# Lake Rotokawau:

# Water quality and sediment study

**CBER Report 127** 

Prepared for Ngati Rangiteaorere

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# **Abstract**

Lake Rotokawau is a small (0.52 km<sup>2</sup>), deep (74 m), oligotrophic lake in the Rotorua Lakes District, located approximately 4.1 km east of Lake Rotorua. The lake is privately owned and managed by the local iwi, Ngati Rangiteaorere. During a site visit carried out on the 25 July 2010, surface and bottom water samples and a sediment core were collected, together with a water column profile (CTD) of temperature, dissolved oxygen, fluorescence, conductivity and depth. The CTD cast showed an anoxic hypolimnion and that the lake likely had not mixed during at the time of sampling, in mid-winter. This observation is highly unusual amongst the Te Arawa lakes and suggests that the lake may remain stratified for multiple years. The lack of mixing could be due to several factors including: presence of higher-salinity bottom waters, high water depth to area ratio, and sheltered aspect. The sediment core collected in the central basin revealed the presence of Ruapehu ash (1995-6 eruption) preserved in the upper 5 cm of the sediment record and the Tarawera Tephra (1886 eruption) located at 13 cm below the sediment water interface. The Ruapehu Ash layer is not preserved in sediment from any other Rotorua lakes and has likely been preserved due to the lack of seasonal mixing. The sediment and pore water chemistry are similar to that of the other lakes in the Rotorua region but however multiple sediment cores are necessary to fully assess variability across the whole lake area.

It is recommended that a routine monitoring programme be established so that any improvement or degradation in water quality can be detected and the mixing frequency of the lake determined. The water quality monitoring should include water column profiles of temperature, dissolved oxygen, fluorescence, conductivity and depth, nutrient analysis (ammonium, nitrate, nitrite, phosphate, silicon, total nitrogen and total phosphorus) of surface and bottom waters and water clarity readings (e.g. Secchi disk and light attenuation). Our observations point to the highly unusual nature of Lake Rotokawau in terms of mixing status and indicate a strong need to preserve significant biological and landscape features of this lake which has not been subject to problems with invasive species that characterise several other lakes in this region.

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Cover photo: Andy Bruere (Bay of Plenty Regional Council)

# 1.0 Literature Review

# 1.1 Site location and description

Lake Rotokawau is a small, oligotrophic lake in the Rotorua Lakes District (Figure 1). The lake is located approximately 4.1 km east of Lake Rotorua and accessed via lake Rotokawau Road, from State Highway 30. The lake is privately owned and managed by the local iwi, Ngati Rangiteaorere.

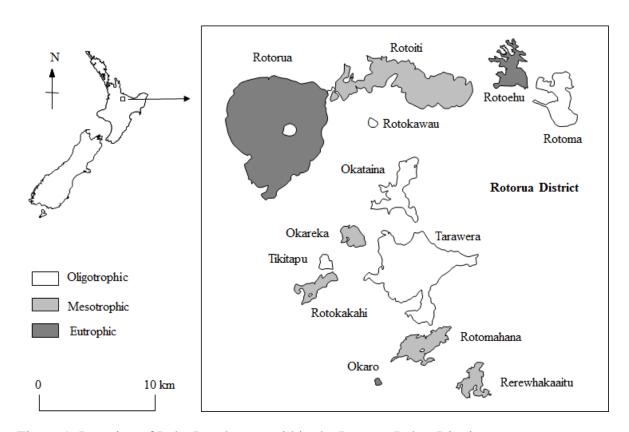


Figure 1: Location of Lake Rotokawau within the Rotorua Lakes District.

The lake was formed by the infilling of an explosion creator approximately 4000 years ago, producing steep cliffs around the lake up to 90 m in height (Figure 2). The local geology of the area is volcanic rhyolite and pumice with areas of alluvial sand and silt. The lake has a surface area of 0.52 km² and an average depth of 43.7 m (Pang et al., 1996). A maximum water depth of 74 m was recorded by James (1987) near the centre of the lake. The lake has a catchment area of approximately 2.23 km² of which 65% is forested and a further 25% is in agriculture (Freshwater Environments New Zealand database (FWENZ)). The lake has one major inflow, the Waimata Stream, which enters the lake on the southern side. White et al. (2007) reports the lake discharges via groundwater to the Waiohewa Stream, near Hells Gate; no surface water outlet exists. The lake also receives geothermal discharges through small springs on the beach located on the north-western shore (Pang et al., 1996).



Figure 2: Images of Lake Rotokawau and sampling the lake with Ngati Rangiteaorere.

# 1.2 Water quality

There have been few water quality assessments carried out on Lake Rotokawau. Green (1975) measured water clarity by light transmission, recording values of 78.4 and 81.1 % transmission m<sup>-1</sup>. James (1987) recorded measurements of ammonium and chlorophyll *a* at four locations (2, 6 and 10 m water depths) around the lake perimeter. Ammonium concentrations ranged from 4.6 to 8.9 µg L<sup>-1</sup> with a mean of 6.84 µg L<sup>-1</sup> (James, 1987). Chlorophyll *a* concentrations ranged from 0.15 to 1.89 µg L<sup>-1</sup> with a mean of 0.76 µg L<sup>-1</sup>. In

2009, water quality was accessed by Tonkin and Taylor Consultants by sampling from the littoral zone at the main beach. Tonkin and Taylor (2009) found concentrations of inorganic nitrogen < 0.002 mg L<sup>-1</sup> and reactive phosphorus < 0.004 mg L<sup>-1</sup>. From these assessments the lake trophic state can be classified as oligotrophic, with low levels of nutrients and chlorophyll a.

The contribution of nutrients to the lake from groundwater is not well known. Typically groundwater entering the Rotorua lakes receives phosphorus inputs from the natural weathering of rhyolite rock and nitrogen occurs mostly from nitrate that arises from agricultural land uses (White, 1983). With a lag time of between 50-100 years for groundwater in many Rotorua lakes' catchments, the impact of past land conversions from native vegetation to pastoral may not yet have impacted significantly on the water quality of Lake Rotokawau. The Waimata Stream drains an area of native forest in the upper reaches, passing through an area of pastoral land in the mid reaches and in the lower reaches the stream passes through an area of plantation pine forest.

# 1.3 Lake ecology

The ecology of the lake and catchment area have been described in an Ecological Restoration Plan by Wildland Consultants (2009) and in a Management Plan by Tonkin and Taylor (2009). Lake Rotokawau has been found previously to have low levels of phytoplankton biomass, consisting mostly of green algae *Sphaerocystis schroeteri*, *Staurastrum* sp. and *Dinobryon* sp. (Thomasson, 1974). It has a dense band of kakahi (*Hyridella menziesi*) around the lake at water depths of 1 to 10 m (James, 1987) and no macrophyte growth. Koaro (*Galaxias brevipinnis*), banded kokopu (*Galaxias fasciatus*), long-finned eel (*Anguilla dieffenbachia*), short-finned eel (*Anguilla australis*), smelt (*Retropinna retropinna*) and common bully (*Gobiomorphus cotidianus*) have been recorded in Lake Rotokawau and its tributaries (Wildland Consultants, 2009). Trout was once stocked in the lake but have now died out due to the lack of suitable breeding habitat (Tonkin and Taylor, 2009).

Ngati Rangiteaorere has a potential interest in using the lake for salmon aquaculture. The feasibility of the aquaculture of salmon and other native species has been assessed by Pryor (2009).

# 2.0 Sampling and Analytical Methods

A site visit to Lake Rotokawau was carried out on 25 July 2010 in which a water column profile of temperature, dissolved oxygen, conductivity and depth was taken with a Sea Bird Electronics 19 plus SEACAT Profiler (CTD, Sea-Bird Electronics Inc., Washington), fitted with a dissolved oxygen sensor (DO, Seabird Electronics; detection limit 0.1 mg L<sup>-1</sup>). The

CTD probe was lowered slowly while sampling at a frequency of 4 Hz to provide a vertical resolution of the order of c. 0.02 m. Lake water samples were collected from the surface and bottom waters along with an intact sediment core. The core was collected using a Swedish gravity corer (Pylonex HTH 70 mm) with a 60 x 600 mm Perspex (Plexiglas) core barrel to capture undisturbed sediments along with c. 20 cm of the overlying water. Once the core was retrieved, a custom-made, gas-tight sampling chamber, designed to minimise exposure of potentially anoxic sediment to the air, was fitted to the core barrel and the core was extruded by a piston from the base of the core. Excess supernatant water overflowed the top of the core upon extrusion until 2 cm of water was overlying the sediment-water interface. This water was collected in a 50 mL polypropylene centrifuge tube and herewith is termed the benthic boundary layer (BBL) sample. Sediment samples were extruded at 1 cm vertical intervals and transferred into 50 mL polypropylene centrifuge tubes; the sediment completely filled the tubes and small amounts of residual sediment were discarded.

In the laboratory, the gravity core sediments were weighed to determine bulk density before pore waters were separated by centrifugation at 4000 rpm (2900 G) for 40 min. The sediment sections were dried at 105 °C for 48 h and ground lightly using a mortar and pestle. The pore water was filtered through a 0.45 μm Millipore filter and split into two polypropylene vials; one vial was acidified with nitric acid (2%) and the other was frozen immediately. The sediments were digested with reverse Aqua Regia at 50 °C for one hour based on a modified standard procedure. The resulting digest along with the acidified pore water was analysed using inductively coupled plasma mass spectrometry (ICP-MS model ELAN DRC II; Perkin-Elmer SCIEX). Analysis for concentrations of ammonium (NH<sub>4</sub>-N), nitrite (NO<sub>2</sub>-N), total oxidised nitrogen (NO<sub>x</sub>-N) and phosphate (PO<sub>4</sub>-P) was carried out on the thawed lake water and pore water samples using a Aquakem discrete analyser. Nitrate was calculated as the residual of NO<sub>x</sub> - NO<sub>2</sub>-.

# 3.0 Results and Discussion

#### 3.1 CTD Cast

The CTD cast showed the lake was stratified during the time of sampling, with a thermocline depth of 30 m (Figure 3). The surface temperature of the lake was 10.8 °C declining to 9.8 °C in the bottom waters (Figure 3a). Dissolved oxygen concentrations reached a maximum of 8.14 mg L<sup>-1</sup> (73.6 % saturation) in the epilimnion and steadily declined in the hypolimnion to a minimum of 0.26 mg L<sup>-1</sup> (2.3 % saturation) just above the sediment-water interface (Figure 3b). Highest fluorescence (a proxy for phytoplankton biomass) was between 20 and 30 m water depth with a maximum reading of 8.7 RFU, indicating the presence of a deep chlorophyll maximum. The declining values at the surface could have been due to a phenomenon known as 'quenching', in which phytoplankton emission of fluorescence is inhibited by bright light at the surface; this was almost certainly the case on the top 2-3 m of water where there was a small temperature gradient that would

expose phytoplankton in this layer to continuously high light levels while this layer persisted (likely from early in the morning under the calm conditions on the day of sampling). Fluorescence rapidly declined in the hypolimnion to less than 0.5 RFU by 40 m water depth (Figure 3c). At the surface fluorescence was 1.2 RFU. The specific conductivity of the epilimnion (surface waters) was fairly uniform, with an average of 63.1 µS cm<sup>-1</sup>, while specific conductivity increased in the hypolimnion up to 66.7 µS cm<sup>-1</sup> near the sediment surface (Figure 3d). This change in conductivity may be sufficient to produce a density gradient the lake that could prevent seasonal mixing.

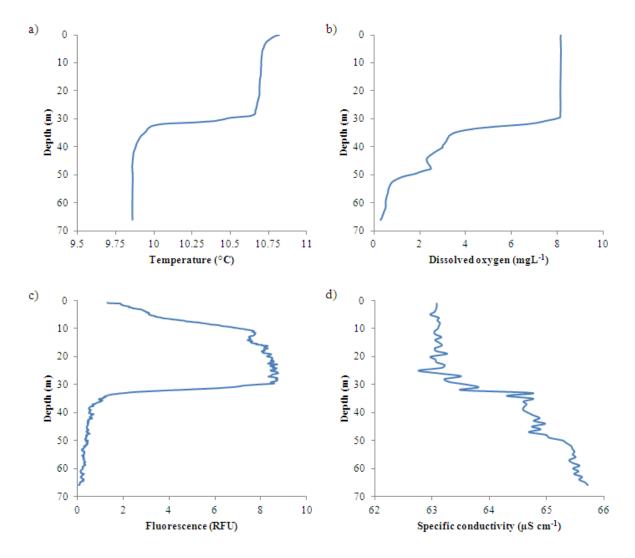


Figure 3: a) Temperature, b) dissolved oxygen c) chlorophyll fluorescence and d) conductivity of Lake Rotokawau sampled on 25 July 2010. Note: depth has been adjusted by applying the pressure reading in air (-0.492 m) as an offset to the CTD output of pressure. Fluorescence is measured in Relative Fluorescence Units (i.e. un-scaled fluorescence measurements as a proxy for chlorophyll *a* concentration). Specific conductivity is presented as an average of 1 m depth intervals.

# 3.2 Lake water chemistry

The surface and bottom water samples collected from a site in the central basin of the lake show similar water chemistry to those collected in the littoral zone (north-western beach) by Tonkin and Taylor (2009) (Table 1). Concentrations of ammonium in surface and bottom waters were higher than those recorded in the littoral zone. Sulfur is lower than the 2009 sampling which may be due to a geothermal discharge to the lake at the north-western beach. Dissolved silicon concentrations in the lake water are sufficient diatom phytoplankton productivity should not be limited. The low levels of dissolved inorganic N and P are unlikely to support cyanobacterial blooms which could otherwise dominate at the lake surface.

Table 1: Water chemistry of Lake Rotokawau compared to Tonkin and Taylor (2009) study. TDP is total dissolved phosphorus. Variables not already given in the text include: Li (lithium), Na (sodium), Mg (magnesium), Al (aluminium), S (sulphur), K (potassium), Ca (calcium), Fe (iron), Mn (manganese), Ni (nickel), Cu (copper), Zn (zinc), As (arsenic), Cd (cadmium), Ba (barium), Pb (lead), U (uranium).

	Surface water (mg L <sup>-1</sup> )	Bottom water (mg L <sup>-1</sup> )	Tonkin and Taylor (2009) Surface water (mg L <sup>-1</sup> )
NH <sub>4</sub> -N	0.0422	0.0383	< 0.001
NO <sub>2</sub> -N	0.0004	0.0007	< 0.002
NO <sub>3</sub> -N	0.0142	< 0.0001	< 0.002
TDP	0.0196	0.0254	n/a
PO <sub>4</sub> -P	0.0094	0.0014	< 0.004
Li	0.0025	0.0028	0.002
Na	6.1441	6.4948	6.5
Mg	1.7915	1.8589	1.6
Al	0.0079	0.0093	0.005
Si	11.9312	12.4374	n/a
S	1.2748	1.0197	4.7
K	2.3556	2.5071	2.1
Ca	3.7348	3.7703	3.4
Fe	0.0100	0.0100	<0.02
Mn	0.0022	0.0019	<0.0005
Ni	0.0004	0.0004	< 0.0005
Cu	0.0006	0.0006	< 0.0005
Zn	0.1947	0.1496	0.0017
As	0.0006	0.0012	< 0.001
Cd	0.0149	0.0146	< 0.00005
Ba	0.0117	0.0114	0.0095
Pb	0.0006	0.0005	<0.0001
U	0.0000	0.0000	< 0.00002

# 3.3 Sediment core description

The core retrieved from the central basin of Lake Rotokawau contained a number of tephra layers from multiple eruptions (Figure 4). The surface tephra layers are likely to have originated from the 1995-96 Ruapehu eruptions and the deeper tephra layers from the 1886 eruption of Mt Tarawera. In between the tephra layers diatomaceous sediment has accumulated as a preserved remnant from diatom deposition, combined with deposition of preserved or partially decomposed biota from within the lake. The black diatomaceous sediment is indicative of anoxic conditions in the hypolimnion.

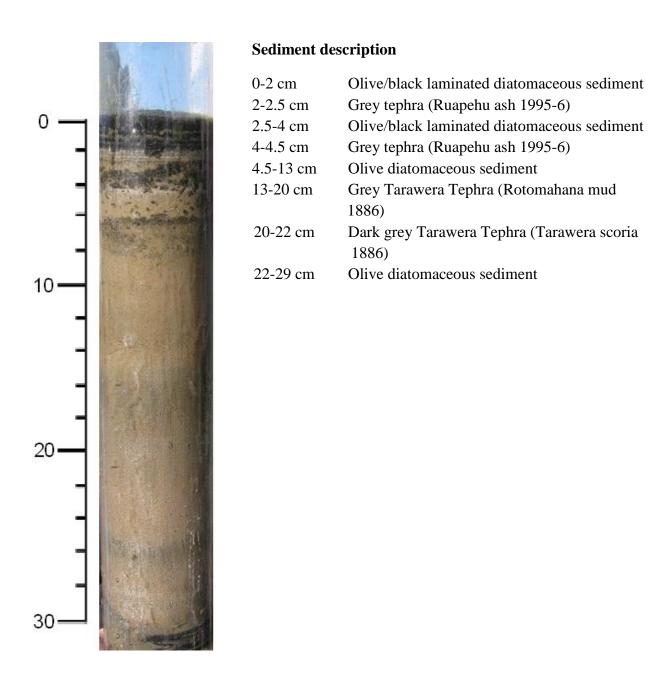


Figure 4: Lake Rotokawau sediment core.

# 3.4 Physical properties of the sediments

The surface sediments are very loose, with a bulk density of 0.01 g cm<sup>-3</sup>, which corresponds to a porosity of 99.5% (Figure 5). The bulk density increases with depth up to 0.28 g cm<sup>-3</sup> near the base of the Tarawera Tephra at 22 cm, before declining slightly to 0.17 g cm<sup>-3</sup> at the base of the core. Sediment porosity ranges between 99.5% at the sediment-water interface to 86.6% at the base of the Tarawera Tephra. The Tarawera Tephra increases in bulk density with depth as the denser Tarawera Scoria was erupted first, followed by the Rotomahana mud layer which has graded as the mud particles settled in the lake.

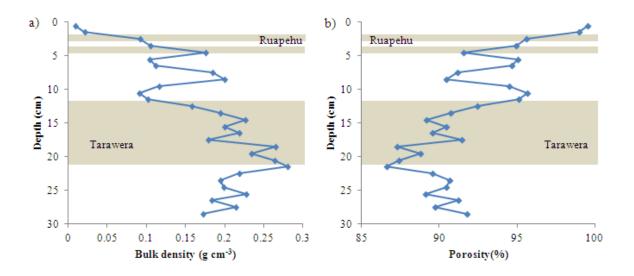


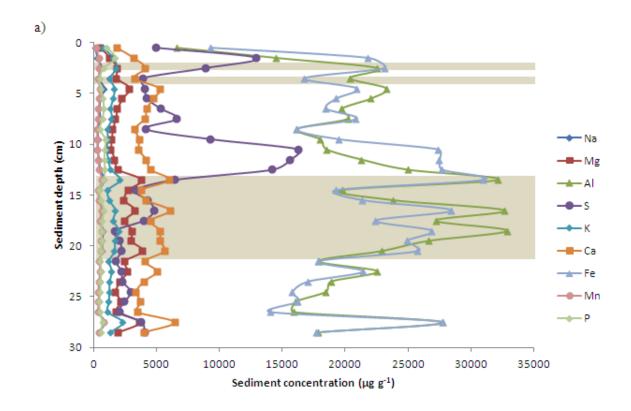
Figure 5: a) Bulk density and b) porosity of Lake Rotokawau sediment.

# 3.5 Sediment chemistry

Lake sediments in the Rotorua lakes area are predominantly made up of the remains of diatoms; unicellular algae in the size range 2-200 µm. They persist due to limited degradation of their structural frustule, which is composed of opaline or biogenic silica (SiO<sub>2</sub>.nH<sub>2</sub>O; Round, 1990). Diatom frustules may comprise the bulk of the sediment in these lakes (see also McColl, 1972; Pickrill, 1991; Pearson, 2007; Trolle et al., 2008). Sedimentation arising from cyanobacteria and other phytoplankton appears to contribute relatively small amounts of residual material to the bottom sediments, but diatom frustules remain largely intact and dominate the finer, low-density component of the sediments. Dissolution of diatom frustules in the Rotorua lakes appears to have been limited by moderate levels of silicic acid arising from volcanic material deposited in the lakes from the Taupo Volcanic Zone (TVZ), the discharge of silica-laden geothermal waters and ignimbrite aquifers that contribute groundwater with high silica concentrations (Rawlence, 1985). The other dominant elements in the sediment are aluminium and iron originating from catchment weathering and volcanic

tephras. The major and minor elements in the lake sediment are presented in Figure 6. For full analysis of the sediment composition see Appendix 1.

Ejecta from the Ruapehu and Tarawera eruptions are present in the lake sediment. These tephra layers provide markers for dating the sediment and estimating sedimentation rate in the lake. The sedimentation rate between the Tarawera eruption (1886) and the Ruapehu eruption (1995) is in the order of 0.08 cm yr<sup>-1</sup> while the sedimentation rate between Ruapehu (1996) and the present sediment surface is approximately 0.14 cm yr<sup>-1</sup>; however the compaction of the sediment has not been taken into account with these calculations.



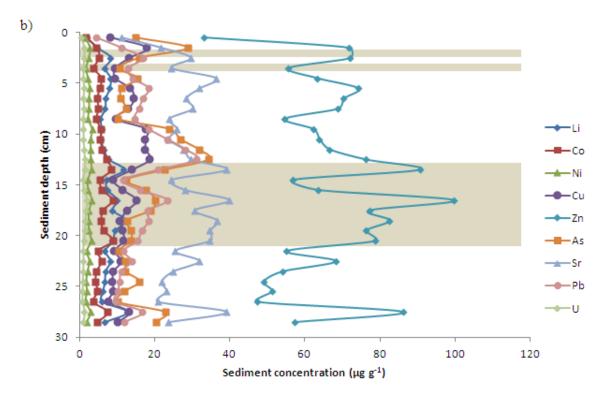


Figure 6: Concentration of a) major and b) minor elements in the sediment of Lake Rotokawau. Tephra layers are indicated by the shaded area.

# 3.6 Pore water chemistry

The dominant diagenetic process that occurs in sediment pore waters is the reduction of oxidised species as organic matter is metabolised and dissolved oxygen depleted, with nitrate converted to ammonium, manganese to manganous, iron reduced to ferrous and sulfur to sulfate. As sediments generally become more reducing at greater depth, the zones in which individual species were reduced vary from species to species and seasonally. Releases of silicon to pore waters occur with weathering of alumno-silicate glass within the sediments as well as from dissolution of diatom frustules. Silicon concentrations decrease towards the sediment water interface while sulfur, iron and manganese all increase in concentration (Figure 7). Iron and manganese are mobilised upwards in pore water towards the sediment-water interface and can act as a co-precipitator for many other trace species, especially phosphate. For full analysis of the pore water see Appendix 2.

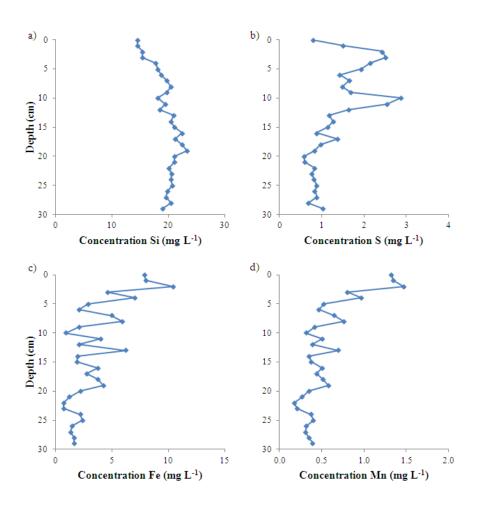


Figure 7: Concentrations of a) silicon, b) sulfur, c) iron and d) manganese in Lake Rotokawau pore water.

The dominant nitrogen species in the pore waters is ammonium, which increases in concentration towards the sediment-water interface from 2.9 mg L<sup>-1</sup> at 30 cm to 4.8 mg L<sup>-1</sup> at 2 cm sediment depth (Figure 8a) while nitrate concentrations range between 0.02-0.08 mg L<sup>-1</sup>, indicating that the sediments are anoxic, i.e. largely devoid of readily oxidised species (Figure 8b). Phosphate in the pore waters is highest in the Tarawera Tephra layer between 13 and 22 cm sediment depth and decreases towards the sediment-water interface. The proportion of reactive phosphate is shown compared to total dissolved phosphorus in Figure 8c.

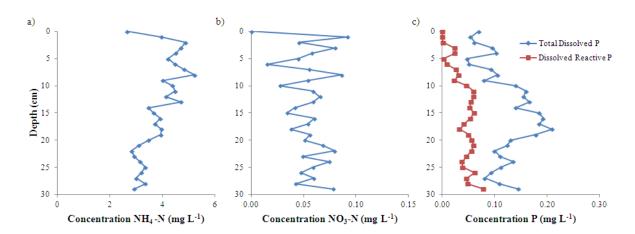


Figure 8: Concentration of a) ammonium, b) nitrate and c) phosphorus species in Lake Rotokawau pore waters.

# 4.0 Summary and Future Management

The CTD cast taken on the lake in July showed an anoxic hypolimnion and that the lake likely had not mixed during the coldest period of winter. This suggests that the lake may remain stratified for multiple years either due to, or leading to, the presence of higher salinity bottom waters. The sheltered aspect and the very low ratio of area to depth for Lake Rotokawau reinforce the lack of mixing. Monthly CTD casts would be necessary to determine the mixing regime of the lake and to determine appropriate management options for within the lake itself. Like all of the Rotorua lakes, however, nutrients will strongly influence the quality and clarity of water in Lake Rotokawau and land uses appropriate to support low nutrient loads to the lake should be considered in the management of the lake. Long-term plans for access to the lake should also be considered carefully. Lake Rotokawau is a weed-free lake with much of its indigenous biodiversity still largely intact. It is the best remnant of what many deep Rotorua lakes once were like.

The sediment core collected in the central basin revealed the presence of Ruapehu Ash preserved in the sediment record. This tephra layer is not preserved in any other Rotorua lake sediments and has likely remained largely intact due to the lake depth and apparent lack of seasonal mixing. The sediment and pore water chemistry is similar to that of the other lakes in the Rotorua region, however multiple sediment cores are necessary to fully assess the spatial variability around the sample site and across the whole lake area.

It is recommended that a routine monitoring programme be established so that any improvement or degradation in water quality or lake resources – particularly invasive species - can be detected. The water quality monitoring should include water column profiles of temperature, dissolved oxygen, chlorophyll fluorescence and conductivity, nutrient analysis (ammonium, nitrate, nitrite, phosphate, silicon, total nitrogen and total phosphorus) of surface and bottom waters and water clarity readings (Secchi disk and light attenuation).

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# Appendix 1: Sediment profile concentrations (µg g<sup>-1</sup>)

Depth	Li	Na	Mg	Al	P	S	K	Ca	Cr	Fe	Mn	Co	Ni	Cu	Zn	As	Se	Sr	Cd	Ba	Ti	Pb	Bi	U
0-1 cm	2.03	164.85	549.79	6612.27	1086.16	4969.30	730.84	1845.72	1.72	9328.12	228.93	1.73	1.60	8.36	33.29	15.07	1.38	11.19	0.10	71.46	0.12	4.53	0.07	0.51
1-2 cm	4.79	337.30	1271.83	14527.89	1746.78	12967.91	1578.84	3198.29	3.07	21812.71	423.16	4.64	2.86	17.98	71.76	28.88	3.41	21.80	0.22	185.75	0.30	11.29	0.25	1.28
2-3 cm	8.35	616.85	1887.38	22554.82	819.87	8935.17	1827.21	4130.86	3.68	23139.18	480.49	5.32	2.56	13.26	72.22	15.90	1.83	29.67	0.21	269.71	0.23	16.90	0.33	1.29
3-4 cm	6.80	438.01	1819.97	20411.45	498.69	3923.30	1309.58	3257.85	2.53	16736.86	418.03	3.90	1.85	9.54	55.74	10.65	1.53	24.53	0.18	258.05	0.18	13.07	0.28	1.11
4-5 cm	8.25	824.24	2859.52	23293.41	587.90	4116.95	1668.30	5269.10	3.04	20939.15	496.69	5.89	2.34	9.47	63.36	15.46	1.21	36.40	0.15	310.78	0.22	14.22	0.31	1.04
5-6 cm	8.04	566.75	2281.67	22079.56	774.31	4263.39	1542.58	4769.64	4.31	19286.05	489.09	5.44	2.79	13.47	74.27	11.31	1.97	32.07	0.27	265.15	0.28	18.56	0.32	1.22
6-7 cm	6.98	470.34	1897.88	19771.75	827.16	5369.90	1368.33	4249.01	4.28	18485.72	420.14	4.75	2.63	14.54	70.42	11.05	2.02	28.44	0.23	238.95	0.27	16.88	0.28	1.12
7-8 cm	6.88	523.40	1734.30	20230.99	728.41	6669.46	1445.78	4082.14	4.29	20889.56	400.91	5.12	2.65	12.95	68.81	12.56	1.58	30.19	0.26	281.31	0.22	15.94	0.30	1.23
8-9 cm	5.62	343.99	1520.49	16167.44	502.22	4188.47	1118.39	3276.88	3.62	16151.87	309.77	4.50	2.39	9.69	54.73	10.31	1.37	23.90	0.23	245.14	0.18	14.72	0.23	1.04
9-10 cm	5.95	384.32	1424.57	18023.20	966.90	9330.80	1138.34	3680.10	4.81	19490.01	323.24	5.70	3.41	17.86	62.26	24.02	2.51	25.93	0.25	223.91	0.22	18.42	0.40	1.11
10-11 cm	5.70	334.88	1385.88	18560.45	905.53	16301.68	1045.04	3585.83	4.64	27382.44	326.48	5.62	3.05	17.57	63.99	26.94	2.90	23.85	0.30	159.05	0.24	23.43	0.30	1.12
11-12 cm	6.47	449.05	1672.89	21334.32	869.86	15677.13	1173.69	4213.10	4.98	27504.00	407.10	6.09	3.05	17.58	66.67	31.85	2.80	27.77	0.30	175.13	0.29	28.31	0.32	1.28
12-13 cm	7.82	529.99	1935.20	25020.02	917.32	14242.57	1389.77	4548.89	4.73	27707.84	465.02	7.21	3.11	18.75	76.40	34.42	2.84	29.78	0.36	173.58	0.32	31.20	0.37	1.42
13-14 cm	11.78	824.22	3811.40	32187.90	820.35	6476.68	2112.01	6051.88	4.52	30950.26	672.68	8.57	3.21	13.99	90.70	22.75	1.65	39.23	0.26	306.64	0.37	21.09	0.46	1.51
14-15 cm	7.38	470.54	2747.70	19845.74	480.56	3384.78	1148.43	3788.56	2.90	19317.08	405.74	5.60	2.29	9.09	56.88	12.47	0.87	24.60	0.19	222.08	0.20	11.78	0.23	0.93
15-16 cm	7.47	487.87	2423.55	23865.56	614.63	4343.87	1257.63	4211.97	3.64	21392.70	461.78	6.13	2.41	11.48	63.71	17.82	1.32	28.13	0.27	285.24	0.25	16.25	0.31	1.27
16-17 cm	10.00	669.34	3266.26	32726.06	832.55	4841.51	1735.22	6097.99	5.19	28481.94	651.99	8.90	3.39	15.19	99.75	20.31	2.23	39.91	0.37	408.51	0.48	23.52	0.50	2.10
17-18 cm	8.83	516.99	2438.03	27219.73	694.62	4013.69	1563.25	4558.11	4.03	22431.94	546.01	6.32	2.56	12.66	77.26	18.92	1.68	30.68	0.36	342.59	0.33	18.26	0.46	1.72
18-19 cm	12.33	747.24	3074.29	32915.70	673.99	1744.33	2014.23	5322.35	3.84	26889.28	667.42	5.82	2.54	10.77	82.70	12.71	0.99	36.71	0.25	412.54	0.32	18.57	0.54	1.65
19-20 cm	9.49	653.01	2963.20	26653.77	654.89	2097.72	1693.50	5285.79	4.00	24916.06	598.06	6.44	2.59	11.45	76.31	13.80	1.26	34.79	0.24	351.49	0.30	16.67	0.44	1.47
20-21 cm	8.88	664.57	3882.95	22907.39	619.85	2271.33	1674.27	5663.86	4.56	25780.70	630.05	8.97	3.19	11.73	78.79	13.66	1.32	34.75	0.22	301.68	0.32	15.40	0.36	1.23
21-22 cm	6.85	459.53	2468.81	17930.00	536.90	1805.64	1240.79	4126.42	3.06	17864.25	464.95	4.93	2.03	9.31	55.20	10.50	0.85	25.44	0.18	228.63	0.21	11.75	0.28	0.98
22-23 cm	8.19	579.52	2670.07	22584.59	626.17	2257.96	1448.71	5049.09	3.79	21422.17	548.82	5.91	2.71	11.10	68.26	12.35	1.44	31.90	0.23	277.74	0.24	13.97	0.31	1.16
23-24 cm	6.97	509.84	2096.44	18899.54	554.76	2324.65	1274.64	4011.18	2.55	17026.09	424.89	4.61	2.20	9.02	54.17	12.35	1.25	25.02	0.20	222.84	0.21	11.14	0.24	0.95
24-25 cm	6.76	436.45	1734.48	18508.59	542.83	2983.35	1255.45	3397.18	2.14	15808.41	411.59	4.28	1.85	8.76	49.06	16.01	1.18	21.94	0.18	218.32	0.19	10.77	0.26	0.95
25-26 cm	6.26	453.62	2135.61	16066.11	481.22	2503.18	1231.87	3766.76	2.27	16252.30	421.58	4.87	2.08	8.97	51.37	11.90	1.29	23.19	0.16	204.98	0.20	10.30	0.22	0.87
26-27 cm	6.09	415.26	1835.35	15911.90	524.94	2118.34	1139.23	3529.71	2.14	14057.25	396.45	3.74	1.71	7.81	47.39	10.22	1.07	20.98	0.19	183.62	0.19	9.64	0.21	0.84
27-28 cm	12.67	833.41	3652.28	27774.46	726.47	3833.43	2317.76	6480.52	3.68	27797.44	796.62	7.50	2.97	13.15	86.34	22.92	2.15	39.22	0.21	346.35	0.41	16.86	0.42	1.41
28-29 cm	6.83	463.19	1979.14	17850.09	580.38	4073.97	1341.60	4037.44	2.55	17757.04	452.70	4.86	2.03	10.22	57.28	20.44	1.71	23.83	0.19	208.42	0.30	11.95	0.28	1.04

# Appendix 2: Lake and pore water profile concentrations ( $\mu g \ L^{-1}$ )

Depth	NH <sub>4</sub> -N	NO <sub>2</sub> -N	NO <sub>3</sub> -N	Li	Na	Mg	Al	Si	TDP	PO <sub>4</sub> -P	S	K	Ca	Fe	Mn	Co	Ni	Cu	Zn	As	Cd	Ba	Pb	Bi	U
Surface	42.20	0.40	14.19	2.49	6144.08	1791.53	7.95	11931.17	19.63	9.37	1274.76	2355.62	3734.81	10.00	2.22	0.02	0.36	0.60	194.66	0.61	14.93	11.67	0.59	0.002	0.003
Bottom	38.27	0.69	<1	2.82	6494.80	1858.88	9.25	12437.38	25.44	1.43	1019.66	2507.12	3770.29	10.00	1.95	0.02	0.36	0.61	149.58	1.16	14.58	11.43	0.50	-0.002	0.003
0 cm	2652.38	<1	<1	2.84	6708.06	2547.59	8.96	14544.70	69.39	0.10	1089.23	3227.84	9100.55	7481.63	1222.69	0.57	0.96	0.83	47.81	5.18	37.71	20.83	0.71	0.001	0.007
0-1 cm	3971.10	<1	91.57	3.08	6751.12	2609.86	8.88	14533.72	54.09	0.10	1480.32	3443.37	8207.07	7186.43	1174.28	0.52	0.85	0.62	410.47	26.80	36.16	48.69	0.64	0.012	0.014
1-2 cm	4881.33	<1	45.38	3.22	7012.48	3041.49	24.50	15431.98	61.27	1.91	2200.12	3776.05	9284.35	9671.42	1310.13	0.43	1.13	1.14	286.73	20.06	42.71	66.95	0.85	0.016	0.033
2-3 cm	4707.35	<1	79.78	3.22	6784.15	2098.35	124.34	15332.37	95.95	23.67	2470.76	3830.63	6100.96	4124.24	711.88	0.35	0.69	2.62	367.48	8.81	28.32	61.91	1.10	0.025	0.056
3-4 cm	4511.57	<1	57.93	3.34	6790.85	2736.86	570.62	17731.99	103.62	24.27	2091.36	3883.66	7542.70	6680.80	853.62	0.42	0.85	2.65	88.13	5.84	35.37	69.62	1.99	0.039	0.089
4-5 cm	4202.39	<1	44.86	3.22	6264.05	1718.53	991.21	18060.34	47.74	2.79	1600.73	3704.29	4776.67	2586.31	455.71	0.51	0.59	4.08	151.50	7.65	22.59	58.65	2.71	0.036	0.128
5-6 cm	4485.85	<1	15.14	3.38	6783.35	1844.36	203.02	18723.94	50.81	9.24	1033.95	3793.45	4794.67	1900.51	407.69	0.34	0.52	1.73	128.54	3.07	22.14	46.20	0.79	0.002	0.028
6-7 cm	4821.58	<1	55.15	3.58	7115.28	2624.81	157.43	19709.43	93.36	25.90	1066.30	4095.38	6732.22	4684.55	569.15	0.29	0.64	2.13	249.72	5.10	30.51	55.20	1.05	0.017	0.032
7-8 cm	5228.34	<1	86.15	3.60	7354.07	3100.46	337.78	20413.06	105.57	30.97	773.98	4405.17	7979.58	5875.41	674.05	0.31	0.88	3.60	573.93	8.39	36.22	62.44	1.53	0.007	0.070
8-9 cm	4014.73	<1	53.82	3.47	6786.14	1787.17	458.45	19735.18	79.98	22.99	1208.55	4038.32	4707.08	1956.42	367.46	0.44	0.76	4.38	317.86	8.48	21.43	47.80	1.51	0.028	0.067
9-10 cm	4395.42	<1	27.24	3.23	6673.39	1339.75	190.77	18156.06	140.28	46.69	2377.37	3931.22	3774.02	907.79	270.66	0.51	0.66	5.38	416.74	10.53	16.32	38.98	1.57	0.016	0.068
10-11 cm	4474.77	<1	58.91	3.39	7221.86	2100.86	222.87	19424.23	159.54	59.95	1727.38	4124.45	5694.17	3801.71	447.02	0.49	1.04	5.83	153.25	13.60	25.11	50.07	2.05	0.031	0.072
11-12 cm	4142.16	<1	65.61	3.25	6876.17	1560.50	365.32	18515.18	155.18	60.42	1023.21	3961.87	4485.05	1982.13	338.40	0.61	0.82	7.64	159.60	16.35	19.44	46.43	2.50	0.047	0.106
12-13 cm	4717.47	<1	59.11	3.41	7407.13	2638.50	552.42	20925.71	166.04	54.97	391.35	4212.27	7430.36	6478.00	613.62	0.65	0.85	6.33	131.41	17.64	32.75	64.81	4.01	0.048	0.123
13-14 cm	3481.75	<1	41.55	3.04	6048.58	1240.42	1853.69	20498.53	139.83	51.86	819.67	3716.10	3942.00	1920.22	308.10	0.86	0.68	8.60	212.03	13.20	18.05	66.68	4.19	0.049	0.212
14-15 cm	3667.02	<1	34.00	3.04	6441.92	1371.52	1303.21	21016.07	184.20	60.68	632.83	3999.12	4280.19	1899.74	334.35	0.74	0.72	7.02	121.34	10.64	18.96	60.32	2.92	0.056	0.155
15-16 cm	3919.27	<1	60.48	3.14	6840.99	1689.27	1789.72	22417.53	192.45	53.81	297.18	4020.38	5361.86	3773.45	454.60	0.81	0.77	10.79	123.38	13.70	23.66	71.34	5.55	0.076	0.266
16-17 cm	3723.82	<1	53.87	3.06	6391.50	1435.92	1776.42	21155.67	185.10	41.72	857.00	3890.85	4691.26	2765.00	395.24	0.78	0.81	8.96	283.75	11.49	20.85	70.23	4.51	0.056	0.246
17-18 cm	3975.91	<1	37.67	3.15	6655.34	1570.53	2722.08	22464.03	209.31	33.27	605.58	4017.93	5373.70	3872.32	464.48	0.94	0.84	11.28	122.66	15.13	24.20	90.37	6.40	0.114	0.362
18-19 cm	3936.77	<1	56.13	3.54	6830.41	1755.35	3483.30	23350.76	178.17	50.53	496.48	4326.39	5987.39	4367.47	530.12	0.75	0.94	10.22	500.25	14.28	27.62	109.50	7.88	0.139	0.410
19-20 cm	3482.77	<1	51.08	3.09	6069.56	1068.22	1619.18	21056.56	130.26	56.67	487.87	3956.96	3742.66	2288.55	319.80	0.44	0.89	8.15	182.88	10.08	16.67	56.29	4.63	0.098	0.231
20-21 cm	3097.02	<1	68.56	2.99	6086.00	768.80	1098.75	21093.94	123.78	59.88	553.77	3973.89	2787.02	1290.82	229.56	0.58	0.74	4.14	237.62	6.57	12.21	43.96	2.65	0.052	0.117
21-22 cm	2837.22	<1	79.61	2.68	5241.86	504.17	1224.13	20075.29	99.97	55.97	770.56	3414.88	1999.12	836.33	155.21	0.45	0.93	3.94	183.17	7.11	8.95	37.30	2.32	0.036	0.122
22-23 cm	2940.08	<1	48.88	2.88	5554.81	564.65	840.90	20536.88	109.98	46.26	540.31	3541.49	2207.16	825.93	180.90	0.33	0.69	3.24	181.54	6.58	9.32	32.82	1.60	0.014	0.092
23-24 cm	3142.09	<1	74.73	3.29	6289.22	987.15	1300.33	20449.59	135.41	38.19	595.91	3997.31	3875.95	2349.72	335.09	0.53	0.76	7.78	154.43	15.25	16.42	48.11	3.14	0.067	0.166
24-25 cm	3341.93	<1	59.18	3.44	6546.45	1042.78	1559.22	20657.11	112.25	38.40	594.54	4138.05	4123.82	2589.33	366.30	0.60	0.91	8.33	192.42	15.32	17.73	57.66	3.62	0.062	0.201
25-26 cm	3199.64	<1	47.34	3.43	6145.42	802.44	1053.48	19794.25	93.29	62.33	625.73	3947.81	3233.40	1587.78	281.10	0.48	0.71	4.76	216.23	11.34	13.59	42.29	2.56	0.053	0.126
26-27 cm	3014.12	<1	59.88	3.50	5988.76	771.66	1091.11	19599.14	81.39	46.78	729.77	3766.08	3160.48	1468.47	271.73	0.40	0.89	5.17	205.30	10.35	13.16	40.35	2.45	0.054	0.128
27-28 cm	3357.87	<1	42.43	3.72	6582.97	918.39	622.38	20473.91	108.98	48.44	539.37	4091.04	3687.08	1853.20	322.49	0.38	0.64	3.06	136.85	9.80	15.11	38.38	1.51	0.032	0.071
28-29 cm	2919.15	<1	77.85	3.84	6480.66	985.07	521.89	18991.46	145.20	78.90	730.18	4055.10	4008.13	1779.99	361.44	0.61	0.68	3.97	157.12	17.70	15.66	36.20	1.48	0.047	0.079