slower release of pollutant from the road surface.

Concentrations found for the dissolved metal constituents at the River Road site were low, variable and inconsistent. Sansalone & Buchberger (1997), in contrast, found a pronounced first flush for the dissolved metals. A first flush of dissolved constituents is the expected result and was observed for the electrolyte species contributing to the conductivity results.

### 5.5.3 Frequency of Rainfall Events

The effect of the frequency of rainfall events was estimated by considering the number of dry days preceding a given event. On the basis of plots of accumulated pollutant levels versus the number of preceding dry days clearly there was no correlation for pyrene and particulate-bound Fe for the events studied. This result is in agreement with that of Shinya et al. (2000) where the highest total load was not shown for the event with the longest antecedent dry period.

### 5.5.4 Effect of Total Volume of Runoff

A reasonable correlation between total pollutant and total volume of runoff collected during the first 2 h of a rainfall event was obtained in the case of particulate-bound Fe. It was similar in the case of the accumulated pyrene. Shinya et al. (2000), by contrast, found the highest total load was not obtained for the event with the highest precipitation.

## 5.6 Calculation of Event Mean Concentrations (EMC) & Comparison with Literature Values & Water Quality Standards

To characterise runoff water concentrations, the EMC is often used, because contaminant concentrations may vary by several orders of magnitude during a runoff event (Huber 1993). Event mean concentrations represent a flow average concentration computed as the total pollutant load (mass) divided by the total runoff volume rounded off to a maximum of 3 significant figures. It can be compared with other road runoff data (Barrett et al. 1998). The EMCs for heavy metal and PAH constituents present in the road runoff samples for the first 2 h of the six rainfall events are given in Table 5.1.

**Table 5.1 EMCs for PAHs (ng/L) and heavy metals ($\mu$g/L) in road runoff from six rainfall events.**

| Event | Phen | Flu | Pyrene | D Zn | P Zn | D Fe | P Fe | D Ni | P Ni |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 356 | 555 | 1410 | 708 | 1990 | - | 50300 | - | - |
| 2 | 376 | 665 | 1490 | 548 | 902 | 224 | 18100 | - | - |
| 3 | 90 | 152 | 317 | 224 | - | - | 7240 | - | - |
| 4 | 173 | 275 | 653 | - | - | - | 15200 | - | - |
| 5 | 166 | 123 | 185 | 92 | 232 | - | 7460 | 588 | 1690 |
| 6 | 147 | 104 | 211 | 274 | 328 | 287 | 9250 | 638 | 2160 |

– indicates not determined, D = dissolved, P = Particulate-bound, Phen = phenanthrene, Flu = fluoranthene

When observed, concentrations of P Fe, D Fe, P Ni, D Ni and PAHs were high relative to water quality criteria (Table 5.2); however, D Fe, P Ni and D Ni were often undetectable in the events studied. The Australian and New Zealand water quality guideline values for general recreational purposes for Ni, Fe and Zn were 100, 300 and 5000$\mu$g/L respectively. Of the metal constituents detected, only P Fe, D Ni and P Ni exceeded these values.

**Table 5.2 Maximum acceptable value (MAV) and guideline value (GV) in $\mu$g/L for New Zealand Drinking Water Standards (MoH 2000).**

| Contaminant | MAV | GV |
|---|---|---|
| Ni | 20 | |
| Fe | | 200 |
| Zn | | 3000 |
| Total PAH | 1 | |

The total EMCs (addition of dissolved and particulate-bound metals) for Fe in low rainfall low runoff volume events collected from River Road were found to be at least 20 times higher that that in the low rainfall low runoff volume events from the Millcreek Expressway in Cincinnati. This was so even though the higher traffic density of 150 000 AADT was observed in the latter study (Sansalone & Buchberger 1997).

The concentrations of Zn reported here resemble those reported in Osaka in Japan by Shinya et al. (2000) for an urban highway with 75 000 AADT; while Ni and Fe from Hamilton exceeded results for the Japanese study. Nickel at River Road for events E5 and E6 also exceeded the results found from a highway with 25 000 AADT (Wu et al. 1998). The higher presence of Ni from the River Road site could be attributed to the new road surface present for E5 and E6. Nickel has been found to be a constituent of asphalt (Ball et al. 1998).

The concentrations of PAHs at the River Road site ranged from 90–1490ng/L, which were slightly higher than the values reported in Shinya et al. (2000) of between 86–455ng/L for rainfall events of similar duration.

The results of the present study indicated that the lead content was consistently below detection and is consistent with the phasing out of Pb as a petrol additive in 1996 (Raksasataya et al. 1996).

## 5.7 Treatment Options for Minimising Environment Impact of Road Runoff

The working hypothesis underlying the present investigation was that concentration of pollutants in road runoff would follow the first flush effect previously reported from overseas studies.

The results from the study give some support to the first flush hypothesis for particulate-bound Fe and pyrene where the rainfall event was preceded by a prolonged dry spell. Under these circumstances, approximately 30% of the total load for the 2-h monitoring period was contained within the first 275L of runoff irrespective of rainfall intensity. Thus the diversion and treatment of the runoff from the early stages of a rainfall have potential for the removal of a disproportionate fraction of total runoff pollutant. The fact that most of the pollutant species of concern are bound to particulates indicates that the diverted runoff should be treated by technologies that remove suspended solids. These could include clarifying devices or filtration devices.

## 5.8 Summary

The principal pollutants present in runoff from a suburban roundabout carrying moderate traffic densities include PAHs (pyrene, phenanthrene, fluoranthene), particle-bound metals (Fe, Ni, Zn), and dissolved metals (Fe, Ni, Zn). Pyrene made up approximately 60% of the PAHs. The principal metal constituent was Fe, although readily detectable levels of Zn and Ni were present in most samples in both particle-bound and dissolved forms. Generally most of the metal was particle bound.

One metal notable for its absence at detectable concentrations was Pb. Although Pb was commonly cited in the stormwater studies of the 1970s, the phasing out of Pb in gasoline in 1996 appears to have been effective in preventing the pollution of road runoff with Pb.

The patterns of heavy metal and PAH constituents at the River Road suburban roundabout runoff were investigated. Where the rainfall event was preceded by a prolonged dry period, the pollutant wash-off patterns for particulate-bound Fe and PAHs demonstrated a first flush regardless of rainfall conditions. Particulate-bound Ni and Zn followed a similar behaviour. Phenanthrene and fluoranthene patterns resembled those of pyrene.

The trends for pyrene and particulate-bound Fe were similar It was concluded that PAHs were predominantly bound to the suspended solids, and that particulate-bound Fe and particulate-bound PAH behaved similarly.

Pollutant wash-off behaviour was not correlated with the intensity of the rainfall, and the amount of pollutant load washed of the road over a 2-h period was not related to the number of preceding dry days. Total pollutant load did appear to depend on total runoff volume collected over the 2-h period.

An important practical outcome from the work is the demonstration of a first flush effect for runoff following periods of dry weather. Treatment technologies designed to treat the first flush offer the possibility of cost-effective improvement of the water quality of road runoff.

## 5.9 Recommendations for Further Work

A difficulty faced in the interpretation of the data obtained in the current study was the limited duration of the sampling period. There is a need for data covering the entire event rather than the first 2 hours. In addition, sampling needs to continue over at least a complete annual weather cycle. In this way, the data necessary to test rigorously the effects of first flush, the number of preceding dry days, and the total volume of runoff, can be obtained.

The explanation offered for trends in conductivity and pH has been very tentative. It is of interest to determine the causes of these trends and whether they are vehicle-related or precipitation-related.

The use of particulate-bound Fe has the potential to simplify the analytical processes required to monitor patterns of runoff, since particulate-bound heavy metals and PAHs correlated well with particulate-bound Fe. The advantages of using particulate-bound Fe as a tracer for runoff pollutants are that the determination of Fe is analytically simpler, errors are small because of the large amounts present, and low sample volumes are required.

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# Appendix 1 Calibration Experiments for Metal Analysis[§]

[§] Values presented in this appendix are raw data, and have not been rounded to 3 significant figures.

**Table A1.1.1** Six replicate Cd concentrations ($\mu$g/L), with CV (%) and Er (%) in the water and sediment standard solutions analysed.

| Known Conc | n = 6 | | | | | | Mean | Stdev | C | Absolute Error (AE) | | | | | | Mean AE | Er |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Cal. (water)* | | | | | | | | | | | | | | | | | |
| 0 | 0.2218 | -0.3036 | -0.067 | 0.558 | -0.4612 | 0.4057 | 0.1 | 0.40 | 68 | 0.222 | -0.304 | -0.067 | 0.558 | -0.461 | 0.406 | 0.059 | - |
| 10 | 10.27 | 10.52 | 9.75 | 10.83 | 9.993 | 10.12 | 10.2 | 0.39 | 3. | 0.27 | 0.52 | -0.249 | 0.83 | -0.007 | 0.12 | 0.25 | 2.5 |
| 100 | 95.72 | 97.44 | 97.1 | 96.54 | 94.81 | 95.49 | 96 | 1.0 | | -4.28 | -2.56 | -2.87 | -3.46 | -5.19 | -4.51 | -3.8 | -3.8 |
| 250 | 252.5 | 250.7 | 250. | 254.2 | 248.3 | 249.9 | 251 | 2.1 | 0.8 | 2.5 | 0.7 | 0.8 | 4.2 | -1.7 | -0.1 | 1.1 | 0.44 |
| 500 | 499.3 | 497.1 | 500. | 500.1 | 501.7 | | 500 | 1.7 | 0.3 | -0.7 | -2.9 | 0.4 | 0.1 | 1.7 | -500 | -84 | -17 |
| *Cal. (sed)* | | | | | | | | | | | | | | | | | |
| 0 | 22.97 | 22.22 | 22.8 | 22.03 | 22.37 | 22.1 | 22 | 0.39 | 1. | 22.97 | 22.22 | 22.81 | 22.03 | 22.37 | 22.1 | 22 | - |
| 500 | 562.1 | 556.5 | 558. | 561 | 562.7 | 556.2 | 560 | 2.8 | 0. | 62.1 | 56.5 | 58.6 | 61 | 62.7 | 56.2 | 60 | 12 |
| 1000 | 1069 | 1082 | 105 | 1074 | 1094 | 1086 | 1080 | 15 | 1. | 69 | 82 | 52 | 74 | 94 | 86 | 77 | 7.7 |
| 10 000 | 10550 | 10600 | 1052 | 10530 | 10690 | 10570 | 10580 | 63 | 0. | 550 | 600 | 520 | 530 | 690 | 570 | 580 | 5.8 |
| 20 000 | 20820 | 21310 | 2127 | 20980 | 20860 | 21020 | 21000 | 205 | 1. | 820 | 1310 | 1270 | 980 | 860 | 1020 | 1000 | 5 |

**Table A1.1.2** Six replicate Cr concentrations ($\mu$g/L), with CV (%) and Er (%) in the water and sediment standard solutions analysed.

| Known Conc | n = 6 | | | | | | Mean | Stdev | C | Absolute Error (AE) | | | | | | Mean AE | Er |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Cal. (water)* | | | | | | | | | | | | | | | | | |
| 0 | 31.88 | 33.86 | 33.0 | 34.13 | 32.62 | 35.21 | 33 | 1.2 | 3. | 31.88 | 33.86 | 33.03 | 34.13 | 32.62 | 35.21 | 33 | - |
| 10 | 35.76 | 36.24 | 35.8 | 35.66 | 39.32 | - | 37 | 1.6 | 4. | 25.76 | 26.24 | 25.82 | 25.66 | - | 29.32 | 27 | 270 |
| 100 | 98.81 | 93.07 | 97.7 | 97.06 | 94.46 | 97.62 | 96 | 2.2 | 2. | -1.19 | -6.93 | -2.28 | -2.94 | -5.54 | -2.38 | -3.5 | -3.5 |
| 250 | 254.5 | 257.3 | 257. | 253.4 | 245.9 | 253.5 | 254 | 4.2 | 1. | 4.5 | 7.3 | 7.6 | 3.4 | -4.1 | 3.5 | 3.7 | 1.5 |
| 500 | 502.7 | 497.7 | 500. | 507.6 | 504.3 | 494.7 | 501 | 4.7 | 0.9 | 2.7 | -2.3 | 0.1 | 7.6 | 4.3 | -5.3 | 1.2 | 0.24 |
| *Cal. (sed)* | | | | | | | | | | | | | | | | | |
| 0 | 103.7 | 94.57 | 96.3 | 104.7 | 101.6 | 102.3 | 101 | 4.1 | 4. | 103.7 | 94.57 | 96.34 | 104.7 | 101.6 | 102.3 | 100 | - |
| 500 | 621.9 | 589.4 | 572. | 591.5 | 589.5 | 599.4 | 590 | 16 | 2. | 121.9 | 89.4 | 72.8 | 91.5 | 89.5 | 99.4 | 94 | 19 |
| 1000 | 1178 | 1101 | 107 | 1109 | 1113 | 1087 | 1110 | 36 | 3. | 178 | 101 | 75 | 109 | 113 | 87 | 110 | 11 |
| 10 000 | 10810 | 10220 | 1018 | 10370 | 99870* | 10270 | 10400 | 260 | 2. | 810 | 220 | 180 | 370 | | 270 | 370 | 3.7 |
| 20 000 | 21740 | 20150 | 1987 | 15450 | 20670 | 20180 | 20000 | 2200 | 1 | 1740 | 150 | -130 | -4550 | 670 | 180 | -320 | -1.6 |

Table A1.1.3 Six replicate Cu concentrations ($\mu$g/L), with CV (%) and Er (%) in the water and sediment standard solutions analysed.

| Known Conc | n = 6 | | | | | | Mean | Stde | CV | Absolute Error (AE) | | | | | | Mean AE | Er |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Cal. (water)* | | | | | | | | | | | | | | | | | |
| 0 | 2.637 | 2.5 | 2.702 | 2.066 | 2.079 | 2.718 | 2.5 | 0. | 12 | 2.637 | 2.55 | 2.702 | 2.066 | 2.079 | 2.718 | 2.5 | - |
| 10 | 10.69 | 12.1 | 11.72 | 12.65 | 12.19 | 11.81 | 11.9 | 0.6 | 5.6 | 0.69 | 2.17 | 1.72 | 2.65 | 2.19 | 1.81 | 1.9 | 18.7 |
| 100 | 98.74 | 101. | 99.71 | 99.11 | 100.7 | 100.3 | 100 | 1. | 1.1 | -1.26 | 1.6 | -0.29 | -0.89 | 0.7 | 0.3 | 0.027 | 0.027 |
| 250 | 248.3 | 254. | 256.5 | 256.3 | 256.2 | - | 254 | 3. | 1.4 | -1.7 | 4.5 | 6.5 | - | 6.3 | 6.2 | 4.4 | 1.7 |
| 500 | 471.4 | 491. | 485.2 | 488.2 | 482 | 474.7 | 482 | 7. | 1.6 | -28.6 | -8.1 | -14.8 | -11.8 | -18 | -25.3 | -17.8 | -3.6 |
| *Cal. (sed)* | | | | | | | | | | | | | | | | | |
| 0 | -66.67 | -64.2 | -66.81 | -66.99 | -68.02 | -68.77 | 67 | 1. | -2.3 | -66.67 | -64.22 | -66.81 | -66.99 | -68.02 | -68.77 | -67 | - |
| 500 | 463.3 | 470. | 469.8 | 466.3 | 476.1 | 475.1 | 470 | 4. | 1.1 | -36.7 | -29.4 | -30.2 | -33.7 | -23.9 | -24.9 | -30 | -6.0 |
| 1000 | 989 | 988. | 1006 | 971.8 | 989 | 986.2 | 990 | 1 | 1.1 | -11 | -11.1 | 6 | -28.2 | -11 | -13.8 | -12 | -1.2 |
| 10 000 | 10470 | 1038 | 10370 | 10360 | 10560 | 10480 | 10400 | 8 | 0.76 | 470 | 380 | 370 | 360 | 560 | 480 | 440 | 4.4 |
| 20 000 | 20560 | 2076 | 20880 | 20280 | 20470 | 20780 | 20600 | 23 | 1.1 | 560 | 760 | 880 | 280 | 470 | 780 | 620 | 3.1 |

Table A1.1.4 Six replicate Fe concentrations ($\mu$g/L), with CV (%) and Er (%) in the water and sediment standard solutions analysed.

| Known Conc | n = 6 | | | | | | Mean | Stde | CV | Absolute Error (AE) | | | | | | Mean AE | Er |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Cal. (water)* | | | | | | | | | | | | | | | | | |
| 0 | 35.5 | 36.1 | 17.08 | 19.56 | 21.56 | 22.5 | 25 | 8. | 33 | 35.5 | 36.15 | 17.08 | 19.56 | 21.56 | 22.5 | 25 | - |
| 10 | 27.79 | 27.8 | 24.99 | 22.49 | 22.29 | 22.99 | 25 | 2. | 10 | 17.79 | 17.82 | 14.99 | 12.49 | 12.29 | 12.99 | 15 | 150 |
| 100 | 103.9 | 98.2 | 97.42 | 94.42 | 94.86 | 94.53 | 97 | 3. | 3.7 | 3.9 | -1.71 | -2.58 | -5.58 | -5.14 | -5.47 | -2.8 | -2.8 |
| 250 | 251 | 250. | 226.3 | 225.7 | 229.5 | - | 240 | 1 | 5.4 | 1 | 0.9 | -23.7 | - | -24.3 | -20.5 | -13 | -5.3 |
| 500 | 440.7 | 427. | 429.5 | 434.9 | 425.3 | 423.5 | 430 | 6. | 1.5 | -59.3 | -72.9 | -70.5 | -65.1 | -74.7 | -76.5 | -70 | -14 |
| *Cal. (sed)* | | | | | | | | | | | | | | | | | |
| 0 | 8816 | 876 | 8768 | 8783 | 8805 | 8794 | 8790 | 2 | 0.23 | 8816 | 8767 | 8768 | 8783 | 8805 | 8794 | 8800 | - |
| 250 000 | 275200 | 25460 | 260400 | 254100 | 258300 | 263900 | 261000 | 780 | 3.0 | 25200 | 4600 | 10400 | 4100 | 8300 | 13900 | 11000 | 4.4 |
| 500 000 | 553400 | 54220 | 531700 | 527500 | 529800 | 531300 | 536000 | 990 | 1.8 | 53400 | 42200 | 31700 | 27500 | 29800 | 31300 | 36000 | 7.2 |
| 750 000 | 825100 | 80210 | 791700 | 796000 | 759400 | 797900 | 800000 | 2100 | 2.6 | 75100 | 52100 | 41700 | 46000 | 9400 | 47900 | 45000 | 6.0 |

**Table A1.1.5** Six replicate Ni concentrations ($\mu g/L$), with CV (%) and Er (%) in the water and sediment standard solutions analysed.

| Known Conc | n = 6 | | | | | | Mean | Stde | CV | Absolute Error (AE) | | | | | | Mean AE | Er |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Cal. (water)* | | | | | | | | | | | | | | | | | |
| 0 | 2.957 | 2.41 | 3.323 | 1.843 | 4.548 | 3.371 | 3.1 | 0.9 | 30 | 2.957 | 2.416 | 3.323 | 1.843 | 4.548 | 3.371 | 3.1 | - |
| 10 | 6.204 | 0.203 | 13.32 | 11.84 | 13.06 | 11.19 | 9 | 5. | 58 | -3.796 | -9.797 | 3.32 | 1.84 | 3.06 | 1.19 | -0.70 | -7.0 |
| 100 | 98.78 | 99.7 | 98.16 | 92.37 | 95.6 | 96.57 | 97 | 2. | 2.8 | -1.22 | -0.29 | -1.84 | -7.63 | -4.4 | -3.43 | -3.1 | -3.1 |
| 250 | 248.9 | 250. | 246.9 | 246.6 | 256.3 | 256.2 | 251 | 4. | 1.7 | -1.1 | 0.1 | -3.1 | -3.4 | 6.3 | 6.2 | 0.83 | 0.33 |
| 500 | 471.4 | 491. | 485.2 | 488.2 | 482 | 474.7 | 482 | 7. | 1.6 | -28.6 | -8.1 | -14.8 | -11.8 | -18 | -25.3 | -18 | -3.6 |
| *Cal. (sed)* | | | | | | | | | | | | | | | | | |
| 0 | -23.43 | -20.5 | -21.79 | -20.27 | -21.25 | -22.13 | 22 | 1. | 5.5 | -23.43 | -20.53 | -21.79 | -20.27 | -21.25 | -22.13 | -22 | - |
| 500 | 503.3 | 505. | 508.4 | 512.3 | 508.5 | 514.1 | 509 | | 0.79 | 3.3 | 5.8 | 8.4 | 12.3 | 8.5 | 14.1 | 8.7 | 1.7 |
| 1000 | 1026 | 103 | 1031 | 983.1 | 1031 | 1016 | 1020 | 1 | 1.9 | 26 | 34 | 31 | -16.9 | 31 | 16 | 20 | 2.0 |
| 10 000 | 10320 | 1035 | 10350 | 10230 | 10180 | 10470 | 10300 | 10 | 0.97 | 320 | 350 | 350 | 230 | 180 | 470 | 320 | 3.2 |
| 20 000 | 20720 | 1983 | 20280 | 20230 | 20410 | 20770 | 20400 | 35 | 1.7 | 720 | -170 | 280 | 230 | 410 | 770 | 370 | 1.9 |

**Table A1.1.6** Six replicate Pb concentrations ($\mu g/L$), with CV (%) and Er (%) in the water and sediment standard solutions analysed.

| Known Conc | n = 6 | | | | | | Mean | Stde | CV | Absolute Error (AE) | | | | | | Mean AE | Er |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Cal. (water)* | | | | | | | | | | | | | | | | | |
| 0 | 24.7 | 29. | 27.67 | 36.72 | 40.27 | 31.69 | 32 | 5. | 18 | 24.7 | 29.7 | 27.67 | 36.72 | 40.2 | 31.69 | 32 | - |
| 10 | 39.22 | 45.8 | 41.63 | 31.32 | 34.15 | 43.48 | 39 | 5. | 14 | 29.22 | 35.81 | 31.63 | 21.32 | 24.1 | 33.48 | 29 | 290 |
| 100 | 131.7 | 119. | 117.3 | 117.9 | 112.2 | 113.6 | 119 | 6. | 5.8 | 31.7 | 19.8 | 17.3 | 17.9 | 12. | 13.6 | 19 | 19 |
| 250 | 260.1 | 265. | 254.4 | 256.1 | 270.5 | 253.7 | 260 | 6. | 2.6 | 10.1 | 15.3 | 4.4 | 6.1 | 20. | 3.7 | 10 | 4.0 |
| 500 | 489.7 | 500. | 464.9 | 491 | 477.5 | 472.9 | 480 | 1 | 2.7 | -10.3 | 0.7 | -35.1 | -9 | -22. | -27.1 | -17 | -3.4 |
| *Cal. (sed)* | | | | | | | | | | | | | | | | | |
| 0 | -3.417 | 7.25 | 1.155 | -14.66 | 7.265 | 0.4132 | 0 | 8. | - | -3.417 | 7.252 | 1.155 | -14.66 | 7.26 | 0.413 | -0.33 | - |
| 500 | 509.7 | 53 | 520.3 | 518.1 | 527.2 | 534.5 | 520 | 1 | 2.1 | 9.7 | 38 | 20.3 | 18.1 | 27. | 34.5 | 25 | 5.0 |
| 1000 | 1031 | 103 | 1035 | 1027 | 1063 | 1069 | 1040 | 1 | 1.7 | 31 | 38 | 35 | 27 | 6 | 69 | 44 | 4.4 |
| 10 000 | 10200 | 1034 | 10170 | 10080 | 10150 | 10400 | 10200 | 12 | 1.2 | 200 | 340 | 170 | 80 | 15 | 400 | 220 | 2.2 |
| 20 000 | 20470 | 2029 | 20030 | 19930 | 20300 | 20280 | 20200 | 20 | 0.99 | 470 | 290 | 30 | -70 | 30 | 280 | 220 | 1.1 |

**Table A1.1.7 Six replicate Zn concentrations ($\mu$g/L), with CV (%) and Er (%) in the water and sediment standard solutions analysed.**

| Known Conc | n = 6 | | | | | | Mean | Stde | CV | Absolute Error (AE) | | | | | | Mean AE | Er |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Cal. (water)* | | | | | | | | | | | | | | | | | |
| 0 | -1.397 | -1.80 | -1.065 | 0.5961 | -1.36 | -1.493 | -1.1 | 0.8 | -78 | -1.397 | -1.803 | -1.065 | 0.596 | -1.3 | -1.493 | -1.1 | - |
| 10 | 16.89 | 16.5 | 12.3 | 12.59 | 10.99 | 11.51 | 13 | 2. | 19 | 6.89 | 6.56 | 2.3 | 2.59 | 0.9 | 1.51 | 3.5 | 35 |
| 100 | 98.77 | 99.6 | 95 | 93.45 | 93.27 | 94.64 | 96 | 2. | 2.9 | -1.23 | -0.38 | -5 | -6.55 | -6.7 | -5.36 | -4.2 | -4.2 |
| 250 | 249.1 | 251. | 247.7 | 245.1 | 249.2 | 245.3 | 248 | 2. | 1.0 | -0.9 | 1.7 | -2.3 | -4.9 | -0. | -4.7 | -2.0 | -0.8 |
| 500 | 495.6 | 49 | 490.7 | 494 | 495.1 | 492 | 494 | 2. | 0.53 | -4.4 | -2 | -9.3 | -6 | -4. | -8 | -5.8 | -1.2 |
| *Cal. (sed)* | | | | | | | | | | | | | | | | | |
| 0 | 11.15 | 11.0 | 3.092 | 4.473 | 3.961 | 2.96 | 6 | 3. | -64 | 11.15 | 11.05 | 3.092 | 4.473 | 3.96 | 2.96 | 6.1 | - |
| 500 | 495.1 | 507. | 493.3 | 503.1 | 504.1 | 507.8 | 502 | 6. | 1.3 | -4.9 | 7.9 | -6.7 | 3.1 | 4. | 7.8 | 1.9 | 0.4 |
| 1000 | 1022 | 102 | 1025 | 997.5 | 1057 | 1049 | 1030 | 2 | 2.1 | 22 | 20 | 25 | -2.5 | 5 | 49 | 28 | 2.8 |
| 10 000 | 10260 | 1024 | 10270 | 10030 | 10270 | 10410 | 10200 | 12 | 1.2 | 260 | 240 | 270 | 30 | 27 | 410 | 250 | 2.5 |
| 20 000 | 20400 | 2027 | 20210 | 20050 | 20200 | 20300 | 20200 | 12 | 0.58 | 400 | 270 | 210 | 50 | 20 | 300 | 240 | 1.2 |

# Appendix 2 Properties Required of an Ideal Internal Standard

§ **Table A2.2.1 Properties required of an ideal internal standard.**

The internal standard should resemble the analyte as closely as possible in terms of chemical and physical properties.

The internal standard should not be a normal constituent of the sample.

The internal standard should be incorporated into the matrix in exactly the same way as the analyte, a situation rarely achieved.

The internal standard and analyte should be resolved chromatographically to baseline (except for isotopically labelled samples when mass discrimination or radioactive counting are used for detection), elute close together, respond to the detection in a similar way, and be present in nearly equal concentrations.

§ See Poole & Schuette (1984), outlined in Corban (1994), for this table and further details.

# Appendix 3 Results of Road Runoff Collected from Six Rainfall Events §

§ Values presented in this appendix are raw data, and have not been rounded to 3 significant figures.

**Table A3.3.1 Time of sampling, runoff flowrate, accumulated (acc) volume, parameters (conductivity, DO, pH and temperature), concentration of PAHs (ng/L) (with recovery) and heavy metals ($\mu$g/L) P (particulate-bound) and D (dissolved), mass and accumulated mass of PAHS (ng) and heavy metals ($\mu$g) for rainfall Event 1 on the 26/1/2001.**

| Name | Actual Tim | Time (min) | Runoff (L/s | Acc Vol (L) | Conductivity (mS/cm) | DO (mg/L) | pH | Temp (°C |
|---|---|---|---|---|---|---|---|---|
| E1 1 | 12:47 - 12:5 | 4.00 | 0.06 | 31.33 | 0.21 | 4.58 | 7.10 | 20.3 |
| E1 2 | 12:53 - 12:5 | 10.00 | 0.04 | 48.22 | 0.21 | 6.44 | 7.18 | 20.8 |
| E1 3 | 13:59 - 13:0 | 16.00 | 0.04 | 63.01 | 0.19 | 7.46 | 7.20 | 21.1 |
| E1 4 | 13:05 - 13:0 | 22.00 | 0.08 | 91.08 | 0.18 | 8.08 | 7.28 | 21.3 |
| E1 5 | 13:11 - 13:1 | 28.00 | 0.1 | 130.84 | 0.15 | 8.66 | 7.32 | 21.7 |
| E1 6 | 13:17 - 13:2 | 34.00 | 0.09 | 164.50 | 0.13 | 9.12 | 7.40 | 21.9 |
| E1 7 | 13:26 - 13:3 | 44.00 | 0.03 | 203.91 | 0.11 | 9.22 | 7.50 | 22.0 |
| E1 8 | 13:41 - 13:5 | 59.00 | 0.02 | 231.34 | 0.12 | 9.05 | 7.42 | 22.0 |
| E1 9 | 13:56 - 14:0 | 74.00 | 0.01 | 248.90 | 0.12 | 8.82 | 7.40 | 21.9 |
| E1 10 | 14:11 - 14:2 | 89.00 | 0.003 | 254.24 | 0.13 | 8.72 | 7.39 | 21.8 |
| E1 11 | 14:26 - 14:3 | 104.00 | 0.001 | 255.23 | 0.13 | 8.57 | 7.30 | 21.6 |
| E1 12 | 14:41 - 14:5 | 119.00 | 0.001 | 256.67 | 0.13 | 8.22 | 7.30 | 21.5 |

| Name | Conc Phen | Mass Phen | Acc Mass Phe | Conc Flu | Mass Flu | Acc Mass Flu | Conc Pyren | Mass Pyrene | Acc Mass Pyrene | Recovery (% |
|---|---|---|---|---|---|---|---|---|---|---|
| E1 1 | 15.7 | 493 | 49 | 19.8 | 620 | 620 | 57. | 1799 | 1799 | 6 |
| E1 2 | 41.4 | 1997 | 249 | 57.6 | 2777 | 3398 | 127. | 6166 | 7965 | 9 |
| E1 3 | 58.0 | 3654 | 614 | 91.6 | 5769 | 9167 | 218 | 13742 | 21707 | 9 |
| E1 4 | 61.2 | 5571 | 1171 | 97.6 | 8889 | 18055 | 228. | 20846 | 42553 | 8 |
| E1 5 | 66.8 | 8742 | 2045 | 103.2 | 13501 | 31556 | 238. | 31149 | 73702 | 10 |
| E1 6 | 86.9 | 14303 | 3476 | 132.2 | 21750 | 53306 | 368. | 60628 | 134330 | 8 |
| E1 7 | 71.7 | 14624 | 4938 | 110.6 | 22559 | 75865 | 296. | 60376 | 194706 | 10 |
| E1 8 | 47.9 | 11078 | 6046 | 72.6 | 16807 | 92671 | 181. | 41974 | 236680 | 9 |
| E1 9 | 28.3 | 7037 | 6749 | 47.9 | 11914 | 104585 | 119. | 29797 | 266477 | 9 |
| E1 10 | 30.1 | 7654 | 7515 | 58.2 | 14808 | 119393 | 154 | 39357 | 305834 | 9 |
| E1 11 | 37.4 | 9551 | 8470 | 47.2 | 12050 | 131443 | 110. | 28070 | 333904 | 10 |
| E1 12 | 25.6 | 6577 | 9128 | 42.3 | 10868 | 142311 | 104. | 26842 | 360746 | 10 |

| Name | D Zn | Mass D Zn | Acc Mass D Zn | P Fe | Mass P Fe | Acc Mass P Fe | P Zn | Mass P Zn | Acc Mass P Zn |
|---|---|---|---|---|---|---|---|---|---|
| E1 1 | 50.9 | 1594 | 1594 | 2121.0 | 66442 | 66442 | 121.9 | 3819 | 3819 |
| E1 2 | 59.4 | 2866 | 4460 | 3358.0 | 161909 | 228352 | 165.2 | 7965 | 11784 |
| E1 3 | 66.6 | 4199 | 8659 | 4624.0 | 291367 | 519719 | 237.7 | 14978 | 26762 |
| E1 4 | 67.1 | 6111 | 14770 | 6305.0 | 574259 | 1093979 | 269.2 | 24519 | 51281 |
| E1 5 | 107.7 | 14092 | 28861 | 6468.0 | 846286 | 1940265 | 327.3 | 42825 | 94105 |
| E1 6 | 94.9 | 15613 | 44474 | 6419.0 | 1055938 | 2996203 | 275.1 | 45255 | 139360 |
| E1 7 | 171.5 | 34971 | 79445 | 6340.0 | 1292789 | 4288992 | 219.9 | 44840 | 184200 |
| E1 8 | 89.8 | 20775 | 100219 | 7034.0 | 1627260 | 5916252 | 232.0 | 53671 | 237871 |
| E1 9 | 104.1 | 25911 | 126130 | 7190.0 | 1789620 | 7705872 | 205.7 | 51200 | 289070 |
| E1 10 | 66.8 | 16993 | 143123 | 6924.0 | 1760344 | 9466216 | 335.8 | 85373 | 374444 |
| E1 11 | 75.1 | 19155 | 162279 | 6975.0 | 1780257 | 11246473 | 273.5 | 69806 | 444250 |
| E1 12 | 75.6 | 19402 | 181681 | 6552.0 | 1681728 | 12928201 | 255.3 | 65529 | 509779 |

Table A3.3.2 Time of sampling, runoff flowrate, accumulated (acc) volume, parameters (conductivity, DO, pH and temperature), concentration of PAHs (ng/L) (with recovery) and heavy metals ($\mu$g/L) P (particulate-bound) and D (dissolved), mass and accumulated mass of PAHS (ng) and heavy metals ($\mu$g) for rainfall Event 2 on the 7/2/2001.

| Name | Actual Time | Time (min) | Runoff (L/s) | Acc Vol (L) | Conductivity (mS/cm | DO (mg/L) | pH | Temp (°C |
|---|---|---|---|---|---|---|---|---|
| E2 1 | 16:56 - 17:00 | 4.00 | 0.036 | 20.42 | 0.2 | 4.28 | 7.28 | 18.6 |
| E2 2 | 17:02 - 17:06 | 10.00 | 0.020 | 28.31 | 0.2 | 5.64 | 7.36 | 19.2 |
| E2 3 | 17:08 - 17:12 | 16.00 | 0.0096 | 31.99 | 0.2 | 6.30 | 7.40 | 19.3 |
| E2 4 | 17:14 - 17:18 | 22 00 | 0.011 | 35.66 | 0.2 | 6.54 | 7.40 | 19.4 |
| E2 5 | 17:20 - 17:24 | 28.00 | 0.034 | 46.94 | 0.2 | 6.16 | 7.40 | 19.5 |
| E2 6 | 17:26 - 17:30 | 34.00 | 0.080 | 74.30 | 0.2 | 7.22 | 7.40 | 19.7 |
| E2 7 | 17:35 - 17:45 | 44.00 | 0.069 | 144.05 | 0.1 | 8.48 | 7.50 | 20.0 |
| E2 8 | 17:50 - 18:00 | 59.00 | 0.013 | 159.26 | 0.1 | 8.93 | 7 50 | 19.9 |
| E2 9 | 18:05 - 18:15 | 74.00 | 0.0049 | 164.48 | 0.1 | 8.55 | 7.40 | 19.8 |
| E2 10 | 18:20 - 18:30 | 89.00 | 0.0013 | 165.87 | 0.1 | 8.28 | 7.40 | 19.8 |
| E2 11 | 18:35 - 18:45 | 104.00 | 0.0012 | 166.87 | 0.1 | 8.12 | 7.38 | 19.7 |
| E2 12 | 18:50 - 19:00 | 119.00 | 0.015 | 178.03 | 0.1 | 8.43 | 7.40 | 19.7 |

| Name | Conc Phen | Mass Phen | Acc Mass Phen | Conc Fl | Mass Flu | Acc Mass Flu | Conc Pyren | Mass Pyrene | Acc Mass Pyrene | Recovery (% |
|---|---|---|---|---|---|---|---|---|---|---|
| E2 1 | 11.4 | 233 | 233 | 20. | 412 | 412 | 49. | 1002 | 1002 | 112. |
| E2 2 | 26.1 | 740 | 973 | 48. | 1370 | 1782 | 109. | 3107 | 4108 | 107. |
| E2 3 | 31.8 | 1017 | 1990 | 46. | 1499 | 3281 | 115. | 3678 | 7786 | 36. |
| E2 4 | 30.8 | 1099 | 3089 | 59. | 2109 | 5390 | 141. | 5041 | 12827 | 85. |
| E2 5 | 46.4 | 2179 | 5268 | 77. | 3656 | 9046 | 179. | 8419 | 21246 | 77. |
| E2 6 | 57.1 | 4240 | 9508 | 101. | 7523 | 16570 | 222. | 16551 | 37797 | 91 |
| E2 7 | 58.0 | 8349 | 17857 | 110. | 15923 | 32492 | 256. | 37007 | 74804 | 78. |
| E2 8 | 70.7 | 11254 | 29111 | 111. | 17802 | 50295 | 255. | 40636 | 115440 | 139. |
| E2 9 | 77.2 | 12694 | 41805 | 117. | 19237 | 69531 | 252. | 41588 | 157028 | 105. |
| E2 10 | 57.1 | 9478 | 51283 | 111. | 18552 | 88084 | 244. | 40504 | 197532 | 120. |
| E2 11 | 49.8 | 8303 | 59586 | 98. | 16407 | 104491 | 203. | 33898 | 231430 | 111. |
| E2 12 | 40.8 | 7261 | 66847 | 78. | 13945 | 118436 | 188. | 33530 | 264960 | 75. |

| Name | D Zn | Mass D Zn | Acc Mass D Zn | P F | Mass P Fe | Acc Mass P F | P Zn | Mass P Zn | Acc Mass P Zn | D F | Mass D Fe | Acc Mass D F |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 1 | 25.6 | 523 | 523 | 1334. | 27264 | 2726 | 65.9 | 1345 | 1345 | 136. | 2785 | 278 |
| E2 2 | 28.5 | 807 | 1330 | 1590. | 45037 | 7230 | 78.8 | 2230 | 3575 | 114. | 3250 | 603 |
| E2 3 | 29.8 | 953 | 2283 | 1658. | 53057 | 12535 | 86.0 | 2751 | 6326 | 102. | 3284 | 931 |
| E2 4 | 26.7 | 952 | 3235 | 1857. | 66255 | 19161 | 77.1 | 2750 | 9076 | 101. | 3604 | 1292 |
| E2 5 | 79.3 | 3723 | 6959 | 2105. | 98823 | 29043 | 81.1 | 3807 | 12883 | 80. | 3753 | 1667 |
| E2 6 | 50.6 | 3763 | 10722 | 2415. | 179450 | 46988 | 148.2 | 11013 | 23896 | 59 | 4411 | 2108 |
| E2 7 | 127.0 | 18288 | 29010 | 3050. | 439460 | 90934 | 154.3 | 22227 | 46123 | 28. | 4118 | 2520 |
| E2 8 | 85.8 | 13672 | 42682 | 2948. | 469581 | 137892 | 160.6 | 25583 | 71706 | 27 | 4377 | 2958 |
| E2 9 | 87.3 | 14361 | 57043 | 2948. | 485001 | 186392 | 153.9 | 25313 | 97019 | 12. | 2106 | 3168 |
| E2 10 | 80.9 | 13417 | 70461 | 2742. | 454819 | 231874 | 121.6 | 20165 | 117184 | 22 | 3709 | 3539 |
| E2 11 | 81.9 | 13663 | 84124 | 2556. | 426573 | 274531 | 131.8 | 21999 | 139183 | 13. | 2276 | 3767 |
| E2 12 | 75.7 | 13470 | 97593 | 2637. | 469618 | 321493 | 120.1 | 21377 | 160560 | 12 | 2212 | 3988 |

**Table A3.3.3 Time of sampling, runoff flowrate, accumulated (acc) volume, parameters (conductivity, DO, pH and temperature), concentration of PAHs (ng/L) (with recovery) and heavy metals ($\mu$g/L) P (particulate-bound) and D (dissolved), mass and accumulated mass of PAHS (ng) and heavy metals ($\mu$g) for rainfall Event 3 on the 11/2/2001.**

| Name | Actual Time | Time (min) | Runoff (L/s | Acc Vol (L) | Conductivity (mS/cm | DO (mg/L) | pH | Temp (°C |
|---|---|---|---|---|---|---|---|---|
| E3 1 | 8:58 - 9:02 | 4.00 | 0.6 | 254.12 | 0.1 | 6.48 | 7.22 | 21.7 |
| E3 2 | 9:04 - 9:08 | 10.00 | 0.7 | 514.86 | 0.0 | 8.04 | 7.44 | 22.5 |
| E3 3 | 9:10 - 9:14 | 16.00 | 0.6 | 766.18 | 0.0 | 8.10 | 7.50 | 22.6 |
| E3 4 | 9:16 - 9:20 | 22.00 | 0.5 | 949.34 | 0.0 | 8.08 | 7.50 | 22.7 |
| E3 5 | 9:22 - 9:26 | 28.00 | 0.3 | 1078.23 | 0.0 | 7.98 | 7.50 | 22.7 |
| E3 6 | 9:28 - 9:32 | 34.00 | 0.3 | 1190.41 | 0.0 | 7.92 | 7.50 | 22.8 |
| E3 7 | 9:37 - 9:47 | 44.00 | 0.3 | 1481.76 | 0.0 | 7.89 | 7.54 | 23.0 |
| E3 8 | 9:52 -10:02 | 59.00 | 0.3 | 1800.43 | 0.0 | 7.80 | 7.60 | 23.2 |
| E3 9 | 10:07 - 10:17 | 74.00 | 0.6 | 2402.84 | 0.0 | 7.91 | 7.58 | 23.2 |
| E3 10 | 10:22 - 10:32 | 89.00 | 0.3 | 2772.98 | 0.0 | 7.76 | 7.50 | 23.4 |
| E3 11 | 10:37 - 10:47 | 104.00 | 0.1 | 2951.51 | 0.0 | 7.64 | 7.52 | 23.3 |
| E3 12 | 10:52 - 11:02 | 119.00 | 0.1 | 3060.37 | 0.0 | 7.50 | 7.50 | 23.3 |

| Name | Conc Phen | Mass Phen | Acc Mass Phen | Conc Fl | Mass Flu | Acc Mass Flu | Conc Pyren | Mass Pyrene | Acc Mass Pyren | Recovery (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| E3 1 | 38.7 | 9828 | 9828 | 69. | 17726 | 17726 | 143. | 36479 | 3647 | 100.2 |
| E3 2 | 45.9 | 23656 | 33484 | 63 | 32468 | 50195 | 129. | 66725 | 10320 | 135.7 |
| E3 3 | 33.3 | 25477 | 58962 | 45. | 34766 | 84960 | 105. | 80549 | 18375 | 122.7 |
| E3 4 | 20.0 | 18972 | 77934 | 31. | 29753 | 114713 | 53. | 50682 | 23443 | 98.1 |
| E3 5 | 12.1 | 13076 | 91010 | 23. | 25169 | 139882 | 39 | 42752 | 27718 | 137.9 |
| E3 6 | 15.3 | 18265 | 109275 | 17. | 21076 | 160958 | 31. | 36985 | 31417 | 150.4 |
| E3 7 | 10.2 | 15101 | 124376 | 31. | 47155 | 208113 | 78. | 116825 | 43099 | 121.0 |
| E3 8 | 14.8 | 26650 | 151026 | 20. | 36654 | 244766 | 41. | 74833 | 50582 | 160.7 |
| E3 9 | 17.8 | 42756 | 193782 | 32. | 77778 | 322545 | 62. | 150209 | 65603 | 146.8 |
| E3 10 | 14.3 | 39656 | 233438 | 23. | 63987 | 386532 | 54. | 150158 | 80619 | 87.2 |
| E3 11 | 6.2 | 18269 | 251707 | 13. | 38359 | 424891 | 28. | 84392 | 89058 | 144.1 |
| E3 12 | 7.4 | 22608 | 274315 | 12. | 39445 | 464336 | 26. | 79844 | 97043 | 159.6 |

| Name | D Zn | Mass D Z | Acc Mass D Zn | P Fe | Mass P F | Acc Mass P Fe |
|---|---|---|---|---|---|---|
| E3 1 | 94.8 | 2409 | 24093 | 2864.1 | 72783 | 727834 |
| E3 2 | 79.5 | 4095 | 65048 | 1702.1 | 87632 | 1604161 |
| E3 3 | 68.5 | 5249 | 117541 | 1612.3 | 123532 | 2839488 |
| E3 4 | 25.4 | 2413 | 141674 | 1126.1 | 106908 | 3908571 |
| E3 5 | 38.3 | 4130 | 182977 | 857.4 | 92452 | 4833093 |
| E3 6 | 19.2 | 2290 | 205885 | 783.2 | 93234 | 5765438 |
| E3 7 | 41.3 | 6112 | 267011 | 922.2 | 136641 | 7131850 |
| E3 8 | 39.8 | 7166 | 338679 | 1275.2 | 229584 | 9427693 |
| E3 9 | 25.3 | 6071 | 399389 | 1583.2 | 380413 | 13231831 |
| E3 10 | 21.7 | 6025 | 459646 | 1261.9 | 349909 | 16730930 |
| E3 11 | 32.7 | 9655 | 556204 | 1049.2 | 309671 | 19827644 |
| E3 12 | 42.6 | 13028 | 686492 | 764.0 | 233804 | 22165694 |

**Table A3.3.4 Time of sampling, runoff flowrate, accumulated (acc) volume, parameters (conductivity, DO, pH and temperature), concentration of PAHs (ng/L) (with recovery) and heavy metals ($\mu$g/L) P (particulate-bound) and D (dissolved), mass and accumulated mass of PAHS (ng) and heavy metals ($\mu$g) for rainfall Event 4 on the 17/2/2001.**

| Name | Actual Time | Time (min | Runoff (L/s) | Acc Vol (L) | Conductivity (mS/cm) | DO (mg/L | pH | Temp (°C) |
|---|---|---|---|---|---|---|---|---|
| E4 1 | 7:46 - 7:50 | 4.0 | 0.18 | 112.36 | 0.16 | 5.0 | 7.20 | 21.90 |
| E4 2 | 7:52 - 7:56 | 10.0 | 0.22 | 189.94 | 0.10 | 6.9 | 7.20 | 21.96 |
| E4 3 | 7:58 - 8:02 | 16.0 | 0.21 | 267.60 | 0.07 | 7.3 | 7.26 | 21.90 |
| E4 4 | 8:04 - 8:08 | 22.0 | 0.19 | 336.95 | 0.06 | 7.4 | 7.20 | 21.90 |
| E4 5 | 8:10 - 8:14 | 28.0 | 0.17 | 398.92 | 0.05 | 7.3 | 7.20 | 21.90 |
| E4 6 | 8:16 - 8:20 | 34.0 | 0.13 | 446.78 | 0.05 | 6.9 | 7.20 | 21.94 |
| E4 7 | 8:25 - 8:35 | 44.0 | 0.23 | 645.70 | 0.05 | 7.3 | 7.20 | 22.00 |
| E4 8 | 8:40 - 8:50 | 59.0 | 0.19 | 823.51 | 0.04 | 7.4 | 7.20 | 22.00 |
| E4 9 | 8:55 - 9:05 | 74.0 | 0.24 | 1033.81 | 0.04 | 7.4 | 7.20 | 22.00 |
| E4 10 | 9:10 - 9:20 | 89.0 | 0.18 | 1216.29 | 0.04 | 7.4 | 7.19 | 22.10 |
| E4 11 | 9:25 - 9:35 | 104.0 | 0.23 | 1414.69 | 0.04 | 7.3 | 7.15 | 22.12 |
| E4 12 | 9:40 - 9:50 | 119.0 | 0.23 | 1621.76 | 0.03 | 7.3 | 7.20 | 22.41 |

| Name | Conc Phen | Mass Phen | Acc Mass Phen | Conc Fl | Mass Flu | Acc Mass Fl | Conc Pyrene | Mass Pyren | Acc Mass Pyrene | Recovery (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| E4 1 | 37.1 | 4164 | 4164 | 56. | 6340 | 634 | 128.8 | 1447 | 14474 | 140.8 |
| E4 2 | 41.9 | 7953 | 12117 | 78. | 14918 | 2125 | 172.9 | 3283 | 47310 | 107 7 |
| E4 3 | 64.8 | 17352 | 29469 | 102. | 27385 | 4864 | 222.5 | 5955 | 106861 | 160.0 |
| E4 4 | 52 2 | 17577 | 47046 | 72. | 24273 | 7291 | 171.1 | 5764 | 164510 | 145.1 |
| E4 5 | 33.3 | 13285 | 60331 | 41. | 16574 | 8948 | 116.9 | 4661 | 211127 | 123.6 |
| E4 6 | 18.9 | 8439 | 68770 | 30 | 13627 | 10311 | 69.9 | 3124 | 242367 | 123.8 |
| E4 7 | 32.2 | 20824 | 89594 | 38. | 25136 | 12825 | 101.8 | 6571 | 308082 | 153.0 |
| E4 8 | 33.0 | 27149 | 116743 | 48. | 39601 | 16785 | 107.6 | 8861 | 396700 | 142.3 |
| E4 9 | 43.7 | 45194 | 161937 | 60. | 62658 | 23051 | 156.4 | 16167 | 558377 | 150.7 |
| E4 10 | 37.8 | 46004 | 207941 | 54. | 66588 | 29710 | 133.6 | 16253 | 720912 | 149.4 |
| E4 11 | 24.6 | 34759 | 242700 | 41. | 58031 | 35513 | 99.7 | 14098 | 861893 | 127.1 |
| E4 12 | 23.2 | 37631 | 280331 | 55. | 90120 | 44525 | 121.3 | 19673 | 1058626 | 246.6 |

| Name | P Fe | Mass P F | Acc Mass P Fe |
|---|---|---|---|
| E4 1 | 2748.0 | 30875 | 308758 |
| E4 2 | 3580.1 | 68000 | 988768 |
| E4 3 | 3584.6 | 95923 | 1947999 |
| E4 4 | 3222.5 | 108584 | 3033843 |
| E4 5 | 2607.3 | 104008 | 4073932 |
| E4 6 | 2161.6 | 96578 | 5039715 |
| E4 7 | 2541.3 | 164090 | 6680615 |
| E4 8 | 2774 0 | 228444 | 8965059 |
| E4 9 | 3267.2 | 327768 | 12342742 |
| E4 10 | 3167.5 | 385255 | 16195293 |
| E4 11 | 2757.2 | 390062 | 20095922 |
| E4 12 | 2802.5 | 454490 | 24640825 |

**Table A3.3.5 Time of sampling, runoff flowrate, accumulated (acc) volume, parameters (conductivity, DO, pH and temperature), concentration of PAHs (ng/L) (with recovery) and heavy metals ($\mu$g/L) P (particulate-bound) and D (dissolved), mass and accumulated mass of PAHS (ng) and heavy metals ($\mu$g) for rainfall Event 5 on the 9/3/2001.**

| Name | Actual Time | Time (min) | Runoff (L/s) | Acc Vol (L) | Conductivity (mS/cm) | DO (mg/L) | pH | Temp (°C |
|---|---|---|---|---|---|---|---|---|
| E5 1 | 23:58 - 00:02 | 4.00 | 0.27 | 98.48 | 0.23 | 5.32 | 7.26 | 20.8 |
| E5 2 | 00:04 - 00:08 | 10.00 | 0.19 | 167.94 | 0.16 | 7.90 | 7.56 | 21.0 |
| E5 3 | 00:10 - 00:14 | 16.00 | 0.16 | 229.47 | 0.13 | 7.72 | 7.68 | 20.9 |
| E5 4 | 00:16 - 00:20 | 22.00 | 0.091 | 264.20 | 0.11 | 7.28 | 7.70 | 20.9 |
| E5 5 | 00:22 - 00:26 | 28.00 | 0.047 | 282.07 | 0.11 | 7.70 | 7.70 | 20.9 |
| E5 6 | 00:28 - 00:32 | 34.00 | 0.029 | 292.82 | 0.11 | 7.64 | 7.70 | 21.0 |
| E5 7 | 00:37 - 00:47 | 44.00 | 0.016 | 308.35 | 0.12 | 7.60 | 7.63 | 21.0 |
| E5 8 | 00:52 - 01:02 | 59.00 | 0.13 | 404.59 | 0.12 | 7.39 | 7.62 | 20.9 |
| E5 9 | 01:07 - 01:17 | 74.00 | 0.35 | 683.75 | 0.07 | 7.82 | 7.70 | 20.6 |
| E5 10 | 01:22 - 01:32 | 89.00 | 0.71 | 1373.60 | 0.03 | 7.92 | 7.70 | 20.3 |
| E5 11 | 01:37 - 01:47 | 104.00 | 0.14 | 1540.45 | 0.04 | 7.83 | 7.60 | 20.4 |
| E5 12 | 01:52 - 02:02 | 119.00 | 0.30 | 1792.40 | 0.04 | 7.99 | 7.60 | 20.3 |

| Name | Conc Phen | Mass Phen | Acc Mass Phen | Conc Flu | Mass Flu | Acc Mass Fl | Conc Pyrene | Mass Pyren | Acc Mass Pyrene | Recovery (% |
|---|---|---|---|---|---|---|---|---|---|---|
| E5 1 | 262.7 | 25873 | 25873 | 175.7 | 17303 | 1730 | 304.7 | 3000 | 30009 | 184. |
| E5 2 | 70.0 | 11750 | 37623 | 65.1 | 10928 | 2823 | 112.6 | 1890 | 48911 | 100. |
| E5 3 | 9.6 | 2200 | 39823 | 74.1 | 17010 | 4524 | 114.9 | 2636 | 75277 | 102. |
| E5 4 | 104.4 | 27579 | 67402 | 49.3 | 13029 | 5827 | 96.1 | 2538 | 100664 | 65. |
| E5 5 | 56.1 | 15812 | 83214 | 49.9 | 14081 | 7235 | 62.0 | 1747 | 118141 | 75. |
| E5 6 | 45.4 | 13291 | 96506 | 34.1 | 9981 | 8233 | 47.0 | 1376 | 131903 | 44. |
| E5 7 | 56.9 | 17547 | 114052 | 48.8 | 15039 | 9737 | 52.4 | 1614 | 148049 | 72. |
| E5 8 | 40.3 | 16290 | 130343 | 30.3 | 12255 | 10962 | 48.4 | 1956 | 167615 | 53. |
| E5 9 | 46.1 | 31524 | 161866 | 41.5 | 28354 | 13797 | 63.2 | 4323 | 210853 | 42. |
| E5 10 | 56.1 | 77084 | 238951 | 31.7 | 43495 | 18147 | 54.3 | 7459 | 285445 | 102. |
| E5 11 | 13.1 | 20116 | 259066 | 8.4 | 12891 | 19436 | 13.1 | 2015 | 305604 | 48. |
| E5 12 | 20.8 | 37332 | 296398 | 14.2 | 25471 | 21983 | 14.0 | 2505 | 330653 | 51. |

| Name | D Ni | Mass Ni | Acc Mass Ni | D Zn | Mass Z | Acc Mass Zn | P Fe | Mass P Fe | Acc Mass P F | P Ni | Mass P Ni | Acc Mass P Ni | P Zn | Mass P Zn | Acc Mass Z |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| E5 1 | 297.5 | 29304 | 29304 | 37.7 | 371 | 3714 | 11482 | 1130742 | 113074 | 872.6 | 85935 | 85935 | 378.9 | 37315.5 | 37315. |
| E5 2 | 225.7 | 37900 | 67204 | 53 | 889 | 12614 | 4071.7 | 683805 | 181454 | 759.2 | 127508 | 213443 | 136.4 | 22913.3 | 60228. |
| E5 3 | 167.7 | 38475 | 105678 | 63.2 | 1450 | 27122 | 2988.9 | 685855 | 250040 | 599.8 | 137630 | 351073 | 88.75 | 20364.4 | 80593. |
| E5 4 | 211.7 | 55937 | 161616 | 45.8 | 1209 | 39221 | 2474.2 | 653679 | 315408 | 583.8 | 154235 | 505307 | 70.84 | 18716.3 | 99309. |
| E5 5 | 173.8 | 49029 | 210644 | 51.4 | 1448 | 53709 | 2012.8 | 567756 | 372183 | 519.3 | 146481 | 651788 | 58.96 | 16630.0 | 115939. |
| E5 6 | 186.7 | 54656 | 265301 | 42.8 | 1254 | 66251 | 1958.7 | 573544 | 429538 | 465.5 | 136313 | 788100 | 59.41 | 17397.2 | 133336. |
| E5 7 | 202.5 | 62450 | 327750 | 35.7 | 1101 | 77266 | 1895.2 | 584388 | 487976 | 506.7 | 156239 | 944339 | 46.88 | 14455.4 | 147792. |
| E5 8 | 213.6 | 86417 | 414167 | 25.7 | 1041 | 87676 | 1819 | 735934 | 561570 | 449.8 | 181966 | 1126305 | 50.11 | 20275.7 | 168067. |
| E5 9 | 139.8 | 95567 | 509734 | 26.1 | 1786 | 105543 | 3285.2 | 2246273 | 786197 | 587.7 | 401871 | 1528176 | 93.82 | 64150.4 | 232218. |
| E5 10 | 78.3 | 107537 | 617271 | 18.1 | 2490 | 130448 | 2517.2 | 3457622 | 1131959 | 587.7 | 807222 | 2335399 | 82.86 | 113817.4 | 346035. |
| E5 11 | 86.4 | 133035 | 750306 | 15.5 | 2386 | 154313 | 692.21 | 1066312 | 1238590 | 236.6 | 364524 | 2699922 | 14.01 | 21587.6 | 367623. |
| E5 12 | 169.8 | 304345 | 1054651 | 5.86 | 1050 | 164815 | 550.48 | 986690 | 1337259 | 184.9 | 331499 | 3031421 | 26.93 | 48264.4 | 415887. |

**Table A3.3.6 Time of sampling, runoff flowrate, accumulated (acc) volume, parameters (conductivity, DO, pH and temperature), concentration of PAHs (ng/L) (with recovery) and heavy metals ($\mu$g/L) P (particulate-bound) and D (dissolved), mass and accumulated mass of PAHS (ng) and heavy metals ($\mu$g) for rainfall Event 6 on the 28/3/2001.**

| Name | Actual Time | Time (min) | Runoff (L/s | Acc Vol (L) | Conductivity (mS/cm) | DO (mg/L) | pH | Temp (°C) |
|---|---|---|---|---|---|---|---|---|
| E6 1 | 12:59 - 13:03 | 4.00 | 0.06 | 67.05 | 0.13 | 5.70 | 7.70 | 21.18 |
| E6 2 | 13:05 - 13:09 | 10.00 | 0.06 | 90.68 | 0.12 | 4.22 | 7.80 | 21.46 |
| E6 3 | 13:11 - 13:15 | 16.00 | 0.04 | 108.19 | 0.12 | 5.04 | 7.80 | 21.56 |
| E6 4 | 13:17 - 13:21 | 22.00 | 0.03 | 121.19 | 0.12 | 3.74 | 7.80 | 21.60 |
| E6 5 | 13:23 - 13:27 | 28.00 | 0.04 | 135.52 | 0.12 | 5.06 | 7.80 | 21.60 |
| E6 6 | 13:29 - 13:33 | 34.00 | 0.07 | 159.91 | 0.12 | 5.32 | 7.70 | 21.68 |
| E6 7 | 13:38 - 13:48 | 44.00 | 0.1 | 270.49 | 0.11 | 6.13 | 7.76 | 21.76 |
| E6 8 | 13:53 - 14:03 | 59.00 | 0.1 | 389.62 | 0.10 | 6.51 | 7.80 | 22.05 |
| E6 9 | 14:08 - 14:18 | 74.00 | 0.1 | 518.94 | 0.10 | 5.83 | 7.72 | 22.13 |
| E6 10 | 14:23 - 14:33 | 89.00 | 0.2 | 726.10 | 0.08 | 6.19 | 7.70 | 22.07 |
| E6 11 | 14:38 - 14:48 | 104.00 | 0.2 | 946.00 | 0.07 | 7.26 | 7.70 | 22.00 |
| E6 12 | 14:53 - 15:03 | 119.00 | 0.1 | 1088.19 | 0.08 | 5.97 | 7.70 | 22.00 |

| Name | Conc Phen | Mass Phen | Acc Mass Phen | Conc Fl | Mass Flu | Acc Mass Flu | Conc Pyren | Mass Pyrene | Acc Mass Pyrene | Recovery[§] (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| E6 1 | 47.3 | 3168 | 3168 | 37. | 2482 | 2482 | 76. | 5103 | 5103 | 45.6 |
| E6 2 | 41.2 | 3739 | 6907 | 33. | 3044 | 5525 | 70 | 6351 | 11454 | 33.2 |
| E6 3 | 47.1 | 5092 | 12000 | 30. | 3283 | 8808 | 46. | 5058 | 16513 | 43.6 |
| E6 4 | 39.1 | 4738 | 16737 | 27. | 3316 | 12124 | 54. | 6557 | 23069 | 38.0 |
| E6 5 | 33.9 | 4589 | 21326 | 22. | 3099 | 15223 | 41. | 5612 | 28681 | 44.1 |
| E6 6 | 37.8 | 6042 | 27368 | 32. | 5201 | 20424 | 40. | 6536 | 35217 | 38.6 |
| E6 7 | 46.8 | 12650 | 40018 | 44. | 12036 | 32460 | 74. | 20068 | 55286 | 29.0 |
| E6 8 | 45.4 | 17672 | 57691 | 33. | 12894 | 45354 | 57 | 22492 | 77778 | 39.1 |
| E6 9 | 34.4 | 17862 | 75553 | 14. | 7359 | 52713 | 43. | 22390 | 100168 | 29.2 |
| E6 10 | 40.0 | 29013 | 104566 | 35. | 26039 | 78752 | 73. | 53145 | 153313 | 35.2 |
| E6 11 | 38.0 | 35973 | 140540 | 18. | 17447 | 96199 | 42. | 39798 | 193111 | 41.4 |
| E6 12 | 17.9 | 19454 | 159994 | 15. | 16725 | 112924 | 33. | 36190 | 229301 | 27.2 |

[§] Recoveries are not considered to be reliable due to a probable inadvertent volumetric error in addition of standard solutions.

| Name | D Nl | Mass D Nl | Acc Mass N | D Zn | Mass D Zn | Acc Mass D Zn | P F | Mass P Fe | Acc Mass F | P Nl | Mass P Nl | Acc Mass N | P Zn | Mass P Zn | Acc Mass Z | D Fe | Mass D Fe | Acc Mass D Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| E6 1 | 220.2 | 14765 | 1476 | 97.3 | 6527 | 6527 | 3997. | 268025 | 26802 | 870.3 | 58351 | 5835 | 143.9 | 9648 | 964 | 108.4 | 7269 | 7269 |
| E6 2 | 210.1 | 19049 | 3381 | 85.8 | 7782 | 14309 | 3669. | 332728 | 60075 | 783.9 | 71083 | 12943 | 124.9 | 11326 | 2097 | 117.7 | 10671 | 17940 |
| E6 3 | 203.0 | 21967 | 5578 | 96.3 | 10421 | 24730 | 2792. | 302136 | 90288 | 694.4 | 75124 | 20455 | 94.2 | 10191 | 3116 | 98.7 | 10677 | 28617 |
| E6 4 | 202.7 | 24559 | 8034 | 91.6 | 11096 | 35826 | 2211. | 268034 | 117092 | 544.2 | 65956 | 27051 | 69.7 | 8449 | 3961 | 111.2 | 13472 | 42089 |
| E6 5 | 195.2 | 26450 | 10679 | 88.7 | 12018 | 47843 | 1870. | 253431 | 142435 | 487.4 | 66056 | 33657 | 64.5 | 8738 | 4835 | 90.1 | 12217 | 54306 |
| E6 6 | 208.3 | 33313 | 14010 | 87.0 | 13912 | 61755 | 2255. | 360707 | 178506 | 547.4 | 87530 | 42409 | 77.9 | 12452 | 6080 | 125.3 | 20038 | 74344 |
| E6 7 | 183.4 | 49615 | 18971 | 100.9 | 27286 | 89042 | 4130. | 1117115 | 290217 | 828.0 | 223975 | 64807 | 158.6 | 42897 | 10370 | 100.1 | 27087 | 101431 |
| E6 8 | 180.4 | 70302 | 26002 | 83.4 | 32504 | 121546 | 2832. | 1103552 | 400572 | 629.1 | 245115 | 89318 | 91.0 | 35461 | 13916 | 104.8 | 40850 | 142281 |
| E6 9 | 161.1 | 33608 | 34362 | 68.1 | 35321 | 156867 | 1971. | 1022889 | 502861 | 475.1 | 246542 | 113973 | 62.2 | 32300 | 17146 | 81.5 | 42293 | 184574 |
| E6 10 | 136.2 | 98930 | 44255 | 61.5 | 44675 | 201542 | 2926. | 2125196 | 715381 | 615.3 | 446742 | 158647 | 95.4 | 69235 | 24069 | 62.1 | 45093 | 229666 |
| E6 11 | 130.3 | 123251 | 56581 | 51.0 | 48250 | 249792 | 1839. | 1739994 | 889380 | 452.7 | 428244 | 201471 | 63.0 | 59641 | 30033 | 52.8 | 49969 | 279636 |
| E6 12 | 117.9 | 128255 | 69406 | 44.2 | 48143 | 297935 | 1076. | 1171438 | 1006524 | 307.0 | 334042 | 234875 | 52.0 | 56615 | 35695 | 30.0 | 32608 | 312244 |

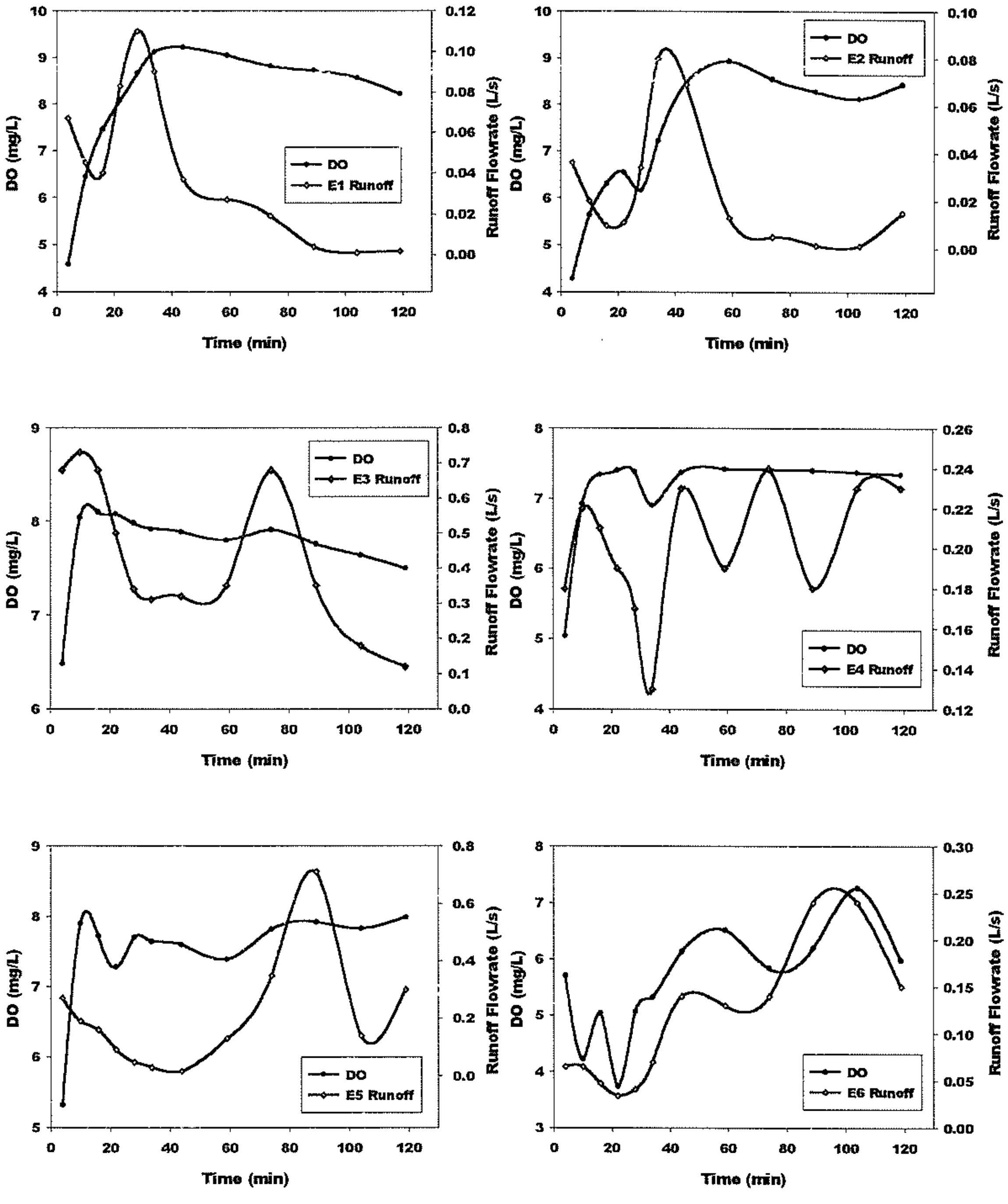

**Figure A3.1.1 Patterns of DO concentrations (mg/L) compared with the runoff flowrates (L/s) during the 2-h sampling period for rainfall runoff E1 to E6.**

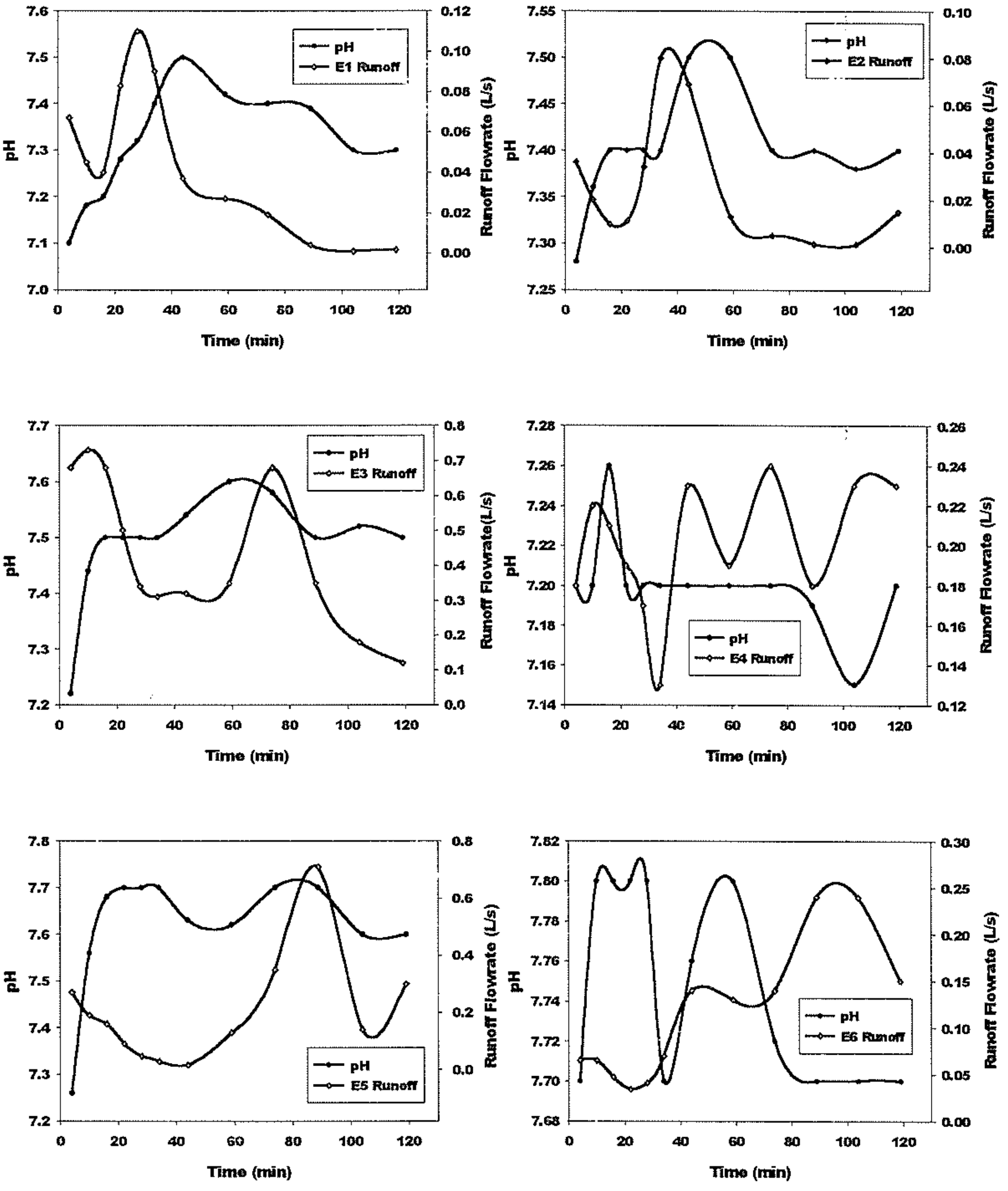

**Figure A3.1.2 Patterns of pH compared with the runoff flowrates (L/s) during the 2-h sampling period for rainfall runoff E1 to E6.**

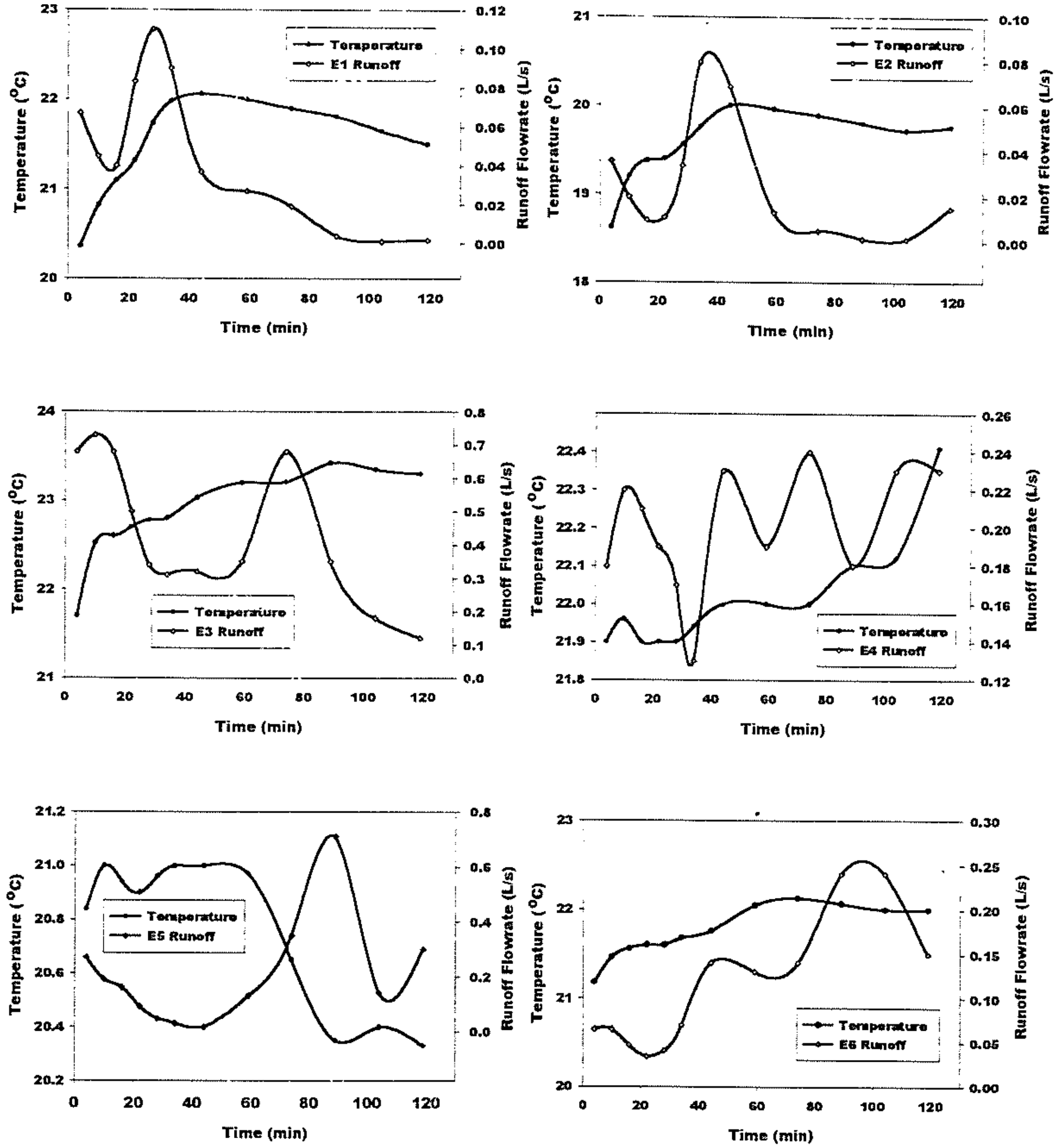

Figure A3.1.3 Patterns of Temperature (°C) compared with the runoff flowrates (L/s) during the 2-h sampling period for rainfall runoff E1 to E6.

## INSTRUCTIONS FOR TRANSFUND NEW ZEALAND RESEARCH REPORT NO. 228

Text: 120pp.
To be copied both sides, in usual way.
Cover page: single side

pp. 43, 68, 69, 70 have colour photos, which could go B/W depending on decisions. An extra set of pages with rather contrasty colour versions of photos from Chapters 2, 3, is provided. If the photos are to be reproduced in colour, maybe best to take from the disc.

If the decision is to use colour for these figures, can the same weight matt surfaced paper be used throughout, for consistency of colour, rather than an art paper.

Pages with photos:
43, 68, 69, 70
B/W pages with much paste up of labels: 36, 45

## FILES FOR ARCHIVING for RR228 (PR3-0422)

Following files:

| | |
|---|---|
| 228.cov | cover page |
| 228prelim.422 | preliminary pages 1-12 |
| roadrunoff.1 | Ch. 1 pp. 13-35 |
| matsmeths.2 | Ch. 2 pp.36-60 |
| methodsite.3 | Ch. 3 pp.61-71 |
| contprof.4 | Ch. 4 pp.72-84 |
| discsum.5 | Ch. 5 pp.85-90 |
| references.422 | Ch.6 references pp.91-98 |
| Appendix 1a.422 | pp.99-100 |
| Appendix 1b.422 | pp.101-104 |
| Appendix 2.422 | pp.105-106 |
| Appendix3.422 | pp.107-113 |
| Appendix DO.422 | |
| Appendix pH.422 | |
| Appendix Temp.422 | |

These have been condensed as Zip file RR228.422, and this is too large to put onto floppies.

Figure 3.3

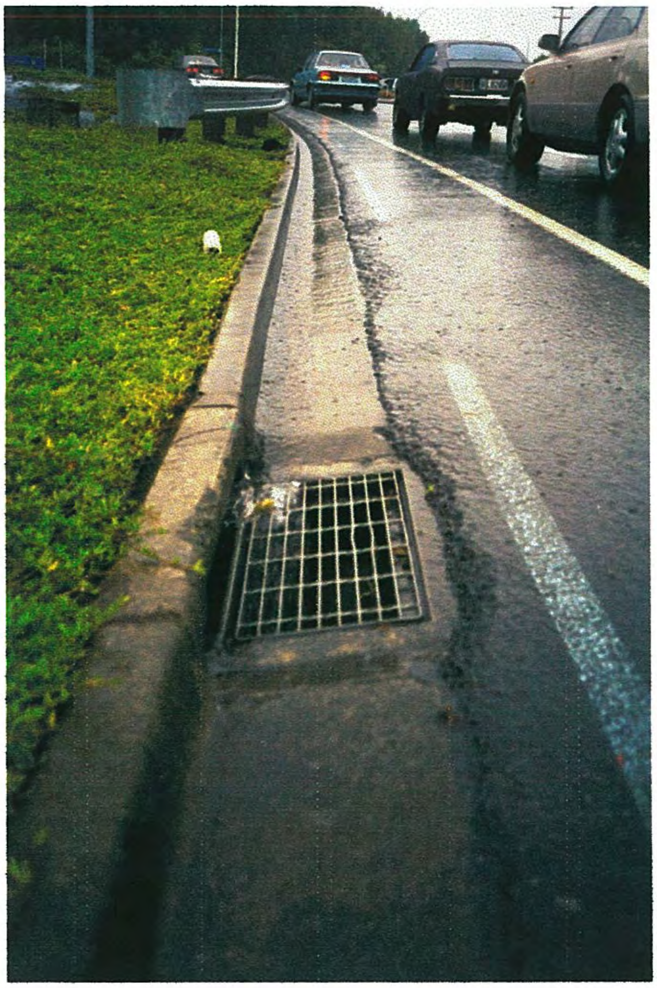

**Figure 3.4 The catchpit that received the roundabout runoff.**

$$\text{Concentration (target compound } \mu g/L) = \frac{(\text{Peak area of the target compound}) \times (\text{concentration of benzo(a)anthracene})}{(\text{Peak area of benzo(a)anthracene}) \times (R_F \text{ of target compound})}$$

All calculations were performed using purpose written Microsoft Excel™ spreadsheets.

Quantification results were accepted if the recovery of naphthalene was in the range 80–120%.

### 2.3.10 Sample Pre-treatment & Extraction

Sample pre-treatment can influence the recovery of organic species from water samples. For example, filtration before extraction can remove particle-bound organic species (pollutants) and lead to the recovery of only free (soluble) species. A detailed study of resin acid and resin neutral speciation in Tarawera River samples has shown that 0.45-$\mu$m filtration before extraction typically removes 60% of the resin compounds (Ali Kanber et al. 2000).

PAHs are likely to behave similarly to resin neutrals as they have similar chemical structures and properties. There is little literature on the distribution of PAHs over the different particle sizes found in road runoff. An investigation of this, while of interest, was beyond the scope of the present project.

The continuous liquid/liquid extraction method requires a purpose-built apparatus designed to achieve exhaustive extraction, because hundreds of droplets are produced per hour, each one being a mini-extraction. Experimental work has shown that many small volume extractions are more effective than a single large volume extraction such as the separating funnel method.

Liquid/liquid extraction initially recovers low solubility organics in the aqueous phase, and after a long extraction will recover high solubility organics in the aqueous phase. Therefore, it achieves a complete recovery of about 99.5% with longer extraction times. Typically, 4–8 h is required, but in the present study overnight extraction for 16–24 h ensured complete extraction.

Comparison with the separating funnel extraction method shows that although ideally, a single extraction would recover all (or at least >95–99%) of an organic species from an aqueous phase, this is not always the case. The recovery is dependent on the partitioning of the organic species from the aqueous phase, and the volume of both the extracting solvent and aqueous phase.

### 2.3.11 Methodology applied in Present Study

Water samples (c.900mL) were pre-filtered through a 400-$\mu$m mesh filter, and then liquid/liquid extracted for 16–24 h with redistilled dichloromethane (c.200mL). Naphthalene (typically 100$\mu$L of a 100.2mg/L solution in dichloromethane) was added to the water phase as a surrogate (recovery) standard immediately before the extraction began. After extraction, benzo(a)anthracene (typically 100$\mu$L of a

100.2mg/L solution in dichloromethane) was added to the dichloromethane extractive solution as primary (quantification) standard, and the extraction solvent was removed until a concentrated extract of 1mL remained using a rotary evaporator. Concentrated extract was transferred to a GC/MS vial, which was capped and stored at 4°C before GC/MS analysis. A schematic outline of the SIM GC/MS analytical protocol used to identify the levels of PAHs in the runoff samples is presented in Figure 2.7.

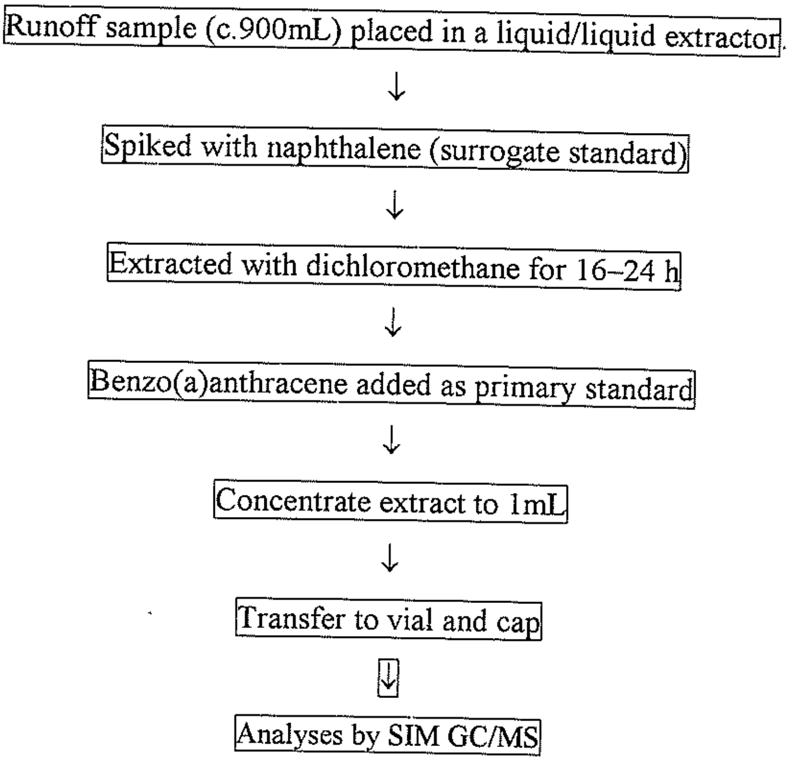

**Figure 2.7** **Flow diagram for the analysis of PAHs.**

### 2.3.12 Summary

Response curves for the PAH standards revealed that linear ranges varied from 0.5 to 20$\mu$g for injected PAHs. Regression coefficients for all target compounds were in the vicinity of 0.99. A reproducibility experiment found that instrument precision was excellent with the CV being less than 5% for all compounds. The recoverability of the organic compounds from the aqueous medium was shown to be within 80 and 120%. Sample results indicated reasonable precision for the extraction and analytical protocol with CV values in the vicinity of 20%.