



Trace Elements in the Sediments of

Lake Forsyth/Wairewa

Summer Scholarship Report

WCFM Report 2012-003

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TITLE: **Trace Elements in the Sediments of Lake Forsyth/Wairewa**

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

PREPARED BY: **Rosemary Parry** BSc (Chemistry)

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

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

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Executive Summary

In support of initiatives to restore Wairewa/Lake Forsyth and improve its water quality, this report investigates trace element concentrations in the lake sediments. Field sampling and chemical analyses for key contaminant trace elements were undertaken, and the data analysed with respect to correlations between elements and comparison to other lake sediments and sediment quality guidelines for the protection of aquatic life.

Surface sediment samples were collected at 20 sites on the lake, and then dried and separated into two size fractions; <63 μ m and <2mm. These were analyzed for chromium (3.7-12.8mg/kg), manganese (90-795 mg/kg), nickel (2.3-10.4 mg/kg), copper (1.3-11.6 mg/kg), zinc (19-55 mg/kg), arsenic (0.2-3.2 mg/kg), cadmium (0.02-0.08 mg/kg) and lead (3.4-16.4 mg/kg) using ICP-MS, and for iron (1.0-3.2 wt%) using AAS. Organic matter (2.6-13.6 wt%) was determined from LOI in a muffle furnace.

All of the trace element concentrations were close to natural background levels, and seemingly unaffected by anthropogenic inputs. Concentrations were below those anticipated to adversely affect aquatic life (i.e., below ANZECC interim sediment quality guidelines) and low relative to the sediments of Te Waihora and Lake Taupo.

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Section 1 Introduction

1.1 Background

Lake Forsyth/Wairewa has high cultural and aesthetic value to the local community, but due to land use intensification, has become hypertrophic. This change has led to a decrease in biodiversity; Maori oral tradition recalls a more diverse and ample fish population (Woodward & Shulmeister, 2005) for example. It has also decreased the aesthetic value of the lake, as green algal blooms now regularly appear over the summer months (e.g., Fig 1). Due to the steep topography of the area, pollution of the lake could include the contribution of fertilizers, which contain trace elements, leaching from steep pastures in the catchment.

There has been limited research undertaken on the condition of Wairewa's sediments and the aim of this project is to see whether trace element concentrations are elevated or at a natural background level, as this has implications for ecosystem restoration, and for sediment removal and reuse or disposal, if required.



Figure 1 Summer algal bloom at Lake Forsyth/Te Wairewa in December 2012.

1.1.1. Characteristics

Lake Forsyth/Wairewa is a shallow lake, with a maximum depth of 4m and an average depth of 1-1.15m and, as with most shallow lakes, it is highly turbid (Main, 2003). Wairewa is fed by the Okana River, which receives flow from the Okuti River and the Opuahau and Hikuika Streams (Elliott, 2002). In addition to this, the steep sides of the lake basin, particularly to the southeast, allow for direct runoff from pasture to the lake.

The lake is hypertrophic. The concentration of nitrate-nitrogen is twice the recommended ANZECC water quality guidelines to minimize algal growth, the phosphorous concentration is three times the recommended limit (Main, 2003). Artificial openings of the lake to the sea through the gravel bar, and seawater overtopping the gravel bar, contribute to the brackish nature of the water. The higher salinity can favour the growth of certain nuisance algae species, such as *Nodularia* (Elliott, 2002)

1.1.2 History

Wairewa's condition today has been strongly influenced by past natural and anthropogenic changes. The lake was originally a tidal estuary and surrounded by forest (Main, 2003). This was altered in the middle of the 19th century when the Kaitorete Spit formed from the avulsion of the Waimakariri river from the Lake Ellesmere basin (Soons et al., 1997). This almost permanently severed the lake from the seawater (Main, 2003), leaving it in a brackish, rather than fluctuating salinity, state. With no outlet to the sea, there was a high risk of flooding adjacent farms, so in 1866 the lake started to be periodically artificially opened by physically removing gravel to create a channel through the bar (Woodward & Shulmeister, 2005).

The forest surrounding Wairewa was removed for timber or burnt off to create pasture. This increased the amount of sediment entering the lake. Before the European settlers arrived, the sedimentation rate was 0.1 mm per year, but this has increased to 20 times this rate over the last 150 years (Reid et al., 2004). Deforestation made land available for farming which became more intensive in the area. The combination of increased nutrients from farming, and the closure regime, has led to reduced water quality in the lake and consequent algal blooms from 1907 (Elliott, 2002; Main, 2003).

1.2 Potential sources of trace elements

Due to the location of Wairewa there are both anthropogenic and natural potential sources of trace metals. Fertilizer use in the catchment could contaminate the lake with the minor trace element concentrations typically contained. New Zealand has traditionally obtained phosphate from ancient avian guano deposits on Christmas Island (Taylor, 1997). The phosphate-blended fertilizer contains trace elements such as cadmium (Cd), uranium (U), molybdenum (Mo), arsenic (As), zinc (Zn), chromium (Cr), lead (Pb), nickel (Ni), vanadium (V), antimony (Sb) and beryllium (Be) (McBride & Spiers, 2001). Increased use of phosphate fertilizer in New Zealand has, for example, increased the amount of Cd in the topsoil over the last 50 years (Taylor, 1997).

Other potential anthropogenic sources of trace elements include urban runoff. The lake is located near two townships; Little River and Birdlings Flat, which include ca. 1000 people and 400 households (Statistics New Zealand, 2006). Runoff from buildings and roof surfaces can include copper (Cu), Pb and Zn, and treated timber can leach Cu, Cr and As, for example. The road running the length of the lake on the north-west shore, is also a potential source of metal discharge into the lake. A vehicle's brake components can contaminate road surfaces

with antimony (Sb) Cu, Pb, Zn, aluminium (Al), manganese (Mn) and iron (Fe) and tyre wear can deposit Zn, Cu, Pb and Fe (Pattle Delamore Partners Ltd, 2008).

In addition, both townships use septic tanks (Asset and Network Planning, 2011). The treated sewage is released into a leaching field, and could reach the lake given the close proximity.

The natural sources of trace elements that could enter the lake include the predominantly volcanic rocks of Banks Peninsula, created by the eruption of two volcanoes; Akaroa and Lyttelton, millions of years ago (Boffa Miskell Limited, 2007). In Lake Taupo, for example, the volcanic catchment is the source of the trace metals present in the lake sediments, which appear largely uninfluenced by anthropogenic change (Koyama et al., 1989).

Section 2 Methodology

2.1 Sediment sampling

Samples were collected at 20 different locations on the lake (Figure 2) in December 2011. GPS Locations for the sites are given in Appendix 1. To provide a representative sample set, the lake was split into five sampling zones; the cliffs zone (C) with 5 samples, the Little River zone (L) with 3 samples, road zone (R) with 5 samples, middle zone (M) with 3 samples and Birdlings Flat zone (B) with 4 samples. While sampling it was noted that in the cliff zone, at C4 and C5, there were sheep grazing on the flat by the lake, and these sites are both offshore from distinctive gullies draining this steep terrain.



Figure 2. Sampling locations on Wairewa/Lake Forsyth. GPS co-ordinates are given in Appendix 1.

The oxidised surface layer of the sediments was collected into a container using a grab sampler, as seen in Figure 3. Before sediment collection, the 200ml LabServ plastic containers being used for sediment storage were rinsed three times with the lake water at

each site. To avoid cross contamination, each filled container was stored in two sealable bags, and all were placed in a chiller bag to keep them cool.



Figure 3. The grab sampler used to collect soft surface sediment from the lake bed.

2.2 Sample preparation

The method used to determine the trace element content of the sediments was EPA Method 200.8 (EPA, 1994). The sediments were first placed in individual acid washed trays and dried for five days at 30° C. Following this, they were double bagged and disaggregated by using a metal rolling pin.

The sediments were divided into two-grain sizes, <63µm which is classified as silt and <2mm, which is classified as sand. To obtain the less than 63µm fraction, the sediment was sieved through nylon mesh. To acquire the less than 2mm fraction, the sediment was sieved through a plastic sieve.

2.3 Trace element analysis

For each sample, 1g was weighed out into acid-washed digestion tubes and 4ml of HNO₃ (8N) and 10ml HCl (2N) were added. The samples were digested at 95°C for 30 minutes, cooled and made up to 20ml. The digestions were diluted a further 21 times and then analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

For quality control, a standard reference marine sediment (#2702) was also digested (in triplicate) and a blank digestion (no sediment) included to check method accuracy. Every 10

samples a duplicate digestion was undertaken, and every 20 samples, a triplicate digestion was undertaken and used for spike recovery.

Results for the standard reference sediment analysis are given in Table 1, showing recoveries of between 60 and 95%. Pb and Cd are fully recovered, while Mn, Cu, Zn and As are only 77-80% recovered by this digestion method. Ni and Cr are only 55-60% recovered by this digestion. The digestion method we used targets only elements bound to the surface of minerals in the sediment, not those included in the mineral structure (which *are* included in the analysis that comes with the standard reference material). Our digestion method therefore provides an indication of readily available trace elements, rather than total trace elements. Elements such as Pb and Cd were evidently bound predominantly to the surface of minerals in the provided standard reference material, whereas Ni and Cr occurred at least partly within the mineral matrix itself.

Table 1 Standard reference marine sediment trace element percentage recovery using the described digestion procedure, rather than a total digestion of the sediment.

Element	% Recovery
Cr	60.9
Mn	80.5
Ni	55.2
Cu	79.0
Zn	77.0
As	77.6
Cd	92.7
Pb	95.6

2.4 Organic content analysis

The percentage weight of organic matter (OM) was determined using loss on ignition (LOI). Samples were oven dried to a constant weight at 105°C for 21 hours, weighed and then heated at 500-550°C in a muffle furnace for four hours to oxidize the organic matter. The LOI was calculated as the difference in the weights and taken to be equal to the organic matter content (Heiri et al, 2001).

2.5 Iron analysis

The Fe concentration was analyzed by Atomic Adsorption Spectrometry (AAS) rather than ICP-MS. This was because the high level of dilution required for ICP-MS analysis would have give a very high error in the Fe analysis. The iron analysis was undertaken on a Varian SpectraAA 220FS atomic adsorption spectrometer, using a wavelength of 248.3 and silt width of 0.2, for a working concentration range of 0.06-15 mg/L.

2.6 Statistical analysis

Microsoft Excel 2008 for Mac was used in the analysis of the results. A paired t-test was used to determine whether the levels of trace elements in the >2mm and the <63 μ m were statistically significantly different. To test whether there was statistically significant correlation between the trace elements and between OM and the trace elements, a Pearson Product Table was produced. (Appendix 1)

Section 3 Results

The results are presented in Table 2a and 2b, for the different sediment size fractions. The concentrations of trace elements (apart from Fe) are shown as an average of the duplicates analyzed. The average difference between duplicates was 8.6%; just within the analytical error of 10%. The heterogeneous nature of the samples will be a contributing factor. Organic matter had two duplicates analyzed, with an average difference of 1.9%. The average difference in the four duplicates in the Fe analysis was 1.4%.

Table 2a Concentrations of trace elements (mg/kg unless otherwise noted) in the <2mm sediment size fraction in Lake Forsyth/Wairewa.

Site	OM Wt%	Fe Wt%	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
R1	8.2	2.7	9.4	559	6.8	8.2	42	2.1	0.05	10.2
R2	10.5	3.0	9.7	795	7.1	10.0	45	2.3	0.06	11.3
R3	8.0	2.4	5.8	160	4.3	4.5	28	1.3	0.03	7.5
R4	7.7	2.2	6.6	221	4.9	5.5	34	1.5	0.04	8.1
R5	7.1	2.0	5.0	176	3.6	3.8	25	1.0	0.03	5.8
L1	3.9	1.3	4.8	132	2.9	2.6	21	0.7	0.02	4.1
L2	4.0	1.4	5.3	165	3.1	2.9	24	0.8	0.03	4.6
L3	4.0	1.4	6.2	161	3.7	3.4	26	0.8	0.03	4.9
C1	9.1	2.7	9.2	242	7.6	7.6	42	1.9	0.05	10.9
C2	5.6	2.0	6.8	399	5.7	5.3	30	1.5	0.03	6.8
C3	6.5	2.1	7.5	333	6.2	5.6	34	1.6	0.04	8.3
C4	8.0	2.3	9.0	272	7.5	7.0	41	1.9	0.05	10.4
C5	6.7	1.9	5.9	293	5.7	4.9	29	1.4	0.04	6.0
M1	11.7	3.2	10.7	653	8.5	10.2	51	2.9	0.07	13.5
M2	9.6	2.8	9.0	330	7.1	7.6	44	2.4	0.05	11.4
M3	8.6	2.2	8.2	299	6.2	6.8	43	1.8	0.06	10.2
B1	7.8	2.4	11.5	242	9.7	8.7	41	2.5	0.05	11.3
B2	11.5	2.8	11.6	380	9.4	10.9	51	2.9	0.07	13.9
B3	13.6	3.1	11.9	257	9.6	11.1	55	3.2	0.08	15.3
B4	12.0	3.0	12.8	214	10.4	11.6	54	2.9	0.08	15.7
Min	3.9	1.3	4.8	132	2.9	2.6	21	0.7	0.02	4.1
Max	13.6	3.2	12.8	795	10.4	11.6	55	3.2	0.08	15.7
Median	8.0	2.3	8.6	265	6.5	6.9	41	1.8	0.05	10.2
Mean	8.2	2.3	8.3	314	6.5	6.9	38	1.9	0.05	9.5

Table 2b Concentrations of trace elements (mg/kg unless otherwise noted) in the <63µm sediment size fraction in Lake Forsyth/Wairewa.

Site	OM wt%	Fe wt%	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
R1	5.4	1.9	7.1	289	5.1	4.8	33	1.5	0.04	7.9
R2	8.2	2.2	7.9	393	5.9	6.6	37	1.8	0.05	9.2
R3	5.8	1.8	6.1	164	4.6	3.0	30	0.8	0.03	9.7
R4	5.3	1.7	4.8	142	3.6	3.7	26	1.0	0.03	6.0
R5	4.5	1.4	3.9	124	2.9	2.8	21	0.8	0.02	4.9
L1	2.7	1.0	4.3	107	2.7	1.3	23	0.3	0.02	4.2
L2	2.6	1.1	4.5	124	2.7	2.3	21	0.6	0.02	3.9
L3	2.7	1.1	3.7	90	2.3	1.5	19	0.2	0.02	4.2
C1	7.0	2.0	7.9	200	6.6	6.1	36	1.6	0.04	8.9
C2	4.0	1.5	5.7	210	4.7	4.1	26	1.1	0.03	5.9
C3	4.0	1.6	6.2	216	5.0	2.3	32	0.6	0.03	7.8
C4	6.0	1.9	7.4	223	6.0	5.3	34	1.6	0.04	8.3
C5	4.1	1.3	5.1	177	4.0	2.0	27	0.5	0.03	6.0
M1	10.1	2.7	1.0	516	7.8	8.8	47	2.7	0.06	12.3
M2	8.0	2.3	6.6	180	4.9	2.8	35	0.6	0.04	7.8
M3	5.5	1.7	12.1	250	10.2	9.3	45	2.7	0.06	12.6
B1	7.8	2.4	10.7	237	8.6	4.9	45	1.3	0.07	12.6
B2	9.5	2.4	10.3	237	8.4	8.7	45	2.5	0.06	11.8
B3	11.1	3.1	10.8	233	8.8	5.3	48	1.5	0.07	13.4
B4	10.0	2.6	11.9	201	9.9	10.5	50	2.6	0.06	14.3
Min	2.6	1.0	3.7	90	2.3	1.3	19	0.2	0.02	3.9
Max	11.1	3.1	12.1	516	10.2	10.5	50	2.7	0.07	14.3
Median	5.7	1.9	6.9	206	5.1	4.4	34	1.2	0.04	8.1
Mean	6.2	1.9	7.4	216	5.7	4.8	34	1.3	0.04	6.6

Section 4 Discussion

4.1 Sediment quality

Excluding Mn & Fe, trace element concentrations were highest for Zn (mean 36mg/kg) and lowest for Cd (mean 0.04 mg/kg). Cu, Pb, Ni and Cr mean concentrations were in the range 5.9 to 9.3 mg/kg, with As somewhat lower at 1.6 mg/kg (Figure 4). All concentrations of trace elements were low in comparison to the ANZECC ISQG (interim sediment quality guidelines; ANZECC, 2000) i.e., trace element concentrations are unlikely to have an adverse impact on benthic (sediment hosted) plants and animals (Table 3).

Table 3 Trace element concentrations in the sediment of Wairewa, compared with previously recorded concentrations and ANZECC sediment quality guidelines, Te Waihora sediments (Joynt, 2011) and Lake Taupo Sediments (Koyama et al., 1989). Units in mg/kg unless otherwise noted.

	Lake Wairewa concentrations				Quality guidelines and other lakes			
	Min	Max	Median	Mean	ANZECC ISQG Low	ANZECC ISQG High	Lake Ellesmere (mean)	Lake Taupo (mean)
OM (%)	2.56	13.59	6.83	7.21			3.6	
Fe (%)	1.04	3.20	2.10	2.12			4.3	2.1
Cr	3.69	12.76	7.72	7.84	80	370	18.6	19.0
Mn	89.7	794	235	264			300	
Ni	2.29	10.42	5.79	6.12	21	52	13.6	4.0
Cu	1.32	11.63	5.66	5.86	65	270	9.6	20.0
Zn	19.09	54.8	37.5	36.0	200	410	56.9	61.0
As	0.24	3.19	1.52	1.59	20	70	4.5	47.0
Cd	0.02	0.08	0.04	0.04	1.50	10	0.04	
Pb	3.41	16.40	9.50	9.34	50	220	17.9	

A study on the neighbouring lake, Te Waihora/Lake Ellesmere (Joynt, 2011), used similar methods and analytical techniques to this study. Although adjacent to each other, the two lakes are quite different in terms of the nature of their inflow, and their size. The inflows to Te Waihora are largely groundwater-fed lowland streams, whereas the inflows to Wairewa are predominantly surface runoff. Te Waihora/ Lake Ellesmere is much bigger, with a surface area of ca. 19000 hectares (Selwyn District Council). Notably the average organic matter content of Wairewa sediment is double that of Te Waihora, while the trace element concentrations were generally lower than those of the larger lake.

A study on Lake Taupo (Koyama et al., 1989) was undertaken to provide a baseline for sediment trace elements in a volcanic catchment environment relatively uninfluenced by anthropogenic pollution. For all comparable trace elements, the concentrations in Wairewa sediments are considerably lower than in Taupo sediments (Table 3). For example, the

mean arsenic concentration for Lake Taupo sediments is 47 mg/kg whereas in Wairewa sediments it is 1.6 mg/kg.

From this we conclude that the trace elements concentrations in the sediments of Wairewa/Lake Forsyth are at background levels and not influenced by land use in the catchment or other anthropogenic effects.

4.2 The source of trace elements

Figure 4 shows how the key trace element concentrations all vary consistently at each site, indicating a natural (rock or soil) source. If it were anthropogenic contamination, some elements would peak, while the others remained at background level. Instead, with the exception Mn, all show peaks at R2, C1, C4, M1 and generally higher values near the outlet B2-B4.

The Pearson-correlation moment (refer Appendix 2) confirms a high correlation between OM and trace elements in the sediments (apart from Mn). The strongest correlations were seen between OM-Fe-Cu-Pb-Zn-As-Cd. A moderate to low correlation was observed for OM-Cr-Ni-Fe, and no correlation was observed for Mn with other OM or trace element components.

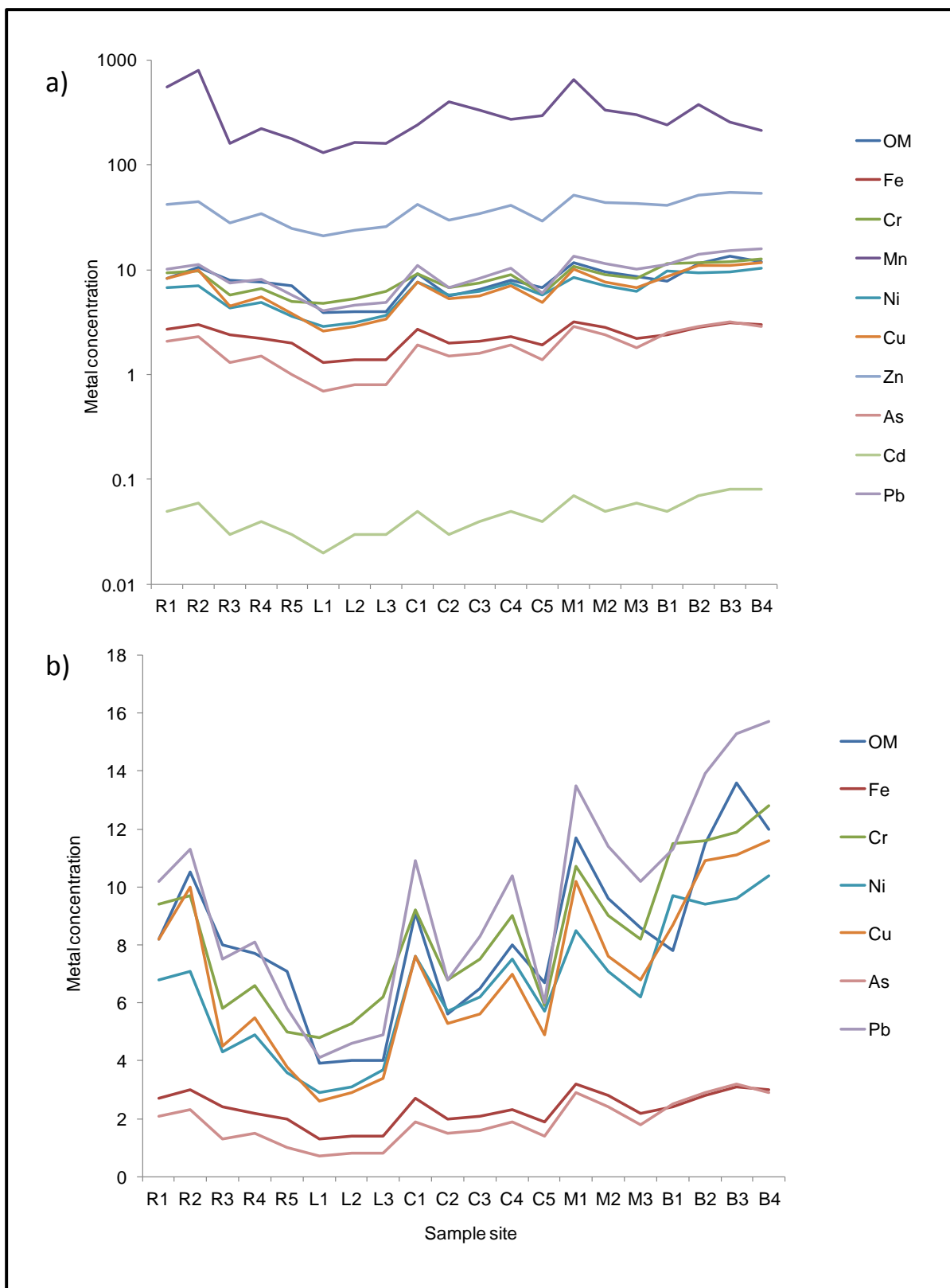


Figure 4. Concentrations in Wairewa sediments (<2mm size fraction) for all trace elements and OM (a) (note the log scale), and for key covariant trace elements and OM (b). Units are mg/kg for all plotted parameters, except OM and Fe (wt%).

4.3 The effect of the size fractions

A paired t-test was undertaken to look at differences in concentrations between the two grain size fractions (Table 4). For all elements there is a 5% statistically significant difference in trace element concentrations between the silt and the coarser sand in the sediment, with the sand (>63 μ m) fraction containing slightly more trace element. This difference may have been even more apparent if the <2mm fraction had excluded the silt (<63 μ m) fraction.

This is somewhat unusual as the finer fraction usually contains more trace elements bound to the surface of minerals, due to the higher surface area of the sediments. This may be indirect evidence of the natural provenance of the trace metals, which are still bound in the original detrital volcanic minerals, or suggest a different mechanism of trace element binding in the sediments.

Table 4 Paired t-test for <63 μ m vs <2mm

Element	p-value
%OM	0.00
Fe	0.02
Cr	0.00
Mn	0.00
Ni	0.01
Cu	0.00
Zn	0.00
As	0.00
Cd	0.00
Pb	0.00

Section 5 Conclusion

This investigation has shown that trace elements in Lake Forsyth/Wairewa sediments appear to be present at the concentrations that would be expected for natural background levels, and below ANZECC interim sediment quality guidelines for the protection of aquatic life. The concentrations are similar to, and generally slightly lower than those in the neighbouring Te Waihora/Lake Ellesmere.

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Appendix 1 Sampling sites GPS location

Sediment Sampling Lake Wairewa 02/12/2011			
Zone	Site	GPS (Latitude)	GPS (Longitude)
Road	R1	43°48.381' S	43°48.152' S
Road	R2	43°48.152' S	43°47.856' S
Road	R3	43°47.856' S	43°47.650' S
Road	R4	43°47.650' S	43°47.447' S
Road	R5	43°47.447' S	43°48.152' S
Little River	L1	43°47.324' S	172°46.176' E
Little River	L2	43°47.487' S	172°46.245' E
Little River	L3	43°47.447' S	172°46.334' E
Cliff	C1	43°48.755' S	172°44.220' E
Cliff	C2	43°48.464' S	172°44.524' E
Cliff	C3	43°48.281' S	172°44.884' E
Cliff	C4	43°48.245' S	172°45.281' E
Cliff	C5	43°47.971' S	172°45.962' E
Middle	M1	43°48.388' S	172°44.043' E
Middle	M2	43°48.002' S	172°45.063' E
Middle	M3	43°47.719' S	172°45.716' E
Birdlings	B1	43°49.427' S	172°42.614' E
Birdlings	B2	43°49.072' S	172°42.788' E
Birdlings	B3	43°48.946' S	172°43.075' E
Birdlings	B4	43°49.055' S	172°43.605' E

Appendix 2 Pearson product-moment correlations

Pearson Product-Moment Correlations for <2mm Fraction

	Log OM%	Log Fe%	Log Cr	Log Mn	Log Ni	Log Cu	Log Zn	Log As	Log Cd	Log Pb
Log OM	1.00									
Log Fe%	0.94	1.00								
Log Cr	0.66	0.70	1.00							
Log Mn	0.29	0.42	0.30	1.00						
Log Ni	0.72	0.75	0.92	0.33	1.00					
Log Cu	0.85	0.89	0.92	0.43	0.93	1.00				
Log Zn	0.82	0.82	0.93	0.36	0.90	0.96	1.00			
Log As	0.86	0.89	0.87	0.42	0.94	0.97	0.93	1.00		
Log Cd	0.88	0.83	0.86	0.35	0.87	0.95	0.96	0.92	1.00	
Log Pb	0.88	0.89	0.90	0.31	0.90	0.96	0.97	0.95	0.94	1.00

Pearson Product-Moment Correlations for <63µm fraction

	Log OM%	Log Fe%	Log Cr	Log Mn	Log Ni	Log Cu	Log Zn	Log As	Log Cd	Log Pb
Log OM	1.00									
Log Fe	0.96	1.00								
Log Cr	0.69	0.70	1.00							
Log Mn	0.50	0.53	0.55	1.00						
Log Ni	0.71	0.71	0.97	0.56	1.00					
Log Cu	0.65	0.61	0.77	0.57	0.78	1.00				
Log Zn	0.78	0.79	0.97	0.59	0.95	0.71	1.00			
Log As	0.63	0.60	0.73	0.62	0.76	0.98	0.68	1.00		
Log Cd	0.86	0.85	0.92	0.57	0.92	0.75	0.94	0.74	1.00	
Log Pb	0.80	0.80	0.92	0.53	0.93	0.70	0.95	0.68	0.92	1.00

Waterways Centre for Freshwater Management

University of Canterbury & Lincoln University

Private Bag 4800

Christchurch

New Zealand

Phone +64 3 364 2330

Fax: +64 3 364 2365

www.waterways.ac.nz