ISSN 2463-6029 (Print)
ISSN 2350-3432 (Online)

Lake Rotorua sediment survey

21 June 2014

ERI report 041

Prepared for Bay of Plenty Regional Council

By Deniz Özkundakci, Lisa Pearson, Chris G. McBride, David P. Hamilton

Environmental Research Institute

The University of Waikato, Private Bag 3105,

Hamilton 3240, New Zealand

THE UNIVERSITY OF WAIKATO
Te Whare Wānanga o Waikato

Environmental Research Institute
Te Pūtahi Rangahau Taiao

Reviewed by:

Mathew Allan

Research Officer

Environmental Research Institute

University of Waikato

Approved for release by:

John Tyrrell

Research Developer

Environmental Research Institute

University of Waikato

Executive summary

Water quality in Lake Rotorua has improved over recent years, with reductions of nitrogen, phosphorus and chloropyll *a* concentrations, and increased water clarity. These changes coincide with alum dosing of the Utuhina and Puarenga inflows, commenced in 2007 and 2010 respectively. The aim of inflow alum dosing is to reduce external phosphorus load by binding (inactivation of) phosphorus flowing into the lake, however, it has been hypothesised that dosing these streams has had subsidiary beneficial effects on the water quality in the lake itself. Namely, the hypothesised effects relate to adsorption of P in the water column and the settling of alum flocs onto bottom sediments, which in turn could reduce sediment release of phosphorus into the overlying water column (internal loading). This report was commissioned by Bay of Plenty Regional Council to investigate the possibility of stream-dosed alum improving water quality in Lake Rotorua. The objective of this study was to assess how much of the dosed alum, if any, could have been deposited onto the bottom sediments of Lake Rotorua where it could reduce internal phosphorus loading. This objective was achieved by two approaches: (i) a field survey of Lake Rotorua bottom sediments in order to observe any changes in sediment aluminium and phosphorus concentrations following the alum dosing of Utuhina and Puarenga streams and (ii) an aluminium mass balance for the inflows and lake, to explore the potential amount of alum settling out of the water column and onto the bottom sediment, taking into account the potential phosphorus uptake rate of alum.

In comparison with sediment samples collected in 2006, sediment Al concentrations in 2012 were lower in the main basin of the lake. Phosphorus concentrations in the sediments were reduced at four sites located near to the discharges of the Utuhina and Puarenga Streams, but sites further from the stream (i.e. deep basin and close to the Ohau Channel outlet) showed increased concentrations of phosphorus in the sediment.

The aluminium mass balance for Lake Rotorua provided insights into the potential amount of alum reaching the lake and sediments after some proportion of the aluminium had bound phosphorus in the preceding 'reactor', including the inflows. There was a low probability that a large proportion of the dosed Al would have reached the sediments in Lake Rotorua. Only in the years 2010 and 2011, when alum dose rate to the streams was comparably high, some of the dosed alum was likely to have reached the lake sediments.

There was a high probability that a large fraction of the Al reached the lake water column with the potential to reduce in-lake water column P concentrations.

Scenarios in the aluminium mass balance were developed to ascertain the conditions needed to achieve a given target for percentage uptake of lake water column P, with respect to the parameters for the fraction of TP available for uptake by alum and the effective Al: P ratio. Only when simulating a 90% reduction of water column P concentrations was the range of possible parameter values for achieving such a reduction relatively constrained. In simulated scenarios where a substantial reduction of internal P loading was the target, parameter values in both the inflows and water column were considerably constrained, indicating that phosphorus uptake by aluminium was likely to be considerable in the inflow and water column. Even with constraint of the parameter values in the inflows and water column, it appeared unlikely that an amount of alum could reach the sediment sufficient to significantly reduce internal P loading.

Changes in sediment P concentrations observed in this study are suggested to have occurred through the synergistic effects of changes in external nutrient loading, sediment focusing and changes in duration and severity of anoxic events in the hypolimnion of the lake driven by unusual climatic events during that time which may have reduced water column stability. The alum mass balance results suggest that although it is possible that some alum reached the bottom sediments in Lake Rotorua, any effect on internal loading was likely to be minor, even in the years 2010 and 2011 when the alum dose rates were comparably high. The conditions under which a substantial reduction of internal P loading would have been possible (with respect to the fraction of the P pool available for uptake and the effective Al:P ratio), are considered highly optimistic (i.e. Al:P ratio ~ 3.5) when compared to literature values of Al:P ratios in other alum-dosed eutrophic lakes.

This study suggests that the amount of Al dosed to the streams is unlikely to explain completely the recent improvement of water quality in Lake Rotorua. Any claim otherwise, should be viewed with caution and can be regarded as optimistic.

Table of contents

List of figures

List of tables

1 Introduction

Alum treatment is a well-established lake restoration method used worldwide for controlling bioavailable phosphorus (P) in the water column and/or bottom sediments. It has been used for more than four decades with varying degrees of success (Cooke et al. 1993; Welch and Cooke, 1999; Lewandowski et al. 2003; Pilgrim et al. 2007; Egemose et al. 2013). The chemical treatment of wastewater and drinking water using alum for P removal or flocculation is also widely used and accepted. Despite the frequent use of alum in wastewater systems, dosing alum to surface inflows of lakes is a relatively new method which has received little attention in the literature (Pilgrim and Brezonik, 2005; Churchill et al. 2009). Stream dosing with alum could potentially combine the benefits of reducing both external and internal P loading to a lake. It could be used for water column P adsorption and to produce a greater proportion of sediment P bound to aluminium as opposed to other metal cations (e.g., iron and manganese) which are redox-sensitive. However, the fate of alum entering lakes via the inflows, and thus the effectiveness of alum in reducing internal loading, is poorly understood.

There are several in-lake processes which may potentially affect the fate of alum in a lake. Alum (applied as a surface inflow and/or water column application) may settle permanently into the bottom sediment, and once settled, continue to adsorb P from these bottom sediments and/or from the water column at the sediment-water interface. In shallow lakes or margins, however, wind-driven resuspension is a common phenomenon and during these events, sediment (including alum) can be transported and focused in deeper parts of the lake or even washed out of the lake. Bioturbation, gas ebullition and advection, as well as stormflows, can disturb or bury surface sediment and thus, move alum into deeper sediment layers, potentially rendering it ineffective for controlling bioavailable P in the lake.

Alum dose rates for lake applications are often determined using laboratory batch experiments using lake water in jar tests or sediment incubations. While several parameters can be measured to determine alum dose rates for whole lake applications, the effective Al:P binding ratio (i.e., the molar or mass ratio of alum to bind phosphorus) is one of the most important variables to be measured because it directly informs on the amount of alum needed to bind with, and by implication inactivate, a given amount of P. In controlled experiments using laboratory grade phosphate solution and alum, the theoretical molar binding ratio of Al:P is 1:1. There are, however, several mechanisms which can reduce the P uptake efficiency of alum in natural waters, which almost certainly increases the effective Al:P binding ratio. Aging of alum flocs has been shown to decrease P binding capacity, presumably as a result of changes in the crystalline structure of the floc and decreased surface area (Lijklema, 1980; Berkowitz et al. 2006). Competitive adsorption with other compounds in natural waters can also render some of the aluminium binding sites unavailable for P. For example, humic substances and the presence of silica and magnesium have been found to negatively affect the P uptake efficiency of alum but can be compensated for in practical applications by increasing the alum dose rate (de Vicente et al. 2008b). The pH of natural water also substantially influences the P uptake efficacy of aluminium as it influences the solubility and form of aluminium following an alum treatment (Berkowitz et al. 2005). When aluminium sulphate is added to water it hydrates immediately:

$$Al^{3+} + 6H_2O \quad \leftrightarrows \quad [Al(H_2O)_6]^{3+} \qquad (1)$$

A progressive series of hydrolysis reactions occur subsequently, which are pH dependent:

$$[Al(H_2O)_6]^{3+} \leftrightarrows [Al(OH)(H_2O)_5]^{2+} + H^+ \qquad pH = 3\text{-}7 \qquad (2)$$

$$[Al(OH)(H_2O)_5]^{2+} \leftrightarrows [Al(OH)_2(H_2O)_4]^{+} + H^+ \qquad pH = 4\text{-}8 \qquad (3)$$

$$[Al(OH)_2(H_2O)_4]^{+} \leftrightarrows Al(OH)_3(H_2O)_3 + H^+ \downarrow \qquad pH = 5\text{-}9 \qquad (4)$$

$$Al(OH)_3(H_2O)_3 \leftrightarrows [Al(OH)_4(H_2O)_2]^{-} + H^+ \qquad pH \geq 6 \qquad (5)$$

The $Al(OH)_3$ complex is of greatest interest due to its ability to adsorb large amounts of inorganic P. Therefore the ideal conditions when alum can be added to the water are within the pH range described by Eq. 5. For alum applications in lakes, a pH between 6 and 8 is generally considered preferable (Cooke et al. 1993). However, equations 2 to 4 highlight that not all the aluminium species formed may be available for P uptake. Furthermore, some aluminium complexes may have toxic side effects. It is also clear from these equations that the Al:P ratio of alum applications in natural waters needs to be relatively high to account for the hydrolysis reactions.

The Lake Rotorua Action Plan (Bay of Plenty Regional Council, 2009) recommended the dosing of inflows to Lake Rotorua with alum in order to reduce the overall phosphorus load to the lake. The Utuhina stream and two other streams were proposed to be dosed with alum. To date, alum has been used in the Utuhina and Puarenga streams entering Lake Rotorua (McIntosh, 2012). Alum dosing began in the Utuhina Stream in 2007 and was extended to the Puarenga Stream in 2010. Since 2007 a total of 269 tonnes of aluminium has been added to Lake Rotorua. Water quality in Lake Rotorua has improved concurrently with alum dosing and the annual TLI target was reached in 2012 (Abell et al. 2012). It has been hypothesised that alum dosing carried out in the Utuhina and Puarenga steams has had subsidiary beneficial effects on the water quality in Lake Rotorua. Namely, these effects relate to adsorption of P in the water column and the settling of alum flocs onto the bottom sediments of the lake which in turn could reduce the bottom-sediment release of phosphorus into the overlying water column (internal loading). Data presented by McIntosh (2012) and Abell et al. (2012) showed that bottom water phosphorus concentrations in Lake Rotorua have declined in 2011 and 2012 compared with previous long term records, coinciding with relatively high alum dose rates to the two streams. However, there is currently no direct evidence which could explain the mechanism for the reduction of water column P concentrations. Thus, accumulation of aluminium onto the bottom sediments, forming what is termed a capping layer, is regarded as speculative at this point and warrants further investigation.

This report was commissioned by the Bay of Plenty Regional Council to investigate the possibility of stream-dosed alum improving the water quality in Lake Rotorua. The objective of this study was to assess how much of the dosed alum, if any, had been deposited onto the bottom sediments of Lake Rotorua where it could reduce internal phosphorus loading. This objective was achieved by using two approaches: (i) a field survey of Lake Rotorua bottom sediments in order to observe any changes in sediment aluminium and phosphorus concentrations following the alum dosing of Utuhina and Puarenga streams and (ii) constructing an aluminium mass balance for Lake Rotorua to explore the potential amount of alum settling out of the water column and onto the bottom sediment, taking into account the potential phosphorus uptake rate of alum. A previous sediment survey was carried out on Lake Rotorua by Pearson (2007) to assess the nature and composition of the lake sediment. This earlier study was undertaken over 2005/06, which provides a pre-alum dosing baseline for comparison with present sediment Al and P concentrations. Pearson (2007) observed Al content in the surface sediment of Lake Rotorua between 2.5 to 10.5 g m^{-2}. This provides a reference point with which to compare the current Al content in the surface sediment which has resulted from 5 years of alum dosing of the Utuhina and Puarenga inflows; a total additional load of 3.4 g Al m^{-2} averaged across the entire lake basin.

2 Methods

2.1 Study site

The Lake Rotorua catchment has an area of approximately 425 km^2. The hydrogeology of the catchment is complex, with permeable pumiceous tephra overlying massive deep rhyolite and ignimbrite unconfined aquifers that retain groundwater for potentially long periods. The urban area has expanded substantially during this time but with progressive reticulation of septic tanks into the centralised Rotorua Wastewater Treatment Plant. Relatively low-intensity pastoral land cover comprising mostly sheep and beef farms covered a considerable area of the lower catchment as early as 1940 but also expanded rapidly around the lake margin and then progressively into the upper catchment. Dairy farming has more recently (past 3-4 decades) replaced both forest and sheep and beef farming in parts of the north-west of the catchment, mostly in and around the Mamaku Plateau. In general there has been a gradual loss of native forest and scrub with the expansion of pasture in the Rotorua catchment to the point where pasture now makes up more than 50% of the total catchment area.

In Lake Rotorua itself, phytoplankton biomass and production may be limited by nitrogen and/or phosphorus, as well as other environmental factors depending on time of year and the location within the lake (Burger et al. 2007). Ratios of N:P are low by comparison with many other lakes in New Zealand and particularly overseas, and, based on Redfield ratios (see Abell et al. 2010), suggest that either of these nutrients could potential limit phytoplankton productivity. White (1977) found using bioassays that N consistently limited algal biomass. Burger et al. (2007) ran similar but in situ-deployed bioassays and also used a model to show that in different seasons co-limitation by N and P was the norm. Bioassays carried out in large-scale mesocosms in Lake Rotorua in summer 2009-10 also indicated that co-limitation was most frequent, as opposed to limitation by either N or P. It is for these reasons that the Technical Advisory Group for the Rotorua lakes has consistently advocated for maintaining controls on loads of both N and P; focus solely on P could lead, at least in the short-term, to significant increases in algal biomass at times of N-limitation, which would result in a P-limitation condition that could prove difficult to obtain with the naturally geologically-enriched phosphorus in aquifers within the Rotorua catchment. In an analogous way, a focus solely on N control could lead to continued eutrophication at times when P was limiting but could also increase the risk of cyanobacterial blooms if there were periods of adequate P and limitation by N to an extent that induced proliferations of heterocystous species as a result of their ability to fix atmospheric N to meet the shortfall in their nutritional requirements for N.

2.2 Sediment survey

To provide empirical data on the potential aluminium and phosphorus accumulation in the Lake Rotorua basin, a sediment survey was conducted. Fifteen sediment cores were collected during August 2012 in a transect starting from close to the inlet of the Utuhina and Puarenga streams continuing north, passing Mokoia Island to the west and progressing towards the Ohau channel before finishing just north of Mokoia Island (Figure 1). Sites were selected from sampling locations previously cored by Pearson (2007), to allow for direct comparison with sediment composition prior to stream alum dosing. The sites chosen for the proposed survey are: 129, 90, 130, 131, 116, 161, 158, 162, 128, 124, 154, 144, 96, 155, and 110 (Table 1). These sites run through the deepest zone of the lake and most sites are greater than 15 m water depth. The sites were chosen to represent three different depositional zones: Zone 1 (Sites 1- 4) to represent the likely immediate depositional area of the treated streams, Zone 2 (Sites 5-11) to represent the main sediment accumulation basin (≥ 20 m water depth) and Zone 3 (Sites 12-15) to represent an area of low sediment accumulation (< 20 m water depth), as identified by Pearson (2007).

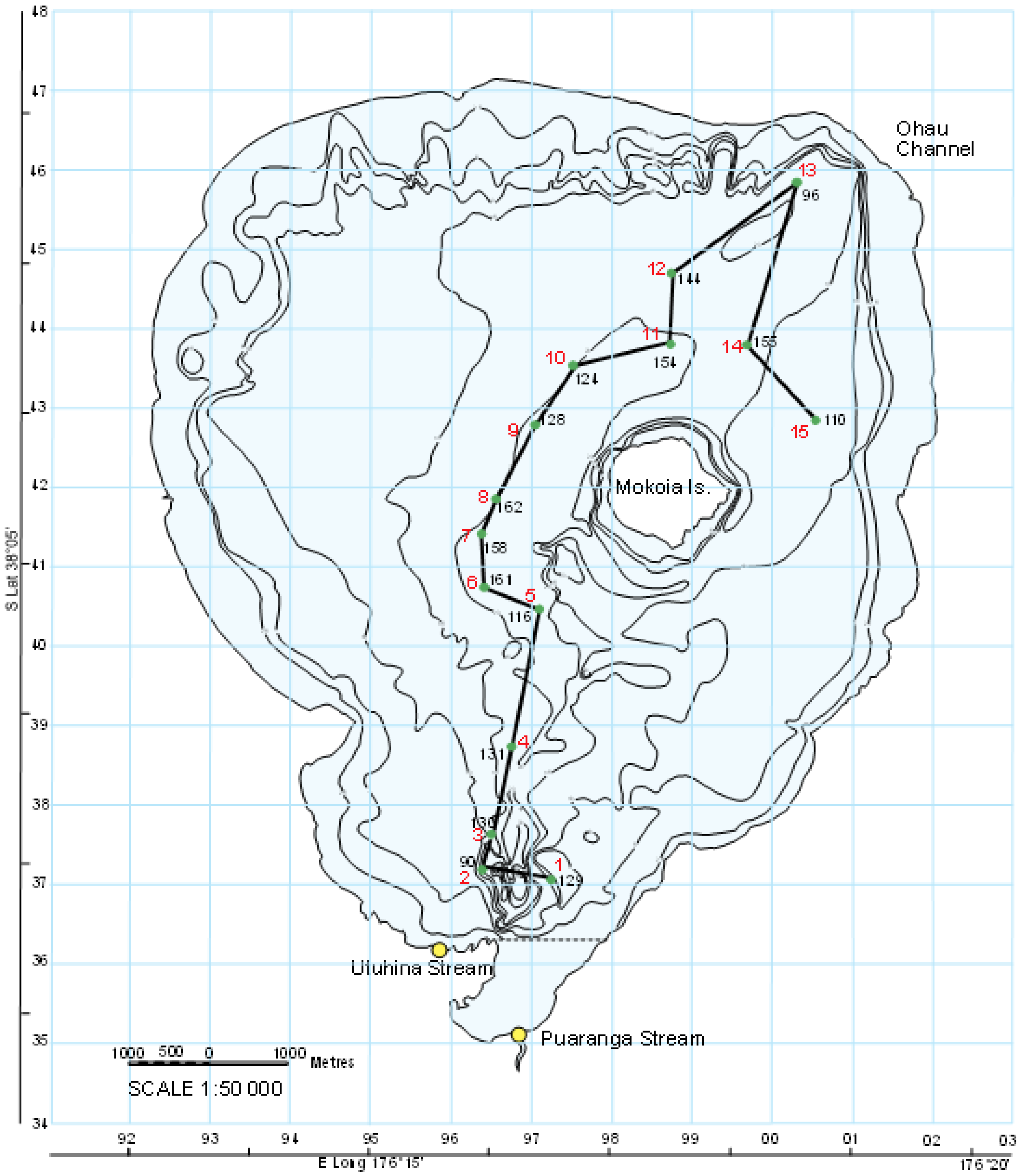


Figure 1: Core locations sampled by Pearson (2007) with sampling transect for this study shown by a black line and location numbers shown in red. The Utuhina and Puarenga Streams are shown with yellow dots where they enter Lake Rotorua.

Table 1: Core sampling locations and water depth.

Core No.	Pearson (2007)	Water depth (m)	Latitude	Longitude
Ru12 1	Ru129	11.0	38 07.485 S	176 16.215 E
Ru12 2	Ru90	20.0	38 07.394 S	176 15.955 E
Ru12 3	Ru130	21.4	38 07.144 S	176 15.997 E
Ru12 4	Ru131	17.9	38 06.551 S	176 16.126 E
Ru12 5	Ru116	21.0	38 05.594 S	176 16.337 E
Ru12 6	Ru161	21.0	38 05.468 S	176 15.869 E
Ru12 7	Ru158	20.8	38 05.106 S	176 15.812 E
Ru12 8	Ru162	21.6	38 04.878 S	176 15.944 E
Ru12 9	Ru128	21.0	38 04.391 S	176 16.225 E
Ru12 10	Ru124	20.4	38 03.962 S	176 16.541 E
Ru12 11	Ru154	20.4	38 03.790 S	176 17.362 E
Ru12 12	Ru144	18.0	38 03.290 S	176 17.337 E
Ru12 13	Ru96	16.1	38 02.646 S	176 18.402 E
Ru12 14	Ru155	16.6	38 03.768 S	176 18.022 E
Ru12 15	Ru110	12.4	38 04.274 S	176 18.625 E

The cores were collected using a Swedish gravity corer (Pylonex HTH 70 mm) with a 60 x 600 mm Perspex (Plexiglas) core barrel to capture undisturbed sediments along with c. 20 cm of the overlying water. Once the core was retrieved and photographed, a custom-made, gas-tight sampling chamber, designed to minimise exposure of potentially anoxic sediment to the air, was fitted to the core barrel and the core was extruded by a piston from the base of the core. Excess supernatant water overflowed the top of the core upon extrusion until the sediment-water interface was exposed. Sediment samples were extruded at 1-cm vertical intervals up to 4 cm sediment depth and transferred into 50 mL polypropylene centrifuge tubes. From 4 to 20 cm sediment depth the sediment was added to tubes at 2 cm intervals. Small amounts of residual overflowing sediment were discarded. Sediment samples were stored on ice until analysis in the laboratory.

In the laboratory, the gravity core sediments were weighed to determine bulk density before pore waters were separated by centrifugation at 4000 rpm (2900 G) for 40 min. The sediment sections were dried at 50 °C for 72 h and ground lightly using a mortar and pestle. The pore water was filtered through a 0.45 µm Millipore filter and acidified with nitric acid (2%). The sediments were digested with reverse Aqua Regia at 50 °C for one hour. The resulting digest along with the acidified pore water was analysed for phosphorus and aluminium using inductively coupled plasma mass spectrometry (ICP-MS model ELAN DRC II; Perkin-Elmer SCIEX).

2.3 Alum mass balance

Our hypothesis is that alum has brought about a significant improvement of water quality in Lake Rotorua, presumably through reduction of internal loading and/or reduction of water column P concentrations. To test this hypothesis potential P uptake capacity of the dosed alum in the water column and bottom sediments needs to be determined. A total of 269 t of aluminium has been added to the Puarenga and Uthuhina streams between 2007 and 2011, with most of the alum applied in 2010 (84 t) and 2011 (110 t). It is reasonable to assume that alum would also take up phosphorus in the streams and lake water column, rendering some of the added aluminium unavailable for P uptake from the sediments.

To explore this hypothesis and the potential amount of aluminium available for reducing internal P loading in Lake Rotorua further, a simple alum mass balance model for Lake Rotorua was constructed. The mass balance tracks the amount of alum available for phosphorus uptake across three coupled reactors (without feedback), representing the inflows, lake and sediment (Figure 2). The main objective of the alum mass balance model was therefore to quantify the P reduction potential by alum from the inflow (Inf), water column (Lk) and sediment (Sed) for a range of different uptake conditions.

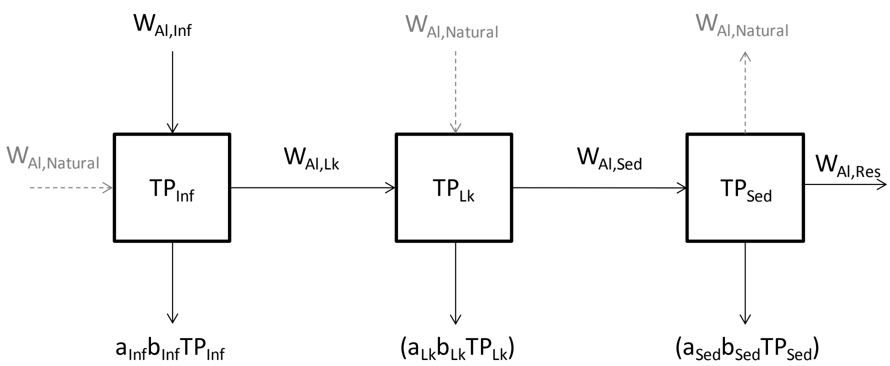


Figure 2: Conceptual diagram of alum mass balance model for Lake Rotorua. The subscripts Inf, Lk and Sed represent the inflows, lakes water column and sediment, respectively. Symbols are described in equation 6. Note: The grey arrows represent the natural aluminium inputs and outputs of aluminium and were not explicitly accounted for here.

Phosphorus uptake by alum was modelled using simple zero-order reaction kinetics for which the uptake was proportional to the TP mass in the reactor (i.e. a fraction of TP) taking into account a potential effective Al:TP uptake ratio. Thus, as alum takes up P in each reactor, the alum load entering the next reactor is reduced by the following amount:

$$W_{Al,j} = W_{Al,i} - a_i\, b_i\, TP_i \tag{6}$$

Where, $W_{Al,j}$ is the alum load leaving the reactor (i and j are used as identifiers for Inf, Lk, and Sed), $W_{Al,i}$ is the incoming alum load into the next reactor, a is the fraction of TP which is available for uptake by alum, and b is the effective Al: P ratio. The mass balance for the three reactors can be written as:

$$\boldsymbol{V_{Inf}\frac{dc_{Al,Inf}}{dt} = W_{Al,Inf} - W_{Al,Lk} - a_{Inf}b_{Inf}V_{Inf}c_{TP,Inf}} \tag{7}$$

$$V_{Lk}\frac{dc_{Al,Lk}}{dt} = W_{Al,Lk} - W_{Al,Sed} - a_{Lk}b_{Lk}V_{Lk}c_{TP,Lk} \tag{8}$$

$$V_{Sed}\frac{dc_{Al,Sed}}{dt} = W_{Al,Sed} - W_{Al,Res} - a_{Sed}b_{Sed}V_{Sed}c_{TP,Sed} \tag{9}$$

With

$$W_{Al,Lk} = \begin{cases} 0, & [W_{Al,Inf} - a_{Inf}b_{Inf}V_{Inf}c_{TP,Inf}] < 0 \\ (W_{Al,Inf} - a_{Inf}b_{Inf}V_{Inf}c_{TP,Inf}), & [W_{Al,Inf} - a_{Inf}b_{Inf}V_{Inf}c_{TP,Inf}] > 0 \end{cases} \tag{10}$$

$$W_{Al,Sed} = \begin{cases} 0, & [W_{Al,Lk} - a_{Lk}b_{Lk}V_{Lk}c_{TP,Lk}] < 0 \\ (W_{Al,Lk} - a_{Lk}b_{Lk}V_{Lk}c_{TP,Lk}), & [W_{Al,Lk} - a_{Lk}b_{Lk}V_{Lk}c_{TP,Lk}] > 0 \end{cases} \tag{11}$$

$$W_{Al,Res} = \begin{cases} 0, & [W_{Al,Sed} - a_{Sed}b_{Sed}V_{Sed}c_{TP,Sed}] < 0 \\ (W_{Al,Sed} - a_{Sed}b_{Sed}V_{Sed}c_{TP,Sed}), & [W_{Al,Sed} - a_{Sed}b_{Sed}V_{Sed}c_{TP,Sed}] > 0 \end{cases} \tag{12}$$

The conditions above (Eq. 10-12) reflect that alum may in some cases become exhausted when the mass of TP in a given reactor exceeds the uptake capacity of alum (i.e. $W_{Al,i} < 0$). In this case, the alum outflow from that reactor is $W_{Al,j} = 0$. The total alum content was tracked internally to maintain mass conservation. The mass balance was computed annually for the years 2007 to 2011 assuming steady state conditions. The mass balance equations show that the model only accounts for the fate of added alum to the Utuhina and Puarenga streams and natural occurring aluminium is not modelled. It is assumed that the import and export of natural aluminium is not influenced by the alum dosing.

Because of uncertainties in determining the values for the reaction coefficients *a* and *b*, a Monte Carlo simulation was implemented comprising of 10,000 model runs, for which *a* and *b* were varied randomly within their respective bounds. The coefficient *a* was varied between 0.27 and 1 for the inflow and between 0 and 1 for the water column and sediment. The bounds for *a* in the inflow were constrained because field data showed that dissolved reactive phosphorus was at the detection limit in the Puarenga stream downstream of the alum dosing plant, but on average constituted 27% of TP upstream of the dosing plant between 2010 and 2011 (J. McIntosh, unpublished data). There was no evidence, however, that a constraint for the parameter *a* would also be valid for the water column and sediment. Thus, the lower bound for *a* (i.e. $a \rightarrow 0$) in the water column and sediment may reflect certain unusual conditions during which alum cannot take up any phosphorus. The bounds for the coefficient *b* (Al:P ratio by weight) were 3.5 and 10 (or 4 – 11.5 molar ratio). This range was chosen based on a series of published values (Table 2). These literature values were assessed based on their method of determination and only Al:P ratios were used which reflect the actual effective binding ratio, not the dose ratio. In rare circumstances, Al:P ratios have been found in the order of ~30:1 to 100:1, but were not included in this model application.

Scenarios were developed to investigate the conditions (i.e. fraction of TP available for uptake by alum and the effective Al:P ratio, respectively) needed for achieving a certain percentage P uptake by alum in the lake water column and sediment. The scenarios involved the determination of the parameter values for *a* and *b* in the three reactors to achieve a reduction of 50, 75 and 90% of water column P concentrations and internal loading. The range of parameters values of the scenarios was summarised in box-whisker plots.

Table 2: Molar binding ratios of Al:P reported in the literature. Direct comparison should be done with caution due to differences in the analytical methods (e.g. extraction protocols). The range reported reflects the effective binding ratios of Al:P in natural waters and laboratory experiments.

Reference	Range molar of $Al:P_{Al}$ ratios	Comments
Pilgrim et al. (2007)	25-100	Sediment cores taken from four lakes in Minneapolis, USA, and treated with alum at different dose rates. Sediment P fractionation using a NaOH extraction was carried out to determine Al bound P.
Rydin et al. (2000)	34.8-40.4	Sediment cores were taken from six alum treated lakes in Washington, USA. Sediment P fractionation P fractionation using a NaOH extraction was carried out to determine Al bound P.
Rydin and Welch (1999)	10-100	Estimated from Al-bound P relative to the added Al added in short-term laboratory experiments with lake sediments.
Huser (2012)	5.6-15	Sediment cores from six alum treated lakes in Minneapolis, USA. Sediment P fractionation using a NaOH extraction was carried out to determine Al bound P.
Egemose et al. (2013)	4-10 (dose ratios) 5-31 (recovered)	Sediment cores were taken at 6-8 sites in six Danish lakes. Phosphorus bound to aluminium was determined using NaOH extractions.
de Vicente et al. (2008a)	7.7-9	Sediment cores were taken from 2 Danish lakes. Phosphorus bound to aluminium was determined using NaOH extractions. Laboratory adsorption experiments were also carried out using synthesised alum flocs with the aim to determine the effect of alum floc aging on P adsorption properties. The results of these experiments are not listed here, because the calculated ratios partially reflect hypothetical maximum adsorption capacities based on adsorption isotherms.
Lewandowski et al. (2003)	2.1	Ratio was calculated based on NaOH extractable phosphorus in laboratory sediment core experiments relative to the added aluminium.
Gibbs et al. (2010)	1.11	Ratio was calculated based on the dose rate required to block 100% of the P release from Lake Rotorua sediments in a short-term laboratory sediment incubation experiment. The dose rate was 77 g m^{-2} of alum to block the P release from 3.168 g P m^{-2}, assuming that ~4% of alum is the form of aluminium.

3 Results

3.1 Sediment survey

On visual inspection of the sediment surface there was no Al floc present at the sediment-water interface in any of the sediment cores (Appendix 1). The bulk density of the sediment ranged from 0.02 g/cm^3 at the sediment surface to 0.2 g/cm^3 at 20 cm sediment depth. The lowest bulk density values at the sediment surface were found in water depths greater than 16 m (Sites 3 to 14) which suggests this area has a high sedimentation rate and is likely influenced by sediment focusing that transports finest sediments into the deep basin.

The overall range of sediment Al concentrations in samples taken as part of the present survey was 4784 to 10921 mg kg^{-1} DW with an average 6381 mg kg^{-1} DW. Generally, Al concentrations increased with sediment depth. The transect sites with elevated Al were those closest to the Utuhina Stream outlet (Sites 1-3). Sediment P concentrations ranged from 418 to 1986 mg kg^{-1} DW with an average of 834 mg kg^{-1} DW. Sediment P concentrations generally decreased with increasing sediment depth (Appendix 2: Raw data from sediment survey.

To allow for direct comparison between the survey carried out as part of this study and the survey carried out in 2006, an estimate of sediment accumulation over the 6-year time period between the studies was made. This rate was determined by preceding studies, and a visual best fit for the data. Trolle et al. (2008) calculated a net sedimentation rate for the period between 1886–2006 of 0.3 cm yr^{-1}, and Pearson (2007) estimated up to 1.0 cm yr^{-1}. Because the Tarawera tephra was not captured in the present sediment survey (see Appendix 1 for core photos), the method of calculation of the accumulation rate used by Trolle et al. (2008) and Pearson (2007) only provides an estimated range for total sediment accumulation over the 6-year period of 1.8 - 6 cm. A visual inspection of the Al and P concentration profiles of the sediment suggest accumulation of 4 cm since 2006. Direct comparison for Al between this study and Pearson (2007) was unable to be made for sites 2 and 13 because of analytical differences.

In comparison with sediment collected in 2006, Al concentrations in 2012 were lower in the main basin of the lake (Figure 3); however, an increase in sediment Al concentration of at least 1000 mg kg^{-1} DW was found at site 9. Phosphorus concentrations in the sediments were reduced in zone 1 (sites 1 to 4) directly out from the discharge of the Utuhina and Puarenga Streams, but other sites further from the stream (i.e. zones 2 and 3) showed increased concentrations of phosphorus in the sediment (Figure 3).

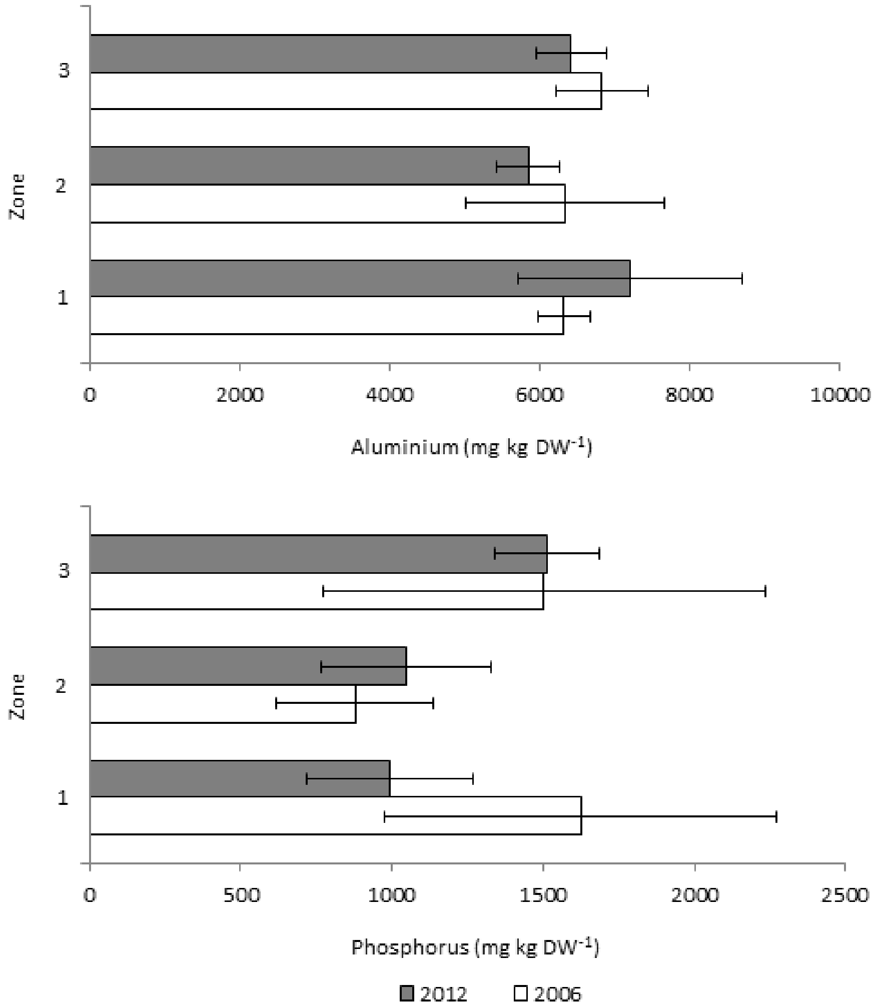


Figure 3: Mean aluminium and phosphorus concentration in Lake Rotorua sediments (0–4 cm) by depositional zone for the present (2012) and 2006 surveys (Pearson, 2007). Bars represent ranges for the respective zone. Zone 1: N=4; zone 2: N=7; zone 3: N=4.

3.2 Aluminium and phosphorus in pore waters

Aluminium in pore waters was highest at the sediment surface near the discharges of the Puarenga and Utuhina Streams (Sites 1 and 2, Appendix 2). At sites 10 to 15, concentrations were lowest at the sediment-water interface and increased with sediment depth. No Al pore-water data from 2006 were available for comparison. Phosphorus concentrations in pore waters were lowest at the sediment water interface and increased with sediment depth. The highest phosphorus concentrations were observed at Sites 1 to 3. Phosphorus concentrations in pore waters have generally decreased since 2006, to the greatest extent at site 15.

3.3 Alum mass balance

In Table 3, the boundary conditions for the alum mass balance model are presented. The annual cumulative alum dose rates to the streams, the cumulative TP loading from the streams and the TP mass in Lake Rotorua varied with time between 2007-2011, whereas the internal P loading from the sediment was assumed to be constant for the entire period. In the mass balance, the sediment is the last reactor (see Figure 2) and thus the internal loading values do not influence the alum mass balance and serve only as a rough point for comparison with the calculated P uptake by alum in that reactor.

Table 3: Overview of alum dosing and TP content in streams and water column and internal P loading in Lake Rotorua

Year	Cumulative alum dosing to streams ($t\ yr^{-1}$)[a]	Cumulative TP loading from streams ($t\ yr^{-1}$)[b]	TP mass in Lake Rotorua water column (t)[c]	Internal P load from sediment (t) [d]
2007	30.17	8.59	21.89	36
2008	17.51	11.29	20.93	36
2009	26.52	7.82	24.02	36
2010	84.01	7.62	22.66	36
2011	110.74	9.95	12.41	36

[a] Values taken from McIntosh (2012); [b] Values calculated from Hamilton et al. (2012); [c] TP mass calculated from data collected by BoPRC; [d] Estimates taken from BoPRC (2009)

A probability distribution of $W_{Al,j}$ (see Eq. 6) was derived from the Monte Carlo simulation, encompassing 10,000 model runs aimed at providing insights into the potential amount of alum reaching the lake and sediments after some proportion of the aluminium had bound phosphorus in the preceding reactor, including the inflows (Figure 4). Because of the relatively wide range of values for the parameters *a* and *b* (fraction of TP available for uptake by alum and the effective Al:P ratio, respectively), the range of $W_{Al,j}$ for each reactor was likewise large. However, Figure 4 shows a low probability that a large amount of the dosed Al would have reached the sediments in Lake Rotorua. This is especially so for the years 2007 to 2009 when the alum dose to the streams was comparatively low. Only in the years 2010 and 2011, was some of the dosed alum likely to have reached the lake sediments. There was a high probability that a large fraction of the Al reached the lake water column. This is due to the high alum dose rates in the streams relative to the low phosphorus loading from the Puarenga and Utuhina streams.

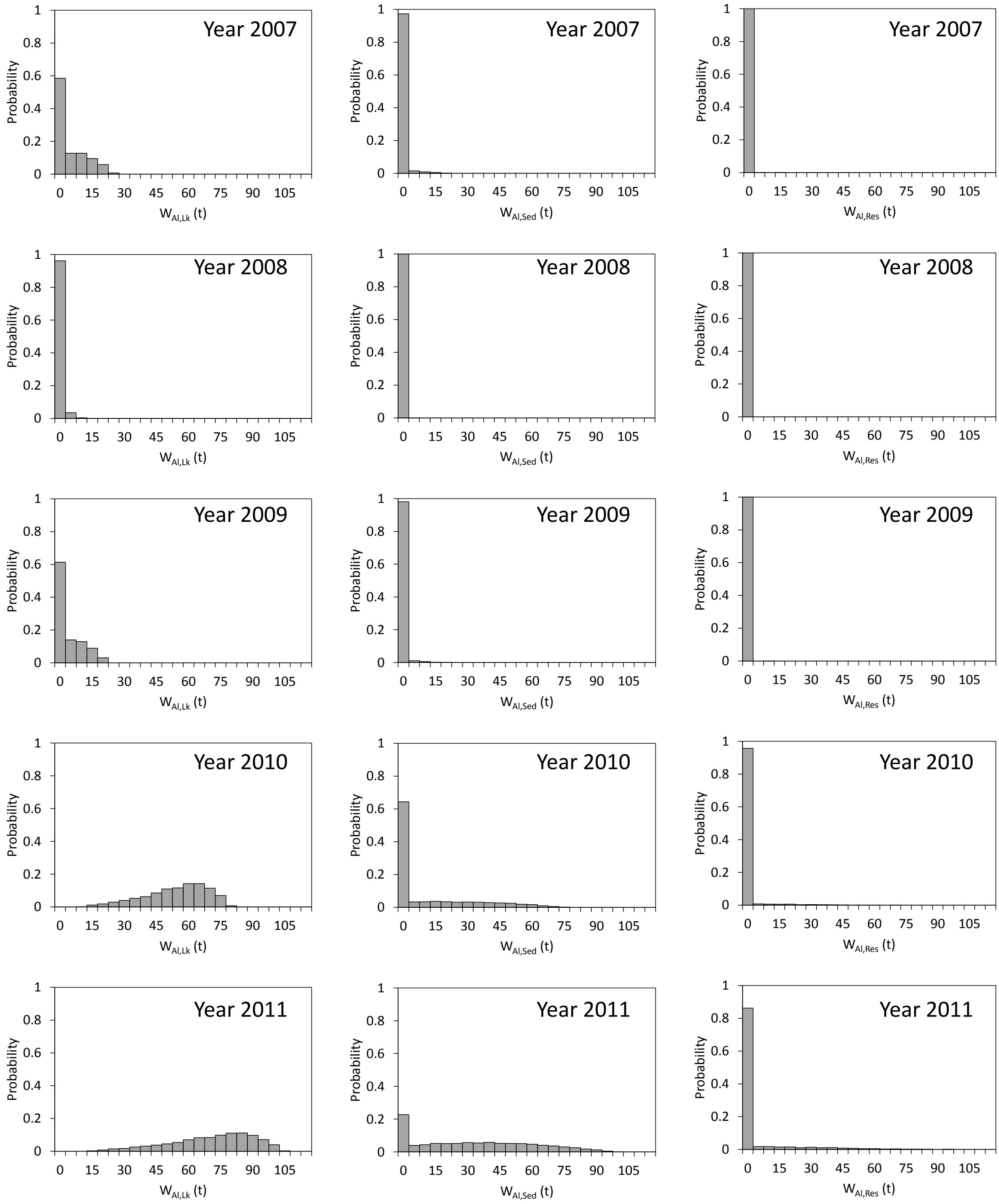


Figure 4: Probability distribution of $W_{Al,j}$, which is the amount of alum leaving the respective reactor after phosphorus uptake is considered in the modelling approach described by Equation 6 (subscripts Lk, Sed, Res lake, sediment and the residual aluminium, see Figure 2 for detailed conceptual diagram) for the years 2007 to 2011. The probability distribution was derived from a Monte Carlo simulation encompassing 10000 simulations for which parameter values for phosphorus uptake were varied randomly within their respective bounds (see text for further details).

Based on the Monte Carlo simulations, the mean P uptake in all three reactors suggests it is unlikely that the alum would have significantly reduced internal P loading (Figure 5). It is possible, however, that alum would have reduced a considerable proportion of the P loading from the streams and the P concentration in the water column P, provided the alum would have had sufficient contact time in the water.

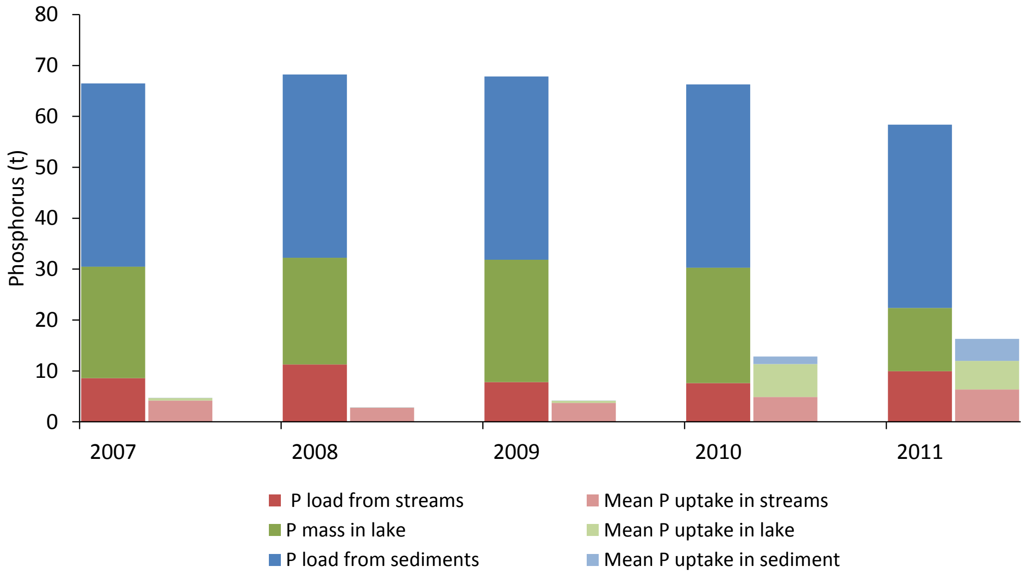


Figure 5: Clustered stacked histogram comparing the annual contribution of the total phosphorus mass of each of the three reactors of the alum mass balance (see Figure 2) between 2007 and 2011 and the mean P uptake in each reactor simulated using a Monte Carlo approach which encompasses 1000 simulations (see text for detailed description).

Although the range of values for the alum mass balance parameter *b* was well within the range found in the literature, it could still be argued that these values are artificially low (see Table 2). Even by using these lower values, it appears that only a small proportion of dosed alum could reach the lake sediments. The question then arises as to what conditions would be needed to achieve a given target for percentage uptake of lake water column P, with respect to the parameters for the fraction of TP available for uptake by alum and the effective Al: P ratio. Figure 6 illustrates that the range of parameter values for *a* and *b* used in this study could bring about a significant reduction in water column P concentrations. Only when simulating a 90% reduction of water column P concentrations was the range of possible parameter values for achieving such a reduction relatively constrained. This is especially so for the fraction of water column TP which is available for uptake by alum with a median value of 0.97.

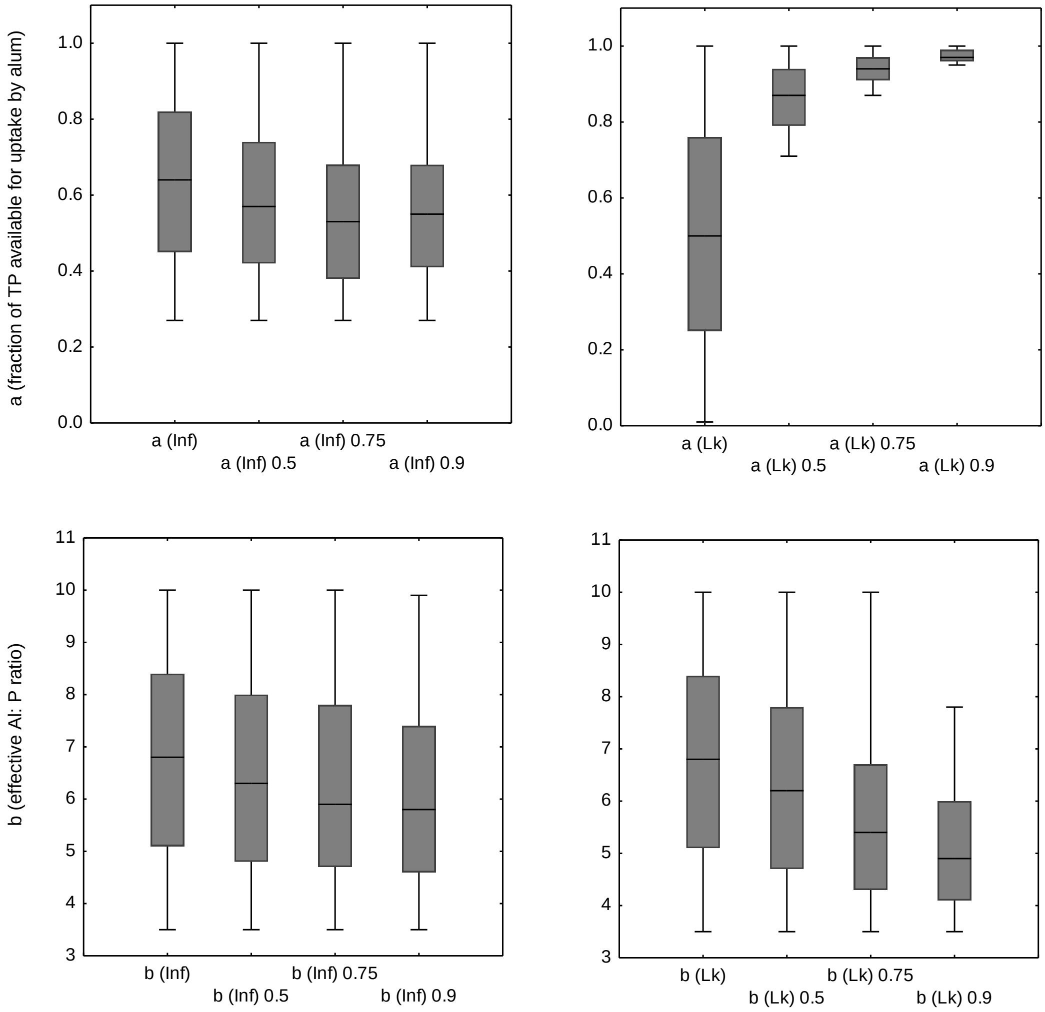


Figure 6: Summary of scenarios for determining the parameter values *a* and *b* in two alum mass balance reactors (inflows and lake) for the baseline and for achieving a 50, 75 and 90% reduction in water column P concentrations. The line represents the median, the boxes are the 25 and 75% percentiles and the bars are the parameter value range < ±1 Standard deviation.

In simulated scenarios where a substantial reduction of internal P loading was the target, parameter values for *a* and *b* in both the inflows and water column were considerably constrained (Figure 7). This was more pronounced for the parameter *a* than it was for *b*, in particular in the water column where median values reached 0.05 in order to achieve a 90% reduction of internal P loading. Even with the constraint of the parameter values in the inflows and water column, there did not appear to be a large amount of alum reaching the sediment to take up a significant proportion of internal P loading. This was reflected in very low median values of the parameter *b* (as low as 3.95 for achieving a 90% reduction in internal P loading).

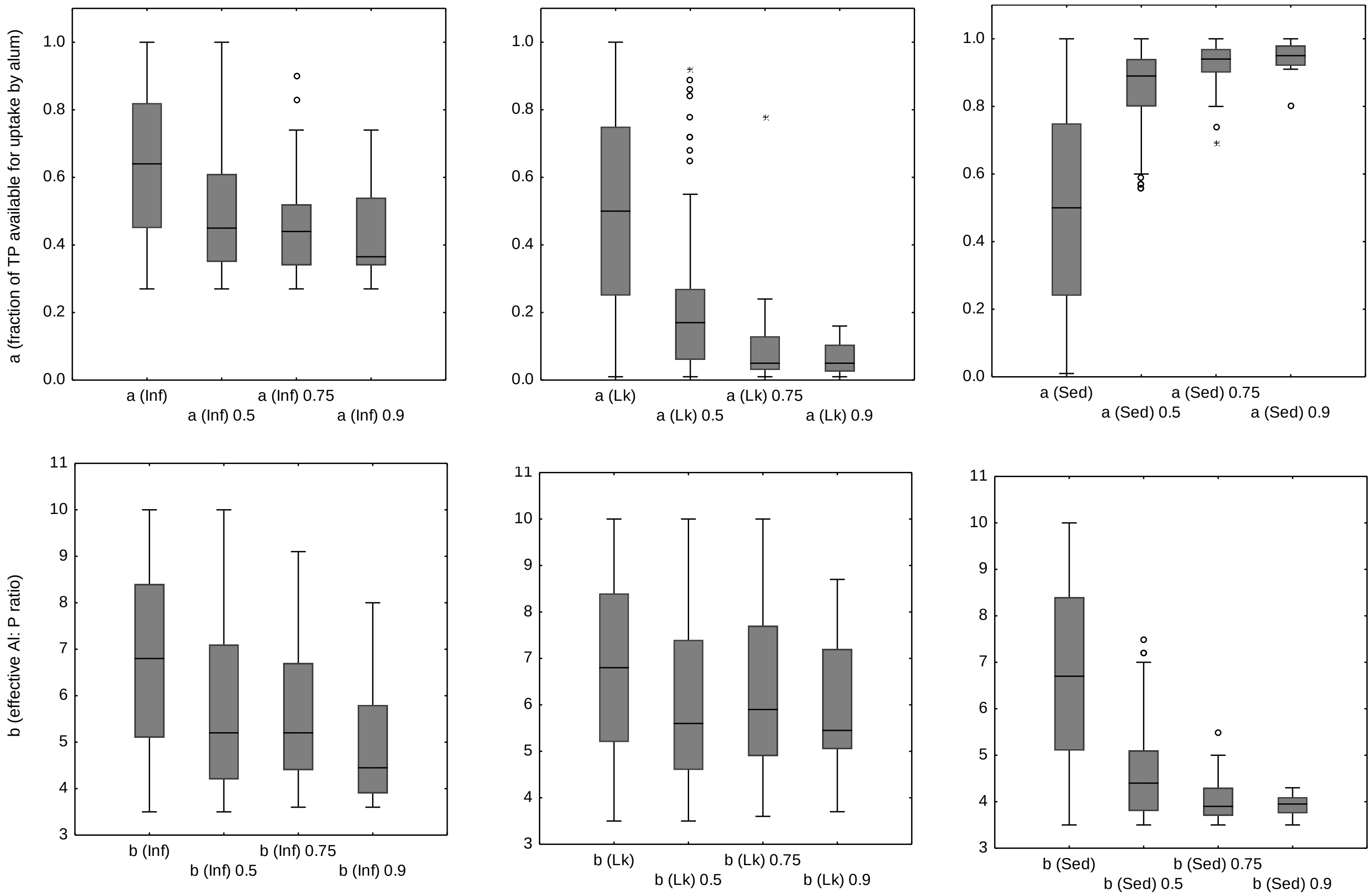


Figure 7: Summary of scenarios for determining the parameter values *a* and *b* in three alum mass balance reactors (inflows and lake) for the baseline and for achieving a 50, 75 and 90% reduction in internal P loading. The line represents the median, the boxes are the 25 and 75% percentiles and the bars are the parameter value range < ±1 Standard deviation, circles are outliers and stars are extreme values.

4 Discussion

4.1 Temporal changes in sediment P and Al concentrations

Longer-term (i.e. multiple year) changes in the lake and catchment need to be accounted for to explain the increase in sediment P content in zone 2. Trolle et al. (2008) found that the sediment P concentrations in Lake Rotorua had decreased substantially between an earlier sediment survey in 1995 (Blomkvist and Lundstedt, 1995) and 2006, at a rate of 63 mg P kg^{-1} DW yr^{-1} for the surficial (0-2 cm) layer. We sampled the same locations in zone 2 at 7 out of 8 sites used by Trolle et al. (2008), therefore, direct comparison can be made. We found an increase of 62 mg P kg^{-1} DW yr^{-1} in the surficial sediments since 2006.

While no direct explanation was offered in Trolle et al. (2008) as to why a reduction in sediment P concentrations had occurred, it was hypothesised that the sewage diversion in 1991, which had significantly reduced the external nutrient load to the lake, resulted in feedback between external loading and sediment nutrient concentrations. This is a plausible explanation, because the relationship between water column P concentration in lakes and external P loading has long been established (e.g. Vollenweider, 1976), suggesting that sediment P concentrations would also respond to changes in external load. This is further supported by a significant relationship between external P load and surficial sediment P concentrations observed in Danish lakes (Søndergaard et al. 1996). It is therefore possible that the sediment P concentrations would decrease in Lake Rotorua with a reduction in external loading (i.e. sewage diversion in 1991) but could also increase as a result of increased external loading.

The time scale of sediment responses to changes in external nutrient loading has been subject of some debate in the literature, due to the fact that the sediment P pool can accumulate over many decades which would prevent a rapid response, although it remains unclear how fast this P pool may become exhausted. In other stratified lakes with anoxic hypolimnia, recovery after P input reduction was observed at time scales of around 10-15 years (Jeppesen et al. 2005). Rutherford et al. (1996) predicted marked improvements of water quality in Lake Rotorua after 20 years following load reductions, but argued that the time scales with which the sediment P concentration may respond was in the order of 195 years. By contrast, Özkundakci et al. (2012) found a significant relationship between medium-term external N loads and surficial sediment N concentrations in Lake Rotorua using a 4-year average of external N loading. This finding would suggest that the surface sediment (i.e. 0-2cm) response time to changes in external loading in Lake Rotorua may be in the order of a decade. If sediment P concentrations are closely related to external loading on relatively short time scales, it follows that the external P load to Lake Rotorua over the last years has increased.

Other mechanisms that may lead to increases in sediment P concentrations may be related to changes in the status of hypolimnetic oxygen and to sediment P accumulation through alum flocculation. These mechanisms may not be independent. Sediment focusing may explain some of the increased sediment P concentrations, but in this case one would also expect an increase in sediment Al concentrations. However, this process should be assumed to be continuous and can, therefore, not necessarily explain a reduction of sediment P concentrations found by Trolle et al. (2008). Flocculation of P by alum is an unlikely explanation, because if flocculation had occurred an increase in sediment Al concentrations would also be expected, but such an increase in Al was not observed. A more plausible explanation is that there have been less frequent and less severe anoxic events during years within the current observation period (C. McBride, unpublished data; Appendix 3), which would likely result in less sediment nutrient release and therefore elevated sediment P concentrations. Changes in the oxygen status of bottom waters could have been a direct result of recently reductions in water column P concentrations observed in Lake Rotorua (see Chapra & Reckhow 1983), unusual climatic events during that time which may have reduced water column stability, or a positive feedback of both.

It is possible that some of the alum deposited onto bottom sediments is buried in deeper sediment layers, thus rendering it less effective for reducing internal loading, assuming that the sorption capacity at this point is not exhausted. Mixing of sediment due to bioturbation is not uncommon in lakes. Generally, maximum diversity of benthic organisms is within sublittoral zones, with decreasing diversity towards the main basin of a lake (White and Miller 2008). However, a quantitative evaluation of macroinvertebrate density (i.e. individuals m^{-2}) during the current sediment survey in Lake Rotorua suggests that the total abundance of benthos may increase with increasing depth (see Appendix 4). Moreover, oligochaete worms, which are often assumed to have a significant impact on sediment mixing due to their feeding patterns (Boes et al. 2005), were the most abundant genus at all sites sampled. Therefore, the likelihood of burial of aluminium into deeper sediment layers due to bioturbation may be higher in the deeper part of Lake Rotorua.

4.2 Alum mass balance

While the primary restoration target for the alum dosing of Puarenga and Utuhina streams in Lake Rotorua is to reduce external loading, the alum may, to some extent, have reduced internal loading (sediment nutrient release) of P as well as external loading.

The alum mass balance results suggest that although it is possible that some alum reached the bottom sediments in Lake Rotorua, any effect on internal loading was likely to be minor, even in the years 2010 and 2011 when the alum dose rates were comparably high. The conditions under which a substantial reduction of internal P loading would have been possible (with respect to the fraction of the P pool available for uptake and the effective Al:P ratio), can be considered highly optimistic (i.e. Al:P ratio ~ 3.5) when compared to literature values of Al:P ratios in other alum-dosed eutrophic lakes.

The alum mass balance is a simplification of complex and dynamic interactions between stream inflows, lake water column and sediments. One of the assumptions in our approach was to omit feedback between the three different reactors. Wind-driven resuspension of the bottom sediments in Lake Rotorua (Burger et al. 2007), for example, could potentially mix alum flocs back into the overlying water column. This resuspended material for which the P sorption capacity is not exhausted, may have potential to take up P and could therefore further reduce water column P concentrations. There is only circumstantial evidence that Al resuspension has occurred in Lake Rotorua since alum dosing began, based on occasional observations of increased total aluminium concentrations in the lake (Appendix 5). However, Burger et al. (2007) showed that sediment resuspension is an important process in the lake. Because this feedback was not included in our approach, the potential P uptake calculated in the water column may be somewhat underestimated whereas the reduction of internal P loading may be overestimated.

The effect of pH on the P uptake efficacy by Al is well known. Peterson et al. (1976) found in a laboratory assay on pond water that the P uptake efficacy of Al varied greatly within a pH range of 4 to 7 and that the maximum P removal capacity occurred at pH 4 to 6 but was reduced significantly on either side of this range. They found that multiple pH adjustments of pond water to pH between 4 and 7 were necessary to achieve a Al:P ratio of 5.7:1 (molar) for a 90% P uptake by Al. By comparison, a single adjustment of pH to a value of 7 resulted in a Al:P ratio of 7.2:1 (molar) for a 90% P uptake efficacy. The pH in Lake Rotorua generally fluctuates between 6 and 8 (Appendix 6), and values in the main basin appear to display relatively little spatial heterogeneity. By contrast, pH around the Sulphur Bay area tends to show high spatial heterogeneity with values as low as 3.9 and as high as 8.5 (Appendix 6). It should be noted that Al-bound P has been found to be re-released at pH above 8.5-9 (Welch and Cooke 1999). Furthermore, the alum dosing in the Puarenga Stream appears to reduce pH downstream of the dose location compared with values upstream. Given the large range of pH values found in the dosed streams and Lake Rotorua itself, it is reasonable to assume that complex hydrolysis reactions (see Equation 2-5) occur, rendering some of the Al species unavailable for P uptake, i.e. increasing the effective Al:P ratio.

While comparing effective Al:P ratios across lakes (see Table 2) provides a point of reference, direct comparisons can be difficult due to differences in chemical composition of individual water bodies and analytical differences between studies. Extrapolation from laboratory experiments (e.g. batch and/or sediment incubation studies) to whole lake ecosystems can also be difficult because many of the natural processes occurring in the lake cannot be reproduced in incubation chambers and the area of the sediment surface being tested is very small relative to the potentially high spatial variability across the bed of the lake (Özkundakci et al. 2011). We regard the range of values for the reaction parameters in our mass balance as reasonable based on values reported in the literature. Validation of the effective Al:P ratio in the streams, lake and sediment using a laboratory study would certainly improve the model accuracy and help to quantify the effective amount of dosed alum available for P uptake in Lake Rotorua.

For the comparison of alum dose rates across different lakes, the unit g Al m^{-3} has been used traditionally with reference to the lake volume. Depending on the restoration objective for a given lake, however, this unit may be misleading in lakes where coverage of the bottom sediments with alum is the target. More recently, authors have used areal dose rates (g Al m^{-2}) which is a more appropriate unit for comparing lakes with different area:volume ratios when the reduction of internal loading is the restoration target.

The conversion of total alum dose rates in the streams (usually reported as t Al yr^{-1}, see McIntosh, 2012) to areal dose rates (g Al m^{-2}) for Lake Rotorua is a valid approach to compare the magnitude of the alum dose rates across various other lakes where internal P loading has been a problem. Egemose et al. (2013) compared the horizontal and vertical distribution of Al in the sediment of six Danish lakes and reported areal dose rates ranging from 10 to 54 g Al m^{-2}. Huser (2012) reported areal dose rates ranging from 18 to 70 g Al m^{-2} in six lakes in Minnesota, USA. By contrast, the cumulative areal dose rate of alum for Lake Rotorua for the years 2007 to 2011 was 3.4 g Al m^{-2} for the entire lake area. This dose rate for Lake Rotorua is arguably an underestimation because the process of sediment focusing could redistribute the sedimented material from shallower to deeper zones of the lake where much of the internal loading occurs (see Burger et al. 2007). By accounting for sediment focusing following the method developed by Blais and Kalff (1995), which calculates the area occupied by the zone of accumulation in the lake (see Appendix 7 for calculations), the cumulative areal dose rate of alum for sediments in depositional areas in Lake Rotorua would be 7 g Al m^{-2}. This dose rate assumes that all alum reaches the bottom sediments; the mass balance shows that the fraction of alum reaching the sediments unbound is likely to be relatively small. Therefore, the areal dose rate of alum to Lake Rotorua sediments is up to 10-fold (or more) lower than in other alum-dosed lakes reported in the literature. This suggests that, while alum may have reduced internal P loading to some extent, other processes affecting internal loading are likely to have contributed to the marked improvement of water quality in Lake Rotorua.

5 Conclusions

The current study was designed to consider the possibility that stream-dosed alum could explain changes in the water quality in Lake Rotorua, through the mechanism of sediment deposition and subsequent reduction of internal P loading. It is likely that alum dosed to the Puarenga and Utuhina Streams has substantially reduced in-stream, and to some extent water column, P concentrations. It appears less likely that alum has reduced internal loading in Lake Rotorua to a comparable proportional extent. Accumulation of sediment Al concentrations was observed in zone 1 (Figure 8), adjacent to the inlets of the Puarenga and Utuhina Streams, and this zone also comprises a 40-m deep depression which may act as a sink for Al. This accumulation, however, cannot explain the fate of the total 269 t Al between 2007 and 2011 dosed to the streams. A mass balance approach showed that the amount of Al dosed to the streams is unlikely to explain completely the recently observed improvement of water quality in Lake Rotorua. Any claim otherwise, should be viewed with caution and regarded as overly optimistic.

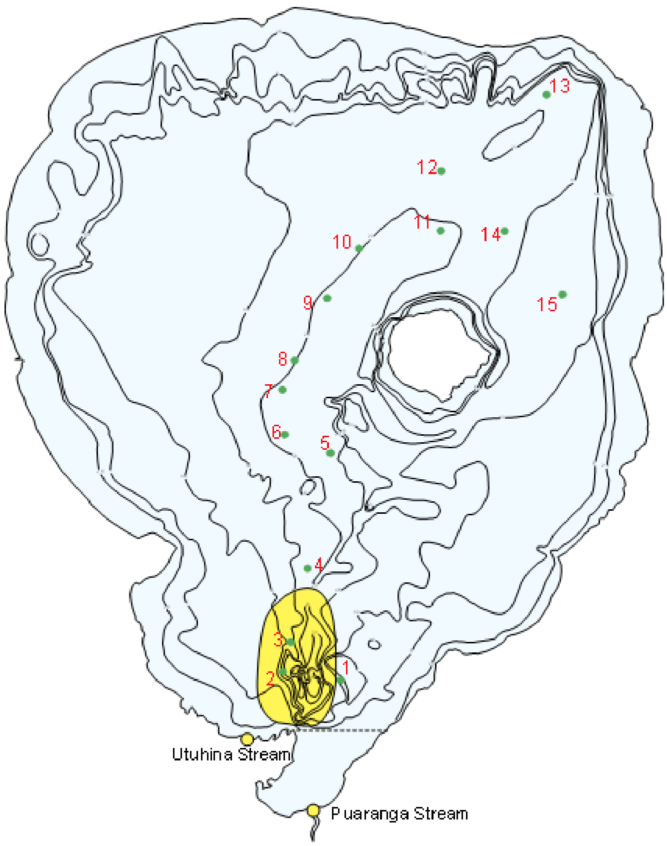


Figure 8 Area of aluminium accumulation in Lake Rotorua sediment. The dashed line represents the boundary of the Sulphur Bay area with high spatial heterogeneity of pH values (Appendix 6).

Further research into the possible synergistic causes of improved water quality in Lake Rotorua is recommended, and could include:

- **One-dimensional dynamic process based modelling**: The modelling period should encompass at least the entire period of the present report. This modelling exercise could include a coupled catchment, climate and lake model to capture any potentially unusual climatic conditions which may affect catchment hydrology and nutrient runoff, recent nutrient management actions within the catchment, in-lake stratification and/or nutrient cycling in the lake.
- **Three-dimensional (3-D) modelling**. The 3-D modelling could help determine the transport patterns and fate of alum in the Lake Rotorua basin. Long-term simulations using a 3-D model are likely to be computationally expensive, and simulations should therefore focus on key short-term events. These events should include a range of stream flow conditions (i.e. base flow and storm events), winter and summer periods and prevailing wind speeds and directions.
- **Tracer experiment(s)**. Tracer experiments within the Puarenga and/or Utuhina stream could be used to track the pathway of the stream water through the Lake Rotorua basin and determine the fate of stream water within the basin.
- **Aluminium monitoring in the Ohau Channel**: To accurately calculate aluminium export from the lake, aluminium concentrations need to be known for the outflow. This information could ultimately be used to refine the alum mass balance approach implemented in this study.
- **Validation the effective Al:P ratios:** The Al:P ratio in streams, lake and sediment can be achieved using a relatively simple laboratory jar test and would aid in constraining the parameter range in the alum mass balance calculations. It should be noted though, that these experiments may only reflect site specific Al:P ratios at the time of sampling. In order to extrapolate findings, it may therefore be necessary to carry repeated trials at different times to account for temporal (e.g. seasonal) variations.

6 References

Abell, J., Hamilton, D., McBride, C., Stephens, T. & Scarsbrook, M., 2012. Analysis of Lake Rotorua water quality trends: 2001-2012. Environmental Research Institute Report: 10, Prepared in response to an Environment Court mediation for the Bay of Plenty Regional Policy Statement of 21 November 2012, University of Waikato, Hamilton, New Zealand, 25pp.

Abell, J.M., Özkundakci, D. & Hamilton, D.P., 2010. Nitrogen and phosphorus limitation of phytoplankton growth in New Zealand lakes: Implications for eutrophication control. Ecosystems, 13: 966-977.

Berkowitz, J., Anderson, M.A. & Graham, R.C., 2005. Laboratory investigation of aluminum solubility and solid-phase properties following alum treatment of lake waters. Water Research, 39: 3918-3928.

Berkowitz, J., Anderson, M.A. & Amrhein, C., 2006. Influence of aging on phosphorus sorption to alum floc in lake water. Water Research, 40: 911-916.

Blais, J.M. & Kalff, J., 1995. The influence of lake morphometry on sediment focusing. Limnology and Oceanography, 40: 582-588.

Blomkvist, D. & Lundstedt, L., 1995. Sediment investigation of the Rotorua lakes. Environmental Report 95/23. Environment Bay of Plenty, Whakatane, New Zealand.

Burger, D.F., Hamilton, D.P., Hall, J.A. & Ryan, E.F., 2007. Phytoplankton nutrient limitation in a polymictic eutrophic lake: community versus species-specific responses. Archiv für Hydrobiologie 169(1): 57-68.

Chapra, S.C. & Reckhow, K.H., 1983. Engineering Approaches for Lake Management. Vol. 2. Mechanistic Modeling. Butterworth Publishers, Boston, MA, 492 pp.

Chruchill, J.J., Beutel, M.W. & Burgoon, P.S., 2009. Evaluation of optimal dose and mixing regime for alum treatment of Matthieson Creek inflow to Jameson Lake, Washington. Lake and Reservoir Management, 25: 102-110.

Cooke, G.D., E.B. Welch, S.A. Peterson & Newroth, P.R., 1993. Restoration and management of lakes and reservoirs, 2nd ed., CRC Press, Inc., Lewis Publishers, Boca Raton, 548 pp.

de Vicente, I., Huang, P., Andersen, F.Ø. & Jense, H.S., 2008a. Phosphate adsorption by fresh and aged aluminum hydroxide. Consequences for lake restoration. Environmental Science & Technology, 42: 6650-6655.

de Vicente, I., Jensen, H.S. & Andersen F.Ø., 2008b. Factors affecting phosphate adsorption to aluminium in lake water: Implications for lake restoration. Science of the Total Environment, 389: 29-36.

Egemose, S., Reitzel, K., Andersen, F.Ø. & Jensen, H.S., 2013. Resuspension-mediated aluminium and phosphorus distribution in lake sediments after aluminium treatment. Hydrobiologia, 701: 79-88.

Environment Bay of Plenty, 2009. Lakes Rotorua and Rotoiti Action Plan. Environmental Publication 2009/03, July 2009, Environment Bay of Plenty, Rotorua District Council, Te Arawa Lakes Trust, Rotorua, New Zealand, 35pp.

Gibbs, M.M., Hickey, C.W. & Özkundakci, D., 2010. Sustainability assessment and comparison of efficacy of four P-inactivation agents for managing internal phosphorus loads in lakes: sediment incubations. Hydrobiologia, 658: 253-275.

Hamilton, D.P., Özkundakci, D., McBride, C., Ye, W., Silvester, W. & White, P., 2012. Prediction of the effects of nutrient loads, management regimes and climate change on water quality of Lake Rotorua. CBER Contract Report 123 prepared for the Bay of Plenty Regional Council, Environmental Research Institute, Department of Biological Sciences, School of Science and Engineering, The University of Waikato, Hamilton.

Huser, B. J., 2012. Variability in phosphorus binding by aluminum in alum treated lakes explained by lake morphology and aluminium dose. Water Research, 46: 4697-4704.

Jeppesen, E., Søndergaard, M., Jensen, J.P., Havens, K.E., Anneville, O., Carvalho, L., Coveney, M.F., Deneke, R., Dokulil, M.T., Foy, B., Gerdeux, D., Hampton, S.E., Hilt, S., Kangur, K.L., Hler, J. K., Lammens, E.H.H.R., Lauridsen, T.L., Manca, M., Miracle, M.A.R., Moss, B., Ges, P.N., Persson, G., Phillips, G., Portielje, B., Romo, S., Schelske, C.L., Straile, D., Tatrai, I., Wille E. & Winder, M., 2005. Lake responses to reduced nutrient loading -

an analysis of contemporary long-term data from 35 case studies. Freshwater Biology, 50: 1747-1771.

Lewandowski, J., Schauer, I. & Hupfer, M., 2003. Long term effects of phosphorus precipitations with alum in hypereutrophic Lake Süusser See (Germany). Water Research, 37: 3194-3204.

Lijklema, L., 1980. Interaction of orthophosphate with iron(III) and aluminium hydroxide. Environmental Science & Technology, 14: 537-541.

Martin, P., Boes, X., Goddeeris B., & Fagel. N., 2005. A qualitative assessment of the influence of bioturbation in Lake Baikal sediments. Global and Planetary Change, 46: 87-99.

McIntosh, J., 2012. Alum dosing of two stream discharges to Lake Rotorua. Internal Report prepared for the Bay of Plenty Regional Council, Whakatane, New Zealand.

Özkundakci, D., Hamilton, D.P. & Gibbs, M.M., 2011. Hypolimnetic phosphorus and nitrogen dynamics in a small, eutrophic lake with a seasonally anoxic hypolimnion. Hydrobiologia, 661: 5-20.

Özkundakci, D., McBride, C.G. & Hamilton, D.P., 2012. Parameterisation of sediment geochemistry for simulating water quality responses to long-term catchment and climate changes in polymictic, eutrophic Lake Rotorua, New Zealand. Water Pollution X, WIT Transactions on Ecology and the Environment, 171-182.

Pearson, L.K., 2007. The nature, composition and distribution of sediment in Lake Rotorua, New Zealand. Masters of Science Thesis, University of Waikato.

Peterson, A., Sanville, W.D., Stay, F.S. & Powers, C.F., 1976. Laboratory evaluation of nutrient Inactivation compounds for lake restoration. Water Pollution Control Federation, 48: 817-831.

Pilgrim, K.M. & Brezonik, P.L., 2005. Treatment of lake inflows with alum for phosphorus removal. Lake and Reservoir Management, 21: 1-9.

Pilgrim, K.M., Huser, B.J. & Brezonik, P.L., 2007. A method for comparative evaluation of whole-lake and inflow alum treatment. Water Research, 41: 1215-1224.

Rutherford, J.C., Dumnov, S.M. & Ross, A.H., 1996. Prediction of phosphorus in Lake Rotorua following load reductions. New Zealand Journal of Marine and Freshwater Research, 30: 383-396.

Rydin, E., Huser, B. & Welch, E.B., 2000. Amount of phosphorus inactivated by alum treatments in Washington Lakes. Limnology and Oceanography, 45: 226-230.

Rydin, E., & Welch, E.B., 1999. Dosing of alum to Wisconsin lake sediments based on *in vitro* formation of aluminium bound phosphate. Journal of Lake and Reservoir Management, 15: 324-331.

Søndergaard, M.,Windolf, J. & Jeppesen, E., 1996. Phosphorus fractions and profiles in the sediment of shallow Danish lakes as related to phosphorus load, sediment composition and lake chemistry. Water Research, 30: 992–1002.

Trolle D., Hamilton, D.P., Hendy, C., Pilditch, C., 2008. Sediment and nutrient accumulation rates in sediments of twelve New Zealand lakes: influence of lake morphology, catchment characteristics and trophic state. Marine and Freshwater Research, 59: 1067 – 1078.

Vollenweider, R.A., 1976. Advances in defining critical loading levels for phosphorus in lake eutrophication. Memorie dell'Istituto Italiano di Idrobiologia, 33: 53-83.

Welch, E.B. & Cooke, G.D., 1999. Effectiveness and longevity of phosphorus inactivation with alum. Lake and Reservoir Management, 15: 5-27.

White, E., Law, K., Payne, G.W., Pickmere, S., 1977. Nutrient demand and availability among planktonic communities-an attempt to assess nutrient limitation to plant growth in 12 central volcanic plateau lakes. New Zealand Journal of Marine and Freshwater Research, 19: 49-62.

White, D.S. & Miller, M.F., 2008. Benthic invertebrate activity in lakes: linking present and historical bioturbation patterns. Aquatic Biology, 2: 269-277.

Acknowledgments

This study was commissioned by the Bay of Plenty Regional Council. We thank John McIntosh for providing the pH and aluminium data for the Puarenga and Utuhina streams and Lake Rotorua. Paul Scholes provided water quality and lake level data for Lake Rotorua. Thanks to Joseph Butterworth and Rob Williamson for providing assistance in the field. This study was also supported through the Lake Biodiversity Restoration program funded by the New Ministry of Business, Innovation and Employment (UOWX0505) and the University of Waikato Lakes Chair supported by BOPRC.

Appendices

Appendix 1: Field photos

Site 1

Site 2

Site 3

Site 4

Site 5

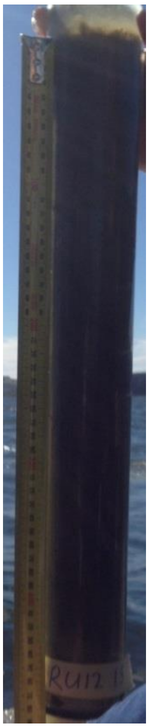
Site 6

Site 7

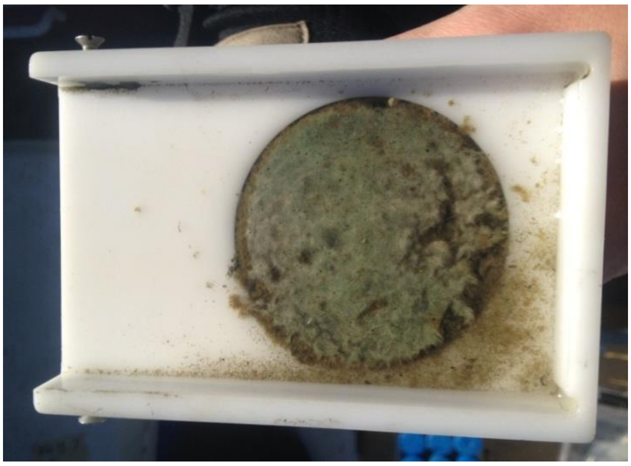
Site 8

Site 9

Site 10

				
Site 11	Site 12	Site 13	Site 14	Site 15

Site 1 core top had an algal mat less than 1 mm thick covering the sediment surface. This mat may be *Beggiatoa* sp. (a sulfur oxidising species), which is possibly why it was only found in the site directly by Sulfur Point, which has a large geothermal discharge to the lake, with high sulphur levels.



Appendix 2: Raw data from sediment survey

Sediment aluminium concentrations (mg kg^{-1} DW) in 2012.

Depth	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15
0-1 cm	6644	7056	7956	5683	5835	6099	6621	5247	6239	5704	6304	6328	7051	6166	6925
1-2 cm	6473	7086	7923	5198	4877	6396	6040	5308	6233	5911	6095	5941	6661	5544	7368
2-3 cm	6723	7279	8011	5455	5867	6025	5583	5301	6056	6172	6062	6057	5835	6157	6596
3-4 cm	7410	10922	9986	5586	5642	5743	5321	5376	5761	5950	6146	5910	6467	6571	7114
4-6 cm	7404	8169	6957	5171	4964	5630	5428	5006	5881	5837	6011	5631	6642	6357	6214
6-8 cm	7539	6527	6460	5361	4794	5388	5144	5317	5693	5934	5206	5730	5791	6057	7702
8-10 cm	6460	9613	7532	5891	5929	5786	4785	5687	5422	5607	5809	5845	6103	5401	6394
10-12 cm	6540	7985	7447	6241	6180	5175	5657	5943	5680	6204	6387	5309	6449	5812	5973
12-14 cm	5572	7440	6428	6401	6931	5708	5291	6352	6302	6291	5978	6142	6046	5941	7017
14-16 cm	5345	8669	8358	6355	7070	6042	5931	7203	6553	6965	7437	6151	5707	6621	6489
16-18 cm	6791	7545	9062	6374	7293	6671	6375	7399	7151	7164	6364	6270	5996	5939	7015
18-20 cm	6225	6755	7988	5883	6926	7589	7161	6348	7247	7040	7069	7531	6493	5936	7220

Sediment aluminium concentrations (mg kg^{-1} DW) in 2006 (Pearson, 2007)

Depth	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15
0-2 cm	5512		6274	6283	5697	7205	6942	6615	4294	7799	6736	6085		6380	6808
2-4 cm	6914		7190	5809	5879	7186	7312	7621	4797	4545	6216	6085		8253	7351
4-6 cm	6970		6699	6123	5387	6882	7776	8706	4715	4254	6635	5335		9389	7367
6-8 cm	6827		6225	6004	6068	8537	7552	5971	5167	4232	6335	6024		9630	
8-10 cm	7607		7096	6992	5881	6917	8633	6080	5425	4416	7500	6426			
10-12 cm	7528		7220	7335	6108	5848	8289	6634	5305	4285	5935	6071			
12-14 cm	8534		8343	6757	4887	5937	7318	7392	5061	4443	6118	6292			
14-16 cm	8396		9550	6861	3709	6174	6411	6985	5713	4746	6587	8129			6994
16-18 cm	7861		7947	6061	4186	6749	6754	8838	5381	5012	6534	7797			6170
18-20 cm	9137		9594	6481	4449	7266	7195	10193	5817	4340	6780	8525			5787

Sediment phosphorus concentrations (mg kg^{-1} DW) in 2012

Depth	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15
0-1 cm	888	1087	1102	940	986	1447	1748	727	1636	872	1487	1745	1779	1670	1162
1-2 cm	1069	922	1197	694	656	1562	1432	809	1665	1036	1205	1546	1797	1331	1315
2-3 cm	948	916	1184	573	690	1119	933	771	1168	1151	783	1306	1238	1919	1987
3-4 cm	978	1474	1425	503	634	1007	688	1067	749	731	623	972	1575	1904	957
4-6 cm	1261	958	1002	441	486	1096	554	805	673	597	558	683	1554	1143	768
6-8 cm	1338	727	908	440	431	725	479	501	602	494	436	575	873	752	750
8-10 cm	1032	1233	940	676	547	659	429	476	500	438	490	519	709	602	609
10-12 cm	999	1094	994	538	594	492	480	485	485	471	501	430	747	565	483
12-14 cm	754	1091	853	521	709	500	488	489	589	478	588	493	574	552	525
14-16 cm	809	1190	1062	476	715	588	524	492	554	578	592	468	552	548	419
16-18 cm	980	1210	1267	544	582	591	527	566	677	483	531	510	558	487	448
18-20 cm	868	1238	1195	545	634	696	558	560	528	479	707	608	562	482	472

Sediment phosphorus concentrations (mg kg^{-1} DW) in 2006 (Pearson, 2007)

Depth	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15
0-2 cm	1476	1330	2979	1130	870	1066	1110	947	589	964	911	2953	1526	1230	1323
2-4 cm	1370	1163	2107	1451	716	989	1139	1085	622	539	764	1850	1407	648	1084
4-6 cm	1572	1163	1607	1155	862	1036	1211	1467	633	541	749	1247	1407	656	884
6-8 cm	1375	1021	1612	936	1039	1421	1073	868	682	550	754	1052	1320	644	830
8-10 cm	1362	1021	1649	961	857	960	1221	795	606	606	768	1004	1320		875
10-12 cm	1297	1138	1717	909	719	813	1178	885	649	658	677	1053	1133		803
12-14 cm	1649	1138	1751	798	588	810	1029	967	894	713	634	931	1133		867
14-16 cm	1576	884	1904	790	509	852	845	842	741	737	561	1193	950		703
16-18 cm	1379	884	1640	652	592	968	853	1115	696	734	552	1096	950		587
18-20 cm	1639	897	2221	760	601	942	942	1310	733	696	516	1250	950		557

Pore water aluminium concentrations (mg L^{-1}) in 2012

Depth	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15
0-1 cm	0.083	0.063	0.025	0.030	0.032	0.038	0.027	0.021	0.013	0.015	0.020	0.019	0.009	0.014	0.021
1-2 cm	0.081	0.092	0.033	0.077	0.041	0.066	0.020	0.031	0.046	0.027	0.040	0.041	0.017	0.038	0.041
2-3 cm	0.089	0.073	0.050	0.081	0.046	0.068	0.021	0.030	0.069	0.054	0.060	0.055	0.047	0.035	0.052
3-4 cm	0.097	0.073	0.047	0.057	0.032	0.062	0.014	0.031	0.054	0.070	0.052	0.060	0.053	0.073	0.079
4-6 cm	0.073	0.070	0.038	0.030	0.011	0.018	0.016	0.042	0.028	0.046	0.034	0.056	0.035	0.077	0.055
6-8 cm	0.104	0.097	0.036	0.025	0.007	0.015	0.011	0.015	0.044	0.035	0.023	0.045	0.050	0.066	0.077
8-10 cm	0.073	0.135	0.020	0.045	0.017	0.020	0.009	0.022	0.027	0.026	0.021	0.037	0.056	0.086	0.116
10-12 cm	0.041	0.114	0.041	0.027	0.015	0.020	0.016	0.021	0.024	0.059	0.034	0.026	0.054	0.087	0.101
12-14 cm	0.070	0.116	0.022	0.012	0.012	0.017	0.055	0.021	0.032	0.053	0.054	0.035	0.061	0.085	0.143
14-16 cm	0.025	0.093	0.029	0.026	0.016	0.019	0.033	0.030	0.017	0.057	0.055	0.059	0.030	0.098	0.096
16-18 cm	0.084	0.063	0.020	0.022	0.007	0.007	0.019	0.017	0.020	0.039	0.044	0.024	0.037	0.066	0.071
18-20 cm	0.035	0.062	0.046	0.023	0.018	0.008	0.050	0.015	0.013	0.048	0.044	0.018	0.097	0.047	0.074

Pore water phosphorus concentrations (mg L^{-1}) in 2012

Depth	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15
0-1 cm	0.041	0.030	0.118	0.125	0.036	0.046	0.032	0.110	0.014	0.005	0.027	0.120	0.025	0.027	0.039
1-2 cm	0.028	0.029	0.246	0.499	0.059	0.171	0.077	0.476	0.267	0.010	0.314	0.103	0.029	0.044	0.095
2-3 cm	0.042	0.028	1.004	0.911	0.346	0.211	0.351	0.959	0.853	0.236	1.088	0.513	0.424	0.337	0.432
3-4 cm	0.161	0.035	0.916	1.301	0.526	0.255	0.516	1.081	1.373	0.582	1.568	1.064	0.910	0.968	0.666
4-6 cm	1.854	0.076	3.466	1.452	3.396	0.608	1.759	2.732	1.666	1.979	2.431	2.257	2.026	1.196	0.883
6-8 cm	1.186	0.189	5.805	0.983	2.032	2.307	1.950	3.212	3.103	2.300	2.277	2.077	2.414	1.794	0.929
8-10 cm	2.783	0.436	6.699	1.657	2.417	1.594	1.894	2.926	3.851	2.562	2.253	2.587	2.645	1.481	0.817
10-12 cm	3.810	0.791	8.299	2.099	2.409	2.210	2.694	2.760	3.188	2.397	2.172	2.411	1.862	2.000	0.648
12-14 cm	4.032	1.568	4.561	3.148	1.880	3.155	3.486	3.421	2.350	2.110	2.310	2.318	2.213	1.869	0.901
14-16 cm	4.013	2.461	6.125	2.458	3.216	1.898	3.117	2.167	2.135	2.557	2.658	3.436	2.704	1.534	0.979
16-18 cm	5.576	3.487	4.518	1.613	0.949	1.686	3.038	2.047	1.966	2.715	1.967	1.909	2.629	1.599	0.865
18-20 cm	4.264	4.340	0.469	1.198	0.072	2.545	3.972	1.679	2.570	2.193	3.508	2.956	2.231	2.050	0.945

Bulk density (g cm^{-3}) in 2012

Depth	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15
0-1 cm	0.086	0.054	0.030	0.027	0.028	0.024	0.007	0.024	0.021	0.015	0.016	0.016	0.014	0.020	0.043
1-2 cm	0.074	0.071	0.074	0.068	0.049	0.051	0.040	0.045	0.045	0.029	0.047	0.043	0.027	0.045	0.073
2-3 cm	0.071	0.102	0.089	0.090	0.079	0.045	0.056	0.058	0.054	0.055	0.072	0.058	0.071	0.048	0.076
3-4 cm	0.072	0.090	0.084	0.120	0.083	0.059	0.065	0.054	0.067	0.067	0.095	0.065	0.075	0.066	0.162
4-6 cm	0.107	0.100	0.081	0.110	0.093	0.061	0.075	0.063	0.068	0.084	0.099	0.086	0.105	0.081	0.091
6-8 cm	0.089	0.106	0.101	0.121	0.098	0.075	0.082	0.083	0.080	0.089	0.102	0.099	0.127	0.097	0.118
8-10 cm	0.116	0.116	0.132	0.168	0.120	0.086	0.084	0.121	0.086	0.099	0.116	0.101	0.123	0.098	0.128
10-12 cm	0.083	0.111	0.158	0.139	0.134	0.096	0.105	0.113	0.104	0.138	0.145	0.114	0.120	0.119	0.117
12-14 cm	0.091	0.122	0.149	0.142	0.137	0.135	0.127	0.127	0.143	0.124	0.164	0.129	0.134	0.115	0.130
14-16 cm	0.077	0.136	0.199	0.150	0.145	0.144	0.119	0.131	0.127	0.135	0.179	0.180	0.127	0.135	0.141
16-18 cm	0.127	0.124	0.205	0.148	0.143	0.123	0.122	0.113	0.147	0.163	0.142	0.145	0.141	0.125	0.131
18-20 cm	0.128	0.111		0.167	0.133	0.134	0.143	0.138	0.145	0.151	0.173	0.146	0.161	0.117	0.143

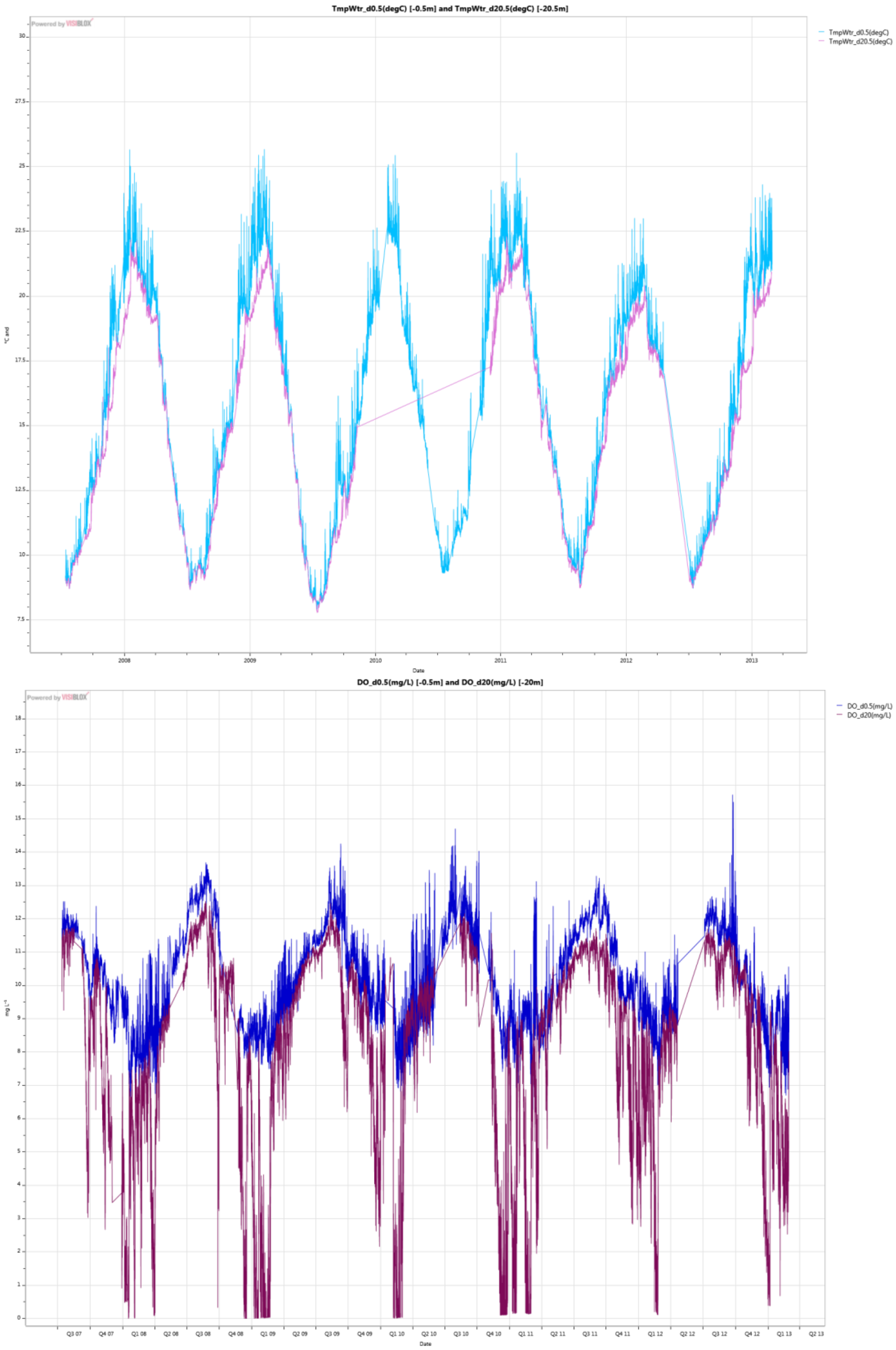
Pore water pH in 2012.

Depth	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15
0-1 cm	6.07	5.82	5.81	5.97	5.94	6.02	5.72	6.03	6.08	5.92	5.94	6.01	5.82	5.76	6.14
1-2 cm	6.06	6.02	6.06	6.00	6.03	6.01	5.88	6.04	6.20	6.08	6.12	6.19	6.27	6.31	6.08
2-3 cm	6.00	6.11	6.11	6.04	6.05	6.04	5.92	6.06	6.24	6.13	6.14	6.19	6.19	6.36	6.13
3-4 cm	6.02	6.14	6.07	6.07	6.11	6.08	5.93	6.09	6.22	6.26	6.14	6.20	6.26	6.32	6.12
4-6 cm	6.02	6.11	6.06	6.10	6.07	6.10	5.93	6.13	6.14	6.23	6.18	6.15	6.28	6.29	6.15
6-8 cm	6.04	6.12	6.05	6.10	6.11	6.18	5.99	6.07	6.25	6.17	6.16	6.21	6.30	6.24	6.19
8-10 cm	6.07	6.02	6.04	6.11	6.14	6.06	5.99	6.09	6.22	6.16	6.19	6.13	6.30	6.22	6.14
10-12 cm	6.06	5.92	6.08	6.11	6.19	6.07	6.00	6.13	6.16	6.23	6.30	6.19	6.33	6.29	6.15
12-14 cm	6.13	5.96	6.07	6.11	6.15	6.12	6.03	6.12	6.29	6.29	6.27	6.21	6.32	6.29	6.16
14-16 cm	6.11	6.02	6.12	6.11	6.19	6.24	6.06	6.22	6.27	6.20	6.33	6.30	6.29	6.25	6.19
16-18 cm	6.10	6.08	6.13	6.16	6.19	6.23	6.11	6.19	6.31	6.24	6.34	6.34	6.28	6.29	6.16
18-20 cm	6.12	6.08		6.16	6.18	6.20	6.09	6.21	6.34	6.29	6.37	6.32	6.30	6.31	6.16

Redox, Eh (mV) in 2012.

Depth	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15
0-1 cm	-14	-37	-3	-38	29	-52	53	-39	73	2	-24	-34	-13	-51	-42
1-2 cm	-71	-144	-38	-40	-1	-67	55	-28	5	-1	-43	-42	-34	-59	-41
2-3 cm	-64	-137	-58	-49	-9	-93	13	-33	-57	-31	-56	-106	-40	-106	-75
3-4 cm	-82	-151	-74	-59	-25	-90	7	-41	-68	-35	-68	-103	-87	-110	-101
4-6 cm	-90	-158	-89	-81	-47	-95	-19	-53	-64	-52	-78	-107	-109	-118	-119
6-8 cm	-106	-153	-95	-89	-67	-101	-30	-60	-73	-62	-85	-110	-114	-124	-129
8-10 cm	-109	-149	-109	-106	-81	-100	-38	-77	-83	-68	-88	-112	-116	-129	-130
10-12 cm	-117	-146	-117	-118	-92	-96	-50	-83	-86	-87	-85	-108	-126	-133	-127
12-14 cm	-119	-149	-120	-139	-95	-100	-65	-90	-85	-90	-88	-108	-127	-121	-131
14-16 cm	-122	-152	-129	-135	-106	-121	-71	-97	-79	-95	-102	-123	-134	-124	-139
16-18 cm	-126	-154	-132	-132	-113	-114	-74	-103	-91	-101	-114	-129	-136	-128	-145
18-20 cm	-136	-147		-129	-119	-122	-85	-99	-101	-82	-122	-133	-137	-130	-141

Appendix 3: High frequency data from the mid-lake monitoring buoy in Lake Rotorua for temperature (top panel) and dissolved oxygen concentrations (bottom panel) at 0.5 and 20.5m depths.



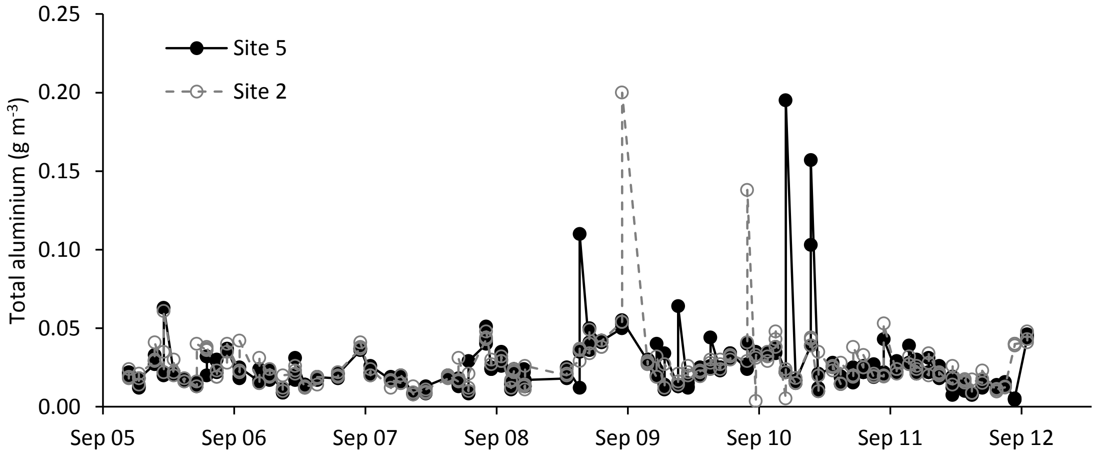
Apendix 4: Quantitative assessment of macroinvertebrate density in Lake Rotorua.

Samples were taken with a Petitie Ponar grab sampler in triplicate and organisms sorted from samples were identified to the genus level. Number of individuals were recorded for each genus (No. of individuals m^{-2}) and were averaged for triplicate samples at each site.

Site	Water depth (m)	Oligocheate	Ilyocryptus	Chironominae	Bivalve	Gastropod	Acarina
1	11	101	333	14	0	0	0
2	20	652	116	348	0	14	0
3	21.4	971	217	101	0	29	14
4	17.9	725	72	58	0	29	0
5	21	507	43	72	0	0	0
6	21	957	87	43	0	0	0
7	20.8	623	0	0	0	0	0
8	21.6	1290	0	116	0	0	14
9	21	826	87	29	0	0	14
10	20.4	435	72	29	0	0	0
11	20.4	420	159	29	0	0	0
12	18	971	87	58	0	0	0
13	16.1	594	362	87	0	0	0
14	16.6	362	14	0	0	0	0
15	12.4	391	101	145	14	29	0

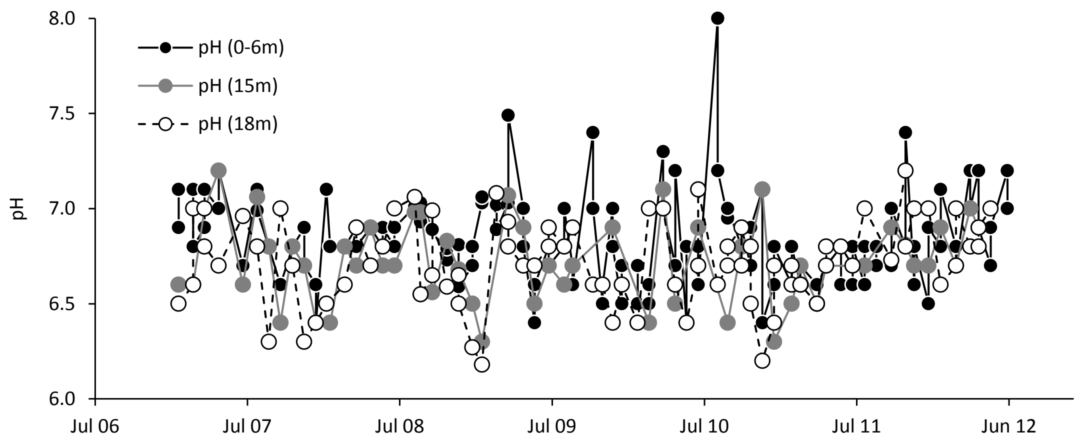
Appendix 5: Total aluminium measurements in Lake Rotorua.

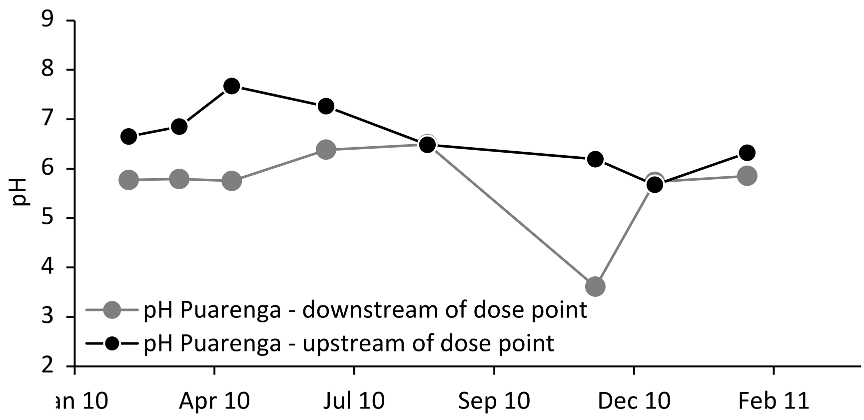
Data provided by John McIntosh (unpublished).

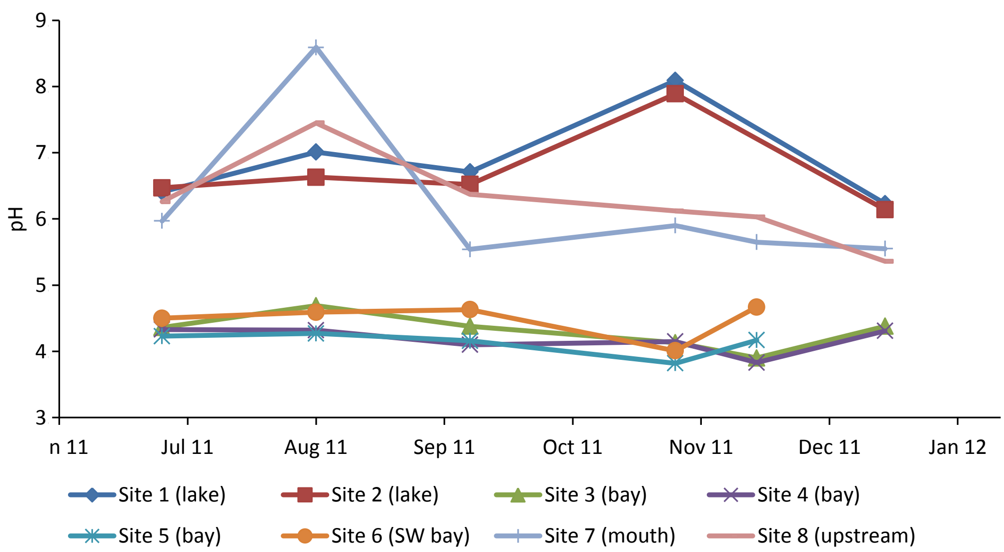


Appendix 6: pH values for Lake Rotorua (BoPRC and John McIntosh, unpublished data).

Upper panel: Lake Rotorua; Middle panel: Puarenga Stream upstream and downstream of alum dosing plant; Lower panel: Multiple sites around Sulphur Bay.







Appendix 7: Calculation of accumulation zone for Lake Rotorua

The percent area occupied by the accumulation zone (*%ZA*) was determined by calculating the area occupied by the region below the depth of the transition from the transportation zone to the accumulation zone as a percentage of the entire lake area:

$$\%ZA = 49.92 - 2.50 \times \alpha'_p$$

Where, α'_p is the mean basin slope, calculated as:

$$\alpha'_p = \left(\frac{l_0}{2} + l_1 + l_2 + \cdots + l_{n-1} + \frac{l_n}{2}\right)\frac{z_{max}}{10nA_L}$$

Where, l_i are the lengths of the contour lines (km), l_0 is the shoreline length (km), z_{max} is the maximum depth of the lake (m), n is the number of contour lines, and A_l is the lake surface area (km^2).

For Lake Rotorua, the mean basin slope (α'_p) was 0.507% and the percent area occupied by the accumulation zone (*%ZA*) was 45.65 % or 38.42 km^2.