

# Trace elements in Christchurch road dust

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by

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## Abstract

Trace elements in road dust were measured from 30 sites across Christchurch over a 7 month sampling programme. Concentrations of all trace elements (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V and Zn) in road dust were lower than previously reported in New Zealand or international studies. For most elements there was no relationship between road dust concentration and traffic, age or weather, nor any temporal trends. Most trace elements were identified as being largely vehicle-derived. Zinc concentrations were greater in industrial/commercial sites compared to residential sites ( $p < 0.05$ ). Trace element concentrations were significantly greater in the 63  $\mu\text{m}$  fraction compared to the 2 mm fraction. Cadmium, copper, lead and zinc concentrations were all significantly enriched compared to background soil concentrations. Four methods for extracting platinum group elements were trialled, with the aqua regia digestion the most successful at determining platinum concentrations. Platinum is emitted as relatively large particulates into road dust, resulting in poor homogeneity. Rainwater and stream water leaches identified limited solubility for trace elements in road dust, leaving accumulation in waterway sediments as the most likely environmental fate. Copper, lead and zinc concentrations in road dust from the majority of sites were high enough to result in sediment exceeding ANZECC guidelines. These elements were also the most bioavailable as assessed using a 1 M HCl leach. Copper, lead and zinc concentrations in road dust therefore could pose a risk to benthic organisms in Christchurch waterways.

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## Abbreviations

AAS – Atomic Absorption Spectroscopy

ANOVA – Analysis of Variance

ANZECC – Australian and New Zealand Environment and Conservation Council

AVS-SEM – Acid Volatile Sulfide – Simultaneously Extracted Metals

CBD – Central Business District

CRM – Certified Reference Material

ECan – Environment Canterbury

HS/AB – ‘Hard and Soft Acids and Bases’ Theory

IARC – International Agency for Research on Cancer

ICP-MS – Inductively Coupled Plasma – Mass Spectrometry

LRI – Land Resource Inventory

MSDS – Material Safety Data Sheet

NIWA – National Institute of Water and Atmospheric Research

OM – Organic Matter

PGEs – Platinum Group Elements

PM – Particulate Matter

USEPA – United States Environmental Protection Agency

# 1. Introduction

## 1.1 Urban waterways

Urban waterways are considered to be highly important in New Zealand society. Each waterway has its own unique ecosystem, such as the Avon River catchment in which various species of trout, eel and bullies can be found.<sup>1</sup> They can be used for recreational activities such as swimming, and the aesthetics of a waterway are often socially important. There is a strong cultural link between waterways and Maori, with local iwi viewing water as a foundation of life and a basis of tribal identity.<sup>2</sup> Various forms of pollution can negatively affect a waterway, including sediment, bacteria, nutrients and trace element pollution, resulting in effects ranging from reduced access to the water to a loss of biodiversity. Trace elements in particular are a significant issue, as they are often persistent, are key contaminants in urban areas and accumulate in waterways.<sup>3</sup> This thesis focuses on road dust as a potential non-point source of trace element contamination to urban waterways.

## 1.2 Road dust

Road dust is the term used to describe resuspended particulate matter found on roads, predominately in gutters. It consists largely of soil and sand particles that become airborne from being disturbed by vehicles. These particles are mixed with litter and larger debris.<sup>4</sup> The quantity of dust varies on roads, due to a multitude of factors including weather and road sweeping, and differing environments (such as soil types). The particle size also varies, with a higher soil content likely to mean coarser particles, while a higher sand content is likely to have finer particles. Road dust can also contain several trace elements released from wear and friction of vehicle parts and road abrasion, resulting in elevated concentrations compared to surrounding soils.<sup>5</sup> This can create a pathway for the pollution of soils, sediments and waterways, as rainfall can transport road dust through stormwater drains and into waterways.

### 1.3 Trace elements in road dust

Road dust is a potential source of contaminants because of the various trace elements it can contain. These elements can be important because they can be accumulative and toxic.<sup>3</sup> Some of these elements can come from natural sources, such as erosion processes from soils and rocks, or from anthropogenic sources. Many automobile parts consist of environmentally important trace elements, and friction forces on these parts can result in the generation of these elements as dust particles (Table 1.1). These key elements include cadmium, copper, nickel, lead, antimony and zinc. Braking systems in cars (especially disc brakes at the front of the car) can contain copper, lead, nickel and zinc in the brake pad and lining, with the concentrations varying brand to brand.<sup>6</sup> Car tyres contain zinc oxide as an activator for the vulcanisation process, as well as other trace elements such as antimony in pigments.<sup>7</sup> Lead is used in adhesive weights to balance wheels, due to its relatively low cost and malleability.<sup>8</sup> Historically, lead was also used as an anti-knocking agent in fuel as tetraethyl lead, as well as in some house paints. Catalytic converters can produce platinum group elements (PGEs), which are discussed later (Section 1.5). Other concentrations of trace elements found in road dust can be from direct contamination, such as cadmium from cigarettes.<sup>9</sup> Road dust can also contain trace elements from airborne deposition, road bitumen and road markings.<sup>12</sup>

Table 1.1: Sources of trace elements found in road dust

Source:	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	V	Zn
<b>Tyres<sup>7,10</sup></b>		✓	✓		✓	✓			✓	✓		✓
<b>Brakes<sup>6</sup></b>	✓	✓	✓	✓	✓	✓		✓	✓	✓		✓
<b>Bitumen<sup>11</sup></b>		✓	✓	✓	✓			✓	✓			✓
<b>Road</b>	✓	✓		✓					✓	✓		
<b>Markings<sup>12</sup></b>												
<b>Batteries<sup>13</sup></b>	✓	✓						✓	✓			
<b>Car Paint<sup>5</sup></b>				✓								✓
<b>Fuel/ Oil<sup>10</sup></b>		✓		✓	✓	✓	✓	✓			✓	✓
<b>Exhaust<sup>5</sup></b>		✓						✓				✓
<b>Bodywork<sup>5</sup></b>				✓		✓	✓	✓			✓	
<b>Historical<sup>5</sup></b>									✓			
<b>Other<sup>13</sup></b>		✓			✓	✓			✓			

## 1.4 Concentrations of road dust

### 1.4.1 New Zealand data

Two major road dust studies were performed in New Zealand, in Wellington 1978 and Christchurch 1984 respectively (Table 1.2).<sup>10,14</sup> For most elements Wellington road dust had higher concentrations than measured in Christchurch road dust, which may be due to the larger traffic density. Several elements, such as lead and zinc, also had large concentration ranges in both studies. It is important to note that the Wellington data was from a <2mm fraction, while the Christchurch data was from a <0.9633 mm fraction. This however only further illustrates the difference between cities, as typically higher concentrations are found in smaller size fractions of road dust.<sup>15</sup>

*Table 1.2: Summary of trace element concentrations in road dust from two studies in Wellington<sup>10</sup> and Christchurch<sup>14</sup>, in  $\mu\text{g g}^{-1}$  except iron (%).*

<b>Element:</b>	<b>Location:</b>	<b>Median:</b>	<b>Minimum:</b>	<b>Maximum:</b>
<b>Antimony</b>	Wellington	11.4	5.0	43.6
	Christchurch	8.9	3.9	22.0
<b>Arsenic</b>	Wellington	6.1	2.0	10.6
	Christchurch	8.25	5.3	11.2
<b>Cadmium</b>	Wellington	2.2	0.18	8.9
	Christchurch	1.1	0.8	1.1
<b>Chromium</b>	Wellington	73	35	703
	Christchurch	58	38	76
<b>Copper</b>	Wellington	184	32	1,572
	Christchurch	106	48	258
<b>Iron (%)</b>	Wellington	3.39	1.64	7.23
	Christchurch	2.39	2.36	5.82
<b>Lead</b>	Wellington	1,977	207	20,842
	Christchurch	1,294	887	10,070
<b>Manganese</b>	Wellington	525	251	1,036
	Christchurch	399	381	399
<b>Nickel</b>	Wellington	22	12	48
<b>Vanadium</b>	Wellington	68	37	92
	Christchurch	48	41	68
<b>Zinc</b>	Wellington	689	141	4,377
	Christchurch	429	365	850

*N.B. Christchurch data is from a <0.9633 mm fraction while Wellington data is from a <2mm fraction*



### 1.4.2 International data

International studies on trace elements in road dust are summarised in Table 1.3.<sup>14, 16-20</sup> Comparing the road dust concentrations in the 1980s with New Zealand concentrations from Table 1.2, New Zealand concentrations were typically the same or lower than other cities around the world. Larger populations tend to have higher concentrations of trace elements in road dust, with London and New York much higher than Halifax, Kingston and the New Zealand concentrations. Recent data also shows the effect of reducing the use of lead in fuel and paint, as lead concentrations are much lower in studies after 2000 compared to the 1984 study. Other elements such as chromium and manganese show an increase over time, potentially due to changing compositions of fuel.<sup>12</sup>

*Table 1.3: Summary of trace element concentrations in road dust from various cities around the world. All values in  $\mu\text{g g}^{-1}$ , except iron (%).*

City:	Year	Sb	As	Cd	Cr	Co	Cu	Fe	Pb	Mn	Ni	V	Zn
<b>London<sup>14</sup></b>	1984	15.2	20	6.6	116	7.3	198	2.4	3031	440.5	-	71	1174
<b>New York<sup>14</sup></b>	1984	6	4.7	8	125	10.8	356	3.3	2582	453.5	-	73	1811
<b>Halifax<sup>14</sup></b>	1984	2	7.4	1	69	7.9	86.5	4.5	1296	579	-	142	467.5
<b>Kingston<sup>14</sup></b>	1984	1.65	5.1	0.8	24.5	7.2	65.5	3.2	863	373.5	-	113	764.5
<b>Ottawa<sup>16</sup></b>	1993	0.42	1.4	0.3	41.8	8.7	29.5	1.8	32.9	426.4	14.6	34.2	98.7
<b>Birmingham<sup>17</sup></b>	2003	-	-	1.62	-	-	166	-	48.6	-	16.6	-	388.4
<b>Delhi<sup>18</sup></b>	2014	-	-	-	171	23.3	169	2.7	129	699.2	37.2	-	263.7
<b>Honolulu<sup>19</sup></b>	2000	3	4	0.5	436	42	162	7.1	313	1078	260	248	439
<b>Hong Kong<sup>20</sup></b>	2003	-	67	-	124	9.5	110	1.4	120	594	28.6	36.6	3840

## 1.5 Platinum Group Elements (PGEs)

Platinum group elements (PGEs) are a group of noble, precious heavy metals in the middle of the periodic table, with similar chemical properties. Their main use is as catalysts. PGEs are used as catalysts in a variety of uses, in particular as catalytic converters in vehicles. Catalytic converters were introduced to reduce toxic car emissions, and contain various amounts of platinum, palladium and rhodium as catalysts. Platinum and palladium are both effective because they can oxidise CO and hydrocarbons into CO<sub>2</sub> and water, while rhodium reduces NO<sub>x</sub> into O<sub>2</sub> and N.<sup>21</sup> Compared to other transition metals these elements are more commonly used in catalysts as they can operate at much higher temperatures, and are more resistant to sulfur-containing molecules.<sup>21</sup> The mandatory use of these catalytic converters in New Zealand, however, presents a potential pathway from these elements to enter the environment. One study found emission of platinum from catalytic converters to range from 0.5 - 0.8 µg per km travelled.<sup>22</sup> Catalytic converters were only made mandatory in New Zealand in 2004, while in other countries they have been compulsory since the 1980's.<sup>23</sup>

### 1.5.1 Typical platinum group element concentrations

Platinum group element concentrations in road dust measured around the world range from 30 – 450 ng g<sup>-1</sup> (Table 1.4). There is significant variability between different cities and different countries. There have been several studies performed to analyse PGEs in road dust throughout the world, however there is no data available for PGE levels in New Zealand, which presents a significant gap in our knowledge of environmental pollution.

*Table 1.4: Concentrations of platinum group elements in road dust measured in several cities. All values in ng g<sup>-1</sup>.*

Location	Platinum	Palladium	Rhodium
Australia <sup>24</sup>	53.5-419.4	58.2-440.5	8.8-91.4
Goteburg <sup>25</sup>	325.5	70.8	101.8
Rome <sup>25</sup>	34	202.7	4.8
Germany <sup>26</sup>	135-303	60-95	30-42

## 1.6 Trace element toxicity

Trace elements in road dust pose an environmental risk due to their inherent toxicity. These trace elements can cause a wide variety of toxicological effects, depending on factors such as concentration and speciation. Although there are several trace elements that are considered “essential” for biological functions (iron, copper, manganese, zinc and cobalt), often there is a narrow range of concentrations of these elements tolerated for beneficial roles, and exceeding this range can have toxic effects.<sup>27</sup> Many trace elements, such as copper, act as co-factors with oxidative stress enzymes, which can result in the generation of reactive oxygen species and free radicals in excess concentrations, causing severe cell and tissue damage through lipid peroxidation.<sup>28</sup> Several of these trace elements, particularly arsenic, cadmium, chromium and lead, are highly toxic, and are classed as either “probable” or “known” carcinogens by the International Agency for Research on Cancer (IARC).<sup>29</sup>

Road dust can also cause toxic effects due to the size of the particles. Particulate matter is studied widely around the world, with emphasis on PM<sub>10</sub> and PM<sub>2.5</sub> (suspended particles with a diameter of 10 micrometres or less and 2.5 micrometres or less respectively). Particles of these sizes can be inhaled in and end up in the lungs, penetrating deep into the smallest parts such as the bronchi, potentially causing lung cancer.<sup>30</sup> PM<sub>2.5</sub> particles are small enough pass

through the lungs and get transported around the body through the blood stream into other organs.<sup>30</sup>

The individual toxicity of each element for humans, plants and other organisms is briefly described in the below sections. Although the toxicity of these elements is mostly well known, it is important to note that so-called “cocktail effect” can make the combined toxic effect of road dust greater or less than each individual element. This is because the presence of multiple elements can have a synergistic or antagonistic effects on toxicity, especially if the elements involved follow similar mechanisms of toxicity.<sup>27</sup> The difficulty in measuring this combined effect means that toxicity is usually characterised per element.

#### 1.6.1 Antimony

The toxicology of antimony is similar to arsenic, as they are both group 15 metalloids, however it is much less toxic.<sup>31</sup> It has been shown to be phytotoxic to some plants by uptake from contaminated soil.<sup>32</sup> Plant growth can also be hindered by excess antimony.<sup>33</sup> Antimony trioxide has been linked to being potentially carcinogenic, particularly when inhaled.<sup>34</sup> The biochemical interactions of antimony are relatively unknown compared to other trace elements.<sup>35</sup>

#### 1.6.2 Arsenic

Arsenic typically is found in the environment in 3 forms - inorganic, organic and elemental. Inorganic arsenic is the most toxic form, particularly in its trivalent state. Trivalent arsenic has been documented to inactivate over 200 enzymes, through protein binding. It can also cause neurological damage and strokes, by increasing the permeability of the blood-brain barrier.<sup>36-</sup>  
<sup>37</sup> Arsenic inhalation in high doses can result in effects on the gastrointestinal tract such as nausea and vomiting, the central nervous and cardiovascular systems, as well as damage to the liver, kidneys and blood. Arsenic can act as a phosphate analog, and therefore be transported quickly within a plant. Aquatic organisms exposed to high concentrations of arsenic can suffer from oxidative stress and cell damage.<sup>38</sup>

### 1.6.3 Cadmium

Cadmium has no biological role in the human body. Excess cadmium can increase the permeability of the blood-brain barrier, causing oxidative stress.<sup>36</sup> It is also very toxic to kidneys, causing dysfunction of renal tubules.<sup>39</sup> In plants, high concentrations of cadmium can cause decreased growth and biomass.<sup>40</sup> The mechanism of cadmium toxicity in fish is largely through oxidative stress, causing lipid peroxidation.<sup>41</sup> Cadmium also can bioaccumulate in organs.<sup>41</sup>

### 1.6.4 Chromium

Chromium is a non-essential element in the human body. It is up taken by replacing other essential cations, depending on oxidation states. Typically hexavalent chromium is more toxic than trivalent chromium.<sup>42</sup> In several fish species, chromium exposure caused damage to gills, kidney and liver tissue.<sup>43-44</sup> Chromium also causes stunted plant growth (particularly in the stem and leaves), and in high concentrations causes chlorosis and necrosis.<sup>45-46</sup>

### 1.6.5 Cobalt

Cobalt is an essential element in organisms for metabolism. The effect of cobalt in plants is largely turbagenic (affects mitosis processes in cells); high concentrations of cobalt can hinder the replication of RNA.<sup>46</sup> Cobalt also reduces the uptake of other essential elements, particularly iron and cadmium in roots.<sup>46</sup> In fish, as well as the generation of reactive oxygen species, cobalt exposure can cause reduced weight and appetite.<sup>47</sup>

### 1.6.6 Copper

Copper is an essential element, particularly as a co-factor for many enzymes. It also functions in electron transport and oxygen transport in some organisms. Excess copper can reduce the uptake of iron and zinc.<sup>48</sup> Low levels of copper have been shown to cause neurological damage to mice after long term exposure.<sup>49</sup> In fish, high copper concentrations can affect fertility and hatching success.<sup>50</sup> It can also replace sodium ions in sodium homeostasis, resulting in a lack of sodium causing death.<sup>51</sup> In plants, excess copper can cause necrosis, and

significantly impact the synthesis of chlorophyll and uptake of key nutrients such as nitrogen and phosphate.<sup>52</sup>

#### 1.6.7 Iron

Iron is a crucial essential element for many processes in the body, particularly oxygen transport in the form of haemoglobin and myoglobin. Because of the importance of this, almost all iron is recycled, and there is no passive mechanism for the excretion of iron. Excess iron is therefore easily accumulated, resulting in effects such as liver and heart damage and endocrine dysfunction.<sup>53</sup> Iron has been found to cause gill damage to brown trout, reducing oxygen uptake and impairing ion regulation.<sup>54</sup> Similar to copper, excess iron can cause necrosis, significantly reduced chlorophyll synthesis and inhibited uptake of phosphate and nitrogen.<sup>52</sup>

#### 1.6.8 Lead

Lead is not an essential element for organisms and plays no biological role. It is extremely toxic due to its ability to displace calcium ions. This allows lead to cross the blood-brain barrier, causing damage to the nervous system.<sup>55</sup> Lead has been shown to cause a drop in human IQ, especially in children, as well as other neurological and behaviour impairments.<sup>56</sup> It can interfere with neuronal signalling and transduction in the brain.<sup>57</sup> Studies on mice and rats show lead can cause tumours, gene mutations and can inhibit DNA synthesis and repair.<sup>58-59</sup> These effects were the major reason in the removal of lead from automobile fuel and paints. In fish, lead and lead compounds have been shown to damage immune systems and cause hyperplasia and hyperglycemia.<sup>60-61</sup> Excess lead in plants can inhibit plant growth, photosynthesis and affect membrane structure and permeability.<sup>62</sup>

#### 1.6.9 Manganese

Manganese is an essential trace element in most organisms, particularly as an antioxidant. In humans, manganese forms part of superoxide dismutase, which turns reactive oxygen species into less reactive hydrogen peroxide and diatomic oxygen. Manganese has been shown to

bioaccumulate in bones, and can cause dysfunction with dopamine processes.<sup>63</sup> In plants, manganese can reduce growth, particularly in the roots where it can hinder root cell wall modification and lignification.<sup>64</sup>

#### 1.6.10 Nickel

Nickel is an essential element in organisms, found as a part of all organs of vertebrates. It is required for biosynthesis of hydrogenase, a process for the conversion of  $H_2$  into  $H^+$  for energy.<sup>65</sup> Excess nickel cause damage through oxidative stress, and through replacing essential metals in the body.<sup>66</sup> In plants, high nickel concentrations can stunt root and stem growth, cause deformities, and cause iron deficiencies which lead to necrosis.<sup>67</sup>

#### 1.6.11 Vanadium

The role of vanadium is limited in the human body. It has been linked to improving glucose transport and metabolism.<sup>68</sup> Vanadium is typically more toxic in the pentavalent form, and can cause an array of haematological and neurobehavioral effects.<sup>69</sup> Excess vanadium in plants has been linked to a reduction in biomass, but only in some species.<sup>70</sup> In fish, high concentrations have been shown to cause higher levels of glucose while decreasing protein content in several organs.<sup>71</sup>

#### 1.6.12 Zinc

Zinc is an essential element for humans, and many plants, animals and microorganisms, playing a key role in many enzymatic reactions. The free ion acts in a structural role for several DNA transcription factors, and is also a strong Lewis acid, acting as a catalyst in reactions such as hydroxylation. Like other trace elements however, excess zinc suppresses uptake of other metals, particularly copper and iron.<sup>48</sup> Zinc ions can replace iron and magnesium ions in enzymes due to its similar ionic radii, interfering with basic cellular functions.<sup>72</sup> As a strong Lewis acid, zinc can be corrosive, and has been shown to reduce plant root and shoot biomass.<sup>73</sup> In fish, high concentrations of zinc can cause hypoxia in gill tissues, and inhibit uptake of calcium by suppressing calcium homeostasis.<sup>74-75</sup>

#### 1.6.13 Platinum group elements

There is limited information on toxicity of platinum group elements in road dust due to both the relatively recent detection of these elements and the low concentrations present in the environment. Available data indicates that PGEs are bioavailable to some degree when digested from road dust or exhaust emissions, which could cause toxic effects due to the formation of PGE-chloride complexes.<sup>76</sup> Further research is needed to determine potential effects of PGEs in the environment, especially if PGEs accumulate in road dust.

### **1.7 Factors affecting road dust generation**

The accumulation of road dust has been shown to depend on a variety of factors. The most significant factor is likely to be traffic density.<sup>77</sup> As particulate matter containing trace elements is generated by vehicles, a greater traffic density should result in more road dust accumulating in nearby gutters, with a greater concentration of trace elements. Another major factor is rainfall, as higher rainfall could wash some or all of the road dust down drains.<sup>78</sup> Road sweeping has a large effect on both the quantity of dust and concentration of trace elements in the dust. Previous research has shown that both the frequency of street cleaning and type of sweeper (typically mechanical, vacuum or regenerative air sweepers) can have an effect on road dust.<sup>79</sup> Other factors may include the land type and housing age of the area, as these factors could indicate the level of anthropogenic impact.

### **1.8 Environmental Fate**

Understanding the environmental fate of trace elements in road dust is crucial to determining the impacts of road dust. As each trace element has different physical and chemical properties, they can take different pathways into the environment. Depending on parameters of the soil, such as pH and moisture content, these elements could be transported through the soil, and potentially enter the ground water supply.<sup>80</sup> Conversely, some elements may bind strongly to the soil, making the soil more toxic to organisms exposed to the soil. High and/or regular rainfall can also wash road dust down drains, resulting in these elements ending up in storm water (especially in overflow scenarios). In addition, the suspended dust could direct enter nearby waterways, in areas such as the Avon River in Christchurch, where



stretches of the river run alongside major roads. Trace elements in the dust would then be most likely to be incorporated into the sediment, with a small fraction that could be transported down the river.<sup>81</sup> Largely insoluble elements could simply remain in the road dust, resulting in the accumulation in gutters of these elements. Lastly, although an organism may be exposed through these pathways to road dust, the trace elements can only have an effect if they are taken up.<sup>27</sup> Therefore, the bioavailability of the elements in road dust is very important to predict if road dust could have toxic effects.

Leaching studies, whereby a solution is mixed through a dust sample to simulate environmental conditions, can be used to simulate environmental availability. By using a Simulated Rainwater solution, the effects of rainfall can be predicted.<sup>82</sup> If the concentration of an element is relatively high in this solution then in the event of rainfall it is likely that this element will be transported into the stormwater system. A low concentration however means the element will likely remain in the gutter in road dust. Similarly a river sample can be used to predict if an element will be transported down a waterway or stay in the sediment layer. Finally, to measure bioavailability to aquatic organisms, a leach using 1 M HCl is a simple method to estimate what fraction of each element is bioavailable.<sup>83</sup>

## **1.9 Christchurch**

This research was conducted within the city of Christchurch. Christchurch is the largest city in the South Island of New Zealand, with a population of 375,000 in June 2016.<sup>84</sup> It is largely made up of residential suburbs, with a small Central Business District (CBD) in the centre, and a large industrial area out west. There are four major waterways that flow through Christchurch, the Avon, Heathcote, Halswell and Styx rivers. In addition, there is over 350km of uncovered streams and other watercourses.<sup>85</sup> There is therefore a large area of exposed urban waterways that could potentially be exposed to contamination from road dust, through both direct airborne pollution and through storm water overflows.

## 1.10 Analysis of platinum group elements

### 1.10.1 Difficulties in detection

Platinum group elements (PGEs) are difficult to analyse in environmental samples. Firstly, environmentally relevant concentrations are very small, typically in the  $\text{ng g}^{-1}$  range. As a result common analytical techniques, such as Atomic Absorption Spectroscopy (AAS), can have too high a detection limit to measure these elements. Due to this, pre-concentration steps are often used to effectively lower the detection limit. Secondly, they can suffer from interferences in detection. The chosen instrument for detection, Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS), can solve the first issue of low concentrations, however it can suffer from several forms of interferences due to the formation of polyatomic and doubly charged ions in the plasma.<sup>86</sup> These interfering ions can have the same mass-to-charge ratio as the PGE being measured, resulting in a falsely inflated result.<sup>24</sup> To combat this, the ICP-MS used contains a helium collision cell that uses kinetic energy discrimination to overcome unwanted polyatomic molecules generated.<sup>86</sup> For the best removal of interfering ions, digestion and separation methods can be used to separate out elements known to interfere (described below).

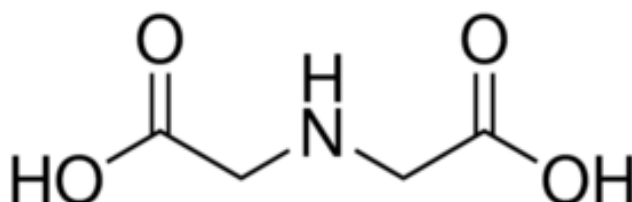
### 1.10.2 Digestion and separation methods

There are several methods currently available for digestion, separation and analysis of PGEs in road dust samples. Acid digestion is a commonly used first step to prepare samples for analysis, usually with aqua regia, as nitric acid breaks down the matrix of the road dust while hydrochloric acid extracts the PGEs.<sup>87</sup> Separation or extraction of PGEs is typically done by ion exchange, co-precipitation or fire assays. Ion exchange uses cationic, anionic or chelating resins to selectively bind metals from a sample, which can then be elucidated from the resin to be analysed, therefore reducing interferences. Co-precipitation involves using a precipitating agent, typically tellurium which forms PGE containing precipitates, which can then be separated and redissolved in acid and analysed. These methods can suffer from poor recoveries, and even the addition of iodide ions (usually KI, which inhibits the co-precipitation of copper forming the  $\text{CuAr}^+$  species) does not completely fix this.<sup>24</sup> Fire assay methods use a flux to reduce a sample at very high temperatures, with the PGEs concentrating into a so

called 'button', which can then be analysed. Fire assays can result in very low detection limits, however usually use relatively large sample amounts, and require expensive and specialized equipment and training. Due to the difficulties of the other methods, acid digestion followed by ion exchange was chosen to be developed as a method to separate PGEs.

#### 1.10.3 Ion exchange method

The ion exchange resin selected for PGE analysis was Amberlite IRC 718. This chelating resin contains iminodiacetic acid functional groups (Figure 1.1), a tridentate ligand able to bind to a transition metal through both the nitrogen atom and the two oxygen atoms from the hydroxyl groups:



*Figure 1.1: Iminodiacetic acid, the functional group in Amberlite IRC 718*

This binding is particularly stable as binding a metal centre will form two 5 membered rings.<sup>88</sup> Amberlite IRC 718 is shipped in the sodium form, meaning that sodium is bound in the active sites of the function groups. This allows for easy ion exchange, as the sodium is readily replaced by most transition metals. Thiourea is then used to extract the PGEs from the resin. Amberlite IRC 718 was relatively inexpensive to purchase, and as resins can be regenerated (by adding strong acid or base to form the  $H^+$  or  $Na^+$  form respectively), this method could potentially create an inexpensive, reproducible method to analyse PGEs in road dust sediments.

#### 1.10.4 Thiourea as an extractant

Thiourea is an ambidentate, organosulfur compound. It can bind through either the nitrogen or sulfur atom, resulting in a wide variety of binding affinities depending on the metal ion.<sup>89</sup> These binding affinities follow hard acid/ soft base (HSAB) theory, where a hard Lewis acid

will preferentially bind to a hard Lewis base, and vice versa. In this scenario, thiourea binding through the sulfur atom is a soft Lewis base, and will strongly bind and complex with PGEs, which are soft Lewis acids. This makes thiourea a good extractant to desorb PGEs from the iminodiacetic acid resin. In addition to the resin method, thiourea was also used in two other complexation methods for analysing PGEs. The modified USEPA 200.8 method used acid digested samples and diluted them with thiourea in nitric acid before analysis. The concentration method took a portion of an acid digested sample, evaporated off the acid then the sample was made up to a reduced volume with the same thiourea/nitric acid mixture, thus preconcentrating the sample.

#### 1.10.5 Aqua regia

A fourth method was attempted to measure PGEs using aqua regia as an extractant. This was to see if a harsher acid would release more PGEs from the road dust matrix. This method was based on a method by De Silva et al (2016).<sup>90</sup> Road dust samples were digested in a small amount of aqua regia, then made up to volume with thiourea in nitric acid before ICP-MS analysis.

### **1.11 Thesis introduction**

There is a large range of data concerning the concentration of trace elements worldwide, however the available data in New Zealand is both limited and outdated. As the only study conducted in Christchurch was performed in the late 1970's, several changes, such as removal of lead, the growth of the city and the Christchurch earthquakes, are likely to have had an effect on trace element concentrations in road dust. There are also few studies that measure environmental availability of trace elements in road dust, which is important to estimate the potential risk road dust presents. In addition to this, the introduction of catalytic converters have made PGEs potential contaminants in road dust. This thesis therefore will provide updated data on Christchurch road dust trace element concentrations, predict the impact these elements could have on waterways and attempt to develop a method to detect platinum group elements in road dust.

### **1.12 Aims**

The aims of this research were to:

- Determine spacial and temporal concentrations of trace elements in road dust in Christchurch
- Compare trace element concentrations in road dust to historical data for Christchurch and other cities
- Examine links between road dust trace element concentrations and traffic density, weather and other parameters
- Determine trace element concentrations in different particle size fractions of road dust
- Develop a method to measure PGEs in road dust
- Simulate the environmental availability of trace elements in road dust through leaching studies

### **1.13 Thesis structure**

Chapter 2 describes the sites around Christchurch selected for sampling. It also includes methods for trace element and PGEs analysis, and for the leaching studies. Chapter 3 presents road dust characteristics and trace element concentrations. It also examines the effects of various factors that could affect road dust, as well as temporal and spatial trends. Platinum group element results are presented for each method. Chapter 4 contains the results from leaching studies, and the implications of these. Chapter 5 summarises the results of this thesis, discusses the environmental impact and identifies potential future work.

## 2. Methods

### 2.1 Sample sites

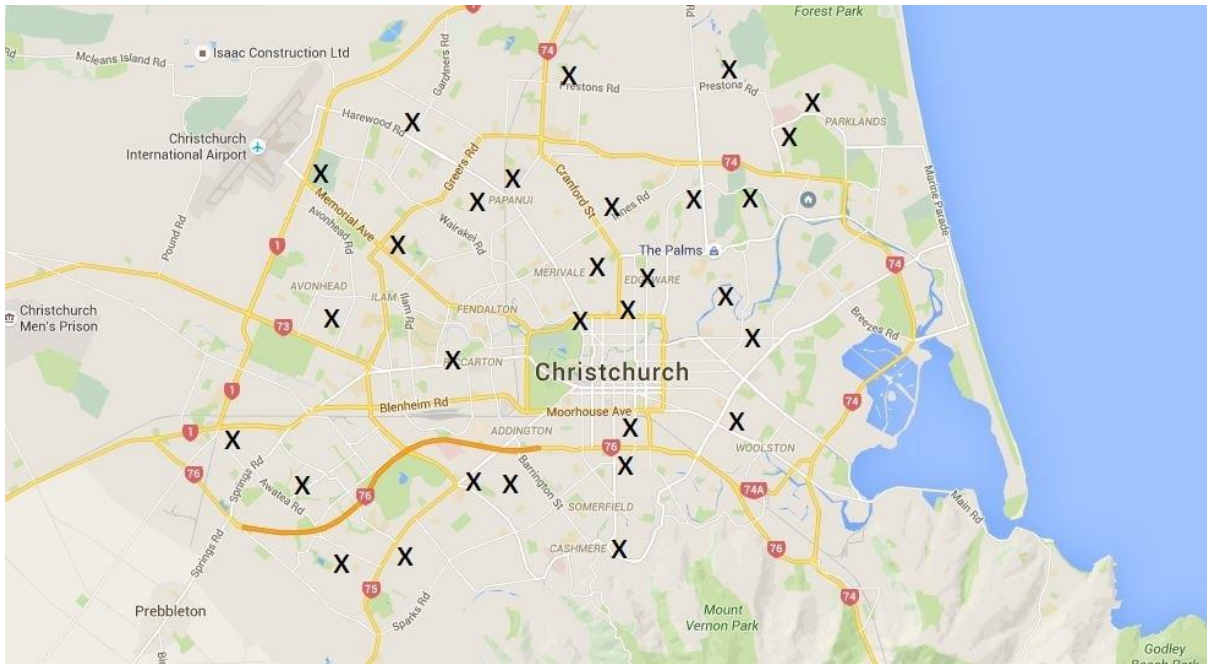
Sampling sites (n= 30) were chosen to reflect a range of traffic densities across Christchurch roads. (Presented in Appendix 1, with GPS coordinates and site parameters). The traffic densities were obtained from the Christchurch City Council, and as not every road was surveyed in the same year, the sites were grouped into traffic density ranges (Table 2.1).<sup>91</sup> The 30 sites were selected to provide both a large spatial variety over the urban Christchurch area, and a pairwise comparison of traffic density (Figure 2.1). Sites of high traffic density such as Lincoln Rd were paired with sites of low density such as Edinburgh Street to compare road dust concentrations within the same environment. Data was collected for each site on land type, soil type and housing age.

*Table 2.1: Traffic category levels, based on data from Christchurch City Council<sup>91</sup>*

<b>Traffic Category</b>	<b>Daily traffic average, averaged over 1 week</b>
<b>Very Low</b>	<5,000
<b>Low</b>	5,000 - 10,000
<b>Medium</b>	10,000 - 20,000
<b>High</b>	>20,000

Several sites were chosen based on the age of the area. Both Tumara Park (Amoka Crescent site) and Aidanfield (Aidanfield Dr site) subdivisions were only opened for residential use in the early 2000's.<sup>92</sup> These sites allowed for comparison of any legacy contaminants such as lead from leaded fuel, as these sites should be relatively free from lead from these sources due to their previous land use. For example, Tumara Park prior to subdivision was part of Bottle Lake Forest (and therefore should be relatively free of lead). Bealey Ave, Harper Ave, Lincoln Rd, Main South Rd, Papanui Rd, Riccarton Rd and Woodham Rd sites were chosen based on the previous research conducted by Jack Fergusson, to provide a historical comparison.<sup>14-15</sup> Sample sites were not selected within the CBD, as this was where most of

the damage occurred from the several earthquakes that have occurred since 2010, which would be likely to affect trace element concentrations. The 30 sites were sampled in July and November to provide a seasonal comparison, while 10 of the sites were sampled monthly to examine the impact of varying factors such as rainfall on trace element concentrations.



*Figure 2.1: Location of 30 sampling sites across Christchurch city (Google Maps)*

## 2.2 Sampling

Dust samples were collected using a modified portable ZIP vacuum cleaner (Figure 2.2). The filter was lined with 20  $\mu\text{m}$  SEFAR NYTAL sieving mesh to protect the motor from fine dust particles, and the polycarbonate bowl lined with a polyethylene zipper storage bag to collect each sample. A smaller polyethylene zipper storage bag was used to collect the dust collected by both the mesh fabric and the filter. To collect the samples, 1 m of gutter was measured, and all dust within the measured area was collected by vacuum. Samples were then weighed in the lab to measure quantities of dust per site.

A water sample was collected for use as a stream water leach. This was collected from Avon River, adjacent to the Harper Ave site. The water sample was collected in an acid washed polycarbonate container that was rinsed with water from the Avon River several times before the sample was collected. A sample of this water was sent to Hills Laboratories for anion concentration measurement, while pH was measured by a pH meter (results in Appendix 2).



*Figure 2.2: Modified vacuum cleaner used for sampling road dust. (Left) Assembled vacuum cleaner. (Right) Filter and pre filter, separated by 20  $\mu\text{m}$  mesh.*

### **2.3 Contamination**

Contamination of dust samples during sampling was minimised by the large volume of sample taken. With most samples being larger than 10 g small traces of previous samples will have limited effect on the concentrations measured in the sample. Between each sample collection, the vacuum cleaner was cleaned by using a can of compressed air, followed by wiping out with a paper towel. The pre filter, filter and 20  $\mu\text{m}$  mesh were cleaned by a fine paintbrush, and the 20  $\mu\text{m}$  mesh was replaced after every 5 samples. All samples were double bagged to prevent loss of sample or contamination from other samples. Between sampling



events the vacuum cleaner was further cleaned using a high pressure air compressor to blow out any remaining dust.

## 2.4 Materials

Table 2.2 lists the materials and reagents used in this research.

*Table 2.2 List of materials used and brand/supplier*

<b>Material</b>	<b>Supplier/Brand</b>
Ultra-pure quartz distilled HCl (24%)	University of Otago
Ultra-pure quartz distilled HNO <sub>3</sub> (70%)	University of Otago
AR Grade H <sub>2</sub> SO <sub>4</sub> (98.5%)	Ixom
Thiourea (powder form)	Sigma Aldrich (Merck)
Amberlite 748 IRC chelating resin	Alfa Aesar (Thermofisher)
50 ml polycarbonate falcon tubes	LabServe
50 ml centrifuge tubes	LabServe
Syringes (blue)	Chirana
0.45 µm disposable membrane filters	Strata
NYTAL sieving mesh (20 & 63 µm size)	SEFAR

## 2.5 Acid digestion

Road dust samples were prepared for ICP-MS analysis using a modified version of USEPA method 200.8.<sup>93</sup> Samples were firstly sieved using a 2mm stainless steel sieve, then 1g of each sample was accurately weighed out into acid washed polycarbonate falcon tubes. To each sample, 4 ml of (1+1) nitric acid and 10 ml of (1+4) hydrochloric acid was added and samples left to stand overnight. Samples were refluxed at 85°C in heating blocks for 40 minutes. Once cooled, the tubes were made up to 20 ml with ultrapure water while swirling, then left overnight to settle out particulates. Finally, the samples were diluted by a factor of 21 by adding 0.5 ml of sample to 10 ml of 2% nitric acid in ICP-MS tubes, and submitted for analysis (Agilent 7500 ICP-MS, operating conditions in Appendix 2). For particle size analysis, road dust was sieved using 63 µm SEFAR NYTAL sieving mesh before digestion.

An internal Certified Reference Material (CRM) of NIST SRM 1643f was analysed with all batches, with acceptable recoveries for all elements (Table 2.2). NIST SRM 2702 was used as an external CRM. This was used as it is from a sediment sample, which is similar to a road dust matrix. Four replicates of this CRM were analysed. Recoveries for most trace elements were within expected values. Iron results were included, despite the removal of iron values from the CRM certificate for revision, as the results were within expected values. Excluding antimony, all other element CRM recoveries were within 10% of the reference value. Detection limits were calculated as three times the standard deviation of all blanks run throughout analysis. This was raised to  $0.1 \mu\text{g L}^{-1}$  if lower than  $0.1 \mu\text{g L}^{-1}$ , as this was the lowest concentration of standard run at the beginning of each ICP-MS run. Manganese was reported as  $1.0 \mu\text{g L}^{-1}$  because the  $0.1 \mu\text{g L}^{-1}$  standard result was inaccurate by more than 10%. All duplicates were less than 10% in difference. Every 20<sup>th</sup> sample was spiked as a measure of accuracy. Spike values were all within expected values, except for iron which had much greater recovery (143.0%), likely due to the small spike concentration relative to the sample concentration.

Table 2.3 Accuracy and precision measures for acid digestion method

Element	<sup>75</sup> As	<sup>111</sup> Cd	<sup>59</sup> Co	<sup>52</sup> Cr	<sup>63</sup> Cu	<sup>56</sup> Fe	<sup>55</sup> Mn	<sup>60</sup> Ni	<sup>208</sup> Pb	<sup>121</sup> Sb	<sup>51</sup> V	<sup>66</sup> Zn
<b>Internal</b>	109.3	105.0	105.4	104.6	96.9	106.3	105.8	100.2	100.3	108.7	108.2	100.0
<b>Recovery %</b>												
<b>SRM 2702</b>	35.5	0.74	27.8	224	94.3	5.57%	1485	46.2	117.6	0.4	25	393.2
<b>(Mean)</b>												
<b>Certified</b>	45.3	0.82	27.8	352	117.7	7.9%	1757	75.4	132.8	5.6	357.6	485.3
<b>Value</b>												
<b>%Recovery</b>	78.4	90.7	79.3	63.7	80.1	70.5	84.5	61.3	88.5	8.0	71.2	81.0
<b>Detection</b>	0.002	0.002	0.002	0.012	0.002	0.2	0.2	0.002	0.002	0.003	0.004	0.2
<b>Limit (µg g<sup>-1</sup>)</b>												
<b>Mean</b>	2.04	1.96	3.56	4.96	2.89	2.79	2.82	2.48	3.14	1.06	3.76	2.24
<b>Duplicates</b>												
<b>%Difference</b>												
<b>Spike</b>	98.3	98.5	99.1	107.3	111.4	143.0	113.6	91.2	118.2	95.1	92.3	112.8
<b>Recovery</b>												

## 2.6 PGE method testing

Four methods were used to separate and concentrate PGEs for analysis. These were chosen as they allowed comparison to measure the effectiveness of the Amberlite resin as a separating reagent. <sup>101</sup>Ru, <sup>105</sup>Pd and <sup>195</sup>Pt were the isotopes analysed to minimise ICP-MS interferences. Each method is detailed below.

### 2.6.1 Modified USEPA 200.8 method<sup>93</sup>

Samples were acid digested with hydrochloric and nitric acids as described previously (Section 2.5). After leaving to stand, 1 ml of each sample was transferred to ICP-MS submission tubes, and 9 ml of 0.5 g L<sup>-1</sup> thiourea in 2% nitric acid was added for dilution and the samples mixed thoroughly.

### 2.6.2 Concentration method

Samples were acid digested with hydrochloric and nitric acids as described for acid digestion. After leaving to stand, 15 ml of each acidified sample was transferred to a new polycarbonate falcon tube. The tubes were heated at 90 °C in a heating block with the lids off, until all the solution had evaporated (Figure 2.3). The samples were then made up to 5 ml with 0.5 gL<sup>-1</sup> thiourea in 2% nitric acid, transferred to ICP-MS tubes and submitted for analysis.

### 2.6.3 Resin method

This method is based on a method by Park (2000).<sup>89</sup> Samples were digested as described in acid digestion step. A 15ml aliquot was then evaporated as described in the Evaporation method. The samples were brought up to 10 ml with 1 M HCl acid. 0.5 g of Amberlite IRC 748 resin was added to the tube, and rotated on an end-over-end mixer for 2 hours at approximately 40 rpm (Figure 2.3). This solution was then decanted into a separate tube for analysis, and to the remaining resin a further 10 ml of 1 M HCl acid was added. This was rotated again on the end-over-end mixer then decanted and 4 ml of 0.25 M thiourea solution was added and rotated with the resin to extract the PGEs. Both decanted HCl solutions and the final thiourea solution were diluted 5 times with 0.5 gL<sup>-1</sup> thiourea in 2% nitric acid to reduce the salt content, and submitted for ICP-MS analysis.



*Figure 2.3 End-over-end mixer for slow mixing of samples*

#### 2.6.4 Aqua regia

A fourth method using concentrated aqua regia was also used to determine whether the harshness of the acid affects the release of PGEs from road dust. This method is based on a method by De Silva (2016).<sup>90</sup> 0.5 g of road dust was accurately weighed out into a 50 ml polycarbonate falcon tube. 2.5 ml of aqua regia (1:3 24 % HCl to 70% HNO<sub>3</sub> ratio) was added and left to digest overnight. Samples were refluxed at 85 °C for 2 hours, made up to 50 ml with 0.5 gL<sup>-1</sup> thiourea in 2% nitric acid, left overnight to allow particulates to settle, then the top 10 ml was taken off and submitted for ICP-MS analysis.

### **2.7 Loss on ignition**

Loss on ignition was used as a method to measure the organic matter of road dust samples, using a modified method from Dean (1974).<sup>94</sup> Ceramic crucibles were washed with 70% ethanol and weighed. Approximately 5 g of road dust was added to the crucible and then reweighed. The crucibles were loosely covered with lids, and placed in a muffle furnace at 550 °C for four hours, then left to cool overnight. The crucibles were reweighed the next day, and the weight loss expressed as percentage of organic matter in a road dust sample.

### **2.8 Leaching Protocols**

Three separate leaching experiments were performed to simulate leachability of trace elements in Christchurch road dust. These were conducted on road dust from the same 5 sites from different sampling events, with 1 duplicate to measure precision (Table 2.4). These samples were selected as there was sufficient material to complete the study. Each method is summarised below.

*Table 2.4 Sites selected for leaching studies*

Site	Month
Corsair Dr	May
Centaurus Rd	June
Te Korari St	June
Prestons Rd	July
Lake Terrace Rd	July

### 2.8.1 Synthetic rain water

A synthetic rain water solution was used to simulate the leaching of trace elements by rain water in storm water drains, from a modified version of USEPA method SW846/1312.<sup>82</sup> The synthetic rain water solution was prepared by making a 60:40 weight percentage mixture of concentrated sulfuric and nitric acids (3.26 ml of 99% AR grade sulfuric acid with 2.65 ml of 70% AR grade nitric acid). This mixture was added in 100 µL volumes to 300 ml of ultrapure water until the solution reached a pH of 4.2. As the solution was unbuffered, it was freshly prepared each time as required.

### 2.8.2 Stream water

Stream water was used to simulate the leaching of trace elements in waterways. This leach reflects what proportion of the trace elements could be transported through the waterway as opposed to remaining in sediment. This method was based on the same USEPA method as the simulated rainwater leach (SW846/1312).<sup>82</sup> A water sample was taken from the Avon River, adjacent to the Harper Ave road dust site. This water sample was analysed for trace element concentrations by first filtering using a 0.45 µm membrane filter, followed by acidification by HNO<sub>3</sub>, then submitted for ICP-MS analysis. A subsample of the water was sent to Hills Laboratories in Hamilton for anion concentration analysis. The pH of the water sample was 7.2.

### 2.8.3 Bioavailability

A bioavailability leach was performed using hydrochloric acid to estimate uptake of trace elements through a digestive tract. Bioavailability is difficult to measure as it is different for every organism, however 1 M HCl is commonly used in Acid Volatile Sulphide/ Simultaneously Extracted Metals (AVS-SEM) methods.<sup>83</sup> The strength of the acid used means that this method can be considered a good measure of “non-bioavailability”, as although the fraction leached could be bioavailable depending on the organism, the fraction not leached is very likely to not be bioavailable.

### 2.8.4 Leaching protocols

All leaching experiments were conducted in centrifuge tubes. The samples were weighed out into the tubes, the leaching solution was added and left to rotate on an end-over-end mixer overnight at approximately 40 rpm. Both the stream and storm water leaches were filtered using 0.45 µm membrane filters using blue Chirana syringes, to remove particulate matter. The bioavailability leach was not filtered because due to the much greater liquid: solid ratio, the extractant could be removed for analysis without disturbing any particulate matter. The solutions were diluted by a factor of 10 with 2% HNO<sub>3</sub> analysed by ICP-MS. The quantities and reagents used for each leaching experiment are summarised in Table 2.5.

*Table 2.5: Summary of leaching protocols*

Leaching Protocol	Solution	Volume	Sample weight
<b>Storm water</b>	Synthetic rain water	20 ml	1 g of road dust
<b>Stream water</b>	Stream sample	20 ml	1 g of road dust
<b>Bioavailability</b>	1 M HCl	50 ml	0.5 g of road dust

Detection limits and duplicates were calculated the same as per the acid digestion method (Table 2.6). Additional spikes were not performed due to the low number of samples involved. The variability between duplicates was much greater compared to the duplicates for acid digestion (for example, 22.3 % for lead compared to 3.14% during acid digestion method).

Table 2.6 Detection limits and ICP-MS duplicates for leaching tests

Element	<sup>75</sup> As	<sup>111</sup> Cd	<sup>59</sup> Co	<sup>52</sup> Cr	<sup>63</sup> Cu	<sup>55</sup> Mn	<sup>60</sup> Ni	<sup>208</sup> Pb	<sup>121</sup> Sb	<sup>51</sup> V	<sup>66</sup> Zn
Detection Limit (µg L <sup>-1</sup> )	0.26	0.1	0.1	0.1	0.37	1	0.1	0.12	0.22	0.1	0.5
Duplicates	17.2	0.6	12.8	4.8	8.3	5.5	5.0	22.3	11.4	5.3	11.0
%Difference											

## 2.9 Health and Safety

The major health and safety hazards associated with this research were around the sampling programme. To understand the risks involved with sampling, such as traffic and weather, a risk assessment and field activity plan was prepared for every sampling trip. Samples were collected where possible from beside a parked car, in order to minimise the risk from traffic driving past. A hi-vis vest and suitable footwear were also worn at all times. Constant contact was kept with the university through a cell phone, and sampling was conducted in pairs in case of emergency. In the lab, all work was performed while wearing a lab coat, safety glasses and gloves. Work involving solvents or heating was done inside a fume hood, to isolate any hazards involved. All lab procedures that were classed as a risk category of 3 or 4 had a risk assessment form completed before they were performed, and the MSDS of each reagent was checked. In particular, care was taken when using concentrated acids, as they are extremely corrosive.

## 2.10 Statistical Analysis

RStudio statistical software was used for all statistical analysis of data. Linear regression was used to establish significant and relevant relationships between factors and trace element concentrations. Student and paired t-tests were used for determining statistical differences, with equivalent nonparametric methods used when the data was not normally distributed. Spearman rank correlation coefficients were used to determine element-element relationships for source identification. For categorical data such as soil types, analysis of



variance (ANOVA) was used, with Tukey tests as post hoc tests for cases of significance. Inkscape was used to generate geochemical maps for spatial analysis.

## 3. Trace elements in road dust

### 3.1 Introduction

Road dust is a source of trace elements in cities across the world. There are however limited, previous studies in New Zealand, with the two main studies conducted in 1978 and 1984.<sup>10,14</sup> These studies are decades out of date, and only measured a limited number of elements. Changes to the composition of fuel and car components are likely to have altered the concentrations of trace elements in road dust. Road dust as a source of contaminants is important for Christchurch, as it contains a large urban waterway network that could be exposed to pollution from road dust. This research was designed to determine current trace element concentrations in Christchurch road dust.

Road dust samples were collected from 30 sites across Christchurch over a 7-month sampling programme. Quantities were recorded for each road dust sample collected throughout sampling. Data was divided into two sets of data. The temporal dataset includes data from the 10 sites that were sampled monthly, while the spatial dataset includes data from the summer and winter sampling of all 30 sites, as well as an average of these two sampling events. These data sets were used to compare trace element concentrations between this study, historical, national and international road dust studies. The spatial data set was used to examine trends between trace elements in Christchurch road dust with traffic, weather and other parameters described below (Section 3.1.1). The temporal data was used for repeated measures analysis.

### 3.1.1 Study objectives

- Determine spatial and temporal concentrations of trace elements in road dust in Christchurch
- Compare trace element concentrations in road dust to historical data for Christchurch and other cities
- Examine relationships between road dust trace element concentrations and traffic density, weather and other parameters
- Determine trace element concentrations in different particle size fractions of road dust
- Develop a method to measure PGEs in road dust

## **3.2 Results and discussion**

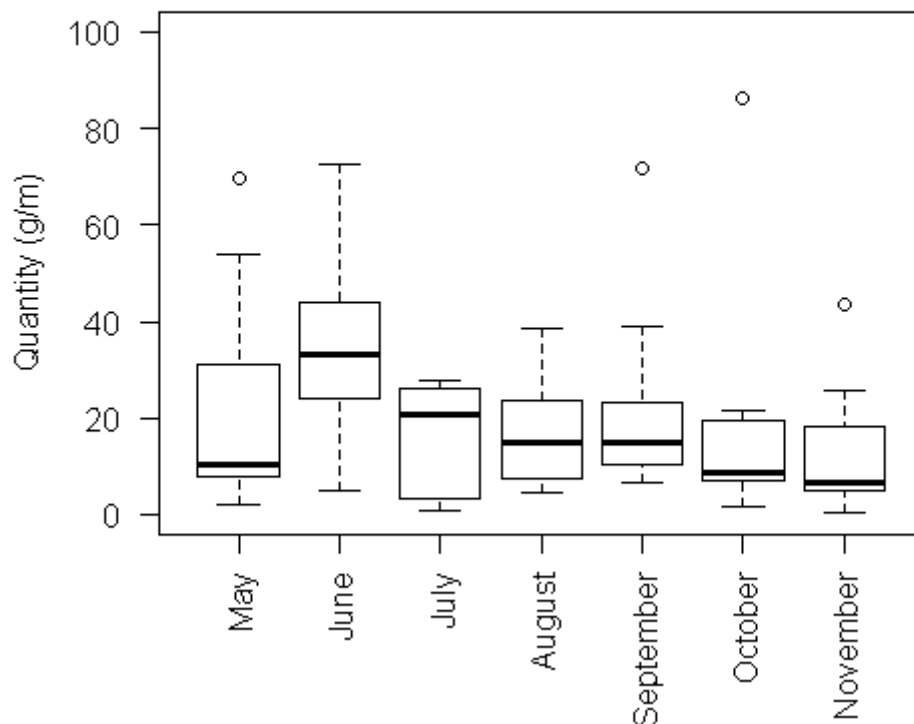
### 3.2.1 Site Parameters

Soil types for each site were determined using the Land Resource Inventory (LRI) portal, based on data by Landcare Research.<sup>97</sup> Background trace element concentrations in soils for each soil type were sourced from a Tonkin and Taylor report prepared for Environment Canterbury (ECan, Appendix 3).<sup>98</sup> Residential housing age and land use was determined from QV property reports of adjacent properties to the sampling site.<sup>99</sup> The age of the area of each site was estimated based on the age of houses adjacent to the site. Although some sites had several rebuilt houses adjacent to the site, all sites had several houses of a similar age that were the oldest in the site area, indicating the age of the suburb. Weather data on monthly rainfall, temperature and number of rain days was collected from the National Institute of Water and Atmospheric Research (NIWA), and the antecedent 5 and 10 days rainfall was recorded from NIWA before each sampling run (Appendix 4).<sup>100</sup>

### 3.2.2 Road dust quantities

Quantities of road dust obtained from each of the 10 sites in the temporal dataset are presented in Figure 3.1 (Data in Table 3.1). Road dust quantities ranged from 0.36 to 163.48 g m<sup>-1</sup>. The highest median road dust quantity for a month was in June, while the lowest was

in November, with the median road dust quantity decreasing each month from June to November. There was no significant relationship between quantity and month, although this may be due to the large outliers at some of the sites. There was also no relationship between quantity of road dust and any of the rainfall parameters described in section 3.2.1.



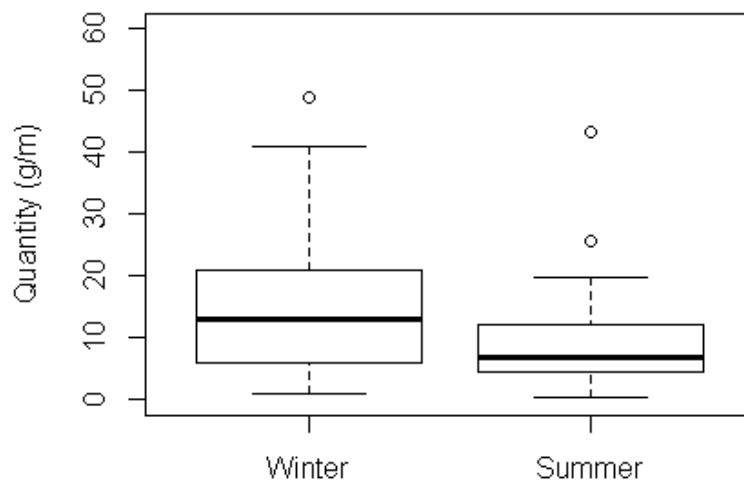
*Figure 3.1 Quantities of road dust sampled at monthly monitoring sites in Christchurch in  $g\ m^{-1}$  ( $n = 10$  for 7 months)*

The lack of significant relationships between road dust quantities and factors is consistent with literature. Although there are few studies that investigate the quantity of road dust, the general consensus is that due to the interaction of many different factors affecting road dust generation significant relationships with a single factor is unlikely.<sup>101</sup> Road dust quantities were also highly variable (Table 3.1). Road dust has been shown however to increase in quantity in areas of greater vehicle speed.<sup>102</sup> This was not observed in this study, as all sites were located on 50 km h<sup>-1</sup> roads.

*Table 3.1 Christchurch road dust median quantities for each month in  $\text{g m}^{-1}$  ( $n = 10$  for each month). Full dataset in Appendix 5*

Month	Quantity median	Standard deviation
May	10.53	22.98
June	33.31	37.69
July	20.57	48.78
August	14.97	11.85
September	14.86	19.95
October	8.75	24.92
November	6.62	13.89

There was also no significant difference in road dust quantities between summer and winter from the spatial dataset (Figure 3.2). The winter and summer medians were  $12.97 \text{ g m}^{-1}$  and  $7.03 \text{ g m}^{-1}$  respectively, and as 8 of the 10 largest quantities of road dust were collected occurred during the winter sampling, while 6 of the smallest 10 were collected during the summer sampling, the lack of significance may be due to statistical outliers.



*Figure 3.2 Comparison of Christchurch road dust quantities between winter and summer sampling in  $\text{g m}^{-1}$  ( $n = 30$ )*

### 3.2.3 Trace element concentrations and characterisation of Christchurch road dust

Trace element concentrations in road dust are presented in Appendices 6 & 7. Trace elements were detected in the following order of concentrations: Fe >> Zn > Mn > Pb > Cu > Cr > V > Ni > As ≈ Co > Sb >> Cd. This order is similar to the two previous New Zealand studies in Table 3.1, with the exception of lead and antimony. Antimony and lead concentrations were both significantly lower in order than for the previous Wellington and Christchurch studies. For all trace elements concentrations were much lower in the current study compared to other New Zealand studies (Table 3.2). This is despite the population increase in Christchurch from 1984 to 2016.<sup>84</sup> The lower lead concentrations can be attributed to the removal of tetraethyl lead from fuel and paint.<sup>5</sup> This is further shown with the comparison with the Jack Fergusson lead study in 1980.<sup>15</sup> Six of the sites from this study were resurveyed in this study (Table 3.3). Lead concentrations for these sites had greatly decreased, with the biggest decrease being a 99.0% reduction.

Table 3.2 Median trace element concentrations in road dust in New Zealand. All values in  $\mu\text{g g}^{-1}$  unless stated.

Element	This Study (Winter)		This Study (Summer)		This Study (Mean Data)		Christchurch (1984) <sup>5</sup>	Wellington (1978) <sup>11</sup>
	Median	$\sigma$	Median	$\sigma$	Median	$\sigma$	Median	Median
<b>Antimony</b>	1.43	0.84	1.42	0.83	1.40	0.59	8.9	11.4
<b>Arsenic</b>	4.69	1.94	3.70	1.71	4.61	1.44	8.25	6.1
<b>Cadmium</b>	0.14	0.39	0.14	0.42	0.18	0.37	1.1	2.2
<b>Chromium</b>	24.1	11.4	19.8	10.7	23.5	7.7	58	73
<b>Copper</b>	55.3	53.3	52.9	56.9	53.7	39.2	106	184
<b>Cobalt</b>	3.91	0.71	3.57	4.50	3.94	2.29	-	-
<b>Iron (%)</b>	1.36	0.17	1.09	0.22	1.21	0.17	2.39	3.39
<b>Lead</b>	65.0	69.1	54.9	44.1	62.4	44.7	1294	1977
<b>Manganese</b>	222.4	48.0	188.6	55.4	214.6	39.4	399	525
<b>Nickel</b>	10.5	6.8	8.77	4.59	9.68	4.79	-	22
<b>Vanadium</b>	16.2	2.2	12.6	3.0	14.7	2.3	48	68
<b>Zinc</b>	307.5	162.9	284.7	110.2	285.8	113.6	429	689

*N.B. Christchurch data was from a <0.9633 mm fraction, while Wellington data was from a 2 mm fraction.*

*Table 3.3 Mean lead concentrations in road dust ( $\mu\text{g g}^{-1}$ ) from 6 sites across Christchurch. 1980's data from Jack Fergusson study.<sup>15</sup>*

Site	This Study	1980's	Percentage Decrease
Bealey Ave	32.2	3380	99.0
Riccarton Rd	25.1	2200	98.9
Halswell Rd	35.0	2110	98.3
Papanui Rd	57.8	2860	98.0
Woodham Dr	59.2	2560	97.7
Lincoln Rd	113.1	1820	93.8

Trace element concentrations in Christchurch road dust were generally lower compared to previous international studies (from Table 1.3). Concentrations of cadmium, chromium, cobalt, iron, manganese, nickel and vanadium were all lower in the current study than all other cities previously measured. Antimony, copper and zinc were lower than all cities other than Ottawa, which generally had the lowest concentrations for most trace elements. Lead was lower than all concentrations measured in 1984, but higher than Ottawa and Birmingham (Pictured in Figure 3.3, along with New Zealand data). This again is likely to the removal of lead from fuel and paint.<sup>5</sup> Arsenic concentrations were similar to other international cities.



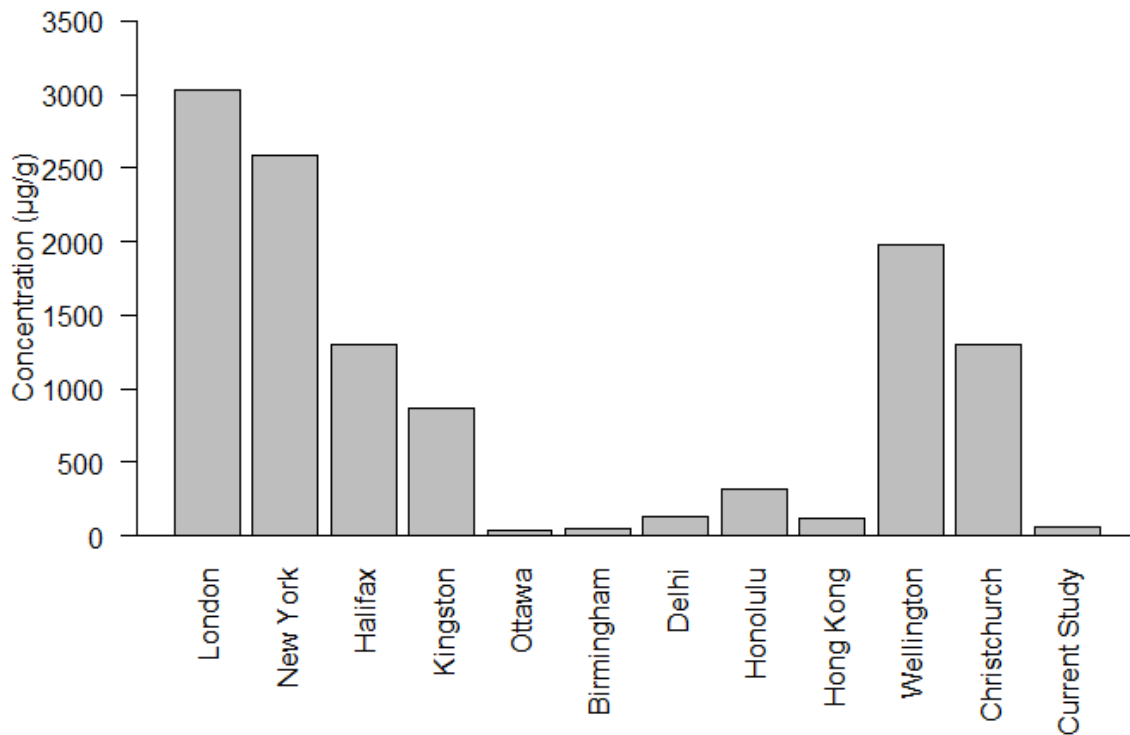


Figure 3.3 Median lead concentrations across different cities in  $\mu\text{g g}^{-1}$ . Data from Tables 1.3 and 3.1.

#### 3.2.3.1 Particle size fractioning

The effect of particle size on trace element concentrations was determined for 8 sites. Trace element concentrations were greater in the  $63\ \mu\text{m}$  fraction compared to the  $2\text{mm}$  fraction (Figure 3.4). Using Wilcoxon signed rank tests, chromium, copper, nickel and zinc were all significantly greater ( $p < 0.05$ ), while cobalt, iron, manganese and vanadium were strongly significantly greater ( $p < 0.01$ ). This increase with decreased particle size was expected, as previous New Zealand and international research has shown that trace elements in road dust tend to be greater in smaller fractions (greatest in fractions smaller than  $250\ \mu\text{m}$ ).<sup>95</sup> This is significant because smaller particles are more easily transported into waterways, and also have a higher surface area which increases adsorption of trace elements.<sup>103</sup>

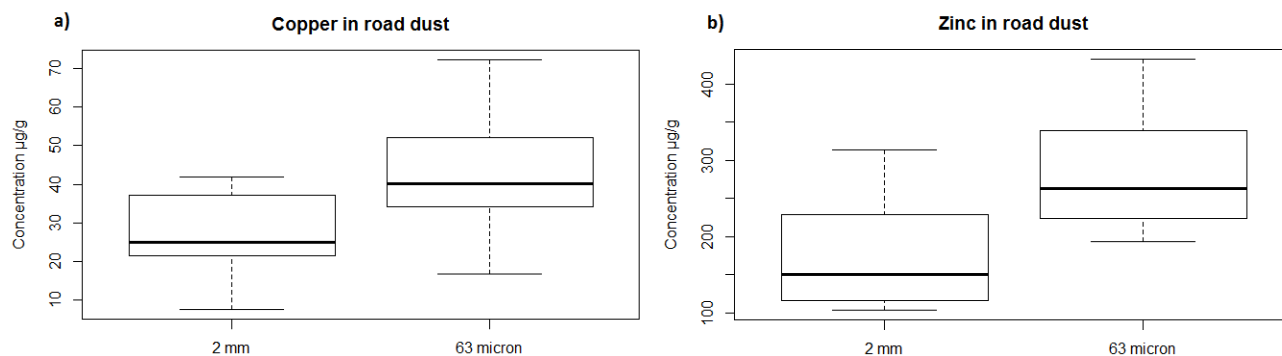


Figure 3.4 Comparisons between 2 mm and 63 µm road dust size fractions for copper (a) and zinc (b). All concentrations in  $\mu\text{g g}^{-1}$ .

### 3.2.3.2 Organic matter

Loss on ignition was used to measure the organic matter (OM) of road dust in Christchurch for 8 samples from the winter sampling sites. The average OM was 5.4% (standard deviation of 3.44%, range of 2.25% - 13.87%). The relatively high range of values is likely a reflection of the various environments each site is from (i.e sites where the gutter is adjacent to a berm would be likely to have a higher OM than sites where gutter is surrounded by pavement). The OM values measured are similar to reported OM road dust results around the world, which vary greatly depending on their soil content.<sup>5,96</sup>

### 3.2.3.4 Enrichment Factors

As road dust largely consists of soil, the background concentrations of trace elements in Christchurch soils are important in measuring the effect of vehicles on trace element concentrations. Enrichment Factors were calculated for the mean data from the spatial data set using the below equation, based on background soil trace element concentrations:

$$\text{Enrichment Factor} = \frac{\text{Road dust concentration}}{\text{Background soil concentration}}$$

The Enrichment Factors are presented below in Figure 3.5. The horizontal line at  $y=1$  reflects when trace element concentrations have the same value as background concentrations. Values higher than this line show enrichment, in this case likely generated from vehicles. Cadmium, copper, lead and zinc were all elevated above background concentrations, while arsenic, manganese and nickel were all reduced. Literature enrichment factors of road dust show similar enrichment of trace elements. Comparison of enrichment factors between different studies can be problematic as many different calculation methods are used, however copper, zinc and lead have all been regularly shown to have enrichment factors greater than 2.<sup>104</sup> A study of road dust in Ghana showed chromium, copper, lead, vanadium and zinc all with enrichment factors larger than 2, with lead and zinc the largest at 13.9 and 6.7 respectively.<sup>105</sup> Copper, lead and vanadium enrichment factors were all above 2 in a urban study in China.<sup>106</sup> These studies all had low enrichment values for cadmium, which means that either Christchurch has very low background cadmium concentrations or the deposition of cadmium in road dust is significant. This may be from the use of cadmium in yellow paint road markings.<sup>12</sup> Overall the magnitude of trace element enrichment factors for road dust were much lower than literature values, implying that trace element concentrations in Christchurch road dust are low in comparison to other countries.

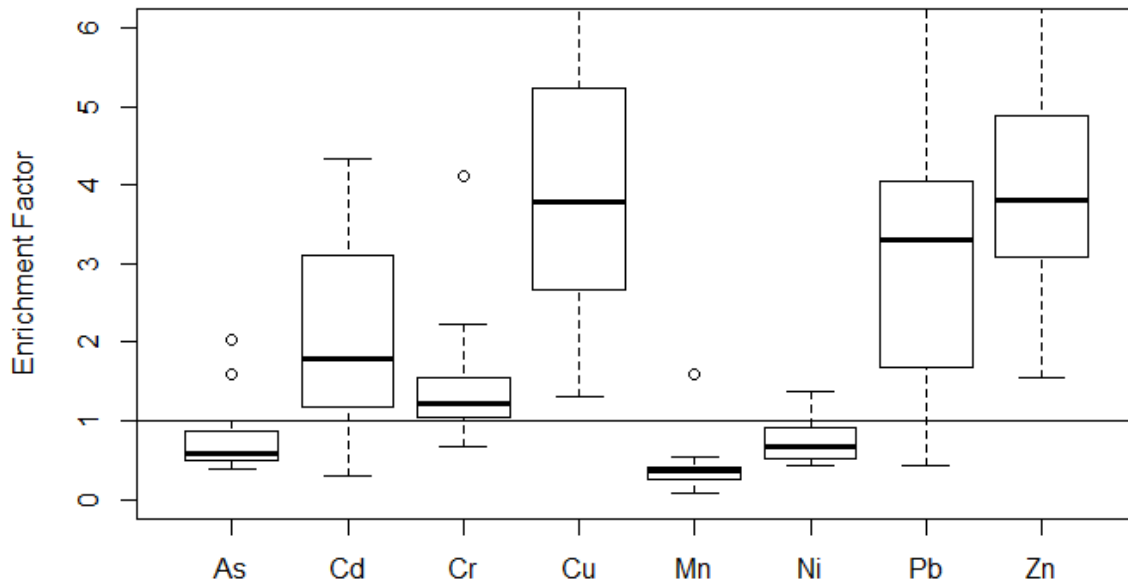


Figure 3.5 Enrichment Factors for trace elements in Christchurch road dust compared to background soil concentrations

### 3.2.4 Factors affecting trace element concentrations

#### *3.2.4.1 Traffic density*

Due to the generation and emission of trace elements by vehicles, the most likely factor affecting trace element concentrations in road dust is traffic density. The spatial data set was used for this analysis. Antimony concentrations increased with increasing traffic densities for both the winter and summer data, while chromium concentrations increased for the summer and mean data ( $p$ -values  $< 0.05$ , Figure 3.6). The lack of a relationship between traffic density and most road dust trace element concentrations is may be due to the fact there are several other sources of these elements for road dust. These include atmospherical deposition (particularly copper lead and zinc)<sup>107</sup> and home heating through wood burning as Christchurch has a high use of wood burners which could release arsenic if the treated timber is burnt.<sup>108</sup> The antimony result likely reflects the limited use of antimony outside of vehicle brake parts.<sup>6</sup>

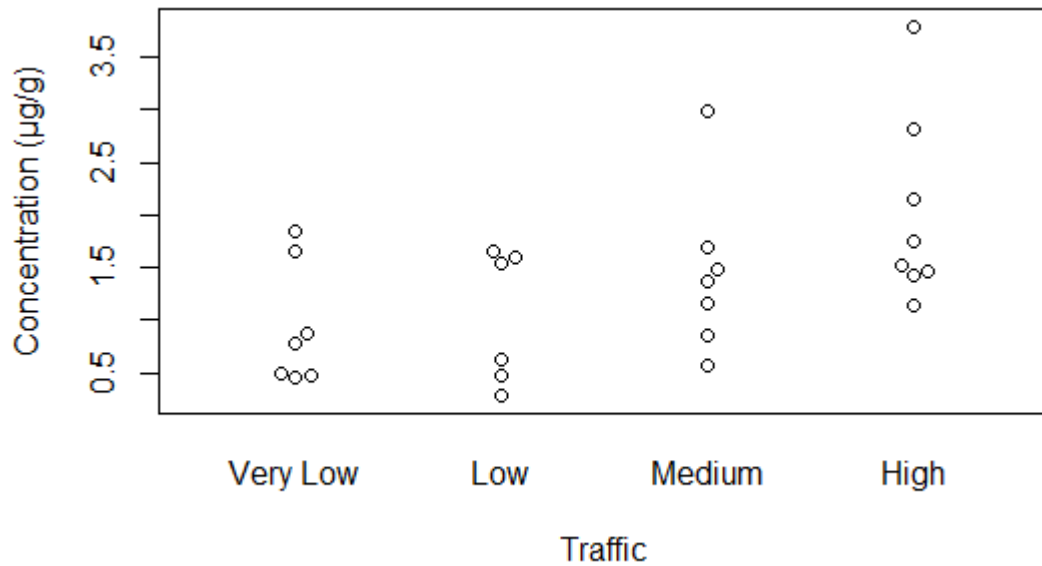


Figure 3.6 Chromium concentrations ( $\mu\text{g g}^{-1}$ ) in Christchurch road dust from summer data from sites of different traffic densities ( $n = 30$ )

Road dust studies conducted both internationally and in New Zealand have previously shown significant relationships between various trace elements and traffic density.<sup>5,109,110</sup> In some cities this may be because of the high concentrations present, of which a large proportion of is vehicle-derived. In addition, studies have shown increasing soil trace element concentrations as the proximity to a nearby road increases.<sup>111</sup> Apart from other contributing sources, another reason for a lack of significant relationships is the estimation of traffic density. As the traffic density groups were only estimated from traffic data from multiple years, a more accurate traffic density for each site may reveal the more significant relationships seen in other studies. Traffic density for each site may also have a large variance throughout the year.

#### 3.2.4.2 Land use

Trace element concentrations in road dust from sites of residential and commercial land use were compared using Wilcoxon rank sum tests with the spatial dataset. Road dust collected adjacent to commercial land had higher concentrations of antimony, iron and zinc compared to residential land ( $p\text{-value} < 0.05$ , Figure 3.7). This trend may reflect the businesses that

operate nearby the sample site. For example, the Papanui Rd site is located next to a tyre repair company, the Ferry Rd site is next to a car sales yard and the Woodham Dr site is next to a fuel station. These three business types would explain the higher zinc concentrations, as tyres are a source of zinc.<sup>7</sup> Research conducted on the Gold Coast, Australia, has also shown that road dust zinc concentrations are higher in commercial and industrial areas compared with residential areas.<sup>112</sup>

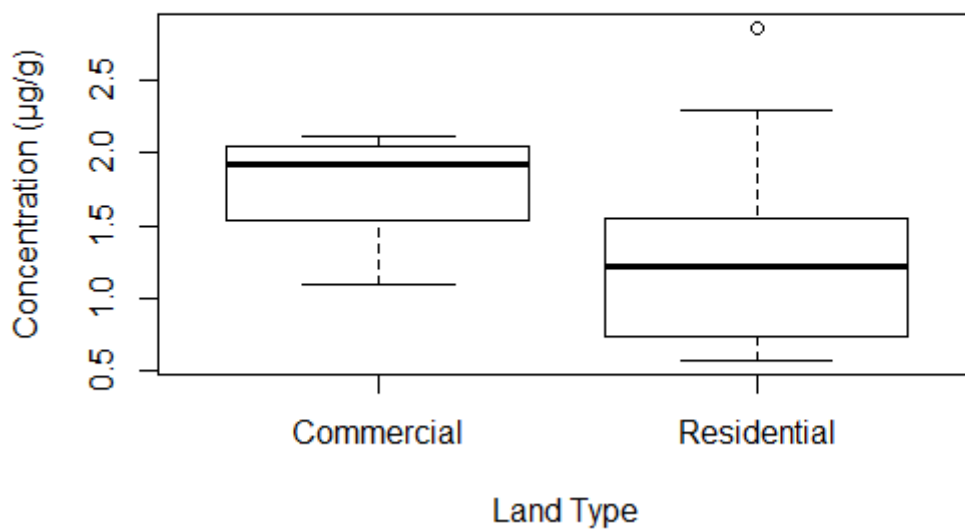


Figure 3.7 Antimony concentrations in Christchurch road dust collected from sites ( $n = 30$ ) adjacent to properties of different land uses. All concentrations in  $\mu\text{g g}^{-1}$ .

#### 3.2.4.3 Subdivision age

The effect of subdivision age on trace element concentrations in road dust was investigated. Average house age was modelled against trace element concentrations from the spatial dataset (Figure 3.8). Antimony, copper and lead concentrations were higher in newer subdivisions ( $p\text{-value} < 0.05$ ). This result was unexpected as typically older areas have higher trace element concentrations, as they accumulate over time.<sup>113-114</sup> This effect could potentially be a reflection of increasing vehicle numbers in Christchurch, however this is unlikely for lead. The lead relationship may be due to previous land use, such as the Wigram

Skies site, which is a new subdivision. This site was previously an aircraft base, so the presence of aviation fuel at the base would explain the high lead concentration.<sup>115</sup> There was no significant relationship between age and road dust trace element concentration for commercial sites.

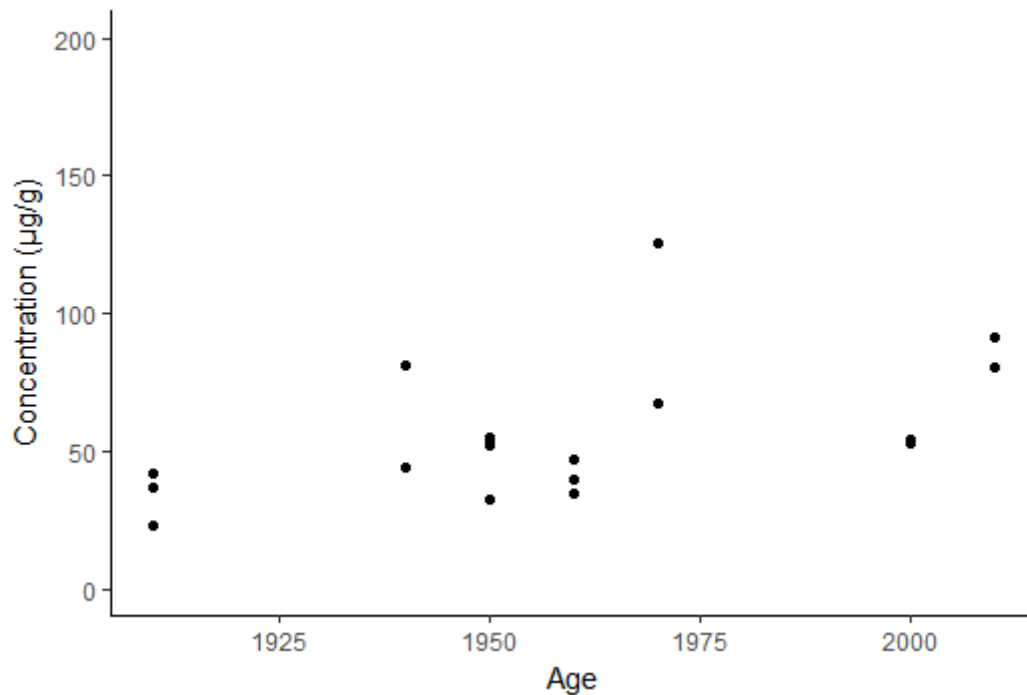


Figure 3.8 Mean copper concentrations in Christchurch road dust from sites of varying residential ages ( $n = 30$ , all concentrations in  $\mu\text{g g}^{-1}$ ).

Four pairs of sites, each containing a post 2000 subdivision and a nearby older main road, were used to further investigate the effect of subdivision age on road dust trace element concentrations. Paired t-tests were used to identify differences between these two groups. There were no statistically significant differences between the groups were found. Despite this, the four new subdivisions had some of the lower trace element concentrations, with all four sites having concentrations of chromium and antimony that were in the lower 50% of all spatial dataset values, while lead concentrations of the four sites were within the lowest 7 recorded values.

#### 3.2.4.4 Weather

Weather parameters as rainfall and temperature have been demonstrated to have an effect on the generation of road dust and trace elements concentrations.<sup>78</sup> Vanadium was the only element to show a statistically significant relationship with number of days of rain, with a positive relationship suggesting vanadium concentrations were highest during months that are regularly wet, however the slope of the line was very shallow ( $p$ -value  $< 0.01$ ,  $R^2 = 0.4403$ , presented in Figure 3.9). No elements showed relationships with any other weather parameter. Studies comparing rainfall and trace element concentrations show similar results, with many trace element concentrations independent to these factors.<sup>116,117</sup>

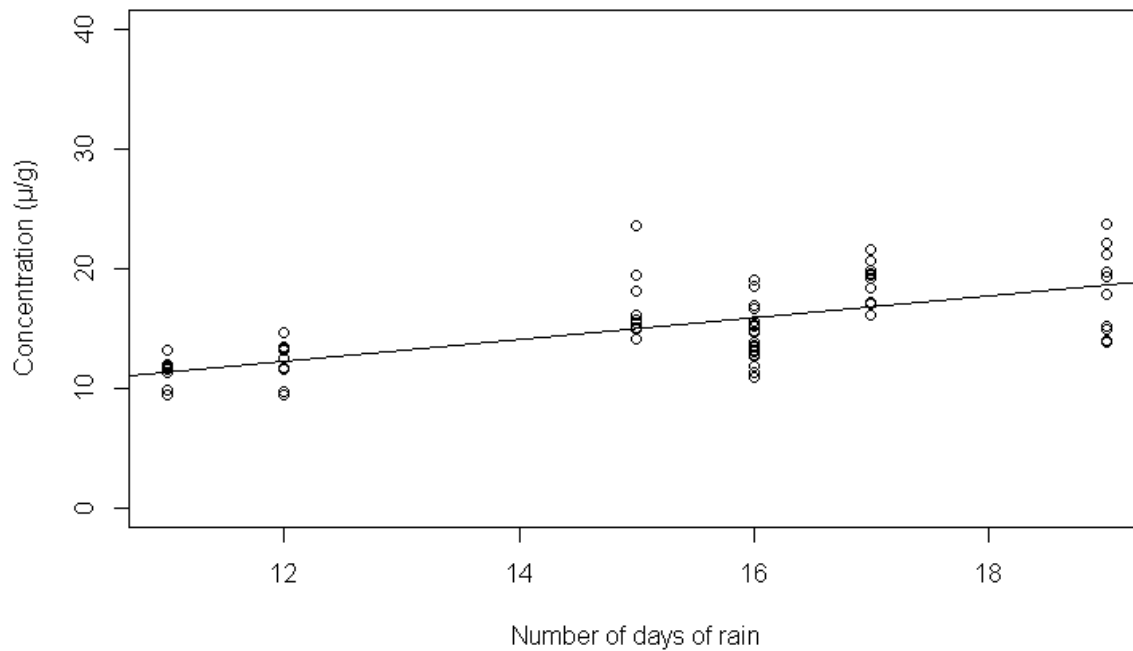


Figure 3.9 Vanadium concentrations in Christchurch road dust from monthly sampling, by number of days of rain per month ( $n = 30$ , all concentrations in  $\mu\text{g g}^{-1}$ ).



### 3.2.5 Temporal trends of concentrations of trace elements in road dust

Road dust samples were collected from 30 sites in July and again in November to allow for a seasonal comparison (spatial dataset). Arsenic, chromium, iron, manganese and vanadium concentrations in road dust were greater in winter compared to summer (p-value <0.05, presented in Figure 3.10).

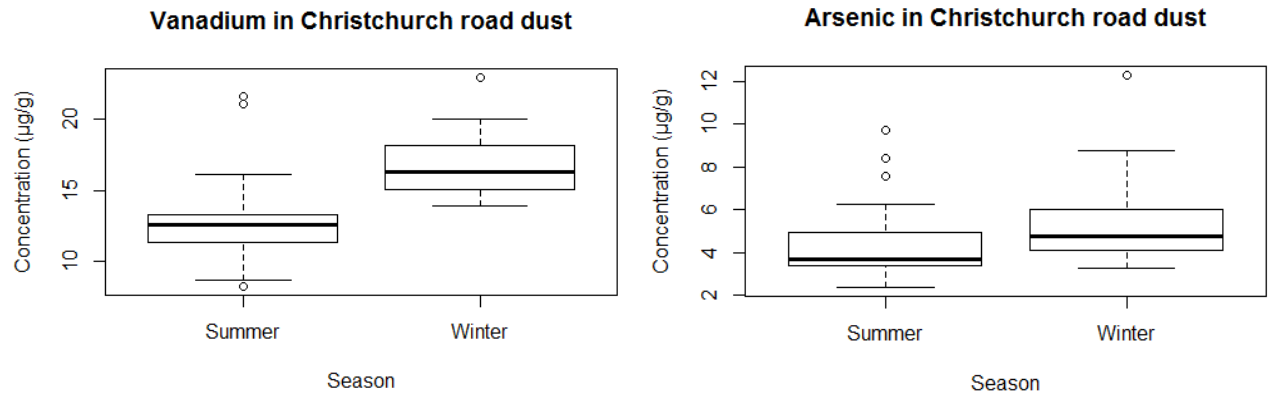


Figure 3.10 Summer/winter comparisons for vanadium and arsenic concentrations in road dust respectively ( $n = 30$ , all concentrations in  $\mu\text{g g}^{-1}$ ).

Monthly data from the temporal dataset was analysed using one-way repeated measures ANOVA. Concentrations of iron and vanadium decreased over time ( $p < 0.05$ , Figure 3.11). This reinforces the difference identified for the spatial dataset (Figure 3.10), where vanadium concentrations were higher in winter compared to summer.

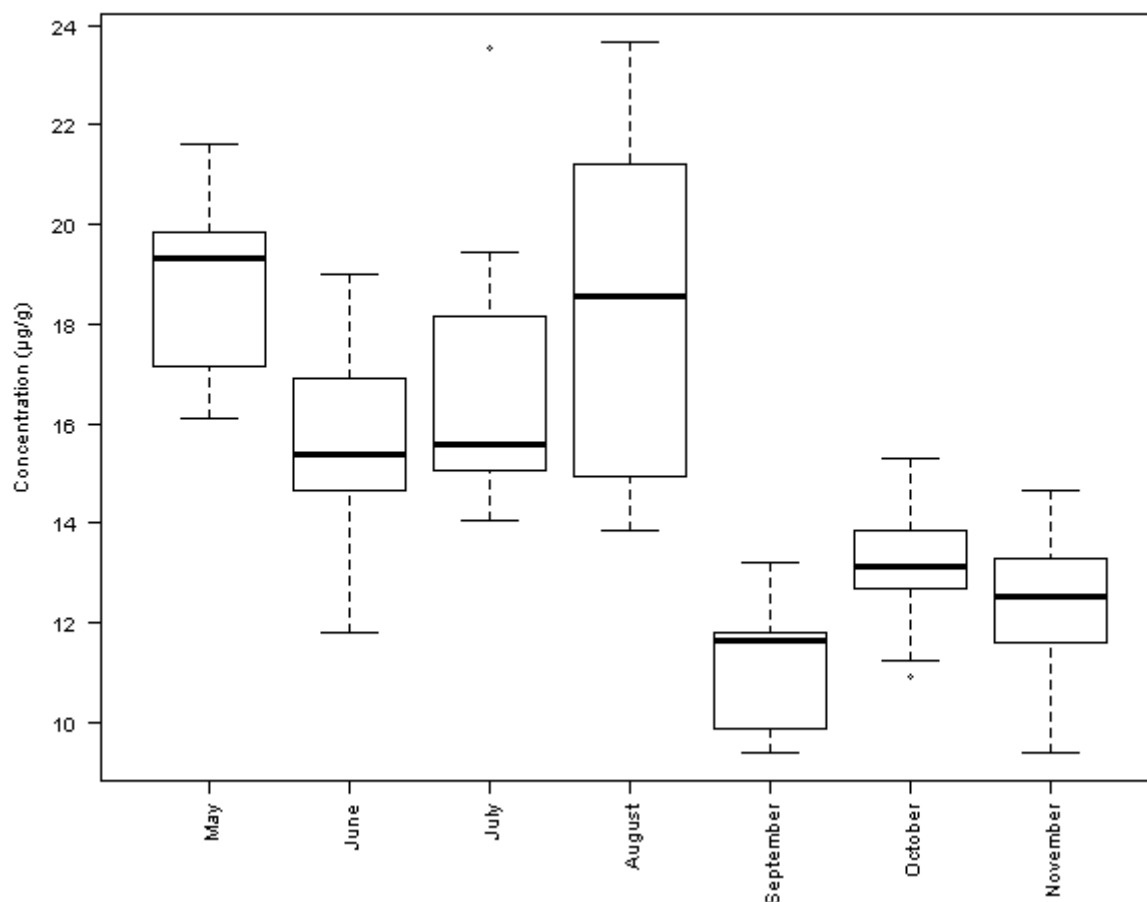


Figure 3.11 Vanadium concentrations in Christchurch road dust sampled monthly ( $n = 10$  for 7 months, all concentrations in  $\mu\text{g g}^{-1}$ )

There is no clear seasonal trend in road dust trace element concentrations reported for previous studies around the world. Different studies have different months or seasons of the year where concentrations of trace elements are highest.<sup>118-121</sup> The trends in this research could be due to the generally colder and wetter weather in winter leading to more cars being driven as compared with walking or cycling, which could result in more trace elements being generated from vehicles.

### 3.2.6 Spatial trends of concentrations of trace elements in road dust

Concentrations of trace elements in Christchurch were plotted to identify potential spatial trends (Figure 3.12). The only element to show a spatial trend was zinc. South of Riccarton Rd, sites tended to have higher concentration of zinc than sites north of Riccarton Rd. This difference was statistically significant (t-test, p-value <0.05, Figure 3.13). This southern area of Christchurch is largely industrial/commercial businesses rather than residential, and may reflect the land type difference determined in 3.2.3, and is consistent with the previous Gold Coast study.<sup>112</sup>

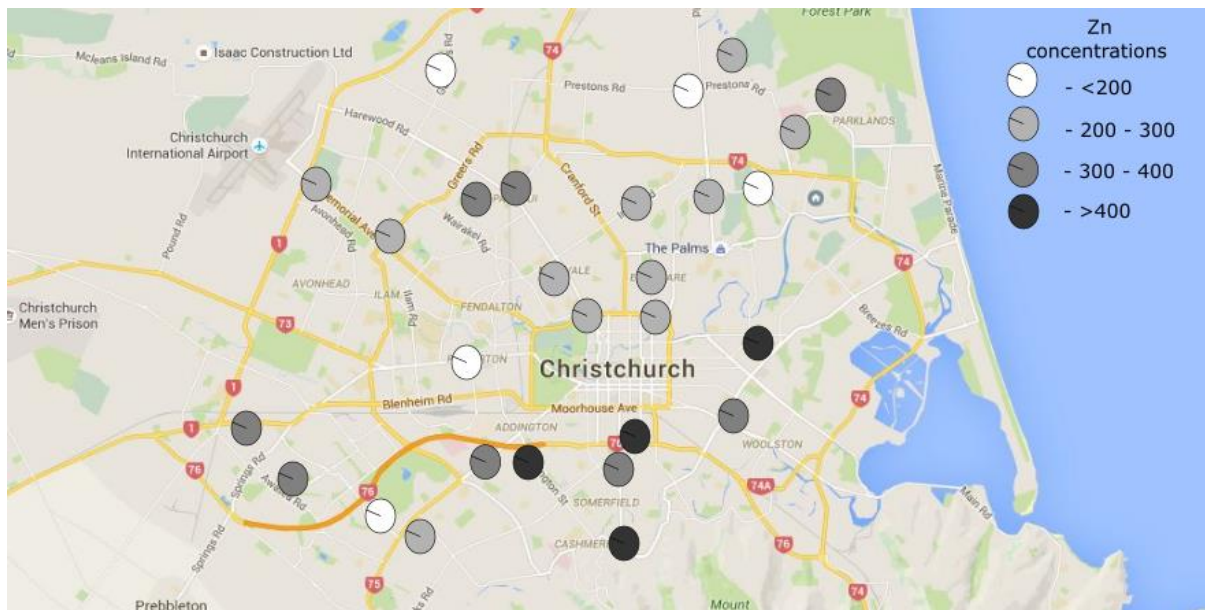
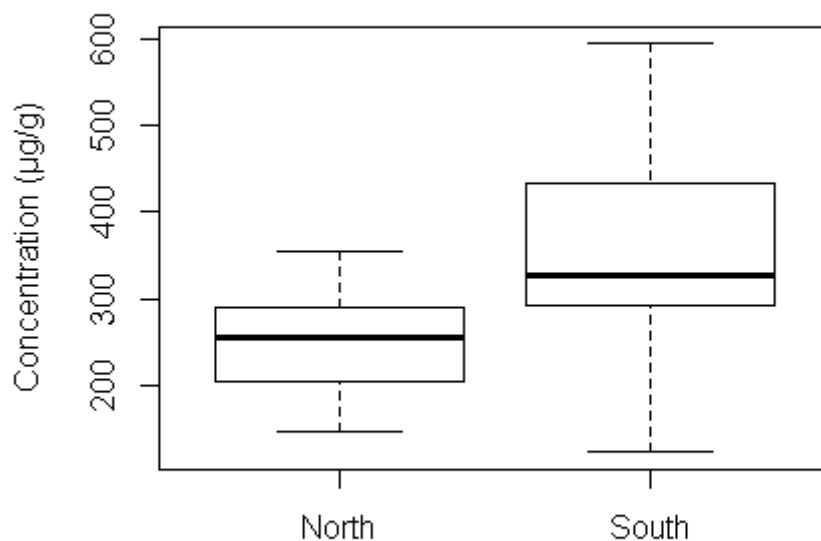


Figure 3.12 Map of zinc concentrations in Christchurch road dust ( $n = 30$ , all concentrations in  $\mu\text{g g}^{-1}$ )



*Figure 3.13 Difference in Christchurch zinc concentrations in road dust between areas north and south of Riccarton Rd ( $n = 30$ , all concentrations in  $\mu\text{g g}^{-1}$ ).*

### 3.2.7 Correlation studies

There were many correlations between trace elements that were significant or strongly significant across all three sets of data (Relationships from mean data in spatial dataset presented in Table 3.4). Of these, several indicate likely sources of trace elements from vehicles. Copper, nickel and chromium all have a significant relationships with each other, which is most likely from the use of these elements in brake pads.<sup>6</sup> The significant relationships between iron and zinc are likely due to emissions from tyre wear.<sup>7</sup> Overall there were more significant relationships in the winter data compared with the summer and mean data.

*Table 3.4 Spearman's rank correlation coefficients for trace elements in road dust using mean data (Light and dark grey shading indicating p-values of <0.05 and <0.01 respectively).*

	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	V	Zn
As	1	0.51	0.69	0.58	0.74	0.63	0.60	0.70	0.65	0.46	0.14	0.44
Cd	-	1	0.24	0.60	0.29	0.74	0.18	0.64	0.21	0.27	0.20	-0.20
Co	-	-	1	0.58	0.79	0.59	0.76	0.58	0.44	0.37	0.18	0.36
Cr	-	-	-	1	0.49	0.79	0.34	0.73	0.11	0.26	-0.18	-0.04
Cu	-	-	-	-	1	0.49	0.72	0.54	0.58	0.30	0.02	0.38
Fe	-	-	-	-	-	1	0.36	0.79	0.28	0.24	-0.20	0.05
Mn	-	-	-	-	-	-	1	0.38	0.66	0.57	0.04	0.55
Ni	-	-	-	-	-	-	-	1	0.35	0.33	-0.30	0.14
Pb	-	-	-	-	-	-	-	-	1	0.35	-0.29	0.59
Sb	-	-	-	-	-	-	-	-	-	1	-0.10	0.21
V	-	-	-	-	-	-	-	-	-	-	1	-0.22
Zn	-	-	-	-	-	-	-	-	-	-	-	1

Several of these Spearman correlations have been previously reported in literature as a data analysis method to identify sources. Copper and nickel are often correlated as they are emitted from brake pads.<sup>122,123</sup> Cadmium correlations with nickel and chromium are also typical, reflecting emissions from fuel combustion and road markings.<sup>124</sup> Nickel and lead correlations have been reported for road dust, which could be from brake emissions or road bitumen.<sup>125</sup> Correlations involving iron and other trace elements are likely from emissions from car bodywork, while nickel correlations with cadmium, chromium, cobalt and copper reflect road bitumen as a source.<sup>5,11</sup> These previously reported correlations were all present in this study.

### 3.2.8 Platinum Group Elements (PGEs)

Three methods were trialled for extracting platinum group elements (PGEs) from road dust. These were trialled initially on a bulk road dust sample (Table 3.5). This was due to two reasons 1) the relatively high cost of the BCR-723 road dust CRM, and 2) the quantity of sample available (The Lake Terrace Rd site in July had 163 g of dust compared to the 25g of CRM). All methods were subsequently trialled using duplicate BCR-723 CRM samples (Table 3.6). Full dataset located in Appendix 8.

*Table 3.5 - Summary of results for all three analytical methods for platinum group elements using a bulk road dust sample*

Method	Detection limit (ng g <sup>-1</sup> )	Pt (ng g <sup>-1</sup> )	Pd (ng g <sup>-1</sup> )	
		Concentration:	Mean:	2σ:
<b>Modified USEPA 200.8</b>	20	<0.000	30.4	33.0
<b>Concentration</b>	10	<0.000	28.2	6.8
<b>Resin A</b>	4	<0.000	19.8	0.8
<b>Resin B</b>	4	<0.000	<DL	-
<b>Resin Final</b>	4	<0.000	4.3	4.0

*Table 3.6 - Summary of BCR-723 road dust CRM results for three different analytical methods*

Method	Rh (ng g <sup>-1</sup> )		Pd (ng g <sup>-1</sup> )		Pt (ng g <sup>-1</sup> )	
	Mean:	2σ:	Mean:	2σ:	Mean:	2σ:
<b>Modified USEPA 200.8</b>	30.1	2.4	72.8	2.42	35.1	14.87
<b>Concentration</b>	8.8	2.6	30.9	4.0	12.0	9.4
<b>Resin</b>	-	-	<DL	-	<DL	-
<b>CRM reference</b>	12.8		6.1		81.3	

#### *3.2.8.1 Modified USEPA 200.8 method (from Section 2.6.1)*

The modified USEPA 200.8 method had the highest detection limit of the three methods. Platinum concentrations were undetectable using this method. At this stage it was unclear whether these results were due to incomplete extraction, or if platinum concentrations in Christchurch road dust were undetectable. The mean concentration of palladium was 30.4 ng g<sup>-1</sup>, however there was a high range of variability. Analysis of the BCR-723 CRM resulted in rhodium, palladium and platinum recoveries of 235.2 %, 1193 % and 43.2 % respectively. Based on these results this method was deemed unsuitable for determination of PGEs in road dust.

#### *3.2.8.2 Concentration method (from Section 2.6.2)*

The concentration method also had undetectable platinum concentrations for bulk sample testing. Palladium concentrations however were detectable and repeatable, with a lower range of values than the modified USEPA 200.8 method. CRM analysis showed rhodium, palladium and platinum recoveries of 68.8 %, 506.6 % and 14.8% respectively. Variability between duplicates was greater for palladium using this method compared with the modified USEPA200.8 method, but smaller for platinum. Despite satisfactory recoveries for rhodium, as platinum and palladium were the main analytes of interest this method was deemed unsuitable for determination of PGEs in road dust.

#### *3.2.8.3 Resin method (from Section 2.6.3)*

Like the other three methods, platinum concentrations were undetectable in the bulk sample. As the resin method involved two decanting steps, the two decanted solutions were also analysed to see if PGE concentrations were lost during these steps (Resin A & B in Table 3.5). Palladium concentrations were greatest in the first decanted solution, indicating that the resin did not bind the PGEs strongly. CRM trials showed no detectable concentrations of platinum or palladium using the resin method. Poor recoveries of the internal standard 9Indium, 55-88 %) meant that the internal standard was changed to rhodium for resin method testing, so rhodium concentrations were unable to be measured. The resin method also had very high blank concentrations, with values up to 84% of sample value (potentially

due to matrix interferences). Based on these results the resin method was deemed unsuitable for determination of PGEs in road dust.

#### 3.2.8.4 Aqua Regia tests

A fourth method using acid digestion with aqua regia (1:3 24 % HCl to 70% HNO<sub>3</sub> ratio) was subsequently trialled to attempt to release a greater proportion of PGEs from the road dust matrix. This method was initially applied to the road dust CRM (n=4, results in Table 3.7). The palladium concentrations were excessively high, indicating potential interferences in the ICP-MS analysis. The platinum results, however had acceptable recoveries and had a high level of precision based on low standard deviation values. The method was therefore deemed suitable for platinum detection.

*Table 3.7 Aqua regia BCR-723 CRM test results*

	Detection limit (ng g <sup>-1</sup> )	Pd (ng g <sup>-1</sup> )	Pt (ng g <sup>-1</sup> )
<b>Mean concentration</b>	10	77.1	58.6
<b>2 σ</b>	-	8.6	5.5
<b>CRM certified value</b>	-	6.1	81.3
<b>Recovery %</b>	-	1263.7	72.0

The aqua regia method was then used to analyse the road dust sampled from the spatial sampling (Appendix 8.5). Results from this testing was inconclusive. Samples ranged in platinum concentration from below detection limit to 767 ng g<sup>-1</sup>, while variance between duplicates were regularly orders of magnitude. This could indicate that platinum is emitted from vehicles as particulates, and a thorough homogenisation is required to analyse platinum concentrations accurately. A lack of homogeneity for platinum in road dust has been shown in previous research.<sup>126</sup> The measured range of platinum concentrations were similar to those in Table 1.4, particularly the range of Australia concentrations.



### 3.3 Conclusions

Trace elements were detected in urban road dust across Christchurch at concentrations generally lower than other cities both in New Zealand and internationally. Correlations between trace elements identified that a significant proportion of these elements were vehicle-derived, particularly copper, zinc and lead. These three elements have also been shown to be significantly enriched above background soil concentrations. Lead concentrations are considered to be largely as a result of historical use of lead in fuel and paint, when compared to the previous study in Christchurch. Factor analysis largely showed no relationships due to the multitude of factors involved. Land use analysis indicated that zinc concentrations may be largely be due to industry emissions rather than vehicle emissions. All four methods were unsuitable for measuring palladium concentrations, while the aqua regia method was suitable for measuring platinum. Platinum concentrations ranged from below detection limit to  $767 \text{ ng g}^{-1}$  but results were highly variable, indicating poor homogeneity.

## 4. Leaching studies

### 4.1 Introduction

The previous chapter showed that several vehicle-derived trace elements in road dust, particularly copper, zinc and lead were elevated above background soil concentrations. To determine if these elements could pose a risk to the environment, the availability of these elements needs to be assessed. There are several pathways that these elements could take through different environments (Figure 4.1). As road dust accumulates in gutters rainfall can wash road dust down stormwater drains. Trace elements can be released within this rainfall or remain bound to the road dust matrix, and therefore remain in gutters. Finer fractions of road dust in the gutter can be resuspended when disturbed, where the particles can return to the gutter or be deposited on soil or nearby waterways.<sup>107</sup> Water containing these elements can be discharged into urban waterways, where the elements could be transported down the waterway or settle into sediment.<sup>10</sup> Due to the poor solubility of most trace elements in water they are most likely to remain bound to the road dust or sediment matrices. Road dust trace elements could also enter groundwater either through stormwater discharge or by passing through soil. Transport to groundwater is an important pathway in Christchurch, as groundwater provides the city's drinking water supply.<sup>127</sup>

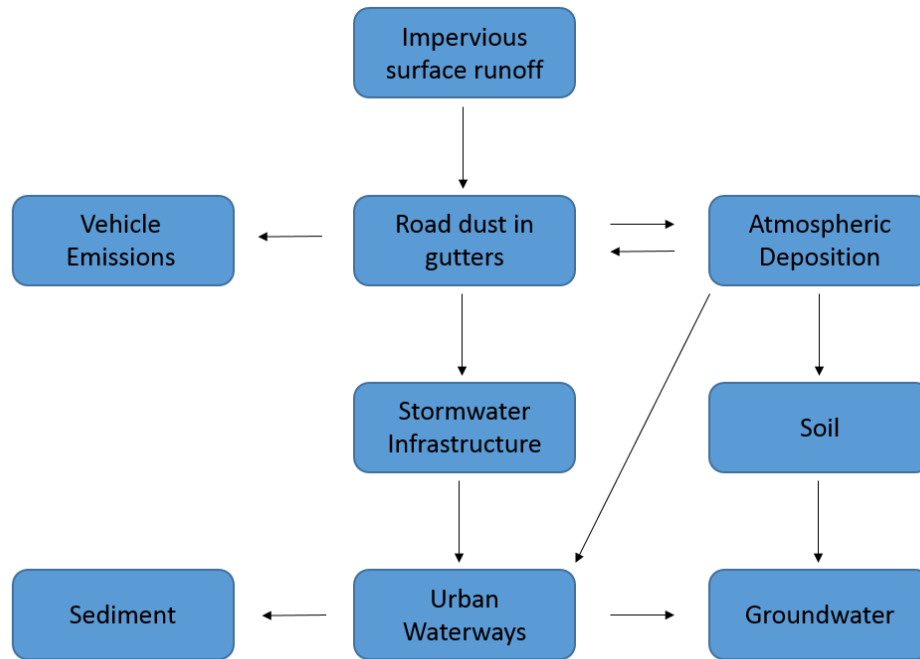


Figure 4.1 Flowchart of the environmental fate of trace elements in Christchurch road dust

#### 4.1.1 Mobility

Leaching studies were performed to simulate environmental conditions for estimating the environmental fate of trace elements in road dust. The rainwater and stream water leaches were selected because they are suitable surrogates of the environmental conditions in Christchurch. Other mobility methods commonly used for trace elements in road dust, sediment and soil include diffusion and speciation methods.<sup>128</sup> Both methods were modified from the USEPA method 1312.<sup>82</sup> The method for making synthetic rainwater was chosen based on the simplicity of preparing the solution, and is usually used for sediment or soil leaching analysis. Other methods exist for making synthetic rainwater, however they tend to be more complex.<sup>129</sup> The chosen method is also USEPA accredited.<sup>82</sup> The stream water sample was collected from Avon River in Christchurch, at a section of water adjacent to both a stormwater outflow and a road dust sampling site

#### 4.1.2 Bioavailability

Toxicity tests are often performed for measuring the effect of trace elements on a variety of organisms, however these can be hard to relate to real world scenarios. Bioavailability tests can be used to show the fraction of the total trace element concentration that an organism could be exposed to, and therefore toxic effects can be predicted. There are many different methods to measure the bioavailability of trace elements in road dust. Bioavailability depends on a wide range of factors such as pH, temperature, organic content and speciation.<sup>130</sup> BCR sequential extraction methods can be used to measure four different fractions, the exchangeable and bound to carbonate fraction, the iron oxide- and manganese oxide-bound fraction, the organic and sulphide fraction and the insoluble/silicate fraction.<sup>131</sup> Other methods include Neutral Salt Solutions or Toxicity Characteristic Leaching Procedures.<sup>132</sup> These methods however can be time consuming and require expensive/dangerous solvents. Single step cold acid extraction methods have been shown to be much faster to perform than sequential extraction methods, while being still as effective.<sup>133</sup> The single step cold acid method chosen was based on Acid Volatile Sulphide – Simultaneously Extracted Metals methods.<sup>83</sup> This method releases the sulphide-bound fraction of trace elements. 1 M HCl is also a reasonable approximation for stomach acid, and therefore is a good measurement of bioavailability to organisms.

#### 4.1.3 Objectives

The objective of this chapter were to:

- Simulate the environmental availability of trace elements in road dust through leaching studies
- Simulate the bioavailability of trace elements in road dust

## 4.2 Results

### 4.2.1 Rainwater

Trace elements were leached using simulated rainwater in the following order of concentrations: Fe > Zn > Mn > Cu  $\approx$  Pb > As > V  $\approx$  Ni  $\approx$  Cr > Co  $\approx$  Sb  $\approx$  Cd (Appendix 9). The maximum amounts of each trace element leached as percentages of total recoverable element concentrations were all less than 4%, indicating that the majority of each trace element is likely to remain associated with the road dust matrix (Figure 4.2). Arsenic, iron, chromium, cobalt, manganese and vanadium all had the lowest leaching percentages, with values less than 0.30% (Table 4.1). The highest leached percentages were for arsenic, cadmium, copper and zinc.

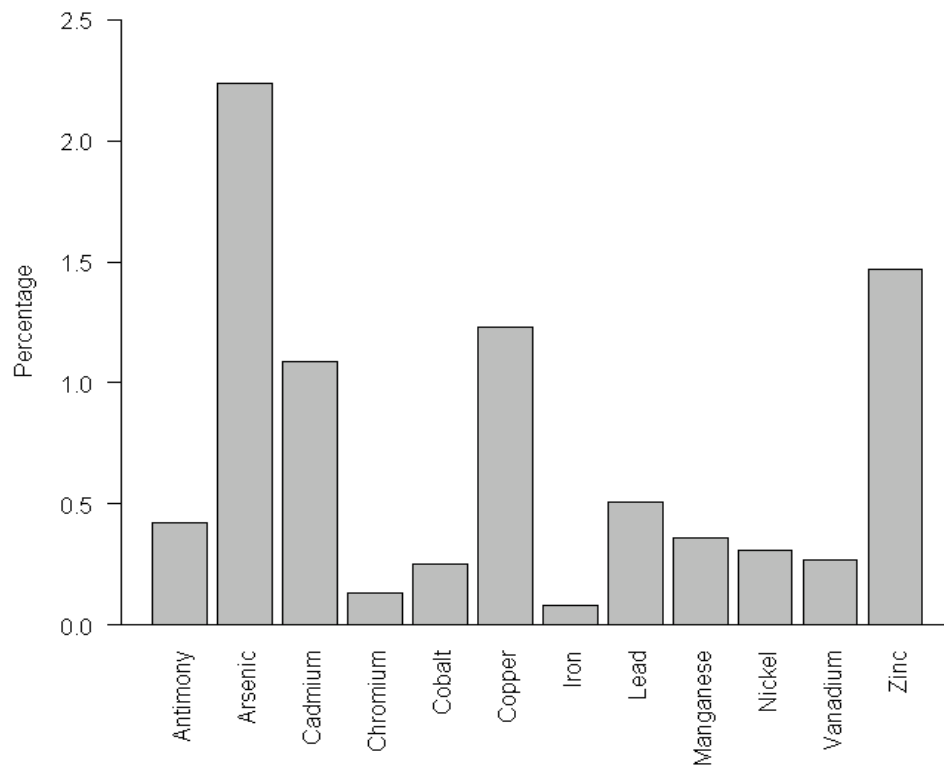


Figure 4.2 Mean percentage rainwater leachate fraction of trace elements in road dust (%  
n=5).

Table 4.1 Mean leachable concentrations compared with mean total recoverable concentrations.

Element	Total	Rainwater		Stream water		Bioavailability (1 M HCl)	
	( $\mu\text{g g}^{-1}$ )	Concentration ( $\mu\text{g g}^{-1}$ )	Percentage (%)	Concentration ( $\mu\text{g g}^{-1}$ )	Percentage (%)	Concentration ( $\mu\text{g g}^{-1}$ )	Percentage (%)
Antimony	0.79	0.003	0.42	0.04	4.50	0.45	56.79
Arsenic	3.92	0.09	2.24	0.12	3.00	2.07	52.86
Cadmium	0.23	0.003	1.09	0.005	2.26	0.11	49.39
Chromium	20.45	0.03	0.13	0.11	0.52	6.02	29.42
Cobalt	3.71	0.009	0.25	0.03	0.85	1.57	42.24
Copper	23.81	0.29	1.23	0.68	2.85	21.71	91.19
Iron	11935	9.19	0.08	45.90	0.38	2774	23.24
Lead	50.78	0.26	0.51	0.99	1.95	38.51	75.85
Manganese	191.92	0.69	0.36	1.59	0.83	76.18	39.69
Nickel	9.99	0.03	0.31	0.06	0.62	2.47	24.73
Vanadium	16.13	0.04	0.27	0.10	0.60	3.34	20.73
Zinc	190.46	2.81	1.47	8.00	4.20	144.80	76.03

For both methods, partitioning coefficients were calculated using the below equation:

$$\log K_D = \log \frac{[Fraction\ not\ leached]}{[Fraction\ leached]} = \frac{\mu g\ g^{-1}}{\mu g\ L^{-1}}$$

These were compared to reference values from the USEPA for both sediment and suspended matter (Table 4.2).<sup>134</sup>

*Table 4.2  $K_D$  values for sediment-water and suspended matter-water from USEPA.<sup>134</sup>*

Element	Sediment-water (ml g <sup>-1</sup> )	Suspended-water (ml g <sup>-1</sup> )
Arsenic	2.5	4.0
Cadmium	3.6	4.7
Cobalt	3.3	4.7
Chromium	4.5	5.1
Copper	4.2	4.7
Nickel	4.0	4.6
Lead	5.1	5.6
Antimony	4.0	-
Zinc	3.7	5.1

All rainwater log  $K_D$  values were significantly lower than the reference values in Table 4.2. This likely indicates that the trace elements in road dust are bound to the matrix by weaker bonds than in typical river sediment or suspended matter. This suggests that trace elements in road dust are more mobile than from sediment or suspended matter in rainwater. This increased mobility is consistent with previous studies.<sup>135</sup>

*Table 4.3 Mean log  $K_D$  values for rainwater leach*

Element	log $K_D$ (ml g <sup>-1</sup> )	$\sigma$
Antimony	1.20	0.12
Arsenic	0.97	0.18
Cadmium	1.03	0.46
Chromium	2.17	0.32
Cobalt	1.93	0.21
Copper	1.17	0.19
Iron	2.45	0.30
Lead	1.60	0.34
Manganese	1.80	0.26
Nickel	1.79	1.49
Vanadium	1.88	0.17
Zinc	1.15	0.17

#### 4.2.2 Stream water

A river water sample was collected from the Avon River and was used to simulate the leaching of trace elements in waterways. Trace elements were leached in the following order of concentrations: Fe >> Zn > Mn > Pb > Cu > As  $\approx$  Cr  $\approx$  V > Ni  $\approx$  Sb  $\approx$  Co > Cd (Figure 4.3). This order is similar to the rainwater leach, except with a lower order for copper and a higher order for arsenic. The lowest leached concentrations were for chromium, iron, nickel and vanadium (all below 0.65% of total recoverable concentration). The highest leached percentages were for antimony and zinc (4.5% and 4.2% respectively), which means for all elements almost all (>95%) of the element will remain in sediment rather than be transported down a waterway in the dissolved phase. For all trace elements, the percentage leached by stream water was greater than the percentage leached by rainwater.



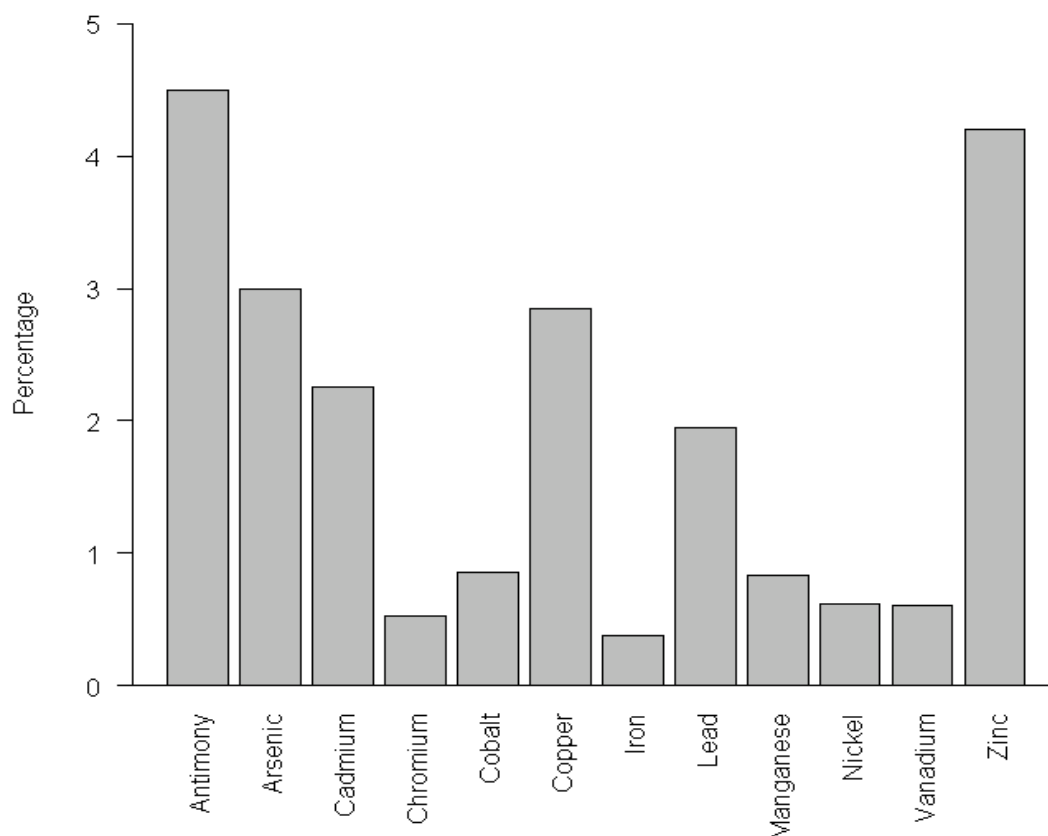


Figure 4.3 Mean percentage stream water fractions of trace elements in road dust (%;  $n=5$ ).

Log  $K_D$  values were calculated for each trace element from the stream water leach to allow comparison to literature values (Table 4.4). Compared to the reference values in Table 4.1, these values are significantly lower, similar to the rainwater log  $K_D$  values, indicating that trace elements in road dust are much more mobile than trace elements from typical sediment and suspended matter in water. Stream water log  $K_D$  values were lower than rainwater log  $K_D$  values for all trace elements.

*Table 4.4 Mean log  $K_D$  values for stream water leach*

Element	log $K_D$ (ml g <sup>-1</sup> )	$\sigma$
Antimony	0.64	0.23
Arsenic	0.81	0.06
Cadmium	0.76	0.26
Chromium	1.58	0.16
Cobalt	1.37	0.05
Copper	0.81	0.16
Iron	1.72	0.11
Lead	1.03	0.27
Manganese	1.39	0.11
Nickel	1.49	0.12
Vanadium	1.53	0.13
Zinc	0.65	0.13

#### 4.2.3 Comparison to Water and Sediment Guidelines

The Australian and New Zealand Environment and Conservation Council (ANZECC) has derived trigger values for water and sediment quality.<sup>136</sup> These values are based on the potential risk a contaminant may cause to aquatic organisms. For water quality, trigger values are given that are designed to protect 95% and 99% of the species in an ecosystem. For sediments, the trigger values represent low and high levels of risk to species. It is important to note that for both arsenic and chromium, there are two prevalent oxidation states that are found in the environment, so for this research the lower trigger value of the two was used.

*Table 4.5 ANZECC trigger values for water and sediment quality. All water concentrations are  $\mu\text{g L}^{-1}$ , while all sediment concentrations are  $\mu\text{g g}^{-1}$ .<sup>136</sup>*

Element	Water Quality		Sediment Quality	
	95%	99%	Low	High
Antimony	-	-	2	25
Arsenic	13	0.8	20	70
Cadmium	0.2	0.06	1.5	10
Chromium	1	0.01	80	370
Copper	1.4	1	65	270
Lead	3.4	1	50	220
Manganese	1900	1200	-	-
Nickel	11	8	21	52
Zinc	8	2.4	200	410

#### 4.2.3.1 Freshwater

The rainwater and stream water leachate concentrations were compared to the ANZECC water quality guidelines to determine if any exceeded the 95% or 99% trigger values (Table 4.6). Chromium, copper, lead and zinc were all greater than the 99% ANZECC protection trigger value, while copper, lead and zinc were also greater than the 95% trigger value. It is important to note that these values are only for 20 ml samples (sediment : solute ratio of 1:20). A 50 fold dilution would reduce all concentrations below 99% trigger values, however in waterways of low water volume where little dilution will occur road dust may release concentrations that still exceed trigger values.

*Table 4.6 Rainwater and stream water leaching concentrations for 20 ml sample of Christchurch road dust ( $\mu\text{g L}^{-1}$ ). Bold values exceed ANZECC trigger values.*

Element	Rainwater	Stream water
Arsenic	0.44	0.59
Cadmium	0.01	0.03
Chromium	<b>0.14</b>	<b>0.54</b>
Copper	<b>1.46</b>	<b>3.41</b>
Lead	<b>1.28</b>	<b>4.95</b>
Manganese	3.46	8.01
Nickel	0.16	0.31
Zinc	<b>14.05</b>	<b>40.22</b>

#### 4.2.3.2 Sediment

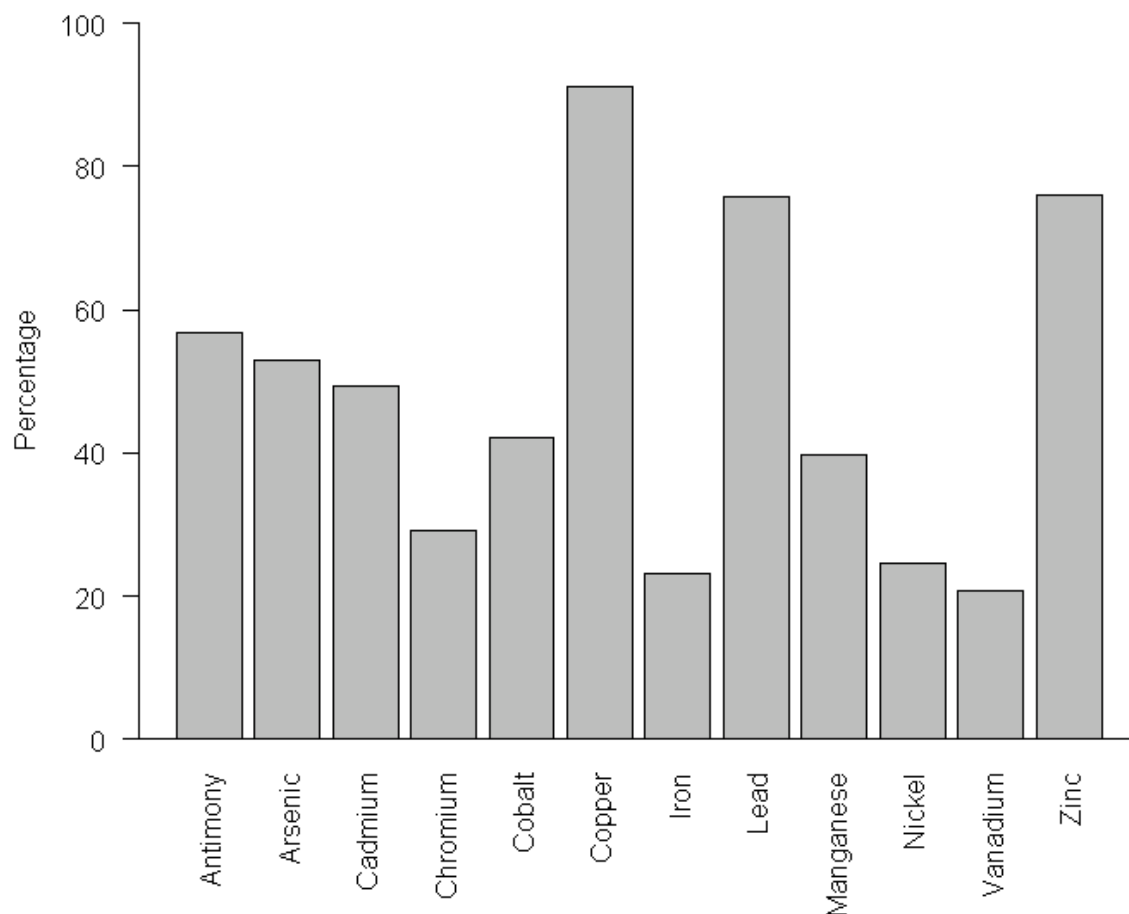
The percentage of road dust that is likely to remain associated to the road dust matrix was compared to the ANZECC sediment guidelines. The percentage of trace element concentrations that did not leach was used to estimate the bound concentrations in the 110 samples from both the spatial and temporal datasets. The percentage of samples that exceeded ANZECC guidelines for sediment following leaching with rainwater or stream water is presented below in Table 4.7. The trace elements that exceeded the guidelines the most frequently were zinc, lead and copper. Zinc in particular exceeded the High trigger value in 13.64% of samples. Over 20% of all sites exceeded the Low antimony trigger value. This means that localised areas within waterways by stormwater outflows could contain sediment sourced from road dust exceeding trigger values for these four elements.

*Table 4.7 Percentage of road dust samples (n = 110) that would exceed ANZECC sediment trigger values after the leach with rainwater or stream water.*

Element	Exceeded Low (%)	Exceeded High (%)
Antimony	20.91	0
Arsenic	0	0
Cadmium	3.64	0
Chromium	1.82	0
Copper	36.36	1.82
Lead	54.55	1.82
Nickel	7.27	0
Zinc	75.45	13.64

#### 4.2.4 Bioavailable Fraction

Dilute HCl (1 M) was used to measure the potential bioavailability of trace elements in road dust. Trace elements were leached in the following order of concentrations: Fe > Zn > Mn > Pb > Cu > Cr > V > Ni  $\approx$  As  $\approx$  Co > Sb > Cd. For vanadium, nickel, chromium and iron the average percentage of the total recoverable fraction that leached was less than 30%, while manganese was less than 40% (Figure 4.4). For cadmium, copper, lead and zinc, there was no statistical difference between the total recoverable and bioavailable fractions, so the bioavailable fraction is equivalent to the total recoverable fraction. The average percentage of the total recoverable fraction that was leached for lead, zinc and copper was 76%, 76% and 91% respectively. These trace elements therefore could pose the greatest risk of toxic effects to organisms in waterways, as the majority fraction of these elements ingested from road dust are likely to be bioavailable.



*Figure 4.4 Bioavailability leach concentrations from Christchurch road dust as a percentage of total recoverable concentrations for each trace element (n=5).*

The concentrations of HCl extractable trace elements particularly for lead and zinc are consistent with previous 1 M HCl bioavailability assessments of road dust.<sup>137-139</sup> Copper was more extractable than in other studies (91.2 % compared to 8%-38%). This may be due to the small sample size (n=5), but could also suggest that copper in Christchurch road dust is present in a more available form than what typically occurs. As copper is used in the production of vehicle brake pads, this could mean that copper is emitted as particulates.<sup>6</sup>

### 4.3 Discussion

The small percentages of leaching for both the rain and stream water leaches means that the majority of all trace elements will remain bound in the road dust matrix. A proportion of the road dust could be physically transported through the stormwater system and be incorporated in waterway sediment. It is unlikely that a significant amount of trace elements would be transported into and down a waterway in the dissolved phase, so higher concentrations of trace elements near drainage outlets would be expected, excluding effects of other sources. Arsenic, copper and zinc are the most likely trace elements to be introduced into waterways via road dust, as these three elements had the greatest leached fraction for both the rain and stream leaches.

It is also interesting to note that overall leaching percentages were generally higher in the stream water leach than in the rainwater leach. Most metals tend to have increased solubility the lower the pH of the solution, and the pH of the synthetic rainwater used in the rainwater leach was significantly lower than the stream water (4.2 compared with 7.2). This may indicate that the anions present are important in releasing trace elements from the road dust matrix, as the rainwater leach was prepared from ultrapure water, so there was little to no anions present. A known example of this is copper, which favours dissolution in water with higher nitrate and chloride concentrations.<sup>140</sup> The stream water sample used had detectable sulphate, chloride and nitrate (Appendix 10).

The bioavailability leach with 1M HCl results indicate that for many trace elements, a large proportion of certain elements are likely to be readily bioavailable. In particular, copper, lead and zinc had the greatest fraction leached. The high bioavailability of copper and zinc is very important because as mentioned, these elements had some of the highest leaching percentages for the other two leaches. Conversely, the trace elements with the smallest leached fraction for the rain and stream leaches (e.g. chromium and iron) also had the lowest bioavailability leaches. The relatively high bioavailability leach fractions combined with the low stream water leach fractions means that the trace elements in road dust pose the greatest threat to benthic organisms, as the trace elements are likely to be in the sediment as opposed to the water.

The toxicity of a trace element depends on both the hazardous effects it can cause and also the exposure. Due to the very low leaching fractions for rain and stream water leaches it is unlikely that dissolved trace elements leached from road dust alone would provide enough exposure to cause toxic effects to organisms in waterways. However in waterways of low volume these concentrations may not be sufficiently diluted and exceed ANZECC trigger values. Trace element concentrations in road dust however could contaminate sediment to the extent that an area of the waterway could exceed the ANZECC sediment guidelines. Only a small fraction of trace elements in road dust leached in the rainwater leach, however road dust could be physically washed down through stormwater drains during rainfall events.<sup>141</sup> This could provide another pathway into waterways other than leaching.

An important factor to consider is the accumulation of trace elements in waterways. Although concentrations of trace elements in road dust are relatively low, and only a small fraction is likely to end up in waterways, trace elements are constantly being released from vehicles.<sup>5</sup> This means that these elements could accumulate over time, allowing for greater concentrations to be found in the sediment in particular and therefore increasing the exposure to organisms. The low leaching fractions further illustrate this, as this means that the trace elements are unlikely to be leached from road dust into the water and dispersed. Several of these trace elements, in particular copper also have the potential for bioaccumulation and biomagnification.<sup>142</sup> A constant supply of these elements, particularly the highly bioavailable ones like copper and zinc, could be accumulated within an organism, potentially exposing the organism to a higher dose than present in the waterway. Biomagnification could also mean that higher trophic level organisms that eat benthic organisms could be exposed to elevated trace element concentrations, as benthic organisms bioaccumulate trace elements.<sup>143</sup> Copper and zinc are both essential elements, so many organisms often have pathways to control these concentrations, however the range of concentrations that can be dealt with is often small and easily exceeded.<sup>27</sup>



#### **4.4 Conclusion**

Leaching studies were used to simulate the environmental availability of trace elements in road dust. Results from these studies showed that trace elements are poorly soluble in both rainwater and stream water, so dissolved concentrations from road dust are unlikely to pose any risk. Sediment concentrations however have the potential to accumulate in concentrations that exceed ANZECC trigger values, particularly of copper, lead and zinc. These elements are also highly bioavailable as shown by the 1M HCl leach, so potentially could be toxic to organisms near stormwater discharge points.

## 5. Summary

### 5.1 Conclusions

This thesis investigated trace element concentrations in Christchurch road dust. Road dust was sampled from 30 sites during a 7 month sampling programme. Trace element concentrations were analysed by ICP-MS. Leaching studies were then used to simulate environment availability. The following conclusions were drawn:

- Trace element concentrations in road dust in Christchurch are lower than historical Christchurch concentrations. Christchurch concentrations were also lower than in previous national and international studies.
- Trace element concentrations were greater in the 63  $\mu\text{m}$  size fraction compared to the 2mm fraction
- Correlation analysis showed that a large portion of these trace element concentrations is vehicle derived
- There is little relationship between traffic, season, age, land use or weather and trace element concentrations in Christchurch. This is likely due to the many factors impacting road dust.
- Cadmium, copper, lead and zinc concentrations were all significantly enriched above background soil concentrations
- Platinum concentrations were detected using an aqua regia method of digestion. These concentrations were highly variable, reflecting PGE emissions as large particulates
- Trace elements in road dust were more mobile in rainfall and stream water than trace elements in sediment, however accumulation in sediment is still the mostly likely environmental fate
- Copper, lead and zinc concentrations in road dust were high enough to result in sediment exceeding ANZECC guidelines
- A 1 M HCl leach identified that copper, lead and zinc are the most bioavailable trace elements

## 5.2 Recommendations

As copper, lead and zinc concentrations in road dust have been identified as posing risks to urban waterways, solutions are needed to minimise the impact these trace elements could have on waterways. Several methods are available for either reducing trace elements in road dust or reducing the amount of sediment that can enter waterways. Three of these are described below:

### 5.2.1 Altering brake pad composition

Brake pads are composed of, among other elements, copper and zinc, and have been shown to emit these elements during wear and tear. Therefore a solution to reduce concentrations of these trace elements is to change the composition of brake pads. This has occurred in both Washington and California in the USA, where legislation in 2010 was passed to require copper concentrations in brake pads to be less than 0.5 weight % by 2025. This legislation was extended nationwide in a Memorandum of Understanding between the USEPA and various automobile organisations.<sup>144</sup> This would be a long-term solution, as it would take many years to phase out copper-containing brake pads from in Christchurch. Alternative brake pads are typically made from either ceramics or organics. Organic brake pads can be made from a mixture of glass, rubber, resin and Kevlar fibres. These are generally cheap, very quiet, but as they wear down a lot faster, have a poor performance at high temperature and have been shown to emit the most dust.<sup>145</sup> Ceramic brake pads are made from fibres of clay and porcelain bound to copper filaments, and are very light and durable. They are also very quiet, but are generally more expensive, dissipate heat poorly and may not be suitable for large vehicles such as trucks.<sup>146</sup> There is therefore no ideal solution for current metallic brakes, however with the deadlines introduced internationally to reduce copper in brake pads, new brake pad materials are likely to become available. This is a long term solution, is a relatively cheaper option for governing bodies as they would not bear the costs and reduces the generation of trace elements rather than attempting to remove them post hoc.

### 5.2.2 Road sweeping

Road sweeping has been shown to strongly impact both road dust quantity and trace element concentrations in road dust. Both the type of road sweeper used and the regularity of road sweeping can alter how effective road sweeping is at reducing road dust.<sup>4</sup> There are three main categories of sweepers: mechanical, vacuum and regenerative air. Of the three types regenerative air sweepers are the most effective at removing smaller particles from gutters.<sup>147,148</sup> This is important as it was shown previously that trace elements concentrations are greater in smaller size fractions (Section . In Christchurch, road sweeping is contracted to CityCare, who use a combination of vacuum and regenerative air sweepers. The frequency of sweeping for the sampled sites was not known, however only one of the sampled sites showed signs of being recently swept out of all 110 sampling events. A more frequent sweeping programme may significantly lower the amount of road dust in gutters, and if used in areas adjacent to waterways may reduce the amount of trace elements entering waterways.

### 5.2.3 Sediment catchpits

Sediment catchpits are designed to stop sediment and debris passing through drains and entering waterways. They are very successful in removing large debris and sediment larger than 500  $\mu\text{m}$  in size, however they remove less of smaller particle-sized sediment.<sup>149</sup> As trace elements are in greater concentration in finer particles, this means that catchpits may not reduce the concentrations of trace elements in road dust entering waterways. Catchpits also have to be emptied when full.

### 5.2.4 Discussion

As catchpits are less successful at reducing finer particles they are unsuitable as the only method of reducing the load of trace elements entering waterways. Road sweeping is a more immediate fix, however it does not alter the generation of these trace elements so these trace elements will still be released as airborne  $\text{PM}_{10}$ . The fate of road dust once collected is also an issue, as it has the potential to leach through soil in landfills.<sup>150</sup> This leaves changing the composition of brake pads as the best option for reducing trace elements in road dust,

particularly as it reduces the generation of trace elements rather than cleaning them up. This could also be applied to other car components that release trace elements, such as tyres and bodywork.<sup>5,7</sup>

### 5.3 Future work

This research provides a good overview of current trace element concentrations in Christchurch road dust. There is however further research that could be done to improve the knowledge and potential impact of urban road dust in Christchurch. A larger, longer and more regular sampling programme may be able to better identify any season trends. By sampling more sites particular sources of trace elements to road dust could be better identified, such as industrial worksites. A longer sampling programme would allow for a comparison between all seasons, and trends such as the higher concentrations of chromium, iron, manganese and vanadium in winter could then be tested to see if they were cyclic (i.e. occurred every year). A more regular sampling programme than once a month may reduce any outliers from contamination by rubbish, etc.

A detailed traffic analysis would allow for a better comparison between traffic and trace element concentrations. As traffic density groups were estimated from traffic data across many years, it is likely that traffic densities reported for each site are inaccurate. The traffic density at any site would also likely vary across months. A current survey of traffic at each site may reveal relationships between traffic and trace element concentrations consistent with literature that were not found in this study.

Road dust toxicity tests could be performed to measure the toxic effects trace elements could have on specific species. As copper, lead and zinc were shown to exceed ANZECC trigger values in sediment, urban waterways may contain these elements in concentrations that could be harmful to benthic organisms. Acute or chronic toxicity tests could show how these organisms are affected, especially New Zealand native species.

Platinum group elements have been identified in this research as being highly variable due to the emission of platinum as particulates. A method involving grinding and mixing road dust

to homogenise samples would allow for factor comparisons and temporal/spatial trend investigations.

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## Appendices

### Appendix 1: Sampling sites

Site	GPS location (NZTM)	Traffic	Sampling	Soil type	Land use	Housing age
<b>Avonhead Rd</b>	5180679.437 N 1564361.629 E	Medium	Monthly	Recent	Residential	1970
<b>Ilam Rd</b>	5182268.829 N 1566187.906 E	Low	Seasonally	Recent	Residential	1940
<b>Memorial Ave</b>	5183593.750 N 1564431.962 E	Medium	Seasonally	Pallic	Residential	1960
<b>Condell Ave</b>	5183834.351 N 1567289.872 E	Very Low	Monthly	Recent	Residential	1950
<b>Papanui Rd</b>	5183938.298 N 1568258.846 E	High	Seasonally	Recent	Commercial	-
<b>Gardiners Rd</b>	5185588.207 N 1566185.469 E	Low	Monthly	Recent	Residential	1960
<b>Prestons Rd</b>	5186436.867 N 1572376.549 E	Medium	Seasonally	Organic	Residential	1940

<b>Te Korari St</b>	5186909.139 N 1572935.229 E	Very Low	Monthly	Brown sand	Residential	2010
<b>Mairehau Rd</b>	5185550.552 N 1574238.651 E	Medium	Seasonally	Brown sand	Residential	1950
<b>Amoka Crescent</b>	5186011.260 N 1574894.383 E	Very Low	Seasonally	Brown sand	Residential	2000
<b>Lake Terrace Rd</b>	5184244.113 N 1573738.156 E	Low	Monthly	Brown sand	Residential	1970
<b>Marshlands Rd</b>	5184183.989 N 1572645.343 E	High	Seasonally	Gley	Residential	1960
<b>Innes Rd</b>	5183858.116 N 1571146.030 E	Medium	Seasonally	Gley	Residential	1950
<b>Normans Rd</b>	5182923.838 N 1568946.149 E	Low	Seasonally	Recent	Residential	1910
<b>Geraldine St</b>	5181839.951 N 1571516.053 E	Very Low	Seasonally	Gley	Residential	1910
<b>Harper Ave</b>	5181245.469 N 1569721.332 E	High	Monthly	Recent	None	-
<b>Bealey Ave</b>	5181302.116 N 1571527.773 E	High	Seasonally	Gley	Residential	1910

<b>Avonside Dr</b>	5181438.930 N 1572922.871 E	Very Low	Monthly	Recent	Residential	-*
<b>Woodham Dr</b>	5180837.901 N 1574254.588 E	Low	Seasonally	Recent	Commercial	-
<b>Ferry Rd</b>	5178837.981 N 1573055.512 E	Medium	Seasonally	Gley	Commercial	-
<b>Wordsworth St</b>	5178638.216 N 1570672.218 E	Low	Seasonally	Recent	Commercial	-
<b>Colombo St</b>	5178570.732 N 1570660.408 E	Medium	Seasonally	Recent	Commercial	-
<b>Centaurus Rd</b>	5176059.339 N 1570563.327 E	Medium	Monthly	Pallic	Residential	1950
<b>Edinburgh St</b>	5177811.075 N 1567962.621 E	Very Low	Seasonally	Recent	Residential	1970
<b>Lincoln Rd</b>	5177985.283 N 1567739.970 E	High	Seasonally	Recent	Commercial	-
<b>Halswell Rd</b>	5176202.370 N 1565715.781 E	High	Seasonally	Recent	None	-
<b>Aidanfield Dr</b>	5176338.703 N 1565532.245 E	Very Low	Seasonally	Recent	Residential	2000

<b>Corsair Dr</b>	5177637.681 N 1564134.719 E	Very Low	Monthly	Recent	Residential	2010
<b>Main South Rd</b>	5178730.180 N 1561774.292 E	High	Seasonally	Recent	Commercial	-
<b>Riccarton Rd</b>	5180191.063 N 1567008.916 E	High	Monthly	Gley	Residential	-*

\* Housing ages unavailable for these sites

## Appendix 2 – ICP-MS operating conditions

<b>Model</b>	<b>Agilent 7500 cx</b>
<b>Collision Cell</b>	Octopole reaction system
<b>Radio frequency power</b>	1560 W
<b>Radio frequency</b>	Matching 1.66 V
<b>Sample depth</b>	8.3 mm
<b>Argon Carrier gas</b>	0.92 L min <sup>-1</sup>
<b>Argon Makeup gas</b>	0.22 L min <sup>-1</sup>
<b>Helium gas</b>	4.5 ml min <sup>-1</sup>
<b>Spray Chamber</b>	2 °C
<b>Nebuliser</b>	Burgener, at 0.1 RPS

Appendix 3 – Background trace element concentrations in Christchurch soil types. All concentrations in mg kg<sup>-1</sup>

<b>Soil Type</b>	<b>Mn</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
<b>Gley</b>	758	8.7	0.24	16.8	15.5	13.4	17.8	65.6
<b>Recent</b>	536	8.4	0.07	20.0	18.8	19.0	21.4	84.0
<b>Organic</b>	114	2.9	0.34	13.8	18.4	7.2	25.9	53.5
<b>Brown Sand</b>	1110	3.4	0.06	11.0	7.1	8.7	31.9	50.7
<b>Pallic</b>	877	4.6	0.11	15.6	11.5	11.6	18.8	62.4

## Appendix 4 – Weather parameters

<b>Sampling month</b>	<b>Monthly rain (mm)</b>	<b>Last 5 days rain (mm)</b>	<b>Last 10 days rain (mm)</b>	<b>Days of rain in month</b>	<b>Average temperature (°C)</b>
<b>May</b>	99	0	0	17	11.9
<b>June</b>	23	1.4	2.2	16	8.1
<b>July</b>	24	1.2	11.4	15	6.6
<b>August</b>	39	6.4	9	19	6.4
<b>September</b>	37	8	14.2	11	10.3
<b>October</b>	67	1.7	15.9	16	12
<b>November</b>	47	0.8	0.8	12	13.8

Appendix 5 – Monthly road dust sample quantities after 2mm filtering, in g m<sup>-1</sup>

Site	May	June	July	August	September	October	November
Avonhead Rd	2.01	4.92	20.03	21.10	6.48	8.20	43.38
Condell Ave	4.57	42.49	27.80	7.64	11.16	4.91	25.70
Gardiners Rd	7.97	31.60	3.09	21.41	23.03	9.30	2.17
Te Korari St	69.74	137.93	21.93	23.51	39.05	21.53	18.35
Lake Terrace Rd	31.00	24.22	163.48	38.35	8.36	19.45	10.44
Harper Ave	13.04	35.03	0.90	5.64	10.49	10.00	6.41
Avonside Dr	7.70	43.80	26.21	36.12	71.86	86.38	-
Centaurus Dr	8.01	29.72	3.47	13.76	17.72	7.40	0.36
Corsair Dr	53.82	72.47	21.12	14.85	12.01	7.22	6.62
Riccarton Rd	21.16	15.84	6.84	4.56	19.04	1.80	4.99



Appendix 6 – Temporal Dataset: Trace elements in road dust from monthly sampling programme. All concentrations (except iron) in  $\mu\text{g g}^{-1}$ .

### 5.1 Arsenic

Site	May	June	July	August	September	October	November
Avonhead Rd	5.48	5.24	12.08	11.37	4.80	6.93	4.20
Condell Ave	5.75	6.34	5.43	5.12	4.60	8.17	4.40
Gardiners Rd	5.31	5.22	5.65	4.71	5.45	5.80	3.46
Te Korari St	3.42	3.00	3.33	2.74	2.22	3.06	3.40
Lake Terrace Rd	3.90	3.58	3.42	3.25	2.70	2.66	2.37
Harper Ave	5.11	3.40	3.71	3.66	5.03	3.32	3.82
Avonside Dr	5.87	4.17	3.97	3.66	2.93	2.48	-
Centaurus Rd	5.29	5.43	5.99	4.91	3.80	4.05	3.10
Corsair Dr	3.66	3.03	4.10	4.41	2.72	3.55	3.27
Riccarton Rd	4.62	3.76	3.94	3.08	3.65	4.11	3.48

### 5.2 Cadmium

Site	May	June	July	August	September	October	November
Avonhead Rd	0.18	0.18	0.43	0.21	0.22	0.21	0.08
Condell Ave	0.21	0.13	0.12	0.12	0.24	0.20	0.14
Gardiners Rd	0.08	0.13	0.14	0.10	0.12	0.10	0.07
Te Korari St	0.05	0.07	0.08	0.04	0.04	0.07	0.06
Lake Terrace Rd	0.09	0.12	0.07	0.08	0.09	0.06	0.05
Harper Ave	0.14	0.24	0.16	0.14	0.17	0.12	0.18
Avonside Dr	0.13	0.08	0.11	0.10	0.07	0.06	-
Centaurus Rd	0.11	0.11	0.15	0.14	0.10	0.12	0.12
Corsair Dr	0.07	0.06	0.09	0.10	0.08	0.10	0.08
Riccarton Rd	2.80	1.14	1.59	0.64	1.09	1.07	0.58

### 5.3 Cobalt

Site	May	June	July	August	September	October	November
Avonhead Rd	15.15	7.87	8.91	6.98	4.62	7.19	3.81
Condell Ave	5.29	11.74	3.97	3.95	3.87	4.03	3.85
Gardiners Rd	20.67	4.15	3.89	6.74	7.91	6.46	3.10
Te Korari St	3.39	2.88	2.95	3.10	2.61	3.14	3.19
Lake Terrace Rd	3.64	3.06	3.49	2.93	3.05	2.82	2.90
Harper Ave	4.96	3.74	3.85	4.28	4.21	3.63	4.33
Avonside Dr	4.16	3.94	3.50	3.32	3.03	2.97	-
Centaurus Rd	4.09	4.19	4.37	4.58	3.85	3.30	2.66
Corsair Dr	4.37	3.62	4.32	3.96	3.47	4.01	3.90
Riccarton Rd	5.09	4.05	4.02	3.61	4.53	4.33	3.89

### 5.4 Chromium

Site	May	June	July	August	September	October	November
Avonhead Rd	27.3	20.8	61.3	28.5	20.9	21.9	13.0
Condell Ave	52.4	21.6	24.0	34.4	25.3	19.8	24.9
Gardiners Rd	22.0	22.2	20.7	20.2	16.5	16.4	13.5
Te Korari St	14.2	10.8	11.6	10.8	8.7	11.1	11.6
Lake Terrace Rd	38.2	15.6	13.8	22.0	15.6	16.0	19.7
Harper Ave	57.5	35.7	32.7	38.3	30.4	25.1	31.5
Avonside Dr	73.8	62.2	43.7	39.5	21.9	21.5	-
Centaurus Rd	42.0	25.4	22.3	34.2	30.2	22.5	16.5
Corsair Dr	30.3	16.4	18.1	16.4	14.8	18.3	14.6
Riccarton Rd	106.0	53.3	73.0	42.1	56.1	106.6	63.9

### 5.5 Copper

Site	May	June	July	August	September	October	November
Avonhead Rd	135.9	60.0	54.0	136.3	56.1	51.5	44.1
Condell Ave	404.6	62.8	41.3	59.6	83.7	54.6	61.4
Gardiners Rd	58.8	35.3	36.8	31.9	33.8	101.8	52.9
Te Korari St	10.9	7.6	24.8	13.0	13.6	11.8	13.6
Lake Terrace Rd	45.4	45.0	25.2	35.1	41.9	30.8	80.3
Harper Ave	193.1	68.5	287.9	98.2	123.2	73.5	106.8
Avonside Dr	86.1	40.6	40.7	31.7	25.1	41.8	-
Centaurus Rd	102.6	39.2	48.6	52.0	95.0	55.1	37.7
Corsair Dr	21.8	73.0	31.8	37.5	78.7	46.6	57.5
Riccarton Rd	117.0	70.8	72.3	47.8	97.8	142.8	81.0

### 5.6 Iron

Site	May	June	July	August	September	October	November
Avonhead Rd	1.51	1.38	2.59	1.23	1.33	1.30	1.04
Condell Ave	1.97	1.29	1.45	1.23	1.30	1.21	1.32
Gardiners Rd	1.37	1.39	1.26	1.18	1.19	1.13	0.88
Te Korari St	1.13	0.94	1.04	1.02	0.89	0.97	0.92
Lake Terrace Rd	1.41	0.97	1.06	0.90	0.96	0.97	0.97
Harper Ave	2.19	1.39	1.47	1.40	1.52	1.35	1.24
Avonside Dr	1.67	1.63	1.32	1.08	1.05	1.03	-
Centaurus Rd	1.45	1.36	1.37	1.30	1.22	1.08	0.84
Corsair Dr	1.42	1.20	1.37	1.14	1.13	1.17	1.12
Riccarton Rd	1.79	1.44	1.50	1.25	1.75	1.66	1.47

## 5.7 Manganese

Site	May	June	July	August	September	October	November
Avonhead Rd	320.9	252.6	1649.2	294.2	257.6	386.4	334.1
Condell Ave	288.9	275.1	244.2	241.7	206.8	209.0	201.6
Gardiners Rd	222.6	236.6	274.6	250.6	244.9	197.9	149.1
Te Korari St	175.3	152.5	163.0	174.6	133.5	162.2	166.3
Lake Terrace Rd	197.7	162.5	174.0	177.4	170.5	153.4	145.7
Harper Ave	264.7	204.1	217.9	234.4	211.4	193.9	216.6
Avonside Dr	216.4	209.4	194.8	212.8	162.7	147.5	-
Centaurus Rd	212.0	222.2	220.2	255.8	216.7	177.3	157.7
Corsair Dr	222.4	192.9	223.7	227.0	178.7	203.4	201.3
Riccarton Rd	246.7	259.5	228.7	200.8	228.6	221.4	200.8

## 5.8 Nickel

Site	May	June	July	August	September	October	November
Avonhead Rd	26.83	13.03	18.24	31.43	10.16	10.87	9.16
Condell Ave	16.71	10.52	9.61	9.83	9.51	8.95	10.84
Gardiners Rd	10.44	9.04	9.50	9.68	9.29	8.75	7.67
Te Korari St	7.08	6.09	6.96	6.86	6.00	6.63	7.02
Lake Terrace Rd	10.10	6.30	8.04	9.00	17.00	6.48	6.69
Harper Ave	17.82	9.25	10.84	9.88	11.65	8.98	9.30
Avonside Dr	13.27	11.04	9.54	8.57	7.81	9.72	-
Centaurus Rd	12.36	13.61	14.57	10.49	9.94	9.57	7.15
Corsair Dr	13.73	8.73	10.47	9.41	7.81	8.50	11.19
Riccarton Rd	25.73	14.56	18.89	13.97	20.80	19.82	20.87

## 5.9 Lead

Site	May	June	July	August	September	October	November
Avonhead Rd	45.2	43.6	593.8	88.7	67.1	141.3	72.4
Condell Ave	66.1	85.3	65.0	56.8	76.6	104.4	75.5
Gardiners Rd	48.2	78.0	40.2	118.8	56.8	49.6	37.0
Te Korari St	17.8	69.9	14.3	11.3	11.9	15.5	13.9
Lake Terrace Rd	38.6	38.2	30.1	31.3	30.5	27.8	31.7
Harper Ave	89.9	102.1	83.1	100.0	79.5	48.1	96.6
Avonside Dr	101.6	45.4	50.5	39.3	44.8	25.6	-
Centaurus Rd	74.8	79.2	76.7	68.4	89.6	71.0	54.9
Corsair Dr	18.9	18.2	23.6	18.8	159.3	21.1	30.2
Riccarton Rd	90.4	61.1	72.4	50.7	59.1	43.9	50.1

## 5.10 Antimony

Site	May	June	July	August	September	October	November
Avonhead Rd	1.71	1.99	1.04	2.17	1.31	2.28	0.54
Condell Ave	1.72	1.80	0.96	0.75	1.10	1.11	0.87
Gardiners Rd	1.89	0.97	1.28	1.13	0.88	0.84	0.63
Te Korari St	0.43	0.85	0.29	0.18	0.21	0.35	0.50
Lake Terrace Rd	2.62	0.92	0.55	0.35	0.48	0.54	0.28
Harper Ave	3.71	2.96	2.56	2.52	3.67	2.82	3.77
Avonside Dr	1.80	1.37	1.43	0.76	0.59	0.46	-
Centaurus Rd	2.08	1.18	0.82	0.98	1.01	1.20	2.98
Corsair Dr	0.57	0.51	0.98	0.67	1.14	1.29	0.77
Riccarton Rd	4.14	2.59	2.67	1.26	2.25	1.93	1.52

### 5.11 Vanadium

Site	May	June	July	August	September	October	November
Avonhead Rd	20.6	16.7	23.5	23.7	11.3	14.7	11.8
Condell Ave	19.9	19.0	16.2	17.8	12.0	13.8	13.2
Gardiners Rd	19.6	16.9	15.7	19.3	13.2	13.5	9.7
Te Korari St	16.1	13.6	15.1	14.9	9.9	12.8	12.5
Lake Terrace Rd	17.0	11.8	14.1	14.0	9.4	10.9	11.6
Harper Ave	21.6	14.8	15.1	19.8	11.7	13.0	13.4
Avonside Dr	18.3	15.6	14.8	15.2	9.8	11.3	-
Centaurus Rd	19.5	18.5	18.1	22.1	11.7	12.7	9.4
Corsair Dr	19.1	15.2	19.4	21.2	11.6	15.3	14.6
Riccarton Rd	17.1	14.6	15.4	13.8	11.8	13.2	13.3

### 5.12 Zinc

Site	May	June	July	August	September	October	November
Avonhead Rd	612.0	345.9	2751.3	1311.8	420.6	705.8	434.0
Condell Ave	285.8	300.0	314.3	333.0	336.2	385.6	302.9
Gardiners Rd	190.1	255.8	233.1	296.5	285.5	231.3	154.3
Te Korari St	121.9	116.8	117.9	97.7	89.5	146.5	182.4
Lake Terrace Rd	332.7	368.1	204.8	270.1	269.5	241.2	152.8
Harper Ave	258.5	180.9	361.8	187.9	275.7	231.9	303.8
Avonside Dr	410.5	290.9	325.1	181.1	115.2	104.0	-
Centaurus Rd	500.3	254.9	251.8	373.5	282.8	277.6	252.2
Corsair Dr	195.8	143.7	266.0	249.1	219.0	305.8	317.6
Riccarton Rd	395.2	273.5	307.5	242.4	323.2	269.7	247.5

Appendix 7 – Spatial dataset: Trace elements in Christchurch road dust from seasonal sampling. All concentrations in  $\mu\text{g g}^{-1}$  unless stated.

6.1 Winter data

Site	As	Cd	Co	Cr	Cu	Fe (%)	Mn	Ni	Pb	Sb	V	Zn
Avonhead Rd	12.08	0.431	8.91	61.3	54.0	2.59	1649.2	18.24	593.8	1.04	23.5	2751.3
Ilam Rd	4.69	0.224	4.40	25.4	96.6	1.31	228.3	10.13	85.6	2.33	16.5	399.4
Memorial Ave	3.57	0.096	3.62	28.9	144.5	1.47	211.1	9.13	77.3	1.64	15.2	191.7
Condell Ave	5.43	0.123	3.97	24.0	41.3	1.45	244.2	9.61	65.0	0.96	16.2	314.3
Papanui Rd	4.64	0.126	3.63	25.0	97.3	1.48	197.6	10.32	77.8	1.82	14.3	384.7
Gardiners Rd	5.65	0.136	3.89	20.7	36.8	1.26	274.6	9.50	40.2	1.28	15.7	233.1
Prestons Rd	4.11	0.819	3.65	22.1	25.2	1.19	188.5	8.47	55.7	0.80	15.4	180.1
Te Korari St	3.29	0.083	2.92	11.5	24.5	1.03	161.2	6.89	14.2	0.29	14.9	116.7
Mairehau Rd	4.51	0.108	3.54	14.8	41.5	1.12	187.1	7.75	41.4	0.87	14.9	239.5
Amoka Crescent	6.29	0.117	4.70	19.4	22.4	1.30	340.2	10.66	24.6	0.66	18.0	228.2
Lake Terrace Rd	3.38	0.073	3.45	13.6	24.9	1.04	171.9	7.94	29.8	0.55	13.9	202.4
Marshlands Rd	5.09	0.080	3.46	23.4	55.3	1.24	169.3	9.16	50.4	2.14	14.0	189.4
Innes Rd	4.34	0.126	3.64	35.6	69.2	1.35	193.2	26.85	84.2	1.76	15.0	255.6
Normans Rd	6.54	0.126	4.39	24.1	40.8	1.38	280.3	10.61	44.6	1.07	18.5	237.0
Geraldine St	5.89	0.172	4.65	24.2	81.8	1.36	293.8	11.01	168.0	2.17	16.6	343.4
Harper Ave	3.71	0.155	3.85	32.7	287.9	1.47	217.9	10.84	83.1	2.56	15.1	361.8
Bealey Ave	5.77	0.178	3.91	20.9	66.2	1.27	226.3	9.46	159.0	1.20	16.5	235.9
Avonside Dr	3.97	0.105	3.50	43.7	40.7	1.32	194.8	9.54	50.5	1.43	14.8	325.1
Woodham Dr	4.22	0.348	3.53	23.3	69.4	1.31	184.6	10.01	49.4	1.02	13.9	428.7
Ferry Rd	5.98	0.345	4.72	31.3	77.1	1.55	233.7	14.11	88.3	2.30	18.2	533.1
Wordsworth St	4.59	0.236	4.53	36.3	64.0	1.57	222.5	16.92	102.8	1.11	17.5	470.3
Colombo St	4.77	0.243	5.55	28.1	152.4	1.76	286.4	37.58	96.9	1.69	23.0	509.7
Centaurus Rd	5.99	0.152	4.37	22.3	48.6	1.37	220.2	14.57	76.7	0.82	18.1	251.8
Edinburgh St	8.23	0.237	5.73	22.8	29.7	1.50	317.9	12.22	69.9	1.61	20.0	727.7
Lincoln Rd	12.29	0.342	5.17	30.2	54.7	1.73	311.4	26.72	383.8	3.86	18.6	835.8

<b>Halswell Rd</b>	8.78	0.130	5.03	29.5	77.8	1.46	253.7	12.21	46.3	3.09	19.8	359.3
<b>Aidanfield Dr</b>	3.33	0.070	3.05	16.0	37.2	1.25	173.5	7.49	23.8	0.61	15.3	153.7
<b>Corsair Dr</b>	4.10	0.086	4.32	18.1	31.8	1.37	223.7	10.47	23.6	0.98	19.4	266.0
<b>Main South Rd</b>	7.04	1.571	3.44	28.2	76.4	1.28	209.5	11.10	44.5	1.80	17.9	319.2
<b>Riccarton Rd</b>	3.94	1.591	4.02	73.0	72.3	1.50	228.7	18.89	72.4	2.67	15.4	307.5

## 6.2 Summer

<b>Site</b>	<b>As</b>	<b>Cd</b>	<b>Co</b>	<b>Cr</b>	<b>Cu</b>	<b>Fe (%)</b>	<b>Mn</b>	<b>Ni</b>	<b>Pb</b>	<b>Sb</b>	<b>V</b>	<b>Zn</b>
<b>Avonhead Rd</b>	4.20	0.08	3.81	13.0	44.1	1.04	334.1	9.16	72.4	0.54	11.8	434.0
<b>Ilam Rd</b>	6.23	0.24	4.78	23.5	53.6	1.11	239.3	9.37	102.8	1.60	15.2	359.0
<b>Memorial Ave</b>	2.90	0.34	2.96	19.8	67.1	0.98	178.2	7.79	67.7	1.48	10.0	263.5
<b>Condell Ave</b>	4.40	0.14	3.85	24.9	61.4	1.32	201.6	10.84	75.5	0.87	13.2	302.9
<b>Papanui Rd</b>	3.21	0.09	3.00	23.6	272.9	1.33	172.0	22.14	160.6	2.81	8.7	477.3
<b>Gardiners Rd</b>	3.46	0.07	3.10	13.5	52.9	0.88	149.1	7.67	37.0	0.63	9.7	154.3
<b>Prestons Rd</b>	5.16	0.36	3.38	15.4	23.3	1.02	172.9	6.99	32.7	0.86	11.5	177.8
<b>Te Korari St</b>	3.40	0.06	3.19	11.6	13.6	0.92	166.3	7.02	13.9	0.50	12.5	182.4
<b>Mairehau Rd</b>	3.76	0.07	3.13	14.8	24.4	1.03	163.0	7.72	32.1	0.57	12.8	179.5
<b>Amoka Crescent</b>	7.55	0.15	6.48	29.8	46.3	1.75	380.0	13.07	48.7	1.66	21.7	399.9
<b>Lake Terrace Rd</b>	2.37	0.05	2.90	19.7	80.3	0.97	145.7	6.69	31.7	0.28	11.6	152.8
<b>Marshlands Rd</b>	3.56	0.06	2.46	16.4	80.3	0.86	126.7	8.11	32.7	1.47	8.3	155.4
<b>Innes Rd</b>	3.98	0.19	3.47	19.9	39.5	1.09	180.9	7.67	41.6	1.16	11.3	223.0
<b>Normans Rd</b>	3.67	0.09	3.79	13.3	23.9	1.09	213.7	8.06	26.7	0.47	12.9	137.4
<b>Geraldine St</b>	4.65	0.12	3.57	9.8	14.2	0.95	214.1	6.24	97.3	0.48	11.3	221.9
<b>Harper Ave</b>	3.82	0.18	4.33	31.5	106.8	1.24	216.6	9.30	96.6	3.77	13.4	303.8
<b>Bealey Ave</b>	3.70	0.10	27.54	20.2	66.0	1.07	188.6	8.77	148.5	1.75	12.6	246.5
<b>Avonside Dr</b>	-	-	-	-	-	-	-	-	-	-	-	-
<b>Woodham Dr</b>	5.64	0.17	4.96	15.8	30.0	0.99	220.2	8.49	62.2	1.54	13.0	348.0



<b>Ferry Rd</b>	2.94	0.18	3.53	21.8	186.3	1.13	174.4	9.24	54.8	1.69	9.9	284.7
<b>Wordsworth St</b>	4.46	0.21	4.40	38.6	179.8	1.62	217.0	23.34	179.9	1.66	12.1	563.3
<b>Colombo St</b>	3.58	0.19	3.50	19.3	58.9	1.02	182.1	11.22	46.3	1.36	11.4	401.5
<b>Centaurus Rd</b>	3.10	0.12	2.66	16.5	37.7	0.84	157.7	7.15	54.9	2.98	9.4	252.2
<b>Edinburgh St</b>	8.39	0.37	4.15	23.3	50.5	1.13	265.4	8.73	83.9	1.85	12.6	351.5
<b>Lincoln Rd</b>	3.51	0.11	3.29	23.2	28.5	1.13	175.5	8.94	154.3	1.15	12.9	315.4
<b>Halswell Rd</b>	9.72	0.15	5.06	30.9	84.9	1.31	275.8	11.86	62.9	2.15	16.2	396.6
<b>Aidanfield Dr</b>	3.30	0.10	3.30	16.1	47.8	1.14	179.9	8.10	27.4	0.46	13.3	117.6
<b>Corsair Dr</b>	3.27	0.08	3.90	14.6	57.5	1.12	201.3	11.19	30.2	0.77	14.6	317.6
<b>Main South Rd</b>	5.59	2.36	4.28	34.5	37.9	1.40	261.3	16.61	56.2	1.42	21.1	314.9
<b>Riccarton Rd</b>	3.48	0.58	3.89	63.9	81.0	1.47	200.8	20.87	50.1	1.52	13.3	247.5

## Appendix 8 – Platinum Group Element concentrations.

## 8.1 Dilution method trial results

Sample number	Platinum (ng g <sup>-1</sup> )	Palladium (ng g <sup>-1</sup> )
1	<0.000	32.59
2	<0.000	51.97
3	<0.000	41.31
4	<0.000	46.60
5	<0.000	23.57
6	<0.000	0.61
7	<0.000	21.21
8	<0.000	25.40

## 8.2 Evaporation method trial results

Sample number	Platinum (ng g <sup>-1</sup> )	Palladium (ng g <sup>-1</sup> )
5	<0.000	28.99
6	<0.000	24.51
7	<0.000	32.52
8	<0.000	26.65

## 8.3 Resin method results

Sample number	Solution	Platinum (ng g <sup>-1</sup> )	Palladium (ng g <sup>-1</sup> )
1	A	<0.000	19.83
1	B	<0.000	1.83
1	Final	<0.000	2.67
2	A	<0.000	19.71
2	B	<0.000	2.14
2	Final	<0.000	6.24
3	A	<0.000	20.31
3	B	<0.000	1.62
3	Final	<0.000	5.80
4	A	<0.000	19.45
4	B	<0.000	1.32
4	Final	<0.000	2.33

#### 8.4 CRM test

Sample	Method	Rhodium (ng g <sup>-1</sup> )	Platinum (ng g <sup>-1</sup> )	Palladium (ng g <sup>-1</sup> )
1	Dilution	30.97	40.41	73.65
2	Dilution	29.27	29.89	71.94
1	Evaporation	9.74	15.31	32.48
2	Evaporation	7.84	8.61	29.46
3	Resin	<DL	<DL	<DL
4	Resin	<DL	<DL	<DL

#### 8.5 Aqua regia analysis of spatial dataset

	Pt (ng g <sup>-1</sup> )
Mean	112.60
Median	63.50
Standard Deviation	140.78
Minimum	< DL
Maximum	766.89
Duplicate Recovery	319.36 %

Appendix 9 – Trace element concentrations from leaching studies. All concentrations in µg g<sup>-1</sup>.

#### 9.1 Arsenic

Site	Sampling month	Stormwater	Stream water	HCl
Corsair Dr	May	0.038	0.131	1.50
Centaurus Rd	June	0.141	0.161	3.36
Te Korari St	June	0.061	0.087	1.31
Prestons Rd	July	0.093	0.120	2.45
Lake Terrace Rd	July	0.107	0.091	1.75

#### 9.2 Cadmium

Site	Sampling month	Stormwater	Stream water	HCl
Corsair Dr	May	0.0012	0.0021	0.057
Centaurus Rd	June	0.0038	0.0059	0.123
Te Korari St	June	0.0025	0.0040	0.031
Prestons Rd	July	0.0025	0.0113	0.300
Lake Terrace Rd	July	0.0024	0.0027	0.058

### 9.3 Cobalt

Site	Sampling month	Stormwater	Stream water	HCl
<b>Corsair Dr</b>	May	0.0062	0.038	1.75
<b>Centaurus Rd</b>	June	0.0130	0.039	2.12
<b>Te Korari St</b>	June	0.0100	0.025	0.90
<b>Prestons Rd</b>	July	0.0047	0.030	1.62
<b>Lake Terrace Rd</b>	July	0.0119	0.025	1.45

### 9.4 Chromium

Site	Sampling month	Stormwater	Stream water	HCl
<b>Corsair Dr</b>	May	0.027	0.148	3.42
<b>Centaurus Rd</b>	June	0.023	0.098	8.92
<b>Te Korari St</b>	June	0.050	0.086	2.04
<b>Prestons Rd</b>	July	0.019	0.148	13.38
<b>Lake Terrace Rd</b>	July	0.019	0.051	2.34

### 9.5 Copper

Site	Sampling month	Stormwater	Stream water	HCl
<b>Corsair Dr</b>	May	0.31	0.74	25.03
<b>Centaurus Rd</b>	June	0.45	1.04	44.23
<b>Te Korari St</b>	June	0.21	0.33	6.21
<b>Prestons Rd</b>	July	0.25	0.84	17.84
<b>Lake Terrace Rd</b>	July	0.25	0.45	15.24

### 9.6 Iron

Site	Sampling month	Stormwater	Stream water	HCl
<b>Corsair Dr</b>	May	8.79	54.65	2870.35
<b>Centaurus Rd</b>	June	7.84	48.18	3768.84
<b>Te Korari St</b>	June	20.01	47.39	1881.09
<b>Prestons Rd</b>	July	4.07	50.78	3292.79
<b>Lake Terrace Rd</b>	July	5.26	28.49	2056.53

### 9.7 Manganese

Site	Sampling month	Stormwater	Stream water	HCl
<b>Corsair Dr</b>	May	0.34	1.94	85.10
<b>Centaurus Rd</b>	June	1.48	1.83	107.72
<b>Te Korari St</b>	June	0.53	1.45	44.58
<b>Prestons Rd</b>	July	0.34	1.78	81.24
<b>Lake Terrace Rd</b>	July	0.78	0.94	62.23

### 9.8 Nickel

Site	Sampling month	Stormwater	Stream water	HCl
<b>Corsair Dr</b>	May	0.024	0.061	2.29
<b>Centaurus Rd</b>	June	0.044	0.088	3.29
<b>Te Korari St</b>	June	0.027	0.050	1.60
<b>Prestons Rd</b>	July	0.029	0.066	2.69
<b>Lake Terrace Rd</b>	July	0.030	0.045	2.47

### 9.9 Lead

Site	Sampling month	Stormwater	Stream water	HCl
<b>Corsair Dr</b>	May	0.181	0.49	13.49
<b>Centaurus Rd</b>	June	0.516	2.28	72.32
<b>Te Korari St</b>	June	0.209	0.43	9.92
<b>Prestons Rd</b>	July	0.095	1.03	67.29
<b>Lake Terrace Rd</b>	July	0.281	0.72	29.56

### 9.10 Antimony

Site	Sampling month	Stormwater	Stream water	HCl
<b>Corsair Dr</b>	May	0.0084	0.043	0.44
<b>Centaurus Rd</b>	June	<0.000	0.033	0.62
<b>Te Korari St</b>	June	<0.000	0.041	0.24
<b>Prestons Rd</b>	July	0.0083	0.047	0.61
<b>Lake Terrace Rd</b>	July	<0.000	0.014	0.33

### 9.11 Vanadium

Site	Sampling month	Stormwater	Stream water	HCl
<b>Corsair Dr</b>	May	0.044	0.114	3.62
<b>Centaurus Rd</b>	June	0.035	0.094	4.05
<b>Te Korari St</b>	June	0.068	0.101	2.62
<b>Prestons Rd</b>	July	0.042	0.116	3.80
<b>Lake Terrace Rd</b>	July	0.029	0.056	2.64

### 9.12 Zinc

Site	Sampling month	Stormwater	Stream water	HCl
<b>Corsair Dr</b>	May	2.01	6.44	138.66
<b>Centaurus Rd</b>	June	4.74	9.74	210.12
<b>Te Korari St</b>	June	2.29	7.98	78.75
<b>Prestons Rd</b>	July	1.44	7.28	138.00
<b>Lake Terrace Rd</b>	July	3.58	8.54	158.48

Appendix 10 – Anion concentrations in Avon River water sample from Hill Laboratory testing.

<b>Test</b>	<b>Method</b>	<b>Detection Limit (mg L<sup>-1</sup>)</b>	<b>Concentration (mg l<sup>-1</sup>)</b>
<b>Chloride</b>	Ferric thiocyanate colourimetry	0.5	6.5
<b>Fluoride</b>	Ion selective electrode	0.05	0.05
<b>Nitrite</b>	Azo dye colourimetry	0.1	<0.1
<b>Nitrate</b>	Cadmium reduction	0.001	1.07
<b>Reactive phosphorus</b>	Molybdenum blue colourimetry	0.004	<0.004
<b>Phosphate</b>	Calculation from reactive phosphorus	0.004	<0.013
<b>Sulphate</b>	Ion chromatography	0.5	8.1