SPECIATION AND DYNAMICS

OF PHOSPHORUS IN RELATION TO

LAKE RESTORATION METHODS

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View from Rainbow Mountain on Lake Okaro (Photo by Deniz Özkundakci)

Abstract

Lake Okaro is a small, warm monomictic lake in the central North Island of New Zealand. It has remained highly eutrophic despite an intensive catchment and in-lake restoration program which commenced in 2003. The program has included the implementation of a constructed wetland, riparian protection, an alum application and application of a modified zeolite mineral (Z2G1) to reduce internal nutrient loading. This study examines water column and sediment nutrient dynamics; focusing on phosphorus (P) and the ecosystem response to lake restoration designed to reduce levels of P.

Trends in P concentrations in Lake Okaro were linked to the restoration efforts over a six-year period (2002-08) including the period shortly before the restoration program. Over the entire study period, the annual average total phosphorus (TP) concentration in the lake decreased by 56 %. Two predictive models, which derive the annual average P concentration in the water column based on external P loading, generally underestimated the measured TP concentrations in the water column due to internal P loading. Of all restoration methods, the application of Z2G1 produced the most effective reduction in water column TP concentrations. However the lake trophic state showed high resilience to reduced internal P loading even though the combined effect of all restoration procedures resulted in significantly decreased TP concentrations in the lake.

The sources and sinks of nutrients in the hypolimnion of Lake Okaro were investigated using field measurements in a comprehensive nutrient budget model in order to determine changes in sediment nutrient fluxes resulting from a whole lake sediment capping trial using Z2G1. Sediment nutrient fluxes in the hypolimnion were estimated as the residual term in the nutrient budget model that accounted for mineralisation of organic nutrients, nutrient uptake by phytoplankton, nitrification, adsorption or desorption of P from inorganic particulate material in the water column, and diffusion of dissolved nutrients at the thermocline. The model indicated that during a period of seasonal

stratification in 2007-08 up to 60% of hypolimnetic phosphate fluxes and 50% of ammonium fluxes were derived from bottom sediments. Diffusion across the thermocline, adsorption/desorption of phosphate to suspended solids, and nitrification were of relatively minor importance ($\leq$ 9%) to the total fluxes. Any reduction in sediment nutrient release by Z2G1 was small compared with both the total sediment nutrient flux and the sum of other hypolimnetic fluxes.

Sediment and settling seston organic P composition was determined using ^{31}P nuclear magnetic resonance (NMR). Settling seston and sediment samples were analysed during winter and summer, representing, respectively, a mixing period when the water column was well oxygenated and a stratified period when the hypolimnion was anoxic. The bottom sediments and settling seston contained orthophosphate, orthophosphate mono- and diesters, pyrophosphates, polyphosphates, and phosphonates with organic P content exceeding 60% of the total extracted P occasionally. Phosphorus content in settling seston increased 2.5-fold in winter, with a marked increase in orthophosphate content. The ^{31}P NMR analyses revealed the presence of several potentially bioavailable P compounds, which may be recycled from the sediment to the water column. An 'apparent half-life' value was used to quantify the time scales on which these compounds are degraded within the sediment and likely being recycled to the overlying water column. Relatively long half-life values, ranging from 8 to 23 years, indicate that this recycling could potentially reduce the efficacy and longevity of in-lake restoration procedures that have been applied to Lake Okaro.

A one-dimensional process based ecosystem model (DYRESM-CAEDYM) was used to simulate the potential effect on water quality of Lake Okaro of separate and combined reductions in external and internal loads of nitrogen (N) and P. The model was calibrated against field data for a two-year period and validated over two separate one-year periods including a year immediately following a Z2G1 application and a year when there was an extraordinary algal bloom from an invasive, highly buoyant, N-fixing cyanobacterium, *Anabaena planktonica*. The model simulations reproduced the scale of phosphate and ammonium concentrations at 14 m depth, corresponding to the deeper region of the hypolimnion, both before and after the application of Z2G1, with no adjustment of parameters, suggesting that there was little effect of the Z2G1, at least within the uncertainties of the model runs. The model

simulations were less successful in reproducing the *Anabaena planktonica* bloom. This was attributed to a lake of flexibility in the conceptualisation and calibration of the model, which meant that it could not encompass this invasive species. In the model scenarios with reduced nutrient loading, the trophic status of Lake Okaro, given quantitatively by the Trophic Level Index (TLI), decreased to a greater extent with a given fractional reduction of the internal load than a reduction of the external load. The control of both N and P was shown in simulations to be more effective in reducing phytoplankton biomass than for N or P alone, tending to affirm an N+P control paradigm.

Undesirable shifts in zooplankton and phytoplankton species composition due to the application of Z2G1 were investigated by comparing the plankton community structure before and after the Z2G1 application. No significant differences in species composition were found at the depths investigated (surface and 9 m). However, further analyses showed statistically significant differences between seasons, indicating that seasonal variations in plankton composition far outweighed changes that occurred as a result of the Z2G1 application.

In this study, field measurements and numerical modelling provided a comprehensive assessment methodology of testing the response of Lake Okaro to reduced nutrient loading, with a focus on P dynamics. Although nutrient loads to Lake Okaro were reduced using catchment and in-lake restoration methods, further substantial and prolonged reduction in both N and P loading appear to be required to decrease phytoplankton biomass and the trophic state of the lake. This study highlights the need for investigating water column P content and sediment P composition for evaluating the potential magnitude of internal loading, and emphasises the importance of using process based numerical modelling as a decision support tool for lake management.

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Acknowledgments

Preface

This thesis is comprised of seven chapters, which describe the results relating to this study. Chapters 2-6 have been written for publication in peer-reviewed scientific journals. Except where referenced, the work presented in this thesis, including field work and laboratory work, data analysis, interpretation and writing was produced from my own ideas, undertaken while under the supervision of Professor David Hamilton and Associate Professor Alan Langdon (University of Waikato).

Co-authors of the papers listed below have contributed with discussions and revisions of the manuscript. Ian Duggan assisted with zooplankton and statistical analysis for Chapter 6. Long-term water quality data for Chapter 2 have been obtained from Environment Bay of Plenty. For Appendix I, I participated in planning of the study, performing sample analysis and writing the article.

Chapter 2 has been accepted for publication in Ecological Engineering under the title 'Effect of intensive catchment and in-lake restoration procedures on phosphorus concentrations in a eutrophic lake' by Deniz Özkundakci, David P. Hamilton and Paul Scholes.

Chapter 3 has been prepared for submission to Hydrobiologia under the title 'Hypolimnetic phosphorus and nitrogen dynamics in a small, eutrophic lake with a seasonally anoxic hypolimnion' by Deniz Özkundakci, David P. Hamilton and Max M. Gibbs.

Chapter 4 is in preparation for submission to Environmental Science and Technology under the title 'Phosphorus dynamics in sediments of eutrophic lake derived from ^{31}P nuclear magnetic resonance assays' by Deniz Özkundakci, David P. Hamilton, Stefan Hill and Richard McDowell.

Chapter 5 has been submitted for publication to Ecological Modelling under the title 'Modelling the response of a highly eutrophic lake to reduction in

external and internal nutrient loading' by Deniz Özkundakci, David P. Hamilton and Dennis Trolle.

Chapter 6 has been accepted for publication in Hydrobiologia under the title 'Does sediment capping have post-application effects on zooplankton and phytoplankton?', DOI:10.1007/s10750-009-9938-y, by Deniz Özkundakci, Ian C. Duggan and David P. Hamilton.

Appendix I has been submitted for publication in Hydrobiologia under the title 'Effects of a modified zeolite on P and N processes and fluxes across the lake sediment-water interface using core incubations' by Max M. Gibbs and Deniz Özkundakci.

1   General introduction

1.1   Motivation

The importance of phosphorus in lakes

Phosphorus (P) is an essential life-supporting element and can be a limiting nutrient controlling biological productivity in many terrestrial and aquatic environments (Oelkers & Valsami-Jones, 2008). However, inadvertent additions of P to aquatic systems have intensified eutrophication (Wetzel, 1992; Carpenter, 2008). One of the most frequently observed symptoms of eutrophication is the formation of surface algal blooms that often consist of potentially toxic cyanobacteria, some of which may also fix nitrogen (Scheffer, 1998; Carmichael, 2001). Despite advances in understanding the causes and effects of eutrophication during the last 50 years, management of eutrophic freshwater and costal marine ecosystems remains a global challenge (Schindler, 2006). The control of eutrophication by reducing nitrogen (N) alone has been shown to have only limited effect in many freshwater systems, and is considered by some to exacerbate the occurrence of algal blooms (Schindler *et al.*, 2008). Recently, there have been renewed arguments to suggest that P reduction alone may alleviate eutrophication (Schindler & Hecky, 2009) while other studies have recognised the importance of simultaneous control of P and N (e.g. Jeppesen *et al.*, 2007; Carpenter, 2008; Conley *et al.*, 2009).

Internal nutrient loads

Phosphorus can reach aquatic ecosystems by a number of vectors including natural weathering of rocks, mining and runoff from other land disturbances. Point sources come primarily from industrial and municipal waste water discharges while most diffuse additions of P to lakes originate from fertilisers added to crop and pastoral land (Carpenter, 2008). Globally, P production for use as fertiliser will reach a maximum production rate around the year 2030 (Cordell

et al., 2009). While this may subsequently drive an improvement in water quality, reductions in lake nutrient levels are likely to be gradual, due to the fact that the bottom sediments of lakes often have a large pool of P. Lake sediments play an important role in nutrient dynamics and eutrophication because internal nutrient loads, i.e. transfers of nutrients from the sediments to the water column, can markedly increase the total nutrient load (Søndergaard *et al.*, 2003; Burger *et al.*, 2007a). In addition, internal loads can delay the improvement of water quality after restoration measures have been conducted in the catchment (Jeppesen *et al.*, 2005).

It was generally believed until the 1970s, that sediments acted as sinks for P and iron-bound phosphate was released to the hypolimnion in periods of anoxia (Mortimer, 1941, 1971). Since that time a much more complicated picture has developed. Phosphorus release from sediments depends on a variety of physical, chemical and biological processes. Gächter (1988) and Sinke *et al.* (1990) showed that sediment microorganisms can rapidly uptake and release inorganic P. Holdren & Armstrong (1980) demonstrated that P release rates increased with increasing temperature. There is also evidence that bioturbation from benthic invertebrates enhances phosphorus release rates, particularly in sediments low in total iron (Phillips *et al.*, 1994). Resuspension by waves can increase total phosphorus (TP) concentrations in the water column of shallow lakes (Hamilton & Mitchell, 1997). Furthermore, remobilisation of P from the sediment is controlled by its speciation (Selig & Schlungbaum, 2003), therefore knowing the TP content of the sediment is not sufficient for defining the amount of P that can be released (Nürnberg, 1988). Phosphorus speciation in sediments can be determined using a technique of sequential chemical extraction in order to give a more precise description of the potential for sediment P release and to predict its future influence on lake water concentrations (e.g. Golterman, 1982; Pettersson *et al.*, 1988; Spivakov *et al.*, 1999). On this basis, it was shown that calcium-bound P gives low release rates, while phosphorus bound to iron and, and to a smaller extent aluminium, is released in anoxic conditions and at high pH levels (Pettersson *et al.*, 1988). However, the exclusive use of chemical extraction to infer release rates based on P to metal cation ratios and using Fick's Law (Sinke *et al.*, 1990) has also been criticised (Barbanti *et al.*, 1994; Ruban *et al.*, 1999). Today, a great variety of extraction schemes are being utilised, none of which

appear to be generally applicable for different sediment compositions. Despite advances in the understanding of internal nutrient loading, there is little information concerning the reactivity of various organic P species in the sediments; at what rates they are transformed and made available again for biological uptake; and which forms can be considered as refractory and thus will be buried in deeper sediment layers (Ahlgren *et al.*, 2005).

Management of internal nutrient loads

Today there is a great variety of lake restoration methods for controlling both external and internal nutrient loads. Reviews have been conducted for North American and European Lakes (Dunst *et al.*, 1974; Cooke *et al.*, 1993; Klapper, 2003). Rowe (2004) has provided a comprehensive review of the types of problems in New Zealand lakes and identified potential restoration approaches, particularly to control eutrophication. More recently, Hickey & Gibbs (2009) have outlined a decision support and risk assessment framework for sediment P release management.

Flocculation or P precipitation with iron or aluminium salts is the most common method utilised to decrease P content in the free-water of lakes with long retention times (Welch & Cooke, 1999; Klapper, 2003). The formation of hydroxides predominates in the process of P binding using metal salts. The metal phosphate is either occluded within the flocs or deposited on the outside of the floc (Cooke *et al.*, 1993). Aluminium is often preferred over iron, because iron is more strongly redox sensitive and can cause a re-dissolution of phosphate under anoxic conditions. However, during formation of the hydroxide flocs following aluminium application, considerable quantities of H^+ ions are released. This can potentially result in an ecologically unacceptable decrease in pH (Cooke *et al.*, 1993). The chemical process of phosphate precipitation with aluminium appears simple:

$$Al^{3+} + PO_4^{3-} \quad \longrightarrow \quad AlPO_4 \downarrow \qquad (1.1)$$

but the solubility and aquatic chemistry of aluminium following alum treatment is complex. When alum is added to water, a series of hydrolysis reactions occur subsequently, which are pH dependent. The $Al(OH)_3$ complex, dominating the Al species at a pH range between 6 and 8, is of greatest interest due to its ability to adsorb large amounts of inorganic phosphorus. Therefore, the ideal conditions for alum to be added to the water would be within the pH range described (Cooke *et al.*, 1993). However, because some aluminium species may have toxic side-effects, several factors must be considered before an application of alum to a lake can be carried out. The aluminium solubility is dependent on the buffering capacity of the lake and the pH, as well as the water temperature (Cooke *et al.*, 1993). At low pH for example, aluminium becomes more soluble and potentially toxic to aquatic biota. Furthermore, decisions are required concerning the water depth of application, dependent on the treatment objective, and the optimal dose rate.

Sediment capping is another method of preventing phosphorus release from lake sediments (Klapper, 2003). In this respect, sand, mineral soils, iron slag and clay minerals have been used to physically seal affected areas of the lake bottom sediment (Yamada *et al.*, 1987; Robb *et al.*, 2003; Berg *et al.*, 2004). The sorption capacity and ion exchange capacity of some of these materials can be enhanced by chemical modification. The efficacy of these types of materials for nutrient uptake (i.e. preventing P being released from the sediments back into the overlying water column) depends predominantly on the adsorption capacity and the ion exchange capacity, the amount of the application, as well as potentially confounding influences of sediment (e.g. resuspension, bioturbation).

In New Zealand, the use of a new proprietary modified zeolite (Z2G1) for eutrophication control has become increasingly popular. Zeolites are microporous crystalline hydrated alumina-silicates with a three dimensional framework structure formed of silica and aluminium molecules (SiO_4^{4-} and AlO_4^{5-}) bound by oxygen atoms. Due to isomorphous substitution of AlO_4 for SiO_4, a permanent negative charge is produced which can be balanced by exchangeable cations, such as ammonium (NH_4^+). The most abundant naturally occurring zeolites in New Zealand are clinoptilolite and mordenite (Nguyen & Tanner, 1998). Both materials have high affinity for NH_4^+ but typically at relatively high concentrations generally similar to those of wastewater (Nguyen & Tanner, 1998;

Weatherley & Miladinovic, 2004). It has also been shown that these two zeolites have an affinity for other cations, such as calcium, potassium and magnesium, however they have low NH_4^+ uptake capacity. Natural zeolites are often modified to enhance their properties to meet particular requirements. The modification process of Z2G1 is proprietary, but in general terms involves the insertion of an aluminium compound into the clay framework of the zeolite without substantial changes of the structure, in order to maintain some ion exchange capacity for NH_4^+. During the development of Z2G1, Yang et al. (2004) showed the material has a high and irreversible binding capacity of phosphate, with up to 95% phosphate removal in solutions similar to lake conditions.

Overview of Lake Okaro

Lake Okaro, the focus of this research, is the smallest of the major Te Arawa Lakes in the Rotorua region with an area of 0.32 km^2 and a catchment of 3.89 km^2 (Irwin, 1968; McColl, 1972). It is located in the Waiotapu geothermal area, 27 km south of Rotorua and 2 km north of Rainbow Mountain (38° 15' S, 176° 25' E). Formed in a geothermal explosion crater about 800 years ago, it is now fed by rain- and groundwater as well as two small unnamed streams entering the lake from the north-west (Irwin, 1968). The Haumi Stream in the south-east of the lake is the only outflow of Lake Okaro and connects it with Lake Rotomahana via the Thermal Valley Stream (Forsyth *et al.*, 1988). The lake catchment area had been almost entirely cleared of native vegetation by the early 1950s and more than 95% is now in pasture, primarily for dairy production (McColl, 1972).

Lake Okaro is a monomictic lake and stratifies for around eight months during summer. The hypolimnion typically becomes anoxic shortly after the onset of stratification, and experiences subsequent sediment nutrient releases (Environment Bay of Plenty, 2006). Limnological records for Lake Okaro extend back to 1955 (Jolly, 1977) when no cyanobacteria were observed in the lake. By 1963, persistent cyanobacterial blooms were observed (Forsyth *et al.*, 1988) and today, Lake Okaro is the most eutrophic lake in the region.

The regional environmental manager, Environment Bay of Plenty, has established the Rotorua Lakes Protection and Restoration Programme for which

action plans were developed for each of the Rotorua District lakes. The water quality targets for those lakes action plans are set on the basis of a numerical water quality index, namely the Trophic Level Index (TLI; Burns *et al.*, 1999). The TLI is determined annually from annual mean surface water concentrations of chlorophyll *a* (chl *a*), total nitrogen (TN), total phosphorus (TP), and Secchi depth (SD). Lake action plans are initiated when the TLI value of a lake exceeds the target value which is specified in the Regional Water and Land Plan. The Lake Okaro Action Plan TLI target still places the lake as being in a eutrophic category. The lake has undergone an intensive catchment and in-lake restoration program which was initiated in 2003. Restoration efforts include the implementation of a constructed wetland (Tanner *et al.*, 2007), riparian protection, an alum application (Paul *et al.*, 2008), and a sediment capping application using an aluminium modified zeolite (Z2G1). The restoration of Lake Okaro provides an example for integrated lake management and planning, involving co-operation of several different institutions and public support.

This study focused on Lake Okaro and is, due to its current active restoration program, a unique study site in New Zealand to examine nutrient dynamics and ecosystem response to lake restoration. The insights presented in this research have important implications for lake restoration of other eutrophic lakes in New Zealand and globally.

1.2   Major objectives

Field study

Despite intensive restoration actions to restore the water quality, little is known about the time scale of response in Lake Okaro to reduction of external and internal loading. In attempts to manage eutrophication in other lakes the reduction of external nutrient loading has lead to improved water quality, though there may be a time lag due to persistent internal loading (Jeppesen *et al.*, 2005). A more rapid response of water quality to lake restoration has been demonstrated in lakes where internal and external loading have been addressed simultaneously (Mehner et al., 2008). I hypothesised, that the progressive catchment and in-lake restoration programme in Lake Okaro would result in improved water quality.

The hypothesis was tested by analysing long-term field observations of water quality data, obtained from Environment Bay of Plenty, using predictive models, which derive the annual average P concentration in the water column from the external P loading. Furthermore, I investigated changes in water quality within the study period using two closely related trophic level indicators.

Before the full scale application of Z2G1 was carried out in Lake Okaro, the efficacy of the material was tested in a lab based sediment incubation study where it was shown to substantially reduce sediment releases of phosphate and to absorb some ammonium (Gibbs & Özkundakci, Appendix I). Based on these results, I hypothesised that the whole lake application of Z2G1 would significantly reduce sediment release of phosphate, and to some extent ammonium. To test this hypothesis, a hypolimnetic P and N mass balance was developed to calculate the relative contribution of different processes (mixing, mineralisation, phytoplankton uptake, adsorption/desorption, nitrification and diffusion across the thermocline) to the observed hypolimnetic accumulation rates of phosphate and ammonium. This quantified the most important sources of nutrients in the hypolimnion.

Organic P in lake sediments has increasingly been recognised to contribute significantly to internal loading and the overall P dynamics in lakes (Hupfer *et al.*, 2004; Ahlgren *et al.*, 2005). A number of studies, utilising ^{31}P Nuclear Magnetic Resonance (NMR) for P speciation of mostly marine sediments and some lake sediments, suggest that seasonal changes in redox chemistry and water column oxygen regime could play an important role in the digenesis of organic P (Cade-Menun, 2005; Reitzel *et al.*, 2006). I hypothesised that seasonal water column dynamics (i.e. oxic and anoxic hypolimnion) in Lake Okaro would result in changes in sediment P species composition, particularly in the sediment surface. I examined the seasonal changes in P species composition in settling seston and bottom sediments of Lake Okaro by using ^{31}P NMR. This assessment is the first measurement of lake sediment organic P in New Zealand.

A general problem with in-lake restoration using sediment capping, flocculation or P precipitation is the risk of undesirable short-term effects on plankton species composition. The use of alum and iron salts reduces zooplankton abundance, biomass and species richness (Schumaker et al., 1993) as

well as increasing mortality and reducing numbers of broods per female (Randall et al., 1999). Increased water column turbidity, as it would be expected after a sediment capping application, could result in the reductions in the standing stock of daphnid zooplankton (Hart, 1986) and reduced zooplankton feeding rates (Kirk, 1991). I hypothesised that the Z2G1 application in Lake Okaro may cause a significant shift in species composition of both zooplankton and phytoplankton. To identify any adverse effects of Z2G1 on zooplankton and phytoplankton species composition, the community structure was analysed before and after the Z2G1 application.

Model application

In aquatic sciences, water quality models have long been used to analyse physical, chemical and/or trophic dynamics (Norberg & DeAngelis, 1997) and also for management and forecasting purposes (Friedman *et al.*, 1984; Arhonditsis & Brett, 2005). The model application in this study was based on the one-dimensional lake ecosystem model DYRESM-CAEDYM, which has been developed at the Centre for Water Research, University of Western Australia. Several successful applications of the model have been made for the purpose of assisting lake management decisions (e.g. Burger *et al.*, 2007b; Trolle *et al.*, 2008; Gal *et al.*, 2009). A critical evaluation of different processes in the model (e.g. algae growth limitation by light and/or nutrients) has rarely been made, however, and could provide additional insight into the ecosystem response to changes in nutrient loadings. The objective of the model application to Lake Okaro was to better understand the response of the lake ecosystem to intensive restoration efforts, especially the response of nutrient limitation status of the simulated phytoplankton groups to reduced nutrient loadings.

1.3   Thesis overview

This thesis consists of five independent research chapters (Chapters 2-6) which have been written in a format of scientific papers. In the final chapter (Chapter 7), the research of this thesis is summarised and conclusions are drawn based on the results from chapters 2-6. As a result of the format required to document Lake

Okaro for these independent papers there is some overlap and repetition for the sake of completeness as standalone scientific papers.

In Chapter 2, the P dynamics in Lake Okaro are analysed to document an intensive catchment and in-lake restoration procedure carried out during the period from 2003 until 2007. The trophic state was put into the context of the historical water quality of Lake Okaro using numerical trophic level indices and basin wide TP budget models to evaluate the individual effects of different restoration methods.

In Chapter 3, water column nutrient dynamics in Lake Okaro were examined before and after the application of Z2G1 in 2007. The magnitude of internal loading of both P and N during summer stratification was quantified using a hypolimnetic flux model to account for changes in nutrient mass due to mixing, mineralisation, phytoplankton uptake, nitrification, adsorption or desorption of P, and diffusion across the thermocline.

In Chapter 4, spatial and temporal variations in sediment P composition and sedimentation rates were examined to better understand the causal factors and extent of internal P loading and to assess the importance of sediment P composition for in-lake restoration methods. Bottom sediments and settling seston were analysed for organic P using ^{31}P NMR to determine the origin and fate of potentially bioavailable P in Lake Okaro. The slope of a regression fit to the exponential decay of P concentration with sediment profile depth was used to estimate the time scale over which various P compounds are being released into the overlaying water column.

In Chapter 5, the coupled one-dimensional (1D) hydrodynamic model Dynamic Reservoir Simulation Model (DYRESM) and aquatic ecological model Computational Aquatic Ecosystem Dynamics Model (CAEDYM) was applied to Lake Okaro for the period 2004-2008. The model simulations were calibrated and validated over the four year period against field data during the active restoration period in Lake Okaro which coincided with the period of model simulations. Model scenarios of nutrient reductions of both external and internal loading were used to quantify the response of the trophic state of the lake to different management strategies.

With the basal positions of phytoplankton and zooplankton in aquatic food webs, alterations in these components as a result of in-lake restoration may alter the nutrient dynamics and energy flow to higher trophic levels and have ecosystem-wide effects. In Chapter 6, multidimensional scaling (MDS) and Analysis of Similarity (ANOSIM) was used to identify any adverse effects on zooplankton and phytoplankton species composition of the full scale application of Z2G1 in Lake Okaro by comparing the community structure before and after the application.

In Appendix I, the P-removal efficacy of Z2G1 on Lake Okaro sediment was examined by treating cores with two different grain sizes and dose rates of Z2G1 under aerobic and anoxic conditions. Furthermore, the different layer thicknesses were used to examine the effect of the Z2G1 capping layer on the microbial processes of nitrification and denitrification and the potential release of metals such as arsenic (As) and mercury (Hg) from lake sediments under aerobic and anoxic conditions.

This study provides a critical assessment of in-lake restoration using sediment capping and a fundamental understanding of sources of internal loading. The extent and time scale of responses of water quality to multiple catchment and in-lake restoration efforts have been established and this study offers insights to the challenges for future lake management to address the persistence of eutrophication. This study also represents the first qualification and quantification of organic P in New Zealand lake sediments utilising ^{31}P NMR.

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2 Effect of intensive catchment and in-lake restoration procedures on phosphorus concentrations in a eutrophic lake

2.1 Introduction

Attempts to manage lake eutrophication have most frequently involved controls of nitrogen (N) and/or phosphorus (P) loads from both diffuse sources (Jeppesen *et al.*, 1999) and point sources (Ahlgren, 1978), as well as internal loads from lakebed sediments (Cooke *et al.*, 2005). Many of these restoration attempts have fallen short of expectations for improvement in water quality as the persistence or re-establishment of internal loading from lakebed sediments has significantly reduced the effectiveness of restoration efforts and delayed improvements in water quality (Jeppesen *et al.*, 2005). This ecological resilience in lakes is defined by the amount of disturbance that the system can absorb, which tends to reinforce a eutrophic state, without a change in its structure or composition (Carpenter, 2003). It may therefore be possible to further hasten recovery with the control of internal nutrient loading, but the longevity of treatment effects is a major issue, particularly if external loads are not reduced concurrently.

Flocculation or P precipitation with iron-, calcium- or aluminium-salts has in several cases been effective in reducing internal P loading and water column total phosphorus (TP) concentrations (Cooke *et al.*, 2005). Aluminium sulfate (alum) is often a preferred choice of flocculent because the resulting floc is chemically relatively stable, even under low redox states commonly encountered under anoxic conditions. Sediment capping with calcite (Berg *et al.*, 2004), modified clay minerals (Robb *et al.*, 2003) and iron slag (Yamada *et al.*, 1987) have all been used to attempt to permanently bind P in the sediments or isolate it from the water column, with varying levels of success. The longevity of sediment capping with calcite, for example, was found to be only of the order of 2 to 10

months for different calcite materials (Berg *et al.*, 2004), and of the order of 6 months for Phoslock[TM] (Robb *et al.*, 2003).

The management of external nutrient loads has become increasingly important in New Zealand, where only 10% of the pre-European colonisation wetlands remain (Cromarty & Scott, 1996). In the Bay of Plenty Region, where my study lake is located, only 3% of the original wetland area is intact (Park, 2002). Constructed wetlands and riparian buffer zones have been used successfully in New Zealand, some for many years (Collier, 1994; Howard-Williams & Pickmere, 1999) to partially compensate for the loss of natural wetlands. There is growing interest in their application in reducing catchment nutrient loads to surface waters (Tanner *et al.*, 2004) which are also affected by increasing agricultural land use intensity (Hamilton, 2005). These engineered systems are designed to take advantage of natural nutrient removal processes such as sedimentation, denitrification and plant uptake that take place in natural wetlands (Mitsch *et al.*, 2000; Vymazal, 2007).

Water quality in several of the Rotorua Lakes, which are located in the Rotorua Region, has declined on time scales that fit with relatively recent development of land for agriculture (mostly since the 1950s) (McColl & Hughes, 1981; Hamilton, 2005) and with increasing fertilizer applications (Parliamentary Commissioner for the Environment, 2006). The Regional Water and Land Plan for the Environment Bay of Plenty region sets water quality targets for the Rotorua Lakes on the basis of the Trophic Level Index (TLI) (Burns *et al.*, 1999). Values of TLI are determined annually from annual mean surface water concentrations of chlorophyll *a* (chl *a*), total nitrogen (TN) and TP, and Secchi depth (SD) (Table 2.1). This index is used as part of the Regional Land Water Plan to evaluate long term trends in lakes' water quality, as management actions are triggered with a pre-defined statistically significant trend in annual TLI value with time. With alternative trophic level indicator schemes (e.g. Trophic State Index; Carlson, 1977) being considered less appropriate for New Zealand lake conditions because of lack of direct dependence on nitrogen (Burns *et al.*, 1999), the TLI was developed to facilitate shortcomings in the performance of these other trophic level indicators for New Zealand lakes. For the TLI, chl *a* is used as the primary variable defining productivity of a lake. To incorporate variables like TP, TN and SD into this multi-parameter index, regression models between these

variables and chl *a* are used to calculate individual trophic level values for each parameter, with values then averaged into one numerical TLI. The inclusion of TN into the TLI was mainly based on the observation that phytoplankton in many lakes in New Zealand show potential for N-limitation (White *et al.*, 1985) as opposed to the predominance of P limitation observed in most Northern Hemisphere lakes (OECD, 1982).

Here I document the changes in water quality as a result of a unique combination of restoration measures in Lake Okaro, New Zealand. I hypothesized that a progressive catchment and in-lake restoration programme should produce a rapid improvement in water quality. I assessed trends in P dynamics in Lake Okaro over six years, including periods immediately before and during the active restoration period. I compared observations in Lake Okaro during the restoration period with two predictive models, which derive the annual average P concentration in the water column from the external P loading. These models were necessary to evaluate the individual effects of restoration measures, because detailed pre-restoration data were limited. Furthermore, I investigated if short-term changes in water quality could be tracked within the study period using two closely related trophic level indicators.

Table 2.1: Equations for calculating Trophic Level Index (TLI) (Burns *et al.*, 1999) and Trophic State Index (TSI) (Carlson, 1977) using annual mean surface water values of the parameters chlorophyll *a* (Chl *a*) concentration (mg m^{-3}), Secchi depth (SD) (m), total phosphorus (TP) concentration (mg m^{-3}), and total nitrogen (TN) concentration (mg m^{-3}).

Parameter	TLI equation	TSI equation
Chl *a*	$TLI_{(Chl\ a)} = 2.22 + 2.54 \log(Chl\ a)$	$TSI_{(Chl\ a)} = 9.81 \ln(Chl\ a) + 30.6$
SD	$TLI_{(SD)} = 5.10 + 2.27 \log(1/SD - 1/40)$	$TSI_{(SD)} = 60 - 14.41 \ln(SD)$
TP	$TLI_{(TP)} = 0.218 + 2.92 \log(TP)$	$TSI_{(TP)} = 10(6-(\ln(48/TP)/\ln2))$
TN	$TLI_{(TN)} = -3.61 + 3.01 \log(TN)$	
Index	$\sum (TLI_{(TN)} + TLI_{(TP)} + TLI_{(SD)} + TLI_{(Chl\ a)})/4$	$\sum (TSI_{(TP)} + TSI_{(SD)} + TSI_{(Chl\ a)})/3$

2.2 Methods

Study site

Lake Okaro (Figure 2.1) is a small (area 0.32 km^2), shallow lake (max. depth 18 m) that is seasonally stratified for c. 8 months each year and mixes fully for c. 4 months. It is the smallest of twelve lakes in the Rotorua region that are collectively referred to as the Rotorua Lakes. Lake Okaro is located in the Waiotapu geothermal area, and was filled after a geothermal explosion crater about 800 years ago (Lloyd, 1959). It has surface water inputs from two small unnamed streams that enter in the north-west of the lake and the only surface outflow is via Haumi Stream in the south-east of the lake (Forsyth *et al.*, 1988). The lake catchment area (3.89 km^2) had been almost entirely cleared of native vegetation by the early 1950s and more than 95% is now in pasture, primarily for dairy production.
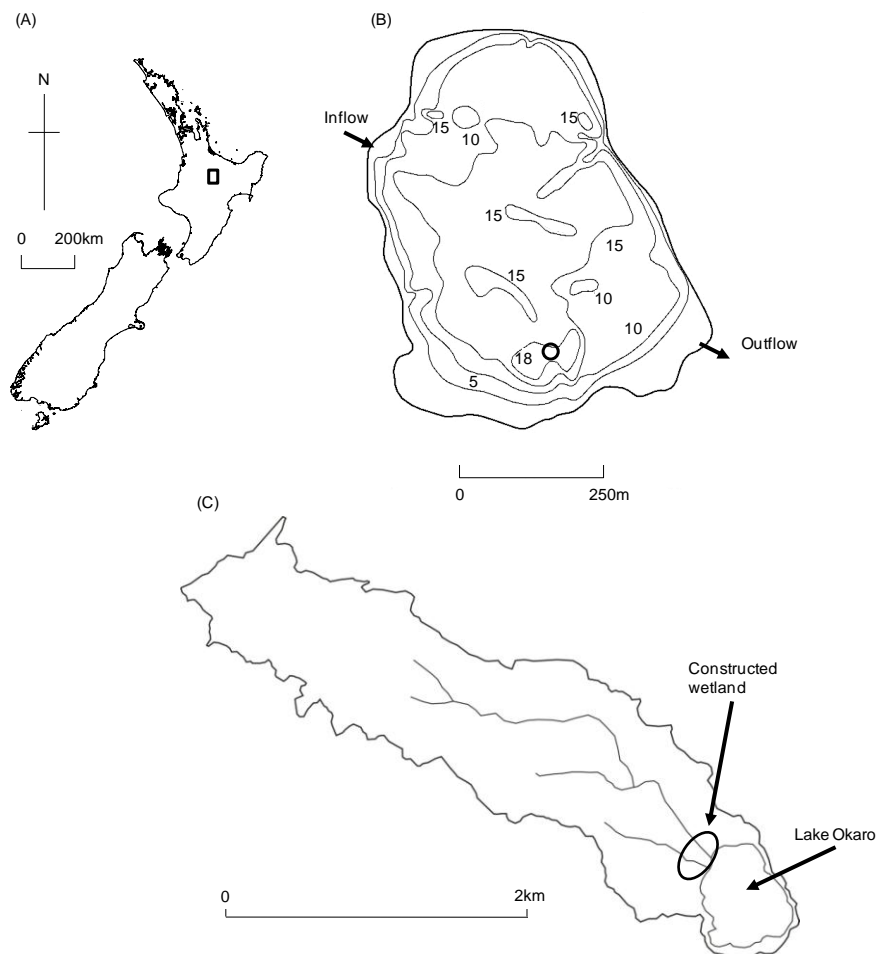
Figure 2.1: Map of New Zealand showing location of Lake Okaro (solid circle), Lake Okaro and its depth contours of 5, 10, 15, and 18 m, inflows and outflow and the location of the lake sampling station (B), and the lake catchment and location of the constructed wetland (C).

Limnological records for Lake Okaro extend back to 1955 (Jolly, 1977) when no cyanobacteria were observed in the lake. By contrast, persistent cyanobacterial blooms were observed in 1963 (Forsyth *et al.*, 1988) and the lake was the study site for an international scientific investigation on cyanobacterial blooms in 1987 (Vincent, 1987). At the outset of the period under consideration in this study (2002-8) Lake Okaro was the most eutrophic of the Rotorua Lakes and had persistent cyanobacterial blooms (Environment Bay of Plenty, 2006).

Overview of restoration procedure

Environment Bay of Plenty, the regional environmental manager, developed an Action Plan for Lake Okaro as a part of its Regional Land and Water Plan. Lake Okaro is the second lake of the Rotorua Lakes to have an Action Plan established. In the Lake Okaro Action Plan, the TLI goal for the lake is a reduction from 5.5 (three-year average to June 2004) to 5.0 (Environment Bay of Plenty, 2006), which still categorizes the lake as eutrophic. An even reduction was applied across the four TLI parameters (TP, TN, chl *a*, SD) in order to calculate the required TN and TP reduction. The following actions were formulated to assist with meeting both N and P reduction targets: (i) a phosphorus-adsorbent lakebed cap, (ii) a constructed wetland to remove nutrients from stream flows, (iii) protection of all riparian margins in the permanently flowing streams of the catchment, and (iv) the introduction of agricultural nutrient management practices to reduce nitrogen leaching from this source.

Alum application

The first attempt at in-lake removal of phosphorus was the application of 13 m^3 of alum solution on 16 and 17 December 2003. Alum was applied to the surface of the lake by spraying from a moving boat as aluminium sulphate solution (47% $Al_2(SO_4)_3$ $14H_2O$) to achieve a concentration of 0.6 g Al m^{-3} in the epilimnion (0-3 m). A relatively low Al concentration was chosen by Environment Bay of Plenty in order to avoid the need for addition of buffering chemicals to the lake, as Lake Okaro has relatively low alkalinity (McColl, 1972). Intensive monitoring was carried out from 2 December 2003 to 13 January 2004 in order to document the short-term effects of the alum application (Paul *et al.*, 2008).

Constructed wetland

In February 2006, the two permanent stream inflows were diverted into a 2.3 ha surface–flow constructed wetland. The annual percentage removal of TN and TP was estimated *a priori* to be 45% (165-210 kg N yr^{-1}) and 10-15% (5-6 kg P yr^{-1}), respectively, of the lake load from this source (Tanner *et al.*, 2007). More than 60,000 plants, including tall spike-rush (*Eleocharis sphacelata*), lake clubrush (*Bolboschoenus fluviatilis*), and jointed twigrush (*Baumea articulata*), were planted throughout the wetland.

Riparian protection

Riparian protection works were undertaken progressively through the study period, including livestock exclusion, fencing and planting of native plant species along the stream banks and lake margins. The importance of the riparian protection of waterways is reflected in the Regional Water and Land Plan which defines a goal of complete riparian protection of all Rotorua lakes' streams and margins by 2012 (Environment Bay of Plenty, 2006).

Modified zeolite application

Between 25 and 28 September 2007, 110 metric tonnes of a proprietary P-inactivation agent, aluminium-modified zeolite (distributed by Blue Pacific Minerals, Matamata, New Zealand), equivalent to a dose rate of 350 g m^{-2} (grain size 1-3 mm), was applied as a sediment capping agent to Lake Okaro. Zeolite is a porous alumino-silicate material that has a large specific surface area for nutrient adsorption due to a fine pore structure. Zeolite can be formed synthetically at great expense, but also occurs naturally in large volcanic deposits in the Rotorua region. Scion (Rotorua, New Zealand) has developed an aluminium-modified zeolite that significantly improves the nutrient uptake capacity of the natural mineral. Modified zeolite was applied over the surface area corresponding to where lake depths were greater than 5 m; equivalent to 20 ha of lakebed above which the waters become anoxic during the seasonal stratification period of around 8 months annually. The primary objective of the modified zeolite application was an immediate (within one stratification cycle)

reduction in concentrations of phosphate in the hypolimnion to less than 50% of historical values (2002-07).

Farm nutrient budget

Under the Resource Management Act, implemented by the New Zealand Government in 1991, regional councils regulate non-point discharges through land use controls or discharge permits. However, to date there are no national standards and most councils advocate a voluntary approach (Drummond, 2006). Environment Bay of Plenty takes an approach more reliant on regulations and is applying environmental programmes as a contractual agreement between rural landowners and the Regional Council or the Rotorua District Council in order to assist landowners to implement various best practice options on their farms. In this regard, nutrient budgets have been constructed for farms within the Lake Okaro catchment using a farm-scale model, Overseer[®]. This model allows determination of nutrient inputs and outputs from a farm for a variety of input data (e.g. stock numbers, soil type, fertilizer regime, and climate). The model also provides a means to investigate mitigation options to reduce the environmental impact of nutrients for a specific land use as discussed at the Fertiliser and Lime workshop (Currie & Hanly, 2003).

Sampling and monitoring

Samples for water column nutrients and chl *a* were taken monthly at 0-4 m (integrated sample) and 14 m depths from a sampling station at the deepest site (18 m; Figure 2.1) as part of a Natural Environment Regional Monitoring Network conducted by Environment Bay of Plenty. Secchi depth was determined with a disk of 20 cm diameter. Sampling of inflows for nutrient concentrations and measurements of discharge were added to the programme in July 2004 and are included in this study to June 2008. Inflows were measured some 10 m upstream of the lake margin. Discharge was measured for only one year, from July 2007 - June 2008. Unfiltered water samples were frozen prior to analysis for concentrations of TP and total Kjeldahl nitrogen (TKN). Additional samples were filtered (Whatman GF/C) and frozen for subsequent analysis as nitrate of the total oxidised nitrogen (TON = $NO_2 + NO_3$) using APHA method 4500 NO_3-N (APHA,

2005) and soluble reactive phosphorus (SRP) using a standardised molybdate blue method. Analysis of TKN was carried out using APHA method 4500B (APHA, 2005). Total nitrogen was then calculated as TN = TKN + TON. Total phosphorus was analysed using an acid persulphate digestion procedure (APHA, 2005). The filters were frozen for subsequent analysis of chl *a* concentration using an acetone extraction procedure (Arar & Collins, 1997).

Conductivity-temperature-depth (CTD) profiles (SBE 19 *plus* SEACAT Profiler, Seabird Electronics Inc.), with additional CTD mounted sensors for dissolved oxygen (DO) concentration (Seabird Electronics), were taken at each sampling occasion. The sensors were calibrated annually in accordance with Seabird Electronics recommendations. To calculate the water balance incorporating evaporation climate data were obtained from Rotorua Airport AWS - Station B86133 (20 km north of Lake Okaro). Daily averages were calculated from hourly observations of wind speed (m s^{-1}), atmospheric pressure (hPa), ambient temperature (ºC) and rainfall (mm) over the whole sampling period.

Data analysis

For the variables chl *a*, SD, TP, and TN, arithmetic means for the surface waters (from 0-4 m) during the period between July and June for each year were calculated. A TLI was then calculated annually for Lake Okaro according to Burns *et al.* (1999) for the period of July 2002 until June 2007 (Table 2.1). In addition, a Trophic State Index (TSI) was calculated annually according to Carlson (1977) for the same period, for comparison (Table 2.1). The TLI is a numerical value of lake trophic level and can range from 0 (ultra-microtrophic) to 7 (hypertrophic) with major divisions of 1 (e.g. 0-1, 1-2, 2-3, etc.). The TSI is a numerical value in a scale of 0 to 100 with major divisions of 10 (10, 20, 30, etc.). It is notable that both values can in extreme cases exceed their nominal upper values.

A critical external P loading for Lake Okaro, using a target trophic state value for TP (68 mg m^{-3}) (Environment Bay of Plenty, 2006), was determined from the equation of Vollenweider (1976):

$$\text{Critical loading} \left(\text{mg m}^{-2}\text{yr}^{-1}\right) = \left[TP_{\text{target}}\left(1 + \sqrt{\tau}\right) z_m \right]/\tau \tag{2.1}$$

where z_m is the mean depth of the lake (m). The theoretical water retention time τ (yr) was calculated as discharge (Q_{out}) divided by lake volume (V). For the periods of July 2004 until June 2007, Q_{out} was calculated as the residual term in a complete lake water balance from July 2007 until June 2008, using the methodology of Wetzel & Likens (2000). The critical loading was calculated for the period from 2004-08.

An approach to predict annual average TP within a lake is given by OECD (1982) and is hereafter referred to as the Vollenweider model:

$$TP = 1.55 \left[TP_{\text{inflow}}/\left(1 + \sqrt{\tau}\right) \right]^{0.82} \tag{2.2}$$

where TP is the annual average in-lake TP concentration, and TP_{inflow} is the discharge weighted annual mean inflow TP concentration.

An alternate model to predict TP in cases where it is still responding to a change in loading, i.e. non-equilibrium, is given by Sas (1989) and is hereafter referred to as the Sas model:

$$TP = TP_{\text{lake pre}} \left(TP_{\text{inflow post}}/TP_{\text{inflow pre}} \right)^{0.65} \tag{2.3}$$

where the subscripts pre and post refer to pre-reduction and post-reduction periods. Both models were applied to one-year periods (July-June) from 2004-08. Predictive models that account for internal P loading as well as external P loading were not considered in this study.

The Pearson Chi-Square (X^2) test was used to compare annual average water column TP with values derived from the Vollenweider and Sas models. A non-parametric Wilcoxon matched pairs test was used to compare arithmetic mean bottom and surface water concentrations of TP and SRP for one year before the restoration programme was started (2002-2003) and for five years during the active restoration period (2003-2008). Annual means of surface concentrations for chl *a*, TP, and TN and SD were tested for significant correlations using Spearman rank correlation coefficient (r_S) values.

2.3   Results

Temperature, stratification and dissolved oxygen distribution

Lake Okaro was thermally stratified for an average of eight months each year based on monthly sampling (Figure 2.2) with the criteria for stratification defined as the presence of a thermocline where dT/dz = minimum, and T is the water temperature (°C) and z is water depth (m), measured positive downward. The lake was considered to be fully mixed when dT/dz was > -0.25 ^{o}C m^{-1} throughout the water column. Stratification usually commenced in September, was strongest at the end of January and broke down in June. The period of stratification was one month longer in my study than that recorded in the 1970s (McColl, 1972). Temperature in surface waters ranged from 23.5 °C to 9.1 °C over the entire study period. During stratification, temperature near the bottom of the lake remained close to the winter value of c. 8.5°C but increased slightly (c. 2-3°C) towards the end of summer (Figure 2.2).

Surface waters (0-4 m integrated depth) were regularly supersaturated in DO during stratification, with a maximum concentration of 17.3 mg L^{-1} during the study period (Figure 2.2). However, the water near the bottom of the lake became anoxic shortly after onset of stratification, though monthly sampling prevents

more detailed resolution of the timing. The duration of bottom water (14 m depth) anoxia was 28 weeks on average. For comparison, in 1962 bottom waters did not become anoxic (Jolly, 1977) while between 1965 and 1986 the hypolimnion was anoxic for an average of 21 weeks during each seasonal stratification period (Forsyth *et al.*, 1988).
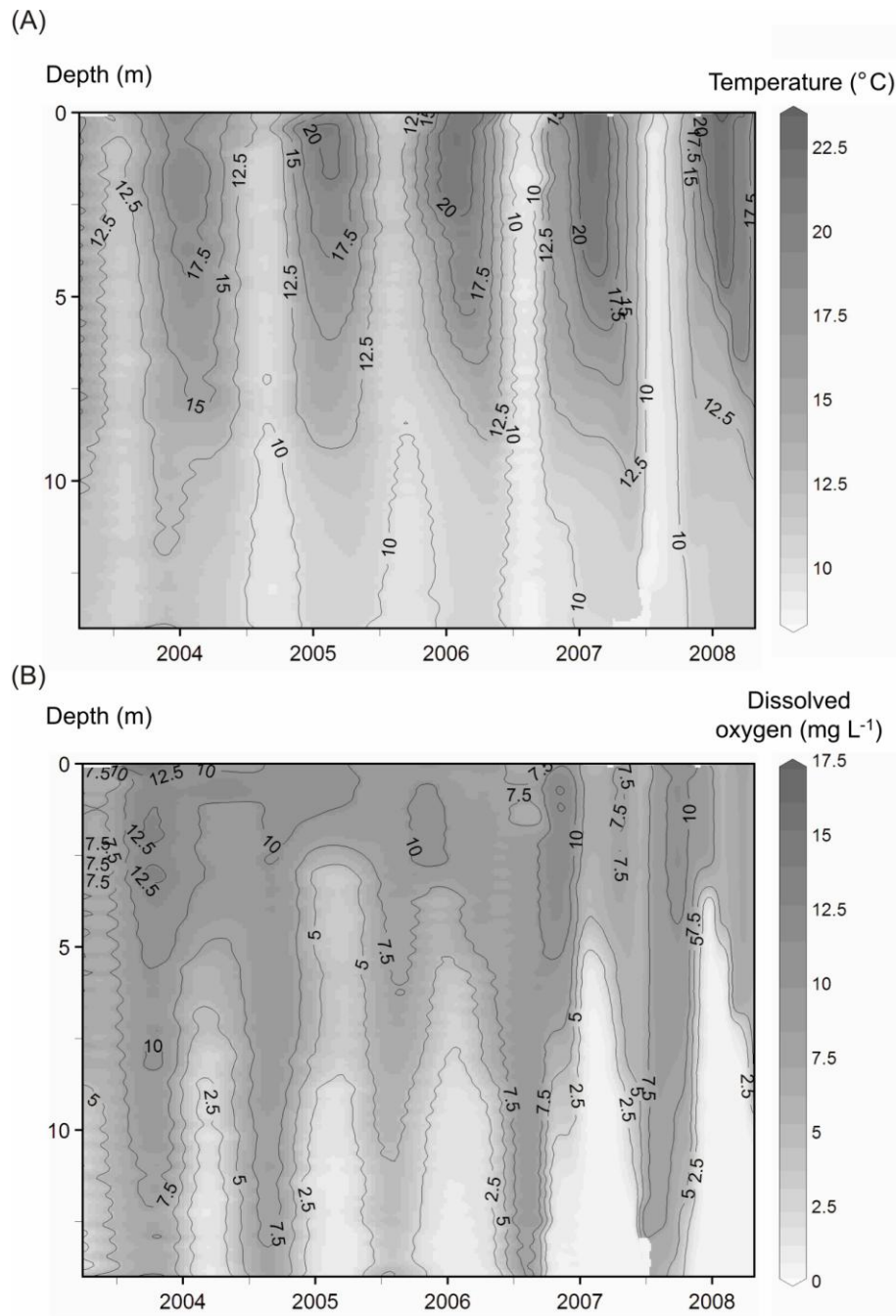
Figure 2.2: Temperature (°C) (A), and dissolved oxygen concentrations (mg L^{-1}) (B) in Lake Okaro for March 2003 until June 2008.

Total phosphorus trend in the bottom and surface waters

Figure 2.3 shows monthly TP and DO concentrations in Lake Okaro at 14 m depth from July 2002 until June 2008. Total phosphorus concentrations usually increased shortly after onset of anoxic conditions in the bottom waters, indicating P release from the sediments. Concentrations of TP at 14 m were up to 769 mg m^{-3} during the period of July 2002 – June 2003 while in the following year, following the December 2003 alum dosing, the maximum declined to 531 mg m^{-3}. Concentrations were further reduced for the periods July 2004 – June 2007 with a maximum TP of 448 mg m^{-3} (March 2007), although there was no obvious decline in TP immediately after the construction of the wetland (February 2006). Following the modified zeolite application in September 2007, TP was lower than recorded in previous years, with a maximum of 310 mg m^{-3} in April 2008.
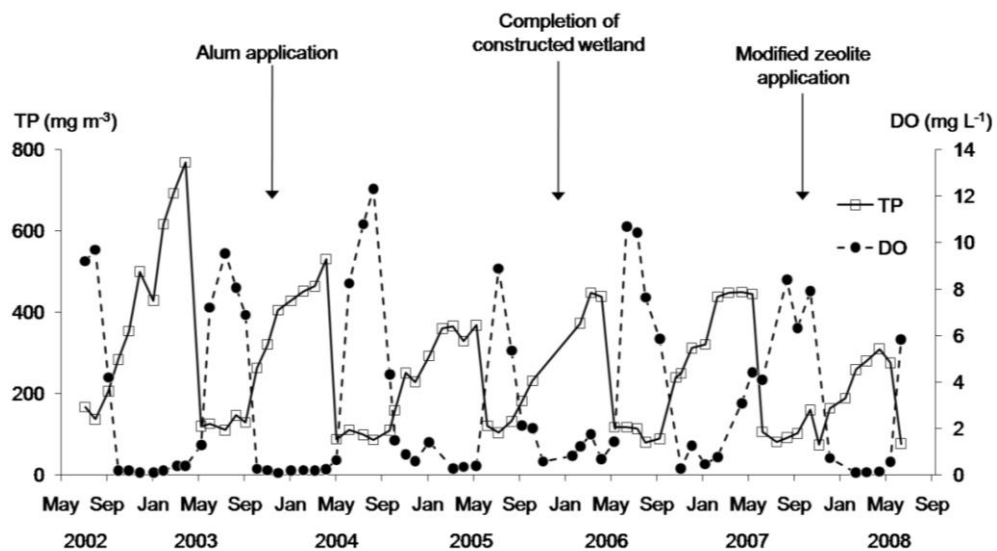
Figure 2.3: TP concentration (mg L^{-1}) and dissolved oxygen concentration (mg L^{-1}) at 14 m depth in Lake Okaro for the period of July 2002 until June 2008.

The mean concentration of TP in surface waters (0-4 m) in 2002-03 was 106.1 mg m^{-3} (Figure 2.4) and decreased following the alum application of December 2003 to 73.1 mg m^{-3} (2003-04), however, this reduction was not statistically significant (Wilcoxon matched pairs test, $p > 0.05$; Table 2.2). In contrast, a reduction in the annual mean TP in bottom waters, from 337 mg m^{-3} (2002-03) to 274.7 mg m^{-3} (2003-04), was statistically significant ($p < 0.05$). Annual mean water TP concentration decreased significantly ($p < 0.05$) from 274.4 mg m^{-3} (2006-07) to 172 mg m^{-3} (2007-08) at 14 m depth and from 62.3 mg

m^{-3} (2006-07) to 46.5 mg m^{-3} (2007-08) in surface waters. Annual mean concentrations of SRP in the bottom waters declined significantly ($p < 0.05$) from 298.4 mg m^{-3} (2002-03) to 230.8 mg m^{-3} (2003-04), while concentrations of SRP at 14 m were also significantly lower ($p < 0.05$) for the period 2007-08 (139.6 mg m^{-3}) compared to 2006-07 (223.4 mg m^{-3}).

Table 2.2: Results of Wilcoxon matched pair tests for annual mean concentrations of total phosphorus (TP) and soluble reactive phosphorus (SRP) at the surface and 14 m depth for periods of July – June between 2002 and 2008 (* denotes significant difference at $p < 0.05$).

	P levels for Wilcoxon matched pairs test			
	TP (surface)	**TP** (bottom)	**SRP** (surface)	**SRP** (bottom)
2002-2003 vs 2003-2004	0.29	0.01*	0.01*	0.01*
2003-2004 vs 2004-2005	0.86	0.06	0.03*	0.05
2004-2005 vs 2005-2006	0.67	0.21	0.46	0.75
2005-2006 vs 2006-2007	0.29	0.40	0.06	0.09
2006-2007 vs 2007-2008	0.01*	0.01*	0.20	0.02*
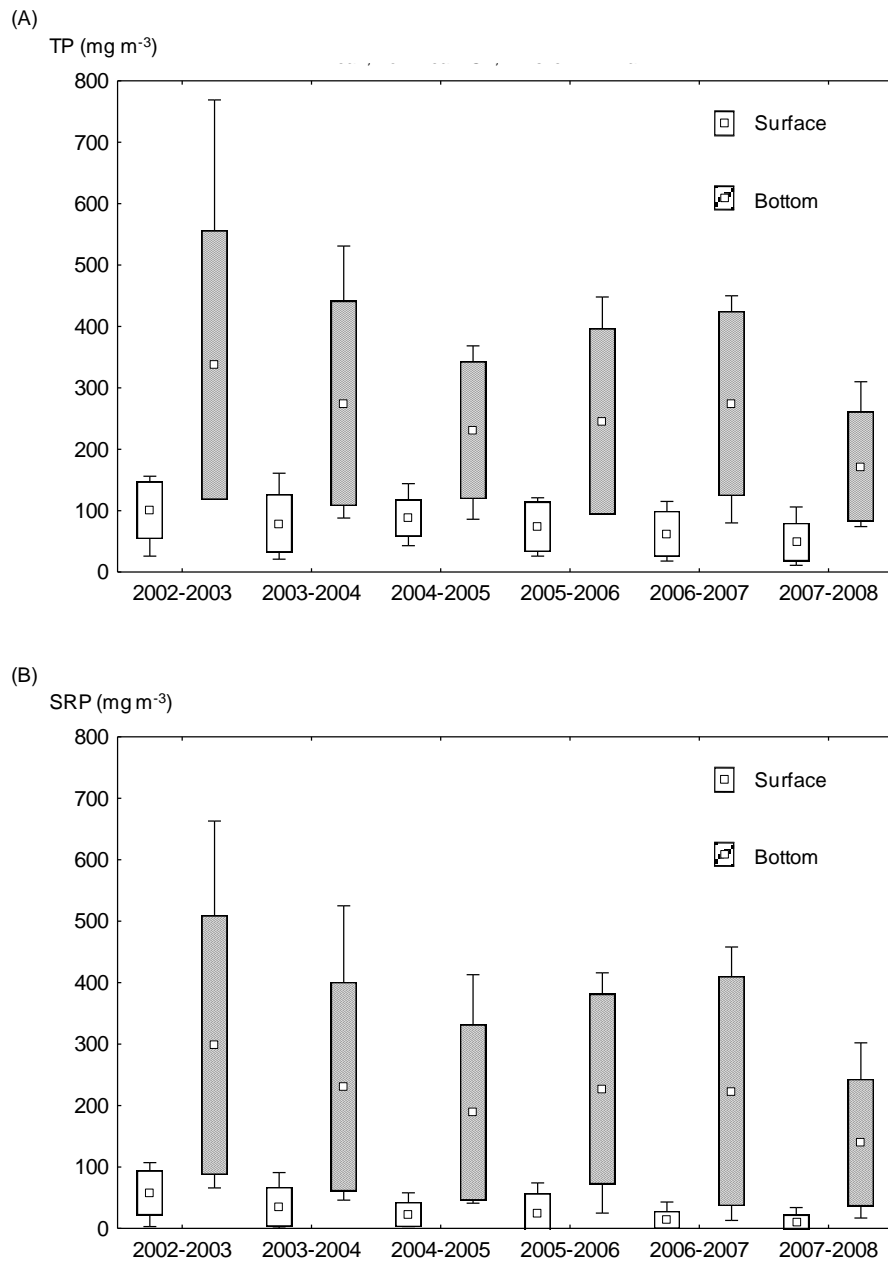
Figure 2.4: Annual mean (July - June) surface and 14 m concentrations of TP (A) and SRP (B). Box represents ± one standard deviation, and bars represent the range.

External and internal phosphorus loads

Figure 2.5 shows the external P load, TP_{ext}, which was 571 mg m^{-2} yr^{-1} for 2004-05 and 575.2 mg m^{-2} yr^{-1} for 2005-06. Following implementation of the wetland in February 2006, TP_{ext} decreased to 367.2 mg m^{-2} yr^{-1} (2006-07) and declined further to 306 mg m^{-2} yr^{-1} in 2007-08. The annual percentage removal of TP in the surface inflow was 42% for the two years following the construction of the wetland compared with the two years preceding its construction.

The calculated average critical TP loading (Vollenweider, 1976) for 2004-05 and 2005-06 was 35 % higher on average than measured TP_{ext} and 100 % higher for the years after the wetland had been implemented (2006-08). The critical TP loading ranged from 626.7 to 822.4 mg m^{-2} yr^{-1} across all years.

Annual mean water column (average of 0-4 and 14 m depth) concentrations of TP (Figure 2.5) declined from 241.8 to 192.7 mg m^{-3} between the years 2002-03 and 2005-06, respectively, increased to 215.5 mg m^{-3} in 2006-07 and then declined again to 141.1 mg m^{-3} for 2007-08. The Vollenweider model produced TP concentrations ranging from 111.1 mg m^{-3} (2005-06) to 59.6 mg m^{-3} (2007-08), with values consistently lower than both the Sas model and the measured data for this period. The Vollenweider model underestimated TP concentrations in the lake (Pearson Chi-Square test, $X^2 = 533.9$) by 45 % for 2004-06 and by 65% lower for 2006-07. For the period of 2007-08, which included the modified zeolite application, Vollenweider-predicted TP was 57% lower than the measured value. The Sas model predictions matched the measured TP concentrations in the water column better throughout the entire study period (Pearson Chi-Square test, $X^2 = 22.5$) and produced a range from 206.9 mg m^{-3} (2004-05) to 122.1 mg m^{-3} (2007-08). This model matched the measured TP concentration most closely for 2004-05 and was 16 % on average lower than measured TP for the remainder of the study period (2005-08).
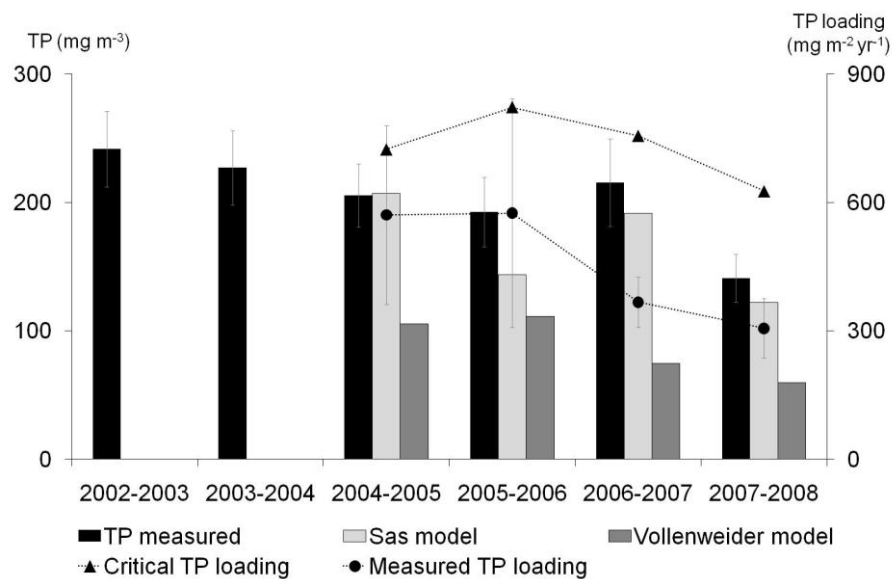
Figure 2.5: Annual mean water column (July - June) measured (±SE) and modelled total phosphorus (TP) concentrations (mg m^{-3}) for Lake Okaro and measured (±SE) and critical areal TP loading (mg m^{-2} yr^{-1}). Critical loading is the value required to achieve a target TP concentration of 68 mg m^{-3} (Environment Bay of Plenty, 2006).

Trophic Level Index and Trophic State Index

Annual values of the TLI ranged from 5.06 (July 2005 – June 2006) to 5.82 (July 2004 – June 2005; Table 2.3), indicating that Lake Okaro is hypertrophic. For the same period TSI ranged from 54.9 (July 2005 – June 2006) to 63.3 (July 2004 – June 2005; Table 2.3), representing a highly eutrophic state. TSI was highly significantly correlated (R = 0.99, p < 0.01) with TLI for the entire study period.

Annual mean chl *a* concentration ranged from 17.1 mg m^{-3} (2006-06) to 77.2 mg m^{-3} (2004-05) and showed no apparent decline towards the end of the study period, i.e. after implementation of all restoration procedures. Annual mean SD increased overall from 1.86 m (2002-03) to 2.37 m (2007-08) with the lowest annual mean SD of 1.48 m for the period 2004-05. Annual mean surface water TP concentrations declined throughout the study period from a maximum of 106.1 mg m^{-3} (2002-03) to a minimum of 46.5 mg m^{-3} (2007-08), while TN was relatively consistent at 803 mg m^{-3}, with a peak of 1236.5 mg m^{-3} in 2004-05. Ratios of TN:TP increased progressively over the duration of the study, from a minimum of 8.2 (2002-03) to a maximum of 17.3 (2007-08). Annual mean concentrations of chl *a* were not correlated with annual mean concentrations of TP (Spearman rank correlation coefficient r_S = 0.14, p > 0.05), but chl *a* was significantly correlated with 1/SD (r_S = 0.89, p < 0.05) (Table 2.4).

Table 2.3: Annual mean values (July – June) for Secchi depth (SD) (m), surface concentrations of chlorophyll *a* (Chl *a*) (mg m^{-3}), total phosphorus (TP) (mg m^{-3}), total nitrogen (TN) (mg m^{-3}), Trophic Level Index (TLI), Trophic State Index (TSI) and the TN:TP. TLI$_{Chla}$, TLI$_{SD}$, TLI$_{TP}$ and TLI$_{TN}$, TSI$_{Chla}$, TSI$_{SD}$ and TSI$_{TP}$ represent the individual values for the trophic level indices for the each variable.

		Jul 2002 – Jun 2003	Jul 2003 – Jun 2004	Jul 2004 – Jun 2005	Jul 2005 – Jun 2006	Jul 2006 – Jun 2007	Jul 2007 – Jun 2008
Chl *a*	**mg m^{-3}**	26.54	19.73	77.18	17.05	19.97	27.28
	TLI$_{(Chla)}$	5.84	5.51	7.01	5.35	5.52	5.87
	TSI$_{(Chla)}$	62.76	59.85	73.24	58.42	59.97	63.03
SD	**m**	1.86	2.38	1.48	2.74	2.42	2.37
	TLI$_{(SD)}$	4.44	4.18	4.68	4.04	4.17	4.19
	TSI$_{(SD)}$	51.08	47.50	54.36	45.50	47.25	47.59
TP	**mg m^{-3}**	106.09	73.10	87.82	74.78	62.25	46.50
	TLI$_{(TP)}$	6.13	5.66	5.89	5.69	5.46	5.09
	TSI$_{(TP)}$	64.27	60.54	62.38	60.77	58.93	56.02
TN	**mg m^{-3}**	867.22	849.82	1236.45	830.93	894.42	803.00
	TLI$_{(TN)}$	5.23	5.21	5.70	5.18	5.27	5.13
TLI		5.41	5.14	5.82	5.06	5.11	5.07
TSI		59.37	55.96	63.32	54.89	55.39	55.55
TN:TP ratio		8.17	11.63	14.08	11.11	14.37	17.27

Table 2.4: Spearman rank correlation coefficients (r_S) for annual mean concentrations of surface chlorophyll *a* (chl *a*), total nitrogen (TN), total phosphorus TP, and Secchi depth (SD) (* denotes significant difference at $p < 0.05$).

	Spearman rank correlation coefficients (r_S)		
	1/SD	**TP**	**TN**
Chl *a*	$r_S = 0.89*$	$r_S = 0.14$	$r_S = 0.37$
1/SD		$r_S = 0.54$	$r_S = 0.43$
TP			$r_S = 0.54$

2.4   Discussion

External P loading vs internal P loading

Both external and internal P loading were reduced during the study period, however, Lake Okaro remains eutrophic. The external TP loading reduction can be attributed to the riparian protection measures, the farm nutrient budgeting, and the constructed wetland, the combination of which was estimated to reduce TP loading by c. 53 kg yr^{-1} (Environment Bay of Plenty, 2006). This loading reduction would be the comparable to c. 13.4% of the total TP catchment loading (395.9 kg yr^{-1}) and c. 6.8% of the total TP loading (777.9 kg yr^{-1}). The TP loading from the surface inflow alone produced a reduction of c. 40 kg yr^{-1}.

Although the Sas loading model yielded better agreement with measured TP than the Vollenweider model, both models consistently underestimated lake water TP concentrations as a result of either ignoring or underestimating, respectively, internal P loading. If it is assumed that the difference between measured TP concentrations and those calculated from the Vollenweider model emanates from internal loading, then this source contributes c. 50 % of the water column TP in Lake Okaro. The critical P loading model, which was used to quantify the external P loading to meet the target trophic state value for TP for Lake Okaro, also indicates clearly that internal P loading is important, since the measured P load was consistently lower than the model prediction, but TP

concentrations in the lake were still higher than either of the models and the target water column TP concentration of 68 mg m^{-3} (Environment Bay of Plenty, 2006) which was used as the basis to define the TLI target of 5.0.

Internal loading decreased following the alum application (December 2003) when P concentrations were lower in both surface and bottom waters. Although annual mean phosphorus concentrations in bottom waters remained lower for the remainder of the study period when compared with 2002-03, the effectiveness of the alum application appeared to be only temporary and TP concentrations increased slightly in 2006-07.

The mean hypolimnetic SRP concentration in 2007-08 was 38% lower than in previous years (2002-07). The reduction in SRP concentration did not reach the restoration target of 50%. Internal loading was clearly reduced for the last period (2007-08) when the Vollenweider model began to more closely approximate the measured TP, most likely as a response to the modified zeolite application.

Longevity of restoration measures

The decrease in external P loading indicates efficient P retention in the constructed wetland for the two years of measurements after its construction. The P removal mechanisms in constructed wetlands are dominated by sorption on soil substrates, storage in biomass, and the formation and accumulation of new sediments and soils rather than processes relating to the gaseous phase as with the N cycle. As a result, P retention in constructed wetlands can be high in the period immediately following construction, but decreases as the soil substrate of the wetland becomes saturated with P and potentially acts as a P source (Mitsch *et al.,* 2000; Fink & Mitsch, 2004). This is not always the case, as White *et al.* (2000) found that wetland sediments were not saturated with P despite several years of high P inputs in a large (1250 ha) restored prairie marsh. Successful reduction of P loading to Lake Okaro through the farm nutrient management system and riparian protection could significantly extend P retention in the constructed wetland.

Lake Okaro appeared to respond relatively quickly to reduced external nutrient loading compared with other stratified lakes with anoxic hypolimnia, where recovery after P input reduction was observed on time scales of around 10-15 years (Jeppesen *et al.*, 2005). Rapid recovery by external load control has generally been observed in lakes with permanently oxic hypolimnetic waters, short residence time and a short history of nutrient enrichment (Cooke *et al.*, 2005). By contrast, with Lake Okaro having a persistent anoxic hypolimnion, the reduction of both internal and external P loading appeared to have caused a response in Lake Okaro similar to that of lakes with oxic hypolimnia. However, the relatively short residence time of Lake Okaro (~ 2.8 years) may have contributed to a reasonably rapid response to reduced external nutrient loading.

Phosphorus inactivation by aluminium has been shown to be very effective in the long term in polymictic lakes (Reitzel *et al.*, 2005) and efficacy has remained high for periods up to 18 years in stratified lakes (Welch & Cooke, 1999). The alum application in Lake Okaro had limited persistent effects on internal loading, however, most likely due to the low alum concentrations (0.6 g m^{-3}; Paul *et al.,* 2008), which was at the lower range (0.05 – 30 g m^{-3}) used in most case studies (Welch & Cooke, 1999). A further factor influencing the effectiveness of alum in Lake Okaro may be associated with pH in surface waters exceeding 9, as observed during the time of the alum application (Paul *et al.,* 2008). While an alum floc is stable and re-dissolution of phosphate under anoxic conditions is unlikely, an unfavourable water column pH (i.e. outside the recommended range of 6 to 8 in which the desirable $Al(OH)_3$ complex dominates) can significantly reduce the P sorption capacity of alum due to the prevalence of more soluble Al complexes (Cooke *et al.*, 2005).

The sediment capping layer created with modified zeolite was intended to form a diffusion barrier by binding free orthophosphate released from the bottom sediments, however, visual inspection revealed an incomplete coverage of the bottom sediments. Insufficient dose size combined with a coarse grain size (1-3 mm) may have contributed to the incomplete coverage and reduced the efficacy of the sediment capping. Berg *et al.* (2004) showed that an increase in layer thickness of calcite barriers, from 1 cm to 2-4.5 cm, reduced P release for more than six months with different grain sizes tested ranging from 2-1200 μm. Other studies confirm that smaller grain size of the sediment capping material, resulting

in increased coverage, yields greater suppression of sediment P release (Yamada *et al.*, 1987). However, a diversity of pathways of P transport, such as biologically mediated transport, and gas ebullition can also be equally important in affecting the effectiveness of sediment capping (Förstner & Apitz, 2007). As aluminium is the active component leading to P adsorption in Z2G1, water column pH, particularly in the bottom waters close the sediment-water interface during the application may also affect its P uptake capacity. For both the alum and modified zeolite applications, consideration of dose rate, coverage of the capping material and application timing with regard to water column pH appear to be critical factors in the long-term reduction of internal P loading.

Criteria for improved water quality using trophic level indicators

Both water quality indices (TLI and TSI) indicate that Lake Okaro is highly eutrophic (Burns *et al.*, 1999; Carlson, 1977), but the TSI shows that Lake Okaro has moved across different trophic divisions (56.0 in 2003-04, 63.3 in 2004-05) over the study period, indicating that TSI may be a more sensitive indicator. For example, for the period of July 2004 - June 2005, Lake Okaro remained supertrophic according to the TLI whereas the TSI changed from 50 to 60 in divisions. Interestingly however, the TSI failed to describe an improvement in water quality as a result of TP reductions for 2007-08 because chl *a* for this period showed a slight increase compared with the previous year.

Both indexes indicate, however, that the trophic state has not responded in a way that might be commensurate with changes in P concentration. Rapid and efficient recycling of P within the lake can maintain an initially high trophic status despite reduction of inputs (Sas, 1989). Although internal loading was reduced in Lake Okaro, the lake trophic state appeared to be resilient to the reduced P loading. Apart from external and internal nutrient loading, a number of feedback mechanisms, including the persistence of an anoxic hypolimnion, have been proposed. Eutrophic lakes may therefore be highly resilient to restoration efforts, and multiple factors beyond TP reduction may be required to shift a lake back to a 'pristine' state (Suding *et al.*, 2004). It is inconclusive if there is a threshold for TP loading reduction required to effect a rapid improvement in lake trophic status analogous to the well-known hysteresis of alternative stable states of macrophyte

dominance and phytoplankton dominance in shallow lakes (Scheffer & Carpenter, 2003). Furthermore, in Lake Okaro reduction of P in the water column was not accompanied with a reduction in N, which could compromise the effectiveness of restoration measures in Lake Okaro until P-limitation becomes dominant.

Although the regional management organisation, Environment Bay of Plenty, acknowledges the importance of controlling both N and P, in its restoration efforts, the focus of nutrient control in Lake Okaro has been on P, partly because of the potential for N-fixation by cyanobacteria when N availability is low (Schindler *et al.*, 2008). The TN:TP ratio increased largely due to decreasing TP concentration in this study. Lean *et al.* (1987) raised doubts as to the importance of TN:TP ratios in controlling cyanobacterial dominance in Lake Okaro and showed that high internal P concentrations in the phytoplankton would allow a substantial increase in biomass to relieve the shortage of N.

Neither the TLI nor the TSI appears to be suitable for tracking pre-defined water quality restoration targets for short periods. Targeting only one of the index input variables (e.g. TP) during lake restoration when all are weighted equally may not adequately account for stabilisation of the eutrophic status by longer lasting feedback mechanisms. When loadings of both, N and P where reduced simultaneously, algal biomass may also be reduced without substantial delays (Köhler *et al.*, 2005). In other lakes however, where only P loading was reduced, water quality has improved without delay as measured by algal biomass, i.e. chl *a* (Coveney *et al.*, 2005).

Relative success of restoration methods

The observed significant decline in P concentration in the bottom waters of Lake Okaro in response to the modified zeolite application suggests that sediment capping was the most effective amongst all of the restoration procedures carried out in this lake. The constructed wetland, farm nutrient management, and the riparian restoration were collectively very effective in reducing external loading of TP, however, I could not actually isolate their individual contributions. Case studies have shown that a combination of several restoration measures is often more successful in achieving a sustained improvement in the water quality of lakes than applying a single procedure alone (Bergman *et al.*, 1999; Ruley &

Rusch, 2004; Kasprzak *et al.*, 2007). While restoration methods and procedures must have a foundation in the basic science of limnology (Cooke *et al.*, 2005), the reductionism approach of classical scientific studies makes lake restoration difficult to achieve. As degradation may have occurred via multiple stressors, restoration at an ecosystem level should take a more holistic approach. Further research using a watershed P balance model (Schussler *et al.,* 2007) may enable resolution of the individual contributions of restoration methods in the catchment.
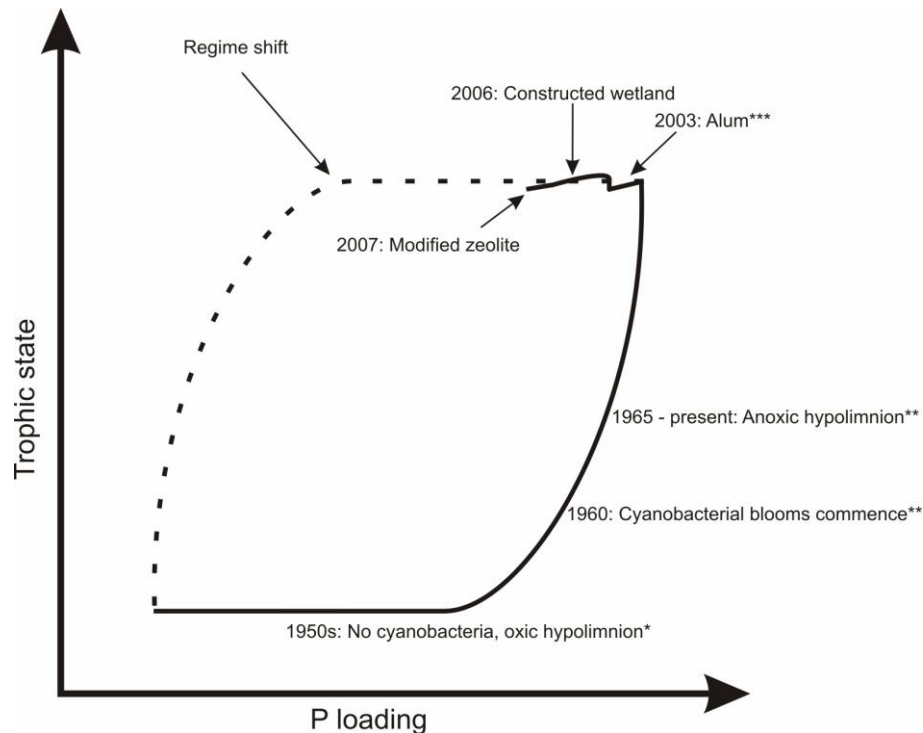
Figure 2.6: Conceptual model of trophic state in relation to P loading (internal and external) in Lake Okaro demonstrating possible regime shifts in response to changes in P loading in Lake Okaro (dashed line) (* Jolly, 1977; ** Forsyth *et al.*, 1988, *** Paul *et al.*, 2008).

The results presented here reflect the short- to medium-term restoration outcome in a single stratified lake (Figure 2.6). Efficient restoration of stratified lakes with anoxic hypolimnia requires that the external load is reduced below a critical threshold, and to avoid delays in recovery, prevention of P recycling from the sediment by phosphorus inactivation or sediment capping can substantially increase the probability that the threshold value might be obtained. Even with a multi-pronged approach, it is still a significant challenge to reach the threshold for P loading that might bring about a regime shift to a distinctly different trophic state with a permanently oxic hypolimnion. Intensive long-term monitoring of

restoration measures can be time consuming and costly. However, as shown with the restoration of Lake Okaro, such monitoring is critical to accurate performance analysis and is only possible by pre-defining restoration targets and monitoring appropriate variables, to draw conclusions as to the success of the restoration procedures.

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3 Hypolimnetic phosphorus and nitrogen dynamics in a small, eutrophic lake with a seasonally anoxic hypolimnion

3.1 Introduction

Internal loading plays a critical role in the nutrient dynamics of many lakes, especially eutrophic lakes whose hypolimnion may become seasonally anoxic (Søndergaard *et al.*, 2003a). Under anoxic conditions, fluxes of the biologically available nutrients, soluble reactive phosphate (SRP) and ammonium-nitrogen (NH_4-N), from internal releases can exceed those from external sources (e.g. Burger *et al.*, 2007), and may therefore delay or negate the effects on water quality of catchment focused restorative procedures (Jeppesen *et al.*, 2005). The total phosphorus (TP) concentration in the lake water column, including the sediment release of SRP, is affected by a number of interacting factors such as temperature (Holdren & Armstrong, 1980), microbial activity (Sinke *et al.*, 1990), bioturbation (Phillips *et al.*, 1994), and sediment re-suspension by currents or wave action (Hamilton & Mitchell, 1997). Furthermore, remobilisation from the sediment is controlled by the complex inorganic and organic speciation of phosphorus (P) (Penn *et al.*, 2000; Spears *et al.*, 2007).

Sediment nutrient releases can be estimated experimentally from benthic chambers (Burger *et al.*, 2007) or sediment core incubations (Anderson & Ring, 1999; Penn *et al.*, 2000; Gibbs & Özkundakci, Appendix I). However, it is difficult to extrapolate these results to whole-lake basins because many of the natural processes occurring in the lake cannot be reproduced in the incubation chamber and the area of the sediment surface being tested is very small given the potentially high spatial variability across the bed of the lake (Auer *et al.*, 1993). Hypolimnetic nutrient accumulation rates can be used to estimate net nutrient release rates, which integrate all processes including mixing, diffusion, and mineralisation (e.g. Nürnberg, 1988).

For effective lake remediation to improve water quality, both N and P loads need to be reduced (e.g. Lewis & Wurtsbaugh, 2008; Pearl, 2009). There are a variety of methods to reduce internal nutrient loading (Smolders *et al.*, 2006), particularly for P, including hypolimnetic oxygenation to promote P binding by iron (Fe^{3+}) in the sediments, although it has been shown that aerobic conditions alone do not necessarily lead to complete P removal (Gächter & Müller, 2003). The addition of nitrate can also reduce P release from the sediment because it is an electron acceptor that helps to prevent the reduction of Fe^{3+} that would otherwise liberate P from the bottom sediments (Wauer *et al.*, 2005).

Phosphorus-inactivation agents, such as calcite (Berg *et al.*, 2004), modified clay minerals (Robb *et al.*, 2003) and iron slag (Yamada *et al.*, 1987), have also been used as sediment capping materials with varying degrees of success, to isolate or permanently bind P within the sediments for sustained long-term management of internal loads. However, because of the potential for sediment capping materials to change the biogeochemical processes across the sediment-water interface (Vopel *et al.*, 2008), application of these materials should be excluded from the permanently aerobic littoral zones to reduce to avoid adverse impacts on benthic biota.

Where aluminium salts (e.g. alum) have been used, reduction of internal P loads has sometimes been effective for 15 years or more, although sometimes only for periods as short as 2-3 years (Welch & Cooke, 1999). Commonly used measures of sediment capping efficacy include P levels in sediment, visual inspection of capping material coverage in cores/grabs, and changes in concentrations of nutrients in the water column (Welch & Cooke, 1999). Hypolimnetic net accumulation rates of nutrients have been used to estimate internal nutrient loads (e.g. Nürnberg, 1987), but these rates rarely include specific process of nutrient source and sink fluxes in the hypolimnion.

In September 2007, an aluminium-amended, modified zeolite, P-inactivation agent, Z2G1, a proprietary product developed by Scion, Rotorua, New Zealand, was applied as a sediment capping material in a small, eutrophic lake (Lake Okaro, New Zealand), in an attempt to reduce the internal P load from the anoxic sediment during seasonal stratification. The aluminium amendment gives the natural zeolite mineral, which is a strong cation absorber, a strong

affinity for phosphate and thus the ability to permanently sequester SRP being released from the anoxic sediments. Laboratory tests and sediment core incubations have shown that Z2G1 has a natural ammonium absorption capacity of around 4.5 g NH_4-N kg^{-1} and a phosphate-binding capacity of about 20 g P kg^{-1} giving it the potential to substantially reduce sediment releases of SRP while retaining the capacity to absorb some NH_4-N at dose rates comparable to the whole lake dose rate (Gibbs & Özkundakci, Appendix I). Because Z2G1 is a granular product with a bulk density of 2, it has the ability to settle rapidly through the water column allowing targeted application to avoid biologically sensitive zones of the lake (e.g. littoral zone). I hypothesized that the "whole lake" treatment of Lake Okaro with Z2G1 would significantly reduce sediment release of SRP, and to some extent NH_4-N. I test this using a comprehensive model of nutrient fluxes in the hypolimnion. Temporal changes in release rates of SRP and NH_4-N were examined for a period of seasonal stratification which included before and after the Z2G1 application. I calculated the relative contribution of different processes (sediment release, mixing, diffusion, mineralisation, and uptake) to the observed hypolimnetic accumulation rates of SRP and NH_4-N, in order to quantify the most important sources of these nutrients in the hypolimnion.

3.2   Materials and methods

Study site

Lake Okaro (Figure 3.1) has a maximum depth of 18 m and is the smallest (0.32 km^2) and most eutrophic of twelve major lakes in the Rotorua region, New Zealand. It is located 27 km south of Rotorua township and was formed from a geothermal explosion crater about 800 years before present (Lloyd, 1959). The catchment area (3.89 km^2) of Lake Okaro is mostly pasture, used for dairy production. Two small unnamed streams enter the lake from the north-west through a recently constructed wetland, designed to reduce catchment nutrient loads to the lake (Tanner *et al.*, 2007), and the Haumi Stream in the south-east of the lake is the only outflow (Forsyth *et al.*, 1988). The lake has a theoretical mean residence time of about 1.5 years. Water quality in Lake Okaro declined

significantly between 1955 and 1963 (Jolly, 1977) and the lake has become eutrophic with persistent cyanobacteria blooms in spring and summer (Forsyth *et al.*, 1988; Paul *et al.*, 2008). Water quality data from the lake show that the hypolimnion is anoxic throughout most of the stratified period and indicates a substantial internal P load which was thought to be driving the cyanobacteria blooms (Environment Bay of Plenty, 2006). In order to reduce the internal P load in Lake Okaro, between 25 and 28 September 2007, 110 tonnes of Z2G1, equivalent to a dose rate of 350 g m^{-2} (grain size 1-3 mm), was applied as a sediment cap. The Z2G1 capping material was applied using a fertiliser spreader over the lake surface corresponding to the area beneath the thermocline (> 5 m; equivalent to c. 0.2 km^2). The application was targeted to avoid the capping material coating the sediments in the littoral zone above 5 m.
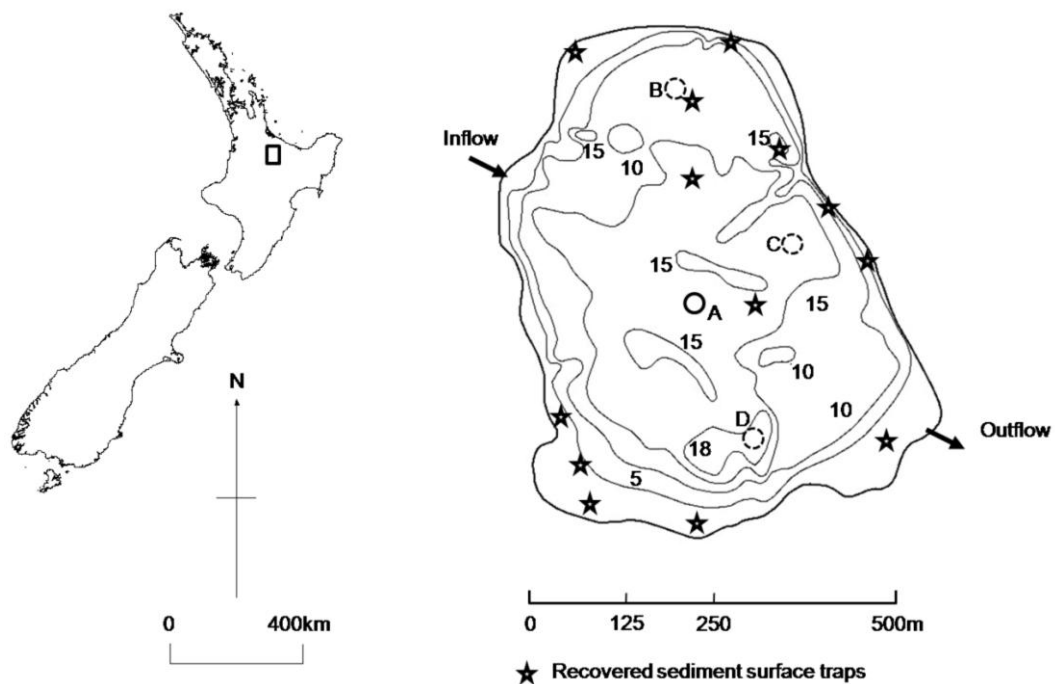
Figure 3.1: Location map of Lake Okaro with depth contours 5 m, 10 m, 15 m, and 18 m, showing the location of the mid lake sampling station (circle marked A), sediment sampling sites (dashed circles marked B, C, and D), and sediment trap sampling sites marked by stars.

Water column sampling

Water column samples were collected monthly from 27 July 2007 (winter, southern hemisphere) to 19 June 2008 from a mid-lake station (A, Figure 3.1) at the surface (0 m) and at 3, 6, 9, and 14 m depths using a 10 L Schindler-Patalas trap. In a small stratified lake, such as Lake Okaro, a reasonable assumption is

that a mid lake fixed-depth sample is sufficient, as conditions are relatively homogeneous horizontally. Göransson et al., (2004) showed that a mid-lake water sample can be considered more representative than a sample taken further away from the centre of the lake. Samples were also collected weekly for two weeks before and immediately following the Z2G1 application in September 2007. Water samples were syringe-filtered through Whatman GF/C filters immediately upon collection and frozen before analysis for SRP, nitrate (NO_3-N), nitrite (NO_2-N), and NH_4-N. Dissolved inorganic nitrogen (DIN) was calculated as the sum of NO_3-N + NO_2-N + NH_4-N. (In most samples NO_2-N concentrations were < 0.002 mg L^{-1}.). The filters for chlorophyll *a* (chl *a*) were stored frozen pending analysis. Unfiltered water samples were also collected and frozen pending analysis of total phosphorus (TP) and total nitrogen (TN).

Depth-referenced (< 0.2 m) temperature, conductivity, oxygen, chlorophyll fluorescence, and irradiance data were measured on each sampling occasion with a conductivity-temperature-depth (CTD) profiler (SBE 19 plus, Seabird Electronics), fitted with a dissolved oxygen (DO, Seabird Electronics) sensor. pH was measured on each sampling occasion at depths of 0 and 14 m using a YSI 6000 UPG Multi Parameter Sonde.

Filterable nutrients were analysed on a Lachat QuickChem® Flow Injection Analyser (FIA+ 8000 Series, Zellweger Analytics, Inc.). Total P and TN were analysed as for SRP and NO_3-N, respectively, following persulphate digestion (Ebina *et al.*, 1983). Chlorophyll *a* concentrations were determined by extracting pigments from the thawed filters using 90% acetone and measuring fluorescence of the extract with a 10-AU Fluorometer (Turner Designs), with correction for phaeophytin using acidification (Arar & Collins, 1997). Contour plots with horizontal axis of time and vertical axis of depth were produced for temperature, DO, chl *a*, and nutrients using Ocean Data View (Version 3.3.2), with interpolation between measured values based on a linear, least-square interpolation.

Data analysis

Thermocline depth (z_{mix}) was calculated from vertical temperature profiles using the temperature gradient as dT/dz = minimum (e.g. Hoare & Spigel, 1987).

Smoothing of the profile was carried out using the robust Lowess method (Cleveland, 1979) with a linear least squares fitting of a first order polynomial function with a span width of 0.3 m, where T is the water temperature (°C) at depth z (m) measured positive downwards. Smoothing was performed to omit noise between measurements in the profile. The lake was considered to be fully mixed when dT/dz was > -0.25 °C m^{-1} throughout the water column (Sherman *et al.*, 1998). The top of the metalimnion was calculated as the depth where dT/dz was initially < -0.25 °C m^{-1} from the surface downwards and the bottom of the metalimnion as the maximum depth where dT/dz was < -0.25 °C m^{-1}.

The hypolimnetic fluxes of SRP and NH$_4$-N were estimated from the change in mass of SRP and NH$_4$-N in the hypolimnion over the time period between successive sampling dates (Δt). Mass values were determined in 0.2 m horizontal layers, calculated by linear interpolation of measured values from the 0, 3, 6, 9 and 14 m water samples, and multiplied by the volume of each layer obtained from a hypsographic curve. Effluxes of SRP and NH$_4$-N from the sediments were calculated on a daily basis and expressed as the net flux per unit area of sediment (A$_{Sed}$, in mg m^{-2} d^{-1}). Nutrient fluxes were not calculated after 27 March as temperature profiles indicated that the deepest sampling depth (14 m) was within the metalimnion and not the hypolimnion. During the stratified period between 20 September 2007 and 27 March 2008, Δt ranged from 6 to 46 days.

Conceptual models were developed for nutrients in the hypolimnion (Figure 3.2), as a first step for quantitative estimates of net fluxes (F) of SRP and NH$_4$-N from the sediment. These models included nutrient loss or gain from hypolimnetic mixing, diffusion across the thermocline, water column mineralisation, phytoplankton uptake, adsorption/desorption associated with P suspended solids (SS), and nitrification (Table 3.1). Fluxes due to mixing were calculated from changes in the thermocline depth. Fluxes due to diffusion (D) across the thermocline were calculated from the concentration gradient (MacIntyre *et al.*, 1999) and a lake-wide average of the vertical eddy diffusivity (K$_Z$; Yeates & Imberger, 2004; Eq. 3.1 and 3.2). The depth-dependent expression for K$_Z$ is based on Lake Number (L$_N$, Imberger & Patterson, 1990) and Brunt-Väisälä frequency (N^2). Lake Number and N^2 were calculated from CTD casts and linearly interpolated between successive sampling dates to approximate daily values for D. Water column mineralisation (M) of organic nutrients (Org) to

inorganic nutrients (i.e. SRP and NH_4-N) was modelled as a first order, temperature-dependent process (Eq. 3.3). Mineralisation rates of Org were separated into an aerobic phase (coefficients k_{OP} and k_{ON}) and an anaerobic phase (coefficients k_{OAN} and k_{OAP}). Nutrient stoichiometry of phytoplankton (internal storage of phytoplankton P and N) was based on the Redfield ratio as discussed in Hecky *et al.* (1993) and set to 1.22 mg P mg^{-1} chl *a* and 8.8 mg N mg^{-1} chl *a*. For P, the pool available for mineralisation was assigned as the difference between concentrations of TP and the sum of SRP and internal P storage of phytoplankton, and for N it was the difference between the concentrations of TN and the sum of DIN and internal N storage of phytoplankton. Values for M were calculated daily from linear interpolation of measured concentrations of nutrients and DO, and temperature. (Eq. 3.3) Phytoplankton nutrient uptake rates (U) in the hypolimnion were modelled as a function of external concentrations of SRP and DIN based on a Michaelis-Menten function that also included an assigned growth (uptake) rate (Eq. 3.4 and 3.5). The model was applied daily from linearly interpolated measured concentrations of nutrients and chl *a* between successive sampling dates. Parameter values used in the models are given in Table 3.2. Values for the half saturation constants for nitrogen (K_N) and phosphorus (K_P) limitation, respectively, were derived for the cyanobacteria species commonly observed in Lake Okaro (*Anabaena* spp. and *Microcystis aeruginosa*; Paul *et al.*, 2008) based on ranges given in Hamilton & Schladow (1997) and Robson & Hamilton (2004). Values for the maximum rate of uptake of N and P (UN_{max} and UP_{max}, respectively) were derived from Hamilton & Schladow (1997). Adsorption and desorption of SRP onto SS, the conversion of SRP to particulate P and vice-versa, were assumed to take place at a rate proportional to the SRP concentration (Eq. 3.6 and 3.7). This process is described using a Langmuir isotherm (Chapra & Reckhow, 1983) where the sorbed P concentration (q_e, mg kg^{-1} SS) varies as a function of the phosphate concentration, the maximum potential adsorbed particulate P concentration ($q_{e,max}$; mg kg^{-1} SS), and the half-saturation constant for P adsorption/desorption (K_f; mg m^{-3}). The effect of redox conditions (i.e. using dissolved oxygen as a proxy) was adjusted by using different values of K_f with a ratio of $K_{f,anoxic}$ to $K_{f,oxic}$ of 1.7 for the pH levels observed in Lake Okaro (Furumai & Ohgaki, 1989). Suspended solids concentrations in Lake Okaro were based on Vant & Davies-Colley (1986) and were varied from 0.8 to 2.5 g m^{-3}. Nitrification was modelled following Monod kinetics using a nitrification rate

coefficient (d^{-1}) and a half-saturation constant for the effect of oxygen on nitrification $(g\ m^{-3})$, with values for both parameters obtained from the literature (Eq. 3.8). The limiting effect of oxygen on nitrification is commonly at values between 0.2 and 0.5 mg O_2 L^{-1} (Downes, 1988; Hanaki *et al.*, 1990) and I assigned a value of 0.4 mg O_2 L^{-1}. A sensitivity analysis was conducted on the parameter values for UN_{max}, UP_{max}, K_N, K_P, k_{ON}, k_{OP}, $q_{e,max}$, K_f, k_{Nit} and K_{DO} using minimum and maximum values found in the literature (Table 3.2). The models for P and N were computed daily, commencing on the first day of stratification corresponding to development of a seasonal thermocline.
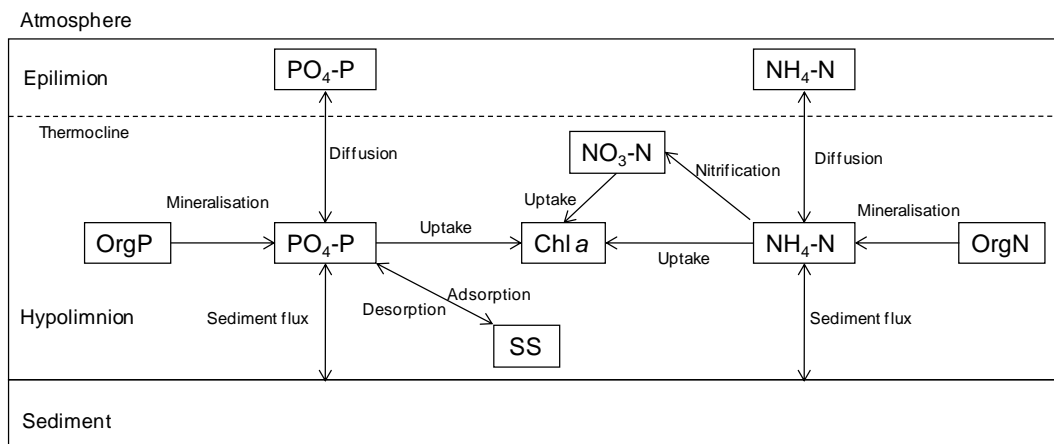
Figure 3.2: Conceptual model for nutrient dynamics in the hypolimnion of Lake Okaro during stratification period.

The distribution of Z2G1 on the bottom sediments following the application was assessed visually using an underwater video camera (Deep Blue, Ocean Systems Inc.) deployed from a boat. Visual inspection was based on a transect between the inflow and the outflow of the lake at depths >10 m (Figure 3.1). A separate visual inspection was based on sediment cores taken from sites B, C, and D (Figure 3.1). Sediment surface traps were also used at the lake bed to determine the amount of Z2G1 that reached the sediment surface. Locations of retrieved traps are shown in Figure 3.1. The traps consisted of Astroturf[TM] sheets (19 mm fibre length, 0.1 m^2) held in plastic trays. The Z2G1 caught in the traps was retrieved after the Z2G1 application and then dried and weighed to obtain an aerial application rate (g Z2G1 m^{-2}) at each location.

Table 3.1: Parameterisations of processes used to model nutrient dynamics in the hypolimnion. The symbol i is used as a generic identifier for phosphorus and nitrogen. See Table 3.2 for definitions of symbols.

Eq.	Process	Units	Equation
3.1	Vertical eddy diffusion coefficient	$(m^2\ s^{-1})$	$K_Z = \dfrac{200 N_{(z)}^2}{L_N N_{max}^2} K_M$
3.2	Diffusion across thermocline of P and N	$(mg\ m^{-2}\ d^{-1})$	$D_i = \dfrac{dc_i}{dz} K_Z$
3.3	Mineralisation of organic P and N	$(mg\ m^{-3}\ d^{-1})$	$M_i = \left(k_{OAi} v^{T-20} \dfrac{K_{MIN}}{K_{MIN} + DO} + k_{Oi} v^{T-20} \dfrac{DO}{K_{MIN} + DO} \right) Org_i$
3.4	Phytoplankton N uptake	$(mg\ m^{-3}\ d^{-1})$	$U_N = v^{T-20} UN_{max} \left(\dfrac{NO_3 + NH_4}{K_N + NO_3 + NH_4} \right) C_{chla}$
3.5	Phytoplankton P uptake	$(mg\ m^{-3}\ d^{-1})$	$U_P = v^{T-20} UP_{max} \left(\dfrac{PO_4}{K_P + PO_4} \right) C_{chla}$
3.6	Langmuir isotherm for P adsorption/desorption	$(mg\ kg^{-1}\ SS)$	$q_e = q_{e,max} \dfrac{PO_4}{K_f + PO_4}$
3.7	Adsorption/desorption	$(mg\ m^{-2}\ d^{-1})$	$AD = \dfrac{d(q_e SS\ V_{Hypo})}{dt} \dfrac{1}{A_{Sed}}$
3.8	Nitrification	$(mg\ m^{-3}\ d^{-1})$	$Nit = v^{T-20} k_{Nit} \left(\dfrac{K_{DO}}{K_{DO} + DO} \right) NH_4$
3.9	Sediment N flux	$(mg\ m^{-2}\ d^{-1})$	$F_N = \dfrac{d(V_{Hypo} c_N)}{dt} \dfrac{1}{A_{Sed}} + \left[D_N + \dfrac{(U_N - M_N + Nit) V_{Hypo}}{A_{Sed}} \right]$
3.10	Sediment P flux	$(mg\ m^{-2}\ d^{-1})$	$F_P = \dfrac{d(V_{Hypo} c_P)}{dt} \dfrac{1}{A_{Sed}} + \left[D_P + AD + \dfrac{(U_P - M_P) V_{Hypo}}{A_{Sed}} \right]$

Table 3.2: Parameter symbols definitions and values used in equations to model nutrient dynamics in the hypolimnion. See Table 3.1 for equations.

Symbol	Description	Parameters values used in sensitivity analysis
UN_{max}	Maximum rate of nitrogen uptake (mg N (mg chl *a*)$^{-1}$ d^{-1}	0.5, 0.75, 1*
UP_{max}	Maximum rate of phosphorus uptake (mg P (mg chl *a*)$^{-1}$ d^{-1}	0.01, 0.05, 0.075, 0.1*
K_N	Half-saturation constant for nitrogen uptake (mg m^{-3})	20, 50, 100, 150, 200*
K_P	Half-saturation constant for phosphorus uptake (mg m^{-3})	1, 5, 10, 15, 25*
K_M	Molecular diffusivity of heat (m s^{-2})	1.4×10^{-7}**
k_{OAN}	Anaerobic organic nitrogen mineralisation rate coefficient (d^{-1})	0.007***
k_{OAP}	Anaerobic organic phosphorus mineralisation rate coefficient (d^{-1})	0.007***
k_{ON}	Aerobic organic nitrogen mineralisation rate coefficient (d^{-1})	0.05, 0.1, 0.15, 0.2*
k_{OP}	Aerobic organic phosphorus mineralisation rate coefficient (d^{-1})	0.07, 0.1, 0.15, 0.2*
K_{MIN}	Mineralisation half-saturation constant for effect of dissolved oxygen on organic breakdown (g m^{-3})	1.5*
k_{Nit}	Nitrification rate coefficient (d^{-1})	0.005, 0.01, 0.025, 0.05*
K_{DO}	Oxygen half-saturation constant for nitrification (g m^{-3})	1, 2, 3, 4*
ν	Temperature multiplier (-)	1.08*
$q_{e,max}$	Maximum adsorbed particulate P (mg kg^{-1} SS)	300, 1000, 2000, 4500****
K_f	Half-saturation constant for P adsorption/desorption (mg m^{-3})	50, 70, 100, 120****

*Hamilton & Schladow (1997, and references therein), Gal *et al.* (2009); **Yeates & Imberger (2003);
***Robson & Hamilton (2004); ****Chapra & Reckhow (1983)

3.3   Results

Distribution of Z2G1 on lake bed

The distribution of Z2G1 was variable across the lake bed and sediments, ranging from 115 to 1520 g Z2G1 m^{-2} across the hypolimnion, but no capping material was detected in the littoral zone. Visual inspection of sediment cores showed that

some granules of Z2G1 penetrated into the surface sediments to depths of up to 10 cm.

Stratification

Lake Okaro was thermally stratified for c. 261 days during the 12-month sampling period (Figure 3.3). Thermocline depth (z_{mix}) ranged from 1.4 m (21 November 2007) to 13.8 m (26 May 2008) and fluctuated between 2.1 m and 11.7 m during the first two months of stratification (September to October 2007). The average thickness of the metalimnion was 2.4 m.
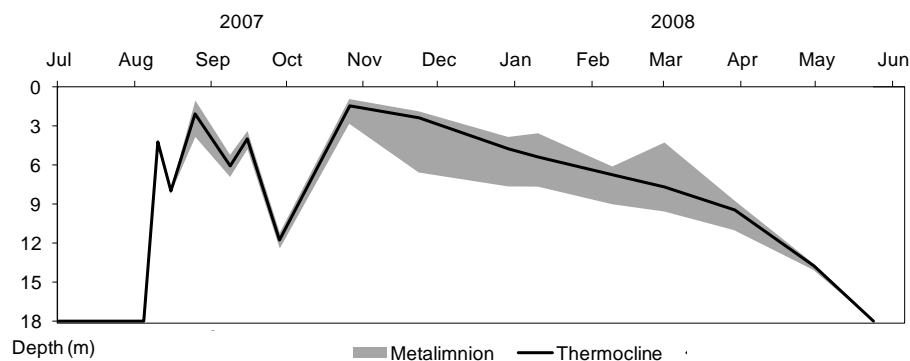
Figure 3.3: Thermocline depth and thickness of metalimnion in Lake Okaro during the study period. Note: During the mixing period, thermocline and metalimnion depths were set to the maximum lake depth of 18 m.

Temperature, dissolved oxygen concentration, and chlorophyll a fluorescence

Depth-averaged water column temperature during the 2007 winter mixing period in Lake Okaro was 9.3 °C (Figure 3.4A). At the onset of stratification, temperature in the surface waters increased steadily and reached a peak of 22.7 °C in mid summer (5 February 2008). Temperature near the bottom of the lake increased about 2-3 °C over the stratified period. The lake was isothermal again by 19 June 2008 when the water column temperature was 10.3 °C (Figure 3.4A).

The maximum dissolved oxygen (DO) concentration was 14.1 mg L^{-1} at the surface on 20 September 2007 (Figure 3.4B). During the stratified period, the hypolimnion was essentially anoxic (< 1 mg L^{-1}) for about 199 days between 20 September 2007 and 26 May 2008. However, between sampling on 4 and 11 October 2007, DO in the hypolimnion increased by 2.5 mg L^{-1}, but was anoxic again on the subsequent sampling day (24 October 2007).
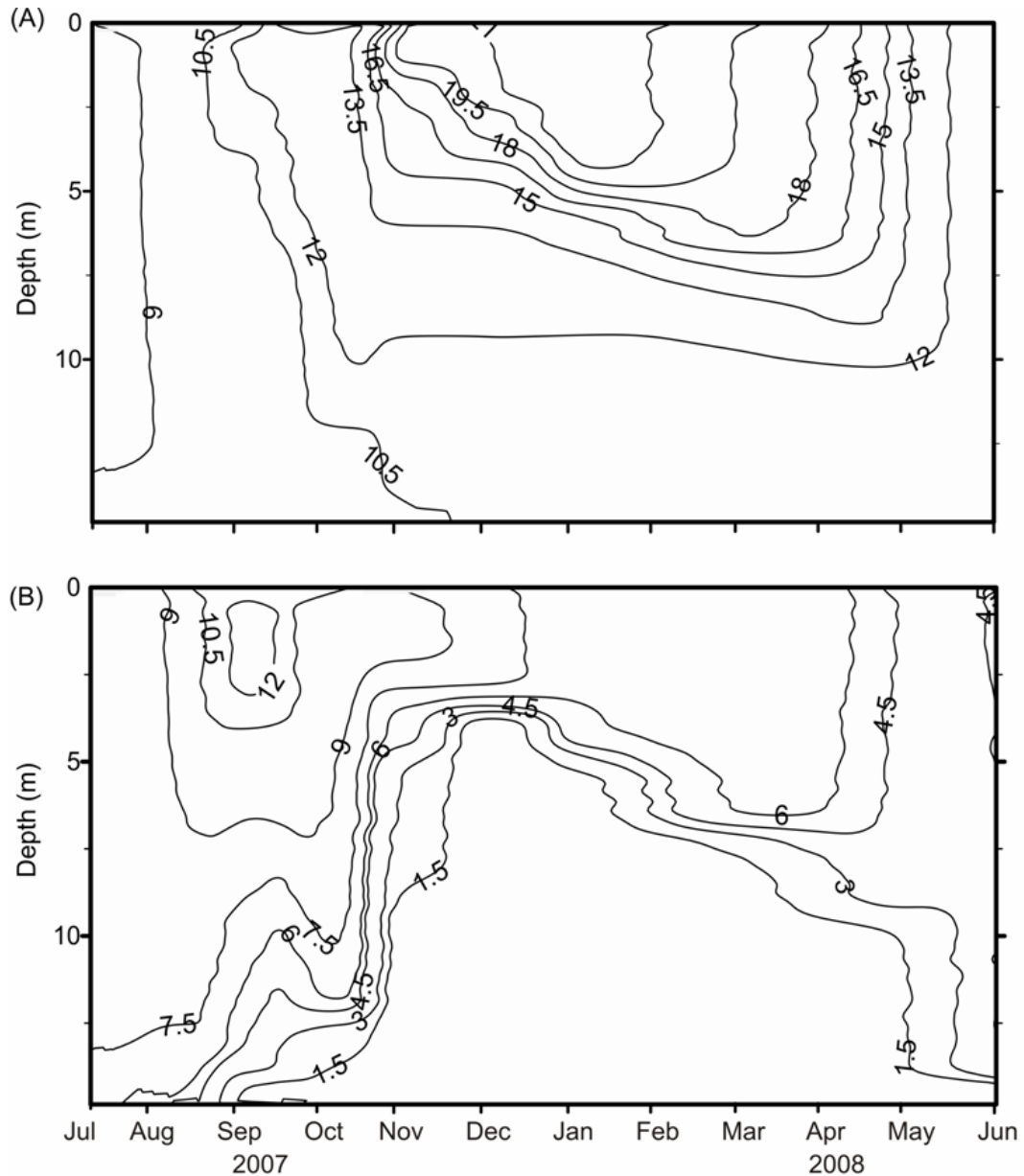
Figure 3.4: Contour plot of (A) temperature (°C), (B) dissolved oxygen concentration (mg L^{-1}) with depth in Lake Okaro for the period July 2007 until June 2008.

Vertical profiles of chl *a* concentration were relatively uniform during the mixed period (July – August 2007, Figure 3.5) and averaged 17.8 µg L^{-1}, before the development of the spring bloom (September to November 2007). During the stratified period, there was a subsurface peak of chl *a* just below the thermocline on 21 November 2007, and 6 and 27 March 2008, with concentrations often 10-fold higher than in the epilimnion and reaching a maximum of 106.3 µg L^{-1} at 6 m on 3 March 2008.
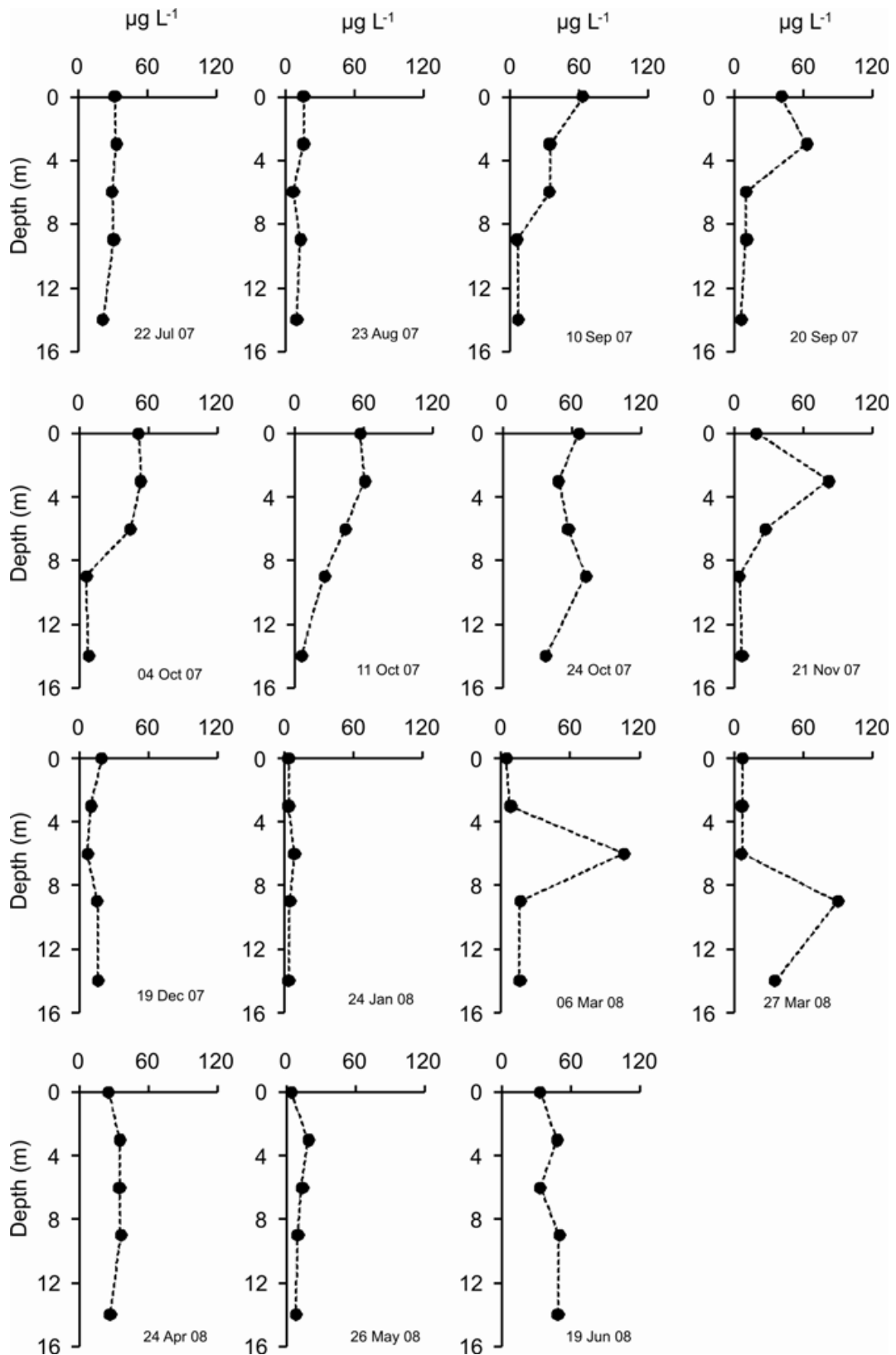
Figure 3.5: Vertical profiles of chlorophyll *a* (µg L^{-1}) obtained from pigment extraction in Lake Okaro for the period July 2007 until June 2008.

pH

Values of pH were similar at 0 and 14 m depth during the mixing period with a depth-average of 7.32 (Figure 3.6). pH at 0 m increased during the spring bloom to a maximum of 10.47 on 21 November 2007 and then decreased gradually over the remainder of the stratified period. pH at 14 m decreased slightly during the stratified period, to a minimum of 6.53 on 19 June 2008.
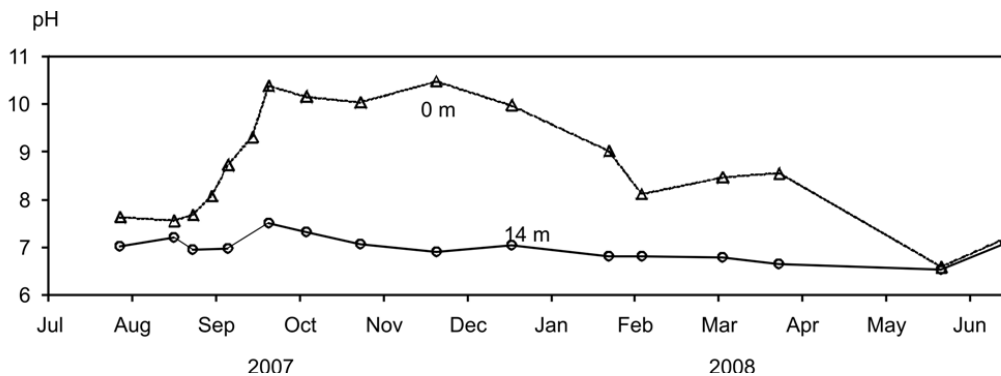
Figure 3.6: Values of pH measured at 0 and 14 m depth for the period July 2007 until June 2008.

Nutrient concentrations

Total phosphorus concentrations at 14 m depth in Lake Okaro followed a similar pattern to those of SRP (R = 0.83, p < 0.05), with SRP contributing up to 70% of the TP. The maximum concentration of TP was 0.266 mg L^{-1} on 6 March 2008 (Figures 3.7A and 3.7B). At the surface, TP concentrations over the entire study period averaged 0.06 mg L^{-1} compared with SRP concentrations of 0.009 mg L^{-1}, and with no correlation between the two measurements at this depth. Concentrations of SRP were relatively uniform throughout the water column during the mixing period at around 0.015 mg L^{-1} but increased rapidly in the hypolimnion after the onset of thermal stratification at the beginning of September to reach 0.105 mg L^{-1} at 14 m on 4 October 2007. Concentrations at 14 m depth continued to increase before reaching a maximum of 0.189 mg L^{-1} on 6 March 2008 (Figure 3.7B).
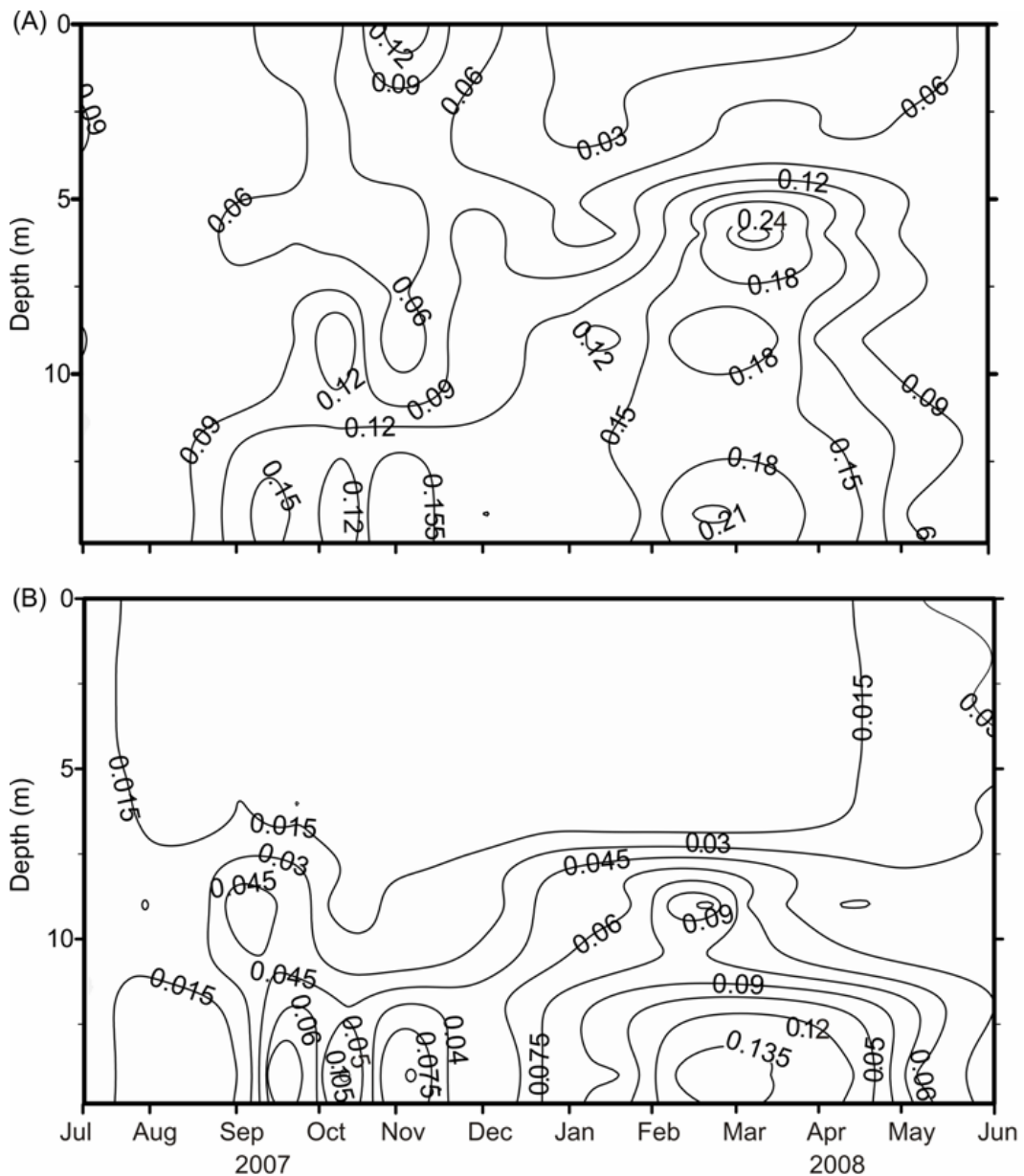
Figure 3.7: Contour plot of (A) TP (mg L^{-1}), and (B) SRP (mg L^{-1}) with depth in Lake Okaro for the period July 2007 until June 2008.

Total nitrogen at 14 m depth followed a similar pattern to NH$_4$-N, which contributed an average of 86% of TN between 24 January 2008 and 26 May 2008 but only 36% across the mixing period. Total nitrogen concentrations reached a maximum of 2.68 mg L^{-1} on 6 March 2008 (Figure 3.8A). Concentrations of NH$_4$-N were reasonably uniform throughout the water column through to 5 October 2007 averaging 0.44 mg L^{-1} (Figure 3.8B), then increased steadily at 14 m to a maximum of 2.47 mg L^{-1} on 6 March 2008, before declining to 0.54 mg L^{-1} on 19 June 2008, when the lake was once again mixed. Concentrations in surface waters declined steadily throughout the stratified period, to 0.1 mg L^{-1}, and then increased to 0.53 mg L^{-1} after winter mixing in June 2008. Concentrations of

NO_3-N were high during the mixed period (Figure 3.8C), reaching a maximum of 0.12 mg L^{-1} on 23 August 2007 at the beginning of stratification, and declined during the stratified period at all depths, with concentrations in the hypolimnion falling below detection (<0.002 mg L^{-1}) by 5 February 2008.

Mass ratios of TN:TP in the hypolimnion were higher at the onset of stratification (17:1 on average from 10 to 20 September 2007, before the Z2G1 application) and then declined after the Z2G1 application to an average ratio of 11:1 for the remainder of the stratified period. In contrast, TN:TP ratios in surface waters showed large seasonal variations, ranging from 8:1 to 47:1 during the same period. An alternative nutrient ratio for deciphering potential for N or P limitation uses DIN:TP (Morris & Lewis, 1988). This ratio was < 1:1 in the surface waters and averaged 7.4:1 in the hypolimnion for the majority of the stratified period.
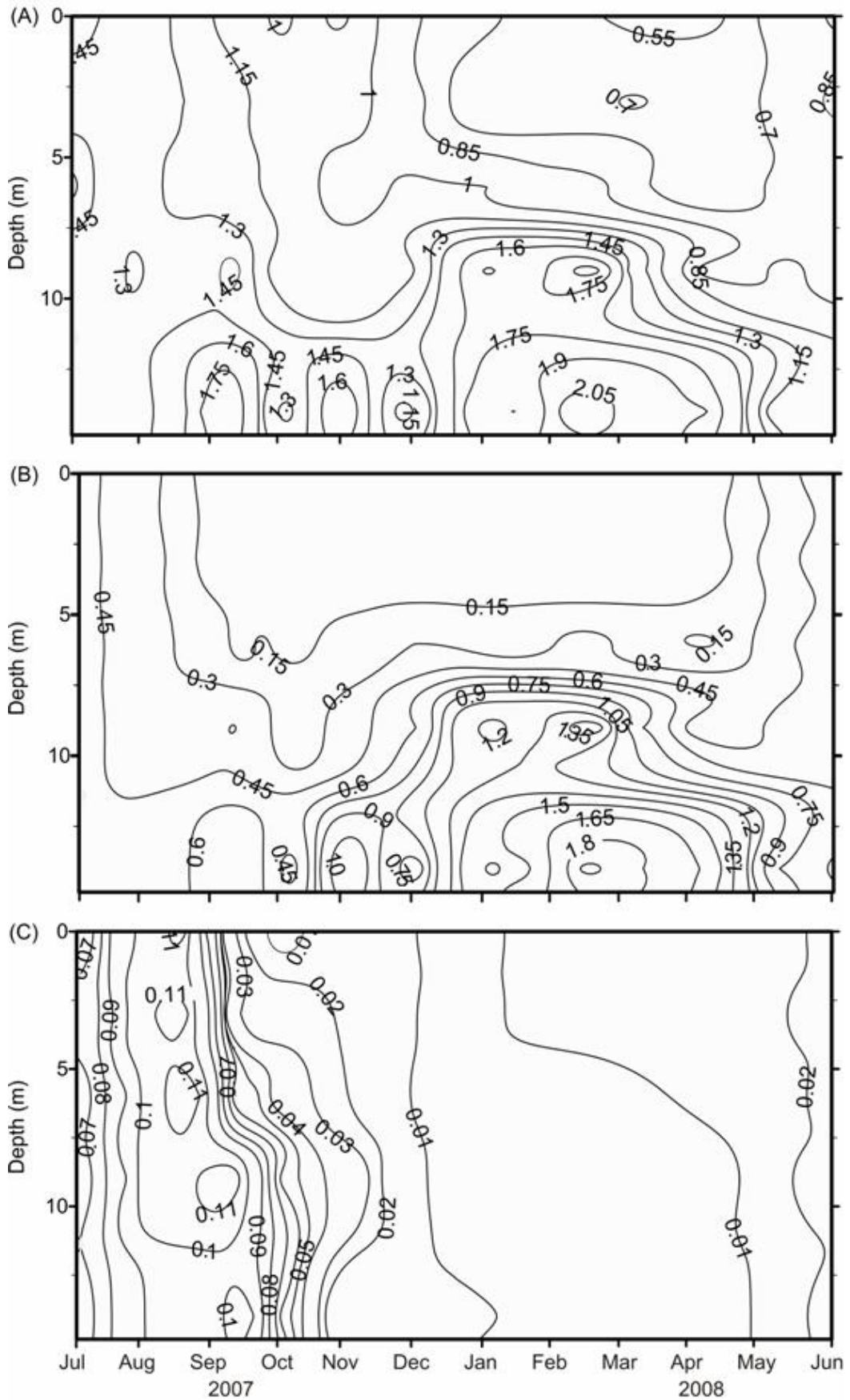
Figure 3.8: Contour plot of (A) TN (mg L^{-1}), (B) NH$_4$-N (mg L^{-1}), and (C) NO$_3$-N (mg L^{-1}) with depth in Lake Okaro for the period July 2007 until June 2008.

Hypolimnetic fluxes of SRP and NH$_4$-N

Hypolimnetic fluxes of SRP and NH$_4$-N in Lake Okaro are presented in Figure 3.9A and 3.9B, respectively. Accumulation rates of both SRP and NH$_4$-N in the hypolimnion varied during the stratified period, initially rising to 25.6 mg m^{-2} d^{-1} and 207 mg m^{-2} d^{-1}, respectively, on 20 September 2007 then falling to -22.3 mg m^{-2} d^{-1} and -145 mg m^{-2} d^{-1}, respectively, on 24 October 2007 before rising again (Figure 3.9).

Mineralisation of organic P contributed up to 11.7 mg m^{-2} d^{-1} of SRP to the hypolimnion and was higher earlier in the stratification period, prior to the disappearance of DO (Figure 3.9A). Mineralisation of organic N in the hypolimnion followed a similar pattern and contributed up to 363 mg m^{-2} d^{-1} NH$_4$-N (Figure 3.9B).

Uptake of SRP and NH$_4$-N by phytoplankton in the hypolimnion was highest at -26.9 mg P m^{-2} d^{-1} and -267 mg N m^{-2} d^{-1} during November 2007 (Figure 3.9A, B). The loss of SRP from the hypolimnion as a result of diffusion across the thermocline, based on daily interpolated values, was relatively low, but reached a maximum of -13.3 mg m^{-2} d^{-1} in September 2007 (Figure 3.9A). Mean diffusion of NH$_4$-N across the thermocline over the entire stratification period was 9.4 mg m^{-2} d^{-1} with a maximum of -46 mg m^{-2} d^{-1} in October 2007 (Figure 3.9B).

Nitrification in the hypolimnion was highest at -72 mg N m^{-2} d^{-1} during oxic conditions in September 2007 and was zero during the anoxic period. Adsorption of phosphate peaked at 3.2 mg m^{-2} d^{-1} in September 2007 and desorption was highest in November 2007 at 8.5 mg m^{-2} d^{-1}.

The sediment flux of SRP varied from a minimum of -26.4 mg m^{-2} d^{-1} (i.e. uptake by the sediment) in October 2007 to a maximum of 36.8 mg m^{-2} d^{-1} in November 2007 (Figure 3.9A). Sediment fluxes of NH$_4$-N varied considerably, with a maximum of 440 mg m^{-2} d^{-1} in November 2007 and a minimum (i.e. sediment uptake) of -251 mg m^{-2} d^{-1} in September 2007 (Figure 3.9B).

As part of the sensitivity analysis for the model, phytoplankton uptake and mineralisation parameters were altered individually. Values for UN$_{max}$ and UP$_{max}$ were varied from 0.5 to 1 mg N (mg chl *a*)$^{-1}$ d^{-1} and 0.01 to 0.1 mg P (mg chl *a*)$^{-1}$ d^{-1}, respectively. Half-saturation constants for nutrient uptake (K$_N$ and K$_P$) were

assigned values ranging from 20 to 200 mg m^{-3} and 1 to 25 mg m^{-3}, respectively. Furthermore, the aerobic organic N mineralisation rate coefficient was varied between 0.05 d^{-1} and 0.2 d^{-1} and the aerobic organic P mineralisation rate coefficient was varied between 0.07 d^{-1} and 0.2 d^{-1}. The maximum adsorbed particulate P ($q_{e,max}$) was varied from 300 to 4500 mg kg^{-1} SS and the half-saturation constant for P adsorption/desorption (K_f) was varied from 50 to 120 mg m^{-3}. The oxygen half-saturation constant for nitrification (K_{DO}) was assigned values ranging from 1 to 4 g m^{-3} and the nitrification rate coefficient (k_{Nit}) was varied from 0.005 to 0.05 d^{-1}. By applying a range to the key parameters used in the models, the average sediment SRP and NH$_4$-N flux in the hypolimnion over the entire stratification period may have ranged from 0.84 to 13.89 mg P m^{-2} d^{-1}, and 17.2 to 160.8 mg N m^{-2} d^{-1} (Table 3.3).

Table 3.3: Average values for SRP and NH$_4$-N flux (mg m^{-2} d^{-1}) in the hypolimnion for the period of stratification in Lake Okaro. For modelled mineralisation and uptake process averages were calculated by output from average parameter values used in the sensitivity analysis, where Max and Min reflect the upper and lower end, respectively, of the parameter ranges. Mean absolute contribution (%) of total hypolimnetic fluxes are given in parentheses. Sediment flux was estimated as the missing term in a nutrient budget as shown in Table 3.1. Negative values represent loss of nutrients and positive values represent gain of nutrients in the hypolimnion.

		Mineralisation	Phytoplankton uptake	Diffusion	Nitrification	Adsorption /desorption	Sediment flux
SRP	**Average**	1.95 (13)	-3.78 (28)	-0.9 (5)	-	-0.01 (2)	5.66 (51)
	Max	2.78 (10)	-10.59(36)	-0.9 (3)	-	0.61 (2)	13.89 (50)
	Min	1.13 (18)	-0.37 (7)	-0.9 (9)	-	-0.58 (7)	0.84 (60)
NH$_4$-N	**Average**	60.4 (24)	-69.9 (28)	-9.4 (4)	-6.0 (2)	-	84.0 (43)
	Max	92.0 (23)	-106.4 (28)	-9.4 (3)	-14.7 (3)	-	160.8 (43)
	Min	28.8 (17)	-40.1 (26)	-9.4 (6)	-0.7 (0.3)	-	17.2 (50)

The mean absolute contributions (%) to the total flux for each process included in the hypolimnetic flux model are presented in Table 3.3. Changes in the mostly derived phosphate and ammonium concentrations in the hypolimnion from the sediments were 50 to 60% and 43 to 50%, respectively, where the range reflects different parameter ranges tested. The contributions of mineralisation of

organic nutrients to the overall hypolimnetic nutrient flux were lower than the net sediment flux for both phosphate (13 to 18%) and ammonium (17 to 24%). Nutrient uptake by phytoplankton accounted for 26 to 28% of the variation in hypolimnetic ammonium fluxes, and 7 to 36% for phosphate, while diffusion of P and N across the thermocline accounted for only 3-9% and 3-6%, respectively, of hypolimnetic fluxes. Contributions of adsorption/desorption and nitrification were comparatively minor at 2 to 7% and 0.3 to 3%, respectively. By comparison, the mean contributions of the net sediment flux of phosphate and ammonium before the Z2G1 application were 55 to 65% for P and 25 to 52% for N, compared with 49 to 59% for P and 45 to 50% for N after the application of Z2G1.
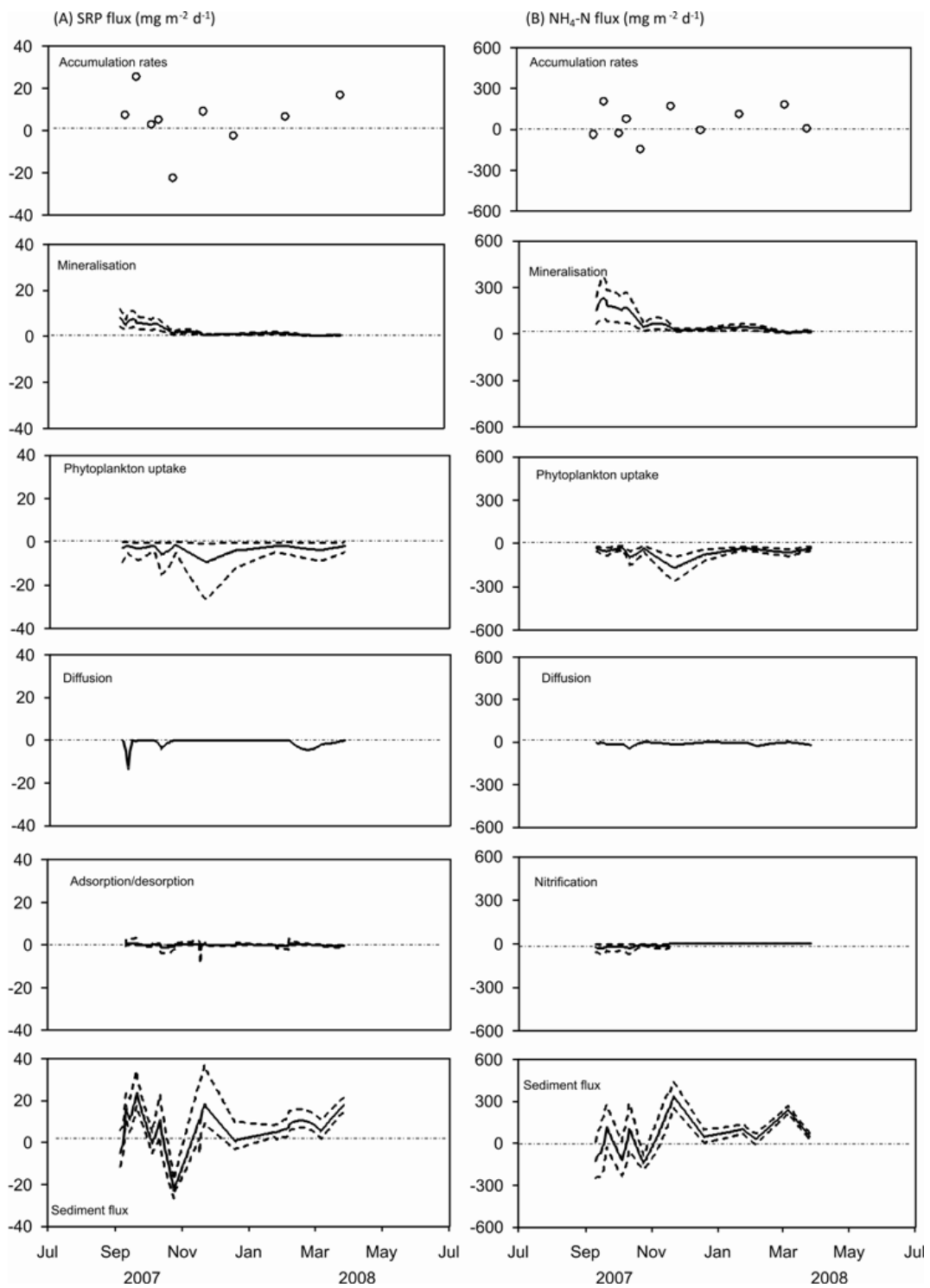
Figure 3.9: Hypolimnetic fluxes (mg m^{-2} d^{-1}) of (A) SRP and (B) NH$_4$-N; accumulation rates between successive sampling days, mineralisation of organic nutrient pool, phytoplankton uptake, diffusion across the thermocline, adsorption/desorption, nitrification, and sediment flux. Negative flux indicates loss and positive flux indicates gain in the hypolimnion. Solid lines represent average result of assigned parameter ranges from the literature and dashed lines represent maximum and minimum, respectively, obtained with selected parameter ranges of Table 3.2.

3.4 Discussion

The results of this study show that during summer stratification the hypolimnetic sediments within a lake can act as both a source and a sink for phosphate and ammonium to the water column. Rates of sediment nutrient release in Lake Okaro are comparable to studies from other lakes (Penn *et al.*, 2000; Beutel, 2001). However, my study has shown that changes in the mass of P and N in the hypolimnion contributed by processes such as mineralisation, nutrient uptake, nitrification, adsorption/desorption and diffusion are very important and can collectively contribute up to 48% of P and 58% of N of the respective total hypolimnetic fluxes.

Effects of Z2G1 on nutrient dynamics

There was a net positive flux of P and N soon after the Z2G1 application, up to 36 mg P m^{-2} d^{-1} and 440 mg N m^{-2} d^{-1}, suggesting that sediment nutrient release was not reduced substantially by Z2G1 compared with identical application rates (350 g m^{-2}) in a lab-based study by Gibbs & Özkundakci (Appendix I). The latter study found that Z2G1 completely blocked the release of both phosphate and ammonium. The lab-based study found that the nutrient binding capacity of Z2G1 was around 20,000 mg P kg^{-1} Z2G1 (dry weight) and showed that the uptake capacity of the sediment capping material was not exhausted for application rates of 350 g Z2G1 m^{-2}. Hupfer & Lewandowski (2008) found that the release rates in sediment incubation studies depend on both duration of the experiment and initial conditions. They concluded that results from short-term laboratory or *in situ* studies cannot be extrapolated to long-term P retention under natural conditions. The duration of anoxia in the hypolimnion of Lake Okaro in my study was long (199 days) compared to the duration of incubations of sediment cores from Lake Okaro (5 days of anoxic conditions; Gibbs & Özkundakci, Appendix I), making it difficult to project the longevity of Z2G1 *in situ*.

The sediment nutrient release rates observed in my study represent an average for the whole sediment surface area below the thermocline, but the sediment nutrient flux is likely to vary locally. Sediment incubations with cores

or using benthic chambers at different sites reinforce high spatial variability of nutrient release rates (Auer *et al.*, 1993; Nowlin *et al.*, 2005; Burger *et al.*, 2007). The efficacy of a uniform layer of Z2G1 will be affected by spatial variability of sediments and, together with high horizontal and vertical patchiness of Z2G1 found in my study, would likely magnify differential sediment nutrient release rates.

There appears to be no consensus on optimal application timing for sediment capping material in a seasonally stratified lake, despite the frequent use of *in situ* capping (e.g. Robb *et al.*, 2003; Berg *et al.*, 2004). An application during winter mixing would ensure that the sediment capping material is applied before the onset of anoxic conditions and any major sediment nutrient release events in the hypolimnion. However, a winter application would hold the risk of burial of material due to high sedimentation rates of P or resuspension (Pettersson, 2001). This suggests that a sediment capping application should be carried out after the onset of stratification, when the risk of burial and resuspension is reduced, but before onset of anoxic conditions and associated nutrient releases in the hypolimnion (Søndergaard *et al.*, 2003b).

Ebullition of gas as methane from lake sediments increases with increasing trophic state (Liikanen *et al.*, 2002). This process disturbs the surface sediments and may possibly enhance P release (Förstner & Apitz, 2007). The degassing of freshly collected sediment cores noted by Gibbs & Özkundakci (Appendix I) suggests that gas ebullition in Lake Okaro may substantially enhance P transport to the water column as well as disturbing the soft sediment and increasing pore water diffusion and advection. This process will have been captured indirectly in the hypolimnetic P budget, but the physical disturbance was likely responsible for the Z2G1 granules sinking deeper into the sediment, thus reducing efficacy of the Z2G1 application.

Any reduction in internal loading is difficult to assign to one particular restoration method in Lake Okaro, as the effects of an alum application in 2003 and constructed wetland implemented in 2006 may have coincided with the effects of the Z2G1 application. Søndergaard *et al.* (1996) showed that surface sediment TP concentration can be related to external TP loading but a reduction in external loading shifted the equilibrium state between sediment and water

nutrients only after a period of 10 to 15 years for P and 5 to 10 years for N (Jeppesen *et al.*, 2005). The time lag before a new equilibrium state is reached in Lake Okaro is however, difficult to estimate due to the possible interacting effects of different overlapping catchment and in-lake restoration methods.

Mineralisation was identified as one of the most important factors influencing the mass balance of dissolved inorganic nutrients in the hypolimnion in Lake Okaro, contributing up to 15% to the overall hypolimnetic P fluxes. In Lake Mikołajskie, Poland, it was found to be strongly influenced by aerobic decomposition following diatom blooms (Kufel & Kalinowska, 1997) and it may be responsible for higher hypolimnion ammonium accumulation rates compared to those observed in sediment incubation chambers (Beutel, 2001). Both Auer *et al.* (1993) and Nowlin *et al.* (2005) corrected hypolimnetic P accumulation rates only for diffusive fluxes of phosphate across the thermocline, which were found to be relatively small in the present study. My study indicates the importance of adjusting nutrient fluxes for water column mineralisation when considering the efficacy of sediment capping.

Restoration methods directed towards reducing water column P concentrations in Lake Okaro would have the potential to increase P-limitation of phytoplankton. While mass ratios of TN:TP in the hypolimnion of Lake Okaro have previously been found to vary little during the stratified period (Paul *et al.*, 2008), my study showed that ratios declined during the stratification period indicating N limitation. However, the nutrient limitation assessment based on ratios of DIN:TP (Morris & Lewis 1988) suggests favourable nutrient conditions for phytoplankton growth in the hypolimnion according to the Redfield ratio, and strong N limitation (DIN:TP < 1) in the surface waters, with the latter suggesting potential for prevalence of N fixing cyanobacteria (Schindler *et al.*, 2008). This highlights the need for further reductions in P concentrations to strongly limit cyanobacteria production in Lake Okaro.

Validation of nutrient flux model

The parameters in the function for phytoplankton nutrient uptake in the nutrient flux model were chosen to match responses of the dominant cyanobacteria species in Lake Okaro, but may not adequately reflect the seasonal variability contributed

by changes in species composition of the phytoplankton community. Lake Okaro contains a diverse phytoplankton community relative to other eutrophic lakes in the central North Island (Forsyth *et al.*, 1988; Paul *et al.*, 2008). Consequently, the hypolimnetic nutrient fluxes arising from phytoplankton uptake may only be interpreted as indicative.

The mineralisation rate coefficients (k_{OP}, k_{ON}) used in my study appear to be at the upper limit of values used in the literature (Hamilton & Schladow, 1997; Gal *et al.*, 2009), but average rates (~ 0.12 d^{-1}) are consistent with values found in nearby Lake Rotoiti (Priscu *et al.*, 1986) and the relative contribution of mineralisation to hypolimnetic nutrient fluxes (c.25%) is similar to values found in other lakes (Carignan & Lean, 1991).

Potential P release mechanisms in Lake Okaro

The net sediment flux in the model for Lake Okaro is a residual term of a hypolimnetic P budget. This value also represents a collation of a number of different P-release mechanisms from the sediment. Conventional P-release models (e.g., Mortimer, 1971) describe how increasing release of P may occur after depletion of DO. Iron(III) oxides are considered to be the main iron compounds in P binding. Sediments contain a multitude of iron(III) oxides, often in complex mixtures, that range widely in degree of crystallinity, particle size, available surface area, reactivity and oxidation state. In this case, when P is sorbed to iron(III) compounds during oxic conditions, iron(III) is reduced to iron(II) and P and iron is returned into solution. There also appears to be a threshold for hypolimnetic nitrate concentrations of c.0.5 mg L^{-1} below which releases of iron hydroxide-bound P are greatly increased (Søndergaard *et al.*, 2000). A decrease in pH in the water column above the sediment, as a result of CO_2 production from mineralisation of organic matter, can also affect the strength of ionic phosphate sorption onto sediment surfaces, and may increase P release, although pH appears to remain relatively constant seasonally in the hypolimnion of Lake Okaro. The stimulation of organic matter mineralisation with increasing temperature can also lead to enhanced nutrient release (Gomez *et al.*, 1998) but bottom waters of Lake Okaro increased by only c.2.5 $^{\circ}$C during seasonal stratification, suggesting temperature changes may be of lesser importance.

The importance of different P release mechanisms may vary during the stratified period. Roden & Edmonds (1997) showed that at very low redox potentials, sulphate reduction increases P efflux from the sediments through mobilization of iron-bound P. McColl (1972) found sulphate concentrations in the bottom waters of Lake Okaro were up to 10 mg L^{-1} at the onset of summer stratification, with reduction of sulphate to hydrogen sulphide during the course of the anoxic period. Sulphides can displace phosphorus from iron, which has been related to enhanced releases of phosphorus to the overlying water (Holmer & Storkholm, 2001). Although sulphate was not measured in this study, I assume that the same process of sulphate reduction still occurs in Lake Okaro and would have been partially responsible for the increase in phosphate concentrations during the stratified period.

3.5 Conclusions

While the laboratory incubation study (Gibbs & Özkundakci, Appendix I) indicated that Z2G1 had the potential to completely block the release of P from the sediments of Lake Okaro, results from the whole lake treatment study indicated that the sediment P release occurred after the application of Z2G1. Similarly, the reduction in N release was lower than expected when compared to the laboratory incubation study. These differences illustrate the difficulty of extrapolating laboratory results to a whole lake. There are likely to be a number factors contributing to these differences including the timing of the Z2G1 application, which occurred after the lake had stratified and the release of SRP from the sediment had begun, the uneven coating of the capping material on the sediment surface, and the sinking of the heavy granules into the sediment surface rendering them ineffective. As the sediment inactivation agent Z2G1 can be milled to a finer grain size, its efficacy and behaviour on the sediment surface requires assessment.

The comprehensive nutrient flux model results provided insight into the relative importance of different source-sink fluxes in the hypolimnion, showing that > 50% of the SRP and NH$_4$-N came from the sediment and a further 20% was released to the water column by mineralisation of organic species, and that around

30% of these nutrients were removed by phytoplankton uptake within the hypolimnion. As found in other studies, diffusive losses across the thermocline and adsorption/desorption on suspended solids were relatively minor components of the hypolimnetic fluxes. The model provided a relatively simple tool to investigate nutrient fluxes in the hypolimnion which need to be accounted when interpreting hypolimnetic nutrient accumulation rates.

3.6 References

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4 Phosphorus dynamics in sediments of a eutrophic lake derived from ³¹P nuclear magnetic resonance spectroscopy

4.1 Introduction

Phosphorus (P) has long been recognized as a key nutrient in many aquatic ecosystems due to its potential to limit primary productivity (Vollenweider, 1976; Carpenter, 2008). Lake sediments are a key source of phosphorus, especially in eutrophic lakes (Søndergaard *et al.*, 2003), in addition to contributions from the catchment and, to a lesser extent, wet and dry deposition from the atmosphere (Reed-Andersen *et al.*, 2000). Phosphorus release from lake sediments depends on the interactions amongst physical, chemical and biological processes (Smolders *et al.*, 2006). Despite recent advances in understanding the mechanisms of internal P loading there is still little known about the compounds and reactivity of organic P compounds in lake sediments (Ahlgren *et al.*, 2005).

Since the first use of ³¹P nuclear magnetic resonance (NMR) to investigate organic P in New Zealand grassland soils in 1980 (Newman & Tate, 1980), this method has become a valuable tool to determine different organic P compounds in soils and sediments worldwide (Cade-Menun, 2005). While several studies have discussed organic P groups in agricultural soils in New Zealand (McDowell *et al.*, 2005), there have been few studies on organic P speciation in freshwater lake sediments. Marine sediments have generally received substantially more attention than lake sediments in studies utilising ³¹P NMR to determine P speciation (Cade-Menun, 2005). The limited number of studies in lake sediments have identified several different organic P compounds, including orthophosphate monoesters, orthophosphate diesters, and polyphosphates (Hupfer *et al.*, 1995; Ahlgren *et al.*, 2006).

Different organic P compounds in lake sediments have been related to exposure of sediments to the presence of either oxic or anoxic conditions.

Carman *et al.* (2000) describe the presence of pyro- and polyphosphates in oxic surface sediments, whereas these compounds were absent in anoxic conditions. Changes in redox chemistry appear to play an important role in the diagenesis of phosphate diesters (Ingall & Jahnke, 1994). In addition, P compounds in settling material can vary substantially with season, and may therefore have an important role in changing P compounds found in bottom sediments (Pettersson 2001). To date there have been no ^{31}P NMR studies that could contribute to an understanding of the effect of seasonal variations in P sedimentation on the P compounds in bottom sediments of lakes.

In New Zealand, the water quality of many of the Te Arawa lakes of the Rotorua region has declined significantly with development of surrounding catchments for agriculture (Hamilton, 2005). Several of the lakes have high internal nutrient loadings due to eutrophication and the enrichment of the bottom sediments with organic matter (White *et al.*, 1978; Burger *et al.*, 2007; Trolle *et al.*, 2008). Lake Okaro, the focus of this study, is the most eutrophic lake of the Te Arawa lakes. It is a monomictic lake with a hypolimnion that becomes anoxic approximately one month after onset of seasonal stratification, which is of duration approximately 9 months (Paul *et al.*, 2008). The lake has been subject to intensive catchment and in-lake restoration techniques, including an alum application in December 2003 and sediment capping with an aluminium-modified zeolite (Z2G1) in September 2007. Previous studies of alum-treated lakes have shown that the amount of P recovered as orthophosphate is increased in the bottom sediments (Reitzel *et al.*, 2006).

I hypothesised that sediment organic P is an important source of internal loading in Lake Okaro. Because seasonal changes in the water column of Lake Okaro (oxic and anoxic hypolimnion) could lead to changes in P sedimentation and sediment P compounds in the surface sediments of the lake, I investigated the P compounds in settling seston and at different depths in the bottom sediments of Lake Okaro using ^{31}P NMR. I chose periods of seasonal stratification, when bottom waters were anoxic, as well as periods of mixing, when the entire water column was well oxygenated, to test for the effects of seasonal variations caused by mixing patterns and redox status.

4.2 Methods

Study site

Lake Okaro is a small lake (0.32 km^2) with a maximum depth of 18 m (Figure 4.1). The catchment area (3.89 km^2) is now used mostly for dairy production. The lake has been eutrophic since the early 1960s (Jolly, 1977) accompanied by regular cyanobacterial blooms and an anoxic hypolimnion during summer stratification (Forsyth *et al.*, 1988; Paul *et al.*, 2008). Two unnamed streams enter the lake from the north-west, have both of which were diverted through a 2.3 ha constructed wetland in 2006 to reduce nutrient loads to the lake (Tanner *et al.*, 2007). On 16 and 17 December 2003, 13 m^3 of alum, equivalent to a dose rate of 0.6 g Al m^{-3}, were applied to the lake as a first attempt to control internal loads of P (Paul *et al.*, 2008). In September 2007, 110 metric tonnes of aluminium-modified zeolite (Z2G1, Blue Pacific Minerals, New Zealand) were applied to Lake Okaro to act as a sediment capping agent to reduced internal loading of P, and to some extent N.
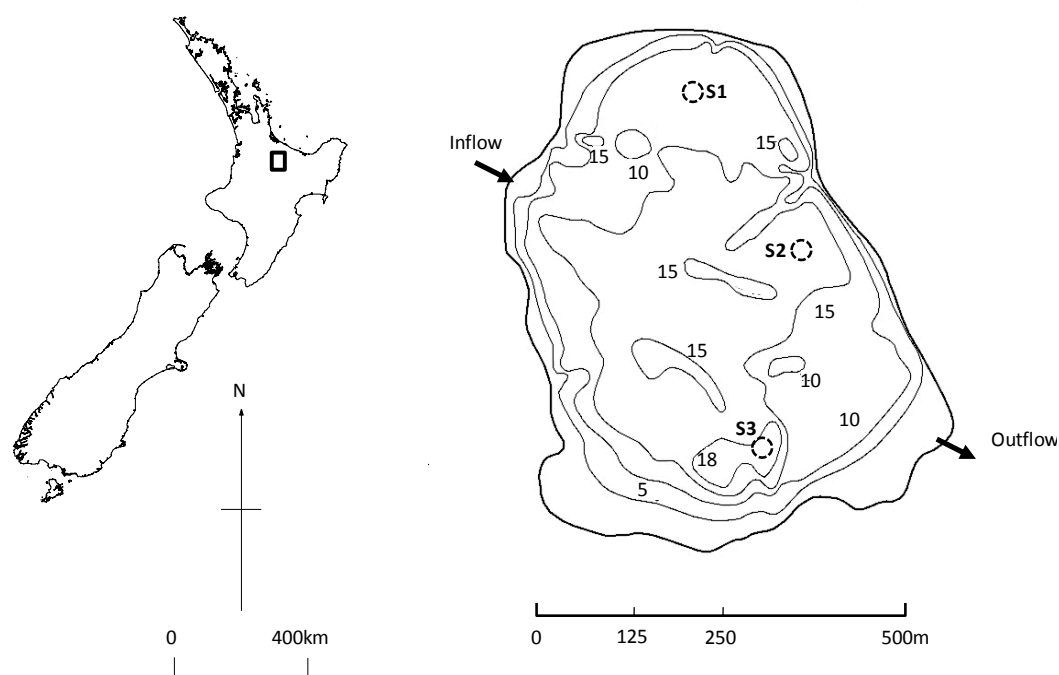
Figure 4.1: Location map of Lake Okaro with depth contours 5 m, 10 m, 15 m, and 18 m, showing the location of sediment trap and sediment sampling sites (dashed circle marked S1, S2 and S3).

Sedimentation rates

Sedimentation rates of seston in Lake Okaro were measured with cylindrical sediment traps (PVC, 0.065m diameter, 0.65m height). Traps were deployed at three sites (S1, S2 and S3, 18 m depth; Figure 4.1), representing bottom depths of 11, 14 and 18 m, when the lake was stratified between 26 January 2007 and 28 February 2007 and when the lake was mixed between 23 May and 22 June 2007. No inhibitors or preservatives were added to the traps so P compounds analyzed in this study represent the integrated effects of aging and degradation over the deployment period. At all sites traps were placed at 3 and 9 m depth. At each trapping depth, four replicate traps were supported by a wooden frame and attached to a central rope suspended vertically in the water column between a bottom anchor and a subsurface buoy (1 m depth). Replicate traps were separated by a distance of at least three times the trap diameter to minimise inter-trap hydrodynamic bias. Once retrieved, traps were settled for 30 minutes before supernatant water was siphoned off and the remaining 500 mL capped and placed on ice for the return to the laboratory. This material was homogenized immediately upon return to the laboratory and sub-samples were taken for analysis of TP and total particulate matter (TPM). Samples for the analysis of TP were digested using persulphate digestion (Ebina *et al.*, 1983) followed by analysis as molybdate-reactive P on a Lachat QuickChem® Flow Injection Analyser (FIA+ 8000 Series, Zellweger Analytics, Inc.). Dry weight of TPM and particulate inorganic material (PIM) were determined from sub-samples filtered onto pre combusted (550 °C) and pre-weighed Whatman GF/C filters. Filters were dried at 105 °C for 24 h for determination of TPM, then combusted at 550 °C for 4 h to determine particulate inorganic matter (PIM). Particulate organic matter (POM) was determined as the difference between TPM and PIM. Subsamples from trapped material were taken from each depth at site S2 for ^{31}P NMR analysis on each sampling occasion.

Sediment sampling

Undisturbed sediment cores were collected with a gravity corer from three sites (S1, S2 and S3; Figure 4.1) on 28 February 2007 and 22 June 2007. Sampling days were chosen to reflect different seasons with February and June representing stratification and mixing periods, respectively. In the field, sediment cores were

sliced into 2 cm intervals down to 30 cm depth, and stored on ice in 50 mL plastic tubes until return to the laboratory where each tube was centrifuged for 40 min at 4000 rpm to separate pore waters from sediment, before filtering pore waters through Whatman GF/C filters. Sediment dry weight (DW) was measured by drying sediment samples at 105 °C over approximately 24 h or until constant weight was obtained. Organic content was measured as loss on ignition (LOI) by combusting the dried sample for 4 h at 550 °C. Analysis of P, total iron (Fe), total manganese (Mn), and total aluminium (Al) was carried out on extracts of dried sediment samples which had been homogenized by grinding following the procedure of Trolle *et al.* (2008). Briefly, approximately 0.5 g of the dried sample was digested with Aqua Regia and the extract was then analyzed for P, Fe, Mn, and Al by Inductive Coupled Plasma Mass Spectrometry (ICP-MS, model ELAN DRC II). Additional sediment core samples were collected from S2 for ^{31}P NMR analysis and sliced horizontally at 2 cm intervals down to 10 cm on each sampling occasion.

^{31}P NMR analysis

Bottom sediment samples were pooled as well as sediment trap samples were pooled for the discrete depth intervals. A subsample of ~10 g wet weight was shaken with 30 mL of 0.25 M NaOH + 0.05 M Na_2-EDTA for 16 h. Samples were then centrifuged (15000 rpm) prior to filtering supernatant through Whatman GF/C filters. Subsamples of the extract were analyzed by ICP-MS for TP. Each extract was pre-concentrated (~10-fold) by rotary evaporation (Büch Rotavopor R110) at 30 °C and then frozen. This process has previously been shown not to alter the P compound composition (Hupfer *et al.*, 2004). Prior to analysis, samples were centrifuged at 4000 rpm and sufficient pure deuterium oxide (D_2O) was added to the samples to obtain a stable lock signal. Samples were transferred to 5 mm NMR tubes and ^{31}P NMR spectra were obtained on solutions at a frequency of 161.97 MHz on a Bruker 400 spectrometer. An identical number of scans (10240) was used for each sample using a pulse angle of 90° with a pulse delay of 5 s and an acquisition time of 0.34 s. The long delay between pulses was chosen in order to reach the spin-lattice relaxation time (T_1), examined by an inversion recovery sequence. Chemical shifts were recorded relative to an external phosphoric acid standard ($\delta = 0$ ppm). Spectra were processed with a 10

Hz line broadening and fitting exponential line shapes using Mestre-C software (V. 2.3a). Peak areas exceeding a signal to noise ratio of 30 were calculated by integration on processed spectra and subsequent grouping into P compounds groups using peak assignments derived from the literature (Hupfer *et al.*, 1995; Cade-Menun, 2005; Ahlgren *et al.*, 2006). The contribution of the P compound groups was calculated relative to the TP in the extracts.

Data analysis

Sedimentation rates of TP and TPM, were examined for spatial (i.e. differences among sites and depths) and temporal variations (i.e. differences amongst sampling days) using one-way analysis of variance (ANOVA) with *post hoc* analysis using a Newman-Keuls test at confidence interval of 95%. Data were tested for normal distribution and homogeneity of variance by visual inspection of residuals.

Apparent half life times (τ) of P compounds in sediments were calculated as $\tau = \ln(2)/k$, where k is a rate constant (yr^{-1}) for the decay of the P compounds (Reitzel *et al.,* 2007). Sediment age for each 2 cm layer was calculated according to the net sedimentation rate in Lake Okaro (Trolle *et al.*, 2008). Short-term effects of changes in sediment P composition on half life time were compensated for by using averaged values of the corresponding 2 cm intervals between February and June 2007.

4.3 Results

Sedimentation rates

Mean sedimentation rates of TP across the three sites for the period 26 January 2007 – 28 February 2007, when the water column was stratified, were 2.06 mg m^{-2} d^{-1} at 3 m depth and 3.52 mg m^{-2} d^{-1} at 9 m. Rates were approximately five-fold higher from 23 May 2007 – 22 June 2007, when the water column was mixed, at 14.30 mg m^{-2} d^{-1} and 14.26 mg m^{-2} d^{-1} at 3 and 9 m depth, respectively. Rates of sedimentation of TPM and TP for individual stations at 3 and 9 m were in several instances significantly lower for the stratified period than the mixed period

(ANOVA, p < 0.05; Table 4.1). Spatial variations in sedimentation rates (i.e. differences amongst sites and depths) were lower than the variations between the two time periods corresponding to mixed and stratified conditions. Sedimentation rates of both TP and TPM were significantly higher (p < 0.05) at 9 m depth than at 3 m depth during the stratified period but during the mixed period rates were not statistically different between depths (p ≥ 0.05). The mean sedimentation rate of TPM across sites during stratification was 0.56 g m^{-2} d^{-1} at 3 m and 0.80 g m^{-2} d^{-1} at 9 m depth compared with 1.40 g m^{-2} d^{-1} at 3 m and 1.42 g m^{-2} d^{-1} at 9 m during mixing. On average, POM constituted 61 % of TPM across all sites and depths during stratification and 56 % of TPM during mixing (Figure 4.2).
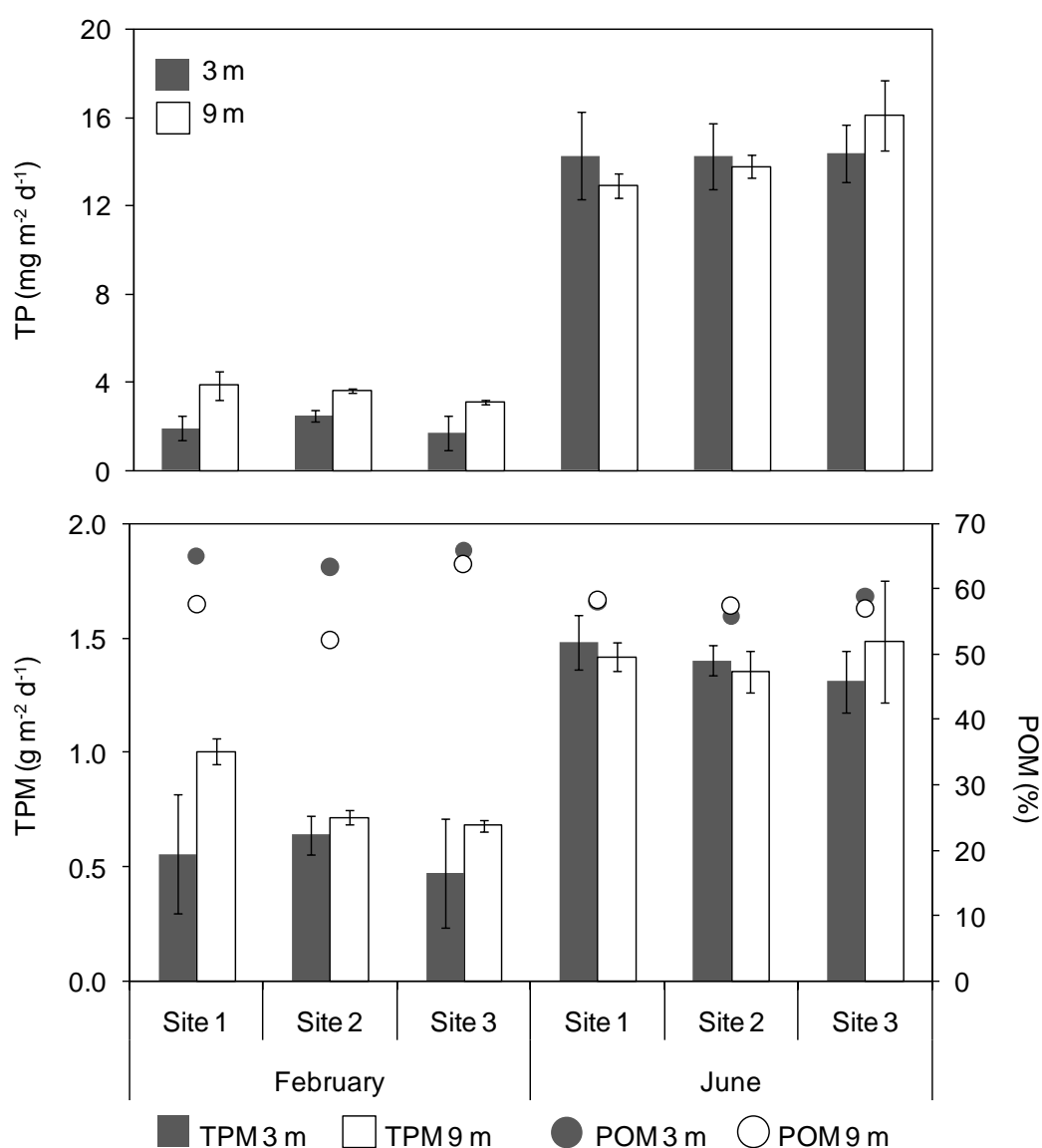
Figure 4.2: Sedimentation rates of total phosphorus (mg TP m^{-2} d^{-1}) and total particulate material (g TPM m^{-2} d^{-1}), and particulate organic matter (POM) as a percentage of TPM, for traps at 3 and 9 m depth at sites S1, S2, and S3 for stratified and mixed periods.

Table 4.1: Summary of results of *post-hoc* Newman-Keuls test to determine differences at significance level p < 0.05 among sites, depths, and sampling days for sedimentations rates of total phosphorus (TP) and total particulate material (TPM). Note: NS = not significant, p ≥ 0.05.

		S1	S2	S3	3 m	9 m
Feb	**TPM**	9 m>3 m	NS	NS	NS	NS
	TP	9 m>3 m	9 m>3 m	9 m>3 m	(S2>S3)=S1	NS
Jun	**TPM**	NS	NS	NS	NS	NS
	TP	NS	NS	NS	NS	(S3>S1)=S2
3 m	**TPM**	Jun>Feb	Jun>Feb	Jun>Feb		
	TP	Jun>Feb	Jun>Feb	Jun>Feb		
9 m	**TPM**	Jun>Feb	Jun>Feb	Jun>Feb		
	TP	Jun>Feb	Jun>Feb	Jun>Feb		

Vertical sediment profiles

Vertical sediment profiles showed P concentrations ranging from 1965 mg P kg^{-1} DW (0-2 cm, S1, June 2007) to 366 mg P kg^{-1} DW (28-30 cm, S3, June 2007; Figure 4.3). Generally, P concentrations in the sediment decreased with increasing sediment depth. Concentrations of measured elements in sediments ranged from 24,901 to 11,208 mg Fe kg^{-1} DW, 600 to 244 mg Mn kg^{-1} DW, and 16,833 to 6,711 mg Al kg^{-1} DW, respectively. Loss on ignition generally decreased with increasing sediment depth and ranged from 29.5% (0-2 cm, S1, February 2007) to 5.1% (28-30 cm, S1, February 2007). Over both sediment sampling days, the vertical profiles of P were significantly correlated ($p < 0.001$) with LOI at all sites (Table 4.2). However, P was only correlated with vertical profiles of Fe at S2 ($p < 0.05$) and showed no correlation with vertical profiles of either Al or Mn ($p \geq 0.05$).
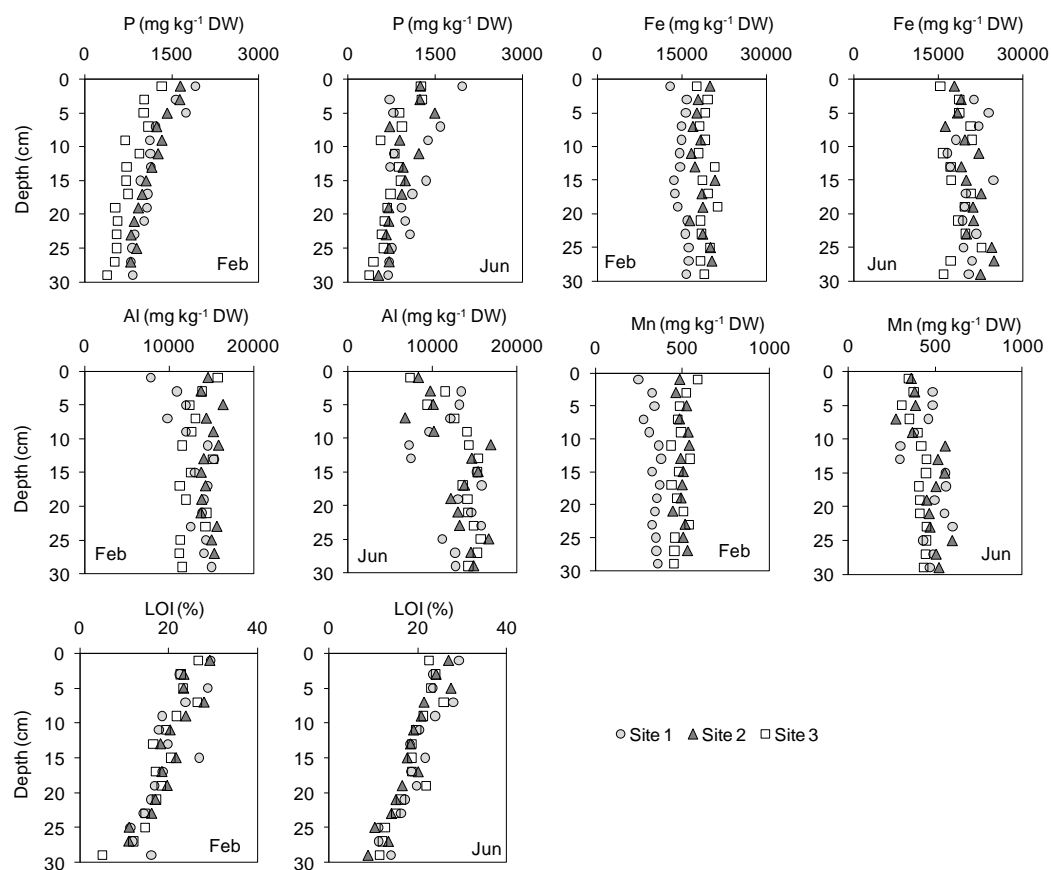
Figure 4.3: Vertical profiles of sediment concentrations of total phosphorus (mg TP kg^{-1} DW), total iron (mg Fe kg^{-1} DW), total aluminium (mg Al kg^{-1} DW), total manganese (mg Mn kg^{-1} DW), and loss on ignition (LOI; %) at sites S1, S2, and S3 for February and June.

Table 4.2: Pearson correlation coefficients, R (N = 30), between Al, P, Fe, Mn and LOI in vertical profiles at sites 1, 2 and 3 based on sediment cores collected in February and June 2007. Note: significant R at * $p < 0.05$, **$p < 0.01$ and *** $p < 0.001$.

		P	Fe	Mn	LOI
Site 1	**Al**	-0.19	0.22	0.58**	-0.35
	P	-	-0.22	-0.21	0.71***
	Fe		-	0.83***	-0.06
	Mn			-	-0.19
Site 2	**Al**	0.01	0.31	0.97***	-0.38*
	P	-	-0.45*	-0.05	0.82***
	Fe		-	0.43*	-0.55**
	Mn			-	-0.42*
Site 3	**Al**	-0.24	0.14	0.53**	-0.14
	P	-	-0.24	-0.07	0.81***
	Fe		-	0.06	-0.03
	M			-	-0.10

^{31}P NMR analysis

Eight P groups or compounds were identified in the sediment extracts, however, only seven groups were found in the sediment trap extracts (Figure 4.4). The eight groups were phosphonates, orthophosphate, orthophosphate monoesters, pyrophosphates, polyphosphates, and three different compounds in the orthophosphate diester region. The latter compounds were identified as deoxyribonucleic acid (DNA) P, microbial P lipids, and teichoic acid P according to peak assignments by Ahlgren *et al.* (2006).
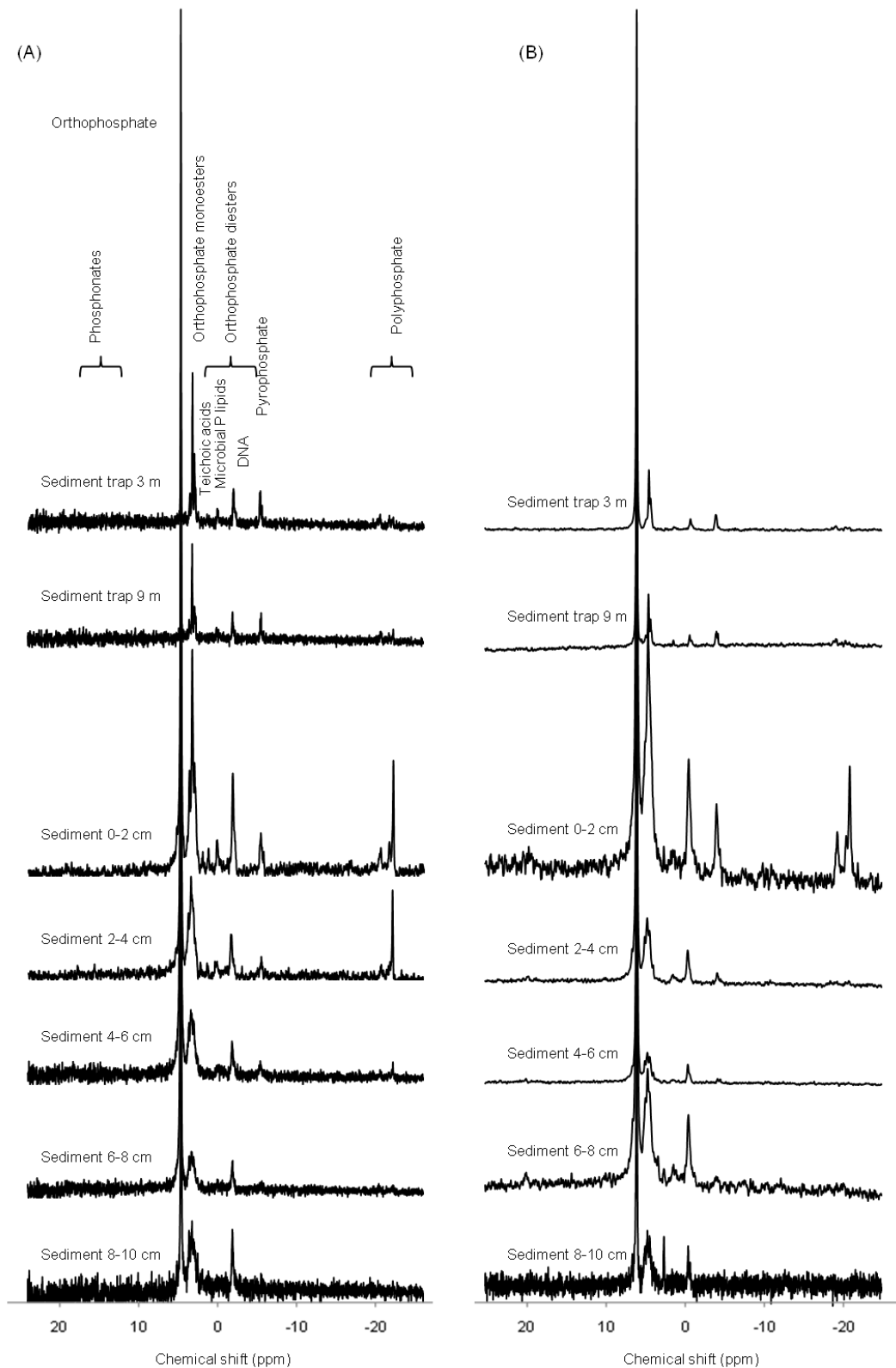
Figure 4.4: ^{31}P nuclear magnetic resonance (NMR) spectra of depth profiles of sediment samples to 10 cm depth from site S2, collected in (A) February and (B) June 2007.

The average percentage P recovery extracted in the bottom sediments was 75% of sediment P concentrations and generally decreased with increasing depth (Table 4.3). Orthophosphate was the most abundant P compound in the sediment extracts, contributing up to 64.3% of the total extracted P while orthophosphate monoesters contributed up to 32.9%, orthophosphate diesters up to 12.9%, polyphosphates up to 11.1%, pyrophosphates up to 6.7% and phosphonates only as much as 1.8% on average of the total P extracted. Orthophosphate concentrations generally increased with increasing sediment depth while all other identified P groups declined with increasing sediment depth.

Generally, the ^{31}P NMR signal in the surface sediment was weaker in June 2007 than in February 2007, with less well developed peaks for microbial P lipids and teichoic acid P in particular. While polyphosphates were present throughout the entire profile in February 2007, this group was not observed in sediment layers of 4-6 and 8-10 cm in June 2007. Due to the low concentrations of phosphonates throughout the profiles, with levels close to detection limits, it is not possible to differentiate if differences between sampling days were due to the analytical sensitivity limitations or a distinct change through time.

The average extraction efficiency across all depths in the sediment trap material increased from 50% in February 2007 to 83% in June 2007 (Table 4.4). The percentage of orthophosphate in the sediment trap extract was 35% on average across all depths in February and increased to 69% in June, while for all other P groups there was decrease in the percentage P, by approximately 50% for orthophosphate monoesters and polyphosphates.

Apparent half life times were determined from the slope of a significant regression fit ($p < 0.05$) to the exponential decay of P concentration with sediment profile age, derived from net sedimentation rates in Lake Okaro (Trolle *et al.*, 2008). Values determined for orthophosphate monoesters, orthophosphate diesters, pyrophosphates and polyphosphates ranged from 8 to 23 years (Figure 4.5). By contrast, exponential regression fit of orthophosphate and phosphonates concentrations with sediment depth had low R^2 and were not significant ($p \geq 0.05$), indicating that these groups behaved differently.

Table 4.3: Concentration (mg kg^{-1} DW) and relative contribution (in parentheses) of P compounds in sediment extracts at different depths from Lake Okaro at site 2, averaged for February and June 2007.

Sediment depth (cm)	Sediment age (yr)	Phosphorus extraction efficiency (%)	Orthophosphate mg kg^{-1} DW (%)	Orthophosphate monoesters mg kg^{-1} DW (%)	Orthophosphate diesters mg kg^{-1} DW (%)	Pyrophosphates mg kg^{-1} DW (%)	Polyphosphates mg kg^{-1} DW (%)	Phosphonates mg kg^{-1} DW (%)
0-2	4.3	77.2	415.6 (36.5)	396.3 (32.9)	156.8 (12.9)	53.2 (4.5)	125.2 (11.1)	8.5 (1.3)
2-4	13.0	89.5	673.2 (53.4)	376.3 (29.8)	120.0 (9.5)	26.8 (2.1)	53.3 (4.2)	25.6 (2.1)
4-6	21.7	76.6	739.9 (64.3)	245.2 (22.5)	77.8 (7.3)	23.7 (2.3)	34.0 (3.9)	14.8 (1.4)
6-8	30.4	71.7	445.2 (57.2)	176.0 (26.9)	75.9 (11.8)	13.3 (1.3)	15.7 (2.2)	8.6 (1.3)
8-10	39.1	44.3	263.3 (54.4)	147.0 (29.8)	52.6 (9.5)	25.6 (6.7)	15.3 (2.5)	19.3 (3.2)

Table 4.4: Sedimentation rate of total phosphorus (TP; mg m^{-2} d^{-1}) ± 1SD at site 2, loss on ignition (LOI), and relative sedimentation (mg m^{-2} d^{-1}), and contribution in parentheses of identified P compounds in the extracts from sediment traps at site 2 for February and June 2007.

Month	Depth (m)	TP (mg m^{-2} d^{-1})	LOI (%)	Extraction efficiency (%)	Orthophosphate mg m^{-2} d^{-1} (%)	Orthophosphate monoesters mg m^{-2} d^{-1} (%)	Orthophosphate diesters mg m^{-2} d^{-1} (%)	Pyrophosphates mg m^{-2} d^{-1} (%)	Polyphosphates mg m^{-2} d^{-1} (%)
Feb	3	2.50 ±0.27	64.7	44.5	0.36 (32.7)	0.39 (34.9)	0.15 (13.7)	0.09 (7.8)	0.12 (10.9)
	9	3.61 ±0.10	57.8	53.6	0.75 (38.9)	0.58 (30.0)	0.22 (11.6)	0.13 (6.9)	0.24 (12.6)
Jun	3	14.26 ±1.49	57.5	82.8	8.33 (70.6)	2.16 (18.3)	0.48 (4.1)	0.48 (4.0)	0.35 (3.0)
	9	13.78 ±0.52	57.6	84.3	7.88 (67.8)	2.11 (18.1)	0.53 (4.6)	0.48 (4.1)	0.62 (5.3)
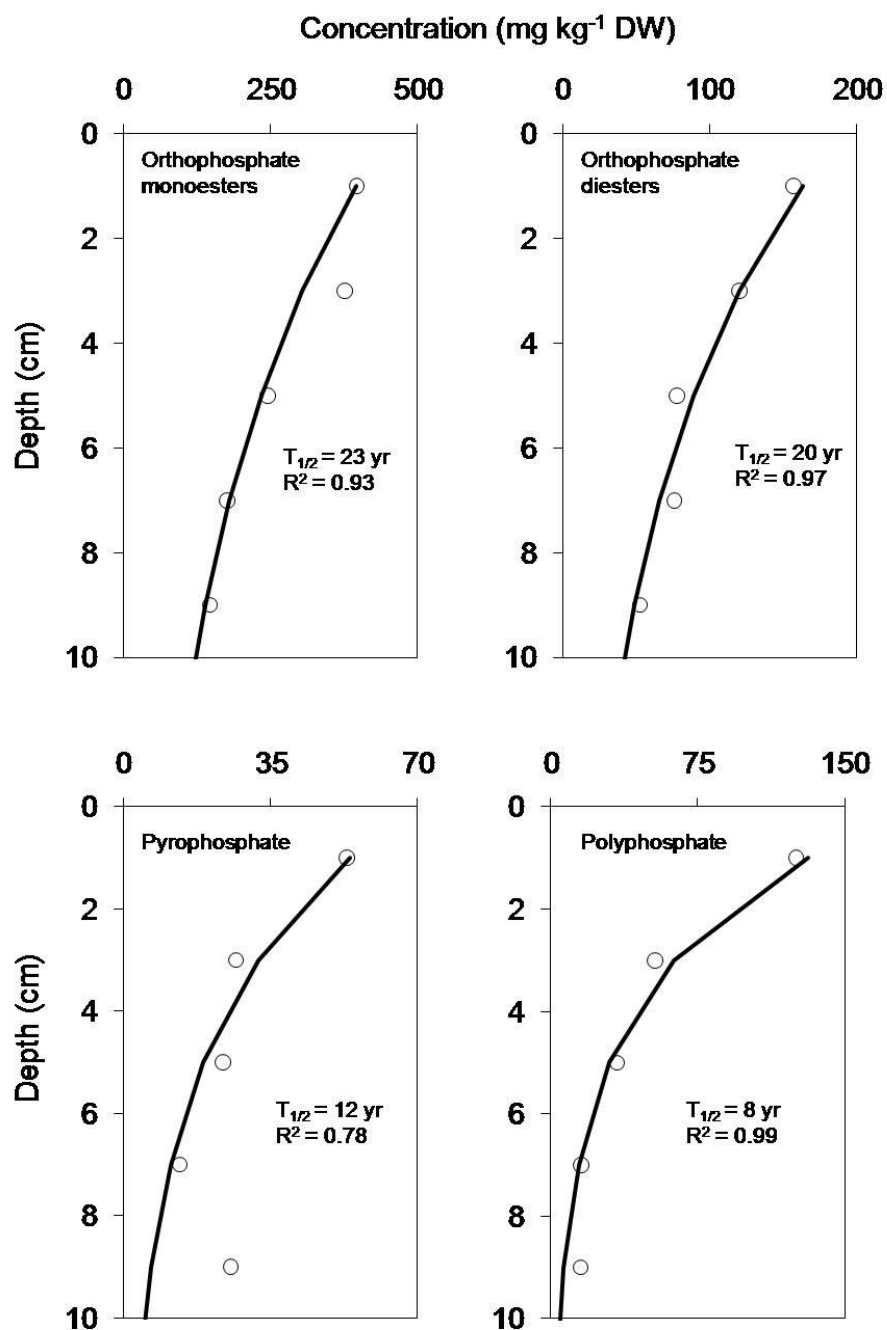
Figure 4.5: Average concentrations of phosphorus groups (mg P kg^{-1} DW) between samples taken in February and June identified using ^{31}P nuclear magnetic resonance (NMR) in the Lake Okaro sediment profiles and exponential regression (solid line) fit to averaged measured concentrations of the corresponding 2 cm intervals between February and June 2007 (best fit of R^2 significant at p<0.05).

4.4   Discussion

Seasonally induced changes due to mixing and resulting changes in oxygen status in bottom waters appear to affect not only P concentrations but also the relative contributions of P compounds in the settling seston. These changes were largely evident as increased P content in the settling seston and increased recovery as orthophosphate and tend to be more pronounced for the water column than the surface sediments of Lake Okaro. There appeared to be no discernible difference in polyphosphate concentrations in the surface sediments of Lake Okaro during periods of stratification and mixing corresponding to anoxic and oxic periods, respectively, in bottom waters. By contrast Hupfer *et al.* (2004) found a general decrease of polyphosphate concentrations in surface sediments during mixing periods, which they attributed to changes in accumulation and hydrolysis (i.e. uptake and release, respectively) by the different microorganism communities prevailing under oxic and anoxic conditions (Hupfer *et al.*, 2004). While the present study did not prove that there is no such synthesis of polyphosphate by microorganisms, changes in sediment microorganism communities due to mixing may be less important during the early diagenesis of polyphosphates in Lake Okaro. This study indicates an increased breakdown of orthophosphate diesters during oxic compared to anoxic conditions and is consistent with previous findings (Ingall & Jahnke, 1994).

Interpretation of P speciation

The P compounds detected in the sediments of Lake Okaro, with the exception of phosphonates, have also been detected in sediments of other eutrophic lakes (Reitzel *et al.*, 2006). The relative proportions of the P compounds are mostly comparable to less eutrophic lakes (Ahlgren *et al.*, 2005; Reitzel *et al.*, 2007). However, care should be taken when making direct comparisons amongst different studies. Methodological variations associated with analytical procedures and NMR instrumentation can result in non-quantitative NMR spectra. These differences may relate to pre-treatments of the sample, extractants, a higher field spectrometer and delay times between pulses when generating quantitative ^{31}P NMR spectra of environmental samples (Cade-Menun, 2005), which affected

comparisons of Lake Erken sediment NMR spectra between the study by Ahlgren *et al.* (2005) and that by Reitzel *et al.* (2007).

In my study, pre-treatments and extractants used for preparation of ^{31}P NMR sediment material were similar to those used in other studies (Ahlgren *et al.*, 2005; Turner *et al.*, 2005; Reitzel *et al.*, 2007). Any extraction procedure for organic P, however, is likely to induce some hydrolysis and there is no general agreement on the most suitable extractant for organic P (Cade-Menun, 2005). The combination of EDTA + NaOH appears to be the most universally accepted technique and reduces degradation of polyphosphates due to the complexation of free metals with EDTA (Turner *et al.*, 2003, 2005). Severe pH stress of the alkaline extraction procedure can, however, alter extracted compounds from their original form. The degradation of ribonucleic acid (RNA)-P into orthophosphate monoesters, for example, has been shown to occur within 24 h in NaOH solution (Makarov *et al.*, 2002). Considering the instability of RNA P during extraction, orthophosphate diesters may be under-represented in my NMR spectra, while orthophosphate monoesters may be over-represented. The degradation of polyphosphates into pyrophosphates has also been shown to occur within 2 h of extraction in NaOH (Hupfer *et al.*, 1995), indicating that the 16 h extraction procedure in my study may have reduced the proportion of polyphosphates to pyrophosphates (Ahlgren *et al.*, 2006). Partial degradation of polyphosphates may still have resulted in underestimation of this group in my spectra.

The method used in my study to calculate apparent half life times for different P compounds is based on sediment ages derived from net sedimentation rates found in Trolle *et al.* (2008). These rates are derived from a volcanic eruption of Mt Tarawera in 1886 which dispersed volcanic ash over much of the Rotorua district, including Lake Okaro and provided a well delineated tephra in the lake sediments. Therefore, the net sedimentation rates represent averages for the entire period 1886-2007. It should be noted that sedimentation rates in Lake Okaro are likely to have varied within this period, especially during the last 50 years when the lake has undergone eutrophication (Forsyth *et al.*, 1988). Furthermore, the apparent half life time is calculated with only one exponential decay parameter which, from a diagenetic perspective, must be interpreted carefully because it will not reflect generation of the specific compound from other sources. The apparent half life times calculated in this study may therefore

only be interpreted as indicative, representing the net effect of several different diagenetic processes.

Forms of phosphorus

Orthophosphate monoesters are usually the major organic P compound in soils and sediments (Turner *et al.*, 2003) and were anticipated to be the most abundant in Lake Okaro. This group comprises several compounds with varying lability, of which the inositol phosphates are usually dominant, but orthophosphate monoesters are generally considered chemically inert in lake sediments (DeGroot & Golterman, 1993). This is supported by my value of apparent half life time for this group, which is the longest of all P compounds in the sediment of Lake Okaro at 23 years. Some orthophosphate monoesters can degrade to orthophosphate under anaerobic conditions (Suzumura & Kamatani, 1995) and, given the prolonged periods of anoxia of bottom waters in this lake, they may be an important long-term source of internal P loading in Lake Okaro.

Orthophosphate diesters from soil organic P tend to be more labile and readily mineralized than monoesters (Makarov *et al.*, 2002). However, the apparent half life time of orthophosphate diesters found in my study is relatively high (20 years) and is similar to those found in other studies (Ahlgren *et al.*, 2005). The presence of two of the minor constituents of the orthophosphate diester group in the sediments, phospholipids and techoic acids, may indicate low rates of microbial activity (Makarov *et al.*, 2002), which may partially explain this relatively long half life time. DNA-P was found to be the largest fraction of orthophosphate diesters. This group arises mostly from bacterial DNA and to some extent decomposing phytoplankton (Ahlgren *et al.*, 2006). DNA-P can have half life times of less than a decade, suggesting that its degradation may be an important contribution to internal P loading (Ahlgren *et al.*, 2005).

Pyrophosphates are bioavailable and can support the growth of heterotrophic bacteria from different environments even when phosphate concentrations are high (Liu *et al.*, 1982; Sundareshwar *et al.*, 2001). Pyrophosphates have been found in sediments arising from urban catchments mostly covered with impervious surfaces (Sundareshwar *et al.,* 2001). My study suggests that pyrophosphates occur naturally in Lake Okaro, where the catchment

is 95% pasture. I found an apparent half life time for pyrophosphates of 12 years, which is similar to the value (13 years) found in mesotrophic Lake Erken (Ahlgren *et al.*, 2005), but much longer than the value of 3 years found for sediments of the Baltic Sea (Ahlgren *et al.*, 2006). There may be several possible reasons for the long half in relatively shallow lakes, including low concentrations or activity of specific breakdown enzymes such as pyrophosphatase and high mineralisation rates in seasonally anoxic hypolimnia of lakes which could cause degradation of substantial fractions of labile P in the settling seston before it reaches the sediment surface.

The detection of phosphonates in the sediment of Lake Okaro, though intermittent, was unexpected. Phosphonates in sediments have been found to be a by-product of protozoan metabolism, which is common to almost all aquatic habitats with high primary productivity except where anoxic conditions exist (Carman *et al.*, 2000; Ahlgren *et al.*, 2005). They also accumulate in alkaline soils, however, where bacteria specifically adapted to this substrate contain a phosphonatase enzyme (Hawkes *et al.*, 1984). In Lake Okaro, pH in surface waters can sometimes exceed 10 as a result of inorganic carbon depletion during severe algal blooms (Paul *et al.*, 2008), which could facilitate the presence of bacteria with phosphonatase. Phosphonates are considered to be very stable compounds and are not readily hydrolysed even after long exposure to acidic and alkaline conditions (Ahlgren *et al.*, 2006), especially compared with orthophosphates, which are more likely to contribute to internal P loading (Ahlgren *et al.*, 2006).

The half life time of polyphosphates was only 8 years. Polyphosphates contribute significantly to P-release following diagenesis, at rates comparable to P-release from iron oxyhydroxides (Hupfer *et al.*, 2004). The short half life time of polyphosphates found in my study suggests rather high degradation rates that may induce high internal loading rates. These results are not consistent with those of Kenney *et al.* (2001) who considered that polyphosphates are not geochemically reactive.

Loss on ignition explained 73% of the variation in sediment P concentrations in Lake Okaro, emphasising that organic P is likely to be one of the dominant forms of P. However, my study did not verify that sediment P was

not associated with other metals, despite weak or no relationships between P and Al, Fe and Mn. The stabilisation of P by Al, for example, depends on several different redox insensitive chemical processes, such as the adsorption of P onto Al hydroxides. Only small portions of the total Al pool may be involved, however, which could partially explain the lack of correlation between P and Al.

Implications of P speciation for sediment remediation

Phosphorus was recovered mostly as orthophosphate in sediments layers of Lake Sønderby corresponding to the time of an alum application (Reitzel *et al.*, 2006) but in Lake Okaro there was no detectable change in P compounds in sediment layers representing an alum treatment application in 2003. One explanation for this is that the low dose rate of alum in Lake Okaro (Paul *et al.*, 2008) resulted in a thin layer of aluminium in the bottom sediments, which was not resolved within the sediment sampling resolution (2 cm intervals) used in my study. Furthermore, once the alum floc reaches the sediment, it may be mixed into sediments to depths of several centimetres (Rydin, 2000).

The presence of organic P in lake sediments has important implications for using aluminium or iron based P-inactivation or sediment capping materials as an in-lake restoration method. Organic P has been found to adsorb strongly to iron and aluminium in soils and sediments (DeGroot & Golterman, 1993). Phosphate monoesters such as *myo*-inositol hexakisphosphate for example, adsorb on the same sites of iron oxides as phosphate ions but with a greater affinity (Celi & Barberis, 2005). Among different phosphate monoesters, *myo*-inositol hexakisphosphate has the highest binding affinity to aluminium oxide surfaces (Shang *et al.*, 1996). The competitive binding of organic P compounds to aluminium could potentially reduce the uptake capacity of aluminium based P-inactivation agents used for Lake Okaro (i.e. alum or Z2G1) by occupying free binding sites for inorganic phosphate.

Sedimentation rates of TPM in Lake Okaro were within the same range as those observed in other eutrophic lakes (Koski-Vähälä *et al.*, 2000; Chalar & Tundisi, 2001; Pettersson, 2001). Values were highest during mixing when P content of TPM increased 2.5-fold while the content of organic matter in the trapped material showed little variation compared with the stratified period. On

average, particulate matter in traps in Lake Okaro was highly enriched in P (7.1 mg TP g^{-1} TPM) compared with other eutrophic lakes (1.3 - 5.8 mg TP g^{-1} TPM; Pettersson, 2001). During stratification seston was dominated to a greater extent by organic P than during mixing, when orthophosphate comprised up to 70.6% of the total extracted P. Phytoplankton biomass in Lake Okaro increases rapidly in spring and summer (Paul *et al.*, 2008) and likely contributes to a greater proportion of P in the resulting organic detritus, similar to what has been observed in Lake Erken (Pettersson, 2001). The persistent supply and decomposition of P-rich organic material in sediment layers above a P-inactivation material, may limit the longevity of effectiveness of sediment capping, both through burial and through continuing sediment P releases to the overlying water column.

It has been suggested that pyrophosphates and polyphosphates in settling seston originate from the bacterial community colonizing and mineralizing settling particles (Hupfer *et al.*, 2004; Reitzel *et al.*, 2007). Such organisms accumulate and store phosphate as cellular polyphosphates under oxic conditions and these polyphosphates are then hydrolysed during anoxia, enhancing releases of orthophosphate (Hupfer *et al.*, 2004). The reactivity and the relatively high abundance of polyphosphates in the settling seston in Lake Okaro suggest that this compound is likely to contribute to increased water column phosphate levels before the P reaches the bottom sediments, particularly during summer stratification when the hypolimnion is anoxic for several months (Forsyth *et al.*, 1988). High mineralisation rates of organic P contributing internal P loading could potentially reduce the efficacy of sediment capping materials such as Z2G1.

The ^{31}P NMR study of the bottom sediments of Lake Okaro has demonstrated that mineralisation of organic P is an important long-term source in internal P loading. However, relatively long apparent half life times of some organic P fractions indicate that a large fraction of the labile P of the settling seston is mineralised in the water column before reaching the sediment surface. The high abundance of organic P compounds in the sediments has to be accounted for when considering in-lake restoration using P-inactivation agents, as competitive sorption processes between free orthophosphate and organic P for free binding sites of these materials may reduce the effectiveness of P-inactivation.

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5 Modelling the response of a highly eutrophic lake to reductions in external and internal nutrient loading

5.1 Introduction

Control of diffuse and point sources of phosphorus (P) and nitrogen (N) remains a global challenge (Schindler, 2006; Carpenter, 2008; Conley *et al.*, 2009) despite more than 50 years of understanding of the role of nutrients as a cause of lake eutrophication. While net phytoplankton growth can be constrained by factors other than nutrients (e.g. light and grazing), there is continued recognition of the critical role of P in the eutrophication process (OECD, 1982; Schindler *et al.*, 2008) though many lake restoration efforts focused predominantly on P control have fallen short of expectations (Conley *et al.*, 2009). Similarly, in management focused predominantly on N there is risk of enhanced growth of N-fixing cyanobacteria that may negate the effectiveness of this control strategy (Schindler *et al.*, 2008). Lewis & Wurtsbaugh (2008) proposed a N+P control paradigm which emerged from evidence of co-limitation of N and P for phytoplankton growth across a large number of inland waters.

Numerical models of aquatic ecosystems that couple physics and biogeochemistry (e.g. Kamykowski *et al.*, 1994; Hamilton & Schladow, 1997) are a valuable tool in aquatic ecosystem research. They have been used for examining theoretical aspects of ecosystem behaviour which may be unattainable by other means (Franks, 1995) and the interactions between trophic dynamics and, for example, climate variability (Norberg & DeAngelis, 1997). These models have been used for forecasting purposes and as environmental management decision support tools, particularly for the control of eutrophication (Friedman *et al.*, 1984; Burger *et al.*, 2007a; Trolle *et al.*, 2008). They have also been used in combination with water quality indices to collate the detailed temporal and spatial information on model output variables into numerical rating values (Gal *et al.*, 2009). There are other water quality indices directly related to

eutrophication assessment such as the Trophic Level Index (TLI; Burns *et al.*, 1999) and Trophic State Index (Carlson, 1977), but I am not aware of any applications of these indices for interpreting the outcomes for different scenarios simulated with numerical water quality models.

The decline over the past 30 to 40 years of water quality in the Te Arawa (Rotorua) lakes and in New Zealand lakes generally has been linked to increasing nutrient loads from land development for agriculture and greater use of artificial fertilisers (Hamilton, 2005; Parliamentary Commissioner for the Environment, 2004). Steps are beginning to be taken to redress the decline in water quality, including changing land use around some lakes (Quinn, 2009). Amongst the Te Arawa lakes there has been an intensive restoration program in Lake Okaro, the focal lake in this study, which commenced in 2003. The TLI is used as the cornerstone by which to gauge the effect of action plans developed to improve water quality of this lake and other Te Arawa lakes, with water quality targets based on its input data of annual mean surface water concentrations of chlorophyll *a* (chl *a*), total nitrogen (TN), total phosphorus (TP), and Secchi depth (SD). Despite a series of actions implemented at Lake Okaro, including an alum application (Paul *et al.*, 2008), a constructed wetland (Tanner *et al.*, 2007) and most recently a sediment capping application using an aluminium modified zeolite mineral (Z2G1), the TLI has remained within the highly eutrophic range. These restoration methods were collectively designed to reduce both N and P loading to the lake, but were mostly directed towards reducing P loads. I hypothesised that a further substantial reduction in nutrient loading of both N and P, including from both external and internal sources, would be required to reduce nutrient and chl *a* concentrations and improve the trophic state of Lake Okaro. I used a numerical model and multi-year simulations to simulate the response of the lake to different N and P loading rates. I also examined the likely response of reduced water column N and P on the duration and severity of nutrient limitation in phytoplankton, using specific outputs of nutrient limitation status from the model.

5.2   Methods

Study site

Lake Okaro (Figure 5.1) is a small lake (area 0.32 km^2) of moderate depth (max. depth 18 m), in the Rotorua district on the Central Volcanic Plateau of North Island, New Zealand. The lake is the most eutrophic of the Te Arawa lakes in the region (Paul *et al.*, 2008). It is a monomictic lake and stratifies for around eight months during summer when there are substantial sediment nutrient releases (Environment Bay of Plenty, 2006). The Regional Water and Land Plan for Bay of Plenty has set a TLI target reduction from the current value of 5.5, which categorises the lake as supertrophic, (three-year average to June 2004) to 5.0 (Environment Bay of Plenty, 2006) as part of a lake action plan. This value will, however, not shift the trophic status of the lake from its current eutrophic category, but the TLI value would be lower than annual values observed since 1992 when continuous monitoring of Lake Okaro commenced (Environment Bay of Plenty, 2006).
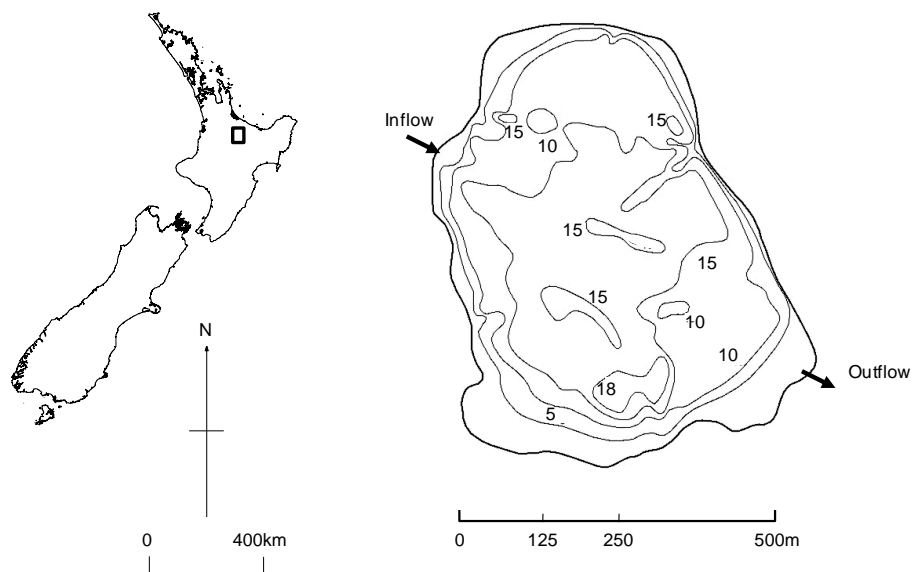
Figure 5.1: Location map of Lake Okaro showing depth contours of 5, 10, 15 and 18 m.

Intensive catchment and in-lake restoration has been carried out at Lake Okaro to reduce both external and internal nutrient loading, to assist with meeting the TLI target. Two permanent stream inflows were diverted into a 2.3 ha surface–flow constructed wetland in February 2006 primarily to reduce N and P loads (Tanner *et al.*, 2007). Riparian protection works were undertaken

progressively through the study period (2004-2008), including livestock exclusion, fencing, and planting of native plant species along the stream banks and lake margins. A low-level alum dose (lake-wide concentration 0.6 g Al m^{-3}) was applied on 16 and 17 December 2003 (Paul *et al.*, 2008). In a more recent restoration attempt to control internal phosphorus loads, 110 t of aluminium-modified zeolite (Z2G1, Blue Pacific Minerals, Matamata, New Zealand) was applied to the lake surface as a sediment capping agent between 25 and 28 September 2007.

Model description

In this study, the one-dimensional (1D) hydrodynamic model DYRESM (version 3.1.0-03) was coupled with the aquatic ecological model CAEDYM (version 3.1.0-06), both developed at the Centre for Water Research, The University of Western Australia, to simulate water quality in Lake Okaro. DYRESM resolves the vertical distribution of temperature, salinity, and density in lakes and reservoirs, while CAEDYM simulates time varying fluxes of biogeochemical variables (e.g. nutrient species, phytoplankton biomass). The model includes comprehensive process representations for carbon (C), N, P, and dissolved oxygen (DO) cycles, and several size classes of inorganic suspended solids. Several applications have been made of DYRESM-CAEDYM to different lakes (e.g. Bruce *et al.*, 2006; Burger *et al.*, 2007a; Trolle *et al.*, 2008; Gal *et al.*, 2009) and these applications are associated with detailed descriptions of the model equations.

The variables in CAEDYM may be configured according to the goals of the model application and availability of data. For example, it is possible to simulate up to seven different phytoplankton groups, five zooplankton groups, fish, and macrophytes. In this study, two groups of phytoplankton were included in CAEDYM, represented by cyanophytes and a combined group termed chlorophytes. The interactions between phytoplankton growth and losses, sediment nutrient fluxes and the mineralisation and decomposition of particulate organic matter influence N and P cycling in the model, as shown in the conceptual model in Figure 5.2. Fluxes of dissolved inorganic and organic nutrients from the bottom sediments are dependent on the temperature, NO_3-N and DO

concentration of the water layer immediately above the sediment surface based on field studies (e.g. Søndergaard *et al.*, 2003), but with calibration of parameters specific to each application.
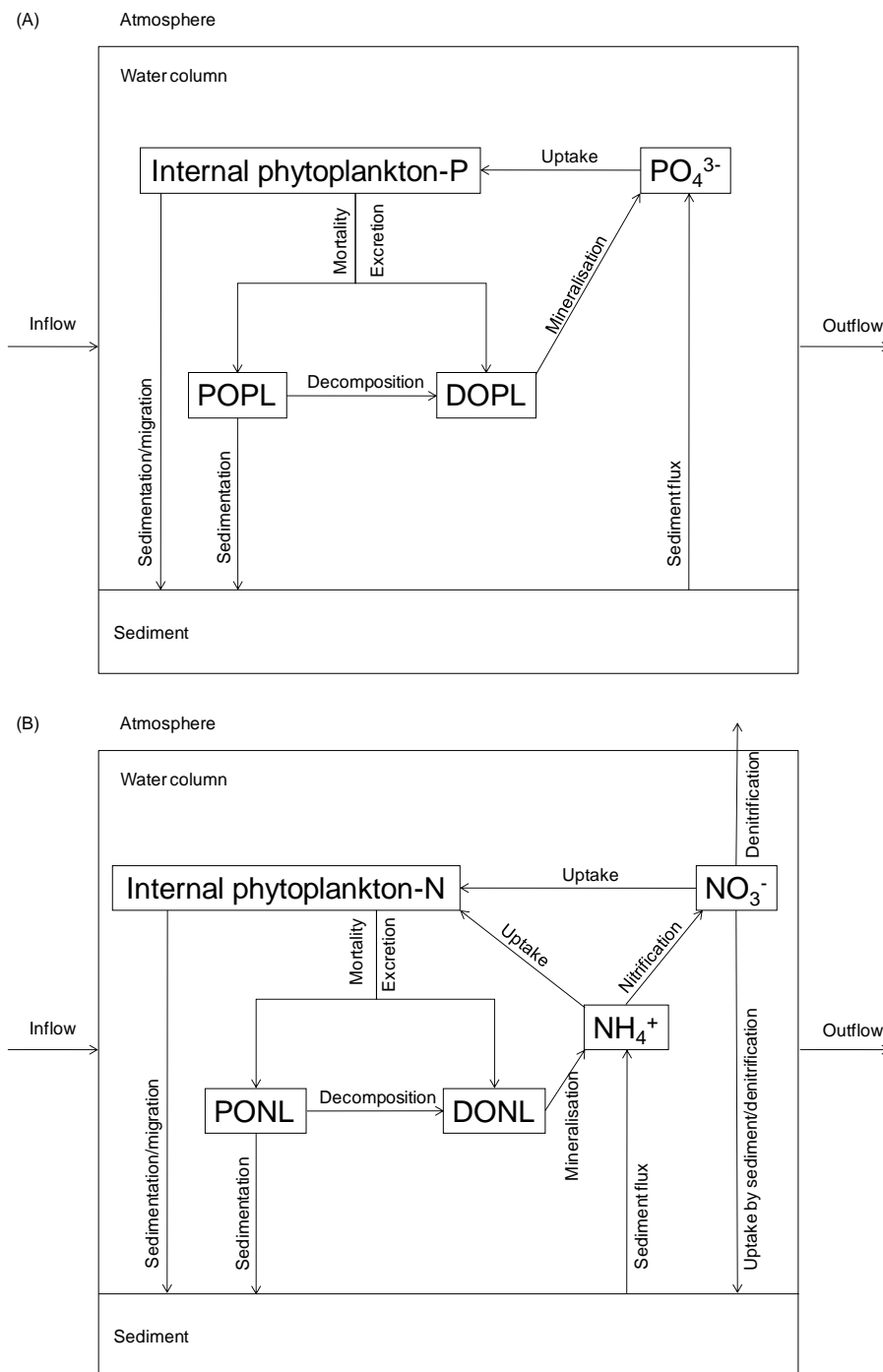
Figure 5.2: Conceptual model of the phosphorus (A) and nitrogen (B) cycle used in DYRESM-CAEDYM for the present study. POPL, PONL, DOPL and DONL represent particulate labile organic phosphorus and nitrogen, and dissolved labile organic phosphorus and nitrogen, respectively.

Model input data

In this study, the model was run at hourly time steps between July 2004 and June 2008, with daily averaged input data and daily output data at midday. Meteorological data required for the simulation period were obtained from Rotorua Airport climate station c. 20 km north of Lake Okaro. Air temperature (°C), shortwave radiation (W m^{-2}), cloud cover (fraction of whole sky), vapour pressure (hPa), wind speed (m s^{-1}) and rainfall (m) data are shown in Figure 5.3. Linear interpolation between monthly samples was used to obtain daily values for stream inflow and nutrient concentrations. Daily values for the outflow volume were calculated as a residual term of a water balance for the simulation period (Wetzel & Likens, 2000), with evaporation calculated from the latent heat flux (Fisher *et al.*, 1979) and saturation vapour pressure (Wunderlich, 1972).
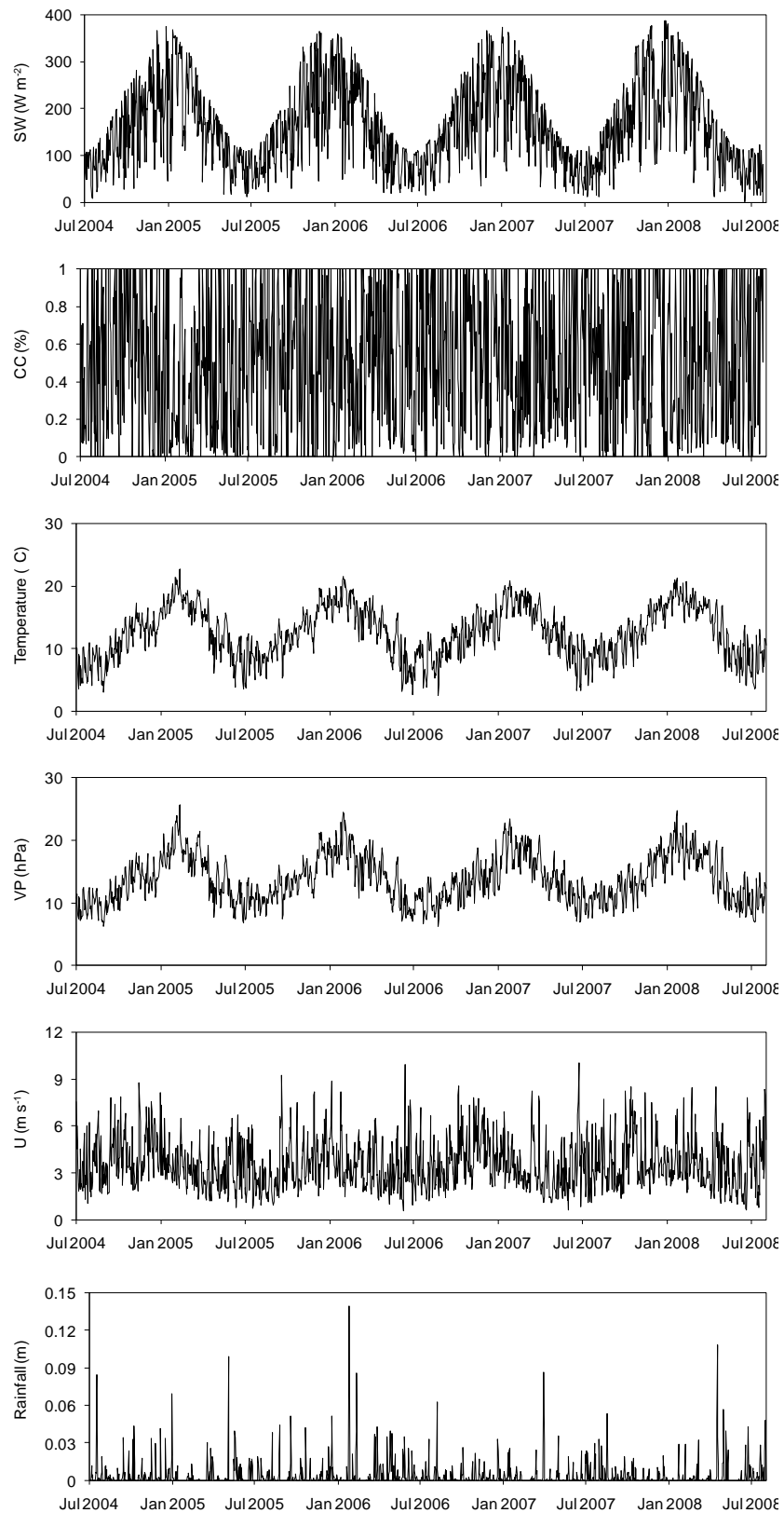
Figure 5.3: Meteorological data used as input to the DYRESM model (July 2004 – June 2008), including short wave radiation (SW), cloud cover (CC), air temperature (T), vapour pressure (VP), wind speed (U), and rainfall. Data were obtained from the Rotorua Airport climate station with daily means calculated from hourly measurements.

Model calibration and validation

DYRESM-CAEDYM was calibrated against field data for a two year period between July 2005 and June 2007 for variables of temperature, DO, PO_4-P, TP, NH_4-N, NO_3-N and TN at the surface (0 m) and near the bottom (14 m) of the lake, using monthly samples collected by Environment Bay of Plenty. Nutrient samples were analysed using standardised methods (APHA, 2005). The two simulated phytoplankton groups were calibrated to represent seasonal variation of chl *a* concentrations, where cyanophytes are assumed to dominate during summer and chlorophytes during winter and early spring, with the sum of their chlorophyll concentration calibrated against chlorophyll *a* measured at the surface only using an acetone extraction procedure (Arar & Collins, 1997). Model parameters were adjusted manually using a trial and error approach using values within literature ranges (e.g. Schladow & Hamilton, 1997; Trolle *et al.*, 2008). The model error, represented by the root-mean-square-error (RMSE) and Pearson correlation coefficient (R) for each output variable, was quantified after each simulation for which parameter values were adjusted. Calibration continued until there was negligible improvement in RMSE and R values. The model was validated over two separate one-year periods outside of the calibration period for which parameters were manipulated. The first validation period between July 2007 and June 2008 was used to evaluate the performance of the model to reproduce a period when the Z2G1 material was applied to Lake Okaro as a P-inactivation agent to reduce internal loading of P. The model was also validated with an additional period between July 2005 and June 2006 when there was an extraordinary cyanobacteria bloom consisting of an invasive, highly buoyant, N-fixing cyanobacterium, *Anabaena planktonica,* which was the dominant species in Lake Okaro over the period between November 2004 and March 2005 (Wood *et al.*, 2005; Environment Bay of Plenty, unpub. data).

Scenarios

A series of nutrient loading scenarios were simulated by adjusting nutrient loads (internal and/or external) over the period between July 2005 and June 2008 where this period was used to represent a base scenario. Lake restoration scenarios were simulated by reducing the external and/or internal loading of either N or P (N_{ext}, N_{int}, N_{comb}, P_{ext}, P_{int} and P_{comb}), or both nutrients (N+P_{ext}, N+P_{int} and N+P_{comb}), by

10, 25, 50, 75, and 90% from the base simulation inputs (subscripts ext, int and comb represent external, internal and combined external/internal loading, respectively). For reduced external loading, a uniform reduction was applied to particulate and dissolved nutrient species, whereas for reduced internal loading, only dissolved inorganic nutrients were decreased. The TLI value was calculated for each scenario and compared with the base scenario. The relevant equations for determination of the TLI are:

$$TL_{Chla} = 2.22 + 2.54\log\left(Chla\right) \tag{5.1}$$

$$TL_{SD} = 5.1 + 2.27\log\left(\frac{1}{SD} - \frac{1}{40}\right) \tag{5.2}$$

$$TL_{TP} = 0.218 + 2.92\log(TP) \tag{5.3}$$

$$TL_{TN} = -3.61 + 3.01\log\left(TN\right) \tag{5.4}$$

$$TLI = \frac{1}{4}\sum\left(TL_{Chla}, TL_{SD}, TL_{TP}, TL_{TN}\right) \tag{5.5}$$

Where TL_{Chla}, TL_{SD}, TL_{TP} and TL_{TN} represent the individual level trophic level indices for the each variable. As Secchi depth is not explicitly included in the model, this variable was derived from a model-predicted attenuation coefficient as:

$$z_{SD} = \frac{\alpha}{K_d} \tag{5.6}$$

Where z_{SD} is the Secchi depth (m), K_d is the diffuse attenuation coefficient (m^{-1}) and α is a constant determined by comparing field measurements of Secchi depth with corresponding values of K_d (R = 0.78, p < 0.01). In CAEDYM, K_d is calculated as:

$$K_{d(CAEDYM)} = K_w + \sum\left(K_a A_a\right) + K_{POC}POC + K_{DOC}DOC \tag{5.7}$$

Where K_w is the background extinction coefficient and K_a is the specific attenuation coefficient for chl *a* (A) for each simulated phytoplankton group (a) and K_{POC} and K_{DOC} are the specific attenuation coefficients for particulate (POC) and dissolved organic matter (DOC), respectively.

The nutrient limitation status of the two phytoplankton groups in the model was investigated by extracting daily basin-average values of the nutrient limitation functions of both N and P for each simulated phytoplankton group from the DYRESM-CAEDYM simulations. The simulated growth of phytoplankton in CAEDYM is based on a minimum expression for light, P and N:

$$\mu_{g_a} = \mu_{max_a} \min\left[f(I)_a, f(N)_a, f(P)_a\right] f_a(T) \qquad (5.8)$$

Where $\mu_{g,a}$ is the growth rate (d^{-1}), $\mu_{max,a}$ (d^{-1}) is the maximum potential growth rate at 20 °C in the absence of significant limitation by light and nutrients, $f(I)$, $f(N)$, and $f(P)$ represent fractional limitation for light, N and P, respectively, and $f(T)$ is a temperature function. The subscript a is used here as a generic identifier for the two simulated phytoplankton groups. A dynamic internal nutrient model in CAEDYM allows phytoplankton to have luxury nutrient stores:

$$f(j)_a = \frac{AI_{j_{MAXa}}}{AI_{j_{MAXa}} - AI_{j_{MINa}}} \left[1 - \frac{AI_{j_{MINa}}}{AI_{j_a}}\right] \qquad (5.9)$$

Where $AI_{jMAX,a}$ and $AI_{jMIN,a}$ are user-defined maximum and minimum internal nutrient concentrations, respectively, and $AI_{j,a}$ is the actual internal nutrient concentration and j represents either P or N. Growth of phytoplankton declines as internal nutrient concentrations of the prevailing limiting nutrient (or light, Eq. 5.8) decrease (i.e. $f(j) \rightarrow 0$) whereas growth is free of nutrient limitation when $f(j) \rightarrow 1$.

5.3   Results

Calibration and validation

The model parameters adjusted during the calibration of DYRESM and CAEDYM are presented in Tables 5.1 and 5.2, respectively. The model was generally able to reproduce the magnitude and dynamics of field measurements using parameter values within the range found in the literature (e.g. Schladow & Hamilton, 1997; Trolle *et al.*, 2008). The parameter for the effect of DO on sediment ammonium release was higher than that found in other eutrophic lakes while the maximum potential release rates for N and P were generally lower (e.g.

Burger *et al.,* 2007a; Gal *et al.*, 2009). The magnitude and timing of chl *a* concentrations during the calibration period were reproduced by allowing cyanophytes luxury uptake of P (Reynolds, 2006) which is reflected by a relatively high maximum internal P concentration (4.0 mg P mg^{-1} chl *a*) as observed in field studies in Lake Okaro (Lean *et al.*, 1987). Chlorophyll *a* concentrations observed during summer and early spring were represented in the model predominantly as contributions from the 'chlorophyte' group using parameters within literature ranges (Schladow & Hamilton 1997; Trolle *et al.,* 2008).

Table 5.1: Assigned values for parameters used in DYRESM.

Parameter	Unit	Calibrated value	Reference/remarks
Critical wind speed	m s^{-1}	3.0	Spigel *et al.* (1986)
Emissivity of water surface	-	0.96	Imberger & Patterson (1981)
Mean albedo of water	-	0.1	Patten *et al.* (1975)
Potential energy mixing efficiency	-	0.2	Spigel *et al.* (1986)
Shear production efficiency	-	0.21	Spigel *et al.* (1986)
Vertical mixing coefficient	-	600	Yeates & Imberger (2003)
Wind stirring efficiency	-	0.2	Spigel *et al.* (1986)
Benthic boundary layer dissipation coefficient	m^2 s^{-1}	7.5 x 10^{-6}	Calibrated
Effective surface area coefficient	m^{-2}	1.45 x 10^6	Calibrated

The model simulations of temperature, DO, total nutrients, and dissolved nutrients in both surface (0 m) and bottom waters (14 m) for the calibration period in Lake Okaro produced low RMSE values and high R values (Table 5.3) compared with these statistics for similar model applications (Arhonditsis & Brett, 2005; Burger *et al.*, 2007a; Trolle *et al.*, 2008). The simulations captured the seasonal transitions of stratification, deoxygenation of bottom waters and subsequent build up of bottom-water concentrations of PO$_4$-P (Figure 5.4). By contrast, the timing of the increase of NH$_4$-N concentrations in the bottom water was not captured as accurately (Figure 5.5) which was also reflected by a relatively low R value of 0.83 (Table 5.3). The observed rapid increase in NO$_3$-N concentrations while DO was still present in the hypolimnion early in the stratification period was also reproduced by the model simulations (Figure 5.5).

Table 5.2: Assigned values for parameters used in CAEDYM for Lake Okaro; DOPL and DONL are dissolved organic phosphorus and nitrogen, respectively.

Parameter	Unit	Calibrated value	Reference source
Sediment parameters			
Sediment oxygen demand	g m^{-2} d^{-1}	2.0	Schladow & Hamilton (1997)
Half-saturation coefficient for sediment oxygen demand	mg L^{-1}	0.25	Schladow & Hamilton (1997)
Maximum potential PO$_4$ release rate	g m^{-2} d^{-1}	0.0160	
Oxygen and nitrate half-saturation for release of phosphate from bottom sediments	g m^{-3}	1.5	
Maximum potential NH$_4$ release rate	g m^{-2} d^{-1}	0.1	
Oxygen half-saturation constant for release of ammonium from bottom sediments	g m^{-3}	5.0	
Temperature multiplier for nutrient release	-	1.05	Robson & Hamilton (2004)
Nutrient parameters			
Decomposition rate of POPL to DOPL	d^{-1}	0.001	Schladow & Hamilton (1997)
Mineralisation rate of DOPL to PO$_4$	d^{-1}	0.025	Schladow & Hamilton (1997)
Decomposition rate of PONL to DONL	d^{-1}	0.007	Schladow & Hamilton (1997)
Mineralisation rate of DONL to NH$_4$	d^{-1}	0.01	Schladow & Hamilton (1997)
Denitrification rate coefficient	d^{-1}	0.1	
Oxygen half-saturation constant for denitrification	mg L^{-1}	2.0	
Nitrification rate coefficient	d^{-1}	0.008	
Nitrification half-saturation constant for oxygen	mg L^{-1}	2.0	
Phytoplankton parameters		Cyanophytes, chlorophytes	
Maximum potential growth rate at 20°C	d^{-1}	0.6, 1.3	Robson & Hamilton (2004)
Irradiance parameter non-photoinhibited growth	µmol m^{-2} s^{-1}	150, 20	Robson & Hamilton (2004)
Half saturation constant for phosphorus uptake	mg L^{-1}	0.032, 0.025	Trolle *et al.* (2008)
Half saturation constant for nitrogen uptake	mg L^{-1}	0.02, 0.03	Trolle *et al.* (2008)
Minimum internal nitrogen concentration	mg N (mg chl *a*)$^{-1}$	4.0, 2.0	Schladow & Hamilton (1997)
Maximum internal nitrogen concentration	mg N (mg chl *a*)$^{-1}$	9.0, 9.0	Schladow & Hamilton (1997)
Maximum rate of nitrogen uptake	mg N (mg chl *a*)$^{-1}$ d^{-1}	3.0, 2.0	Schladow & Hamilton (1997)
Minimum internal phosphorus concentration	mg P (mg chl *a*)$^{-1}$	0.2, 0.25	Schladow & Hamilton (1997)
Maximum internal phosphorus concentration	mg P (mg chl *a*)$^{-1}$	4.0, 2.0	Schladow & Hamilton (1997)
Maximum rate of phosphorus uptake	mg P (mg chl *a*)$^{-1}$ d^{-1}	0.5, 0.25	Schladow & Hamilton (1997)
Temperature multiplier for growth limitation	-	1.05, 1.06	Schladow & Hamilton (1997)
Standard temperature for growth	°C	19.0, 20.0	Gal *et al.* (2009)
Optimum temperature for growth	°C	26.0, 28.0	Gal *et al.* (2009)
Maximum temperature for growth	°C	34.0, 34.0	Gal *et al.* (2009)
Respiration rate coefficient	d^{-1}	0.055, 0.055	Schladow & Hamilton (1997)
Temperature multiplier for respiration	-	1.06, 1.06	Schladow & Hamilton (1997)
Constant settling velocity	m d^{-1}	0.0, -0.43	Burger *et al.* (2007a)
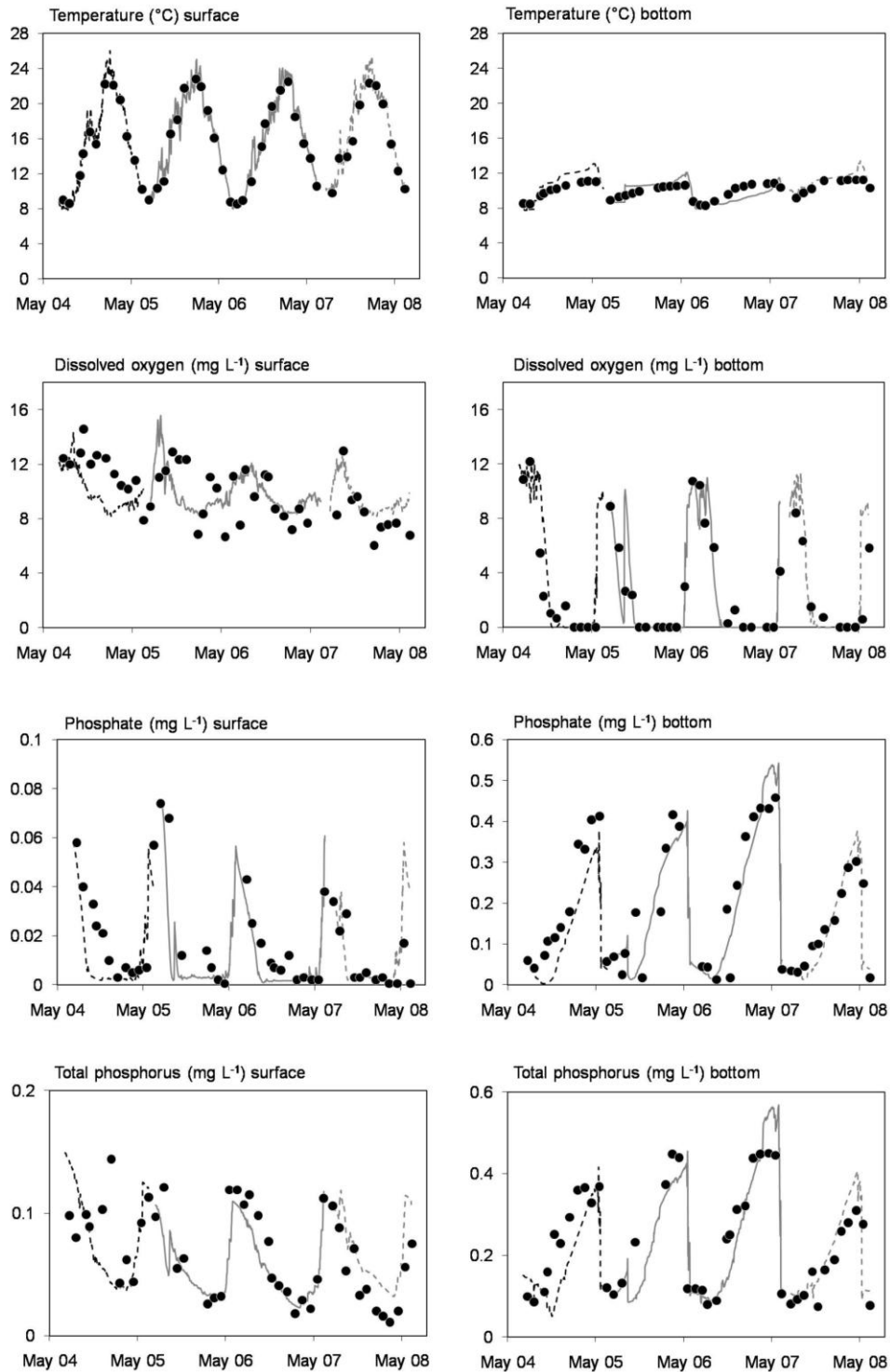
Figure 5.4: Comparison of model simulation results (grey lines) against field observations (black circles) in the surface (0 m) and bottom (14 m) waters of Lake Okaro during the calibration period (solid grey line) and validation periods (dashed grey and black line) for temperature, dissolved oxygen, phosphate and total phosphorus.
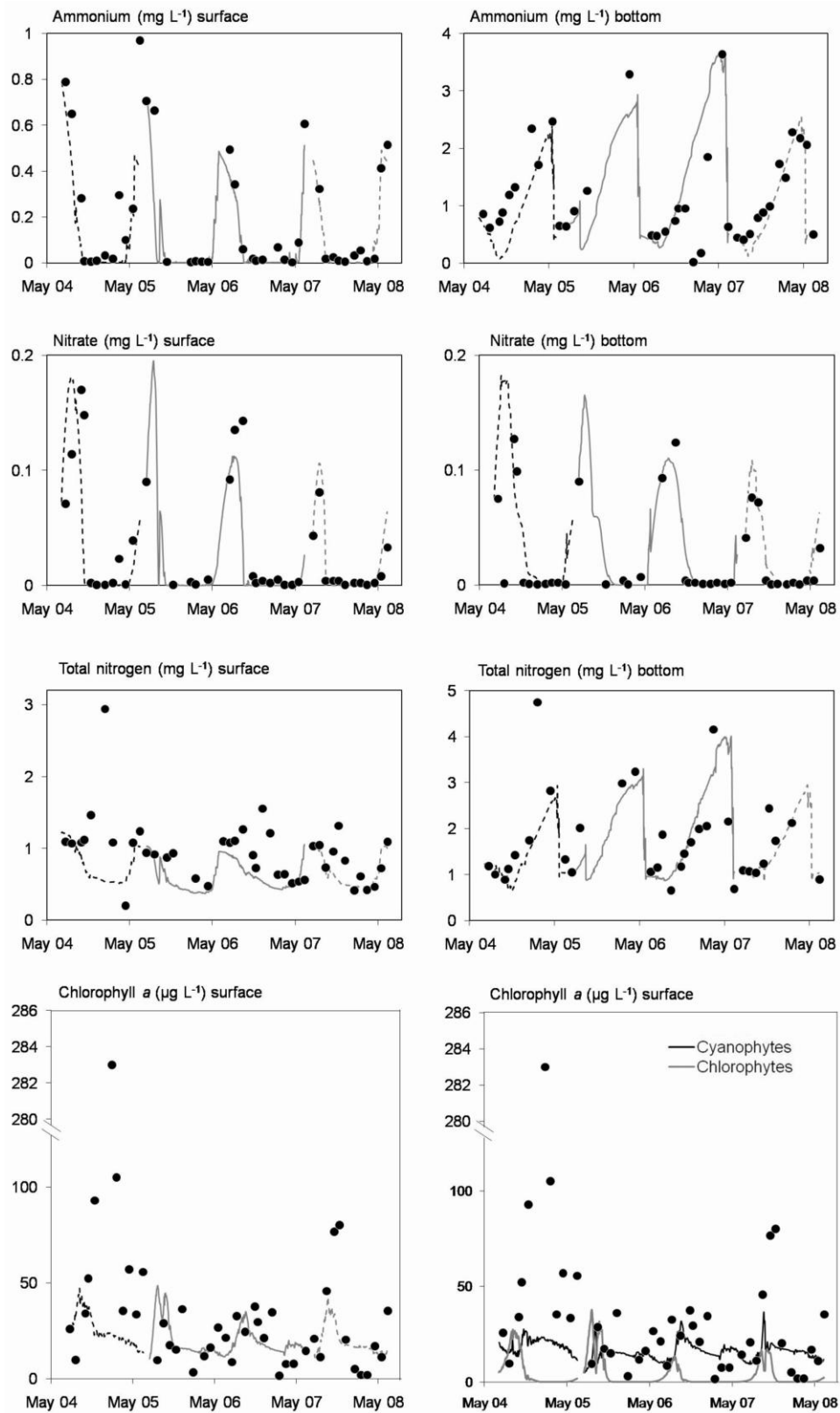
Figure 5.5: Comparison of model simulation results (grey lines) against field observations (black circles) in the surface and bottom waters of Lake Okaro during the calibration period (solid grey line) and validation periods (dashed grey and black line) for ammonium, nitrate, total nitrogen and surface water chlorophyll *a*.

During the validation period between July 2007 and June 2008, the model simulations reproduced the field data with similar RMSE and R values observed to those of the calibration period (Table 5.3). However, R values for bottom water concentrations of TN and TP were lower than for the calibration period. The model reproduced the scale of phosphate and ammonium build up in the bottom waters during the validation period between 2007 and 2008, despite the application of Z2G1 to Lake Okaro in September 2007. Attempts to adjust the maximum potential release rates for both PO_4-P and NH_4-N did not result in better correspondence between model output and field measurements, suggesting that there was little effect of the Z2G1 application, at least not within the uncertainties of the model calibration.

The other validation period between July 2004 and June 2005 produced generally higher RMSE and lower R values than for the calibration period (Table 5.3). In particular, the model did not reproduce a peak of chl *a*, which was dominated by the invasive, highly buoyant and N-fixing cyanobacterium, *Anabaena planktonica*, between November 2004 and March 2005 (Environment Bay of Plenty, unpub. data). The simultaneous peaks of surface TP and TN concentrations, which were likely associated with the substantial phytoplankton biomass corresponding to the *Anabaena planktonica* bloom observed during this period, were also not reproduced by the model.

Base scenario

Over the entire base scenario period (July 2005 - June 2008), average TP (63.5 mg m^{-3}) and chl *a* concentrations (19.3 mg m^{-3}) were in the supertrophic range (Burns *et al.*, 1999) according to the Trophic Level Index value for TP and chl *a* (6.0> TL_{TP}, TL_{Chla} > 5.0; Figure 5.6). Average TN concentration was 652.8 mg m^{-3}, in the eutrophic range (5.0> TL_{TN} > 4.0), while Secchi depth averaged 2.6 m, which was also in the eutrophic range (5.0 >TL_{SD} > 4.0). The TLI value for the base scenario averaged 4.97, slightly lower than the TLI calculated from measured data (5.08) over the same period.
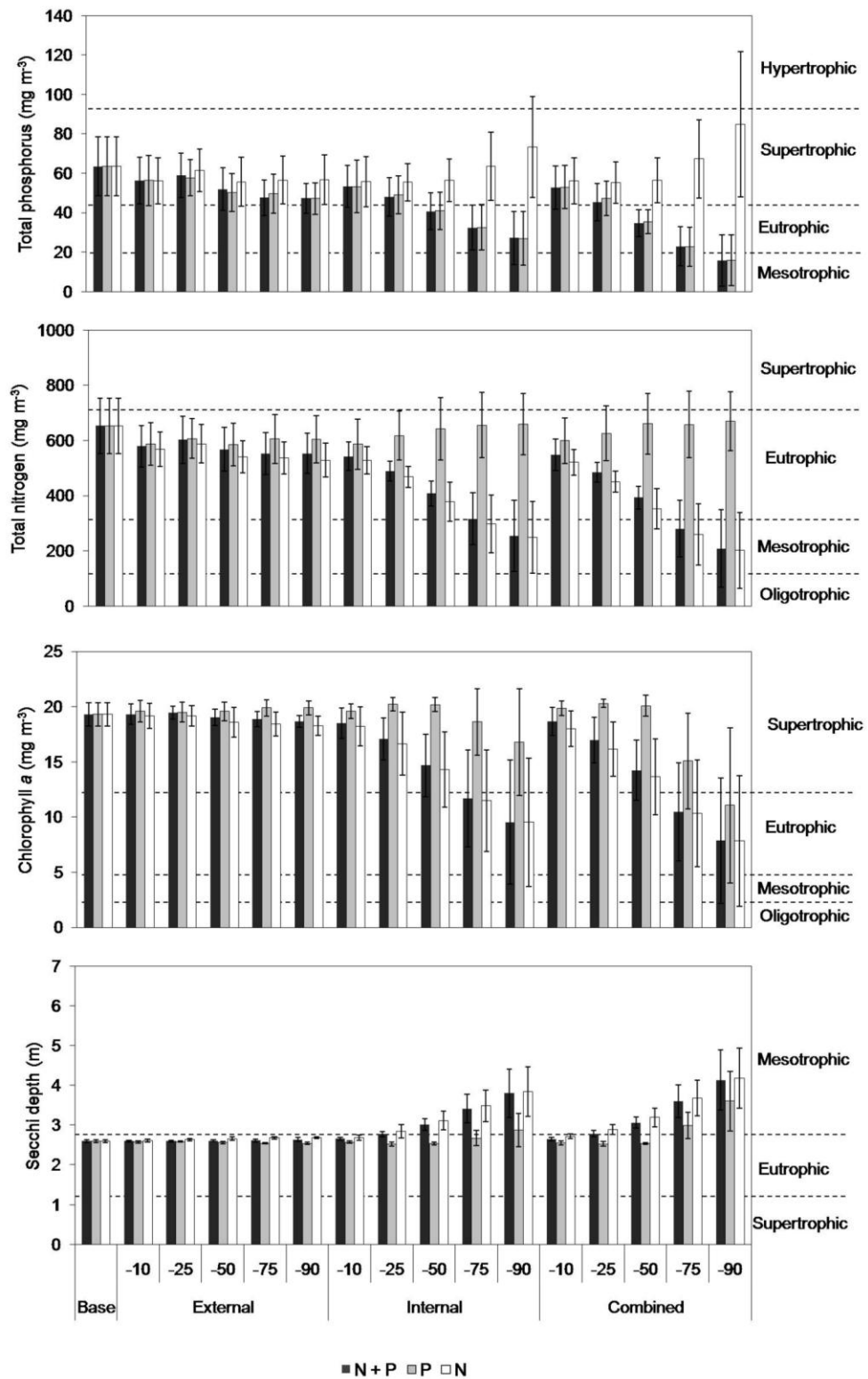
Figure 5.6: Simulated annual average total nitrogen, total phosphorus and chlorophyll *a* concentrations (mg m^{-3}) and Secchi depth (m) with seasonal variation represented by ± one standard deviation compared with the base scenario (July 2005 - June 2008) for simultaneous reduction of both nitrogen (N) and phosphorus (P) and individual reduction of P or N for reductions in external loading, internal loading, and a combined reduction of both external and internal loading (-10%, -25%, -50%, -75%, and -90%).

Table 5.3: Statistical comparison between model simulations and field data of surface (0 m) and bottom (14 m) waters in Lake Okaro using root-mean-square-error (RMSE) and Pearson correlation coefficient (R) for each variable.

	Calibration (2005-2007)				Validation (2007-2008)				Validation (2004-2005)			
	Surface waters		Bottom waters		Surface waters		Bottom waters		Surface waters		Bottom waters	
	RMSE	R	RMSE	R	RMSE	R	RMSE	R	RMSE	R	RMSE	R
Temperature	0.822	0.99	0.786	0.99	1.165	0.98	0.723	0.90	0.801	0.99	1.176	0.98
Dissolved oxygen	1.814	0.39	2.205	0.83	1.781	0.72	2.952	0.82	2.242	0.34	2.665	0.85
Phosphate	0.014	0.83	0.064	0.93	0.018	0.44	0.064	0.85	0.015	0.82	0.091	0.95
Ammonium	0.114	0.92	0.509	0.83	0.048	0.97	0.509	0.96	0.208	0.89	0.626	0.84
Nitrate	0.030	0.83	0.016	0.96	0.014	0.96	0.016	0.93	0.059	0.56	0.060	0.43
Total phosphorus	0.018	0.91	0.064	0.81	0.028	0.88	0.064	0.79	0.040	0.29	0.087	0.80
Total nitrogen	0.382	0.28	0.465	0.78	0.277	0.50	0.465	0.67	0.851	-0.19	0.988	0.74
Chlorophyll *a*	13.519	0.07	-	-	23.774	0.59	-	-	90.147	-0.17	-	-

Cyanophytes generally dominated chl *a* concentrations for the base scenario and comprised 80% on average of the total chl *a* concentration over the entire simulation period. The model output used to determine nutrient limitation status of the two simulated phytoplankton groups suggests that N was more often likely to limit growth of cyanophytes than P (i.e. $f(N) < f(P)$) for the majority of the simulation period (Figure 5.7). Nitrogen limitation for cyanophytes increased (i.e. decreasing $f(N)$) during stratification but neither N or P was strongly limiting during mixing periods (i.e. $f(N)$, $f(P) \rightarrow 1$). Growth of the 'chlorophyte' group was mostly limited by P over N (i.e. $f(P) < f(N)$) with limitation strongest (i.e. low $f(P)$) during stratification least (i.e. $f(P) \rightarrow 1$) when the lake was isothermal.
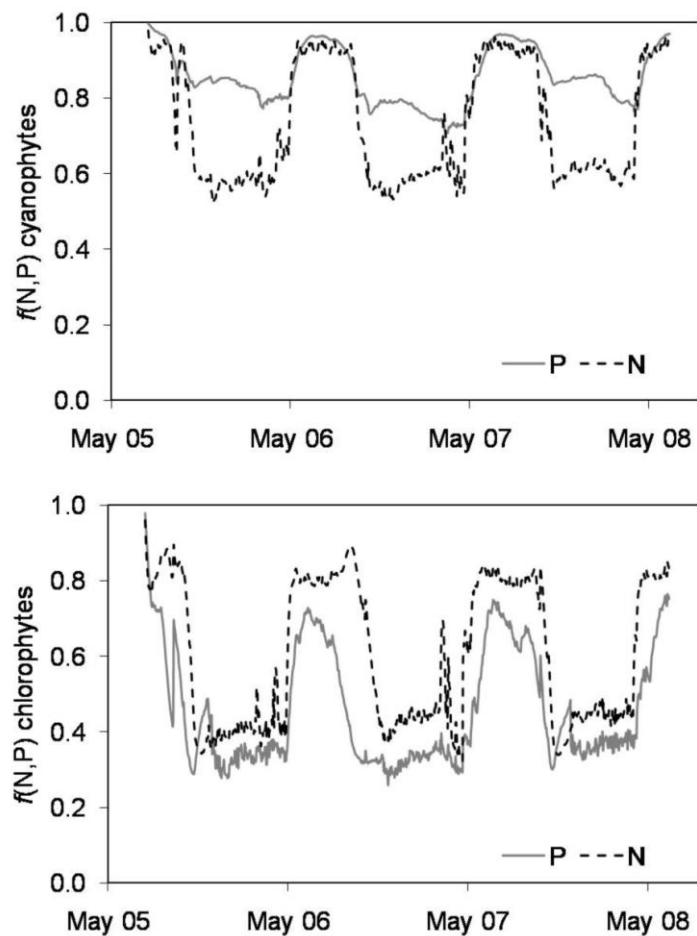
Figure 5.7: Limitation function (*f*) of phosphorus (P) and nitrogen (N) for cyanophytes and chlorophytes for the base scenario of July 2005 - June 2008.

Nutrient loading reduction scenarios

Model simulations show that reducing N and/or P loading results in the expected decrease in annual average water column concentrations of N and P, respectively but at a lower relative rate than the corresponding percentage of reduction in external and/or internal loading (Figure 5.8). Reducing external loading was generally less effective in reducing water column TP, TN and chl *a* concentrations relative to an equivalent reduction in internal loading. Generally, chl *a* concentrations decreased more as a response to a given percentage loading reduction of N compared with P reduction. Not surprisingly, a combined reduction of external and internal loading for both N and P was most effective in reducing annual average water column concentrations of TP, TN and chl *a*.

Annual average TP concentrations in Lake Okaro generally remained in the eutrophic to supertrophic range, according to the TLI value for TP ($6.0 > TL_{TP} > 5.0$; Burns *et al.*, 1999), until P_{comb} was reduced by 90% (Figure 5.6), when the index ($3.0 < TL_{TP} < 4.0$) indicated that a mesotrophic state had been attained. Total N concentrations were usually in the eutrophic range according to the TL_{TN}, but fell into a mesotrophic category ($3.0 < TL_{TN} < 4.0$) when N_{int}, N_{comb}, $N+P_{int}$ and $N+P_{comb}$ were reduced by more than 75% (Figure 5.6). Annual average water column concentrations of chl *a* were in the supertrophic range until N_{int}, N_{comb}, $N+P_{int}$ and $N+P_{comb}$ and P_{comb} were reduced by more than 75% and TLI values for chl *a* fell into the eutrophic range ($5.0 > TL_{Chla} > 4.0$). Water quality indices were naturally reduced most in scenarios when N and P loadings were reduced simultaneously. Generally, reduction in N loading was more effective in increasing Secchi depth transparency than P loading reduction. TLI values were generally in the eutrophic range for all scenarios except for $N+P_{comb}$ at 90%, when the TLI corresponded to a mesotrophic state ($3.0 < TLI < 4.0$; Figure 5.9). Reduced N+P internal loading was more effective in reducing TLI values than the equivalent fractional reduction of external N+P loading alone.
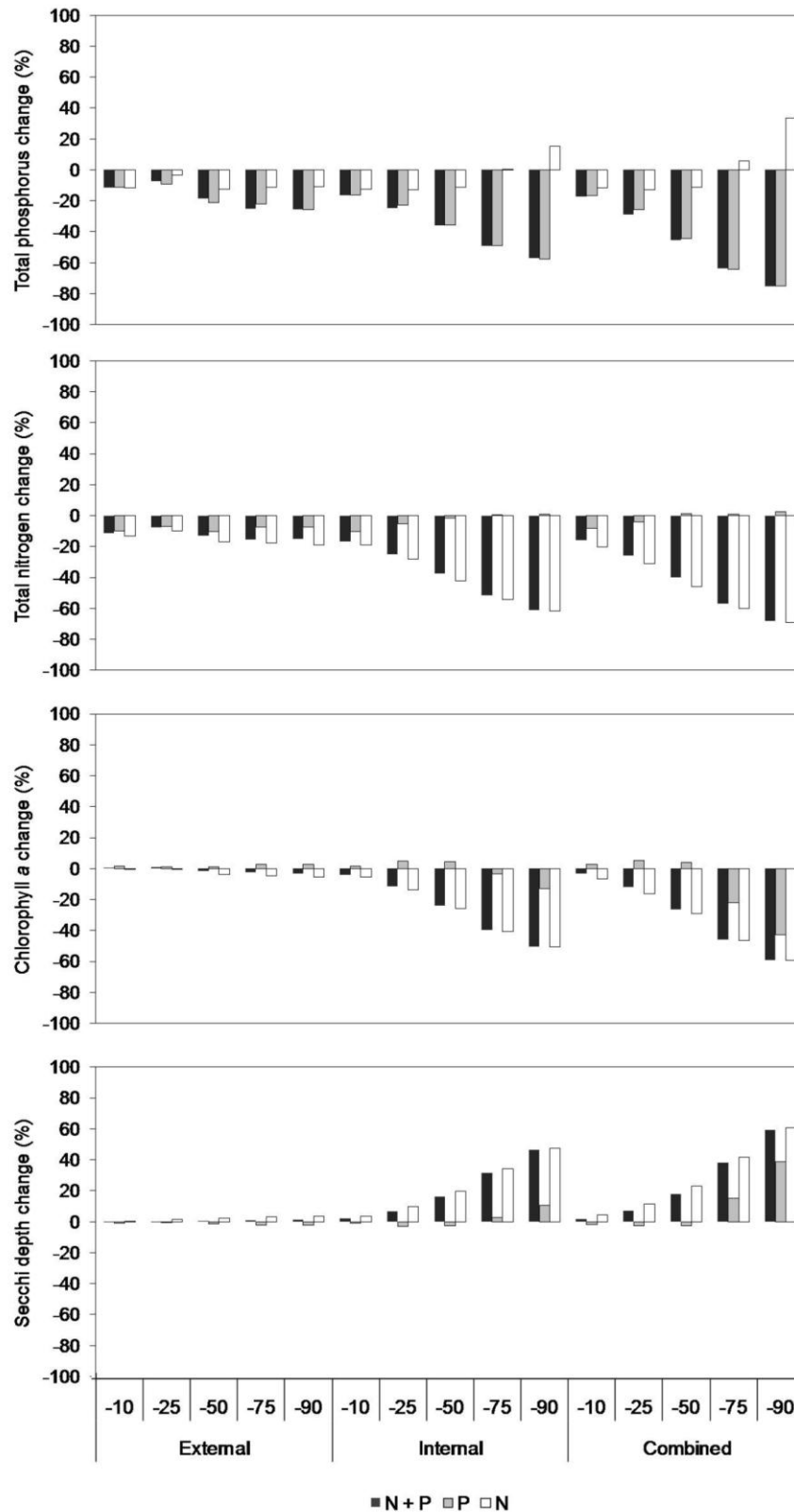
Figure 5.8: Mean relative simulated change of annual average total phosphorus, total nitrogen and chlorophyll *a* concentrations and Secchi depth as a response to reductions in external loading, internal loading, and a combined reduction of both external and internal loading (-10%, -25%, -50%, -75%, and -90%) compared to the base scenario of July 2005 - June 2008.

Effect of nutrient load reductions on nutrient limitation

The proportion of nutrient limitation over the simulation period for cyanophytes changed from almost entirely N-limited to almost entirely P-limited in scenarios when P_{int} and P_{comb} exceeded a 75% reduction (Figure 5.10). Nitrogen limitation of cyanophytes predominated in all scenarios when only N or N+P was reduced. A change in nutrient limitation from almost exclusively P-limited to almost entirely N-limited was observed for chlorophytes in scenarios when external and/or internal N loading was reduced by more than 50%. Chlorophytes were predominantly P-limited for all other scenarios. The proportion of the total chl *a* concentration represented by cyanophytes appeared to decrease with increasing N loading reduction whereas the proportion of cyanophytes increased with increasing P loading reduction.
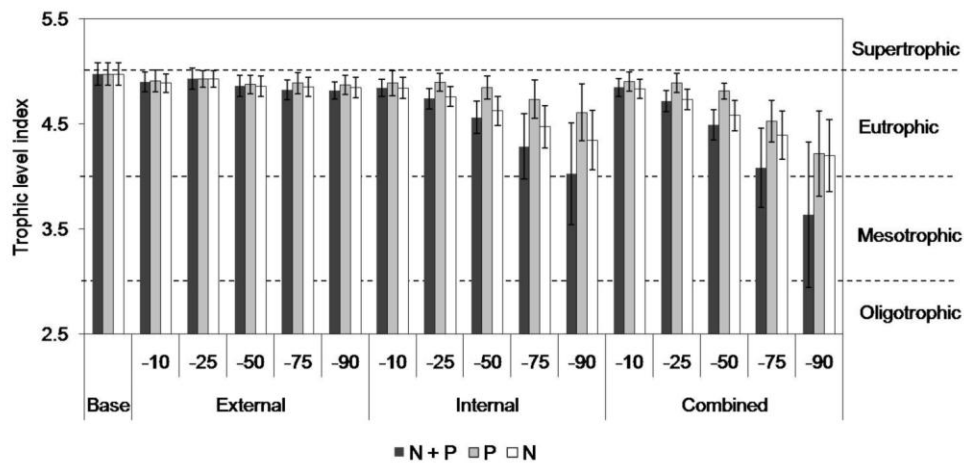
Figure 5.9: Simulated Trophic Level Index values with seasonal variation represented by ± one standard deviation compared with the base scenario (July 2005 - June 2008) for simultaneous reduction of both nitrogen (N) and phosphorus (P) and individual reduction of P or N for reductions in external loading, internal loading, and combined reduction of both external and internal loading (-10%, -25%, -50%, -75%, and -90%).
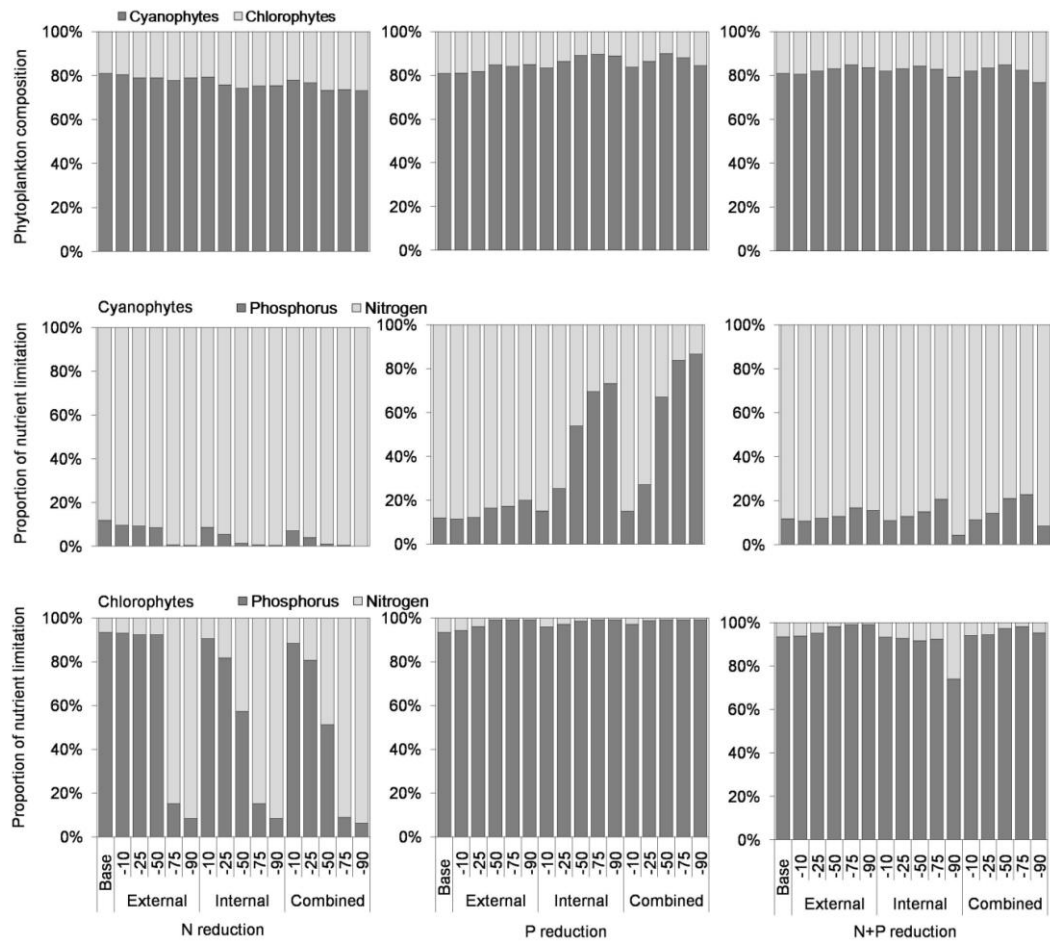
Figure 5.10: Average proportion of phytoplankton composition of total chl *a* concentrations (cyanophytes and chlorophytes), average proportion of nutrient limitation of cyanophytes (N and P), and average proportion of nutrient limitation of chlorophytes phytoplankton (N and P) over the entire simulation period.

5.4 Discussion

In this study, DYRESM-CAEDYM was applied to Lake Okaro to investigate the need for nutrient load reduction to improve the trophic state in the lake, which was represented by the TLI. Previously, it has been suggested that a simultaneous reduction of both N and P loads would be more successful in reducing phytoplankton than the reduction of one of these nutrients alone (Lewis & Wurtsbaugh, 2008). This strategy appears to be suitable for Lake Okaro, where a combined N+P loading reduction resulted in a greater decrease of TLI values than the equivalent reduction of either N or P loading. This study also shows that P loading reductions have to be substantial to induce dominance of P-limitation to compensate for high background levels of P that saturate demand.

Model performance and constraints

There were occasionally higher surface concentrations of phosphate in the winter mixed period in the model simulation compared with field data, mostly during the calibration period. This could be partially an effect of the relatively simplistic process representation of sediment nutrient dynamics in CAEDYM. The current version of the model regulates the sediment phosphate release according to concentrations of dissolved oxygen and nitrate, and temperature in the overlying water layer. Thus changes in sediment P release in the model reflect only the relevant water layer variables and not any changes in sediment P content (e.g. Hupfer & Lewandowski, 2008) or related processes, such as the time scales on which P is resupplied from sediments at depths of up to 20 cm (Søndergaard *et al.*, 2003). A further confounding factor is the fact that the simulation falls within a period when several different restoration procedures were implemented in Lake Okaro, commencing in 2003 (Environment Bay of Plenty, 2006). Changes in external nutrient loading will likely feedback to sediment nutrient releases, tending towards a new equilibrium between external and internal loading (Søndergaard *et al.*, 2003). As there is no such feedback on the bottom sediment composition in the current version of CAEDYM, the scenarios with combined nutrient reduction (i.e. external and internal loading) may perhaps best reflect this feedback, but without demonstrating the typical period of 10-15 years that could be expected before small to medium sized lakes reach a new equilibrium state in response to reduced loading (Jeppesen *et al.*, 2005). The inclusion of a dynamic response of sediment nutrient releases to changes in sedimentation in the water column after reduced external loading as well as sediment diagenetic processes could, however, provide a better understanding of the temporal variability of sediment nutrient releases.

Conceptual simplifications of the system being modelled are unavoidable (Harris, 1994) and it is important to acknowledge the effect of these simplifications on the outcome of various model scenarios. Data for fish, submerged macrophytes, and zooplankton were not available for the simulation period and were not included in the conceptual model. The impact of major nutrient loading changes on phytoplankton community structure can be substantial (Schindler, 2006) and food webs can undergo significant shifts in their trophic cascade by, for example, increased zooplankton grazing pressure on smaller

phytoplankton following nutrient load reductions (Carpenter, 2003; Jeppesen *et al.*, 2005) that may not be represented adequately with a dynamic ecosystem model such as DYRESM-CAEDYM (Trolle *et al.*, 2008). Therefore, the phytoplankton response to reduced nutrient loading may be underestimated in the model as no higher trophic levels and sediment diagenetic processes were included in the conceptual model.

A further limitation of most ecosystem models is their inability to predict ecosystem changes that may occur due to the introduction of a new species. For example, DYRESM-CAEDYM did not reproduce to any great extent the chl *a* peak observed in December 2004. During this period there was a dense (> 70 000 cells ml^{-1}) mono-specific bloom of *Anabaena planktonica* present in Lake Okaro. This species was first detected in New Zealand and in Lake Okaro in 2000, and has since spread rapidly throughout the North Island of N.Z. (Wood *et al.*, 2005, Environment Bay of Plenty, unpub. data). It has been reported to dominate the phytoplankton community for short periods within 2-3 years of its introduction into a water body (Ryan *et al.*, 2003, Wood, pers. comm., 2009), after which time its dominance tend to decline, supposedly due to a natural response and adaptation of the overall lake ecosystem to a new invasive species. Although, *Anabaena planktonica* still occurs in Lake Okaro, blooms of the magnitude reported in December 2004 are not a common occurrence (Environment Bay of Plenty, unpub. data).

The inclusion of an additional phytoplankton group in the conceptual model could not be justified based on the lack of differentiation of total chl *a* concentrations to taxonomic level. However, different phytoplankton groups or even different species within groups (e.g. *Microcystis* vs. *Anabaena* amongst the cyanobacteria) may have different nutrient requirements. As *Anabaena planktonica* is heterocystous and can potentially supplement nitrogen requirements through N-fixation when inorganic nitrogen concentrations are low, the model in its present form, with cyanophytes not assigned an N-fixation function, should be re-examined in future model development. This limitation may have had subsidiary effects, for example, compromising ability to accurately reproduce N concentrations in the water column because N-fixation may account for modest proportions (6 - 82%) of total N loads to a lake (Oliver & Ganf, 2000).

The question of whether dynamic, process based ecosystem models have the desired predictive power to forecast the future (e.g. restoration scenarios) has been discussed previously (Flynn, 2005; Jakeman *et al.*, 2006). Validating a calibrated model against an independent data set to determine if the model not only fits measured data but also functions adequately (i.e. adequate response of trophic structure) is often thought to be a satisfactory performance evaluation (Arhonditsis & Brett, 2004; Robson *et al.*, 2008). However, even validation cases are only applicable to those conditions under which the model is tested and consistent with the modelling objectives (Power, 1993; Rykiel, 1996). Therefore, the predictions presented in this study should be viewed with some caution, in particular with regards to a potential new arrival of phytoplankton species which can out-compete all other phytoplankton.

The implications of model scenarios for lake restoration

The model simulations indicate that water column TN, TP and chl *a* concentrations change little with a reduction in external loading compared with internal loading. A modelling study of eutrophic Lake Rotorua by Burger *et al.* (2007a) also found that reducing external loading had only a minor impact on chl *a* concentrations compared with the same percentage reduction in internal loading. Direct comparisons between percentage reduction of external and internal nutrient loading can, however, be somewhat misleading. External nutrient loading includes various fractions of dissolved and particulate organic and inorganic nutrients which may not be immediately available for phytoplankton and may also be partially lost from the system due to settling of organic matter. By contrast, internal loading in this model comprises entirely of dissolved inorganic nutrient species.

Reductions in external N loading were more effective than for P in reducing the TLI, reflecting the predominance of N-limitation of cyanobacteria and their ability for luxury P uptake (Lean *et al.*, 1987). The control of external N loading, however, may be more easily achieved than control of P loading. Constructed wetlands, for example, are generally effective in reducing N loading via denitrification, whereas P retention can be relatively short-lived and the saturation of the soil substrate of the wetland can potentially lead to an increase in

P loading (Fink & Mitch, 2004). The management of nutrient loads is also a sensitive issue due to the national importance of pastoral farming to the New Zealand economy. For the Te Arawa lakes in the Volcanic Plateau, which is an area that contains P-rich volcanic ash in the soil profile, a considerable portion of N inputs to the lakes originates from diffuse sources and relates to patches created by animal excreta and urine which are driven by ongoing intensification of agriculture involving increases in N fertiliser additions (White *et al.*, 1985; Hamilton, 2005; Parliamentary Commissioner for the Environment, 2004).

An increase in N-limitation as a result of N loading reduction could promote dominance of N-fixing cyanobacteria (Smith, 1983; Howarth *et al.*, 1988; Schindler *et al.*, 2008) resulting in cyanobacterial blooms, especially when there are high levels of inorganic P (e.g. in Lake Okaro). Schindler *et al.* (2008), for example, indicated with a 37-year experiment of managing nutrient inputs to a single lake, that the control of N loading alone could promote eutrophication. It appears to be counter-intuitive to reduce N loading alone, considering the risk of promoting N-fixing cyanobacteria in an ecosystem which is already eutrophic. However, while reducing P loading alone has been shown to result in major reductions in chl *a* concentrations in a series of Danish lakes (Jeppesen *et al.*, 2007), it may be difficult to achieve P-limitation in many lakes of the central North Island of New Zealand, which have a tendency to be N-limited or co-limited by both N and P due to P-rich volcanic soils (White *et al.*, 1985; Burger *et al.*, 2007b). This trend towards N-limitation may be exacerbated by the dominance of cyanobacteria with the ability for luxury P uptake (Reynolds, 2006). The status and strength of nutrient limitation in Lake Okaro was shown to vary seasonally for both of the simulated phytoplankton groups (i.e. cyanophytes and chlorophytes). This suggests that a dual control of N and P would be more successful in reducing phytoplankton growth while compensating for any shortcomings of reducing N or P individually. Furthermore, the control of N and P appears on the basis of my model results, to be more effective in reducing phytoplankton biomass than for N or P alone, tending to affirm a N+P control paradigm (Lewis & Wurtsbaugh, 2008).

The model application to Lake Okaro suggests through a series of nutrient loading reduction scenarios that the lake will remain eutrophic until external and internal nutrient loadings of both N and P are reduced by more than 75%.

According to the model, N loading reduction may be more successful in improving water quality measured by the TLI, than reducing P loading alone. Evaluation of the nutrient limitation status of the simulated phytoplankton groups revealed that N is a major limiting factor for cyanobacteria growth while P limitation of this dominant phytoplankton group would require severe reductions in P loadings.

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6 Does sediment capping have post-application effects on zooplankton and phytoplankton?

6.1 Introduction

Internal loading of phosphorus (P) and nitrogen (N) can contribute significantly to nutrient loads entering the water column of lakes (Søndergaard *et al.*, 2003). Such inputs can delay the improvement of water quality following restoration measures (Jeppesen *et al.*, 2005). Several methods have therefore been developed to reduce P in both the water column and bottom sediments of lakes (Klapper, 2003). Flocculation or P precipitation with iron or aluminium salts (alum) is the most common method to decrease P content in the water column of lakes with long retention times (Cooke *et al.*, 1993). Alum can form a P-adsorbing floc cap on the surface layer of sediments, or alternatively mixes within the sediments, where it continues to reduce P release to the overlying water (Cooke *et al.*, 1993; Rydin *et al.*, 2000; Pilgrim *et al.*, 2007). Another technique to address internal loading is sediment capping, for which the aim is to prevent nutrients (or other contaminants) being released from the sediments (Förstner & Apitz, 2007). In this respect, sand, mineral soils and clay minerals are applied to the lake as passive capping agents to physically seal off affected areas of the lake bottom sediment (Klapper, 2003). Sediment capping agents can also be chemically active P-inactivation agents designed to permanently bind P. These may be naturally occurring clay minerals modified to enhance P uptake capacity (Hickey & Gibbs, 2009).

Despite the frequent use of *in situ* capping (e.g. Yamada *et al.*, 1987; Robb *et al.*, 2003; Berg *et al.*, 2004), post-application assessment has typically focused on reductions in the concentration of the targeted substance (e.g. P). Rarely have there been investigations of the potential undesirable short term effects on, for example, plankton species composition. Naturally, species composition of phytoplankton can be influenced by a number of factors such as mixing regime,

light climate and nutrient status (Ryan *et al.*, 2006). As nutrient concentrations are reduced after in-lake restoration, potentially resulting in reduced dominance of cyanobacteria (Reynolds, 1998), this could lead to improved food quality for zooplankton (Gulati & Demott 1997; Duggan *et al.*, 2002a). The lack of recognition of the potential direct effects of sediment capping materials on plankton community structure is surprising, however, given some of the known acute and chronic toxic effects of flocculants such as alum, which may be exacerbated by excessive dose rates, poor application timing or inappropriate environmental conditions (e.g. low pH; Lamb & Bailey, 1981; Gensemer & Playle, 1999). For example, applications of the flocculent alum have been shown to lead to short term reductions in zooplankton abundance, biomass and species richness in Newman Lake, Washington, USA (Schumaker *et al.*, 1993). An alum application in Lake Okaro, New Zealand, led to increased ammonium concentrations in the water column, possibly as a result of zooplankton mortality (Paul *et al.*, 2008). Randall *et al.* (1999) tested the acute toxicity of iron salts on daphnid zooplankton in a laboratory scale study and found that the presence of particulate iron caused increased mortalities and reduced the number of broods per female.

The deposition of large volumes of sediment into a lake might be expected to affect zooplankton and phytoplankton species composition immediately following application in several ways. For example, experimental studies on the impacts of inorganic sediments have shown that with increasing turbidity there are reductions in the standing stocks of daphnid zooplankton (Hart, 1986) and reduced zooplankton feeding rates (Kirk, 1991). Consequently, lakes with high suspended sediment loads commonly have a limited richness of zooplankton species (e.g. Duggan *et al.*, 2002a). Robb *et al.* (2003) suggested that an increase in phytoplankton growth rates following treatment with the capping agent Phoslock™ at sites in the Swan-Canning Estuary, Australia, may have been caused by a loss of grazers (i.e. zooplankton). Finally, burial of phytoplankton cysts and zooplankton diapausing eggs by the capping agent also have the potential to reduce plankton recruitment following application of these agents. With the basal positions of phytoplankton and zooplankton in aquatic food webs, alterations in these components may alter the energy flow to higher trophic levels and have ecosystem-wide effects.

In New Zealand, the water quality of many of the Te Arawa Lakes of the Rotorua region has declined significantly, coinciding with the development of surrounding catchments for agriculture (McColl & Hughes, 1981; Hamilton, 2005). Due to high external nutrient loading over many decades, the bottom sediments have become enriched with organic matter, and consequently several of the lakes have high internal nutrient loadings (White *et al.*, 1978; Burger *et al.*, 2007). An aluminium modified zeolite (Z2G1; Blue Pacific Minerals, Matamata, New Zealand) application in Lake Okaro, Rotorua, was carried out in September 2007. Zeolite is a porous alumino-silicate material that has a large specific adsorptive surface area due to a fine porous structure. A naturally occurring zeolite in the Rotorua region has been modified by Scion to significantly improve the nutrient uptake capacity of the natural material. The modified zeolite was applied as a sediment capping agent with the primary purpose of reducing internal loading of phosphate, but also targeting ammonium. I hypothesised that the Z2G1 application may cause significant shifts in species composition of zooplankton and phytoplankton due to burial of resting stages or through interference of zooplankton grazing. Alternatively, Z2G1 might have no effect on plankton species composition due to, for example, a restricted sediment capping target area and the relatively coarse grain size of the application. The objective of this study was to identify any adverse effects of Z2G1 on zooplankton and phytoplankton species composition (e.g. shifts in community structure, including species loss) by comparing the community structure before and after the Z2G1 application in Lake Okaro.

6.2   Materials and Methods

Study site

Lake Okaro (Figure 6.1) is a small (0.32 km^2), shallow lake (18 m max. depth) in the Rotorua region, New Zealand. It is located 27 km south of Rotorua township and was formed c. 800 years ago from a geothermal explosion crater (Lloyd, 1959). The inflows to the lake are two unnamed streams that enter from the north-west. Both have been diverted through a 2.3 ha constructed wetland since 2006 to reduce external nutrient loads (Tanner *et al.*, 2007). The Haumi Stream in

the south-east of the lake is the only outflow (Forsyth *et al.*, 1988). The catchment area (3.89 km^2) is now mostly used for dairy production. Lake Okaro has been eutrophic since the early 1960s (Jolly, 1977) and regular cyanobacterial blooms have persisted to this point in time (Forsyth *et al.*, 1988; Paul *et al.*, 2008). Z2G1 was applied between 25 and 28 September 2007. A total of 110 tonnes of the material (grain size 1 – 3 mm) was applied over the water surface, corresponding to the area where lake depths are greater than 5 m. This was equivalent to the 0.2 km^2 area of lakebed above which the hypolimnetic waters become anoxic during the seasonal stratification period of c. 8 months in this warm monomictic lake.

Sampling

Zooplankton samples were collected in duplicate using a 10 L Schindler-Patalas trap at site A (Figure 6.1) from 0 m and 9 m depths. Samples were taken monthly (26 January 2007 – 19 June 2008) and weekly two weeks before and after the Z2G1 application. Water from the trap was passed through a 40 μm mesh filter, and the retained zooplankton were preserved in 50% ethanol (final concentration). For enumeration, samples were passed through a 40 μm mesh to remove ethanol and to attain a final known volume of 30 and 40 mL depending on the density of algae. Samples were enumerated in 5 mL aliquots in a gridded Perspex tray until at least 300 counts were obtained, or the entire sample was enumerated. Species were identified using standard guides (e.g. Chapman & Lewis, 1976; Shiel, 1995).

Phytoplankton samples were collected using a 10 L Schindler-Patalas trap at site A (Figure 6.1) from 0 m and 9 m depths, and transferred to 150 mL polycarbonate jars. Samples were collected from the same days and depths as the zooplankton samples. Samples were preserved using Lugol's iodine solution and stored in the dark until analysis. Phytoplankton cell counts were carried out on settled samples in Utermöhl chambers (Utermöhl, 1958) using keys and descriptions from Prescott (1978), Cox (1996), John *et al.* (2003), and Baker & Fabbro (1999). Depending on cell densities, 1 to 3 mL aliquots were settled in the chambers and enumerated at 200 to 400x magnification.
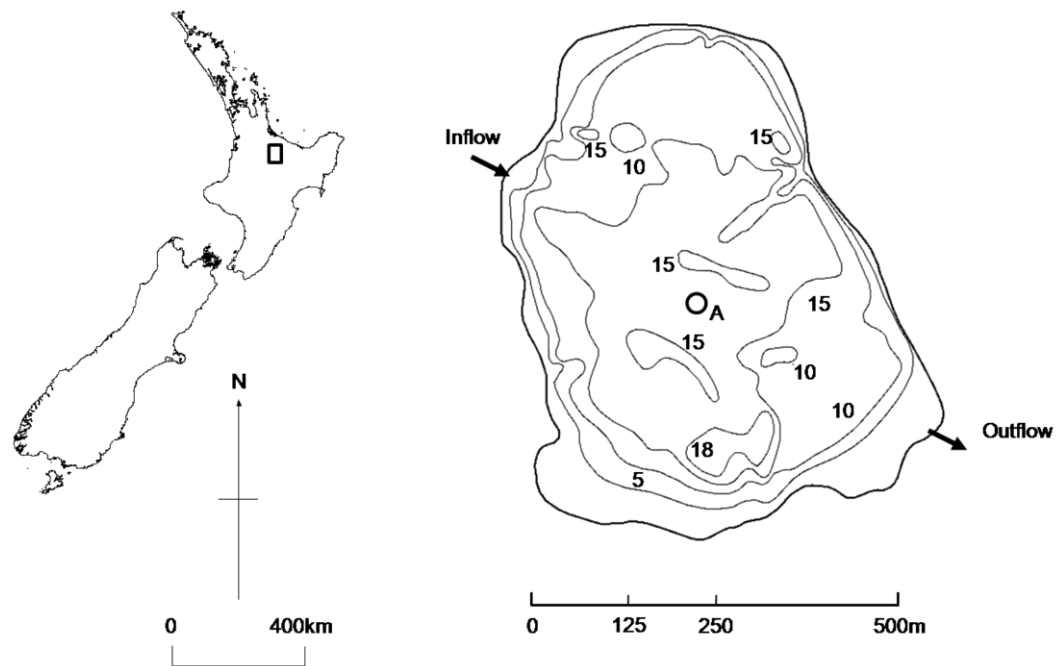
Figure 6.1: Map of New Zealand and of Lake Okaro showing depth contours 5 m, 10 m, 15 m, and 18 m and location of lake sampling station.

Analytical methods

Non-metric Multidimensional Scaling (MDS) and Analysis of Similarities (ANOSIM) were used to detect patterns in species composition of both zooplankton and phytoplankton at each depth, and to test for differences before and after the Z2G1 application. MDS was performed on a similarity matrix based on the Bray-Curtis similarity coefficient calculated on fourth-root transformed abundance data of dominant taxa. MDS builds a 2-D "map" based on the similarities among samples as defined by the similarity matrix. A stress value is provided as a measure of the goodness of the map's fit relative to the similarity matrix. Phytoplankton and zooplankton were considered dominant if they comprised >5% of the total abundance on any date, for either of the depth combinations, over the study period. The fourth-root transformation was chosen to reduce any undue influence of highly abundant community members. To determine whether changes in taxonomic composition before and after the Z2G1 application were significant, I applied ANOSIM to the similarity matrix underlying the MDS ordination. ANOSIM is a non-parametric permutation test to examine a priori hypotheses. Sample periods were split into two groups for testing; before and after application (January 2007–September 2007 and October

2007–June 2008). ANOSIM provides a measure of dissimilarity of groups of samples in the form of an R-statistic that lies between 0 and 1; values close to 1 imply the groups are dissimilar while those approaching zero are very similar. Additionally, I tested for the influence of season on community composition relative to the influence of Z2G1, with sample groups divided seasonally into summer (December-February), autumn (March-May), winter (June-August) and spring (September-November). I adjusted the acceptable P-value (α=0.05) using a Dunn-Šidák correction to allow for the non-independence of these tests. MDS and ANOSIM were performed using the PRIMER 6 statistical software package (PRIMER 6.1.6, Plymouth Marine Laboratory).

6.3   Results

Zooplankton dynamics

Amongst the zooplankton rotifers were numerically dominant over crustaceans during the study (Figure 6.2). Nine species comprised greater than 5% of the total abundance on any date (Figure 6.2). The dominant crustacean *Bosmina meridionalis* and rotifers *Pompholyx sulcata*, *Keratella cochlearis* and *Polyarthra dolichoptera* were generally found to have highest abundances in the surface waters when the lake was mixed (peaking in July), although they also showed peaks in abundance in the 9 m samples at other times (typically in summer). The calanoid copepod *Calamoecia lucasi* and rotifer *Trichocerca similis* were most abundant in winter and spring (June to November). *Hexarthra intermedia* and *Filinia longiseta* were most abundant during summer and autumn (December to May), while *Filinia novaezealandiae* had short-lived peaks of abundance in February 2007 and December 2007 at 9 m only. Overall, abundance peaks were more predictable in the surface waters than at 9 m. The application of Z2G1 did not appear to alter the dynamics of any of the dominant species.

Phytoplankton dynamics

Twenty-one phytoplankton species were found to comprise greater than 5% of any sample over the entire study period. The dominant species that comprised

greater than 10% of any samples are presented in Figure 6.3. *Fragilaria crotonensis* was dominant during summer months (February to March) at depths 0 and 9 m. *Asterionella formosa* and *Microcystis aeruginosa* were most abundant at the end of the stratification period (May to June). *Anabaena spiroides* and *Dictyosphaerium sp.* had peaks in abundance during spring (September to October) but were almost absent for the remainder of the study period. *Staurastrum cingulum* varied little throughout the study period but with a peak in the 9 m sample in February 2007. *Oocystis sp.* and *Pseudanabaena limnetica* were most abundant during October 2007. *Microcystis flos-aquae* showed highest abundance during summer 2007 (January to May) but was often close to detection limits (< 10 planktonic units mL^{-1}) during 2008. Green algae were the dominant taxonomic group during summer (July to January), representing up to 90% of total cell counts at 0 and 9 m depth, followed by Cyanobacteria, Bacillariophyta, Eulenophyta, and Cryptophyta. The application of Z2G1 did not appear to alter the abundance of any of the dominant species or taxonomic groups.
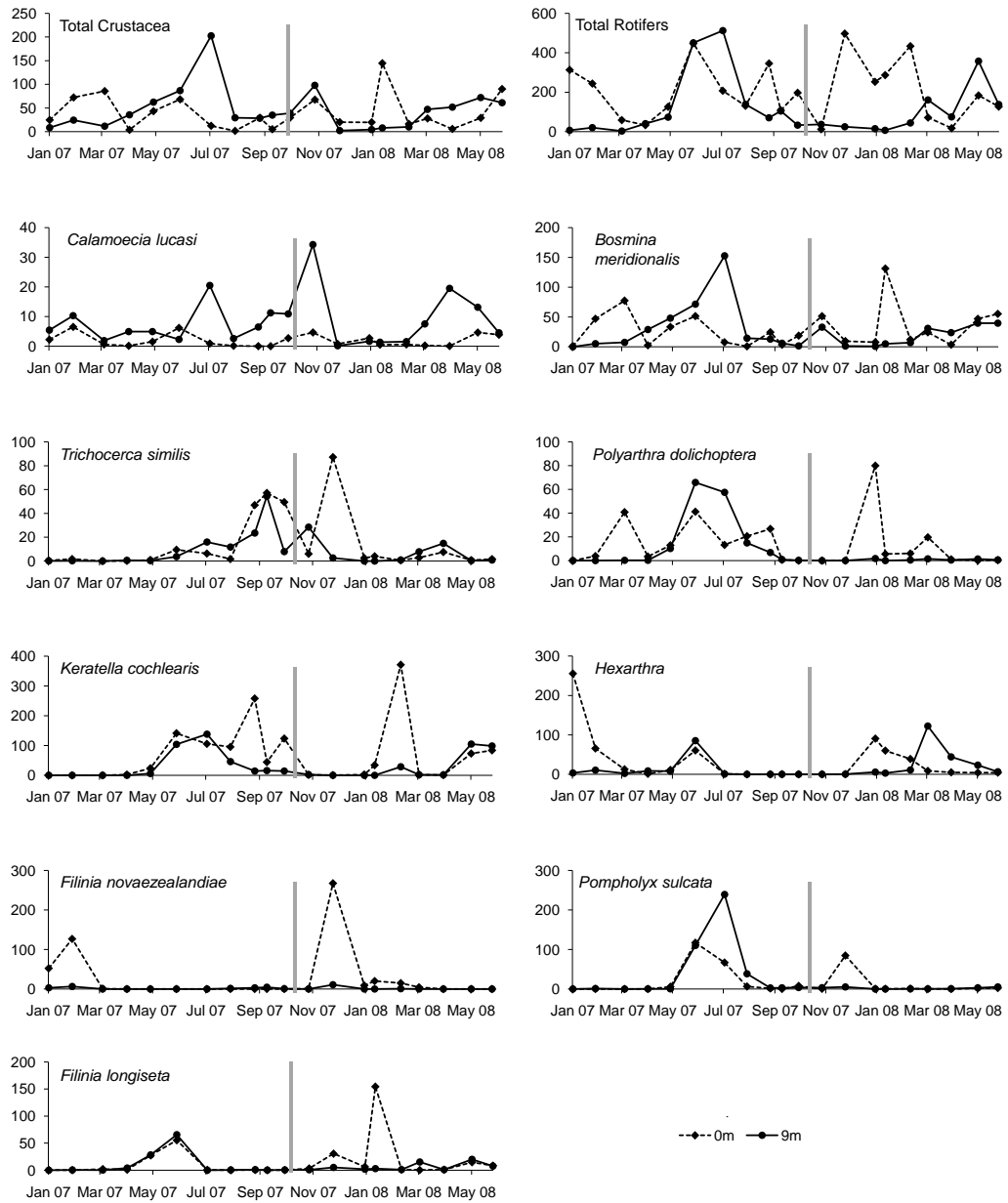
Figure 6.2: Temporal and spatial distribution of total crustaceans and total rotifers and abundant zooplankton species comprising greater than 5% of any sample (numbers L^{-1}). Shaded area represents days of modified zeolite application.
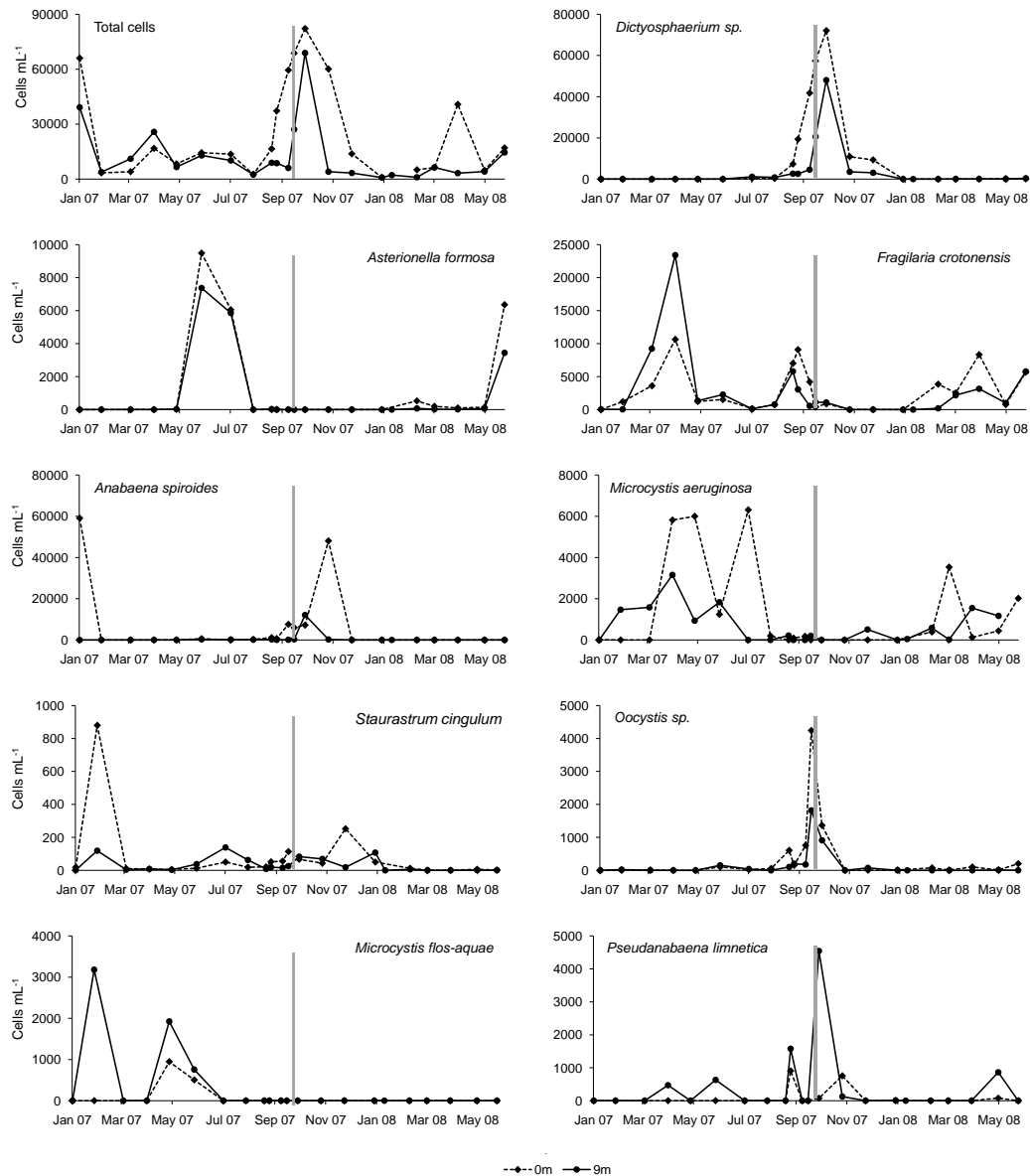
Figure 6.3: Temporal and spatial distributions of total phytoplankton concentrations (cells mL^{-1}) and abundant phytoplankton species comprising greater than 10% on most sampling days. Shaded area represents days of modified zeolite application.

Community analyses

The low stress values of the MDS plots (Figure 6.4) indicate that the ordinations provide good representations of the relationships among samples (Clarke & Warrick, 2001). In all plots a strong seasonal influence is apparent. Samples for each season were typically closely associated with one another, regardless of year, while there was a reasonable separation of samples from different seasons. For example, in the ordination of zooplankton at 0 m, summer (December-February) samples are located in the top left region of the ordination, autumn samples in the

bottom left, and winter and spring samples in the bottom right. Samples from equivalent times in 2007 and 2008 were typically found closely associated in the MDS plot (e.g. summer and autumn samples), despite the application of Z2G1 between these dates.

Results from ANOSIM supported these findings (Table 6.1). All of the analyses of zooplankton and phytoplankton communities showed composition to be statistically indistinguishable before and after the Z2G1 application ($P > 0.05$). However, all of the analyses showed statistically significant differences among seasons (all $P < 0.01$), indicating seasonal variation in plankton composition far outweighed any variation caused by Z2G1 application.

Table 6.1: Results (R and P values) from ANOSIM tests for differences in zooplankton and phytoplankton community composition before and after application of Z2G1 and for seasonal change.

Taxon	Treatment	0 m	9 m
Zooplankton	Application before/after	0.003 (0.67)	0.037 (0.41)
	Season	0.406 (<0.01)	0.518 (<0.01)
Phytoplankton	Application before/after	0.090 (0.16)	0.043 (0.36)
	Season	0.664 (<0.01)	0.447 (<0.01)
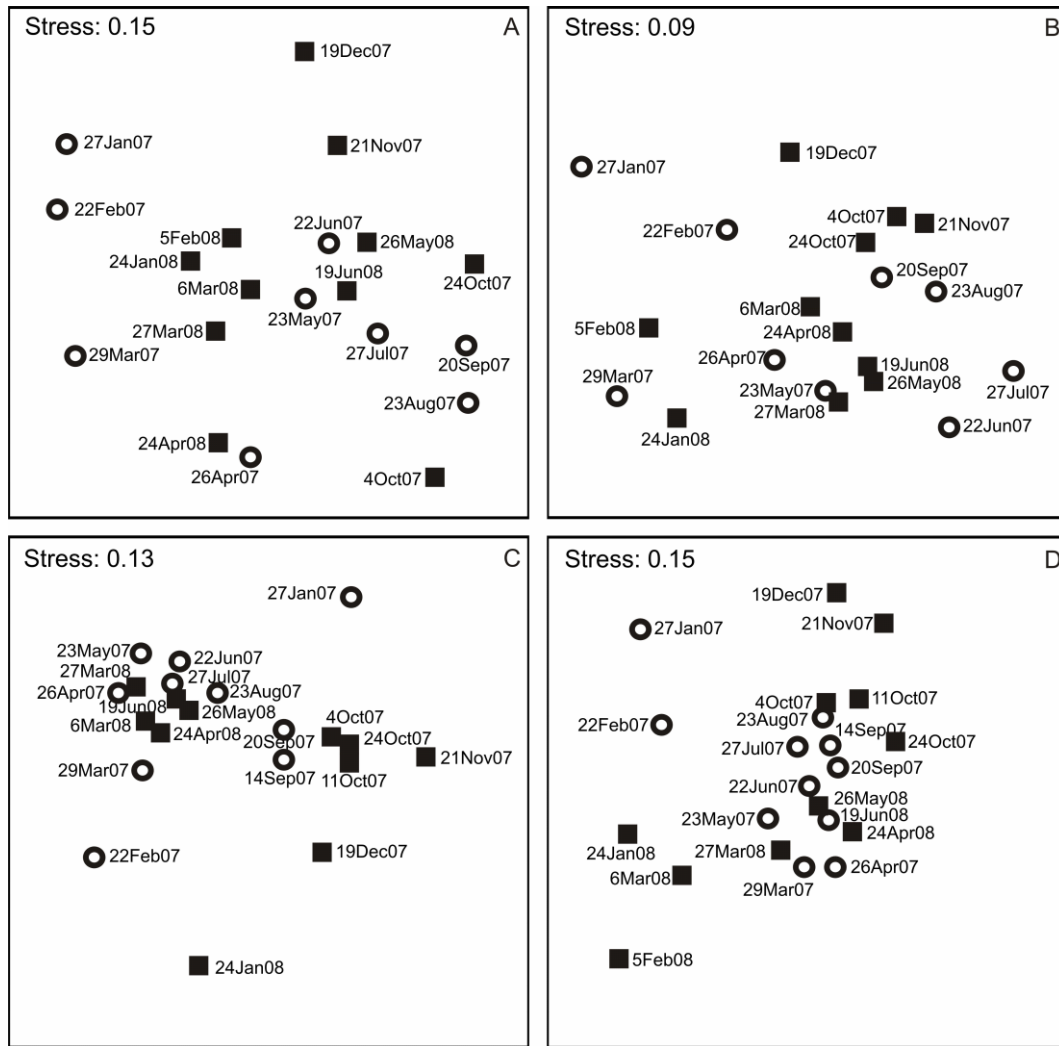
Figure 6.4: Multidimensional scaling (MDS) ordinations of sampling days based on abundant taxa with A: zooplankton at 0 m, B: zooplankton at 9 m, C: phytoplankton at 0 m, and D: phytoplankton at 9 m. Triangles signify dates before application of Z2G1, while inverted triangles signify dates post-application.

6.4   Discussion

There appeared to be no discernible effect of the Z2G1 application in Lake Okaro on zooplankton or phytoplankton composition in the days or months immediately following its application. Seasonally induced changes were the over-riding factor determining plankton composition during my study. The lack of effects on plankton species composition observed in the Z2G1 application to Lake Okaro indicates that it may have fewer undesirable direct (e.g. from free Al^{3+}) and indirect (e.g. from low pH) effects on biota over other methods for reducing internal nutrient loadings (e.g. where alum application is inappropriate, because of

low pH), providing it is sufficiently efficacious in removing P. Major reasons for a lack of undesirable impacts may include the coarse particle sizes (1-3 mm) of the Z2G1 material and the limited area of the lake where it was applied.

Sediment particle size is a significant factor influencing algal ingestion rates of zooplankton, and the large size of particles used in the current Z2G1 application may have reduced any negative effects on zooplankton grazing. Kirk (1991) demonstrated that coarse clay (mean particle size of 1 µm) can significantly reduce the feeding rate of *Daphnia*. In Lake Okaro, however, the sediment capping agent was applied as a coarse material (grain size 1-3 mm), larger than the size of particles ingested by zooplankton (or indeed of most zooplankton themselves). The increased settling rates of larger particles (Gibbs & Özkundakci, Appendix I) would also minimise any potential risk for filter feeders. However, finer particle sizes are known to achieve a more complete coverage of sediment by capping agents and to have higher efficiency of P removal (Gibbs & Özkundakci, Appendix I), and may therefore be preferred for future applications. Choice of the material and its size must therefore be made with caution, considering potential effects on filter feeding zooplankton; finer particles could lead to adverse food web or water quality effects, such as those observed for some alum applications (e.g. Schumaker *et al.*, 1993; Paul *et al.*, 2008) and for Phoslock™ (Robb *et al.*, 2003).

Burial of zooplankton eggs was also likely not a problem during the current Z2G1 application. Zooplankton diapausing eggs are less successful at hatching when buried in sediments than when exposed to open water (e.g. Vandekerkhove *et al.*, 2004; Bailey *et al.*, 2005), and burial might therefore prevent a high proportion of emergence. However, even if zooplankton were unable to emerge from below the sediment that was capped, the area of the application was designed to occur only where water overlying sediments becomes anoxic, leaving significant areas that should remain unaffected by the application. The abundances of zooplankton diapausing eggs in the sediments of Lake Okaro are known to be extremely high (Duggan *et al.*, 2002b), which will also ensure high numbers are able to emerge. Visual inspection of the sediment showed, however, that small quantities of the capping agent had settled out in non-targeted areas (i.e. outside of the 0.2 km^2 area). This has implications on the application of Z2G1. Dose rate is likely an important factor influencing the extent of bottom

coverage. While the current dose rate of Z2G1 in Lake Okaro (350 g m^{-2}) appeared to have little influence in non-target areas, higher dose rates may bury such areas to a greater extent, potentially reducing hatching rates of zooplankton in the following months. Accurate placement of the material is therefore important to achieve high efficacy, and will also minimise the risk to zooplankton diapausing eggs.

Phytoplankton communities also did not change in composition with the addition of Z2G1 in the time period considered. These species are unlikely to be influenced directly by Z2G1application, although a long-term change could be expected with reduction in P levels. For example, Lake Okaro underwent a shift in phytoplankton community structure in the early 1960s, from no observed cyanobacteria (Jolly, 1977) to persistent cyanobacteria blooms (Vincent, 1987; Paul *et al.*, 2008). Ideally, the long-term effects of lake restoration at Lake Okaro, including Z2G1 application, would result in a return to pre-eutrophication phytoplankton communities. The most probable cause of any effect on phytoplankton community structure, had it occurred, would have been indirectly through release from zooplankton grazing if these had been affected, as well as from changes in availability of nutrients. In the long term, zooplankton are likely to change in composition with reduction of nutrient and algal levels. Duggan *et al.* (2002a), for example, found clear patterns in zooplankton community composition associated with trophic state in New Zealand lakes. If Z2G1 is successful in reducing nutrient concentrations in Lake Okaro, then a lower incidence of cyanobacteria can be expected accompanied by a shift in zooplankton species composition.

6.5   Conclusions

In this study I investigated the impact of sediment capping using a modified zeolite, Z2G1, on zooplankton and phytoplankton community structure in Lake Okaro. The addition of Z2G1 to the surface of the lake for the control of internal nutrient loading resulted in no discernable changes in plankton species composition in the water column in the short term, possibly because the sediment capping agent was applied as a coarse-grained material that settled out of the

water column rapidly. As P-inactivation agents, including Z2G1, can be milled to finer grain sizes, these finer materials require assessment for their effect on plankton, and a hypolimnetic application is recommended to avoid undesirable direct and indirect effects on plankton communities.

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7   Conclusions

7.1   Research summary

Eutrophication is considered to be one the most widespread freshwater pollution problems on a global scale. In most cases, the cause of eutrophication is excess addition of nutrients to water bodies. Generally, it is advisable to decrease the source of nutrients to surface waters by reducing their use as fertilisers or manure in the catchment. However, the reduction of external loadings does not always produce the desired improvement of water quality. Phosphorus (P) has been identified as a key nutrient causing excessive algae growth. The beneficial effects of reductions in external P loading can be offset by P release from bottom sediments into the overlying water column, commonly referred to as internal loading. The P pool responsible for this internal loading has in many cases accumulated for many decades. To disrupt the internal loading, in-lake restoration methods are frequently used concurrently or alternatively to catchment restoration designed to reduce external loading. In this study, the effects were investigated of an intensive catchment and in-lake restoration program on nutrient dynamics and ecosystem response in Lake Okaro, New Zealand. The restoration procedures included a 2.3 ha constructed wetland established in February 2006 and riparian margin protection to reduce external loading, as well as an alum application in December 2003 and sediment capping using a modified-zeolite P-inactivation agent (Z2G1) in September 2008 which was designed to reduce internal loading.

In Chapter 2, the response of water column P concentrations in Lake Okaro to progressive catchment and in-lake restoration methods was analysed over a period of six years (2002-08) which included the period shortly before the restoration program. It was shown that the magnitude of internal P loads in Lake Okaro is comparable to external loads. In terms of total impact, the internal nutrient load has the potential to be as influential on the total phosphorus concentration in the water column as the external loading. Due to the temporal

overlap of different restoration methods in the catchment and in the lake, individual effects of each method could not be determined. Despite a significant reduction in P concentrations in the lake, two numerical trophic level indices, the Trophic State Index (TSI) and the Trophic Level Index (TLI), used to track changes in water quality during the restoration period between 2003 and 2008 indicated only a minor improvement in water quality. The trophic state of Lake Okaro appeared to demonstrate a level of resilience to reduced P loading. This means that an improvement in the trophic state of a eutrophic water body appears to occur at a much lower P loading level than during the degradation phase. Determining the P loading level at which the trophic level will improve remains a major challenge for controlling eutrophication in Lake Okaro.

In Chapter 3, the relative importance of sources and sinks of nitrogen (N) and P concentrations in the hypolimnion were determined using a comprehensive hypolimnetic mass balance model. The model accounted for mineralisation of organic nutrients, nutrient uptake by phytoplankton, nitrification, adsorption or desorption of P onto inorganic suspended solids, and diffusion of dissolved nutrients at the thermocline. This model was also used to determine changes in sediment nutrient fluxes resulting from the whole lake sediment capping trial using Z2G1. It demonstrated the significance of these different processes and their relative contribution to hypolimnetic nutrient fluxes during stratified periods. The findings of this study are important for quantifying *in situ* sediment nutrient releases in monomictic lakes, as a comprehensive array of processes is seldom taken into account when hypolimnetic nutrient accumulation rates are calculated for the purpose of estimating internal loading. The hypolimnetic mass balance model demonstrated that the bottom sediments can act as a source and sink for nutrients during the stratified period, within which there are short intervals of relatively high nutrient releases. Initial releases of P from the sediment after the onset of stratification coincided with anoxic conditions in the hypolimnion, and fit with classical theory of oxidized ferric complexes that are reduced and release previously sorbed P from the iron complex. With ongoing anoxia in the hypolimnion during the stratified period, however, P releases still occurred indicating that Z2G1 did not block sediment P releases completely. In the long-term, these P releases have important implications for the timing and magnitude of in-lake nutrient control measures such as P-inactivation agents that are used to

reduce internal loading. Long-term P releases suggest that results obtained from the short-term laboratory studies (see Appendix I) should be viewed with caution and in a specific context. The debate surrounding the extrapolation of results from small scale experiments to whole ecosystems is not new and this study re-emphasises the need for care when basing management decisions on the results of laboratory experiments.

While the precise reason was not established for the inability of the whole lake application of Z2G1 (Chapter 3) to be as successful as the laboratory study (Appendix I), there may be several possible explanations. A number of processes occurring in the bottom sediments may counteract the stability and thus efficacy of a uniform sediment capping layer. For example, bioturbation, gas ebullition and advection can disturb or bury an intact sediment capping layer and these processes can vary in magnitude between lakes and across trophic gradients. Furthermore, the transformation and degradation of biogenic P into dissolved inorganic P, which in turn is released from the sediment, could provide a more long-term supply of orthophosphate to the water column than has previously been considered. It is therefore recommended that prior to any application of P-inactivation agents, the extent of these processes are assessed and quantified, and the material quantity evaluated appropriately.

Chapter 4 provides an investigation of the source of internal loading in Lake Okaro. Settling seston and the bottom sediments were analysed for organic P using ^{31}P nuclear magnetic resonance (NMR). Organic P was found to be intimately involved in processes that drive internal loading, and the high abundance of various organic P compounds in the bottom sediments of Lake Okaro was identified as an important long-term source of internal P loading. Organic P compounds occur in the environment in chemically diverse forms and organic P speciation is brought about by complex cell synthesis pathways by plants and microorganisms. The effect of removing dissolved inorganic P in the bottom sediments, which may only account for a small fraction of total P, may be negligible when using P-inactivation agents, as it may simply create a different equilibrium between the reactive phosphorus and the other pools of phosphorus that contribute to it. Many in-lake restoration methods, including P-inactivation, aim to reduce the amount of P in its simplest ionic form of dissolved inorganic P, orthophosphate, which is the most bioavailable species, whilst failing to fully

appreciate the relative importance of organic P in lake management. The importance of advancing our knowledge of organic P biogeochemistry is a key factor in understanding the role of P in aquatic ecosystem processes, particularly when considering that in Lake Okaro organic P can contribute more than 60 % of the total extracted P in settling seston and bottom.

In Chapter 5, the one-dimensional hydrodynamic model DYRESM was coupled with the aquatic ecological model CAEDYM to examine the water quality response of Lake Okaro to reduced nutrient loading. Model simulations indicate that reducing internal nutrient loads is more important in decreasing phytoplankton biomass in the surface waters, than external nutrient loads. This was most likely due to prolonged stratification periods in Lake Okaro, which are accompanied by long periods of anoxia in the hypolimnion. However, the effect of reduced internal loading may have been overestimated due to conceptual simplifications in the sediment nutrient release mechanism in the model. Nevertheless, there was a pronounced improvement of trophic state, indicated quantitatively by reductions in the Trophic Level Index (TLI), after reductions in internal load compared with the same relative reduction in external load. A critical evaluation of the phytoplankton nutrient limitation status and its response to reduced internal and external loading of N and P revealed insights into the potential consequences of reducing with N or P loads individually. Nitrogen was found to be at least as likely to be limiting to phytoplankton growth as P in Lake Okaro. Inducing P-limitation alone would require major reduction of P loading to achieve the desired result and is likely to be costly and potentially take some time. Alternatively, undertaking N-limitation by reducing N loading alone could have the negative effect of promoting the dominance of N-fixing cyanobacteria. It was demonstrated that a combined reduction of N and P would produce a greater reduction in phytoplankton biomass while compensating for any shortcomings of reducing N or P individually.

The analysis of zooplankton and phytoplankton species composition in Chapter 6 has shown that Z2G1 did not cause discernible changes in species composition in the period of 9 months following its application. However, with future applications of Z2G1 or other P-inactivation agents considered in different Te Arawa Lakes, the deposition of large volumes of suspended sediments into the water column remains a threat for filter feeders. Potential applications of any P-

inactivation agent, especially when fine-grain sized materials are used, should include an evaluation of short-term effects on zooplankton and phytoplankton species composition. The nutrient reduction targets for any lake restoration methods must not outweigh any possible adverse effects on the aquatic fauna as there remains potential for disastrous ecological consequences.

The control of P loads is undoubtedly crucial for mitigating eutrophication. The use of P-inactivation agents as sediment capping materials for in-lake restoration may be viewed as only a treatment for the symptoms of eutrophication and not a solution for the factors causing the eutrophication. The fate of the P-inactivation agents in any case is ultimately the burial into deeper sediment layers with P permanently locked up. This is generally the desired outcome of in-lake nutrient control. However, one must ask if the burial of P in the sediment is a sustainable measure as the demand for fertiliser is increasing while the world is facing a global P supply shortage. At present, the recovery of P from lake sediments may not provide a profitable commodity as large scale P extraction costs probably exceed the market value. Therefore, the recovery of P from lake sediments in the immediate future is unlikely without the development of a cost effective technological solution. There is, however, no doubt about the significance of reducing external nutrient loads by controlling nutrient run-off and optimising fertiliser applications on farm land. However, despite time intensive and costly restoration efforts, this importance is often overshadowed or ignored by the substantial value of farming to New Zealand's overall economy.

7.2 Recommendations for future work

By using ^{31}P NMR, various organic P compounds can be identified within the extract of an environmental sample. Originally developed for soil P analysis, ^{31}P NMR was shown in this study to be suitable for determining organic P compounds in lake sediments. The approach used in this study, however, only partially identified the source of sediment organic P compounds from the water column. The analysis of soils in the catchment using ^{31}P NMR could reveal more insight into the origin of different P compounds in the lake sediment. Lakes which are under increasing pressure from agricultural intensification may

demonstrate the presence of different biogenic P forms, for example due to P originating from increased run-off from manure, compared to lakes with substantial remaining areas with native vegetation. A multi-lake comparison of organic P compounds across a range of trophic levels with different catchment land use could provide comprehensive information about the sources and fate of potentially bioavailable P in lake sediments and ultimately provide for a targeted management approach for different land uses.

Subsurface maxima of phytoplankton biomass have often been recorded in clear waters of oceans and lakes. The occurrence of these subsurface phytoplankton biomass maxima in the highly eutrophic Lake Okaro during this study, measured using chlorophyll *a* (chl *a*) as a proxy, may have caused an underestimation of the trophic state of the lake using the TLI, which is calculated using surface water concentrations only. A basic understanding of the mechanisms generating these maxima in a highly eutrophic lake is important for accurately assessing phytoplankton biomass and the application of trophic level indices to quantify water quality. This knowledge will also help to evaluate restoration targets, as a reduction of phytoplankton biomass is often considered a measure of success for lake restoration.

The use of P-inactivation agents, whether being used as a flocculent or sediment capping agent, has become increasingly popular. However, there are several alternatives to these in-lake P control methods for lake restoration. Hypolimnetic aeration or oxygenation in Lake Okaro may arguably need to be maintained to result in the desired outcome of sustained sediment P retention. Although high iron concentrations were found in the surface sediment of Lake Okaro, oxygen may not penetrate sufficiently deeply into the organic rich sediments to allow iron to adsorb P. A micro-layer of oxidised iron in the surface may become saturated and P from deeper sediment layers moving towards the sediment-water interface may simply diffuse through the thin oxidised layer. With the prospect of increasing demand and market price for P, the recovery of sediment P by dredging may provide the opportunity to cover some of the costs of this restoration method. However, the ecological impact of dredging has to be evaluated carefully to avoid any undesirable effects on the aquatic life. As indicated above, the reduction of nutrient inputs into the lake by reducing the external nutrient loads is the most sustainable method to mitigate eutrophication,

though often accompanied with considerable response lag time. The best measure prophylaxis against eutrophication is not to allow it to occur in the first instance, and there need to be socio-political tools to assist with sustainable water quality management. These need to include the enforcement of regulations to protect the lakes and their catchment on a long-term, planned basis in order to prevent the need for more costly restoration measures.

Appendix I

Effects of a modified zeolite on P and N processes and fluxes across the lake sediment-water interface using core incubations

Introduction

The problem of internal phosphorus (P) loads in lakes is worldwide. For example, a recent study of over 14,000 lakes >1 ha in size in Great Britain found that 51% are likely to require P-reduction measures to meet the Water Framework Directive to achieve "good status" by the year 2015 (Carvalho *et al.*, 2005). Results from that study also showed strong regional patterns with Scotland having the least and England having the highest number of lakes at risk at 18 % and 88%, respectively. New Zealand has many lakes affected by internal P loads. However, because of the high P content of their catchment soils and thus their inflow streams (Timperley, 1983), lakes in the Taupo volcanic zone (TVZ) of the North Island are more likely to require internal P load management than elsewhere in New Zealand (Parliamentary Commissioner for the Environment, 2006; Edgar, 2009).

Internal P loads are derived from the release of phosphate sequestered by oxidised iron species and the decomposition of organic matter in the lake sediments releasing biologically available (bioavailable) P as soluble phosphate into the water column during periods of anoxia, usually in summer (Smolders *et al.* 2006). Not all of the P in the lake sediments is bioavailable (Spears *et al.*, 2007).

Internal P load management strategies in Northern Hemisphere countries, to reduce algal biomass and the incidence of cyanobacteria blooms, have included binding the P in the lake with an inactivation agent applied either as a flocculation

agent to strip P from the water column or as a capping agent to seal the sediments against the release of P during periods of anoxia (Cooke *et al.*, 2005). The P-inactivation agent of choice is typically alum (aluminium sulphate) which, in neutral to alkaline water, produces a flocculent gelatinous precipitate of aluminium hydroxide, $Al(OH)_3$, which is chemically relatively stable, even under low redox states commonly encountered under anoxic conditions.

The effectiveness of the alum treatment usually lasts for more than just the year of treatment. In an evaluation of the effectiveness of reducing total P (TP) and longevity of alum treatments in 21 lakes across USA, Welch & Cooke (1999) found that the internal loading rate was reduced by around two-thirds and TP was reduced by around one-half for a period of 5 to 11 years. In some dimictic lakes, the internal loading may be controlled for at least 13 and up to 18 to 20 years, with a reasonable expectation of 15 years longevity (Welch & Cooke, 1999). A decline in treatment effectiveness over time was thought to be due to bioturbation and burial of the alum floc. It is likely that the continued input of P from the catchment was also a contributing factor.

While N can be permanently removed from the lake by the microbial processes of coupled nitrification and denitrification (e.g. McCarthy *et al.*, 2007), there is no comparable removal process for P. In general, denitrification accounts for about 36% of the TN input to lakes (Molot & Dillon, 1993), with denitrification rates of up to 229 mg N m^{-2} d^{-1} in some hyper-eutrophic lakes (Jensen *et al.*, 1992). Lake Rotorua, located nearby Lake Okaro, has similar highly organically enriched sediments, and mean annual denitrification rates are likely to be around 30 mg N m^{-2} d^{-1} (White *et al.*, 1978) and mean P release rates were around 44 mg P m^{-2} d^{-1} (White *et al.*, 1978; Burger *et al.*, 2007). Given the similarity in soil type, geothermal influence, catchment land-use and trophic condition (Hickey & Gibbs 2009), comparable N and P fluxes might be expected in Lake Okaro, the focus of this study, with the high internal P load negating the benefits of controlling the external P loads from the catchments.

Internationally attempts to reduce internal P loadings in eutrophic lakes also include sediment capping using calcite (Berg *et al.* 2004), modified clay minerals (Robb *et al.*, 2003) and iron slag (Yamada *et al.*, 1987). P-inactivation agents considered for the reduction of internal P loads in Lake Okaro were alum

and a new proprietary granular P-inactivation agent, Z2G1, that has been developed as a capping agent by Scion, Rotorua, and manufactured by Blue Pacific Minerals Ltd., Matamata, New Zealand.

Z2G1 is also an Al-based P-inactivation agent that uses a zeolite clay as a carrier for the Al and does not require buffering to avoid lake water acidification as can occur using alum in poorly buffered lakes (Cooke *et al.*, 2005). Zeolites are good cation absorbers that can remove ammonium ions (NH_4^+) (Wen *et al.*, 2006), and the modified zeolite retains the NH_4^+ absorption properties of the base material. Z2G1 has been designed to be applied as a sediment capping material with a granular formulation that improves the settling rate and thus accuracy of treating specific areas of lake bed. This is necessary to avoid lateral drift of the capping material into the littoral zone.

Environment Bay of Plenty, the regional environmental manager, used Z2G1 on Lake Okaro (surface area 0.32 km^2) in September 2007 as a "whole lake trial to test its effectiveness in reducing the internal P load by blocking the release of P from the sediments, and to assess whether Z2G1 could be used in the restoration of other Rotorua lakes, including Lake Rotorua (surface area 81 km^2). The main objective of this study was to assess if Z2G1 could block the release of P from lake sediments before undertaking the whole lake trial. We examined the P-removal efficacy of Z2G1 on Lake Okaro sediment by treating cores with two different grain sizes and dose rates of Z2G1 under aerobic and anoxic conditions. We also used the different layer thicknesses to examine the effect of the Z2G1 capping layer on the microbial processes of nitrification and denitrification and the potential release of metals such as arsenic (As) and mercury (Hg) from Lake Okaro's geothermally influenced sediments under aerobic and anoxic conditions.

Methods

Study site

Lake Okaro, a relatively small (0.32 km^2) low alkalinity (HCO$_3$ 36.8 g m^{-3}), hyper-eutrophic crater lake in the TVZ that lies in a mostly agricultural (>95% pasture) catchment. It has a mean depth 12.1 m (max. depth 18.0 m) and thermally stratifies annually between 4 and 8 m. Summer surface temperatures reach up to 23ºC with hypolimnetic temperatures of around 18ºC. Water clarity is variable (Secchi depth 0.6-3.6 m) associated with chlorophyll *a* concentrations ranging from 1.4 to 200 mg m^{-3} (mean 28 mg m^{-3}). Total phosphorus concentrations range from 18 to 573 mg m^{-3} (mean 103 mg m^{-3}) and total nitrogen concentrations range from 430 to 4690 mg m^{-3} (mean 1161 mg m^{-3}) (Timperley & Vigor-Brown 1986; Environment Bay of Plenty, 2006; Hickey & Gibbs 2009). Lake Okaro has highly organically enriched sediments from agricultural catchment runoff (Forsyth *et al.*, 1988), with high nitrogen (N) inputs from the catchment and a high internal P load (Burns, 2001) from the sediments during summer stratification. These are the main nutrient drivers of nuisance cyanobacteria blooms (Dryden & Vincent, 1986) which occur through summer and autumn. Because Lake Okaro is an important recreational lake in the Bay of Plenty region, Environment Bay of Plenty, have made a commitment to improve its water quality through the use of catchment and in-lake remediation techniques, to reduce both N and P. The sustained control of phytoplankton biomass requires the reduction of both N and P loads (e.g. Lewis & Wurtsbaugh, 2008); however, the reduction of P loading often can be the most effective approach in eutrophic lakes (e.g. Schindler *et al.* 2008). Catchment remediation work including restricting stock access to the lake, enhancing riparian buffer zones, and installing a large constructed wetland on the main inflow have been completed (Tanner *et al.*, 2007) and the present focus is on managing the internal P load.

Core collection

In this study it was assumed that releases of P from lake sediments were mainly by diffusion mostly from the top 4 cm (Cooke *et al.*, 2005). Sediment P release rates, and the efficacy of Z2G1 as a capping agent to block that release, were

measured on composite degassed sediment using a continuous-flow incubation system (e.g. Miller-Way & Twilley, 1996). Multiple sediment cores were collected from a depth of 12 m in Lake Okaro in winter (June 2006) when the lake was fully mixed, using a Jenkins Corer (Mortimer, 1971). Sampling at this time of year ensures the maximum sequestration of P into the sediments and simulates the expected time of application of the Z2G1 as a capping layer for the whole lake treatment. The top 10 cm of sediment in each core was extruded upwards into a 25-cm long incubation tube the same diameter as the corer tube (7.0 cm ID), using a manual push piston. The bottom of the incubation tube was sealed with plug of 3 cm thick high density foam (cut from a sheet with a 7.5 cm hole saw without the drill bit). This process spilled most of the overlying water. The top of each incubation tube was closed with another plug of high density foam but with a vent hole to relieve any pressure. The vent hole was subsequently closed with a rubber bung and the incubation tube placed vertically in a rack in container of lake water for transport to the laboratory.

A sample of the near-sediment overlying water was collected for nutrient and dissolved metal analyses from one corer tube using a syringe fitted with a length of narrow-bore hard nylon tube. Four 100-L barrels of unfiltered surface lake water were also collected as the source water for the incubations. The barrels were sealable wide-mouth black alkathene barrels lined with clean heavy-walled plastic bags (bin liners) to prevent cross contamination.

Set up procedure

While the intention was to use the undisturbed sediment in the incubation tubes, sediment disturbance by degassing of methane and CO_2 during transport to the laboratory made this impossible. Consequently, the sediment in each incubation tube was stirred gently to remove remaining gas bubbles and then allowed to reconstitute under aerobic lake water for 5 days before starting the experiment.

After treatment (see below), the incubation tubes were converted to incubation chambers by closing the top with a high density foam plug with a vent port, a 2-mm ID nylon inlet tube, and a 3.5-mm ID nylon outlet tube; both tubes were inserted through the plug (Figure 1A). With the top closed, the water space above the sediment was reduced to 2.5 cm (volume ~100 mL) by pushing the

bottom plug further up inside the incubation tube. The vent port spilled the excess water and air bubbles, and was then sealed with a rubber bung. The incubation chambers were placed vertically in a rack in a temperature–controlled water bath at 18ºC (i.e. summer hypolimnion temperature), with the incubation chamber tops just under water. The experiments were run in a controlled temperature room at 18ºC.

Continuous flow incubation system

The continuous flow incubation system (CFIS) (Figure 1B) comprised a multi-channel peristaltic pump (ex-AutoAnalyzer[®]) drawing water from the source-water drum and pushing it into each incubation chamber at a flow rate of 1.5 mL min^{-1} i.e. each incubation chamber received identical water. The inflow water mixed with water in contact with the sediment in each incubation chamber and an equal volume of the mixed water was displaced via the outflow tube into individual sample collectors. The larger diameter of the outlet tube was to prevent pressure build up in the sediment under test. Apart from the Tygon[®] pump tube, all tubing was hard nylon (automotive brake fluid transmission tubing) which had low internal friction and was impermeable to oxygen.

With a chamber volume of 100 mL and a flow rate of 1.5 mL min^{-1}, the water in each chamber was exchanged about 24 times d[-1]. It took about 24 h for the CFIS to reach a steady state after the initial disturbance of closing the chambers. Nutrient fluxes from the sediments were estimated from the difference between inflow and outflow concentrations at steady state.
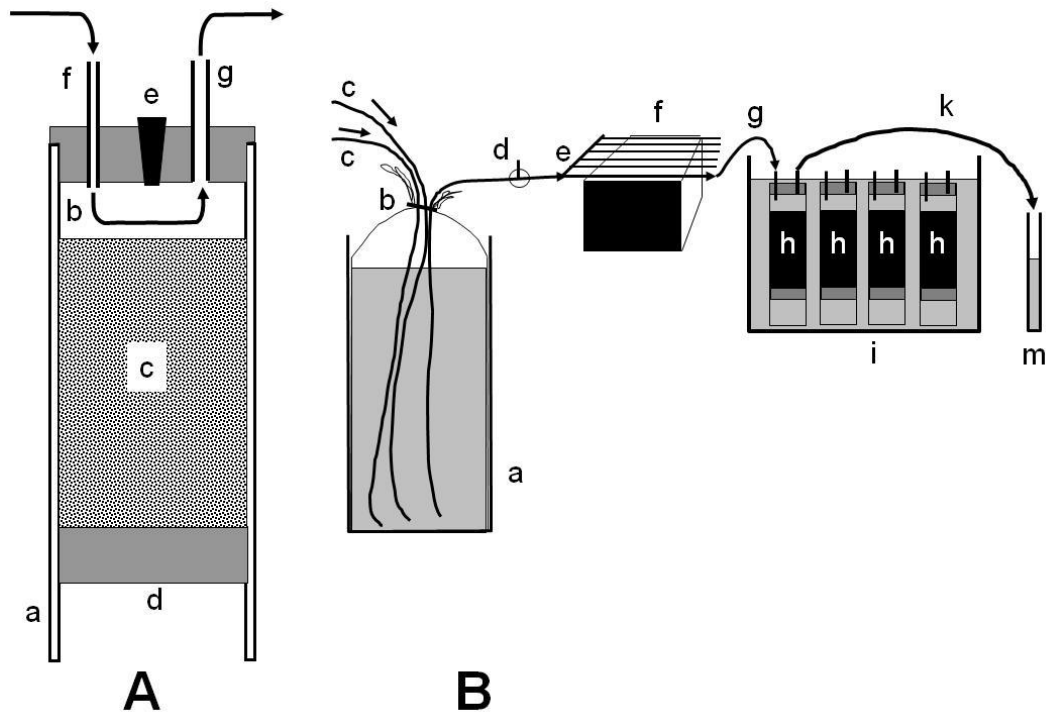
Figure 1: (A) Schematic of the incubation chamber (a) with flow-through cavity (b) above the sediment (c) showing the movable bottom plug (d), vent hole and bung in the chamber cap (e), the 2-mm ID inlet tube (f), and the 3.5-mm ID outlet tube (g). (B) Schematic of the continuous flow incubation system showing the bulk water drum (a) with the plastic liner (b) bound around the gas lines (c), the 3-way tap for inflow water sampling (d), the distribution manifold to the individual pump tubes (e), the multi-channel peristaltic pump (f), the inflow transmission tubes to each incubation chamber (g), the incubation chamber (h) submerged in a controlled temperature water bath (i), the outflow transmission tubes (k) to the sample collection tube (m). Arrows indicate flow direction.

Experimental design

To achieve rapid settling of Z2G1 as a capping layer in Lake Okaro, a 1-3 mm grain size was used at a dose rate of 350 g m^{-2}. Experimental treatments used this dose rate and 700 g Z2G1 m^{-2} in the CFIS in one set (3 replicates of each treatment) of incubation chambers. The 1-3 mm grain size material was sieved from a bulk <3 mm grain size Z2G1 sample. Because fine-grained materials have a greater surface area per unit mass and thus potentially could absorb more P, this was tested by treating a second set of incubation chambers with the same dose rates of the residual <1 mm grain size. Control treatments where chambers containing bare sediment, and a single blank treatment consisted of a chamber dosed with 700 g m^{-2} of <1 mm grain size Z2G1 without sediment, to distinguish

between trace metals released from the Z2G1 and releases from the sediment because of the Z2G1 capping layer. The 1-3 mm grain size treatments and controls were run in triplicate and the <1 mm grain size treatments were run in duplicate.

Two identical experiments were set up and run concurrently, one with natural lake water and the other with natural lake water amended with nutrients to evaluate natural and potential fluxes of N and P. The nutrient amendments increased the DRP concentration to about 200 mg DRP m^{-3} (sodium dihydrogen phosphate) and the nitrate (NO_3-N) concentration to about 1500 mg NO_3-N m^{-3} (potassium nitrate). The NO_3-N amendment was also used to check the effect of Z2G1 capping layer on denitrification. No ammoniacal-N (NH_4-N) was added.

Aerobic versus anoxic treatments

Because sediment release of P can be predominantly regulated by oxygen concentrations at the sediment-water interface (Gächter & Müller, 2003), each experiment was first run with natural lake water under aerobic conditions, to simulate mixed or littoral zone effects, and then under anoxic conditions to simulate hypolimnetic conditions after thermal stratification.

The bulk lake water for aerobic tests was aerated using an aquarium air stone and filtered air from outside the laboratory. Lake water was made anoxic using the plastic liner as an air barrier bound tightly around two gas lines and the pump line to the CFIS installed in the bulk water drum. One gas line was used to continuously bubble oxygen-free dry nitrogen gas through the bulk water to remove all dissolved oxygen. Anoxia was achieved in about 1 hour. The other gas line was used to bubble CO_2 gas into the anoxic water as required (30-second bursts) to adjust the pH to around 7.5. A nylon Luer lock 3-way tap in the pump line allowed the bulk water to be sampled for measuring pH and DO. The plastic bag trapped the excess N_2 gas under positive pressure in the head-space, preventing any significant diffusion of oxygen into the water from the atmosphere.

Sampling

Each experimental condition was run for 5 days. Sample collection was daily after the first day. For nutrient analyses, a 50 mL water was collected from each chamber in an open 50-mL plastic syringe (plunger removed) with a tap in place of the needle. Refitting the plunger enabled the sample to be syringe–filtered into a sample bottle without an intermediate transfer step. Inflow water samples were drawn by syringe from the 3-way tap in the pump line. Filtration was through a 2.5 cm Whatman® GF/C glass fibre filter in a 2.5 cm Swinnex® filter holder. A 10-mL aliquot of each filtered sample was transferred to a specially prepared sample bottle containing nitric acid preservative for trace metal analysis.

At the completion of the experiment, the incubation chambers were opened and samples of the Z2G1 capping layer material were recovered from each chamber under low vacuum and placed in plastic centrifuge tubes. The sediment adhering to the Z2G1 capping material was removed by sequential washing with deionised water, which was discarded. The recovered Z2G1 and a similar amount of fresh Z2G1 as a reference material were dried at 105ºC for 24 h before being ground to a fine powder with a mortar and pestle. The Z2G1 samples and a dried ground sample of untreated sediment were digested using aqua regia solution at 90°C for 2 hours before analysis for metals and trace elements.

P-saturation

To determine the maximum P-binding capacity of Z2G1 and its P-uptake rate, 5 g of the <3 mm grain size product were placed in 1 litre of water containing 200 mg P (2 g $NaH_2PO_4.2H_2O$). The mixture was shaken vigorously for 1 minute then allowed to settle for 10 minutes before removing about 0.5 g of granules by suction tube. The mixture was shaken and sampled at timed intervals over a period of 200 h to provide a time-series uptake curve. The samples were centrifuged immediately on collection (3000 rpm for 10 minutes) and the aqueous phase was discarded. The samples were rinsed twice with deionised water before drying, grinding and digestion as above.

Analytical

The nutrient bottles were frozen at -20ºC pending batch analysis for DRP, NO_3-N, and ammoniacal-N (NH_4-N) on a Lachat flow injection analyser (FIA) using standard Lachat methods for freshwaters. The acidified water samples were analysed for the metals iron (Fe), manganese (Mn), aluminium (Al), zinc (Zn), and As, using an ICP-mass spectrometer (ICP-MS) and the Z2G1 and sediment sample digests were analysed for metals and trace elements using an ICP-MS.

Sediment bulk density was determined on an aliquot of wet sediment and was calculated from the water loss from a measured volume of sediment after drying at 105^0C for 24 h.

Statistical analysis

A T-test was carried out to test for significant differences between dose rates and grain size with natural and nutrient enriched lake water. Because of the limited sample size (3), significance was assumed when P <0.05.

Results

P-binding capacity

The P-uptake results (Figure 2) showed a rapid uptake of DRP over the first few hours with uptake reaching a plateau of around 20,000 mg P kg^{-1} Z2G1 dry weight over the 200 hour experiment. As the fitted curve indicates little increase after 24 h, this is a best estimate of the P-binding capacity of Z2G1. The use of sodium di-hydrogen phosphate as the source of the DRP gave the solution a pH of around 6.
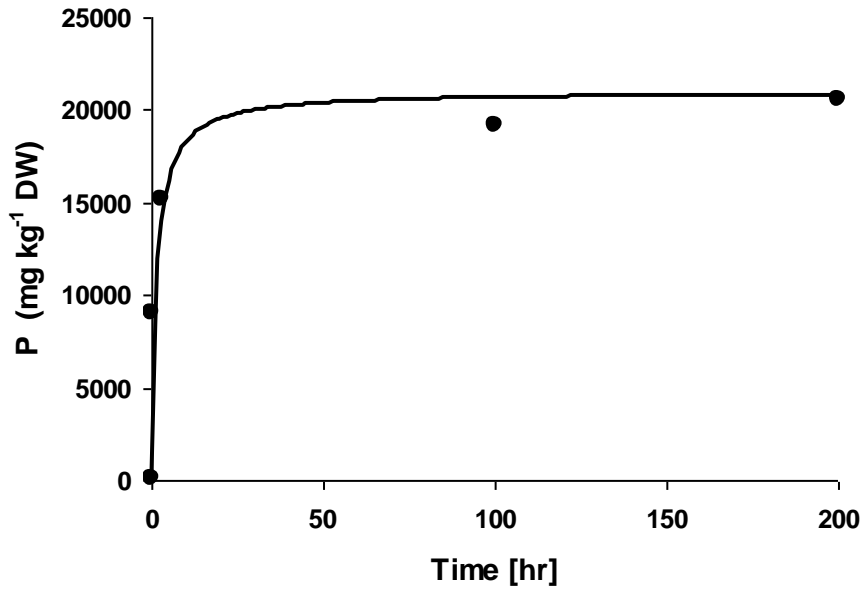
Figure 2: Time-series total P concentration changes in Z2G1 over the 200 h P-saturation experiment. Curve modelled to account for the measured (dots) rapid initial uptake and final concentration, gives an indication of maximum P-binding capacity of Z2G1.

Sediment coverage

Sediment coverage was judged visually. The sediment coverage by the 1-3 mm grain size 350 g m^{-2} layer was incomplete with large gaps between the Z2G1 granules (Figure 3B), while the <1 mm grain size 350 g m^{-2} layer gave almost complete coverage (Figure 3A). At the 700 g m^{-2} dose rates, the 1-3 mm grain size still did not achieve complete coverage of the sediment.
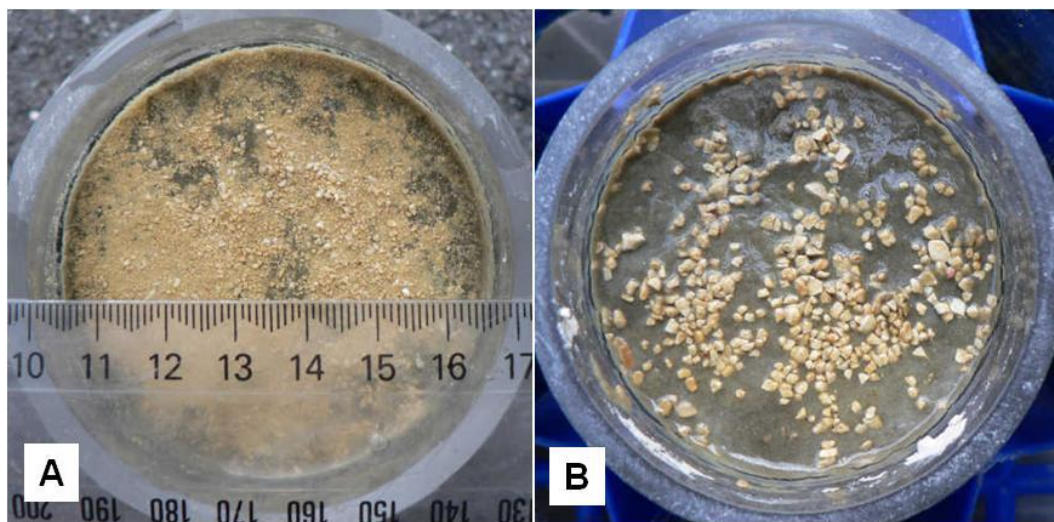
Figure 3: Comparison of sediment coverage by Z2G1 at a dose rate of 350 g m^{-2} for A) <1 mm grain size, and B) 1-3 mm grain size.

P-fluxes

Sequential analyses of the inflow and outflow DRP concentrations from the incubation chambers showed that the system was at equilibrium from the beginning of the sampling at the end of day 2 and through to the final sampling on day 5 (Figure 4). Concentrations higher than those of the inflow (Figure 4, control) indicate that DRP was released from the sediment. Concentrations lower than the inflow (Figure 4, all treatments) indicate that the Z2G1 blocked the release of DRP from the sediment as well as absorbing DRP from the lake water above the sediment.
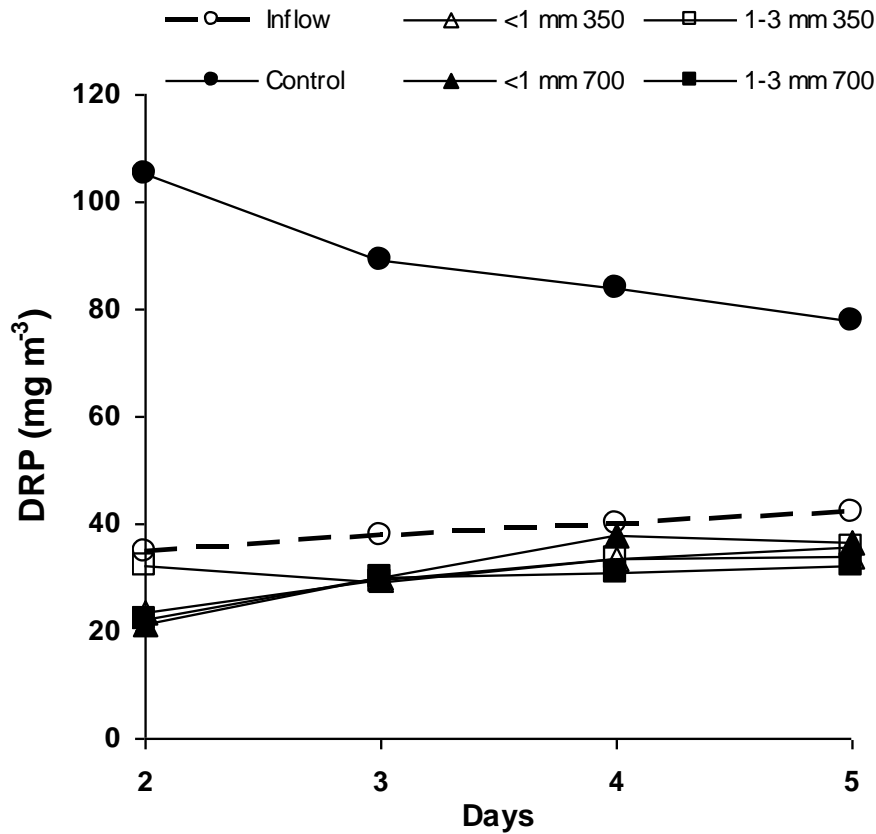
Figure 4: Sequential analyses of DRP concentrations in the inflow and outflow water from the anoxic natural lake water chambers over days 2 to 5. Graph key values 350 and 700 are dose rates of Z2G1 in g m^{-2}.

Under aerobic conditions, DRP was removed from the overlying water column in all incubation chambers including the control (Figure 5). The results showed that all of the Z2G1 treatments sequestered a similar amount of P which was about double the amount sequestered by the natural sediment from the natural lake water. There was no statistically significant (T-test; $P < 0.05$) difference between dose rates ($P = 0.96$). Adding DRP to the lake water enhanced the amount of DRP sequestered but while the lower dose rate of each grain size appeared to sequester more than the higher dose rate, the difference was not statistically significant ($P = 0.16$).

Figure 5: P-fluxes (mg m^{-2} d^{-1} $\pm$ 1 SD) in the sediment incubation chambers under aerobic conditions using natural lake water (open bar, DRP concentration 27 mg m^{-3}) and amended lake water (solid bar, DRP concentration 253 mg m^{-3}). Graph values 350 and 700 are dose rates of Z2G1 in g m^{-2} for that grain size. The blank was a 700 g m^{-2} dose of <1 mm grain size Z2G1 applied to an incubation tube without any sediment using amended lake water, only.

Under anoxic conditions, DRP was released into the overlying water column in the control with natural lake water but not with DRP amended lake water (Figure 6). In the incubation chambers dosed with Z2G1 the release of DRP from the sediments was blocked and some of the DRP in the overlying water column was sequestered. While there was no statistically significant (T-test; P <0.05) difference between dose rates (P = 0.85) for the <1 mm grain size, there was a significant difference (P <0.02) between dose rates for the 1-3 mm grain size, with higher sequestration of P at the higher dose rate. In the chambers exposed to DRP amended lake water, the amount of P sequestered by the Z2G1 treatments was higher than in the control but not as high as in the aerobic incubations. The lower dose rate of each grain size sequestered significantly (P <0.02) more P than the higher dose rate, but overall there was no statistically significant (P = 0.59) difference with grain size (Figure 6).
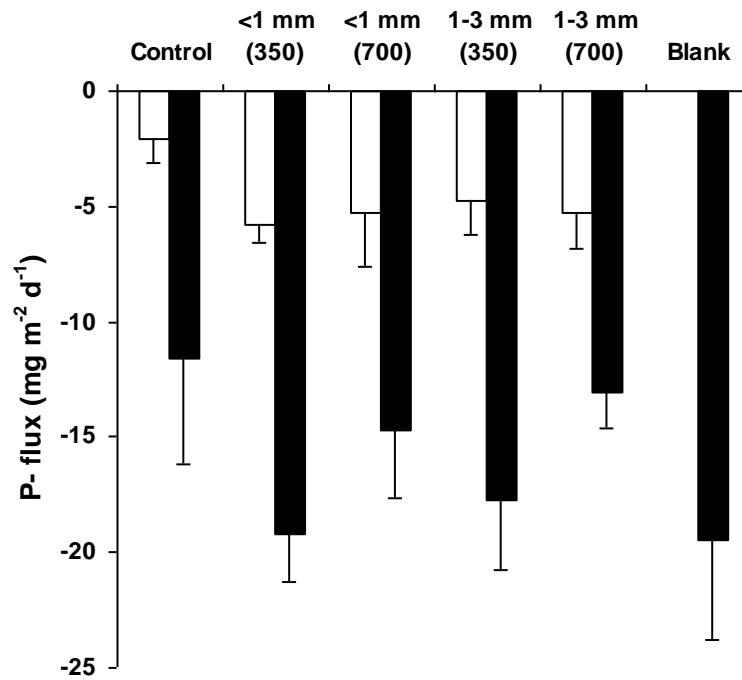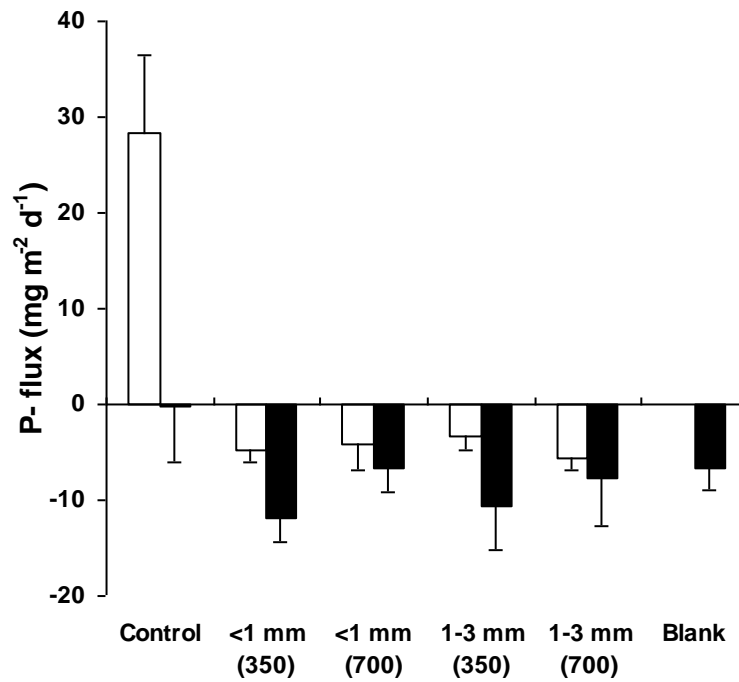
Figure 6: P-fluxes (mg m^{-2} d^{-1} ± 1 SD) in the sediment incubation chambers under anoxic conditions using natural lake water (open bar, DRP concentration 39 mg m^{-3}) and amended lake water (solid bar, DRP concentration 267 mg m^{-3}). Graph values 350 and 700 are dose rates of Z2G1 in g m^{-2} for that grain size. The blank was a 700 g m^{-2} dose of < 1 mm grain size Z2G1 applied to an incubation tube without any sediment using amended lake water, only.

N-fluxes

The NH$_4$-N fluxes under aerobic and anoxic conditions (Figs. 7 and 8) showed that Z2G1 absorbed NH$_4$-N released from the sediment from the overlying water. Under aerobic conditions and natural lake water (mean NH$_4$-N concentration 450 mg m^{-3}) there was little or no change in the NH$_4$-N concentrations from the control chambers while the incubation chambers treated with Z2G1 had significantly reduced NH$_4$-N concentrations (Figure 7). The addition of NO$_3$-N to the natural lake water (NO$_3$-N 1540 mg m^{-3}; no change to the NH$_4$-N concentration) produced a greater loss of NH$_4$-N from all chambers (Figure 7). There was no statistically significant (T-test; P <0.05) difference between dose rates (P >0.4).
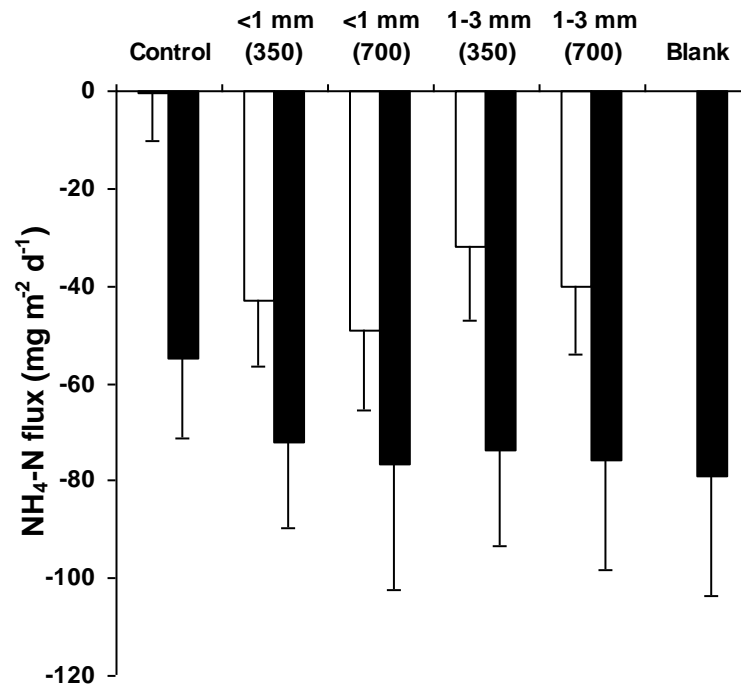
Figure 7: NH$_4$-N fluxes (mg m^{-2} d^{-1} ± 1 SD) in the sediment incubation chambers under aerobic conditions using natural lake water (open bar, NH$_4$-N concentration 450 mg m^{-3}) and lake water amended with NO$_3$-N (solid bar, NO$_3$-N concentration 1540 mg m^{-3}). Graph values 350 and 700 are dose rates of Z2G1 in g m^{-2} for that grain size. The blank was a 700 g m^{-2} dose of < 1 mm grain size Z2G1 applied to an incubation tube without any sediment, using amended lake water, only.

Under anoxic conditions there was a significant release of NH$_4$-N from the control sediments with natural lake water (mean NH$_4$-N concentration 480 mg m^{-3}) but not with the lake water amended with NO$_3$-N (1590 mg m^{-3}) (Figure 8). In contrast, the incubation chambers treated with Z2G1 had significantly reduced NH$_4$-N concentrations (Figure 8). The addition of NO$_3$-N to the natural lake water (no change to the NH$_4$-N concentration) produced a greater loss of NH$_4$-N from all chambers (Figure 8). There was no statistically significant (T-test; P <0.05) difference between dose rates with natural lake water (P = 0.61). With the addition of NO$_3$-N, the higher dose rates appeared to have a greater loss of NH$_4$-N, although this difference was not statistically significant (P = 0.06).
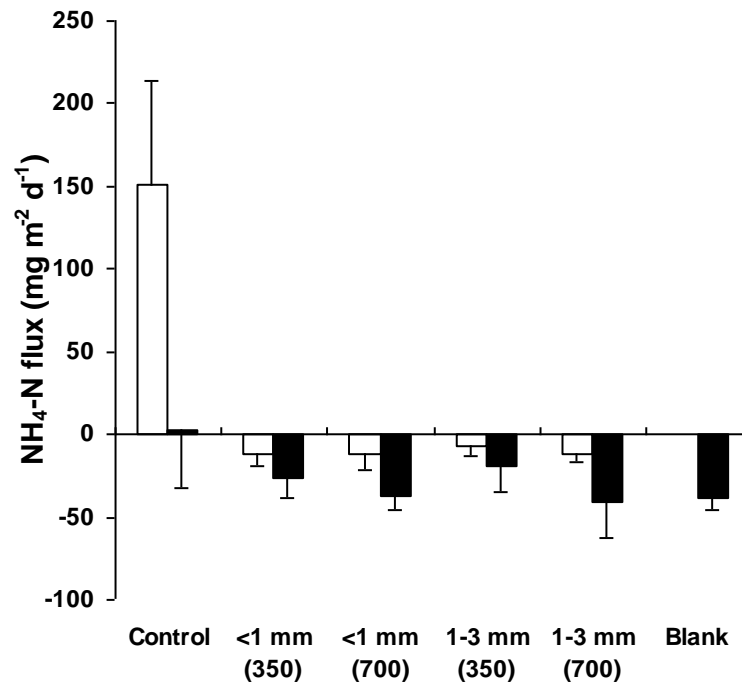
Figure 8: NH$_4$-N fluxes (mg m^{-2} d^{-1} ± 1 SD) in the sediment incubation chambers under anoxic conditions using natural lake water (open bar, NH$_4$-N concentration 480 mg m^{-3}) and lake water amended with NO$_3$-N (solid bar, NO$_3$-N concentration 1590 mg m^{-3}). Graph values 350 and 700 are dose rates of Z2G1 in g m^{-2} for that grain size. The blank was a 700 g m^{-2} dose of < 1 mm grain size Z2G1 applied to an incubation tube without any sediment using amended lake water, only.

The NO$_3$-N fluxes under aerobic conditions (Figure 9) showed N reductions in all treatments. With natural lake water (NO$_3$-N concentration 17 mg m^{-3}), the loss of NO$_3$-N from the Z2G1 treated chambers was similar to the loss from the control and there was no statistically significant (T-test; P,0.05) difference between dose rates (P = 0.73). With the lake water amended with NO$_3$-N (NO$_3$-N concentration 1540 mg m^{-3}), there was a significant increase in the loss of NO$_3$-N from all chambers. The loss of NO$_3$-N from the chambers treated with Z2G1 was equal to or greater than the loss from the control chambers. The apparent difference between dose rates, with the lower dose rate producing a greater NO$_3$-N loss than the higher dose rate, was highly significant (P << 0.001).
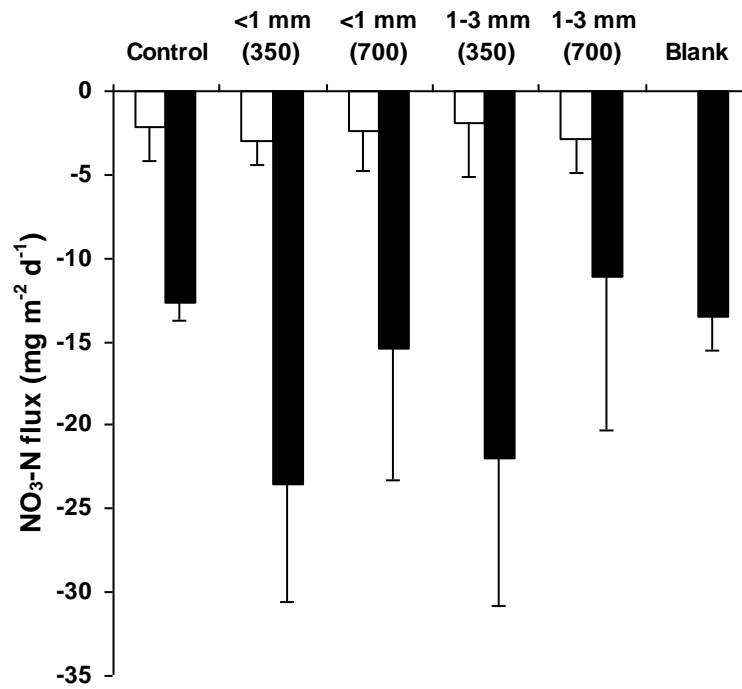
Figure 9: NO$_3$-N fluxes (mg m^{-2} d^{-1} ± 1 SD) in the sediment incubation chambers under aerobic conditions using natural lake water (open bar, NO$_3$-N concentration 17 mg m^{-3}) and lake water amended with NO$_3$-N (solid bar, NO$_3$-N concentration 1540 mg m^{-3}). Graph values 350 and 700 are dose rates of Z2G1 in g m^{-2} for that grain size. The blank was a 700 g m^{-2} dose of < 1 mm grain size Z2G1 applied to an incubation tube without any sediment using amended lake water, only.

Metal fluxes

The fluxes of metals between the sediment and water column in the incubation chambers were generally small (Table 1). Even when the incubation chambers were taken to anoxia, the concentrations of metals in the water from the chambers were generally much lower than in the water sample collected from just above the sediment in the corer tube at the time of sampling (Table 1). This may indicate that the bottom water metal concentrations were augmented by disturbance of the pore waters during coring.

Table 1: Total dissolved metal concentrations (g m^{-3}) and dissolved oxygen (% saturation) in the outflow water relative to the inflow water (lake surface) and lake bottom water from just above the sediments in the corer tube.

Sample	Fe	Mn	Al	Zn	As	DO
	(g m^{-3})	(g m^{-3})	(g m^{-3})	(g m^{-3})	(g m^{-3})	(% sat)
Lake Okaro						
Surface water	0.027	0.002	0.013	0.127	0.003	56.5
Bottom water	0.510	0.197	0.009	0.029	0.004	16.5
Aerobic chambers						
Control	0.027	0.002	0.013	0.127	0.003	92.1
<1 mm (350)	0.027	0.003	0.018	0.088	0.003	87.4
<1 mm (700)	0.03	0.005	0.014	0.07	0.003	89.0
1-3 mm (350)	0.03	0.007	0.007	0.115	0.003	89.4
1-3 mm (700)	0.033	0.004	0.011	0.068	0.003	90.2
Blank (<1 mm 700)	0.037	0.003	0.022	0.095	0.003	89.1
Anoxic chambers						
Control	0.068	0.018	0.023	0.061	0.004	<0.5
<1 mm (350)	0.025	0.010	0.036	0.055	0.003	<0.5
<1 mm (700)	0.020	0.010	0.036	0.055	0.003	<0.5
1-3 mm (350)	0.030	0.011	0.009	0.045	0.003	<0.5
1-3 mm (700)	0.027	0.009	0.008	0.030	0.003	<0.5

Sediment and Z2G1

The wet sediment had a bulk density of 1039 kg m^{-3}, therefore 1 m^3 of wet sediment will have 39 kg dry weight of sediment. The TP content of the sediments was 2000 mg kg^{-1} dry weight (Table 2) and therefore each 1 cm thick slice of wet sediment had an areal TP content of 780 mg P m^{-2}. This indicates a potential internal P load of up to 3.12 g P m^{-2} from the top 4 cm of sediment. Note that TP is a maximum which will be greater than the total bioavailable P.

Metal and trace element analyses of different fractions of Z2G1 (Table 2) showed considerable variability in composition between different size fractions, which may be a function of the grain size or the analytical procedure. Analyses of the recovered Z2G1 (Table 2, used) showed that material had elevated P concentrations, with the <1 mm grain size adsorbing about 50% more P than the 1-3 mm grain size. There was little difference in P absorption by Z2G1 from the incubation chambers exposed to natural lake water or P-amended lake water (Table 2, +P) indicating that the majority of the P absorbed was from the sediment.

Comparison of the other elemental composition of the new and recovered Z2G1 with that of the sediment shows that there were elemental changes occurring in the Z2G1 in contact with the sediments. For example, the sediment had a higher Fe content than the Z2G1 applied. The Fe content in the recovered Z2G1 was about double after the 14-day incubation period. While this change may have been due to precipitation of Fe onto the zeolite matrix during the Z2G1 recovery under aerobic conditions, other changes occurred which would require a different mechanism. Arsenic and mercury increased in the Z2G1 indicating absorption of these elements from the geothermally influenced sediment. Sodium, calcium, and magnesium decreased and potassium increased, especially in the Z2G1 recovered from the chambers exposed to P and NO$_3$-N-amended lake water (Table 2, +P).

Table 2: Concentrations (mg kg^{-1} dry weight) of metals and trace elements in Lake Okaro sediment and different fractions of Z2G1, measured by ICP-MS. Results are means of 3 analyses of each digest. Used Z2G1 is material recovered from the sediment surface at the end of the incubation experiment; +P indicates those samples were exposed to the P-amended lake water.

Sample	Grain size	P	Al	Fe	Mn	Zn	As	Hg	Na	K	Ca	Mg
Sediment		2000	10700	17800	315	78	38	13.1	565	1980	2430	1500
Z2G1 new	<3 mm	110	18100	3200	200	57	8	0.6	10200	6560	8410	1570
Z2G1 new	<1 mm	180	24800	5700	275	60	9	0.7	12200	8220	5260	1810
Z2G1 new	1-3 mm	80	14900	5100	170	37	9	0.5	12800	8220	5260	1430
Z2G1 used	<1 mm	1380	29700	9100	250	96	17	9.9	2760	8910	3000	735
Z2G1 used	1-3 mm	900	19000	6400	150	43	11	8.3	4360	9200	2860	520
Z2G1 used + P	<1 mm	1360	28800	8300	295	90	19	9.3	2420	12600	2820	665
Z2G1 used + P	1-3 mm	940	18400	8300	310	48	14	7	3910	11500	2880	590

Discussion

Comparisons between control and treatment fluxes under aerobic and anoxic conditions show that, at the dose rates used in this study, the thin layer of Z2G1 was capable to completely block the release of P from the sediments of Lake Okaro. Under natural lake water and anoxic conditions, the higher dose rate of the 1-3 mm Z2G1 removed significantly more P than the lower dose rate, consistent with a better coverage of the sediment surface. Of interest, however, the lower dose rate of Z2G1 at both grain sizes removed significantly more P from the water column than the higher dose rate when the phosphate concentration was increased under anoxic conditions. The increase in P content of the Z2G1 recovered from the treated sediment cores relative to the unused Z2G1 confirmed that the Z2G1 was removing the P and that it was not just the passive action of the granular material on the sediment surface. These results also show that the <1 mm grain size absorbed around 50% more P than the 1-3 mm grain size in both the natural and phosphate enriched incubations for the same period of sediment exposure. This is consistent with the finer material having a greater active surface area than the coarser material (e.g. Wen *et al.*, 2006).

Under aerobic conditions and natural lake water concentrations, the natural sediment in the control also removed P from the overlying water column. This is consistent with iron oxides and oxyhydroxides in the natural sediment sequestering phosphate from the water in contact with the sediment (Søndergaard *et al.*, 2003). Adding more phosphate to the overlying aerobic water increased the concentration gradient between the water column and the sediment, inducing a greater uptake flux. These results indicate that under aerobic conditions, internal P loads in Lake Okaro are unlikely to occur.

Under anoxic conditions and natural lake water concentrations, P was released from the sediment in the control cores but there was still a reduction of P in the Z2G1 treated sediment cores. This indicates that we had achieved anoxic conditions and that in the anoxic control cores, phosphate sequestered by iron under aerobic conditions had been released under the resultant reducing conditions (Perkins & Underwood, 2001). It also indicated that Z2G1 was

sequestering the phosphate released from the iron and had sufficient P-binding capacity to also remove some of the P from the overlying water column. Adding more phosphate to the overlying water increased the amount of P removed by the Z2G1 but caused the P release flux from the control sediments to reduce to near zero. This apparent anomaly can be explained if the mechanism for release of P from the sediments is considered, namely chemical or molecular diffusion as a function of concentration gradient with movement of a compound towards the low concentration. Under natural lake water, the P concentrations in the sediment pore water can be expected to be very much higher than in the lake water (Enell & Löfgren, 1988), causing the observed efflux of P. Increasing the overlying water P concentrations reduced the concentration gradient to near zero causing the efflux also to be reduced to near zero. This indicates that the pore water P concentrations were likely to be in the order of 200 mg m^{-3}.

Efficiency of Z2G1

From the analysis of the Z2G1 granules recovered from the incubation cores, it is clear that particle size of the granular material has a strong influence on the efficiency of Z2G1 to bind P, with the finer material being around 50% more efficient than the coarser material. Based on the efflux of P from the anoxic untreated sediments of up to 38 mg m^{-2} d^{-1}, and the additional reduction in P from the water column of up 15 mg m^{-2} d^{-1}, Z2G1 has a P uptake rate of at least 53 mg m^{-2} d^{-1}.

This P uptake rate would be effective on lakes in New Zealand and around the world with similar sediment P release rates. For example, Burger *et al.* (2007) measured P release rates of 2.1 to 85.6 mg P m^{-2} d^{-1} in nearby Lake Rotorua (mean rate 44.3 mg P m^{-2} d^{-1}), values which included both seasonal changes and differences between sites at different depths. White *et al.* (1978) also estimated a mean sediment P release of ~44 mg m^{-2} d^{-1} in Lake Rotorua. Penn *et al.* (2000) measured seasonal variations in P release rates of 3 to 38 mg P m^{-2} d^{-1} in hyper-eutrophic Onondaga Lake, USA. The similarity in P release rates from these three lakes is consistent with P release being limited by the rate of diffusion across the sediment-water interface (Perkins & Underwood, 2001).

The zeolite substrate in Z2G1 also absorbed NH_4^+ from water and this was seen in the NH_4-N flux data. The aerobic results showed that Z2G1 absorbed a mean of 40 mg NH_4-N m^{-2} d^{-1} from the overlying water across all treatments, but with apparently higher absorption rates by the <1 mm than the 1-3 mm grain size material, however, not statistically significant. Addition of NO_3-N to the incubation water almost doubled the NH_4-N absorption rates to around 75 mg m^{-2} d^{-1} with maximum values of >100 mg m^{-2} d^{-1}, and induced a comparable reduction of NH_4-N in the controls. The extra NH_4-N reduction in the presence of high NO_3-N concentrations is consistent with coupled nitrification-denitrification. However, while these results show that nitrification is occurring, they do not show whether there has been suppression of the nitrification by the Z2G1. As nitrification biochemically oxidises NH_4-N to NO_3-N, an adverse effect on nitrification would result in an increase in NH_4-N in the water column. Any increase in NH_4-N in these experiments was masked by the uptake of NH_4-N by the zeolite substrate.

Under anoxic bottom water conditions, nitrification and thus denitrification would not be expected at the sediment-water interface (Downes, 1988), and the DIN released from the sediments would all appear as NH_4-N, as seen in the controls where the NH_4-N efflux was up to 212 mg m^{-2} d^{-1}. Notwithstanding this, the Z2G1 capping layers absorbed all of the NH_4-N released from the sediments as well as additional NH_4-N from the water column. These results indicate that Z2G1 could absorb NH_4-N at up to almost 300 mg m^{-2} d^{-1} under anoxic conditions. As the NH_4-N absorption capacity of the Z2G1 was not tested, it is uncertain how long this uptake would continue. A best estimate from this study would indicate an NH_4-N absorption capacity of around 4.5 mg NH_4-N g^{-1} Z2G1, which is comparable with other New Zealand zeolites (e.g. Nguyen & Tanner, 1998).

Potential effects of sediment capping on benthic fauna

While not specifically part of this study, it is important to recognise that excessive applications of capping materials are undesirable as they may cause unexpected effects such as Fe release from the sediments (Douglas *et al.*, 2008). Low dose rates based on laboratory estimates of the internal P load were preferred because these are sufficient to bind the P release without smothering sensitive benthic

biota, an unacceptable ecological outcome. These comments are supported by a study by Vopel *et al.* (2008) who showed that excessively thick capping layers (>2-mm) caused the reduction-oxidation (redox) boundary to moved out of the sediment into the capping layer thus completely blocking oxygen diffusion into the sediment. The sediment immediately below the capping layer became anaerobic, which would smother infauna, and had the potential to release metals and sulphides which could diffuse out of the capping layer. Vopel *et al.* (2008) also tested Z2G1 at a range of dose rates with a dose rate of 400 g m^{-2} of <125 μm sieved Z2G1 producing a layer about 2 mm thick. This suggests that the <1 mm grain size, 350 g Z2G1 m^{-2} treatments in this study probably had a thickness of around 2 mm and thus were at the top end of an acceptable dose rate range without causing adverse effects on benthic fauna. However, in other studies it was found that macrozoobenthic organisms were not affected by layer thickness of calcite and applications achieving up to 5 mm were taken into consideration to compensate for possible mechanical instability of the capping agent (Berg *et al.*, 2003).

The implications from the different grain size results are that the larger granules did not completely block oxygen diffusion into the sediment and thus would be less likely to smother benthic biota. They would also settle faster and make application of the capping layer to selected areas of lake bed more precise. Small residence time of the material in the water column could also be beneficial in reducing the impact on zooplankton. Kirk & Gilbert (1990) for example showed that population growth rate of rotifers was reduced by coarse clay in the water column.

However, the greater density of coarse grain size capping agents could cause them to sink into sediment where the surface had a nepheloid layer, potentially rendering them ineffective as a capping layer. Consequently, a lower dose rate of the <1 mm grain size material could be as effective as the 350 g m^{-2} dose rate used in these tests as it would be less likely to completely block oxygen diffusion and less likely to sink into the sediments, while retaining a relatively rapid settling rate.\

Potential effects of sediment capping on denitrification

Under aerobic conditions, any NO_3-N in the over lying water in contact with the anoxic sediments would most likely be removed by denitrification (e.g. Downes, 1988). Consequently, the loss of NO_3-N from all incubation chambers under aerobic conditions is consistent with denitrification. The addition of high NO_3-N concentrations produced a larger reduction in NO_3-N confirming denitrification activity and indicating that the denitrification potential of the Lake Okaro sediments was in excess of 30 mg N m^{-2} d^{-1}.

Any adverse effect on denitrification by the Z2G1 capping layer would be expected to result in a reduction in the rate of removal of NO_3-N under aerobic conditions. Comparison of the mean denitrification potential values show a highly significant dose-rate effect with lower potentials in the 700 g m^{-2} than in the 350 g m^{-2} treatments at around 35% and 50% for the <1 mm and 1-3 mm grain size, respectively. Although not conclusive, this dose-rate and thus layer-thickness-dependent reduction in denitrification indicates partial suppression of denitrification by the Z2G1 capping material. While the Z2G1 may only be affecting the denitrification microbial community, it is more likely that the nitrification microbial community was also being affected.

The implication of a 50% reduction in denitrification means that additional N would be available in the water column for algal production. This effect may have been the cause of an increase in NH_4-N concentrations for a short period after an alum application to Lake Okaro (Paul *et al.*, 2008). As the apparent suppression effect occurred under aerobic conditions in the laboratory, it may be very important to avoid application of this, or any other capping material, to the permanently aerobic zones of a lake, such as the littoral zone. Consequently, accurate application of the capping material on the lake bed is very important.

Effect of Z2G1 on metal fluxes

A vertical shift of the redox boundary into the sediment capping layer could potentially lead to the release of redox-sensitive metals that are mobile under anaerobic conditions (Himmelheber *et al.*, 2008). Although the layer thickness of the Z2G1 capping material had the potential to enhance metal mobilization from

the sediments, there was little or no effect on metal fluxes from the sediments under aerobic or anoxic conditions. A small increase of 0.005 g m^{-3} and 0.013 g m^{-3} in Al under aerobic and anoxic conditions, respectively, from the 350 g m^{-2} of the <1 mm grain size treatments was not seen in the other treatments, including the higher dose rates. The lack of significant changes in metal concentrations in the overlying water column, even under anoxic conditions, may be attributed to the zeolite substrate which is a good cation absorber. The Al content in the Z2G1 recovered from <1 mm grain size treatments was variable but higher than in the new Z2G1, consistent with Z2G1 absorbing Al from the sediments. Apart from P, Z2G1 absorbed a range of metals from the sediment including Fe, Al, As, Hg, and K. Reduction in Na, Ca, and Mg content indicates an ionic exchange process may also be occurring between the zeolite substrate and the geothermally influenced sediments. These exchanges may also reflect the soft water and low alkalinity characteristics of Lake Okaro.

In this study we found Lake Okaro sediment contains about 2 g P kg^{-1} dry weight, which is consistent other studies (e.g. Trolle *et al.*, 2008) and gives a potential P load of about 0.78 g P m^{-2} per cm thick layer. With a P-binding capacity of around 20 g P kg^{-1} dry weight, the Z2G1 application rate of 350 g m^{-2} is capable of absorbing about 7 g P m^{-2} of sediment, which is equivalent to all of the P in the top 8 cm of sediment, assuming a uniform P content. However, as the majority of P released for internal loads has been found to come from the top 4 cm of the sediments (e.g. Cooke *et al.*, 2005; Heggie *et al.*, 2008), the dose rate of 350 g Z2G1 m^{-2} may be up to twice the required treatment rate for Lake Okaro. However, P releases have also been shown from sediment depths of up to 20 cm (Søndergaard *et al.*, 2003) but these contribute only a small part of the total P release.

The relative sediment coverage by the different grain size Z2G1 particles at the same dose rates showed that capping material particle size was important. While the larger particle size increased the settling rate and thus improved the ability to apply Z2G1 to selected areas of a lake bed, it reduced the coverage of the sediment per unit mass of material applied. The degree of sediment coverage affected the efficiency of the capping layer. Both grain size treatments completely blocked the release of P from the sediments indicating that the larger grain size granules could absorb P released from the sediments across the gaps between the

granules. However, subsequent analysis of the Z2G1 granules recovered from the sediments showed that the <1 mm grain size material had absorbed around 50% more P than the 1-3 mm grain size material over the 14-day incubation period. This greater P absorption is consistent with the expected higher P-removal efficiency by finer material. However, as no P was released from either grain size treatments, the extra P in the <1 mm grain size treatments implies a faster P release with the more complete coverage. This is also consistent with the blocking of oxygen diffusion into the sediments and the movement of the redox boundary into the <1 mm capping layer, as suggested by Vopel *et al.* (2008).

Conclusions

This study shows that Z2G1 P-inactivation agent is a potentially effective sediment capping material which completely blocked the release of P from the sediments under anoxic conditions, at the dose rates tested, and removed additional phosphate from the overlying water column in contact with the capping layer. While there was little difference in P removal between the high and low dose rates and fine and coarse grain sizes relative to the controls, there was a significant difference in uptake efficiency with finer material absorbing around 50% more P than the coarser material under the same conditions. This is likely to be a surface area effect with the finer material having a greater surface area per unit mass applied than the coarser material.

The cation absorption characteristics of the zeolite substrate allowed Z2G1 to adsorb some metals including As and Hg, as well as NH_4^+ from the water in contact with it and to completely block the release of NH_4-N from the sediments at the dose rates tested. Consequently, Z2G1 is the only sediment capping agent that inactivates both P and N.

The study results indicate a potential for Z2G1 to inhibit nitrification and denitrification under aerobic conditions. This means that Z2G1 could enhance N retention in the lake if it was applied in the permanently aerobic zones (e.g. littoral zone) of a lake. This is especially important in Lake Okaro where the narrow permanently aerobic littoral zone above 5 m is the only habitable area of lake bed for most of the year. To protect that habitat, any sediment capping agent would

need to be applied only to the lake bed below 5 m. That requires great precision in the treatment of the lake. Given that the granular nature of Z2G1 allows it to settle very quickly through the water column, Z2G1 will be more easily applied to that targeted zone than alum or most other P-inactivation agents.

Overall, the higher P absorption of the finer grain size material coupled with results that show a significantly greater P removal by the 350 g m^{-2} than 700 g m^{-2} dose rate, and a significantly lower effect on denitrification at the this rate, it would be reasonable to conclude that Z2G1 might best be used as a <1-mm grain size material at a dose rate of 350 g m^{-2} or less.

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