

## Low-dose alum application trialled as a management tool for internal nutrient loads in Lake Okaro, New Zealand

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**Abstract** Aluminium sulfate (alum) was applied to Lake Okaro, a eutrophic New Zealand lake with recurrent cyanobacterial blooms, to evaluate its suitability for reducing trophic status and bloom frequency. The dose yielded 0.6 g aluminium m<sup>-3</sup> in the epilimnion. Before dosing, pH exceeded 8 in epilimnetic waters but was optimal for flocculation (6–8) below 4 m depth. After dosing, there was no significant change in water clarity, hypolimnetic pH decreased to 5.5, and soluble aluminium exceeded recommended guidelines for protection of freshwater organisms. Epilimnetic phosphate concentrations decreased from 40 to 5 mg m<sup>-3</sup> and total nitrogen (TN):total phosphorus (TP) mass ratios increased from 7:1 to 37:1. The dominant phytoplankton species changed from *Anabaena* spp. before dosing, to *Ceratium hirudinella*, then *Staurastrum* sp. after dosing. Detection of effectiveness of dosing may have been limited by sampling duration and design, as well as the low alum dose. The decrease in hypolimnetic pH and epilimnetic TP, and increase in Al<sup>3+</sup> and chlorophyll *a*, are attributed to the low alkalinity lake water and coincidence of alum dosing with a cyanobacterial bloom and high pH.

**Keywords** flocculation; alkalinity; *Anabaena*; *Ceratium hirudinella*; phosphorus

## INTRODUCTION

A number of New Zealand lakes have become eutrophic and water quality has become degraded since quantitative scientific assessments of lake water composition began in the 1950s (Rowe 2004). Although trophic state of most Rotorua lakes (Central Volcanic Plateau of North Island, New Zealand), was considered to have stabilised during the 1990s (Burns et al. 1997), further measurements have provided evidence of recent increases in trophic state in several of these lakes (Burns et al. 2005). Lakes Rotorua and Rotoiti, for example, are characterised by high internal nutrient loads supplied from bottom sediments, and these loads are comparable to catchment loads on an annual basis (Hamilton et al. 2004; Burger et al. 2005). Increasing nutrient loads of many New Zealand waterways in association with intensification of agriculture (Parliamentary Commissioner for the Environment 2004) and increasing groundwater nitrate concentrations (Schipper et al. 2004) may necessitate measures to control lake eutrophication. These measures may include control of land-use activities, innovative techniques for maintaining nutrients on land, and in-lake nutrient inactivation (Hamilton 2005).

Deoxygenation of bottom waters during stratification in monomictic lakes can be used as an indicator of change of lake trophic state over time (Burns et al. 1999). Dissolved oxygen (DO) levels have been documented previously in several Rotorua lakes during stratified periods in 1955–57 (Jolly 1968), 1962–66 (Fish 1968, 1969, 1970), 1970–71 (McColl 1972), 1955–81 (Vincent et al. 1984), and 1977–86 (Forsyth et al. 1988). The data demonstrate an increasing extent and duration of anoxia in several of the lakes through time (e.g., Lake Rotoiti; Hamilton et al. 2005).

Lake Okaro is a Rotorua lake that has had 95% of its catchment converted to pasture (McColl 1972). Pastoral farming was established in the lake catchment as early as 1953 (Jolly 1968). Anoxia of the hypolimnion (taken to be DO <1 mg litre<sup>-1</sup>) was not observed in water samples collected in

April 1955 (Jolly 1968). Hypolimnetic anoxia was evident, however, in each year from 1963, for up to 6 months of the year (Fish 1968, 1969, 1970; McColl 1972; Forsyth et al. 1988). Changes in phytoplankton species composition have occurred that are consistent with eutrophication; no cyanobacterial species were recorded in a December 1955 survey by Jolly (1968) whereas by 1963 cyanobacterial blooms had become a regular occurrence (Forsyth et al. 1988), and in 1979–80 *Microcystis aeruginosa* and *Anabaena* spp. dominated the phytoplankton assemblage (Dryden & Vincent 1986).

A number of lake restoration programmes have addressed internal phosphorus (P) loading through biomanipulation, applications of chemical flocculants and adsorbents such as alum, and sediment dredging (Søndergaard et al. 2003). In other instances, diversion of nutrient-laden inflows has been possible (Edmondson & Lehman 1981; Beklioglu et al. 1999). Lake Okaro, the focus lake for the present study, is the subject of a long-term restoration plan that addresses both external and internal nutrient loads (Burns et al. 2005; Scholes & Bloxham 2005)

Water column applications of alum have been used extensively to attempt to bind P in bottom sediments following flocculation and sedimentation of P from the water column (Cooke & Kennedy 1981; Rydin & Welch 1998). Application rates in lakes commonly range from 0.05 to 30 g m<sup>-3</sup> as soluble aluminium (Al<sup>3+</sup>) (Lund & Chester 1991; Welch & Cooke 1999; Van Hullebusch et al. 2002). Effectiveness of alum treatment can be assessed in terms of reduction in water column P concentrations, longevity of P inactivation and effects on phytoplankton populations, whereas potential for toxicity from elevated levels of Al<sup>3+</sup> is also an important consideration. Cooke et al. (1993) indicate that most lake treatments reduce sediment P release, but their effectiveness may in some instances be compromised by low application rates or focusing of alum flocs by wind. Refinements in application rates have been based on Al:P ratios in bottom sediments with emphasis on more effective inactivation of P under anoxic conditions (Rydin & Welch 1999; Reitzel et al. 2003).

This study was the first full-scale alum application for eutrophication control in a New Zealand lake. It provided an opportunity to assess the effectiveness of a whole lake application of alum in Lake Okaro, which has low alkalinity comparable to many other New Zealand lakes (Timperley 1987). The objective of this study was to document the impacts of the alum application, primarily on water column

nutrient concentrations and chlorophyll *a* (Chl. *a*), and to provide insights into how the methodology associated with the application and sampling could be optimised to be relevant to other New Zealand softwater lakes.

## MATERIALS AND METHODS

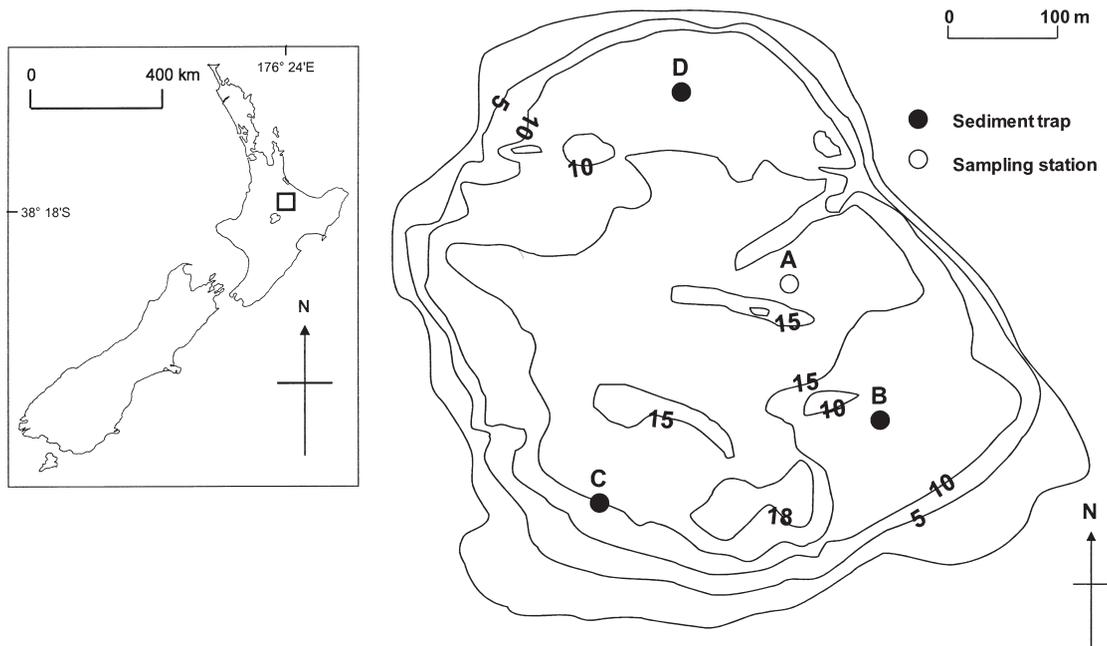
### Study site

Lake Okaro (38°18'S, 176°24'E) is c. 27 km southeast of Rotorua city in the Bay of Plenty region of New Zealand. It is approximately circular and occupies a hydrothermal explosion crater formed 900 years B.P. (Healy 1975). It has a maximum depth of 18 m and an area of 0.32 km<sup>2</sup> (Irwin 1968; McColl 1975) (Fig. 1). It has a catchment area of 3.3 km<sup>2</sup> with three small inflows and one outflow, Haumi Stream.

Lake Okaro has the poorest water quality of the lakes within the Rotorua district and has recurrent cyanobacteria blooms (Dryden & Vincent 1986). The lake usually stratifies from September to May (early spring to late autumn). Concentrations of total phosphorus (TP), total nitrogen (TN) and Chl. *a* in water samples taken from the surface waters for the period 1992 to 2004 ranged from 20 to 220 mg m<sup>-3</sup>, 600 to 2400 mg m<sup>-3</sup>, and 5 to 200 mg m<sup>-3</sup>, respectively (Scholes 2004). The alkalinity of Lake Okaro is c. 22 mg litre<sup>-1</sup> as CaCO<sub>3</sub> (Timperley & Vigor-Brown 1986), in common with generally low alkalinities for lakes in the Rotorua district (Jolly 1968).

### Alum trial

Three agencies (Environment Bay of Plenty, National Institute of Water and Atmospheric Research Ltd, and University of Waikato) were responsible for sampling different lake variables, with dates and depths of sampling not optimally coordinated, and limitations for data interpretation. Alum was applied to Lake Okaro (by Environment Bay of Plenty) on 16 and 17 December 2003. Over 2 days, 13 m<sup>3</sup> of alum solution (47% Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·14H<sub>2</sub>O) was applied to the surface of the lake by spraying from a moving boat, to produce a calculated concentration of 0.6 g Al m<sup>-3</sup> in the epilimnion (0–3 m). This low application rate was used to eliminate the need for addition of a buffer with the alum application, as Lake Okaro has a relatively low alkalinity. There was no mechanical mixing with the alum application and water at the periphery of the lake (depth <2 m) was not treated directly.



**Fig. 1** New Zealand, map of Lake Okaro (after Irwin 1974) showing sampling point A and sediment trap sites B, C, and D with depth contours in metres.

Sampling took place at station A (Fig. 1) on 2, 8, and 12 December 2003 (pre-dosing), and 18, 22 December 2003 and 13 January 2004 (post-dosing). Water column profiles were taken with a profiling instrument that simultaneously measures conductivity, temperature and depth (SBE 19 plus SEACAT Profiler, Sea-Bird Electronics Inc., Washington), dissolved oxygen (Sea-Bird Electronics, Inc.), photosynthetically available radiation (PAR; Li-cor Inc.), beam transmittance (Sea-Bird Electronics, Inc.), and chlorophyll fluorescence (Chelsea Instruments Ltd). Coefficients for attenuation of photosynthetically available radiation (PAR) were derived assuming Beer's Law attenuation, after removing the uppermost 1 m from the profile (Wetzel 2001). Secchi depth measurements were taken with a 20 cm diameter disk with black and white quadrants and an underwater viewing chamber (Nuova Rade spa model 31409). pH was measured (YSI model 610 DM) at 1 m intervals from the water surface to the lake bottom.

Water samples for analysis of Chl. *a* and dissolved nutrients were collected with a Schindler-Patalas trap at depths of 1.5, 7, 10, and 13 m, and filtered on site using 0.45  $\mu\text{m}$  glass fibre filter (GC50, Advantec). Nutrient samples and Chl. *a* filters were placed on ice, transferred to the laboratory and

stored at  $-20^{\circ}\text{C}$  until analysis. Nutrient analyses were performed on thawed samples using a flow injection analyser, according to APHA methods 4500-NH<sub>3</sub>-H for ammonium, 4500-Norg D for total Kjeldahl nitrogen, 4500-NO<sub>3</sub>-I for nitrate-N + nitrite-N, 4500-NO<sub>2</sub>-I for nitrite-N, 4500-P G for soluble reactive phosphorus, and 4500-P H for total phosphorus (Clesceri et al. 1998). Chl. *a* filters were thawed and ground, and chlorophyll was extracted by steeping in 90% MgCO<sub>3</sub>-buffered acetone (Arar & Collins 1997).

Water samples for phytoplankton analysis were collected at a depth of 1.5 m (epilimnion) with a Schindler-Patalas trap. Samples were transferred to polycarbonate jars and fixed with Lugol's iodine solution (Pridmore 1987). Phytoplankton identification was carried out using keys and descriptions of Prescott (1978), Cox (1996), and Baker & Fabbro (1999). Phytoplankton counts were performed on samples settled in Utermöhl chambers (Utermöhl 1958; USEPA 2003). Phytoplankton biomass calculations were based on biovolumes determined from average dimensions for 10 organisms of each species (Pridmore 1987).

Water samples for Al analysis were taken using a Schindler-Patalas trap from 1, 3, and 5 m depths on eleven occasions (total Al) and six occasions

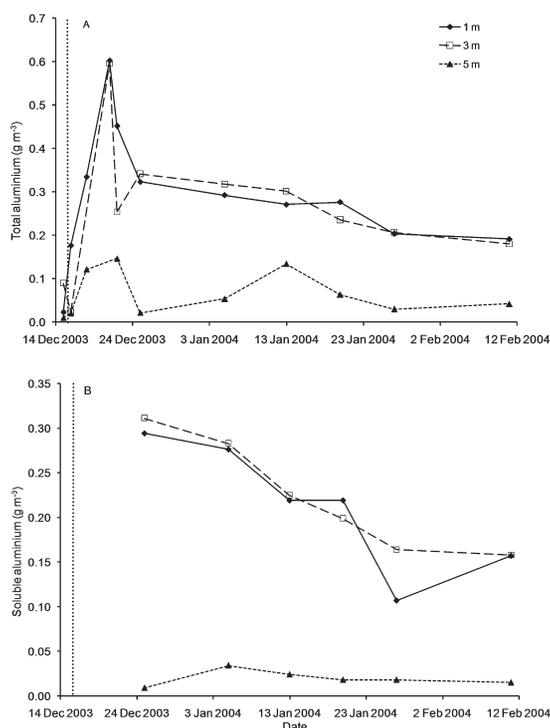
(soluble Al) between 16 December 2003 and 19 February 2004. Soluble aluminium analyses were performed on the thawed filtered samples using an inductively coupled plasma mass spectrometer (ICP-MS) according to APHA method 3125 (Clesceri et al. 1998).

Sedimentation rates of sediment and particulate Al were measured in triplicate with sedimentation traps at three sites (B, C, and D) (Fig. 1). At each site, there were three sediment traps each at depths of 3, 6, and 9 m in separate deployments from 11–16 December and 16–19 December 2003 as recommended by Kozerski (1994). The PVC sediment traps were 0.5 m long with 6.2 cm internal diameter, and had plastic tubing, a nalgene funnel and 6 mm bore tap at the base. Traps were held taut between a weight at the lake bed and a subsurface float. A hole at the mid-point of the trap tube was covered with tape, which was removed immediately on recovery, to drain some of the supernatant water. The remaining slurry of water and sediment was mixed thoroughly before analysis. Suspended solids were measured by filtering duplicate aliquots of the slurry through pre-weighed Whatman GF/C filters that had been pre-combusted (500°C). The filters were dried at 60°C to constant weight, then weighed to determine total suspended solids as the difference in dry filter weight following filtration. These filters were then analysed for particulate Al by digesting with nitric/hydrochloric acid mixture (2.5/0.5, v/v). Digestion was carried out at 90°C for 1 h before dilution with Type 1 water to a final volume of 50 ml making up a final concentration of 5% nitric acid and 1% HCl acid. Analysis for Al was carried out by ICP-MS according to APHA method 3125 (Clesceri et al. 1998).

Difference in concentrations of TP and Chl. *a* in the epilimnion between the first and last day of the sampling period (6 weeks) was used to measure “effectiveness” of the alum application.

### Statistical analysis

Pearson correlation analysis (Statistica 6.1, StatSoft Inc, Oklahoma, United States) was used to calculate the strength of correlation between the light attenuation coefficient ( $K_d$ ) and Chl. *a* (Zar 1996) and between Chl. *a* and phytoplankton biomass. A 2-way factorial treatment model using a randomised block design was applied to the sediment trap and particulate Al data to differentiate changes before and after alum dosing (Zar 1996). The two factors tested were before and after alum dosing, with the blocks site and depth. These analyses were



**Fig. 2** Concentrations of **A**, total aluminium and **B**, soluble aluminium at water depths of 1, 3, and 5 m, in Lake Okaro from 16 December 2003 to 11 February 2004. Dashed line denotes alum dosing.

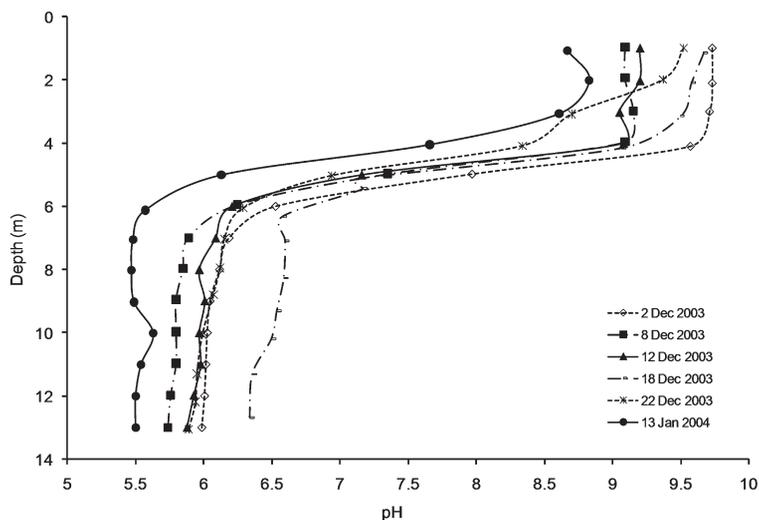
performed on GenStat 9 (VSN International Ltd, Hemel Hempstead, United Kingdom).

## RESULTS

Lake Okaro was thermally stratified throughout the sampling period. The thermocline (i.e., the maximum vertical temperature gradient) was between depths of 4.7 and 5.9 m. Water temperature was in the range 18.0 to 25.6°C in the epilimnion and 11.0 to 12.5°C in the hypolimnion. Concentrations of DO in the hypolimnion were <1 mg litre<sup>-1</sup> throughout sampling and ranged from 4.7 to 12.9 mg litre<sup>-1</sup> in the epilimnion in the period 18 December 2003 to 13 January 2004.

Secchi depths ranged from 1.2 to 3.5 m during the sampling period and decreased after alum dosing. The lowest reading of 1.2 m coincided with the highest value of the light attenuation coefficient ( $K_d$ ) for PAR of 1.53 m<sup>-1</sup> on 22 December 2003. The highest Secchi depth of 3.5 m occurred when

**Fig. 3** Profiles of pH with depth, in Lake Okaro from 2 December 2003 to 13 January 2004.



$K_d$  was lowest at  $0.4 \text{ m}^{-1}$  on 8 December 2003. Values of  $K_d$  were negatively correlated with Chl. *a* concentrations ( $r = 0.93$ ,  $P < 0.05$ ,  $n = 6$ ).

Total Al concentrations were  $<0.09 \text{ g m}^{-3}$  at 1, 3, and 5 m depths before the alum application (Fig. 2A). Total Al concentrations increased at all depths after the application and were maximal ( $0.6 \text{ g m}^{-3}$ ) at 1 and 3 m depths on 21 December 2003. Concentrations at 1 and 3 m depths then declined to  $0.3 \text{ g m}^{-3}$  by 25 December 2003, with ongoing decline in concentrations through the remaining two months of sampling (Fig. 2A). Soluble Al was not measured before the application, but from 25 December 2003 concentrations at the 1 and 3 m depths were  $>0.09 \text{ g m}^{-3}$  for at least 57 days and constituted between 52 to 91% of the total Al at the same depths over the same time period (Fig. 2B). At 5 m depth, soluble Al represented 17 to 64% of total Al (Fig. 2). There was a general decline in concentrations of soluble Al at all depths from 25 December 2003 to 11 February 2004 (Fig. 2B).

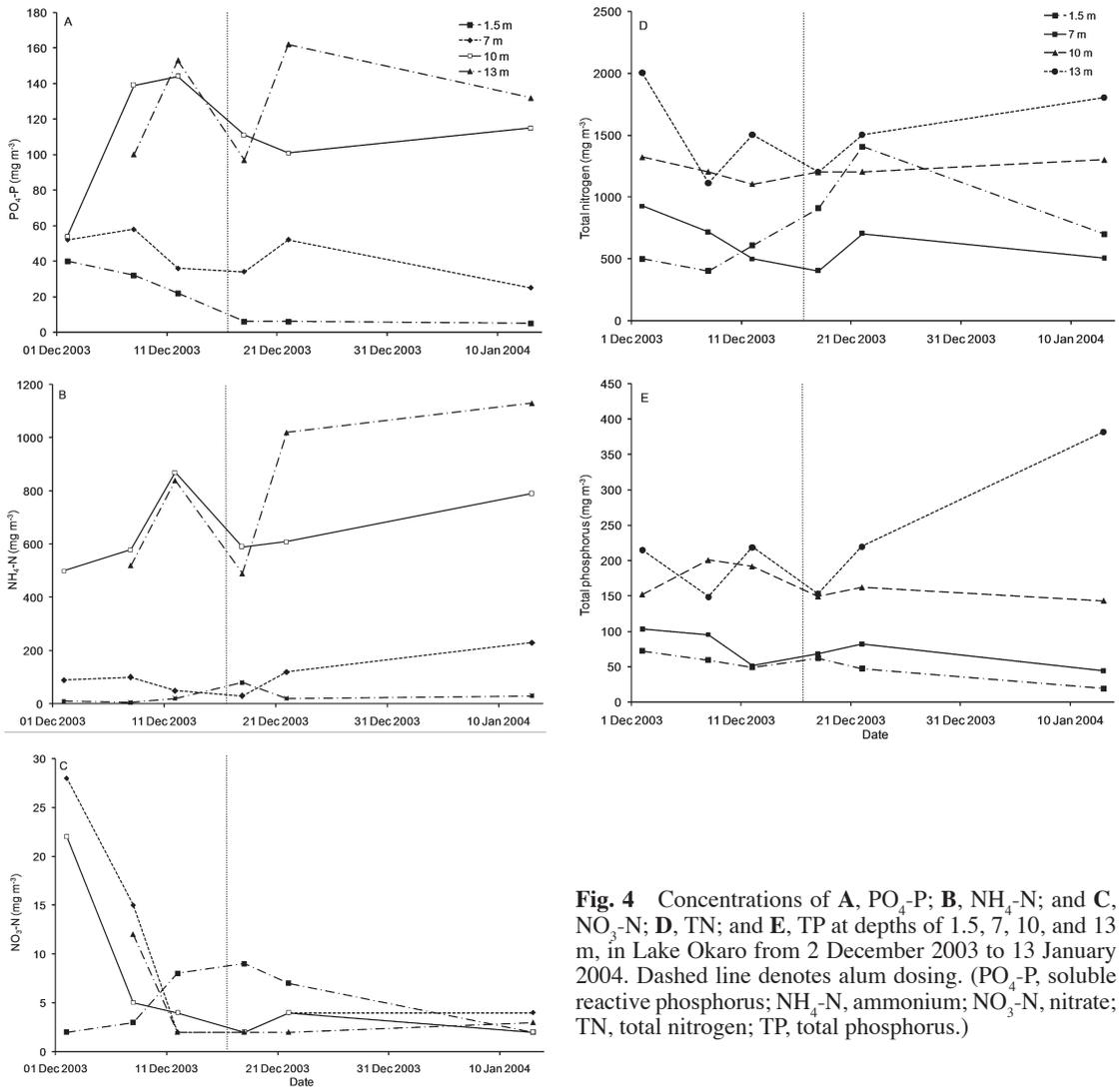
Between 2 December 2003 and 13 January 2004, pH ranged from 8.6 to 9.7 at the surface (1 m) and 5.5 to 6.3 at 13 m depth, whereas around the thermocline (4.7–5.9 m) it was mostly in the range 6–8 (Fig. 3). pH increased at each depth sampled in the period from 8 to 18 December 2003 and generally decreased from 18 December 2003 to 13 January 2004, when it was below 6 through the hypolimnion (Fig. 3).

Between 2 and 18 December 2003, concentrations of  $\text{PO}_4\text{-P}$  decreased from  $40$  to  $6 \text{ mg m}^{-3}$  in the epilimnion with a further decrease to  $5 \text{ mg m}^{-3}$  by 13 January 2004 (Fig. 4A). Hypolimnetic concentrations of  $\text{PO}_4\text{-P}$  varied throughout the

sampling period, but there was a decrease at all depths after the alum application (Fig. 4A). On the day following the alum application, concentrations of  $\text{NH}_4\text{-N}$  decreased by c. 40% at 7, 10, and 13 m but increased four-fold at 1.5 m (Fig. 4B). There was a general trend of increases in  $\text{NH}_4\text{-N}$  at all depths between 2 December 2003 and 13 January 2004 (Fig. 4B). Concentrations of  $\text{NO}_3\text{-N}$  decreased from 25 to  $2 \text{ mg m}^{-3}$  in the hypolimnion from 2 to 12 December 2003, then remained low ( $<5 \text{ mg m}^{-3}$ ) over the remainder of sampling. Concentrations of  $\text{NO}_3\text{-N}$  in the epilimnion were consistently low ( $<13 \text{ mg m}^{-3}$ ) throughout sampling (Fig. 4C). Concentrations of TN fluctuated most at 1.5 m depth, whereas TP fluctuated most at 13 m depth (Fig. 4D,E).

Mass ratios of TN:TP in the epilimnion increased from 7:1 on 2 December 2003 to 37:1 by 13 January 2004. In the hypolimnion, ratios varied little from 2 December 2003 to 13 January 2004 (Fig. 5A). Mass ratios of hypolimnetic dissolved inorganic nitrogen (DIN): soluble reactive phosphorus ( $\text{PO}_4$ ) decreased from 6.1 to 4.9 in the period 2–18 December 2003 then increased to 8.3 by 13 January 2004 (Fig. 5B). Epilimnetic DIN: $\text{PO}_4\text{-P}$  was extremely low at 0.3 to 1.3 before the alum application, but was 14.8 on 18 December 2003, the day following dosing (Fig. 5B).

Chlorophyll *a* concentrations at 1.5 m depth were highest at  $110 \text{ mg m}^{-3}$  on 22 December 2003 and lowest at  $3 \text{ mg m}^{-3}$  on 8 December 2003 (Fig. 6). The peak of phytoplankton biomass occurred in the sample taken 3 days after the peak Chl. *a* concentration, but phytoplankton biomass and Chl. *a* concentrations mirrored each other closely,

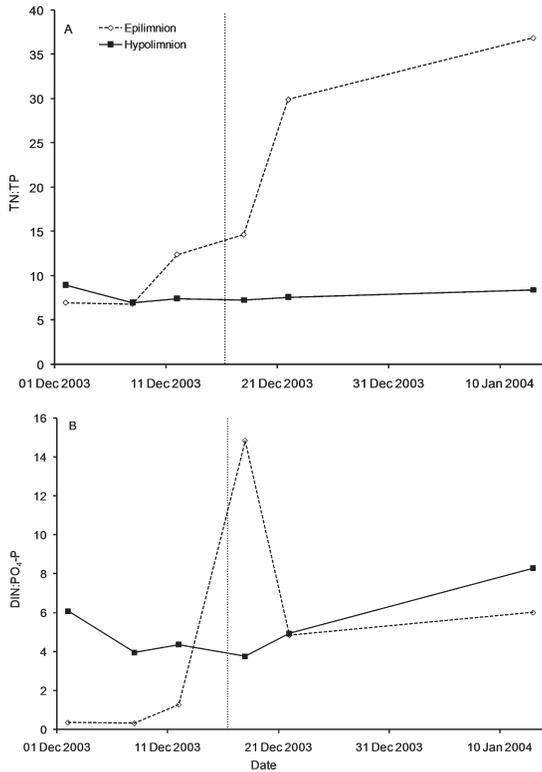


**Fig. 4** Concentrations of **A**,  $\text{PO}_4\text{-P}$ ; **B**,  $\text{NH}_4\text{-N}$ ; and **C**,  $\text{NO}_3\text{-N}$ ; **D**, TN; and **E**, TP at depths of 1.5, 7, 10, and 13 m, in Lake Okaro from 2 December 2003 to 13 January 2004. Dashed line denotes alum dosing. ( $\text{PO}_4\text{-P}$ , soluble reactive phosphorus;  $\text{NH}_4\text{-N}$ , ammonium;  $\text{NO}_3\text{-N}$ , nitrate; TN, total nitrogen; TP, total phosphorus.)

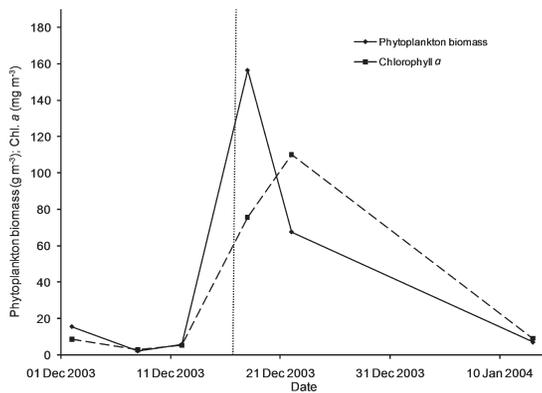
with a rapid increase in both variables between the samples collected on 12 December 2004, before alum dosing, and on 18 December 2004 soon after alum dosing (Fig. 6). Chl. *a* concentrations were closely correlated with phytoplankton biomass ( $r = 0.87$ ,  $P < 0.01$ ,  $n = 6$ ). Amongst the phytoplankton assemblage at 1.5 m depth, the dominant genera or species were *Anabaena* spp., *Ceratium hirudinella*, *Dictyosphaerium* sp., *Nephrocystium agardhianum*, *Oocystis* sp., *Peridinium* sp., *Microcystis aeruginosa*, and *Staurastrum* spp. *Ceratium hirudinella* dominated phytoplankton biomass on 2, 18, and 22 December 2003, measuring 52–82% of total biomass (Fig. 7). *Staurastrum* spp. dominated on 8 December 2003 and 13 January 2004 with 42

and 60% of total biomass, respectively, and on 12 December 2003, *Anabaena* spp. constituted 51% of the total phytoplankton biomass (Fig. 7).

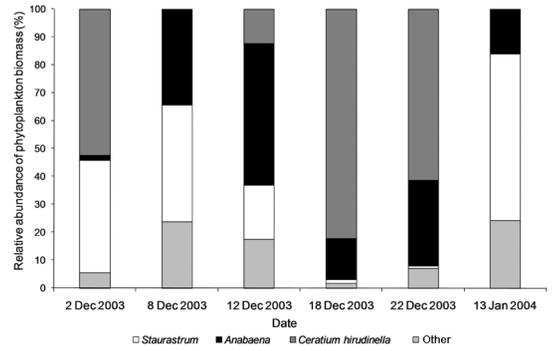
There was a significant difference between trapping rates before and after the alum application at all depths ( $F = 9.84$ , d.f. = 1,  $P < 0.005$ ) and between individual depths ( $F = 9.04$ , d.f. = 2,  $P < 0.005$ ). Sediment trapping rates increased after alum dosing, by 19% at 3 m, 51% at 6 m, and 26% at 9 m depth (Fig. 8A). Particulate Al trapping rates were significantly greater after alum dosing (16–19 December 2003) than before (11–16 December 2003), at all depths ( $F = 114.3$ , d.f. = 1,  $P < 0.001$ ) and between individual depths ( $F = 75.64$ , d.f. = 2,  $P < 0.001$ ; Fig. 8B).



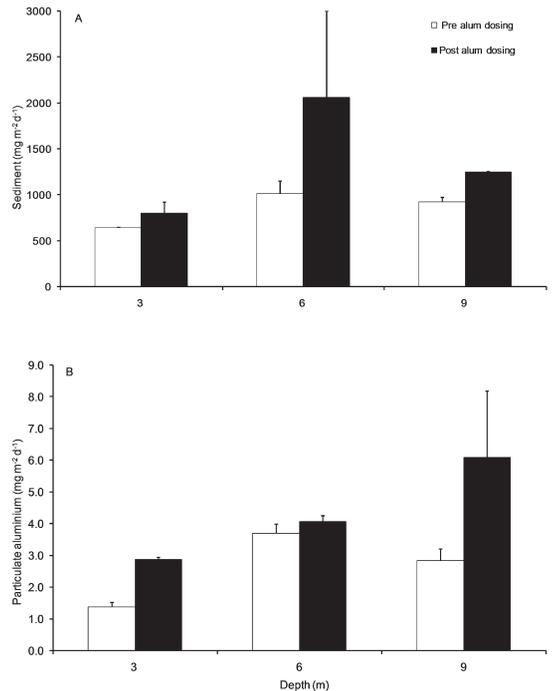
**Fig. 5** Mass ratios of **A**, TN:TP; and **B**, DIN:PO<sub>4</sub>-P in Lake Okaro from 2 December 2003 to 13 January 2004. Dashed line denotes alum dosing. (TN, total nitrogen; TP, total phosphorus; DIN, dissolved organic nitrogen; PO<sub>4</sub>-P, soluble reactive phosphorus.)



**Fig. 6** Chlorophyll *a* concentrations and phytoplankton biomass at 1.5 m depth in Lake Okaro from 2 December 2003 to 13 January 2004. Dashed line denotes alum dosing.



**Fig. 7** Relative abundance of dominant phytoplankton species by percentage biomass in Lake Okaro from 2 December 2003 to 13 January 2004.



**Fig. 8** Trapping rate (mean + SE) of **A**, sediment and **B**, particulate aluminium at depths of 3, 6, and 9 m for 11–16 December 2003 (pre alum dosing,  $n = 9$ ) and 16–19 December 2003 (post alum dosing,  $n = 8$ ) in Lake Okaro.

## DISCUSSION

The effectiveness of alum dosing, based on changes in trophic status indicators such as Chl. *a* and TP concentration in the epilimnion over the sampling period, was somewhat variable. Decrease in TP and increase in Chl. *a* indicate that there may have been some flocculation of phosphorus resulting from the alum application, but that phytoplankton may not have been strongly phosphorus-limited, perhaps as a result of sufficient internal phosphorus stores or limitation by some other factor such as nitrogen.

A number of factors may have influenced the effectiveness of the alum application in Lake Okaro, namely dose rate, timing of the application in relation to water column pH, and availability and concentrations of different phosphorus species. The application rate to Lake Okaro was very low. Treatments of lakes elsewhere have ranged from 0.05 to 30 g m<sup>-3</sup> as soluble aluminium (Al<sup>3+</sup>) (Lund & Chester 1991; Welch & Cooke 1999; Van Hullebusch et al. 2002). This low dose rate was applied because Lake Okaro has low alkalinity (Timperley & Vigor-Brown 1986) and there was a risk of substantial decrease in alkalinity and pH with the alum application. Low buffering capacity and high levels of inorganic carbon assimilation from phytoplankton production in Lake Okaro resulted in pH exceeding 9 in the epilimnion, both before and after dosing. At this pH, floc formation is unlikely, phosphorus sorption capacity is reduced (Koski-Vähälä & Hartikainen 2001), and soluble aluminium may be more persistent. Soluble aluminium concentrations following dosing remained above recommended guidelines for protection of 95% of freshwater species (ANZECC 2000) for at least 3 months (Fig. 2B). At these levels there is potential for fish mortality (Neville 1985), though no fish deaths were reported in the lake. By contrast, pH in the hypolimnion was mostly below the recommended lower limit for adsorption of pH 6 (Cooke et al. 1993). Nevertheless, there were decreases in concentrations of most nutrient species in the hypolimnion immediately after dosing (Fig. 4) although these decreases were temporary, possibly owing to exhaustion of the aluminium sorption capacity, burial of the floc blanket on the bottom sediments (Lewandowski et al. 2003) or bioturbation.

Following alum dosing, there was a progressive decrease in the proportion of soluble to total aluminium with depth (Fig. 2) and an increase in particulate aluminium in the sediment traps (Fig. 8B). There was also a decrease in phosphate concentrations in

the epilimnion after dosing, but at the time of dosing Lake Okaro, epilimnetic concentrations of phosphate were relatively low (Fig. 4A) and comprised only a small proportion of the total phosphorus pool. Most phosphorus in surface waters was therefore likely to have been present within phytoplankton cells or associated with other organic particulates in forms less easily adsorbed by alum flocs than free phosphate ions (Cooke et al. 1993). Alum dosing applications therefore require careful consideration of the abundance and availability of different forms of phosphorus and the relative adsorption capacity of these forms.

A four-fold increase in concentrations of ammonium in the epilimnion (Fig. 4B) soon after alum dosing was similar to that noted by Özkundakci (2006) in mesocosm trials to simulate alum dosing in Lake Okaro. Increased mortality of zooplankton has been observed at relatively low aluminium concentrations (80 µg Al<sup>3+</sup> litre<sup>-1</sup>; Peterson et al. 1976). Mineralisation of dead organisms, including zooplankton, by heterotrophic bacteria might therefore explain the observed increase in ammonium, though mortality of heterotrophic bacteria from alum dosing should also not be discounted. The increase in epilimnetic NH<sub>4</sub>-N which coincided with a decrease in PO<sub>4</sub>-P the day following alum dosing may have led to a reduction in N-limitation of phytoplankton, possibly leading to a shift in numerical dominance from heterocystous, N-fixing *Anabaena* spp. cells to the larger, motile dinoflagellate cells of *C. hirudinella* that compete well for inorganic nitrogen when it becomes available (Reynolds 1997; Graham & Wilcox 2000).

The optimal period for a whole lake alum application in Lake Okaro is likely to be from June to August (winter) when the lake is isothermal (Dryden & Vincent 1986) and pH is well within the recommended range of 6 to 8 throughout the water column. This period of winter mixing is also associated with high concentrations of dissolved oxygen (McCull 1972), however, which would result in a greater proportion of inorganic phosphorus in complexes with redox-sensitive ferric oxides, reducing the potential for formation of aluminium oxides (Søndergaard et al. 2003). Cooke et al. (1993) recommend applications of alum in summer before the occurrence of cyanobacterial blooms and when the pH of the entire water column is in the optimal range for flocculation of 6 to 8, but also when DO concentrations in the hypolimnion are sufficiently low to induce phosphate release from bottom sediments.

Based on historical data (Dryden & Vincent 1986), this period would generally be around September to October in Lake Okaro. A further complication in relation to pH and optimal timing of the dose is that denitrification increases alkalinity (Kadlec & Knight 1996) and this process may have been responsible for an increase in pH in the hypolimnion (8–18 December) that more than compensated for decreases in pH produced by hydrolysis reactions following the alum application (Fig. 3 and 4C).

Problems with pH affecting phosphorus adsorption by alum may also be alleviated by dosing that targets discrete layers of the water column. Concentrations of soluble iron and manganese in the hypolimnion of Lake Okaro have been found to be significantly higher than in five other Rotorua lakes; an observation by McColl (1972) that he related to the highly reducing conditions in the hypolimnion of Lake Okaro. Hence, hypolimnetic applications of alum following stratification could be used when redox potential is reduced sufficiently to favour phosphorus complexation with aluminium, as opposed to oxides and hydroxides of iron and manganese. Addition of a buffering agent such as lime whilst applying alum below the hypolimnion could also be considered if the combination of suitably low redox potential and pH >6 proved difficult to attain.

This study represented an opportunity to document the effects of the alum application on the Lake Okaro ecosystem by collectively enlisting management authorities and research providers, to provide an integrated monitoring approach. Variations in sampling dates and depths between these groups and limited repetition, however, made it difficult to derive statistically significant relationships between variables. The focus of our study was to elucidate short-term responses to alum dosing, but further research is required to document the intermediate and long-term effects of alum dosing on Lake Okaro.

It is somewhat counter-intuitive that highly eutrophic lakes experiencing hypolimnetic anoxia and phytoplankton blooms may not be well suited for alum applications to manage phosphorus levels, particularly when they are poorly buffered. However, discrete applications of alum to the hypolimnion, addition of buffers, and timing of applications based on seasonal patterns of temperature, dissolved oxygen, redox potential and pH profiles could enable use of a higher concentrated alum dose, reduce potential for toxicity and optimise effectiveness of applications.

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