

Lake Rotorua and Lake Rotoehu: Total and Non-crystalline Aluminium Content in Bottom Sediments



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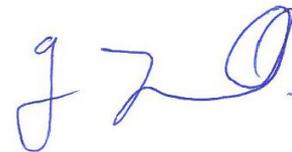
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Executive Summary

The application of alum (aluminium sulphate) is widely used for lake restoration. Aluminium binds dissolved reactive phosphate (DRP) reducing its availability to phytoplankton and inhibiting algal blooms. The Bay of Plenty Regional Council has conducted continuous alum treatment of the Puarenga and Utuhina Streams discharging to Lake Rotorua and the Waitangi Soda Stream entering Lake Rotoehu for nearly 10 years. This has resulted in the addition of more than 722.3 tonnes of aluminium to Lake Rotorua and 80.8 tonnes to Lake Rotoehu. Dissolved reactive phosphorus levels within the streams have been markedly reduced due to alum dosing. This appears to support long-term trends of reducing Trophic Level Index (TLI) levels in both lakes, indicative of water quality improvement, with greater success in Lake Rotorua. In addition, secondary sediment capping effects from the dosing have been suggested as a potential process explaining recent improvements in lake water quality. Accumulation of alum-derived aluminium in lake sediments potentially provides the additional benefit of adsorbing dissolved phosphorus which might otherwise be released from lake sediments under anoxic conditions.

The University of Waikato was contracted by the Bay of Plenty Regional Council to conduct on-going monitoring of sediment aluminium and phosphorus concentrations in lakes Rotorua and Rotoehu. In addition to sediment total aluminium content, the proportion of amorphous (non-crystalline) aluminium was also determined. Amorphous aluminium is recognised as the fraction of total aluminium able to adsorb dissolved phosphorus, sequestering it from the water column. For this study it was assumed that increased proportions of amorphous aluminium were derived from alum dosing.

Fifteen sediment cores were taken from Lake Rotorua and the findings from the analysis of these cores was compared to data collected in 2006 and 2012. Sites were chosen to represent three different depositional zones: zone 1 (Sites Ru1–4) to represent the immediate depositional area of the treated streams, zone 2 (Sites Ru5–11) to represent the main sediment accumulation basin (≥ 20 m water depth) and zone 3 (Sites Ru12–15) to represent an area of low sediment accumulation (< 20 m water depth). Analysis of the sediment showed little or no accumulation of aluminium in either zone 2 or zone 3 compared to similar surveys conducted in 2006 and 2012. There was also no change in the mean sediment total aluminium content for zone 1, however, two zone 1 sites (Ru2 and Ru3) contained notably higher proportions of amorphous aluminium in their surface sediments. In association with these two sites, surface sediment pore water dissolved reactive phosphate (DRP) concentrations were reduced compared to other sampled sites. These findings suggest that alum-derived aluminium is only accumulating in an area close to the discharge points of the Utuhina and Puarenga Streams, although further survey work will be needed for confirmation. The lack of aluminium accumulation in the main lake basin indicates that secondary sediment capping effects are unlikely to be substantial, and recent improvements in the water quality of Lake

Rotorua are driven by other factors, such as a positive feed-back loop between reductions in organic matter sedimentation and nutrient regeneration.

A total of seven sediment cores were taken from Lake Rotoehu in a transect line running from the mouth of the Waitangi Stream out into the main basin. Significant accumulation of alum derived aluminium ($>25,000 \text{ mg kg}^{-1}$) was found in the sediment of Te Weta Bay, however, no observable accumulation of aluminium (i.e., $<5000 \text{ mg kg}^{-1}$) was found in the main basin of Lake Rotoehu. Impedance of flow from the large biomass of *Ceratophyllum demersum* in Te Weta Bay is likely preventing alum flocs from reaching the main lake basin, negating any hoped for benefits of DRP sequestration through sediment capping. In addition, large diel shifts in pH between 6 and 9.5 caused by photosynthesis-respiration cycles of *C. demersum* are causing dissolution of the aluminium-phosphorus bound precipitate, reducing the performance of the alum dosing programme.

It is recommended that an additional sediment survey be conducted around Kawaha Point and the area north of Sulphur Bay in Lake Rotorua to determine if these areas are accumulating aluminium derived from alum flocculent. Given improved understanding of processes through which alum dosing improves lake water quality, alum dosing rates for Lake Rotorua should be reviewed with the aim of testing if lower alum dose rates can achieve the TLI target. The Waitangi Soda Stream alum treatment programme should be reviewed in order to assess whether a more effective strategy can be implemented in the presence of potentially confounding factors such as lake weed and high iron levels in stream inflows.

Acknowledgements

We thank Troy Baiden and John Tyrrell for reviewing this document. Joe Butterworth provided technical field support and Charlotte Caldwell laboratory support. This project was also financially supported through the Enhancing the Health and Resilience of New Zealand Lakes (Contract UOWX1503) and funding for the Bay of Plenty Regional Council Chair in Lake Restoration.

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Introduction

The Bay of Plenty Regional Council initiated several alum dosing programmes in the Rotorua lakes district in an effort to reduce lake trophic levels. Currently, continuous alum dosing is undertaken on the Puarenga and Utuhina Streams discharging to Lake Rotorua and the Waitangi Stream entering Lake Rotoehu. Continuous alum dosing to the Utuhina and Puarenga Streams began in 2006 and 2010, respectively. In mid-2011, a continuous alum dosing station was commissioned for the Waitangi geothermal spring inflow to Lake Rotoehu. A calculated rolling average showed that the combined average aluminium dose for the Utuhina and Puarenga Streams was c. 202 kg Al day⁻¹ with peaks of up to c. 500 kg Al day⁻¹ for the period July 2010 – June 2014 (Figure 1A)(Hamilton et al. 2015). Mean alum dose rates to the Waitangi Stream waters were lower at c. 41 kg Al day⁻¹ (July 2011 – June 2014)(Figure 1B) although Lake Rotoehu is approximately one-tenth of the area of Lake Rotorua. The alum dosing has resulted in the total applications of 722.4 and 80.8 tonnes of aluminium to lakes Rotorua and Rotoehu, respectively.

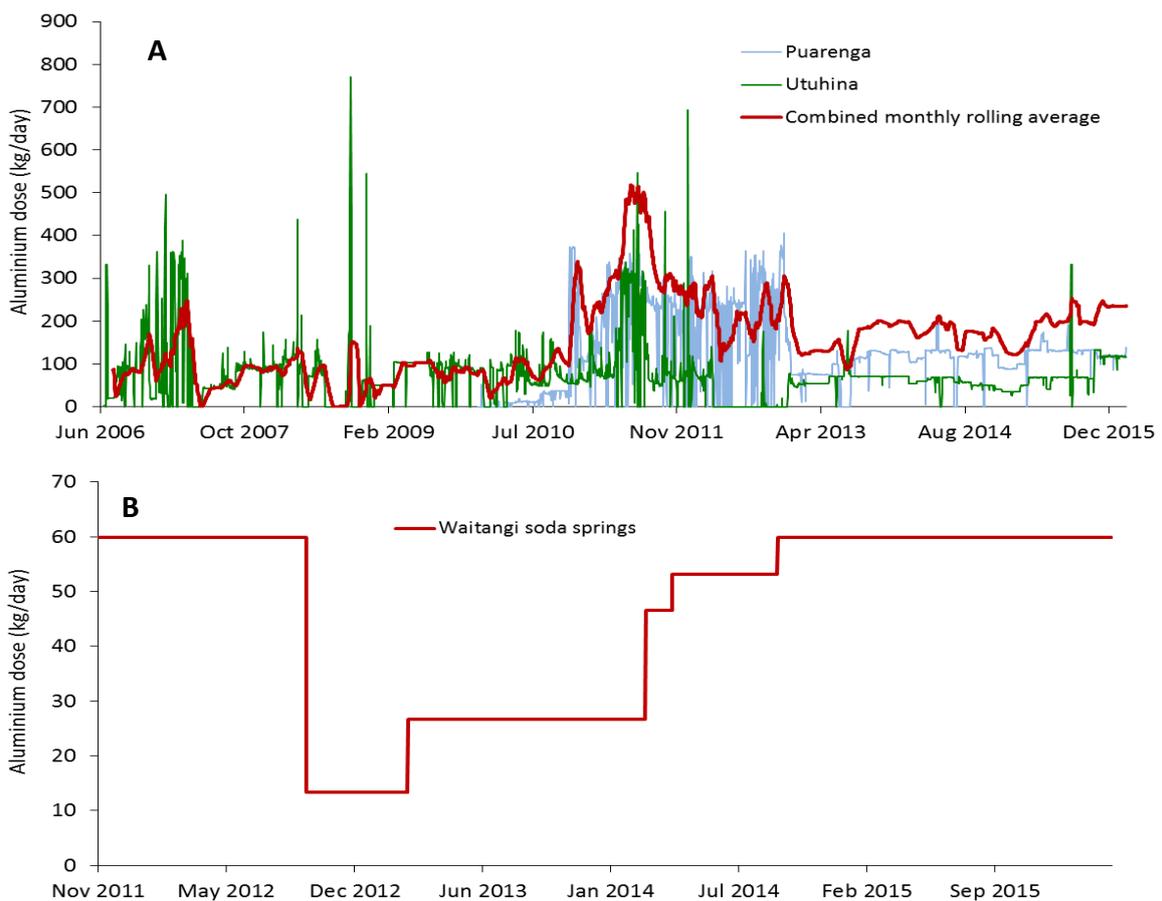


Figure 1. Daily aluminium dose rates for (A) Lake Rotorua and (B) Lake Rotoehu until 1 March 2016.

When added to water, alum ($\text{Al}_2(\text{SO}_4)_3$) dissociates and dissolved aluminium undergoes a series of hydrolysis reactions resulting in the formation of aluminium hydroxide ($\text{Al}(\text{OH})_3$) which adsorbs dissolved phosphorus and coagulates suspended solids. The resulting flocculent sequesters dissolved and particulate phosphorus in the sediment, reducing primary production, thereby improving water clarity (Cooke et al. 2005). Once within the water column, the aluminium flocs may either be lost from the system through outflows or may settle into the bottom sediment. In shallow lakes (i.e., Rotorua and Rotoehu) or lake margins, wind-driven resuspension may cause settled flocs to be transported to deeper parts of the lake (Cooke et al. 2005). Bioturbation, gas ebullition and advection, as well as storm surges, can disturb or bury surface sediment and thus, move the aluminium flocs into deeper sediment layers, potentially rendering it ineffective for controlling bioavailable phosphorus in the lake (Egemo et al. 2013, Özkundakci et al. 2013). Once settled, flocculated $\text{Al}(\text{OH})_3$ undergoes an aging process, changing from a colloidal amorphous solid to microcrystals, and then to the mineral gibbsite in a process that may take up to a year (Cooke et al. 2005). However, during the early part of this process, before crystallisation, $\text{Al}(\text{OH})_3$ is still able to bind bioavailable phosphorus, providing the additional benefit of attenuating sediment phosphorus release under hypoxic conditions (Welch and Cooke 1999).

Previous bottom-sediment surveys of Lake Rotorua were conducted prior to (Pearson 2007), and following (Özkundakci et al. 2013) initiation of alum dosing in Lake Rotorua. Sediment aluminium concentrations in 2012 were lower in the main basin of the lake, compared to 2006. Sediment phosphorus concentrations were reduced at four sites located near to the discharges of the Utuhina and Puarenga Streams, but sites further from the stream (i.e. deep basin and close to the Ohau Channel outlet) showed increased concentrations of phosphorus in the sediment (Özkundakci et al. 2013). However, the proportion of non-crystalline to total aluminium within the sediment was not investigated. Quantification of the non-crystalline aluminium fraction is important, as this is the only form capable of binding phosphorus.

The University of Waikato was commissioned by the Bay of Plenty Regional Council to conduct a sediment survey of Lakes Rotorua and Rotoehu to investigate aluminium and phosphorus concentrations in the lakes' sediments. Comparative sediment aluminium accumulation between 2012 and 2016 was determined and vertical profiles of aluminium concentrations examined for changes between 2012 and 2016. This study established the amorphous (non-crystalline) aluminium fraction in the lake sediment. This information will provide an indication of the relative level of aluminium accumulation and the proportion of aluminium that may be re-mobilised should persistent acidic or alkaline conditions occur in the water column.

Methods

Study Sites

Lake Rotorua has a surface area of 80.6 km², a mean depth of 10.8 m (maximum depth 45 m), and a total water volume of 0.85 km³ and polymictic stratification patterns (Burger et al. 2011). The basin was formed around 220-230 ka ago as a result of a rhyolitic eruption (Wood 1992). The eruption created an extensive plateau, the Mamaku ignimbrite, which contains a substantial portion of the deep aquifer storage within the catchment. Catchment land use is primarily agricultural (47.3%), with smaller areas of native (23.9%) and exotic (21.4%) vegetation (PCE 2006). Lake Rotorua has experienced a generally improving water quality trend over the past 10 years, although prolonged summer stratification conditions in 2014-15 and 2015-16 have resulted in increased Trophic Lake Index (TLI) levels (Figure 2).

Lake Rotoehu is a shallow (mean depth 8.2 m), moderately sized (7.9 km²), polymictic lake in the northeast of the Rotorua in the Te Arawa lakes district (Scholes 2009). The catchment land use is relatively evenly distributed between exotic forestry (32%), native vegetation (33%) and pasture (34%) (Scholes 2009), with small settlements at Ngamimiro Bay and Otautu Bay on the eastern side of the lake. Geothermal waters contribute dissolved nitrogen and phosphorus to the lake, and the trophic state of the lake has historically been classified as mesotrophic to eutrophic (Scholes 2009). The TLI was relatively stable between 1994 to 2010 (~4.5) before showing an improving trend in water quality coinciding with the initiation of alum dosing in 2011. However, Rotoehu has also experienced extensive periods of stratification and algal blooms in 2014-15 and 2015-16 resulting in an increase in TLI levels (Figure 2). As the lake is primarily fed by groundwater discharge it often experiences large fluctuations in water levels, and at the time of sampling the lake level was approximately 1–1.5 m below its mean level.

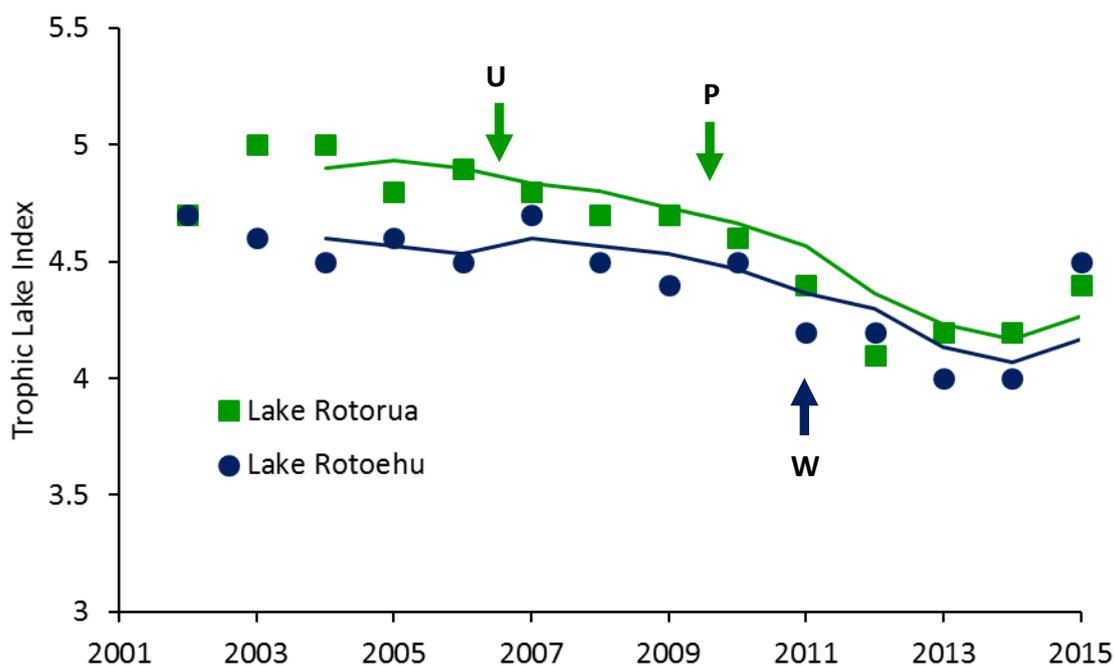


Figure 2. Trophic Lake Index (TLI) of Lake Rotorua and Lake Rotoehu 2002–15. Solid lines indicate 3-yearly running average. Coloured arrows indicate approximate start dates for alum dosing of lake inflows, including the Utuhina Stream (U), Puarenga Stream (P) and Waitangi Soda Stream (W). Data supplied by Bay of Plenty Regional Council.

Sediment surveys

To ascertain aluminium and dissolved phosphorus concentrations in the sediments a sediment survey was conducted across the basins of Lake Rotorua and Lake Rotoehu. In Lake Rotorua, 15 sediment cores were collected over two consecutive days in February 2016. The cores were collected in a transect starting from close to the inlet of the Utuhina and Puarenga streams continuing north, passing Mokoia Island to the west and progressing towards the Ohau channel before finishing just north of Mokoia Island (Figure 3). Coring sites were the same locations previously sampled by Pearson (2007) prior to stream alum dosing and Özkundakci et al. (2013), following 6 years of alum dosing. The sites ran through the deepest zone of the lake and most sites were greater than 15 m water depth. The sites were chosen to represent three different depositional zones: Zone 1 (Sites Ru1–4) to represent the likely immediate depositional area of the treated streams, Zone 2 (Sites Ru5–11) to represent the main sediment accumulation basin (≥ 20 m water depth) and Zone 3 (Sites Ru12–15) to represent an area of low sediment accumulation (< 20 m water depth), as identified by Pearson (2007). The relationship between current site designs and those used by Pearson (2007) and Özkundakci et al. (2013) are presented in Appendix 1.

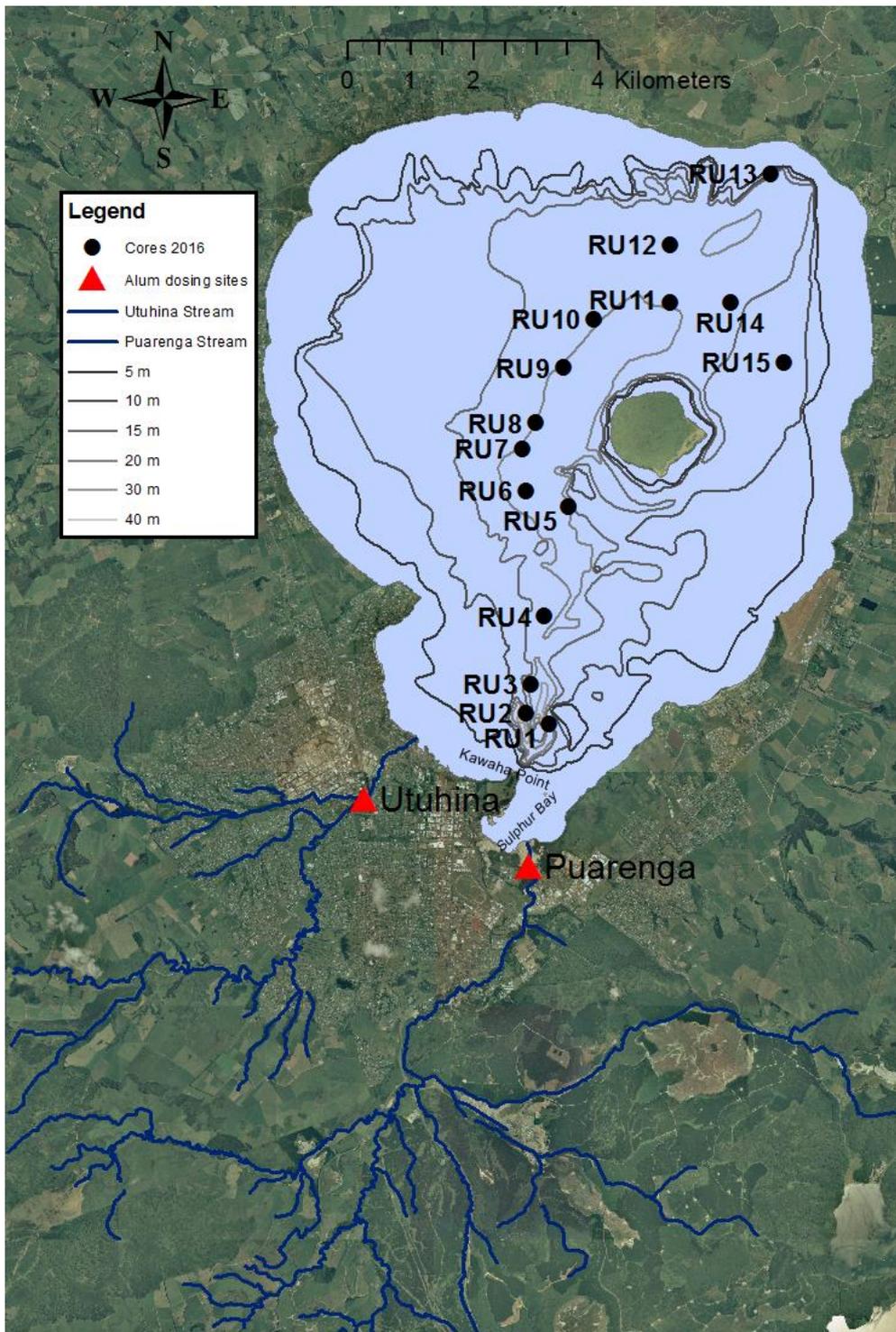


Figure 3. Lake Rotorua February 2016 sediment coring sites. Utuhina and Paarenga sub-catchments with alum dosing sites are also shown.

On 1 March 2016 seven sediment cores were taken in Lake Rotoehu from sites running north-west then north from the mouth of the Waitangi Springs Stream out into the main basin of the lake (Figure 4). Coring sites were chosen to represent a likely gradient of sediment aluminium concentrations running from high levels where the alum dosed Waitangi Springs

Stream enters the lake at Te Weta Bay, out to the most dispersed location in the main basin. Lake Rotoehu core sampling locations are presented in Appendix 2.

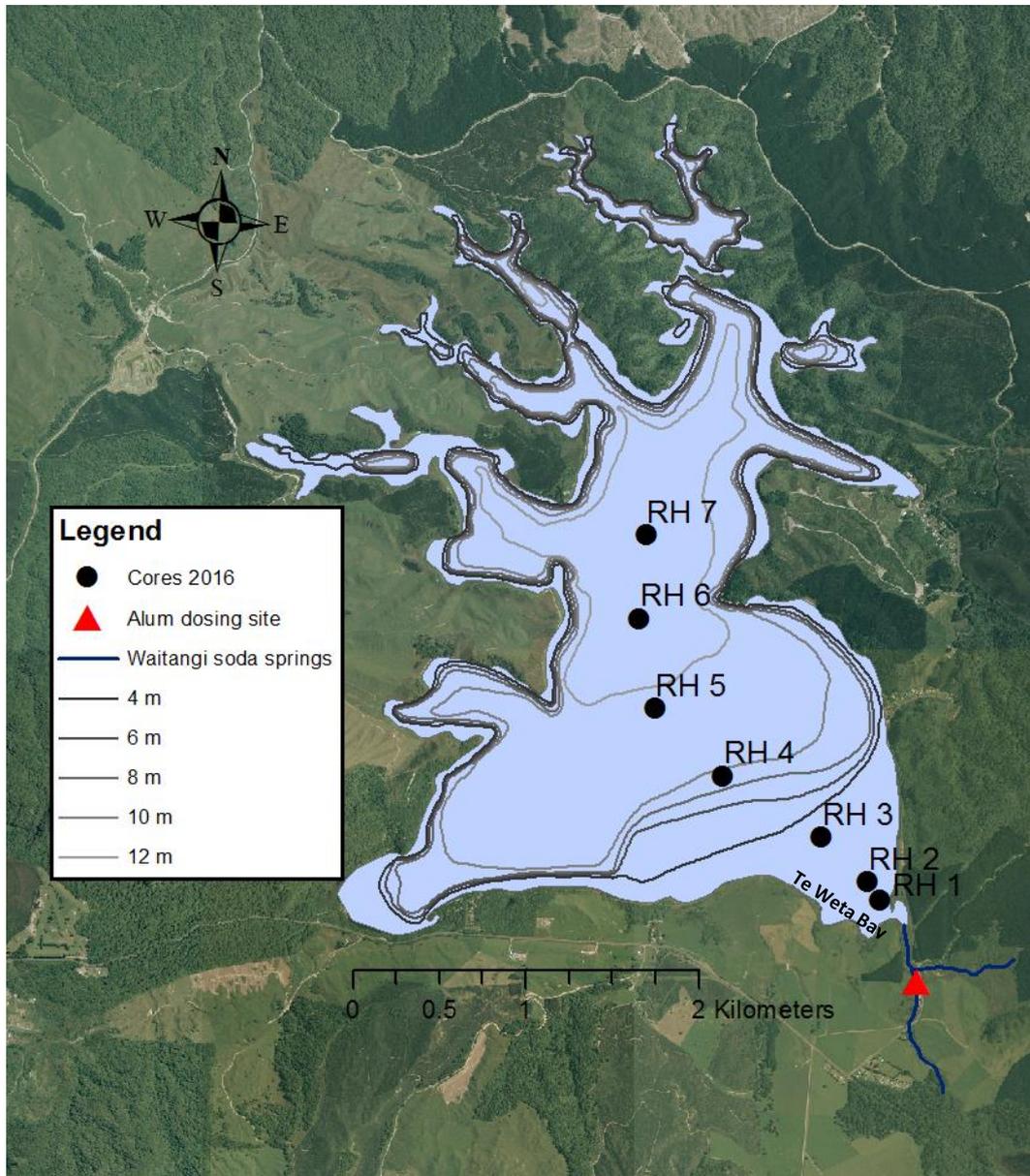


Figure 4. Lake Rotoehu 2016 sediment coring sites. Waitangi Soda Springs Stream and alum dosing station are also shown.

Following Özkundakci et al. (2013) sediment cores were 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. 10 cm of the overlying water. Once the core was retrieved it was photographed and water samples taken from the overlying water for determination of total nutrients (nitrogen and phosphorus) and dissolved nutrients (dissolved reactive phosphate, ammonium, and nitrate). A custom-made, gas-tight sampling chamber, designed to minimise exposure of potentially anoxic sediment to the air, was then 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 the sediment-water interface was exposed. Sediment samples were extruded at 1-cm vertical intervals up to 4 cm sediment depth and transferred into 50 mL polypropylene centrifuge tubes. From 4 to 20 cm sediment depth the sediment was added to tubes at 2-cm intervals. Small amounts of residual overflowing sediment were discarded. Sediment samples were stored on ice until analysis in the laboratory.

In addition to sediment coring, water column profiles were taken at each coring site using a conductivity-temperature-depth (CTD) profiler (SBE 19 plus SEACAT Profiler, Seabird Electronics Inc.), with additional mounted sensors for dissolved oxygen (DO) concentration (Seabird Electronics), chlorophyll fluorescence (Chelsea MiniTracka II) and beam transmittance (WetLabs C-star).

Sediment and nutrient analysis

Sediments were centrifuged at 4000 rpm (2900 G) for 15 minutes and the resulting supernatant pore water filtered using acid washed Swinnex filter holders and Whatman GF/C microfiber filters before being analysed for dissolved reactive phosphate concentrations. The centrifuged sediment was then dried at 50°C for 7 days and then lightly ground using a mortar and pestle.

Sediment total aluminium content was determined by reverse Aqua Regia digestion. Sediment samples (0.2 g) were left to pre-digest overnight at room temperature following the addition of 1 mL conc. HNO₃ and 0.33 mL conc. HCL. Samples were then digested at 50°C for 1 hr in a circulating water bath followed by the addition of 50 mL milli-Q water. Digested samples were centrifuged and 15 mL of the supernatant filtered using 0.45 µm cellulose acetate filters (MicroAnalytix, Auckland). The sample and control blank digests were then analysed for phosphorus and aluminium using inductively coupled plasma mass spectrometry (ICP-MS model ELAN DRC II; Perkin-Elmer SCIEX).

Sediment non-crystalline aluminium content was determined by ammonium oxalate digestion following a modified method of Hodges and Zelazny (1980). Sediment (0.2 g) was shaken with 50 mL 0.2 N ammonium oxalate (Sigma, Australia) (pH 3) for 2 h in the dark, followed by centrifugation for 5 min at 5000 rpm. The supernatant was then filtered using 0.45 µm cellulose acetate filters and aluminium content determined by ICP-MS.

Water nutrient concentrations were analysed using a Flow Injection Analyser 8500 Series II (FIA+ 8000 Series, Zellweger Analytics, Inc. Hach). Phosphate was analysed using LACHAT QuickChem method 31-115-01-1-H; ammonium was analysed using LACHAT QuickChem method 31-107-06-1-B and LACHAT QuickChem Method 31-107-04-1-A was used to analyse

nitrate/nitrite. Limits of detection were 0.001 mg N L⁻¹ for NO₂, NO₃, 0.002 mg N L⁻¹ for NH₄ and 0.001 mg P L⁻¹ for PO₄.

Results

Lake Rotorua

Plots of temperature and dissolved oxygen concentrations from CTD profiles indicate strong stratification of Lake Rotorua on 15 and 16 February 2016 (Figure 5). There was a c. 5°C temperature difference between surface and bottom waters throughout the main basin of the lake with a well-defined thermocline at c. 15 m depth. Epilimnion water temperature was approximately 1°C higher at sites Ru1–4, likely reflecting the more sheltered conditions near Kawaha Point (Figure 3). The following day prevailing weather conditions had changed with increased westerly wind and heavy rain-showers resulting in the epilimnion water temperature declining by approximately 1°C (Figure 5). The lake was anoxic below 15 m depth with some indication of hypoxia at 9–10 m depth at site Ru 1. Other notable features include an area of high conductivity and reduced pH near the lake bottom at site Ru 11 (Figure 5), potentially indicating intrusion of geothermal waters. A plume of higher conductivity water can also be seen at 10 m depth across sites Ru 1–4, which may be the result of geothermally influenced water leaving Sulphur Bay (Figure 3).

Visual inspection of the sediment surface showed no evidence of Al floc at the sediment-water interface in any of the sediment cores (Appendix 3). Intact sediment cores were difficult to obtain from site Ru 4 due to the coarse, compacted nature of the sediment, resulting in sectioning to a depth of 18 cm rather than the full 20 cm. Thick (c. 0.5–1 cm) benthic algal mats were also present on the sediment surface of cores retrieved from depths < 20 m (Appendix 3).

Dissolved reactive phosphate (DRP) and ammonium concentrations from the water overlying the 15 sampled sediment cores were variable, with DRP ranging from 0.018– 0.262 mg L⁻¹ (mean 0.099 mg L⁻¹) and ammonium-N ranging from 0.170 – 3.949 mg L⁻¹ (mean 1.119 mg L⁻¹) (Figure 6). In contrast, there was little variation in nitrate-N (range 0.021 – 0.023 mg L⁻¹; mean 0.022 mg L⁻¹) and nitrite-N (range 0.004 – 0.005 mg L⁻¹; mean 0.004 mg L⁻¹) concentrations (data not presented). Total phosphorus (range 0.086 – 2.249 mg L⁻¹; mean 0.664 mg L⁻¹) and total nitrogen (range 0.678 – 7.221 mg L⁻¹; mean 2.737 mg L⁻¹) concentrations largely reflected the site variations in DRP and ammonium apart from unusually high values at site Ru6 (Figure 6).

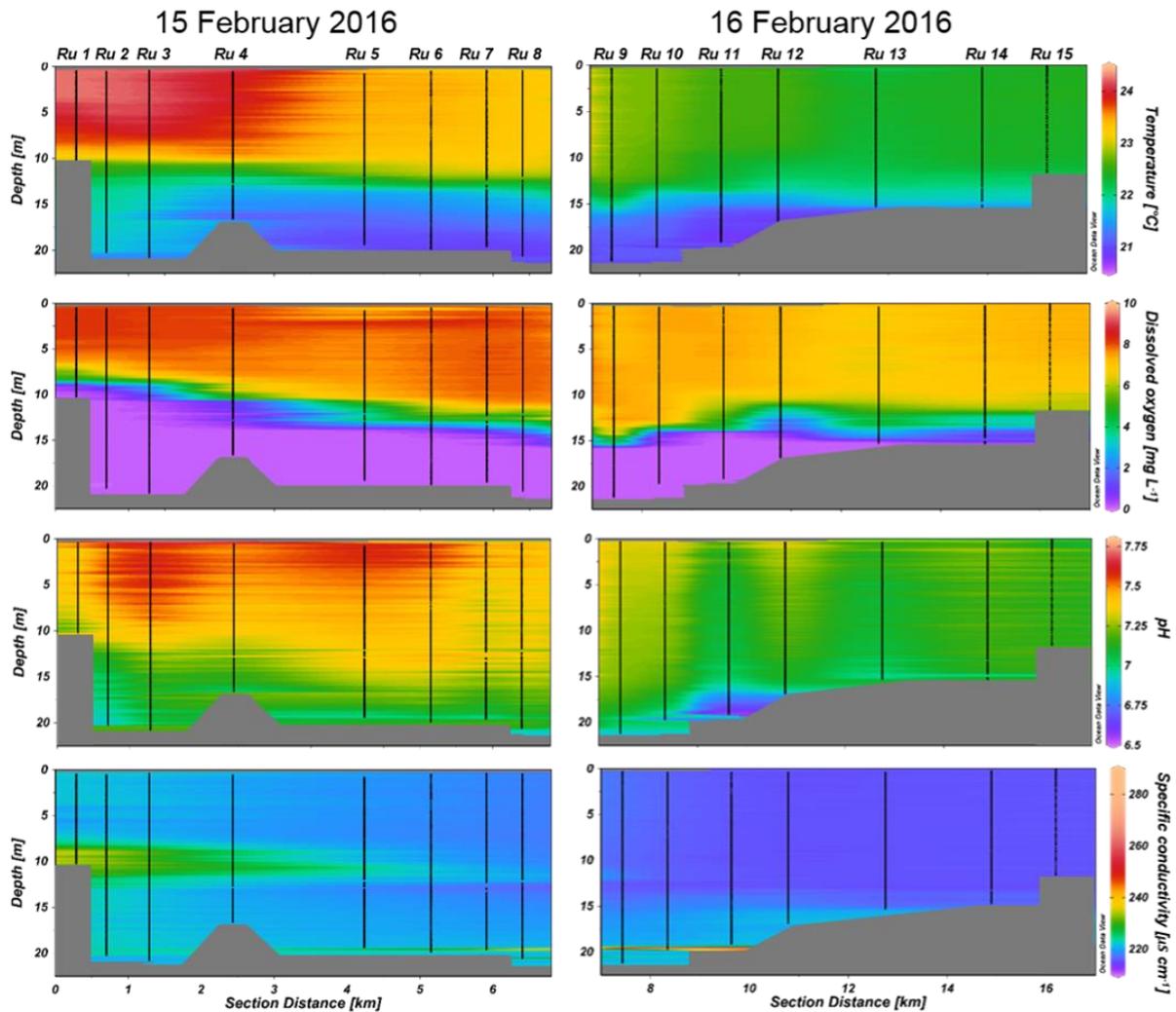


Figure 5. Lake Rotorua temperature, dissolved oxygen, pH and specific conductivity from CTD profiles taken at sediment coring sites (Ru1–15) on 15 and 16 February 2016.

Cores were pooled into three depositional zones (zone 1 cores Ru 1 – 4; zone 2 cores Ru5 – 11; zone 3 Ru12 – Ru15) and mean total aluminium concentrations compared to those previously reported in 2006 and 2012. Surface sediment (0–4 cm depth) total aluminium concentrations had small increases in total aluminium content compared to previously reported concentrations in all three depositional zones of the lake (Figure 7). These increases were not significantly different between years (ANOVA; $P > 0.05$) apart from a significant (ANOVA; $P < 0.05$) increase in total aluminium content in zone 3 between 2012 ($5854 \text{ mg kg}^{-1} \text{ DW} \pm 139 \text{ 95\% CI}$) and 2016 ($7208 \text{ mg kg}^{-1} \text{ DW} \pm 365 \text{ 95\% CI}$); however, there was no significant difference (ANOVA; $P > 0.05$) in total aluminium content between 2006 ($6827 \text{ mg kg}^{-1} \text{ DW} \pm 849 \text{ 95\% CI}$) and 2016 for this zone.

Sub-surface (5–12 cm) sediment mean total aluminium concentrations were compared between sampling years for each depositional zone (Figure 8). Small but statistically

significant increases (ANOVA $p < 0.05$) in total aluminium were observed between 2012 and 2016 in zone 2 ($5588 \text{ mg kg}^{-1} \text{ DW} \pm 145 \text{ 95\% CI}$ and $5910 \text{ mg kg}^{-1} \text{ DW} \pm 230 \text{ 95\% CI}$, respectively) and zone 3 ($6088 \text{ mg kg}^{-1} \text{ DW} \pm 266 \text{ 95\% CI}$ and $6777 \text{ mg kg}^{-1} \text{ DW} \pm 331 \text{ 95\% CI}$, respectively), however, there was no statistically significant (ANOVA $p > 0.05$) increase in total aluminium content between 2006 and 2016 in zone 1 (Figure 8). Zone 2 and zone 3 2016 mean total aluminium content was not significantly different (ANOVA $p > 0.05$) from 2006.

For deeper lake sediments (13–20 cm), all zones had similar mean total aluminium content (Figure 9), with the only statistically significant (ANOVA $p < 0.05$) change in total aluminium content being a small decrease from 2012 ($6708 \text{ mg kg}^{-1} \text{ DW} \pm 226 \text{ 95\% CI}$) to 2016 ($5955 \text{ mg kg}^{-1} \text{ DW} \pm 132 \text{ 95\% CI}$) in zone 2.

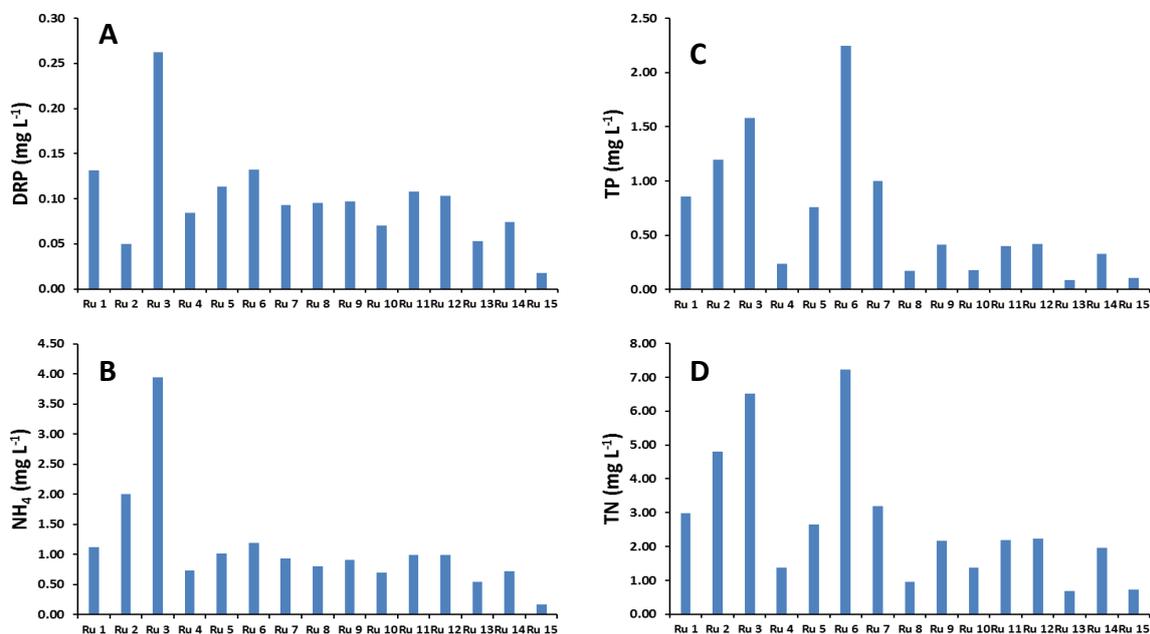


Figure 6. (A) Dissolved reactive phosphate (DRP), (B) ammonium (NH₄-N), (C) total phosphorus (TP) and (D) total nitrogen (TN) concentrations in water overlying each of the 15 sediment cores sampled from Lake Rotorua on 15 and 16 February 2016.

Small but not statistically significant (ANOVA $p > 0.05$) increases in surface sediment (0–4 cm) phosphorus content were observed in zone 1 (sites Ru 1–4) and zone 2 (Ru5–11) between 2012 and 2016 (Figure 10). In comparison, sediment phosphorus content in zone 3 was significantly (ANOVA $P < 0.05$) lower in 2016 ($989 \text{ mg kg}^{-1} \text{ DW} \pm 171 \text{ 95\% CI}$) compared to 2006 ($1502 \text{ mg kg}^{-1} \text{ DW} \pm 569 \text{ 95\% CI}$) and 2012 ($1512 \text{ mg kg}^{-1} \text{ DW} \pm 179 \text{ 95\% CI}$) (Figure 10).

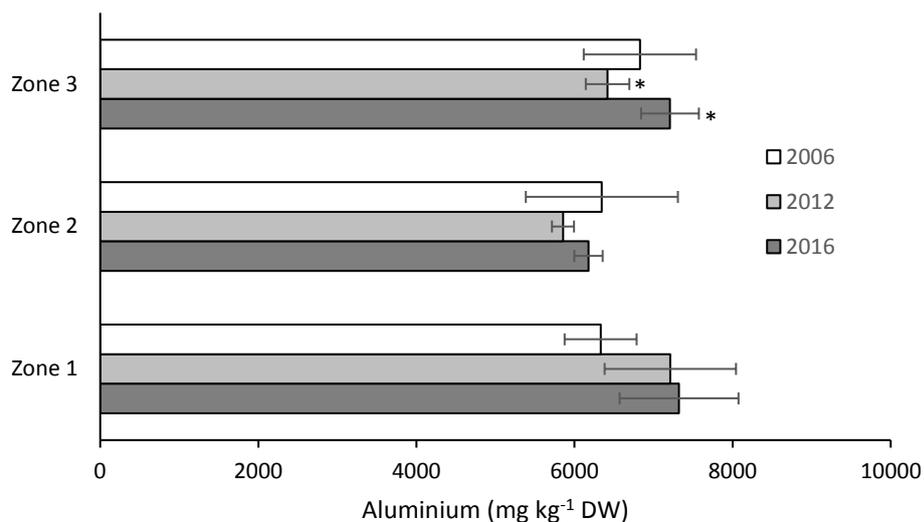


Figure 7. Mean total aluminium content in Lake Rotorua sediments (0–4 cm) by depositional zone for the present (2016), 2012 (Özkundakci et al. 2013) and 2006 (Pearson 2007) surveys. Error bars represent 95% confidence intervals, * indicates significant difference (ANOVA; $P < 0.05$) in total aluminium content between years within the depositional zone.

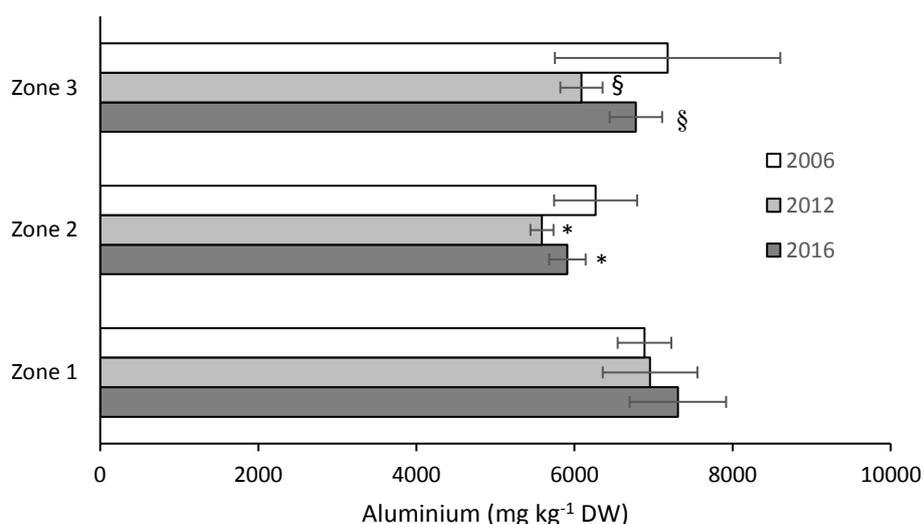


Figure 8. Mean total aluminium content in Lake Rotorua sub-surface sediments (5–12 cm) by depositional zone for the present (2016), 2012 (Özkundakci et al. 2013) and 2006 (Pearson 2007) surveys. Error bars represent 95% confidence intervals. , * and § indicates significant differences (ANOVA; $P < 0.05$) in total aluminium content between years within the depositional zone.

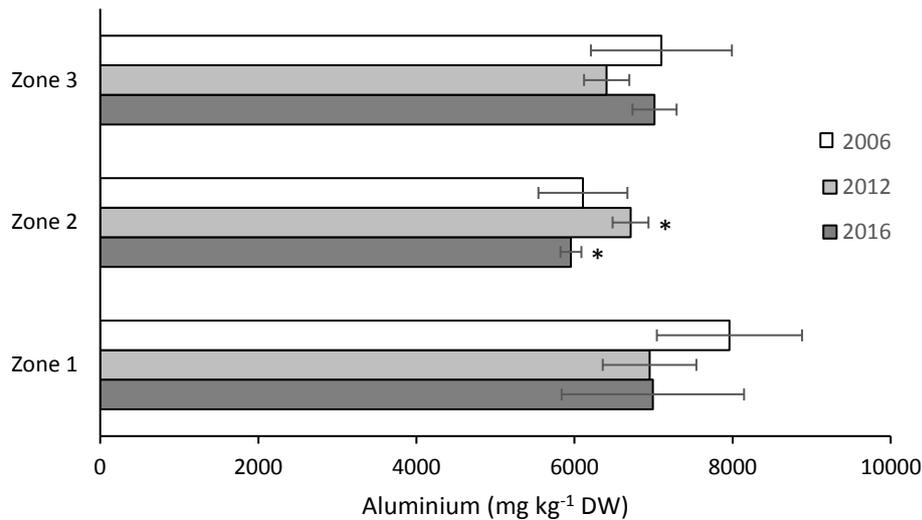


Figure 9. Mean total aluminium content in Lake Rotorua sediments (13–20 cm) by depositional zone for the present (2016), 2012 (Özkundakci et al. 2013) and 2006 (Pearson 2007) surveys. Error bars represent 95% confidence intervals. * indicates significant differences (ANOVA; $P < 0.05$) in total aluminium content between years within the depositional zone.

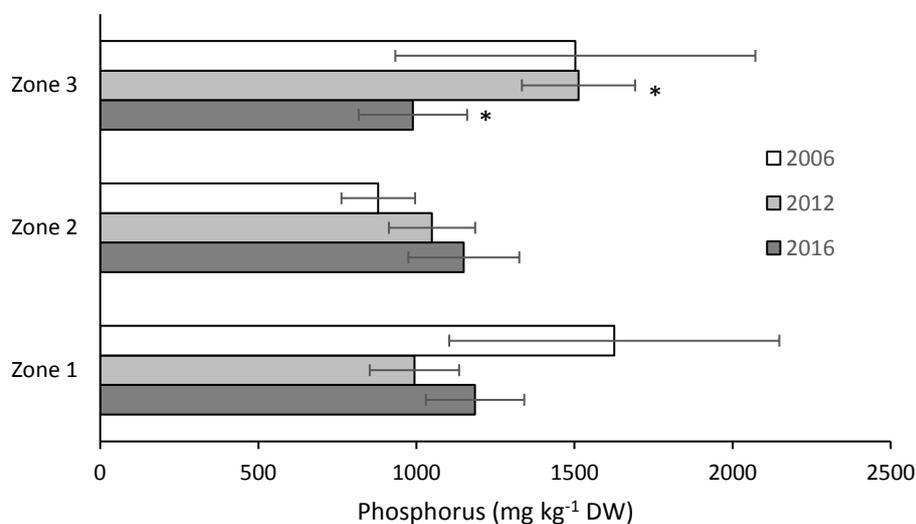


Figure 10. Mean total phosphorus content in Lake Rotorua sediments (0–4 cm) by depositional zone for the for the present (2016), 2012 (Özkundakci et al. 2013) and 2006 (Pearson 2007) surveys. Error bars represent 95% confidence intervals. * indicates significant differences (ANOVA; $P < 0.05$) in total phosphorus content between years within the depositional zone.

Sub-surface (5–12 cm) sediment phosphorus content showed no change between 2012 and 2016 for all three depositional zones (Figure 11). However, all zones were significantly (ANOVA $p < 0.05$) reduced in sediment phosphorus content in 2012 and 2016 compared with 2006. In addition, phosphorus content was noticeably higher in zone 1 compared with zones 2 and 3, within survey years.

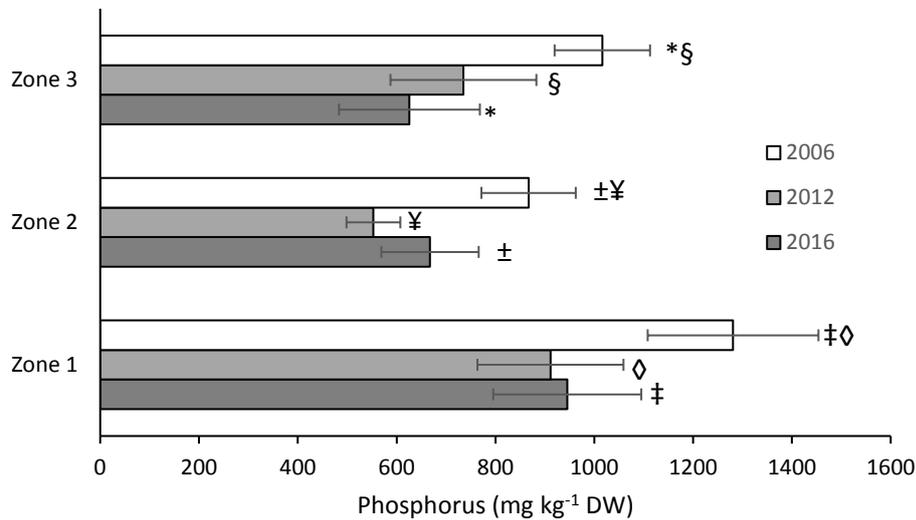


Figure 11. Mean total phosphorus content in Lake Rotorua sub-sediments (5–12 cm) by depositional zone for the for the present (2016), 2012 (Özkundakci et al. 2013) and 2006 (Pearson 2007) surveys. Error bars represent 95% confidence intervals. *, ‡, ◊, ±, ¥ and § indicate significant differences (ANOVA; $P < 0.05$) in total phosphorus content between years within the depositional zone.

Deeper lake sediments (13–20 cm) had variable total phosphorus content between sampling years within each depositional zone (Figure 12). Within zone 1 a significant reduction (ANOVA $p < 0.05$) in total phosphorus content was observed between 2006 (1285 mg kg⁻¹ DW ± 261 95% CI) and 2016 (737 mg kg⁻¹ DW ± 172 95% CI), although neither was significantly different from 2012 (912 mg kg⁻¹ DW ± 150 95% CI). Statistically significant reductions (ANOVA $p < 0.05$) in total phosphorus content were observed from 2006 to 2016 in zone 2, and from 2006 and to 2012 in zone 3.

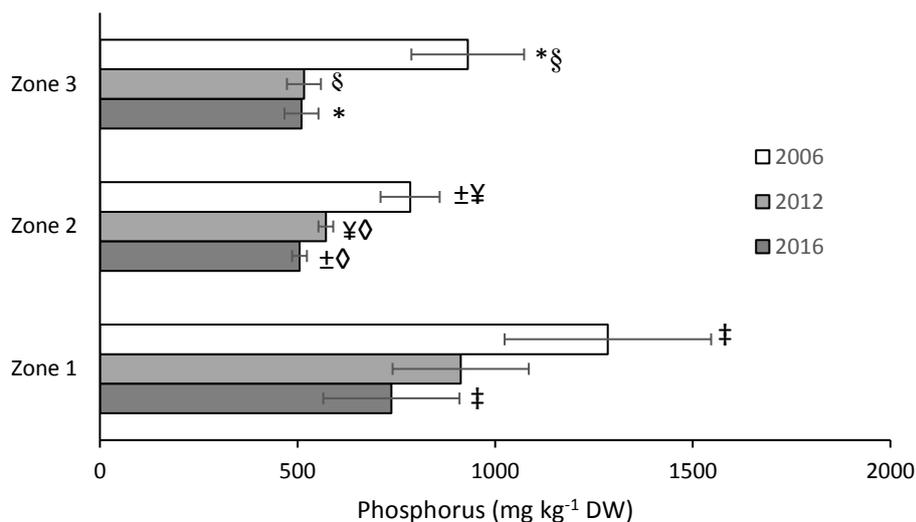


Figure 12. Mean total phosphorus content in Lake Rotorua deep sediments (13–20 cm) by depositional zone for the for the present (2016), 2012 (Özkundakci et al. 2013) and 2006 (Pearson 2007) surveys. Error bars represent 95% confidence intervals. *, ‡, †, ±, ¥ and § indicate significant differences (ANOVA; P<0.05) in total phosphorus content between years within the depositional zone.

The proportion of amorphous (non-crystalline) aluminium in relation to total aluminium was determined and plotted as vertical profiles grouped by depositional zone (Figure 13A–C). Mean values of amorphous aluminium proportions in each depositional zone are also presented (Figure 14D). Vertical profiles of amorphous aluminium proportions in zone 1 were highly variable, while profiles from zone 2 and zone 3 were more consistent. While there was a general negative trend in amorphous aluminium content with depth for most profiles, there was no consistent relationship between amorphous fractions values and specific depths. In contrast to zone 2 and zone 3, two sites (Ru2 and Ru3) in zone 1 had greater amorphous aluminium content in surface (0–4 cm depth) and sub-surface (5–12 cm depth) sediments compared to all other sites (Figure 13). A peak in amorphous aluminium content was observed at 4 cm depth in the Ru4 site profile which may be related to the shallower depth of the site and its location between the small lake basin located north of Kawaha Point and the main lake basin (Figure 2). Similarly, the profile of site Ru1 showed an atypical peak in sediment amorphous aluminium content from 10–16 cm compared to the other profiles, which may be related to the location of the sampling site, sediment disturbance from gas ebullition or bioturbation.

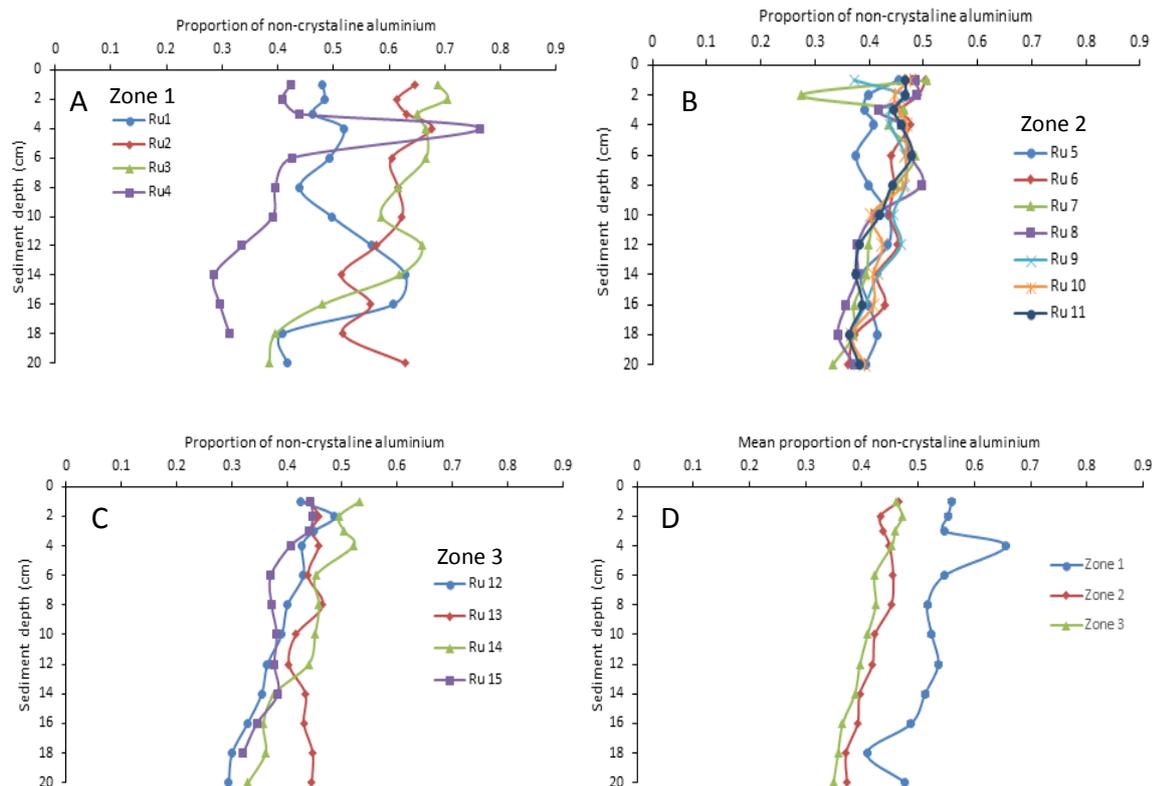


Figure 13. Vertical sediment profiles of the proportion of amorphous (non-crystalline) aluminium from 15 sites in Lake Rotorua. Profiles are grouped by depositional zone (A) zone 1 (Ru1–Ru4), (B) zone 2 (Ru5–Ru11) and (C) zone 3 (Ru12–Ru15); also presented are (D) means of each depth in the three depositional zones.

Mean pore water DRP concentrations for each depositional zone are presented in Figure 14 and individual core profiles are presented in Appendix 4. Dissolved reactive phosphorus concentrations in the sediment pore water were observed to decrease with increasing sediment depth, this is in contrast to data from 2012 where DRP concentrations increased with depth (Figure 14; Appendix 4). Pore water mean DRP concentrations in the surface sediments are lower in zone 1 compared to zone 2 and zone 3. This is primarily driven by lower (c. 0.011 – 0.600 mg L⁻¹) surface sediment pore water DRP concentrations at sites Ru2 and Ru3 (Appendix 1).

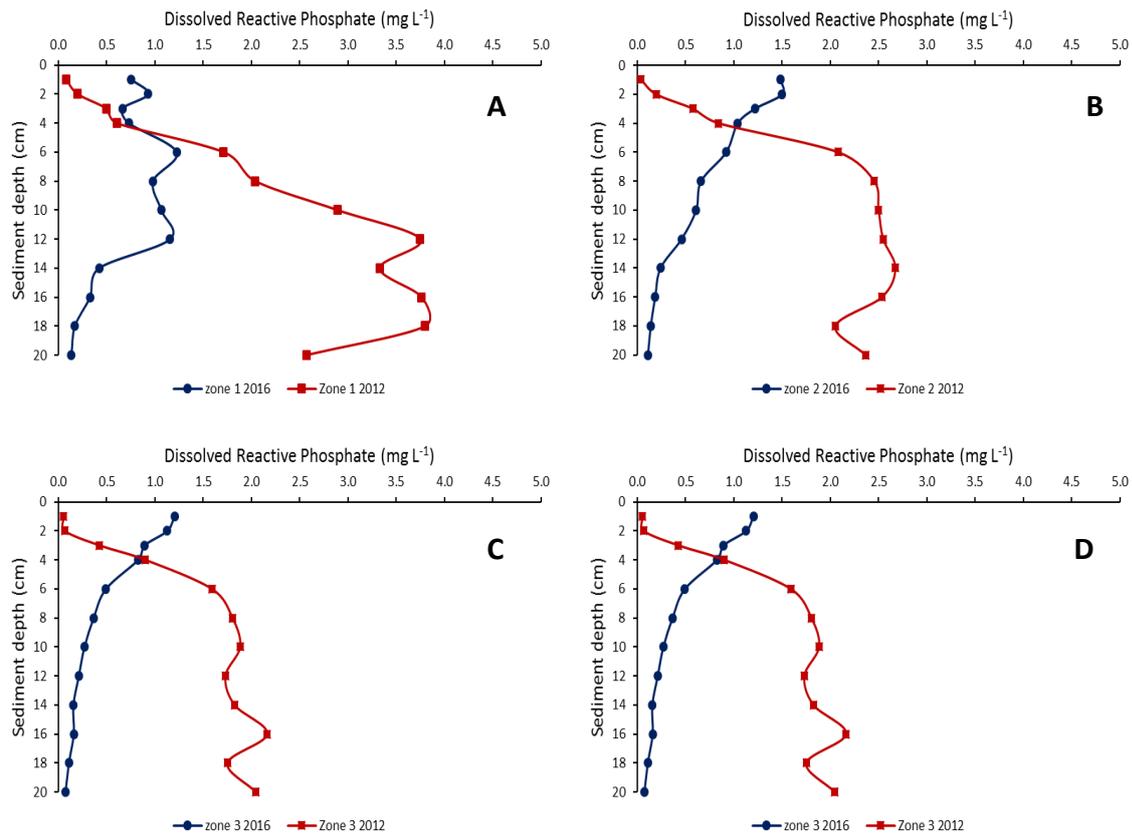


Figure 14. Vertical profiles of mean sediment pore water dissolved reactive phosphate concentrations in Lake Rotorua February 2016. DRP data from August 2012 (Özkundakci et al. 2013) is provided for comparison. Profiles are grouped by depositional zone (A) zone 1 (Ru1–Ru4), (B) zone 2 (Ru5–Ru11) and (C) zone 3 (Ru12–Ru15); also presented are (D) means of each depth in the three depositional zones.

Lake Rotoehu

Lake Rotoehu was sampled on 1 March 2016. There was insufficient water depth at sites Rh1 and Rh2 to conduct CTD casts. Plots of temperature and dissolved oxygen concentrations from CTD profiles indicate weakening stratification with a maximum 1.6°C difference in surface and bottom water temperatures. Dissolved oxygen levels are reduced to near anoxic levels in the bottom waters of the main basin in a zone extending for approximately 2 m above the lake bed (Figure 15). Site Rh4 appears to show some evidence of upwelling with cooler deoxygenated water breaking the thermocline and extending into the epilimnion. There was also notable variation in pH both horizontally and vertically. Water entering lake Rotoehu from Waitangi springs was pH <7 while surface water in the main basin (i.e., Rh6 and Rh7) was >9. This resulted in a surface pH gradient from sites Rh1 to Rh7 (Figure 15). Smaller vertical pH gradients can also be observed between bottom and surface waters at site Rh5–7 (Figure 14). Specific conductivity was higher (c. 530 $\mu\text{S cm}^{-1}$) than in Lake Rotorua (c. 220 $\mu\text{S cm}^{-1}$) but displayed very little spatial variability (Figure 15).

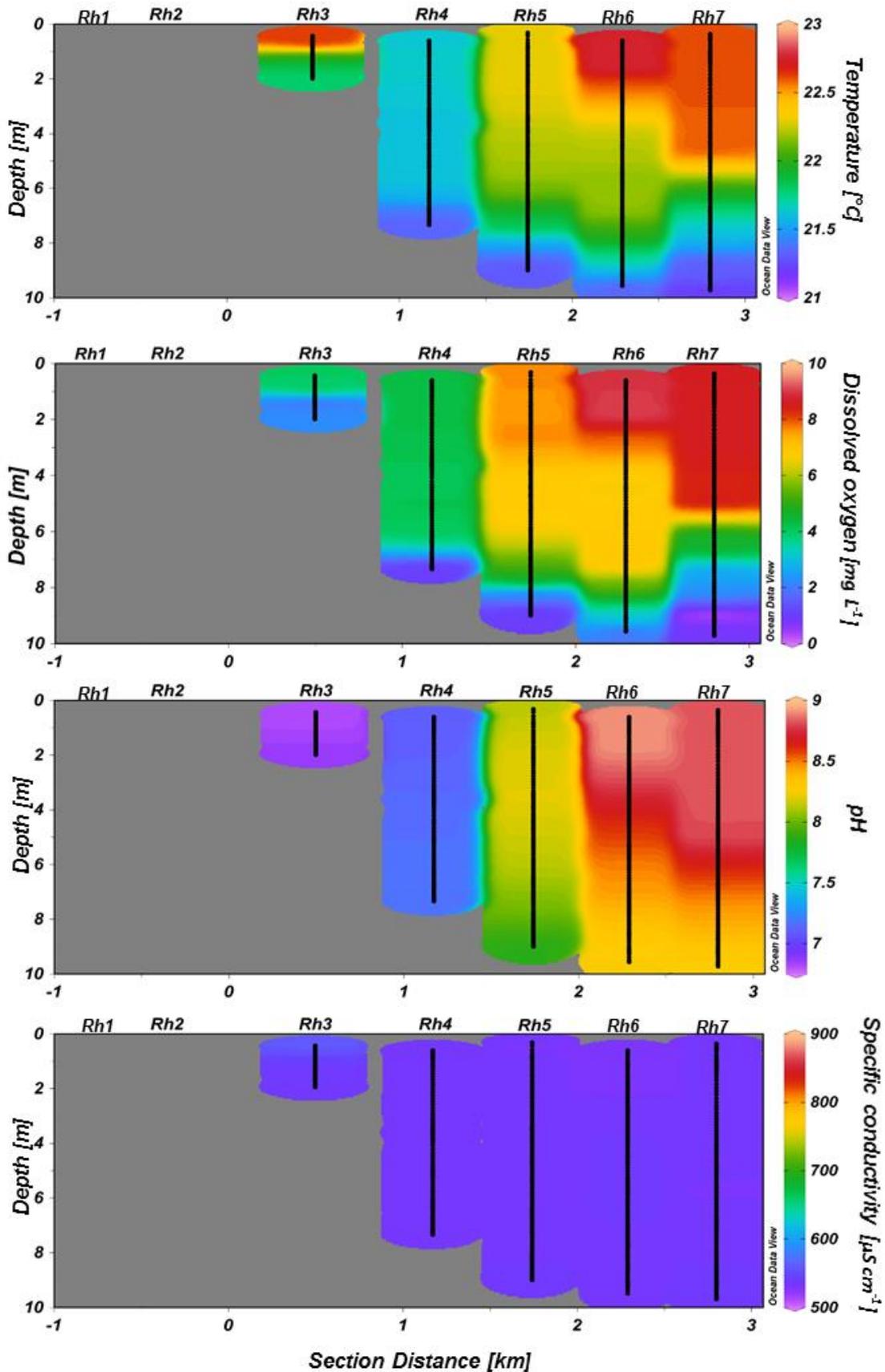


Figure 15. Lake Rotoehu temperature, dissolved oxygen, pH and specific conductivity from CTD profiles taken at sediment coring sites (Rh1-7) on 1 March 2016. There was insufficient water depth for CTD measurements at sites Rh1-2.

Dissolved reactive phosphate concentrations in the water overlying the sediment cores had an increasing trend from the mouth of the Waitangi Stream out into the main basin of the lake, ranging from 0.006 mg L⁻¹ at site Rh3 to 0.682 mg L⁻¹ at site Rh7 (Figure 16A). Ammonium concentrations had a less defined trend, being comparatively low at site Rh1 (0.064 mg L⁻¹) and greatest at site Rh3 (0.740 mg L⁻¹) (Figure 16B). Sediment from Lake Rotoehu was sandier and often contained coarse pumice particles compared to the finer muddier sediment from Lake Rotorua. This made retrieval of intact cores with undisturbed surface sediment more challenging, therefore, total nutrient concentrations are not presented and some cores (i.e., sites Rh1, Rh4, Rh6) have truncated sediment profiles (Appendix 5).

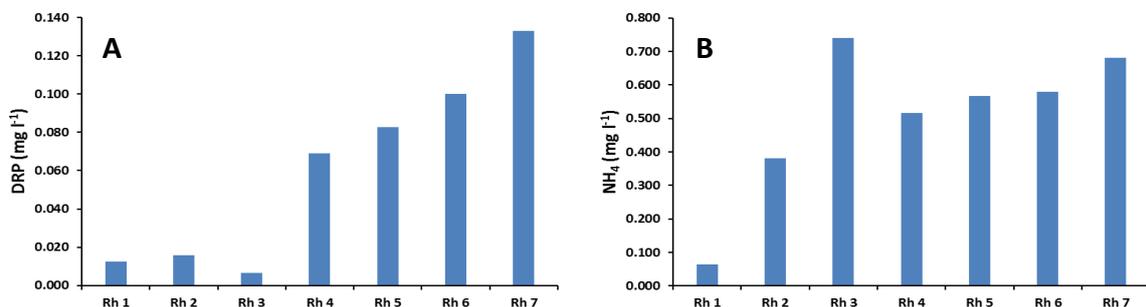


Figure 16. (A) Dissolved reactive phosphate (DRP) and (B) ammonium-N (NH₄), concentrations in water overlying each of the seven sediment cores sampled from Lake Rotoehu on 1 March 2016.

Sediment total aluminium profiles for the seven cores taken from Lake Rotoehu are presented in Figure 17. Surface sediments from cores sampled near the discharge point of the Waitangi Stream (i.e., Rh1 and Rh2; Figure 3) have notably increased aluminium content, in comparison to the main basin of Lake Rotoehu and Lake Rotorua. Below 10 cm depth sediment aluminium content declines and at 20 cm depth is similar to that measured in the main basin of Lake Rotoehu (Figure 16). Aluminium in the surface and subsurface sediments of sites Rh1 and Rh2 is almost entirely amorphous (Figure 18). Sites Rh3 and Rh4 also show increased amorphous aluminium, at levels similar to sites Ru2 and Ru3 in Lake Rotorua (Figure 13A). However, Rotoehu sites Rh5–7, which are located in the main lake basin, show similar proportions of amorphous aluminium to cores from zone 2 and zone 3 in Lake Rotorua (Figure 18).

Sediment total phosphorus content was notably higher at site Rh1 and increased with increasing sediment depth (Figure 19). Phosphorus content was also comparatively higher at sites Rh2 and Rh3 although the same trend was reversed, with phosphorus content decreasing with sediment depth. Total phosphorus content in sediments from sites Rh4–7 was similar throughout the sediment profile and similar to that observed in the deep sediment from zone 2 and zone 3 in Lake Rotorua (i.e., c. 500–600 mg P kg⁻¹) (Figure 12).

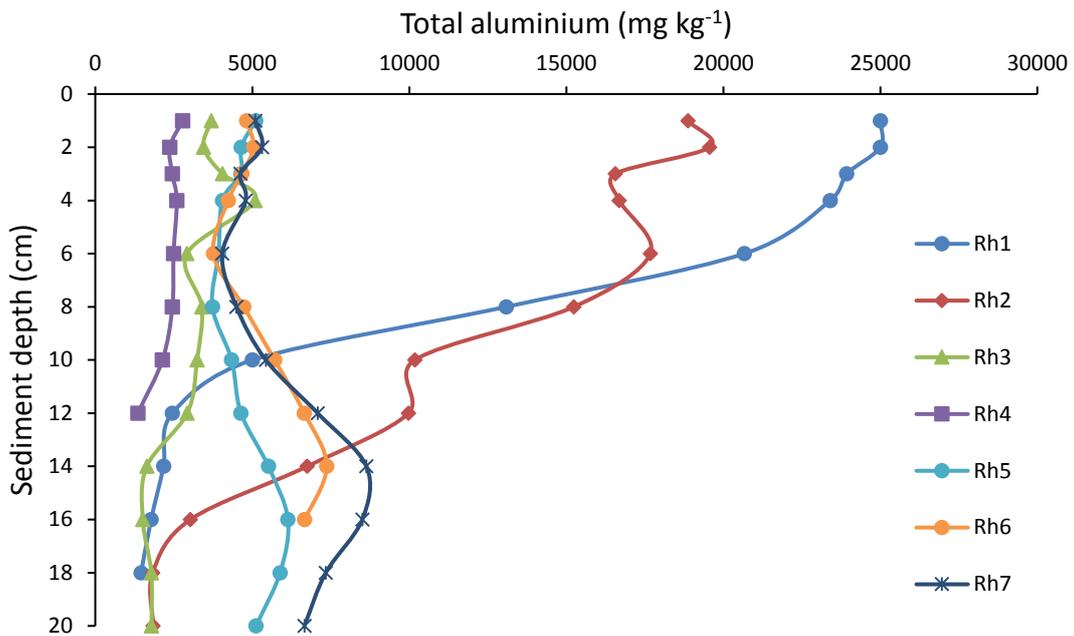


Figure 17. Vertical sediment profiles of total aluminium content in Lake Rotoehu sediments.

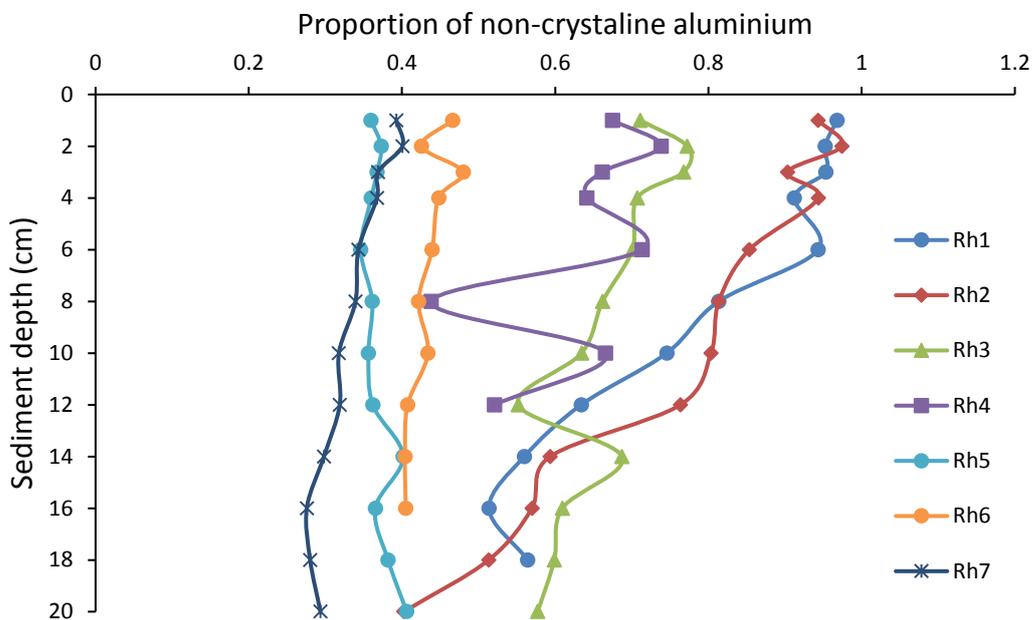


Figure 18. Vertical sediment profiles of the proportion of amorphous (non-crystalline) aluminium from sediment in Lake Rotoehu.

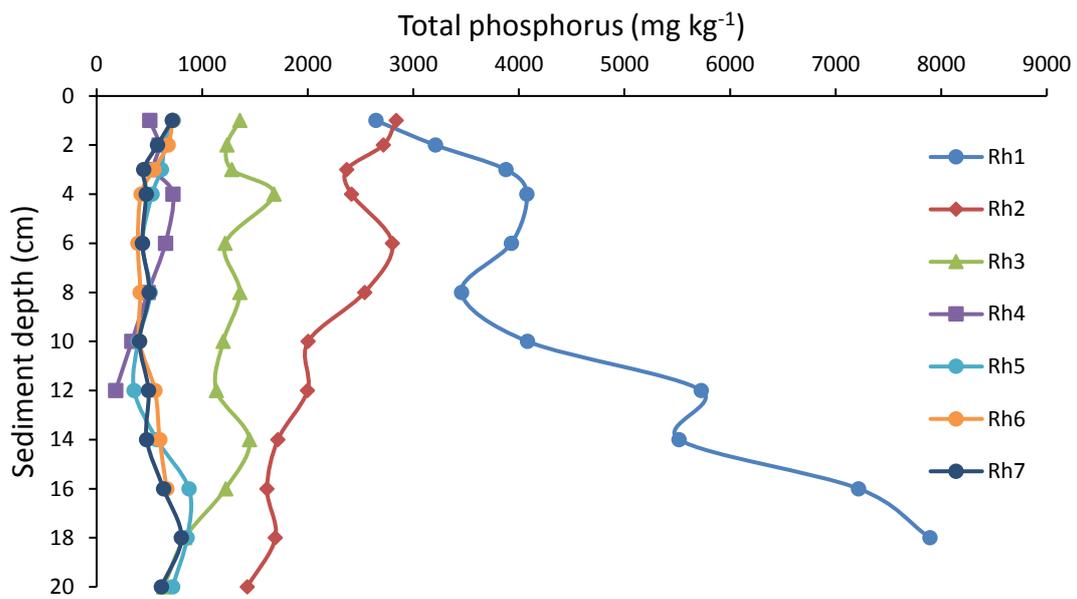


Figure 19. Vertical sediment profiles of sediment total phosphorus content in Lake Rotoehu sediments.

Dissolved reactive phosphate concentrations in the sediment pore water were highly variable with DRP concentrations ranging from below detection limits (i.e., $<0.004 \text{ mg L}^{-1}$) at sites Rh1–3 to $>0.3 \text{ mg L}^{-1}$ in the surface sediment pore waters at site Rh7. Peaks in DRP concentrations at 2 cm depth rather than 1 cm may reflect disturbance at the sediment-water interface resulting in some dilution of pore waters with overlying lake water.

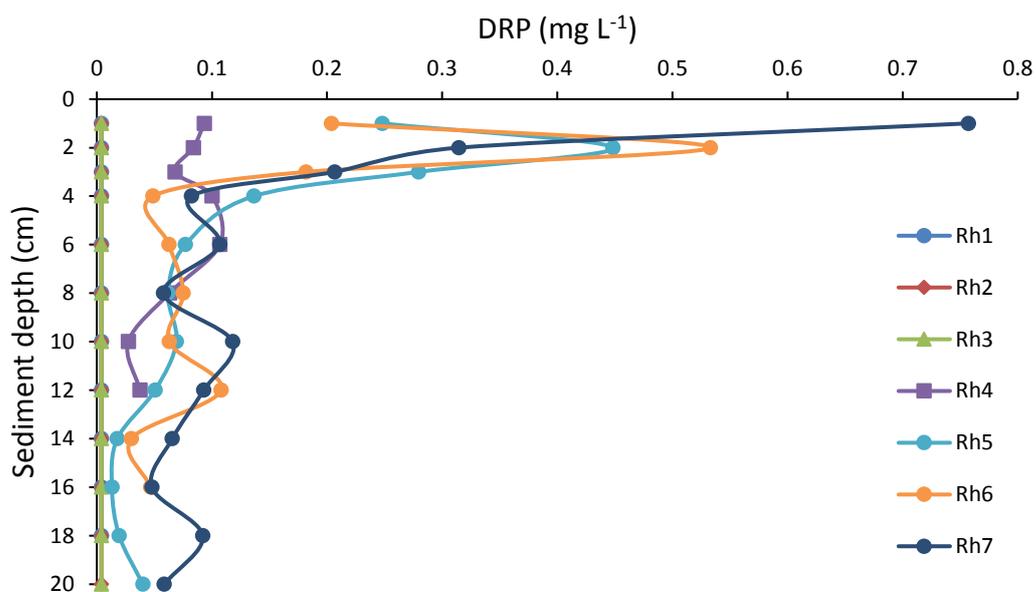


Figure 20. Vertical sediment profiles of sediment pore water dissolved reactive phosphate concentrations in Lake Rotoehu.

Discussion

Selected inflows to Lake Rotorua and Lake Rotoehu have been continuously dosed with alum since 2006 and 2011, respectively. This has resulted in the addition of 444.2 tonnes of aluminium to Lake Rotorua and 55.2 tonnes of aluminium to Lake Rotoehu by 2015 (Tempero 2015). Lake sediment surveys of Rotorua and Rotoehu were undertaken to investigate the fate of aluminium in these lakes and the effect of aluminium dosing on dissolved phosphorus concentrations. Survey sites in Lake Rotorua were selected to provide comparable locations to those used in previous studies conducted by Özkundakci et al. (2013) and Pearson (2007), and utilised the same analytical methodology of Özkundakci et al. (2013) by grouping sites into three different depositional zones. The depositional zones were: zone 1 (sites Ru1–4) to represent the likely immediate depositional area of the treated streams, zone 2 (sites Ru5–11) to represent the main sediment accumulation basin (>20 m water depth) and zone 3 (sites Ru12–15) to represent an area of low sediment accumulation (<20 m water depth), as identified by Pearson (2007). No previous survey of sediment aluminium content had been conducted for Lake Rotoehu. Therefore, a transect of seven cores (Rh1–7) running from the mouth of the Waitangi Stream out into the main lake basin were selected to provide the best spatial coverage for detecting aluminium accumulation in the sediments. Comparative sediment aluminium accumulation between 2012 and 2016 was determined and vertical profiles of aluminium concentrations were examined for changes between 2012 and 2016 in Lake Rotorua. Amorphous (non-crystalline) aluminium fractions in the sediments of both lakes were measured to determine likelihood of aluminium binding DRP released from lake sediments.

Sediment dating layers such as the 1886 Tarawera tephra were not captured in the present sediment survey (see Appendix 3 and Appendix 5 for core photos), precluding direct calculation of sedimentation rates. For Lake Rotorua, Trolle et al. (2008) calculated a net sedimentation rate for the period 1886–2006 of 0.3 cm yr⁻¹, and Pearson (2007) estimated at rate of up to 1.0 cm yr⁻¹. The method of calculation of the accumulation rate used by Trolle et al. (2008) and Pearson (2007) provides an estimated range of 3–10 cm for total sediment accumulation for the period 2006–16 in Lake Rotorua. For Lake Rotoehu, a mean net sedimentation rate of 0.23 cm y⁻¹ for the period 1886–2006 was reported by Trolle et al. (2008). Visual inspection of the aluminium and phosphorus concentration profiles of the sediment suggest accumulation rates of ~7 cm since 2006 in Lake Rotorua and ~5 cm in Lake Rotoehu since 2011, however, it should be noted that alum accumulation is highly spatially variable and not a reliable indicator of sedimentation rate. Sediment bioturbation rates have not been investigated and the impact of macroinvertebrate (i.e., koura) disturbance cannot be quantified.

Lake Rotorua

Fifteen sediment cores were retrieved from Lake Rotorua over two days in mid-February 2016. The lake was strongly stratified during this time, with an extensive anoxic zone below 15 m depth. Under anoxic conditions DRP and ammonium are released from lake sediments into the hypolimnion (Burger et al. 2011), and this was reflected in the elevated concentrations measured in the water above the cores (Figure 6). The release of these nutrients to the epilimnion following lake turnover likely constituted a substantial impediment to reaching the target TLI of 4.2 over the 2015/16 monitoring period.

Analysis of total aluminium content in the sediment of Lake Rotorua showed no evidence of widespread accumulation in the surface sediments (0–4 cm depth) of either zone 1 (closest to the alum dosed streams outflows) or zone 2 (the main lake basin) compared to surveys conducted in 2006 and 2012. A small increase in aluminium content was observed in the sediments of zone 3 (furthest from the inflows) between 2012 and 2016, but the 2016 level was not significantly different from the 2006 level. Aluminium content in the sub-surface sediments (5–12 cm depth) was significantly higher in 2016 compared to 2012 for zone 2 and zone 3, possibly indicating accumulation of aluminium from alum dosing. However, there was no difference in aluminium content between any of the survey years in zone 1 and the differences between years in zone 2 and zone 3 were minor in comparison to the total aluminium content. In the deep sediments (13–20 cm depth) there was no difference between years for zone 1 and zone 2 and a decrease in aluminium content between 2012 and 2016 in zone 2. When considered as a whole there appears little evidence to support a hypothesis of widespread aluminium accumulating on the bed of Lake Rotorua.

Assuming an increased proportion (i.e., >0.5) of amorphous aluminium in lake sediment is due to alum dosing, determination of the amorphous aluminium levels may provide some insight into possible areas of aluminium accumulation. Zone 1 had a higher mean amorphous aluminium content than sediments from zone 2 and zone 3, which can be primarily attributed to higher amorphous aluminium at sites Ru2 and Ru3 (Figure 13). Sites Ru1–3 are located comparatively close (c. 700 m) to Kawaha Point, an area roughly intermediate between discharge points for the Utuhina and Puarenga streams. The area is craterous and contains some of the deepest points in the lake (Jolly and Brown 1975). Site Rh1 (11.2 m deep) sits on the edge of this area, while sites Ru2 and Ru3 are located at depths ≤ 20 m and site Ru4 (17.4 m deep) approximately 1.1 km further north on a ridge between the Kawaha Point basin and the main lake basin. The increased amorphous aluminium at sites Ru2 and Ru3 suggests that this deeper area is accumulating alum derived aluminium, while alum flocculent deposited at the shallower Ru1 site is being resuspended and transported to the adjacent deeper areas. Alternatively, the shallower depth, which is above the anoxic zone, may be more hospitable to benthic burrowing organisms resulting in bioturbation of the surface sediment and burial of alum flocculent (i.e., Figure 13A). However, there appears to be insufficient aluminium accumulation in the zone 1 sites to account for the >450 tonnes of alum derived aluminium

entering the lake. One possible explanation for this is the settling alum floc to the lake bed immediately after it is discharged from the Uthina and Puarenga streams, and the current sampling sites are not sufficiently close to the stream discharge points to detect the area of aluminium floc deposition. In addition, aluminium flocculent discharged from the Puarenga Stream into Sulphur Bay may be dispersing along the south-eastern shore, driven by prevailing westerly winds as evidenced by satellite imagery in Figure 21. Current and past survey sites are not suitable for detecting aluminium flocculants dispersed in this direction.

Özkundakci et al. (2013) refuted claims that sediment capping resulting from alum dosing of the Puarenga and Uthina streams was primarily responsible for observed improvements in the water quality of Lake Rotorua during the years immediately following the initiation of dosing in 2006. This is supported by the current study which provides little evidence for significant aluminium accumulation in the main lake basin or an associated sediment capping effect preventing release of DRP into the water column under anoxic conditions. In addition, major increases in DRP and ammonium concentrations were observed in the bottom waters following a period of prolonged stratification in early 2016 (Sumeran et al., BOPRC, pers. comm.), indicating on effective capping effect. Sediment total phosphorus content was variable between years and zones. However, when this data is grouped within years and depth for each zone there is a notable trend of decreasing phosphorus with increasing depth (Appendix 6). This is expected as phosphorus is known to be mobile within sediment, especially under anoxic conditions, and is primarily driven by natural diagenetic processes rather than eutrophication (Carignan and Flett 1981, Trolle et al. 2010). In lakes undergoing annual alum treatment this process is reversed as alum-derived aluminium permanently binds the DRP fraction increasing the amount of refractory phosphorus within the sediment (Lewandowski et al. 2003). This effect is not observable in the sediment surveys of Lake Rotorua, however, it should be noted that there is considerable variation in the data, which may obscure clear trends.



Figure 21. Satellite imagery of 17 April 2017 sourced from Google Earth illustrating the easterly dispersal of precipitated material from the geothermal area of Sulphur bay, Rotorua. Alum flocculent is discharged from the Puarenga Stream at the head of Sulphur Bay.

Possible aluminium binding of pore water DRP was only observable at sites Rh2 and Rh3, the only two sites with observably higher fractions of amorphous aluminium. This suggests that alum dosing of the Utuhina and Puarenga streams is not sufficient to have a significant mitigating effect on bottom-sediment DRP release from the main lake basin. However, this does not preclude some degree of phosphorus sequestration in the Kawaha point area of Lake Rotorua and reductions in external, particularly bioavailable, phosphorus loading from the Puarenga and Utuhina stream.

Observed improvements in the water quality of Lake Rotorua over the past 10 years have been associated with adjustments to alum dosing of the Utuhina and Puarenga Streams. Moderation of lake phosphorus loading from these streams has been highly effective. However, secondary benefits associated with aluminium accumulation in the sediment of Lake Rotorua are more equivocal. Currently, there is no evidence to suggest widespread alum derived aluminium accumulating in the main basin of Lake Rotorua, the primary site of sediment DRP release following lake stratification. These observations suggest it is likely that the main site of aluminium accumulation is restricted to an area closer to the discharge points of the Utuhina and Puarenga streams. A supporting sediment survey with high spatial

resolution should be conducted in order to confirm this hypothesis, and to inform expert opinion as to what effect such an area would have on lake internal phosphorus loading. Survey sites should include the south-eastern shoreline to confirm whether alum flocculants discharged from the Puarenga Stream is dispersing in easterly direction. If advances in bathymetric mapping make it possible to constrain rates of sediment accumulation in key areas targeted for quantifying aluminium accumulation, it would be beneficial to establish age-depth relationships to better understand spatially-explicit aluminium and phosphorous accumulation rates.

Lake Rotoehu

A total of seven sediment cores were retrieved from Lake Rotoehu on 1 March 2016. Stratification in the lake was beginning to breakdown but a defined hypoxic zone was evident below 8 m depth. A notable gradient in pH from <7 near the mouth of the Waitangi Stream to >9 in the surface waters in the main basin of the lake was also evident. This may potentially affect the efficacy of phosphorus-aluminium binding, as the optimum pH range is for alum dosing is between pH 6 to 8.5 (Tempero 2015). Dissolved reactive phosphorus concentrations in the water overlying sediment cores from Te Wairoa Bay were notably reduced (<0.01 mg L⁻¹) compared to sites from the main lake basin (>0.06 mg L⁻¹), with a defined trend of increasing DRP concentration with increasing site depth. Ammonium concentrations were also elevated (>0.3 mg L⁻¹) in the water overlying the sediment for most sites. This can be attributed to a period of stratification prior to the survey, resulting in reducing conditions in the sediment and release of ammonium and DRP to the water column.

Surface (0–4 cm) sediment total aluminium content at sites Rh1 and Rh2 was 4-5 times higher than surface sediments from the main basin of Lake Rotoehu. In addition, the proportion amorphous aluminium at sites Rh1 and Rh2 was highly elevated (c. 0.9) and moderately elevated at sites Rh3 and Rh4 (c. 0.7). This suggests that the majority of alum dosed to the Waitangi Stream is deposited in Te Wairoa Bay and does not reach the main basin of the lake. Te Wairoa Bay is a broad shallow delta area in the south-eastern end of Lake Rotoehu covering approximately 0.3 km² (c. 3.7% of total lake area), with a mean depth of 1 m, although this value is highly dependent on lake level and can range by more than a metre. Much of the bay is occupied by the invasive submerged macrophyte *Ceratophyllum demersum* in sufficient biomass to cause significant physical and biogeochemical fluctuations. The dense vegetation reduces flow velocities promoting the deposition of aluminium flocs discharged from the Waitangi Stream (Eager 2017). In addition, diel fluctuations in pH and dissolved oxygen resulting from photosynthesis-respiration cycles are sufficient to inhibit aluminium-phosphorus binding within the bay (Eager 2017). Deposition of aluminium flocs in Te Weta Bay does have a localised effect in preventing release of DRP from sediments (i.e. Figure 20), however the shallowness of Te Weta Bay means it is unlikely to undergo extended periods stratification, and sediment DRP release is likely to be small compared with the main lake

basin. Eager (2017) estimates that approximately 50% of the Waitangi Stream DRP load is sequestered by alum dosing and natural ferric hydroxides also contribute to reducing phosphorus availability. The effectiveness of alum sequestering phosphorus from the water column is demonstrated by the atypical sediment total phosphorus vertical profile at site Rh1 (Figure 19), indicating that phosphorus is being permanently bound in the deeper sediments rather than undergoing vertical migration towards the sediment surface. However, this area is comparatively localised and typical profiles of phosphorus distribution are observed in the main basin.

Localised sediment aluminium concentrations at the head of Te Weta Bay (i.e., sites Rh1 and Rh2) are likely to have a toxicological effect on aquatic invertebrates (Gensemer and Playle 1999), however this would be incidental to the observed diel variations in pH and the influence of other dissolved constituents from the geothermal Waitangi Springs. Diel variations in pH within Te Weta Bay may result in the dissolution of aluminium hydroxide precipitate at pH >9 resulting in the release of bound phosphorus (Reitzel et al. 2013). Reitzel et al. (2013) found that up to 24% of the sediment aluminium hydroxide could dissolve within 2 hours at pH 9.5 and a portion of sediment phosphorus was dissolved concomitantly. Lowering pH to 7 caused 30–100% of the dissolved aluminium to precipitate again after 24 hours. Toxicological effects also manifest with the dissolution of aluminium hydroxide at high pH, although exposure times are likely to be limited as the pH shifts to ≤ 7 once respiratory processes of *C. demersum* dominate at night. In addition, larger more mobile species such as fish are likely to actively avoid the Te Weta Bay area (Wauer and Teien 2010). Currently, the dynamics of pH shifts on aluminium-phosphorus binding are poorly studied, but it is likely that the prevailing environmental instability is negatively impacting on the effectiveness of the alum dosing.

Conclusions

Sediment surveys of lakes Rotorua and Rotoehu were conducted in early 2016 to determine aluminium and phosphorus concentrations and identify the impact of the alum dosing programme.

The main conclusions from this for Lake Rotorua work were:

1. Widespread increases in sediment aluminium content resulting from alum treatment of inflows were not observed in either lake.
2. It is likely that alum derived aluminium is accumulating in the Kawaha Point area of Lake Rotorua, as well as the south eastern shores north of Sulphur Bay. Further survey work is necessary to confirm this hypothesis.

3. The lack of alum derived aluminium in the main lake basin moderates the assumption that significant secondary effects of sediment phosphorus sequestration are contributing to recent improvements in the water quality of Lake Rotorua.

The main conclusions from this for Lake Rotoehu work were:

4. Similar to conclusions in Lake Rotorua, the majority of alum derived aluminium dosed to the Waitangi Stream is being deposited in Te Weta Bay rather than being transported into the main basin of Lake Rotoehu.
5. The large biomass of *Ceratophyllum demersum* in Te Weta Bay is causing large diel shifts in pH and dissolved oxygen. This is likely having a negative impact on aluminium binding by shifting the local pH outside of the optimum range for aluminium-phosphorus binding on a diel timescale.
6. In addition, the increased impedance of flow from *Ceratophyllum demersum* is causing the alum-derived aluminium from reaching the main lake basin and achieving secondary benefits of sequestering sediment released phosphorus. The effectiveness of the Waitangi Stream alum treatment programme should be reviewed in order to develop a more efficient and effective strategy for alum dosing.

Recommendations

1. Extend the sediment survey area in Lake Rotorua to include the areas of Kawaha Point and north of Sulphur Bay where aluminium accumulation is more likely. New survey stations should be established as soon as possible so that future time-series surveys are better able to determine the fate of added alum, and associated phosphorus.
2. Given that results suggest that the dominant effect of alum dosing is localised removal of DRP in major inflows, it will be worthwhile to consider testing the hypothesis that DRP concentrations and TLI values for Lake Rotorua may respond rapidly, enabling the trialling of lower dose rates that still achieve target TLI values, and
3. Undertake a review of Rotoehu alum dosing to develop a more effective and efficient strategy for dosing.

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Appendices

Appendix 1. Locations and synonyms of sediment coring sites in Lake Rotorua.

Site designation 2016	Previous site designations		Latitude	Longitude	Water depth (m)
	Pearson (2007)	Özkundakci et al. (2013)			
RU1	Ru129	Site 1	-38 07.485	176 16.215	11.2
RU2	Ru90	Site 2	-38 07.394	176 15.955	20.0
RU3	Ru130	Site 3	-38 07.144	176 15.997	21.2
RU4	Ru131	Site 4	-38 06.551	176 16.126	17.4
RU5	Ru116	Site 5	-38 05.594	176 16.337	20.2
RU6	Ru161	Site 6	-38 05.468	176 15.869	20.7
RU7	Ru158	Site 7	-38 05.106	176 15.812	20.4
RU8	Ru162	Site 8	-38 04.878	176 15.944	21.3
RU9	Ru128	Site 9	-38 04.391	176 16.225	22.0
RU10	Ru124	Site 10	-38 03.962	176 16.541	20.2
RU11	Ru154	Site 11	-38 03.790	176 17.362	19.8
RU12	Ru144	Site 12	-38 03.290	176 17.337	17.6
RU13	Ru96	Site 13	-38 02.646	176 18.402	16.4
RU14	Ru155	Site 14	-38 03.768	176 18.022	16.3
RU15	Ru110	Site 15	-38 04.274	176 18.625	12.3

Appendix 2. Locations of sediment coring sites in Lake Rotoehu

Site	latitude	longitude	Water Depth (m)
RH 1	-38.0333	176.54633	0.7
RH 2	-38.0324	176.54545	1.1
RH 3	-38.0301	176.5423	2.7
RH 4	-38.0271	176.53566	8.0
RH 5	-38.0237	176.53097	9.7
RH 6	-38.019	176.52973	10.5
RH 7	-38.0146	176.52998	10.4

Appendix 3. Sediment cores taken from Lake Rotorua 15 and 16 February 2016.



Ru 1



Ru 2



Ru 3



Ru 4



Ru 5



Ru 6



Ru 7



Ru 8



Ru 9



Ru 10



Ru 11



Ru 12



Ru 13



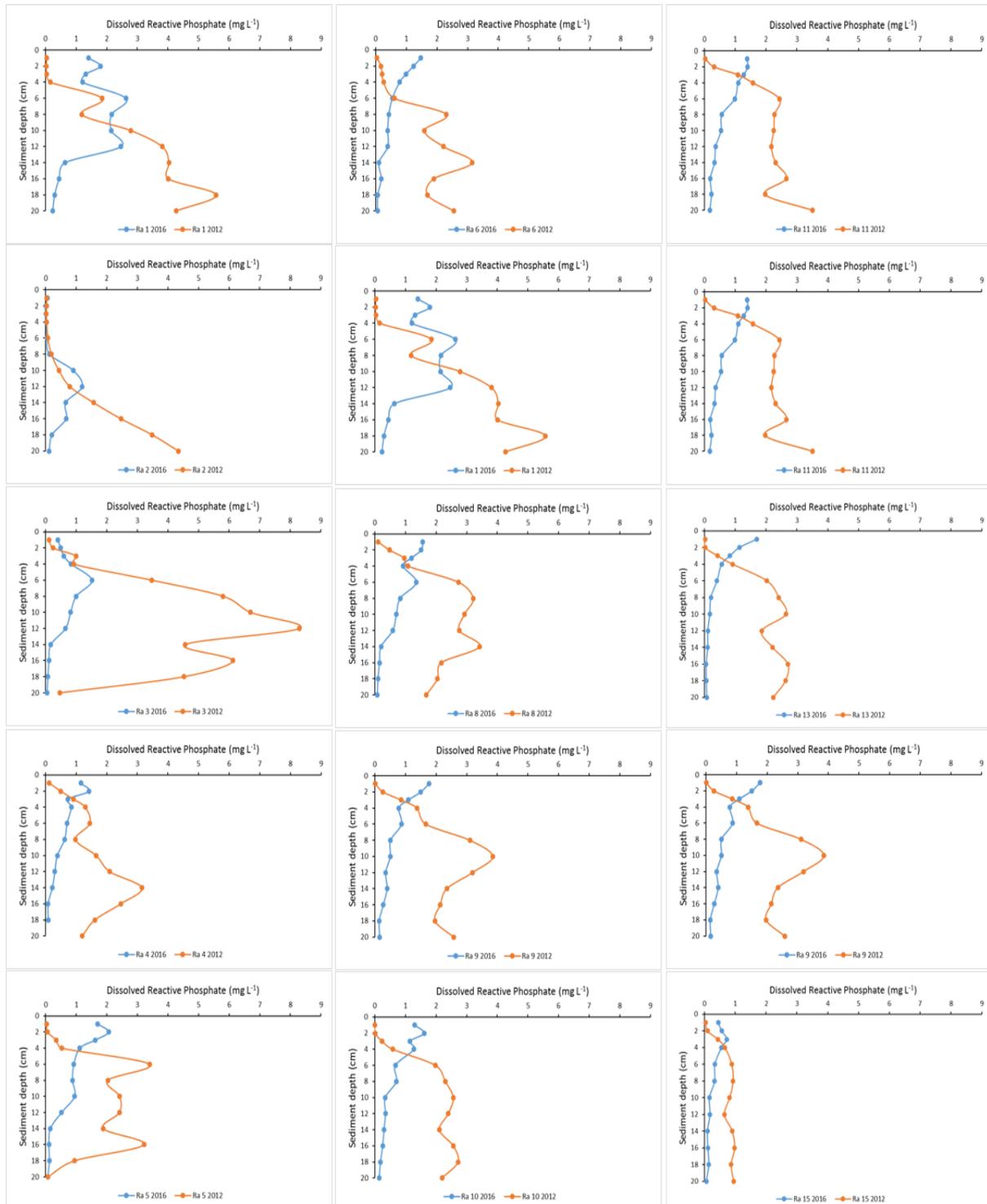
Ru 14



Ru 15



Appendix 4. Sediment pore water dissolved reactive phosphorus (DRP) concentrations in 15 cores taken from Lake Rotorua on 15 and 16 February 2016 and August 2012 (Özkundakci et al. 2013).



Appendix 5. Sediment cores taken from Lake Rotoehu 1 March 2016.



Rh 1



Rh 2



Rh 3



Rh 4



Rh 7



Rh 5



Rh 6

Appendix 6. Mean sediment phosphorus content for Lake Rotorua grouped by depositional zone and year (A) 2016, (B) 2012 and (C) 2006. Error bars represent 95% confidence intervals.

