



Trace Elements in the Sediments of Te Waihora

Summer Scholarship Report

WCFM Report 2011-001

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TITLE: **Trace Elements in the Sediments of Te Waihora**

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Executive Summary

The sediments of Te Waihora contain natural levels of trace metals, at concentrations that are below the ANZECC (2000) interim sediment quality guidelines.

Trace metal concentrations were measured in <2mm and <63µm sediment size fractions for 13 different sites located around the lake. ICP-MS analysis was used to determine trace metal concentrations for vanadium (18.9-45.8mg/kg), chromium (12.5-26.8mg/kg), manganese (194.2-237.5mg/kg), cobalt (6.1-12.4mg/kg), nickel (9.3-18.3mg/kg), copper (3.7-22.7mg/kg), zinc (33.2-82.7mg/kg), arsenic (2.1-9.8mg/kg), cadmium (0.02-0.13mg/kg) and lead (7.1-27.1mg/kg).

The sediments do not show elevated trace metals as a consequence of anthropogenic contamination, despite the intense agricultural influences in the catchment. This is likely due to the fact that drainage reaches the lake mainly via the groundwater system, which retards trace element mobility and transport to the lake environment. Future work could be carried out to assess whether proposed land use changes in the catchment will increase trace metal accumulation in the lake.

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Section 1 Introduction

Te Waihora (Lake Ellesmere) is one of New Zealand's most biodiverse ecosystems and regarded internationally for its conservation values.¹ The lake is a habitat for 43 species of fish and 167 species of birds of which at least 37 species are breeding.¹ It supports a large commercial Eel (*Anguilla australis*), Flounder (*Rhombosolea retiaria*) and Yellow Eyed Mullet (*Aldrichetta forster*) fishing industry which supplies both local and international markets.²

Te Waihora is located at the bottom of an extensive catchment and acts as a sink for nutrients and trace metals. Increased use of nitrate and phosphate fertilizers in the catchment has caused the lake to become highly eutrophic. The lake has an average depth of 1.4m and due to the high average winds the water remains oxygenated enough for aquatic life.² Until now, research has been focussed on nutrient and water conditions in the lake. This projects aims to determine the concentration of trace metals in the lake bed sediments and determine whether these metals occur at natural levels.

1.1 Geology and Hydrology

The Te Waihora catchment covers an area of 276,000 hectares of the Southern Alps, Canterbury Plains and Banks Peninsula (see Figure 1).^{1, 3} The Selwyn River and Banks Peninsula surface water provide one third of the water inflow water to the lake. The other two thirds of inflow water are from artesian spring feed streams and rivers which occur within 20km of the lake.^{3, 4} The ground water in the catchment which feeds the artesian springs is sourced primarily from channel leakage from the Rakaia, Waimakariri and Selwyn rivers with a lesser amount sourced from direct seepage from the Canterbury Plains.⁴

Morphological, stratigraphical, micropaleontological and radiocarbon dating of the Kaitorete Spit indicates the lake formed around 8,000 years ago, creating Te Waihora.⁵ Since the formation of the lake there have been periodic openings of the lake to the sea by avulsion of the Waimakariri River. The last natural opening occurred 200-500 years ago and changed the lake environment to the current lagoonal/estuarine setting.⁵ The lake is now artificially opened to control the lake level. Wind action on the surface of the lake causes it to become highly turbid.

1.2 Natural Sources of Trace Metals

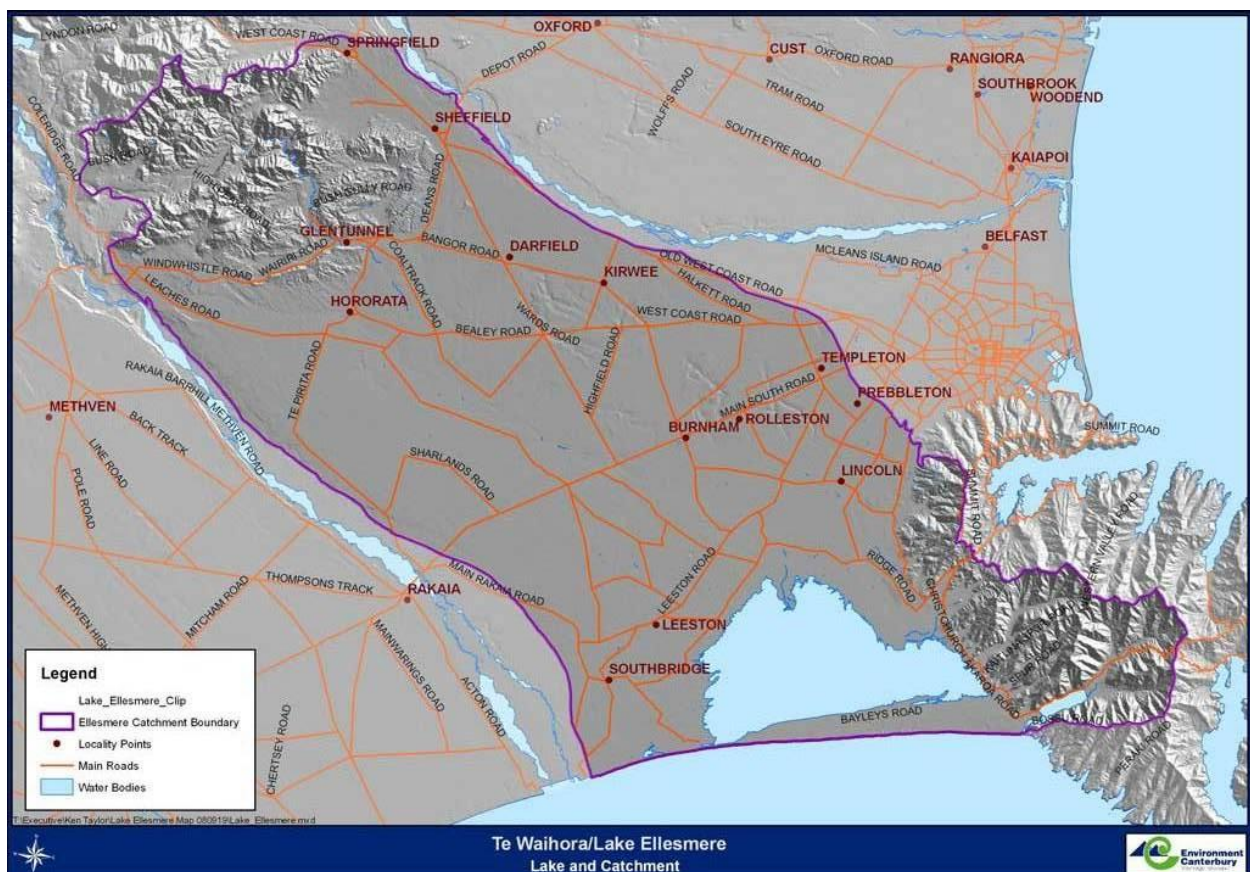
Trace metals occur naturally in varying concentrations depending on the geology of an area. The main natural source of trace metals in Te Waihora is weathering of the Akaroa and Lyttleton volcanoes located at the northern end of the lake (Figure 1). The majority of the rock present is basaltic with minor amounts of rhyolite and trachyte. Basalt contains higher

amounts of Cr, Cu, Ni and Zn than other rocks in the Te Waihora catchment. These metals can substitute for Fe, Mg and Al in mafic minerals due to their similar ionic radii⁶. Pb may also substitute for K in K-Feldspar which is present in felsic rocks such as rhyolites. The rest of the catchment is composed of recent fluvial gravel deposits which are dominantly composed of quartz sandstone. It is important to note that the bulk of detrital trace metals remain bound within the mineral lattice from initial weathering to deposition and are therefore not bioavailable.⁶

1.3 Anthropogenic Source of Trace Metals

The catchment is dominantly used for agricultural purposes. The main anthropogenic source of trace metals in this catchment is most likely from the use of rock phosphate-based fertilisers. Rock phosphate contains a number of trace metals such as Cd, U, Ni, Hg, Mn, Cu, Cr, As, Zn, Mo and Pb but the concentration of these varies depending on the source of the rock phosphate and the geological setting where it formed.^{7,8,9} Cadmium concentrations in pastoral soils have increased over the last 50 years due to phosphate fertiliser use.⁷ The degree of accumulation of cadmium varies depending on the soil type.⁷ Trace elements such as Cu, Zn, Mo, Co, Mn are added to fertilisers in varying amounts to make up for soil deficiencies.

Other potential sources of contamination are CCA-treated timber and timber treatment plants, facial eczema treatment which contains a high amount of Zn, lead from duck shooting which occurs on the lake, and possibly sewage discharge into the lake.



Section 2 Methods

2.1 Sediment Sampling

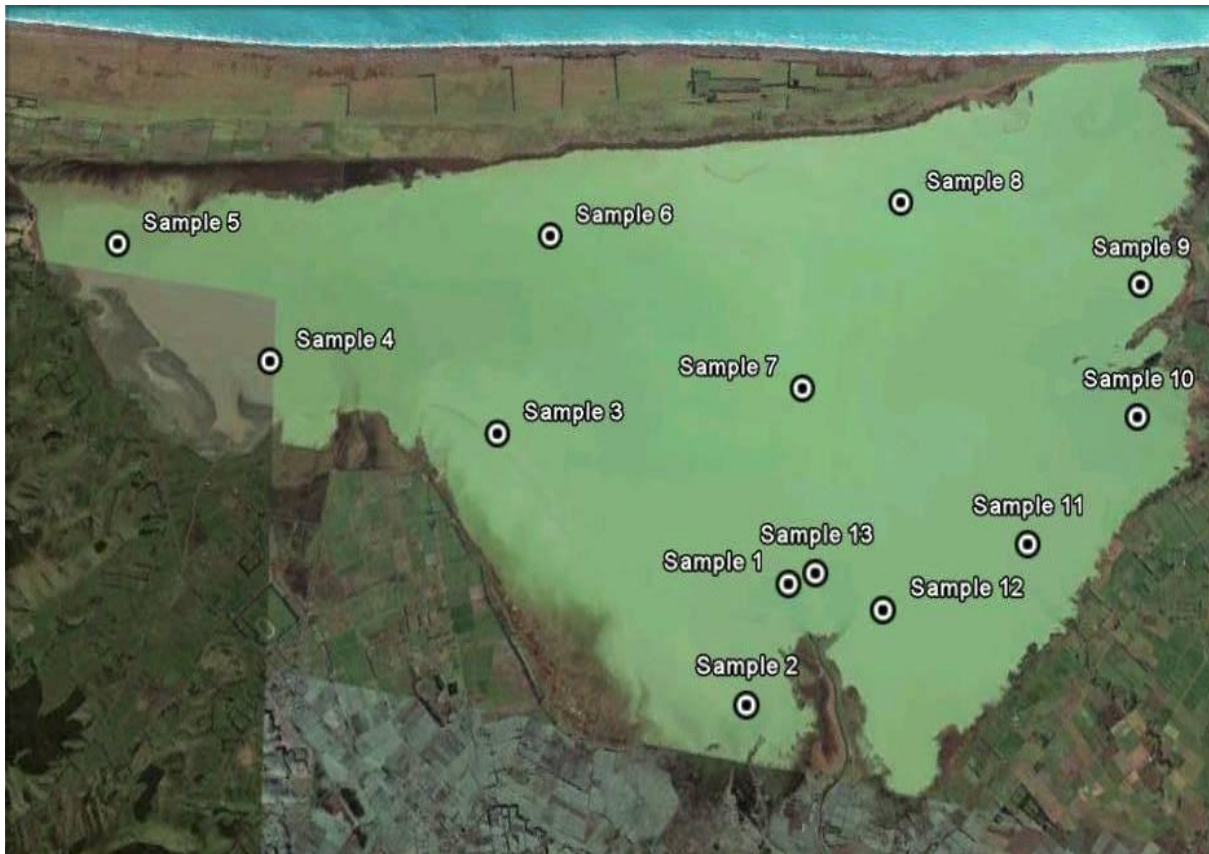


Figure 2. Sample site locations on Lake Ellesmere/Te Waihora (base map, Google Earth, 2010).

The sampling programme was designed to obtain an overview of different diffuse and point source sediment inputs. Seven point source samples were collected from the inflows of the Selwyn River, LII River, Halswell River, Harts Creek and the Irwell River. An additional six samples were collected from the areas located away from point sources (Figure 2). GPS coordinates for the sample sites are recorded in the Appendix. The samples were collected using a stainless steel grab sampler which was thoroughly washed with lake water between samples to avoid cross-contamination between sites (Figure 3). The uppermost portion of brown oxidised sediment was removed from the sampler, placed in an acid washed container and sealed in a bag to avoid contamination. Samples were immediately placed in a cooler at approximately 4°C.

2.2 Analysis for Trace Metals by ICP-MS

Total trace metal content was determined using Method 200.8 from the U.S. Environmental Protection Agency.¹⁰ Samples were placed in acid washed trays and dried at 35°C for five days to prevent the loss of volatile metallic compounds. After drying the samples were disaggregated by double-bagging and rolling with a rolling pin. The ground samples were then dry sieved using 2mm and 63µm nylon sieves to obtain two separate fractions. One gram of each size fraction was weighed out in duplicate and placed in an acid washed digestion tube followed by 4ml of HNO₃ (1+1) and 10ml of HCl (1+4). The digestion tubes were heated to 95°C and refluxed for 30 minutes. To ensure the method's effectiveness and quality, a certified marine sediment reference material (U.S. National Institute of Standards and Technology Standard Reference Material 2702) and blanks were used with each batch digested. Recoveries for the CRM standard reference material are summarised in Table 1. All reagents used in the analysis were of high analytical grade.



Figure 3. Sediment sampling from the University of Canterbury boat, using an aluminium grab sampler (photo credit: Phil Emnet).

For ICP-MS analysis the samples were diluted by a factor of 10 with 2% nitric acid to reduce the interference of salt due to the slightly saline nature of the sediments. This dilution factor was found to be insufficient and caused a build-up of salt on the cones. To reduce the salt effect the dilution was increased to 21 times. To ensure quality control during analysis, at every 10 samples a duplicate was made and every 20 samples a triplicate made for a spike recovery. Spiked samples showed an average recovery of 94%.

2.3 Grain Size Distribution Analysis

To determine the percentage of each size fraction (<63µm, <2mm) present in the samples, 20g of dry sediment were accurately weighed out and sieved with a 63µm nylon mesh sieve. The remaining fraction of >63µm was weighed and the percentage calculated.

2.4 Organic Content

The percent weight of organic matter was determined using loss on ignition. Approximately 1cm³ of sediment from each size fraction was accurately weighed out in a silica crucible. The samples were then placed in an oven at 105°C for 24 hours to remove any residual moisture.¹¹ On immediate removal from the oven, samples were weighed to obtain an accurate dry weight. Samples were then placed in a muffle furnace and heated at 550°C for four hours.¹¹ After heating, samples were transferred to a 60°C oven to cool. Once cooled to 60°C, samples were reweighed and the organic matter determined by the loss in weight.

Table 1. CRM Standard Reference Material recoveries

Element	Standard Reference Material Recovery (Recovery %)
V	74.7
Cr	70.8
Fe	105.2
Mn	84.2
Co	82.6
Ni	62.6
Cu	83.6
Zn	83.2
As	88.6
Cd	98.1
Pb	90.4

2.5 Iron Analysis

Iron analyses were carried using a Varian SpectraAA 220FS atomic absorption spectrometer (AAS). Due to high concentrations of iron, large dilutions would be required to analyse the samples by ICP-MS. To avoid large dilutions and the associated error, AAS was chosen as it would still produce an accurate iron result. The calibration curve was made by dilution of a CertiPUR 1000ppm Fe standard. The wavelength used was 248.3nm with an optimum detection range of 0.6-15ppm.

2.6 Statistical Analysis

Statistical analysis of data was carried out using Data Desk 6.0 and Microsoft Excel. Data Desk was used to log normalise data and create Pearson Product Correlation Coefficients to determine whether there was significant variation between different metals. Paired t-tests were used to determine if metal concentrations were higher in a particular size fraction.

Section 3 Results and Discussion

Metal concentrations, organic matter concentrations and grain size distribution data are presented in Table 2. Trace metal values presented are the average of the two duplicate samples analysed. The mean difference between duplicates was 10.2%. This difference is most likely due to the heterogeneity of the samples. There is no organic matter content value for Sample 1 due to sample use. Antimony was measured for two sites (Samples 2 and 3) in areas which have high amounts of recreational shooting. Antimony concentrations were found to be <1ppb and have not been included as they were below the detection limit.

3.1 Sediment Characterisation

Elevated metal concentrations were found at Site 6 located mid-way along the Kaitorete Spit and Site 11 at the mouth of the Irwell River. The concentration of metals in Te Waihora sediments are well below the Australia and New Zealand Environment Conservation Council (ANZECC) Interim Sediment Quality Guidelines (ISQG) (see Table 3). This means that sediment should have no adverse effects on the aquatic ecosystem of Te Waihora (see Table 3).¹²

A 2003 study by Kingett and Mitchell Ltd. examining sediment quality in Pegasus Bay reported concentrations comparable to those measured in Te Waihora sediments.¹³ Although the bay is a different physical and environmental setting, the natural and anthropogenic sources of contaminants are similar. The study measured trace metal concentrations in 17 (<2mm fraction) samples taken between the mouths of the Waimakariri and Ashley rivers. The method used for digestion and analysis was method 200.2 from the US EPA. The results from this study are shown in Table 3. The majority of results are slightly lower than those of Te Waihora which may be due to the high sedimentation rate making it difficult for metals to accumulate. The site is also located further from the Lyttelton and Banks Peninsula volcanoes therefore receiving less trace metals.

Table 2. Metal concentrations, organic matter concentrations and grain size distribution in Te Waihora. S1-S13 are the <2mm fraction; S1a – S13a are the <0.63um fraction.

Sample	Grain Size Dist. wt%	Organic Matter Wt%	Fe Wt%	Mn (mg/Kg)	Cr (mg/Kg)	V (mg/Kg)	Co (mg/Kg)	Ni (mg/Kg)	Cu (mg/Kg)	Zn (mg/Kg)	As (mg/Kg)	Cd (mg/Kg)	Pb (mg/Kg)
S1	>99	-	3.61	209	13	21	8	10	4	33	2.1	0.02	7
S2	61	3.9	4.08	292	17	27	8	12	7	51	3.0	0.04	15
S3	87	5.2	3.50	234	13	19	6	9	4	33	2.8	0.02	8
S4	59	5.0	4.21	324	16	26	8	12	7	49	3.4	0.03	14
S5	52	3.8	4.59	205	21	34	7	13	9	58	3.6	0.03	18
S6	19	1.6	5.34	328	25	46	11	18	12	83	6.5	0.04	27
S7	7	3.1	4.64	262	17	27	7	12	7	51	2.9	0.02	16
S8	17	2.8	4.20	331	17	28	8	12	7	53	3.9	0.03	16
S9	67	4.6	4.79	284	17	27	10	14	8	49	4.7	0.03	12
S10	38	5.0	5.20	438	21	34	10	15	11	62	5.2	0.03	19
S11	45	3.8	5.82	320	27	43	12	18	12	70	7.0	0.04	20
S12	14	3.6	4.25	372	18	29	9	13	8	56	3.9	0.03	17
S13	14	4.5	5.82	302	22	36	10	15	11	67	4.4	0.04	24
S1a	<1	-	5.02	315	19	32	12	15	14	64	7.5	0.13	24
S2a	39	2.8	3.72	313	18	29	9	14	23	60	3.7	0.04	19
S3a	13	1.9	3.18	333	18	29	8	14	8	59	3.4	0.03	19
S4a	41	1.2	3.31	319	17	27	8	13	8	54	4.1	0.04	17
S5a	48	3.8	4.29	194	18	30	6	12	7	52	3.8	0.03	18
S6a	81	3.8	4.20	312	23	43	11	18	12	80	6.5	0.04	26
S7a	93	3.3	3.32	224	13	21	6	10	6	42	2.3	0.02	13
S8a	83	3.7	3.36	276	14	22	7	10	6	43	3.2	0.02	13
S9a	33	2.4	4.23	305	20	34	11	16	13	66	9.8	0.07	24
S10a	62	4.5	3.86	395	19	30	9	14	10	61	4.8	0.04	20
S11a	55	3.4	4.40	315	27	44	12	18	19	73	7.1	0.04	21
S12a	86	3.7	3.63	317	15	25	8	11	7	48	3.3	0.03	15
S13a	86	4.6	4.26	283	19	32	9	14	11	61	4.4	0.03	21
Min		1.2	3.2	194	12	19	6	9	4	33	2.1	0.02	7
Max		5.2	5.8	437	27	46	12	18	23	83	9.8	0.13	27
Average		3.6	4.3	300	19	31	9	14	10	57	4.5	0.04	18

Table 3. Trace metal concentrations (mg/kg unless noted) in the Te Waihora sediments, compared with those of other studies, and sediment quality guidelines

	Min	Max	Median	Mean	Pegasus Bay Sediments 2003 ¹³	Avon/Heathcote Estuary (1994) ¹⁴		ANZECC ISQG (2000) ¹²	
						<i>Site 1</i>	<i>Site 2</i>	<i>Low</i>	<i>High</i>
Fe	3.2%	5.8%	4.2%	4.3%		2.14%	1.46%		
Mn	194.2	437.5	312.7	300.1		84.4	55.8		
V	18.9	45.8	29.0	30.6					
Cr	12.5	26.8	18.2	18.6	12.7	56.0	34.7	80	370
Ni	9.3	18.3	13.5	13.6	9.5	15.8	10.9	21	52
Cu	3.7	22.7	8.1	9.6	3.9	7.46	7.57	65	270
Zn	33.2	82.7	57.0	56.9	35.8	29.1	43.8	200	410
As	2.1	9.8	3.9	4.5	5.0			20	70
Cd	0.02	0.13	0.03	0.04	0.02			1.5	10
Pb	7.1	27.1	17.8	17.9	10.9	22.3	8.87	50	220

Deely et al 1994 measured the trace metal concentrations in the Avon/Heathcote Estuary and their distributions in the different size fractions.¹⁴ The total metal concentrations recorded at two sites in the estuary are presented Table 3. Site 1 is located at the mouth of the Heathcote River and Site 3 is located near the outflow of the oxidation ponds. The concentration of metals found in the estuary are similar to Te Waihora values, however there are some variations due to urban contamination. The metal concentrations are up to five times higher in the <4µm clay fraction.¹⁴ The increased concentration of metals in the clay fraction has the potential to cause adverse effects to plant and animal life in Te Waihora due to the lake's high turbidity.

3.2 Interpretation

Metal concentrations varied between sites but concentrations observed at the sites were high for all metals (see Figure 4). Statistical analysis of data from Te Waihora sediments suggests that metal concentrations in the lake are close to natural levels. The Pearson Product Correlations for each of the size fractions show a strong relationship with trace metals and iron content in the sediments (see Appendix). There is also a relationship with the vanadium content in the sediments which suggests that the metal concentrations found in the lake are from natural sources. The paired t-test values for the comparison of metal concentrations between the two different size fractions show that Fe, Cu, Zn, As, Cd and Pb are likely to be found in higher concentrations in the <63µm fraction (see Table 4). The differences in metal concentration between the two size fractions were minimal due to the high content of fines in most samples. If samples were sieved within a range (e.g. <2mm-63µm) excluding lower fractions, concentration differences between each size fraction would be more apparent.

Table 4. Paired t-test results for <2mm vs <63µm

Metal	T-test Result
V	0.464
Cr	0.431
Fe	0.003
Mn	0.489
Co	0.316
Ni	0.275
Cu	0.043
Zn	0.016
As	0.085
Cd	0.078
Pb	0.063

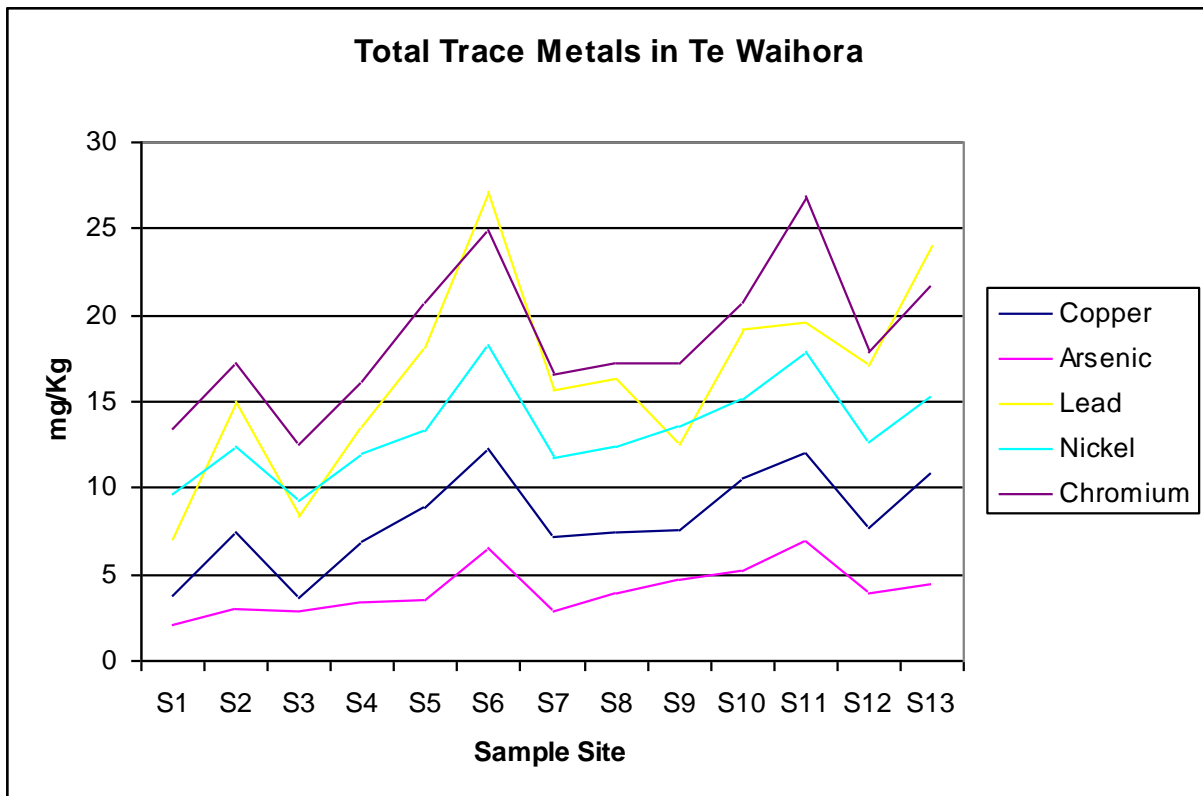


Figure 4. Metal concentrations of the sediment at 13 different sites in Te Waihora for the <2mm fraction of the sediment.

3.3 Further Research

Suspended sediment: Due to Te Waihora's high turbidity, the trace metal load in the suspended sediment should be determined. Suspended sediment has a greater effect on plant and animal life living in the lake and has a higher bioavailability than bottom sediment.

Bioavailability: A bioavailability study should be carried out on the lake looking at the effects of trace metals on high trophic level species (e.g. Eels).

Other lakes: A further study on Lake Wairewa (Forsyth) will allow the differences in natural and anthropogenic contaminants from different catchments to be compared.

Follow-up study: In the past 20 years, the Te Waihora catchment has made a transition from dominantly dry land farming to irrigated dairy farming. This change has resulted in an increased use of phosphate fertiliser to maximise grass production which may cause significant contamination of Te Waihora. A study by Butler and Timperley in 1996 has shown that phosphate-based fertilisers are a source for cadmium contamination into estuaries.⁸ The data gathered from this study on Te Waihora is a baseline to assess whether contamination is occurring. A follow-up study on the sediment contamination should be carried out in the next three to five years to determine any changes.

Section 4 Conclusion

The results from this study show that the trace metal concentrations in the sediments of Te Waihora are at natural levels. The values are within the ANZECC guidelines for sediment quality for the protection of aquatic life.

Concentrations found for lake sediments can act as a baseline for future studies to assess whether Te Waihora is being affected by anthropogenic trace metal input.

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Appendix

Sample GPS Locations

Sample Site	Latitude	Longitude
1	43°45'7.87"S	172°27'12.22"E
2	43°43'53.18"S	172°27'35.87"E
3	43°46'8.89"S	172°31'55.12"E
4	43°46'30.12"S	172°35'36.24"E
5	43°47'28.15"S	172°38'21.53"E
6	43°48'18.86"S	172°31'36.76"E
7	43°47'8.10"S	172°27'21.92"E
8	43°49'17.69"S	172°26'11.17"E
9	43°48'49.02"S	172°22'18.73"E
10	43°47'24.46"S	172°22'11.78"E
11	43°45'55.43"S	172°23'41.56"E
12	43°45'1.81"S	172°25'45.12"E
13	43°45'16.89"S	172°26'49.38"E

Pearson Product-Moment Correlations for <2mm Fraction

	Log V	Log Cr	Log Fe	Log Mn	Log Co	Log Ni	Log Cu	Log Zn	Log As	Log Cd	Log Pb	Log OM%
Log V	1											
Log Cr	0.987	1										
Log Fe	0.899	0.918	1									
Log Mn	0.451	0.443	0.463	1								
Log Co	0.764	0.748	0.789	0.603	1							
Log Ni	0.96	0.952	0.931	0.545	0.887	1						
Log Cu	0.953	0.958	0.937	0.585	0.767	0.956	1					
Log Zn	0.971	0.953	0.883	0.568	0.722	0.937	0.971	1				
Log As	0.871	0.883	0.845	0.619	0.83	0.927	0.885	0.855	1			
Log Cd	0.779	0.773	0.68	0.495	0.715	0.779	0.793	0.803	0.723	1		
Log Pb	0.916	0.902	0.842	0.559	0.596	0.851	0.937	0.977	0.762	0.764	1	
Log OM%	-0.528	-0.425	-0.231	-0.073	-0.252	-0.425	-0.345	-0.572	-0.353	-0.263	-0.56	1

Pearson Product-Moment Correlations for <63μm Fraction

	Log V	Log Cr	Log Fe	Log Mn	Log Co	Log Ni	Log Cu	Log Zn	Log As	Log Cd	Log Pb	Log OM%
Log V	1											
Log Cr	0.984	1										
Log Fe	0.692	0.71	1									
Log Mn	0.39	0.407	0.22	1								
Log Co	0.767	0.757	0.602	0.611	1							
Log Ni	0.954	0.944	0.631	0.512	0.872	1						
Log Cu	0.776	0.778	0.446	0.472	0.743	0.836	1					
Log Zn	0.951	0.924	0.582	0.529	0.754	0.947	0.846	1				
Log As	0.811	0.8	0.571	0.483	0.844	0.87	0.749	0.817	1			
Log Cd	0.547	0.526	0.394	0.385	0.704	0.638	0.672	0.632	0.775	1		
Log Pb	0.849	0.812	0.499	0.479	0.621	0.835	0.809	0.955	0.764	0.67	1	
Log OM%	-0.166	-0.122	0.263	-0.101	-0.088	-0.217	-0.175	-0.28	-0.162	-0.304	-0.326	1

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