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Sediment Aluminium Content of Lakes Rotorua and Rotoehu: 2020 Monitoring Survey

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Executive Summary

The application of aluminium sulphate (alum) to freshwater systems is commonly undertaken in order to restrict the availability of dissolved reactive phosphate (DRP), thereby reducing phytoplankton growth. Alum treatment of inflows to Lake Rotorua was initiated in 2006 and to Lake Rotoehu in 2011. As of December 2020, a total of 773 tonnes of aluminium had been dosed to Lake Rotorua and 124 tonnes to Lake Rotoehu. Improvements in water quality have been subsequently observed in Lake Rotorua with values of the Trophic Lake Index (TLI) decreasing from 4.8 to 4.2. In contrast, water quality has not significantly improved in Lake Rotoehu and alum dosing was halted from July 2018 to December 2020 while a review was conducted.

The University of Waikato was contracted by the Bay of Plenty Regional Council to conduct on-going monitoring of sediment aluminium concentrations in lakes Rotorua and Rotoehu as part of their resource consent conditions for alum dosing of inflows to these lakes. In addition to sediment total aluminium content, the proportion of amorphous (non-crystalline) aluminium was assessed. Amorphous aluminium is recognised as the fraction of total aluminium able to adsorb dissolved phosphorus, sequestering it from the water column. It was assumed that increased proportions of amorphous aluminium were primarily derived from alum dosing.

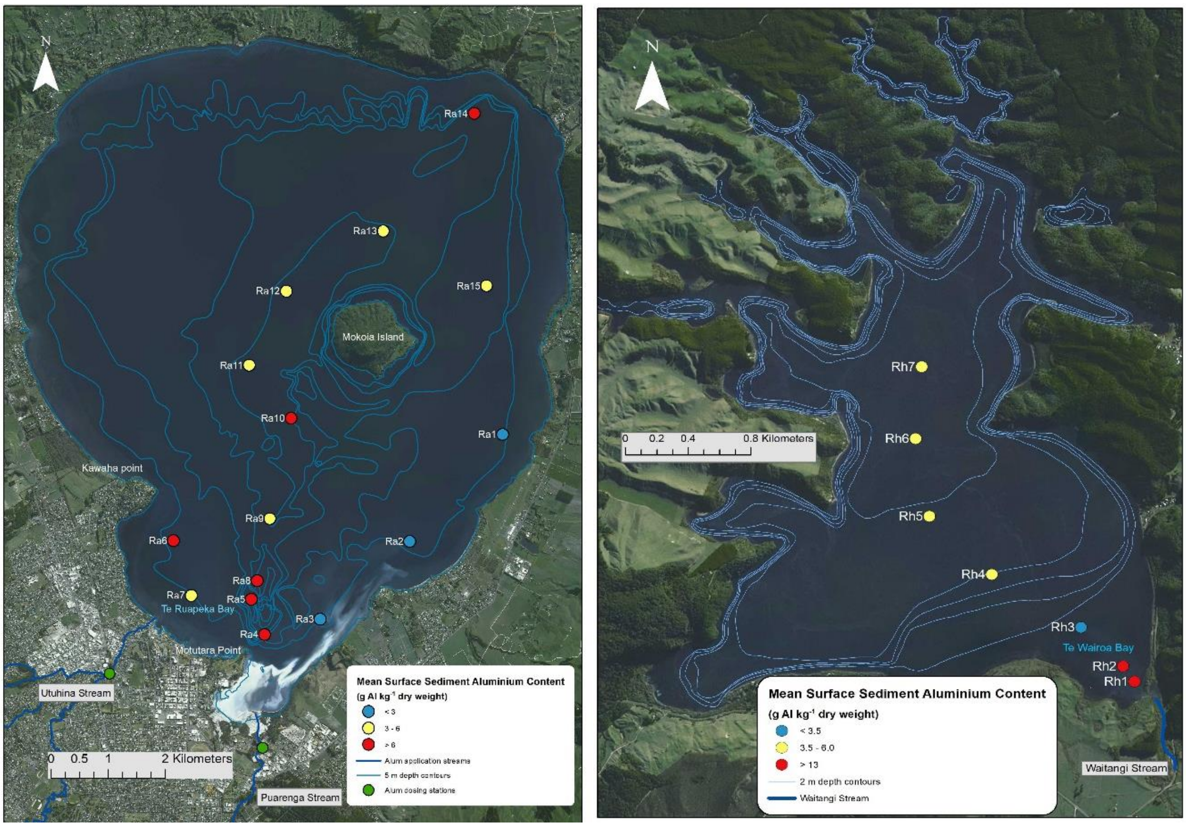
Fifteen sediment cores were taken from Lake Rotorua in December 2020. Previous surveys had reported little aluminium accumulation in the main basin of Lake Rotorua, with aluminium accumulation primarily occurring near the outlet to the Utuhina Stream and the 45 m deep crater north of Motutara Point. Based on this information, coring locations were modified from previous surveys with seven near-shore and crater sites sampled and the number of main basin sites sampled reduced to eight. The background sediment aluminium content for the main basin of Lake Rotorua is approximately 5 g Al kg^{-1} dry weight. The current survey supports the findings of previous sediment surveys with the main depositional areas for alum derived aluminium being the surface (1–4 cm depth) sediments of Te Ruapeka Bay, which can reach 12 g Al kg^{-1} and the crater north of Motutara Point at ~8 g Al kg^{-1}. There was no apparent accumulation of aluminium beyond background levels to the east of Sulphur Bay or in the main basin of Lake Rotorua.

In Lake Rotoehu, seven sites were surveyed in December 2020, extending from the mouth of the Waitangi Stream out into the main basin of the lake. Results were similar to those reported by Tempero and Hamilton (2016), with background sediment aluminium content approximately 5-6 g Al kg^{-1}. Alum derived aluminium was primarily accumulating in Te Wairoa Bay close to the discharge point of the Waitangi Stream with levels exceeding 25 g Al kg^{-1}. However, the two-year cessation of alum dosing resulted in a small decline of ~5 g Al kg^{-1} in

the surface sediments. Despite a five-fold increase in total aluminium content in Te Wairoa Bay over background levels, amorphous aluminium content appears to have declined due to the 2-year halt in alum dosing and aging of alum floc to the mineral gibbsite. There was no evidence of aluminium accumulation in the main basin of Lake Rotoehu.

Recommendations

1. On-going sediment monitoring for alum derived aluminium should incorporate both near-shore zone and deeper basin areas of the lakes.
2. Monitoring of sediment aluminium accumulation should also include assessment of amorphous aluminium content to distinguish alum-derived aluminium from natural background crystalline aluminium.
3. Consideration should be given to alternate alum delivery mechanisms to the lakes to better target areas of sediment phosphorus release, thereby improving phosphorus sequestration and reducing the amount of alum needed to achieve water quality improvements.



Mean total aluminium content in sediment cores from Lake Rotorua (left) and Lake Rotoehu (right). Background aluminium content in the main basin of both lakes is approximately 5 g Al kg^{-1} sediment dry weight.

Acknowledgements

I would like to thank Deniz Özkundakci and John Tyrrell for reviewing this document. Joe Butterworth and Warrick Powrie provided field support. ICP-MS analysis was conducted by Danielle Blackwell and X-ray diffraction analysis by Kirsty Vincent. Additional support and funding were provided by the Bay of Plenty Regional Council Chair in Lakes and Freshwater Science.

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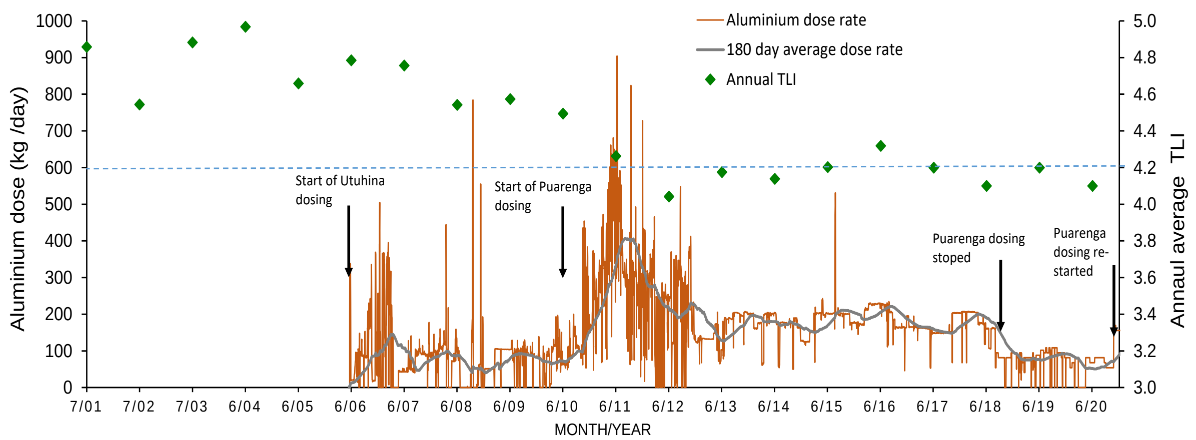
Introduction

Alum (aluminium sulphate) dosing is widely used for lake restoration and is intended to sequester dissolved phosphorus, removing it from the water column, thereby reducing primary production and improving water clarity (Cooke et al. 2005). Near continuous alum dosing of the Utuhina and Puarenga inflows to Lake Rotorua has been conducted by the Bay of Plenty Regional Council since 2006 and 2010, respectively. Dosing to the Puarenga Stream was halted from 30 September 2018 to 22 November 2020, although alum dosing of the Utuhina Stream was increased during this period to partially compensate for the shutdown. Continuous alum dosing of the Waitangi Soda stream which flows into Lake Rotoehu was initiated in 2011, however dosing was halted from 18 July 2018 to 9 December 2020 due to concerns about aquatic weed interference with alum delivery to the lake. Total daily aluminium dose rates and annual trophic lake index for lakes Rotorua and Rotoehu are presented in Figure 1. As of 9 December 2020, a total of 773 tonnes of aluminium had been dosed to Lake Rotorua and 124 tonnes to Lake Rotoehu.



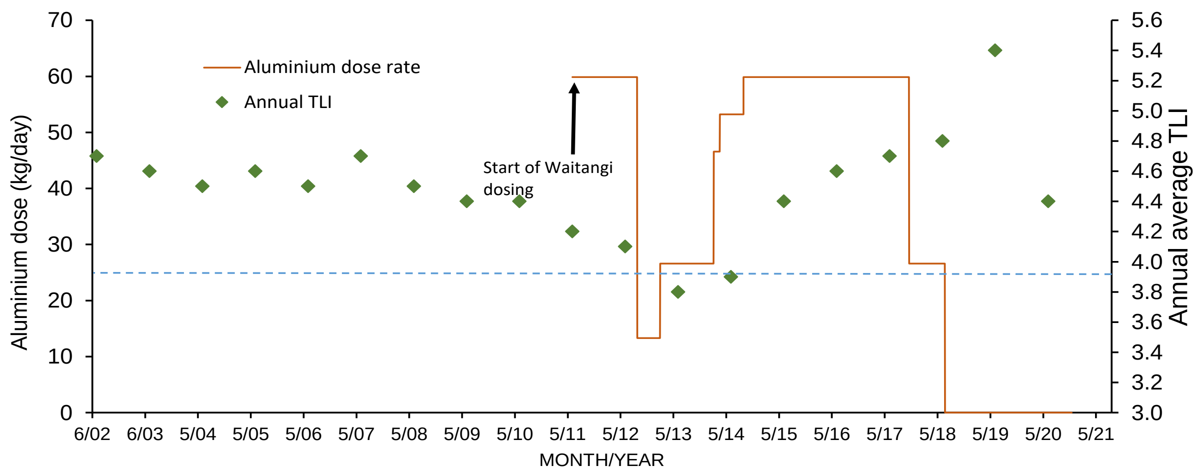


Figure 1. Daily aluminium dose rates to Lake Rotorua (top) and Lake Rotoehu (bottom) with average annual trophic lake index (TLI) from 2001 to 2020. The blue dashed lines indicate the TLI restoration target for each lake.

When added to water alum forms aluminium hydroxide ($Al(OH)_3$) which adsorbs dissolved phosphorus and coagulates suspended solids (Cooke et al. 2005). The resulting aluminium flocs may either be lost from the system through outflows or settle to the bottom sediment. In shallow lakes 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 (Egemose et al. 2013, Özkundakci et al. 2013). Once settled, flocculated $Al(OH)_3$ 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, $Al(OH)_3$ is still able to bind bioavailable phosphorus, providing the additional benefit of attenuating sediment phosphorus release under hypoxic conditions (Welch and Cooke 1999).

Previous sediment surveys of Lake Rotorua were conducted prior to (Pearson 2007), and following (Özkundakci et al. 2013, Tempero and Hamilton 2016) initiation of alum dosing of the inflows. Post-alum dosing surveys primarily focused on the main basin of Lake Rotorua, with sediment coring sites all below 10 m depth (Tempero and Hamilton 2016). Sediment surveys conducted by Özkundakci et al. (2013) and Tempero and Hamilton (2016) did not detect significant increases in surface (0–4 cm) sediment total aluminium concentrations compared to pre-alum dosing in the main basin of the lake. However, Tempero and Hamilton (2016) did report increases in the proportion of surface sediment amorphous aluminium in relation to total aluminium at core sites closest to the Utuhina and Puarenga inflows, indicating the deposition of alum floc. A follow up survey of the near-shore environment primarily at depths of 4-5 m along the southern perimeter of the lake found notable accumulations of amorphous aluminium out from the Utuhina discharge point between Kawaha Point and Motutara Point, including the deep (45 m) volcanic crater off Motutara Point (Tempero 2019). In contrast, cores taken to the east of Sulphur Bay showed little or no accumulation of aluminium. This was attributed to greater wave resuspension of particles, as this area of the lake is subject to greater wind driven wave action (Tempero 2019). Extensive beds of *Lagarosiphon major,* up to several meters in height are present in Te Ruapeka Bay to the west of Sulphur Bay (Tempero 2019). This submerged aquatic vegetation may also dampen wave resuspension of alum floc and prevent it from reaching the main basin of the lake. It was concluded that alum derived aluminium from the Utuhina and Puarenga Streams was not accumulating in the main basin of Lake Rotorua as assumed, but was either being deposited in the nearshore zone (<10 m depth) or remained in suspension and discharged from the lake (Tempero and Hamilton 2016, Tempero 2019).

A survey of sediment aluminium content in Lake Rotoehu was previously conducted by Tempero and Hamilton (2016). Significant accumulation of alum derived aluminium was found in Te Wairoa Bay, at the discharge point of the Waitangi Stream. However, no observable accumulation of aluminium was found in the main basin of Lake Rotoehu. Impedance of flow and dampening of wave resuspension by extensive *Ceratophyllum demersum* weed beds in Te Wairoa Bay likely prevented alum floc from being transported to the main lake basin (Tempero and Hamilton 2016, Eager 2017). Unlike Lake Rotorua, improvements in water quality were not observed with alum dosing of Lake Rotoehu (Figure 1) and dosing was halted from mid-2018 while the effectiveness of alum dosing was reviewed.

The geothermal Waitangi Stream is a significant source of iron and sulphur to Lake Rotoehu, with elevated concentrations in both the water column and lake sediment near the stream discharge point compared to the rest of the lake (Eager 2017). Both iron (Fe) and sulphur (S) play an important role in determining sediment phosphorus flux (Rothe et al. 2015). Under oxidic conditions iron adsorbs phosphorus within the sediments, but during hypoxic/anoxic events lake sediments proceed through the redox gradient where surface sediment $Fe(OH)_3$ is reduced to soluble ferrous iron (Fe^{2+}), releasing sorbed phosphorus (Hupfer and Lewandowski 2008). Sulphur is closely coupled to the transformations of phosphorus and iron. Free sulphide (S^{2-}) can preferentially react with Fe^{2+} over phosphorus to form insoluble iron sulphides. Simultaneously, iron(oxyhydr)oxide-P compounds may undergo reductive dissolution in the presence of free sulphide ions which leads to increased phosphorus-concentrations in the water. Therefore, the extent of sulphide production and the amount of available reactive iron crucially determines the effectiveness of iron in binding phosphorus, significantly influencing phosphorus retention in the short- and also in the long-term (Rothe et al. 2015). Comparative sediment mineral composition in Lake Rotoehu such as the relative prevalence of vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$), gibbsite ($Al(OH)_3$) and pyrite (FeS_2) by X-ray diffraction may provide insight into the effectiveness of alum dosing of the Waitangi Stream and the potential for phosphorus release under reducing conditions.

The University of Waikato was contracted by the Bay of Plenty Regional Council to conduct sediment aluminium content monitoring of Lake Rotorua and Lake Rotoehu as part of their resource consent monitoring of alum dosing. Sediment cores were taken from 15 previously sampled sites in Lake Rotorua, including the seven near-shore sites sampled by Tempero (2019). Seven cores were taken from Lake Rotoehu at the same locations as those sampled by Tempero and Hamilton (2016). Sediment cores were sectioned and analysed for total and non-crystalline aluminium content by inductively coupled plasma mass spectrometry (ICP-MS) in order to determine whether alum derived aluminium was accumulating in the nearshore environment of lakes Rotorua and Rotoehu. Where possible, sediment pore water was extracted and analysed for dissolved reactive phosphate to provide a comparative assessment of effective aluminium binding of available phosphorus.

Based on the sediment core ICP-MS elemental results, selected sediment samples from Lake Rotoehu were analysed by X-ray diffraction to determine their relative mineralogical composition. Results from this analysis will be used to provide recommendations as to the need for further investigation of this area as a potential hot-sport for phosphorus release under reducing conditions.

Methods

Site descriptions

Lake Rotorua is the largest of 12 lakes jointly managed under the Rotorua Te Arawa Lakes Programme. It has a surface area of 80.6 km^2, a mean depth of 10.8 m (maximum depth 45 m), a total water volume of 0.85 km^3 and polymictic stratification patterns (Burger et al. 2011). Lake Rotorua is currently classified as eutrophic but has experienced significant improvements water quality since the mid-2000s, with the TLI fluctuating around the target TLI of 4.2 since 2010 (Donald et al. 2018).

Lake Rotoehu is a shallow (mean depth 8.2 m), moderately sized (7.9 km^2), polymictic lake in the northeast of the Rotorua in the Te Arawa lakes district (Scholes 2009). 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, Lake Rotoehu has also experienced extensive periods of stratification and algal blooms in 2014–15 and 2015–16 along with an increase in TLI levels (Figure 1). 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 above its mean level.

Sediment survey locations

Sediment surveys for aluminium accumulation in Lake Rotorua resulting from alum dosing were previously undertaken in 2012 (Özkundakci et al. 2013) and 2016 (Tempero and Hamilton 2016). The 15 coring sites initially selected focused on the main basin of the lake, based on the assumption that alum derived aluminium was likely to accumulate in the main lake basin. However, results from both these surveys found no evidence of sediment aluminium accumulation in the main lake basin. In 2019, a follow-up survey by Tempero (2019) of seven sites was undertaken in the nearshore region, closer to the discharge points of the Utuhina and Puarenga streams and along the southeast fringe of the lake. Surface sediments (0-4 cm depth) in the wider Te Ruapeka Bay from Kawaha Point to Sulphur Bay and the 45 m deep volcanic crater off Motutara Point were found to have higher aluminium content than deeper sediments, indicating that alum floc was primarily accumulating in the nearshore environment. As a result of these findings, coring locations were altered from previous surveys with the seven nearshore sites (Ra1–7) again surveyed and the number of main basin core locations (Ra8–15) reduced from 15 to eight (Figure 2). Coordinate locations and water depth of sediment coring sites in Lake Rotorua are provided in Appendix 1.

Seven sediment cores were taken from Lake Rotoehu on 9 December 2020 at the same locations sampled by Tempero and Hamilton (2016) (Figure 3). 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 Wairoa Bay, out to the most dispersed location in the main basin. Coordinate locations of the Lake Rotoehu cores are presented in Appendix 2.

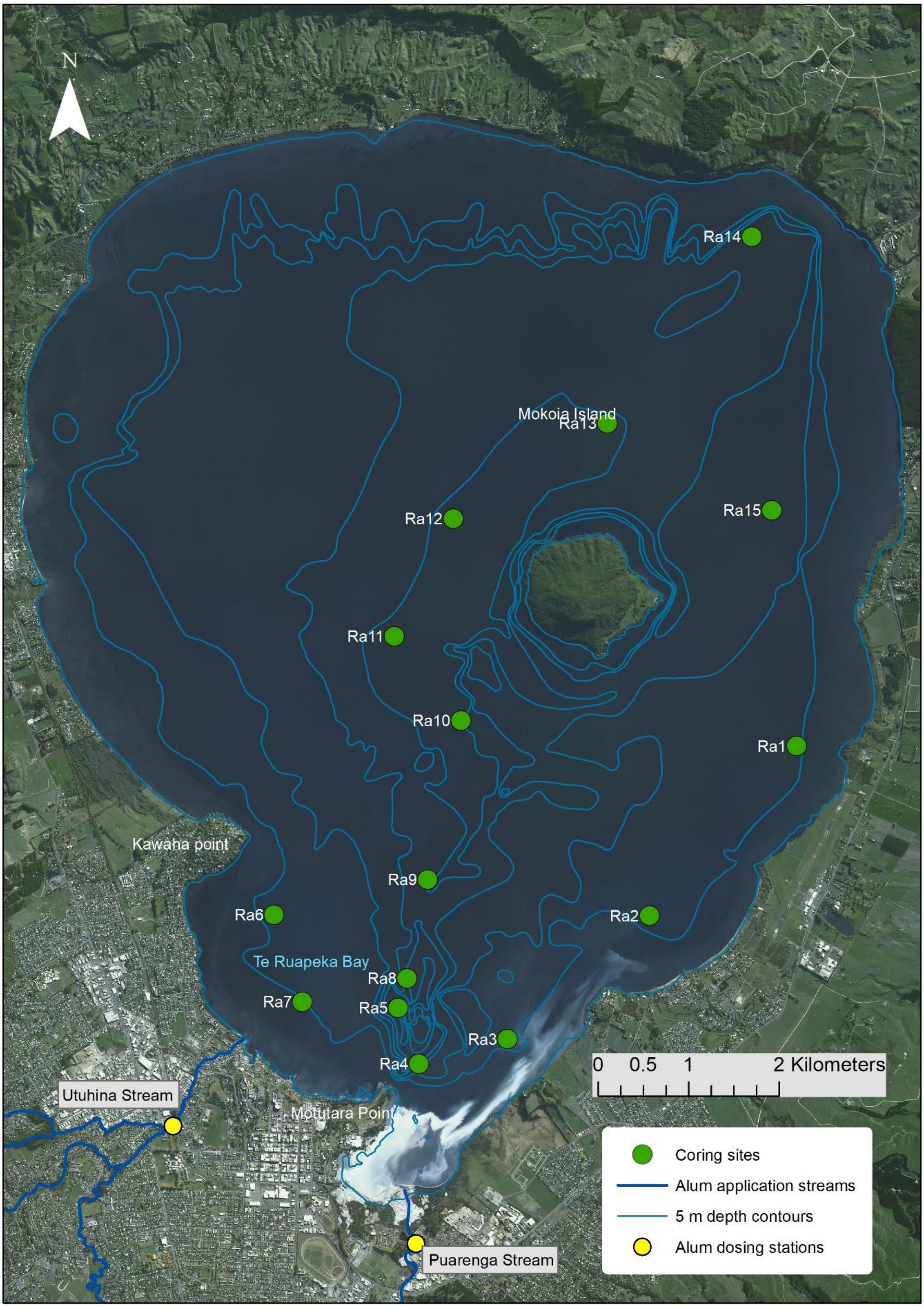


Figure 2. Locations of sediment cores (Ra1–15) taken from Lake Rotorua on 7-8 December 2020.

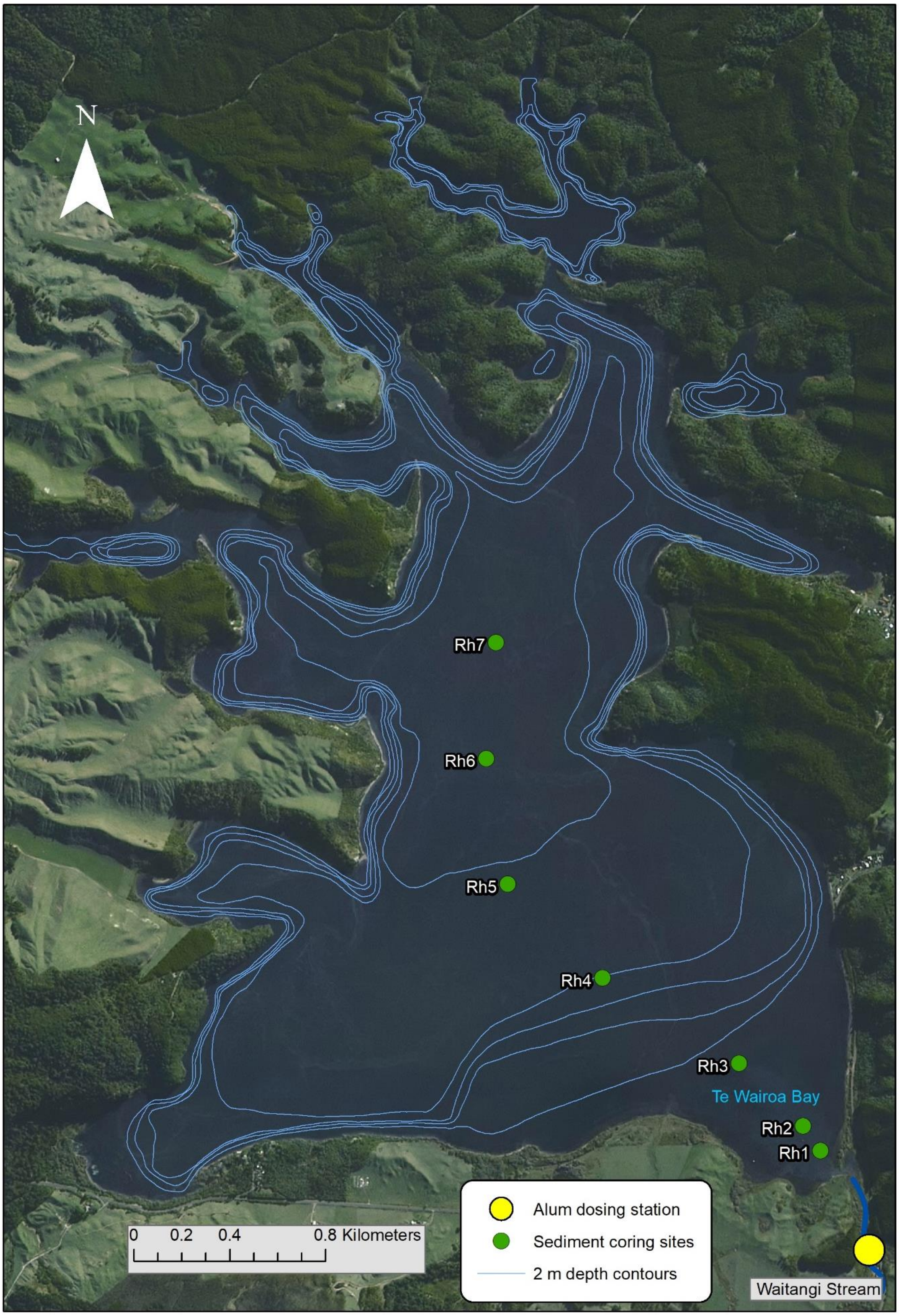


Figure 3. Lake Rotoehu sediment core sites (Rh1–7) sampled on 9 December 2020.

Sediment core retrieval and processing

Following (Özkundakci et al. 2013) and Tempero and Hamilton (2016) sediment cores were collected using a gravity corer (Pylonex HTH 70 mm) with a 60 x 600 mm Perspex (Plexiglas) core barrel to capture undisturbed sediments. 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 Lake Rotorua coring sites Ra1, Ra2, Ra3, Ra6 and Ra7, the sediment composition was primarily coarse gravel and sand, as well as dense beds of *L. major* at sites Ra6 and Ra7 precluding the retrieval of intact cores. A modified technique was employed, whereby the corer barrel was pushed into the sediment and then retrieved by a scuba diver.

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 10 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. Due to the low pore-water extraction volumes from the coarse sediment, samples were pooled into three depth groupings 1–4 cm, 6–12 cm and 14–20 cm. Water nutrient concentrations were analysed using a Flow Injection Analyser 8500 Series II (FIA+ 8000 Series, Zellweger Analytics, Inc. Hach). Dissolved reactive phosphate (PO_4) was analysed using LACHAT QuickChem method 31-115-01-1-H with a detection limit of 0.004 mg P L^{-1}.

The centrifuged sediment was then dried at 60°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 (0.1 g) were left to pre-digest overnight at room temperature following the addition of 1 mL conc. HNO_3 and 0.33 mL conc. HCl. Samples were then digested at 80°C for 1 hr in a circulating water bath followed by the addition of 50 mL ultrapure water. Digested samples were then centrifuged and 15 mL of the supernatant filtered using 0.2 µm cellulose acetate filters (Satorius, Germany). The sample and control blank digests were then analysed for phosphorus and aluminium content using inductively coupled plasma mass spectrometry (ICP-MS model Agilent 8900 with a triple-quadrupole).

Sediment non-crystalline aluminium content was determined by ammonium oxalate digestion following the 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 0.2 µm cellulose acetate filters and aluminium content determined by ICP-MS.

X-ray diffraction

Based on Lake Rotoehu sediment iron, phosphorus, manganese and sulphur concentrations provided by ICP-MS analysis, 18 ground sediment samples were selected for X-ray diffraction analysis. Analysis was carried out using a Panalytical Empyrean Series 2 XRD in the School of Science, University of Waikato. Powdered samples were run from 5-80 °2θ, at 50 seconds per step.

Results

Lake Rotorua

CTD profiles

Conductivity, Temperature, Depth (CTD) profiles were measured at the same time cores were sampled. Core sites Ra1–8 were sampled on 7 December and core sites Ra9–15 on 8 December. There was little variation in temperature (<0.5°C) and dissolved oxygen (<5% saturation) between surface and bottom waters across all sites, although temperature and dissolved oxygen did increase throughout the day. Representative temperature and dissolved oxygen profiles from the deepest sites are presented in Figure 4.

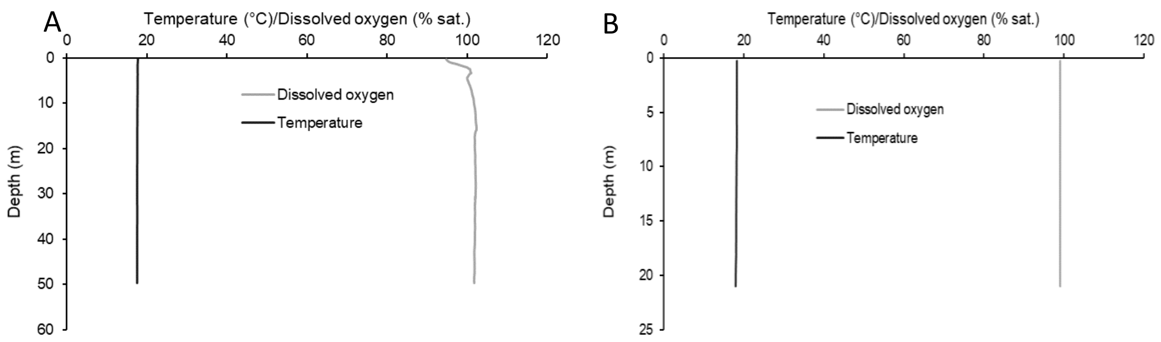


Figure 4. Representative temperature (°C) and dissolved oxygen (% saturation) vertical profiles for Lake Rotorua taken at the deepest core sites on, (A) site Ra5 sampled on 7 December 2020 and, (B) site Ra12 sampled on 8 December 2020.

Core composition

Visual inspection of the sediment cores revealed no evidence of aluminium floc at the sediment-water interface and no distinguishing tephra layers that could be used for dating. At sites Ra1–3 sites, the top 6–10 cm of sediment was composed primarily of coarse sand and gravel transitioning to finer sand and silt below 12 cm depth. Cores from sites Ra3, Ra6 and Ra7 also contained small fragments of vegetative material, likely derived from the *L. major* beds in these areas. The deeper cores from the rest of the lake were composed of silt and clay particles and were free from vegetation.

Sediment aluminium content

Sediment total aluminium content exhibited distinct distribution profiles in relation to geographic location, although there was little variation between sampling periods. Cores taken from the deeper crater sites (Sites Ra4, Ra5 and Ra8) off Motutara Point had notably higher mean total aluminium content (~ 8 g Al kg^{-1} dry weight) than cores taken to the east of

Sulphur Bay (sites Ra1–3) (~1.7 g Al kg^{-1} dry weight)[1]), while sites within the main basin (Ra9–15) fell somewhere in between for mean sediment aluminium content (~5.4 g Al kg^{-1} dry weight) (Figure 5).

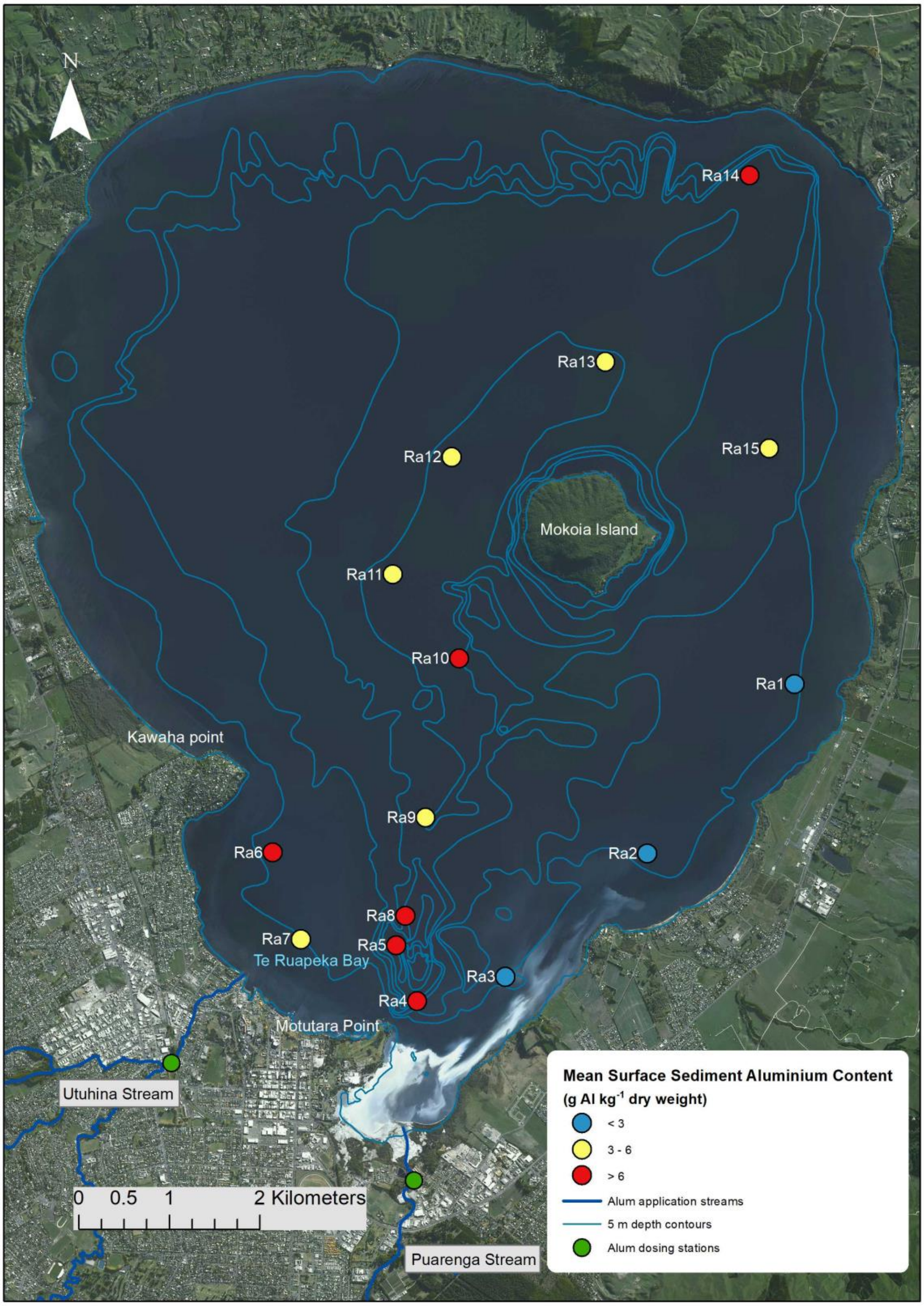


Figure 5. Geographic distribution of mean sediment core total aluminium content for Lake Rotorua, December 2020.

Core sites Ra1–3 showed little difference in total and amorphous aluminium content between May 2019 and December 2020 (Figure 6). In contrast, mean core total aluminium content was slightly reduced at sites Ra4 (2019, 8.1 g Al kg^{-1} cf. 2020, 7.1 g Al kg^{-1}) and Ra5 (2019, 10.0 g Al kg^{-1} cf. 2020, 8.2 g Al kg^{-1}) compared to 2019 (Figure 7), although the proportion of amorphous aluminium was somewhat elevated throughout the core profiles. Cores from sites Ra6 and Ra7, located near the Utuhina Stream inflow, had notably higher mean total aluminium in near surface sediment (0–4 cm depth, Ra6 6.8 g Al kg^{-1}, Ra7 5.8 g Al kg^{-1}) compared to deeper in the sediment profile (12–20 cm, Ra6 2.9 g Al kg^{-1}, Ra7 2.7 g Al kg^{-1}), this difference between surface and deep sediment aluminium was particular evident at site Ra7. Both, total aluminium and amorphous aluminium content was similar between 2019 and 2020 at sites Ra6 and Ra7 (Figure 7).

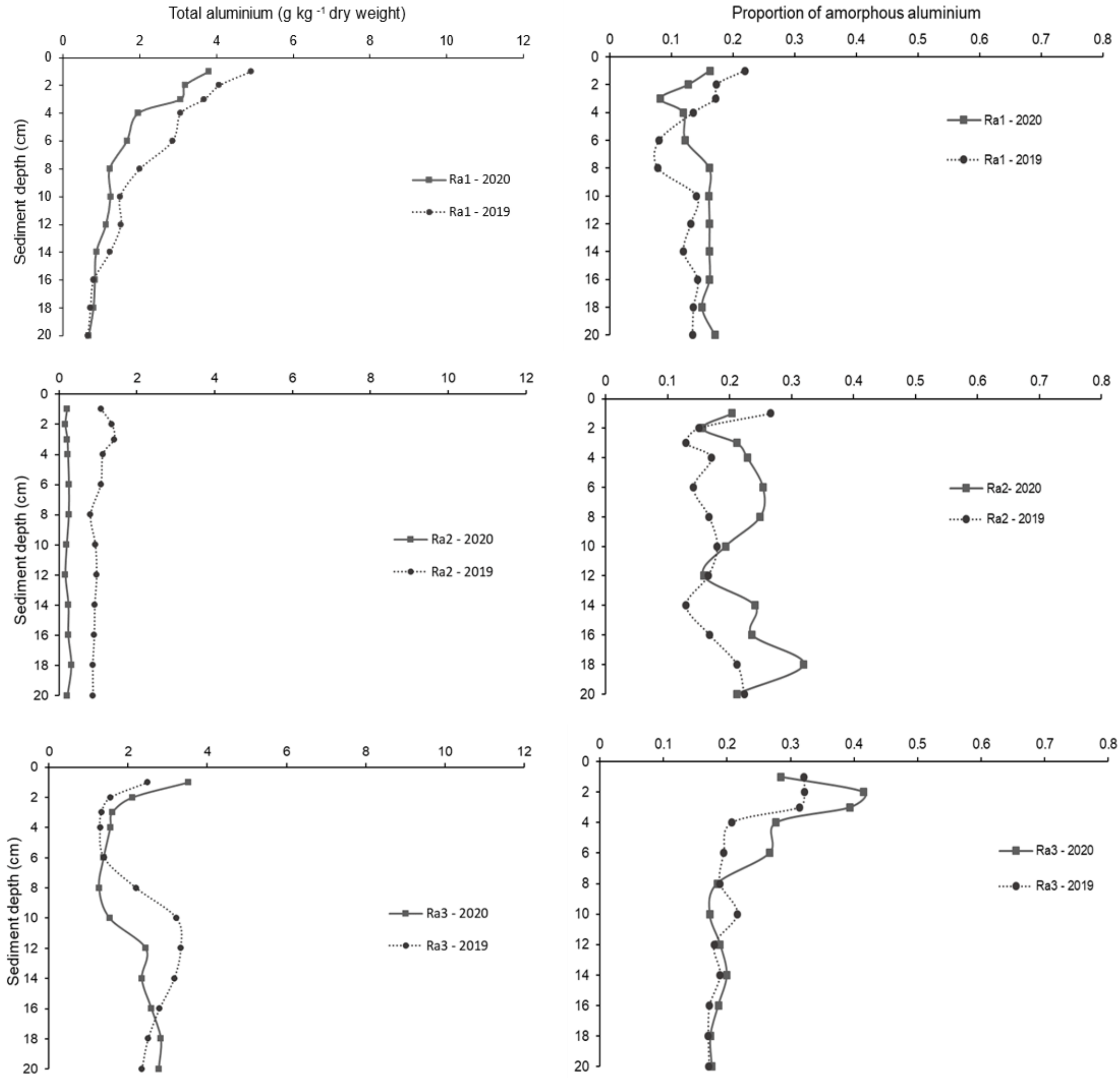


Figure 6. Vertical profiles of sediment total aluminium content (left) and proportion of amorphous (non-crystalline) aluminium at Lake Rotorua sites Ra1, Ra2 and Ra3 from December 2020 with comparisons to 2019 survey data from Tempero (2019).

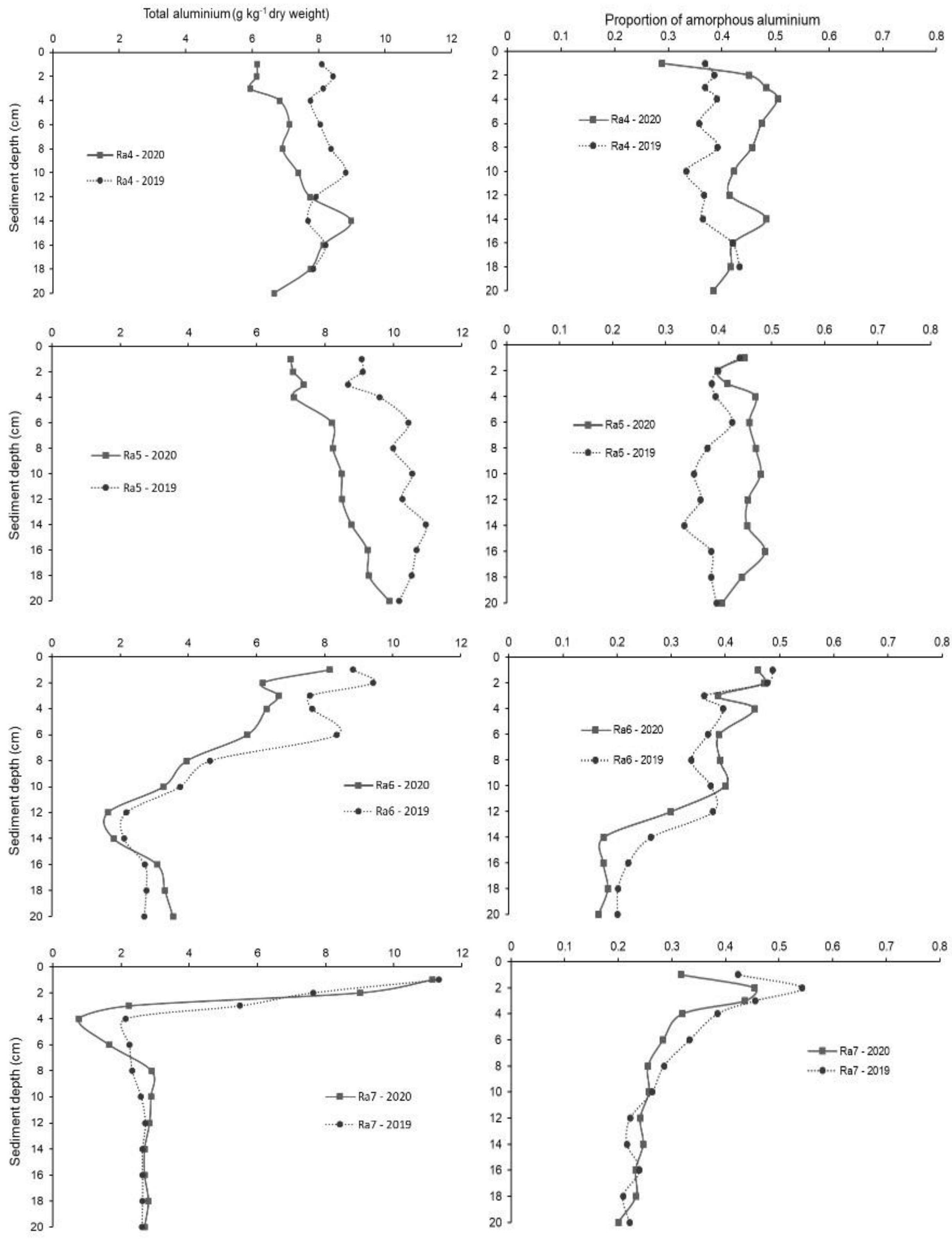


Figure 7. Vertical profiles of sediment total aluminium content (left) and proportion of amorphous (non-crystalline) aluminium at Lake Rotorua sites Ra4, Ra5, Ra6 and Ra7 from December 2020 with comparisons to 2019 survey data from Tempero (2019).

Towards the main basin of Lake Rotorua (sites Ra8, Ra9, Ra10 and Ra11) vertical sediment profiles of total aluminium and amorphous aluminium exhibited a similar pattern to that of previous surveys, with total aluminium declining with increasing distance to the Utuhina and Puarenga inflows (Figure 8). Proportions of amorphous aluminium were similar to 2016 levels at sites Ra9, Ra10 and Ra11, however, amorphous aluminium levels were notably lower but more uniform in 2020 compared to 2015 at site Ra8. Site Ra8 was also unusual in that total aluminium content increased with increasing sediment depth compared to the lower, but more uniform concentrations at the site in 2016 (Figure 8).

To the north of Mokoia Island the sediment cores (sites Ra12, Ra13, Ra 14 and Ra 15) showed very little variation in aluminium content, with mean sediment total aluminium content broadly similar between sites Ra9 to Ra 15 ranging from 4.8 to 5.8 g Al kg^{-1} dry weight sediment (Figure 5). There was also little variation between survey years or in the proportion of amorphous aluminium, although there is some decline in amorphous aluminium with increasing sediment depth (Figure 9).

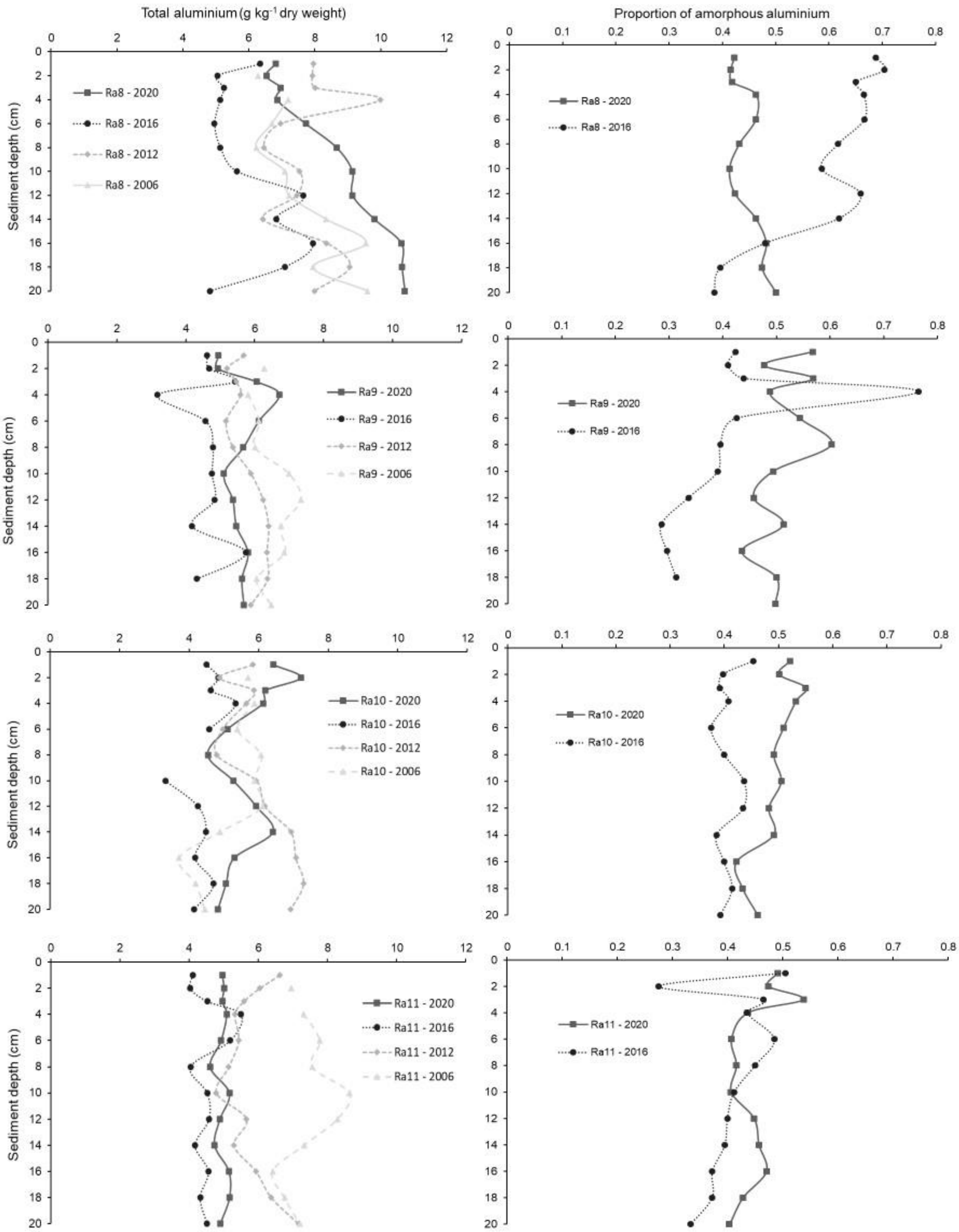


Figure 8. Vertical profiles of sediment total aluminium content (left) and proportion of amorphous (non-crystalline) aluminium at Lake Rotorua sites Ra8, Ra9, Ra10 and Ra11 from December 2020 with comparisons to survey data from Tempero (2019), Tempero and Hamilton (2015), Özkundakci et al. 2013 and Pearson (2006).

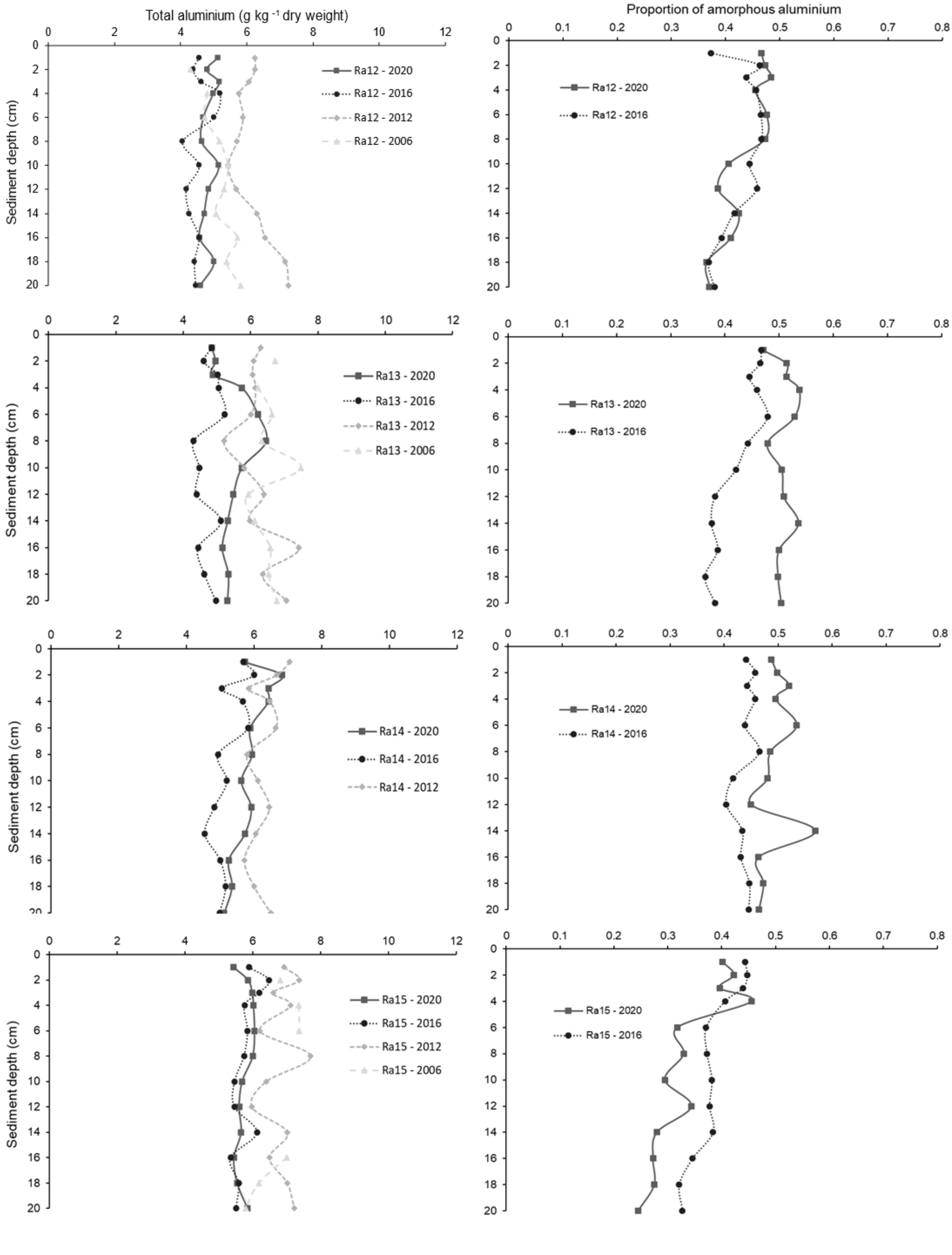


Figure 9. Vertical profiles of sediment total aluminium content (left) and proportion of amorphous (non-crystalline) aluminium at Lake Rotorua sites Ra12, Ra13, Ra14 and Ra15 from December 2020 with comparisons to survey data from Tempero (2019), Tempero and Hamilton (2015), Özkundakci et al. 2013 and Pearson (2006). Note: site Ra14 was not sampled by Pearson (2006).

Sediment phosphorus content

Generally, phosphorus content was highest in the surface sediment (0-4 cm depth), declining slightly with increasing sediment depth (Figure10). Total phosphorus content was lower in the shallow (<5 m depth) sites compared to the deeper sites of the volcanic crater and the main basin of the lake, although there was little variation in concentrations within near-shore and main basin sites.

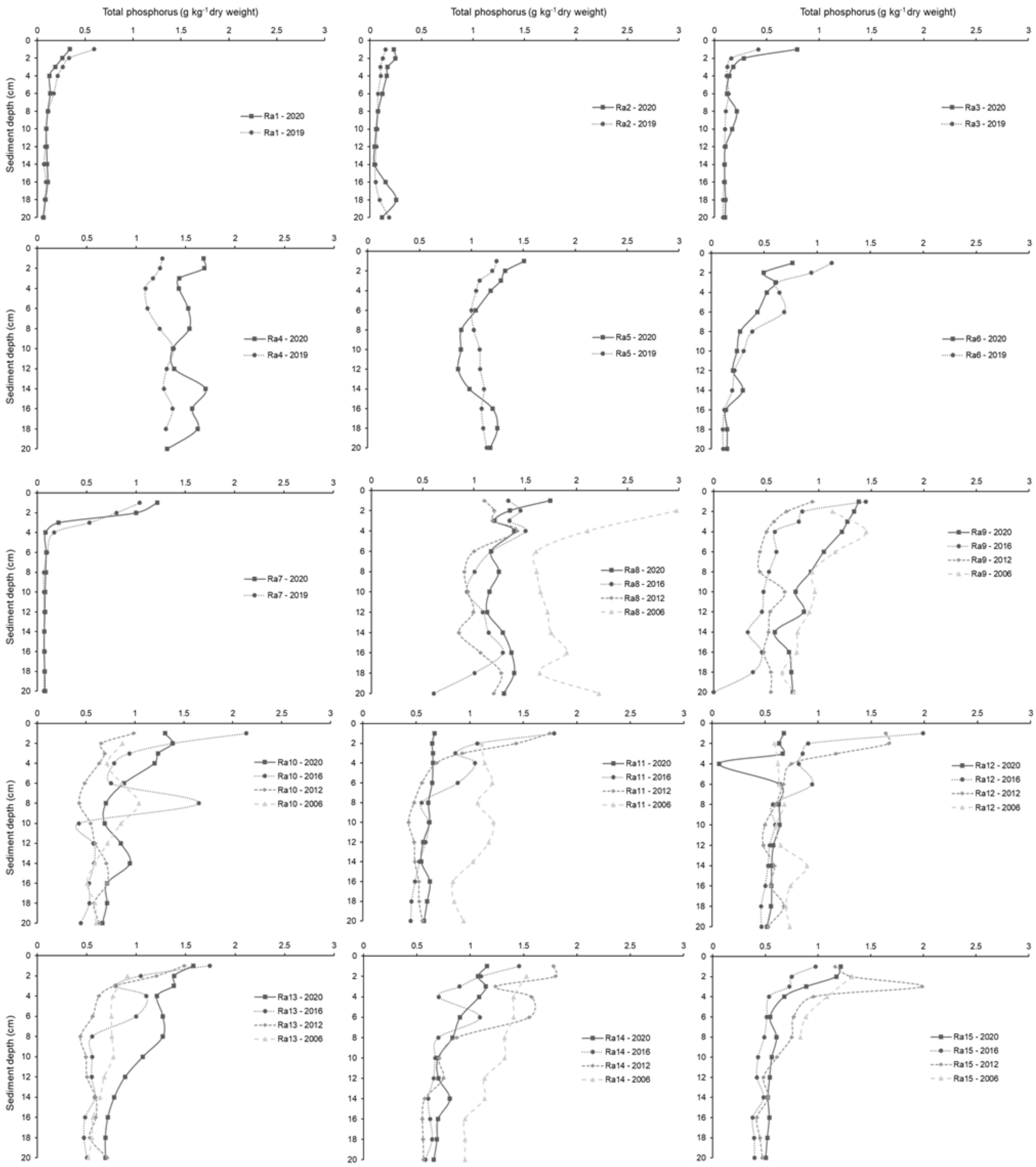


Figure 10. Vertical profiles of sediment total phosphorus from December 2020 with comparisons to survey data from Tempero (2019), Tempero and Hamilton (2016), Özkundakci et al. 2013 and Pearson (2006).

Due to the coarse grain size of the sediment at the near-shore sites it was necessary to pool sediment pore water to obtain sufficient volumes for analysis. Samples were pooled into either sediment surface (0–4 cm), sub-surface (5–12 cm) and deep (13–20 cm) zones at each site before analysis. Dissolved reactive phosphate (DRP) concentrations for each depth zone are compared to surveys from August 2012 and February 2016 (Figure 11). It is plausible that DRP concentrations are related to water depth and time of year rather than sediment aluminium concentration.

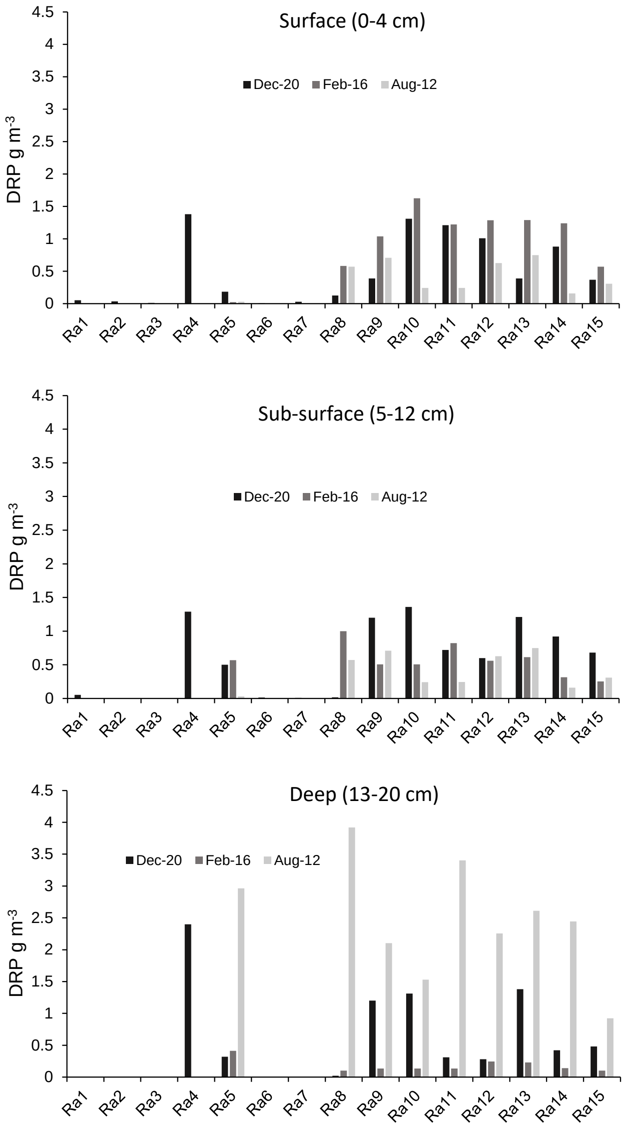


Figure 11. Sediment pore water dissolved reactive phosphate (DRP) concentrations from sediment cores taken from Lake Rotorua, December 2020. Pore water was pooled in three zones based on sediment depth surface (0–4 cm), sub-surface (5–12 cm) and deep (13–20 cm). Comparisons to concentrations from February 2016 (Tempero and Hamilton 2016) and August 2012 (Özkundakci et al. 2013) are also provided.

Lake Rotoehu

CTD profiles

CTD profiles were conducted at each sediment coring site on 9 December 2020. There was no evidence for lake stratification, however, water temperature was approximately 2.5°C warmer at the inflow site of the geothermal Waitangi Stream (sites Rh1 and Rh2) compared to the main lake basin (Rh7). CTD profiles of temperature and dissolved oxygen for sites Rh1 and Rh7 are presented as representative profiles for the lake (Figure 12).

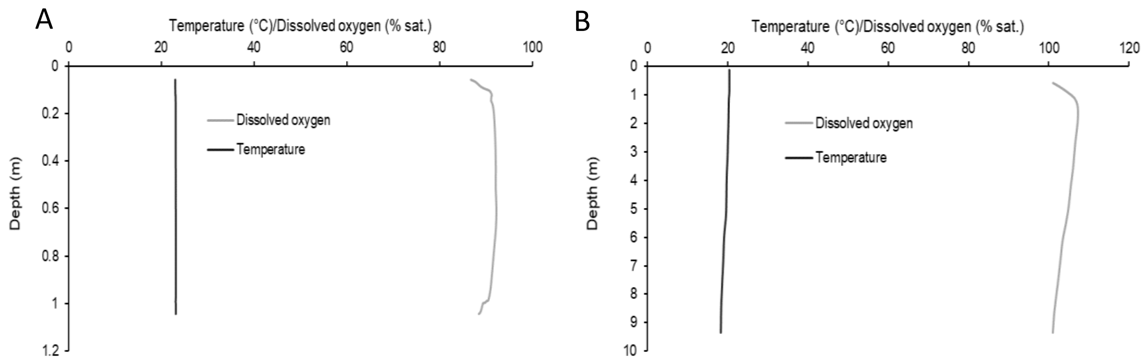


Figure 12. Representative temperature (°C) and dissolved oxygen (% saturation) vertical profiles for Lake Rotoehu taken at (A) Site Rh1, the inflow site of the geothermal Waitangi Stream and, (B) Site Ra7 within the main basin of Lake Rotoehu, 9 December 2020.

Core composition

The lake level of Lake Rotoehu was approximately 1 m higher in December 2020 compared to the previous sediment survey conducted in February 2016. The beds of *Ceratophyllum demersum* in Te Wairoa Bay were largely submerged and the formerly widespread area of raupō (*Typha orientalis*) near the Waitangi Stream discharge point had died out. Surface sediment from core sites Rh1 and Rh2 was finer and infiltrated with root material from raupō compared to the cores taken in 2016 that were sandier in composition. However, deeper sections of the cores were of a similar composition to those observed in 2016. The remaining cores were composed of fine silt and occasional sand particles which was similar to the cores sampled in 2016.

Sediment aluminium content

Mean sediment core total aluminium content in Lake Rotoehu was notably higher at sites Rh1 an Rh2 (13.2 and 13.6 g Al kg^{-1} dry weight, respectively) compared to the other Rotoehu sites (Rh3–7; range 3.3–5.4 g Al kg^{-1} dry weight) (Figure 13). Site Rh3 had the lowest mean aluminium content (3.3 g Al kg^{-1} dry weight) despite being in comparatively close proximity to the discharge point of the Waitangi Stream.

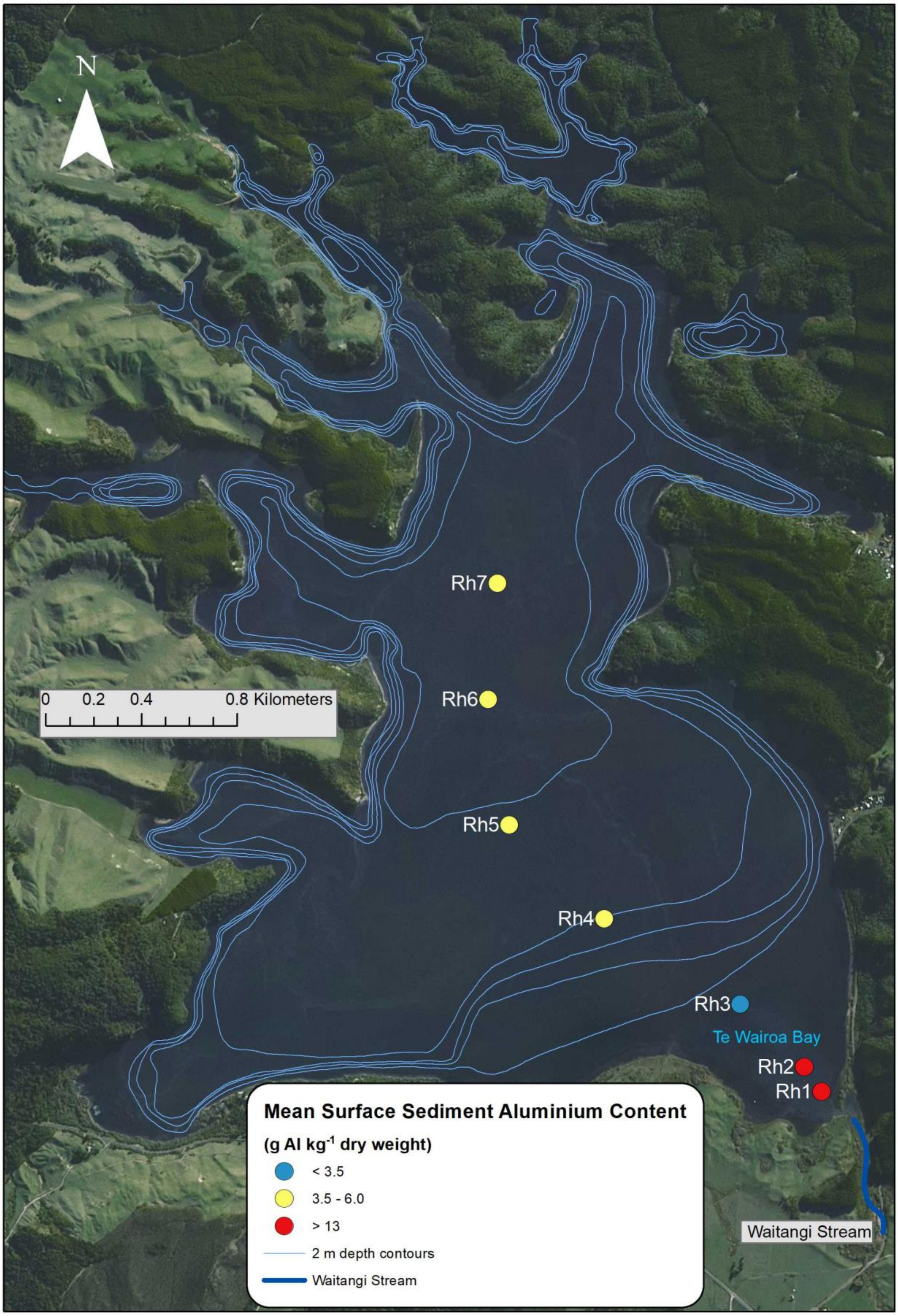


Figure 13. Geographic distribution of mean sediment core total aluminium content for Lake Rotoehu, December 2020.

Distinct changes in the proportions of amorphous aluminium were apparent between the 2020 and 2016 core samples at sites Rh1–3 with a lower proportion of amorphous aluminium in the 2020 cores compared to the 2016 cores. However, sediment total aluminium content was largely similar between surveys across all three sites, although surface sediment total aluminium is lower at sites Rh1 and Rh2 compared to 2016 levels (Figure 14).

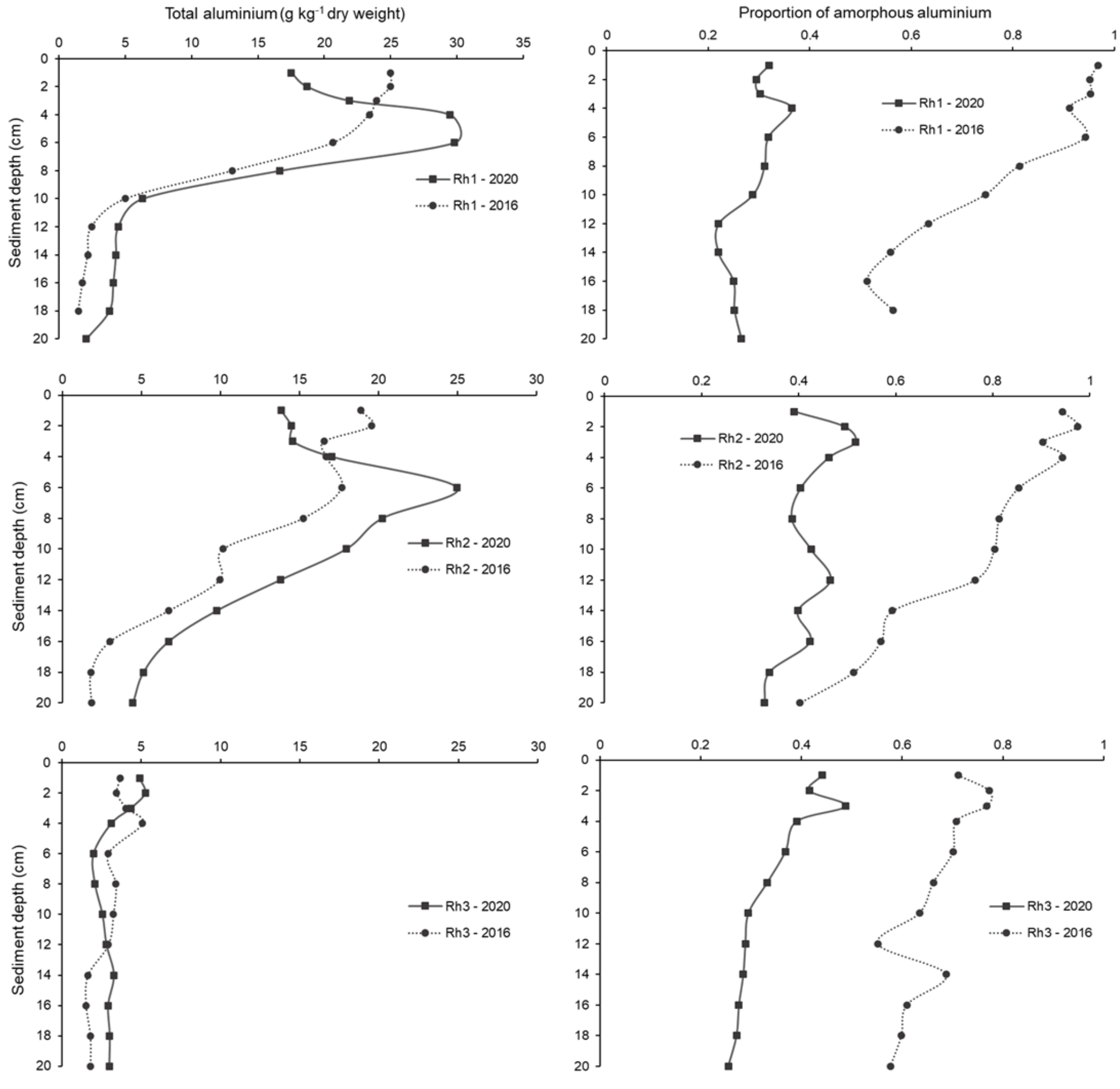


Figure 14. Vertical profiles of sediment total aluminium content (left) and proportion of amorphous (non-crystalline) aluminium from Lake Rotoehu sites Rh1, Rh2 and Rh3 from December 2020 with comparisons to 2016 survey data from Tempero and Hamilton (2016).

Decreases in amorphous aluminium were also present in sediment cores Rh4–7, although to a lesser degree than those observed in Te Wairoa Bay. Sediment total aluminium content was relatively unchanged between the 2016 and 2020 surveys (Figure 15).

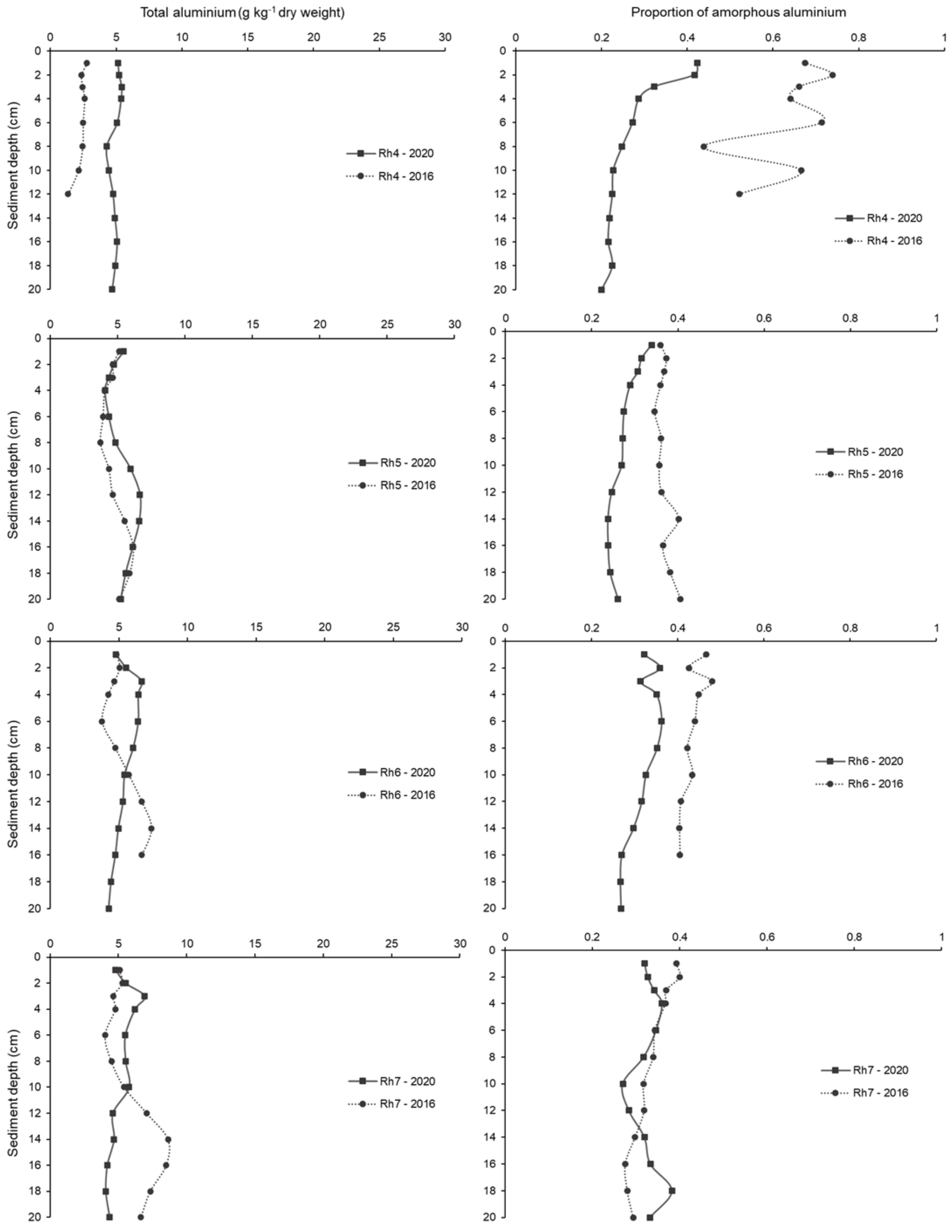


Figure 15. Vertical profiles of sediment total aluminium content (left) and proportion of amorphous (non-crystalline) aluminium from Lake Rotoehu sites Rh4, Rh5, Rh6 and Rh7 from December 2020 with comparisons to 2016 survey data from Tempero and Hamilton (2016).

Sediment phosphorus content

Lake Rotoehu sediment total phosphorus content was highly variable across the sediment sampling sites (Figure 16). Surface sediment total phosphorus content at site Rh1 at the mouth of the Waitangi Stream was significantly higher than the rest of the coring sties with phosphorus content increasing from 3.9 to 24.6 g kg^{-1} with increasing sediment depth. Such changes were not observed at the remaining survey sites, but phosphorus content was higher in the 2020 sediment profiles compared to the 2016 profiles, particularly in the surface sediments of sites Rh4–7.

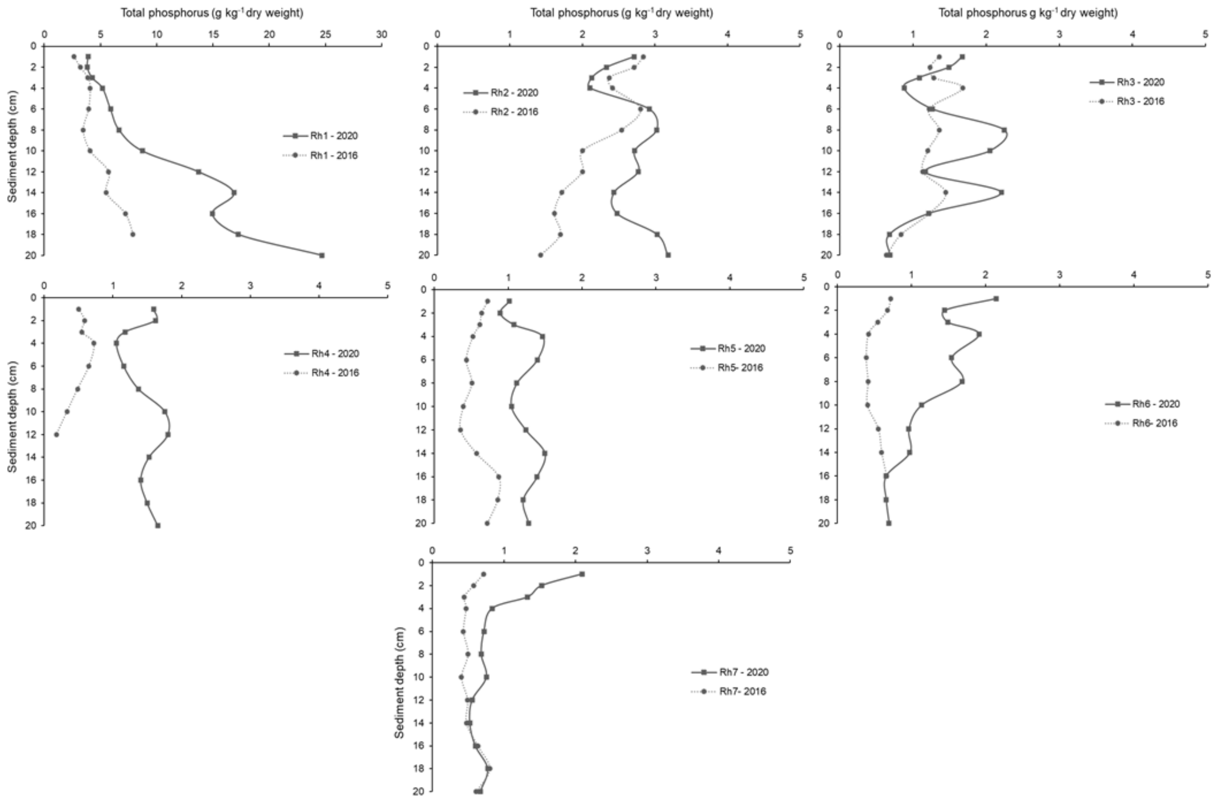


Figure 16. Vertical profiles of Lake Rotoehu sediment total phosphorus from December 2020 with comparisons to survey data from Tempero and Hamilton (2016).

Sediment pore water DRP concentrations varied with water and sediment depth ranging from just above detection limits (i.e., <0.004 g m^{-3}) at sites Rh1–3, to >0.4 g m^{-3} in the surface sediment pore water at site Rh6 (Figure 17). The 2020 DRP pore water concentrations at sites Rh1–3 were slightly elevated compared to the 2016 concentrations although still just above the detection limit. DRP concentrations decreased with increasing sediment depth but increased with water depth in both survey periods. Site Rh6 was the only 2020 core with notably elevated DRP concentrations in the surface sediment compared to 2016.

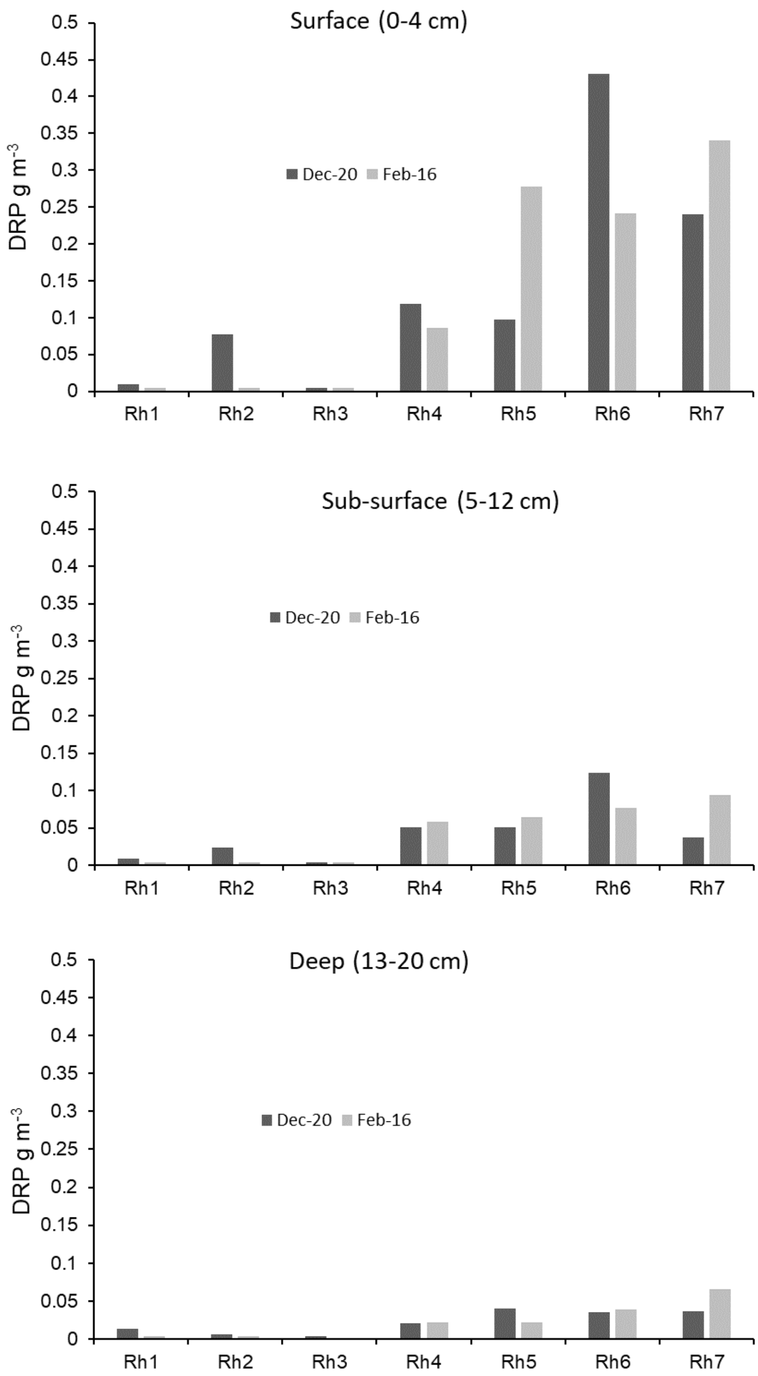


Figure 17. Sediment pore water dissolved reactive phosphate (DRP) concentrations from sediment cores taken from Lake Rotoehu, December 2020. Pore-water was pooled in three zones based on sediment depth surface (0–4 cm), sub-surface (5–12 cm) and deep (13–20 cm). Comparisons to concentrations from February 2016 (Tempero and Hamilton 2016) are also displayed.

Sediment mineral composition

Based on ICP-MS analysis of iron, manganese and sulphur in the sediment samples from Lake Rotoehu, 18 sub-samples were selected for analysis by X-ray diffraction to determine mineral content. Both iron and sulphur were comparatively abundant at sites Rh1 and Rh2, with elevated levels of manganese at 8-10 cm depth at sites Rh2 and Rh3 (see Appendix 3). Pyrite was the only mineral detected at site Rh1 at 16 cm depth (Figure 18). Amorphous (non-crystalline) mineral content was too high in the remaining samples, which obscured detection of targeted minerals by X-ray diffraction (Appendix 4).

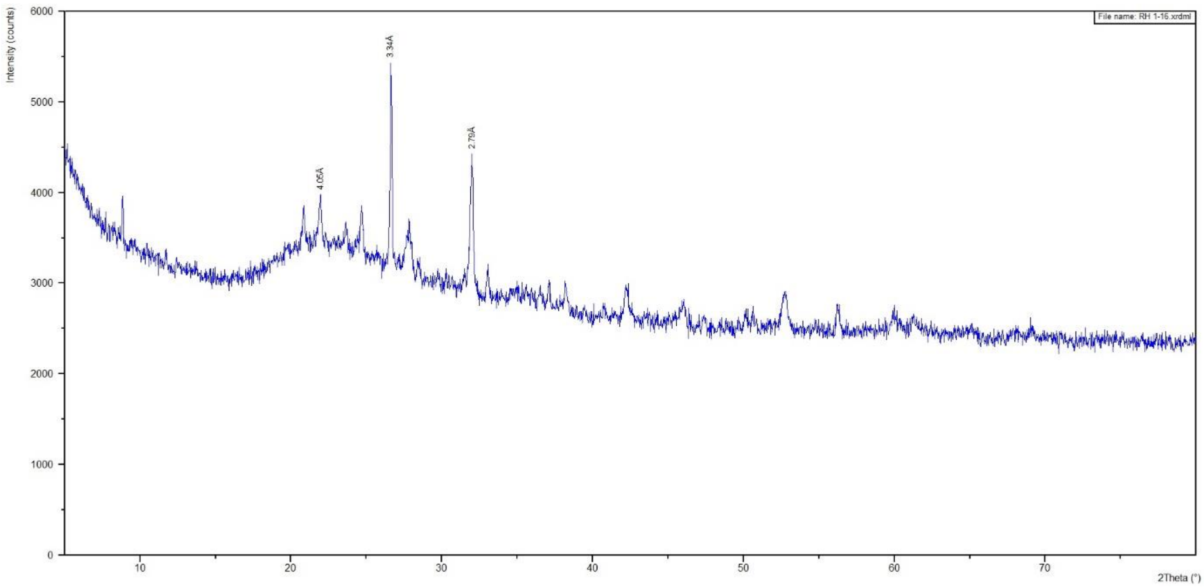


Figure 18. X-ray diffraction analysis of sediment sub-sample from Lake Rotoehu site Rh1 at 16 cm depth was able to distinguish the presence of pyrite.

Discussion

Alum dosing of the Utuhina and Puarenga inflows to Lake Rotorua has resulted in the addition of 773 tonnes of aluminium to Lake Rotorua since 2006. Previous sediment surveys of Lake Rotorua by Özkundakci et al. (2013) and Tempero and Hamilton (2016) as well as a near-shore survey by Tempero (2019) found little evidence for accumulation of aluminium in the main basin of the lake. Elevated levels of aluminium were present in the deep volcanic crater north of Sulphur Bay and in the surface sediments of Te Ruapeka Bay, near the discharge point of the Utuhina Stream. Similarly, a survey of Lake Rotoehu by Tempero and Hamilton (2016) found significant accumulation of aluminium in Te Wairoa Bay near the discharge of the Waitangi Stream, but little evidence for aluminium accumulation above background levels in the remainder of the lake. In December 2020 the University of Waikato was contracted by the Bay of Plenty Regional Council to conduct on-going monitoring of Lake Rotorua and Lake Rotoehu to determine sediment aluminium and phosphorus concentrations. Comparative sediment total aluminium concentrations and amorphous aluminium were determined by ICP-MS and compared to data from previous surveys.

Comparisons between the current and previous sediment surveys found no evidence for aluminium accumulation in the main basin of Lake Rotorua. Sediment background total aluminium content ranged between 5–6 g Al kg^{-1} sediment both within and between the main basin sites (Ra9–15), with no apparent trend to increasing aluminium content over time. Similarly, amorphous aluminium was not abundant in the surface sediments of the main basin sites with relatively minor decreases in abundance with sediment increasing depth, indicating that aluminium is not accumulating in the main basin of Lake Rotorua beyond the natural background rate.

The near-shore survey sites to the east (Ra1–3) and west (Ra6–7) of Sulphur Bay showed no change in aluminium content between the 2019 and 2020 surveys. The sediment to the east of Sulphur Bay was composed of sand and gravel sized particles to a depth of about 12 cm and contained the lowest levels of both total and amorphous aluminium. Alum floc discharged from the Utuhina Stream and Sulphur Bay does not accumulate in this area due to the shallow depth (<10 m) frequent wind-driven wave resuspension. In contrast, Te Ruapeka Bay to the west of Sulphur Bay is more sheltered from wind fetch along with extensive beds of *L. major* also providing increased protection from wave resuspension (Gibbs et al. 2016). However, given that aluminium concentrations were only elevated in the surface sediment it is likely that resuspension of alum floc occurs intermittently, likely during large storm events when northerly winds predominate. Further investigation would be required to determine the proportion of alum derived aluminium discharged from the lake due to wave resuspension.

The primary area of aluminium accumulation in Lake Rotorua appears to be the deep crater area north of Motutara Point. Sites Ra4, Ra5 and Ra8 contained considerably elevated sediment aluminium in comparison to other Lake Rotorua monitoring sites (Figure 5). The crater sites also feature distinctive differences in total aluminium content within the vertical profiles, with aluminium content increasing with depth (see Figures 7 & 8). In addition, the proportion of amorphous aluminium is notably lower at site Ra8 in 2020 compared to 2016, suggesting that less alum floc has been accumulating in this area in the past four years. In contrast amorphous aluminium has become abundant at sites Ra4 and Ra5 which are closer to the Puarenga and Utuhina inflows sites.

Lake Rotorua sediment phosphorus content largely followed the same vertical distribution patterns as the aluminium profiles at each coring site. Coring sites from deeper in the lake had higher mean phosphorus content, although these sites display a greater degree of variability both between sites and survey years, particularly in the surface sediments (e.g., see Figure 10 sites Ra10–12). This may be due to differences in the time of year the sediment surveys were conducted and associated environmental conditions (e.g., hypolimnetic oxygen status). This is reflected in the sediment pore water concentrations with DRP highest in the surface sediment and lowest in the bottom sediment during the summer (February) while the inverse occurs in the winter (August). This suggests that in the main lake basin, sediment release of DRP exceeds the adsorption capacity of any deposited alum floc, however, further investigation would be required to quantify the amount of P loading.

Alum dosing of the Lake Rotoehu inflow was halted from 18 July 2018 to 9 December 2020. This is reflected in the large decreases (~5 g Al kg^{-1}) in both total and amorphous aluminium in the surface sediments at sites Rh1 and Rh2 (Figure 14) compared to 2016. Mean sediment total aluminium content at these sites remains higher compared to the other Lake Rotoehu monitoring sites, indicating that alum floc primarily accumulated in Te Wairoa Bay close to the discharge point of the Waitangi Stream. The proportion of amorphous aluminium at sites Rh1 and Rh2 had also declined markedly, presumably as the aluminium hydroxide floc aged and mineralised to form gibbsite over the two-year halt in alum dosing. Total aluminium content was similar within sites Rh3–7 with no apparent increase between the 2016 and 2020 sampling periods. Background total aluminium content was similar to the main basin of Lake Rotorua at approximately 5 g Al kg^{-1} sediment. As with sites Rh1 and Rh2 amorphous aluminium content had declined but apart from site Rh4 this change was relatively minor.

Sediment total phosphorus content was highly variable across the Rotoehu coring sites, with the highest phosphorus content at sites Rh1 and Rh2. This is likely due to adsorption and then sedimentation of alum dosed to the Waitangi Stream. Phosphorus content declines across sites Rh3–5, but increases again in the surface sediments at sites Rh6 and Rh7 in the main basin of the lake (Figure 16). Lake Rotoehu is primarily groundwater fed with few surface inflows, of which, the Waitangi Stream is the most significant (Scholes 2009). However, the total phosphorus load from this inflow is ~2 kg day^{-1} of which ~0.75 kg day^{-1} is DRP (Dare, unpublished data), this constitutes a relatively minor proportion of phosphorus to the lake (McBride, unpublished data). In addition, lake productivity increased between the 2016 to 2020 period, with significant algal blooms over the 2018-19 summer. The increase in total phosphorus at sites Rh6 and Rh7 may be primarily due to accumulation of seston originating from resuspended littoral material and sedimented organic material from algal blooms, rather than the small increase in external phosphorus loading due to discontinuation of alum dosing.

Inductively coupled plasma mass spectrometry analysis of sediment from Lake Rotoehu confirmed the elevated levels of iron and sulphur at sites Rh1 and Rh2 reported by Eager (2017). Elevated iron (Fe) within the sediment increases the potential for phosphorus binding which would assist sequestering of phosphorus within the wider Te Wairoa Bay. However, free sulphide (S^{2-}) can preferentially react with Fe^{2+} over phosphorus to form insoluble iron sulphides and inhibit phosphorus removal. It was intended that X-ray diffraction analysis of selected sediment sub-samples would provide insight into the mineralogical composition of the sediments in Te Wairoa Bay. This would provide indications as to the relative efficacy of aluminium binding of phosphorus and how it might be influenced by iron-sulphur dynamics.

The background sediment aluminium content for Lake Rotorua is approximately 5 g kg^{-1}. From the current sediment survey and previous surveys of Lake Rotorua the main depositional zones of alum derived aluminium are the surface sediments of Te Ruapeka Bay which can reach 12 g Al kg^{-1} and the crater north of Motutara Point at ~8 g Al kg^{-1}. The sediment accumulation rate for the Motutara Point crater appears to be greater than either the mean lake sedimentation 0.3 cm yr^{-1} estimated by Trolle et al. (2008) or 1.0 cm yr^{-1} by (Pearson 2007), as elevated aluminium levels extend beyond 20 cm depth in cores taken from this zone. There is also some evidence from surface sediment layers of the crater that aluminium accumulation has recently declined, this may be associated with the 2-year break in dosing to the Puarenga Stream. In contrast, little aluminium appears to be accumulating in the main lake basin or in the near-shore environment to the east of Sulphur Bay. The fate of aluminium discharged from Sulphur Bay is likely dependent on the prevailing wind direction, either sedimenting to the deeper crater area under southerly or easterly wind conditions or kept in suspension under westerly wind conditions and discharged from the lake.

Results from the current sediment survey of Lake Rotoehu support the findings of the previous survey conducted in 2016. Background sediment aluminium content is similar to Lake Rotorua at 5 g Al kg^{-1}. Alum derived aluminium is primarily accumulating in Te Wairoa Bay close to the discharge point of the Waitangi Stream with levels exceeding 25 g Al kg^{-1}. However, the two-year cessation of alum dosing has resulted in a small decline of ~5 g Al kg^{-1} in the surface sediments. Despite the five-fold increase in aluminium content in Te Wairoa Bay over background levels amorphous aluminium content appears to be decreasing indicating that the deposited aluminium is crystallising to the more benign mineral gibbsite (Cooke et al. 2005). There was no evidence for aluminium accumulation in the main basin of the lake.

The current sediment coring sites appear suitable for on-going monitoring of surface sediment aluminium content in lakes Rotorua and Rotoehu. Future sediment surveys should continue to include amorphous aluminium content as well as total aluminium as this analysis provides additional insights to sediment aluminium accumulation. However, observed spatial distributions of aluminium sedimentation do not appear optimal for desired secondary sediment phosphorus adsorption post-deposition. For both Rotorua and Rotoehu the spatial extent of sedimented alum derived aluminium is relatively limited in relation to the size of each lake. In addition, the areas of deposition are primarily <5 m in depth, placing them above the thermocline during periods of stratification and unlikely to interact with phosphorus released from the sediment during periods of anoxia. Alterations in the delivery of alum such as lake surface application or subsurface piping may improve dispersion and allow targeting of deeper areas of the lake. Not only would this reduce resuspension and loss of alum floc from the lake (i.e., Lake Rotorua), it would also result in more efficient phosphorus removal per unit of supplied alum, allowing reductions in alum dosing rates while achieving water quality improvements.

Conclusions

Sediment cores were taken from Lake Rotorua and Lake Rotoehu in December 2020 covering both near-shore and main basin sites. Total and amorphous aluminium content and total phosphorus content was assessed to determine where alum derived aluminium was accumulating in Lake Rotorua.

The main conclusions were:

1. Sediment aluminium content was elevated above background levels in the nearshore area between Kawaha Point and the crater area off Motutara Point in Lake Rotorua.
2. Aluminium does not appear to be accumulating in the main basin or south-eastern nearshore zone east of Sulphur Bay in Lake Rotorua.
3. Aluminium content was significantly elevated above background levels at the discharge point of the Waitangi Stream in Te Wairoa Bay, Lake Rotoehu.
4. Aluminium was not elevated in the main basin of Lake Rotoehu.
5. Iron and sulphur sediment content were elevated in Te Wairoa Bay compared to the rest of the lake, but X-ray diffraction analysis of the mineral content was inconclusive.

Recommendations

1. On-going sediment monitoring for alum derived aluminium should incorporate both near-shore zone and deeper basin areas of the lakes.
2. Monitoring of sediment aluminium accumulation should also include assessment of amorphous aluminium content to distinguish alum-derived aluminium from natural background crystalline aluminium.
3. Consideration should be given to alternative alum delivery mechanisms in order to better target areas of sediment phosphorus release, potentially improving phosphorus sequestration and reducing the amount of alum needed to achieve water quality improvements in lakes Rotorua and Rotoehu.

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Appendices

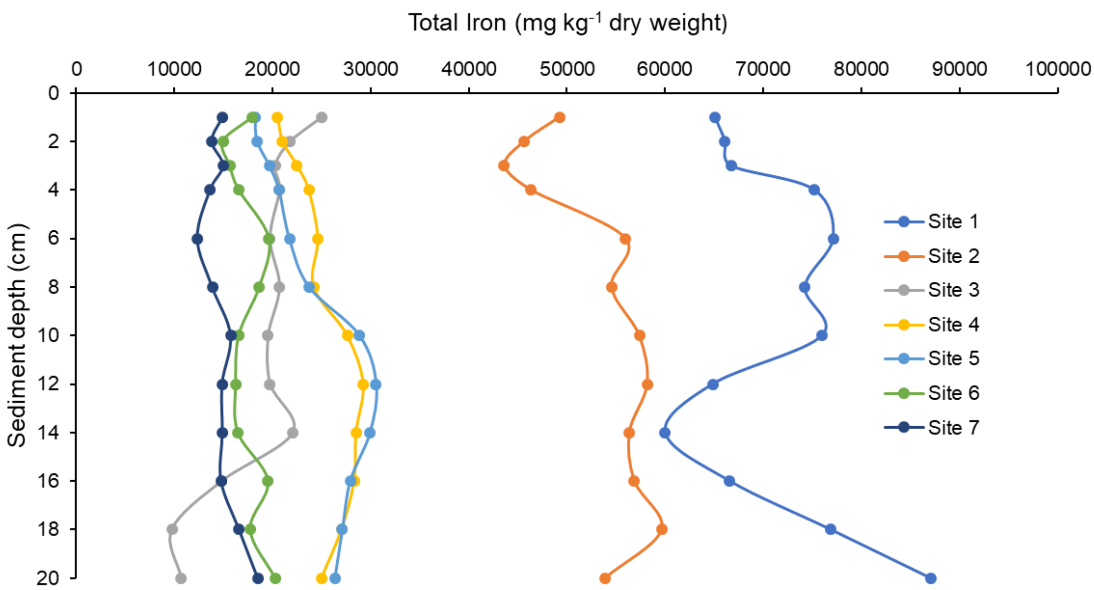
Appendix 1. Locations and water depth of sediment coring sites in Lake Rotorua, December 2020.

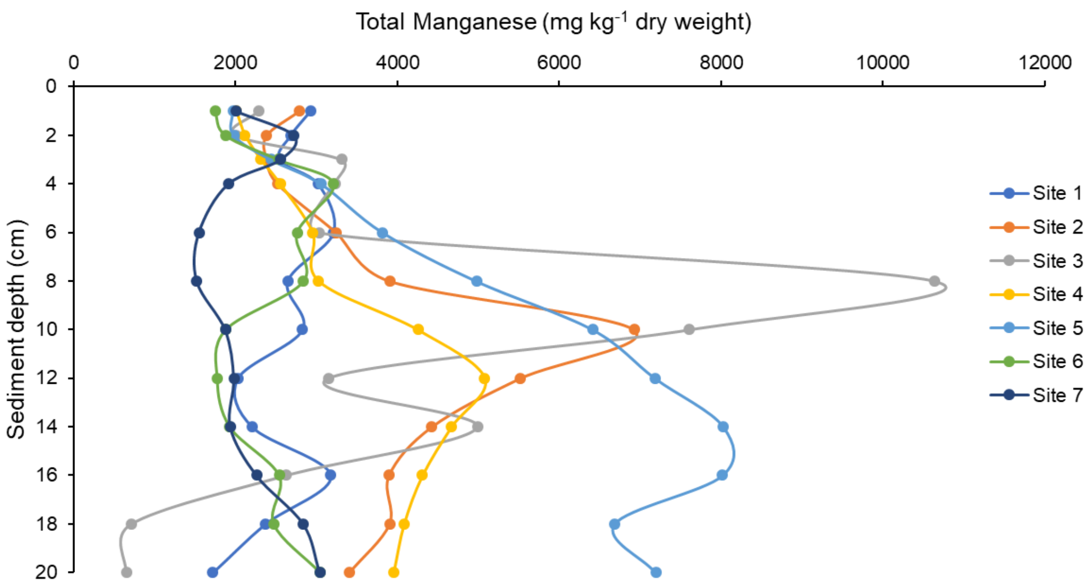
	Previous Site designation					
2020 Core site	Tempero and Hamilton (2016)	Tempero (2019)	2020 Sampling date	Latitude	Longitude	Water depth (m)
Ra1		Site 1	7 December 2020	-38.094591	176.314635	4.8
Ra2		Site 2	7 December 2020	-38.111994	176.296850	4.9
Ra3		Site 3	7 December 2020	-38.124765	176.279512	4.7
Ra4		Site 4	7 December 2020	-38.127519	176.268509	22.1
Ra5	RU2	Site 5	7 December 2020	-38.122032	176.265637	45.1
Ra6		Site 6	7 December 2020	-38.113216	176.249619	4.9
Ra7		Site 7	7 December 2020	-38.121759	176.253555	4.8
Ra8	RU3		8 December 2020	-38.119067	176.266617	21.2
Ra 9	RU4		8 December 2020	-38.109183	176.268767	17.4
Ra10	RU5		8 December 2020	-38.093233	176.272283	20.2
Ra11	RU7		8 December 2020	-38.085100	176.263533	20.4
Ra12	RU9		8 December 2020	-38.073183	176.270417	22.0
Ra13	RU11		8 December 2020	-38.063167	176.289367	19.8
Ra14	RU13		8 December 2020	-38.044100	176.306700	16.4
Ra15	RU15		8 December 2020	-38.071233	176.310417	12.3

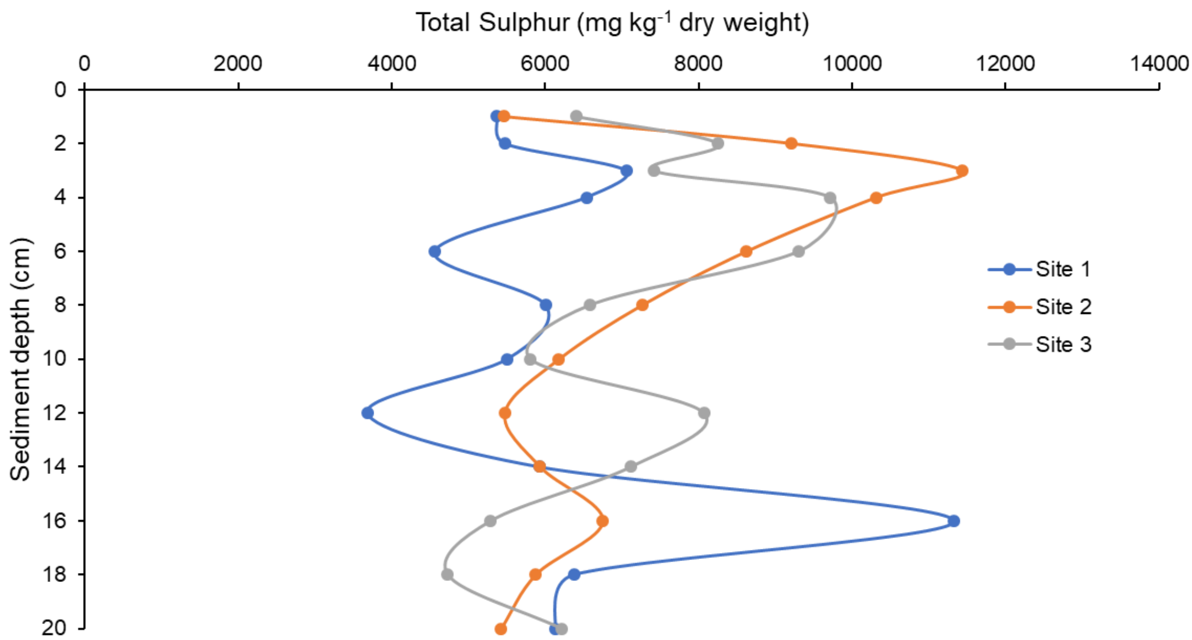
Appendix 2. Locations of sediment coring sites in Lake Rotoehu 2015 and 2020.

Site	latitude	longitude	2020 Water Depth (m)
Rh 1	-38.0333	176.54633	1.2
Rh 2	-38.0324	176.54545	1.6
Rh 3	-38.0301	176.54230	3.2
Rh 4	-38.0271	176.53566	8.5
Rh 5	-38.0237	176.53097	10.2
Rh 6	-38.0190	176.52973	11.0
Rh 7	-38.0146	176.52998	11.0

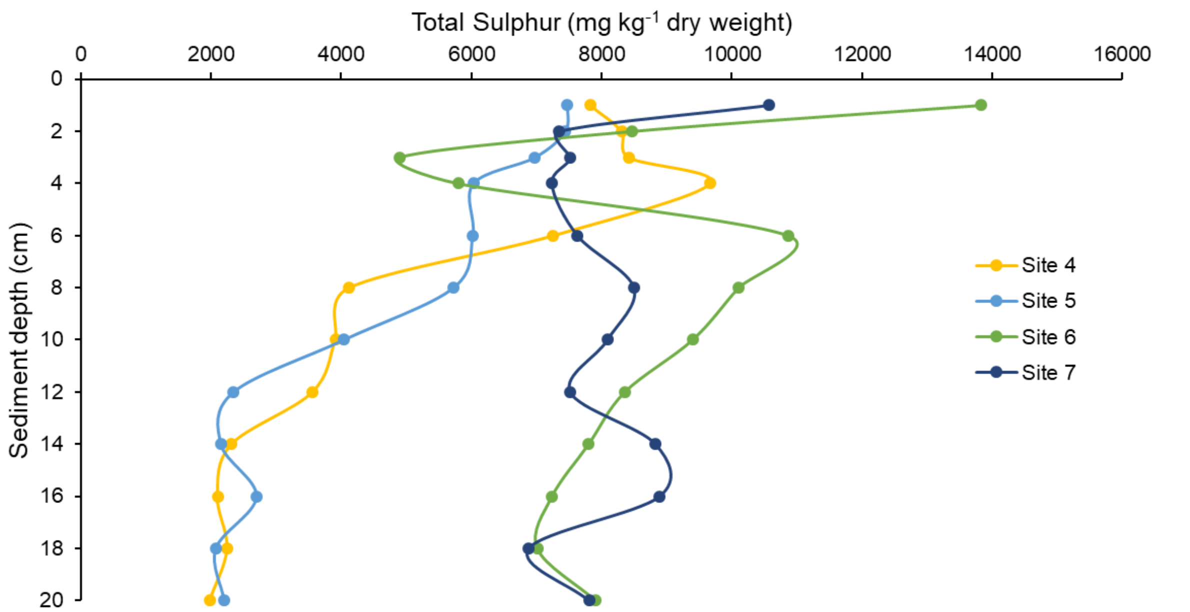
Appendix 3. Sediment profiles of iron, manganese and sulphur from inductively coupled plasma mass spectrometry (ICP-MS), Lake Rotoehu, December 2020.







Total Sulphur (mg kg-1 dry weight)
0
2000
4000
6000
8000
10000
12000
14000
Sediment depth (cm)
0
2
4
6
8
10
12
14
16
18
20
Site 1
Site 2
Site 3



Total Sulphur (mg kg-1 dry weight)
0
2000
4000
6000
8000
10000
12000
14000
16000
Sediment depth (cm)
0
2
4
6
8
10
12
14
16
18
20
Site 4
Site 5
Site 6
Site 7

Appendix 4. X-ray diffraction of sediment sub-samples from Lake Rotoehu, December 2020. High abundance of amorphous material prevented detection of crystalline minerals, apart from pyrite at site Rh1 at 16 cm sediment depth (Rh 1-16).