Taihoro Nukurangi

Alum treatment for rehabilitation of Lake Okaro: ecological surveys and response of sedimentation rates to initial low alum dose trial

NIWA Client Report: HAM2004-052
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NIWA Project: BOP04219

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Prepared for

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Executive Summary

I. Alum dosing to strip phosphorus was trialled as an in-lake restoration measure for the first time in New Zealand in Lake Okaro, a eutrophic lake near Rotorua. Sufficient alum was added by Environment Bay of Plenty (EBOP) to increase the aluminium concentration in the epilimnion (surface water, above a thermocline at c. 4 m) by approximately 0.5 g m^{-3} on 16-18 December 2003.

II. NIWA was contracted by EBOP to measure the effects of the addition on particle settling rates and carry out baseline ecological studies on the plant communities. We also carried out surveys of invertebrate macrofauna (koura/crayfish and kakahi/mussels) and laboratory studies on the relationship between aluminium concentrations, floc formation, phosphorus removal, pH and toxicity to cladoceran zooplankton (*Daphnia* spp.), funded by FRST in the Restoration of Aquatic Ecosystems programme.

III. Prior to alum addition, the perennial, creeping herbs *Glossostigma submersum* and *Glossostigma elatinoides* occurred in the shallows (to 0.8 and 0.4 m depth respectively) and the oxygen weed *Elodea canadensis* occurred to 2.2 m. The turf forming perennial *Lilaeopsis ruthiana* occurred in the shallows at one of five transects. A mat of algae covered the lakebed down to at least 8 m depth.

IV. No koura or kakahi were found in the lake or the main inlet stream.

V. Bullies (*Gobiomorphus cotidianus*) were abundant above the narrow band of oxygenated lake bed around the lake margins to c. 4 m. However, between late November 2003 and early March 2004 (2.5 months after alum dosing) mean abundance declined and larger (2 and 3 year old) fish disappeared from the catch. This may reflect post-spawning mortality or a changed depth distribution, but could also be a response to alum because aluminium concentrations in excess of the ANZEEC guidelines for protection of aquatic life (0.055 g m^{-3}) occurred for 2 months after dosing.

VI. An algal bloom that was in progress when the alum was added obscured effects of alum dosing on particle settling rates and phosphorus concentrations. Particle settling rates increased at 6 m depth after alum application, but this could be explained by an increase in settling rates associated with the algal bloom. EBOP monitoring showed that aluminium concentrations in the surface waters did not decline abruptly, as would be expected if binding to phosphorus and floc formation was occurring. Dissolved aluminium concentrations at 1-3 m depth declined from 0.30 to 0.15 g m^{-3} over two months after dosing, with total aluminium showing a similar pattern of decline from an initial concentration of 0.50 g m^{-3}. The dissolved Al concentrations markedly exceed the ANZECC guideline for this entire period.

VII. Laboratory trials on effects of aluminium concentration (0.5 to 40 g m^{-3}) on Lake Okaro surface water quality showed a marked reduction in pH at 10 g m^{-3} (from pH 7.4 to 5) and no *Daphnia* survival at the alum dosings resulting in $\geq$ 2 g Al m^{-3}, despite relatively minor effects on pH at doses up to 5 g Al m^{-3}. It is not known whether this impact was due to aluminium toxicity or entrapment of *Daphnia* in $Al(OH)_3$ floc.

VII. These results indicate that the initial low dose addition of alum to surface waters in Okaro has not been immediately effective. Factors that probably contributed to this are: (1) high pH (>8) at the time of the application due to an algal bloom reducing the formation of Aluminium hydroxide polymer flocs; (2) the low level of available P at the time resulting from the algal bloom; and (3) the low dose rate. This confirms EBOP's initial judgement that repeat alum dosing over several years will be necessary for low doses to provide control of P and hence nuisance blue-green algal blooms in Lake Okaro. The effectiveness of future alum additions to Okaro is likely to be improved by combinations of: (i) increasing the dosing rate within the constraints of the buffering capacity of the lake water and toxic effects on biota; (ii) adding the alum to hypolimnetic water, if done under stratified conditions, or during winter, when the lake is unstratified, more dissolved P is available in the water column, while pH <8.

VIII. Further research to guide future alum treatment in Okaro should include: (i) sampling of bully populations for abundance and size structure in November 2004 to better evaluate the apparent effects of the low dose alum treatment on these fish; (ii) measurement of the mobile P levels in the surface sediments of the lake bed to determine appropriate alum dose rates to bind that P and related laboratory trials on the actual effectiveness of addition of alum at the levels derived from P availability tests; (iii) laboratory trials of alum dose responses of Lake Okaro hypolimnetic water to evaluate effects of alum concentration on pH, floc formation and dissolved Al; and (iv) laboratory trials on the effects of phosphorus concentration and high pH on floc formation and P stripping in Okaro surface waters. While the above laboratory tests would advance our knowledge of key processes influencing the effectiveness of alum dosing, field experiments using limno-corals (i.e., plastic tubes that isolate columns of lake water and sediment) are also recommended to test the overall environmental effects and sustainability of revised approaches.

1. Introduction

Lake quality criteria in Environment Bay of Plenty's (EBOP) Water and Land Plan indicate that five of the region's lakes need action to bring about improvement. A number of remedial methods are being investigated and trialed by EBOP. Alum dosing to control lake phytoplankton growth by reducing phosphorus has been used widely overseas (e.g., Cooke et al. 1986; Welch & Cooke 1995; Welch & Cooke 1999) and has potential for use in embayments and small lakes, such as Lake Okaro, near Rainbow Mountain. This lake has the poorest quality of the Rotorua lakes and is small enough, at 32 hectares (McIntosh 2003), for alum treatment to be practicable.

The nitrogen: phosphorus (N:P) ratio of Okaro indicates that phytoplankton growth is balanced to nitrogen-limited (McIntosh 2003). Blue-green algae blooms, that are favoured over green algae by N-limited conditions, have been a particular problem in recent years (Wilding 2000). Phosphorus removal by alum dosing has the potential to both reduce the overall phytoplankton growth and increase the N:P ratio, thus reducing the competitive advantage to blue-green algae that can fix atmospheric N. A large proportion of the nutrient loading to the lake is internal, resulting from nutrient release from the sediment under anoxic conditions when the lake stratifies each summer (median values of 0.38 tonnes P yr^{-1} and 2.4 tonnes N yr^{-1}, representing approximately 78% and 47% of total load respectively, Table 5 in McIntosh 2003). This means that eutrophication management in this lake needs to include controls on the internal loads.

This trial was the first use of alum for in-lake remediation in New Zealand and forms part of an EBOP programme for rehabilitation on Lake Okaro that also includes land management options (e.g., use of artificial wetlands and riparian fencing). The basis of alum treatment is the depletion of inorganic phosphorus (P) in the water column and sediments through formation of Aluminium-Phosphorus complexes. When alum is added to the lake water at pH 6-8, it forms predominantly settlable, polymerised aluminium hydroxide, and P is removed by $AlPO_4$ precipitate, via sorption of P on the surface of $Al(OH)_3$ polymer of floc, and by entrainment and sedimentation of P-containing particulate matter in $Al(OH)_3$ floc (Cooke et al. 1986). The settled Al hydroxide floc can form an "Al blanket" at the sediment surface preventing further P release, provided that the rate of sediment P release is not sufficient to swamp the available aluminium. This can control the "internal loading" of P from lake sediments that is usually caused by anoxic conditions leading to reduction of iron (Fe) and subsequent return of both iron and sorbed phosphate to solution (Mortimer 1941).

Appropriate alum doses for precipitation of P from lake waters are often determined based on the acid neutralising capacity of the lake water with the objective of maintaining pH high enough (i.e., >6) to prevent aluminium toxicity (toxic Al (III) predominates at low pH) (Cooke et al. 1986). Acid neutralising capacity provides a guide on how much alum can be added without causing pH <6. However, this method may lack effect in many cases because it does not consider mobile P in sediments, which is the cause of the lake's internal P loading. Alum doses have also been determined from the amount of Al required to bind the measured mobile P (loosely sorbed P + Fe-P) in the top 4 cm of lakebed sediment (Rydin & Welch 1999). In the Okaro case, EBOP set the target for alum dosing at a level to increase the surface water Al concentration to 0.5 g m^{-3} with the aim of evaluating whether a "low alum dose approach" would be effective in phosphorus removal while avoiding potential toxic effects that could occur at higher doses (pers. comm. John McIntosh, EBOP). It was envisaged that further annual treatments would probably be required for up to 5-10 years for effective control of the inlake P levels, and hence blue-green algae blooms, given the highly eutrophic state of the lake.

EBOP contracted NIWA to carry out a general ecological survey of the lake prior to alum addition to characterise baseline conditions against which change could be measured, and to measure the immediate effects of alum addition on sedimentation rates of aluminium and algal particles. The ecological studies focus on the macrophytes, macroscopic invertebrates (crayfish/koura and mussels/kakahi) and benthic fish, and our studies complement research on the responses of lake chemistry and plankton (by University of Waikato), and routine water quality monitoring by EBOP (EBOP monitoring results are included in this report). Forest Research undertook a single initial sampling of lake fish population size (trout, smelt and bullies) with a view to investigating the long-term effects of changes in trophic status (pers. comm. Mike van den Heuvel).

NIWA also conducted preliminary laboratory experiments on the effects of alum addition to Lake Okaro water on flocculation, pH, nutrient removal and grazing cladocerans, funded by the FRST Restoration of Aquatic Ecosystems programme, and the findings are included in this report.

2. Methods

2.1 Macrophyte surveys

Submerged vegetation was surveyed prior to alum treatment (25/11/2003) using the survey method of Clayton (1983b) where SCUBA divers recorded vegetation presence along a depth profile at 5 sites within the lake (Fig. 1). Observations included the depth range of each species encountered. In addition, the average species cover within the depth range was noted and maximum cover present in any 2 m^2 area was recorded following the modified Braun-Blanquet cover scale:

1 = 1-5% cover, 2 = 6-25%, 3 = 26-50%, 4 = 51-75%, 5 = 76-95%, 6 = 96-100%

Average and maximum height was recorded for plants growing over 0.1 m tall.

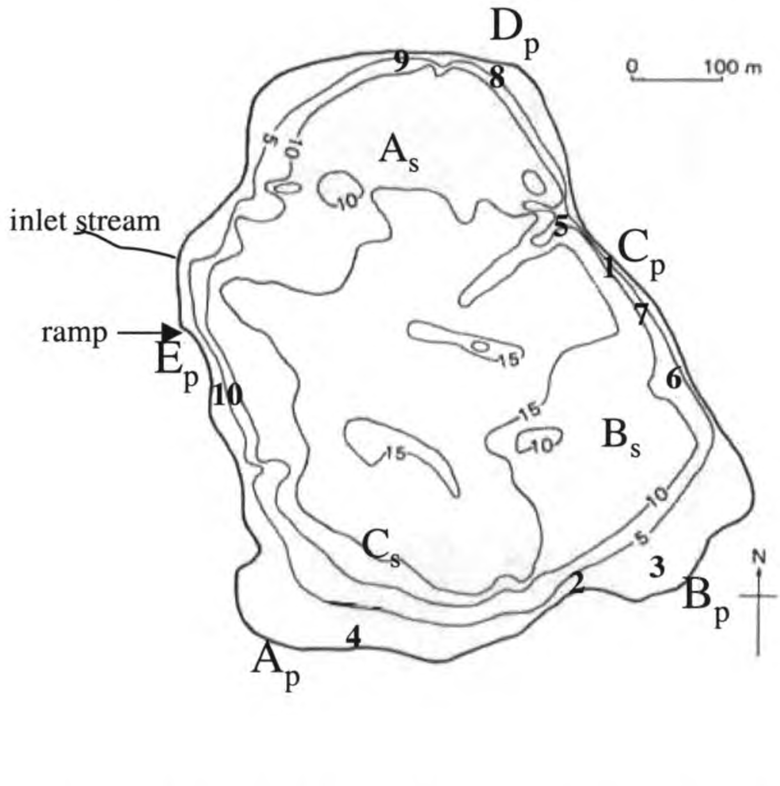


Figure 1: Lake Okaro location map showing points on shoreline from which macrophyte profiles were extended into the lake perpendicular to the shore (A_p-E_p), sediment traps (A_s-C_s), and the g-minnow sampling sites (1-10).

Biomass samples of *Elodea canadensis* were collected from 1 site (Site B, Fig. 1) by removing all material from 5 replicate 0.1 m areas. Samples were dried (80°C) to constant weight (±0.01 g).

Sediment cores were collected using 1 m long perspex tubes at c. 8 m depth at each of the 5 macrophyte survey lines and photographed to display the nature of the surficial sediments and benthic microbial growth. Lakebed sediment was also sampled at c. 8 m depth using an Ekman grab from which a core (7.5 cm ID) was taken and separated into the surficial microbial/detrital mat (top 0-1 cm), upper sediment layer (1-5 cm) and underlying sediments (5-10 cm). These cores were labelled and stored frozen in case they were needed later for sediment chemistry studies (currently stored in the upright freezer in the Ecotoxicology Laboratory, NIWA Hamilton).

2.2 Koura, kakahi and bully surveys

SCUBA searches for koura and kakahi were made at each of the macrophyte transects and broader areas of the lake bed were surveyed for the presence of koura and kakahi using an underwater camera lowered from a cable from a boat. G-minnow baited traps (with perforated sachets of "Chef Ocean Bounty" catfood and either "Friskies" catfood pellets or burley-bait pellets) were set at 2-3 m depth near the shore in the epilimnion at each of the 5 survey sites overnight on 25-26 November 2003 in an attempt to catch koura and bullies. Bullies caught were counted (to measure catch per unit effort, CPUE) and, at two sites (4 and 10), representative samples measured for length. The main tributary stream was inspected for presence of macrophytes, koura and kakahi near the lake inlet.

Minnow trapping was repeated in mid-March 2004 at four sites (sites 1, 3, 4 and 7) to measure bully CPUE and size range to evaluate the medium term effects of alum dosing on these abundant benthic fish.

2.3 Sedimentation rates

Sedimentation of algae and aluminium was measured at depths of 3 m, 6 m and 9 m at 3 sites at the 11 m bottom depth contour on the north eastern (Site A_s), south eastern (site B_s) and south western (site C_s, near pumps) sides of the lake. Trap arrays were lowered into the lake, and filled with lake water as they descended.

Sediment trap cups consisted of a 0.5 m x 6.2 cm ID plastic tube terminated with a nalgene funnel and a 6 mm bore tap at the bottom (Fig. 2). A quick dump release hole

25 mm ID was drilled into the tube at the mid-point of the tube length, and covered with a single layer of parcel tape. This hole is needed to release the upper water column in the trap immediately on recovery to eliminate contamination from upper-layer water entering the trap on retrieval. Wooden frames, each holding three trap cups, were attached to a rope 1 m above the sediments, just below the thermocline (6 m deep) and in the epilimnion (3 m deep). The rope was held taut between a bottom weight and a subsurface float (2 m deep) and a surface marker from the subsurface float was used to locate the trap array. Prior to installing the sediment trap array, the inside of each trap cup was scrubbed clean with a large soft mop/brush, the tap inspected, cleaned and closed, and a new piece of parcel tape fitted over the quick release hole.

Prior to recovery of the trap arrays, a water column sample was collected (van Dorn sampling bottle) at the depth of the top of the trap cups at each site. When the traps were lifted, the parcel tap was broken with a knife and the upper water column in the trap cups allowed to spill. The remaining contents of the trap cup were run into a 1-litre bottle through the tap. The water samples were transported to the laboratory on crushed ice, then processed immediately.

The total volume from each cup was measured and then, after mixing, the samples were partitioned for chlorophyll *a* and suspended solids analyses. For chlorophyll *a*, duplicate aliquots were filtered through untreated 2.5 cm Whatman GF/C glass fibre filters, extracted with 95% acetone and measured spectrophotometrically.

For suspended solids, duplicate aliquots (either 100 ml or 250 ml) were filtered under reduced pressure (20%) through pre-combusted (500°C), pre-weighed 2.5 cm Whatman GF/C glass fibre filters. Aliquots of the ambient water at each depth were also filtered. The filters were air-oven dried at 60°C overnight then weighed to constant weight. The sediment trapping rate was calculated as the mass caught per unit time through the area of the trap cup in g m^{-2} day^{-1}. Settling velocity (m day^{-1}) at each trap depth was estimated by dividing the trapping rate at each depth by the concentration at that depth.

These filters were subsequently analysed for total aluminium (Al) by R.J. Hill Laboratories. Trapping and settling rates for Al were calculated as for the suspended solids. It is assumed that if Al is linked to the suspended solids, the ratio of trapping rates and the settling velocities will be the same.

Figure 2: Sedimentation traps being retrieved from Lake Okaro on 19 December 2003.

Trap arrays were installed on 11/12/2003 between 13:00 and 15:00 and retrieved and reset on 16/12/2003 between 06:30 and 08:00, just prior to alum dosing commencing on the same day, then retrieved and removed on 19/12/2003 between 12:00 and 13:30 (daylight saving time). On each lake visit, Secchi depth was measured, and dissolved oxygen and temperature vertical profiles were made. Samples were also collected at 3, 6 and 9 m depths on 16 and 19 December 2003 and analysed for DRP, TDN, DOP, NH_4-N, NO_3-N, DON and Chlorophyll *a*, *b*, and *c*.

2.4 Laboratory alum dosing trials

The effects of addition of alum to Lake Okaro surface (epilimnetic) water were investigated at a range of alum dosing levels in the laboratory. Twenty litres of water were collected on 8 March 2004 and maintained under constant aeration in the laboratory for use in the two trials starting on 17 and 18 March.

In Trial 1, 1 litre measuring cylinders were filled with Lake Okaro water to which alum was added to give final aluminium concentrations of 0, 5, 10, 20, 40 g m^{-3}. This includes the range of concentrations commonly used in successful alum additions for in-lake P control overseas (e.g., Cooke et al. 1986; Welch & Cooke 1999). Alum was added to the top of the measuring cylinders and mixed using a pipette. Background dissolved reactive phosphorus (DRP) concentrations were raised by 50 mg DRP m^{-3} as Na_2HPO_4, except in the experiment control (no additions) and a P enhancement control (no P added, but alum increased to 5 g Al m^{-3}), because of expectations that background levels were likely to be too low for the effects of alum on P precipitation to be observable. We added 10 cladoceran grazers (*Daphnia magna*) to each treatment. After 24 hours, we photographed the waters to show settling of floc, measured pH, turbidity of the surface water, and counted the number of surviving cladocerans. DRP and aluminium concentrations were also measured for the 5 g m^{-3} aluminium treatment by ICP-MS at Hill Laboratories (detection limits = 0.02 and 0.003 g m^{-3}, respectively).

Trial 2 was conducted using the same protocol as Trial 1 but at lower aluminium concentrations of 0.5, 1, 2 and 4 g m^{-3}, after Trial 1 showed marked pH declines at Al levels >5 g m^{-3} and no cladoceran survival in any of the Al additions (see below). The native cladoceran *Daphnia carinata* was used in this trial.

3. Results and discussion

3.1 Submerged vegetation

The submerged vegetation comprised 4 species and was very similar in composition to the earlier data (Table 1), with the introduced weed *E. canadensis* dominant. At the time of the recent survey, *E. canadensis* plants were only rooted to a maximum depth of 2.2 m, but comprised drift material in deeper depths. This drift material was exclusively of stems without a root crown or roots.

The average biomass of rooted *E. canadensis* was 85.0 g m^2 (±36.7 SD).

Comparison of the recent survey results with previous surveys (Table 1) shows variation in the depth extent and frequency (proportion of sites) of rooted *E. canadensis*. For example, two months before the recent survey along the same survey transects (Table 1, 17/09/2003), *E. canadensis* beds were recorded to 4.6 m depth and were present at all investigated sites.

Table 1: Summary of submerged vegetation development in Lake Okaro according to available NIWA records.

Technique	Date	Species	No. of sites present	Depth range		Cover scale		Height	
				Min	Max	Ave	Max	Ave	Max
Survey	19/10/1989	*Elodea canadensis* Michaux	2/5	0.5	2.7	1/2	3		0.5
		Glossostigma elatinoides Benth.	2/5	0.5	0.5	1	2	-	-
		Lilaeopsis ruthiana J.M. Affolter	1/5	0.5	0.5	1	1	-	-
		Myriophyllum pedunculatum Hook.f.	1/5	0.5	0.6	2	3	-	-
		Myriophyllum triphyllum Orchard	1/5	0.5	0.5	1	1	-	-
LakeSPI	24/04/2002	*Elodea canadensis* Michaux	8/8	0.5	5				0.35
		Glossostigma sp.	2/8		0.5				
LakeSPI	17/09/2003	*Elodea canadensis* Michaux	5/5	0.3	4.6				0.5
		Glossostigma elatinoides Benth.	2/5		0.5				
		Glossostigma submersum Petrie	2/5		0.6				
		Lilaeopsis ruthiana J.M. Affolter	1/5		0.5				
Survey	25/11/2003	*Elodea canadensis* Michaux	3/5	0.3	2.2	3	6	0.5	0.6
		Glossostigma submersum Petrie	2/5	0.3	0.8	5	6	-	-
		Glossostigma elatinoides Benth.	2/5	0.1	0.4	3/5	6	-	-
		Lilaeopsis ruthiana J.M. Affolter	1/5	0.3	0.8	2	2	-	-

The lower depth limit of *Elodea canadensis* in Lake Okaro appears to be relatively unstable with unusually large variations in the extent and depth range of weed beds apparent over time. Specifically, there had been a big regression in the maximum depth for *E. canadensis* between mid-September and late November, 2003. It appears that plants growing in the deeper littoral (2.2. to 4.6 m) suffered root mortality and then persisted as drift debris. Possible causes of this change are a de-oxygenation event that extended to within a few metres of the water surface, or an extended turbid event which meant plants could not maintain a photosynthetic oxygen supply to their roots. If Environment BOP could detect evidence of either event within the water quality data that is collected at Lake Okaro, then we would get a better understanding of the cause of this vegetation instability.

Cores of the lakebed showed a thick algal/microbial mat covered the bed (Fig. 3 & 4). The top 1 cm was green with a whitish biofilm on the top surface, we suspect was sulphur-oxidising bacteria (e.g., *Beggiatoa*). Beneath this surface layer was an organic layer of about 5 cm thickness, then the sediments became more inorganic, changing to lighter brown and then to grey with increasing depth.

Figure 3: Lake Okaro sediment core at site E_p adjacent to (east of) the boat-ramp on 24/11/03 showing whole core and a close-up of the surface material.

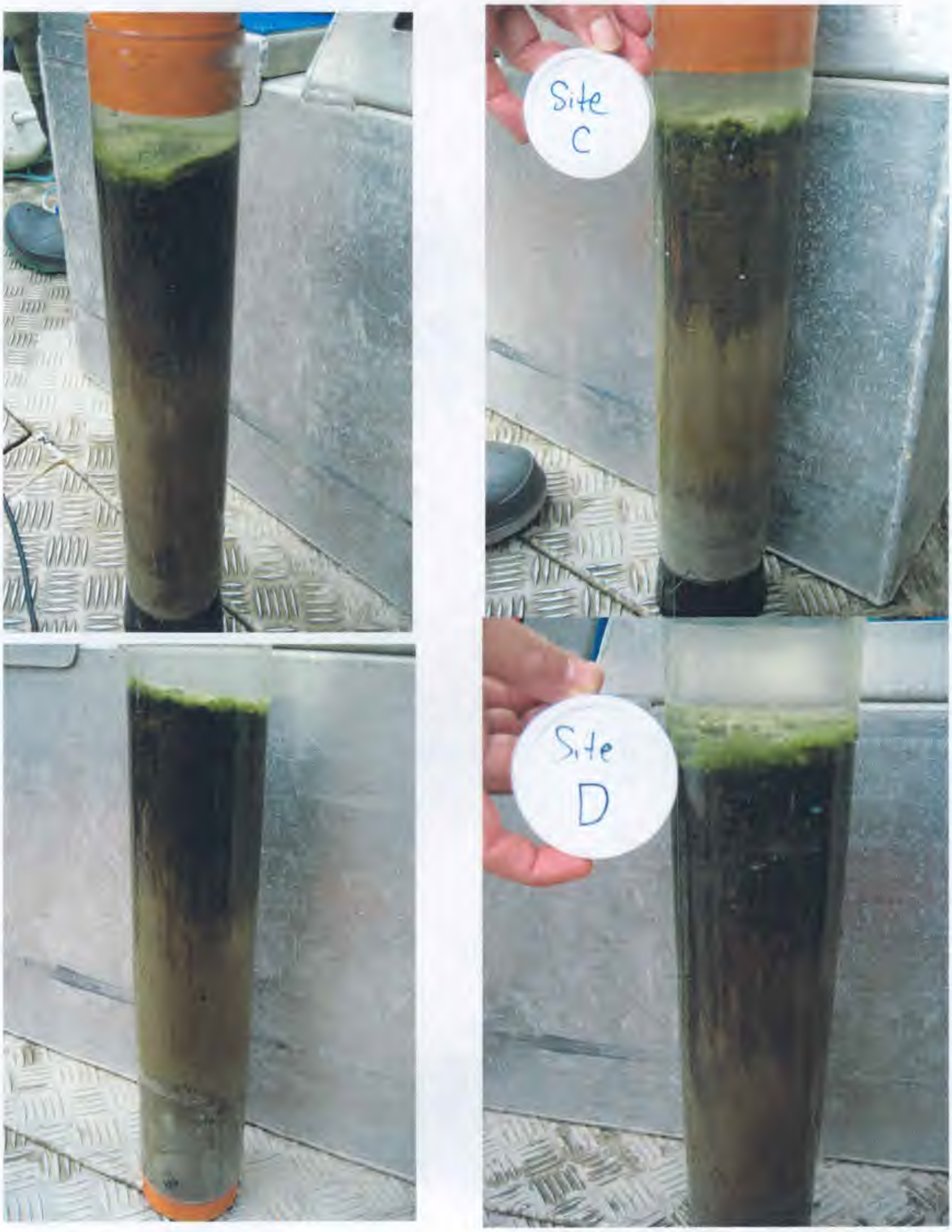


Figure 4: Photographs of Lake Okaro sediment cores collected from 8 m depth at sites A_p, B_p, C_p and D_p (see Fig. 1 for locations) on 25/11/03.

3.2 Koura, kakahi and bully surveys

A combination of SCUBA diving, of extensive bed surveys using an underwater camera, and of trapping with baited G-minnow traps overnight did not result in any observations of koura or kakahi in the lake prior to alum dosing. Preliminary searching of the lower reaches of the inflow stream also indicated neither of these species was present. This confirms previous observations that koura have been lost from the lake due to deterioration in habitat quality (Donald et al. 1991).

Bullies (*Gobiomorphus cotidianus*) were very abundant in the shallow, littoral, surface waters, with overnight trapping using g-minnow traps yielding catches of 43 ± 29 fish/trap (mean ± S.D.) for 8 traps around the lake edge. Two of the traps had apparently moved below the thermocline and contained 0-2 fish. These high densities in the epilimnion reflect the fact that these benthic fish were confined to a narrow band of the lakebed (like the ring around the bathtub) where the bed was in contact with oxygenated, epilimnetic, water. Repeat sampling at 4 of these sites on 12-13 March 2004 (2.5 months after alum treatment) yielded 12.2 ±10.9 bullies/trap, representing a 72% reduction in catch per unit effort. This difference was statistically significant (ANOVA on log transformed CPUE data, $F_{11,2} = 8.87$, $P = 0.014$). The size range of fish caught in March was also narrower than in November (Fig. 5), with no fish >65 mm length (= 2-3 year old fish, pers. comm. David Rowe) caught, whereas these represented 35% of the catch in November 2003.

These results may indicate a decline in abundance of larger, 2-3 year old, individuals, between late November 2003 and early March 2004. An alternative explanation is that larger bullies moved to shallower depths in March. Bully spawning occurs in December, and post-spawning mortality may have contributed to this pattern, since the larger fish that are the repeat spawners (pers. comm. David Rowe) showed the greatest decline in abundance. However, the apparent complete absence of larger fish in March was not expected, and suggests the possibility that the larger fish may be particularly susceptible to impacts associated with alum dosing (perhaps resulting from combined effects of aluminium toxicity and factors such as spawning stress and higher parasite burdens than younger fish). The potential for seasonal factors to have influenced the results suggests that repeating the sampling in late November 2004 would help to clarify the magnitude of the alum effects (if any). Such sampling would also provide information on the effects of alum dosing at the time of spawning on bully recruitment (e.g., via effects on larval fish). Notably, EBOP's monitoring indicates that aluminium concentrations (see Fig. 9 below) exceeded the ANZEEC guideline values (Table 3.4.1, (ANZECC 2000) of 55 and 150 mg m^{-3} for protection of 95% and 80% of species, respectively.

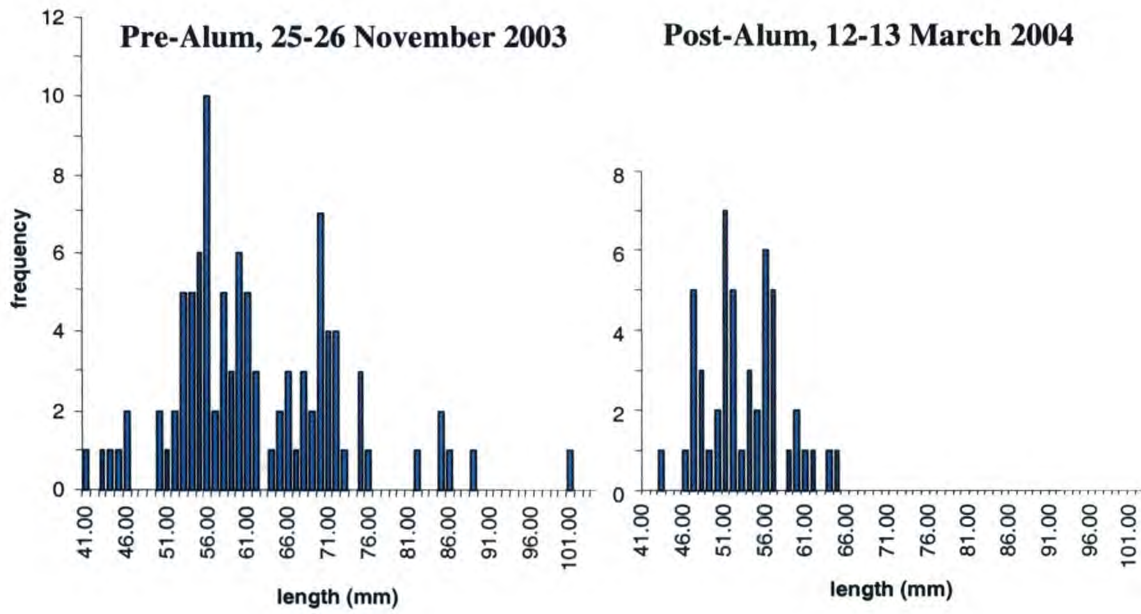


Figure 5: Length-frequency distributions of bullies caught in g-minnow traps set overnight in lake Okaro before (n = 99) and after (n = 49) Alum dosing.

3.3 Effects of alum dosing on water quality and sedimentation rates Lake Okaro

3.3.1 Particle settling rates and related studies

Secchi depth declined from 3.0 m on 11 December 2003 to 2.25 m on 16 December. On 19 December a phytoplankton bloom was obviously occurring on 19 December (Fig. 6) and Secchi depth varied from 0.85 at site A_s (downwind part of lake) to 2.25 at B_s (upwind part of lake) with intermediate levels of 1.1 m at site C_s (see Fig. 1 for site locations). These temporal and spatial patterns in Secchi depth are mirrored by patterns in Chlorophyll *a* that increased between the sampling dates and were greater on 19 December at sites A_s and C_s than at B_s (Table 2).

The lake was stratified on each occasion, with fairly uniformly warm waters in the top 3-4 m and declining temperatures with depth below this level. Dissolved oxygen levels were <0.6 g m^{-3} below 5 m on 11 December and below 4 m on 16 and 19 December. DO saturation was 133-178% in the top 3 m on 19 December, reflecting the very high productivity due to the algal bloom at this time.

Figure 6: Algal bloom at Lake Okaro on 19 December 2003.

Table 2: Water Quality at 3 lake sedimentation sampling sites (Fig. 1) before (16/12/03) and after alum addition (19/12/03).

Site/depth	Date Collected	DRP (mg m^{-3})	TDP (mg m^{-3})	NH_4-N (mg m^{-3})	NO_3-N (mg m^{-3})	TDN (mg m^{-3})	Chl. *a* (mg m^{-3})
A_s 3m	16/12/2003	16	40	10	<1	420	30
A_s 6m	16/12/2003	38	57	8	<1	366	18
A_s 9m	16/12/2003	114	135	705	<1	1020	18
B_s 3m	16/12/2003						31
B_s 6m	16/12/2003						11
B_s 9m	16/12/2003						15
C_s 3m	16/12/2003						34
C_s 6m	16/12/2003						16
C_s 9m	16/12/2003						13
A_s 3m	19/12/2003	2	22	12	2	421	64
A_s 6m	19/12/2003	35	56	4	<1	374	8.4
A_s 9m	19/12/2003	163	203	1010	<1	1330	12
B_s 3m	19/12/2003						24
B_s 6m	19/12/2003						8.7
B_s 9m	19/12/2003						11
C_s 3m	19/12/2003						91
C_s 6m	19/12/2003						13
C_s 9m	19/12/2003						3.9

DRP and TDP at site A_s declined in the surface water (i.e., by 14 and 18 mg m^{-3}, respectively, at 3 m depth) between 16 and 19 December after alum addition (Table

2). Although alum addition may have contributed to the decline in DRP during this period, the increase in chlorophyll *a* from 30 to 60 g m^{-3} (Table 2) could also more than account for this, assuming that synthesis of 1 g Chlorophyll a requires 1 g phosphorus. Dissolved inorganic nitrogen (DIN = NH_4-N + NO_3-N) levels were very low at this time and neither DIN not TDN declined in the surface water over the 3 day period 16-19 December, suggesting that the bloom was driven by cyanobacteria that were obtaining the necessary N for growth by fixing atmospheric N.

Particle settling rates over 11-16 December, before alum addition, were similar at the 3 sites around the lake and were higher at 6 and 9 m than at 3 m (Fig. 7). However, over 16-19 December, during/after alum addition, rates varied spatially amongst the sites, reflecting the accumulation of algae in the downwind part of the lake (site A_s) where Secchi depth was also much lower than in the upwind site (B_s), as discussed above. Thus, although increased particle settling occurred during and after alum addition to the lake, this effect was obscured by a natural increase in settling rate expected during the algal bloom that was occurring at the time of alum addition to the surface waters.

Particulate aluminium settling rates at site A_s were very similar before and after alum dosing (Fig. 8). Aluminium trapping rate (Fig. 8) increased at A_s after dosing, reflecting the increase in total particle settling resulting from the algal bloom. In general, the ratio of total particle:Al trapping rates were consistent and the Al settling rates were comparable with those of the total particles. However, Al trapping and settling rates did not increase at the 6 m depth at site A_s, as was seen for the total particles (Fig. 7), indicating that that increase in particle settling was probably due to the algal bloom not the alum dosing. Similarly, the high Al trapping rate and settling velocity estimated for the 9 m depth at site B (Fig. 8) were not accompanied by a similar change in the rates for the particles, again indicating that the Al component was not directly related to the total particle component.

Environment Bay of Plenty's aluminium monitoring (Fig. 9) shows that the target Al concentration of 0.5 g m^{-3} was achieved after dosing. However, the expected rapid decline in Al, due to flocculation and associated rapid settling, did not occur. Instead it took approximately 2 months for the dissolved Al concentration to drop below the 150 mg m^{-3} level recommended for protection of 80% of biota (ANZEEC 2000) and the trend suggests it would have taken at least another month to drop below the 50 mg m^{-3} recommended level for protection of 95% of biota (ANZEEC 2000). The reduction in Al in the water column is most likely the result of slow settling from the surface waters, rather than flushing from the lake since the residence time of the epilimnetic water is approximately 3.4 years (assuming mean outflow is 15 l s^{-1}, epilimnion = 5 m deep and surface area is 32 ha). The expected high pH (up to 8.5, pers. comm. John McIntosh) due to the algal bloom at the time of the alum dosing probably contributed to poor floc formation that is optimal at pH 6-8 (Cooke et al. 1986). Low DRP in the water column may have also limited floc formation (see 3.2 and 3.4).

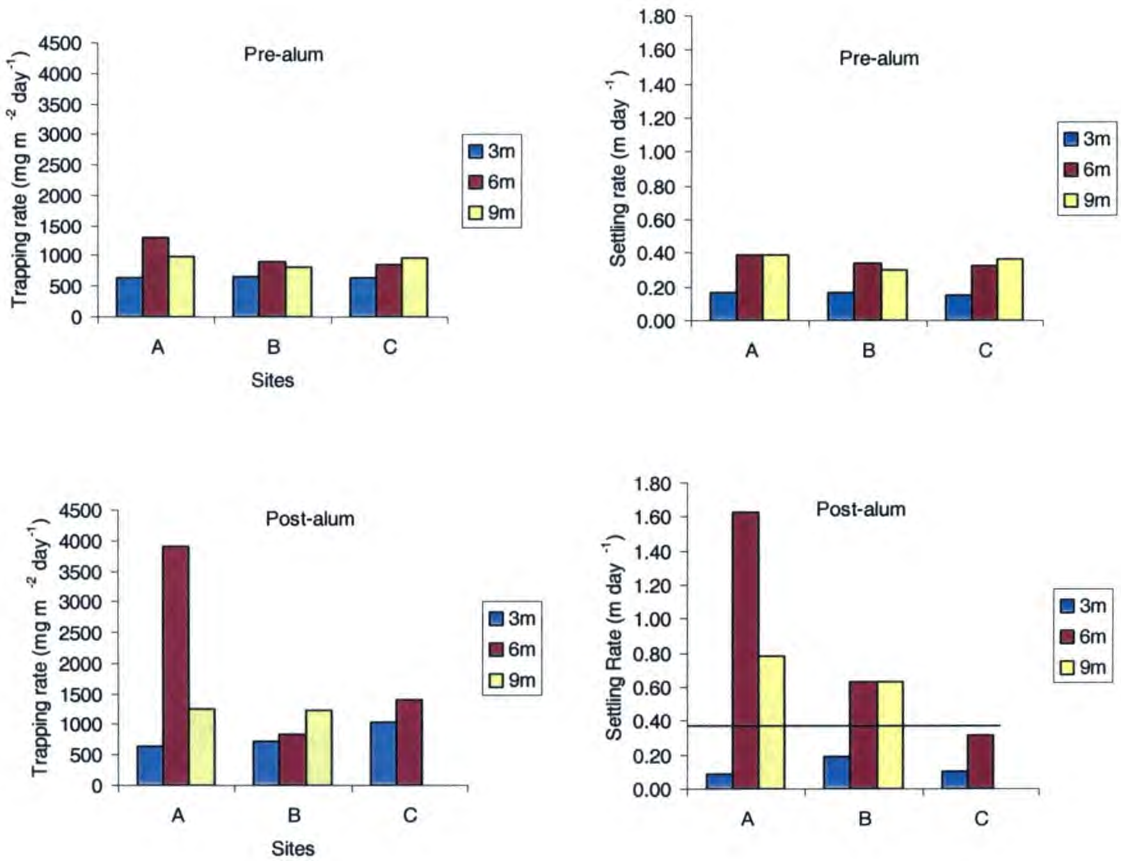
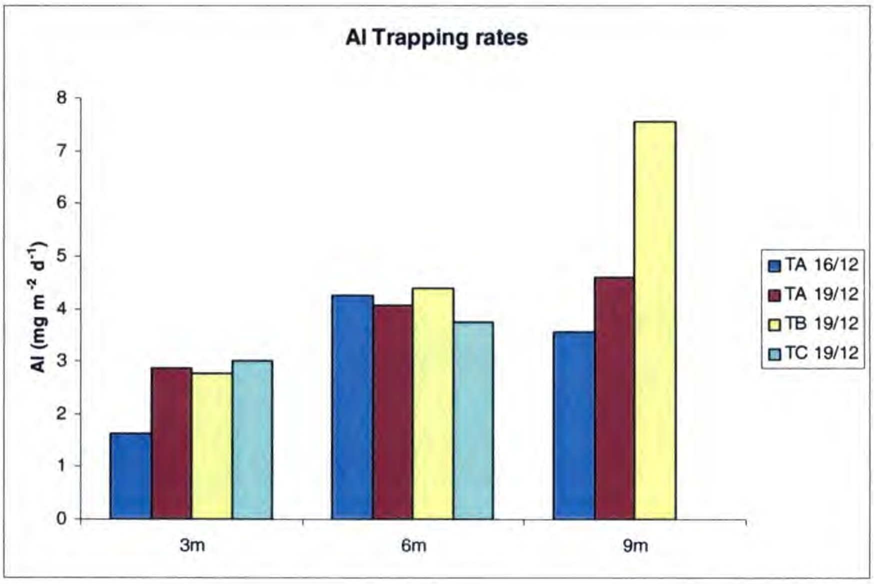


Figure 7: Average rates of particle trapping and settling (=trapping rate/water column concentration) on Lake Okaro on 11-16 December (pre-alum) and 16-19 December (post-alum). The horizontal line on the post-alum settling rate plot shows the mean pre-alum rate at 3 m and 6 m.



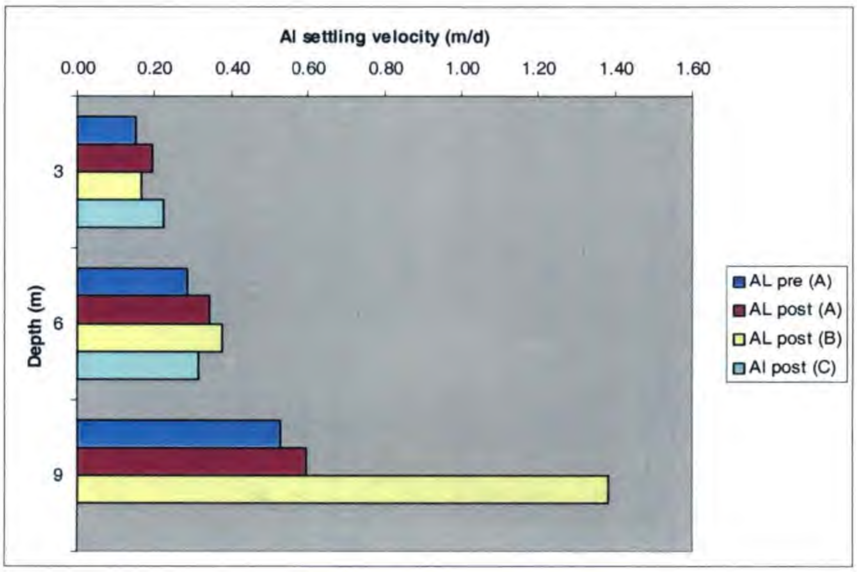
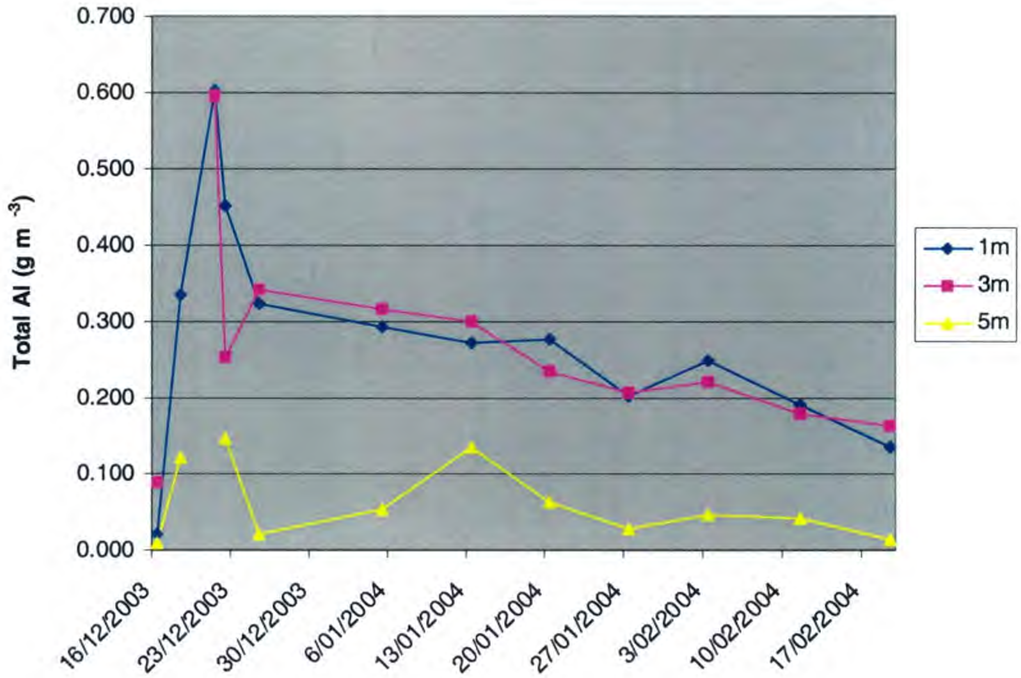


Figure 8: Particulate aluminium settling and trapping rates at 3 depths before (11-16 December) alum dosing at sites A_s and after (16-19 December 2003) alum dosing at sites A_s, B_s and C_s (see Fig. 1).



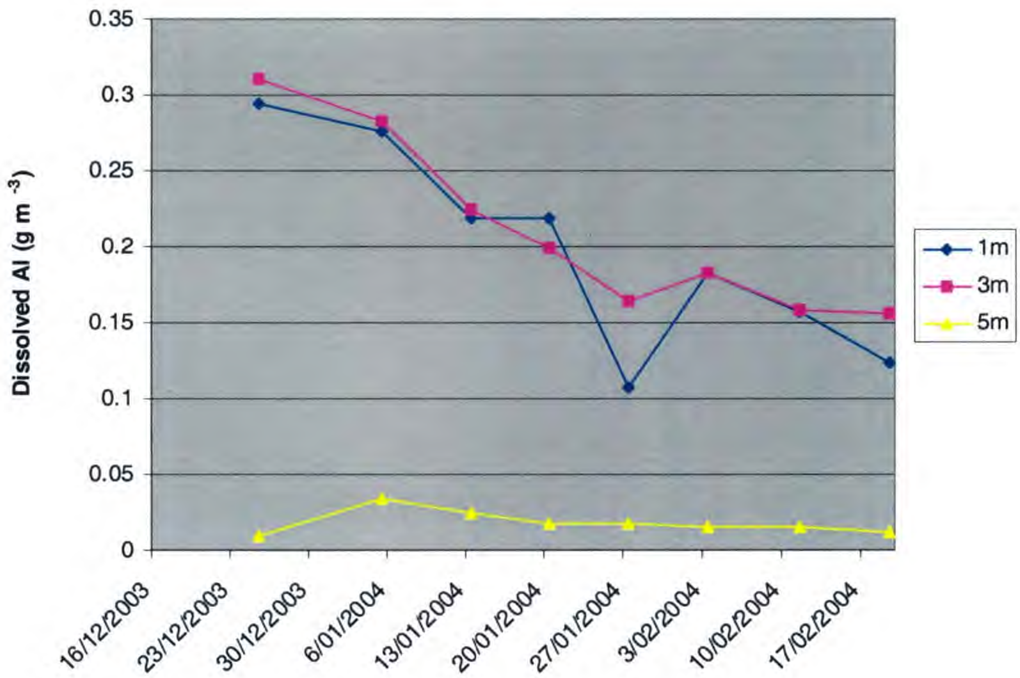


Figure 9: Changes in total (upper) and dissolved (lower) aluminium concentration in Lake Okaro during and after alum dosing on 16-18 December 2003 (EBOP data).

3.4 Laboratory experiments on alum dosing effects on Lake Okaro water chemistry and floc formation

The results of trials 1 and 2 are summarised in Table 3 and photographs of the columns are shown in Figure 10. Aluminium dosing of 10 g m^{-3} and higher caused marked reduction in pH, from 7.4 to 5 and lower, whereas the pH drop was much less severe at dosing up to 5 g Al m^{-3} (to pH of approx. 6.6). This response of pH to alum addition is more rapid than typical data shown in a classic lakes restoration reference (Cooke et al. 1986), and this is likely due to lower alkalinity in Okaro (i.e., 22 g m^{-3} as $CaCO_3$, pers. comm. John McIntosh EBOP).

Table 3: Results of laboratory trials on effects of Alum additions on Lake Okaro water quality 24 h after Alum dosing. +P, P increased by 50 mg m^{-3}; NA = not applicable, ND = not determined.

Trial	Treatment	*Daphnia* % survival	pH	Turbidity (NTU)	DRP (g m^{-3})	Al (g m^{-3})
1.1	Control_No P_Al = 5 g m^{-3}	0	6.75	0.66	ND	ND
1.2	Control + P	100	7.42	0.643	ND	ND
1.3	Al_5 g m^{-3} + P	0	6.8	0.54	< 0.02	< 0.003
1.4	Al_10 g m^{-3} + P	0	5	0.243	ND	ND
1.5	Al_20 g m^{-3} + P	0	4.27	0.285	ND	ND
1.6	Al_40 g m^{-3} + P	0	4.18	0.324	ND	ND
1.7	Control_No P no Daphnia	NA	7.3	0.62	ND	ND
2.1	Control_No P_AL_0.5	80	7.24	0.389	<0.02	0.035
2.2	Control + P	90	7.12	0.413	0.08	0.007
2.3	Al_0.5 g m^{-3} + P	70	7.13	0.377	<0.02	0.005
2.4	Al_1.0 g m^{-3} + P	70	6.98	0.459	<0.02	0.004
2.5	Al_2.0 g m^{-3} + P	0	6.91	0.498	<0.02	0.004
2.6	Al_4.0 g m^{-3} + P	0	6.62	0.395	<0.02	0.004
2.7	Control_No P no Daphnia	NA	7.15	0.468	<0.02	< 0.003

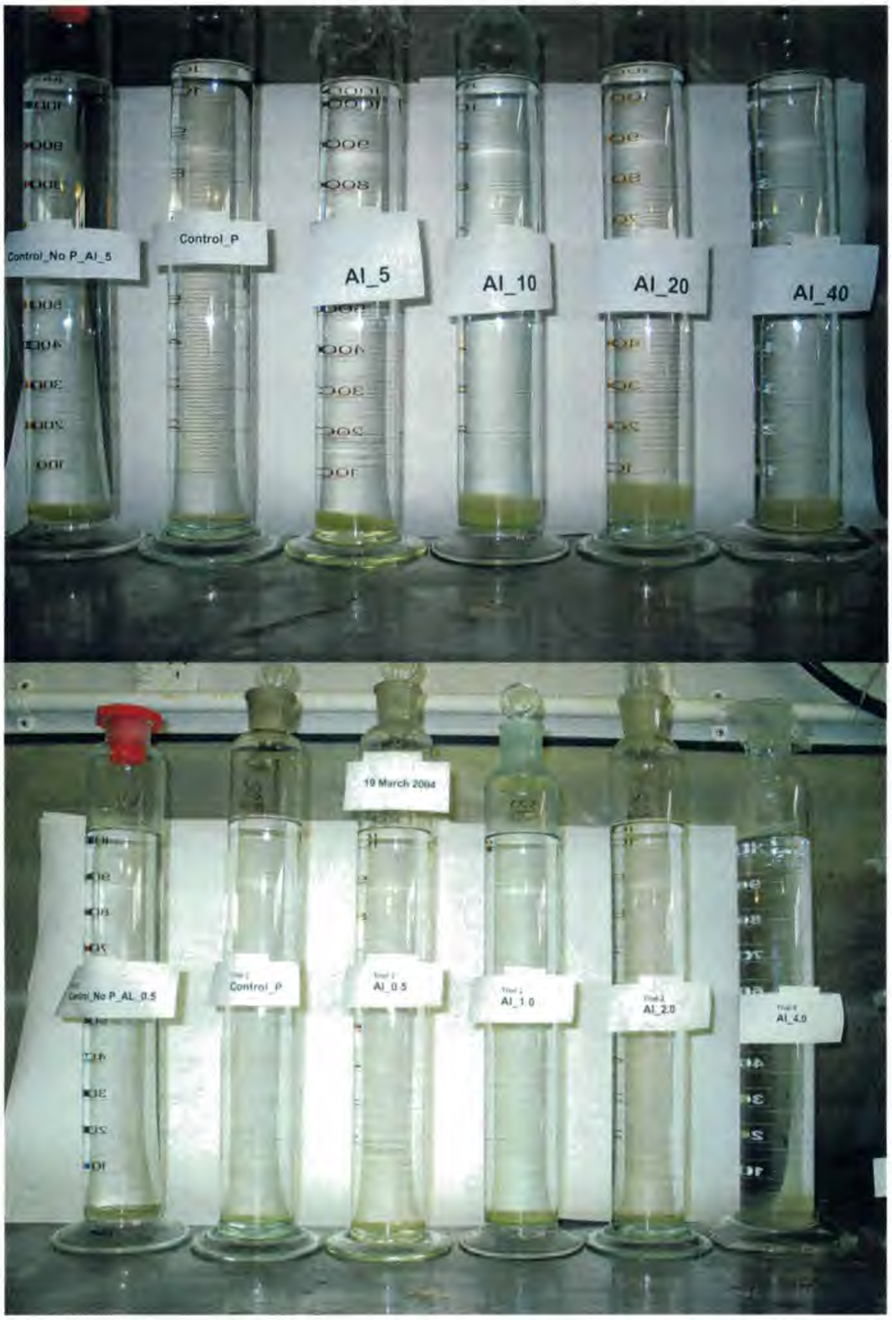


Figure 10: Photo of glass cylinders of Lake Okaro water 24 hours after alum addition in Trial 1 (upper photo) and 2 (lower photo). Al levels are calculated Aluminium concentrations in whole column after mixing.

Flocs of settled algae occurred in all the cylinders after 24 h, but the floc thickness increased with aluminium dosing up to 20 g Al m^{-3} (Fig. 10). In Trial 2, there was little discernable difference in the thickness of the floc formed at dosings of 0.5 and the controls, whereas that at 4 g m^{-3} was obviously thicker than the controls (Fig. 10).

Turbidity (a measure of suspended particles in the water column, presumed mostly algae) 24 h after dosing was approximately 40-50% of the control level in the 10-40 g Al m^{-3} treatments and 80% of the control level at 5 g Al m^{-3}, whereas variable low reductions occurred at 0.5-4 g Al m^{-3} (Table 3).

The residual dissolved aluminium measured 24 h after dosing up to 5 g Al m^{-3} was below the level of 50 mg Al m^{-3} (dissolved) adopted as a maximum safe level (based on protection of rainbow trout) by Cooke et al. (1986) and as the trigger value for protection of 95% of biota by ANZEEC (2000). However, levels were greater where no DRP had been added to the Okaro water, presumably reflecting less P available for binding aluminium. Nevertheless, no *Daphnia* survived the alum dosings resulting in $\geq$ 2 g Al m^{-3}, despite relatively minor effects on pH at doses up to 5 g Al m^{-3}. It is not known whether this impact was due to aluminium toxicity or entrapment of *Daphnia* in $Al(OH)_3$ floc.

The results of these preliminary trials suggest the following:

- Alum dosing of surface waters needs to be managed to avoid impacts caused by a significant reduction in pH, which had both direct adverse effects on lake biota and indirect effects via increasing the proportion of the aluminium that is toxic Al (III). At pH 6-8 insoluble $Al(OH)_3$ is formed and the concentration of dissolved Al (III) should be very low (Cooke et al. 1986). In Okaro, Al dosing of up to 5 g Al m^{-3} appears to avoid undesirable pH lowering, whereas 10 g Al m^{-3} does not.

- Alum dosing to surface waters needs to be managed to avoid impacts on zooplankton grazers, such as cladocerans, because they may play an important role in controlling phytoplankton blooms. Our results indicate that the threshold Al dose concentrations after mixing to avoid such effects is between 1 and 2 g Al m^{-3}. Addition of alum to the anoxic hypolimnetic waters would provide a way of achieving higher dosing without impacting on zooplankton grazers that are confined to the oxygenated surface (epilimnetic) waters.

3.5 General discussion and conclusions

The results of the initial monitoring of particle and aluminium settling and aluminium concentrations indicate that the approach to alum treatment used in this trial was not immediately effective and that, as anticipated by EBOP (pers. comm. John McIntosh), low rate alum dosing will need to recur over a number of years for control of P levels and hence reduction in nuisance blue-green phytoplankton blooms. Further monitoring of Al and P by EBOP at the time of winter mixing will provide a more complete assessment on the effectiveness of the initial low-dose alum application (pers. comm. John McIntosh). The low settling rates and slow decline of Al in the water column immediately after alum dosing indicate that the alum did not form rapidly settling $Al(PO_4)$ precipitate or $Al(OH)_3$ flocs. The laboratory trials suggest that this may have been due to the very low DRP level at the time (few PO_4-P molecules to bind with the Al) and/or low alum dosing rate. High pH (>8), due to photosynthetic uptake of CO_2 and HCO_3 by the blooming phytoplankton would also have reduced the formation of polymeric aluminium hydroxides that form flocs to which P binds (Cooke et al. 1986). Although the pH was 7.5 at the time of the alum addition, level up to 8.5 were measured during summer (pers. comm. John McIntosh). High pH can also result in Al toxicity in some conditions (NALMS 2004).

Laboratory trials also indicated that alum dosing that increases in-lake Al concentrations to 2 g m^{-3} are likely to be toxic to cladoceran grazers, so there are obvious constraints on how much the Al concentration can be increased. These findings indicate that alum dosing may be more effective if added to hypolimnetic waters where DRP is abundant, pH is likely to be <8, and low dissolved oxygen levels mean that Al toxicity effects are not of concern. This would require a specialised dosing system that can deliver the alum to a depth of c. 6 m. Another option would be to carry out surface water dosing during the winter when the lake is unstratified, but taking care to avoid toxicity impacts.

Studies that would help to guide further alum additions include: (1) repeat sampling of bully populations for CPUE and size structure in November 2004 to better evaluate the apparent effects of the low dose alum treatment on these fish; (2) measurement of the mobile P levels in the surface sediments of the lake bed to determine appropriate alum dose rates to bind that P (after Rydin and Welch 1999); and (3) laboratory trials of alum dose responses of Lake Okaro hypolimnetic water (i.e., effects on pH, floc formation and dissolved Al). While the above laboratory tests would advance our knowledge of key processes influencing the effectiveness of alum dosing, field experiments using limno-corals (i.e., plastic tubes that isolate columns of lake water and sediment) are also recommended to test the overall environmental effects and sustainability of revised approaches. These studies could also evaluate alternative chemical approaches (e.g., alum, Phosloc) and would support laboratory studies to measure the effectiveness of dosing approaches in limiting nutrient releases from lake-bed sediments. The use of chemical dosing approaches complements catchment measures for nutrient reduction, and is an essential component for management of lakes with high internal loading.

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