



# Silver (and Other Metals) in Christchurch's Urban Waterways

Summer Scholarship Report

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TITLE: **Silver (and other metals) in Christchurch's Urban Waterways**

PREPARED FOR: **Waterways Centre for Freshwater Management**

PREPARED BY: **Phil Clunies-Ross** BBiomedSc, BSc(Hons)

REVIEWED BY: Prof. Jenny Webster-Brown (Waterways Centre) and Dr Sally Gaw  
(Chemistry, University of Canterbury)

AFFILIATION: Waterways Centre for Freshwater Management  
University of Canterbury & Lincoln University  
Private Bag 4800  
Christchurch  
New Zealand

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## Executive Summary

The purpose of this study was to conduct a preliminary investigation of the environmental fate of silver nanoparticles in Christchurch's freshwater environments.

Sediment samples were collected from nine sites in Christchurch representing waterways that are likely to be impacted by residential and industrial activities. Two sites were sampled for the purposes of experimental control. The total concentrations of silver was measured by ICP-MS in the <2 mm and <63 µm sediment size fractions. Additionally, the silver content was measured in a primary sludge sample obtained from the Bromley wastewater treatment plant.

The greatest concentrations of silver were measured in the dry wastewater sludge samples (3.1 – 3.7 mg/kg). However, these concentrations were found to be considerably lower than a previous analysis of Bromley sludge (36.3 mg/kg). The concentrations measured in freshwater sediments varied from <0.4 – 0.43 mg/kg. No samples were found to exceed relevant sediment quality guidelines for the protection of aquatic life. However, statistically significantly higher concentrations were measured in sites associated with industrial and residential activities.

The proportion of silver in samples attributable to silver nanoparticles was not able to be determined using ICP-MS alone. Additional studies are recommended to characterise the silver present in Christchurch's freshwater sediments and wastewater sludge. Regular monitoring of sites is also recommended to assess whether the increasing use of Ag-NPs may be enhancing environmental concentrations.

The concentrations of other contaminant trace metals were also determined in the course of this study. This dataset is presented in Appendix 3, but results have not been interpreted as part of this study.

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## Section 1 Introduction

### 1.1 Background

Silver is a soft white transition metal with the chemical symbol Ag and atomic number of 47. It is insoluble in water, has excellent electrical conductivity and is utilised in industrial catalytic applications and the production of high performance electrical equipment. In its pure form, metallic silver is a lustrous metal that is extensively used in the production of jewellery, currency and other precious items.<sup>1</sup>

Silver nanoparticles (Ag-NPs), also known as “colloidal silver”, are tiny particles of silver metal ranging in size from 1-100 nm. Ag-NPs have a large surface area and area of chemical reactivity compared to metallic silver and are also commonly utilised in a variety of catalytic and electronic applications owing to their unique size-dependant properties.<sup>2</sup> More importantly, Ag-NPs are increasingly being used as a potent antimicrobial agent. Before the advent of modern antibiotics, solutions of Ag-NPs were used for more than 100 years to treat bacterial infections.<sup>3</sup> Particles are now frequently incorporated into medical equipment and consumables to prevent bacterial and fungal growth. Ag-NPs are also increasingly being incorporated into textiles, food packaging, ‘health’ supplements and other household applications.<sup>4</sup> However, many of the benefits of these non-medical applications are scientifically proven.

The ever-increasing use of Ag-NPs in everyday applications will ultimately result in increasing quantities entering the environment. Approximately 500 tonnes are produced annually worldwide and this quantity is predicted to steadily increase as the number of consumer products utilising Ag-NPs increases.<sup>2</sup>

### 1.2 Properties of Silver Nanoparticles

Ag-NPs may be synthesized using a variety of physical, chemical and biosynthetic processes. A frequently used method involves the reduction of silver ions ( $\text{Ag}^+$ ) with a reductant (such as citrate or borohyride) to form particles with a metallic silver ( $\text{Ag}^0$ ) core.<sup>5</sup> The synthetic method used in production strongly influences the characteristics of the particles. For example, the final size, morphology and stability of particles is determined by the experimental conditions.<sup>6</sup> Pure Ag-NPs are unstable in suspension and will aggregate to form clusters. The presence of divalent ions (such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) will exacerbate this effect.<sup>7</sup> Aggregation is typically prevented by coating particles with an organic compound, or “capping agent”, that promotes their dispersion by steric or electrostatic repulsion forces. Commonly used examples include citrate, cysteine, polyethylene glycol and starch.<sup>5</sup>

Ag-NPs have unique chemical, physical and optical properties that are not present in bulk silver. In particular, particles exert a strong antimicrobial activity against a broad spectrum of gram positive and negative bacteria.<sup>6</sup> The exact mechanism of toxicity is not fully understood. However, the majority of studies suggest that the dissolution of Ag<sup>+</sup> from the nanoparticle is responsible for the bactericidal effect.<sup>2</sup> The rate of dissolution is determined by the size, shape and surface charge of the particle. Fine Ag-NPs typically release Ag<sup>+</sup> at a greater rate than larger particles resulting in an enhanced antibacterial activity.<sup>8</sup> Additionally, particles with triangular shapes have been found to generate a stronger biocidal effect than spherical or rod shaped particles.<sup>6</sup> It may also be possible that the uptake or adhesion of Ag-NPs on cell surfaces may exacerbate toxicity.<sup>3</sup> However more research is required to elucidate these mechanisms.

### **1.3 Sources in the Freshwater Environment**

Prior to the use of Ag-NPs in everyday applications, the majority of silver in freshwater environments originated from natural leaching, mining and the photographic industry.<sup>5</sup> In 1978 it was reported that an estimated 2,500 tons of silver was lost to the environment in the USA alone, 29% of which was released to the aquatic environment.<sup>1</sup>

Ag-NPs may be formed naturally in freshwater environments, occurring when dissolved Ag<sup>+</sup> reacts with naturally occurring reducing agents, such as humic acids.<sup>2</sup> However, there is little doubt that the majority of Ag-NPs originate from anthropogenic sources. Household products containing nanoparticles, such as cosmetics and personal care products, are likely to be washed off into wastewater. Studies have also demonstrated that Ag-NPs impregnated into clothing may be lost during washing in both dissolved (Ag<sup>+</sup> and Ag complexes) and nanoparticle form.<sup>9-10</sup> The majority of these sources, along with any input from industry, are expected to enter sewer systems where it will be subjected to waste water treatment processes.<sup>11</sup> The removal of this silver from wastewater can greatly decrease the potential environmental burden, but creates a silver-rich sludge that is typically disposed of in landfills, incinerated, or converted to biosolids. Incomplete removal of silver from wastewater may contaminate waters receiving effluent.<sup>3</sup>

A significant proportion of products containing Ag-NPs, such as medical consumables, textiles and electronic devices will also be disposed of in landfills or incinerated. Subsequent leaching from landfills may contaminate both ground and surface waters, while emissions from the incineration of solid waste may result in contamination of the atmosphere that could eventually deposit in soils and aquatic environments.<sup>3</sup> It has been previously estimated that up to 50% of silver nanoparticles produced will be discharged to air, soil or water during their manufacture, use and disposal.<sup>12</sup>

The extent of silver contamination in the urban waterways of Christchurch is not known. However, it is possible that residual contamination may be present in the vicinity of old electroplating businesses as well as chemical and photographic laboratories. Various waterways within the city have been impacted by wastewater released from the sewage network that was extensively damaged during the major earthquakes of 2010/2011. This may have provided a pathway for Ag-NPs to enter waterways originating from wastewater.

#### 1.4 Environmental Fate

The ultimate environmental fate of Ag-NPs and their degradation products, in receiving water environments, is not well understood. Much of the current understanding of the speciation of Ag-NPs stems from past research conducted in response to silver pollution from the photographic industry. In freshwater, silver forms a variety of different complexes dependant on the chemical composition and redox conditions of the environment. Under oxidising conditions the dissolution of silver releases  $\text{Ag}^+$ , a highly reactive ion that is known to bind with a variety of organic and inorganic ligands.<sup>2</sup> For example,  $\text{Ag}^+$  forms complexes with bromides, chlorides and iodides. In brackish and marine waters, the concentrations of silver complexes with chlorine ( $\text{AgCl}$ ,  $\text{AgCl}^{2-}$ ,  $\text{AgCl}_3^{2-}$ ,  $\text{AgCl}_4^{3-}$ ) increases. Soluble silver species will also quickly react with a variety of naturally occurring ligands such as organic acids (humic acids) and suspended particulates.<sup>3</sup> Under reducing conditions metallic  $\text{Ag}^0$  can be formed. However, the majority typically reacts with sulphide ( $\text{S}^{2-}$ ) to form silver sulphide ( $\text{Ag}_2\text{S}$ ).<sup>1</sup>  $\text{Ag}_2\text{S}$  is highly insoluble ( $K_{sp} = 5.92 \times 10^{-51}$ ) and quickly settles in the process of sedimentation. Silver species will also adsorb to manganese dioxide, ferric compounds and clay minerals which are present in high concentrations in sediments.

Silver nanoparticles are much more reactive than bulk silver on account of their large surface area. Dissolution is typically faster, yielding larger quantities of reactive  $\text{Ag}^+$  and other degradation products. A major challenge in assessing the ultimate environmental fate of Ag-NPs is predicting their stability. Nanosilver particles aggregate under a variety of environmental conditions which affects their mobility, bioavailability and toxicity in freshwater environments.<sup>5</sup> Divalent ions (such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), ubiquitous in freshwater environments, induce a potent aggregation effect to most nanoparticles. This could potentially mitigate ecological toxicity from the dissolution and ingestion of particles.<sup>7</sup> The type of capping agent used to stabilise particles also affects the stability of particles, particularly the rate of dissolution. Other considerations include the pH, ionic strength, the presence of suspended particulate material (such as natural organic matter) and reactive ligands present in the environment.<sup>6</sup> The presence of oxygen in solution is required for nanosilver particle dissolution, with  $\text{Ag}^+$  release enhanced with reducing pH in oxygen saturated water.  $\text{Ag}^+$  release from Ag-NPs is completely inhibited by removing dissolved

oxygen, suggesting that Ag-NPs may remain stable and accumulate in anoxic environments.<sup>13</sup>

Waste water treatment plants have proven to be very efficient at removing silver from wastewaters, including those highly enriched from photo processing activities. Waste waters contain high concentrations of  $S^{2-}$  compared to natural waters. It has therefore been proposed that silver will begin to be transformed to  $Ag_2S$  before entering treatment plants.<sup>7</sup> The majority of the remaining silver is then efficiently removed from the wastewater and retained in the sludge as insoluble  $Ag_2S$ .<sup>14</sup> Ag-NPs are also efficiently removed in this process, with a recent study reporting 99% removal efficiency from a spiked urban treatment plant, irrespective of the particle size and capping agent used. The majority was diverted to the digester and only a small fraction was released to surface waters.<sup>15</sup> Despite this observation, concentrations of silver near sewage outfalls tend to be one to two orders of magnitude higher than pristine waters.<sup>16</sup> Previous analysis of Bromley sewage sludge in 1996 measured concentrations of silver at 36.3 and 38.9 mg/kg in lagoon and dry sludges respectively.<sup>17</sup>

## 1.5 Toxicity

The toxicity and bioavailability of silver in aquatic environments is highly variable and is thought to be correlated with the quantity of free  $Ag^+$  in solution.<sup>1</sup> In freshwater fish,  $Ag^+$  damages the gills and can cause acute toxicity at extremely low concentrations.<sup>18</sup> As a result, silver has been listed as a priority pollutant by the USEPA (1977) and in the EEC Dangerous Substance Directive List II (1976).<sup>5</sup>

Ag-NPs are considered to be relatively harmless to humans and numerous products are now available that market solutions of Ag-NPs as 'health' supplements for the remedy of certain medical ailments.<sup>6</sup> The majority of these claims are scientifically unproven. In fact, over-exposure to silver can result in argyria, a condition in which the skin turns a bluish-grey colour due to the accumulation of silver in body tissues.<sup>5</sup>

Ag-NPs have been shown to be toxic to a variety of aquatic species including fish, invertebrates and algae.<sup>5</sup> However, toxicity may vary dependant on the concentration, size, morphology and surface properties of the particles.<sup>5</sup> The majority of studies suggest that the toxicity of particles is in direct proportion to the rate of dissolution.  $Ag^+$  is extremely reactive in biological systems and is known to interact with the thiol groups of vital enzymes and proteins, inhibiting metabolic pathways.<sup>5</sup> Smaller particles, with higher rates of dissolution, cause greater toxic responses in model organisms.<sup>7</sup> However, *in vivo* and *in vitro* toxicity studies have also demonstrated that silver nanoparticles can enter cells in biological tissues and cause cellular damage.<sup>5</sup> Nanoparticles may be taken up into biological tissues where they may undergo dissolution to deliver  $Ag^+$  to critical metabolic pathways. The capping



agents used to disperse silver nanoparticles could enhance the translocation of particles across biological membranes.<sup>5</sup>

The toxicity of Ag-NPs in freshwater environments is likely to be mitigated by the metals propensity to form complexes with surrounding chemical species that are not readily bioavailable.<sup>6</sup> However, increasing loads of Ag-NPs into the environment may result in concentrations that have environmental impacts. This has generated considerable concerns from both scientists and government agencies.

## Section 2 Methods

### 2.1 Sediment Sampling

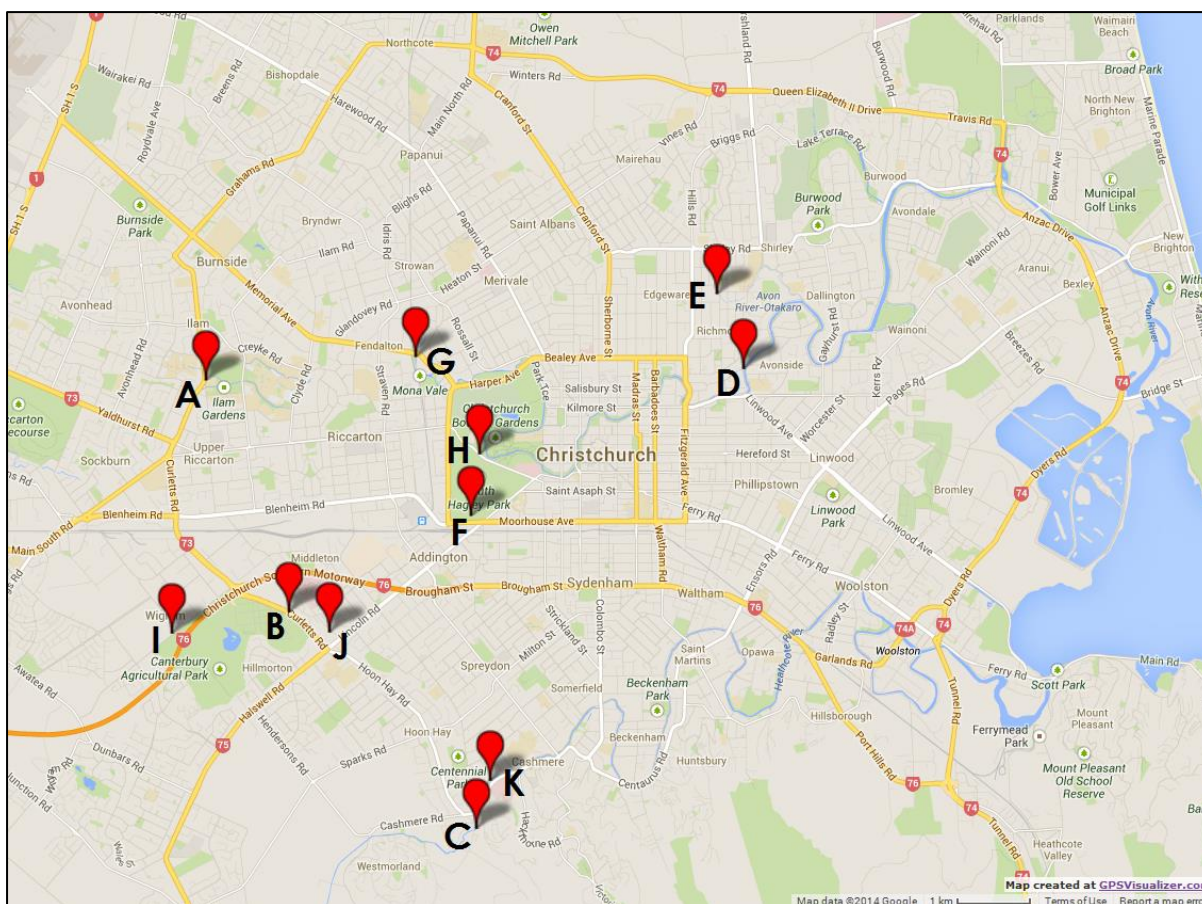
Sediment samples were collected from 11 locations in the city of Christchurch (**Table 1, Figure 1**) on the 17<sup>th</sup> December 2013 and 8<sup>th</sup> January 2014. Two locations, the headwaters of the Ilam Stream and a semi-urban section of the Cashmere Stream, were chosen as control sites unlikely to be impacted by anthropogenic activities. The remaining sites were selected for their historic contamination with sewage or heavy metals. Detailed descriptions of samples sites and GPS locations are provided in **Appendix 1**.

**Table 1** Sample ID and locations where sediment was collected for analysis.

Sample ID	Location	Sample ID	Location
Site A	Head of Ilam Stream	Site G	Avon River at Mona Vale
Site B	Curlett's Rd Drain	Site H	Riccarton Drain
Site C	Cashmere Stream	Site I	Hayton's Drain at Wigrams Rd
Site D	Avon River at Swanns Rd Bridge	Site J	Heathcote River at Annex Rd
Site E	Dudley Creek at Stapletons Rd.	Site K	Heathcote River at Cashmere Rd
Site F	Addington Drain		

At each location a composite sample of sediment was collected from a 1 m<sup>3</sup> area. The brown oxidised surface layer of sediment was collected into a 200 ml LabServ plastic container using a thoroughly rinsed plastic hand trowel or grab sampler. Excess water was drained before being sealed in a bag to prevent cross contamination.

A single sample of wastewater primary settled sludge was also collected from the Bromley wastewater treatment plant that services the greater Christchurch population. This sample was collected from the primary sedimentation tanks by staff at the Christchurch City Council.



**Figure 1** Overview of Christchurch city and locations of sample sites in the Avon/Ōtākaro and Heathcote/Ōpāwaho river catchments (Map generated GPS visualizer).

## 2.2 Sample Preparation and Analytical Method

All samples were initially dried at 70°C for three days to remove all moisture and deactivate any potentially harmful pathogens. Samples were then double bagged and disaggregated with a metal rolling pin before dry sieving with a 2 mm stainless steel and 63 µm nylon sieve to separate size fractions. One gram of each size fraction was weighed out and placed in acid washed digestion tubes.

Four ml of 1:1 nitric acid (HNO<sub>3</sub>) and 10 ml of a 1:4 hydrochloric acid (HCl) was added to each tube before allowing to sit for one hour. The solutions were next heated to 85°C and refluxed for 40 minutes, cooled to room temperature and then made up to 40 ml with milliQ water. For the purposes of quality control, duplicate samples of certified reference material (U.S National Institute of Standards and Technology Reference Material 2702) and experimental blanks were included in the digestion process. All digested samples were left to stand overnight. Sewage sludge samples were filtered with MILLEX HA 0.45 µm filter units to remove particulate material. All samples were then diluted by a factor of 10 by adding 0.5 ml of the digested sediment solution to 4.5 ml of 2% HNO<sub>3</sub> and 0.5% HCl solution. A duplicate sample was included every 10 samples to measure method consistency. Additionally, a

triplicate sample was spiked and included every 20 samples to measure the recovery of trace metals.

Analysis of trace metal content was performed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) as per Method 200.8 from the U.S. Environmental Protection Agency.<sup>19</sup> Samples were analysed for aluminium (Al), vanadium (V), chromium (Cr), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), ruthenium (Ru), palladium (Pd), silver (Ag), cadmium (Cd), antimony (Sb), platinum (Pt) and lead (Pb).

### **2.3 Statistical Analysis**

Statistical Analysis was performed using XLSTAT Version 2013.5.03.

## Section 3 Results

### 3.1 Analysis by ICP-MS

The percentage recovery of silver was measured to be 110.93% from concentrations measured in the certified reference material. Recoveries for all metals analysed are detailed in **Appendix 2**. The detection limit for silver was found to be 0.1 µg/l, or 0.04 mg/kg.

Concentrations of silver determined by ICP-MS are presented for both the <2 mm and < 63 µm sediment size fractions in **Tables 2 and 3**, respectively. Silver concentrations were converted to mg/kg for the purposes of comparative analysis with relevant sediment quality guidelines. Concentrations of Ag measured in the primary sewage sludge are included in **Table 1**. Concentrations of all trace metals measured in sediment samples are presented as **Appendix 3**.

The highest concentrations of silver, measured at 3.11 and 3.69 mg/kg dry sample, were detected in the wastewater sludge samples. Concentrations measured in Christchurch urban streams were at least one order of magnitude lower in the <2 mm size fraction (**Table 2**). The highest was measured at the Curlett's Rd drain with 0.28 mg/kg. Cashmere stream, the Avon River at Schwann's Rd, Riccarton Drain and the Heathcote River at Cashmere Ave had levels below the detection limit of 0.4 mg/kg. Concentrations of silver measured in the <63 µm size fraction (**Table 3**) were typically higher than those in the <2 mm size fraction. The highest concentration was once again measured at the Curlett's Rd drain with 0.43 mg/kg. Cashmere Stream was the only site with a concentration below the detection limit.

**Table 2** Silver concentrations (mg/kg) measured in the <2 mm sediment size fraction in Christchurch's urban waterways and waste water treatment sludge.

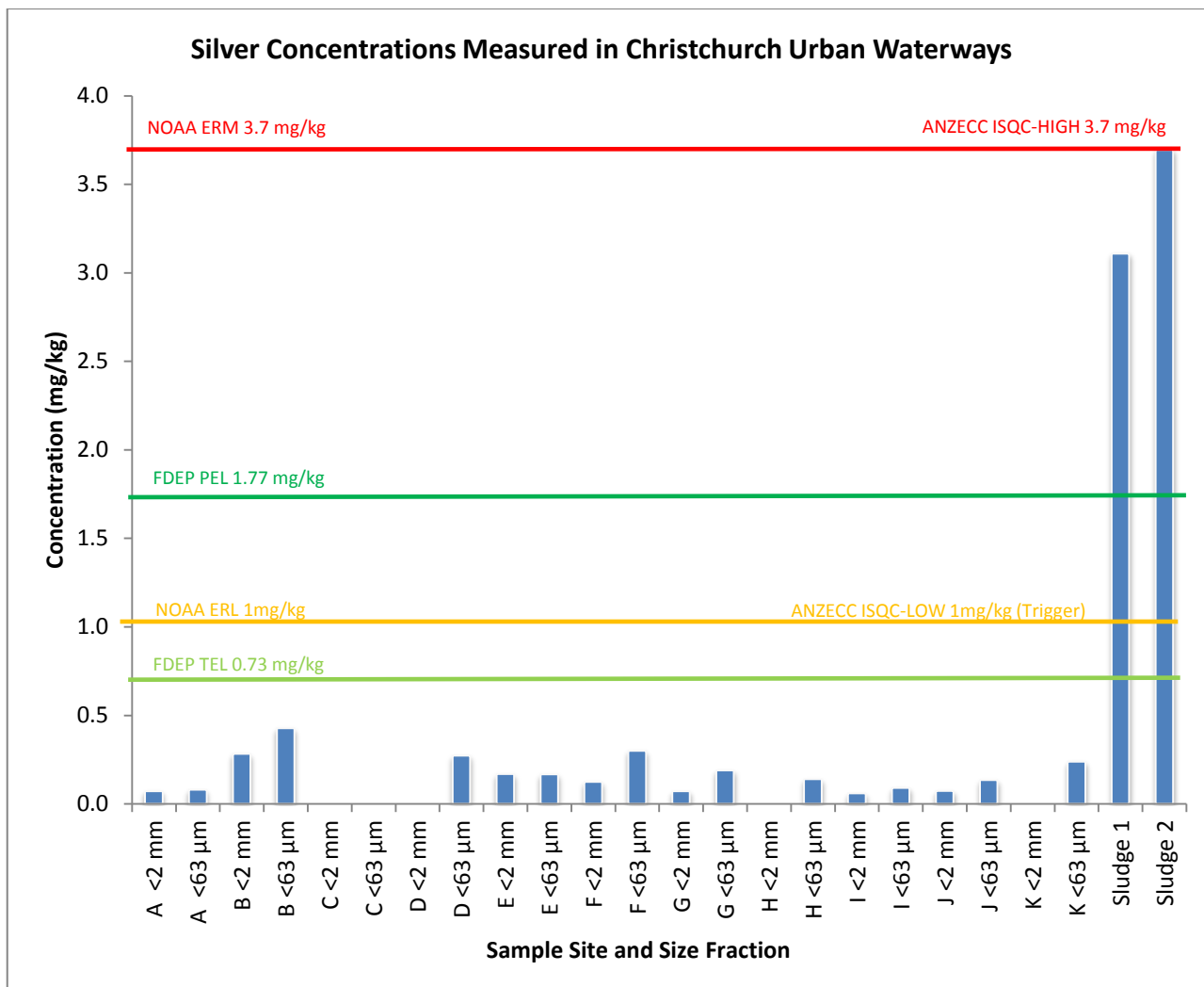
Sample Code	Site	Sample Site-	Ag (mg/kg)
PCR01	A	Ilam Stream	0.07
PCR03	B	Curlett's Rd Drain	0.28
PCR05	C	Cashmere Stream	<0.4
PCR07	D	Avon @ Schwanns Rd	<0.4
PCR09	E	Dudley Creek	0.17
PCR11	F	Addington Drain	0.12
PCR13	G	Avon @ Mona Vale	0.07
PCR15	H	Riccarton Drain	<0.4
PCR17	I	Hayton's Drain	0.06
PCR19	J	Heathcote @ Annex Rd	0.07
PCR21	K	Heathcote @ Cashmere Ave	<0.4
Sludge 1	WWTP	Bromley Sludge Sample 1	3.11
Sludge 2	WWTP	Bromley Sludge Sample 2	3.69

**Table 3** Silver concentrations (mg/kg) measured in the <63  $\mu\text{m}$  sediment size fraction in Christchurch’s urban waterways.

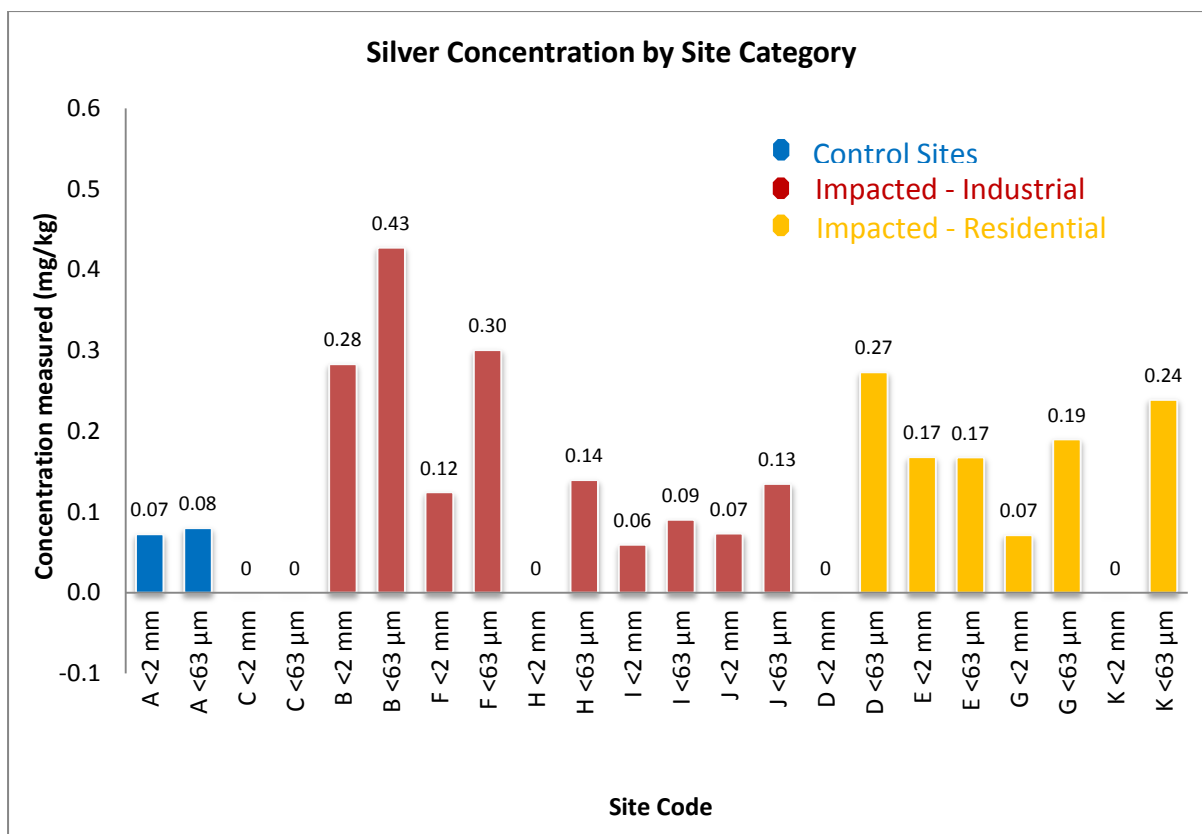
Sample Code	Site	Sample Site	Ag (mg/kg)
PCR02	A	Ilam Stream	0.08
PCR04	B	Curlett's Rd Drain	0.43
PCR06	C	Cashmere Stream	<0.4
PCR08	D	Avon @ Schwanns Rd	0.27
PCR10	E	Dudley Creek	0.17
PCR12	F	Addington Drain	0.30
PCR14	G	Avon @ Mona Vale	0.19
PCR16	H	Riccarton Drain	0.14
PCR18	I	Hayton's Drain	0.09
PCR20	J	Heathcote @ Annex Rd	0.13
PCR22	K	Heathcote @ Cashmere Ave	0.24

**Figure 2** illustrates the silver concentrations measured at all locations for both <2 mm and < 63  $\mu\text{m}$  size fractions as well as the wastewater sludge samples. These are presented along with the most frequently utilised sediment quality guidelines including those from the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC)<sup>18</sup>, the US National Oceanic and Atmospheric Administration (NOAA) and the Florida Department of Environmental Protection (FDEP). Concentrations of silver in wastewater sludge were found to exceed most sediment quality guidelines, with the exception of the NOAA effects range medium (ERM) and the ANZECC ISQC-High (derived from the same value). Concentrations of silver in sediments collected from Christchurch’s urban waterways were all below relevant guideline values.

The data was rearranged to compare the differences in silver concentrations measured at control sites compared to those impacted by anthropogenic activities (**Figure 3**). The concentrations measured in the control sites (blue) appear to be lower than those impacted in industrial (red) and residential (yellow) areas.



**Figure 2** Concentrations (mg/kg) of silver measured in Christchurch’s urban waterways (both <2 mm and <63 µm sediment size fractions) and wastewater sludge. Relevant sediment quality guidelines are included for comparative analysis.



**Figure 3** Concentrations (mg/kg) of silver measured in Christchurch’s urban waterways (<2 mm and <63 μm sediment size fractions) at control sites (blue) and those impacted in industrial (red) and residential (yellow) areas.

### 3.2 Statistical Analysis

A paired Students T-test was used to determine that concentrations of Ag measured in <2 mm and <63 μm sediment size fractions were statistically significantly different at the 5% significance level ( $p = 0.004 < 0.05$ ).

A one-way analysis of variance (ANOVA) was used to determine that sample means in “control”, “industrial” and “residential” sites were not statistically significantly different at the 5% significance level ( $p = 0.19 > 0.05$ ). Two sample T-tests were then performed to establish that concentrations of Ag measured in the control sites were statistically different than industrial ( $p = 0.02 < 0.05$ ) and residential sites ( $p = 0.04 < 0.05$ ) at the 5% significance level. Concentrations of Ag measured at industrial and residential sites were found to not be significantly different ( $p = 0.66 > 0.05$ ).



## Section 4 Discussion

The concentrations of silver measured in the sediments of Christchurch's urban waterways were variable dependant on the sample site and the size fraction of sediment analysed. Sample sites associated with industrial and residential activities were found to have significantly greater concentrations of silver than control sites. However, no significant difference was observed at residential and industrial locations. The fine sediment size fraction (<63  $\mu\text{m}$ ) was found to have significantly more bound silver than the larger <2 mm fraction, no doubt due to the greater surface area available for the binding of metals in the finer sediment.

The data suggests that anthropogenic activities have led to a greater degree of silver in the sediments of Christchurch's urban waterways. However, it is not clear when or how this contamination occurred. The highest concentrations were measured at the Curlett's Rd and Addington drains, locations that are known to have legacy issues with industrial pollution. It is possible that these waterways have at one stage been located in the vicinity of photographic development and chemical laboratories, electroplaters and other industry that may have utilised some form of silver. The elevated concentrations observed in residential locations may also be due to similar legacy effects, as well as the indiscriminate contamination from household silver containing items such as silverware, electrical components and silver-plated metals. It is also possible that the use of Ag-NPs may be contributing to the levels of contamination observed. Despite the elevated concentrations, no sites were found to have concentrations of silver exceeding any relevant sediment quality guidelines. This indicates that the ecological health of sediments are unlikely to be impacted by current levels of contamination at this time.

Unsurprisingly, the concentrations of silver measured in wastewater sludge were high compared to sediment samples. This silver is likely to be sourced from domestic and industrial applications that has been washed into wastewater systems and subsequently retained in the wastewater sludge as insoluble  $\text{Ag}_2\text{S}$ . The concentrations measured in both samples (3.1 - 3.7 mg/kg) were an order of magnitude lower than a previous analysis of Bromley sludge conducted in 1996 (36.3 mg/kg).<sup>17</sup> This may be attributed to a reduction in the use of silver in photographic processing with the widespread adoption of digital cameras.

The major limitation of this study was the inability to distinguish Ag-NPs from other species of silver. ICP-MS is a valuable tool that quantifies the overall concentrations of silver in samples. However, it is not able to determine what proportion of contamination is attributable to Ag-NPs and cannot characterise between silver species. Detecting engineered Ag-NPs in the environment can be achieved but has proven to be a significant challenge. Cloud point extraction, field-flow fractionation and a variety of chromatographic methods have been used to first separate Ag-NPs from environmental samples. Particles may then be

characterised with transmission electron microscopy (TEM) or scanning electron microscopy (SEM). Energy-dispersive X-ray spectroscopy (EDS) is often coupled with these techniques to analyse the elemental composition of particles. The quantity of silver is then typically measured with ICP-MS.<sup>20</sup>

This investigation has provided a preliminary indication of the levels of silver contamination present in the sediments of Christchurch's urban waterways. No samples were found to exceed relevant sediment quality guidelines for the protection of aquatic life. However, elevated concentrations were measured in sites associated with industrial and residential activities. The concentrations measured in primary sludge obtained from the Bromley WWTP were found to have decreased since a previous investigation in 1996. ICP-MS analysis successfully quantified the total concentrations of silver in all samples. However, it was not possible to identify and characterise Ag-NPs using this method alone. Additional studies are recommended to characterise the silver present in sediment samples using a combination of separation and characterisation techniques. Regular monitoring of sites is also recommended to assess whether the increasing use of Ag-NPs may be enhancing environmental concentrations.

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## Appendices

### Appendix 1 Detailed descriptions of sites where sediment samples were collected including site ID, date, location, GPS and field observations.

Sample ID	Date	Location	GPS Coordinates	Field Observations
Site A	17/12/2013	Head of Ilam Stream	S 43°31.397 E172° 34.398	Control Site in residential location. Unlikely to be impacted by anthropogenic activities. Springs at head of Ilam stream were not flowing. Small stream character with shallow banks of natural character. Slow flowing with low water level (~0.2 m/s). Samples collected in residential area between University halls of residence and Ilam park. Large quantities of rubbish observed in general area. Approximately a 1 cm layer of brown-grey oxidised sediment. Dark anoxic sediments below this layer. Confirmed with detection of hydrogen sulphide. Eel seen in sample area.
Site B	17/12/2013	Curlett's Rd Drain	S 43°33.022 E172° 35.195	Impacted site in industrial location. Historic Cu and Zn and Pb contamination. This was a steep-sided, square channelled drain located next to busy road. Flow of water relatively fast (~0.5 m/s). Unable to see bed of drain due to high levels of sediment in water. Small quantities of loose sediment present amongst rocks and weeds. Composite sample taken within 1 m <sup>3</sup> area.
Site C	17/12/2013	Cashmere Stream	S 43°34.536 E172° 37.008	Control site in residential location. Historically has had good water quality values. Cashmere Stream Sampled at Worsely's Rd in park area (just entered residential setting). Levels of suspended sediment low enough to view stream bed. Bed sampled on river left (shallow bank side). Very thin layer of oxidised sediment ~ 0.5 cm. Composite sample taken from 1 m <sup>3</sup> area.
Site D	17/12/2013	Avon River at Swanns Rd Bridge.	S 43°31.320 E172° 39.600	Impacted site in residential location. Location of ongoing sewage leak caused by major earthquakes. Avon River sampled at site of historic sewage leak. Sampled downstream of bridge on river left. Gentle gradient at sample site. Medium river flow. Thick layer of oxidized sediment (> 2 cm thick). Composite sample taken from 1 m <sup>3</sup> area.
Site E	17/12/2013	Dudley Creek sampled at Stapletons Rd.	S 43°30.790 E172° 39.336	Impacted site in residential location. Historic contamination issues with Zn, Pb and E. Coli. Steep sided, square channelled creek. Located in residential setting. Unable to see stream bed due to high levels of suspended sediment in water. However, thick layer of oxidised sediment present on stream bed (> 2 cm thick). Composite sample taken from 1 m <sup>3</sup> area.
Site F	17/12/2013	Addington Drain	S 43°32.344 E172° 36.962	Impacted site located downstream of industrial area. Historic Zn and As contamination. Steep sided, square channelled drain. Sampled in south Hagley Park alongside Moorhouse Ave. Site had smell of oil or solvent. Distinctive film observed on surface of water. Medium quantities of sediment in water but stream bed able to be observed. Thick oxidised sediment layer present (> 2 cm thick). Composite sample taken from 1 m <sup>3</sup> area.

**Appendix 1 (Cont)** Detailed descriptions of sites where sediment samples were collected including site ID, date, location, GPS and field observations.

Sample ID	Date	Location	GPS Coordinates	Field Observations
Site G	8/01/2014	Avon River at Mona Vale	S 43° 31.232 E172° 36.425	Impacted site in residential area. Historic Zn and Pb contamination. Wide (~7 m) boxed channel. Sample obtained north western side of site, directly beside Fendalton Rd as the river flows under the road. Slow water flow (approximately 0.25 m/s). Muddy substrate with some rocks. Thin layer of oxidised sediment. Ducks present. Composite sample taken from 1 m <sup>3</sup> area.
Site H	8/01/2014	Riccarton Drain	S 43° 31.916 E172° 37.046	Likely impacted site downstream of commercial area. Site not known to have historic contamination legacy. Boxed drain, approximately 2m wide. Located next to Riccarton Avenue in Hagley park. Sample obtained on north side of park before drain runs in Avon River. Slow moving water flow approximately 0.1-0.2 m/s. Rocky substrate. Composite sample of sediment taken from 1 m <sup>3</sup> area.
Site I	8/01/2014	Hayton's Drain at Wigrams Rd	S 43° 33.168 E172° 34.069	Impacted site downstream of industrial area. Historic nutrient, sediment and Zn contamination. Stream running through new subdivision on corner of Hayton's and Wigram's Rd. Low flow stream with large quantities of rubbish in waters. Sample obtained from pooling area before water flows under Haytons rd. Site of new riparian planting. Gentle bank gradient. Stream smelled anoxic. Composite sample taken from 1 m <sup>3</sup> area.
Site J	8/01/2014	Heathcote River at Annex Rd	S 43° 33.163 E172° 35.590	Impacted site located in residential and industrial area. Historic Cu and Zn contamination. River sampled alongside Annex Rd, downstream of a minor drain. Very slow moving water (approximately 0.1 m/s). River approximately 5 m wide. Grassy bank with gentle gradient. Muddy substrate. Thin layer of top sediment. Composite sample taken from 1 m <sup>3</sup> area.
Site K	8/01/2014	Heathcote River at Cashmere Rd	S 43° 34.200 E172° 37.141	Impacted site located in residential area. Historic Zn contamination. River sampled opposite Princess Margaret Hospital. Approximately 5 m wide. Faster moving water (approximately 0.5 m/s). Steep grassy river banks. Large trees sheltering river. Large quantities of organic matter on river bed. Composite sample taken from 1 m <sup>3</sup> area.

**Appendix 2** Percentage recovery of trace metals analysed by ICP-MS.

<b>Element (atomic mass)</b>	<b>Standard Reference<sup>19</sup> (mg/kg)</b>	<b>Reference Recovery (mg/kg)</b>	<b>% Recovery</b>
V (51)	357.6 ± 9.2	283.97	79.4
Cr (53)	352 ± 22	249.43	70.9
Mn (55)	1757 ± 58	1594	90.7
Co (59)	27.76 ± 0.58	23.1	83.2
Ni (60)	75.4 ± 1.5	51.24	67.9
Cu (63)	117.7 ± 5.6	100.38	85.3
Zn (66)	485.3 ± 4.2	405.86	83.6
As (75)	45.3 ± 1.8	42.08	92.9
Ru (101)	ND	0	-
Pd (105)	ND	0.11	-
Ag (107)	0.622 ± 0.078	0.69	110.9
Cd (111)	0.817 ± 0.011	0.85	104.0
Sb (121)	5.60 ± 0.24	3.95	70.5
Pt (195)	ND	0.02	-
Pb (208)	132.8 ± 1.1	134.95	101.6

**Appendix 3** Concentrations of trace metals measured by ICP-MS.

<b>Trace Metal Concentrations (mg/kg)</b>										
<b>Sample Code</b>	<b>Sample Site</b>	<b>Size Fraction</b>	<b>Metal Concentrations (mg/kg)</b>							
			<b>Al (27)</b>	<b>V (51)</b>	<b>Cr (53)</b>	<b>Fe (54)</b>	<b>Mn (55)</b>	<b>Co (59)</b>	<b>Ni (60)</b>	<b>Cu (63)</b>
PCR01	Ilam Stream	<2 mm	7445.20	15.56	12.31	7199.18	156.64	4.08	8.65	11.63
PCR02	Ilam Stream	< 63 µm	8622.79	16.68	15.84	7678.43	159.16	4.16	9.63	20.54
PCR03	Curlett's Rd Drain	<2 mm	13187.12	30.00	41.54	15121.03	533.34	8.72	19.78	249.50
PCR04	Curlett's Rd Drain	< 63 µm	15205.33	34.37	47.30	17270.81	540.91	9.55	22.47	302.98
PCR05	Cashmere Stream	<2 mm	7481.64	16.68	11.06	8979.10	257.56	8.15	9.34	5.50
PCR06	Cashmere Stream	< 63 µm	9300.55	19.79	13.29	9858.01	370.25	8.81	9.79	9.25
PCR07	Avon @ Schwanns Rd	<2 mm	7725.51	17.69	11.44	9152.98	226.92	5.12	9.80	6.17
PCR08	Avon @ Schwanns Rd	< 63 µm	9696.49	21.76	15.25	11248.97	311.56	6.11	11.58	13.36
PCR09	Dudley Creek	<2 mm	12503.93	28.41	22.30	14730.60	394.04	10.56	16.27	43.11
PCR10	Dudley Creek	< 63 µm	14922.84	31.59	25.01	16334.71	399.20	10.53	17.01	105.20
PCR10 D1	Duplicate	< 63 µm	14290.40	30.78	24.28	16006.88	389.52	10.32	16.75	42.59
PCR11	Addington Drain	<2 mm	9931.61	24.57	28.59	18506.03	558.33	7.60	17.92	32.41
PCR12	Addington Drain	< 63 µm	12194.74	29.71	29.62	21434.26	607.18	8.89	18.85	45.50
PCR13	Avon @ Mona Vale	<2 mm	8204.81	18.88	17.80	8888.08	183.00	4.87	10.49	33.09
PCR14	Avon @ Mona Vale	< 63 µm	8974.97	19.37	18.25	9014.09	173.55	4.60	10.18	33.28
PCR15	Riccarton Drain	<2 mm	6656.02	16.42	13.23	8899.30	250.64	4.53	8.84	14.86
PCR16	Riccarton Drain	< 63 µm	7410.24	20.12	25.96	11795.70	434.11	5.65	12.11	48.25
PCR17	Hayton's Drain	<2 mm	9540.81	21.87	20.42	11084.01	262.16	6.29	12.69	23.55
PCR18	Hayton's Drain	< 63 µm	12094.46	26.37	26.98	12986.23	294.64	7.36	15.74	35.73



**Appendix 3 (Cont)** Concentrations of trace metals measured by ICP-MS.

<b>Trace Metal Concentrations (mg/kg)</b>											
<b>Sample Code</b>	<b>Sample Site</b>	<b>Size Fraction</b>	<b>Metal Concentrations (mg/kg)</b>								
			<b>Zn (66)</b>	<b>As (75)</b>	<b>Ru (101)</b>	<b>Pd (105)</b>	<b>Ag (107)</b>	<b>Cd (111)</b>	<b>Sb (121)</b>	<b>Pt (195)</b>	<b>Pb (206)</b>
PCR01	Ilam Stream	<2 mm	361.3	3.08	0.00	0.09	0.07	0.13	0.43	0.00	53.80
PCR02	Ilam Stream	< 63 µm	437.6	4.57	0.00	0.09	0.08	0.15	0.52	0.01	80.34
PCR03	Curlett's Rd Drain	<2 mm	138	12.66	0.00	0.10	0.28	1.42	4.81	0.00	102.2
PCR04	Curlett's Rd Drain	< 63 µm	1488	14.15	0.00	0.11	0.43	1.38	6.24	0.01	123.2
PCR05	Cashmere Stream	<2 mm	83.42	3.66	0.00	0.05	0.02	0.09	0.09	0.00	11.74
PCR06	Cashmere Stream	< 63 µm	103.2	5.97	0.00	0.07	0.03	0.09	0.16	0.00	18.57
PCR07	Avon @ Schwanns Rd	<2 mm	111.9	2.83	0.00	0.04	0.02	0.05	0.12	0.00	19.65
PCR08	Avon @ Schwanns Rd	< 63 µm	194.6	5.18	0.00	0.06	0.27	0.10	0.48	0.00	41.72
PCR09	Dudley Creek	<2 mm	419.0	14.53	0.00	0.08	0.17	0.43	1.15	0.00	136.1
PCR10	Dudley Creek	< 63 µm	445.1	15.79	0.00	0.08	0.17	0.42	1.12	0.00	128.9
PCR10 D1	Duplicate	< 63 µm	437.0	15.48	0.00	0.07	0.17	0.41	1.14	0.00	127.5
PCR11	Addington Drain	<2 mm	471.8	18.57	0.00	0.05	0.12	0.25	1.31	0.00	56.03
PCR12	Addington Drain	< 63 µm	560.9	18.82	0.00	0.06	0.30	0.27	2.01	0.00	62.53
PCR13	Avon @ Mona Vale	<2 mm	210.6	4.78	0.00	0.04	0.07	0.33	0.47	0.00	81.47
PCR14	Avon @ Mona Vale	< 63 µm	191.9	5.75	0.00	0.05	0.19	0.21	0.64	0.00	80.77
PCR15	Riccarton Drain	<2 mm	203.6	6.26	0.00	0.03	0.03	0.10	1.06	0.00	71.95
<b>PCR16</b>	Riccarton Drain	< 63 µm	383.6	17.69	0.00	0.07	0.14	0.21	1.39	0.02	108.8
PCR17	Hayton's Drain	<2 mm	275.0	6.13	0.00	0.05	0.06	0.15	0.47	0.00	34.69
PCR18	Hayton's Drain	< 63 µm	411.1	7.46	0.00	0.06	0.09	0.23	0.71	0.00	47.41

**Appendix 3 (Cont)** Concentrations of trace metals measured by ICP-MS.

<b>Trace Metal Concentrations (mg/kg)</b>										
<b>Sample Code</b>	<b>Sample Site</b>	<b>Size Fraction</b>	<b>Metal Concentrations (mg/kg)</b>							
			<b>Al (27)</b>	<b>V (51)</b>	<b>Cr (53)</b>	<b>Fe (54)</b>	<b>Mn (55)</b>	<b>Co (59)</b>	<b>Ni (60)</b>	<b>Cu (63)</b>
PCR19	Heathcote @ Annex Rd	<2 mm	7706	18.11	17.60	9921	261.9	5.65	10.85	61.48
PCR20	Heathcote @ Annex Rd	< 63 µm	8587	19.73	21.82	11751	335.2	6.43	12.46	78.82
PCR 20 D1	Duplicate	< 63 µm	9016	20.64	23.29	12340	348.3	6.74	13.03	82.56
PCR20 D2	TriPLICATE (Spiked)	< 63 µm	9009	29.16	31.42	12240	354.8	14.87	21.16	89.22
PCR21	Heathcote @ Cashmere Ave	<2 mm	6262	15.91	10.73	7611	194.1	7.97	8.45	16.96
PCR22	Heathcote @ Cashmere Ave	< 63 µm	9140	21.56	17.05	10950	341.9	11.41	11.86	33.11
PCR23	Bromley Sludge 1	-	3081	6.31	142.8	4051	110.8	1.55	8.86	107.8
PCR24	Bromley Sludge Duplicate	-	3380	6.78	154.7	4115	122.5	1.60	8.99	114.8
PCR25	Ref 1	-	17010	278.6	247.1	37972	1601	22.40	49.71	98.35
PCR26	Ref 2	-	17240	284.0	249.4	38329	1594	23.10	51.24	100.4
PCR B1	Blank 1 - acid washed	-	0.96	0.04	0.11	1.75	0.03	0.00	0.00	0.03
PCR B2	Blank 2 - acid washed	-	2.95	0.04	0.13	0.54	0.01	0.00	0.00	0.03
PCR B3	Blank 3 - Non	-	0.44	0.00	0.01	0.21	0.00	0.00	0.00	0.02
PCR B4	Blank 4 - Non	-	0.35	0.00	0.00	0.38	0.01	0.00	0.00	0.01
PCR B4 D1	Duplicate	-	0.54	0.00	0.03	0.35	0.00	0.00	0.00	0.01
PCR B5	Blank 5 - A/W + filtered	-	1.13	0.04	0.04	0.36	0.01	0.00	0.00	0.04

**Appendix 3 (Cont)** Concentrations of trace metals measured by ICP-MS.

<b>Trace Metal Concentrations (mg/kg)</b>											
Sample Code	Sample Site	Size Fraction	Metal Concentrations (mg/kg)								
			Zn (66)	As (75)	Ru (101)	Pd (105)	Ag (107)	Cd (111)	Sb (121)	Pt (195)	Pb (206)
PCR19	Heathcote @ Annex Rd	<2 mm	512.6	5.77	0.00	0.03	0.07	1.08	0.48	0.00	39.29
PCR20	Heathcote @ Annex Rd	< 63 µm	600.7	9.21	0.00	0.03	0.13	0.64	1.18	0.00	60.33
PCR 20 D1	Duplicate	< 63 µm	622.9	9.68	0.00	0.04	0.14	0.69	1.26	0.00	62.84
PCR20 D2	Triplicate (Spiked)	< 63 µm	632.5	17.91	8.73	8.60	8.57	9.11	10.05	8.62	70.84
PCR21	Heathcote @ Cashmere Ave	<2 mm	154.6	3.04	0.00	0.03	0.02	0.24	0.12	0.00	17.28
PCR22	Heathcote @ Cashmere Ave	< 63 µm	266.6	8.00	0.00	0.05	0.24	0.28	0.38	0.00	53.68
PCR23	Bromley Sludge 1	NA	329.2	4.49	0.00	0.02	3.11	0.51	0.86	0.01	23.91
PCR24	Bromley Sludge Duplicate	NA	362.4	3.98	0.00	0.04	3.69	0.58	0.92	0.01	28.78
PCR25	Ref 1		403.1	41.19	0.00	0.10	0.66	0.85	4.12	0.01	138.8
PCR26	Ref 2		405.9	42.08	0.00	0.11	0.69	0.85	3.95	0.02	134.9
PCR B1	Blank 1 - acid washed	NA	0.35	0.03	0.00	0.00	0.00	0.00	0.01	0.00	0.02
PCR B2	Blank 2 - acid washed	NA	0.47	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00
PCR B3	Blank 3 - Non	NA	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCR B4	Blank 4 - Non	NA	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCR B4 D1	Duplicate	NA	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCR B5	Blank 5 - A/W + filtered	NA	0.79	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00

**Appendix 4** Results for paired T-test statistical analysis.

<b>Paired T -Test Analysis. &lt; 2mm vs &lt;63 µm sediment size fractions</b>									
Element	Al (27)	V (51)	Cr (53)	Fe (54)	Mn (55)	Co (59)	Ni (60)	Cu (63)	Zn (66)
<b>P-Value</b>	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00
Element	As (75)	Ru (101)	Pd (105)	Ag (107)	Cd (111)	Sb (121)	Pt (195)	Pb (206)	
<b>P-Value</b>	0.01	0.51	0.01	0.00	0.56	0.01	0.15	0.00	

**Waterways Centre for Freshwater Management**

University of Canterbury & Lincoln University

Private Bag 4800

Christchurch

New Zealand

Phone +64 3 364 2330

Fax: +64 3 364 2365

**[www.waterways.ac.nz](http://www.waterways.ac.nz)**