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Sediment Aluminium Content of Lake Okaro: 2021 Monitoring Survey

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Cover photo: Lake Okaro, Bay of Plenty. Photo: Deniz Özkundakci

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Executive Summary

The application of aluminium salts such as polyaluminium chloride and aluminium sulphate has been widely used to assist in the remediation of eutrophic freshwater ecosystems. Aluminium binds to phosphorus, reducing its availability for phytoplankton growth, with the additional benefit that sediment phosphorus is reduced under anoxic lake conditions. Since 2013, alum (aluminium sulphate) has been applied twice per year to Lake Okaro to reduce dissolved reactive phosphorus availability. The lake's annual Trophic Lake Index has decreased from 5.5 in the early 2000s to 4.5 in 2020. Alum dosing has resulted in the addition of 3.8 t of aluminium to the lake, however, the spatial distribution and sediment accumulation rate of alum derived aluminium has not been investigated.

The University of Waikato was contracted by the Bay of Plenty Regional Council to survey sediment aluminium concentrations in Lake Okaro to determine the distribution and accumulation of alum derived aluminium. In addition to sediment total aluminium content, the proportion of amorphous (non-crystalline) aluminium was assessed. Amorphous aluminium is the fraction of total aluminium able to adsorb dissolved phosphorus, sequestering it from uptake by phytoplankton. It was assumed that increased proportions of amorphous aluminium were primarily derived from alum dosing.

Four sediment cores were taken from Lake Okaro in November 2021. Sediment total aluminium content was broadly similar at all four core sites, with mean total aluminium increasing from 5.9 g Al kg^{-1} (± 0.58 95% CI) sediment dry weight (dw) in the surface (0–4 cm) sediment to 6.8 g Al kg^{-1} (± 0.76 95% CI) in the deeper (14–20 cm) sediments. The vertical distribution of amorphous aluminium was similar in all four cores, with higher proportions (>0.65) in the surface (0–4 cm depth) sediments, declining to 0.3–0.4 at the bottom of the core (14–20 cm sediment depth). Monitoring buoy data indicated that the lake was stratified and the hypolimnion was anoxic during the sampling; under these conditions, it was unsurprising that sediment porewater dissolved reactive phosphate concentrations were highest in the surface sediments (mean 0.30 g m^{-3} ± 0.06 95% CI; 0–4 cm depth) and declined with increasing sediment depth (mean 0.07 g m^{-3} ± 0.02 95% CI; 14–20 cm depth).

A comparison of mean sediment total aluminium to a 2007 study conducted prior to the start of regular alum dosing in 2013 indicated that sediment aluminium content has increased from 4.6 g kg^{-1} sediment dw in 2007 to 6.3 g kg^{-1} sediment dw in 2021. However, the mean aluminium accumulation rate of appears to be modest (~0.12 g Al kg^{-1} $year^{-1}$), with similar total aluminium concentrations (6–7 g Al kg^{-1} sediment dw) observed in moderate depositional areas of lakes Rotorua and Rotoehu. Based on biota monitoring of alum dosing to lakes Rotorua and Rotoehu, the observed sediment total aluminium levels in Lake Okaro are highly unlikely to result in acute ecological impacts.

Recommendations

1. On-going monitoring of sediment for alum derived aluminium should be conducted on a 3–5 year basis.
2. On-going monitoring of sediment aluminium accumulation should also include assessment of amorphous aluminium content to distinguish alum derived aluminium from natural background crystalline aluminium.

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Introduction

Lake Okaro is located in the Bay of Plenty Region, approximately 20 km south-east of Rotorua City. The lake has undergone significant eutrophication due to extensive deforestation and land use intensification (Forsyth et al. 1988). Several management actions have been implemented to improve lake water quality including sediment capping with 110 t of modified zeolite (Z2G1) (Gibbs and Özkundakci 2011), development of farm nutrient management plans and riparian planting (Burns et al. 2009), constructed wetlands (Özkundakci et al. 2010), and alum dosing (Paul et al. 2008). The application of alum (aluminium sulphate) to freshwater systems is commonly undertaken to restrict the availability of dissolved reactive phosphate (DRP), thereby inhibiting phytoplankton growth (Cooke et al. 2005). An initial bulk dosing trial of alum to Lake Okaro was conducted in December 2003, with approximately 550 kg of aluminium applied to the lake (Paul et al. 2008). Since 2013, seasonal (spring and autumn) bulk dosing has been conducted, with a total of 3.8 tonnes of aluminium applied to the lake as aluminium sulphate. This has been associated with an improving, but variable, trend in Lake Okaro's Trophic Lake Index (TLI) (Figure 1).

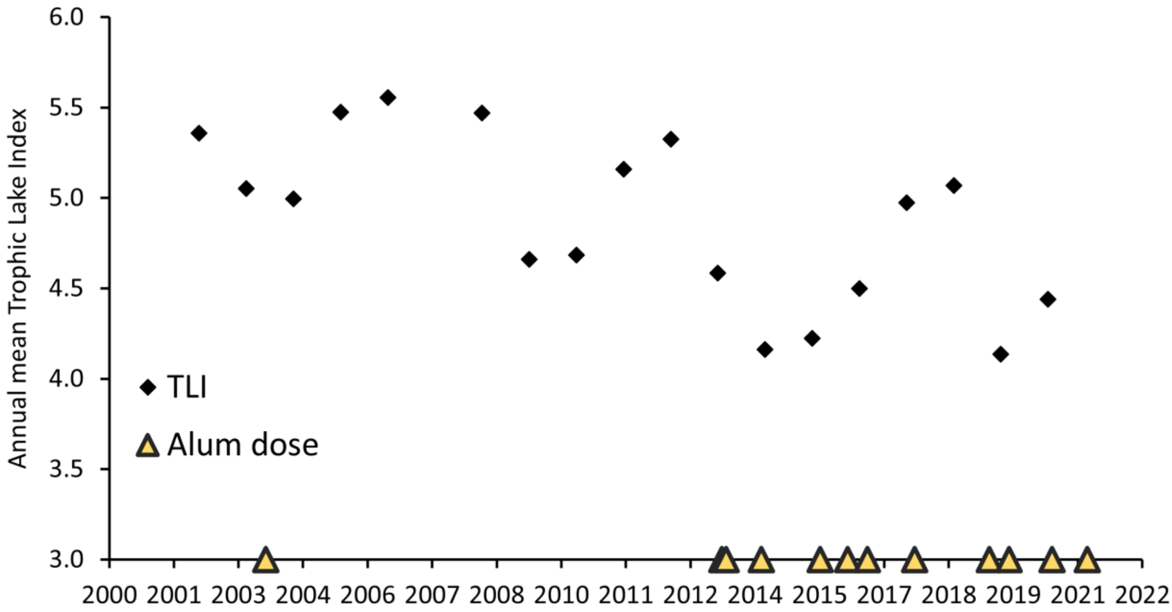

Figure 1. Lake Okaro mean annual (hydrological year) Trophic Lake Index and timing of bulk alum dosing events (yellow triangles). Note: no alum dosing was conducted in 2018.

Sediment surveys to monitor accumulation of alum derived aluminium have been conducted every 3 years in Lakes Rotorua and Rotoehu as part of the Bay of Plenty Regional Council's resource consent for alum dosing. However, regular monitoring surveys have not been conducted for Lake Okaro. Sediment aluminium content in Lake Okaro was determined by

Özkundakci et al. (2013a) in 2007, with mean sediment total aluminium content ~4.5 g Al kg^{-1} of dry sediment. Despite an initial alum dosing trial in 2003, there was no apparent increase in surface sediment total aluminium at this time, although the low application rates likely made it difficult to distinguish applied total aluminium from natural background aluminium concentrations. Previous sediment surveys of lakes Rotorua and Rotoehu by Tempero and Hamilton et al. (2016) and Tempero (2019) have found quantification of amorphous aluminium content to be useful in distinguishing alum derived aluminium from background total aluminium, as this fraction of the total aluminium content can be primarily attributed to aluminium application.

The Bay of Plenty Regional Council contracted the University of Waikato to conduct sediment aluminium content monitoring of Lake Okaro to support their resource consent for alum dosing. Sediment cores were taken from four sites in Lake Okaro, three of which were previously sampled by Özkundakci et al. (2013a). Sediment cores were sectioned and analysed for total and non-crystalline aluminium content by inductively coupled plasma mass spectrometry (ICP-MS). Sediment porewater was extracted and analysed for dissolved reactive phosphate to provide a relative assessment of effective aluminium binding of porewater dissolved phosphorus.

Methods

Study site

Lake Okaro is the smallest of the 12 Te Awara lakes, covering 32 ha with a maximum depth of 18 m and a mean depth of 12.5 m (Santoso et al. 2021). It was formed in a hydrothermal explosion crater approximately 700 years ago, and much of the catchment surface geology is composed of Rotomahana mud from the 1886 Tarawera eruption (Hardy 2005). The lake has a catchment area of 330 ha, with three small inflows and one outflow, the Haumi Stream (Paul et al. 2008). Water quality has significantly declined since the 1960s, and the lake has become eutrophic with persistent phytoplankton blooms during the spring and summer (Jolly and Chapman 1977). Lake Okaro is monomictic and may be stratified for up to 10 months of the year (Özkundakci et al. 2011). The hypolimnion is anoxic throughout most of the stratified period and substantial internal phosphorus loading appears to be driving the phytoplankton blooms (Environment Bay of Plenty 2006, Özkundakci et al. 2011).

Four sediment cores were retrieved from Lake Okaro on 26 November 2021, including three sites (S1–S3) previously cored by Özkundakci et al. (2013a) (Figure 2). A fourth site (S4) was included to complete spatial coverage of the lakebed.

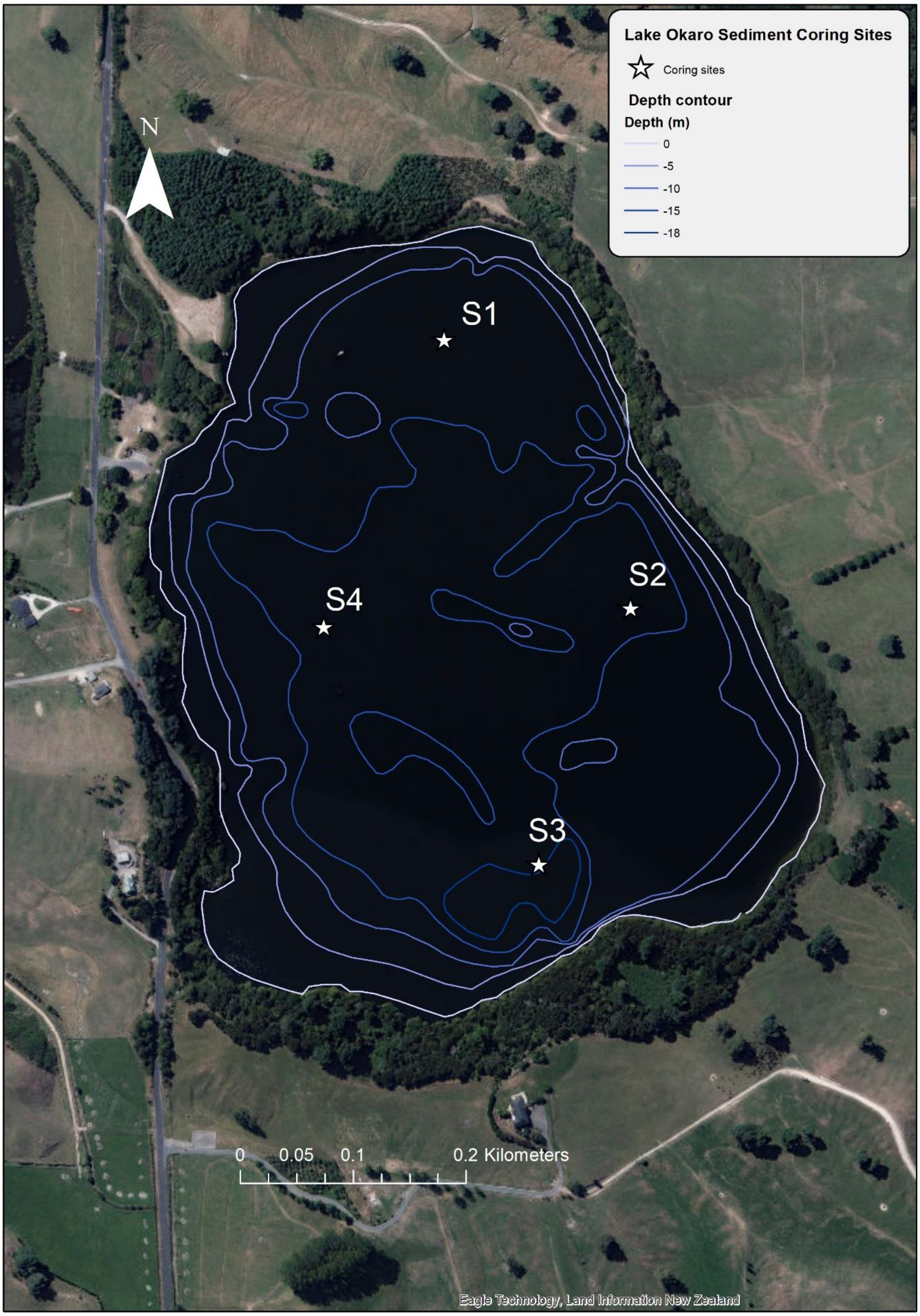

Figure 2. Location of sediment cores sampled from Lake Okaro on 26 November 2021.

Sediment core retrieval and processing

Following Tempero and Davies-Calway (2021), 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.

Sediment and nutrient analysis

Sediments were centrifuged at 4000 rpm (2900 G) for 10 minutes and the resulting supernatant porewater 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 extraction volumes, porewater 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 lower detection limit of 0.004 mg P L^{-1}.

The centrifuged sediment was then dried at 60°C for 7 days, followed by grinding 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 concentrated nitric acid and 0.33 mL concentrated hydrochloric acid. Samples were then digested at 80°C for 1 hour 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 was filtered using 0.2 µm cellulose acetate filters (Sartorius, Germany). The sample and control blank digests were then analysed for aluminium content using inductively coupled plasma mass spectrometry (ICP-MS model Agilent 8900 with a triple-quadrupole). Sediment total phosphorus content data was available but was not analysed as previous studies have found phosphorus concentrations to be highly spatially and temporally variable (Tempero and Hamilton 2016, Tempero 2019, Tempero and Davies-Calway 2021).

Sediment amorphous (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 hours in the dark, followed by centrifugation for 5-minutes at 5000 rpm. The supernatant was then filtered using 0.2 µm cellulose acetate filters and aluminium content determined by ICP-MS.

Results

Lake profile data provided by Limnotrack indicated that the lake was strongly stratified and the hypolimnion was anoxic (Appendix 1). Visual inspection of the four sediment cores revealed no evidence of aluminium floc at the sediment-water interface and no distinguishing tephra layers that could be used for dating. However, once the sediment was sectioned and dried, small (1–3 mm), light granular inclusions were distinguishable in the core sections from 10–14 cm sediment depth (Figure 3). These particles were likely zeolite which had been applied to the lake in 2008 to cap the sediment and reduce internal phosphorus loading (Özkundakci et al. 2010).

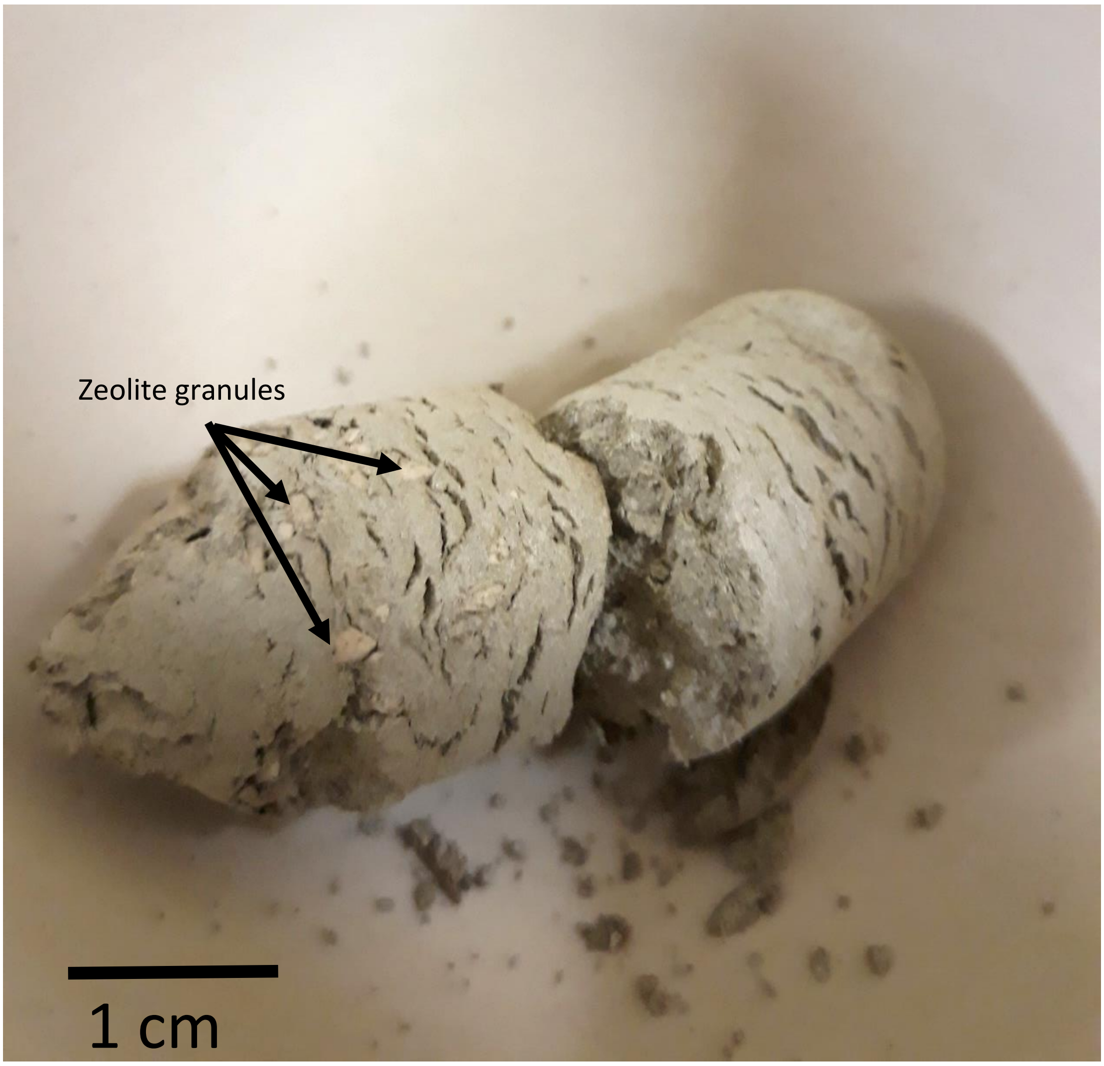

Figure 3. Small zeolite granules were present in sediment sections from 10–14 cm depth in Lake Okaro.

Sediment aluminium content

Sediment total aluminium content was broadly similar at all four core sites, with mean total aluminium increasing from 5.9 g Al kg^{-1} (± 0.58 95% CI) sediment dry weight in the surface (0–4 cm) sediment to 6.8 g Al kg^{-1} (± 0.76 95% CI) sediment in the deeper (14–20 cm) sediments. This difference is primarily attributable to site 1 (S1) which had higher aluminium content from 12–18 cm depth compared to the other Okaro sites (Figure 4).

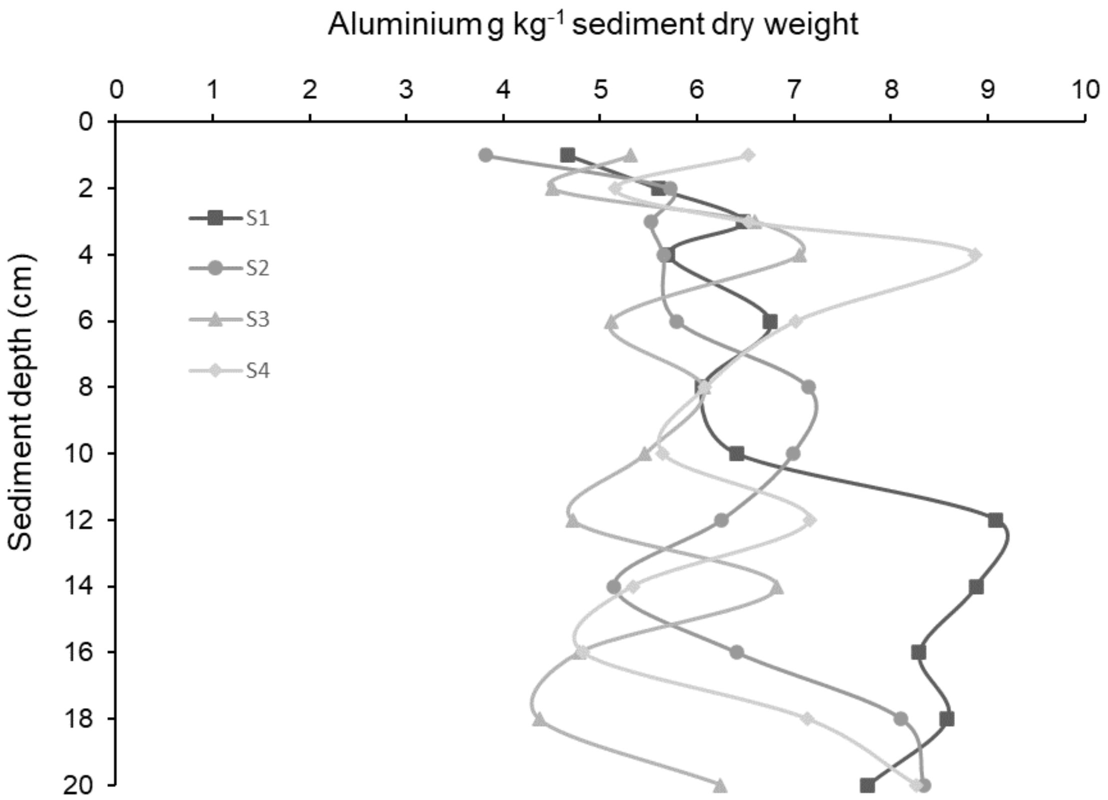

Figure 4. Vertical profiles of sediment total aluminium content from four core sites (S1–S4) in Lake Okaro, sampled 26 November 2021.

The proportion of amorphous aluminium was highest in the surface sediments (mean proportion 0.57 ± 0.05 95% CI) and declined with increasing sediment depth to 0.34 (± 0.02 95% CI) in the bottom sediment sections. Transient increases in the proportion of sediment amorphous aluminium did occur between 4–8 cm depth at sites S3 and S4, but the profiles were generally similar at all for sites (Figure 5).

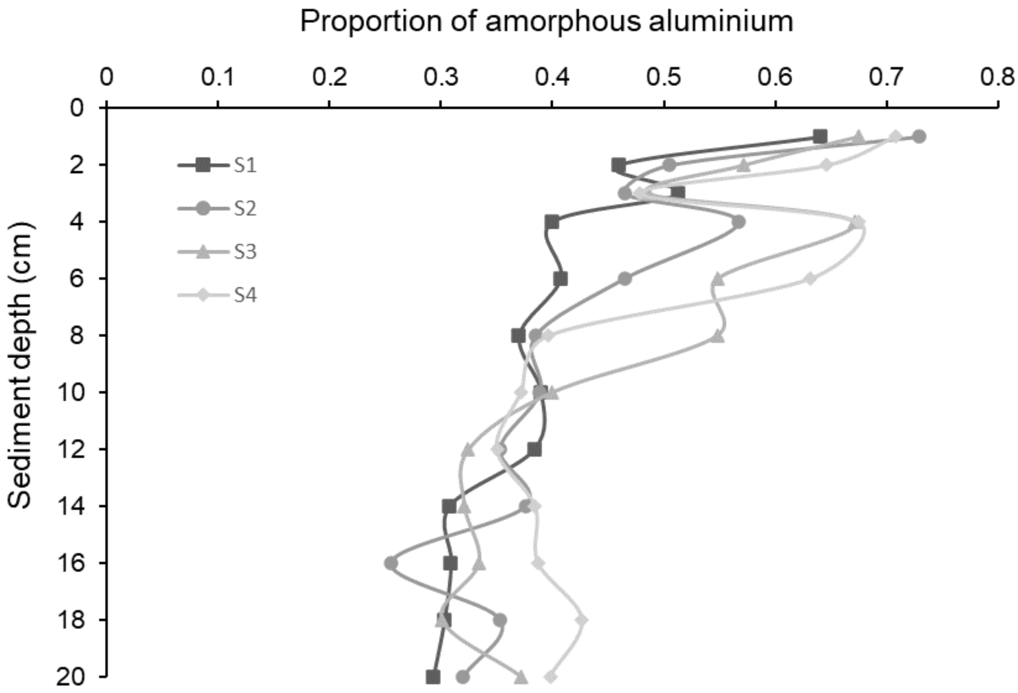

Figure 5. Vertical profiles of sediment amorphous (non-crystalline) aluminium content from four core sites (S1–S4) in Lake Okaro, sampled 26 November 2021.

Sediment porewater was aggregated into surface (0–4 cm), middle (4–12 cm) and bottom (12–20 cm) fractions and DRP concentrations determined for each fraction. Dissolved reactive phosphate concentrations were highest in the surface sediments and declined with increasing sediment depth (Figure 6).

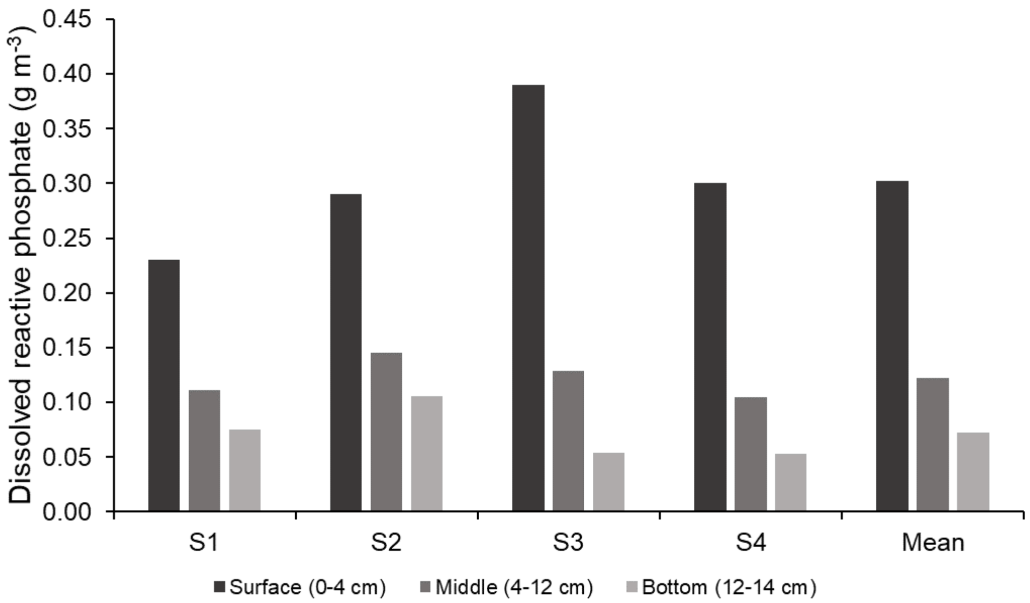

Figure 6. Aggregated sediment porewater dissolved reactive phosphate concentration from four Lake Okaro core sites, sampled 26 November 2021.

Discussion

Alum dosing of lake Okaro was first trialled in 2003, with regular bulk dosing occurring from 2013, resulting in the addition of 3.8 tonnes of aluminium to the lake. Monitoring surveys for alum derived aluminium have not been previously conducted, but the distribution of aluminium appears to be fairly consistent across the lake basin, with only limited evidence of accumulation in sections of the sediment profiles (Figures 4 & 5), likely due to uneven application of the alum. Sediment total aluminium content was collected by Özkundakci et al. (2013a) in 2007, prior to the current period of regular alum dosing. Comparison of sediment (i.e., 0–20 cm depth) mean total aluminium content between the current study and Özkundakci's (2007) survey indicates that aluminium content has increased from 4.6 g kg^{-1} sediment dry weight (dw) in 2007, to 6.3 g kg^{-1} sediment dw in 2021 (Figure 7). However, direct comparison of aluminium content at specific depths is not advisable due to differences in the core sectioning between the current study and Özkundakci et al. (2013a) study, in addition, effects from bioturbation, gas ebullition and advection, which can disturb or bury surface sediment and move the aluminium flocs into deeper sediment layers (Egemose et al. 2013, Özkundakci et al. 2013b).

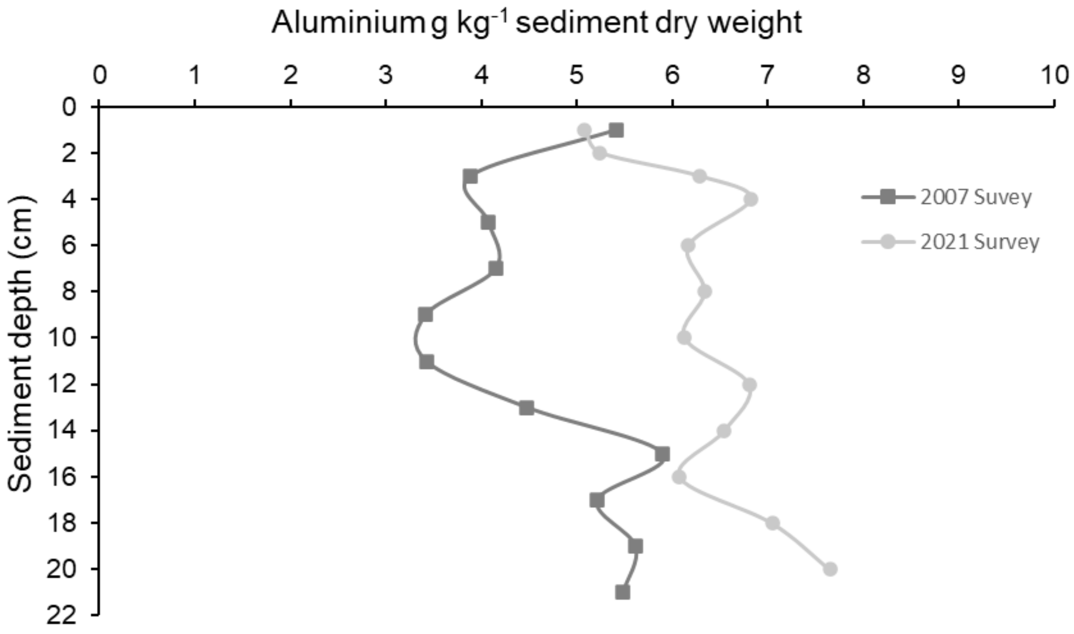

Figure 7. Comparison of sediment profile mean total aluminium content from sites S1–S4 in the current study and sites S1–S3 which were sampled by Özkundakci et al. (2013a) in 2007.

The accumulation rate of aluminium in Lake Okaro appears to be modest (~0.12 g Al kg^{-1} $year^{-1}$), with similar total aluminium concentrations (6–7 g Al kg^{-1} sediment dw) observed in moderate depositional areas of lakes Rotorua and Rotoehu (Tempero and Davies-Calway 2021), and well below the higher depositional areas (i.e., >8 g Al kg^{-1} sediment dw) near the lake discharge points of the alum dosed Utuhina (Rotorua) and Waitangi (Rotoehu) streams (Tempero and Hamilton 2016, Tempero 2019). Monitoring of biota at the discharge points of the Utuhina and Waitangi streams has found no significant impact from alum dosing, and it is unlikely that acute toxicological impacts would occur in Lake Okaro given the comparatively conservative application rates employed by the Bay of Plenty Regional Council (Tempero 2015, Tempero 2018, Ling 2021a,b).

All four vertical sediment profiles of amorphous aluminium were similar to alum floc deposition sites in lakes Rotorua and Rotoehu, with higher proportions (>0.65) of amorphous aluminium in the surface (0–4 cm depth) sediments, declining to 0.3–0.4 at the bottom of the profile (i.e., 14–20 cm) (Tempero and Davies-Calway 2021). This pattern presumably reflects the mineralisation of alum floc to gibbsite. This is a natural process that can continue for more than a year, although this has not been widely investigated (Berkowitz et al. 2006). The gap in alum dosing in 2018 is possibly reflected in the lower proportion of amorphous aluminium at 2–3 cm depth in the sediment profile (Figure 5), although this does not appear to be reflected in the total aluminium data (Figure 4).

Dissolved reactive phosphate concentrations were greatest in the surface sediments and declined with increasing depth. This trend has also been observed in Lake Rotorua during periods of stratification (Özkundakci et al. 2013b; Tempero and Hamilton 2016) and likely represents the mobilisation DRP from the breakdown of sedimented organic matter. The higher levels of DRP in the surface sediments indicate that sediment release of DRP is exceeding the adsorption capacity of naturally occurring phosphorus binding substances and recently deposited alum floc. Benthic incubation chambers would aid in the quantification of internal phosphorus release and assist with optimising future alum dose rates.

Conclusions

To determine the rate and spatial distribution of alum derived aluminium accumulation in Lake Okaro, four sediment cores were taken from Lake Okaro in November 2021. The cores were analysed for total and amorphous aluminium content by ICP-MS, and sediment porewater DRP concentrations were determined by flow injection analysis.

The main conclusions were:

1. Alum dosing of Lake Okaro has resulted in a minor and comparatively uniform accumulation of aluminium in lake sediments.
2. Observed sediment aluminium concentrations are similar to those in alum floc deposition zones of lakes Rotorua and Rotoehu, and unlikely to result in acute toxic effects to lake biota.
3. There was an observable trend of increasing aluminium mineralisation with sediment depth, likely representing the natural formation of inert gibbsite.

4. The high concentration of DRP in surface sediments indicates that sediment release of DRP exceeds the adsorption capacity of recently deposited alum floc.

Recommendations

1. On-going monitoring of sediment for alum derived aluminium should be conducted on a 3–5-year basis.
2. Monitoring of sediment aluminium accumulation should also include assessment of amorphous aluminium content to distinguish alum derived aluminium from natural background crystalline aluminium.

Acknowledgements

I would like to thank Deniz Özkundakci and Charles Lee for reviewing this report. Field support was provided by Joe Butterworth of JFB Enviro. ICP-MS analysis was conducted by Danielle Blackwell at the University of Waikato. Lake Okaro monitoring buoy data was sourced from Limnotrack. Additional support and funding were provided by the Bay of Plenty Regional Council Chair in Lakes and Freshwater Science.

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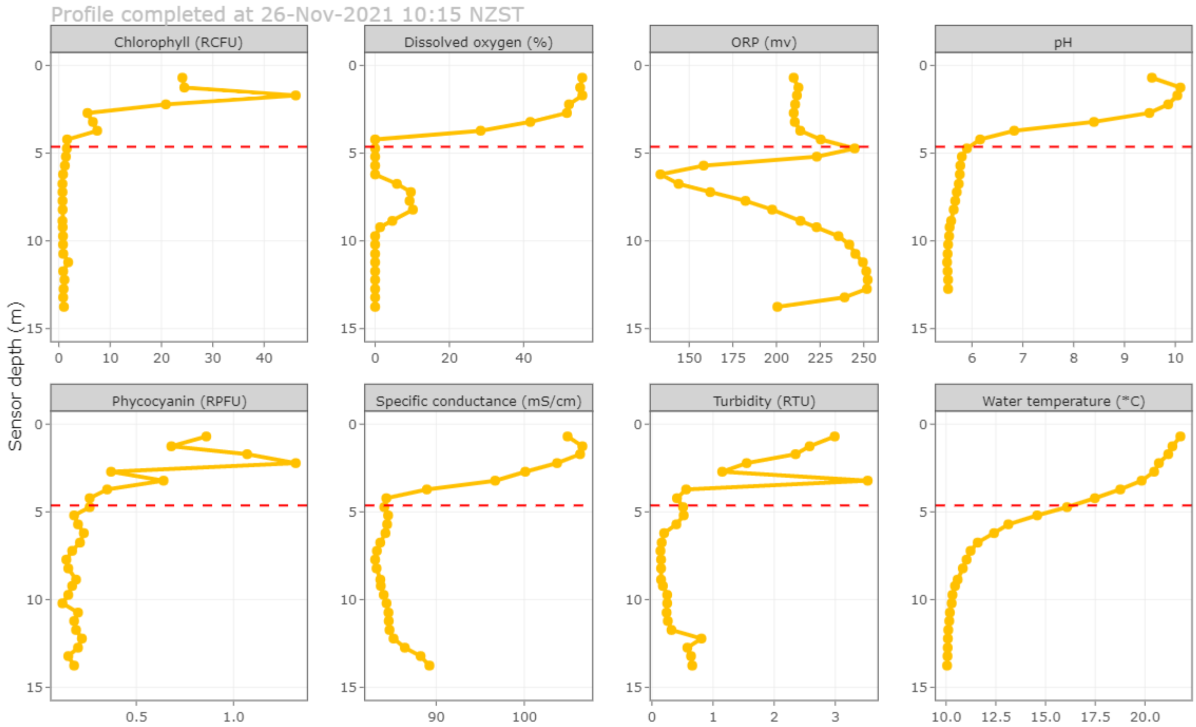
Appendices

Appendix 1. Vertical lake profiles of chlorophyll, dissolved oxygen, ORP, pH, phycocyanin, specific conductance, turbidity, and water temperature. 26 November 2021 10:15 am.



Appendix 2. Locations of Lake Okaro sediment coring sites, 26 November 2021.

Site	latitude	longitude	Water Depth (m)
S1	-38.296359	176.394351	12
S2	-38.298303	176.396265	15
S3	-38.300386	176.395402	16
S4	-38.298539	176.393288	15