

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

**Use of Zinc in Agriculture: an Assessment of Data for
Evidence of Accumulation in Waikato Soils, Surface Water
and Sediments.**

A thesis presented in partial fulfillment of the requirements
for the degree of

Master of Health Science
in
Environmental Health

at Massey University, Wellington
New Zealand.

Vanessa Vermeulen
2015

Copyright is owned by the Author of this thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Abstract

Pastoral soils in the Waikato region of New Zealand have received high mass loads of Zn since the advent of facial eczema remedies. This activity could potentially cause widespread Zn accumulation in receiving soils, and mobilisation and contamination of nearby receiving environments, presenting risk to ecological health. Currently, no studies have examined the environmental fate of significant sources of anthropogenic Zn used in farming. This study assessed the extent and nature of any evidence that facial eczema Zn is causing significant contamination of agricultural soils and associated ecosystems in the Waikato region of New Zealand by examining extensive soil, surface water, and sediment datasets. Farmed surface soils contained two times more AR Zn on average (60.6 mg/kg, $p < 0.0001$) than natural soils and significant relative enrichment of SSP fertiliser elements Cd, P, Ca, U, F and Ni. Including Zn, these elements decreased down the soil profile, indicating anthropogenic sources. Zn accumulation occurred more readily in inorganic, granular, and allophanic soils. Laboratory experiments showed rapid Zn adsorption in granular soil at the natural soil pH level of 5.70 (>90% of the total concentration within 5 mins and ~97% at equilibrium). This reduced to ~62% adsorption at pH 4.70, indicating Zn re-mobilization in acid soils. No significant change in Zn concentration was observed in farmed soils (average of 7 years) but a 25% decrease ($p < 0.05$) was observed in forestry soils (average of 7.4 years). Approximately 11% of sampled pastoral soils exceeded 100 mg/kg AR Zn but all were below the Biosolids Guideline value of 300 mg/kg. Approximately 112.5 kg Zn/day is carried by the Waikato River ($p < 0.0001$), with ~50% in the dissolved fraction. Zn concentrations peaked twice with distance along the Waikato River: first in the upper reaches, along with B, Li, and As, consistent with local geothermal inputs; and again in the lower reaches, as with increased nutrient elements N, P, and turbidity, consistent with runoff from pastoral farming in the catchment area. Rapidly decreasing Zn concentrations in the River's med-section indicated fast adsorption to bed sediments. Zn concentrations and mass load increased during high-flow events in pastoral catchments of the Waikato River and other regional rivers ($p < 0.001$), suggesting that soluble Zn is being mobilised. Relative to background levels, 86% of sampled Waikato lake sediments have more than twice as much Zn, and up to 73% of sampled sediments have more than twice as much Co and Ca, suggesting

substantial agricultural surface soil inputs and possible mobilization to bed sediments. Presently, sediment Zn concentrations are not high enough to cause toxicity to sediment dwelling organisms and rural lake ecosystems. Overall, results indicate that Zn is accumulating in agricultural soils and some of this is likely to be mobilised in surface runoff leading to likely accumulation of Zn in receiving lake sediments. Potential issues associated with continued Zn accumulation include loss of soil function, trace element imbalances, potential phytotoxicity, and reduction of habitable lakebeds. A number of recommendations are made, including the need for ongoing monitoring and development of suitable New Zealand ecological guideline values for protection of soil receptors and function.

Acknowledgements

I would like to gratefully acknowledge and thank Matthew Taylor of Waikato Regional Council, for supplying the environmental data used in this thesis and for providing ongoing assistance and clarification when required.

Thank you to the chief supervisor of this project, Dr. Nick Kim, who went beyond the call of duty to equip me with the knowledge and skills I needed to complete this thesis. I am grateful for his vast understanding of environmental science, and appreciate his patience and professionalism.

Thank you also to co-supervisor Dr. Stuart McLaren for overseeing the projects progression and ensuring I had access to the required resources. His knowledge of environmental health issues and passion for student advocacy are highly appreciated.

Lastly, but not least, thank you to my husband Joshua Vermeulen, whose love, encouragement and support made completion of this project possible.

Table of Contents

ABSTRACT	I
ACKNOWLEDGEMENTS	III
TABLE OF CONTENTS	IV
LIST OF TABLES	VII
LIST OF FIGURES	X
CHAPTER 1. INTRODUCTION	1
1.1 Environmental Chemistry of Zinc.....	1
1.2 Essentiality of Zinc	3
1.2.1 Zinc as an essential element.....	3
1.2.2 Toxicity of zinc	4
1.2.3 Guideline values for ecological health protection	5
1.3 Sources of Zinc to the Environment.....	9
1.3.1 General outline.....	9
1.3.2 Facial eczema remedies	10
1.3.3 Mobility of zinc	12
1.4 Statement of the Problem	12
1.5 Aims and Structure.....	13
1.6 References	14
CHAPTER 2. METHODS	21
2.1 Background	21
2.2 Data Sources.....	23
2.2.1 Waikato regional soils monitoring.....	23
2.2.2 Waikato regional freshwater monitoring	25
2.2.3 Waikato freshwater lake sediments	27
2.3 Statistical Methods	28
2.3.1 Soils data analysis	28
2.3.2 Preliminary Adsorption Trial.....	29
2.3.3 Freshwater data analysis	30
2.3.4 Sediment data analysis.....	32

2.4	Appendices	33
2.5	References	39
CHAPTER 3. ZINC IN WAIKATO SURFACE SOILS		41
3.1	Summary statistics	41
3.2	Evidence for Zinc Enrichment in Soils	45
3.2.1	Considerations based on XRF zinc and AR/XRF ratios.....	45
3.2.2	Variation in AR zinc with land use.....	47
3.2.3	Comparison to other elements in pastoral soils	51
3.2.4	Zinc concentrations over time.....	53
3.2.5	Zinc concentrations with depth.....	61
3.2.6	Facial eczema remedies and zinc loadings on pastoral soils	65
3.3	Apparent Accumulation – Relationship to Soil Order	68
3.4	Preliminary Adsorption Trial Results	71
3.5	Correlations	74
3.5.1	Natural soils	74
3.5.2	Anthropogenically influenced soils	76
3.5.3	Comparison of background to farmed soils.....	78
3.6	Comparison to Soil Quality Guidelines	78
3.7	Potential Human Health Issues	79
3.8	Comparisons to Other Regions of New Zealand.....	80
3.9	Chapter Summary.....	83
3.10	Appendices	84
3.11	References	95
CHAPTER 4. ZINC IN WAIKATO RIVER SURFACE WATER.....		98
4.1	Summary Statistics.....	98
4.2	Compliance with Water Quality Guidelines	101
4.3	Concentration vs Distance.....	102
4.4	Sources of Additional Zinc	106
4.5	Influence of Rainfall and Flows on Zinc Concentrations	113
4.6	Chapter Summary.....	115
4.7	References	116
CHAPTER 5. ZINC IN REGIONAL WAIKATO SURFACE WATER		119

5.1	Summary Statistics.....	119
5.2	Comparison to ANZECC Guidelines.....	121
5.3	Correlations	123
5.4	Influence of Rainfall and River Flow.....	124
5.5	Chapter Summary.....	125
5.6	References	126
CHAPTER 6. ZINC IN WAIKATO FRESHWATER LAKE SEDIMENTS ...		127
6.1	Raw Data and Summary Statistics	127
6.2	Apparent Enrichments and Possible Sources.....	132
6.2.1	Enrichment estimates	132
6.2.2	Zinc	137
6.2.3	Cobalt.....	138
6.2.4	Other Trace Elements	140
6.3	Comparison to ANZECC Guidelines for Sediment Quality.....	141
6.4	Correlations	144
6.5	Chapter Summary.....	147
6.6	Appendices	149
6.7	References	162
CHAPTER 7. SUMMARY AND CONCLUSIONS		167

List of Tables

Table 1.1 <i>Summary of New Zealand Documents Containing Guideline Values for Zn in Soils</i>	6
Table 2.1 <i>Metadata Relating to Zinc and Other Potentially Relevant Variables in Waikato Soils Examined as Part of this Research</i>	23
Table 2.2 <i>Metadata Relating to Zinc and Other Potentially Relevant Variables in Waikato River Surface Water Examined as Part of this Research</i>	25
Table 2.3 <i>Metadata Relating to Zinc and Other Potentially Relevant Variables in Waikato Freshwaters Examined as Part of this Research</i>	25
Table 2.4 <i>Waikato River Sampling Locations</i>	26
Table 2.5 <i>Metadata Relating to Zinc and Other Potentially Relevant Variables in Waikato Lake Sediments Examined as Part of this Research</i>	27
Table 3.1 <i>Summary Statistics for Zinc and Other Variables in Waikato Surface Soils</i>	42
Table 3.2 <i>Summary Statistics for AR and XRF Zn in Natural, Horticultural, Pastoral, and Farmed soils, using the Subset of Samples for which Both Fractions of Zn were Measured</i>	44
Table 3.3 <i>Differences between Mean and Median XRF Zn in Background Samples in each Farmed Soils Category</i>	46
Table 3.4 <i>Summary Statistics for AR Zn in Waikato Background, Forestry, Natural (B+F), Horticultural, Pastoral and Farmed (P+H) Surface Soil (mg/kg, apart from n)</i>	48
Table 3.5 <i>Summary Statistics for Zinc Concentration Ratios at Sites Sampled More than Once, According to Land Use Category</i>	55
Table 3.6 <i>Newer/Older Date-Pair Ratios for Each Measured Variable on Properties Sampled Twice or More (N=136 for Zn)</i>	56
Table 3.7 <i>Summary of Paired t-test Results (all possible pairs) for Zn at Sites Sampled on Two or More Occasions (mean time between samplings 6-7 years)</i>	60

Table 3.8 <i>Summary Statistics for Waikato Pastoral and Background Surface (0-10 cm) and Deeper (10-20 cm) Soil Samples, Ranked by Surface Enrichment Ratio for Pastoral Soils</i>	62
Table 3.9 <i>Ratios of Cd, Pb, and Zn in Surface (0-10 cm)/deeper (10-20 cm) Soils in Native, Forestry, Background, Horticultural and Pastoral Waikato Land Use Categories</i>	64
Table 3.10 <i>Summary Statistics for AR Zn (mg/kg) for Allophanic, Brown, Gley, Granular, Organic, Podzol, Pumice, Recent and Ultic Surface Soils (0 - 10 cm) of the Waikato Region</i>	69
Table 3.11 <i>Adsorption Trial Results for Zinc in pH 5.7 Buffer in 100 mL Solution</i> ..	72
Table 3.12 <i>Correlation Coefficients and p-values for AR Zinc and Other Variables in Regional Waikato Background and Forestry Soils. Relationships of $p < 0.001$ or better are in Bold Italic*</i>	74
Table 3.13 <i>Soil Order Percentages of Background and Forestry Samples</i>	76
Table 3.14 <i>Correlation Coefficients p-values for AR Zinc and Other Variables in Regional Waikato Horticultural (including Arable) and Pastoral Soils. Relationships of $p < 0.001$ or better are in Bold Italic</i>	76
Table 3.15 <i>Distribution of Individual Zn Concentrations in Waikato Farmed soils</i> .	78
Table 3.16 <i>Estimated Number of Years before Guideline Values are Reached</i>	79
Table 3.17 <i>Summary Statistics for AR Zn (mg/kg) in New Zealand Surface Soils</i>	81
Table 3.18 <i>Average (arithmetic) Zn (mg/kg) in Background, Forestry, Pastoral and Horticultural Soils in the Auckland, Bay of Plenty, Marlborough, Taranaki, Waikato and Wellington Regions of New Zealand</i>	81
Table 4.1 <i>Summary Statistics for Waikato River Surface Water Sampling</i>	99
Table 4.2 <i>Annual Mean Total Zn by Sample Site</i>	102
Table 4.3 <i>Annual Mean Dissolved Zn by Sample Site</i>	103
Table 4.4 <i>Results of Pooled t-tests on Differences in Mean Zn Concentrations Between the Upper, Mid and Lower Reaches of the Waikato River</i>	104

Table 4.5 <i>Correlation Coefficients for Zn and other Variables, Distance, and Dissolved/Total Zn Ratios in Waikato River Surface Water. Relationships of $p < 0.001$ or better are shown in Bold Italic*</i>	107
Table 4.6 <i>Mass Flows and Ratios of Total and Dissolved Zn in the Waikato River</i>	113
Table 4.7 <i>Correlation Matrix for Relationships between Mean Monthly River Flow at Huntly (m^3/s), Dissolved and Total Zn Concentrations, and Mass Loads of Zn.....</i>	114
Table 5.1 <i>Summary Statistics for Zinc and other Variables in Regional Waikato Surface Water.....</i>	120
Table 5.2 <i>Regional Waikato Surface Water Sites that Exceeded the ANZECC Guideline Trigger Value for Zn ($8 \mu g/L$)</i>	122
Table 5.3 <i>Correlation Coefficients and p-values for Zn and other Variables in Regional Waikato Surface Water. For all relationships, $N=1113$ pairs</i>	123
Table 5.4 <i>Correlation Coefficients for River Flow and Sample Variables at Sites where Zn Concentrations Exceeded the ANZECC GV on Two or More Occasions. Relationships of $p < 0.001$ are shown in Bold Italic*</i>	124
Table 6.1 <i>Individual Zn Concentrations (mg/kg dry weight) in Waikato Lake Sediments</i>	128
Table 6.2 <i>Summary Statistics for Zn and other Variables in Waikato Lake Sediment Grab Samples (mg/kg dry weight).....</i>	129
Table 6.3 <i>Average Enrichment Factors for Zn and other Variables in Waikato Lake Sediments. Variables Enriched by a Factor of 2 or more are in Bold Italic*</i>	133
Table 6.4 <i>Summary of Elements with an Enrichment Factor of 2.0 or More in >33% of Waikato Lakes Studied, and initial attribution of possible sources.....</i>	136
Table 6.5 <i>Recommended Sediment Quality Guidelines (ANZECC, 2000, pp. 3.5-4)</i>	141
Table 6.6 <i>Correlations for Zn and other Variables in Waikato Lake Sediments. Relationships of $p < 0.0001$ or greater are in Bold Italic*</i>	145

List of Figures

Figure 3.1 <i>Histogram showing the Distribution of AR Zn Concentrations Measured in the 369 Waikato Region Soil Samples</i>	44
Figure 3.2 <i>Histogram of the Distribution of AR Zn Concentrations in Natural (B + F) Compared to Farmed (H + P) Waikato Surface Soils</i>	50
Figure 3.3 <i>Pastoral/Natural (B+F) AR Trace Element Ratios for Waikato Surface Soils, based on Mean Concentrations in Each Category</i>	52
Figure 3.4 <i>Correlations between Years In-Between Sampling of Waikato Forest Soils and Zn Ratios</i>	58
Figure 3.5 <i>Mean AR Zn Concentrations (mg/kg) in Addition to Background Zn Levels in Pastoral and Horticultural Surface Soils of Different Orders (Kim, 2011).</i>	70
Figure 3.6 <i>Comparison of Zn adsorption to soil in pH 5.70 and pH 4.70 buffer solution over time</i>	73
Figure 3.7 <i>Comparison of Regional Mean AR Zn Concentrations (mg/kg) in Natural and Farmed Soils</i>	82
Figure 4.1 <i>Changes in Annual Mean Dissolved and Total Zn Concentrations with Distance Along the Waikato River</i>	103
Figure 4.2 <i>Changes in annual mean ratios of dissolved/total Zn with distance from Taupo Gates</i>	105
Figure 4.3 <i>Changes in annual mean turbidity in Waikato River water with distance from Taupo Gates</i>	106
Figure 4.4 <i>Relative Changes in Annual Mean Concentrations of As, Li and B in Waikato River Water with Distance from Taupo Gates</i>	109
Figure 4.5 <i>Changes in annual mean concentration of nitrite (NO₃), nitrite-n + nitrate-n (NO₃ + NO₂), nitrate (NO₂), total ammoniacal-n (NH₄) and total kjeldahl-n (TKN) in Waikato River water with distance from Taupo Gates</i>	111
Figure 4.6 <i>Changes in annual mean concentration of total phosphorus (TP) and dissolved reactive phosphorus (DRP) in Waikato River water with distance from Taupo Gates</i>	112

Figure 4.7 <i>Changes in annual mean concentration of non-purgeable organic carbon (NPOC) and dissolved non-purgeable organic carbon (DNPOC) in Waikato River water with distance from Taupo Gates</i>	112
Figure 5.1 <i>Seasonal Fluctuations of Zn in Surface Water at Three Waikato Sites Regularly Exceeding the ANZECC GV for Zn</i>	125
Figure 6.1 <i>Histogram Showing the Distribution of Zn Concentrations Measured in the 68 Freshwater Lake Sediment Samples</i>	131
Figure 6.2 <i>Enrichment Rankings for Zn in Waikato Lake Sediments</i>	137
Figure 6.3 <i>Enrichment Rankings for Co in Waikato Lake Sediments</i>	139
Figure 6.4 <i>Scatterplot showing the Relationship between Zn and Cd Concentrations in Waikato Lake Sediments</i>	146

Chapter 1. Introduction

1.1 Environmental Chemistry of Zinc

Zinc (Zn), atomic number 30, is a transition metal belonging to Group 12 (IIB) of the Periodic Table. Because of its nature as a transition element, Zn possesses chemical properties that are extremely useful and important in biological systems (Brown, Wuehler, & Peerson, 2001). This section will provide a brief overview of some applicable aspects of the chemistry of Zn in soils, freshwaters, and sediments. Sources of Zn to the environment are discussed in Section 1.3 and the essentiality of Zn is discussed in Section 1.2.

The total amount of Zn in soils is distributed over several distinct fractions, which have been defined by Kabata-Pendias (2011) as:

1. the water soluble pool, which is the fraction of Zn present in the soil solution,
2. the exchangeable pool, which are Zn ions bound to soil particles by electrical charges,
3. the adsorbed, chelated or complexed pool, where Zn binds to organic ligands,
4. the pool of clayey secondary minerals and insoluble metal oxides, and
5. the pool of primary minerals.

It is only the amount of Zn that is in the soluble fractions, and those from which ions can be easily desorbed, that are available for uptake by plants and potentially leachable in water infiltrating down through the soil profile (Alloway, 2008; Kiekens, 1995). In soils, Zn occurs in three forms:

1. free ions (Zn^{2+} and ZnOH^+) and organically complexed Zn in solution,
2. adsorbed and exchangeable Zn on surfaces of the colloidal soil fraction, such as clay particles, humic compounds and iron and aluminium hydrated oxides, and
3. secondary minerals and insoluble complexes in the solid phase of the soil.

The distribution of Zn between these forms is governed by precipitation and dissolution, complexation and decomplexation, and adsorption and desorption (Kabata & Pendias, 2001). Factors controlling the interactions of Zn include:

1. the concentration of Zn^{2+} and other ions in the soil solution,
2. the type and amount of adsorption sites in the solid phase of the soil,
3. the concentration of ligands which are able to form complexes with Zn,
4. pH and redox potential of the soil.

Zn^{2+} is the main species of Zn in the soil solution at or below pH 7.7. Above pH 7.7, $ZnOH^+$ predominates and at pH 9.11 or higher, $Zn(OH)_2$ is dominant (Alloway, 2008). It is generally considered that Zn^{2+} is the form of Zn primarily responsible for eliciting a toxic response in aquatic organisms. Typically, inorganic and organic complexes ameliorate the uptake and toxicity of Zn by reducing the concentration of Zn^{2+} (ANZECC, 2000a).

Zn forms soluble complexes with chloride, phosphate, nitrate, and sulphate ions. Of importance are the sulphate ($ZnSO_4^0$) and phosphate ($ZnHPO_4^0$) species, as these complexes may increase Zn solubility of Zn^{2+} in soils and increased availability when acidifying fertilisers (e.g. ammonium sulphate) are used.

Zn concentration in soils is a key source of Zn for aquatic receiving environments (Van Sprang, Verdonck, Van Assche, Regoli, & De Schampelaere, 2009). However, the extent to which the total concentration of Zn in a soil is available for uptake by plants or mobilisation down the soil profile depends on a range of soil parameters, including total Zn content, pH, organic matter content, redox conditions, microbial activity in the rhizosphere, soil moisture content, and concentrations of other trace elements and macronutrients (Alloway, 2008). For example, the availability of Zn decreases with increasing soil pH due to increasing adsorptive capacity, formation of hydrolysed forms of Zn, possible chemisorption on calcium carbonate, and co-precipitation in iron oxides. Higher concentrations of other trace elements relative to Zn, such as Cu (copper), in the soil solution can reduce the

availability of Zn to a plant (and *vice versa*) due to competition for absorption sites into the plant root. This could occur after the application of Cu fertilizer (Alloway, 2008; Kiekens, 1995).

1.2 Essentiality of Zinc

1.2.1 Zinc as an essential element

The essentiality of Zn for organisms was first discovered in 1869, when scientists observed the relationship between Zn presence and successful growth of the fungus *Aspergillus niger*. Then, in 1934, the beneficial role of Zn in the nutrition of the rat was established by comparing rats supplemented with Zn salts to rats supplemented a diet low in Zn (Todd, Elvehjem, & Hart, 1934). It was not until 1961 that the essentiality of Zn in the human diet was established by way of investigating the causes of adolescent dwarfism and hypogonadism in Iran (Prasad, Halsted, & Nadimi, 1961). Soon after, Sommer and Lipman (1926) explored the relationship between higher plants and Zn, determining its necessity for greenhouse-grown sunflower and barley.

Further research has identified the essentiality of Zn in plant carbohydrate metabolism (both in photosynthesis and conversion of sugars to starch), protein metabolism, auxin metabolism, pollen formation, maintenance of the integrity of cell membranes and resistance to several infectious fungal diseases (Alloway, 2008; Kiekens, 1995). In animals, Zn functions both as a component of several metalloenzymes and as an activator of enzymes in protein synthesis, carbohydrate metabolism and nucleic acid metabolism (Kiekens, 1995). In the human body, Zn is involved in essential catalytic, structural, and regulatory processes, specifically: homeostasis, immune responses, oxidative stress, apoptosis (the process of programmed cell death), aging, and age-related diseases (Plum, Rink, & Haase, 2010; Prasad, 1998; Stefanidou, Maravelias, Dona, & Spiliopoulou, 2006).

It is now unequivocally accepted that all living organisms require Zn at small but precise levels in order to successfully grow and reproduce (Alloway, 2008; Frassinetti, Bronzetti, Caltavuturo, Cini, & Croce, 2006; Kiekens, 1995). For this reason, Zn has been termed an ‘essential micronutrient’.

1.2.2 Toxicity of zinc

While essential for life, Zn cannot be synthesised by an organism and must therefore exist within the environment at the required concentrations. The potential for Zn toxicity is increased when environmental Zn levels are greater than those required by an organism. Industrial activities, such as the burning of fossil fuels and smelting of non-ferrous metals, as well as leaching from galvanized materials, dispersion in particles of tyre rubber, and land application of sewage sludge and agrichemicals (e.g. fertilisers, pesticides and animal remedies) largely contribute to high levels of Zn in the environment (Bailey, Clark, Ferris, Krause, & Strong, 2002; Kiekens, 1995).

Zn toxicity in soils has been associated with the prohibition of fundamental soil microbial processes. Tyler, Pålsson, Bengtsson, Bååth, and Tranvik (1989) reported that Zn concentrations at 2-10 times the regional background levels caused the decline of most biological activities in forest litter/soil by 20 - 40%. Specific biological properties inhibited, either fully or partially, by excess Zn in soils include nitrate reductase, potential nitrification β -glucosidase and dehydrogenase (Coppolecchia et al., 2011; Porter & Sheridan, 1981; Vesper & Weidensaul, 1978).

Zn is also toxic to plants in high amounts, with evidence of Zn phytotoxicity occurring most commonly between soil concentrations of 100-500 mg/kg (Kabata-Pendias, 2011). Symptoms such as chlorosis (insufficient chlorophyll production) and depressed plant growth were observed (Chaney, 1993; Kabata-Pendias, 2011). The effect of high Zn in soils was also reported as inducing deficiency in another essential elements, e.g. Co (cobalt) or Cu, and inducing desorption of Cd (cadmium) (Kim, 2011).

Of increasing significance, particularly in New Zealand but in other countries also, is the substantial increase in the use of Zn in agriculture that has occurred from the mid twentieth century – specifically through the use of facial eczema remedies. Anthropogenic sources of Zn to the environment are discussed further in Section 1.3.

1.2.3 Guideline values for ecological health protection

Soil Quality Guidelines

A number of documents provide soil guideline values (SGVs) that are used to interpret state of environment trace element data in New Zealand; most of which are developed primarily for the management of contaminated land (Table 1.1). In New Zealand, five documents provide soils guideline values for Zn on either a national or regional scale (Cavanagh, 2006).

For this study, the most applicable guidelines are those provided by the Guidelines for the Safe Application of Biosolids to Land (herein referred to as the 'Biosolids Guidelines'). These guidelines were developed to provide guidance on the application of biosolids to land, and include soil limits for a range of metal and metalloid contaminants, including Zn (Cavanagh, 2006; NZWWA, 2003). The Biosolids Guidelines represent recommended maximum concentrations of these metals and metalloids for the receiving environment and set a soil limit of 300 mg/kg for Zn. This is a 'lowest observed adverse effect concentration' (LOAEC), which is to provide protection for human health and ecological receptors (NZWWA, 2003). The limit was set at 300 mg/kg because of evidence that such a level is protective against phytotoxicity in soils treated with biosolids and minimise leaching to groundwater (NZWWA, 2003).

Table 1.1 Summary of New Zealand Documents Containing Guideline Values for Zn in Soils

Document	Guideline value (total recoverable Zn, mg/kg)	Guideline rationale	Reference
Biosolids Guidelines	300	Protection of plants (avoid phytotoxicity) and soil microbial health	(NZWWA, 2003)
Landfill Waste Acceptance Criteria	20 - 200	Protection of human health and ecological receptors	(MfE, 2004)
Soil Acceptance Criteria	180 - 200	Protection of ecological receptors	(Cavanagh & O'Halloran, 2006)
Auckland City Council (Residential + Parks and recreational)	7000 - 1400	Protection of human health	(Tonkin and Taylor, 2006)
Waikato residential soil sub-division	300 and 23000	Protection of ecological receptors and human health (suggested default value)	(Kim, 2004)

ANZECC Guidelines

The Australian and New Zealand Guidelines for Fresh and Marine Water Quality, herein referred to as the ‘ANZECC Guidelines’, are an authoritative reference for water quality management in New Zealand, particularly for toxic contaminants. The primary purpose of the ANZECC Guidelines is “...to provide an authoritative guide for setting water quality objectives required to sustain current, or likely future, environmental values [uses] for natural and semi-natural water resources in Australia and New Zealand” (ANZECC, 2000b, p. 6).

The ANZECC Guidelines set out ‘trigger values’ (guidelines) for protecting a range of aquatic ecosystems. Trigger values are bioavailable concentrations of contaminants or stressors that, if exceeded, “...would indicate a potential environmental problem, and so ‘trigger’ a management response, e.g. further investigation and subsequent refinement of the guidelines according to local conditions” (ANZECC, 2000b, pp. 2-15). Usual practice in New Zealand has been to apply 95% protection values representing slightly-to-moderately disturbed aquatic ecosystems as default figures unless there is good reason to apply higher or lower degrees of protection (e.g. in pristine or substantively degraded ecosystems, respectively) (Valler, 2013).

Essentially, 95% protection values are concentrations above which 5% of aquatic organisms in an ecosystem may begin to experience the onset of toxic effects from the contaminant (ANZECC, 2000b). For metals, the dissolved fraction is most directly comparable to the guideline because this is thought to best reflect the bioavailable and potentially toxic component. Comparison of the total metal concentration with the guideline is also accepted practice, but this is done on the basis that it will over-estimate risk (the comparison is said to be ‘conservative’), because the dissolved component will always be equal to or less than the total concentration.

The 95% freshwater trigger value of 8 µg/L applies to the dissolved Zn results obtained in this study. This is regarded as a high reliability trigger value that would apply to slightly-moderately disturbed systems and was determined on the basis of chronic Zn toxicity data covering six taxonomic groups (fish, crustaceans,

echinoderm, mollusks, annelids, and algae (ANZECC, 2000a). Toxicity of Zn decreases with increasing hardness and alkalinity, and the 95% guideline applies to a default hardness of 30 mg/L of CaCO₃.

ANZECC Interim Sediment Quality Guidelines

The rural lake sediment results obtained during the study period were assessed for compliance with the ANZECC Interim Sediment Quality Guidelines (ISQGs). ISQG values are based on the best available overseas data and have been refined using knowledge of existing baseline concentrations, as well as by local effects data as it become available (ANZECC, 2000b). ISQG guideline values are given as low and high ISQG values, corresponding to the effects range-low (ERL) and effects range-medium (ERM) used by Long, MacDonald, Smith, and Calder (1995).

The two trigger values define three concentration ranges for a particular chemical: concentrations below the low trigger value represent a ‘minimal-effects’ range, where effects would rarely be observed. Concentrations equal to or above the low trigger value, but below the high trigger value, are deemed the ‘possible effects’ range, within which effects would occasionally occur. Lastly, concentrations equal to or above the high trigger value represent a ‘probable effects’ range, where effects would frequently occur (ANZECC, 2000b; Long et al., 1995). For Zn, the ISQG-Low trigger value is 200-mg/kg dry weight and the ISQG-High trigger value is 410 mg/kg dry weight.

It is important to note that the Guidelines provide indicative, rather than absolute, evidence for adverse effects (Stephenson, Milne, & Sorensen, 2008). Principally, the guidelines aim to: “...identify sediments where contaminant concentrations are likely to result in adverse effects on sediment ecological health; facilitate decisions about the potential remobilisation of contaminants into the water column and/or into aquatic food chains; and identify and enable protection of uncontaminated sediments” (ANZECC, 2000b, pp. 3.5-1).

Initial screening typically compares the trigger value to the total concentration of the contaminant and any exceedance of the trigger value then triggers management/remedial action or further investigation to consider the readily

bioavailable and mobile fractions of the contaminant. In the case of metals, the dilute-acid-soluble metal concentration is likely to be a more meaningful measure than the total value (ANZECC, 2000b). Further investigations are required (such as ecological evaluations, toxicity testing, source identification, prediction of future sediment quality, and an evaluation of management options) to determine with greater certainty whether or not effects are actually occurring at the affected site(s) (ANZECC, 2000b; Stephenson et al., 2008). Concentrations above this point indicate a progressively increasing risk of ecotoxic effects on aquatic organisms as a result of both exposure to high Zn in the water column and the accumulation of toxic levels of Zn in lake bed sediments (Kim, 2011).

1.3 Sources of Zinc to the Environment

1.3.1 General outline

Zn is a natural component of the Earth's crust and is one of the most common elements found naturally. It exists ubiquitously in the environment as well as in all plants, animals and humans (Alloway, 2008).

The average Zn content of the earth's crust is estimated as being between 70-80 mg/kg (Alloway, 2008; Kabata-Pendias, 2011; Kiekens, 1995). In magmatic rock, Zn concentrations appear to be evenly distributed (Kabata-Pendias, 2011; Kiekens, 1995); while concentrations in sedimentary rocks typically range from 10 to 30 mg/kg in sandstones, limestones and dolomites, or to higher concentrations of 80 to 120 mg/kg in shales and clayey sediments (Kiekens, 1995).

Total Zn concentrations in soils are largely derived from the geochemical weathering of the parent rock material from which the soil was made (Alloway, 2008). General values for the average Zn content of soils of different groups, worldwide, range between 60 and 89 mg/kg (Kabata-Pendias, 2011).

In many cases, anthropogenic sources of Zn influence the total concentration beyond natural amounts. Atmospheric deposits of pollution via industrial emissions (e.g. smelting) and urban air pollution (e.g. car exhaust fumes) contribute to the atmospheric deposition of Zn to soils. Two other dominant sources of Zn

contamination in the urban environment include runoff from galvanised iron surfaces, and particles of car tyre rubber (which contains ~1% Zn) (Davis, Shokouhian, & Ni, 2001; Kim, 2011).

Pastoral soils are known to contain enriched amounts of certain trace elements due to the application and use of agrichemicals, e.g. lime and superphosphate fertilisers, facial eczema remedies and pesticides (Alloway, 2008; Kabata-Pendias, 2011; Taylor, Kim, & Hill, 2011). For horticultural soils, the most likely source of Zn includes common dithiocarbamate fungicide sprays containing Zn in chelated form (e.g. Ziram) (Kim, 2008). Although these will break down, they will leave behind Zn as an inorganic payload. A plausible explanation for pastoral soils, and one that is becoming more widely accepted, is that the increasing use of facial eczema remedies over the last decade and a half is substantially increasing Zn enrichment in farmed soils. (Land Monitoring Forum, 2009; Taylor et al., 2011; Taylor, Kim, Hill, Stevenson, & Gilkes, 2010).

1.3.2 Facial eczema remedies

Zn dosing of animals is used to prevent development of the mycotoxic ruminant disease pithomycotoxicosis (commonly termed Facial Eczema). Facial Eczema is “...a hepatogenous photosensitisation of ruminants caused by sporidesmin produced by the saprophytic fungus, *Pithomyces chartarum*, which grows on pasture litter” (Smith & Towers, 2002, p. 28). Facial Eczema is characterised by photosensitivity of areas of the animal’s skin that is exposed to sunlight and by the animal experiencing severe sunburn. The disease was first discovered in New Zealand and is seasonally common here and in other temperate climate zones of the world (Alloway, 2008).

In New Zealand, the disease typically occurs throughout late summer and early autumn, during periods of warm, humid weather and light rain (Smith & Towers, 2002). Under these conditions, pastures become heavily contaminated with *P. chartarum*. As the fungus spores, it produces the hepatotoxin sporidesmin which, when ingested, causes liver injury and inflammation and blockage of the bile duct (Di Menna, Smith, & Miles, 2009). As a result, the photosensitising pigment phylloerythrin (a breakdown product of chlorophyll), which is normally secreted, is

retained in the circulating blood. Retention of this causes lesions to occur on unpigmented skin when the animal is exposed to sunlight (Bennison, Nottingham, Key, & Parkins, 2010; Di Menna et al., 2009; Munday et al., 1997). By and large, the mechanisms by which Zn prevents the disease from occurring is still largely unknown, however it is believed that Zn forms a stable mercaptide with sporidesmin, thereby removing the toxin from the autoxidation cycle, that leads to the cascade generation of reactive oxygen radicals responsible for causing cell damage (Waring, Egan, Braithwaite, Mullbacher, & Sjaarda, 1990).

Facial Eczema causes significant farming production losses due to a reduction of milk production, loss of body weight and animal death (Smith & Towers, 2002). Dosing of ruminants with high levels of Zn (up to 50mg/kg) is an effective prophylactic treatment for facial eczema (Bennison et al., 2010; Munday et al., 1997; Munday et al., 2001; Smith, Embling, Towers, Wright, & Payne, 1977; Towers & Smith, 1978). Zinc oxide is either sprayed directly onto pasture herbage or administered directly to the animal (and subsequently excreted onto pastures). The most effective method for reducing the occurrence of facial eczema in farmed animals is by using a controlled slow-release intraruminal bolus (Towers, 1999). Boluses contain up to 80% Zn (depending on the animal type and weight). Once administered, Zn is released into the rumen for up to 4 weeks continuously.

Remedial Zn use for facial eczema has increased markedly in New Zealand over the last decade and a half. In a scoping report to Waikato Regional Council, Sowry (2011) estimated that at least 60 percent of farmers in the Waikato region of New Zealand alone use Zn based facial eczema remedies in a given year. When spore counts are particularly high, this figure could be as high as 100 percent (Sowry, 2011). N. Kim (personal communication, August 17, 2004) and Sowry (2011) estimated that up to 8500 tons/yr of facial eczema Zn is applied over dairy, beef and sheep pastures in the Waikato region. Such amounts are likely to have contributed to the observed increase in average acid recoverable Zn in Waikato pastoral soils (Taylor et al., 2011; Taylor et al., 2010).

1.3.3 Mobility of zinc

Currently, most of the concern about excessive Zn in soils relates to its possible uptake by crops and consequent adverse effects on crops themselves and on animal and human diets as a result (Alloway, 1995). However, there is mounting awareness of the potential fate pathways of Zn in soils and the impacts of high Zn concentrations on receiving environments, such as surface waters and bed sediments.

Due to the chemical nature of Zn and its mobility in the environment, Zn contamination of soils has a direct impact on water quality (Taylor et al., 2011). As Zn concentrations in soil increase, so does the potential for Zn enrichment of waterbodies and accumulation in bed sediments (Land Monitoring Forum, 2009). Lakes and streams are susceptible to Zn toxicity, particularly those receiving storm water, domestic and industrial wastewater and agricultural runoff (Fergusson, 1990).

Of particular concern in New Zealand are the receiving freshwater environments in the Waikato region, such as the Waikato River and a number of rural lakes, due to the intensification of agricultural practices in the catchment area (Chapman, 1996). Pastoral farming (predominantly sheep and cattle rearing) accounts for 58% of land use in the Waikato region (Chapman, 1996; Waikato Regional Council, 2014). Freshwater sediments are the ultimate receiving environments, and it is likely that Zn moving from land to freshwater environments will accumulate in the bed sediments.

1.4 Statement of the Problem

It is now evident that, for the last ~3 decades, Waikato pastoral soils have been receiving high mass loadings of Zn as facial eczema treatments, in the order of 5-7 kg/ha/yr (Sowry, 2011). The advent of this source of Zn dwarfs other sources. This activity has the potential to cause:

1. accumulation of Zn in receiving soils,
2. contamination of surface waters through mobilization of the mobile fraction of Zn, and

3. an increase of Zn in freshwater receiving environments, including potential accumulation in bed sediments.

If occurring, these outcomes have the potential cause a range of adverse effects that may include toxicity to ecological receptors (Section 1.2.2).

1.5 Aims and Structure

The primary aim of this research was to examine applicable datasets to determine the extent and nature of any evidence that facial eczema Zn is causing significant contamination of agricultural soils and associated ecosystems in the Waikato Region of New Zealand. Specific aims were to:

1. examine evidence for and magnitude of Zn enrichment and accumulation in Waikato farmed soils and associated factors. This is the subject of Chapter 3. This included the statistical analysis of soil data in relation to land use, Zn concentration over time and with soil depth and soil order, and correlations with other elements;
2. examine evidence relating to possible entry of anthropogenic Zn into Waikato freshwaters and lake sediments. This component involved detailed investigation of analytical and other data relating to the Waikato River (Chapter 4), regional rivers (Chapter 5) and freshwater lake sediments (Chapter 6); and
3. review potential environmental and human health implications that may be linked to the findings.

1.6 References

- Alloway, B. (1995). *Heavy metals in soils*: Springer Science & Business Media.
- Alloway, B. (2008). *Zinc in soils and crop nutrition*. France: International Zinc Association & International Fertilizer Industry Association.
- ANZECC. (2000a). National water quality management strategy paper 4. *Australian and New Zealand guidelines for fresh and marine water quality. Volume 2: Aquatic ecosystems - rationale and background information*. Canberra, Australia: ANZECC with ARMCANZ.
- ANZECC. (2000b). National water quality management strategy paper 4. *Australian and New Zealand guidelines for fresh and marine water quality*. Canberra, Australia: ANZECC with ARMCANZ.
- Bailey, R, Clark, H, Ferris, J, Krause, S, & Strong, R. (2002). *Chemistry of the environment* (2nd ed.). New York: Academic Press.
- Bennison, J., Nottingham, R., Key, E., & Parkins, J. (2010). The effect of zinc oxide and elemental zinc boluses on the concentrations of Zn in serum and faeces, and on providing protection from natural *Pithomyces chartarum* challenge in sheep. *New Zealand Veterinary Journal*, 58(4), 201-206.
- Brown, K., Wuehler, S., & Peerson, J. (2001). The importance of zinc in human nutrition and estimation of the global prevalence of zinc deficiency. *Food & Nutrition Bulletin*, 22(2), 113-125.
- Cavanagh, J. (2006). *Comparison of soil guideline values used in New Zealand and their derivations. Landcare Research contract report: LC0607/025*. Lincoln, New Zealand: Prepared for Environment Canterbury.
- Cavanagh, J., & O'Halloran, K. (2006). *Development of soil guideline values protective of ecological receptors in the Auckland region. Landcare Research contract report: LC00605/065*. Lincoln, New Zealand: Prepared for Auckland Regional Council.

- Chaney, R. (1993). Zinc phytotoxicity. In A. Robson (Ed.), *Zinc in soils and plants* (Vol. 55, pp. 135-150): Springer Netherlands.
- Chapman, M. (1996). Human impacts on the Waikato River system, New Zealand. *GeoJournal*, 40(1-2), 85-99.
- Coppolecchia, D., Puglisi, E., Vasileiadis, S., Suciu, N., Hamon, R., Maria Beone, G., & Trevisan, M. (2011). Relative sensitivity of different soil biological properties to zinc. *Soil Biology and Biochemistry*, 43(9), 1798-1807.
- Davis, A., Shokouhian, M., & Ni, S. (2001). Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere*, 44(5), 997-1009.
- Di Menna, M., Smith, B., & Miles, C. (2009). A history of facial eczema (pithomycotoxicosis) research. *New Zealand Journal of Agricultural Research*, 52(4), 345-376.
- Fergusson, J. (1990). *The heavy elements: chemistry, environmental impact, and health effects*. Oxford, New York: Pergamon Press.
- Frassinetti, S., Bronzetti, G., Caltavuturo, L., Cini, M., & Croce, C. (2006). The role of zinc in life: a review. *Journal of environmental pathology, toxicology and oncology : official organ of the International Society for Environmental Toxicology and Cancer*, 25(3), 597-610.
- Kabata-Pendias, A. (2011). *Trace elements in soils and plants* (4th ed.). Boca Raton: CRC Press.
- Kabata, A., & Pendias, H. (2001). *Trace elements in soils and plants*. New York: CRC Press.
- Kiekens, L. (1995). Zinc. In B. Alloway (Ed.), *Heavy Metals in Soils*. London: Blackie Academic and Professional.
- Kim, N. (2004). *Suggested guidelines for residential soil sub-division in the Waikato region*. Hamilton, New Zealand: Environment Waikato.

- Kim, N. (2008). *Cadmium accumulation in Waikato soils*. Environment Waikato Regional Council.
- Kim, N. (2011). [Agricultural zinc – issue characterisation and management options notes].
- Land Monitoring Forum. (2009). *Land and soil monitoring: A guide for SoE and regional council reporting*. New Zealand: Land Monitoring Forum.
- Long, E., MacDonald, D., Smith, S., & Calder, F. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental management*, 19(1), 81-97.
- MfE. (2004). *Hazardous waste guidelines: Landfill waste acceptance criteria and landfill classification*. Wellington, New Zealand: Ministry for the Environment.
- Munday, R., Thompson, A., Fowke, E., Wesselink, C., Smith, B., Towers, N., . . . Ford, A. (1997). A zinc-containing intraruminal device for facial eczema control in lambs. *New Zealand Veterinary Journal*, 45(3), 93-98.
- Munday, R., Thompson, A., Smith, B., Towers, N., O'Donnell, K., McDonald, R., & Stirnemann, M. (2001). A zinc-containing intraruminal device for prevention of the sporidesmin-induced cholangiopathy of facial eczema in calves. *New Zealand Veterinary Journal*, 49(1), 29-33.
- NZWWA. (2003). *Guidelines for the safe application of biosolids to land in New Zealand*. Wellington, New Zealand: New Zealand Water and Wastes Association.
- Plum, L., Rink, L., & Haase, H. (2010). The essential toxin: impact of zinc on human health. *International journal of environmental research and public health*, 7(4), 1342-1365.
- Porter, J., & Sheridan, R. (1981). Inhibition of nitrogen fixation in alfalfa by arsenate, heavy metals, fluoride, and simulated acid rain. *Plant physiology*, 68(1), 143-148.

- Prasad, A. (1998). Zinc in human health: An update. *The Journal of Trace Elements in Experimental Medicine*, 11(2-3), 63-87.
- Prasad, A., Halsted, J., & Nadimi, M. (1961). Syndrome of iron deficiency anemia, hepatosplenomegaly, hypogonadism, dwarfism and geophagia. *The American Journal of Medicine*, 31(4), 532-546.
- Smith, B., Embling, P., Towers, N., Wright, D., & Payne, E. (1977). The protective effect of zinc sulphate in experimental sporidesmin poisoning of sheep. *New Zealand Veterinary Journal*, 25(5), 124-127.
- Smith, B., & Towers, N. (2002). Mycotoxicoses of grazing animals in New Zealand. *New Zealand Veterinary Journal*, 50(sup3), 28-34.
- Sommer, A., & Lipman, C. (1926). Evidence on the indispensable nature of zinc and boron for higher green plants. *Plant physiology*, 1(3), 231.
- Sowry, G. (2011). *Scoping report - volumes and quality of facial eczema zinc. Prepared for Environment Waikato*. Hamilton, New Zealand: Contaminated Site Investigations.
- Stefanidou, M., Maravelias, C., Dona, A., & Spiliopoulou, C. (2006). Zinc: a multipurpose trace element. *Archives of Toxicology*, 80(1), 1-9.
- Stephenson, G., Milne, J., & Sorensen, P. (2008). *Wellington harbour marine sediment quality investigation*: Greater Wellington Regional Council.
- Taylor, M., Kim, N., & Hill, R. (2011). *A trace element analysis of soil quality samples from the Waikato region*. Paper presented at the 24th Annual FLRC Workshop: Adding to the knowledge base for the nutrient manager.
- Taylor, M., Kim, N., Hill, R., Stevenson, B., & Gilkes, R. (2010). *Comparison of soil quality targets and background concentrations in soil of the Waikato Region, New Zealand*. Paper presented at the Proceedings of the 19th World Congress of Soil Science: Soil solutions for a changing world, Brisbane, Australia, 1-6 August 2010. Symposium 1.5. 1 Quantitative monitoring of soil change.

- Todd, W., Elvehjem, C., & Hart, E. (1934). Zinc in the nutrition of the rat. *American Journal of Physiology*, 107, 146-156.
- Tonkin and Taylor. (2006). *Ferndale kindergarten, 830 New North Road, Mt Albert Site Validation Report. Report for Auckland City Council Environmental and Utility Management*. Auckland, New Zealand: Tonkin and Taylor.
- Towers, N. (1999). Facial eczema: zinc treatment for dairy cattle. Hamilton, New Zealand: Agresearch.
- Towers, N., & Smith, B. (1978). The protective effect of zinc sulphate in experimental sporidesmin intoxication of lactating dairy cows. *New Zealand veterinary journal*, 26(8), 199-202.
- Tyler, G., Pålsson, A., Bengtsson, G., Bååth, E., & Tranvik, L. (1989). Heavy-metal ecology of terrestrial plants, microorganisms and invertebrates. *Water, Air, and Soil Pollution*, 47(3-4), 189-215.
- Valler, T. (2013). *Sources and effects of catchment derived bioavailable contaminants in Hamilton urban streams*. Masters thesis. The University of Waikato. Hamilton, New Zealand. Retrieved from <http://researchcommons.waikato.ac.nz/bitstream/handle/10289/7942/thesis.pdf?sequence=3>
- Van Sprang, P., Verdonck, F., Van Assche, F., Regoli, L., & De Schamphelaere, K. (2009). Environmental risk assessment of zinc in European freshwaters: a critical appraisal. *Science of the total environment*, 407(20), 5373-5391.
- Vesper, S., & Weidensaul, T. (1978). Effects of cadmium, nickel, copper, and zinc on nitrogen fixation by soybeans. *Water, Air, and Soil Pollution*, 9(4), 413-422.
- Waikato Regional Council. (2014). Land use in the Waikato. Retrieved 5 November, 2014, from <http://www.waikatoregion.govt.nz/Environment/Natural-resources/Land-and-soil/Land-use-in-the-Waikato/>

Waring, P, Egan, M, Braithwaite, A, Mullbacher, A, & Sjaarda, A. (1990). Apoptosis induced in macrophages and T blasts by the mycotoxin sporidesmin and protection by Zn ²⁺ salts. *International journal of immunopharmacology*, 12(4), 445-457.

Chapter 2. Methods

2.1 Background

As outlined in Chapter 1, a core aim of this thesis was to examine available existing data to determine whether evidence exists that anthropogenic Zn is accumulating in agricultural soils where facial eczema remedies are being used and if migration of this Zn to wider environmental compartments is occurring. The primary scope of this assessment was intended to be large-scale, rather than field or laboratory scale.

The Waikato region was selected as the most suitable study area for this assessment for five reasons:

1. Facial eczema remedies are in widespread use in the Waikato region (Sowry, 2011). The Waikato region is a long-standing farming region (Kim, 2008) with an estimated 1,430,000 hectares (57%) of pastoral land (including sheep, dairy and beef) and a further 26,843 hectares (1.6%) used as horticultural land (including arable cropping) (Kim, 2008). A full breakdown of land uses in the Waikato region by area is provided in Appendix 2.1. Use of Zn for treatment and then prevention of facial eczema was invented, trialed and developed in the Waikato region (Di Menna, Smith, & Miles, 2009).
2. Of all regions in New Zealand, the Waikato region is thought to have the most extensive set of systematic monitoring data available describing concentrations of Zn in agricultural soils, freshwaters, and lake sediments (N. Kim, personal communication, February 2, 2015). Although there have been many individual soil and water surveys carried out by researchers in New Zealand Universities and Crown Research Institutes over the years, very few of these have been designed with representative wide-scale environmental state monitoring in mind. By contrast, since the advent of the Resource Management Act 1991, regional councils in New Zealand have instituted a range of systematic overlapping environmental monitoring programmes, of which the Waikato Regional Council's monitoring is considered the most extensive. Measurements for Zn in Waikato soils have been carried out as part of an on-

going Regional Soil Quality Monitoring Programme (Taylor, 2013) that covers a representative range of land uses and soil types, as well as in samples collected at two depths along sub-regional transects (Taylor & Kim, 2010). Measurements for dissolved and total Zn in water have been carried out monthly for 12 months in samples collected from the Waikato River and over 100 other Waikato streams and rivers as part of a parallel Regional Water Quality Monitoring Programme (Vant, 2013), with sampling for sites that showed elevated Zn continuing for a second year. Sampling and measurement of Zn and other trace elements in Waikato lake sediments have also been carried in two years (2004 and 2009), at a subset of the lakes that form part of ongoing monitoring programmes relating to ecological and chemical lake health and stability.

3. Most sites and samples described in (2) have been both well characterised and analysed for a range of other variables, providing suitable context for Zn measurements and a better ability to interpret likely meaning of results. For example, ‘soil order’ and ‘land use’ are recorded characteristics of each soil monitoring site, and all soil samples have been analysed for a range of over 30 trace elements, some of which may correlate with Zn.
4. All samples described in (2) had been analysed at an IANZ accredited laboratory (Hill Laboratories Hamilton) or other suitable research facility following appropriate quality assurance and quality control (QA/QC) procedures. The level of rigor applied by commercial laboratories who maintain IANZ accreditation was seen as providing assurance that the majority of data being assessed in this work was likely to be accurate and precise. As part of this work, further screening tests were run on each data-set to identify and eliminate potential outliers (Section 2.3), but being able to start with IANZ accredited analytical results was seen as an ideal way to minimise one of the common uncertainties in interpretation that could otherwise arise.
5. The fifth important consideration was that the Waikato Regional Council were willing to provide the available data for use in this project, for which the author is grateful. Most data was provided in the form of large multi-page Microsoft Excel spreadsheets.

A more detailed description of each data source is provided in Section 2.2, and processing and statistical handling is covered in Section 2.3.

During the course of this research, a small amount of additional laboratory work was undertaken at Massey University’s Wellington campus after an Atomic Absorption instrument was purchased and became available to use. This work involved examining the extent of Zn adsorption on soils at two pH values, and the methodology followed is outlined in Section 2.3.2.

2.2 Data Sources

2.2.1 Waikato regional soils monitoring

Metadata summarizing the information available for Zn and potentially relevant variables in Waikato soils that was assessed as part of this work is provided in Table 2.1.

Table 2.1 Metadata Relating to Zinc and Other Potentially Relevant Variables in Waikato Soils Examined as Part of this Research

Data Aspect	Quantity
Sampling timeframe	1995 - 2012 (17 years)
Number of unique sampling events ¹	342
Number of site characteristics recorded (excluding location, address and sampling date)	22
Number of variables measured in each sample	Up to 9-10 major soil variables, up to 34 trace elements (ICP-MS), up to 51 major and trace elements (XRF) (depending on sample)
Approx. total data points	~20,000

The majority of samples were collected as part of a the Waikato Regional Soils Monitoring Programme, targeted to capture a representative range of land uses and soil types, by methods described in Hill and Sparling (2009) and Kim and Taylor

¹ Includes return visits to a given property

(2009). Sample locations are given in Taylor (2013) and are reproduced in Appendix 2.2. All analyses were carried out at IANZ-accredited laboratories (Landcare Research, Hill Laboratories, both of Hamilton, and Plant & Food Research, Lincoln).

In total, 369 soil samples from the Waikato region were tested for Zn by acid recoverable (AR) extraction and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Of these, 133 samples were also tested for Zn by X-ray fluorescence (XRF). Samples were tested for a range of other parameters in addition to Zn.

136 properties were sampled on either two or three occasions with a mean time between sampling events of 7 years. Each standard sample was a composite of 40 cores and taken at depths of 0-10cm. At another 105 sites, samples from two depths (0-10 cm and 10-20 cm) were collected at ~2 km intervals as part of three large-scale transect studies.

Land uses were classified as either dairy (pasture grazed with milking cows), drystock (pasture grazed with all other animals), arable (annually cultivated plants), horticultural (long-term growth of plants), forestry (production tree growth) and background (native) (Taylor, Kim, & Hill, 2011). Additional categories 'natural' soils and 'farmed' soils were added. In terms of their Zn content, forestry soils were statistically indistinguishable from the background soils subset, thus, it made sense to merge the two data subsets to provide the greatest number of samples that represent 'clean' soils. More discussion on this is given in Section 3.2.2.

Soils were classified according to the New Zealand Soil Classification System (Hewitt, 1998) and the FAO (1998). Soil order classifications used (and equivalent in World Reference Base) were Allophanic soils (Andosols), Brown soils (Cambisols), Gley soils (Gleysols), Granular soils (Ferralsols), Podzols (Podzols), Pumice soils (Andosols), Recent soils (Fluvisols & Arenosols), Ultic soils (Acrisols) and Organic soils (Histosols).

Each site was assigned a unique three digit identifier to which sample results and accompanying metadata was assigned to, such as catchment details, spatial

information, data quality information, soil and land use information and data acquisition history.

Soil results from other regions were supplied to Waikato Regional Council and have been used, with permission, in this thesis. Statistical methods used for these datasets were the same as were used for the Waikato region soils dataset.

2.2.2 Waikato regional freshwater monitoring

Metadata summarizing the data available for Zn and potentially relevant variables in surface water of the Waikato River is summarised in Table 2.2, and for regional Waikato freshwaters, Table 2.3.

Table 2.2 Metadata Relating to Zinc and Other Potentially Relevant Variables in Waikato River Surface Water Examined as Part of this Research

Data Aspect	Quantity
Sampling timeframe	August 2009 – July 2010 (12 months)
Number of unique sampling events	118
Number of site characteristics recorded (excluding location, address and sampling date)	2 (distance from Taupo Gates and flow (m ³ /s))
Number of variables measured in each sample	27 (including total and dissolved Zn, 8 major bulk parameters, 9 nutrient elements, 4 geothermal indicator elements, 4 microbial indicators)
Approx. total data points	~3,248

Table 2.3 Metadata Relating to Zinc and Other Potentially Relevant Variables in Waikato Freshwaters Examined as Part of this Research

Data Aspect	Quantity
Sampling timeframe	August 2009 – June 2011 (22 months, not all sites sampled in 2011)
Number of unique sampling events	1,367 (including repeat samples)
Number of site characteristics recorded (excluding location, address and sampling date)	5
Number of variables measured in each sample	14
Approx. total data points	~22,937

In total, 118 Waikato River surface water samples were collected monthly between August 2009 and July 2010 from 10 sites along the River. Site information is provided in Table 2.4 and shown in Appendix 2.3. Collection was done according to methods set out in Tulagi (2014).

Regional Waikato surface water samples were collected from 100 sites between August 2009 and July 2010 as part of the Regional River Monitoring Programme (RERIMP). Monthly sampling continued for 15 regional sites for an additional 12 months. Sample locations for each are given in Vant (2013) and reproduced in Appendices 2.3 and 2.4. Samples were analysed at an IANZ accredited laboratory, using standard analytical methods, for dissolved and total Zn concentrations as well as a range of other parameters

Hydrological flow data were provided by Mighty River Power (Hydro Lakes, Wai-O-Tapu stream and Waikato River at Reid’s Farm), Contact Energy (Ohaaki Bridge) and Genesis Power (Huntly) through agents Opus and NIWA (Tulagi, 2014).

Table 2.4 Waikato River Sampling Locations

Location Number	Distance² (km)	Location Name	Map Ref
1131.127	0.1	Taupo Gates	U18:772-757
1131.105	36.5	Ohaaki Bridge	U17:981-914
1131.107	75.8	Ohakuri Tailrace Bridge	U17:796-061
1131.147	105	Whakamaru Tailrace	T17:552-056
1131.143	126.1	Waipapa Tailrace	T16:448-200
1131.328	202.2	Hamilton – Narrows	S14:168-710
1131.69	225.6	Horotiu Bridge	S14:048-871
1131.77	246.5	Huntly – Tainui Bridge	S13:003-018
1131.91	286.3	Mercer Bridge	S12:919-336
1131.133	296.8	Tuakau Bridge	R12:828-320

² Approximate distance (in kilometres) from Lake Taupo’s outlet

2.2.3 Waikato freshwater lake sediments

Metadata summarizing the information available for Zn and potentially relevant variables in Waikato lake sediments assessed as part of this work is provided in Table 2.5.

Table 2.5 Metadata Relating to Zinc and Other Potentially Relevant Variables in Waikato Lake Sediments Examined as Part of this Research

Data Aspect	Quantity
Sampling timeframe	One off study in 2011, with additional samples for some lakes, taken in 2004 and 2005, included in the overall dataset
Number of unique sampling events	68
Number of site characteristics recorded (excluding location, address and sampling date)	0
Number of variables measured in each sample	36
Approx. total data points	2,357

Sediment samples were taken from 22 Waikato regional lakes (21 rural and one urban), as part of a one-off lake sediments survey. In total, 68 sediment samples were tested for total recoverable Zn (USEPA 200.2 strong acid digestion), with exception of fluorine, which is total based on alkali fusion. All analyses were conducted at an IANZ accredited laboratory.

Bed sediment samples were collected using an Ekman grab sampler. For most (17) of these, three grab samples were collected from each lakebed: one in the deepest part (the basin) and two at different locations midway between the basin and shore.

Waikato lakes included in the sediment study include: Rotokotuku, Maratoto, Waikare, Whangapae, Harihari, Penewaka, Waahi, Omatearoa, Ohinewai, Taharoa, Mangahia, Hakanoa, Puketi, Areare, Serpentine East, Ngaroto, Serpentine North, Rotomanuka, Mangakaware, Serpentine South, Parkinson, and Te Koutu.

2.3 Statistical Methods

All data analysis was completed using Data Desk version 6.3 for students, including summary statistics, correlations, and t-testing. Graphs were produced using Microsoft Excel 2011.

2.3.1 Soils data analysis

Prior to data analysis, all soil data was compiled, tidied, and simplified by removing non-applicable metadata. Each step of data analysis was completed a new Excel workbook, to ensure no data was lost or overwritten in the analysis process. For the purpose of data analysis, non-detect results (i.e. results with ‘less than’ values) were assumed to be equal to half the corresponding limit of detection, e.g. < 2 mg/kg became 1 mg/kg for AR Zn (Zn by *aqua regia* digestion and ICP-MS has a detection limit of 2 mg/kg).

Eight soil data outliers were identified and removed prior to data analysis:

1. four background sites had one result each that showed evidence of fertiliser contamination,
2. two pastoral soil results were from ironpan soils that contained very high iron (20-30%) and so did not fit within the conventional pastoral soils dataset,
3. one forestry soil contained unusually high Zn, lead (Pb), and tin (Sn), which suggested presence of a paint flake in the subsample, and
4. one pastoral soil result was omitted due to the historic land application of slag (a metal by-product of smelting).

Summary statistics were first calculating using the entire surface soils dataset (including the top 0-10 cm of transect soils) to provide a direct comparison across all variables. More focused analysis involved calculating summary statistics for all variables according to land use type, then by using Zn data only (including the subset of data tested for both AR and XRF Zn). These statistics provided an overall picture of the distribution of Zn across land use types to determine if a change in Zn

concentrations had occurred. Correlation data and tests of significance were used to further analyse changes with land use.

To assess changes in concentration over time and with depth (using the subset of data for sites that have been sampled on two or more occasions) two approaches were used: The first of these involved calculating the ratio of later/earlier results for each sample site, then establishing whether the average ratio for the whole set was significantly greater or less than one. The second parallel approach was to carry out a series of paired Student's t-tests based on sample occasions.

Four outliers were removed from the main dataset prior to derivation of results; sites 9 (2004), 10 (2004), and site 15 (2002) were excluded because they represented samples that appeared to be influenced by fertiliser (confirmed by the presence of increased phosphorus (P) and Cd). Site 13 (1997) represented an unusually high Zn result that had only occurred once in the sample run from 1997 and was therefore excluded.

For the ratios method, evidence for Zn accumulation or loss over time was established when the mean was significantly greater or less than 1.0. Evidence for this was not established if the mean was indistinguishable from 1.0 (i.e. if the confidence interval included 1.0). Student's paired t-tests were conducted to support the ratios method, using the data subset for soils sampled on more than once occasion.

2.3.2 Preliminary Adsorption Trial

A preliminary Zn adsorption time experiment was conducted to determine the time required for adsorption equilibrium to be achieved for Zn in a soil solution. A Flame Atomic Absorption Spectrophotometer (AAS) was used to analyse the Zn/soil solutions. Two trials were run, the first was using a pH 5.70 buffer and 100 mL Zn solution and the second trial was using a pH 4.70 in a 50 mL Zn solution.

The soil used for the experiments was 'Patumahoe Clay Loam', of the granular soil order. The soil was prepared by lightly crushing and sieving through a 600 μm

copper sieve. 0.5 g of the processed soil was then accurately weighed into 20 pre-acid washed conical flasks (10 pairs). Pairs of flasks were labelled with the pre-determined time intervals of 5 min, 20 min, 1 hour, 3 hours, 6 hours, 16 hours, 24 hours, 48 hours, 72 hours, and 115 hours.

35 mL of a 4 mg/L working AR Zn $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Zn sulphate heptahydrate) solution with 0.02 M pH 5.70 or pH 4.70 buffer was then added to each flask and the timer set for the corresponding times specified on each pair of flasks.

After each time period was up, the contents of each flask were filtered through Whatman 54 filter papers into 100 mL volumetric flasks and made up to the mark with distilled water and set aside at room temperature.

Analysis of the filtered Zn solutions was done by AAS using matrix matched standard calibration solutions. Once the calibration of the AAS had been completed, the analysis sequence for all Zn solutions was initiated.

2.3.3 Freshwater data analysis

For analysis of Waikato River results, five total Zn outliers and three dissolved Zn outliers identified and removed prior to calculating the summary statistics. These included:

1. Taupo gates: a total Zn result of 0.046 ppm. This result did not fit with the dissolved Zn results from the same sample in terms of ratio expected (d/t is less than 0.1) and it also did not fit with the next downstream site where total Zn was suddenly 5 times lower;
2. Ohaaki Bridge: both total and dissolved Zn results for this sample occasion were rejected on the basis that the dissolved Zn result was 11 times higher than the corresponding total Zn result;
3. Ohakuri Tailrace Bridge: both total and dissolved Zn results for this sample occasion were rejected because they were not in keeping with downstream

results and well outside expected variation due to analytical error, (to keep this would mean there was a lot of extra Zn that suddenly went missing);

4. Mercer Bridge: both total and dissolved Zn results for this sample occasion were rejected because they were not in keeping with upstream results and did not fit with the result for the following date; and
5. Mercer Bridge: a total Zn outlier was removed as it is likely that the sample had slightly more suspended sediment in it than usual (because of the way that dissolved Zn also increased from $<1 \mu\text{g/L}$ to $> 7 \mu\text{g/L}$ to $> 2.2 \mu\text{g/L}$).

The Zn data included 12 (10.6%) non-detections which were set to the detection limit of $1 \mu\text{g/L}$ when estimating summary statistics. Summary statistics were using the entire Waikato River surface water dataset, and then calculated by site. These statistics, in combination with correlations and significance tests, were used to analyse the differences in Zn concentrations with distance and flow.

In estimating mass flows of Zn being carried by the Waikato River, a decision was made to focus on the first site downstream of the hydrodams (Hamilton-Narrows) and the first site after the confluence of the Waipa River (Huntly). This was because flow data relating to hydrodams is difficult to interpret due to varying flows being released from the dam tailraces on each day. Additionally, on the majority of sampling dates, Zn concentrations at the Hamilton-Narrows site were at or below the analytical detection limit (0.001 mg/L or $1 \mu\text{g/L}$). Results for Huntly showed Zn detections and thus more of the data could be used. Flows from the Waipa River were calculated using the difference in measured flow before convergence with the Waikato River, and again after convergence.

For regional surface water data analysis, the statistics were based on detected Zn concentrations of $>1\mu\text{g/L}$. This is because, when analysing Zn data, consideration of the usual ratio of dissolved to total Zn (in cases where both were detected) suggested that that, in most cases, a non-detected value of $<0.001 \text{ mg/L}$ would lie closer to 0.001 mg/L than 0.0005 mg/L . Data analysis was conducted in much the same way as for the Waikato River dataset.

Flow data specific to the regional surface water monitoring sites included in the study has been integrated with site data to explore the influences of rainfall and flows on the mass of Zn being carried in surface waters at each sample location. The relationship between flow and Zn concentrations was examined using a subset of ongoing surface water quality monitoring and flow data for regional rivers (referred to in Section 2.2.2).

2.3.4 Sediment data analysis

To determine if enrichment in sediments was occurring, lake sediment data needed to be compared to naturally occurring levels of Zn and other elements. As no background lakes are available in the Waikato region that could be considered to be unaffected by anthropogenic influence, enrichment estimates were made by comparing trace element concentrations in the lake sediments with mean concentrations across background and forest soil sites.

Although this is not ideal, it was reasoned that natural soil parent materials would also contribute to the inorganic background in lake sediments and provide reliable order-of-magnitudes for the natural concentration of each element in crustal material. Before estimating enrichments, results for multiple samples from each lake were averaged. Enrichments relative to background and forest soils are provided with sediment summary statistics.

2.4 Appendices

Appendix 2.1 *Land Use in the Waikato Region by Area*

Land type	Hectares	Percent of Waikato
Tussock and danthonia used for grazing	23471	1.4
Pasture: sheep	333442	13.3
Pasture: dairy	623013	24.9
Pasture: beef	471345	18.9
Arable crop land, fodder crop land and fallow land	16698	1.0
Land in horticulture	10145	0.6
Planted production forest	329781	19.1
Mature native bush	52024	3.0
Native scrub and regenerated native bush	80266	4.6
Other land	62245	3.6

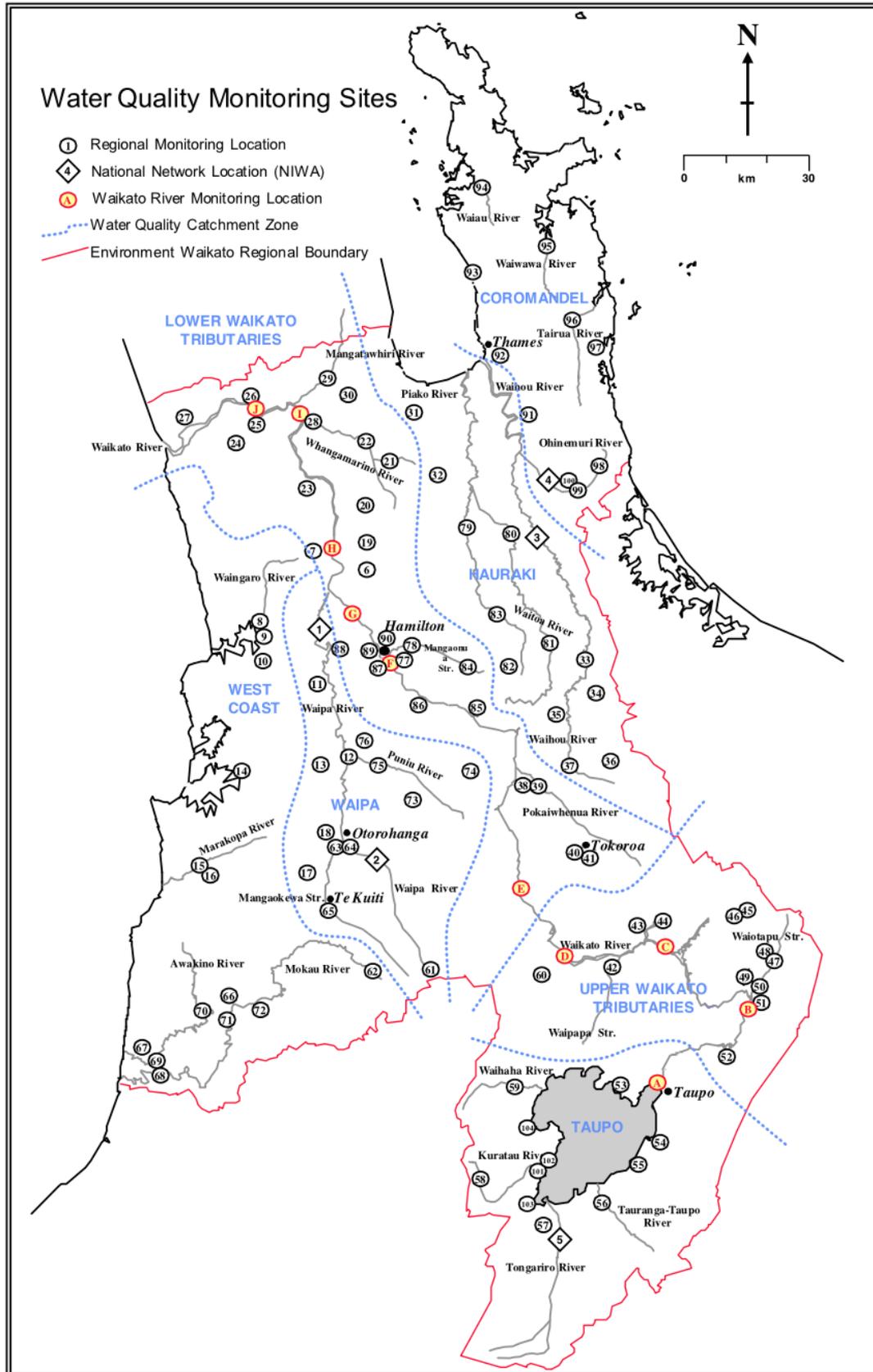
Note: Table from Kim (2008), used with permission.

Appendix 2.2 Map of Waikato Regional Soil Quality Monitoring Sites (excluding transect sites)



Note: Image from Taylor (2013), used with permission.

Appendix 2.3 Map of Waikato River and Regional Waikato Surface Water Sample Locations



Note: Image from Vant (2013), used with permission.

Appendix 2.4 Table of Regional Waikato Surface Water Quality Monitoring Sites

Map No.	Location	Location Id
<i>Coromandel</i>		
91	Hikutaia River @ Old Maratoto Rd	169.2
92	Kauaeranga River @ Smiths Cableway/Recorder	234.11
99	Ohinemuri River @ Queens Head	619.19
98	Ohinemuri River @ SH25 Bridge	619.2
96	Tairua River @ Morrisons Bridge Hikuia	940.1
93	Tapu River @ Tapu-Coroglen Rd	954.5
94	Waiau River @ E309 Rd Ford	1105.3
100	Waitekauri River @ U/S Ohinemuri Confluence	1239.32
95	Waiwawa River @ SH25 Coroglen	1257.3
97	Wharekawa River @ SH25	1312.3
<i>Map No.</i>	<i>Location</i>	<i>Location Id</i>
<i>Hauraki</i>		
32	Mangawhero Stm (Kaihere) @ Mangawara Rd	489.2
35	Oraka Stm @ Lake Rd	669.6
83	Piako River @ Kiwitahi	749.1
79	Piako River @ Paeroa-Tahuna Rd Bridge	749.15
82	Piakonui Stm @ Piakonui Rd	753.4
33	Waihou River @ Okauia	1122.18
37	Waihou River @ Whites Rd	1122.41
36	Waiohotu Stm @ Waiohotu Rd (Off SH5)	1173.2
34	Waiomou Stm @ Matamata-Tauranga Rd	1174.4
31	Waitakaruru River (Hauraki Plains) @ Coxhead Rd Bridge	1230.1
81	Waitoa River @ Landsdowne Rd Bridge	1249.15
80	Waitoa River @ Mellon Rd Recorder	1249.18
<i>Map No.</i>	<i>Location</i>	<i>Location Id</i>
<i>Tributaries to the lower Waikato River</i>		
27	Awaroa River (Waiuku) @ Otaua Rd Bridge opp Moseley Rd	41.9
7	Awaroa Stm (Rotowaro) @ Sansons Bridge–Rotowaro–Huntly	39.11
85	Karapiro Stm @ Hickey Rd Bridge	230.5
90	Kirikiroa Stm @ Tauhara Drive	253.4
6	Komakorau Stm @ Henry Rd	258.4
38	Little Waipa Stm @ Arapuni – Putaruru Rd	335.1
87	Mangakotukutuku Stm (Rukuhia) @ Peacock Rd	398.1
40	Mangamingi Stm (Tokoroa) @ Paraonui Rd Bridge	407.1
77	Mangaone Stm @ Annebrooke Rd Bridge	417.7
78	Mangaonua Stm @ Hoeka Rd	421.1
84	Mangaonua Stm @ Te Miro Rd	421.16
30	Mangatangi River @ SH2 Maramarua	453.6
29	Mangatawhiri River @ Lyons Rd at Buckingham Bridge	459.6
19	Mangawara Stm @ Rutherford Rd Bridge	481.7
86	Mangawhero Stm (Cambridge) @ Cambridge-Ohaupo Rd	488.1
20	Matahuru Stm @ Waiterimu Rd Br	516.5

Appendix 2.4 Continued

Map No	Location	Location Id
	<i>Tributaries to the lower Waikato River</i>	
25	Ohaeroa Stm @ SH22 Bridge	612.9
24	Opuatia Stm @ Ponganui Rd	665.5
39	Pokaiwhenua Stm @ Arapuni-Putaruru Rd	786.2
21	Waerenga Stm @ Taniwha Rd	1098.1
89	Waitawhiriwhiri Stm @ Edgecumbe Street	1236.2
26	Whakapipi Stm @ SH22 Bridge	1282.8
41	Whakauru Stm @ U/S SH1 Bridge	1287.7
28	Whangamarino River @ Island Block Rd	1293.7
22	Whangamarino River @ Jefferies Rd Bridge	1293.9
23	Whangape Stm @ Rangiriri-Glen Murray Rd	1302.1
<i>Map No.</i>	<i>Location</i>	<i>Location Id</i>
	<i>Waipa River and Tributaries</i>	
11	Kaniwhaniwha Stm @ Wright Rd	222.16
74	Mangaohoi Stm @ South Branch Maru Rd	411.9
65	Mangaokewa Stm @ Te Kuiti Borough Water Supply Intake	414.12
76	Mangapiko Stm (Pirongia/Te Awamutu) @ Bowman Rd	438.3
63	Mangapu River @ Otorohanga	443.3
73	Mangatutu Stm (Waikeria) @ Walker Rd Bridge	476.7
13	Mangauika Stm @ Te Awamutu Borough Water Supply Intake	477.1
88	Ohote Stm @ Whatawhata/Horotiu Rd	624.5
75	Puniu River @ Bartons Corner Rd Bridge	818.2
61	Waipa River @ Mangaokewa Rd	1191.5
12	Waipa River @ Pirongia-Ngutunui Rd Bridge	1191.1
64	Waipa River @ SH3 Otorohanga	1191.12
18	Waitomo Stm @ SH31 Otorohanga	1253.5
17	Waitomo Stm @ Tumutumu Rd	1253.7
<i>Map No.</i>	<i>Location</i>	<i>Location Id</i>
	<i>Tributaries to the upper Waikato River</i>	
48	Kawaunui Stm @ SH5 Bridge	240.5
43	Mangaharakeke Stm (Atiamuri) @ SH30 (Off Jct SH1)	359.1
49	Mangakara Stm (Reporoa) @ SH5	380.2
60	Mangakino River (Whakamaru) @ Sandel Rd	388.1
46	Otamakokore Stm @ Hossack Rd	683.4
52	Pueto Stm @ Broadlands Rd Bridge	802.1
44	Tahunaatara Stm @ Ohakuri Rd	934.1
51	Torepatutahi Stm @ Vaile Rd Bridge	1057.6
47	Wai-O-Tapu Stm @ Campbell Rd Bridge	1186.2
50	Wai-O-Tapu Stm @ Homestead Rd Bridge	1186.4
42	Waipapa Stm (Mokai) @ Tirohanga Rd Bridge	1202.7
45	Whirinaki Stm @ Corbett Rd	1323.1

Appendix 2.4 Continued

<i>Map No.</i>	<i>Location</i>	<i>Location Id</i>
	<i>West Coast</i>	
70	Awakino River @ Gribbon Rd	33.6
69	Awakino River @ SH3 Awakau Rd Junction	33.9
67	Manganui River @ Off Manganui Rd	410.4
66	Mangaotaki River @ SH3 Bridge	428.3
15	Marokopa River @ Speedies Rd (Off Te Anga Rd)	513.3
68	Mokau River @ Awakau Rd	556.2
62	Mokau River @ Mangaokewa Rd (Off SH30)	556.5
71	Mokau River @ Totoro Rd Recorder	556.9
72	Mokauiti Stm @ Three Way Point – Aria	557.5
9	Ohautira River @ Waingaro - Te Uku Rd	616.1
14	Oparau River @ Langdon Rd (Off Okupata Rd)	658.1
16	Tawarau River @ Off Speedies Rd	976.1
8	Waingaro River (Pukemiro) @ Ruakiwi Rd Off SH22	1167.4
10	Waitetuna River @ Te Uku-Waingaro Rd	1247.2
<i>Map No.</i>	<i>Location</i>	<i>Location Id</i>
	<i>Inflows to Lake Taupo</i>	
55	Hinemaiaia River @ SH1	171.5
101	Kuratau River @ Te Rae Street	282.5
58	Kuratau River @ SH41 Moerangi	282.4
53	Mapara Stm @ Off Mapara Rd (Whakaipo Reserve)	504.2
56	Tauranga-Taupo River @ Te Kono Slackline	971.4
105	Tokaanu Power Station Tailrace Canal @ SH41 Bridge	1491.1
57	Tokaanu Stm @ Off SH41 Turangi	1045.3
59	Waihaha River @ SH32	1106.4
54	Waitahanui River @ Blake Rd	1226.1
104	Whanganui Stream @ Lakeside Lake Taupo	1301.1
102	Whareroa Stream @ Lakeside Lake Taupo	1318.4
103	Whangamata Stm (Kinloch) @ Whangamata Rd	1300.1

2.5 References

- Di Menna, M., Smith, B., & Miles, C. (2009). A history of facial eczema (pithomycotoxicosis) research. *New Zealand Journal of Agricultural Research*, 52(4), 345-376.
- FAO, ISSS. (1998). World reference base for soil resources. *World soil resources reports*, 84, 21-22.
- Hewitt, A. (1998). *New Zealand soil classification* (2nd ed.). Lincoln, New Zealand: Manaaki Whenua Press.
- Hill, R., & Sparling, G. (2009). Soil quality monitoring. *Land and soil monitoring: A guide for SoE and regional council reporting*. Hamilton, New Zealand: Land Monitoring Forum.
- Kim, N. (2008). *Cadmium accumulation in Waikato soils*. Environment Waikato Regional Council.
- Kim, N., & Taylor, M. (2009). Trace element monitoring. *Land and soil monitoring: A guide for SoE and regional council reporting*. (pp. 117-166). Hamilton, New Zealand: Land Monitoring Forum.
- Sowry, G. (2011). *Scoping report - volumes and quality of facial eczema zinc. Prepared for Environment Waikato*. Hamilton, New Zealand: Contaminated Site Investigations.
- Taylor, M. (2013). *Soil quality monitoring in the Waikato region 2011* (Technical report 2013/49). Hamilton, New Zealand: Waikato Regional Council.
- Taylor, M., & Kim, N. (2010). Dealumination as a mechanism for increased acid recoverable aluminium in Waikato mineral soils. *Soil Research*, 47(8), 828-838.

Taylor, M., Kim, N., & Hill, R. (2011). *A trace element analysis of soil quality samples from the Waikato region*. Paper presented at the 24th Annual FLRC Workshop: Adding to the knowledge base for the nutrient manager.

Tulagi, A. (2014). *Waikato River water quality monitoring programme: Data report 2013* (Technical report 2014/31). Waikato, New Zealand: Waikato Regional Council.

Vant, B. (2013). *Trends in river water quality in the Waikato region, 1993-2012* (Technical report 2013/20). Hamilton, New Zealand: Waikato Regional Council.

Chapter 3. Zinc in Waikato surface soils

In total, 369 surface soil samples from the Waikato region were tested for Zn by AR extraction and ICP-MS. Of these, 133 samples were also tested for Zn by XRF. Samples were also tested for a range of other variables. For soil sampling methodology, please refer to Section 2.2.1.

Results are discussed in this chapter in the order of summary statistics (Section 3.1), evidence for Zn enrichment in soils (Section 3.2), Zn accumulation and relation to soil order (Section 3.3) the influence of pH on adsorption in laboratory trials (Section 3.4), correlations in natural soils and anthropogenically influenced soils (Section 3.5), comparisons to soil quality guidelines (Section 3.6), potential human health issues (Section 3.7) and comparisons to other regions of New Zealand (Section 3.8).

3.1 Summary statistics

Summary statistics for AR Zn and other variables in Waikato surface soils are presented in Table 3.1. Summary statistics comparing AR and XRF Zn results are given in Table 3.2. All results for Zn and other variables tested by XRF are provided in Appendix 3.1.

Table 3.1 Summary Statistics for Zinc and Other Variables in Waikato Surface Soils

Variable	n	Mean	Mdn	SD	Min	Max	5th %tile	95th %tile
pH	367	5.77	5.73	0.536	3.50	7.20	4.90	6.67
TOC	320	25.0	8.97	28.1	0.50	158	3.68	77.7
TN	302	2.04	0.780	2.19	0.020	9.34	0.300	6.35
Ag	342	0.153	0.110	0.147	0.020	1.10	0.036	0.378
Al	346	31985	29250	19496	750	104000	6200	69200
As	350	8.33	5.70	24.6	0.44	440	1.55	18.0
B	296	4.61	4.00	3.91	2.00	60.0	2.00	9.00
Ba	346	127	97.0	95.0	11.6	520	26.8	351
Bi	338	0.220	0.210	0.143	0.030	2.05	0.086	0.406
Ca	346	4211	3545	3235	114	25650	882	9220
Cd	369	0.533	0.470	0.380	0.012	2.30	0.065	1.20
Co	346	5.10	4.10	4.66	0.160	42.0	0.892	12.7
Cr	351	13.2	9.10	21.0	1.50	220	2.42	29.5
Cs	346	2.35	1.95	1.78	0.093	12.1	0.504	5.62
Cu	351	20.9	16.5	17.3	0.400	216	5.60	45.0
F	249	417	418	158	16.0	900	144	661
Fe	346	20508	17000	15468	550	110000	4016	52840
Hg	365	0.148	0.120	0.148	0.021	1.65	0.036	0.325
K	345	730	630	427	141	4200	271	1600
La	346	20.3	10.7	25.6	0.370	150	2.42	83.5
Li	342	8.58	7.60	5.81	0.480	33.0	0.910	19.4
Mg	346	993	730	834	97.0	6400	306	2600
Mn	346	1004	550	1170	9.30	7590	80.8	3700
Mo	346	0.859	0.710	0.561	0.090	3.00	0.259	2.02
Na	343	170	160	73.4	43.0	619	84.7	290
Ni	349	5.80	4.55	5.97	0.530	76.0	1.15	12.1

Table 3.1 continues on pg.43

Table 3.1 Continued

Variable	<i>n</i>	Mean	Mdn	SD	Min	Max	5th %tile	95th %tile
OP	303	44.7	34.9	41.8	0.500	307	3.00	121
P	363	1530	1340	1011	57.0	10000	290	3139
Pb	369	23.9	13.9	42.7	1.58	650	3.69	81.0
Rb	346	9.40	7.96	6.23	0.850	41.0	2.04	21.6
Sb	321	0.201	0.100	0.618	0.040	10.2	0.047	0.545
Se	91	3.03	3.00	0.788	2.00	6.00	2.00	4.48
Sn	346	1.67	1.40	1.42	0.110	20.0	0.399	3.62
Sr	346	23.6	19.0	16.9	2.10	148	8.42	52.5
Tl	340	0.267	0.188	0.220	0.020	1.25	0.051	0.717
U	364	1.56	1.44	0.846	0.052	4.20	0.414	3.05
V	300	50.6	37.5	39.9	10.0	300	14.5	130
Zn	369	60.0	53.0	35.4	3.60	220	17.0	130

Note: Trace element concentrations (all mg/kg dry weight) are acid recoverable with exception of F, which is total F by alkaline fusion. Total organic carbon (TOC) and total nitrogen (TN) are in %.

Abbreviations: TOC, Total Organic Carbon; TN, Total Nitrogen; Ag, Silver; Al, aluminium; As, arsenic; B, boron; Ba, barium; Bi, bismuth; Ca, calcium; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; F, fluorine; Fe, iron; Hg, mercury; K, potassium; La, lanthanum; Li, lithium; Mg, magnesium; Mn, manganese; Mo, molybdenum; Na, sodium; Ni, nickel; OP, Olsen phosphorus; P, phosphorus (acid recoverable); Pb, lead, Rb, rubidium; Sb, antimony; Se, selenium; Sn, tin; Sr, strontium; Tl, thallium; U, uranium; V, vanadium; Zn, Zn.

On average, Waikato surface soils contained 60.0 mg/kg as AR Zn. Individual soil Zn results ranged from 3.60 mg/kg to 220 mg/kg AR, with most results between 20 mg/kg and 80 mg/kg (Figure 3.1).

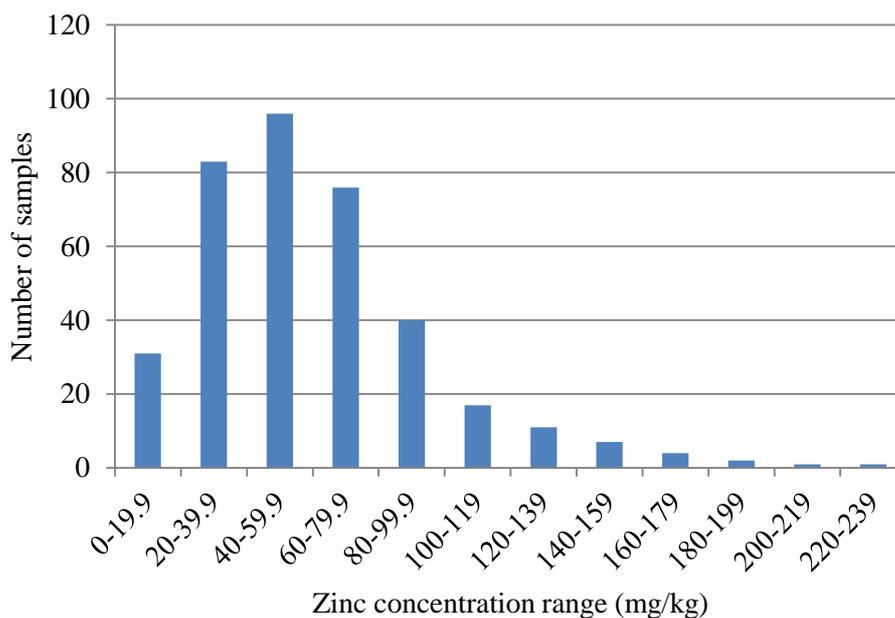


Figure 3.1 Histogram showing the Distribution of AR Zn Concentrations Measured in the 369 Waikato Region Soil Samples

Table 3.2 Summary Statistics for AR and XRF Zn in Natural, Horticultural, Pastoral, and Farmed soils, using the Subset of Samples for which Both Fractions of Zn were Measured

Land use	Fraction	n	Zn concentrations (mg/kg)				
			Mean	SD	Mdn	Min	Max
Natural (B + F) soils	Acid recoverable (AR)	20	32.7	16.5	32.6	12.7	65.0
	XRF (total)	20	69.9	22.0	72.2	16.2	100
	Ratio AR/XRF	20	0.47	0.16	0.47	0.22	0.80
Horticultural soils	Acid recoverable (AR)	26	75.1	33.4	71.8	19.3	190
	XRF (total)	26	124	41.1	122	56.6	245
	Ratio AR/XRF	26	0.59	0.09	0.58	0.34	0.77
Pastoral soils	Acid recoverable (AR)	86	62.9	31.0	59.0	18.1	170
	XRF (total)	86	100	37.6	90.2	34.4	208
	Ratio AR/XRF	86	0.61	0.11	0.62	0.27	0.82
Farmed (H + P) soils	Acid recoverable (AR)	112	65.7	31.9	61.0	18.1	190
	XRF (total)	112	106	39.6	101	34.4	245
	Ratio AR/XRF	112	0.60	0.10	0.61	0.27	0.82

AR and total (XRF) Zn concentrations in Waikato soils (Table 3.2, Appendix 3.1) are generally in keeping with soil Zn data provided in the literature. A survey by Longhurst, Roberts, and Waller (2004) reported median AR Zn in New Zealand pastoral soils as between 42 mg/kg - 91 mg/kg.

Worldwide background total concentrations have been reported on by many and summarized by Alloway (2008a) as being between 50-64 mg/kg. By comparison, for sites that could be reliably classified as representing background in this work (including forestry sites not significantly influenced by anthropogenic enrichment), total (XRF) Zn averaged 70 mg/kg (Table 3.2).

Overall means across the mix of Waikato land uses reported on in this work were 60 mg/kg as AR Zn ($n=369$) but 101 mg/kg as XRF Zn by ($n=133$) (Table 3.2, Appendix 3.1). Variation across land use is discussed further in Section 3.2.2.

On average and as a median, just under half (47%) of the Zn was acid recoverable across the 20 'deemed background' sites, where the same samples were tested for both Zn fractions (Table 3.2). Within these 20 samples, the acid-recoverable portion varied quite widely from a minimum of 22% to a maximum of 80%.

3.2 Evidence for Zinc Enrichment in Soils

3.2.1 Considerations based on XRF zinc and AR/XRF ratios

For the subset of samples that were tested for Zn by XRF (Table 3.2), a preliminary assessment of evidence for Zn enrichment in farmed soils can be made by comparing these with XRF Zn concentrations in background soils. Table 3.3 shows the differences between mean and median total (XRF) Zn in background samples and each farmed soils category.

Table 3.3 Differences between Mean and Median XRF Zn in Background Samples in each Farmed Soils Category

Datasets	Average	Median
Horticultural XRF minus background XRF	+54.6	+50.2
Pastoral XRF minus background XRF	+30.5	+18.0
Farmed XRF minus background XRF	+36.1	+29.0

Substantially more Zn is apparent in soils under both horticulture (+50 to 55 mg/kg) and pasture (+18 to 31 mg/kg) (Table 3.3). On average, horticultural soils had 54.6 mg/kg more Zn than background soils. This amount was slightly less on average for pastoral soils (30.5 mg/kg). Over all farmed soils, the apparent increase in Zn is 29 mg/kg based on medians or 36 mg/kg based on means.

A limitation of this approach is that the background and farmed soils are necessarily from different locations, so that some of the variability may be due to differences in soil types between background and forest sites and (for example) horticultural soils. This limitation also applies to comparison of AR Zn results across land uses (Section 3.2.2), but may be more significant for XRF results due to lower sample numbers tested by this method (see Table 3.2).

Much of the anthropogenic Zn introduced to a farming system is expected to be acid recoverable. For example, facial eczema Zn is introduced as soluble Zn salts and Zn adsorbed to soils in this form can be quantitatively recovered with a strong acid digestion. This may apply less to some forms of anthropogenic Zn, for example Zn in mineral components of fertilisers, but overall and expected pattern with anthropogenic enrichment would be an increase in the relative proportion of available (and acid recoverable) Zn over time.

For this reason, if the apparent increases shown in Table 3.3 do represent anthropogenic Zn enrichment, it would also be expected that the ratio of AR Zn to XRF Zn should be higher in farmed soils than in background soils. This does appear to be the case. Table 3.2 shows that the mean percentage of AR to XRF Zn increases by 13% in moving between these categories, from 47% in background soils to 60% in farmed soils.

3.2.2 Variation in AR zinc with land use

Summary statistics for AR Zn in Waikato soils, categorized by land use, are given in Table 3.4. Mean values for all constituents, categorised according to land use, are given in Appendix 3.2. The distribution of AR Zn concentrations in background and farmed soils are provided in Figure 3.2.

Table 3.4 Summary Statistics for AR Zn in Waikato Background, Forestry, Natural (B+F), Horticultural, Pastoral and Farmed (P+H) Surface Soil (mg/kg, apart from n)

Land use Category	n	Arithmetic Mean	95% CI	Geo Mean	Mdn	SD	Min	Max	5th %tile	95th %tile
All	369	60.0	[56.4 - 63.7]	50.2	53.0	35.4	3.60	220	17.0	130
Background	24	32.1	[24.9 - 39.3]	27.2	34.0	17.1	4.00	77.0	9.53	68.6
Forestry	29	28.0	[21.5 - 34.5]	23.1	22.0	17.1	3.60	77.0	6.93	56.5
Natural (B+F)	53	29.9	[25.2 - 34.6]	24.9	28.5	17.1	3.60	77.0	7.46	63.6
Horticultural	47	73.3	[63.4 - 83.3]	64.4	69.0	33.9	5.15	190	19.5	132
Pastoral	202	57.6	[53.2 - 62.1]	50.1	50.8	32.1	13.0	211	20.8	124
Farmed (H+P)	249	60.6	[56.5 - 64.7]	52.5	55.6	32.9	5.15	211	20.5	128
Urban	67	81.9	[72.5 - 91.3]	74.1	78.0	38.4	26.0	220	32.7	164

As discussed previously in Section 2.2.1, the indigenous background ($n=24$) and forestry ($n=29$) land use categories are indistinguishable from each other in their trace element content, and this result also applies to overlapping confidence intervals for Zn (Table 3.4). Therefore, these two land use categories were grouped together, to increase sample numbers ($n=53$) and provide a better estimate of likely background Zn in Waikato soils.

The average AR Zn concentration of natural soils (including background and forestry soils) was 9.9 mg/kg (arithmetic mean), with a confidence interval of 25.2 mg/kg - 34.6 mg/kg. Individual results ranged from 3.60 mg/kg – 77.0 mg/kg, however the majority of those (77%) were below 40 mg/kg (Table 3.4).

Similar mean background Zn concentrations for Waikato soils have been reported by the Land Monitoring Forum (2009) of 27.6 mg/kg Zn and by Alloway (2008a) as 35.0 mg/kg. However, a concordance of these results is not unexpected because both of the previous estimates are based on earlier results received from the same regional Soil Quality Monitoring Programme, and so represent two subsets of the dataset now under consideration in this work. The earliest estimate of 35 mg/kg is likely to have been based on comparatively fewer background sample sites (N. Kim, personal communication, January 20, 2015).

For the other three land uses, average Zn concentrations follow the order urban soils (81.9 mg/kg) > horticultural soils (73.3 mg/kg) > pastoral soils (57.6 mg/kg) (Table 3.4). Confidence intervals for urban and horticultural soils substantially overlap, whereas those between horticultural and pastoral soils do not. These results indicate that at a 95% confidence level, mean Zn in horticultural soils is indistinguishable from mean Zn in urban soils, and that both of these show higher mean Zn than pastoral soils. Despite the distinction between pastoral ($n=202$) and horticultural ($n=47$) soils, the two groups can be merged to provide an overall land use-weighted estimate for average Zn across the ‘farmed’ soils of 60.6 mg/kg (Table 3.4).

All four categories (urban, pastoral, horticultural, and farmed) show significantly more Zn than natural, background or forestry soils (Table 3.4). Results from this study therefore show that on average, farmed soils contain two times more Zn than in natural soils in the Waikato region ($p < 0.0001$). This distinction also shows up in 95th percentiles (Table 3.4) which follow the order:

urban (164 mg/kg) > horticultural (132 mg/kg) ~ all farmed (128 mg/kg) ~
pastoral (124 mg/kg) >> natural (63.6 mg/kg)

The ratio of farmed to background averages hides an important aspect of the Zn distribution in farmed soils. This is that soil Zn concentrations of some farms may be up to six times higher than typical background values (Figure 3.2). Potential sources of Zn to the environment are outlined in Section 1.3.

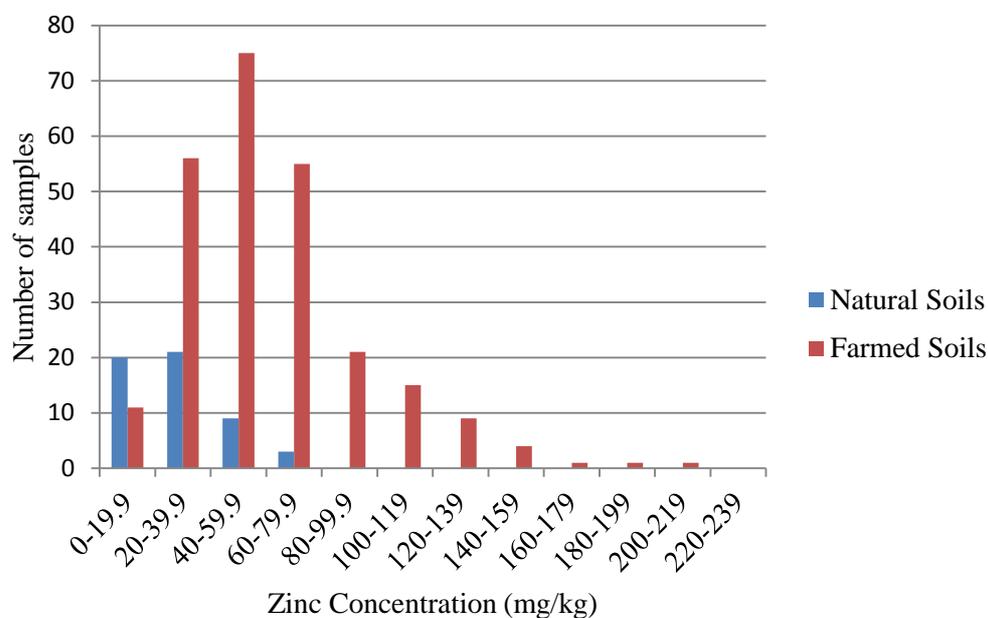


Figure 3.2 Histogram of the Distribution of AR Zn Concentrations in Natural (B + F) Compared to Farmed (H + P) Waikato Surface Soils

3.2.3 Comparison to other elements in pastoral soils

To provide context, results for Zn in pastoral soils were compared with those of all other trace elements and major soil variables that were measured in the same soil samples. Means and medians were calculated for all other variables and each land use category. Results of the comparison of means in pastoral versus background soils are shown in Figure 3.3.

Figure 3.3 is a graph of mean relative enrichments (pastoral/background), ordered from most enriched to least enriched, for all variables measured. For values <1.0 , there is no indication of enrichment in farmed soils. Potential enrichment is also uncertain with values between 1.0-1.5.

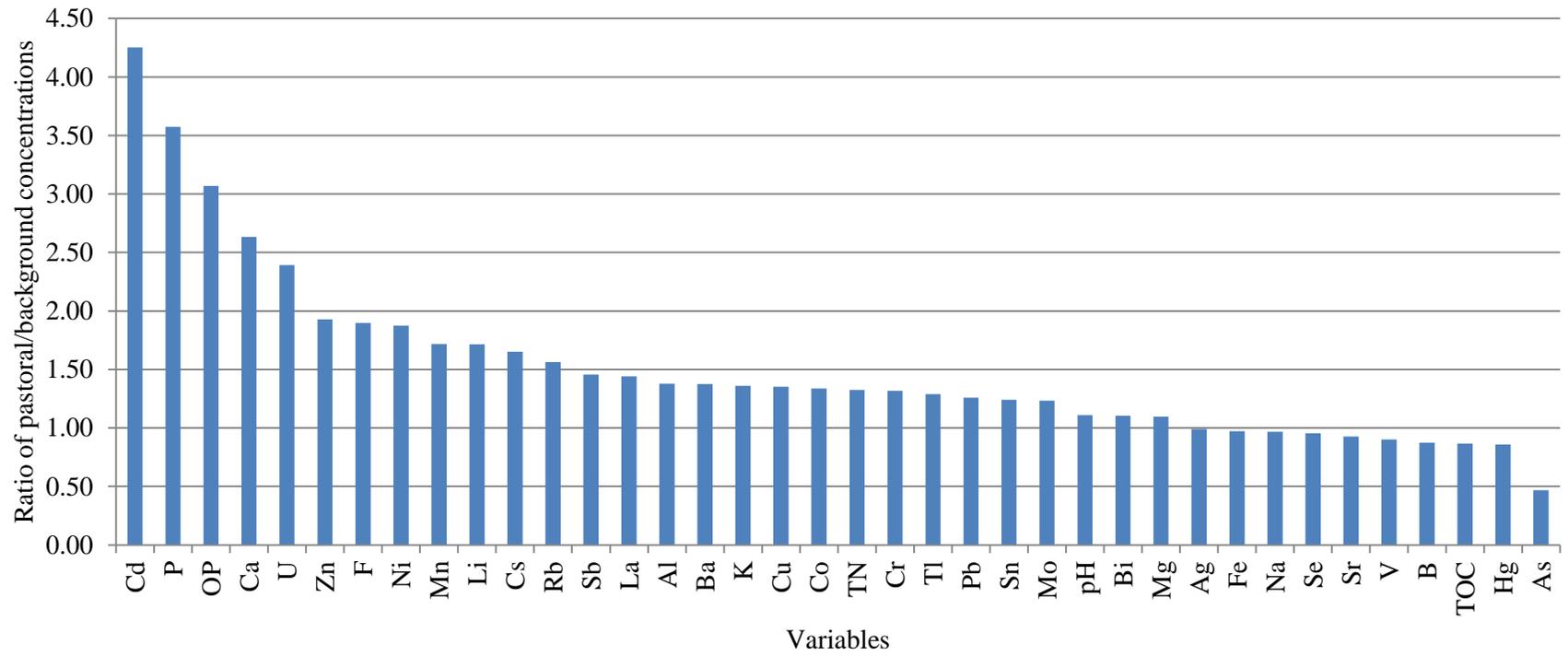


Figure 3.3 Pastoral/Natural (B+F) AR Trace Element Ratios for Waikato Surface Soils, based on Mean Concentrations in Each Category

The six elements showing the greatest mean enrichment in pastoral soils are (in order, shown in Figure 3.3):

$Cd > P \text{ (acid recoverable and Olsen-P)} > Ca > U > Zn \sim F \sim Ni$

Consistent with previous studies, enrichments of Cd, P, Ca, U and F can be attributed to single superphosphate (SSP) fertilizer having become the dominant source of P, S, F, Cd and U in farmed soils (McBride & Spiers, 2001; McLaughlin, Tiller, Naidu, & Stevens, 1996). SSP fertilizer is also a source of Ca as it is 40% gypsum ($CaSO_4$), and this with periodic application of lime to farmed soils explains Ca enrichment.

However, SSP is not considered a significant source of either Zn or Ni, so other sources are required to explain enrichment of these elements in pastoral soils. For Zn, high mass loadings of 5-6 kg/ha/y on pastoral land have been linked with facial eczema remedies (Section 1.3.2). Results for Ni could be the subject of future research, but it is notable that this element is now being used as a dairy-cow supplement (Taranaki Daily News, 2012).

Overall, these results show that enrichment of Zn in pastoral soils has been of a high enough magnitude to place it within range of the better-known trace element contamination caused by application of SSP fertilisers.

3.2.4 Zinc concentrations over time

To examine the relative increase or decrease in Zn concentration between any two sampling dates, ratios of Zn (newer sampling date/earlier sampling date) were calculated for properties sampled on either two or three occasions (mean time between sampling events of 7 years). These resulted in 136 newer/older date pairs.

Table 3.5 provides the summary statistics for these ratios (Zn only) within different land use categories. Table 3.6 provides a contextual summary of how Zn ratios compare with ratios of other elements in soils sampled more than once within different land use categories

Mean concentrations and enrichment ratios for farmed/background and pastoral/background soils are supplied in Appendix 3.2, while Appendix 3.3 provides the raw ratio results for Zn across the different land use categories.

Table 3.5 Summary Statistics for Zinc Concentration Ratios at Sites Sampled More than Once, According to Land Use Category

Variable	Unit	Background soils	Forestry soils	Natural soils	Horticultural soils	Pastoral soils
<i>N</i>		15	23	38	51	67
Average time between samples	yr	7.30	7.40	7.40	6.80	6.00
Mean Zn concentration ratio		0.96	0.76	0.84	0.98	0.99
95% error on mean (Student's t)		0.13	0.10	0.08	0.09	0.06
95% lower boundary		0.82	0.67	0.76	0.90	0.94
95% upper boundary		1.09	0.86	0.92	1.07	1.05
Mdn		0.97	0.81	0.88	0.90	0.98
SD	mg/kg	0.24	0.22	0.25	0.31	0.23
Min		0.53	0.40	0.40	0.57	0.50
Max		1.36	1.11	1.36	2.25	1.63
Lower 5th %tile		0.54	0.42	0.44	0.70	0.62
Upper 95th %tile		1.33	1.10	1.25	1.64	1.46
95% CI (Student's t)		[0.823 - 1.09]	[0.666 - 0.858]	[0.758 - 0.920]	[0.895 - 1.07]	[0.938 - 1.05]
95% CI (Normal Distribution)	[0.932 - 0.982]	[0.742 - 0.782]	[0.823 - 0.855]	[0.969 - 0.997]	[0.982 - 1.01]	

Table 3.6 Newer/Older Date-Pair Ratios for Each Measured Variable on Properties Sampled Twice or More (N=136 for Zn)

Variable	Land use category				
	All soils	Background	Forest	Horticultural	Pastoral
Al	1.01	1.03	0.93	1.09	0.98
As	0.88	0.80	0.82	0.93	0.87
B	0.98	0.86	0.83	0.95	1.03
Ba	0.91	0.93	0.87	0.92	0.91
Bi	0.87	0.83	0.91	0.87	0.86
C:N	0.98	0.95	0.99	0.99	0.97
Ca	0.98	1.05	1.07	0.99	0.93
Cd	0.92	0.89	0.93	0.94	0.91
Co	0.98	1.01	0.96	1.04	0.96
Cr	1.02	1.07	0.97	1.02	1.04
Cs	0.92	0.91	0.94	0.91	0.93
Cu	0.90	0.80	0.93	0.91	0.96
F	1.00	0.96	1.04	1.04	0.98
Fe	0.97	0.98	0.90	1.03	0.95
Hg	1.00	0.86	1.06	1.06	0.98
K	0.95	1.08	0.83	1.07	0.89
La	0.88	0.95	0.84	0.89	0.88
Li	0.95	1.05	0.88	1.03	0.92
Mg	1.07	1.20	0.96	1.15	1.03
Mn	0.91	0.89	0.82	1.01	0.89
Mo	0.86	0.77	0.86	0.85	0.89
Na	0.95	0.98	0.89	1.08	0.89
Ni	1.02	1.15	0.97	1.00	1.01
OP	1.24	1.24	1.42	1.15	1.23
P	0.97	1.08	1.00	0.96	0.95
Pb	0.91	0.95	0.87	0.88	0.93
pH	1.02	1.04	1.01	1.02	1.02
Rb	0.97	1.08	0.90	1.00	0.95
Sn	0.95	0.90	0.90	1.02	0.94
Sr	0.93	0.94	0.89	0.97	0.93
Tl	0.87	0.85	0.92	0.89	0.85
TC	1.02	1.06	1.02	0.98	1.04
TN	1.05	1.11	1.04	0.99	1.07
U	0.92	0.94	0.98	0.89	0.91
Zn	0.94	0.97	0.78	0.97	0.97

Overall, ratio data for soils sampled over time provides no evidence of a substantial change in mean Zn concentration over time in background, horticultural and pastoral soils (average times between samples 7.3 years, 6.8 years and 6.0 years, respectively). However, similar results occur for P, Cd, Ca, F, and U – all of which are likely to be accumulating in farmed soils from the use of SSP fertilisers. On this basis, the results for Zn should not be viewed as positive evidence that Zn accumulation in soils is not occurring.

The more likely interpretation is that the magnitude of change on an individual site over seven years is lower than variation due to spatial heterogeneity, episodic temporal variation (e.g. through re-sowing or ploughing), and analytical errors (i.e. that seven years is too short a timescale to see firm evidence of Zn accumulation in average or geometric mean statistics).

The apparent change in Zn results between two sampling dates (newer/older) also showed quite a large *range* from 0.42 – 2.25 times, suggesting that on some properties samples may have been collected from different locations (paddocks or blocks) between the first and second sampling dates, and/or that Zn accumulation on other properties may have been comparatively rapid.

An alternative explanation is that there may have been some systematic changes to sampling or analytical procedures that have resulted in more recent results for trace elements being slightly lower than the older estimates. Although it is unclear what may have changed which could cause a modest reduction in reported results, one possibility is an increase in sampling depth in pastoral soils from 0-7.5 cm (Longhurst et al., 2004) to a nominal depth of 0-10 cm (Land Monitoring Forum, 2009).

For the elements that show surface enrichment, collection of slightly deeper samples may cause apparent dilution of trace element results, because the deepest part of the 0-10 cm sample contains a slightly lower concentration than is present in the immediate topsoil. This factor would not be expected to influence the results presented in Section 3.2.2 because across all data there was an even spread of sampling dates covering each land use (Table 3.5).

Despite the limitations, the results suggest that there may be more than minor loss of Zn and some other trace elements in soils under forestry (Table 3.5). Over an average of 7.4 years, Zn concentrations in forestry soils decreased by 25% (calculated mean is 0.76 mg/kg, 95% CI is 0.67 mg/kg - 0.86 mg/kg). Reasons for this are unclear; however, there are two possible explanations. The first is that the particular soil types associated with forestry areas (commonly pumice) do not adsorb as much Zn as other soil types (explored in more detail in Section 3.3). The second possibility is that because forestry soils are unlikely to receive any inputs of Zn, plant uptake of Zn from forestry outweighs Zn inputs to forestry soils, thus causing a net loss over time.

The correlation between time in between sampling of forest soils and Zn ratio appears to be weak ($p < 0.05$). Notwithstanding this, overall there appears to be less extractable Zn in forest soils over time, shown by the number of ratios that fall below 1.0 (Table 3.6, Figure 3.4).

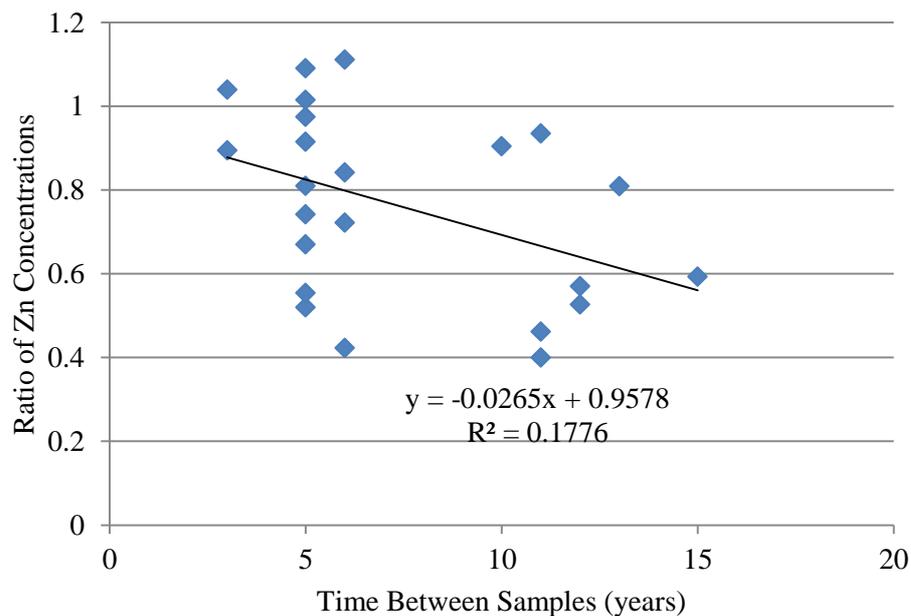


Figure 3.4 *Correlations between Years In-Between Sampling of Waikato Forest Soils and Zn Ratios*

Other elements that are also showing up as depleted in forest soils include B (0.83), K (0.83), La (0.84), and Mn (0.82) (Table 3.6). Possible reasons for this effect may include:

1. leaching through the soil, supported by the fact that As (as arsenate) and B are both known to be mobile elements in soils, and Zn is one of the most mobile cations (Kabata-Pendias, 2010; Kiekens, 1995),
2. facilitated leaching, e.g. complexation with low molecular weight organic matter, such as fulvic acids, from the pine trees (Bradl, 2004; McBride, Sauve, & Hendershot, 1997),
3. uptake by plants - B, Zn, Mn, and K are essential element in plants (Brenchley, 1936; Kabata-Pendias, 2010),
4. planting rotations- uptake by plants in rotation outweighing inputs of Zn into soils.

The second parallel approach to determining if Zn concentrations have changed over time in Waikato soils was to run a series of Student's paired t-tests based on sample occasions. Overall, the results (Table 3.7) provide some support for ratio data (Table 3.5), particularly for the observed loss of Zn in forestry soils ($p < 0.0001$).

The marginal decrease over time in horticultural soils was somewhat significant ($p < 0.002$), while the subtle decrease in Zn from background and pastoral soils were statistically insignificant ($p < 0.16$ and $p < 0.04$ respectively). Student's paired t-tests based on consecutive sample dates (omitting first-third sample occasion pairs) gives the same results ($p < 0.001$).

Table 3.7 Summary of Paired t-test Results (all possible pairs) for Zn at Sites Sampled on Two or More Occasions (mean time between samplings 6-7 years)

Land use category	Paired t-test for Zn concentrations decreasing over time (T1 > T2):			Mean Zn concentration (mg/kg)		Ratio of means	Difference in means (T2-T1)	
	Pairs	p-value	Significance level	Earlier sampling	Subsequent sampling	(time 2/time 1)	Absolute (mg/kg)	% decrease
All data	156	< 0.0001	Highly	52.7	48.4	0.92	4.3	8.2
Background soils	15	< 0.16	Not	29.0	26.8	0.92	2.2	7.7
Forestry soils	20	< 0.0001	Highly	25.5	18.6	0.73	6.9	27.0
Horticultural soils	50	< 0.002	Quite	74.5	67.4	0.91	7.1	9.5
Pastoral soils	71	< 0.04	Just	50.1	48.0	0.96	2.1	4.2

3.2.5 Zinc concentrations with depth

Data for pastoral and background surface (0-10 cm) and deeper (10-20 cm) soils are summarised in Table 3.8. An additional table for raw ratio data for indigenous, forestry and horticultural land use categories is provided in Appendix 3.4. An excerpt of this is included in Table 3.9.

To provide context for pastoral soils ratio results, surface enrichment ratios (0-10 cm/10-20 cm) and absolute concentration differences between the two layers were estimated for background soils also (Table 3.8). For ratio data, a result of 1.5 or more denotes reasonably substantial enrichment at the surface compared with deeper. A ratio of 1 means that concentrations down the soil profile are much the same, while values less than 1 indicate that the highest concentration may be slightly under the surface layer.

Table 3.8 Summary Statistics for Waikato Pastoral and Background Surface (0-10 cm) and Deeper (10-20 cm) Soil Samples, Ranked by Surface Enrichment Ratio for Pastoral Soils

Variable	<i>n</i>		Surface enrichment ratio		Surface average (mg/kg)		Mean difference (surface-deeper) (mg/kg)		Mean percent decrease with depth	
	Background	Pastoral	Background	Pastoral	Background	Pastoral	Background	Pastoral	Background	Pastoral
OP	11	127	1.45	2.19	18.1	37.0	8.09	15.4	44.6	41.5
P	8	89	1.23	1.99	425	1682	127	999	29.9	59.4
Cd	8	89	1.22	1.80	0.124	0.630	0.009	0.360	7.43	57.1
Ca	7	71	2.31	1.79	1609	4595	741	2251	46.0	49.0
TOC	8	89	1.48	1.70	7.35	9.34	3.52	3.86	47.9	41.4
TN	11	109	1.21	1.65	0.485	0.718	0.083	0.1	17.1	13.1
K	8	71	1.25	1.58	494	843	137	359	27.8	42.5
Zn	8	89	1.15	1.52	32.4	58.0	11.8	27.1	36.5	46.7
Sr	8	71	2.12	1.50	29.4	22.9	12.9	8.66	43.9	37.8
Cu	8	71	1.01	1.36	15.0	16.7	9.15	6.77	60.9	40.6
Mg	7	71	1.40	1.35	825	1134	280	352	33.9	31.1
Mn	8	71	1.07	1.35	531	827	301	269	56.7	32.6
Na	8	68	1.12	1.26	180	163	59.0	65.0	32.8	39.9
B	6	45	1.19	1.24	4.50	4.05	1.94	1.81	43.1	44.8
Ni	7	71	0.956	1.22	5.40	6.98	3.42	2.66	63.3	38.1
U	8	89	0.929	1.21	0.784	1.75	0.099	0.761	12.6	43.4
Ag	8	71	1.80	1.18	0.245	0.134	0.028	0.048	11.4	35.9
Rb	8	71	1.03	1.16	3.62	11.2	1.22	3.38	33.5	30.2
F	0	60		1.14	111	439	30.2	160	27.3	36.5
Ba	8	71	1.40	1.10	89.4	118	54.0	38.6	60.4	32.6
Cr	8	71	0.824	1.09	27.9	17.9	22.1	8.00	79.1	44.8

Table 3.8 continues on pg.63

Table 3.8 Continued

Variable	<i>n</i>		Surface enrichment ratio		Surface average (mg/kg)		Mean difference (surface-deeper) (mg/kg)		Mean percent decrease with depth	
	Background	Pastoral	Background	Pastoral	Background	Pastoral	Background	Pastoral	Background	Pastoral
Sb	7	54	0.873	1.08	0.080	0.116	-0.017	0.012	-21.2	10.4
Mo	8	71	0.906	1.08	1.14	0.861	-0.091	0.291	-7.96	33.8
Tl	7	71	0.799	1.08	0.290	0.217	-0.058	0.074	-20.0	34.0
Co	8	71	0.993	1.04	6.41	5.25	2.41	1.45	37.6	27.7
pH	8	89	1.02	1.03	5.23	5.79	1.41	1.82	27.0	31.4
Pb	8	89	1.08	1.02	15.1	15.5	2.17	3.65	14.4	23.5
Li	7	71	0.951	1.01	5.23	9.62	1.45	3.37	27.7	35.0
La	8	71	1.15	1.01	13.0	14.3	6.44	6.23	49.3	43.5
Sn	8	71	0.857	1.00	1.81	1.56	-0.296	0.473	-16.4	30.4
Hg	7	89	0.790	0.972	0.306	0.125	-0.436	0.026	-142	20.6
Cs	8	71	0.862	0.967	0.755	2.44	0.310	0.695	41.0	28.5
V	8	68	0.846	0.961	83.0	51.0	40.8	19.3	49.2	37.9
Al	8	71	0.854	0.954	27727	31653	7864	11443	28.4	36.2
Bi	7	71	0.836	0.953	0.309	0.207	-0.169	0.070	-54.7	33.7
As	8	71	0.908	0.939	45.4	6.53	-12.9	1.49	-28.4	22.9
Se	5	9	0.784	0.930	3.50	2.91	-0.333	0.905	-9.52	31.1
Fe	8	71	0.898	0.916	34700	21748	9245	6922	26.6	31.8

Zn concentrations decreased with depth by 46.7% in pastoral soils, from a surface average of 58.0 mg/kg to an average of 43.8 mg/kg in deeper soils (Table 3.8). The average difference in Zn concentrations with depth was also higher in pastoral soils than in background soils.

Nutrients associated with farming, e.g. P, Cd and TN, show higher surface enrichments in pastoral soils than in background soils (Table 3.8). The occurrence of surface soil enrichment is likely to signify local sources of Zn contamination (Kabata-Pendias, 2011).

In background soils, some elements show evidence of surface enrichment, whereas others do not, or show apparent surface depletion (Table 3.8). One reason for this is likely to be the higher content of organic matter in the topsoil (0-10 cm) than deeper down (10-20 cm). The natural TOC surface enrichment ratio of 1.48 supports this (Table 3.8). More organic matter at the surface will dilute the inorganic mineral content of the topsoil layer, explaining why major elements such as Al show lower concentrations at the surface than at 10-20 cm depth.

Table 3.9 Ratios of Cd, Pb, and Zn in Surface (0-10 cm)/deeper (10-20 cm) Soils in Native, Forestry, Background, Horticultural and Pastoral Waikato Land Use Categories

Variable	Land use				
	Native (indigenous) sites	Forestry sites only	Background (native and forest) sites only	Horticultural sites only	Pastoral sites only
Cd	1.22	1.53	1.40	1.67	1.80
Pb	1.08	0.96	1.01	1.47	1.02
Zn	1.15	1.14	1.14	1.40	1.52

Cd and Pb are two trace elements that are often geochemically associated with Zn and may be compared with it. In background soils, Cd shows similar surface enrichment to Zn (1.22 times *c.f.* 1.15 times, Table 3.9). Relative to the background condition, both elements show surface enrichment in both pastoral and horticultural soils, and enrichment overall (Table 3.9). For Cd, the surface-enrichment source is known to be SSP fertiliser for both land use types. Pb shows no evidence of surface

enrichment in background soils or pastoral soils, and no overall evidence of being enriched in pastoral soils (Section 3.2.3).

Pb is enriched in horticultural soils, consistent with the old orchard sites in this group previously receiving lead arsenate spray as an insecticide. Pb and As contamination is a well-documented feature of old orchard soils (Gaw, Northcott, Kim, Wilkins, & Jensen, 2012). Thus, in the case where an anthropogenic source is not suspected (e.g. Pb in pastoral soils), no relative increase in surface enrichment is observed.

In the cases where anthropogenic sources are known, e.g. SSP as a source of Cd, and lead arsenate as a source of Pb to horticultural soils (Section 3.2.2), overall and surface enrichments are both observed. Zn in horticultural and pastoral soils fits into the second category. For Zn, overall enrichment and surface enrichment are both observed. Surface and overall enrichment results for Zn therefore indicate the existence of substantive source(s) of anthropogenic Zn to both horticultural and pastoral soils. As discussed in Chapter 1, the most likely and substantive sources of Zn in horticultural soils are dithiocarbamate fungicide sprays, and in pastoral soils, facial eczema remedies.

3.2.6 Facial eczema remedies and zinc loadings on pastoral soils

Taylor, Kim, and Hill (2011) reported that the widespread use of facial eczema remedies are increasing annual Zn loadings to between 5-7 kg/ha/yr on Waikato pastoral soils. This data is based on a HortResearch report to the Waikato Regional Council (Mills, Robinson, & Clothier, 2004), in which Zn and Cu loadings were estimated for different land use types. On pastoral properties where facial eczema remedies are being used, Zn loading rates to soils were estimated to be 5.04 mg/kg/yr for beef farming, 5.77 mg/kg/yr for sheep and 6.72 mg/kg/yr for dairy (Kim, 2008).

Estimates of total Zn use across the region can be made based on these figures and land areas involved: 623,013 ha for dairy pasture, 333,442 ha for sheep, and 471,345 for beef. A lower boundary estimate for total use of 5,090 tons per annum assumes 60% of farmers use facial eczema remedies in a given year. However, Sowry (2011)

reported that most farmers were using facial eczema remedies most years, resulting in an upper boundary estimate of 8,500 tons per annum across the Waikato region.

Loadings can also be used to estimate the potential rate of Zn accumulation in soils, in units of mg/kg/yr (Kim, 2008). These estimates are indicative only as they rely on assumptions about soil bulk density, soil mixing depth, and Zn retention.

Loadings: as outlined above, annual loadings of Zn to pastoral soils where facial eczema remedies are used are estimated to be 5-7 kg/ha/y, or $5-7 \times 10^6$ mg/ha.

Dilution weights: added Zn is diluted into the soil receiving it. Using an assumed soil bulk density of 1 g/cm^3 (1 ton/m^3), a 1 ha (100 m x 100 m) area of soil taken to 15 cm (0.15 m) depth weighs 1.5×10^6 kg (1,500 t).

Assuming no Zn loss, a lower estimate for accumulation would therefore be $5 \times 10^6 \text{ mg} / 1.5 \times 10^6 \text{ kg} = 3.3 \text{ mg/kg/yr}$. Assuming that as for Cd and F, about 10% of Zn is lost from topsoil, then a more realistic mid-range figure may be closer 3 mg/kg/yr.

This estimate is approximate and does not account for actual soil bulk densities and variation in soil adsorption capacities (e.g. highly adsorptive allophanic soils compared with likely lower adsorption of Zn in pumice soils). However, assuming a figure in of this magnitude may apply as an average across soil types, the result suggests that on properties where facial eczema remedies are used annually, an increase in soil Zn of ~30 mg/kg may occur over one decade.

For pastoral soils investigated in this work, mean Zn was 62.9 mg/kg and the observed maximum figure was 170 mg/kg (Table 3.2). Both could be compared with an average background Zn estimate of 32.7 mg/kg. The average and maximum observed apparent increase in pastoral soils were therefore 30.2 mg/kg and 137 mg/kg, respectively. The average increase in Zn observed across all pastoral soils is therefore equivalent to one decade of accumulation, if all pastoral properties had received Zn every year.

With a more realistic view that average usage over time has been closer to 50% in any given year, the observed increase in pastoral soils may represent 20 years of Zn accumulation. This figure is commensurate with timing for the wide scale introduction of high-dose facial eczema treatment, since the mean sampling time for soils covered in this work is the year 2008, and twenty years before this is 1988. High dose treatment for facial eczema was getting underway in the mid-to-late 1980s.

For the pastoral property with the highest Zn, an increase of ~130 mg/kg over 20 years would represent an apparent accumulation of 6.5 mg/kg/yr. Such a figure is well within the envelope of possibilities defined by soil density, actual mixing depth, soil adsorption capacity and application time. For example, for an allophanic soil with a bulk density of 0.75 t/m³ and slightly higher (95%) Zn adsorption, under dairy (6.72 kgZn/ha/yr), with a mixing depth of 10 cm, the estimated annual accumulation rate is $(6.72 \times 10^6 \text{ mg/ha/yr} / 7.5 \times 10^5 \text{ kg/ha}) \times 0.95 = 8.5 \text{ mg/kg/yr}$. Under these conditions, achieving a concentration increase of 130 mg/kg would have taken ~15 years of facial eczema Zn use.

Thus, the average increase in soil Zn for pastoral properties routinely using facial eczema Zn may be ~30 mg/kg per decade, but with rates on some properties being 2-3 times higher than this depending on land use and soil type. The average in pastoral soils across the Waikato region as a whole will be a proportion of this figure, because not all properties receive facial eczema Zn every year. Back-projection suggests that on average perhaps half of the pastoral properties in the Waikato region have received facial eczema Zn on any given year, given an historic rate closer to 15 mg/kg/decade.

Various guidelines exist for Zn in soils depending on the endpoint to be protected, and these are discussed in Section 1.2.3.

3.3 Apparent Accumulation – Relationship to Soil Order

Soil adsorption capacity is an important determinant of Zn retention and the potential for accumulation (see Section 1.1). In this study, the effect of soil order on Zn adsorption was studied by focusing on soil order information within the Waikato surface soils dataset (sites sampled on more than one occasion). Table 3.10 contains the summary data for this. A graph showing the excess (compared with background concentrations) Zn by soil order is provided in Figure 3.5.

Table 3.10 Summary Statistics for AR Zn (mg/kg) for Allophanic, Brown, Gley, Granular, Organic, Podzol, Pumice, Recent and Ultic Surface Soils (0 - 10 cm) of the Waikato Region

Soil Order	<i>n</i>	Mean	95% CI	Geo mean	Mdn	SD	Min	Max	5th %tile	95th %tile
ALL	369	60.0	56.4 - 63.7	50.2	53.0	35.4	3.60	220	17.0	130
Al	84	71.4	64.4 - 78.4	63.9	68.0	32.3	12.4	170	27.1	131
Br	39	44.1	36.1 - 52.1	37.3	38.0	24.6	4.00	130	13.0	78.5
Gl	49	59.0	51.1 - 66.8	53.2	56.0	27.3	9.50	153	27.6	113
Gr	51	60.0	51.6 - 68.5	53.7	53.0	30.1	20.0	149	23.2	120
Or	24	51.0	30.3 - 71.7	37.6	39.8	49.1	5.15	211	10.6	196
Po	5	16.5	13.3 - 19.7	16.4	16.3	2.57	12.7	19.7	12.7	19.7
Pu	26	24.8	30.0 - 28.6	23.3	21.4	9.49	13.1	47.0	14.5	46.2
Re	9	68.8	52.7 - 84.8	66.2	67.1	20.9	45.0	110	45.0	110
Ul	13	35.4	25.4 - 45.5	30.9	37.0	16.6	7.10	59.0	8.54	58.6

Across all Waikato surface soils, allophanic and recent soils appeared to have the strongest capacity to adsorb and fix Zn (mean Zn concentrations of 71.4 mg/kg and 68.8 mg/kg respectively) while podzol and pumice soils (mean Zn concentrations of 16.5 mg/kg and 24.8 mg/kg respectively) have the least adsorption capacity, and potentially an increased capacity to leach Zn.

Allophanic soils are formed by layers of volcanic ash and have properties that are strongly influenced by the clay minerals allophane, imogolite, and ferrihydrite (Hewitt, 1998). Podzol soils are strongly acid soils (Hewitt, 1998) and it is likely that this increases the mobilization of Zn within this type of soil, which would result in relatively lower AR Zn concentrations. Pumice soils have low reserves of major nutrient elements and are typically deficient in trace elements (Hewitt, 1998), thus it is likely that the pumice soils had less extractable Zn to begin with.

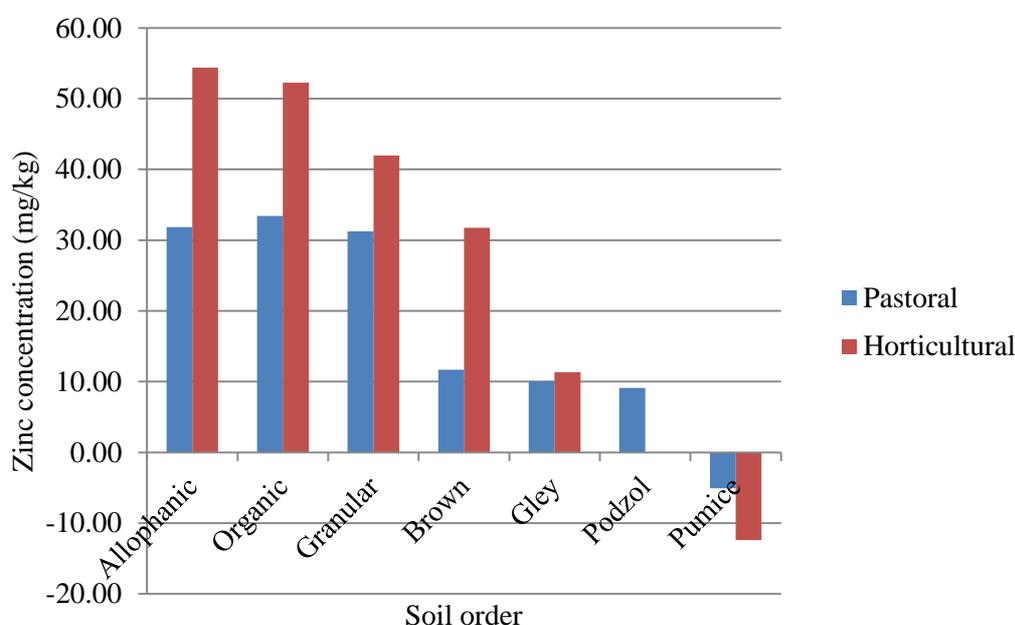


Figure 3.5 Mean AR Zn Concentrations (mg/kg) in Addition to Background Zn Levels in Pastoral and Horticultural Surface Soils of Different Orders (Kim, 2011).

Note: Table from Kim (2011), used with permission.

Zn concentrations appear to be increasing more rapidly in certain soil types. For farmed land, the average additional Zn concentration (i.e. the concentration above background levels) is 30.7 mg/kg (Table 3.4). Within this, organic, granular and

allophanic soils have an average of 30-33 mg/kg more Zn than background soils, gley, brown and podzol soils have 10-12 mg/kg more Zn, and pumice soils have 5 mg/kg less Zn than background soils (Figure 3.5). Thus, apparent additional Zn in farmed soils follows the order:

Allophanic (most) > Organic > Gley > Granular > Brown > Pumice (least)

Within the horticultural soils subset, the average concentration of 44 mg/kg additional Zn is made up of a similar but more exaggerated range that stretches from organic and allophanic soils (52-54 mg/kg more Zn than background) to pumice soils (12 mg/kg less than background) (Figure 3.5).

Though it is clear that more Zn is lost from pumice soils than from other soil types, these findings do not provide sufficient evidence in support of the theory that that soil type is the predominant reason for Zn loss in forestry soils (Section 3.2.4). This is because the number forestry sites comprising pumice soils included in this study are few compared to other soil orders.

3.4 Preliminary Adsorption Trial Results

As outlined in Section 2.3.2, a preliminary Zn adsorption time experiment was conducted to determine the time required for adsorption equilibrium to be achieved for Zn in a soil solution. Table 3.11 provides the results for the first trial using the pH 5.70 buffer in 100 mL Zn solution.

Table 3.11 Adsorption Trial Results for Zinc in pH 5.7 Buffer in 100 mL Solution

Time (h)	Zn concentration mg/L in 100 mL		Total mg of Zn in 100 mL		Originally added (in 35 mL)		Lost from solution		% adsorbed of original	
	Rep 1 mg/L	Rep 2 mg/L	Rep 1 mg	Rep 2 mg	Rep 1 mg	Rep 2 mg	Rep 1 mg	Rep 2 mg	Rep 1	Rep 2
0.08	0.407	0.387	0.041	0.039	0.14	0.14	0.099	0.101	70.92	72.34
0.33	0.284	0.308	0.028	0.031	0.14	0.14	0.112	0.109	79.72	77.99
1	0.177	0.204	0.018	0.020	0.14	0.14	0.122	0.120	87.39	85.41
3	0.151	0.195	0.015	0.019	0.14	0.14	0.125	0.121	89.25	86.09
6	0.103	0.080	0.010	0.008	0.14	0.14	0.130	0.132	92.63	94.31
16	0.191	0.193	0.019	0.019	0.14	0.14	0.121	0.121	86.37	86.24
24	0.050	0.048	0.005	0.005	0.14	0.14	0.135	0.135	96.43	96.58
48	0.087	0.053	0.009	0.005	0.14	0.14	0.131	0.135	93.76	96.25
72	0.063	0.093	0.006	0.009	0.14	0.14	0.134	0.131	95.51	93.39
115	-0.064	0.007	-0.006	0.001	0.14	0.14	0.146	0.139	105	99.50

At pH 5.7, >90% of the original Zn concentrations was adsorbed within 5 minutes, and most (~97%) of the Zn was adsorbed at equilibrium. This indicates that Zn is rapidly adsorbed at the natural soil's pH level of 5.7 in granular soil types.

The second trial was run at a lower pH of 4.70. In this trial, the proportion of Zn adsorbed to the soil significantly decreased to ~62%, indicating that an increase in soil acidity would likely cause re-mobilisation of some of the previously adsorbed Zn. This finding is relevant to environmental situations that involve a decrease in soil pH, e.g. locally around acidic granules of superphosphate fertiliser, or generally as a result of nitrification. Increasing pH (e.g. by addition of lime) would increase Zn adsorption. Figure 3.6 compares adsorption times for both trials.

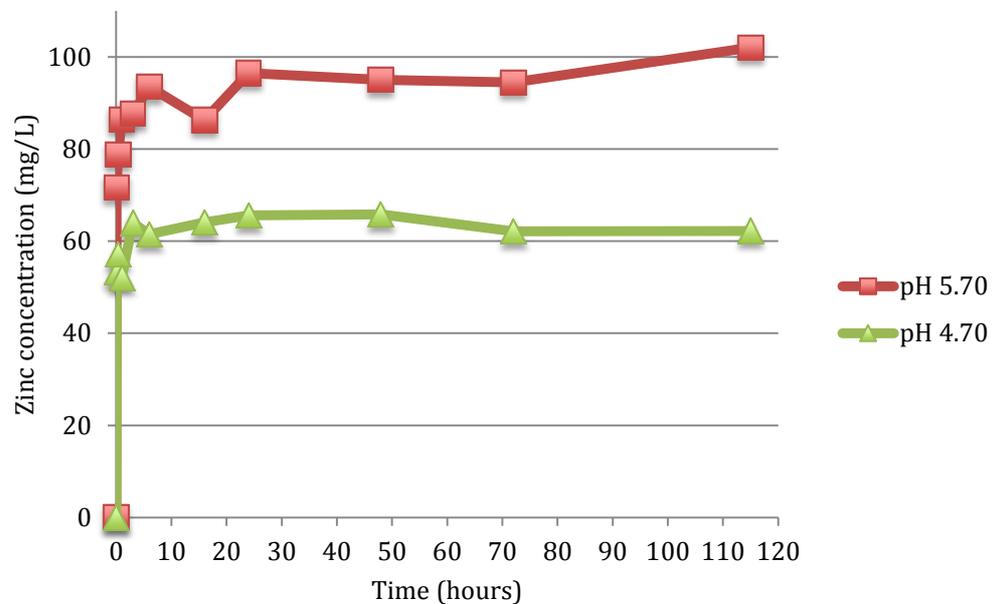


Figure 3.6 Comparison of Zn adsorption to soil in pH 5.70 and pH 4.70 buffer solution over time

3.5 Correlations

All variables apart from pH, F and XRF results were log-normalised prior to derivation of the correlation matrices. One outlier, raw soil site 53, was removed prior to calculating the correlation matrix. This was due to raw soil having characteristically low trace element concentrations for several elements, which caused correlation scatterplots to have an unrepresentative low point, yielding an artificially high R-value.

3.5.1 Natural soils

Table 3.12 Correlation Coefficients and p-values for AR Zinc and Other Variables in Regional Waikato Background and Forestry Soils. Relationships of $p < 0.001$ or better are in Bold Italic*

Background Soils				Forestry Soils			
<i>n</i>	Variable	R value	p value	<i>n</i>	Variable	R value	p value
24	Zn	1		28	Zn	1	
9	XRF Zn	0.94	0.0001	11	XRF Zn	0.766	0.01
24	pH	0.776	0.0001	29	pH	0.218	0.1
21	TOC	-0.04	0.1	20	TOC	0.099	0.1
21	TN	0.039	0.1	20	TN	0.148	0.1
23	Ag	-0.143	0.1	28	Ag	0.319	0.1
24	Al	0.501	0.02	28	Al	0.708	0.0001
24	As	-0.256	0.1	28	As	0.460	0.05
23	B	0.197	0.1	19	B	0.216	0.1
24	Ba	0.442	0.05	28	Ba	0.517	0.01
22	Bi	-0.307	0.1	28	Bi	0.442	0.02
24	Ca	0.789	0.0001	28	Ca	0.417	0.05
24	Cd	0.568	0.01	28	Cd	0.489	0.01
24	Co	0.837	0.0001	28	Co	0.830	0.0001
24	Cr	0.350	0.1	28	Cr	0.720	0.0001
24	Cu	0.499	0.02	28	Cu	0.615	0.001
16	F	-0.172	0.1	18	F	0.021	0.1
24	Fe	0.236	0.1	28	Fe	0.650	0.001
23	Hg	-0.443	0.05	28	Hg	0.356	0.1
24	K	0.237	0.1	28	K	0.530	0.01
24	La	0.339	0.1	28	La	0.427	0.05
22	Li	0.500	0.02	28	Li	0.706	0.0001
24	Mg	0.734	0.0001	28	Mg	0.674	0.0001

Table 3.12 continues on pg.75

Table 3.12 continued

Background Soils				Forestry Soils			
<i>n</i>	Variable	R value	p value	<i>n</i>	Variable	R value	p value
24	Mn	0.830	0.0001	28	Mn	0.600	0.001
24	Mo	-0.003	0.1	28	Mo	0.341	0.1
24	Na	0.03	0.1	27	Na	0.220	0.1
23	Ni	0.562	0.02	28	Ni	0.839	0.0001
24	OP	-0.296	0.1	28	OP	-0.080	0.1
24	P	0.019	0.1	27	P	0.189	0.1
24	Pb	0.129	0.1	28	Pb	0.639	0.001
24	Rb	0.598	0.01	28	Rb	0.132	0.1
21	Sb	-0.188	0.1	24	Sb	0.319	0.1
24	Sn	0.196	0.1	28	Sn	0.604	0.001
24	Sr	0.364	0.1	28	Sr	0.615	0.001
22	Tl	0.006	0.1	28	Tl	0.505	0.01
24	U	0.463	0.05	28	U	0.512	0.01
21	V	0.211	0.1	19	V	0.507	0.05

Notable correlations in background soils include the pH-Zn relationship ($R=0.776$, $p<0.0001$, $n=24$) and the Ca-Zn relationship ($R=0.789$, $p<0.0001$, $n=24$); both of which were lost in forestry soils. The loss of a pH - Zn correlations in forest soils accompanied by similar loss for Ca-Zn suggests that lime (CaCO_3) may have been applied to forest soils, possibly to optimise soil condition for forest growth. This would have raised the pH and may have caused the underlying pH-Zn correlation to be lost.

Some correlations for background and forestry soils may be influenced by a particular soil order for that sample. For example, seven forest soil samples were pumice, as opposed to only in two background soil samples (Table 3.13). This might account for the strong Zn-Cr correlation in forestry soils ($R=0.720$, $p<0.001$, $n=28$) but not in background soils (Table 3.12).

Table 3.13 Soil Order Percentages of Background and Forestry Samples

Soil order	Background soils		Forest soils	
	<i>n</i>	%	<i>n</i>	%
Allophanic	4	16.7	8	25.8
Brown	7	29.2	6	19.4
Gley	3	12.5	1	3.2
Granular	3	12.5	1	3.2
Organic	1	4.2	0	0.0
Podzol	1	4.2	3	9.7
Pumice	2	8.3	7	22.6
Raw	1	4.2	1	3.2
Recent	1	4.2	0	0.0
Ultic	1	4.2	4	12.9

3.5.2 Anthropogenically influenced soils

A number of variables correlate very strongly with Zn in horticultural and pastoral soils (Table 3.14).

Table 3.14 Correlation Coefficients *p*-values for AR Zinc and Other Variables in Regional Waikato Horticultural (including Arable) and Pastoral Soils. Relationships of *p*<0.001 or better are in Bold Italic

Horticultural soils				Pastoral soils			
<i>n</i>	Variable	R-value	<i>p</i> -value	<i>n</i>	Variable	R-value	<i>p</i> -value
47	Zn	1		202	Zn	1	
26	<i>XRF Zn</i>	<i>0.931</i>	<i>0.0001</i>	86	<i>XRF Zn</i>	<i>0.917</i>	<i>0.0001</i>
47	<i>pH</i>	<i>0.723</i>	<i>0.0001</i>	204	pH	0.201	0.01
38	TOC	-0.197	0.1	178	TOC	-0.053	0.1
38	TN	-0.038	0.1	160	TN	0.017	0.05
45	<i>Ag</i>	<i>0.596</i>	<i>0.0001</i>	183	<i>Ag</i>	<i>0.492</i>	<i>0.0001</i>
47	<i>Al</i>	<i>0.716</i>	<i>0.0001</i>	184	<i>Al</i>	<i>0.453</i>	<i>0.0001</i>
47	<i>As</i>	<i>0.577</i>	<i>0.0001</i>	183	<i>As</i>	<i>0.419</i>	<i>0.0001</i>
45	<i>B</i>	<i>0.511</i>	<i>0.001</i>	177	<i>B</i>	<i>0.299</i>	<i>0.0001</i>
47	<i>Ba</i>	<i>0.778</i>	<i>0.0001</i>	184	<i>Ba</i>	<i>0.525</i>	<i>0.0001</i>
44	Bi	0.145	0.1	181	<i>Bi</i>	<i>0.424</i>	<i>0.0001</i>
47	<i>Ca</i>	<i>0.158</i>	<i>0.0001</i>	184	Ca	0.220	0.01
47	<i>Cd</i>	<i>0.509</i>	<i>0.001</i>	202	<i>Cd</i>	<i>0.368</i>	<i>0.0001</i>
47	Co	0.463	0.01	184	<i>Co</i>	<i>0.570</i>	<i>0.0001</i>
47	Cr	0.245	0.01	184	<i>Cr</i>	<i>0.363</i>	<i>0.0001</i>

Table 3.14 continues on pg. 77

Table 3.14 *continued*

Horticultural Soils				Pastoral Soils			
<i>n</i>	Variable	R-value	p-value	<i>n</i>	Variable	R-value	p-value
47	<i>Cs</i>	0.632	0.0001	184	<i>Cs</i>	0.303	0.0001
47	<i>Cu</i>	0.453	0.01	184	<i>Cu</i>	0.583	0.0001
42	<i>F</i>	0.367	0.01	172	<i>F</i>	0.223	0.01
47	<i>Fe</i>	0.501	0.001	184	<i>Fe</i>	0.425	0.0001
46	<i>Hg</i>	0.268	0.1	201	<i>Hg</i>	0.422	0.0001
47	<i>K</i>	0.397	0.01	184	<i>K</i>	0.419	0.0001
47	<i>La</i>	0.719	0.0001	184	<i>La</i>	0.617	0.0001
46	<i>Li</i>	0.593	0.0001	184	<i>Li</i>	0.497	0.0001
47	<i>Mg</i>	0.324	0.05	184	<i>Mg</i>	0.429	0.0001
47	<i>Mn</i>	0.619	0.0001	184	<i>Mn</i>	0.659	0.0001
47	<i>Mo</i>	0.356	0.02	184	<i>Mo</i>	0.527	0.0001
47	<i>Na</i>	0.003	0.1	183	<i>Na</i>	0.143	0.05
47	<i>Ni</i>	0.371	0.1	184	<i>Ni</i>	0.482	0.0001
47	<i>OP</i>	0.297	0.1	202	<i>OP</i>	0.158	0.05
47	<i>P</i>	0.571	0.0001	202	<i>P</i>	0.408	0.0001
47	<i>Pb</i>	0.272	0.1	202	<i>Pb</i>	0.554	0.0001
47	<i>Rb</i>	0.608	0.0001	184	<i>Rb</i>	0.295	0.0001
45	<i>Sb</i>	0.179	0.1	169	<i>Sb</i>	0.302	0.0001
47	<i>Sn</i>	0.533	0.001	184	<i>Sn</i>	0.471	0.0001
47	<i>Sr</i>	0.327	0.05	184	<i>Sr</i>	0.353	0.0001
46	<i>Tl</i>	0.705	0.0001	181	<i>Tl</i>	0.531	0.0001
47	<i>U</i>	0.489	0.001	202	<i>U</i>	0.411	0.0001
43	<i>V</i>	-0.080	0.1	164	<i>V</i>	0.181	0.1

However, caution must be taken when interpreting these as enrichments, as some relationships are likely to be coincidental. For example, P correlates very strongly with Zn in horticultural and pastoral soils (horticultural $n=47$, $R=0.571$, pastoral $n=202$, $R=0.408$, both $p<0.0001$). Farm soils are likely to receive P via fertilisers and Zn concurrently via facial eczema remedies, thus appearing as coincidental correlation.

Both horticultural and, to a less extent, pastoral soils correlate positively with pH (Table 3.12 and Table 3.14). These relationships are consistent with findings in Section 3.4, where adsorption of Zn occurred less in acidic soil. Often, horticultural soils are treated with lime to raise the soil pH in order to meet crop requirements, which may have resulted in a stronger correlation in this data. In contrast, pastoral

soils tend to have a narrower pH range for optimal grass growth, thus resulting in a less significant correlation. This may also apply to forest soils.

3.5.3 Comparison of background to farmed soils

Overall, the correlation data does not provide definitive information regarding differences in Zn relationships to other variables in background vs farmed soils. This is largely due to the uncertainty of a number of high positive correlations in this data. Correlations between two elements can occur for a number of reasons, including similar biogeochemical histories, a common anthropogenic source or sources, common solubilities and enrichment pathways, or the presence of two or more chemically distinct sources that are coincident in time and place.

3.6 Comparison to Soil Quality Guidelines

The Biosolids Guidelines provide a GV of 300 mg/kg for Zn in soils (see Section 1.2.3). No individual soil samples obtained during the study period exceeded this concentration. The majority of concentrations fell below 128 mg/kg (Table 3.15). One result, obtained from organic soil at a pastoral property, fell above 200 mg/kg (211 mg Zn/kg). This particular sample also had very high P, Mg, P, and Ca.

Table 3.15 Distribution of Individual Zn Concentrations in Waikato Farmed soils

Concentration	<i>n</i> (out of 249)	% of all sites
≥200 mg/kg	1	0.4
≥150 mg/kg	6	2.41
≥100 mg/kg	30	12.0
≤95th percentile (128 mg/kg)	90	36.1

While there are no guidelines for the minimum amount of Zn required in soils, Zn deficiency is well recognized in the literature as a globally ubiquitous micronutrient deficiency disorder (Alloway, 2008a). Typical critical concentrations of Zn used in the interpretation of soil and plant analyses have been given by Alloway (2009) as between 0.5 mg/kg - 3 mg/kg extractable Zn in soils and between 15 mg/kg - 20 mg/kg extractable Zn in plant tissue.

Background concentrations in Waikato soils were low, particularly in forestry soils, which had a mean Zn concentration of 28.0 mg/kg. This is less than half of the estimated world average background soil concentration of 64 mg/kg (European Communities, 2004; Kabata & Pendias, 2001; Ure & Berrow, 1982).

Estimated years that it might take to reach three of these guidelines for three general cases are shown in Table 3.16. These are indicative only assumes that current acid recoverable Zn concentration in soils are at the regional mean for pastoral soils of 60 mg/kg.

Table 3.16 Estimated Number of Years before Guideline Values are Reached

Zn concentrations (mg/kg)			Years to Reach Guideline		
Guideline	Current Average	Difference	Average across Region	Average for pastoral properties routinely receiving FE Remedies	Higher end accumulators (e.g. dairy properties on Allophanic soils)
90	60	30	60	10	4
200	60	140	133	47	16
300	60	240	200	80	28

Note: Guidelines values provided in this table refer to those discussed in Section 1.2.3.

3.7 Potential Human Health Issues

Several points can be made in relation to potential human health issues associated with the findings of this chapter. The most significant points are summarised below.

Increased Zn concentrations may cause an increase in Cd mobilisation from soils into soil pore water (by direct competition between Zn^{2+} and Cd^{2+}) (Kim, 2008). That may cause two issues related to human health:

1. a possibility of increased crop uptake of Cd, which would be of concern because tolerable daily intake limits (TDI values) for Cd across all foods are already being approached (Kim, 2008), and

2. potential for increased leaching and movement of Cd to groundwater, which may be used for rural drinking water, as well as stock watering and irrigation.

However, it is important to note that for (a), excess Zn may also cause decreased crop uptake of Cd, as the two may compete during uptake into plants, and that extra Zn in foods may be protective of Cd toxicity. For (b), strong adsorption of both Zn and Cd to subsoil may still prevent the entry of significant amounts of either metal to groundwater in most cases.

Increased concentrations of Zn in soils (mainly from the additional Zn in horticultural soils) may cause an increase in the Zn content of some foods and in the diet, which may actually be beneficial. The Recommended Daily Allowance (RDA) for Zn for men is 14 mg/day and for women is 8 mg/day (NZ Nutrition Foundation, 2015). However, increased Zn in soils may cause deficiencies in crops and dietary intake of other essential elements, such as Cu or Co (Kim, 2008).

Zn accumulation in soils also has the potential to cause widespread development of antibiotic resistance in soil microorganisms, which may be of unknown significance to human health but potentially very important. This type of resistance comes about because Zn (and some other metals) will cause selection of metal-resistance genes, and these same genes often confer resistance to antibiotics (Baker-Austin, Wright, Stepanauskas, & McArthur, 2006).

3.8 Comparisons to Other Regions of New Zealand

In addition to Waikato soils data, samples were also obtained from the Auckland, Bay of Plenty, Marlborough, Taranaki and Wellington regions of New Zealand and analysed for AR Zn and other variables. Methods for this section are provided in Section 2.3. Summary statistics for all New Zealand surface soil data by land use category are given in Table 3.17 and regional averages by land use are provided in Table 3.18. Summary statistics for each region are supplied in Appendices 3.5-3.9.

Table 3.17 Summary Statistics for AR Zn (mg/kg) in New Zealand Surface Soils

Land use category	<i>n</i>	Mean	95% CI	Geo Mean	Mdn	SD	Min	Max	5th %tile	95th %tile
All	838	59.8	57.7 - 61.9	51.7	59.0	31.0	3.60	288	18.0	110.6
Background soils	58	41.5	35.5 - 47.6	34.6	37.0	23.0	4.00	95.0	12.1	86.4
Forestry soils	83	37.2	32.2 - 42.2	30.2	30.0	22.8	3.60	105	8.84	75.7
Natural soils	141	39.0	35.2 - 42.8	31.9	36.0	22.9	3.60	105	10.1	80.2
Horticultural soils	160	66.9	62.6 - 71.2	60.2	68.3	27.5	5.15	190	20.8	108.5
Pastoral soils	422	59.8	56.9 - 62.7	53.0	58.0	30.4	12.0	288	20.5	112.0
Farmed soils	582	61.7	59.3 - 64.2	54.9	60.5	29.8	5.15	288	20.6	111.2
Urban soils	68	81.3	72.0 - 90.6	73.5	77.5	38.4	26.0	220	32.8	163.7

Table 3.18 Average (arithmetic) Zn (mg/kg) in Background, Forestry, Pastoral and Horticultural Soils in the Auckland, Bay of Plenty, Marlborough, Taranaki, Waikato and Wellington Regions of New Zealand

Region	All soils	Background soils	Forestry soils	Natural soils	Horticultural soils	Pastoral soils	Farmed soils	Urban soils
All regions	59.8	41.5	37.2	39.0	66.9	59.8	61.7	81.3
Auckland	43.8	41.1	55.2	49.4	34.8	44.1	41.1	-
Bay of Plenty	42.1	23.3	20.7	21.4	54.9	51.0	52.3	-
Marlborough	68.7	72.3	59.3	62.8	73.1	68.6	69.8	-
Taranaki	69.4	56.0	49.7	52.2	92.0	73.1	75.8	-
Waikato	60.0	32.1	28.0	29.9	73.3	57.6	60.6	81.9
Wellington	67.5	63.1	47.1	56.3	72.5	67.4	69.8	41.0

In total, 838 samples were collected across New Zealand and analysed for AR Zn and other variables. Zn concentrations ranged from 3.60 mg/kg to 288 mg/kg, most within the range of 40-80 mg/kg (Table 3.17). These results are generally in line with the range of mean total Zn in soils reported in the literature, e.g. 50 mg/kg - 64 mg/kg (Alloway, 2008b; Kabata & Pendias, 2001).

Compared to the Waikato region, farmed soils in Taranaki, Marlborough, and Wellington contained higher mean Zn concentrations (75.8 mg/kg, 69.8 mg/kg, and 69.8 mg/kg respectively) (Table 3.18). This may be due, in part, to baseline Zn concentrations (i.e. naturally occurring levels) being slightly higher in these regions (Figure 3.7). Despite this, average additional zinc levels (i.e. Zn concentrations above background levels) were highest in the Waikato and Bay of Plenty region (+30 mg/kg each) (Table 3.4, Figure 3.7, Appendix 3.6).

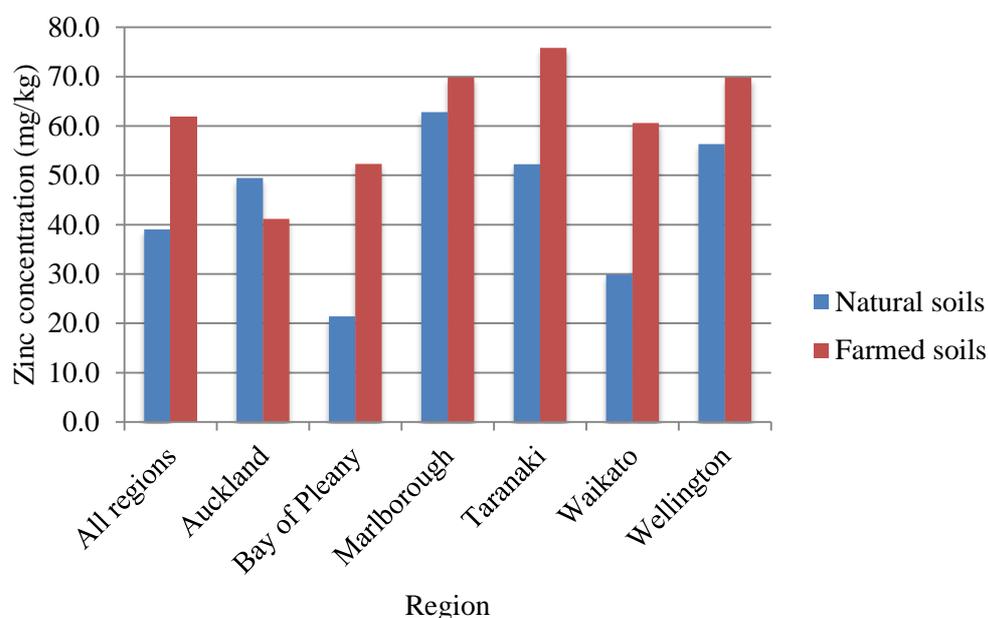


Figure 3.7 Comparison of Regional Mean AR Zn Concentrations (mg/kg) in Natural and Farmed Soils

3.9 Chapter Summary

Overall, mean Zn concentrations are approximately twice as high in farmed (horticultural and pastoral) surface soils as in natural (background and forestry) surface soils in the Waikato region (Section 3.2.2). In pastoral surface soils, Zn enrichment is within the range of other trace element soil contaminants associated with superphosphate fertiliser application, such as Cd, P, Ca, U F and Ni (Section 3.2.3). The decrease in concentration of these elements (including Zn) with soil depth indicates substantial surface agricultural inputs and possible mobilization (Section 3.2.5). Due to several limitations, no substantive evidence is provided for changes in Zn concentrations over time in farmed soils, however there does appear to be an overall loss of Zn from forestry soils (Section 3.2.4).

Zn concentrations also differ according to soil order, and appear higher in farmed organic, granular, and allophanic soils than in the same background soils orders (Section 3.3). Laboratory experiments show that Zn adsorption in granular soil occurs rapidly, and almost entirely (~97% adsorbed at equilibrium) at the natural soil pH level of 5.70. This decreased to ~62% at pH 4.70, indicating that an increase in soil acidity would be likely to cause re-mobilisation of some of the previously adsorbed Zn (Section 3.4).

No soils exceeded 300 mg/kg of Zn; the upper limit recommended for soils the New Zealand Biosolids Guidelines. However, approximately 11% of pastoral soils exceeded 100 mg/kg Zn, an indicative guideline that could be used to denote potential toxicity to soil microbial function. The highest single result from a pastoral farm was 170 mg/kg (AR Zn), and from a horticultural property 190 mg/kg (AR Zn) (Section 3.6).

Continued Zn accumulation in pastoral and horticultural soils may lead to a decrease in soil function and ecological health as a result of Zn toxicity, particularly in relation to microbes, plants, and soil invertebrates. Excess Zn may also affect soil chemistry of other trace elements with which Zn competes or interacts (e.g. Cd or Co). Evidence relating to potential entry of anthropogenic soil Zn into the Waikato River is discussed in the following chapter.

3.10 Appendices

Appendix 3.1 Summary Statistics for XRF Zn (mg/kg) and other Variables in Waikato Surface Soils

Variable	<i>n</i>	Mean	Mdn	SD	Min	Max	5ith %tile	95ith %tile
XAg	0	-	-	-	-	-	-	-
XAl	133	9.05	9.39	2.26	0.160	15.0	5.84	12.3
XAs	133	7.48	6.10	4.48	0.400	32.3	3.15	14.6
XBa	133	403	427	171	30.0	934	139	679
XBi	113	0.949	0.900	0.458	0.300	3.60	0.400	1.79
XBr	133	50.4	43.0	31.6	9.90	182	18.3	111
XCa	133	0.959	0.985	0.396	0.100	1.94	0.281	1.68
XCd	31	0.556	0.500	0.207	0.300	1.10	0.300	0.995
XCe	132	63.7	57.1	33.3	5.20	203	21.2	125
XCl	133	451	401	249	91.0	1120	127	1010
XCo	132	21.9	21.1	9.44	6.00	73.0	8.41	36.0
XCr	104	51.8	25.6	111	2.50	800	3.85	245
XCs	129	12.5	11.7	4.96	3.00	30.0	5.39	21.8
XCu	133	34.5	27.2	31.5	8.50	306	12.5	76.0
XFe	133	3.57	2.97	2.11	0.073	12.6	1.75	7.96
XGa	133	19.5	19.2	4.71	0.900	32.3	14.3	27.0
XGe	130	1.73	1.70	0.514	0.500	3.70	1.00	2.60
XHf	133	8.08	8.05	2.14	1.10	13.9	4.50	11.7
XHg	104	0.884	0.800	0.440	0.30	2.00	0.400	1.80
XI	133	24.2	16.7	20.6	3.70	135	5.305	64.3
XIn	16	0.381	0.300	0.138	0.30	0.800	0.300	0.740
XK	133	0.955	0.98	0.417	0.039	1.98	0.341	1.68
XLa	132	50.0	31.8	45.5	4.40	194	8.48	159
XMg	132	0.232	0.184	0.160	0.040	1.04	0.101	0.554
XMn	133	0.179	0.127	0.160	0.003	0.812	0.023	0.539
XMo	131	2.35	2.20	0.790	0.800	5.00	1.30	3.90
XNa	133	1.37	1.29	0.670	0.080	3.17	0.393	2.72
XNb	133	12.8	11.5	7.00	1.40	63.0	7.20	23.0
XNd	121	42.2	28.4	37.2	9.40	217	11.8	126
XNi	133	13.8	10.8	13.9	1.20	98.0	4.80	33.9
XP	133	0.304	0.285	0.167	0.026	1.18	0.068	0.601
XPb	133	22.6	21.1	9.83	5.40	95.3	12.6	39.1
XPr	124	33.0	26.9	22.6	6.20	169	9.41	70.6
XRb	133	51.2	52.2	19.2	2.20	96.0	17.3	83.0
XS	133	1689	1581	610	702	4177	841	2800

Appendix 3.1 Continued

Variable	<i>n</i>	Mean	Mdn	SD	Min	Max	5ith %tile	95ith %tile
XSb	85	0.983	0.90	0.311	0.300	1.80	0.500	1.53
XSe	133	2.11	1.80	0.974	0.500	5.50	1.06	4.10
XSi	133	23.6	24.1	5.11	0.557	32.7	16.5	30.2
XSn	131	2.17	2.00	2.04	0.350	23.7	0.853	3.40
XSr	133	102	103	41.5	15.7	240	39.6	173
XTa	108	4.13	3.80	1.27	1.90	8.00	2.40	6.40
XTe	106	2.01	1.98	0.706	0.600	4.20	0.880	3.32
XTh	133	13.1	12.8	3.34	2.60	22.6	8.42	18.4
XTi	133	0.411	0.330	0.300	0.008	1.96	0.174	0.813
XTl	132	1.82	1.80	0.555	0.300	3.00	0.900	2.80
XU	133	6.72	6.80	1.36	2.90	10.2	4.46	8.90
XV	133	91.6	71.0	80.19	3.60	558	9.70	261
XW	133	85.5	61.9	85.74	2.70	414	3.20	278
XY	133	31.0	23.5	24.87	1.70	116	8.25	95.7
XZn	133	101	92.0	39.65	16.2	245	48.1	173
XZr	133	248	226	87.04	5.20	491	155	415

Appendix 3.2 Mean Concentrations (mg/kg) and Enrichment Ratios for AR Zn and other Variables Sampled in Natural, Farmed, Pastoral, and Horticultural Waikato Soils

Variable	Natural soils	Farmed soils	Pastoral soils	Horticultural soils	Farmed/ Natural soils ratio	Pastoral/ Natural soils ratio
pH	5.23	5.90	5.80	6.31	1.13	1.11
TOC	30.0	29.3	26	44.7	0.975	0.866
TN	1.72	2.56	2.27	3.77	1.49	1.32
Ag	0.134	0.140	0.133	0.170	1.05	0.99
Al	23209	35583	32002	49606	1.53	1.38
As	12.5	6.32	5.86	8.13	0.504	0.467
B	4.66	4.4	4.07	5.62	0.944	0.874
Ba	87.21	135.2	120	195	1.55	1.37
Bi	0.195	0.224	0.215	0.263	1.15	1.11
Ca	1845	5071	4860	5895	2.75	2.63
Cd	0.154	0.672	0.656	0.737	4.35	4.25
Co	3.95	5.65	5.28	7.13	1.43	1.34
Cr	11.4	15.1	15.0	15.3	1.32	1.32
Cs	1.37	2.39	2.26	2.87	1.74	1.65
Cu	12.8	21.1	17.4	35.3	1.64	1.35
F	233	447	443	461	1.91	1.90
Fe	20760	21925	20212	28634	1.06	0.974
Hg	0.147	0.139	0.127	0.193	0.944	0.860
K	572	770	778	740	1.35	1.36
La	13.3	22.9	19.1	37.4	1.72	1.44
Li	5.24	9.32	8.99	10.6	1.78	1.71
Mg	953	1010	1044	877	1.06	1.10
Mn	558	1176	958	2028	2.11	1.72
Mo	0.701	0.929	0.864	1.18	1.33	1.23
Na	168	158	163	141	0.941	0.967
Ni	3.41	6.49	6.38	6.91	1.91	1.87
OP	15.2	51.1	46.5	71.0	3.37	3.07
P	500	1882	1788	2286	3.76	3.57
Pb	11.2	17.2	14.1	30.8	1.54	1.26
Rb	6.73	10.1	10.5	8.53	1.50	1.56
Sb	0.079	0.162	0.115	0.339	2.06	1.46
Se	3.14	3.08	3.00	3.29	0.982	0.956
Sn	1.17	1.54	1.45	1.87	1.31	1.24
Sr	24.3	23.6	22.5	28.2	0.974	0.926
Tl	0.19	0.291	0.245	0.476	1.54	1.29
U	0.738	1.88	1.77	2.38	2.55	2.39
V	57.0	54.7	51.3	67.4	0.960	0.901
Zn	29.9	60.6	57.6	73.3	2.03	1.93

Appendix 3.3 Ratios of later/earlier Zinc concentrations in Background, Forestry, Natural, Horticultural and Pastoral Soils Sampled Twice or More

Background sites	Forestry sites	Natural sites	Horticultural sites	Pastoral sites
0.97	0.84	0.97	0.95	0.94
1.03	1.04	1.03	1.02	0.94
1.00	0.57	1.00	0.75	0.96
1.09	0.59	1.09	1.19	0.97
0.53	0.53	0.53	0.89	0.76
0.58	1.11	0.58	0.98	1.07
0.91	0.92	0.91	0.87	0.97
0.70	0.89	0.70	0.80	1.00
1.24	0.90	1.24	0.96	0.89
1.14	0.81	1.14	0.77	1.50
1.36	0.93	1.36	0.82	1.45
0.86	0.52	0.86	0.94	0.71
0.90	0.67	0.90	0.77	1.04
0.78	0.55	0.78	0.94	0.50
1.25	0.72	1.25	1.10	1.01
	0.40	0.84	1.13	1.01
	1.09	1.04	0.77	0.78
	0.42	0.57	0.84	1.06
	0.46	0.59	0.78	1.13
	1.02	0.53	1.03	0.89
	0.81	1.11	0.75	1.13
	0.74	0.92	0.70	1.02
	0.98	0.89	2.25	0.85
		0.90	1.58	1.10
		0.81	1.06	0.97
		0.93	1.56	0.93
		0.52	1.65	1.06
		0.67	0.90	1.26
		0.55	0.81	1.33
		0.72	0.94	1.02
		0.40	0.76	0.60
		1.09	0.71	0.90
		0.42	1.02	0.91
		0.46	0.72	0.57
		1.02	0.76	1.17
		0.81	0.85	0.67
		0.74	0.65	1.00
		0.98	0.72	0.90
			0.79	1.36
			0.57	0.62
			0.88	1.05

Appendix 3.3 Continued

Background sites	Forestry sites	Natural sites	Horticultural sites	Pastoral sites
			1.20	1.04
			0.93	0.85
			1.32	0.69
			1.77	0.89
			1.02	0.96
			1.02	1.16
			1.27	0.76
			0.90	1.14
			0.89	1.07
			0.95	1.15
				1.00
				0.89
				1.14
				1.63
				0.85
				1.30
				0.99
				0.84
				1.39
				1.09
				0.84
				0.79
				0.72
				1.58
				0.85
				0.98

Appendix 3.4 Surface Soil (0-10 cm)/Deeper Soil (10-20 cm) Ratios for Zinc and Other Variables in Background, Forestry, Natural, Horticultural and Pastoral Waikato Soils

Variable	Land use				
	Background Soils	Forestry soils	Natural Soils (B + F)	Horticultural Soils	Pastoral Soils
Ag	1.80	1.54	1.66	1.20	1.18
Al	0.85	0.98	0.93	0.89	0.95
As	0.91	1.32	1.15	1.02	0.94
B	1.19	0.94	1.09	0.92	1.24
Ba	1.40	1.15	1.25	0.97	1.10
Bi	0.84	0.89	0.87	1.03	0.95
Ca	2.31	1.61	1.90	1.94	1.79
Cd	1.22	1.53	1.40	1.67	1.80
Co	0.99	1.10	1.06	1.11	1.04
Cr	0.82	1.00	0.93	1.00	1.09
Cs	0.86	0.92	0.90	2.40	0.97
Cu	1.01	1.04	1.03	1.13	1.36
Fe	0.90	1.09	1.01	1.18	0.92
Hg	0.79	1.16	1.01	1.23	0.97
K	1.25	1.22	1.24	1.75	1.58
La	1.15	0.99	1.06	0.97	1.01
Li	0.95	1.00	0.98	1.03	1.01
Mg	1.40	1.14	1.24	1.80	1.35
Mn	1.07	1.54	1.34	2.89	1.35
Mo	0.91	1.15	1.05	1.16	1.08
Na	1.12	0.98	1.04	1.17	1.26
Ni	0.96	1.01	0.99	1.11	1.22
OP	1.45	1.67	1.56	1.11	2.19
P	1.23	1.76	1.50	1.52	1.99
Pb	1.08	0.96	1.01	1.47	1.02
pH	1.02	1.00	1.01	1.03	1.03
Rb	1.03	1.07	1.05	1.76	1.16
Sb	0.87	1.06	0.97	0.95	1.08
Se	0.78	0.91	0.85	1.00	0.93
Sn	0.86	0.91	0.89	1.03	1.00
Sr	2.12	1.76	1.91	1.19	1.50
Tl	0.80	0.96	0.89	1.06	1.08
TN	1.21	1.53	1.37	1.61	1.65
TOC	1.48	2.02	1.79	0.99	1.70
U	0.93	1.00	0.97	1.38	1.21
V	0.85	0.98	0.92	1.02	0.96
Zn	1.15	1.14	1.14	1.40	1.52

Appendix 3.5 Summary Statistics for AR Zinc in Auckland Background, Forest, Natural, Horticultural, Pastoral, Farmed and Urban Soils

Land use category	<i>n</i>	Mean	95% CI	Geo mean	Mdn	SD	Min	Max	5th %tile	95th %tile
All land use types combined	84	43.8	[38.6 - 48.9]	37.0	42.0	23.7	5.10	150	12.0	75.9
Background soils	11	41.1	[25.7 - 56.4]	33.3	36.0	22.8	5.10	75.0	5.65	74.8
Forest soils	16	55.2	[42.7 - 67.6]	46.1	66.0	23.3	6.80	93.0	7.04	85.8
Natural soils	27	49.4	[40.0 - 58.8]	40.4	54.5	23.7	5.10	93.0	6.55	77.7
Horticultural soils	18	34.8	[26.4 - 43.1]	31.2	30.3	16.9	14.0	68.5	14.4	67.9
Pastoral soils	39	44.1	[35.8 - 52.4]	37.7	42.0	25.6	12.0	150	12.9	78.6
Farmed soils	57	41.1	[34.9 - 47.4]	35.5	38.0	23.5	12.0	150	14.0	74.7
Urban soils	-	-	-	-	-	-	-	-	-	-

Appendix 3.6 Summary Statistics for AR Zinc in Bay of Plenty Background, Forest, Natural, Horticultural, Pastoral, Farmed and Urban Soils

Land use category	<i>n</i>	Mean	95% CI	Geo mean	Mdn	SD	Min	Max	5th %tile	95th %tile
All land use types combined	79	42.1	[33.8 - 50.4]	33.8	32.5	37.1	10.5	288	14.5	97.6
Background soils	7	23.3	[17.5 - 29.1]	22.5	27.5	6.26	14.0	29.0	14.0	29.0
Forest soils	19	20.7	[16.5 - 24.9]	19.4	18.0	8.65	10.5	48.0	11.2	42.6
Natural soils	26	21.4	[18.2 - 24.6]	20.2	18.5	8.04	10.5	48.0	11.7	38.4
Horticultural soils	18	54.9	[40.9 – 69.0]	47.8	57.6	28.2	14.0	121	16.7	113
Pastoral soils	35	51.0	[34.8 - 67.1]	41.3	42.0	47.1	18.5	288	18.9	108
Farmed soils	53	52.3	[40.9 - 63.7]	43.4	42.5	41.4	14.0	288	18.7	110
Urban soils	-	-	-	-	-	-	-	-	-	-

Appendix 3.7 Summary Statistics for AR Zinc in Marlborough Background, Forest, Natural, Horticultural, Pastoral, Farmed and Urban Soils

Land use category	<i>n</i>	Mean	95% CI	Geo mean	Mdn	SD	Min	Max	5th %tile	95th %tile
All land use types combined	169	68.7	[65.9 - 71.5]	66.4	68.0	18.5	18.0	170	44.0	102
Background soils	3	72.3	[28.2 - 116]	70.8	76.0	17.8	53.0	88.0	53.0	88.0
Forest soils	8	59.3	[39.1 - 79.4]	55.1	51.5	24.1	27.0	105	27.0	105
Natural soils	11	62.8	[47.7 - 78.0]	59.0	53.0	22.5	27.0	105	27.9	104
Horticultural soils	35	73.1	[68.4 - 77.7]	71.7	75.0	13.5	41.0	97.0	44.3	91.8
Pastoral soils	89	68.6	[64.6 - 72.5]	66.2	68.0	18.8	18.0	170	43.0	95.4
Farmed soils	124	69.8	[66.7 - 73.0]	67.7	69.5	17.6	18.0	170	43.0	94.3
Urban soils	-	-	-	-	-	-	-	-	-	-

Appendix 3.8 Summary Statistics for AR Zinc in Taranaki Background, Forest, Natural, Horticultural, Pastoral, Farmed and Urban Soils

Land use category	<i>n</i>	Mean	95% CI	Geo mean	Mdn	SD	Min	Max	5th %tile	95th %tile
All land use types combined	20	69.4	[55.5 - 83.3]	64.6	65.0	29.8	37.0	164	37.0	136
Background soils	2	56.0	[185 - 297]	52.7	56.0	26.9	37.0	75.0	37.0	75.0
Forest soils	3	49.7	[11.1 - 88.3]	48.1	45.0	15.5	37.0	67.0	37.0	67.0
Natural soils	5	52.2	[30.2 - 74.2]	49.9	45.0	17.7	37.0	75.0	37.0	75.0
Horticultural soils	2	92.0	[73.2 - 257]	91.1	92.0	18.4	79.0	105	79.0	105
Pastoral soils	12	73.1	[51.6 - 94.6]	67.9	63.5	33.8	47.0	164	47.0	158
Farmed soils	14	75.8	[57.2 - 94.4]	70.8	68.0	32.2	47.0	164	47.0	153
Urban soils	-	-	-	-	-	-	-	-	-	-

Appendix 3.9 Summary Statistics for AR Zinc in Wellington Background, Forest, Natural, Horticultural, Pastoral, Farmed and Urban Soils

Land use category	<i>n</i>	Mean	95% CI	Geo mean	Mdn	SD	Min	Max	5th %tile	95th %tile
All land use types combined	117	67.5	[64.0 - 71.1]	64.7	66.3	19.4	28.7	137	37.2	95.3
Background soils	11	63.1	[49.9 - 76.3]	60.5	54.0	19.6	37.0	95.0	37.6	94.8
Forest soils	8	47.1	[31.8 - 62.4]	44.5	45.0	18.3	29.5	87.0	29.5	87.0
Natural soils	19	56.3	[46.6 - 66.1]	53.1	50.0	20.3	29.5	950	29.7	93.2
Horticultural soils	40	72.5	[66.1 - 78.8]	69.7	72.4	19.8	28.7	137	40.6	102
Pastoral soils	47	67.4	[62.2 - 72.7]	65.0	66.0	17.9	29.0	120	40.3	93.9
Farmed soils	87	69.8	[65.7 - 73.8]	67.1	69.0	18.9	28.7	137	40.7	95.7
Urban soils	1	41.0	-	41.0	41.0	-	41.0	41.0	41.0	41.0

3.11 References

- Alloway, B. (2008a). *Copper and zinc in soils: too little or too much?* Paper presented at the New Zealand Trace Elements Group Conference, Waikato University, Hamilton, New Zealand.
- Alloway, B. (2008b). *Zinc in soils and crop nutrition*. France: International Zinc Association & International Fertilizer Industry Association.
- Alloway, B. (2009). Soil factors associated with zinc deficiency in crops and humans. *Environmental Geochemistry and Health*, 31(5), 537-548. doi: 10.1007/s10653-009-9255-4
- Baker-Austin, C., Wright, M., Stepanauskas, R., & McArthur, J. (2006). Co-selection of antibiotic and metal resistance. *Trends in Microbiology*, 14(4), 176-182.
- Bradl, H. (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science*, 277(1), 1-18.
- Brenchley, W. (1936). The essential nature of certain minor elements for plant nutrition. *The Botanical Review*, 2(4), 173-196.
- European Communities. (2004). *Risk assessments on zinc and zinc compounds. EC Regulation 793/93. Draft versions of 9 February 2004 (environment) and October 2003 (health)*. Bilthoven, The Netherlands.
- Gaw, S., Northcott, G., Kim, N., Wilkins, A., & Jensen, J. (2012). Comparison of earthworm and chemical assays of the bioavailability of aged 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene, 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane, and heavy metals in orchard soils. *Environmental Toxicology and Chemistry*, 31(6), 1306-1316.
- Hewitt, A. (1998). *New Zealand soil classification* (2nd ed.). Lincoln, New Zealand: Manaaki Whenua Press.

- Kabata-Pendias, A. (2010). *Trace elements in soils and plants*: CRC press.
- Kabata-Pendias, A. (2011). *Trace elements in soils and plants* (4th ed.). Boca Raton: CRC Press.
- Kabata, A., & Pendias, H. (2001). *Trace elements in soils and plants*. New York: CRC Press.
- Kiekens, L. (1995). Zinc. In B. Alloway (Ed.), *Heavy metals in soils*. London: Blackie Academic and Professional.
- Kim, N. (2008). *Cadmium accumulation in Waikato soils*. Environment Waikato Regional Council.
- Land Monitoring Forum. (2009). *Land and soil monitoring: A guide for SoE and regional council reporting*. New Zealand: Land Monitoring Forum.
- Longhurst, R., Roberts, A., & Waller, J. (2004). Concentrations of arsenic, cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, 47(1), 23-32.
- McBride, M., Sauve, S., & Hendershot, W. (1997). Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science*, 48(2), 337-346.
- McBride, M., & Spiers, G. (2001). Trace element content of selected fertilizers and dairy manures as determined by ICP-MS. *Communications in Soil Science and Plant Analysis*, 32(1-2), 139-156.
- McLaughlin, M., Tiller, K., Naidu, R., & Stevens, D. (1996). Review: the behaviour and environmental impact of contaminants in fertilizers. *Soil Research*, 34(1), 1-54.

- Mills, T., Robinson, B., & Clothier, B. (2004). *The accumulation of heavy metals in Waikato's productive sector environments. HortResearch Client Report 13155/2004*. Hamilton, New Zealand: Environment Waikato.
- NZ Nutrition Foundation. (2015). Zinc. Retrieved March 22, 2015, from <http://www.nutritionfoundation.org.nz/nutrition-facts/minerals/zinc>
- Sowry, G. (2011). *Scoping report - volumes and quality of facial eczema zinc. Prepared for Environment Waikato*. Hamilton, New Zealand: Contaminated Site Investigations.
- Taranaki Daily News. (2012, 23/08/2012). Nickel is found to make all the difference to cows. Retrieved January 7, 2015, from <http://www.stuff.co.nz/taranaki-daily-news/lifestyle/7531473/Nickel-is-found-to-make-all-the-difference-to-cows>
- Taylor, M., Kim, N., & Hill, R. (2011). *A trace element analysis of soil quality samples from the Waikato region*. Paper presented at the 24th Annual FLRC Workshop: Adding to the knowledge base for the nutrient manager.
- Ure, A., & Berrow, M. (1982). The elemental constituents of soils. In H. Bowen (Ed.), *Environmental Chemistry 2*. London: The Royal Society of Chemistry.

Chapter 4. Zinc in Waikato River Surface water

The following chapter will present and discuss surface water data for Waikato River in the order of: summary statistics (Section 4.1), compliance with the ANZECC Guidelines (Section 4.2), changes in Zn concentration with distance down the River (Section 4.3), potential sources of additional Zn (Section 4.4), and the influence of rainfall and flows on Zn concentrations (Section 4.5). Methods for the data analysis can be found in Section 2.3.3.

4.1 Summary Statistics

Summary statistics for Waikato River surface water data are presented in Table 4.1.

Table 4.1 Summary Statistics for Waikato River Surface Water Sampling

Variable	Units	<i>n</i>	Mean	95% CI	Mdn	SD	Min	Max
TZn	µg/L	113‡	4.19	[3.32 - 5.06]	2.70	4.65	1.00	29.0
DZn	µg/L	115§	1.83	[1.49 - 2.17]	1.00	1.82	1.00	11.0
D/T Zn		113	0.547	[0.498 - 0.596]	0.529	0.261	0.127	1.08**
River flow	m ³ /s	106	277	[249 - 305]	245	146	51.0	920
Turb	NTU	118	5.48	[3.95 - 7.02]	1.98	8.42	0.210	52.0
EC	mS/m	118	15.9	[15.5 - 16.3]	16.2	2.08	11.6	21.2
TDS	g/m ³	118	119	[116 - 122]	120	18.0	73.0	155
pH	pH Units	118	7.37	[7.33 - 7.41]	7.40	0.22	6.80	7.80
A340	AU 1cm Cell	118	0.014	[0.012 - 0.016]	0.01	0.013	<0.002	0.060
A440	AU 1cm Cell	118	0.003	[0.003 - 0.004]	0.002	0.002	<0.002	0.011
A780	AU 1cm Cell	118	<0.002	-	<0.002	-	<0.002	<0.002
DO	mg/L	118	9.56	[9.40 - 9.71]	9.50	0.848	8.00	12.2
BOD5	mg/L	118	1.02	[0.935 - 1.11]	0.925	0.472	<0.4	4.10
NPOC	mg/L	118	2.17	[1.90 - 2.44]	1.70	1.48	0.590	7.50
NO3 -N	mg/L	118	0.251	[0.202 - 0.300]	0.170	0.270	<0.002	1.10
NOx -N	mg/L	118	0.255	[0.205 - 0.305]	0.170	0.274	<0.002	1.20
NO2 -N	mg/L	118	0.003	[0.003 - 0.004]	0.002	0.002	<0.002	0.011
NH4 -N	mg/L	118	0.015	[0.013 - 0.016]	0.010	0.008	<0.01	0.051
TKN	mg/L	118	0.212	[0.184 - 0.241]	0.172	0.156	0.050	1.12
TP	mg/L	118	0.040	[0.034 - 0.045]	0.031	0.029	<0.004	0.120
DRP	mg/L	118	0.015	[0.014 - 0.017]	0.015	0.009	<0.004	0.045

Table 4.1 continues on pg. 100

‡ 5 total zinc outliers removed

§ 3 dissolved zinc outliers removed

** Result most likely attributable to normal random measurement error

Table 4.1 Continued

Variable	Units	n	Mean	95% CI	Mdn	SD	Min	Max
As	mg/L	118	0.022	[0.021 - 0.024]	0.023	0.009	0.006	0.050
B	mg/L	118	0.262	[0.247 - 0.277]	0.260	0.082	0.093	0.50
Cl	mg/L	118	18.1	[17.2 - 18.9]	18.0	4.54	8.20	32.0
Li	mg/L	118	0.087	[0.081 - 0.093]	0.088	0.031	0.031	0.170
Chlora	mg/L	118	0.008	[0.007 - 0.009]	0.007	0.006	<0.003	0.043
Ent	cfu/100 mL	118	178	[88.8 - 267]	22.5	489	<1	3100
E coli	cfu/100 mL	118	272	[155 - 389]	42.0	643	<1	3200
FC	cfu/100 mL	118	337	[192 - 481]	50.5	793	<1	4000

Abbreviations: TZn, total Zn; DZn, dissolved Zn; D/T Zn, dissolved to total Zn ratio; Turb, turbidity; EC, electrical conductivity; TDS, total dissolved solids; A340, absorbance at 340 nm ; A440, absorbance at 440 nm; A780, absorbance at 780 nm; DO, dissolved oxygen; BOD5, Biological oxygen demand; NPOC, non-purgeable organic carbon; OC, organic carbon; NO₃ –N, Nitrate nitrogen; NO_x –N, Nitrate-N + Nitrite-N; NO₂ –N, Nitrite-N; NH₄ –N, Total Ammoniacal Nitrogen; TKN, Total Kjeldahl Nitrogen (TKN); TP, Total phosphorus; DRP, Dissolved Reactive Phosphorus; As, Arsenic; B, Boron; Cl, Chloride; Li, Lithium; Chlora, Chlorophyll A; Ent, Enterococci; E coli, Escherichia coli; FC, Faecal coliforms

Excluding outliers, total Zn concentrations in the Waikato River ranged from <1 to 29 µg/L. Most individual sample results were toward the lower end of this range, giving an overall median of 2.7 µg/L (mean 4.2 µg/L).

Typical dissolved Zn concentrations in freshwaters can range from 0.06 µg/L to 2 µg/L, with values between 2 µg/L and 7 µg/L being less common, and >7 µg/L uncommon (Gaillardet, Viers, & Dupré, 2003). It therefore appears that dissolved Zn in the Waikato River is at the high end of the concentration range expected for freshwaters (Table 4.1). Possible reasons for this apparent enrichment include the influence of geothermal sources and farming runoff and these are discussed further below.

On average, just over half (55%) of the Zn in the Waikato River was being carried in the ‘dissolved’ (<0.45 µm) fraction (Table 4.1). Some of the high and low dissolved/total Zn ratios involved non-detections of either dissolved Zn or both fractions: however excluding these cases only changed the mean dissolved/total ratio marginally: from 0.55 to 0.47.

Multiplying the average Zn concentration (4.2 mg/m³) by the average flow (277 m³/s) (e.g. Table 4.1) provides an estimate of the total load of Zn being carried by the Waikato River past an average point: 1163.4 mg/s. This translates to 100.5 kg/day, or 36.7 t/y. It can therefore be seen that the Waikato River transports a substantial amount of Zn because it is (a) a large river and (b) a river with higher than typical Zn.

4.2 Compliance with Water Quality Guidelines

The dissolved Zn results obtained during the study period were assessed for compliance with the 95% freshwater trigger value of 8 µg/L derived in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000) (Section 1.2.3).

Compliance with the 8 µg/L trigger value was achieved 98.3% of the time, with the exception of two results: 11 µg/L dissolved Zn, sampled from the Ohaaki Bridge

sample site on August 3, 2009, and 10 µg/L dissolved Zn, sampled from the Taupo Gates sample site on August 3, 2009. Both exceedances are marginal and could be attributed to contamination of the sample or analytical variability, given that both exceedances occurred on the same day and that such concentrations were recorded only once at each site. These two results were also exceptions, and mean and median concentrations of dissolved Zn ($N=115$) being 1.8 µg/L and 1.0 µg/L, respectively (Table 4.1). Overall, this comparison shows that Zn concentrations in the Waikato River are not at levels that would be expected to cause any noticeable toxicity to aquatic organisms.

4.3 Concentration vs Distance

Summary statistics for total and dissolved Zn (Table 4.2 and Table 4.3 respectively) show that total and dissolved Zn were at higher concentrations in the upper and lower areas of the Waikato River than in its mid reaches. Figure 4.1 shows the relationship between total and dissolved Zn with Waikato River sampling sites during the study period.

Table 4.2 Annual Mean Total Zn by Sample Site

Location	<i>n</i>	Distance from Lake Taupo (km)	Average TZn (µg/L)	SD (µg/L)
Taupo Gates	11	0.1	7.09	5.76
Ohaaki Bridge	11	36.5	5.46	6.35
Ohakuri Tailrace Bridge	11	75.8	7.84	8.22
Whakamaru Tailrace	10	105.0	1.31	0.28
Waipapa Tailrace	12	126.1	1.24	0.25
Hamilton – Narrows	12	202.2	1.60	0.76
Horotiu Bridge	12	225.6	2.36	0.95
Huntly – Tainui Bridge	12	246.5	4.74	2.18
Mercer Bridge	10	286.3	6.96	5.40
Tuakau Bridge	12	296.8	3.95	1.63

Table 4.3 Annual Mean Dissolved Zn by Sample Site

Location	<i>n</i>	Distance from Lake Taupo (km)	Average dissolved Zn ($\mu\text{g/L}$)	SD ($\mu\text{g/L}$)
Taupo Gates	12	0.1	3.45	2.69
Ohaaki Bridge	11	36.5	2.69	3.09
Ohakuri Tailrace Bridge	11	75.8	3.03	2.17
Whakamaru Tailrace	10	105.0	1.01	0.03
Waipapa Tailrace	12	126.1	1.02	0.06
Hamilton – Narrows	12	202.2	1.02	0.06
Horotiu Bridge	12	225.6	1.02	0.04
Huntly – Tainui Bridge	12	246.5	1.56	1.13
Mercer Bridge	11	286.3	2.35	2.19
Tuakau Bridge	12	296.8	1.25	0.39

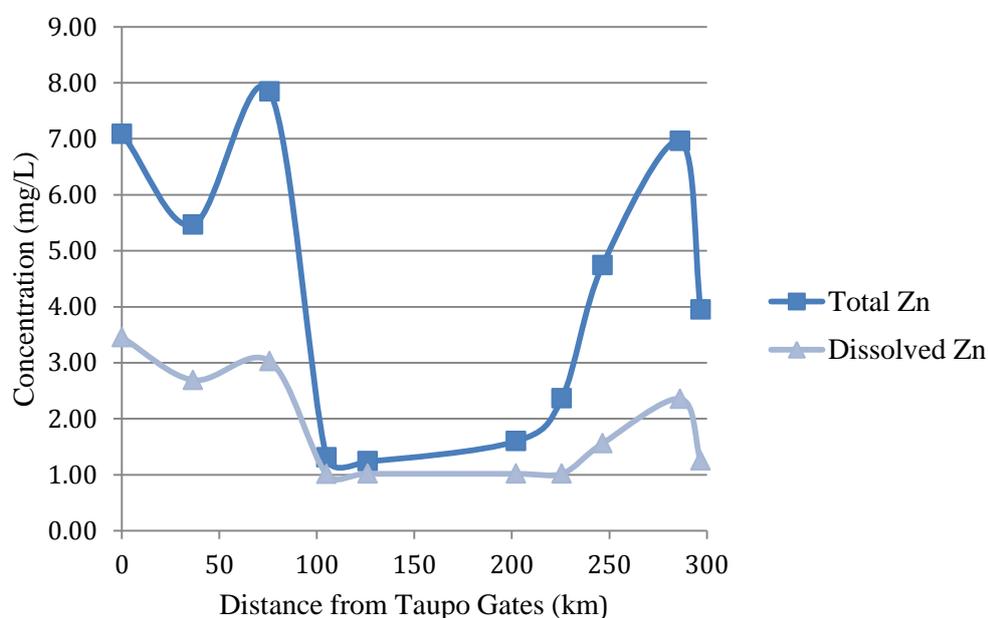


Figure 4.1 Changes in Annual Mean Dissolved and Total Zn Concentrations with Distance Along the Waikato River

To test this idea, data was further grouped into upper, mid and lower reaches of the Waikato River to test for statistical significance of the groups means (Table 4.4). In this analysis, ‘upper’ refers to the three sites from Taupo Gates to Ohakuri Tailrace Bridge, ‘mid’ covers the four sites from Whakamaru Tailrace to Horotiu Bridge, and ‘lower’ refers to the three sites from Huntly/Tainui Bridge to Tuakau Bridge (see Table 4.2 and Table 4.3).

Table 4.4 Results of Pooled t-tests on Differences in Mean Zn Concentrations Between the Upper, Mid and Lower Reaches of the Waikato River

Variable	Pooled t-test hypothesis on means		
	Upper > Mid	Lower > Mid	Upper > Lower
Dissolved Zn, µg/L	Yes, p<0.0001	Yes, p<0.043	No, p=0.32
Total Zn, µg/L	Yes, p<0.0001	Yes, p<0.0017	No, p=0.57
Dissolved/total ratio	No, p=0.29	No, p=1.0*	Yes, p=0.039

* (In this case the alternative hypothesis is that Mid>Lower gives: Yes, p<0.0001)

Results for dissolved and total Zn show two features. Firstly, dissolved and total Zn concentrations in the upper reaches of the Waikato River (0 - 76 km from Lake Taupo) are statistically indistinguishable from those in its lower reaches (from 246 km onward). Secondly, Zn concentrations in both of these areas are statistically higher than those in the Waikato River's mid-reach sampling sites (spanning approximately 105-225 km from Lake Taupo) (Table 4.4).

It was suggested above (Section 4.1) that Zn concentrations in the Waikato River are at the upper end of those expected internationally. For this reason, it is thought that the differences shown in Table 4.2 and Table 4.3 are most likely to represent relative enrichment of Zn in the upper and lower reaches of the Waikato River, rather than depletion of Zn in the river's mid-reaches. This in turn suggests the presence of two distinct sources of additional Zn to the Waikato River, as will be discussed further below.

A third outcome of t-testing was an observation that in lower reaches of the Waikato River, the ratio of dissolve to total Zn drops substantially. The mean ratios of dissolved/total Zn are statistically higher in both the upper and mid reaches than for the lower reaches (Table 4.4, Figure 4.2).

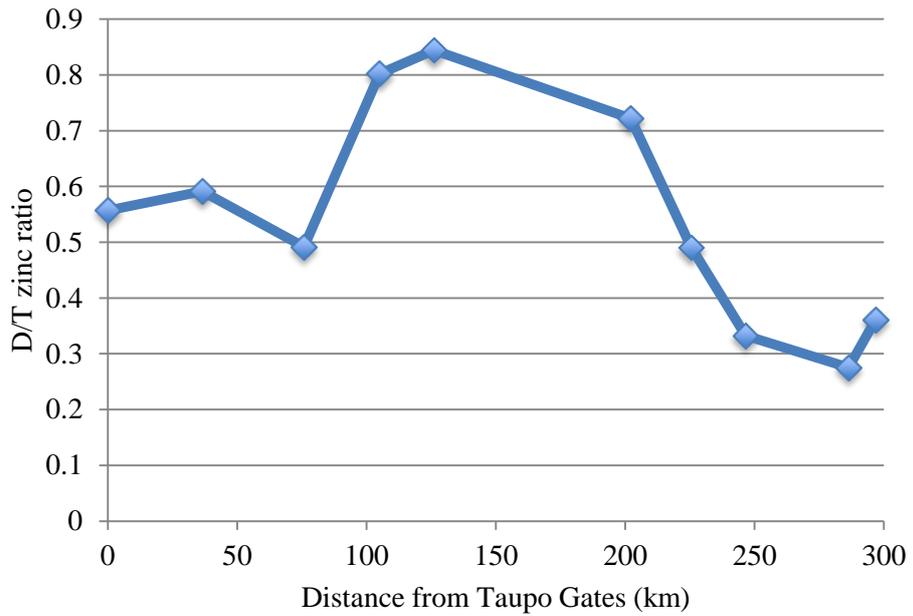


Figure 4.2 *Changes in annual mean ratios of dissolved/total Zn with distance from Taupo Gates*

Given that total Zn is a measure of both dissolved Zn and Zn that is present in the particulate matter, low ratios of dissolved/total Zn probably indicate that more particulate matter is present in the water, which would increase turbidity. This interpretation is supported by an analysis of the behaviour of turbidity with distance along the Waikato River (Figure 4.3) where a substantial increase in mean turbidity can be seen over the same three lower-reach sites that show the lowest dissolved/total Zn ratios. Surface water at sample sites closest to Lake Taupo were found to be less turbid than surface water downstream; the cause of this is discussed below.

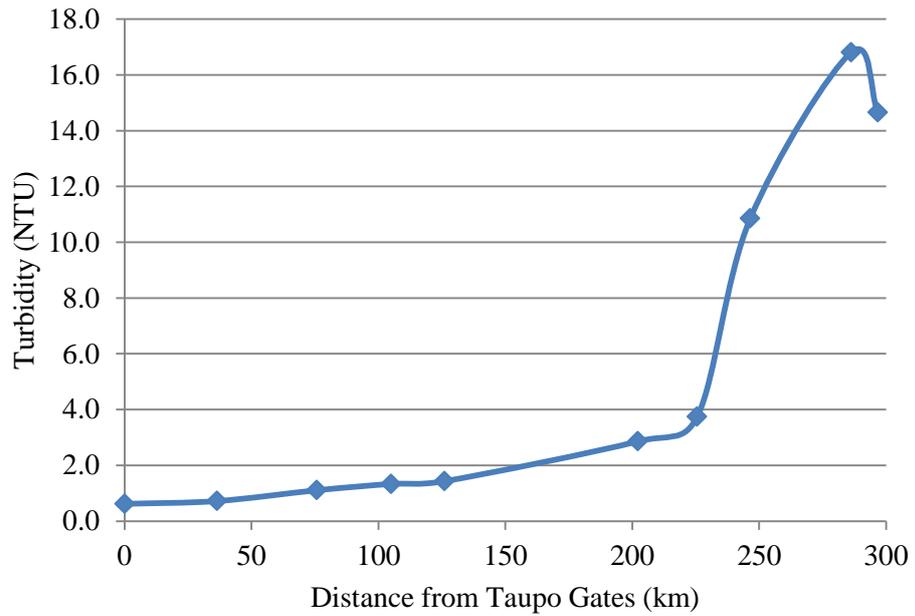


Figure 4.3 *Changes in annual mean turbidity in Waikato River water with distance from Taupo Gates*

4.4 Sources of Additional Zinc

Results of the previous sections suggests that Zn concentrations appear to be enriched in the upper and lower reaches of the River, suggesting the presence of two or more unique sources. To identify potential sources of additional Zn, correlations can be examined for relationships shown by other variables for which sources are known (Table 4.5).

Table 4.5 Correlation Coefficients for Zn and other Variables, Distance, and Dissolved/Total Zn Ratios in Waikato River Surface Water. Relationships of $p < 0.001$ or better are shown in Bold Italic*

Variable	TZn (mg/L)	DZn (mg/L)	Distance (km)	D/T Zn
TZn	1			
DZn	0.788	1		
Distance	-0.125	-0.294	1	
D/T Zn	-0.442	-0.053	-0.382	1
Site	-0.121	-0.291	0.992	-0.384
River Flow	-0.048	-0.189	0.434	-0.294
Turb	0.135	0.072	0.600	-0.522
EC	-0.036	-0.027	0.084	0.173
TDS	-0.099	-0.160	0.217	0.140
pH	0.026	0.000	-0.082	0.030
A340	0.041	-0.112	0.735	-0.474
A440	0.126	0.016	0.581	-0.476
A780	-	-	-	-
DO	0.123	0.117	-0.223	-0.063
BOD ⁵	-0.016	0.055	0.290	-0.276
NPOC	0.042	-0.103	0.707	-0.488
DNPOC	0.025	-0.077	0.667	-0.441
NO ₃ -N	0.054	-0.056	0.681	-0.413
NO _x -N	0.054	-0.055	0.679	-0.411
NO ₂ -N	0.125	0.039	0.44	-0.337
NH ₄ -N	-0.034	-0.076	0.204	-0.014
TKN	0.043	0.008	0.682	-0.494
TP	0.021	-0.121	0.776	-0.464
DRP	-0.065	-0.259	0.680	-0.317
As	-0.032	0.010	-0.29	0.350
B	-0.076	0.009	-0.353	0.337
Cl	-0.028	-0.045	0.110	0.130
Li	-0.097	-0.034	-0.218	0.338
Chlora	-0.099	-0.253	0.580	-0.293
Ent	-0.017	-0.016	0.204	-0.142
E coli	0.065	-0.052	0.375	-0.367
FC	0.044	-0.068	0.364	-0.307

*Note: For most relationships N=115 pairs: $R > \pm 0.183$ is $p < 0.05$; $R > \pm 0.217$ is $p < 0.02$; $R > \pm 0.239$ is $p < 0.01$; $R > \pm 0.303$ is $p < 0.001$, and $R > \pm 0.355$ is $p < 0.0001$.

See Table 4.1 for abbreviations.

Overall, the non-linear variation of Zn concentrations along the Waikato River results in a weak overall correlation between both Zn (either total or dissolved) and distance. Noteworthy relationships include negative correlations between distance

and dissolved/total Zn, As, and B, and positive associations between distance and P, N, and DNPOC (all $p < 0.001$ or better, Table 4.5).

These R-values reflect the strength of overall linear trend lines but obscure some details that are evident in graphs of concentrations versus distance (e.g. Figure 4.1). A closer look these relationships, as well as other potential influencing factors (such as local geology and human activity) may help to explain why Zn concentrations appear higher in the upper and lower areas of the river.

Considering first the negative correlations between distance and dissolved/total Zn, As, and B. Higher concentrations of these particular elements in the upper reaches of the river, relative to the middle and lower reaches, are likely to exist due to the geological makeup of the upper Waikato River, closest to Lake Taupo. This region is classified as the Taupo Volcanic Zone (TVZ) and encompasses a number of geothermal systems which extend across the North Island from Mt Ruapehu to White Island (Harding, Mosley, Pearson, & Sorrell, 2004).

A significant amount of geothermal fluid discharges into lakes and streams in the TVZ, including Lake Taupo, as well as the Waikato River and the Wairakei and Wai-O-Tapu areas near Rotorua (MfE, 2013). According to Timperley and Huser (1996), the Wai-O-Tapu catchment contributes 13.6 t/yr of geothermal fluid. Other catchments, such as the Whirinaki, Whangapoa, and Waipapa/Mokai catchments contribute 2.5 t/yr, 1.8 t/yr, and 4.8 t/yr respectively.

In addition to inflows from geothermal catchments are the geothermal contributions of nine power stations situated within the Waikato region. Four of these are located at the Wairakei geothermal field, before the second sample site (Ohaaki Bridge). Inflows of geothermal fluid chemicals into the Waikato River were studied by Timperley and Huser (1996), who found that 88t/yr of arsenic is contributed to the Waikato river by the Wairakei geothermal Power Station and a further 23 t/yr from other sources in the Wairakei field.

Various trace elements are present in geothermal fluids, at elevated concentrations, e.g. Cu, Ni, Hg, Pb, Al, Mn, As, F, Li, B and Zn (Parfitt, Schipper,

Baisden, & Elliott, 2006). In the present study, Ar, Li and B, are highly inter-correlated with each other (As-Li: $R=0.921$; B-Li: $R=0.957$; As-B: $R=0.898$ for 118 pairs, all $p<0.000001$). Relative changes in annual mean concentrations of these three elements with distance are shown below, in Figure 4.4.

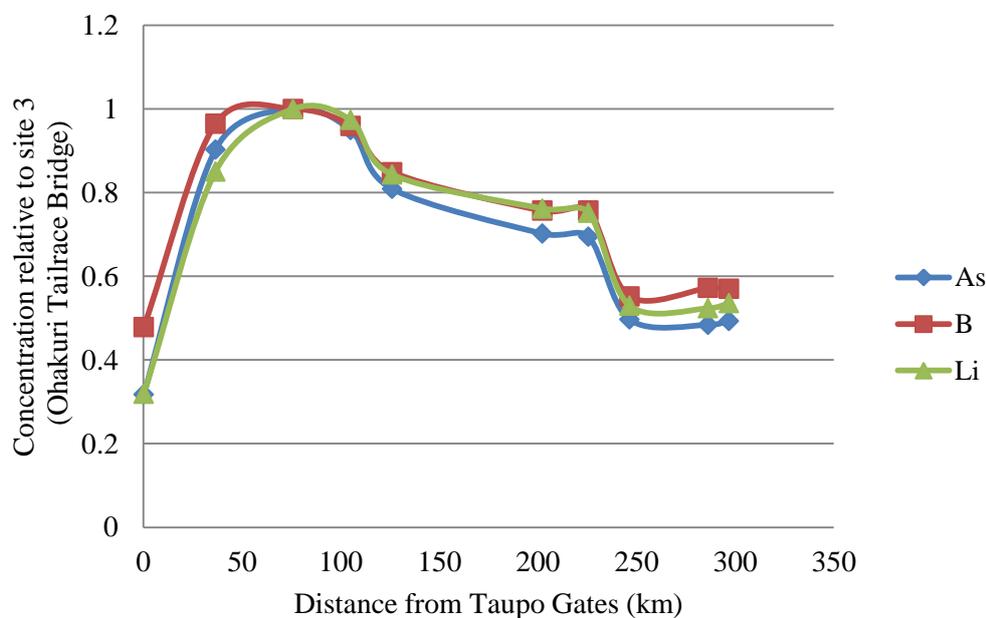


Figure 4.4 *Relative Changes in Annual Mean Concentrations of As, Li and B in Waikato River Water with Distance from Taupo Gates*

Each of these trace elements appear to increase considerably, and are most concentrated within the first 100 km (i.e. Taupo Gates - Ohakuri Tailrace Bridge) (Figure 4.4). The Ohaaki Bridge sample site is located immediately downstream from the Wairakei geothermal field and power stations. As the surface water flows further downstream away from the TVC, dilution, as well as sorption to suspended and bed sediments, is most likely responsible for the reduction in concentrations and would thus have little impact on concentrations in the middle and lower sections of the Waikato River.

It should be noted that As, Li, and B concentrations are already elevated relative to their natural ranges in freshwaters at the origin of the Waikato River at Taupo Gates, reflecting the input of geothermal fluid from the bed of Lake Taupo itself. For example, the annual mean concentration of As at this location is $10.4 \mu\text{g/L}$, which is

marginally higher than the New Zealand Drinking Water Standard of 10 µg/L. In the upper reaches of the Waikato River, Zn concentrations are also high at Taupo Gates (site 1), but then dip at Ohaaki Bridge (site 2), before peaking (like As, B and Li) at Ohakuri Tailrace Bridge (site 3).

The main difference in behaviour between Zn and the geothermal tracer elements is that Zn appears to be lost from the water column more readily than As, B, or Li. This effect can be seen in both the drop in Zn concentrations at site 2, and drop in Zn concentrations between sites 3 and 4 (Figure 4.1). The most likely explanation is that adsorption losses of Zn to suspended and bed sediment is relatively rapid and significant when compared to As, B, or Li.

The existence of two peaks in Zn concentrations, one at Taupo Gates and the other at site 3 (Ohakuri Tailrace Bridge) where As, B and Li also peak, provides strong support for the idea that most Zn in water of the upper Waikato River between these two locations is likely to be of geothermal origin. The rapid decreases once geothermal sources have been passed signal the presence of reasonably efficient removal processes.

Considering now the positive associations between distance and turbidity ($p < 0.0001$, Table 4.5). Mean turbidity levels increase significantly in the lower reach of the River relative to the middle and upper reaches, specifically between the Horotiu Bridge and Tuakau Bridge sample sites, where the Waipa River converges with the Waikato River. The Waipa River - the largest tributary to the Waikato River - flows through farmland with relatively soft erodible land, resulting in generally higher sediment and nutrient loads and a decrease in visual and chemical water quality (Harding et al., 2004; PCE, 2013; Waikato Regional Council, 2014a). Turbidity in rivers usually ranges from 2-50 NTU, but can be in the thousands during flood events (PCE, 2013). Median Waikato River surface water turbidity results ($N=113$) were just under this range, at 1.98 NTU. The maximum turbidity result obtained was 52 NTU.

Increased fine sediment in water not only causes a reduction in visual clarity but also contributes to faecal microbial contamination and enrichment of nutrient

elements N, P, and C (Davies-Colley, 2013; McDowell, Larned, & Houlbrooke, 2009; McDowell, Muirhead, & Monaghan, 2006). N and P are essential for aquatic plant life but high concentrations of these nutrients (i.e. above guideline values) can promote excessive aquatic plant growth, resulting in blooms of algae and nuisance weeds. This, in turn, degrades river water quality, chemically and aesthetically, which can affect fish and other aquatic animals (Harding et al., 2004; MfE, 2013; PCE, 2013).

In the present study, nutrient elements P, N, and C were positively associated with distance from the Taupo Gates sample site, meaning that these elements were most concentrated at sites farthest away from the Taupo Gates sample site (Table 4.5, Figures 4.5 - 4.7). Additionally, low dissolved to total Zn ratios in the lower reach of the River (Figure 4.2) indicate that more particulate matter is present, causing increased turbidity and potentially contributing to nutrient and Zn concentrations.

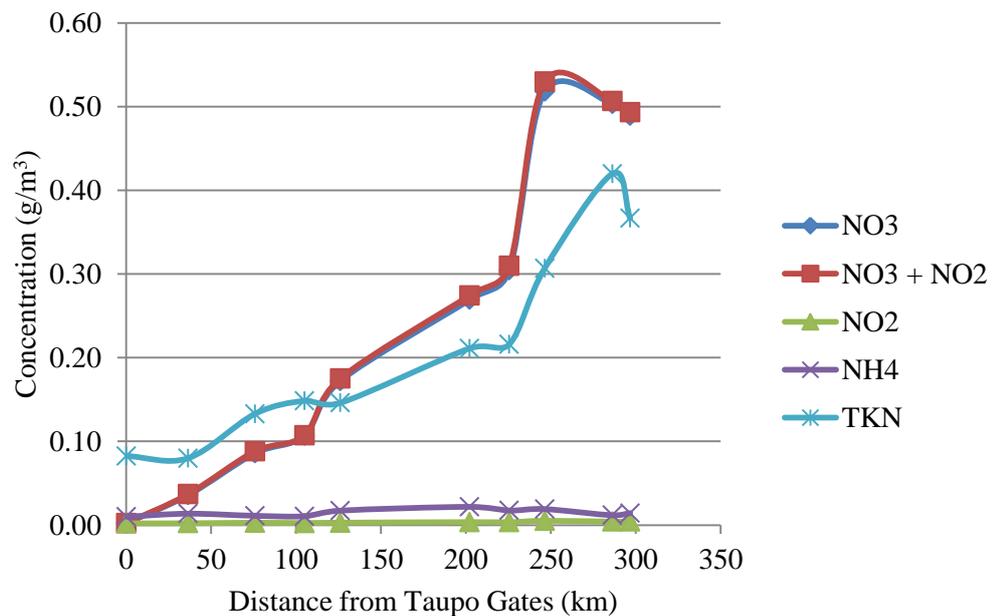


Figure 4.5 Changes in annual mean concentration of nitrite (NO_3), nitrite-n + nitrate-n ($NO_3 + NO_2$), nitrate (NO_2), total ammoniacal-n (NH_4) and total kjeldahl-n (TKN) in Waikato River water with distance from Taupo Gates

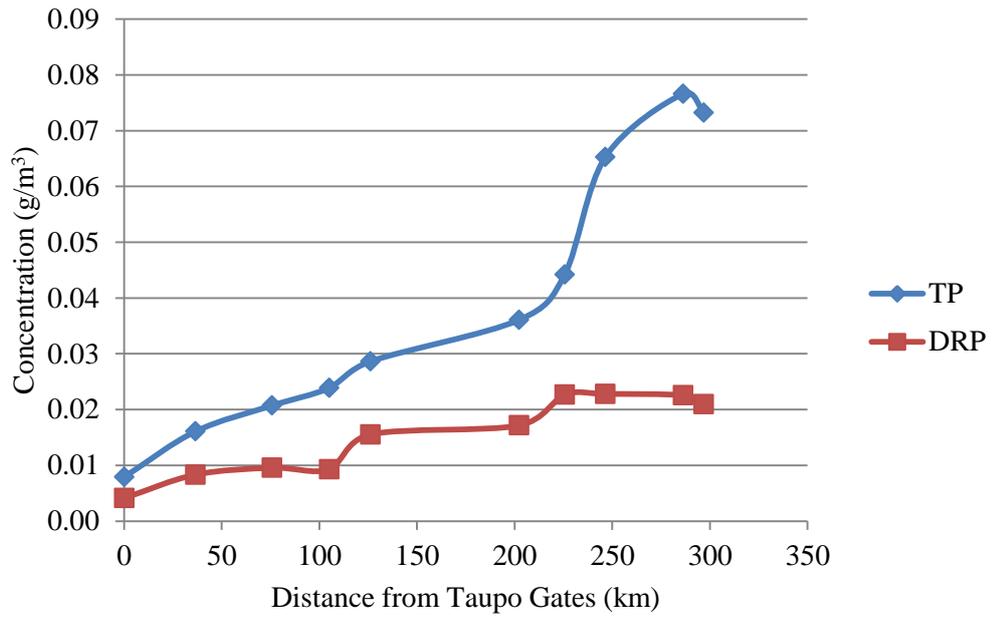


Figure 4.6 Changes in annual mean concentration of total phosphorus (TP) and dissolved reactive phosphorus (DRP) in Waikato River water with distance from Taupo Gates

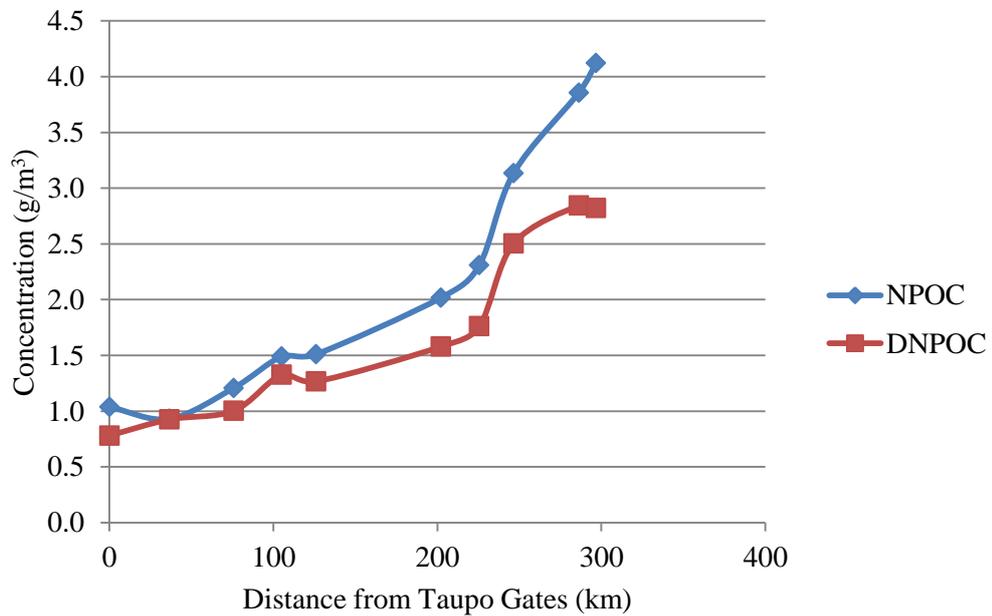


Figure 4.7 Changes in annual mean concentration of non-purgeable organic carbon (NPOC) and dissolved non-purgeable organic carbon (DNPOC) in Waikato River water with distance from Taupo Gates

In the Waikato region, pastoral farming and exotic forestry account for 58% and 12% of land use respectively (Waikato Regional Council, 2014b). Increased cattle stocking rates, fertiliser inputs and soil erosion in agricultural areas can cause significant seepage of these nutrients to groundwater and runoff into lakes and streams (Abell, Özkundakci, Hamilton, & Miller, 2011; Elliott et al., 2005; Monaghan et al., 2007; PCE, 2013; Smith, 2003). The existence of the third peak in Zn concentration along the River (Figure 4.1) in conjunction with peaks in N and P provides strong support for the idea that most Zn in water of the lower Waikato River is likely to be of agricultural origin.

4.5 Influence of Rainfall and Flows on Zinc Concentrations

In estimating mass flows of Zn being carried by the Waikato River, a decision was made to focus on the first site downstream of the hydrodams (Hamilton-Narrows) and the first site after the confluence of the Waipa River (Huntly). Justification for this is included in Section 2.3.3. Flows from the Waipa River were calculated using the difference in measured flow before on the Waikato River and after convergence (Table 4.6).

Table 4.6 Mass Flows and Ratios of Total and Dissolved Zn in the Waikato River

Averages	Flow	Mass of dissolved Zn	Mass of total Zn	D/T	T/D
(Units)	m ³ /s	kg/day	kg/day		
Waikato River at Hamilton	255	22.7	39.1	0.719	1.39
Waipa River & catchment	149	36.9	143	-	-
Total at Huntly	404	59.5	182	0.332	3.01
Percentages	Flow	Mass of dissolved Zn	Mass of total Zn	D/T	T/D
(Units)	%	%	%	-	-
Waikato River at Hamilton	63.2	38.1	21.5	-	-
Waipa River & catchment	36.8	61.9	78.6	-	-
Total at Huntly	100	100	100	-	-

Despite the fact that the Waipa River contributes only 37% of the total flow at Huntly, it contributes an estimated 62% and 79% of the dissolved and total Zn loads, respectively (2009-10) (Table 4.6). Part of the picture for the second figure (79%) is

that the ratio of dissolved/total Zn drops from 0.72 to 0.33, indicating that the Waipa River brings in a high suspended sediment load. This is consistent with earlier findings where turbidity, nutrient concentrations, and Zn concentrations were higher at sample points downstream of the Waipa-Waikato River convergence (Section 4.3).

Table 4.7 Correlation Matrix for Relationships between Mean Monthly River Flow at Huntly (m^3/s), Dissolved and Total Zn Concentrations, and Mass Loads of Zn

Variable	Number of pairs	R-value	p-value
Flow at Huntly	12	1	
Dissolved/total Zn ratio	12	-0.225	>0.1
Dissolved Zn concentration ($\mu g/L$)	12	0.457	>0.1
Total Zn concentration ($\mu g/L$)	12	0.699	<0.02
Dissolved Zn mass load (kg/day)	12	0.847	<0.001
Total Zn mass load (kg/day)	12	0.927	<0.0001

As River flow increased at Huntly, so did mass loads of total and dissolved Zn, and total Zn concentration ($p < 0.0001$, $p < 0.001$ and $p < 0.02$ respectively) (Table 4.7). This effect did not reach $p < 0.05$ for dissolved Zn, where more measurements are close to detection limits. However, having a flow-concentration relationship for total Zn suggests that as rainfall and catchment runoff increase, proportionately more Zn occurs than under typical lower flow conditions.

Three possible scenarios could account for the relationships observed between flow and Zn masses and concentrations presented in Table 4.7. Firstly, a relative increase in Zn concentration is outweighed by river volume, which would result in an overall decrease in Zn concentrations. Secondly, an increase in River flow would balance with the increase in Zn concentrations, which would result in no change. Thirdly, any relative increase in Zn concentration outweighs the increase in River volume, resulting in an overall increase in Zn concentration. This third scenario implies that rainfall is actively ‘scavenging’ available Zn and washing it through the system in significant amount. This scenario may be what is happening at the Huntly sites a significant increase in Zn concentration occurs here, most likely flushing through from surrounding agricultural land (via the Waipa River).

4.6 Chapter Summary

The Waikato River is a large body of water, carrying approximately 100.5 kg Zn/day (Section 4.1). Zn concentrations do not appear to be at levels that are expected to cause any noticeable toxicity to aquatic organisms (Section 4.2).

Zn concentrations peak in the upper reaches of the River, along with geothermal indicator elements Li, As, and B. This is likely to be caused by inputs from geothermal systems of the Taupo Volcanic Zone. Following this, a rapid decrease in Zn concentrations was observed in the mid-section of the River, indicating rapid adsorption to bed sediments. A distinct second peak in Zn concentrations in the lower reaches of the River corresponds to increased concentrations of nutrient elements and turbidity (Section 4.3). Additionally, elevated Zn concentrations during high-flow events suggest that Zn is being added to the water in sufficient quantities as to outweigh a dilution effect (Section 4.5).

These findings, in addition to the knowledge that intense pastoral farming occurs in the lower catchment areas of the Waikato River, suggest that anthropogenic Zn from the soil is being mobilised into the Waikato River (Section 4.4).

Possible entry of anthropogenic Zn into regional Waikato surface water is discussed in the following chapter.

4.7 References

- Abell, J., Özkundakci, D., Hamilton, D., & Miller, S. (2011). Relationships between land use and nitrogen and phosphorus in New Zealand lakes. *Marine and Freshwater Research*, 62(2), 162-175.
- ANZECC. (2000). National water quality management strategy paper 4. *Australian and New Zealand guidelines for fresh and marine water quality. Volume 2: Aquatic ecosystems - rationale and background information*. Canberra, Australia: ANZECC with ARMCANZ.
- Davies-Colley, R. (2013). *River water quality in New Zealand: an introduction and overview*. Lincoln, New Zealand: Manaaki Whenua Press, Landcare Research.
- Elliott, A., Alexander, R., Schwarz, G., Shankar, U., Sukias, J., & McBride, G. (2005). Estimation of nutrient sources and transport for New Zealand using the hybrid mechanistic-statistical model SPARROW. *Journal of Hydrology (New Zealand)*, 44(1), 1.
- Gaillardet, J., Viers, J., & Dupré, B. (2003). Trace elements in river waters. In H. Heinrich & K. Turekian (Eds.), *Treatise on Geochemistry* (pp. 225-272). Oxford: Pergamon.
- Harding, J., Mosley, M., Pearson, C., & Sorrell, B. (Eds.). (2004). *Freshwaters of New Zealand*. Christchurch, New Zealand: New Zealand Hydrological Society Inc and New Zealand Limnological Society Inc.
- McDowell, R., Larned, S., & Houlbrooke, D. (2009). Nitrogen and phosphorus in New Zealand streams and rivers: control and impact of eutrophication and the influence of land management. *New Zealand Journal of Marine and Freshwater Research*, 43(4), 985-995.

- McDowell, R., Muirhead, R., & Monaghan, R. (2006). Nutrient, sediment, and bacterial losses in overland flow from pasture and cropping soils following cattle dung deposition. *Communications in Soil Science and Plant Analysis*, 37(1-2), 93-108.
- MfE. (2013). Nutrients. Retrieved 3 December, 2014, from <http://www.mfe.govt.nz/more/environmental-reporting/fresh-water/river-condition-indicator/nutrients>
- Monaghan, R., Wilcock, R., Smith, L., TikkiSETTY, B., Thorrold, B., & Costall, D. (2007). Linkages between land management activities and water quality in an intensively farmed catchment in southern New Zealand. *Agriculture, Ecosystems & Environment*, 118(1-4), 211-222.
- Parfitt, R., Schipper, L., Baisden, W., & Elliott, A. (2006). Nitrogen inputs and outputs for New Zealand in 2001 at national and regional scales. *Biogeochemistry*, 80(1), 71-88.
- PCE. (2013). *Water quality in New Zealand: Land use and nutrient pollution*. Wellington, New Zealand: Parliamentary Commissioner for the Environment.
- Smith, V. (2003). Eutrophication of freshwater and coastal marine ecosystems a global problem. *Environmental Science and Pollution Research*, 10(2), 126-139.
- Timperley, M., & Huser, B. (1996). Inflows of geothermal fluid chemicals to the Waikato River catchment, New Zealand. *New Zealand Journal of Marine and Freshwater Research*, 30(4), 525-535.
- Waikato Regional Council. (2014a). How clean is the Waipa River? Retrieved 11 November, 2014, from <http://www.waikatoregion.govt.nz/Environment/Natural-resources/Water/Rivers/Waipas-River/How-clean-is-the-Waipas-River/>

Waikato Regional Council. (2014b). Land use in the Waikato. Retrieved 5
November, 2014, from
<http://www.waikatoregion.govt.nz/Environment/Natural-resources/Land-and-soil/Land-use-in-the-Waikato/>

Chapter 5. Zinc in Regional Waikato Surface water

As outlined in Section 2.2.2, regional surface water samples were obtained monthly from 100 sites for 12 months, from 2009-10, and continued for a second year for 15 sites of specific interest. The following subsections will focus predominantly on regional Waikato sites where Zn concentrations exceeded the ANZECC guideline trigger value of $<8 \mu\text{g/L}$; particularly focusing on instances where likely sources of additional Zn are not immediately apparent.

Additionally, River flow data for sites frequently exceeding the guidelines is examined to determine what impacts rainfall and increased river flows have on Zn loadings in Waikato regional surface waters.

5.1 Summary Statistics

Summary statistics for Zn and other variables in regional Waikato surface waters are given in Table 5.1.

Table 5.1 Summary Statistics for Zinc and other Variables in Regional Waikato Surface Water

Variable	Units	n	Mean	95% CI	Mdn	SD	Min	Max
TZn	µg/L	1115	5.62	[4.92 - 6.32]	2.60	11.9	0.500	180
DZn	µg/L	1115	2.72	[2.19 - 3.24]	0.500	8.94	0.500	151
D/T Zn		1115	0.470	[0.45 - 0.49]	0.380	0.340	0.010	3.40
A340	AU, 1 cm cell	1115	0.037	[0.035 - 0.040]	0.025	0.045	0.001	0.500
A440	AU, 1 cm cell	1115	0.007	[0.006 - 0.007]	0.005	0.008	0.001	0.083
A780	AU, 1 cm cell	1115	0.001	[0.001 - 0.001]	0.001	0.0001	0.001	0.004
pH	pH units	1115	7.26	[7.23 - 7.28]	7.30	0.402	3.90	8.70
EC	mS/m	1115	14.6	[13.9 - 15.3]	11.4	11.9	3.00	136
Turb	NTU	1115	11.6	[10.4 - 12.8]	4.90	20.0	0.093	320
DRP	mg/L	1115	0.039	[0.035 - 0.043]	0.017	0.071	0.002	1.20
TP	mg/L	1115	0.082	[0.074 - 0.090]	0.049	0.138	0.002	3.30
NO _x -N	mg/L	1115	0.735	[0.689 - 0.781]	0.470	0.777	0.001	4.60
NH ₄ -N	mg/L	1115	0.051	[0.042 - 0.059]	0.005	0.137	0.005	1.30
TKN	mg/L	1115	0.370	[0.344 - 0.395]	0.230	0.440	0.025	5.00
TN	mg/L	1115	1.10	[1.04 - 1.16]	0.745	1.02	0.026	8.80

Abbreviations: TZn, total Zn; DZn, dissolved Zn; D/T Zn, dissolved to total Zn ratio; A340, absorbance at 340 nm ; A440, absorbance at 440 nm; A780, absorbance at 780 nm; EC, electrical conductivity; Turb, turbidity; TP, Total Phosphorus; DRP, Dissolved Reactive Phosphorus; NO_x -N, Nitrate-N + Nitrite-N; ; NH₄ -N, Total Ammoniacal Nitrogen; TKN, Total Kjeldahl Nitrogen (TKN); TN, Total Nitrogen.

Total Zn concentrations in surface waters sampled in the Waikato region during the study period ranged from 1 µg/L to 180 µg/L, however the majority of individual total Zn concentrations were at the lower end of this range, yielding an overall median of 3 µg/L and an average of 6 µg/L ($N=1115$).

It therefore appears that Zn concentrations in sampled surface waters are, on average, slightly greater than that expected in freshwaters, where concentrations most commonly lie between 0.06 µg/L to 2 µg/L (values between 2 µg/L and 7 µg/L are less common, and >7 µg/L are uncommon (Gaillardet, Viers, & Dupré, 2003). On average, just under half (47%) of the Zn carried by regional surface waters was in the dissolved fraction.

5.2 Comparison to ANZECC Guidelines

Dissolved Zn results obtained during the study period were assessed for compliance with the 95% freshwater trigger value of 8 µg/L, derived in the ANZECC Guidelines. Information relating to the ANZECC Guidelines can be found in Section 1.2.3.

During the study period, 84% of sites monitored in the Waikato region complied with the ANZECC Guidelines on every sampling occasion (ANZECC, 2000). This means that Zn results were on all 12 sampling occasions at 84 of 100 sites. Sixteen sites exceeded <8 µg Zn /L at least once, and these are given in Table 5.2. Of these 16 sites, two exceeded the trigger value on all 12 sampling occasions.

Table 5.2 Regional Waikato Surface Water Sites that Exceeded the ANZECC Guideline Trigger Value for Zn (8 µg/L)

Location	Site Reference	% of sampling occasions trigger value exceeded
Wai-O-Tapu Stream at Campbell Rd Bridge	47	100
Waitawhiriwhiri Stream	89	100
Kirikiroa Stream	90	92
Mangakotukutuku Stream	87	58
Ohote Stream	88	58
Mangawara Stream	19	58
Komakorau Stream	6	42
Mangamingi Stream	40	25
Wai-O-Tapu Stream at Homestead Rd Bridge	50	25
Awaroa River (Waiuku)	27	25
Mangapiko Stm (Pirongia/Te Awamutu)	76	17
Mangawhero Stm (Cambridge)	86	18
Matahuru Stream	20	17
Tokaanu Power Station Tailrace Canal	105	17
Pokaiwhenua Stm	7	8
Unnamed site	-	8

For these sites, local geology and catchment land use are likely to be the primary sources of additional Zn. For example, Site 47 is the upper of two sample sites located on the Wai-O-Tapu stream. This stream is located in the Taupo volcanic Zone and receives significant geothermal inputs (LAWA, 2014) (see also Section 4.4 for a discussion relating to geothermal influences on water quality).

Site 89 also exceeded the guideline trigger value on all sampling occasions. This site is located on the Waitawhiriwhiri Stream, immediately before its convergence with the Waikato River. Land use in that sampling area is predominantly urban, with some pastoral land use in the upper catchment area (LAWA, 2014). It is likely that elevated Zn concentrations in surface water at this site are due to urban storm water pollution (e.g. galvanised iron runoff, wear from car tyres and brake pads, combustion of lubricating oils, corrosion of building materials and metal objects). This is also likely to be the case for Site 90.

The remaining 13 non-compliant sites exceeded the guideline trigger value on up to 58% of sampling occasions. Sources of additional Zn at these sites are not

immediately clear; however notably, most of these sites are situated in catchments comprised predominantly of pasture and farmland (LAWA, 2014). Catchment land use at sites 6 (which converges with site 19), 7, 27 and 87 (geographically close to site 88) are reported by LAWA (2014) as predominantly pasture and dairy farmland.

5.3 Correlations

Table 5.3 gives the correlation coefficients and p-values for Zn and other variables in regional Waikato surface water.

Table 5.3 Correlation Coefficients and p-values for Zn and other Variables in Regional Waikato Surface Water. For all relationships, N=1113 pairs

Variable	TZn		DZn	
	R-value	p-value	R-value	p-value
TZn	1	-	-	-
DZn	0.731	0.0001	1	-
A340	0.503	0.0001	0.407	0.0001
A440	0.494	0.0001	0.389	0.0001
A780	0.00	ns	0.018	ns
pH	-0.407	0.0001	-0.498	0.0001
EC	0.392	0.0001	0.460	0.0001
Turb	0.642	0.0001	0.390	0.0001
DRP	0.148	0.0001	0.153	0.0001
TP	0.496	0.0001	0.373	0.0001
NO _x -N	0.360	0.0001	0.330	0.0001
NH ₄ -N	0.703	0.0001	0.745	0.0001
TKN	0.710	0.0001	0.582	0.0001
TN	0.582	0.0001	0.503	0.0001

Correlation coefficients and p-values in Table 5.3 show high positive correlations with water quality variables already linked to farming and land use (e.g. runoff, erosion), notably, four forms of N and two forms of P, turbidity (from suspended eroded sediments, as well as algal growth due to N and P), and colour (due to organic matter, such as algae). Additionally, high negative correlations with pH show that Zn in water increases as pH decreases. This is expected because pH is a significant

control of adsorption and mobilisation of Zn (see Section 3.4- Preliminary adsorption trials).

5.4 Influence of Rainfall and River Flow

Increased river flow appears to relate strongly to both Zn concentrations and increased total mass of Zn (kg/day) carried by regional Waikato surface water (Table 5.4). This means that, as more rainfall occurs and river flows increase (e.g. during the winter months- seen in Figure 5.1 below). Zn is being mobilised from soils and added to surface water. These relationships show that the extra water is both pushing more Zn through the system, and adding more Zn to the system. Similar findings were reported in Section 4.5 in relation to Waikato River surface water.

Table 5.4 Correlation Coefficients for River Flow and Sample Variables at Sites where Zn Concentrations Exceeded the ANZECC GV on Two or More Occasions. Relationships of $p < 0.001$ are shown in Bold Italic*

Variable	Flow						
	Site 6	Site 7	Site 27	Site 50	Site 87	Site 89	site 90
N	12	11	11	18	12	12	12
Flow	1	1	1	1	1	1	1
AvgF	0.763	0.956	0.99	0.825	0.882	0.558	0.895
cZnD	0.899	0.017	0.578	0.795	0.295	0.727	0.753
cZnT	0.909	0.01	0.641	0.806	0.353	0.814	0.877
mZnD	0.966	0.601	0.577	0.897	0.589	0.926	0.970
mZnT	0.987	0.735	0.644	0.949	0.641	0.949	0.982

*Note: n=11: $R > \pm 0.521$ is $p < 0.1$; $R > \pm 0.602$ is $p < 0.05$; $R > \pm 0.685$ is $p < 0.02$; $R > \pm 0.735$ is $p < 0.01$; $R > \pm 0.847$ is $p < 0.001$; $R > \pm 0.910$ is $p < 0.0001$. n=12: $R > \pm 0.497$ is $p < 0.1$; $R > \pm 0.576$ is $p < 0.05$; $R > \pm 0.658$ is $p < 0.02$; $R > \pm 0.708$ is $p < 0.01$; $R > \pm 0.823$ is $p < 0.001$; $R > \pm 0.891$ is $p < 0.0001$. n=18: $R > \pm 0.400$ is $p < 0.1$; $R > \pm 0.468$ is $p < 0.05$; $R > \pm 0.543$ is $p < 0.02$; $R > \pm 0.590$ is $p < 0.01$; $R > \pm 0.708$ is $p < 0.001$; $R > \pm 0.789$ is $p < 0.0001$.

Abbreviations: AvgF, average flow; cZnD, dissolved zinc concentration; cZnT, total zinc concentration; mZnD, mass of dissolved zinc; mZnT, mass of total zinc.

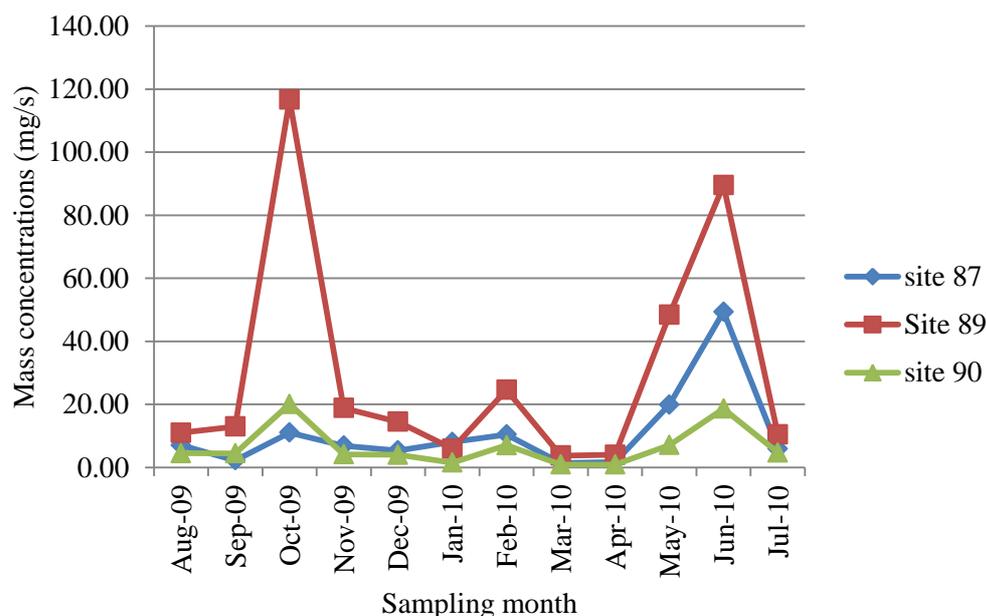


Figure 5.1 *Seasonal Fluctuations of Zn in Surface Water at Three Waikato Sites Regularly Exceeding the ANZECC GV for Zn*

5.5 Chapter Summary

Results for this part of the study highlight that most (84%) of the regional Waikato lakes sampled were below the ANZECC Guideline Value of 8 µg Zn/L on each sampling occasion (Section 5.2). Sixteen sites exceeded the guideline on one or more occasions, and of these, 13 are located in farming catchments (for the others, source of Zn were geothermal, and urban) (Section 5.2). In addition, rainfall events appear to mobilise soluble Zn within pastoral catchments in a way that causes an increase in both the concentration (µg/L) of Zn in the water, as well as the (more expected) increase in mass loading (kg/day) (Section 5.4).

Overall, the potential for facial eczema Zn to cause direct Zn toxicity in regional rivers and streams is considered unlikely. This is because observed GV exceedances were marginal (not orders of magnitude above the guideline, which relates to long term-exposure). However, there is potential for Zn to be accumulating in some sediment receiving environments, and this is discussed in the following chapter.

5.6 References

- ANZECC. (2000). National water quality management strategy paper 4. *Australian and New Zealand guidelines for fresh and marine water quality*. Canberra, Australia: ANZECC with ARMCANZ.
- Gaillardet, J., Viers, J., & Dupré, B. (2003). Trace elements in river waters. In H. Heinrich & K. Turekian (Eds.), *Treatise on Geochemistry* (pp. 225-272). Oxford: Pergamon.
- LAWA. (2014). Explore data: Waikato region. Retrieved 16 December, 2014, from <http://www.lawa.org.nz/explore-data/waikato-region/waikato-river/awaroa-stm-%28rotowaro%29-at-sansons-br-@-rotowaro-huntly-rd/>

Chapter 6. Zinc in Waikato Freshwater Lake Sediments

Sixty-eight sediment samples from 22 regional Waikato lakes (21 rural and one urban) were tested for total recoverable Zn. Sampling methodology is given in Sections 2.2.3 and 2.3.4.

Results are presented and discussed in this chapter, in the order: raw data and summary statistics (Section 6.1), occurrence of Zn enrichment and possible sources (Section 6.2), comparison to sediment quality guidelines (Section 6.3), and relationships between Zn and other elements (Section 6.4).

6.1 Raw Data and Summary Statistics

Raw data covering all individual sample results is provided in Appendix 6.2. Individual sample results for Zn only are reproduced in Table 6.1 below. Summary statistics for variables measured in regional Waikato lake sediments are provided in Table 6.2.

Table 6.1 Individual Zn Concentrations (mg/kg dry weight) in Waikato Lake Sediments

Lake and location	Sampl- ing yr	Zn (mg/kg)	Lake and location	Sampl- ing yr	Zn (mg/kg)
Areare - Deep	2011	132	Rotomanuka	2004	180
Areare - Mid 1	2011	128	Rotomanuka	2011	200
Areare - Mid 2	2011	149	Rotomanuka - Deep	2011	185
Hakanoa	2004	136	Rotomanuka - Mid 1	2011	178
Hakanoa - Deep	2011	112	Rotomanuka - Mid 2	2011	179
Hakanoa - Mid 1	2011	113	Serpentine East	2004	141
Hakanoa - Mid 2	2011	111	Serpentine E - Deep	2011	130
Harihari - Deep	2011	81	Serpentine E - Mid 1	2011	127
Harihari - Mid 1	2011	78	Serpentine E - Mid 2	2011	164
Harihari- Mid 2	2011	95	Serpentine E - Deep, repl. 2	2011	132
Mangahia - Deep	2011	106	Serpentine E - Mid, repl. 2	2011	145
Mangahia - Mid 1	2011	95	Serpentine E - Mid 2, repl. 2	2011	142
Mangahia - Mid 2	2011	130	Serpentine N	2004	133
Mangakaware - Deep	2011	183	Serpentine N - Deep	2011	136
Mangakaware - Mid 1	2011	174	Serpentine N - Deep, repl. 2	2011	146
Mangakaware - Mid 2	2011	198	Serpentine N - Mid 1	2011	162
Maratoto	2004	40	Serpentine N - Mid 2	2011	179
Maratoto	2011	43	Serpentine S - Deep	2011	220
Ngaroto	2004	146	Serpentine S - Mid 1	2011	200
Ngaroto	2011	148	Serpentine S - Mid 2	2011	220
Ohinewai - Deep	2011	89	Taharoa - Deep	2011	89
Ohinewai - Mid 1	2011	90	Taharoa - Mid 1	2011	90
Ohinewai - Mid 2	2011	88	Taharoa - Mid 2	2011	88
Omatearoa	2011	87	Te Koutu	2004	390
Parkinson	2003	260	Waahi	2004	89
Penewaka - Deep	2011	89	Waahi - Deep	2011	87
Penewaka - Mid 1	2011	75	Waahi - Mid 1	2011	86
Penewaka - Mid 2	2011	94	Waahi - Mid 2	2011	84
Puketi - Deep	2011	121	Waikare	2004	50
Puketi - Mid 1	2011	126	Waikare repl. 2	2004	55
Puketi - Mid 2	2011	149	Waikare - deep sample	2011	47
Rotokotuku - Deep	2011	55	Waikare - Mid 1	2011	49
Rotokotuku - Mid 1	2011	32	Waikare - Mid 2	2011	48
Rotokotuku - Mid 2	2011	28	Whangapae	2004	80

Table 6.2 Summary Statistics for Zn and other Variables in Waikato Lake Sediment Grab Samples (mg/kg dry weight)

Variable	n	Mean	95% CI	Mdn	SD	Min	Max
OC	56	12.1	[10.2-13.9]	11.7	6.96	0.400	34.0
TN	56	0.990	[0.872 - 1.11]	1.08	0.441	0.060	1.90
Al	66	26870	[24300 - 29500]	25500	10616	3900	49000
Sb	60	0.339	[0.164 - 0.514]	0.170	0.677	0.040	5.20
As	68	9.08	[6.79 - 11.4]	5.95	9.44	0.90	42.0
Ba	66	199	[170 - 228]	167	119	10.7	470
Bi	65	0.166	[0.149 - 0.183]	0.150	0.069	0.040	0.350
B	65	5.91	[5.13 - 6.69]	5.00	3.16	3.00	18.0
Cd	67	0.451	[0.379 - 0.523]	0.480	0.295	0.022	1.37
Cs	66	2.89	[2.02 - 3.76]	1.63	3.54	0.14	15.5
Ca	66	4973	[4520 - 5420]	4650	1825	1940	8400
Cr	67	10.5	[8.85 - 12.1]	8.30	6.74	4.80	34.0
Co	66	12.8	[11.4 - 14.1]	11.6	5.65	1.02	31.0
Cu	67	19.7	[18 - 21.5]	17.9	7.10	10.2	49.1
F	56	148	[132 - 163]	136	57.8	52.0	290
Fe	66	32858	[27800 - 37900]	27000	20676	1730	102000
La	66	16.1	[14.7 - 17.6]	15.5	5.92	3.80	30.0
Pb	67	35.6	[21.5 - 49.7]	18.3	57.8	4.90	320
Li	65	13.3	[10.9 - 15.7]	10.6	9.70	0.400	48.0
Mg	66	1430	[1170 - 1690]	970	1057	520	5600

Abbreviations: OC, organic carbon; TN, total nitrogen; Al, aluminium; Sb, antimony; Ba, barium; Bi, bismuth; B, boron; Cd, cadmium; Cs, caesium; Ca, calcium; Cr, chromium; Co, cobalt; Cu, copper; F, fluorine; Fe, iron; La, lanthanum; Pb, lead; Li, lithium; Mg, magnesium.

Table 6.2 continues on pg. 130

Table 6.2 Continued

Variable	<i>n</i>	Mean	95% CI	Mdn	SD	Min	Max
Mn	66	840	[654 - 1030]	665	756	50.0	4000
Hg	66	0.157	[0.131 - 0.182]	0.138	0.104	0.038	0.670
Mo	66	0.522	[0.462 - 0.582]	0.570	0.246	0.09	1.79
Ni	67	7.55	[6.54 - 8.55]	5.70	4.12	2.30	19.0
P	66	1178	[1020 - 1340]	1090	659	360	3800
K	66	640	[574 - 706]	618	268	159	1460
Rb	66	9.53	[8.2 - 10.9]	7.90	5.39	0.880	21.0
Se	29	2.83	[2.58 - 3.08]	3.00	0.658	2.00	4.00
Ag	65	0.125	[0.106 - 0.143]	0.100	0.075	0.030	0.50
Na	66	285	[266 - 303]	262	74.53	113	470
Sr	66	47.7	[43.3 - 52.1]	46.7	18.0	10.9	98.0
Tl	65	0.409	[0.346 - 0.472]	0.370	0.254	0.030	0.980
Sn	66	1.36	[1.04 - 1.68]	1.10	1.29	0.140	10.5
U	66	0.797	[0.729 - 0.866]	0.785	0.279	0.129	1.30
V	66	67.7	[47.1 - 88.3]	41.0	83.8	13.0	380
Zn	68	124	[109 - 138]	124	60.4	28.0	390

Abbreviations: Mn, manganese; Hg, mercury; Mo, molybdenum; Ni, nickel; P, phosphorus; K, potassium; Rb, rubidium; Se, selenium; Ag, silver; Na, sodium; Sr, strontium; Tl, thallium; Sn, tin; U, uranium; V, vanadium; Zn, zinc.

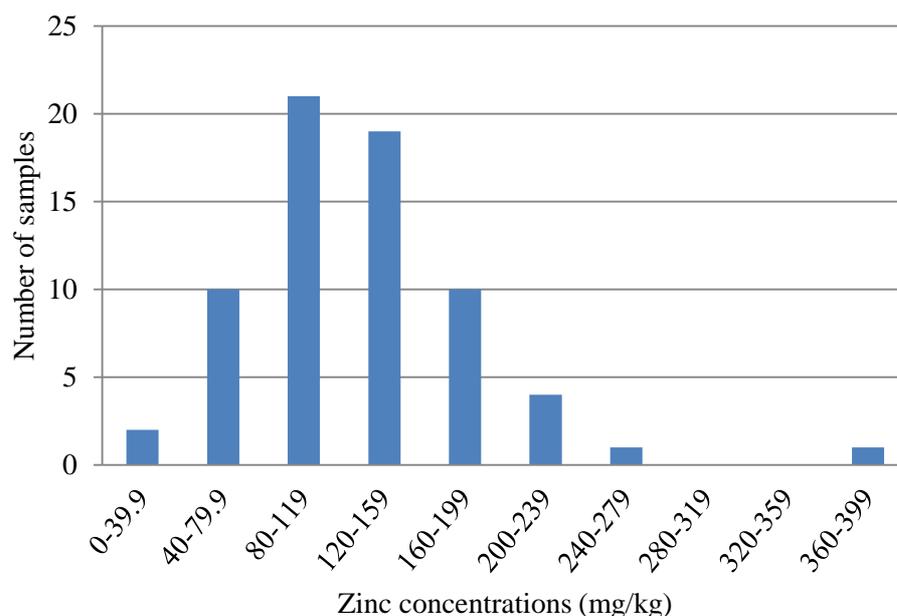


Figure 6.1 Histogram Showing the Distribution of Zn Concentrations Measured in the 68 Freshwater Lake Sediment Samples

In total, 68 sediment samples were tested for AR Zn (mg/kg), with results ranging from 28 mg/kg – 390 mg/kg (Table 6.2, Figure 6.1). With the exception of one outlier, Zn concentrations show an even spread across this range (median of 123.5 mg/kg, mean of 123.7 mg/kg) (Table 6.2).

The single Zn outlier (390 mg/kg) represents the only urban-situated lake in the sample set: Lake Te Koutu in Cambridge. Sediments of this lake also showed elevated Pb (316 mg/kg). Pb and Zn enrichment is a common occurrence in urban lake sediments (Kabata & Pendias, 2001; Taylor, Kim, & Hill, 2011). Two dominant sources of Zn to urban catchments are runoff from galvanized iron surfaces and particles of car tyre rubber (Makepeace, Smith, & Stanley, 1995).

In general, for those lakes sampled at three locations or in different years, Zn concentrations also showed little variability within lakes or across time in the 7 years between from 2004-2011 (Table 6.1). For example, in Lake Rotomanuka, in the 2011 sampling run, the Zn concentration of a sediment grab sample collected from deepest part of the lake (the basin) was 185 mg/kg, compared with 178 mg/kg and 179 mg/kg in two other samples collected on the same day from different locations mid-way

between the basin and the lakeshore. Another single grab sample collected during 2011 (location unspecified) gave a result of 200 mg/kg. These four results (mean 186 mg/kg, std dev 10.1 mg/kg) compare with a figure of 180 mg/kg obtained when the lake was sampled at a midway point during 2004 (Table 6.1).

6.2 Apparent Enrichments and Possible Sources

6.2.1 Enrichment estimates

As there are no background lakes in the Waikato region that can be considered unaffected by anthropogenic trace element contamination, enrichment estimates were made by comparing trace element concentrations in the lake sediments with mean concentrations across background and forest soil sites (see Methodology Section 2.3.4 and mean background soil concentrations for all variables in Appendix 6.1.).

Enrichment estimates for Zn and other variables in studied Waikato lake sediments are provided in Table 6.3. A summary of cases where over one third of lakes show apparent enrichment, and an initial attribution of possible sources, is provided in Table 6.4. Of all the elements Zn and Co showed apparent enrichment in sediments of the most lakes by this method. Relative enrichments across lakes for these two elements are shown in graphical form in Figure 6.2 (Zn) and Figure 6.3 (Co).

Table 6.3 Average Enrichment Factors for Zn and other Variables in Waikato Lake Sediments. Variables Enriched by a Factor of 2 or more are in Bold Italic*

Variable	OC	TN	Al	Sb	As	Ba	Bi	B	Cd	Cs	Ca	Cr
Mean background levels (% for OC and TN, mg/kg for others)	30.02	1.72	23209	0.08	12.5	87	0.19	4.66	0.15	1.37	1845	11.39
Lake Areare	1.57	1.88	1.92	0.98	1.62	1.50	1.06	0.80	3.64	1.04	3.45	0.67
Lake Hakanoa	1.22	2.09	0.89	4.41	2.89	1.95	1.26	1.85	2.89	3.75	1.61	0.55
Lake Harihari	0.45	0.84	0.90	0.58	1.17	1.15	1.25	0.93	0.51	0.65	1.59	1.53
Lake Mangahia	1.85	2.21	1.46	1.11	2.08	2.90	0.68	0.67	4.38	1.17	3.96	0.70
Lake Mangakaware	1.24	1.97	1.76	2.13	2.06	4.42	1.19	0.80	6.57	2.26	2.11	0.63
Lake Maratoto	3.32	2.51	0.74	2.94	0.67	1.32	0.64	0.80	1.33	0.26	3.44	0.39
Lake Ngaroto	0.77	1.43	1.20	1.79	1.28	4.11	0.89	0.70	3.03	1.13	2.32	0.50
Lake Ohinewai	1.10	1.36	0.64	4.26	8.68	2.01	0.70	0.67	1.54	1.68	2.48	0.40
Lake Omatearoa	0.04	0.11	0.17	-	0.24	0.10	-	-	0.12	0.17	1.06	1.84
Lake Parkinson	-	-	-	-	2.63	-	-	-	2.66	-	-	2.06
Lake Penewaka	0.91	1.67	1.01	6.82	9.91	1.59	0.87	1.34	1.53	10.27	1.61	0.60
Lake Puketi	0.83	1.45	0.67	5.20	1.16	0.35	0.30	0.87	0.52	0.38	1.86	2.40
Lake Rotokotuku	2.70	2.77	0.37	1.41	0.32	0.67	1.45	1.00	0.70	0.10	2.09	0.40
Lake Rotomanuka	1.64	3.07	1.22	5.60	1.09	2.22	0.60	1.64	2.82	0.59	3.50	0.73
Lake Serpentine East	1.67	2.52	1.53	1.64	0.79	1.59	0.78	0.77	3.71	0.92	3.66	0.46
Lake Serpentine North	1.76	2.77	1.52	3.02	0.74	1.92	0.84	1.00	2.70	1.01	4.15	0.49
Lake Serpentine South	1.21	2.14	1.91	23.36	1.63	3.79	1.51	1.54	3.48	1.35	2.91	0.59
Lake Taharoa	0.22	0.62	1.16	-	2.28	1.54	2.04	0.73	0.52	0.72	2.66	1.08
Lake Te Koutu	-	-	0.89	16.88	6.66	1.49	1.66	1.00	4.10	2.55	2.45	1.29
Lake Waahi	0.55	1.13	1.11	1.95	2.09	1.43	1.58	3.06	1.26	1.89	2.23	0.74
Lake Waikare	0.30	0.57	0.81	3.77	3.90	1.65	1.37	1.25	0.91	6.42	1.11	0.58
Lake Whangapae	-	-	0.78	3.33	2.24	1.35	1.21	1.60	1.22	1.22	2.96	0.83

Table 6.3 continues on pg. 134

Table 6.3 Continued

Variable	Co	Cu	F	Fe	La	Pb	Li	Mg	Mn	Hg	Mo	Ni
Mean background levels (% for OC and TN, mg/kg for others)	3.95	12.88	233	20760	13.28	11.17	5.24	953	558	0.15	0.70	3.41
Lake Areare	2.54	1.06	0.63	1.05	1.33	1.86	3.55	1.05	0.28	1.04	1.03	1.48
Lake Hakanoa	1.98	0.89	0.63	1.52	0.69	2.19	3.08	1.26	1.47	1.48	0.69	1.57
Lake Harihari	4.24	1.60	0.63	5.14	0.79	1.07	2.60	3.93	1.24	0.63	0.52	2.92
Lake Mangahia	3.75	1.41	0.44	1.56	0.75	1.20	2.17	1.58	0.45	1.49	0.97	1.73
Lake Mangakaware	2.97	1.52	0.38	1.34	1.27	1.63	3.02	1.01	0.48	1.87	0.95	2.16
Lake Maratoto	1.08	0.82	0.42	0.55	0.55	2.17	0.24	1.92	0.15	0.93	0.97	0.75
Lake Ngaroto	3.98	1.09	0.22	2.01	1.69	1.14	2.13	1.11	2.70	1.37	0.53	1.40
Lake Ohinewai	3.13	0.63	0.69	2.11	0.67	0.60	1.82	1.08	2.44	1.07	0.89	1.31
Lake Omatearoa	3.89	0.62	0.89	2.70	0.23	0.45	0.77	3.07	0.55	-	0.14	2.94
Lake Parkinson	-	1.39	-	-	-	1.21	-	-	-	-	-	5.16
Lake Penewaka	2.55	0.88	0.67	1.95	0.61	3.56	5.93	1.77	0.83	1.52	0.53	1.41
Lake Puketi	6.75	1.17	0.93	4.04	0.48	7.01	1.77	3.12	0.84	0.43	0.49	4.26
Lake Rotokotuku	0.37	1.10	0.87	0.11	0.52	1.08	0.10	0.73	0.07	1.17	0.55	0.91
Lake Rotomanuka	4.44	1.21	0.31	1.85	1.08	7.29	1.30	0.92	1.22	0.97	1.10	1.65
Lake Serpentine East	2.97	1.08	0.55	1.27	1.37	1.68	2.29	1.12	0.41	1.27	1.05	1.38
Lake Serpentine North	2.34	1.34	0.59	1.22	1.35	3.40	2.20	1.22	0.43	1.13	1.00	1.53
Lake Serpentine South	3.22	1.92	0.36	1.53	1.41	11.74	3.53	1.14	0.78	1.35	1.01	1.67
Lake Taharoa	3.03	1.92	1.16	3.62	1.07	1.65	11.14	6.79	4.09	0.83	0.32	4.52
Lake Te Koutu	1.51	2.98		0.93	0.83	29.13	3.10	2.87	0.37	1.35	2.84	2.42
Lake Waahi	2.55	0.84	0.96	1.48	0.83	1.53	5.11	2.01	1.44	1.17	0.89	3.67
Lake Waikare	2.09	0.87	0.56	1.25	0.92	1.67	5.49	2.08	1.15	4.28	0.31	1.26
Lake Whangapae	1.58	1.03		2.14	0.68	1.53	3.75	2.36	0.96	1.26	1.43	4.02

Table 6.3 continues on pg. 135

Table 6.3 Continued

Variable	P	K	Rb	Se	Ag	Na	Sr	Tl	Sn	U	V	Zn
Mean background levels (% for OC and TN, mg/kg for others)	500	572	6.73	3.14	0.13	168	24.28	0.19	1.17	0.74	56.96	29.88
Lake Areare	2.94	1.36	0.98	1.19	2.95	1.50	2.39	2.87	4.66	1.45	0.58	4.15
Lake Hakanoa	1.49	1.34	2.23	-	1.01	1.75	2.04	1.35	2.22	1.11	0.37	3.59
Lake Harihari	2.57	1.61	1.55	-	0.56	2.25	1.41	0.47	1.15	1.20	3.40	2.58
Lake Mangahia	5.87	1.18	0.78	-	1.34	1.42	3.56	3.55	0.84	0.98	0.51	3.36
Lake Mangakaware	3.34	1.12	1.13	0.90	2.26	1.22	2.15	4.02	1.40	1.53	0.58	5.63
Lake Maratoto	1.36	0.36	0.20	0.75	0.98	1.88	4.15	0.68	0.64	0.52	0.53	1.27
Lake Ngaroto	1.66	1.13	1.14	-	1.08	1.20	1.98	3.44	0.80	1.19	0.49	4.47
Lake Ohinewai	1.14	0.83	0.91	-	0.85	1.61	1.85	2.17	0.65	0.92	0.29	2.71
Lake Omatearoa	0.68	0.41	0.30	-	-	0.63	0.55	-	0.50	0.32	4.24	2.65
Lake Parkinson	-	-	-	-	-	-	-	-	-	-	-	7.91
Lake Penewaka	1.72	1.68	2.51	-	0.88	1.92	1.34	1.41	1.16	0.89	0.41	2.62
Lake Puketi	1.60	0.81	0.64	-	0.43	1.88	1.30	0.18	0.85	0.82	5.31	4.02
Lake Rotokotuku	1.45	0.31	0.13	0.70	0.36	2.44	2.05	0.56	0.17	0.18	0.20	1.17
Lake Rotomanuka	2.32	1.09	0.59	0.82	1.08	1.36	2.68	2.47	0.73	0.69	0.90	5.61
Lake Serpentine East	2.22	0.82	0.94	0.77	1.80	1.55	3.51	2.60	0.98	0.82	0.63	4.27
Lake Serpentine North	1.81	1.06	0.94	0.82	1.61	1.18	2.95	1.86	1.31	0.89	0.61	4.60
Lake Serpentine South	2.00	1.05	1.34	0.90	2.16	1.27	2.47	3.51	1.57	1.29	0.72	6.49
Lake Taharoa	2.05	2.59	1.75	-	0.75	1.52	2.37	0.47	1.32	1.35	1.13	2.71
Lake Te Koutu	2.23	1.50	1.24	-	1.47	1.57	1.65	1.05	3.91	1.14	0.89	11.87
Lake Waahi	0.71	1.64	2.03	-	0.74	2.04	3.71	1.01	1.50	1.06	0.54	2.63
Lake Waikare	0.65	1.50	2.56	-	0.64	1.20	1.17	0.98	1.51	1.58	0.66	1.52
Lake Whangapae	0.93	1.68	1.75	-	0.79	1.17	2.52	0.87	0.98	1.41	0.51	2.44

Table 6.4 Summary of Elements with an Enrichment Factor of 2.0 or More in >33% of Waikato Lakes Studied, and initial attribution of possible sources

Element	Number of Lakes with Enrichment Factor >2.0	% of Lakes Sampled	Possible Sources
Zn	19	86	Agricultural (<i>e.g.</i> Facial Eczema remedies) and urban runoff (for one lake).
Co	16	73	Agricultural sources (supplement) and/or possible natural enrichment process ^a
Ca	15	68	Superphosphate fertiliser (40% gypsum) and lime
Li	15	68	Unknown (Li enrichment also apparent for Waikato soils)
Sr	13	59	Gypsum in superphosphate and lime (occurs with Ca)
Sb	12	55	Geothermal (co-occurs with As) and gun shot (see Section 6.3)
As	11	50	Geothermal
Cd	11	50	Superphosphate fertiliser
Pb	9	41	Road influence (era of leaded petrol) ^b and gun shot (see Section 6.3)
Ni	9	41	Use in dairy farming ^c
TN	8	36	Pastoral farming
Mg	8	36	Gypsum in superphosphate and lime (occurs with Ca)
P	8	36	Superphosphate fertiliser
Tl	8	36	Unknown (Tl enrichment also apparent for soils) ^d

^aSañudo-Wilhelmy, Gómez-Consarnau, Suffridge, & Webb, 2014

^bPearson, Hendy, Hamilton, & Pickett, 2010

^cTaranaki Daily News, 2012

^dTaylor & Kim, 2010

6.2.2 Zinc

Zn appeared enriched by a factor of two or more at 19 out of 22 lakes included in this study (Table 6.4). This means that over 86% of lakes included in this study appear to have at least twice as much Zn than what is expected to occur naturally. Lakes Te Koutu, Parkinson, and Serpentine South appeared most enriched, with average Zn levels 11.87, 7.91, and 6.49 times higher than expected backgrounds levels, respectively (Figure 6.2). Lakes Rotokotuku, Maratoto and Waikare were the least enriched (respective factors of 1.17, 1.27, and 1.52).

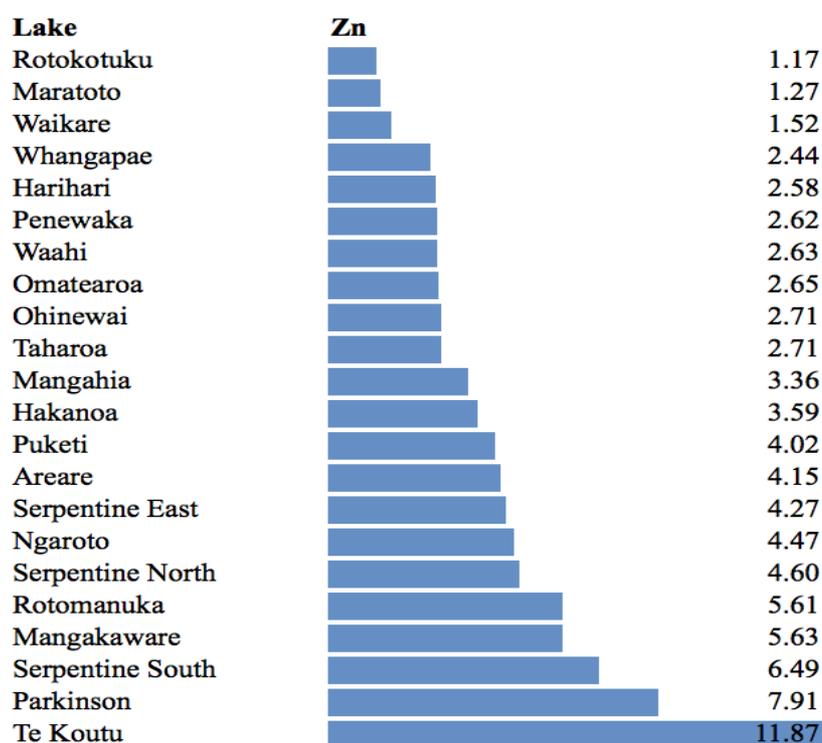


Figure 6.2 *Enrichment Rankings for Zn in Waikato Lake Sediments*

Lake Te Koutu is an urban lake (discussed above as the outlier in Section 6.1) for which Zn enrichment is expected. Lake Te Koutu is located in the town of Cambridge and receives high sediment and nutrient loadings from urban storm water drains and diffuse seepage. As a result, eutrophication of the lake has occurred (Waikato Regional Council, 2014b). For this lake, it is likely that Zn enrichment is due to urban sources, with transport in storm water runoff and seepage.

However, excluding Lake Te Koutu, Zn enrichment is still apparent in 18 of 21 – also 86% – of the rural lakes. Zn is the most consistently elevated of all 36 variables tested (Table 6.4), with apparent enrichment being evident across the most lakes. These initial findings are interesting in that they allude strongly to the occurrence of substantial and widespread Zn enrichment in rural Waikato lake sediments.

Of the rural lakes sediments from Parkinson, Serpentine (South), Rotomakana, and Mangakaware were found to be, on average, the most Zn-enriched. Unlike Lake Te Koutu, these are located in pastoral catchments (Waikato Regional Council, 2014a). These lakes, among others in the Waikato, are classed as having degraded water quality attributable to contaminants from pastoral land drainage (Waikato Regional Council, 2014a).

A common characteristic of the four lakes displaying higher amounts of Zn in sediments is that they are all located in areas of intensive agriculture. Furthermore, each lake has been reported as having varied degrees of degraded water quality attributed to agricultural land use practices within the catchment areas. It is therefore likely that one or more agricultural sources are responsible for the observed Zn enrichment in the rural lake sediments.

Agricultural sources of Zn to the environment include animal supplements, animal remedies, fertilisers, and Zn-containing pesticides (see Section 1.3- Sources of Zn to the Environment). Of these, the highest mass-use appears to be linked with facial eczema remedies, with estimates that most farm soils receive 5-6 kg of Zn per hectare per year from this source alone (Kilbride, Poole, & Hutchings, 2006; Potts, Webb, Williams-Thorpe, & Kilworth, 1995).

6.2.3 Cobalt

After Zn, the next most consistently enriched element is Co, which appears to be elevated in 16 of the 21 (76% of) rural lake beds included in this study (with no evidence for enrichment in the urban lake) (Table 6.4). The three most Co-enriched lakes are Lake Puketi, Lake Rotomanuka, and Lake Harihari, with enrichment factors of 6.75, 4.44 and 4.24 respectively (Figure 6.3).

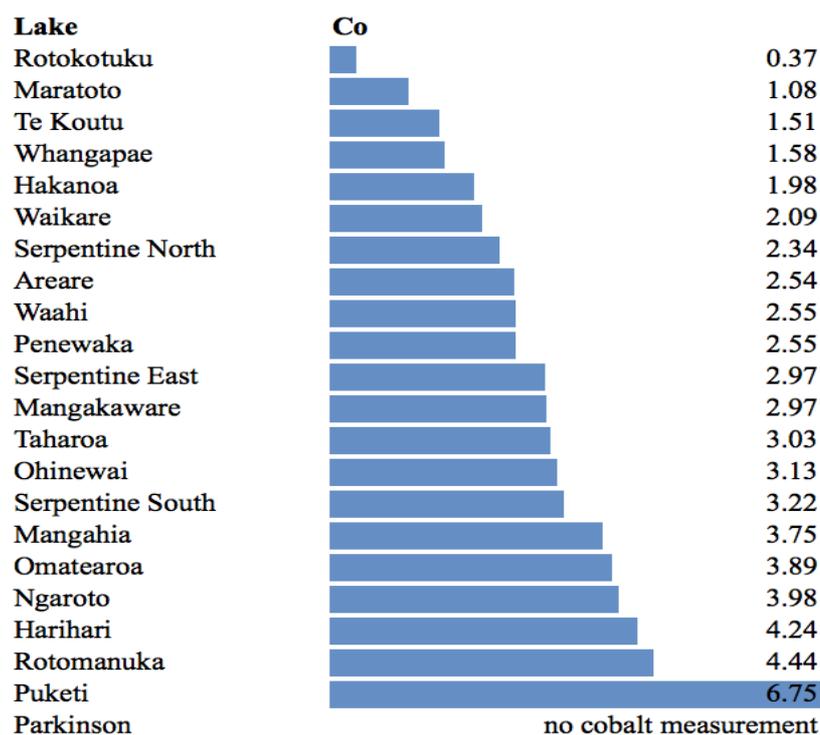


Figure 6.3 *Enrichment Rankings for Co in Waikato Lake Sediments*

Reasons for the apparent widespread Co enrichment are unclear. Co has been applied to agricultural soils in some parts of the Waikato region to correct for deficiencies, and is also an animal supplement. Co is not normally associated with storm water runoff, and this is reflected in the lower concentrations of Co in the urban lake sediments (Lake Te Koutu).

One possibility is therefore that the additional Co in Waikato lake sediments is from agricultural sources, providing sufficient masses of Co have been used and mobilised. Co is a common limiting micronutrient in aquatic systems (MfE, 2004), so the interesting possibility exists that increased productivity and eutrophication of some rural lakes may not have occurred, or been held in check, if they had not been extensively supplemented with additional Co. Alternatively (or as well), the possibility exists that a natural process such as vitamin B12 utilisation and micronutrient cycling in lake ecosystems may result in natural Co accumulation in bed sediments as receiving sinks (Taylor, Kim, Hill, Stevenson, & Gilkes, 2010).

6.2.4 Other Trace Elements

Potential speculative sources of other elements are outlined in Table 6.4. Contamination from pastoral land drainage could also account for the enrichment of some of the other trace elements in rural Waikato lake sediments, e.g. Ca, Sr, Cd, Ni, Mg, and P (as they were all enriched by a factor of two or more in 8-15 of the sampled lakes (Table 6.4).

Phosphate fertiliser (in particular superphosphate) is likely to be a significant anthropogenic source of P and Cd and a number of other trace elements in lake sediments (Adriano, 1986; He, Yang, & Stoffella, 2005; Łukowski & Wiater, 2009; McLaughlin, Tiller, Naidu, & Stevens, 1996; Taylor, 1997). 50% of the lake sediments in this study showed apparent enrichment with Cd, and 36% with P (Table 6.4). Additionally, 68% of lakes appear to show Ca enrichment (Table 6.4).

Both superphosphate fertiliser and lime are sources of Ca to soils (presumably through runoff to lake sediments). These sources could also account for enrichments of Mg and Sr, which are in the same group of the Periodic Table as Ca and geochemically associated with it (Monaghan et al., 2007).

Ni may also come from agricultural sources. This element is increasingly used in dairy farming, with its promoters reporting improved milk yield, quality of pasture, animal health and nitrogen utilisation (Taranaki Daily News, 2012).

Pb shows apparent enrichment in 41% of lakes (Table 6.4). Possible sources include runoff from roading (relating to the era of leaded petrol) and Pb from gun shot. Two lakes show specific evidence for the second source – see Section 6.3.

Enrichments of As (50% of lakes sampled) and Sb (55% of lakes sampled) are often due to a natural geothermal influence (Cavanagh, 2006). This was discussed previously in Section 4.4.

6.3 Comparison to ANZECC Guidelines for Sediment Quality

The rural lake sediment results obtained during the study period were assessed for compliance with the ANZECC Interim Sediment Quality Guidelines (ISQGs). ISQG guideline values are given as low and high ISQG values, corresponding to the effects range-low (ERL) and effects range-medium (ERM) used by Long, MacDonald, Smith, and Calder (1995). For more information on these guidelines, please refer to Section 1.2.3.

For Zn, the ISQG-Low trigger value is 200-mg/kg dry weights and the ISQG-High trigger value is 410 mg/kg dry weight. Table 6.5 is taken from the ANZECC Guidelines and provides the trigger values for Zn and other variables.

It is important to note that the Guidelines provide indicative, rather than absolute, evidence for adverse effects (Stephenson, Milne, & Sorensen, 2008). Principally, the guidelines aim to: "...identify sediments where contaminant concentrations are likely to result in adverse effects on sediment ecological health; facilitate decisions about the potential remobilisation of contaminants into the water column and/or into aquatic food chains; and identify and enable protection of uncontaminated sediments" (ANZECC, 2000, pp. 3.5-1).

Table 6.5 Recommended Sediment Quality Guidelines (ANZECC, 2000, pp. 3.5-4)

Contaminant	ISQG-Low Trigger Value	ISQG-High Trigger Value
METALS (mg/kg dry wt)		
Antimony	2	25
Cadmium	1.5	10
Chromium	80	370
Copper	65	270
Lead	50	220
Mercury	0.15	1
Nickel	21	52
Silver	1	3.7
Zinc	200	410
METALLOIDS (mg/kg dry wt)		
Arsenic	20	70

Data for the 10 elements listed in Table 6.5 were first compared with their ISQG-High values. Only two exceedances of the ISQG-High were found across the whole dataset (Appendix 6.2), and these are both for Pb. The basin of Lake Serpentine South returned a Pb concentration of 320 mg/kg. However, it is questionable whether this result is representative of the basin because the other two samples from mid-points of this lake showed Pb concentrations of one tenth of this value (30 and 32 mg/kg). A possible reason for the high result is that the sediment sample of sub-sample contained fragments or corrosion products of lead shot used for hunting (MfE, 2006). This is supported by the fact that Sb is also present at a high concentration in the same sample (5.2 mg/kg in the basin compared with 0.14 and 0.24 mg/kg at the other sampling points). Sb is used to harden bullet lead (NZWWA, 2003).

Interestingly, there was one other case showing an order-of-magnitude difference in the concentration of these same two trace elements (Pb and Sb) between sampling points in a lake: this is one of the two the mid-point samples from Lake Puketū which contained 200 mg/kg Pb and 0.99 mg/kg Sb. Lake Te Koutu was the other lake with sediments exceeding the ISQG-High for Pb (316 mg/kg compared with ISQG-High of 220 mg/kg). As discussed above for Zn, this is expected because Lake Te Koutu is the single urban lake in the set, and Pb has been well known component of urban storm water. Leaded petrol was previously the key primary source of Pb in urban storm water runoff (Land Monitoring Forum, 2009).

Results were next compared with ISQG-Low values. Results for elements other than Zn were as follows:

1. No lakes exceeded ISQG-Low values for Cd, chromium, Cu, Ni, or Ag;
2. One lake exceeded the ISQG-Low value of 2 mg/kg for Sb, and this was Serpentine South where the source is thought to be related to lead shot (discussed above);
3. Two lakes (Ohinewai and Penekawa) exceed the ISQG-Low for As (20 mg/kg), both by up to a factor of 2. This is likely to be of geothermal origin;

4. Five lakes exceeded the ISQG-Low for Pb of 50 mg/kg. Three of these which exceeded by the greatest amounts were Te Koutu (ratio of concentration/ISQG-Low: 6.32), Serpentine South (6.40), and Puketi (4.00), discussed above. The other two lakes showed modest exceedances of 1.5–2.1 times the ISQG-Low for Lake Rotomanuka and 1.44 times for Lake Serpentine North. These modest levels of enrichment may have several possible sources including an influence of roadside runoff from vehicles; and
5. Sediment of eight lakes showed Hg at concentrations above its ISQG-Low of 0.15 mg/kg. However, this result is unlikely to be of toxicological significance because the ISQG value is the same as the estimated natural concentration of mercury in Waikato soils. Of the eight lakes, seven show enrichments that are only 1.01-1.53 times higher than the ANZECC ISQG-Low for Hg. For this reason, Hg does not show up as being generally enriched across more than 33% of lakes (Table 6.4). Lake Waikare is an exception, which shows up to 4.5 times the ISQG-Low for Hg. This is known to be caused by a natural hydrothermal system in the lakebed. In separate work carried out by the Waikato Regional Council, concentrations of Hg, up to 400 times the ISQG-High, have been determined in sediments near the geothermal source. Warm water flowing into the lake from vents in the bed had a temperature of up to 78°C (Kim, N. personal communication, January 13, 2015).

This leaves Zn. Although Zn does appear to be present at elevated concentration relative to expected natural levels in most lakes (Section 6.2), in most cases the enrichments have not reached toxicological significance. Zn is present at or above its ISQG-Low of 200 mg/kg in only three lakes: Lake Parkinson (1.3 times), Lake Serpentine South (1.0-1.1 times), and Lake Te Koutu (the urban lake).

A major finding from comparing the sediment data to the ANZECC guideline trigger values for Zn is that 63 out of 67 rural sediment samples collected during the study period were below the ISQG-Low trigger value of 200 mg/kg. This means that 94% of Zn results are within a range where the likelihood of adverse ecological effects is very low. 6% of sediments sampled during the study period with equal to or above the ISQG low trigger value, but below the ISQG high trigger value of 410

mg/kg, meaning that minimal effects may be observed occasionally at these sites. No sample results were above the ISQG-High trigger value for Zn.

These results indicate that, although Zn concentrations in many rural lake sediments appear to have substantially increased above their expected natural levels (Section 6.2), in most cases they are not yet at concentrations that would cause toxicity to sediment dwelling organisms and rural lake ecosystems, or levels seen in urban lake sediments.

The results strongly suggest there is a need for future monitoring of rural lakes showing elevated Zn concentrations to determine whether concentrations are continuing to increase, or have reached some form of steady state. A steady state condition might occur in cases where the impact of new anthropogenic Zn is counteracted by the dilution effect of clean sediments being eroded from the same catchment.

6.4 Correlations

R-values for Zn and other variables tested in the lake sediments are provided in Table 6.6. Data for the urban lake (Te Koutu) was excluded from this part of the assessment because urban lakes are likely to represent a distinctly different population of lakes with different source contributions. This left between 56 and 67 pairs between Zn and each other variable, depending on the variable.

The limited number of non-detects (mainly for Se) were set equal to their detection limits, and log values of the following variables were taken before derivation of the correlation matrix to correct for data showing a log-normal distribution: Sb, As, B, Cs, Cr, Cu, Mg, Mn, Hg, Ni, P, Se, Ag and Sn).

Table 6.6 Correlations for Zn and other Variables in Waikato Lake Sediments. Relationships of $p < 0.0001$ or greater are in Bold Italic*

<i>Variable</i>	<i>R-value</i>	<i>p-value</i>
	Zn	
Zn	1	
OC	0.134	ns
TN	0.491	0.001
<i>Al</i>	<i>0.687</i>	<i>0.0001</i>
log Sb	0.236	ns
log As	-0.120	ns
<i>Ba</i>	<i>0.540</i>	<i>0.0001</i>
Bi	-0.263	0.05
log B	0.058	ns
<i>Cd</i>	<i>0.665</i>	<i>0.0001</i>
log Cs	0.009	ns
Ca	0.461	0.001
log Cr	0.127	ns
Co	0.458	0.001
<i>log Cu</i>	<i>0.484</i>	<i>0.0001</i>
<i>F</i>	<i>-0.539</i>	<i>0.0001</i>
Fe	0.358	ns
<i>La</i>	<i>0.627</i>	<i>0.0001</i>
Pb	0.368	0.01
Li	-0.219	ns
log Mg	-0.394	0.01
log Mn	0.091	ns
log Hg	-0.123	ns
<i>Mo</i>	<i>0.532</i>	<i>0.0001</i>
log Ni	0.181	ns
<i>log P</i>	<i>0.506</i>	<i>0.0001</i>
K	-0.093	ns
Rb	-0.247	0.05
<i>log Se</i>	<i>0.497</i>	<i>0.0001</i>
<i>log Ag</i>	<i>0.660</i>	<i>0.0001</i>
Na	-0.438	0.001
Sr	0.194	ns
<i>Tl</i>	<i>0.702</i>	<i>0.0001</i>
log Sn	0.274	0.05
U	0.137	ns
V	0.212	ns

Note that the number of pairs ranges from N=56 to N=67.

For N=56 pairs: $R > \pm 0.496$ is $p < 0.0001$; $R > \pm 0.428$ is $p < 0.001$; $R > \pm 0.341$ is $p < 0.01$; $R < \pm 0.310$ is $p < 0.02$; and $R < \pm 0.263$ is $p < 0.05$.

For N=67 pairs: $R > \pm 0.460$ is $p < 0.0001$; $R > \pm 0.396$ is $p < 0.001$; $R > \pm 0.315$ is $p < 0.01$; $R < \pm 0.286$ is $p < 0.02$; and $R < \pm 0.242$ is $p < 0.05$.

Very strong positive correlations were observed with Zn and Al, Ba, Cd, Cu, La, Mo, P, Se, Ag, and Tl (Table 6.6), the most significant being Zn-Tl ($R=0.702$) and Zn-Cd ($R=0.665$) (Figure 6.4).

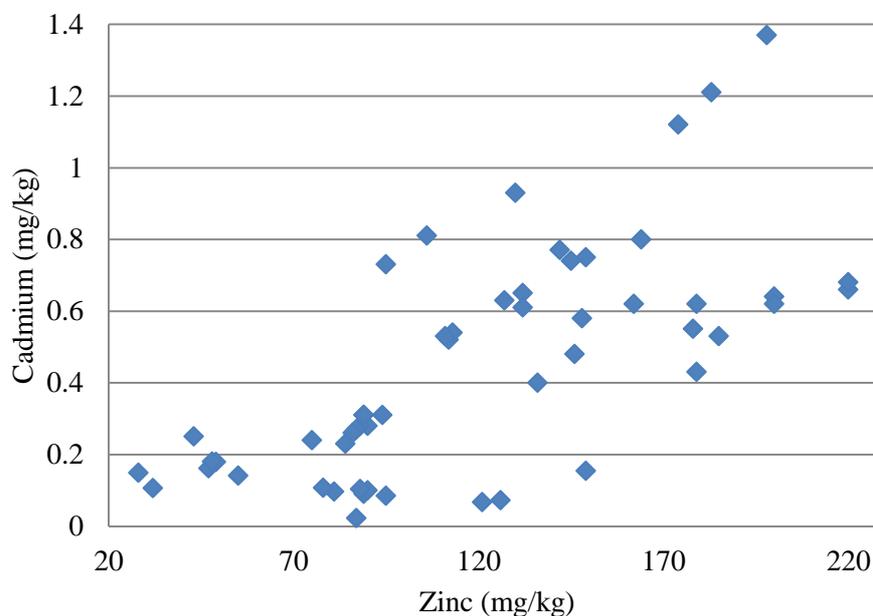


Figure 6.4 Scatterplot showing the Relationship between Zn and Cd Concentrations in Waikato Lake Sediments

The reasons for high positive correlations in this data are largely uncertain. A correlation between two elements may occur for a number of reasons, such as similar biogeochemical histories, common anthropogenic source(s), common solubilities and enrichment pathways, or the presence of two or more chemically distinct sources that are coincident in time and place.

It could be speculated that agricultural surface and groundwater inflows originating from either common or different sources may contribute to the strong positive correlations between Zn and some other elements known to be linked with agriculture (e.g. P, Cd, and Ca, and possibly also Co, Mo and Cu). The Zn - Cd relationship shown in Figure 6.4 may therefore reflect coincident agricultural sources contributing to farming runoff. Much of the additional Cd in sediment may originate from superphosphate fertiliser, while much of the Zn may come from facial eczema remedies. However, the existence of these two known sources to soils (and likely

sources to runoff) does not rule out other reasons why the two elements may correlate in rural lake sediments.

In contrast to sources or pathways being a reason for a positive correlation, the link between Zn and Al may come about if clay (aluminosilicate) minerals in the lake sediments act as a significant adsorptive trap for Zn in the water column. Lake sediments that are richer in clay minerals would be likely to show up as having higher total recoverable Al. Other factors being equal, a correlation with Zn might come about if the lakes with more clay minerals also retain more Zn in their sediments by adsorption. Additionally, taking into account that Al is one of the most abundant element in the earth's crust (and the most abundant metal) (Driscoll & Schecher, 1990; Rosseland, Eldhuset, & Staurnes, 1990), it is not unreasonable to assume that Al enrichment in Waikato lake sediments may also be due, in part, to natural processes (storm water runoff may also play a small role).

Continued Zn accumulation in a given lake, or part of a lake, may depend on an interplay of factors (e.g. the annual mass load of anthropogenic Zn, mass of clean sediment, and nature of sediment deposition in the lake bed). It is possible that Zn concentrations will still be steadily increasing in sediments of all lakebeds that receive runoff from pastoral land. However, it is also possible that some lakebeds will have attained a steady-state concentration of Zn, where the new Zn inputs are balanced by dilution factor represented by the lower Zn concentration of natural sediments.

6.5 Chapter Summary

Nineteen out of twenty two regional Waikato lakes included in this study appear to have at least twice as much Zn in bed sediments than what is expected to occur naturally. Of these, the highest concentration of sediment Zn occurred in lakes located in farming catchments (Section 6.2). However, it can only be speculated that strong positive associations between Zn and agriculturally-associated elements (e.g. P, Cd, Ca, Co, Mo and Cu) are as a result of agricultural surface and groundwater inflows (Section 6.4). In most cases, Zn concentrations are not yet high enough to cause toxicity to sediment dwelling organisms and aquatic ecosystems (Section 6.3).

Further investigation is needed to determine conditions under which Zn concentrations are likely to be increasing in bed sediments (Section 6.4).

6.6 Appendices

Appendix 6.1 Mean Concentrations of Zn and other Variables in Natural, Farmed, Pastoral and Horticultural Land Use Categories

Variable	Land Use Category			
	Natural	Farmed	Pastoral	Horticultural
pH	5.23	5.90	5.80	6.31
TOC	30.0	29.3	26.0	44.7
TN	1.72	2.56	2.27	3.77
Ag	0.13	0.14	0.13	0.17
Al	23209	35583	32002	49606
As	12.5	6.32	5.86	8.13
B	4.66	4.40	4.07	5.62
Ba	87.2	135	120	195
Bi	0.195	0.224	0.215	0.263
Ca	1845	5071	4860	5895
Cd	0.154	0.672	0.656	0.737
Co	3.95	5.65	5.28	7.13
Cr	11.4	15.1	15.0	15.3
Cs	1.37	2.39	2.26	2.87
Cu	12.9	21.1	17.4	35.3
F	233	447	443	461
Fe	20760	21925	20212	28634
Hg	0.147	0.139	0.127	0.193
K	572	770	778	740
La	13.3	22.9	19.1	37.4
Li	5.24	9.32	8.99	10.6
Mg	953	1010	1044	877
Mn	558	1176	958	2028
Mo	0.701	0.929	0.864	1.18
Na	168	158	163	141
Ni	3.41	6.49	6.38	6.91
OP	15.2	51.1	46.5	71.0
P	500	1882	1788	2286
Pb	11.2	17.2	14.1	30.8
Rb	6.73	10.1	10.5	8.53
Sb	0.079	0.162	0.115	0.339
Se	3.14	3.08	3.00	3.29
Sn	1.17	1.54	1.45	1.87
Sr	24.3	23.6	22.5	28.2
Tl	0.190	0.291	0.245	0.476
U	0.738	1.88	1.77	2.38
V	57.0	54.7	51.3	67.4
Zn	29.9	60.6	57.6	73.3

Appendix 6.2 Raw Data for Regional Waikato Lake Sediment Sampling (units in mg/kg, apart from OC and TN which are %)

Lake →	Areare 2011 Deep	Areare 2011 Mid 1	Areare 2011 Mid 2	Hakanoa 2004	Hakanoa 2011 Deep	Hakanoa 2011 Mid 1
Sampling year →	2011	2011	2011	2004	2011	2011
Variable						
OC	14.7	15.4	15.3	-	11.8	11.7
TN	0.980	0.990	1.02	-	1.12	1.11
Al	42000	44000	47000	19400	21000	21000
Sb	0.080	0.070	0.080	0.620	0.250	0.260
As	6.10	5.80	6.60	12.30	10.70	10.60
Ba	146	163	163	220	200	200
Bi	0.170	0.160	0.170	0.220	0.190	0.190
B	4.00	4.00	4.00	9.00	10.0	9.00
Cd	0.650	0.650	0.750	0.580	0.520	0.540
Cs	1.51	1.53	1.59	5.26	5.70	5.80
Ca	6500	6100	6700	3110	3000	3000
Cr	9.20	8.90	9.40	7.20	7.70	7.70
Co	10.9	10.6	11.2	8.65	8.30	8.60
Cu	17.4	17.0	17.9	15.5	14.4	14.5
F	156	150	137	-	145	150
Fe	19700	18100	19600	29300	27000	27000
La	20.0	22.0	24.0	12.0	11.4	11.2
Pb	21.0	18.6	21.0	27.9	22.0	23.0
Li	14.3	14.4	15.6	10.9	13.9	13.3
Mg	830	800	830	1060	940	960
Mn	230	210	240	982	1230	1210
Hg	0.112	0.115	0.122	0.180	0.159	0.165
Mo	0.670	0.640	0.640	0.510	0.400	0.420
Ni	5.30	5.40	5.60	5.80	5.70	5.90
P	1740	1640	1840	969	860	830
K	730	710	750	616	740	770
Rb	7.10	7.60	7.70	14.8	17.6	18.0
Se	4.00	4.00	4.00	< 2	< 2	< 2
Ag	0.200	0.500	0.200	0.100	0.100	0.100
Na	280	270	260	266	340	320
Sr	45.0	47.0	49.0	41.8	40.0	41.0
Tl	0.610	0.600	0.680	0.290	0.300	0.300
Sn	1.86	10.5	1.95	2.00	2.40	2.30
U	1.13	1.15	1.15	0.933	0.850	0.880
V	42.0	39.0	39.0	26.0	25.0	25.0
Zn	132	128	149	136	112	113

Appendix 6.2 *Continued*

Lake →	Hakanoa 2011 Mid 2	Harihari 2011 Deep	Harihari 2011 Mid 1	Harihari 2011 Mid 2	Mangahia 2011 Deep	Mangahia 2011 Mid 1
Sampling year → Variable	2011	2011	2011	2011	2011	2011
OC	11.7	4.400	5.600	3.100	17.600	17.800
TN	1.10	0.420	0.530	0.380	1.13	1.17
Al	21000	20000	25000	17200	34000	34000
Sb	0.250	0.040	< 0.04	0.050	0.080	0.090
As	10.3	4.80	5.30	3.20	8.30	7.50
Ba	197	120	150	90	290	290
Bi	0.190	0.190	0.230	0.170	0.110	0.100
B	9.00	5.00	5.00	4.00	4.00	3.00
Cd	0.530	0.096	0.107	0.085	0.810	0.730
Cs	5.60	0.960	1.09	0.840	1.66	1.68
Ca	2900	3100	3100	2700	7500	7300
Cr	7.50	20.0	19.5	23.0	9.60	9.30
Co	8.50	18.4	17.0	19.2	16.8	14.0
Cu	14.2	25.0	29.0	25.0	23.0	22.0
F	153	139	136	172	84.0	103
Fe	27000	102000	102000	76000	29000	27000
La	10.9	13.7	15.8	9.50	12.3	12.0
Pb	22.0	10.8	12.9	11.0	13.5	12.6
Li	13.2	10.6	12.8	9.10	9.10	8.70
Mg	960	2900	3200	3100	1220	1210
Mn	1260	1050	1180	740	360	360
Hg	0.157	0.071	0.083	0.057	0.192	0.168
Mo	0.400	0.350	0.330	0.310	0.600	0.610
Ni	5.70	10.5	10.6	11.1	6.40	6.00
P	870	1750	1610	1190	3300	3300
K	760	780	960	850	620	600
Rb	17.4	11.3	13.7	10.5	5.60	5.70
Se	< 2	< 2	< 2	< 2	< 2	< 2
Ag	0.110	0.060	0.070	0.040	0.140	0.130
Na	340	430	470	320	260	260
Sr	38.0	29.0	35.0	19.4	68.0	70.0
Tl	0.300	0.100	0.120	0.090	0.770	0.690
Sn	2.40	1.11	1.27	1.16	0.840	0.850
U	0.840	0.870	1.09	0.870	0.770	0.750
V	24.0	220	187	290	36.0	35.0
Zn	111	81.0	78.0	95.0	106	95.0

Appendix 6.2 *Continued*

Lake →	Mangahia 2011 Mid 2	Manga- kaware 2011 Deep	Manga- kaware 2011 Mid 1	Manga- kaware 2011 Mid 2	Maratoto 2004	Maratoto 2011
Sampling year →	2011	2011	2011	2011	2004	2011
Variable						
OC	18.0	11.4	11.3	13.0	-	32.0
TN	1.21	0.970	1.01	1.16	-	1.33
Al	33000	46000	40000	36000	15100	19200
Sb	0.090	0.170	0.170	0.160	0.260	0.200
As	7.90	8.40	7.40	7.70	2.30	2.80
Ba	330	460	470	460	122	155
Bi	0.110	0.200	0.180	0.180	0.100	0.100
B	3.00	4.00	4.00	4.00	4.00	4.00
Cd	0.930	1.210	1.120	1.370	0.250	0.250
Cs	1.87	3.60	3.30	3.20	0.390	0.380
Ca	7400	4100	3800	3900	5740	7100
Cr	9.80	8.80	8.40	8.50	4.80	5.80
Co	17.5	13.0	11.5	13.8	3.80	5.50
Cu	25.0	26.0	23.0	26.0	13.0	13.9
F	126	107	86.0	76.0	-	98.0
Fe	29000	22000	27000	24000	8020	11900
La	12.7	21.0	21.0	21.0	8.85	9.20
Pb	12.8	19.8	16.7	16.5	24.0	23.0
Li	9.30	14.6	11.4	11.7	1.00	1.00
Mg	1260	860	740	770	1420	1570
Mn	360	400	410	350	100	132
Hg	0.138	0.230	0.195	0.200	0.100	0.107
Mo	0.620	0.630	0.580	0.580	0.530	0.690
Ni	6.70	8.00	7.70	8.10	2.50	3.00
P	3800	1860	2300	1770	843	770
K	680	640	590	570	178	210
Rb	6.60	9.40	8.50	8.00	1.43	1.64
Se	< 2	3.000	3.00	3.00	2.00	3.00
Ag	0.140	0.250	0.220	0.220	0.070	0.130
Na	250	220	220	220	308	370
Sr	72.0	47.0	38.0	42.0	65.4	98.0
Tl	0.880	0.890	0.780	0.980	0.130	0.170
Sn	0.89	1.57	1.38	1.35	0.600	0.720
U	0.790	1.23	1.20	1.19	0.388	0.430
V	34.0	42.0	41.0	37.0	32.0	40.0
Zn	130	183	174	198	40.2	43.0

Appendix 6.2 Continued

Lake →	Ngaroto 2004	Ngaroto 2011	Ohinewai 2011 Deep	Ohinewai 2011 Mid 1	Ohinewai 2011 Mid 2	Omatearoa 2011
Sampling year →	2004	2011	2011	2011	2011	2011
Variable						
OC	-	7.40	11.5	10.4	9.90	0.400
TN	-	0.760	0.740	0.700	0.730	0.060
Al	24400	31000	13200	16800	14500	3900
Sb	0.140	< 0.04	0.410	0.300	0.290	< 0.04
As	4.20	5.50	39.0	33.0	27.0	0.900
Ba	410	450	210	240	183	10.7
Bi	0.150	0.130	0.110	0.120	0.100	< 0.02
B	3.00	4.00	4.00	3.00	3.00	< 2
Cd	0.560	0.580	0.310	0.280	0.280	0.022
Cs	1.70	1.66	2.20	2.70	2.60	0.250
Ca	4250	4400	4900	4800	4200	1970
Cr	6.70	6.90	5.10	5.90	5.30	25.0
Co	16.8	17.4	17.3	12.3	10.8	16.7
Cu	18.3	17.6	10.2	10.7	10.2	10.3
F		52.0	153	169	165	210
Fe	34100	39000	41000	41000	33000	49000
La	25.8	30.0	11.5	11.6	10.3	3.80
Pb	13.5	11.3	6.400	7.000	6.200	4.900
Li	8.30	9.40	6.70	8.60	7.40	3.20
Mg	894	840	840	920	770	2400
Mn	1710	2600	2100	2100	1640	440
Hg	0.190	0.115	0.119	0.117	0.120	< 0.010
Mo	0.320	0.350	0.600	0.580	0.510	0.090
Ni	4.90	5.40	4.90	5.00	4.60	10.8
P	929	1030	720	690	620	400
K	629	580	410	490	440	220
Rb	8.35	9.00	6.20	7.60	7.00	2.30
Se	< 2	< 2	< 2	< 2	< 2	< 2
Ag	0.110	0.110	0.090	0.090	0.080	< 0.02
Na	241	191	300	310	260	113
Sr	36.1	42.0	38.0	37.0	34.0	10.9
Tl	0.760	0.750	0.630	0.430	0.370	< 0.02
Sn	0.800	0.830	0.640	0.730	0.630	0.510
U	0.969	0.900	0.730	0.770	0.670	0.250
V	34.0	33.0	20.0	21.0	18.0	290
Zn	146	148	89.0	90.0	88.0	87.0

Appendix 6.2 *Continued*

Lake →	Parkinson 2003	Penewaka 2011 Deep	Penewaka 2011 Mid 1	Penewaka 2011 Mid 2	Puketi 2011 Deep	Puketi 2011 Mid 1
Sampling year →	2003	2011	2011	2011	2011	2011
Variable						
OC	-	8.30	8.10	9.90	4.90	5.60
TN	-	0.860	0.790	1.010	0.440	0.530
Al	-	20000	26000	24000	15000	14200
Sb	-	0.490	0.510	0.600	0.100	0.990
As	10.0	30.0	42.0	41.0	4.00	4.20
Ba	-	147	167	185	35.0	33.0
Bi	-	0.120	0.130	0.160	0.040	0.050
B	-	6.00	7.00	7.00	4.00	3.00
Cd	0.500	0.310	0.240	0.310	0.067	0.072
Cs	-	15.3	15.1	15.5	0.560	0.560
Ca	-	2800	3000	3200	3600	3200
Cr	28.0	7.40	8.60	8.70	32.0	34.0
Co	-	10.2	10.0	12.7	27.0	29.0
Cu	23.0	13.9	13.7	16.0	17.8	19.1
F	-	210	151	115	220	220
Fe	-	31000	34000	41000	83000	73000
La	-	9.30	9.90	10.8	7.80	7.90
Pb	13.1	35.0	36.0	45.0	14.9	200
Li	-	22.0	25.0	27.0	7.80	7.10
Mg	-	1230	1450	1470	2600	2600
Mn	-	580	680	720	730	640
Hg	<0.1	0.162	0.172	0.174	0.039	0.038
Mo	-	0.280	0.320	0.410	0.240	0.280
Ni	19.0	4.90	5.10	5.60	14.5	15.9
P	-	800	1030	1220	970	870
K	-	830	890	990	410	420
Rb	-	18.5	19.4	19.5	4.80	5.00
Se	-	< 2	< 2	< 2	< 2	< 2
Ag	-	0.080	0.090	0.100	0.040	0.040
Na	-	310	320	410	320	290
Sr	-	25.0	27.0	27.0	26.0	23.0
Tl	-	0.320	0.270	0.340	0.030	0.040
Sn	-	1.07	1.19	1.29	0.940	0.790
U	-	0.620	0.680	0.800	0.860	0.550
V	-	24.0	28.0	32.0	370	380
Zn	260	89.0	75.0	94.0	121	126

Appendix 6.2 *Continued*

Lake →	Puketi 2011 Mid 2	Roto- kotuku 2011 Deep	Roto- kotuku 2011 Mid 1	Roto- kotuku 2011 Mid 2	Roto- manuka 2004	Roto- manuka 2011
Sampling year →	2011	2011	2011	2011	2004	2011
Variable						
OC	13.6	34.0	24.0	20.0	-	17.6
TN	1.33	1.90	1.43	1.07	-	1.75
Al	17100	8100	9500	8300	14900	39000
Sb	0.130	0.080	0.090	0.160	0.650	0.380
As	5.00	1.00	1.60	1.00	4.10	4.10
Ba	43.0	71.0	68.0	71.0	129	151
Bi	0.050	0.150	0.350	0.180	0.100	0.110
B	6.00	5.00	5.00	5.00	8.00	9.00
Cd	0.154	0.141	0.106	0.149	0.500	0.640
Cs	0.560	0.140	0.140	0.170	0.930	1.120
Ca	3600	3700	3700	4300	4560	7300
Cr	32.0	5.10	6.10	5.20	9.5	12.7
Co	31.0	1.53	2.20	1.02	16.9	21.0
Cu	21.0	17.9	22.0	14.6	19.2	24.0
F	220	111	260	240	-	101
Fe	64000	2100	2300	1730	19900	32000
La	8.00	7.50	11.1	7.40	18.4	22.0
Pb	13.3	8.30	5.80	21.0	82.6	106
Li	7.20	< 0.4	0.400	0.400	3.20	7.60
Mg	2100	540	540	640	520	810
Mn	640	56.0	50.0	64.0	820	980
Hg	0.066	0.120	0.147	0.123	0.110	0.124
Mo	0.410	0.320	0.400	0.330	0.640	0.690
Ni	16.6	3.30	4.40	2.30	5.60	7.30
P	990	910	950	710	888	1580
K	480	159	172	165	464	520
Rb	4.80	0.880	1.00	1.05	4.35	5.30
Se	< 2	2.00	3.00	2.00	< 3	4.00
Ag	0.050	0.040	0.040	0.030	0.100	0.150
Na	410	440	470	410	238	250
Sr	28.0	43.0	33.0	45.0	48.9	62.0
Tl	0.050	0.100	0.230	0.040	0.520	0.500
Sn	0.880	0.140	0.180	0.200	0.700	0.910
U	0.530	0.129	0.133	0.152	0.540	0.610
V	340	14.0	15.0	13.0	57.0	82.0
Zn	149	55.0	32.0	28.0	180	200

Appendix 6.1 *Continued*

Lake →	Roto- manuka 2011 Deep	Roto- manuka 2011 Mid 1	Roto- manuka 2011 Mid 2	Serpen- tine East 2004	Serpentine East 2011 sample 1	Serpentine East 2011 sample 2
Sampling year →	2011	2011	2011	2004	2011	2011
Variable						
OC	17.0	17.1	11.4	-	15.1	16.9
TN	1.67	1.64	1.44	-	1.22	1.32
Al	30000	35000	22000	34600	36000	36000
Sb	0.420	0.390	0.350	0.170	0.140	0.110
As	4.00	4.00	4.50	3.10	3.10	2.90
Ba	280	290	310	28.0	82.0	64.0
Bi	0.090	0.090	0.080	0.130	0.130	0.120
B	8.00	8.00	8.00	3.00	4.00	4.00
Cd	0.530	0.550	0.430	0.690	0.640	0.630
Cs	0.790	0.880	0.690	1.620	1.320	1.210
Ca	6600	7300	6900	6860	7300	6900
Cr	9.40	10.4	7.90	6.60	6.40	6.40
Co	19.5	18.1	20.0	11.8	13.8	11.8
Cu	19.1	20.0	17.6	18.7	17.0	17.0
F	56.0	74.0	60.0	-	122	124
Fe	38000	34000	44000	22700	23000	24000
La	16.8	17.3	14.9	27.1	22.0	23.0
Pb	77.0	94.0	36.0	17.8	16.7	15.7
Li	5.50	6.50	4.20	9.00	9.20	9.20
Mg	730	820	710	857	970	880
Mn	1010	1050	1010	279	290	280
Hg	0.092	0.114	0.100	0.140	0.137	0.140
Mo	0.730	0.680	0.720	0.660	0.780	0.660
Ni	6.00	6.20	5.20	5.00	5.10	5.10
P	1430	1440	1520	1280	1340	1300
K	560	560	830	463	450	420
Rb	4.10	4.50	4.10	7.31	7.20	6.80
Se	2.00	3.00	2.00	2.00	3.00	3.00
Ag	0.100	0.110	0.090	0.170	0.200	0.190
Na	260	250	230	263	320	270
Sr	53.0	56.0	44.0	65.1	74.0	70.0
Tl	0.550	0.460	0.680	0.530	0.590	0.500
Sn	0.700	0.770	0.640	1.10	1.06	1.01
U	0.530	0.570	0.470	0.680	0.640	0.590
V	58.0	61.0	50.0	45.0	53.0	46.0
Zn	185	178	179	141	130	127

Appendix 6.2 *Continued*

Lake →	Serpentine East 2011 sample 3	Serpentine East 2011 Deep	Serpentine East 2011 Mid 1	Serpentine East 2011 Mid 2	Serpentine North 2004	Serpentine North 2011
Sampling year →	2011	2011 (replicate)	2011 (replicate)	2011 (replicate)	2004	2011
Variable						
OC	18.1	15.2	14.9	16.4	-	18.5
TN	1.45	1.27	1.32	1.44	-	1.36
Al	33000	37000	36000	35000	28000	41000
Sb	0.140	0.110	0.120	0.110	0.250	0.150
As	2.90	3.00	3.00	2.90	2.60	2.60
Ba	49.0	310	310	320	52.6	82.0
Bi	0.100	0.130	0.130	0.120	0.120	0.120
B	4.00	4.00	4.00	4.00	4.00	4.00
Cd	0.800	0.610	0.740	0.770	0.420	0.400
Cs	1.00	1.43	1.50	1.54	1.63	1.20
Ca	7200	6600	6600	6400	6280	7800
Cr	6.10	6.00	5.90	6.00	5.90	7.10
Co	18.8	11.6	11.6	9.90	7.98	11.60
Cu	17.5	17.7	18.1	18.7	18.6	23.0
F	133	129	131	135	-	148
Fe	26000	22000	23000	21000	17400	29000
La	21.0	22.0	22.0	21.0	20.2	27.0
Pb	21.0	16.7	21.0	18.7	25.0	17.2
Li	7.80	10.2	10.3	10.9	7.20	8.60
Mg	880	840	860	820	735	970
Mn	670	260	270	250	201	320
Hg	0.147	0.152	0.128	0.148	0.100	0.132
Mo	0.680	0.660	0.640	0.560	0.510	0.720
Ni	5.30	5.10	5.00	5.00	4.30	6.10
P	1340	1280	1390	1270	826	1050
K	400	440	460	460	470	460
Rb	5.70	7.30	7.70	7.90	6.69	6.00
Se	3.00	3.00	2.00	2.00	< 2	3.00
Ag	0.180	0.200	0.170	0.170	0.120	0.170
Na	300	280	260	260	166	210
Sr	72.0	69.0	67.0	66.0	46.4	67.0
Tl	0.740	0.540	0.540	0.560	0.370	0.340
Sn	0.940	0.950	0.970	1.00	1.10	0.970
U	0.560	0.680	0.680	0.680	0.623	0.650
V	41.0	44.0	40.0	33.0	40.0	46.0
Zn	164	132	145	142	133	136

Appendix 6.2 *Continued*

Lake →	Serpentine North 2011 Deep	Serpentine North 2011 Mid 1	Serpentine North 2011 Mid 2	Serpentine South 2011 Deep	Serpentine South 2011 Mid 1	Serpentine South 2011 Mid 2
Sampling year →	2011	2011	2011	2011	2011	2011
Variable						
OC	16.0	17.0	16.3	12.6	11.5	11.0
TN	1.39	1.61	1.51	1.19	1.13	1.08
Al	35000	36000	36000	41000	42000	49000
Sb	0.370	0.170	0.240	5.200	0.140	0.140
As	2.80	2.90	3.20	8.10	5.30	5.20
Ba	280	300	290	380	390	420
Bi	0.130	0.150	0.140	0.240	0.220	0.250
B	5.00	6.00	6.00	8.00	8.00	7.00
Cd	0.480	0.620	0.620	0.660	0.620	0.680
Cs	1.31	1.76	1.59	1.83	1.89	2.30
Ca	8300	8000	8400	5600	5400	5300
Cr	6.30	7.10	7.20	7.90	7.80	8.50
Co	10.5	9.00	11.2	14.1	13.4	14.0
Cu	21.0	23.0	25.0	45.0	24.0	26.0
F	134	145	132	82.0	80.0	90.0
Fe	24000	19600	21000	27000	28000	28000
La	22.0	21.0	21.0	23.0	23.0	24.0
Pb	72.0	36.0	34.0	320	30.0	32.0
Li	9.50	10.7	9.80	13.0	14.2	16.8
Mg	1020	1020	1010	870	860	930
Mn	330	480	380	660	590	620
Hg	0.120	0.138	0.141	0.155	0.145	0.150
Mo	0.650	0.580	0.700	0.650	0.630	0.630
Ni	5.70	5.70	6.30	6.10	5.90	6.40
P	1070	1230	1180	1170	1180	1190
K	580	710	640	530	550	620
Rb	6.70	8.50	7.90	9.20	9.60	11.8
Se	3.00	2.00	3.00	3.00	3.00	3.00
Ag	0.180	0.170	0.180	0.220	0.210	0.230
Na	230	240	220	240	220	230
Sr	61.0	56.0	60.0	50.0	48.0	48.0
Tl	0.390	0.440	0.500	0.750	0.740	0.820
Sn	1.22	1.67	1.77	1.50	1.57	1.76
U	0.690	0.780	0.780	0.980	0.990	1.09
V	42.0	36.0	43.0	50.0	49.0	49.0
Zn	146	162	179	220	200	220

Appendix 6.2 *Continued*

Lake →	Taharoa 2011 Deep	Taharoa 2011 Mid 1	Taharoa 2011 Mid 2	Te Koutu 2004	Waahi 2004	Waahi 2011 Deep
Sampling year →	2011	2011	2011	2004	2004	2011
Variable						
OC	2.10	1.97	2.40	-	-	5.30
TN	0.310	0.310	0.370	-	-	0.600
Al	29000	25000	26000	20600	24100	29000
Sb	< 0.04	< 0.04	< 0.04	1.320	0.330	0.090
As	9.20	8.40	8.40	25.3	7.80	8.20
Ba	173	155	157	156	143	155
Bi	0.320	0.320	0.320	0.260	0.270	0.240
B	4.00	3.00	4.00	5.00	11.0	18.0
Cd	0.090	0.100	0.103	0.770	0.190	0.270
Cs	1.070	1.050	1.080	3.800	2.170	3.200
Ca	5400	4600	4900	4580	3120	4500
Cr	14.9	14.5	14.6	17.6	9.00	10.9
Co	13.2	12.8	13.1	6.48	10.2	11.0
Cu	31.0	32.0	32.0	49.1	14.0	13.8
F	290	260	270	-	-	220
Fe	71000	65000	61000	16800	25100	28000
La	17.3	17.7	17.9	13.7	12.8	14.3
Pb	18.0	17.9	17.7	316	17.6	16.5
Li	48.0	43.0	48.0	12.9	15.0	24.0
Mg	5600	5000	5300	2240	1280	1710
Mn	4000	2500	3300	296	878	1320
Hg	0.102	0.089	0.087	0.150	0.130	0.140
Mo	0.210	0.200	0.200	1.79	0.820	0.480
Ni	16.2	16.8	16.9	8.90	12.7	14.0
P	1340	1190	1110	1320	414	440
K	1460	1260	1450	806	638	1000
Rb	13.8	12.9	13.2	9.45	12.3	17.0
Se	< 2	< 2	< 2	< 2	< 2	< 2
Ag	0.080	0.070	0.080	0.150	0.070	0.070
Na	310	240	270	283	259	440
Sr	49.0	47.0	44.0	32.4	57.1	79.0
Tl	0.110	0.100	0.100	0.230	0.200	0.240
Sn	1.37	1.36	1.31	4.00	1.30	1.66
U	1.08	1.08	1.04	0.899	0.973	0.800
V	84.0	76.0	71.0	61.0	35.0	38.0
Zn	89.0	90.0	88.0	390	89.1	87.0

Appendix 6.2 Continued

Lake	Waahi 2011 Mid 1	Waahi 2011 Mid 2	Waikare 2004	Waikare 2004B
Sampling year	2011	2011	2004	2004B
Variable				
OC	5.30	5.40	-	-
TN	0.590	0.600	-	-
Al	26000	23000	15000	-
Sb	0.090	0.100	0.510	-
As	8.20	7.60	19.9	15.2
Ba	152	150	169	-
Bi	0.240	0.240	0.230	-
B	17.0	15.0	4.00	-
Cd	0.260	0.230	0.160	-
Cs	3.00	2.90	8.42	-
Ca	4700	4300	2280	-
Cr	10.7	9.60	7.30	-
Co	11.1	11.5	8.12	-
Cu	13.9	13.4	14.4	-
F	230	230	-	-
Fe	27000	27000	21400	-
La	13.9	13.9	15.7	-
Pb	16.0	16.2	18.3	-
Li	24.0	22.0	18.4	-
Mg	1750	1550	1660	-
Mn	1310	1080	1060	-
Hg	0.129	0.124	0.480	0.310
Mo	0.470	0.470	0.290	-
Ni	14.0	13.3	4.00	-
P	420	410	411	-
K	990	890	712	-
Rb	16.6	15.9	17.5	-
Se	< 2	< 2	< 2	-
Ag	0.090	0.070	0.050	-
Na	390	380	195	-
Sr	81.0	75.0	25.9	-
Tl	0.220	0.230	0.200	-
Sn	1.60	1.57	1.10	-
U	0.760	0.820	1.30	-
V	37.0	37.0	45.0	-
Zn	86.0	84.0	49.9	55.1

Appendix 6.2 Continued

Lake →	Waikare 2011 deep	Waikare 2011 Mid 1	Waikare 2011 Mid 2	Whangapae 2004
Sampling year →	2011	2011	2011	2004
Variable				
OC	2.90	3.00	2.70	-
TN	0.300	0.320	0.290	-
Al	19800	21000	19400	18100
Sb	0.200	0.250	0.220	0.260
As	13.0	13.8	12.2	8.50
Ba	167	182	174	141
Bi	0.200	0.220	0.210	0.190
B	6.00	9.00	6.00	8.00
Cd	0.161	0.179	0.180	0.230
Cs	9.60	10.4	9.80	1.82
Ca	2000	2100	1940	5530
Cr	7.90	8.30	8.10	11.3
Co	8.80	9.40	9.60	6.77
Cu	14.0	14.5	14.3	17.0
F	135	131	129	
Fe	22000	24000	23000	38900
La	14.3	15.8	15.3	11.2
Pb	17.2	18.5	18.4	16.6
Li	23.0	26.0	24.0	15.6
Mg	1590	1700	1560	1840
Mn	850	920	830	767
Hg	0.470	0.670	0.450	0.140
Mo	0.170	0.170	0.160	0.900
Ni	4.70	5.00	4.80	14.8
P	370	400	360	552
K	810	880	820	904
Rb	19.5	21.0	19.9	13.3
Se	< 2	< 2	< 2	< 2
Ag	0.070	0.070	0.070	0.080
Na	220	240	210	211
Sr	22.0	23.0	21.0	49.5
Tl	0.210	0.220	0.230	0.190
Sn	1.45	1.53	2.10	1.00
U	1.13	1.27	1.28	1.11
V	43.0	47.0	46.0	35.0
Zn	47.0	49.0	48.0	80.3

6.7 References

- Adriano, D. (1986). *Trace elements in the terrestrial environment*. New York: Springer-Verag.
- ANZECC. (2000). National water quality management strategy paper 4. *Australian and New Zealand guidelines for fresh and marine water quality*. Canberra, Australia: ANZECC with ARMCANZ.
- Cavanagh, J. (2006). *Comparison of soil guideline values used in New Zealand and their derivations. Landcare Research contract report: LC0607/025*. Lincoln, New Zealand: Prepared for Environment Canterbury.
- Driscoll, C., & Schecher, W. (1990). The chemistry of aluminum in the environment. *Environmental Geochemistry and Health*, 12(1-2), 28-49.
- He, Z., Yang, X., & Stoffella, P. (2005). Trace elements in agroecosystems and impacts on the environment. *Journal of Trace Elements in Medicine and Biology*, 19(2-3), 125-140.
- Kabata, A., & Pendias, H. (2001). *Trace elements in soils and plants*. New York: CRC Press.
- Kilbride, C., Poole, J., & Hutchings, T. (2006). A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni and Mn determined by acid extraction/ICP-OES and ex situ field portable X-ray fluorescence analyses. *Environmental Pollution*, 143(1), 16-23.
- Land Monitoring Forum. (2009). *Land and soil monitoring: A guide for SoE and regional council reporting*. New Zealand: Land Monitoring Forum.
- Long, E., MacDonald, D., Smith, S., & Calder, F. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental management*, 19(1), 81-97.

- Łukowski, A., & Wiater, J. (2009). The influence of mineral fertilization on heavy metal fraction contents in soil. Part II: copper and nickel. *Pol J Environ Stud*, 18(4), 645-650.
- Makepeace, D., Smith, D., & Stanley, S. (1995). Urban stormwater quality: Summary of contaminant data. *Critical Reviews in Environmental Science and Technology*, 25(2), 93-139.
- McLaughlin, M., Tiller, K., Naidu, R., & Stevens, D. (1996). Review: the behaviour and environmental impact of contaminants in fertilizers. *Soil Research*, 34(1), 1-54.
- MfE. (2004). *Contaminated land management guidelines No.5: Site investigation and analysis of soils (revised 2011)*. Wellington, New Zealand: Ministry for the Environment.
- MfE. (2006). *Contaminated land management guidelines No. 4: Classification and information management protocols*. Wellington, New Zealand: Ministry for the Environment.
- Monaghan, R., Wilcock, R., Smith, L., TikkiSETTY, B., Thorrold, B., & Costall, D. (2007). Linkages between land management activities and water quality in an intensively farmed catchment in southern New Zealand. *Agriculture, Ecosystems & Environment*, 118(1-4), 211-222.
- NZWWA. (2003). *Guidelines for the safe application of biosolids to land in New Zealand*. Wellington, New Zealand: New Zealand Water and Wastes Association.
- Pearson, L., Hendy, C., Hamilton, D., & Pickett, R. (2010). Natural and anthropogenic lead in sediments of the Rotorua lakes, New Zealand. *Earth and Planetary Science Letters*, 297(3), 536-544.
- Potts, P., Webb, P., Williams-Thorpe, O., & Kilworth, R. (1995). Analysis of silicate rocks using field-portable X-ray fluorescence instrumentation incorporating a

mercury(II) iodide detector: a preliminary assessment of analytical performance. *Analyst*, 120(5), 1273-1278.

Rosseland, B., Eldhuset, T., & Staurnes, M. (1990). Environmental effects of aluminium. *Environmental Geochemistry and Health*, 12(1-2), 17-27.

Sañudo-Wilhelmy, S., Gómez-Consarnau, L., Suffridge, C., & Webb, E. (2014). The role of B vitamins in marine biogeochemistry. *Annual Review of Marine Science*, 6(1), 339-367.

Stephenson, G., Milne, J., & Sorensen, P. (2008). *Wellington harbour marine sediment quality investigation*: Greater Wellington Regional Council.

Taranaki Daily News. (2012, 23/08/2012). Nickel is found to make all the difference to cows. Retrieved January 7, 2015, from <http://www.stuff.co.nz/taranaki-daily-news/lifestyle/7531473/Nickel-is-found-to-make-all-the-difference-to-cows>

Taylor, M. (1997). Accumulation of cadmium derived from fertilisers in New Zealand soils. *Science of the Total Environment*, 208(1), 123-126.

Taylor, M., & Kim, N. (2010). Dealumination as a mechanism for increased acid recoverable aluminium in Waikato mineral soils. *Soil Research*, 47(8), 828-838.

Taylor, M., Kim, N., & Hill, R. (2011). *A trace element analysis of soil quality samples from the Waikato region*. Paper presented at the 24th Annual FLRC Workshop: Adding to the knowledge base for the nutrient manager.

Taylor, M., Kim, N., Hill, R., Stevenson, B., & Gilkes, R. (2010). *Comparison of soil quality targets and background concentrations in soil of the Waikato Region, New Zealand*. Paper presented at the Proceedings of the 19th World Congress of Soil Science: Soil solutions for a changing world, Brisbane, Australia, 1-6 August 2010. Symposium 1.5. 1 Quantitative monitoring of soil change.

Waikato Regional Council. (2014a). Lakes in the Waikato region. Retrieved December 21, 2014, from <http://www.waikatoregion.govt.nz/Environment/Natural-resources/Water/Lakes/Shallow-lakes-of-the-Waikato-region/Peat-lakes/>

Waikato Regional Council. (2014b). *Shallow lakes management plan: Volume 2* (No. 2014/59). Hamilton: Waikato Regional Council. Retrieved from <http://www.waikatoregion.govt.nz/PageFiles/19527/Additional%20information%20for%20Item%206B%20Shallow%20Lakes%20Resource%20Statement.pdf>

Chapter 7. Summary and Conclusions

Since the remedial attributes of Zn for ruminal facial eczema were discovered approximately 3 decades ago, many pastoral soils in the Waikato region of New Zealand have received high mass loadings of Zn (in the order of 5-7 kg/ha/yr). Productive pastoral soils (mainly dairy, beef and sheep farms) comprise 57% of Waikato's land area (about 1,430,000 ha). This activity has potential for both widespread accumulation of Zn in receiving soils, Zn mobilization and contamination of nearby environments, such as surface water and sediments. If occurring, these outcomes have the potential to cause a range of adverse effects that may include toxicity to ecological receptors. Zn compounds have also been used as fungicides for many years on some types of horticultural soils, a category that represents only ~0.6% of Waikato's land area (about 10,145 ha) but is at the base of all fruit and vegetable production.

Although there have been many individual soil and water surveys carried out over the years, none have examined the environmental fate of significant sources of anthropogenic Zn used in farming and few have been designed with representative wide-scale environmental state monitoring in mind. However, as part of their responsibility under the RMA (1991), Waikato Regional Council have instituted a range of systematic and overlapping environmental monitoring programmes, which have generated an extensive set of monitoring data describing concentrations of Zn in Waikato soils and receiving environments. This data was made available for use in this study.

The core aim of this study was to determine the extent and nature of any evidence that facial eczema Zn is causing significant contamination of agricultural soils and associated ecosystems in the Waikato Region of New Zealand. This was achieved by examining Waikato soils datasets for evidence and magnitude of Zn enrichment and accumulation in Waikato farmed soils (Chapter 3) and by examining Waikato surface water and sediment datasets for evidence relating to possible entry of anthropogenic Zn into freshwaters (Chapter 4 and Chapter 5) and lake sediments (Chapter 6).

On average, farmed (horticultural and pastoral) surface soils now contain twice as much Zn as natural (background and forestry) surface soils. Furthermore, Zn enrichment in pastoral surface soils is substantial enough to place it within the enrichment range of better-known trace element soil contaminants associated with superphosphate fertiliser application (e.g. Cd, P, Ca, U F and Ni). Including Zn, these elements also appear to decrease down the soil profile in farmed soils, indicating substantial surface agricultural inputs and possible mobilization.

Zn concentrations vary according to soil order. Farmed organic, granular, and allophanic soils contain an average of 30-33 mg/kg more Zn than background soils of the same orders. Additionally, Zn adsorption in granular soils was observed to occur rapidly (>90% of total Zn amount within 5 mins) at the natural soil pH level of 5.70. Under these conditions most (~97%) of the Zn was adsorbed at equilibrium. The proportion of Zn adsorbed to the granular soil significantly decreased (to ~62%) at pH 4.70, indicating that an increase in soil acidity would be likely to cause re-mobilisation of some of the previously adsorbed Zn.

In relation to potential for toxicity to soil organisms, the upper end of the distribution is of most interest. Approximately 11% of pastoral soils exceeded 100 mg/kg Zn, an indicative guideline that could be used to denote potential toxicity to soil microbial function. No soils exceeded 300 mg/kg; the upper limit recommended for soils the New Zealand Biosolids Guidelines. The highest single result from a pastoral farm was 170 mg/kg (AR Zn), and from a horticultural property 190 mg/kg (AR Zn).

A key implication of continued Zn accumulation in pastoral and horticultural soils is that increasing areas of land may experience a decrease in function and ecological health as a result of Zn toxicity, particularly in relation to microbes, plants, and soil invertebrates. Excess Zn may also affect soil chemistry of other trace elements with which Zn competes or interacts. For example, excess Zn (Zn^{2+}) may increase desorption and mobilisation of Cd (Cd^{2+}) to soil pore water, or decrease plant uptake of the essential trace elements Cu (Cu^{2+}) or Co ($Co^{2+/3+}$), potentially inducing deficiencies in these elements.

Farmed soils did not gain or lose a significant amount of Zn in between sampling occasions (average of 7 years); however, these findings are likely to be limited by the scope of data currently available and potentially by changes over time in sampling methodology and data analysis. Forest soils show an apparent 25% decrease in Zn concentrations over an average of 7.4 years, which may or may not be genuine. Although the reason for this result in forest soils is uncertain, results for forest soils suggest the possibility that soils under plantation forestry may be becoming deficient in essential trace elements. Mechanistically this would make sense because trace elements such as Zn would be exported from the system in wood that is harvested with each rotation.

The Waikato River carries approximately 100.5 kg Zn/day, and the proportion of Zn in the dissolved form is approximately half. A peak in Zn concentration in the upper reaches of the Waikato River is likely to be of geothermal origin. Total and dissolved Zn concentrations quickly decrease in the mid-section of the River, indicating rapid adsorption to bed sediments. A distinct second peak in Zn concentrations in the lower reaches of the River coincides with increased concentrations of nutrient elements, turbidity, and intensive pastoral farming within the catchment area. This, in addition to increased Zn concentrations during high-flow events (over and above the amount needed to outweigh a dilution effect), suggests that Zn from soil in the lower river catchment area is being mobilised into the Waikato River.

Regionally, the same occurrence of increased Zn loadings to surface waters was observed during periods of rainfall and increased river flows. Thirteen of the sixteen non-compliant (i.e. $>8 \mu\text{g Zn/L}$) sampling sites are located in farming catchments (for the others, source of Zn were geothermal, and urban). Results for this part of the work indicated that rainfall events are mobilising soluble Zn within pastoral catchments in a way that usually causes an increase in both the concentration ($\mu\text{g/L}$) of Zn in the water, as well as the (more expected) increase in mass loading (kg/day). Occasional exceedances of guideline values suggest that this may be attributable to anthropogenic Zn, but it was not possible to quantify the relative proportions of mobilised Zn attributable to natural or anthropogenic sources.

A key implication of the results is that it is thought *unlikely* that use of facial eczema Zn is causing (or will cause) direct Zn toxicity in regional rivers and streams. This is because the ANZECC ecological guideline value for dissolved Zn (8 µg/L) relates to long-term exposure, and exceedances that were observed were marginal (not orders of magnitude above the guideline). However, it is thought likely that Zn is accumulating in some sediment receiving environments (see below).

Nineteen regional Waikato lakes included in this study appear to have at least twice as much Zn in bed sediments than what is expected to occur naturally. Although Zn enrichment does appear to be occurring in most lakes studied, in most cases concentrations are not yet high enough to cause toxicity to sediment dwelling organisms and aquatic ecosystems. Whether Zn may continue to accumulate in a given lake, or part of a lake, may depend on an interplay of factors that would include the annual mass load of anthropogenic Zn, the mass of clean sediment (perhaps enhanced by erosion in the catchment) and the nature of sediment deposition in the lake bed. It is possible that Zn concentrations will still be steadily increasing in sediments of all lakebeds that receive runoff from pastoral land. However, it is also possible that some lakebeds will have attained a steady-state concentration of Zn, where the new Zn inputs are balanced by dilution factor represented by the lower Zn concentration of natural sediments.

Overall, findings from this study show that agricultural Zn use in the Waikato region of New Zealand is increasing Zn concentrations in Waikato farmed soils, and that soil Zn may potentially be mobilising to receiving surface water and sediments. As the primary use of Zn in agriculture, facial eczema remedies are likely to be contributing most of the anthropogenic Zn to farmed soils. This is likely to have been the case since Zn was discovered as a facial eczema remedy approximately 3 decades ago. Although Zn concentrations in farmed soils and receiving surface waters and sediments are enriched, concentrations are not, at the present time, high enough to cause toxicity to microbes or sediment ecosystems.

The following recommendations are made based on the results of this research:

1. Development of suitable New Zealand-specific guideline values for Zn in agricultural soils. These could consider (a) protection of soil microbial health and productive function (b) protection of other soil ecological receptors such as plants and invertebrates, and (c) significance of potential for Zn to induce deficiency in another trace element.
2. Investigation of the relationships between increased Zn in soils and the environmental behaviour and plant uptake of toxic or essential elements such as Cd, Cu, and Co.
3. Investigation of the potential for Zn to be causing the widespread development antibiotic resistance in recipient soils and its potential human health significance.
4. Targeted work on regional lakes to determine conditions under which Zn concentrations are likely to be increasing in bed sediments, which lakes are most vulnerable, and mitigation measures that could be undertaken to prevent bed sediments from becoming ecotoxic.
5. Quantification of the proportion of anthropogenic to natural Zn in surface water runoff in a representative stream or river in a pastoral catchment. This may be possible through determination of Zn isotope ratios in receiving waters compared with those in facial eczema treatments and background soils.
6. Investigations of viable and inexpensive alternatives to the use of Zn for facial eczema prevention.
7. Investigation of potential trace element depletion in soils under forestry and its significance in terms of environmental sustainability of plantation forestry and future land uses (i.e. to maintain land-use flexibility as per RMA 1991).