# Copper, Zinc and Iron Contamination in Wellington Streams After Rainfall Events

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#### Abstract

This work set out to determine the concentrations of dissolved copper (Cu), zinc (Zn) and iron (Fe) during base and wet weather flow at streams throughout the Wellington region. The secondary objective was to investigate possible sources of heavy metals during rainfall events.

The concentrations of the three dissolved trace metals Cu, Zn and Fe were measured at 13 sites on five streams during base flow conditions and during runoff events (wet weather flow) in the Wellington region between January and July 2011. More than 240 base flow and 100 wet weather flow samples have been analysed for the three dissolved metals. Additionally, rainfall, roof runoff and paved surface runoff samples have been collected and analysed. The analysis was performed by Flame Atomic Absorption Spectroscopy (FAAS). A pre-concentration procedure using Chelex-100, a chelating polymeric resin bead, was developed and successfully used to enhance the concentrations of dissolved Cu and dissolved Zn. The recorded data were compared to the recommended long-term (chronic) toxicity triggers; the Australian and New Zealand Environment and Conservation Council freshwater toxicity trigger values (ANZECC (2000) TV) for dissolved Cu and Zn, and the Canadian trigger value (CTV) for dissolved Fe. Additionally, the concentrations of dissolved Cu and Zn in storm water samples were compared against the recommended short-term (acute) toxicity triggers, the United States Environmental Protection Agency (USEPA 2006) Criteria Maximum Concentrations (CMC).

The medians of dissolved heavy metals concentrations; Cu, Zn, and Fe, all of which are potentially toxic to aquatic life, exceeded the long-term (chronic) toxicity guidelines at one of the studied sites for Fe, nine sites (69%) for Cu and 10 sites (77%) for Zn in base flow conditions. Comparison of base flow monitoring data to previous reports showed that the concentrations of the studied metals have increased over the last five years.

Storm water (wet weather flow conditions) contained elevated levels of dissolved heavy metals in comparison to base flow concentrations which is consistent with what has been reported previously. Dissolved Cu and Zn exceeded the acute toxicity criteria at sites of suburban residential areas. The median of dissolved Fe concentration exceeded the sustained toxicity exposure trigger at eight of the studied sites (61%).

Distinct catchment type contaminant concentrations (dissolved Cu and Zn) were observed during storm runoff events with a concentration pattern of suburban residential > commercial > light residential > rural catchment. Dissolved Fe exhibited a similar pattern but in this case the concentration in rural catchments was higher than in light residential catchments. These observations were attributed to the high traffic of vehicles passing nearby the area; accumulated particulate materials; and corrosion of materials containing heavy metals, such as galvanised and copper roofs, gutter systems and building construction materials. The strongest and most obvious first flush effect was observed with dissolved Cu followed by Zn where the phenomenon was observed in six storm runoff events for Cu and five events for Zn. The first flush effect of dissolved Fe was present in three out of eight storm runoff events. The concentrations of dissolved metals were of the same order of magnitude as those previously reported for the Wellington region, but this work recorded the highest expected concentrations, particularly, for dissolved Fe. The reported data are consistent with data sets from other New Zealand regions.

The investigation of possible sources of dissolved heavy metals in storm runoff samples showed that rainfall water contained markedly elevated concentrations of dissolved Zn and smaller Cu concentrations, 0.04-0.075 and 0.0018-0.01 mg/L respectively, in comparison to the ANZECC (2000) TVs, 0.008 and 0.0014 mg/L respectively. The concentrations of dissolved Fe were below the CTV level of 0.3 mg/L. Most studies conducted in New Zealand did not take into account the atmospheric precipitation contribution to the elevated concentrations of dissolved metals during runoff events. Roof runoff samples had similar dissolved Cu and Fe concentration to those recorded in atmospheric rainfall water, but Zn was found to be higher in galvanised roof runoff. First flush samples from roof runoff had higher concentrations of all three metals than the delayed runoff samples, indicating the presence of accumulated particles containing metals. Paved surface runoff samples

had concentrations of dissolved Cu and Zn higher than the chronic toxicity triggers, but the medians did not exceed the acute toxicity guidelines. The value of the median for the concentrations of dissolved Fe was below the CTV criteria. Similar results have been published for surface runoff in New Zealand and the international literature related to this field.

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# Glossary

**ANZECC 2000 TV:** Australian and New Zealand Environment and Conservation Council freshwater toxicity trigger values.

**Base flow sample**: a single grab sample collected manually from the studied sites at weekly bases during dry days.

**Chelex-100**: polymeric beads consist of polystyrene cross-linked with divinylbenzene and functionalized with iminodiacetate groups as the chelating sites.

**CMC:** United States Environmental Protection Agency (USEPA 2006) Criteria Maximum Concentrations.

**Composite sample**: the mathematical mean of the concentrations of dissolved metals in the samples collected after the first flush time.

**CTV:** Canadian Trigger Value.

FAAS: Flame Atomic Absorption Spectroscopy.

**First flush sample**: A) in stream water context: the mathematical mean of the concentrations of dissolved metals in the samples collected in the first 25 minutes of the runoff. B) in roof context: a single sample collected at the very early stage of a roof runoff and usually associated with a delayed roof runoff sample.

**GWRC**: Greater Wellington Regional Council.

**ICPMS**: Inductively Coupled Plasma Mass Spectrometry.

**Mg/L**: milligram of the solute per litter of the solution.

SCPS: School of Chemical and Physical Sciences.

**Storm runoff sample**: a single grab sample collected manually at random times during the runoff, excluding the first flush time from the studied sites.

 $PM_{2.5}$  and  $PM_{10}$ : particulate matters with aerodynamic diameters less than 2.5 and 10  $\mu$ m respectively.

VUW: Victoria University of Wellington.

## Chapter 1

## **1** Introduction

#### 1.1 Water and Quality

Water is the most valuable and essential substance on the surface of the planet. There is a direct link between good water quality and health for all known forms of life. However, 'human activity' is responsible for water quality deterioration. In addition, runoff of rain water is well known to play a significant role in lowering water quality by introducing various contaminants to water bodies, including physical and chemical comprising organic and inorganic contaminants. The type and concentration of these contaminants will vary depending upon the environmental characteristics such as natural, pre-urban, urban and industrial areas [1-2].

Heavy metals are one of the most abundant and frequently detected contaminants in natural and storm water in recent years [3-4]. Living organisms require trace amounts of certain heavy metals known as trace metals such as Cu, Zn and Fe, to carry out bio-reactions including nerve and oxygen transportation in the organism. In contrast, if the recommended levels are exceeded, the same metals are considered toxic substances producing adverse effects for all living organisms [5].

Over the last decade, a small number of studies have investigated heavy metal contamination in storm water in New Zealand [6], and particularly in the Wellington region [7-8]. This work indicated that heavy metals, particularly dissolved Cu and Zn concentrations occurred at levels exceeding the recommended chronic and acute toxicity guidelines.

#### **1.2 Objectives and Research Questions**

The primary purpose of the present study was to determine the concentrations of dissolved heavy metal, specifically, Cu, Zn, and Fe in natural waters during base flow and wet-weather flow at various locations throughout the Wellington region. The secondary objective was to examine possible sources of Cu, Zn and Fe present in storm water during rainfall events.

**Research Questions:** 

- 1) What are the concentrations of dissolved Cu, Zn and Fe in Wellington streams?
- 2) How do the concentrations compare with the recommended chronic toxicity guidelines?
- 3) What are the concentrations of dissolved Cu, Zn, and Fe during the runoff events?
- 4) How do the concentrations of Cu, Zn and Fe during the runoff events compare with the recommended chronic and acute toxicity triggers, and to the base flow levels?
- 5) What are the possible sources of dissolved metals, Cu, Zn and Fe, in storm water during rainfall events?

#### **1.3 Research Approach**

In order to answer the first two questions a weekly monitoring program was carried out at seven sites on three urban streams between January and July in 2011. In March, six additional sites on three additional streams were included in the program to obtain detailed information regarding residential and rural sites (sites 8-13). The outcome of the monitoring program (base flow dataset) was utilized to assess base flow water quality from a dissolved Cu, Zn and Fe concentration perspective and to establish background concentrations. The base flow dataset helps one to understand the impact of storm water runoff on dissolved Cu, Zn and Fe concentrations present in the receiving water bodies.

Questions 3 and 4 were answered in two ways: first, collecting a single sample during several runoff events at each site to provide a dataset (so-called storm runoff samples) in parallel to base flow data set; second, continuous monitoring of storm runoff to examine first flush phenomenon (discussed in chapter 2), which potentially carries higher concentrations of dissolved Fe, Cu and Zn.

Question 5 was resolved by collecting and analysing three different types of sample:

- A) Atmospheric rainfall samples, at three main collection sites: 1) VUW campus, 2) a rural site (site 13), and 3) a site with high traffic volumes (Mt Victoria tunnel).
- B) Roof runoff samples: Runoff from two roof types (galvanised and tile) were examined. The selected roofs were located in Wellington City, Porirua, Tawa, and Karori.
- C) Storm water runoff from paved surfaces: Run off from road surfaces and parking areas has been collected and analysed to measure the concentration of dissolved Fe, Cu and Zn. The studied paved surfaces were either close to VUW campus or adjacent to one of the monitored sites.

#### **1.4 Study Area and Sites Classifications**

The monitored sites are located within the Wellington region and represent six streams, having different physical characteristics.

A total of four sites were located on the Porirua Stream, sites 1-4. Porirua stream is classified as an urban stream and is one of the most important streams in the Wellington region. It runs from Johnsonville (residential area), passing through Tawa with residential, light industrial and commercial activity, to Porirua Harbour and drains a total area of more than 3567 hectares. Porirua stream receives storm water from a motorway and a railway for almost all of its length [21]. The lowest water flow is experienced at the zone adjacent to Johnsonville (site 1) and the flow gradually increases, due to mixing with other tributaries, to reach its maximum before entering Porirua Harbour (site 4, ~ 200 meters upstream from Porirua Harbour).

Kenepuru Stream drains a total area of about 1299 hectares and it also drains into Porirua Harbour [21] (site 5 is located ~ 200 meters upstream from the Porirua Harbour). Kenepuru Stream passes through a residential area on the eastern side of Porirua.

Takapu Stream is divided into two regions. The upper reaches of Takapu Stream pass through farm lands, natural bush and unmodified areas (site 6 is located at the end of this zone). The lower reaches of Takapu Stream pass through a commercial area (site 7) before crossing State Highway 1 and before entering Porirua Stream.

Karori Stream is one of the important streams in the Wellington region. It drains a total area of 3093 hectares and is divided into two zones. The upper portion of Karori Stream is extensively modified, piped in concrete channels, while passing through the residential area of Karori and its associated commercial activities, [21], (where site 8 is located). The lower reaches of this stream have light residential activities and light land modifications [21] (site10). Site 9 is located in a tributary of Karori Stream which passes through a light residential zone before entering Karori Stream.

Makara and Ohariu Streams are mostly classified as rural. They drain total areas of 6117 and 1804 hectares respectively and drain into Opau Bay [21]. Sites 11 and 12 are located on Makara Stream, separated by about 4 kilometres. Site 13 is located on Ohariu Stream, which flows into the Makara Stream downstream after site 12.

The monitored sites were adjacent to roads, varying in traffic density, and had single dominant land-uses. To facilitate comparison between sampling sites, all sites were classified under four categories, suburban residential (sites 1, 5, 8), commercial (sites 3, 4, 7) light residential (sites 2, 9 and 11) and rural (sites 6, 11, 12 and 13). With this division, one can evaluate the contaminants of concern and predict the sources of these contaminants. Table 1.1 illustrates characteristics of the monitored sites. Figure 1.1 shows a map of the Wellington region and the location of the monitored sites. Figures 1.2, 1.3, 1.4, and 1.5, [9], show satellite photos of the monitored sites and illustrate the nature of surrounding terrain. Additionally, site coordinates and selected pictures of the monitored sites are in Appendix 2.

Site Site name number		Main characteristics of surrounding terrain
1	Wingfield Place, Porirua Stream	Suburban residential.
2	Middleton Road Tunnel,	Light residential.
2	Glenside, Porirua Stream	
3 Tawa, Main Road, Porirua Stream.		Commercial zone.
4	Kenepuru Drive, next to the flow monitoring station, Porirua Stream.	Commercial zone.
5	Champion Street, Kenpuru Stream	Suburban residential.
6	Woodburn Drive- Takapu Road, Takapu Stream	Rural area.
7	7 Takapu Road, Takapu Stream Commer	
8	Karori Park eastern, Karori Stream	Suburban residential
9 Karori Park western, a tributary of Karori Stream.		Light residential.
10	Makara Peak, Mountain Bike Park, Karori Stream.	Light residential.
11	Makara Road, Makara Stream.	Rural area.
12	Takarau Gorge Road, Makara Stream.	Rural area.
13	Takarau Gorge Road, Ohariu Stream.	Rural area.

 Table 1.1 Main characteristics of the monitored sites.



Figure 1.1 Map of the Wellington region indicating the sampling sites [39].



Figure 1.2 Satellite photos of sites 1, 2 and 3 (the red marks).



Figure 1.3 Satellite photos of sites 4, 5, 6 and 7 (the red marks).



Figure 1.4 Satellite photos of sites 8, 9, 10 and 11 (the red marks).



Figure 1.5 Satellite photos of sites 12 and 13 (the red marks)

# **1.5 Heavy Metals in Natural and Storm Waters: Sources and Effects**

Non-point sources of pollution (diffuse sources) have been identified as the major cause of increasing trace metal concentrations, specifically, Cu, Zn and Fe, within urban watersheds. There is increasing recognition that diffuse sources may contribute to the emission of Cu, Zn and Fe during storm runoff by producing particulate materials constituted of these metals or by producing these metals directly as a result of corrosion. Sources such as road components, wear and tear of tyre components and engine parts, brake pads and the dust generated by their use, rusting process of auto bodies, infrastructure and building components, including materials considered to be the major causes of water quality degradation during runoff events [10-17]. Figure 1.6 illustrates examples of potential sources of heavy metals, Cu, Zn, and Fe [10].



**Figure 1.6** Potential sources of heavy metals in urban environment, obtained from [10].

The principal concern regarding the potential adverse effects of heavy metals is that the long term uptake by sediment leads to sediment toxicity and bioaccumulation of heavy metals in the resident aquatic life [5-6, 18]. Metals exist in either dissolved (dissolved refers to the concentration of metal obtained by filtering the sample through a 0.45µm membrane) or solid form. Metals are persistent and accumulate in filter feeding animals such as shell fish, so elevated concentrations could pose public health issues. Natural aquatic ecosystems may become contaminated and could be adversely effected by heavy metals released from human activities, and this may have disturbing effects on the ecological balance and diversity of aquatic organisms residing in the receiving watershed environment [5]. Dissolved metals are the most bio-available fraction and therefore should be used to assess the potential toxicity and natural waters quality [11].

#### **1.6 The Guidelines**

The Australian and New Zealand Environment and Conservation Council freshwater toxicity trigger values (ANZECC 2000 TV) for heavy metals are intended to provide protection from sustained exposure and are derived from chronic toxicity field tests on multiple species. The ANZECC (2000) toxicity guidelines provide four data sets of protection levels. The commonly applied level to slightly to moderately disturbed aquatic ecosystems is the 95% protection level [11], which in this study was used to interpret base flow and wet-weather data. The toxicity of metals in water depend on the water's hardness, but published toxicity trigger values are only presented for a default hardness value of 30 mg/L as CaCO<sub>3</sub>. ANZECC presented a mathematical expression, represented in eq. 1.1, that allows the modification of the trigger value to the new measured hardness. One can calculate a hardness-modified trigger values for any hardness value.

Hardness modified trigger value for Cu and Zn = Trigger value X (Measured hardness/30)<sup>0.85</sup> (1.1)

It is important to note that ANZECC 2000 toxicity trigger values are not considered to be a pass or fail criteria. In fact, developers of these guidelines emphasise that they are only one of several evidences that will help in judging the potential effects of metal contaminants on a given environment [4, 8, 11, 19]. Table 1.2 and Table 1.3 show unmodified and hardness modified ANZECC (2000) toxicity trigger values for Cu and Zn at 95% species protection. ANZECC noted that there was not enough information to derive a reliable trigger value for Fe, so the Canadian trigger value (CTV) is recommended and was used in this work.

 Table 1.2 ANZECC 2000 toxicity trigger values for Cu and Zn at 95% species

 protection and the Canadian trigger value for Fe [11].

Metal	ANZECC toxicity trigger values and CTV
	[mg/L]
Cu	0.0014
Zn	0.008
Fe	0.3

 Table 1.3 Hardness-modified trigger values for chronic Cu and Zn toxicity.

Stream name	Dissolved Cu HMTV	<b>Dissolved Zn HMTV</b>
	[mg/L]	[mg/L]
Porirua Stream	0.00183	0.01043
Karori Stream	0.00152	0.00868
Makara Stream	0.00171	0.01000
Ohariu Stream <sup>1</sup>	0.00171	0.01000
Kenepuru and	No hardness information is available	
Takapu Streams		

Calculations in Table 1.3 are based on hardness information provided by the Greater Wellington Regional Council (GWRC) [20].

<sup>&</sup>lt;sup>1</sup> A report by the GWRC [7] showed that the value of Ohariu stream water hardness is comparable to Makara stream.

As previously noted, ANZECC 2000 toxicity trigger values are intended for protection from sustained exposure and the exposure to storm water derived dissolved Cu, Zn and Fe is comparably short, therefore, storm runoff data was additionally compared against the United States Environmental Protection Agency (USEPA 2006) Criteria Maximum Concentrations (CMC). CMC values are higher than the ANZECC toxicity trigger values and established maximum protection numbers that do not cause adverse effects on the exposed aquatic population as a result of brief exposure (acute toxicity) to dissolve heavy metals [8].

Metal	Modified USEPA 2006 CMC criteria	
	[mg/L]	
Cu	0.006	
Zn	0.0568	
Fe	No data available	

Table 1.4 Modified USEPA 2006 CMC criteria for dissolved Cu and Zn [8].

In Table 1.4, the original values were derived at a hardness of 100 mg/L as  $CaCO_3$ , and the current numbers were adjusted to meet local water hardness in the range of 0 to 52 mg/L as  $CaCO_3$  [8].

### Chapter 2

# 2 Scope of First Flush and Literature Review

#### 2.1 First Flush Phenomenon

The following questions are addressed below:

- A) What is first flush?
- B) What are the factors effecting the quality of first flush?
- C) Where and how to use first flush gathered information?

Urbanization facilitates the rapid transport of storm water runoff to the nearest watershed [3, 17]. Figure 2.1 shows the relationship between the peak value of water hydrology and a comparison between the speed of water transport in urbanized and pre-urban environments. Urbanization storm runoff peaks occur at shorter times in comparison to pre-urban storm water runoff [21].



Figure 2.1 Changing of stream discharge after urbanisation, obtained from [21].

As rainwater travels over natural and manmade surfaces, it washes the accumulated contaminants off and corrodes surface components. The largest flux of contamination and the most contaminated portion of runoff in urban watersheds is likely to come with the first volume of the runoff event, this phenomenon is known as the first flush [22-28]. First flush is a phenomenon associated with any storm water contaminant variables, for instance first flush of (heavy metals), first flush of (pH) or first flush of (turbidity) [29]. Moreover, several factors affect the quality and the existence of first flush in a given area [27, 29].

- 1) Climate characteristics, the length of antecedent dry weather.
- 2) Rainfall characteristics, the intensity of rainfall.
- 3) Runoff quantity characteristic, the volume of the runoff.
- Characteristics of the catchment (imperviousness of the area as such) in relation to receiving water body.

First flush phenomena have been utilized for 1) the prediction of contamination levels in rain water collected by harvesting systems, [30], and 2) the potential adverse impact on the receiving environments [8].

Firstly, rain water harvesting systems are a common method used to supply water for domestic purposes in many countries such as New Zealand and Australia [31-32]. The quality of potable water collected by this method has to meet the recommended guidelines [33]. Engineering solutions are employed to divert the contaminated first flush of the rain [23]. Figure 2.2 shows a series of samples collected from roof runoff. The analysis of first flush sample indicated high turbidity and conductivity in relation to later runoff samples [23]. The majority of the engineering solutions are based on the elimination of the initial volume of rain water runoff [23, 26, 30]. Figure 2.3 shows an example of a first flush diverter, the mechanical operation is based on elimination of the first contaminated volume of rainwater runoff from roofs [23].



Figure 2.2 Samples, left to right, collected subsequently, earlier to later, from roof runoff, obtained from [23].



**Figure 2.3** First flush diverter which consists of a chamber with a floating ball which isolates the contaminated portion of roof runoff, obtained from [23].

Secondly, first flush has been used for water pollution control and is monitored as an indicator of environmental pollution and associated hazards [8, 29]. In most cases, the concentrations of water variables (physical and chemical, organic and inorganic contaminants) are higher during the first stage of runoff and lower at later stages. This suggests that treating the first portion of storm water, rather than treating all storm runoff, drops the contamination level sharply, and could be cost effective, as shown in Figure 2.4 [29]. Figure 2.4 displays visual observation (turbidity) of storm runoff, monitored in California, wherein the storm water becomes less contaminated as the storm progresses [29].



**Figure 2.4** Visual observation of monitoring urban storm runoff from a highway in California, obtained from [29].

#### **2.2 Literature Review**

As previously mentioned, urban storm runoff discharges introduce various contaminants to the columns of water. There were a limited number of studies found in the literature investigating heavy metals in New Zealand streams. This subchapter provides a discussion of the available New Zealand studies and some examples of international work.

#### 2.2.1 Wellington Region

Before reviewing the literature in storm water, it should be noted that Cu and Zn, which are known contaminants in urban streams, and Fe were incorporated into the regular monthly baseline monitoring program undertaken by the GWRC in 2008. A recent report by the GWRC [4], shows the results of 2009- 2010 annual monitoring at sites across the Wellington region. According to this study, the median values for the concentrations of dissolved Cu and Zn exceeded their respective ANZCC (2000) TV at 3 and 4 urban sites respectively. However, if the previous guidelines were modified to take into account local water hardness, only the median values of dissolved Zn concentrations exceeded the HMTV at 3 sites; the Porirua Stream at Wall Park, Karori Stream at Makara Mountain Bike Park and the Waiwhetu Stream at Wainuiomata Hill Bridge .The data in the present study for site 10 of Karori Stream is compared and discussed further in Chapter 4 with data from the 2009-2010 study [4], and with the unpublished data of the ongoing GWRC monitoring program summarised in Figure A 1.8, [34], in Appendix 1. In addition, a study conducted by the GWRC [8], undertook a base flow survey for 7 sites, in addition to storm runoff monitoring. The concentration of dissolved Cu and Zn in 3 samples exceeded the ANZECC (2000) TVs. The data of Wingfield Place and Kenepuru sites of Porirua Stream are compared and discussed with the corresponding sites in this study in Section 4.2.

Furthermore, over the last decade, the GWRC has provided, in three separate investigations [7-8, 35], evidence that urban catchment delivers contaminated water during runoff events, which could adversely affect the benthic community. Several water contaminants have been considered in these studies, such as heavy metals,

particularly Cu, Zn Pb, Cr, Ni and Fe (in both forms: dissolved and sedimentassociated); polycyclic aromatic hydrocarbons (PAHs), nutrients, pesticides, suspended solids and pH. The studies are discussed further below, particularly the pollutants of concern in this study. The data from the three studies is discussed and compared with the results of our study in greater detail in Section 4.2 and 5.3.

The earliest storm runoff monitoring study in the Wellington region was in 1998, an investigation into the effects of transport on water quality in Wellington carried out by John Sherriff [35]. The investigation was carried out in an area where it was believed that road runoff was not affected by any storm water runoff from any other source prior to discharge into the drainage system. The investigation suggested that the majority of the contaminants were carried by the first flush, and a much reduced amount was carried in a subsequent storm runoff. The data for dissolved Cu and Zn concentrations are discussed in Section 5.3 and compared with paved surface runoff data from this study.

The second investigative programme was undertaken between 2001 and 2004 by the GWRC. The analyses and reporting were undertaken by consultants Kingett Mitchell Ltd [7]. The investigation showed the results of a total eleven storm runoff events at eleven different sampling sites with different catchment types; industrial, commercial and residential. It was found that dissolved Cu, Ni, Co and Zn concentrations exceeded the ANZECC (2000) TVs. Dissolved Fe and Pb did not exceed the sustained toxicity triggers (ANZECC (2000) TV and CTV). In comparison to the guidelines, the most elevated dissolved metal concentrations were for Zn, which were markedly elevated at two industrial catchments.

In 2005 the GWRC embarked on a series of long term (2 years) storm water quality examinations at seven sites on five urban streams in the Wellington region where the concept of first flush was introduced [8]. Dissolved metals were analysed in eighteen storm runoff samples and it was concluded that:

 Dissolved concentrations of Cu and Zn exceeded their respective ANZECC (2000) TV in all first flush and composite samples (later duration sample of runoff).

- Two first flush and eight composite samples exceeded the USEPA (2006) hardness adjusted CMC for Cu.
- Dissolved Zn exceeded the USEPA (2006) hardness-adjusted CMC guideline in five first flush and three composite samples.
- Overall, the concentrations of dissolved Cu were the highest in the composite samples. In contrast, the first flush samples had the highest concentrations of dissolved Zn.

Further discussions of these studies are presented in Section 4.2.

#### 2.2.2 Other New Zealand Literature

In New Zealand, there have been only a few studies which have measured heavy metals in storm runoff during the last decade. In a similar manner to Section 2.2.1, an overview is provided here, and details are discussed more thoroughly in Section 4.2.

Firstly, Rotorua District Council in association with NIWA designed a monitoring program to capture storm runoff water during the period 1999-2002. A total number of thirteen storm runoff events were sampled from three different catchment types; residential, commercial, and industrial [6]. Several parameters commonly associated with urban storm water were measured e.g.; electrical conductivity, suspended solids, chemical oxygen demand, heavy metals (particularly dissolved and solid-attached Cu, Zn, Fe and Pb), petroleum hydrocarbons, indicator microbes, faecal coliforms and *E. coli*. An assessment of potential adverse impacts on water residing organism was made using several means such as toxicity testing and observation of biological surveys in stream and lakes close to storm discharges [6].
In 2005, the Auckland Regional Council conducted study on the identification and quantification of heavy metals (Cu, Zn, and Pb) in three catchment types; commercial, industrial and residential in the Auckland region [36]. The mass budgets (the result of multiplying the contaminant concentration with associated water flow) for Zn, Cu and Pb in the storm water for the three catchments were determined. As a result, the contributions of the known metal sources (Zn: vehicle tyres, galvanised building materials, paints, industrial activities, natural soils; Cu: vehicle brake pads, plumbing, industrial activities, natural soils) to metal loads in urban storm water were identified. Roof runoff, particularly from galvanised roofs, accounted for almost all the Zn found in commercial and industrial catchments. In the residential catchment on the other hand, roofs contributed only to 45% of the total Zn load concentration. In all catchment types, roads contributed only a minor proportion of the total load, as shown in Figure 2.5. The major contributor for Cu in the three catchments was unidentified. The calculation of the mass budget does not account for runoff coming from walls and fittings, Figure 2.6. However, analysis of sediment adjacent to buildings showed very low levels of Cu, indicating a low contribution from this source [36].



**Figure 2.5** Total mass budgets for zinc in the three catchments (left to right 47, 176 and 26 kg/year) and the contribution of each known sources, obtained from [36].



**Figure 2.6** Total mass budgets for Cu in the three catchments (left to right 4.59, 4.21 and 3.57 kg/year) and the contribution of each known source, obtained from [36].

More recently, over the period of 2007-2008, Wicke and co-workers developed a rainfall contaminant relation model for an urban catchment in Christchurch (a car park located in the University of Canterbury campus) [37]. The concept of first flush was considered and investigated. A total of six storm runoff events were monitored for heavy metals, Cu and Zn in particular. The results indicated that A) The concentrations of dissolved Cu and Zn in the first flush were higher than the composite (later duration) samples. B) These metals were measured at levels higher than ANZECC (2000) TVs. The data is compared against our findings of paved surface runoff on Section 4.5.2.

#### **2.2.3 International Literature**

There is increasing recognition in many countries for storm associated issues, particularly the presence of hazardous contaminants. The literature is rich with studies describing monitoring programs and remediation solutions. In this section, a summary of 4 studies is discussed.

The first flush phenomenon in storm runoff collected from a highway in California, USA was studied over a four year period by Stenstrom, *et. al* [29]. More than ten associated storm runoff parameters were examined including heavy metals. Generally, most of the parameters monitored in this study had higher concentrations

in first flush of the runoff than later stages of the runoff, confirming the existence of the first flush phenomenon. One should bear in mind that California weather is typified by rain events preceded by long dry weather periods. The authors attributed the first flush phenomenon to the nature of runoff, which generally has lower flow rate at the beginning of the storm than at the end of the storm, causing the dilution of the contaminants in those events that had longer duration. Another proposal was that the majority of the contaminants were flushed off in the first water-surface contact resulting in high concentration at the beginning of the runoff. It was concluded that, treating the first portion of storm runoff is cost effective. Figure 2.7 and Figure 2.8 are selected two plots of the variation of total and dissolved Cu and Zn concentration of the monitored contaminant versus time, for two monitored runoff events, where the first event displayed first flush for Cu and Zn but the second event did not [29].



**Figure 2.7** Plot of total and dissolved Cu and Zn as a function of time. The highest concentrations of total and dissolved Cu and Zn are in the initial rainstorm runoff compared to the remainder runoff of the storm, obtained from [29].



**Figure 2.8** Plot of total and dissolved Cu and Zn as a function of time. An example of storm runoff that did not show the first flush effect, where the concentrations of total and dissolved Cu and Zn were higher at later stages of the storm, obtained from [29].

Gnecco *et al.* [54], examined first flush phenomenon related to runoff from a variety of urban surfaces (roof and road runoff) in 12 rainfall events in Genoa, Italy. In this study they measured dissolved metals concentrations (Zn, Pb, Cu, Cd, Cr and Ni). The concentrations of Cu, Pb and Zn exceeded the European water quality standards in 70% of the monitored samples of road runoff.

In Xiamen City, China, Wei *et al.* [61], found that the concentrations of heavy metals (Cu, Pb, Cd and Zn) in storm runoff from parking lots and roads were much higher than the concentration of heavy metals in samples from lawn runoff. First flush samples contained higher concentrations of heavy metals, organic matter and nutrients than the samples collected at later time of the runoff events.

Asaf *et al.* studied the variation of chemical and isotopic compositions of urban storm water in the coastal city of Ashdod, Israel [62]. In this study, 68 samples of 46 rainwater events were collected over a two year period (2000-2002). Land use was not a big contributor to the total concentrations of trace metals. The concentrations of trace metals in 97% of the storm water samples were below the drinking water standard.

# 2.2.4 Summary of the Literature

Urban storm water discharges during wet-weather flow deliver pulses of contaminated water to many receiving water bodies. There has been a limited amount of published work on this subject in recent years in New Zealand. The impact and effect magnitude of urban storm on water quality depends on the characteristics of the storm and catchments. A study conducted by the GWRC showed that in a depositional environment such as filter feeding organism and sediment, elevated levels of heavy metals have been observed in places adjacent to urban areas [38]. Accumulation by flora and fauna, which could result in a reduction in biodiversity, is one of the most concerning adverse effects. This could have a negative impact on human health.

# Chapter 3

# 3 Field Work and Experimental 3.1 Field Work and Sampling Strategies

As previously mentioned, the primary objective of this work was to determine the concentrations of the three dissolved metals during base flow (dry weather) and wet weather flow in the Wellington region. A monitoring program was established to capture these two sample types. In the case of wet weather flow samples there are two different sub-types of samples. The first type is a single grab sample collected during runoff events from the studied sites (so-called runoff samples), which were less difficult and challenging than the second type. The second type of samples are obtained while monitoring storm runoff continuously from the beginning which lead to characterise the storm runoff with two samples, first flush and composite samples, defined in Section 3.1.3. The collection of these samples was associated with challenges involving an enormous amount of work. Water flow information was not measured, so event mean concentration and annual mass load cannot be calculated from the data presented in this work. To achieve the identification of possible sources of contaminants, sampling and analysis of three categories of sample was carried out: A) atmospheric rainfall samples, B) roof samples and C) paved surface runoff. This section is intended to provide details of the sampling protocols and a review of associated literature.

#### **3.1.1 Base flow Samples**

A monitoring program was established to collect base flow water samples. A series of sampling events were undertaken on a weekly basis. In most cases, a sampling event covered all monitored sites. The program was started on 7/01/2011 with seven sites (sites 1-7), four sites on Porirua Stream, one site on Kenepuru Stream, and two sites on Takapu Stream. On 03/03 /2011, six additional sites were added to the program (sites 8-13): two sites on Karori Stream and one site on a tributary of Karori

Stream; two sites on Makara Stream, and one site of Ohariu Stream. The purpose of including sites 8-13 was to include more residential sites to the west of the Wellington region and importantly to add rural sites (sites 11-13) to the program. In Appendix 1, the total number of base flow samples for each site is shown.

#### **3.1.2 Storm Runoff Samples**

Previous work by the GWRC [7] conducted storm water runoff sampling based on time-weighted average concentrations; a composite sample from six separate samples. The sampling commenced within the first hour of the storm commencing and continued at hourly intervals. Similarly, Rotorua District Council conducted storm runoff sampling based on flow-weighted samples and a conclusive composite sample for each storm [6]. An automatic sampler was utilised which was programmed to collect samples as soon as a water flow increase was observed. In both studies, each storm runoff was represented by one composite sample, therefore, first flush was not considered.

In the current study a storm runoff event is monitored by a single grab sample collected manually at random times during the runoff, excluding the first flush. This was to enable the author to obtain storm runoff samples from more than one studied site during the same runoff event. In all sites, at least five storm runoff events were sampled; for example, sites 8-13. Sites 1-7 have a larger number of storm runoff samples due to the longer sampling period. The total number of storm runoff samples is detailed in Appendix 1 with each site.

Having base flow and storm runoff datasets, one can use the value of the medians of dissolved metal concentrations for an evaluation against sustainable and acute toxicity guidelines. The ANZECC (2000) noted that the evaluation of a certain contaminant concentration against the guidelines should only be made upon several monitored concentrations [11], which has been fulfilled by the protocols conducted in this study. In addition, acquiring the base flow data set provides an additional comparative element to evaluate the relation between site characteristics and storm water discharges.

# **3.1.3 Continuous Monitoring of Storm Runoff: First Flush and Composite Samples**

Sampling first flush always is difficult and requires meticulous preparation. The weather forecast is an important aspect of first flush sampling. It was necessary to obtain a reliable forecast in order to prepare for sampling events. The New Zealand meteorological service webpage <u>www.metservice.com</u> was consulted for upcoming rainfall events, however, it does not provide an absolute time and there are large variations between the start of the rain in Wellington City and at the collection sites. Usually, first flush sampling involved 1-2 hours of waiting before they actually could be collected. Sampling strategies is an arguable matter amongst researchers, particularly, how much of the storm runoff should be considered as first flush [27]. Herein, three opinions are provided and the protocol used in this work is described.

The GWRC [8] conducted first flush sampling by using an ISCO automatic sampler that triggers automatically when water level rises 35 mm over 15 minutes (water depth dependent). The first flush sample was the average composition of the three samples collected at five minute intervals, and the composite sample (later duration of the storm) consisted of a further eight samples taken at 20 minute intervals [8]. On the other hand, in the study done in California [29], first flush is the mathematical mean concentration value of a certain pollutant during the first hour of runoff samples. Composite samples were obtained using the mean of further runoff samples, collected at hourly intervals, between 4 and 7 hours, as shown in Figure 3.1. The sampling was flow dependent, sampling commenced as soon as the flow was observed, by an automatic sampler. Finally, a study done in Christchurch in 2008 [37] proposed that first flush is the composition of the later duration samples of the storm runoff. The sampling was accomplished using an automatic samples as soon as water flow was observed.



Figure 3.1 General sampling protocol for first flush and composite samples, obtained from [29].

In this work first flush is considered to be the mathematical mean of the concentrations of dissolved metals in samples collected in the first 25 minutes collected at intervals of 5-15 minutes, as shown in Figure 3.2. Composite samples were obtained using the same mean, but for samples collected after the first flush, at different time intervals of 10 minutes to 1 hour with a maximum monitoring time of 6 hours, as shown in Figure 3.2. Note that there were some short storm events therefore only one sample was collected after first flush. All samples were collected manually and the collection was commenced five minutes after rainfall started. It should be remembered that first flush is used to express contamination levels at the beginning of the storm compared to later stages of the same storm runoff.



Figure 3.2 General definitions and sampling protocols for first flush and composite samples.

In total, nine storm runoff events were monitored: Four events at site 1 (one event is a runoff from Middleton Road, adjacent to site 1, this is explained further in Section 3.1.6), two events at site 8; and single events at sites 4, 5 and 9. Additionally, the effect of the length of dry weather before to the storm on first flush was examined between events monitored at sites 1 and 8, and this is discussed in Section 4.2.4. Complete details, in terms of collection time intervals, concentrations of dissolved metals for each collected sample during the runoff, length of antecedent dry weather, and temporal variation of the concentrations of dissolved metals for each event are presented in Appendix 1 for the respective sites.

#### 3.1.4 Atmospheric Rainfall Samples

Rain samples were collected between December 2010 and July 2011. Weather forecasts were consulted in advance from <u>www.metservice.com</u>. Once rainfall was predicted, a non-metallic rainwater collector, as shown in Figure 3.4, was placed on the collection site. Sampling was carried out until approximately 500 ml was collected. In the case of short events, the collector was removed after the rain had stopped; in this way contamination of rain samples by dry deposition was avoided. The samples were collected mainly on the roof of the second floor of Laby Building, School of Chemical and Physical Sciences (SCPS), of Victoria University of Wellington, Kelburn, Wellington, New Zealand. In addition, three atmospheric rainfall samples were collected at the Mt Victoria road tunnel, which has a high traffic density and four rural atmospheric rainfall samples were collected at site 13, located near 257 Takarau Gorge Road.



**Figure 3.3** Wellington map, locations of sites for the atmospheric rainfall sampling. A: VUW, B: Mt. Victoria tunnel, C: 257- Takarau Gorge Road, obtained from [39].



**Figure 3. 4** Pictures of non-metallic atmospheric rainfall samplers: before placing in the holder and after placing in the holder and at the rural site.

# 3.1.5 Roof Runoff Samples.

Roof runoff samples were collected from residential and commercial buildings located in Wellington Central, Porirua, Tawa, Karori and Lower Hutt. The samples were collected from outer pipes of the gutter systems that discharge roof runoff to either storm water drainage systems or directly to the ground. Roof samples were divided into two categories. The first class aimed to capture roof runoff samples during random times of the runoff events, excluding first flush. Runoff from two roof types was measured: Galvanised roofs (the painting quality varied from moderate to bad) and tile roofs. Galvanised roofs are the majority of the samples due to their prevalence and ease of accessibility. The second group of samples involved an examination of first flush in roof runoff. Therefore, weather forecasts were checked for upcoming rainfall events. Galvanised roofs were selected for this purpose, due to ease accessibility. In terms of sampling strategies, one sample was collected as soon as the runoff was observed and the other sample (so-called delayed-runoff sample) was collected at a later time, there was at least a one hour difference between the two collections.

#### 3.1.6 Paved Surface Runoff Samples

Another class of samples was obtained as a runoff from paved surfaces. These samples were collected in accordance with the storm runoff sampling protocol. The paved surfaces chosen were parking areas, roads, and land utilized for human entertainment purposes, located adjacent to one of the monitoring sites or to VUW, Kelburn campus. The samples were collected before the runoff had entered the storm water system or had mixed with stream water. As mentioned earlier, in 3.1.3, a monitoring of a road runoff (Middleton Road) was done at site 1. The samples were obtained from a drainage pipe that drains storm water from a section of the road and this portion of the road probably does not have roof runoff (or little). In the same event, another first flush sample was collected at site 1 but from different drainage pipe that drains runoff water from Wingfield Place which passes through a residential area and could contain roof runoff (this sample was not associated with a composite sample, the water level rose very quickly and the sampling had to stop for safety reasons).

# **3.2 Laboratory Work**

#### **3.2.1 Pre-sampling Preparation**

The work was performed in a clean area to avoid any introduction of contamination to the analysed water samples. All water samples were obtained in 510 ml polyethylene bottles. Before any sampling took place, the containers were washed three times with distilled water, once with 2.5 M HNO<sub>3</sub>, once with 0.1 M ethylenediaminetetraacetic acid (EDTA), and finally rinsed four times with distilled water. Bottles were allowed to dry out, inside a fume hood, and then they were closed with the lids and placed inside sealed plastic bags. The atmospheric rainfall samplers, glassware and other laboratory equipment were treated in the same method. During sampling, the bottles were rinsed twice with sampled water and then filled. The analysis of heavy metals was performed as soon as possible after the sampling with no holding time. This procedure fits well with the recommended sampling criteria protocol [40].

#### 3.2.2 Analytical Procedure

#### 3.2.2.1 Determination of Dissolved Metal Concentrations

Flame Atomic Absorption Spectroscopy (FAAS) was used to analyse the three metals in water samples. FAAS involves irradiation of a sample that has been aspirated and atomised into an oxy-acetylene flame with monochromatic light, measuring the absorption of entering light which is proportional to the concentration of analysed elements. Each element absorbs light at a characteristic wavelength; hence a change in the radiation source is required for each analyte. The detection limits for the studied elements are in the range of 0.01-0.05 mg/L [40-41]. Table 3.1 shows calculated<sup>2</sup> detection limits for FAAS. Calibration curves were established with 5 variable concentrations in the range of (0.00-1.5 mg/L) for Cu and Zn and (0.00- 9.00 mg/L) for Fe before the analysis took place (examples of typical calibration curves are given in appendix 2 Figures A2.4-A2.6). The determination of

<sup>&</sup>lt;sup>2</sup> The calculations are based on the recommended method in [52].

the concentrations of the studied metals is obtained after a triplicate analysis on FAAS. It should be noted that the determination of dissolved metals concentrations is usually preformed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) which has a very low detection limits for the analysed metals, as low as 50  $\mu$ g/L. Unfortunately, this instrument was not available for the daily analysis and the external analysis is highly expensive.

Metal	Limit of detection LOD		
	[mg/L]		
Cu	0.04		
Zn	0.01		
Fe	0.045		

**Table 3. 1** Calculated<sup>3</sup> detection limits for Cu, Zn and Fe.

Based on the results obtained by the Greater Wellington Regional Council (GWRC) [4, 8] and the monitoring data during the earliest two months, the concentrations of dissolved Cu and Zn in some samples were below the detection limits of the FAAS technique. The detection limits are higher than the recommended chronic toxicity guidelines. To overcome this issue, a technique, called pre-concentration was used to enhance the concentrations in the analysed samples. Various reagents and methods have been utilised to enhance the concentration of Cu and other elements prior to their detection in natural waters. These methods include solvent extraction, precipitation, electrochemical analysis, chelation resins, and various chromatographic techniques. Table 3.2 shows some examples of materials and techniques used in the pre-concentration process for trace metals in natural waters.

<sup>&</sup>lt;sup>3</sup> The calculated LODs are at good agreement with that reported in the literature, for example, [40].

Reference	Methods	Advantages	Disadvantages	Target Elements
[42]	Single drop micro-extraction into organic solvent	Inexpensive, easy operation and few complications Simple procedure and high enrichment	Slow kinetics and instability of the drop	Suitable for a wide range of elements.
[43]	resin and of silylated silica gel.	and recovery factors.	Slow process	Eu.
[44]	Hyphan cellulose <sup>4</sup>	satisfactory recovery percentage	Time consuming	Cu
[45-46]	Anodic stripping voltamtry <sup>5</sup> .	Fast and simple procedure.	High detection limit and few interferences	Wide range of elements.
[47]	Solvent extraction by1-nitroso- 2-naphthol and Dowex MWC-1 resin column <sup>6</sup>	Simple procedure and low detection limit	Reagents consuming and expensive	Zn and Cu
[48]	Ethylenediamine functionalized self-assembled monolayers on mesoporous supports	Fast kinetics and High sorption capacities	Complicated preparation of the sorbent	Cu
[49]	Metal ions are sorted as pyrocatechol violet complexes on activated carbon column, followed by detection on AAS	fast and simple method	Chemical consuming method and expensive.	Cu, Mn, Co, Cd, Pb, Ni and Cr
[44, 48, 50-51]	Chelex-100	Simple, cheap and excellent recovery percentage	Slow kinetics	Wide range of elements.

Table 3.2 Various reagents and techniques used for pre-concentrating heavy metals in natural waters.

 <sup>&</sup>lt;sup>4</sup> Hyphan cellulose is a chelating resin in a microcrystalline form with chelating groups 1-(2-hydroxyphenylaza)-2-naphthol.
<sup>5</sup> Deposition of Cu on a suitable working electrode and reverse the reaction in a smaller volume afterwards, and/or observe the correspond signal.
<sup>6</sup> Dowex MWC-1 is chelating resin with a sulfonic acid functional group as the chelating sites.

Among the wide range of pre-concentration methods and reagents available, Chelex-100 is a chelating resin that has durable, insoluble and compatible properties. The polymeric backbone of the resin is polystyrene cross-linked with divinylbenzene, functionalized with iminodiacetate groups as the chelating sites. This resin traps metals from aqueous solution in an efficient and selective way, depending on the pH and the type of ions of the solution [44, 48, 50-51]. It is supplied in the sodium form with 50-100 mesh grain size (obtained from Sigma). This form is very stable and has excellent shelf life; it can be recovered after use by a two steps, firstly soaking in acid (2.5 M HNO<sub>3</sub> in this work) followed by immersion in a strong base (0.3 M NaOH in this work)<sup>7</sup> and warming [51]. In the light of these facts, Chelex-100 chelating resin was chosen as the pre-concentration method prior to the analysis of dissolved Cu and Zn (in these cases where it could not be directly measured) by FAAS.

Cu and Zn speciation studies have shown that fast dynamic adsorption of the metals is exhibited by Chelex-100 [50]. The time for complete uptake from the sample to the resin is some dispute. In the literature, opinions vary from couple of hours [51] to three days [50]. On the other hand, the influence of pH on metal uptake is agreed where protonation of carboxylates and the nitrogen donor group was reported to be complete at pH 2.0  $\pm$  0.1. Therefore, complete metal elution is achieved by soaking the resin in an acid media. Complete Cu and Zn adsorption occurs at pH 5.5  $\pm$ 0.3 [44, 48, 50-51]. In the light of the above facts, a pre-concentration technique using Chelex-100 was developed using a batch equilibration technique. Figure 3.5, is a schematic of the developed batch procedure for Cu and Zn pre-concentration in natural waters.

The decrease in volume from 500 mL to 15 mL enhances the concentration of dissolved Cu and Zn by a factor of 33. The procedure consists of two parts. Part A is to measure the concentration of Fe directly (to avoid particulate contamination, the samples must first be filtered using a 0.45  $\mu$ m pore size membrane), and second, to see whether or not dissolved Zn needs to be considered after the pre-concentration process, in parallel to Cu. If the concentration of dissolved Zn is directly measurable on FAAS, which is commonly the case for residential and commercial sites, the

<sup>&</sup>lt;sup>7</sup> There was no difference between the new and recovered forms of Chelex-100 in term of capability, refer to Table 3.3.

samples were not measured again<sup>8</sup> for dissolved Zn in the pre-concentrated samples (in the 15 mL).

Part B is the pre-concentrating procedure. Chelex-100 chelates the dissolved form of metals and so, there was no need to filter with the 0.45µm membrane because Chelex-100 reacts only with dissolved form of metals, which saved an enormous amount of time, particularly on these occasions where large numbers of samples were being analysed. The pH of the 500 ml has to be adjusted by adding ammonium acetate solution. The buffer solution was a 1:1 mixture of 2.5 M of ammonium chloride and 2.5 M of acetic acid (reagents obtained from Panreac). The pH of the buffer was checked periodically.

After the adjustment of pH, Chelex-100 (either new or recovered forms) was added after being washed with 0.1 M ammonium chloride solution (for fast dissociation through the chelating process [44]). Clean magnetic bars were placed inside the plastic bottles and the samples were stirred for 24 hours, Figure 3.6, is a picture of a water sample containing all reagents and ready for stirring stage. Afterwards, the samples were filtered (with 70 µm pore size) and Chelex-100 beads containing the Cu and Zn were isolated. A one hour contact between Chelex-100 containing Cu and Zn with 1:1 solution of 2.5 M HNO3 and 2.5 M HCl (supplied by Fisher Scientific) followed in order to elute the metals from Chelex-100. Note that all reagents used were metal free and of analytical grads. The latter solution has been reported to be the best ratio for the elution mixture [44]. Finally, a filtration was performed to isolate the Chelex-100. The 15 mL samples containing enhanced concentrations of metals were measured on the FAAS and the original concentrations in the 500 mL were calculated. For example, a sample that contains 0.0045 mg/L of dissolved Cu after pre-concentrating the sample, the FAAS measures 0.15 mg/L of Cu. This assumes having 100 % recovery and an enhancement factor of 33. The procedure is time consuming and required considerable lab work, particularly, during the course of analysing storm water samples, which contain suspended solids. In these circumstances, the first filtration step becomes even more frustrating and time consuming.

<sup>&</sup>lt;sup>8</sup> There were some internal tests where the concentrations of dissolved Zn were measured directly and in the pre-concentrated samples. The results were always consistent.



Figure 3.5 Schematic of the pre-concentration method employed to enhance the concentrations of Cu and Zn.



Figure 3.6 Stirring stage of water sample in the pre-concentration procedure.

The method has been assessed with standard solutions of the metals containing variable concentrations, in the range of 0.01-0.04 mg/L (spiking real samples with variable metal concentrations and testing the recovery). As can be seen in Table 3.3, excellent average recoveries were achieved for both metals, confirming the success of the procedure. The recoverability testing experiments were operated on natural water, from site 1 that contained concentrations of Cu and Zn, previously determined and set as blank. It is important to mention that the recoverability tests were done by a recoverable form of Chelex-100. The same conclusion was reported in other publications [44, 50], however, different procedures were applied.

In addition, an analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was performed on six samples analysed earlier on FAAS. Table 3.4 shows the concentrations of dissolved Cu, Zn and Fe obtained from FAAS and ICP-MS. The analysis reveals reasonable variations for dissolved Cu and Zn between the two analytical methods (except Zn in the sample from site 8). However, it should be noted that the samples were filtered two times, using 0.45  $\mu$ m membrane, before the analysis by ICP-MS took place, which could explain the lower concentrations of dissolved Fe obtained from the analysis by the ICP-MS. Colloidal particles of Fe could have been removed in the second filtration, leading to lower concentrations.

Total relative uncertainties were calculated. Rectangular distributions ( $\sqrt{3}$ ) were assumed for all uncertainty sources, including laboratory apparatus and FAAS. The calculations revealed that the measurements were associated with total relative uncertainty of 4.00%, 5.87%, and 7.83% for Cu, Zn and Fe respectively. Note that the calculations were performed in accordance with the recommendations in [52]. Calculations of consistency and relative uncertainty are detailed in Appendix 2.

**Table 3.3** Examination of Chelex-100 recovery with variable concentrations of Cu and Zn concentrations.

Metal	Number of samples	Initial concentration [mg/L]	Average Concentration [mg/L]	Average recoveries [%]
Cu	$2^*$	0	0	0
	2**	0	0.0035	Not applicable
	2	0.01	0.01	100
	2	0.02	0.02	100
	2	0.03	0.03	100
	2	0.04	0.038	95
Zn	2*	0	0	0
	2**	0	0.02	Not applicable
	2	0.01	0.01	100
	2	0.02	0.02	100
	2	0.03	0.029	97
	2	0.04	0.038	95

\*: performance of Chelex-100 protocol in distilled water. \*\*: the Concentrations of dissolved Cu and Zn in natural samples obtained by Chelex-100 without any addition.

**Table 3.4** Comparison between the concentrations of dissolved Cu, Zn and Fe obtained from the analysis by FAAS and ICPMS.

Site	Metal concentration [mg/L]						
	Cu		Zn		Fe		
	FAAS	ICP-MS	FAAS	ICP-MS	FAAS	ICP-MS	
1	0.0070	0.0089	0.030	0.052	0.116	0.067	
3	0.0042	0.0079	0.015	0.022	0.115	0.060	
4	0.0063	0.0030	0.020	0.013	0.126	0.15	
5	0.0048	0.0059	0.022	0.023	0.255	0.13	
8	0.0075	0.0042	0.034	0.0047	0.100	0.02	
Rainfall	0.017	0.011	0.1	0.046	0.21	0.063	

It should be noted that the pre-concentration procedure had not been developed before 22/03/2011. Before this time, all the three metals in water samples had been analysed following part A in Figure 3.5. Hence, dissolved Cu and Zn (in a few cases) in base flow and storm runoff samples collected prior to this date were below the detection limit. Consequently they were not considered and were omitted from the subsequent statistical calculations. The number of omitted samples for Cu and Zn is detailed with data set of each site in Appendix 1. The concentrations of dissolved Cu that fell below the enhanced detection limit (0.0012 mg/L) were assumed to be equivalent to the enhanced detection limit and were introduced to the statistical calculations. The concentrations of dissolved Zn were always high enough to be measured either directly or by the pre-concentration method and therefore no assumptions were made. The assumption does not affect our judgment on whether the concentration of Cu exceeds the chronic toxicity trigger value (ANZECC (2000) TV and HMTV) or not, because the enhanced detection limit is lower than this guideline. In a similar manner, the concentrations of dissolved Fe that fell below the detection limit of 0.045 mg/L of FAAS particularly for base flow samples of Takapu Stream and Karori Stream sites, were assumed to be the detection limit. It should be noted that **no** assumptions were made for samples collected from atmospheric rainfall samples, roof, and paved surface runoff, because the guidelines are not intended to assess this type of water.

# Chapter 4

# 4 Base Flow and Wet Weather Monitoring Outcome 4.1 Results

The primary objective of the present project was to measure the concentrations of dissolved Cu, Zn and Fe in base flow and investigate the impact of rain runoff on the level of contamination to see whether there was any degradation of water quality. Section 4.1 provides data obtained from the weekly monitoring program (base flow sampling), storm runoff sampling, and monitoring for first flush. For each site, unless stated, dissolved Cu and Zn data are presented separately in tables (Appendix 1) and visualised as box plots and compared against the ANZECC (2000) hardness modified trigger values chronic toxicity (HMTVs). Sites that do not have water hardness information are compared against the default ANZECC (2000) TVs directly without modification. Dissolved Fe data is treated in a similar manner to the data for Cu and Zn, but in this case it is compared against the Canadian sustained Toxicity trigger Value (CTV). Additionally, storm runoff data is compared against the United States Environmental Protection Agency (USEPA 2006) Criteria Maximum Concentrations (CMC) values. Box plots present the data parameters, minimum, 25th percentile, median, 75th percentile and maximum as shown in Figure 4.1. The median values are the basis for all comparisons and discussions against the guidelines. The factor by which the respective toxicity triggers is exceeded is based on the median values and mentioned in the tables for each metal in Appendix 1. Additionally, the impact of storm runoff events on the dissolved metal contamination was evaluated using the medians of the collected data in base flow and runoff events. Results for first flush and composite samples are shown, details are in Appendix 1. The next Section (4.2) provides an overview and a discussion of the data in greater detail, with comparisons to previous works.



Figure 4.1 Interpretation of box plot.

#### 4.1.1 Site1 Data

A total 19 base flow and 10 storm runoff samples were collected at this site. Also, 3 storm runoff events were monitored for first flush resulting in 3 first flush and 3 composite samples. Site 1 is the most contaminated with the presence of high concentrations of dissolved Cu in base flow and run off events, this could be attributed to the fact that this site has low water flow or its location next to residential area. In fact, all dissolved Cu, and the median dissolved Zn in base flow and storm runoff samples exceeded the HMTVs, as shown in Figure 4.2 and Figure 4.3. The median of dissolved Cu and Zn concentrations in storm runoff samples exceeded the CMC. In general, the concentrations of dissolved Cu and Zn were higher in first flush than the composite samples; both were below the CMC and higher than HMTV. The median of dissolved Fe concentrations of dissolved Fe in composite samples tended to be higher than the first flush and both exceeded the CTV, as shown in Figure 4.4.

#### 4.1.1.1 Dissolved Cu



Figure 4.2 (A) HMTV, CMC and statistical parameters of dissolved Cu

concentrations [mg/L] in base flow, storm runoff, first flush and composite samples at site 1 of Porirua Stream. Note that the 75<sup>th</sup> percentile and maximum of storm runoff samples are excluded from Figure 4.2 (A) but are shown in Figure 4.2 (B) (0.081 and 0.14 mg/L respectively).



**Figure 4.3** HMTV, CMC and statistical parameters of dissolved Zn concentrations [mg/L] in base flow, storm runoff, first flush and composite samples at site 1 of Porirua Stream.





**Figure 4.4** CTV and statistical parameters of dissolved Fe concentrations [mg/L] in base flow, storm runoff, first flush and composite samples at site 1 of Porirua Stream.

### 4.1.2 Site 2 Data

A total of 20 base flow and 10 storm runoff samples were collected at this site. It was noted that the median of dissolved Cu and Zn concentrations in base flow and storm runoff samples at sites 2 and 3 were lower in comparison to those for site1, but that they exceeded the HMTVs (refer to Figures 4.2 and 4.3 for site 1 and Figures 4.5 and 4.6 for site 2 and Figures 4.8 and 4.9 for site 3).



#### 4.1.2.1 Dissolved Cu

**Figure 4.5** HMTV, CMC and statistical parameters of dissolved Cu concentrations [mg/L] in base flow and storm runoff samples at site 2 of Porirua Stream.



**Figure 4.6** HMTV, CMC and statistical parameters of dissolved Zn concentrations [mg/L] in base flow and storm runoff samples at site 2 of Porirua Stream.



#### 4.1.2.3 Dissolved Fe

**Figure 4.7** CTV and statistical parameters of dissolved Fe concentrations [mg/L] in base flow and storm runoff samples at site 2 of Porirua Stream.

#### 4.1.3 Site 3 Data

A total of 22 base flow and 8 storm runoff samples were collected at site 3.



#### 4.1.3.1 Dissolved Cu

**Figure 4.8** HMTV, CMC and statistical parameters of dissolved Cu concentrations [mg/L] in base flow and storm runoff samples at site 3 of Porirua Stream.



**Figure 4.9** HMTV, CMC and statistical parameters of dissolved Zn concentrations [mg/L] in base flow and storm runoff samples at site 3 of Porirua Stream.

#### 4.1.3.3 Dissolved Fe



**Figure 4.10** CTV and statistical parameters of dissolved Fe concentrations [mg/L] in base flow and storm runoff samples at site 3 of Porirua Stream.

# 4.1.4 Site 4 Data

A total of 22 base flow and 10 storm runoff samples were obtained at this site. One storm runoff event was observed for first flush, which gave 1 first flush and one composite sample. The data for first flush monitoring is shown in Appendix 1, in site 4 data.

#### 4.1.4.1 Dissolved Cu



**Figure 4.11** HMTV, CMC and statistical parameters of dissolved Cu concentrations [mg/L] in base flow and storm runoff samples at site 4 of Porirua Stream.



**Figure 4.12** HMTV, CMC and statistical parameters of dissolved Zn concentrations [mg/L] in base flow and storm runoff samples at site 4 of Porirua Stream.



#### 4.1.4.3 Dissolved Fe

**Figure 4.13** CTV and statistical parameters of dissolved Fe concentrations [mg/L] in base flow and storm runoff samples at site 4 of Porirua Stream.

## 4.1.5 Site 5 Data

A total of 21 base flow and 10 storm runoff samples were collected and analysed for this site. One storm runoff event was monitored for first flush which resulted in one first flush and one composite sample. First flush monitoring data is reported in Appendix 1, in site 5 data. Notably, this site is the only site that the medians of dissolved Fe exceeded the CTV in base flow samples, this is discussed further in Section 4.2.



#### 4.1.5.1 Dissolved Cu

**Figure 4.14** ANZECC (2000) TV, CMC and statistical parameters of dissolved Cu concentrations [mg/L] in base flow and storm runoff samples at site 5 of Kenepuru Stream.



**Figure 4.15** ANZECC (2000) TV, CMC and statistical parameters of dissolved Zn concentrations [mg/L] in base flow and storm runoff samples at site 5 Kenepuru Stream.







## 4.1.6 Site 6 Data

A total of 20 base flow and 9 storm runoff samples were obtained at this site.



#### 4.1.6.1 Dissolved Cu





**Figure 4.18** ANZECC (2000) TV, CM and statistical parameters of dissolved Zn concentrations [mg/L] in base flow and storm runoff samples obtained from site 6 of Takapu Stream.

4.1.6.3 Dissolved Fe




# 4.1.7 Site 7 Data

A total of 20 base flow and 9 storm runoff samples were collected at this site.

# 4.1.7.1 Dissolved Cu



**Figure 4.20** ANZECC (2000) TV, CMC and statistical parameters of dissolved Cu concentrations [mg/L] in base flow and storm runoff samples collected from site 7 of Takapu Stream.



**Figure 4.21** ANZECC (2000) TV, CM and statistical parameters of dissolved Zn concentrations [mg/L] in base flow and storm runoff samples obtained from site 7 of Takapu Stream.

#### 4.1.7.3 Dissolved Fe



**Figure 4.22** CTV and statistical parameters of dissolved Fe concentrations [mg/L] in base flow and storm runoff samples for site 7 of Takapu Stream.

# 4.1.8 Site 8 Data

A total of 17 base flow and 5 storm runoff samples were obtained at this site. Monitoring of 2 storm runoff events for first flush were accomplished at this site, which resulted in two first flush and 2 composite samples. First flush monitoring data are presented in Appendix 1, in sites 8 and 10 data.



# 4.1.8.1 Dissolved Cu

**Figure 4.23** HMTV, CMC and statistical parameters of dissolved Cu concentrations [mg/L] in base flow and storm runoff samples for site 8 of Karori Stream.



**Figure 4.24** HMTV, CMC and statistical parameters of dissolved Zn concentrations [mg/L] in base flow and storm runoff samples for site 8 of Karori Stream.

4.1.8.3 Dissolved Fe



**Figure 4.25** CTV and statistical parameter of dissolved Fe concentrations [mg/L] in base flow and storm runoff samples for site 8 of Karori Stream.

# 4.1.9 Site 9 Data

A total of 17 base flow and 5 storm runoff samples were obtained at this site. Monitoring of a storm runoff event for first flush at this site was accomplished resulted in 1 first flush and 1 composite sample, presented in Appendix 1.



#### 4.1.9.1 Dissolved Cu

**Figure 4.26** HMTV, CMC and statistical parameters of dissolved Cu concentrations [mg/L] at site 9.



**Figure 4.27** HMTV, CMC and statistical parameters of dissolved Zn concentrations [mg/L] at site 9.





**Figure 4.28** CTV and statistical parameters of dissolved Fe concentrations [mg/L] at site 9.

# 4.1.10 Site 10 Data

A total of 17 base flow and 5 storm runoff samples were obtained at site 10.



#### 4.1.10.1 Dissolved Cu

**Figure 4.29** HMTV, CMC and statistical parameters of dissolved Cu concentrations [mg/L] in base flow and storm runoff samples for site 10 of Karori Stream.

#### 4.1.10.2 Dissolved Zn



**Figure 4.30** HMTV, CMC and statistical parameters of dissolved Zn concentrations [mg/L] in base flow and storm runoff samples for site 10 of Karori Stream.

#### 4.1.10.3 Dissolved Fe



**Figure 4.31** CTV and statistical parameter of dissolved Fe concentrations [mg/L] in base flow and storm runoff samples for site 10 of Karori Stream.

# 4.1.11 Site 11 Data

A total of 17 base flow and 5 storm runoff samples were obtained at this site.



#### 4.1.11.1 Dissolved Cu

**Figure 4.32** HMTV, CMC and statistical parameters of dissolved Cu concentrations [mg/L] in base flow and storm runoff samples for site 11 of Makara Stream.



**Figure 4.33** HMTV, CMC and statistical parameters of dissolved Zn concentrations [mg/L] in base flow and storm runoff samples for site 11 of Makara Stream.



#### 4.1.11.3 Dissolved Fe

**Figure 4.34** CTV and statistical parameters of dissolved Fe concentrations [mg/L] in base flow and storm runoff samples for site 11of Makara Stream.

# 4.1.12 Site 12 Data

A total of 17 base flow and 5 storm runoff samples were obtained at this site.



#### 4.1.12.1 Dissolved Cu

**Figure 4.35** HMTV, CMC and statistical parameters of dissolved Cu concentrations [mg/L] in base flow and storm runoff samples for site 12 of Makara Stream.



**Figure 4.36** HMTV, CMC and statistical parameters of dissolved Zn concentrations [mg/L] in base flow and storm runoff samples for site 12 of Makara Stream.

#### 4.1.12.3 Dissolved Fe



**Figure 4.37** CTV and statistical parameters of dissolved Fe concentrations [mg/L] in base flow and storm runoff samples for site 12 of Makara.

# 4.1.13 Site 13 Data

A total of 17 base flow and 5 storm runoff samples were obtained at this site. There is no water hardness information available for Ohariu Stream. According to data provided in a study conducted by the GWRC [7], the Ohariu water hardness value is comparable to Makara's value and hence the samples from site 13 of Ohariu Stream were evaluate using the HMTV of Makara Stream.



# 4.1.13.1 Dissolved Cu

**Figure 4.38** HMTV, CMC and statistical parameters of dissolved Cu concentrations [mg/L] in base flow and storm runoff samples for site 13 of Ohariu Stream.

#### 4.1.13.2 Dissolved Zn



**Figure 4.39** HMTV, CMC and statistical parameters of dissolved Zn concentrations [mg/L] in base flow and storm runoff samples for site 13 of Ohariu Stream.





**Figure 4.40** CTV and statistical parameters of dissolved Fe concentrations [mg/L] in base flow and storm runoff samples for site 13 of Ohariu Stream.

# **4.2 Discussion of Base Flow and Wet Weather Flow Monitoring Data.**

# 4.2.1 Dissolved Cu

#### 4.2.1.1 Base Flow Samples

The median of dissolved Cu concentrations for base flow samples, as shown in Figure 4.41, exceeded the relative sustained toxicity triggers in all sites on the Porirua Stream (except site 3), site 5 on the Kenepuru Stream, all Karori Stream sites, site 12 on the Makara Stream and site 13 on the Ohariu Stream. The medians for samples from sites 6 and 7 on the Takapu Stream, site 3 on the Porirua Stream and site 11 on the Makara Stream did not exceed the corresponding chronic toxicity values.

Generally, as shown in Figure 4.42, the highest average of the median values of dissolved Cu concentrations in base flow samples were observed at suburban residential sites followed by light residential and then commercial sites. Notably, the average of the median values for dissolved Cu at rural sites did not exceed the ANZECC (2000) TV. This is an indication of the effect of residential discharges on the level of dissolved Cu. Evidently, as shown in Figure 4.41, the highest median of dissolved Cu amongst Porirua Stream sites was found at site 1 which has the lowest water flow and is close to a concentrated residential area, Johnsonville.



**Figure 4.41** Median values for dissolved Cu concentrations, in base flow and storm runoff samples, for sites 1-13. Visual comparisons between the median values and the ANZECC (2000) TV (green line); HMTVs for Karori Stream (yellow line), Makara and Ohariu Streams (purple line) and Porirua Stream (blue line); and the CMC (black line).



**Figure 4.42** ANZECC (2000) TV, CMC and average of the median values for dissolved Cu concentrations in base flow and storm runoff samples for suburban residential (sites 1, 5 and 8), commercial (sites 3, 4, and 7), light residential (sites 2, 9 and 10) and rural sites (6, 11, 12 and 13).

Previous monitoring data obtained between January 2008 and June 2009 of dissolved Cu for site 10 of Karori Stream by the GWRC [34], shown in Figure A1.8 in Appendix 1, reported that the median dissolved Cu concentrations was 0.0013 mg/L. Another study conducted by the GWRC, presented the results of a monitoring program from July 2009 to June 2010 for the same site where the median Cu concentrations was 0.00145 mg/L [4]. In our study the median of dissolved Cu concentrations at this site is 0.0021 mg/L. The values from all three studies exceed the HMTV for this site. In addition, the current study showed that base flow median value for dissolved Cu concentrations at sites 1 and 4 were 0.0033 and 0.0021 mg/L respectively, and were higher than the concentrations measured on 09/05/2006 (0.002 and 0.0015 mg/L respectively) by the GWRC [8], (the GWRC measured a single base flow sample for each of these sites in their study). The three studies clearly demonstrate that the concentrations of dissolved Cu in Wellington urban streams have been increasing over the five years of monitoring<sup>9</sup>.

#### 4.2.1.2 Storm Runoff Samples

The medians of dissolved Cu concentrations are higher in storm runoff samples than the corresponding base flow samples, except at site 2 where they are the same, as shown in Figure 4.41. The medians of dissolved Cu in all storm runoff samples at all sites exceeded the respective sustained exposure toxicity triggers. Notably, the medians of dissolved Cu concentration at sites 1 of Porirua Stream and 8 of Karori Stream are the only figures that exceeded the CMC, and the median of dissolved Cu concentrations at sites 3 almost approached the CMC.

Generally, as illustrated in Figure 4.42, the highest average of the median values for dissolved Cu concentrations was observed at sites located in suburban residential areas, and was the only figure that exceeded the CMC. The concentrations at the other types of sites were lower by a factor of at least two, as shown in Figure 4.42.

<sup>&</sup>lt;sup>9</sup> Different sampling and testing methods used in the three studies could be a factor of the increment found in dissolved Cu concentration.

Storm runoff contained elevated dissolved Cu concentrations that are higher than base flow and the recommended chronic toxicity triggers. The concentrations exceed the acute toxicity triggers in suburban residential catchments.

The observed elevated concentrations could originated from various sources. A study by Kennedy in the Wellington region in 1980, reported elevated concentrations of Cu in accumulated particulate materials of urban gutter and road surfaces [16]. These results showed that Cu contaminated all dust and accumulated particulates samples in the Wellington region. The author suggested the corrosion of trolley bus wires (this could only be applicable for Karori Stream sites) and vehicle brake lining wear could account for some of the elevation in the gutter/road dusts of the Wellington region [16]. More detailed results were provided in another study done by Kennedy and Gadd [15]. They examined several potential sources of Cu in the New Zealand's environment. The results indicated that the highest median of Cu concentration was for brake pad dust samples (219.5 mg/kg); and the median for brake pads, tyres, raw bitumen and road bitumen were 35.5, 1, <1, and 46.3 mg/kg respectively.

Our analysis of rainwater runoff samples from roofs and paved surfaces, discussed in Chapter 5, showed that elevated concentrations of dissolved Cu were found, especially in first flush samples, which agrees with the previously mentioned studies. However this study has identified an additional source of Cu, the analysis of urban atmospheric rainfall samples showed the presence of dissolved Cu at concentrations higher than the ANZECC (2000) TV, and the highest concentrations were observed in samples collected from the Mt. Victoria tunnel. This source has not been considered in previous works in the country. The data on atmospheric rainfall samples are also discussed in Chapter 5.

As noted in Chapter 2, there are only a limited number of storm water studies from New Zealand, particularly investigating heavy metals. The results of the GWRC study [7], concluded that the concentrations of dissolved Cu in Wellington storm water were higher than the ANZECC (2000) TV, which is consistent with this study, Figure 4.41 and Figure 4.43. Moreover, the average of the median values for dissolved Cu concentrations (0.0073 mg/L) at suburban residential catchments is higher than what was observed earlier (0.00545 mg/L) [7]. The same study showed markedly higher median for dissolved Cu in samples collected from commercial

catchments, shown in Figure 4.44, than those observed in this study. This study recorded concentrations for a suburban residential catchment (site 1) similar to those recorded for commercial catchments.



**Figure 4.43** ANZECC (2000) TV and a summary of dissolved Cu, range 0.0025-0.0225 [mg/L], in 11 monitored storm runoff at 11 different sites within the Wellington region by the GWRC [7]. Note that this figure is constructed from data presented in a table in [7].



**Figure 4.44** The median dissolved Cu concentrations  $[g/m^3]$ , standard error and land-use in monitored storm runoff at 6 residential sites: Owhiro Stream; Browns Stream; The Parade; McLeod Park; Duck Creek; Grassleas Reserve and five industrial and commercial sites: Te Roto Drive; Semple Street ; Hutt Park Road; Waring Taylor Street; Parkside Road. Figure taken from [7].

Comparison with the Rotorua data set [6], discussed in Chapter 2, shows that the data are comparable (Table 4.1).

**Table 4.1** Comparison between the average of the median values for dissolved Cu concentrations for residential and commercial catchments obtained by this study and median values of the respective catchments in the study conducted in Rotorua.

Year	Place	Catchment type	Cu concentration [mg/L]	Reference
2011	Wellington	Suburban residential	0.0073	This study
2011	Wellington	Light residential	0.0032	This study
1999-2001	Rotorua City	Residential	0.0041	[6]
2011	Wellington	Commercial	0.0037	This study
1999-2001	Rotorua City	Commercial	0.005	[6]

#### **4.2.1.3 First Flush and Composite Samples**

As can be seen in Figure 4.45, dissolved Cu concentrations in all first flush samples exceeded the respective chronic toxicity triggers except at site 9. Except at sites 4 and 9, composite figures exceeded the relevant sustained toxicity triggers. No exceedance was recorded for the CMC criteria. Six of a total of eight monitored storms runoff showed the first flush effect.



**Figure 4.45** The median values for sites 1 and 8 and single data for sites 4, 5, and 9 of dissolved Cu concentrations in first flush and composite samples. Also shown are visual comparisons of Cu concentrations in first flush and composite samples against the ANZECC (2000) TV (green line); HMTVs for Karori Stream (red line), and Porirua Stream (blue line); and the CMC (black line).

Compared to previous work, the concentrations of dissolved Cu in first flush and composite samples were lower than those observed by the GWRC between 2005 and 2007 [8], as shown in Figure 4.46. Moreover, the same study showed that first flush concentrations of dissolved Cu in 17 storm runoff events were lower than composite samples and two first flush and eight composite samples exceeded the CMC. In contrast, this study demonstrates that dissolved Cu in first flush samples tended to be higher than the composite samples and no sample exceeded the CMC, Figure 4.46.



**Figure 4.46** ANZECC (2000) TV, CMC and summary of dissolved Cu concentrations [mg/L] in first flush, and composite samples by this study and by the GWRC [8].

# **4.2.1.4 Summary of Dissolved Cu Concentration in Base Flow and Wet Weather Flow Waters.**

The median values for dissolved Cu concentrations in base flow exceeded the respective HMTVs and ANZECC (2000) TV at 9 of 13 sites. Severe excedence was recorded for sites 1 and 2 of Porirua Stream. The medians of dissolved Cu concentrations in base flow condition tended to be higher than those reported by the GWRC from previous monitoring.

The medians of dissolved Cu concentrations in storm runoff waters exceeded the CMC at sites 1 and 8, and this is attributed to the sites being adjacent to concentrated residential areas. The average of the median value for samples collected from suburban residential catchments is higher than those collected from other catchments. The average of the median values of dissolved Cu concentrations in storm runoff waters for residential areas was higher than those recorded by the GWRC [7]. The Rotorua study reported comparable concentrations to those reported in this study for storm water runoff from suburban and light residential and commercial catchments.

The first flush effect was exhibited in six storm runoff events and the concentrations of dissolved Cu in first flush and composite samples were higher than the relevant chronic toxicity triggers, except the storm runoff at site 9. All first flush and composite samples were lower than the CMC. Generally, the reported first flush monitoring data is lower what was observed during 2005-2007 by the GWRC [8].

## 4.2.2 Dissolved Zn

#### 4.2.2.1 Base Flow Samples

As can be seen in Figure 4.47, the median of dissolved Zn concentration in base flow samples for all Porirua Stream sites; site 5 of Kenepuru Stream; sites 6 and 7 of Takapu Stream; and all Karori Stream sites exceeded the respective sustained toxicity triggers. The rural sites of Makara and Ohariu Streams however, did not exceed the HMTV but almost equal to it. As shown in Figure 4.48, suburban residential catchments had the highest value of dissolved Zn concentrations followed by commercial and then light residential. The average of the median values for dissolved Zn for the rural sites was the lowest and about equal to the ANZECC (2000) TV.



**Figure 4.47** The median values of dissolved Zn concentrations in base flow and storm runoff samples obtained from sites 1-13. Visual comparisons of the median of dissolved Zn concentrations against the ANZECC (2000) TV (green line); HMTV for Karori Stream (yellow line), Makara and Ohariu Streams (purple line) and Porirua Stream (blue line); and (CMC) (black line).



**Figure 4.48** ANZECC (2000) TV, CMC and the average of the median values for dissolved Zn concentrations in base flow and storm runoff samples for suburban residential (sites1, 5 and 8); commercial (sites 3, 4, and 7); light residential (sites 2, 9 and 10) and rural sites (sites 6, 11, 12 and 13).

According to unpublished data of the GWRC for site 10, summarised in Figure A1.8 in Appendix 1, the median of dissolved Zn data obtained between January 2008 until June 2009 was 0.021 mg/L [34]. Perrie, *et al.* showed the results of the GWRC monitoring program during July 2009 to June 2010 where the median of the data was 0.018 mg/L [4]. The current study observed the median of Zn concentrations for the period of monitoring to be 0.03 mg/L. All the three studies agree in that dissolved Zn concentrations exceeded the HMTV at site 10 of Karori Stream; and the highest value was associated with the current study. In regard to Porirua Stream, the median of dissolved Zn concentrations measured on 09/05/2006 by the GWRC, 0.017 and 0.043 mg/L respectively [8], (the GWRC measured a single base flow sample for each of these sites in their study).

#### 4.2.2.2 Storm Runoff Samples

Overall, the medians for dissolved Zn concentrations were higher in storm runoff samples than the corresponding base flow samples, except for site 12. As can be seen in Figure 4.47, the medians of dissolved Zn in storm runoff samples at all sites, except site 12, exceeded the respective sustained toxicity triggers. The CMC was exceeded by sites 1, 2, 3, 5 and 8.

As with dissolved Cu, the average of the median of dissolved Zn concentrations for samples collected from suburban residential catchments were the highest followed by samples from commercial and then light residential sites. Rural sites showed the lowest value, as shown in Figure 4.48. Clearly, dissolved Zn was more abundant in storm water than dissolved Cu.

Kennedy, reported high Zn concentration in accumulated particulates on gutter and road surfaces in the Wellington region. The presence of Zn as a contaminant in accumulated particulate materials on gutter/road surface was attributed to soil derived Zn; zinc-based alloys (galvanised roofs), motor oils and vehicle emissions, tyres, bake pad/ brake pad dust and paint materials [16]. Kennedy and Gadd measured significantly higher median Zn concentrations in samples, ranging between 5.5 and 8310 mg/kg, for tyres (highest), brake pad dust, brake pads, raw bitumen, and road bitumen (lowest) used in New Zealand [15].

Analysis of rainwater runoff from roofs and paved surface samples in the current study revealed elevated concentrations of dissolved Zn especially in first flush samples, whereas accumulated dust/particulates are flushed off by the first portion of rainfall. Runoff from galvanised roofs showed very high concentrations even after the first flush, indicating that Zn leaches from the surface of the roofs.

The analysis of urban atmospheric rainfall samples showed the presence of dissolved Zn at concentrations higher than ANZECC (2000) TV, and more elevated concentrations were observed at a site adjacent to a road with high traffic density (Mt. Victoria tunnel). Refer to atmospheric rainfall samples in Chapter 5.

Both this study and the data collected by the GWRC [7], illustrated in Figure 4.49, point to the same conclusion, that the concentrations of dissolved Zn in Wellington storm waters are higher than the ANZECC (2000) TV. They also agree that Zn concentrations exceeded the CMC in samples collected from residential catchments. However, they are at odds regarding dissolved Zn from commercial catchments, where the concentration exceeded the CMC in the GWRC data [7] (Figure 4.50). It is worth noting that dissolved Zn concentrations at site 1 were similar to those reported by the GWRC for industrial catchments.



**Figure 4.49** ANZECC (2000) TV and a summary of dissolved Zn, range 0.022-1.05 mg/L, in 11 storm runoff water samples at 11 different sites within the Wellington region by the GWRC, 2002 [7]. Note that this figure is constructed from data presented as a table in [7].



**Figure 4.50** The median Zn concentration, standard error and land-use for the monitored storm water in six residential sites: Owhiro Stream, Browns Stream, The Parade, McLeod Park, Duck Creek, Grassleas Reserve, and five industrial and commercial sites: Te Roto Drive, Semple Street, Hutt Park Road, Waring Taylor Street, Parkside Road. The figure taken from [7].

Dissolved Zn data compared with the data from Roturua City are comparable, but the Rotorua commercial catchment has a markedly higher concentration than the Wellington commercial catchment (Table 4.2) [6].

**Table 4.2** Comparison between the average of the median values for dissolved Zn concentrations for residential and commercial catchments obtained by this study and median values of the respective catchments in the study conducted in Rotorua.

Year	Place	Catchment type	Dissolved Zn concentration [mg/L]	Reference
2011	Wellington	Suburban	0.072	This study
		residential		
2011	Wellington	Light residential	0.050	This study
1999-2001	Rotorua City	Residential	0.033	[6]
2011	Wellington	Commercial	0.053	This study
1999-2001	Rotorua City	Commercial	0.096	[6]

#### 4.2.2.3 First Flush and Composite Samples

All dissolved Zn concentrations in first flush and composite samples exceeded the respective sustained toxicity triggers, as shown in Figure 4.51. Average dissolved Zn exceeded the CMC for first flush and composite samples at site 8, and approached this level at sites 1 and 5. The highest Zn concentrations were observed at site 8 followed by sites 5 and 1. The first flush effect was exhibited in storm runoff monitored at sites 1, 5, 8, and 9 (Figure 4.51).



**Figure 4.51** The medians for sites 1 and 8, and single data for sites 4, 5 and 9 of dissolved Zn concentrations in first flush and composite samples. Shown are visual comparisons of Zn concentrations against the ANZECC (2000) TV (green line), HMTVs for Karori Stream (red line), and Porirua Stream (blue line); and (CMC) (black line).

Comparison with previous work shows that the results of this study and data obtained between 2005-2007 by the GWRC,[8], agree on observing first flush effect for dissolved Zn, shown in Figure 4.52. The concentrations of dissolved Zn in this study however are higher than those reported by the GWRC,[8], in both first flush and composite samples, as shown in Figure 4.52.



**Figure 4.52** ANZECC (2000) TV, CMC and a summary of dissolved Zn concentrations [mg/L] in first flush and composite samples by this study and by the GWRC, between 2005-2007 [8].

# 4.2.2.4 Summary of Dissolved Zn Concentrations in Base Flow and Storm Runoff Monitoring

Overall, the medians of dissolved Zn concentrations in base flow were higher than the respective chronic water quality guidelines at all sites excepting sites of Makara and Ohariu Streams, the rural sites. The median of dissolved Zn concentrations in storm runoff samples were higher than the corresponding base flow samples, and elevated compared to their sustained toxicity triggers. Similarly to the Cu results, the highest concentrations were observed at suburban residential catchments, and were lowest for rural catchments; values of commercial and light residential catchments fall in between.

Comparisons of the data with previous work shows comparable concentrations were observed by the GWRC [7], in the Wellington region of residential catchments; however, the concentrations recorded for site 1 in this study tended to be similar to those observed for industrial catchments. Data from Rotorua and this study are of the same order of magnitude.

The first flush effect was observed in five storm runoff events and the concentrations of dissolved Zn in first flush and composite samples exceeded the CMC at site 8. The study by the GWRC [8], conducted in the Wellington region, reached the same conclusion, however, higher concentrations were recorded in this study.

#### 4.2.3 Dissolved Fe

#### 4.2.3.1 Base flow Samples

As can be seen in Figure 4.53, all the base flow medians of dissolved Fe concentrations were below the CTV except at site 5. Because the results of this site were anomalous, site 5 of Kenepuru Stream was further investigated by analysing base flow stream water samples from up and downstream of the sampling site. A total of eight samples were analysed, with a concentration range of 0.39-1.57 mg/L. Some of the samples were obtained directly from springs that drain directly to the Kenepuru Stream, and the samples contained orange clay. It was concluded that the concentration of dissolved Fe at this stream is naturally elevated. The concentrations of dissolved Fe was reported by Hodder at elevated levels for Ngawha Springs in Taupo, [53], similar to those found in this study for site 5 and they noted that the origin of the elevated level of dissolved Fe concentration is due to hydrothermal activity.

The data provided by the GWRC [34], summarised in Appendix 1, Figure A1.8, for site 10, show that the median of dissolved Fe concentrations was below the CTV which is consistent with this study. However, the median of dissolved Fe concentrations measured in this study is higher.



**Figure 4.53** The median values for dissolved Fe concentrations in base flow and storm runoff samples from sites 1-13, and visual comparisons between the median values and the CTV.



**Figure 4.54** The CTV and average of the median values for dissolved Fe concentrations in base flow and storm runoff samples for suburban residential (sites 1, 5, 8), commercial (sites 3, 4, 7), light residential (sites 2, 9 and 10), and rural sites (sites 6, 11, 12 and 13).

#### 4.2.3.2 Storm Runoff Samples

Figure 4.54 clearly shows the medians of dissolved Fe concentrations were higher in storm runoff than the corresponding base flow samples. The CTV was exceeded in sites 1, 3, 4, 5, 9, 11, 12, and 13.

Suburban residential sites had the highest values of dissolved Fe in storm runoff samples, as shown in Figure 4.54 (remembering that the contribution of site 5 to this figure is not manmade contamination. Rural sites 11, 12, 13 showed high dissolved Fe during runoff events in contrast to what was observed for dissolved Cu and Zn. Fe is a key component element in soils and sediments [16]. At these rural sites, there is very little, if any, piping and tunnelling of the streams, so water during runoff has a greater contact with soil and sediment. Samples collected from the rural sites had higher amount of suspended solid (based on visual observation). This might explain the higher concentrations observed.

The observed elevated dissolved Fe concentrations, particularly those recorded for suburban residential and commercial catchments, could have originated from various sources. Kennedy indicated that Fe is a common contaminant in accumulated materials in the Wellington region, ranging from 1.64 to 4.76% [16]. The prevalence of Fe was attributed to the rusting process of iron in buildings and car components, with a little from tyres, raw bitumen and brake pad/dust. The concentrations of Fe in accumulated dust/particulates in gutter and on road surfaces were higher than what would be expected from soil or sediment samples [16]. Kennedy and Gadd [15] found that samples obtained from New Zealand tyres had the highest median Fe concentration of 105 mg/kg when compared with the other analysed samples; brake pads, raw bitumen and road bitumen.

In the GWRC study, [7], the median for dissolved Fe concentrations of the 11 storm runoff events sampled between June 2002 and September 2004 was 0.08 mg/L (range <0.02-0.24). This range is markedly lower compared with what has been observed for the respective catchments in this study. Nevertheless, comparable medians of the dissolved Fe concentrations were observed at site 7 of Takapu Stream and site 8 of Karori Stream in both studies.

Dissolved Fe concentrations during runoff events were also compared with Rotorua city data [6]. The concentrations recorded in this study are significantly higher than the corresponding concentrations, as shown in Table 4.3.

**Table 4.3** Comparison between the average of the median values for dissolved Fe concentrations for residential and commercial catchments obtained by this study and median values of the respective catchments in the study conducted in Rotorua.

Year	Place	Catchment type	Dissolved Fe concentration [mg/L]	Reference
2011	Wellington	Suburban	0.4	This study
		residential		This study
2011	Wellington	Light residential	0.27	This study
1999-2001	Rotorua City	Residential	0.04	[6]
2011	Wellington	Commercial	0.37	This study
1999-2001	Rotorua City	Commercial	0.08	[6]

#### 4.2.3.3 First Flush and Composite Samples

Figure 4.55 shows that dissolved Fe concentrations at site 1 and site 5 for first flush and composite samples exceeded the CTV. As noted earlier, the elevated dissolved Fe concentration at site 5 is probably natural. First flush monitoring showed that one event at site 5 of Kenepuru Stream and two events at site 8 of Karori Stream exhibited first flush effect. In general, the first flush of dissolved Fe is weak compared with dissolved Cu and Zn.


Figure 4.55 The CTV and the median values for site 1 and site 8, and a single data of dissolved Fe concentrations for sites 4, 5, and 8 in first flush and composite samples.

#### 4.2.3.4 Summary of Dissolved Fe Concentrations in Base Flow and Storm Runoff Monitoring

Base flow median concentrations of dissolved Fe at the monitored catchments were below the CTV except site 5 of Kenpuru Stream which is probably not an anthropogenic contribution. The concentrations of dissolved Fe were higher in storm runoff than the base flow. Dissolved Fe in storm runoff samples at light residential areas is the only figure that does not exceed the CTV. Three storm runoff events showed the first flush effect, one event at sites 5, and two events at 8. Dissolved Fe was recorded during runoff events at markedly higher levels than those recorded by previous work in the Wellington region and within New Zealand [6-7].

#### 4.2.4 First Flush of Dissolved Metals and Antecedent Dry Weather

The longest period of dry weather observed in this study was 10 days. Storm water runoff occurring after this period was observed as a first flush at two sites (sites 8 and 9). The antecedent period of dry weather associated with other first flush monitoring events varied from 1 day to 8 days.

It might be expected that the highest concentration of first flush of dissolved metals would appear with runoff events associated with longest preceding period of dry weather [29]. This does not necessarily seem to be true, although the amount of data is limited, considering the monitored storm runoff events at site 1, as shown in Figure 4.56, the highest concentrations of dissolved Cu and Fe for first flush samples amongst the three storm runoff events appeared with the longest preceding period of dry weather followed by the event with only one preceding non raining day and the lowest concentrations were observed with the event associated with five preceding fine days. There was no obvious relation between the concentrations of dissolved Zn in the three monitored storm runoff events at site 1 in comparison to the other metals. A storm runoff event at site 8 that occurred after 10 days of dry weather, as shown in Figure 4.57, resulted in the highest first flush of dissolved Fe and Zn, but the highest dissolved Cu concentration was associated with the storm runoff that occurred after 1 day of dry weather. It should be noted that there are other factors that contribute to the natural behaviour of heavy metals in a first flush, such as rainfall intensity, runoff volume and the physical characteristics of the runoff land [30, 54], which were not considered in this study. The results of the first flush of Zn at site 1 is at agreement with what has been reported by Schriewer and co-authors [55]. They found higher Zn concentrations were associated with low rain intensities, and were independent of the antecedent dry weather period.



**Figure 4.56** Comparison between the concentrations of dissolved Cu, Zn and Fe [mg/L] in first flush samples associated with different duration of dry weather at site 1 of Porirua Stream.



**Figure 4.57** Comparison between the concentrations of dissolved Cu, Zn and Fe [mg/L] in first flush samples associated with different duration of dry weather at site 8 of Karori Stream.

## Chapter 5

# 5 Investigation of Possible Sources of Dissolved Metals in Storm Water

#### **5.1 Atmospheric Rainfall Samples**

Rainfall samples were collected between December 2010 and July 2011 at the main collection site, the roof of second floor of the Laby building, VUW. A total of 24 rainfall events were sampled at Laby building. The data presented here, shown in Figure 5.1 and Figure 5.2, were obtained using the pre-concentration regime or direct analysis on FAAS. The concentrations are given in Table A. 36 in Appendix 1. In addition, there were seven samplings of atmospheric rainfall events at two other locations in the Wellington region, between April and July 2011; Table 5.1 summarises this data.



**Figure 5.1** Summary of dissolved Cu concentrations [mg/L] in the atmospheric rainfall samples collected at VUW.



Zn in atmospheric rainfall samples Fe in atmospheric rainfall samples

Figure 5.2 Summary of dissolved Zn and Fe concentrations in the atmospheric rainfall samples collected at VUW.

**Table 5.1** Dissolved Cu, Zn and Fe concentrations [mg/L] in atmospheric rainfall samples collected at site 13, Takarau Gorge Road and at the top of Mt. Victoria tunnel between April and July 2011.

Site name and	Number	Concentration range and median			
characteristic	of samples	Cu [mg/L]	Zn [mg/L]	Fe [mg/L]	
Site 13, Rural	4	*<0.0012-0.0066 Median = 0.0025	0.01-0.08 Median = 0.035	**<0.045-0.09 Median = 0.05	
Mt. Victoria tunnel (urban with high traffic volume)	3	0.0045-0.03 Median = 0.0093	0.13-0.25 Median = 0.23	<0.045-0.06 Median = 0.05	

\*: Dissolved Cu in two samples were below the enhanced detection limit of Cu. \*\*: one sample for dissolved Fe below the detection limit of Fe.

Rainwater has no specific toxicity guidelines for heavy metals. The ANZECC (2000) TV, CMC, and CTV would give an indication of contamination levels; therefore, they were used to assess rainwater.

To the best of our knowledge, none of the existing local (in New Zealand) or international storm water literature has considered rainfall as a contributor to the contamination by heavy metals in streams. In most cases the presence of metal contamination was attributed to runoff from roofs and impervious surfaces [1-2, 12-14, 7-8, 29, 32, 35-36]. Rainwater has been recognised as a contributor to metal pollution in drinking water from roof harvesting systems. The data from our rainwater samples clearly illustrates the following points:

- The median dissolved Cu and Zn concentrations in rainwater samples are higher than the ANZECC (2000) TV values.
- 2) The median of dissolved Fe concentrations was lower than the CTV.
- The median of dissolved Cu concentrations was almost equal to and the median of dissolved Zn concentrations was higher than the CMCs.
- Higher concentrations of dissolved Cu and Zn were associated with longer periods of dry weather before the rainfall events.
- 5) Comparison of the different sampling sites shows that the highest median dissolved Cu and Zn concentrations were in samples collected from Mt. Victoria tunnel, followed by VUW. The results are in agreement with what was found by Davy who measured metal concentrations of airborn particulate matter [56]. He found the concentrations of Cu, Zn and Fe in airborne particulates were higher at the Mt. Victoria tunnel than those for residential and rural sites (refer to Table 5.2). In Auckland, Simmons *et al.* [32] found dissolved Cu concentrations in drinking water samples, collected by roof harvesting systems, were higher at urbanised sites than the samples from rural sites. Huston and co-workers [57] in Australia noted that rainfall contributed to dissolved Cu, Zn and Fe concentrations found in drinking water samples collected by roof harvesting systems.

As mentioned in point 5, the concentrations and composition of airborne particulate matter in the Wellington region have been studied by Davy [56]. In that study, it was concluded various sources contributed to  $PM_{2.5}$  and  $PM_{10}^{10}$  aerosols in the Wellington region. Aerosol concentration and elemental composition varied, depending on the site (Table 5.2).

**Table 5.2** Average of the concentrations<sup>11</sup> of Cu, Zn and Fe in airborne particulate  $PM_{2.5}$  and  $PM_{10}$  [56].

Site name	Site characteristics	Cu [ng/m <sup>3</sup> ]	Zn [ng/m <sup>3</sup> ]	Fe [ng/m <sup>3</sup> ]
<b>Bering Head</b>	Rural	Not recorded	Not recorded	24
Masterton	Rural residential	6	11	84
Mt Victoria	Urban with high	170	121	2564
Tunnel	traffic	177	121	2304
Upper Hutt	Residential with light industrial	2	6	49
Lower Hutt	Industrial area	3	28	163

As noted in the experimental section, Chapter 3, metals in this study were measured after filtrating the samples using 0.45  $\mu$ m filters. Consequently, any PM<sub>2.5</sub> and PM<sub>10</sub> might be able to pass through the pores of the filter. Alternatively, the metals attached to the airborne aerosol may be soluble in water.

It is concluded that atmospheric rainwater contains dissolved concentrations of Cu and Zn that contribute to the concentrations of the metals in storm water. The median of dissolved Fe concentrations were found to be below the CTV.

 $<sup>^{10}</sup>$  PM<sub>2.5</sub> and PM<sub>10</sub>: particulate matter with aerodynamic diameters less than 2.5 and 10  $\mu$ m respectively.

<sup>&</sup>lt;sup>11</sup> The concentrations were reported separately for each particle size. In the table, the numbers are the sum of the values for both  $PM_{2.5}$  and  $PM_{10}$ .

#### **5.2 Roof Runoff Samples**

A total of 28 roof runoff samples were collected and analysed for roofs located in the Wellington region mainly commercial roofs in the Wellington Central, Karori, Tawa and Porirua. The samples comprise of:

- 15 samples of galvanised roof runoff, shown in Table A1.37 and visualised in Figures 5.3, 5.4 and 5.5.
- The result of four first flush samples from galvanised roof runoff with their associated delayed runoff samples, shown in Table 5.3.



• Three tile roof runoff samples, shown in Table 5.4.

**Figure 5.3** Summary of dissolved Cu concentrations [mg/L] from galvanised roof runoff samples.



**Figure 5.4** Summary of dissolved Zn concentrations [mg/L] from galvanised roof runoff samples.



**Figure 5.5** Summary of dissolved Fe concentrations [mg/L] from galvanised roof runoff samples.

**Table 5.3** Dissolved Cu, Zn and Fe concentrations [mg/L] in first flush and delayed runoff samples collected from galvanised roofs.

Sample	Cu [mg/]	L]	Zn [mg/L]		Fe [mg/L]	
number	First flush	Delayed	First flush	Delayed	First flush	Delayed
1	0.0099	< 0.0012	0.28	0.28	0.88	< 0.045
2	0.0042	< 0.0012	0.29	0.025	0.26	< 0.045
3	0.0324	0.0021	0.9	<b>1.56</b> <sup>12</sup>	< 0.045	< 0.045
4	0.0021	0.0036	1.37	0.15	< 0.045	< 0.045

**Table 5.4** Dissolved Cu, Zn and Fe concentrations [mg/L] in samples collected from tile roof runoff.

Metal	Concentration range [mg/L]
Cu	<0.0012-0.0024
Zn	0.03-0.06
Fe	< 0.045

ANZECC (2000) TVs, CMCs, and CTV were used to assess metal contamination in roof runoff sample.

As can be seen in Figure 5.3 and Figure 5.4, the median of dissolved Cu and Zn concentrations were higher than the ANZECC (2000) TVs, and Zn exceeded the CMC. Dissolved Fe concentrations on the other hand, did not exceed the CTV except in one sample. The same conclusion can be drawn from data presented in a study reported by Simmons *et al.* in Auckland [32]. The data are for potable water collected using roof harvesting systems, however, they reported significantly higher

<sup>&</sup>lt;sup>12</sup> The concentration in delayed sample is higher than the concentration in first flush sample which could be a result of roof corrosion rather than accumulated particulates.

median dissolved Cu and Zn concentrations (0.06, 0.4 mg/L respectively) than those measured in this study.

Tile roof samples contained less dissolved Cu and Zn concentrations than those observed from galvanised roof runoff samples, as shown Table 5.4. Yaziz *et al.*, who studied the variations in rainwater quality (several water contaminants including heavy metals) from roof catchments in Malaysia [30], demonstrated the same outcome. These concentrations could have been derived from rainfall. Dissolved Fe concentrations were below the detection limit, as shown in Table 5.4.

The concentrations of dissolved metals, particularly Cu and Fe, in first flush samples were higher than in the corresponding delayed roof runoff samples (except dissolved Zn in one event where the concentration in the delayed sample is 0.66 mg/L higher than the concentration in first flush sample), as shown in Table 5.3, suggesting the presence of accumulated material (dust particulates) containing the metal of concern.

The concentrations of dissolved Cu and Fe in rainfall, collected at VUW, and in roof runoff samples (all types) are similar, indicating that the roof runoff Cu and Fe are mainly derived from rainfall. In contrast, dissolved Zn concentrations from galvanised roof runoff samples are higher than the atmospheric rainfall samples. This indicates that galvanised roofs are an additional source of dissolved Zn in storm water, as has been suggested previously [12, 36, 58-60].

#### **5.3 Paved Surface Runoff Samples**

A total of 16 samples were collected and analysed for runoff from paved surfaces that serve road, parking and entertaining usages. In most cases, the samples were collected from places close to VUW and to the monitored sites. Dissolved Cu, Zn and Fe concentrations are presented in Table A1.38, Appendix 1, and visualised below. The result of first flush monitoring is presented in Table A1.39, Appendix 1.



Figure 5.6 Summary of dissolved Cu concentrations [mg/L] in paved surface runoff samples.



Zn in Paved surface runoff samples Fe in Paved surface runoff samples



As can be seen in Figure 5.6 and Figure 5.7, the median of dissolved Cu and Zn concentrations were above the ANZECC (2000) TVs and below the CMCs. The median of dissolved Fe concentrations did not exceed the CTV.

Runoff from Middleton Road was measured at site 1. Notably, there is probably little roof contribution in this runoff because the draining pipe drains storm runoff from a section of the road, which has no houses on it. The concentrations of dissolved Cu and Zn in the first flush sample were 0.0023 and 0.043 and 0.0012, 0.040 mg/L in composite sample respectively (for details of this monitoring refer to Table A1. 39, Appendix 1). During the same runoff event, a single first flush sample was obtained at site 1 but from another drainage outlet that discharges road runoff from Wingfield Place which passes through a residential area and could contain roof runoff. The concentrations of dissolved metals were 0.0015, 0.17, and 0.06 mg/L for Cu, Zn, and Fe respectively (note that there is no composite sample<sup>13</sup>). Dissolved Zn in the latter first flush sample was 4-fold higher than the other first flush of road runoff. This clearly illustrates the effect of roof material on the amount of dissolved Zn in storm water.

As mentioned earlier in Section 4.2.2, Zn has been reported at elevated levels in tyres commonly used in New Zealand and brake pads/dust samples [15]. The mechanical action between tyres and surface causes tyre components to leach into the environment [14]. Sampling of a runoff event from an outdoor field used for go-kart racing in Porirua was carried out in this work. The site is located 400 meters upstream from site 4 on Porirua stream. The concentrations of dissolved Cu, Zn and Fe in first flush sample were 0.0033, 0.93 and 0.06 and 0.0023, 0.33 and 0.1 mg/L in composite sample respectively. This is an indication that worn out materials containing these metals accumulated during the dry period, and were flushed off by the first portion of the rain runoff.

The data from paved surface runoff can be compared with similar New Zealand and international studies. The concentrations of dissolved Cu and Zn are of the same order of magnitude as the data reported in the study done in the Wellington region by Sherriff [35], the study conducted by Wicke *et al.* in Christchurch [37] and the study conducted by Stenstrom *et al.* in California [29].

<sup>&</sup>lt;sup>13</sup> The water level rose very quickly and the sampling had to be stopped for safety reasons.

#### Chapter 6

### **6** Conclusion and recommendations

This work set out to determine the concentrations of dissolved Cu, Zn and Fe during base and wet weather flow at streams throughout the Wellington region. A secondary objective was to investigate possible sources of heavy metals during rainfall events.

Three dissolved trace metals Cu, Zn and Fe were measured at 13 sites on five streams in base flow conditions and during runoff events in the Wellington region between January and July 2011. More than 240 base flow and 100 wet weather flow samples were analysed for the three dissolved metals. Additionally, 24 rainfall events and runoff from different roof types and paved surface were collected and analysed for dissolved Cu, Zn, and Fe. The analysis was performed by Flame Atomic Absorption Spectroscopy (FAAS). A pre-concentration procedure, using Chelex-100, was developed and successfully used to enhance the concentrations of dissolved Cu and Zn.

The medians of dissolved heavy metals, Cu, Zn, and Fe all of which are potentially toxic to aquatic life, exceeded the long-term (chronic) toxicity guidelines at one site for Fe, nine sites (69%) for Cu and 10 sites (77%) for Zn in base flow conditions. Comparison of base flow monitoring data with previously reported concentrations indicated that the concentrations of the studied metals have increased over the last five years.

Storm water (wet weather flow conditions) contained elevated levels of dissolved heavy metals in comparison to base flow concentrations and the recommended guidelines, the ANZECC (2000) TVs and the CTV. Dissolved Cu and Zn exceeded the short-term (acute) toxicity criteria at suburban residential sites. On the other hand, dissolved Fe concentrations exceeded the sustained toxicity exposure trigger at eight sites (61%). A distinct catchment type contaminant concentration (dissolved Cu and Zn) was observed during storm runoff events with the pattern of suburban residential > commercial > light residential > rural catchment of relative metals

abundance. Dissolved Fe showed a similar pattern, but the rural concentration was higher than light residential catchments concentration. The observations were attributed to the high vehicle traffic, accumulated particulate materials and corrosion of materials containing heavy metals such as galvanised or copper roofs, gutter systems and building construction materials. The strongest and most obvious first flush effect was observed with dissolved Cu followed by dissolved Zn; first flush of dissolved Fe however was observed in only three of a total of eight storm runoff events. The concentrations of dissolved metals are in the same order of magnitude as previously reported data for the Wellington region, but higher concentrations were recorded in this work, particularly dissolved Fe. The results are of the same order of magnitude with data sets of other New Zealand regions.

Investigations of possible sources of dissolved heavy metals in storm runoff samples demonstrated that rain water contained markedly elevated dissolved Zn and smaller Cu concentrations in comparison to the ANZECC (2000) TVs. The concentrations of dissolved Fe were below the CTV level.

Roof runoff samples had similar dissolved Cu and Fe concentration to those recorded in atmospheric rainfall water, but Zn was found to be higher in galvanised roof runoff so galvanised roof runoff is an additional contributor to dissolved Zn in storm water. First flush samples from roof runoff had higher concentrations than the delayed runoff samples, indicating the presence of accumulated particulates containing metals. Paved surface runoff samples had concentrations of dissolved Cu and Zn higher than chronic toxicity triggers, and the median of the concentrations of these metals did not exceed the acute toxicity guidelines. Median dissolved Fe concentrations were below the CTV criteria. Comparable results have been reported in the New Zealand and international literature.

The outcomes of this project imply that there could be possible adverse impacts to the residing aquatic life as a result of the exposure to high concentration of the studied metals. Accumulation of Cu, Zn and Fe in sediment which leads to sediment toxicity is most likely. Monitoring dissolved heavy metals (in particular, Cu and Zn) at Wellington's suburban sites should be continued during dry and wet weathers. Biological toxicity surveys should be undertaken in order to provide a definite decision regarding the possible adverse effects. The amount of Cu, Zn and Fe could be reduced during rainfall events by performing surface painting and maintenance processes.

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# Appendix 1

Data and figures from which figures and arguments were constructed the main text body are included below, unless it is already mentioned. In addition, an electronic copy of the raw data is attached to the thesis for further readings.

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# A1.1 Site 1 Data

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	19	3	3	10
Number of omitted samples Minimum [mg/L]	7 0.0021	0 0.0033	0 0.0026	4 0.0033
25 <sup>th</sup> percentile [mg/L]	0.0029	0.0034	0.0027	0.0044
Median [mg/L]	0.0033	0.0036	0.0028	0.0099
75 <sup>th</sup> percentile [mg/L]	0.006	0.0037	0.0033	0.081
Maximum [mg/L]	0.012	0.0039	0.0039	0.14
Average [mg/L]	0.0050	0.0036	0.0031	0.031
Std. dev. [mg/L]	0.0032	0.0030	0.0007	0.053
*Factor of exceeding the HMTV	1.8	2	1.5	5.4
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not exceeding	1.6

 Table A1.1 Dissolved Cu concentrations (mg/L) at site 1 of Porirua Stream.

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	19	3	3	10
Number of omitted samples	1	0	0	0
Minimum [mg/L]	0.020	0.050	0.046	0.034
25 <sup>th</sup> percentile [mg/L]	0.026	0.052	0.047	0.060
Median [mg/L]	0.055	0.055	0.047	0.070
75 <sup>th</sup> percentile [mg/L]	0.087	0.059	0.059	0.18
Maximum [mg/L]	0.150	0.063	0.070	0.560
Average [mg/L]	0.060	0.056	0.0545	0.160
Std. dev. [mg/L]	0.040	0.006	0.013	0.180
*Factor of exceeding the HMTV	5.5	5.5	4.7	7.0
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not exceeding	1.2

 Table A1.2 Dissolved Zn concentrations (mg/L) at site 1 of Porirua Stream.

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	19	3	3	10
Minimum [mg/L]	0.090	0.25	0.31	0.14
25 <sup>th</sup> percentile [mg/L]	0.115	0.3	0.34	0.20
Median [mg/L]	0.15	0.34	0.36	0.38
75 <sup>th</sup> percentile [mg/L]	0.185	0.355	0.37	0.53
Maximum [mg/L]	0.39	0.37	0.38	0.73
Average [mg/L]	0.16	0.321	0.35	0.39
Std. dev. [mg/L]	0.07	0.06	0.035	0.11
*Factor of exceeding the CTV	Not exceeding	1.1	1.2	1.3

 Table A1.3 Dissolved Fe concentrations (mg/L) at site 1of Porirua Stream.

Number of antecedent dry days		1	
Sampling time	Me	tal concentrat [mg/L]	ion
	Cu	Zn	Fe
9:23 a.m.	0.0027	0.04	0.38
9:28 a.m.	0.0042	0.05	0.37
9:34 a.m.	0.0048	0.03	0.33
9:45 a.m.	0.0027	0.10	0.28
10:00 a.m.	0.0039	0.07	0.36

**Table A1.4** Data for the monitored storm runoff on 24/04/2011 at site 1 of PoriruaStream.



**Figure A1.1** Temporal variation of dissolved Cu, Zn and Fe concentrations for the monitored storm runoff on 24/04/2011 at site 1 of Porirua Stream.

Number of antecedent dry days	5		
Sampling time		Metal concentr [mg/L]	ration
	Cu	Zn	Fe
7:10 p.m.	0.0048	0.07	0.22
7:15 p.m.	0.0033	0.07	0.31
7:20 p.m.	0.0027	0.06	0.25
7:25 p.m.	0.0024	0.05	0.24
7:30 p.m.	0.003	0.05	0.29
7:40 p.m.	0.0027	0.05	0.28
7:50 p.m.	0.0021	0.04	0.33
8:00 p.m.	0.0027	0.05	0.35

**Table A1.5** Data for the monitored storm runoff on 29/05/2011 on site 1 of PoriruaStream.



**Figure A1.2** Temporal variation of dissolved Cu, Zn and Fe concentrations for the monitored storm runoff on 29/05/2011, at site 1 of Porirua Stream.

Number of antecedent dry days		7	
Sampling time	Met	tal concentratio [mg/L]	)n
L O	Cu	Zn	Fe
8:45 am	0.0048	0.05	0.41
9:00 am	0.0030	0.05	0.34
9:19 am	0.0030	0.08	0.28
9:27 am	0.0027	0.04	0.43
9:38 am	0.0027	0.04	0.52
10:38 am	0.0024	0.03	0.36
11:27 am	0.0030	0.04	0.42
12:31 pm	0.0033	0.05	0.30

**Table A1.6** Data of the monitored storm runoff on 05/06/2011 at site 1 of PoriruaStream.



**Figure A1.3** Temporal variation of dissolved Cu, Zn and Fe for the monitored storm runoff on 05/06/2011 at site 1 of Porirua Stream.

# A1.2 Sites 2 and 3 Data

Sample type	Base flow site 2	Storm runoff site 2	Base flow site 3	Storm runoff site 3
Number of samples	20	10	22	8
Number of omitted samples	9	3	10	3
Minimum [mg/L]	0.0012	0.0018	0.0012	0.0021
25 <sup>th</sup> percentile [mg/L]	0.0015	0.0022	0.0015	0.0024
Median [mg/L]	0.0027	0.0027	0.0018	0.0051
75 <sup>th</sup> percentile [mg/L]	0.0039	0.0063	0.0026	0.0078
Maximum [mg/L]	0.0063	0.0076	0.0048	0.0088
Average [mg/L]	0.0029	0.0042	0.0023	0.0052
Std. dev. [mg/L]	0.0017	0.0025	0.0012	0.0030
*Factor of exceeding the HMTV	1.5	1.5	Not exceeding	2.8
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not applicable	Not exceeding

 Table A1.7 Dissolved Cu concentrations (mg/L) at sites 2 and site 3 of Porirua Stream.

Sample type	Base flow site 2	Storm runoff site 2	Base flow site 3	Storm runoff site 3
Number of samples	20	10	22	8
Number of omitted samples	1	0	1	0
Minimum [mg/L]	0.0075	0.015	0.0078	0.019
25 <sup>th</sup> percentile [mg/L]	0.010	0.050	0.012	0.027
Median [mg/L]	0.040	0.065	0.040	0.060
75 <sup>th</sup> percentile [mg/L]	0.065	0.087	0.060	0.075
Maximum [mg/L]	0.150	0.250	0.110	0.120
Average [mg/L]	0.043	0.091	0.040	0.059
Std. dev. [mg/L]	0.037	0.0820	0.029	0.035
*Factor of exceeding the HMTV	3.8	6.2	3.8	5.7
*Factor of exceeding the CMC	Not applicable	1	Not exceeding	1

**Table A1.8** Dissolved Zn concentrations (mg/L) at sites 2 and site 3 of Porirua Stream.

Sample type	Base flow site 2	Storm runoff site 2	Base flow site 3	Storm runoff site 3
Number of samples	20	10	22	
	20	10	22	8
Minimum [mg/L]	0.07	0.19	0.05	0.10
25 <sup>th</sup> percentile [mg/L]	0.14	0.21	0.11	0.17
Median [mg/L]	0.17	0.25	0.16	0.52
75 <sup>th</sup> percentile [mg/L]	0.29	0.61	0.22	0.75
Maximum [mg/L]	0.89	1.57	0.64	2.26
Average [mg/L]	0.24	0.50	0.19	0.66
Std. dev. [mg/L]	0.2	0.4	0.1	0.7
*Factor of exceeding the CTV	Not exceeding	Not exceeding	Not exceeding	1.7

Table A1.9 Dissolved Fe concentrations (mg/L) at sites 2 and site 3 of Porirua Stream.

## A1.3 Site 4 Data

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	22	1	1	10
Number of omitted samples	8	0	0	4
Minimum [mg/L]	0.0012	NA	NA	0.0012
25 <sup>th</sup> percentile [mg/L]	0.0021	NA	NA	0.0025
Median [mg/L]	0.0021	NA	NA	0.0037
75 <sup>th</sup> percentile [mg/L]	0.0026	NA	NA	0.0056
Maximum [mg/L]	0.0063	NA	NA	0.016
Average [mg/L]	0.0026	0.0031	0.0015	0.0055
Std. dev. [mg/L]	0.0013	NA	NA	0.0054
*Factor of exceeding the HMTV	1.2	1.7	Not exceeding	2.0
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not exceeding	Not exceeding

 Table A1.10 Dissolved Cu concentrations (mg/L) at site 4 of Porirua Stream.

\*Based on the median values. NA: not applicable. In the table, first flush and composite samples are single data points and the values are placed in average cells.

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	22	1	1	10
Number of omitted samples	1	0	0	0
Minimum [mg/L]	0.010	NA	NA	0.020
25 <sup>th</sup> percentile [mg/L]	0.016	NA	NA	0.034
Median [mg/L]	0.040	NA	NA	0.050
75 <sup>th</sup> percentile [mg/L]	0.070	NA	NA	0.075
Maximum [mg/L]	0.090	NA	NA	0.150
Average [mg/L]	0.044	0.016	0.018	0.060
Std. dev. [mg/L]	0.027	NA	NA	0.041
*Factor of exceeding the HMTV	4	1.7	1.8	5
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not exceeding	Not exceeding

 Table A1.11 Dissolved Zn concentrations (mg/L) obtained at site 4 of Porirua Stream.

\*Based on the median values. NA: not applicable. In the table, first flush and composite samples are single data points and the values are placed in average cells.

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	22	1	1	10
Minimum [mg/L]	0.09	NA	NA	0.14
25 <sup>th</sup> percentile [mg/L]	0.17	NA	NA	0.24
Median [mg/L]	0.20	NA	NA	0.37
75 <sup>th</sup> percentile [mg/L]	0.26	NA	NA	0.77
Maximum [mg/L]	0.51	NA	NA	1.61
Average [mg/L]	0.23	0.21	0.24	0.58
Std. dev. [mg/L]	0.10	NA	NA	0.45
*Factor of exceeding the CTV	Not exceeding	Not exceeding	Not exceeding	1.2

**Table A1.12** Dissolved Fe concentrations (mg/L) obtained at site 4 of Porirua Stream.

\*Based on the median values. NA: not applicable. In the table, first flush and composite samples are single data points and the values are placed in average cells
Number of antecedent		4				
dry days						
Sampling time	Metal concentration (mg/L)					
	Cu	Zn	Fe			
9:38 am	0.0045	0.0192	0.23			
10:00 am	0.0018	0.014	0.19			
10:30 am	0.0018	0.0177	0.23			
11:00 am	0.0012	0.016	0.18			
12:00 pm	0.0015	0.0195	0.31			

**Table A1.13** Data of the monitored storm on 23/06/2011 at site 4 of Porirua Stream.



**Figure A1.4** Temporal variation of dissolved Cu, Zn and Fe in the monitored storm runoff on 23/06/2011 at site 4 of Porirua Stream.

# A1.4 Site 5 Data

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	21	1	1	10
Number of omitted samples	10	0	0	5
Minimum [mg/L]	0.0012	NA	NA	0.0021
25 <sup>th</sup> percentile [mg/L]	0.0016	NA	NA	0.0030
Median [mg/L]	0.0021	NA	NA	0.0033
75 <sup>th</sup> percentile [mg/L]	0.0036	NA	NA	0.0048
Maximum [mg/L]	0.0060	NA	NA	0.020
Average [mg/L]	0.0027	0.0017	0.0019	0.0066
Std. dev. [mg/L]	0.0017	NA	NA	0.0075
*Factor of exceeding the ANZECC (2000) TV	1.5	1.2	1.3	2.4
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not exceeding	Not exceeding

 Table A1.14 Dissolved Cu concentrations (mg/L) at site 5 of Kenepuru Stream.

\*Based on the median values. NA: not applicable. In the table, one base flow data point was below, and assumed to be, the enhanced detection limit. Note that first flush and composite samples are single data points and the values are placed in average cells.

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	21	1	1	10
Number of omitted samples	1	0	0	0
Minimum [mg/L]	0.0081	NA	NA	0.020
25 <sup>th</sup> percentile [mg/L]	0.019	NA	NA	0.035
Median [mg/L]	0.040	NA	NA	0.070
75 <sup>th</sup> percentile [mg/L]	0.070	NA	NA	0.140
Maximum [mg/L]	0.10	NA	NA	0.23
Average [mg/L]	0.044	0.056	0.044	0.089
Std. dev. [mg/L]	0.027	NA	NA	0.071
*Factor of exceeding the ANZECC (2000) TV	5	7	5.5	8.7
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not exceeding	1.2

 Table A1.15 Dissolved Zn concentrations (mg/L) at site 5 of Kenpuru Stream.

\*Based on the median values. NA: not applicable. In the table, first flush and composite samples are single data points and the values are placed in average cells.

Sample type	Base flow	First flush	Composite	Storm runoff
Numbers of samples	21	1	1	10
Minimum [mg/L]	0.26	NA	NA	0.31
25 <sup>th</sup> percentile [mg/L]	0.46	NA	NA	0.49
Median [mg/L]	0.51	NA	NA	0.59
75 <sup>th</sup> percentile [mg/L]	0.56	NA	NA	0.71
Maximum [mg/L]	1.04	NA	NA	2.49
Average [mg/L]	0.53	0.58	0.44	0.78
Std. dev. [mg/L]	0.15	NA	NA	0.63
*Factor of exceeding the CTV	1.7	1.9	1.4	1.9

 Table A1.16 Dissolved Fe concentrations (mg/L) at site 5 of Kenepuru Stream.

\*Based on the median values. NA: not applicable. In the table, first flush and composite samples are a single data points each and were placed in average cells.

Number of antecedent dry days	6					
Sampling time	Metal concentration [mg/L]					
	Cu	Zn	Fe			
8:00 am	0.0024	0.09	0.7			
8:05 am	0.0018	0.06	0.63			
8:10 am	0.0015	0.05	0.49			
8:15 am	0.0012	0.04	0.61			
8:25 am	0.0015	0.04	0.52			
8:35 am	0.0015	0.04	0.5			
8:45 am	0.0015	0.04	0.48			
9:00 am	0.0018	0.05	0.47			
9:35 am	0.0021	0.04	0.39			
10:35 am	0.0021	0.04	0.37			
11:35 am	0.0021	0.06	0.44			
12:35 pm	0.0021	0.04	0.42			

**Table A1.17** Data for the monitored storm on 18/06/2011 at site 5 of KenepuruStream.



**Figure A1.5** Temporal variation of dissolved Cu, Zn and Fe concentrations for the monitored storm runoff on 18/06/2011 at site 5 of Kenepuru Stream.

### A1.5 Sites 6 and 7 Data

Sample type	Base flow site 6	Storm runoff site 6	Base flow site 7	Storm runoff site 7
Number of samples	20	9	20	9
Number of omitted samples	6	3	6	3
Minimum [mg/L]	0.0012	0.0012	0.0012	0.0012
25 <sup>th</sup> percentile [mg/L]	0.0012	0.0014	0.0012	0.0018
Median [mg/L]	0.0012	0.0024	0.0012	0.0022
75 <sup>th</sup> percentile [mg/L]	0.0015	0.0043	0.0020	0.0031
Maximum [mg/L]	0.0027	0.0064	0.0036	0.014
Average [mg/L]	0.0015	0.0030	0.0017	0.0041
Std. dev. [mg/L]	0.000539	0.0021	0.00087	0.0049
*Factor of exceeding the ANZECC (2000) TV	Not exceeding	1.7	Not exceeding	1.6
*Factor of exceeding The CMC	Not applicable	Not exceeding	Not applicable	Not exceeding

Table A1.18 Dissolved Cu concentrations (mg/L) at site 6 and 7 of Takapu Stream.

\*Based on the median values. In the table, the concentration of dissolved Cu in 5 and 7 base flow samples and 1 storm runoff sample for site 6 and site 7 respectively were below, and assumed to be, the enhanced detection limit of Cu.

Sample type	Base flow site 6	Storm runoff site 6	Base flow site 7	Storm runoff site 7
Number of samples	20	9	20	9
Number of omitted samples	1	0	1	0
Minimum [mg/L]	0.0048	0.010	0.0075	0.010
25 <sup>th</sup> percentile [mg/L]	0.0067	0.027	0.0089	0.027
Median [mg/L]	0.013	0.055	0.030	0.050
75 <sup>th</sup> percentile [mg/L]	0.050	0.10	0.055	0.072
Maximum [mg/L]	0.08	0.23	0.09	0.29
Average [mg/L]	0.027	0.085	0.035	0.075
Std. dev. [mg/L]	0.024	0.086	0.028	0.090
*Factor of exceeding the ANZECC (2000) TV	1.6	6.9	3.7	6.2
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not applicable	Not exceeding

 Table A1.19 Dissolved Zn concentrations (mg/L) at site 6 and 7 of Takapu Stream.

\*Based on the median values.

Sample type	Base flow site6	Storm runoff site 6	Base flow site 7	Storm runoff site 7
Number of samples	20	9	20	9
Minimum [mg/L]	0.045	0.08	0.045	0.045
25 <sup>th</sup> percentile [mg/L]	0.045	0.11	0.085	0.15
Median [mg/L]	0.08	0.2	0.13	0.23
75 <sup>th</sup> percentile [mg/L]	0.095	0.42	0.19	0.31
Maximum [mg/L]	0.21	0.75	0.31	2.53
Average [mg/L]	0.084	0.29	0.14	0.49
Std. dev. [mg/L]	0.046	0.23	0.077	0.83
*Factor of exceeding the CTV	Not exceeding	Not exceeding	Not exceeding	Not exceeding

**Table A1.20** Dissolved Fe concentrations (mg/L) at site 6 and 7 of Takapu Stream.

\*Based on the median value. In the table, the concentration of dissolved Fe in 7 base flow samples for site 6 and 3 base flow and 1 storm runoff samples for site 7 were below, and assumed to be, the detection limit of Fe.

### A1.6 Sites 8 and 10 Data

 Table A1.21 Dissolved Cu concentrations (mg/L) at site 8 of Karori Stream.

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	17	2	2	5
Number of omitted samples	2	0	0	0
Minimum [mg/L]	0.0012	NA	NA	0.0042
25 <sup>th</sup> percentile [mg/L]	0.0015	NA	NA	0.0064
Median [mg/L]	0.0021	NA	NA	0.0087
75 <sup>th</sup> percentile [mg/L]	0.0040	NA	NA	0.018
Maximum [mg/L]	0.022	NA	NA	0.03
Average [mg/L]	0.0042	0.0046	0.0031	0.014
Std. dev. [mg/L]	0.0052	0.0011	0.00024	0.010
*Factor of exceeding the HMTV	1.3	3	2	5.7
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not exceeding	1.4

\*Based on the median values. NA: not applicable. In the table, first flush and composite samples are single data points and the values were averaged and compared against the HMTV and CMC.

Sample type	Base flow	Storm runoff
Number of samples	17	5
Number of omitted samples	2	0
Minimum [mg/L]	0.0012	0.0012
25 <sup>th</sup> percentile [mg/L]	0.0012	0.0032
Median [mg/L]	0.0021	0.0036
75 <sup>th</sup> percentile [mg/L]	0.0030	0.0060
Maximum [mg/L]	0.0081	0.011
Average [mg/L]	0.0023	0.0050
Std. dev. [mg/L]	0.0019	0.0038
*Factor of exceeding the HMTV	1.4	2.4
*Factor of exceeding the CMC	Not applicable	Not exceeding

\*Based on the median values. In the table, 5 base flow and 1 storm runoff samples were below, and assumed to be, the enhanced detection limit of Cu.

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	17	2	2	5
Number of omitted samples	1	0	0	0
Minimum [mg/L]	0.017	NA	NA	0.032
25 <sup>th</sup> percentile [mg/L]	0.020	NA	NA	0.060
Median [mg/L]	0.0315	NA	NA	0.077
75 <sup>th</sup> percentile [mg/L]	0.05	NA	NA	0.10
Maximum [mg/L]	0.07	NA	NA	0.120
Average [mg/L]	0.037	0.081	0.065	0.077
Std. dev. [mg/L]	0.018	0.016	0.0070	0.034
*Factor of exceeding the HMTV	3.6	9.4	7.5	8.9
*Factor of exceeding the CMC	Not applicable	1.4	1.1	1.3

 Table A1.23 Dissolved Zn concentrations (mg/L) at site 8 of Karori Stream.

\*Based on the median values. NA: not applicable. In the table, first flush and composite samples are two data points and the values are averaged and compared against the HMTV and CMC.

Sample type	<b>Base flow</b>	Storm runoff
Number of samples	17	5
Number of omitted samples	1	0
Minimum [mg/L]	0.007	0.007
25 <sup>th</sup> percentile [mg/L]	0.023	0.019
Median [mg/L]	0.030	0.050
75 <sup>th</sup> percentile [mg/L]	0.050	0.090
Maximum [mg/L]	0.060	0.11
Average [mg/L]	0.032	0.055
Std. dev. [mg/L]	0.015	0.044
*Factor of exceeding the HMTV	3.5	5.8
*Factor of exceeding the CMC	Not applicable	Not exceeding

Table A1.24 Dissolved Zn concentration	ns (mg/L) at site 10 of Karori Stream.
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\*Based on the median values.

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	17	2	2	5
Minimum [mg/L]	0.045	NA	NA	0.14
25 <sup>th</sup> percentile [mg/L]	0.06	NA	NA	0.17
Median [mg/L]	0.085	NA	NA	0.22
75 <sup>th</sup> percentile [mg/L]	0.11	NA	NA	0.26
Maximum [mg/L]	0.13	NA	NA	0.30
Average [mg/L]	0.08	0.19	0.17	0.22
Std. dev. [mg/L]	0.029	0.025	0.0089	0.065
*Factor of exceeding the CTV	Not exceeding	Not exceeding	Not exceeding	Not exceeding

 Table A1.25 Dissolved Fe concentrations (mg/L) at site 8 of Karori Stream.

\*Based on the median values. NA: not applicable. In the table, first flush and composite samples are two data points and are averaged and compared against the CTV. Note that the concentration of dissolved Fe in 2 base flow samples were below, and assumed to be the detection limit of Fe.

Sample type	Base flow	Storm runoff
Number of samples	17	5
Minimum [mg/L]	0.045	0.09
25 <sup>th</sup> percentile [mg/L]	0.045	0.11
Median [mg/L]	0.090	0.23
75 <sup>th</sup> percentile [mg/L]	0.13	0.30
Maximum [mg/L]	0.16	0.31
Average [mg/L]	0.09	0.2
Std. dev. [mg/L]	0.043	0.10
*Factor of exceeding the CTV.	Not exceeding	Not exceeding

 Table A1.26 Dissolved Fe concentrations (mg/L) at site 10 of Karori Stream.

\*Based on the median values. In the table, the concentration of dissolved Fe in 6 base flow samples was below, and assumed to be the detection limit of Fe.

#### Table A1.27 Data of the monitored storm on 25/04/2011 at site 8 of Karori Stream.

Number of antecedent dry days		1	
Sompling time	Metal	concent [mg/L]	ration
Samping time	Cu	Zn	Fe
8:26 am	0.0030	0.09	0.22
8:28 am	0.0045	0.09	0.14
8:35 am	0.0030	0.09	0.22
8:47 am	0.0048	0.10	0.25
8:56 am	0.0033	0.06	0.18



**Figure A1.6** Temporal variation of dissolved Cu, Zn and Fe concentrations for the monitored storm runoff on 25/04/2011 at site 8 of Karori Stream.

Number of antecedent	10				
dry days					
	Metal concentration				
Sampling time		[mg/L]			
	Cu	Zn	Fe		
7:00 a.m.	0.0063	0.09	0.22		
7:05 a.m.	0.006	0.07	0.15		
7:10 a.m.	0.0054	0.06	0.19		
7:15 a.m.	0.0045	0.06	0.16		
7:20 a.m.	0.0048	0.07	0.14		
7:30 a.m.	0.0063	0.08	0.15		
7:40 a.m.	0.0042	0.08	0.14		
8:30 a.m.	0.003	0.05	0.19		
9:10 a.m.	0.0033	0.09	0.16		
10:00 a.m.	0.0021	0.06	0.18		
11:00 a.m.	0.0024	0.05	0.16		
12:00 p.m.	< 0.0012*	0.06	0.18		
2:00 p.m.	< 0.0012*	0.09	0.18		

 Table A1.28 Data of the monitored storm on 23/07/2011 at site 8 of Karori Stream.

\* The concentrations are assumed to be the enhanced detection limit of Cu.



**Figure A1.7** Temporal variation of dissolved Cu, Zn and Fe concentrations for the monitored storm runoff on 23/07/2011 at site 8 of Karori Stream.



**Figure A1.8** HMTVs for Cu and Zn, CTV for Fe (horizontal red lines) and statistical parameters of dissolved Cu, Zn, and Fe, left to right, unpublished data of monitoring program conducted between January/2008 to Jun/2009 by the GWRC14 at site 9, Karori Stream at Makara Peak, Mountain Bike Park [34].

<sup>&</sup>lt;sup>14</sup> Note that the data was provided in tables.

### A1.7 Site 9 Data

Table A1.29 Dissolved Cu concentrations (mg/L) for site 9, a tributary of Karori Stream.

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	17	1	1	5
Number of omitted samples	2	0	0	0
Minimum [mg/L]	0.0012	NA	NA	0.0015
25 <sup>th</sup> percentile [mg/L]	0.0012	NA	NA	0.0024
Median [mg/L]	0.0019	NA	NA	0.0042
75 <sup>th</sup> percentile [mg/L]	0.0033	NA	NA	0.0048
Maximum [mg/L]	0.0057	0.0013	0.0012	0.0072
Average [mg/L]	0.0024	NA	NA	0.0040
Std. dev. [mg/L]	0.0013	NA	NA	0.0022
*Factor of exceeding the HMTV	1.3	0	0	2.7
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not exceeding	Not exceeding

\*Based on the median values. NA: not applicable. In the table, the concentrations of dissolved Cu in 5 base flow samples were below, and assumed to be, the enhanced detection limit. Note that first flush and composite samples are single data points and they are placed in average cells.

Sample type	<b>Base flow</b>	First flush	Composite	Storm runoff
Number of samples	17	1	1	5
Minimum [mg/L]	0.010	NA	NA	0.014
25 <sup>th</sup> percentile [mg/L]	0.014	NA	NA	0.024
Median [mg/L]	0.023	NA	NA	0.030
75 <sup>th</sup> percentile [mg/L]	0.030	NA	NA	0.080
Maximum [mg/L]	0.050	NA	NA	0.090
Average [mg/L]	0.025	0.045	0.029	0.048
Std. dev. [mg/L]	0.013	NA	NA	0.035
*Factor of exceeding the HMTV	2.6	5.1	3.3	3.4
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not exceeding	Not exceeding

Table A1.30 Dissolved Zn concentrations	(mg/L) for site 9, a tributary of Karori Stream.
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\*Based on the median values. NA: not applicable. In the table, first flush and composite samples are single data points and the values are placed in average cells.

Sample type	Base flow	First flush	Composite	Storm runoff
Number of samples	17	1	1	5
Minimum [mg/L]	0.045	NA	NA	0.23
25 <sup>th</sup> percentile [mg/L]	0.13	NA	NA	0.33
Median [mg/L]	0.19	NA	NA	0.35
75 <sup>th</sup> percentile [mg/L]	0.20	NA	NA	0.37
Maximum [mg/L]	0.37	NA	NA	0.4
Average [mg/L]	0.17	0.21	0.27	0.33
Std. dev. [mg/L]	0.076	NA	NA	0.064
*Factor of exceeding the CTV	Not exceeding	Not exceeding	Not exceeding	1.1

 Table A1.31 Dissolved Fe concentration (mg/L) for site 9, a tributary of Karori Stream.

\*Based on the median values. NA: not applicable. In the table, one base flow sample was below, and assumed to be, the detection limit. Note that, first flush and composite samples are single data points and the values are placed on average cells.

Number of antecedent dry days				
Sampling time	Metal concentration [mg/L]			
	Cu	Zn	Fe	
7:00 a.m.	0.00145	0.048	0.24	
7:05 a.m.	<0.0012*	0.045	0.2	
7:15 a.m.	0.0012*	0.044	0.2	
7:30 a.m.	<0.0012*	0.047	0.21	
7:40 a.m.	0.0012	0.046	0.22	
8:30 a.m.	< 0.0012*	0.012	0.22	
9:10 a.m.	0.0012	0.032	0.35	
10:00 a.m.	< 0.0012*	0.028	0.28	
11:00 a.m.	<0.0012*	0.032	0.33	
12:00 a.m.	<0.0012*	0.01	0.34	
2:00 a.m.	< 0.0012*	0.03	0.27	

Table A1.32 Data of the monitored storm runoff event on 23/07/2011 at site 9.

\* The concentrations are assumed to be the enhanced detection limit of Cu.



**Figure A1.9** Temporal variation of dissolved Cu, Zn and Fe for the monitored storm runoff on 23/07/2011 at site 9, a tributary of Karori Stream.

# A1.2 Sites 11, 12 and 13 Data

Table A1.33 Dissolved Cu concentrations (mg/L) at site 11, site12 of Makara Stream, and site 13 of Ohariu Stream.

	Site 11	Site 11	Site 12	Site 12	Site 13	Site 13
Sample type	base flow	storm runoff	base flow	storm runoff	base flow	storm runoff
Number of samples	17	5	17	5	17	5
Number of omitted samples	3	0	3	0	3	0
Minimum [mg/L]	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012
25 <sup>th</sup> percentile [ mg/L]	0.0012	0.0012	0.0012	0.0012	0.0012	0.0030
Median [mg/L]	0.0012	0.0030	0.0019	0.0030	0.0018	0.0033
75 <sup>th</sup> percentile [mg/L]	0.0021	0.0051	0.0030	0.0044	0.0024	0.0044
Maximum [mg/L]	0.0039	0.0056	0.0039	0.0051	0.0039	0.0090
Average [mg/L]	0.0017	0.0032	0.0021	0.0029	0.0019	0.0042
Std. dev. [mg/L]	0.00086	0.0021	0.0010	0.0018	0.00086	0.0029
*Factor of exceeding the HMTV	Not exceeding	1.7	1.1	1.7	1	1.9
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not applicable	Not exceeding	Not applicable	Not exceeding

\*Based on the median values. In the table, the concentration of dissolved Cu in 8, 4, 6 base flow samples and 2, 1, 1 storm runoff samples were below, and assumed to be, the enhanced detection limit of Cu for sites 11, 12 13 respectively.

Sample type	Site 11 base flow	Site 11 storm runoff	Site 12 base flow	Site 12 storm runoff	Site 13 base flow	Site 13 storm runoff
Number of samples	17	5	17	5	17	5
Number of omitted samples	2	0	2	0	2	0
Minimum [mg/L]	0.0051	0.01	0.0012	0.009	0.006	0.01
25 <sup>th</sup> percentile [mg/L]	0.0087	0.02	0.0075	0.01	0.008	0.01
Median [mg/L]	0.01	0.027	0.01	0.01	0.01	0.014
75 <sup>th</sup> percentile [mg/L]	0.02	0.06	0.025	0.07	0.013	0.05
Maximum [mg/L]	0.05	0.08	0.05	0.07	0.05	0.06
Average [mg/L]	0.016	0.039	0.016	0.034	0.013	0.029
Std. dev. [mg/L}	0.014	0.029	0.014	0.033	0.011	0.024
*Factor of exceeding the HMTV	0	2.7	Not exceeding	Not exceeding	Not exceeding	1.4
*Factor of exceeding the CMC	Not applicable	Not exceeding	Not applicable	Not exceeding	Not applicable	Not exceeding

Table A1.34 Dissolved Zn concentrations (mg/L) at site 11 and site12 of Makara Stream and site 13 of Ohariu Stream.

\*Based on the median values.

Sample type	Site 11 Base flow	Site 11 Storm runoff	Site 12 Base flow	Site 12 Storm runoff	Site 13 Base flow	Site 13 Storm runoff
Number of samples	17	5	17	5	17	5
Minimum [mg/L]	0.045	0.23	0.045	0.16	0.045	0.26
25 <sup>th</sup> percentile [mg/L]	0.07	0.28	0.11	0.18	0.09	0.56
Median [mg/L]	0.12	0.36	0.15	0.43	0.15	0.61
75 <sup>th</sup> percentile [mg/L]	0.14	0.9	0.16	0.59	0.19	0.63
Maximum [mg/L]	0.23	0.9	0.22	0.73	0.29	1.8
Average [mg/L]	0.12	0.53	0.14	0.42	0.15	0.77
Std. dev. [mg/L]	0.05	0.34	0.05	0.250	0.07	0.6
*Factor of exceeding the CTV	Not exceeding	1.2	Not exceeding	1.4	Not exceeding	2

Table A1.35 Dissolved Fe concentrations (mg/L) for site 11 and site 12 of Makara Stream and site 13 of Ohariu Stream.

\*Based on the median values. In the table, the concentration of dissolved Fe in 2 base flow samples for the three sites were below, and assumed to be the detection limit of Fe.

# Atmospheric rainfall samples

Metals	Cu	Zn	Fe
Number of samples	24	24	24
Number of omitted sample	17*	0	6**
Minimum [mg/L]	0.0018	0.007	0.05
25 <sup>th</sup> percentile [mg/L]	0.0021	0.040	0.06
Median [mg/L]	0.0057	0.090	0.10
75 <sup>th</sup> percentile [mg/L]	0.0081	0.135	0.16
Maximum [mg/L]	0.010	0.23	0.44
Average [mg/L]	0.0054	0.094	0.13
Std. dev. [mg/L]	0.0036	0.066	0.096

Table A1.36 Dissolved Cu, Zn and Fe concentrations (mg/L) in the atmospheric rainfall samples collected at VUW.

\*The samples were below the detection limit or the enhanced detection limit.\*\*The samples were below the detection limit of Fe.

# **Roof runoff samples**

Metals	Cu	Zn	Fe
Number of samples	15	15	15
Number of omitted samples	5*	0	7**
Minimum [mg/L]	0.0015	0.02	0.047
25 <sup>th</sup> percentile [mg/L]	0.0022	0.09	0.05
Median [mg/L]	0.0046	0.15	0.065
75 <sup>th</sup> percentile [mg/L]	0.0054	0.70	0.12
Maximum [mg/L]	0.0078	1.9	0.35
Average [mg/L]	0.0044	0.5	0.12
Std. dev. [mg/L]	0.0021	0.62	0.11

**Table A1.37** Dissolved Cu, Zn and Fe concentrations (mg/L) in the galvanised roof runoff samples.

\*The samples are below the detection limit or the enhanced detection limit.\*\*The samples are below the detection limit of Fe.

# **Paved surface runoff Samples**

	9		
Metals	Cu	Zn	Fe
Number of samples	16	16	16
Number of omitted samples	5*	0	5**
Minimum [mg/L]	0.0024	0.010	0.05
25 <sup>th</sup> percentile [mg/L]	0.0033	0.024	0.07
Median [mg/L]	0.0040	0.045	0.16
75 <sup>th</sup> percentile [mg/L]	0.0081	0.22	0.58
Maximum [mg/L]	0.040	0.93	0.74
Average [mg/L]	0.0081	0.17	0.31
Std. dev. [mg/L]	0.01	0.24	0.28

**Table A1.38** Dissolved Cu, Zn and Fe concentrations (mg/L) in paved surfaces runoff off samples.

\*The samples are below the detection limit of Fe.

Number of antecedent dry days		7	
Sampling time	Metal	l concentra [mg/L]	ition
	Cu	Zn	Fe
8:50 am	0.0021	0.03	0.4
9:11 am	0.0024	0.04	0.51
9:18 am	0.0024	0.06	0.39
9:30 am	0.0009	0.04	0.46
11:30 am	0.0012	0.04	0.52
12:30 pm	0.0012	0.04	0.41

 Table A1.39 Data of the monitored street storm runoff at site 1 on 05/06/2011



**Figure A1.10** Temporal variation of dissolved Cu, Zn and Fe for the monitored street storm runoff at site 1 on 05/06/2011.

# **Appendix 2**

#### **Quality assurance**

#### A) Consistency

In order to determine the stability of research results, control chats are used (Shewharts charts). A given concentration of the analyte, subjected to quality control, is monitored over time and the mean and standard deviation are calculated. At least 10-15 data points should be used to satisfy the requirements of this type of test [52]. In this work, the variations of dissolved Cu, Zn and Fe concentrations (1.2, 1.2 and 5 mg/L respectively) were observed between June-July/2011. The means and standard deviations were calculated. Upper and lower action limits (UAL and LAL) were calculated, mean  $\pm$  3 standard deviation. Figures A.2.1, A.2.2 and A2.3 show that the analysis of dissolved Cu, Zn and Fe was statically consistent.



**Figure A2.1** Variation of the analysis of dissolved Cu (1.2 mg/L) between June-July/2011



**Figure A2.2** Variation of the analysis of dissolved Zn (1.2 mg/L) between June-July/2011.



**Figure A2.3** Variation of the analysis of dissolved Fe (5 mg/L) between June-July/2011

#### **B)** Uncertainty

Using equation A2.1, [52], standard uncertainty can be calculated for dissolved Cu, Zn and Fe, as shown in tables A2.1, A2.2, and A2.3. Note that the rectangular distributions ( $\sqrt{3}$ ) were assumed for all uncertainty sources, since no information was provided by the manufacturer regarding to the coverage factor.

By applying equation A2.2, [52], the total relative uncertainty can be calculated. The measurements of Cu, Zn and Fe were associated with 4.00%, 5.87%, and 7.83% respectively.

Standard Uncertainty= Standard deviation/
$$\sqrt{3}$$
 A2.1

Total relative uncertainty= 
$$\sqrt{\sum \left(\frac{\text{Standard uncetainty}}{\text{Absolute value}}\right)^2}$$
 A2.2

Table A2.1 Sources and standard uncertainties associated with dissolved Cu measurements.

Sources	Value	Standard uncertainty
Standard solution	1001 mg/L	2.30
Volumetric flask	25 mL	1.73
Micropipette	1000 µL	0.11
FAAS	1.20 mg/L	0.048
2 x Measuring cylinder	250 mL	0.115
Measuring cylinder	25 mL	0.058

Sources	Value	Standard uncertainty
Standard solution	1000 mg/L	1.15
Micropipette	1000 µL	0.11
FAAS	1.20 mg/L	0.070
Volumetric Flask	25 mL	0.173

**Table A2.2** Sources and standard uncertainties associated with dissolved Zn measurements.

**Table A2.3** Sources and standard uncertainties associated with dissolved Fe measurements.

Sources	Value	Standard uncertainty
Standard solution	1000 mg/L	2.30
Micropipette	1000 µL	0.11
FAAS	5.0 mg/L	0.070
Volumetric Flask	25 mL	0.39

# **D**)Calibration curves



Figure A2.4 Cu calibration curve obtained by analysing 5 standards on FAAS.



Figure A2.5 Zn calibration curve obtained by analysing 5 standards on FAAS.



Figure A2.6 Fe calibration curve obtained by analysing 5 standards on FAAS.

# Sites Coordinates

#### Table A2.4 Coordinates of the monitored sites

Site number	Sites name	Latitude	Longitude
Site 1	Wingfield Place, Porirua Stream	-41.210469	174.812046
Site 2	289 Middleton Road Tunnel, Glenside, Porirua Stream	-41.203140	174.817980
Site 3	Tawa, Main Road, Porirua Stream.	-41.176924	174.825981
Site 4	Kenepuru Drive, next to the flow monitoring station, Porirua Stream.	-41.141651	174.843032
Site 5	Champion Street, Kenpuru Stream	-41.133880	174.853077
Site 6	Woodburn Drive Takapu Road, Takapu Stream	-41.178400	174.838975
Site 7	Takapu Road, Takapu Stream	-41.181254	174.834795
Site 8	Karori Park eastern, Karori Stream	-41.285639	174.725476
Site 9	Karori Park western, a tributary of Karori Stream.	-41.287495	174.723388
Site10	Makara Peak, Mountain Bike Park, Karori Stream.	-41.297278	174.721705
Site 11	Makara Road, Makara Stream	-41.263776	174.711991
Site 12	Takarau Gorge Road, Makara Stream.	-41.239395	174.719154
Site 13	Takarau Gorge Road, Ohariu Stream.	-41.225907	174.748541

# Selected site photos

Site 1



Site 2




Site 4







Site 7



## Site 8







## Site 10









