# SEDIMENT-PORE WATER CHEMISTRY OF TAUPO VOLCANIC ZONE LAKES AND THE EFFECT TROPHIC STATE HAS ON EXCHANGE WITH THE WATER COLUMN

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# ABSTRACT

The Taupo Volcanic Zone (TVZ) is in the Waikato and the Bay of Plenty regions of North Island of New Zealand and contains many volcanic lakes of diverse history, physiography, and limnology. The lakes vary in size (0.2 to 620 $km^2$), mixing regime (monomictic and polymictic), and trophic status (oligotrophic to supertrophic). The purpose of this study is to develop an understanding of the sediment-pore water interactions over a range of trophic conditions and how the biogeochemical cycles influence the lake ecosystem and the implications that this has for management of the TVZ lakes. The monthly changes in composition of lake water, pore water, sediments and stable isotopes of dinitrogen gas were monitored in five monomictic TVZ lakes (Taupo, Tarawera, Okataina, Rotoiti and Ngapouri) of widely varying trophic state, in order to evaluate the interaction between sediments and lake water. In particular, $^{15}N$ enrichment in the benthic nepheloid layer (BNL), sediment-pore water geochemistry, the lead record in the sediment and silicon as a potential limiting nutrient for diatom growth were studied. In addition to the monthly analysis, discrete studies were extended to 9 other lakes of the Rotorua District (Te Arawa Lakes) to reinforce the findings of the monthly study.

The applicability of the natural abundance of nitrogen gas isotope ratios was used to indicate the spatial distribution of nitrogen transformations in the water column and sediment pore waters of Lake Ngapouri. A method is introduced to extract gas from water samples to measure $\delta^{15}N$ [$N_2$] Samples were collected from the epilimnion, hypolimnion, benthic nepheloid layer and at 5 cm intervals from the sediment pore waters at monthly intervals for one year. Values of $\delta^{15}N$ [$N_2$] ranged from -1 to 0.28 ‰ in the epilimnion, -1.5 to 1.25 ‰ in the hypolimnion, -1.8 to 12.2 ‰ in the benthic nepheloid layer and -0.7 to 3.5‰ in sediment pore waters. Values of $\delta^{15}N$ [$N_2$] showed a strong seasonal pattern that was related to the loss of dissolved oxygen in the hypolimnion during seasonal stratification. Increases in $^{15}N$-enriched dinitrogen take place in the benthic nepheloid layer during the periods of anoxia (taken to be dissolved oxygen concentrations < 0.2

mg $L^{-1}$) and may be related to abundant ammonium substrate (up to 3.6 mg $L^{-1}$) to support denitrification. Nitrate concentrations increased up to 0.5 mg $L^{-1}$ with increasing duration of anoxia. We hypothesise that an alternative electron acceptor besides oxygen is required to support the nitrification needed for the production of nitrate. Iron and manganese hydroxides and oxides from material sedimenting out of the water column may have induced chemo-nitrification sufficient to oxidize ammonium in the anoxic benthic nepheloid layer. The nitrate formed would mostly be rapidly denitrified so that the $\delta^{15}N$ [$N_2$] would continue to become enriched during the presence of anoxia, as observed in hypolimnion and benthic nepheloid layer of Lake Ngapouri. The changes in $\delta^{15}N$ [$N_2$] values indicate the potential use of isotope ratios to identify and quantify potential chemo-nitrification/denitrification in the water column and sediment pore waters of lakes.

The study of $\delta^{15}N$ [$N_2$] was extended to 11 Taupo Volcanic Zone lakes in order to test the wider applicability of this method. . The stratified lakes showed enrichment of $\delta^{15}N$ [$N_2$] in the hypolimnion of up to 20.2‰ during stratification (autum 2007). A subset of five lakes was sampled monthly for up to one year. Water samples were taken from the epilimnion, hypolimnion and 0.1 m above the sediment-water interface (benthic boundarynepheloid layer, BNL), and from within the sediment at 5 cm depth intervals. Values of $\delta^{15}N$ [$N_2$] varied widely spatially and temporally. Gas extracted from the surface waters of all lakes remained close to equilibrium with the atmosphere (around 0‰). The hypolimnion showed some enrichment in autumn (up to 1.2‰), whilst samples from the BNL were strongly enriched in $^{15}N$. Maximum BNL values of $^{15}N$ [$N_2$] were 0.4‰ for Lake Taupo, 1.3‰ for Lake Tarawera, 5.3‰ for Lake Okataina, 6.4‰ in Lake Rotoiti and 12.2‰ in Lake Ngapouri. Enrichment of $^{15}N$ [$N_2$] within the BNL was greatest in lakes of highest trophic status and anoxic hypolimnia, suggesting diagenesis of particulate organic matter as the source of fractionation. Hypolimnion and BNL $\delta^{15}N$ [$N_2$] values correlated closely with volumetric hypolimnetic oxygen demand (VHOD) ($R^2$ = 0.92, P <0.001) and 'Trophic Level Index' (TLI) as an indicator of trophic status ($R^2$= 0.77, P <0.001).

Sediment and pore water samples were collected monthly from the central basins of five monomictic Taupo Volcanic Zone lakes of varying trophic state, to examine the diagenetic processes influencing the availability of major, trace elements and nutrients. A wide range of redox, diagenetic, dissolution and precipitation processes occurred, and these were specific to the compound examined, the lake and season. The dominant process associated with the onset of anoxia involved reduction, with nitrate to ammonium, manganic to manganous, ferric reduced to ferrous and sulfate to sulfide, as organic carbon was metabolised to carbon dioxide. The products of reduction were either reprecipitated as sulfides (especially pyrite) or transported to the oxic zone and oxidised (especially Mn). Ammonium was oxidised to nitrate and in the presence of anoxic conditions was denitrified. With burial the processes of hydrolysis and hydration of the siliceous sediments (including diatoms) released silicon and aluminium to the pore waters, with the Si diffusing to the lake and Al forming colloids and clay minerals. Phosphate, arsenate and many trace heavy metals (Cu, Zn, Hg, Pb and U) were released to the pore waters as the particulates containing them were dissolved and then adsorbed onto newly formed colloids or mineral phases. Protonation of small amounts of biogenic carbonates raised the concentrations of magnesium, calcium and strontium in the near-surface pore waters. Barium appeared to be transported as barite to the sediments and released into solution once sulfate concentrations decreased under reducing conditions. Geothermal fluid inputs in lakes Tarawera (surface-water) and Rotoiti (sub-surface) were important for inputs of conservative elements (Li, B, Na and K). The pore waters showed strong seasonal changes in Fe, Mn, $NH_4^+$, $SO_4^{2-}$ and associated ions such as the phosphates ($H_2PO_4^-$, $HPO_4^{2-}$ $PO_4^{3-}$) driven mostly by changes in redox potential and the depth to which oxygen penetrated during mixed lake conditions. With hypolimnetic anoxia in lakes Okataina, Rotoiti and Ngapouri, concentrations of Fe, Mn and $NH_4^+$ increased in upper pore waters and $SO_4^{2-}$ decreased. It is likely that polyoxides ($PO_4$ and $AsO_4$ species) and chalcophilic elements (Cu, Zn, Pb, Hg) undergo some degree of redox cycling, either directly or indirectly in association primarily with Fe, Mn and $SO_4^{2-}$. Average annual fluxes of nutrient species were calculated from near-surface diffusion gradients using Ficks first law. Oligotrophic lakes (Taupo, Tarawera and Okataina) typically had higher fluxes of Fe, Mn and Si from the sediment to the overlying lake water while eutrophic lakes (Rotoiti and Ngapouri) had higher fluxes of $NH_4^+$ and total dissolved P from the sediment and S and $NO_3^-$ into the sediments. Geothermal fluid inputs to Lake Rotoiti had influenced conservative element concentrations, especially Na (2006 mg $m^{-2}$ $yr^{-1}$). The range of fluxes of nutrients in the five lakes was 16.5 to 377 mg $m^{-2}$ $yr^{-1}$ for $NH_4^+$, 1.3 to 110 mg $m^{-2}$ $yr^{-1}$ for total dissolved phosphorus and 0.05 to 18.5 mg $m^{-2}$ $yr^{-1}$ for reactive $PO_4$ species.

In lakes there is rapid deposition and often little bioturbation of lead, resulting in an excellent depositional history of changes in both natural and anthropogenic sources. The objective of this study was to use sediments from a regionally bounded set of lakes to provide an indication of the rates of environmental inputs of lead whilst taking into account differences of trophic state and lead exposure between lakes. Intact sediment gravity cores were collected from 13 Rotorua lakes in North Island of New Zealand between March 2006 and January 2007. Cores penetrated sediments to a depth of 16-30 cm and contained volcanic tephra from the 1886 AD Tarawera eruption. The upper depth of the Tarawera tephra enabled prescription of a date for the associated depth in the core (120 years). Each core showed a sub-surface peak in lead concentration above the Tarawera tephra which was contemporaneous with the peak use of lead alkyl as a petroleum additive in New Zealand. An 8 m piston core was taken in the largest of the lakes, Lake Rotorua, in March 2007. The lake is antipodal to the pre-industrial sources of atmospheric lead but still shows increasing lead concentrations from < 2 up to 3.5 µg $g^{-1}$ between the Whakatane eruption (5530 ± 60 cal. yr BP) and the Tarawera eruption. Peaks in lead concentration in Lake Rotorua are associated with volcanic tephras, but are small compared with those arising from recent anthropogenic-derived lead deposition. These results show that diagenetic processes associated with iron, manganese and sulfate oxidation-reduction, and sulfide precipitation, act to smooth distributions of lead from anthropogenic sources in the lake sediments. The extent of this smoothing can be related to changes in sulfate availability and reduction in sulfide driven by differences in trophic status amongst the lakes. Greatest lead mobilisation occurs in mesotrophic lakes during seasonal anoxia as iron and manganese are released to the pore water, allowing upward migration of lead towards the sediment-water interface. This lead mobilisation can only occur if sulfides are not present. The sub-surface peak in lead concentrations in lake sediments ascribed to lead alkyl in petroleum persists despite the diagenetic processes acting to disperse lead within the sediments and into the overlying water.

Intact sediment cores were taken from the deepest basins of nine lakes in the Taupo Volcanic Zone, New Zealand, to investigate the factors controlling silicon (Si) concentrations in sediment pore waters and the flux of Si to the overlying lake water. The lakes ranged in trophic state from oligotrophic to highly eutrophic. A Si transport model developed from the vertical gradients of pore water concentrations simulated Si gradients with high precision ($r^2 > 0.95$, $p < 0.01$) in lakes where there were no volcanic tephra layers or significant geothermal inflows. The ubiquitous presence of diatom frustules in the sediment was likely responsible for release of silicon to the pore waters and subsequent diffusion to overlying lake waters. Fluxes of silicon were related to the trophic status of the lake and were greatest in eutrophic lakes where diatom populations reduced epilimnetic silicon concentrations to <1 mg $L^{-1}$. Temporal variations in the concentrations of Si, N, and P suggest that over most of the year diatom growth in the oligotrophic lakes is limited by nitrogen, or co-limited by nitrogen and phosphorus, whilst in some eutrophic lakes silicon may limit diatom growth during mixed conditions and phosphorus and/or nitrogen may limit phytoplankton growth when the lake is stratified. The rapid decline in Si concentrations below 0.1 mg $L^{-1}$ after lake mixing is likely to increase dominance of non-siliceous flagellated species and cyanobacteria over diatoms.

The challenge facing lake managers is there is not one single factor that controls water quality. Biogeochemical cycles controlling the availability and cycling of nutrients cannot be separated from those processes controlling other chemical species. Conservative components are needed to compare, contrast and understand non-conservative transitions. The overall budget of the lake cannot be fully understood without including these processes. Where lead has not been significantly remobilised its peak concentration in combination with the depth to the Tarawera Tephra (a non-mobile marker) can be used to assess sedimentation rates by dating the sediments and allowing historical nutrient concentrations TVZ lakes to be derived. Understanding the lake specific sediment diagenetic processes coupled with ecological modelling should enable remediation strategies to be better targeted. The rapid depletion in silicon in some TVZ lakes suggests there is potential for the use of reactive silicon as a remediation method. $\delta^{15}N$ [$N_2$] extracted from the BNL or near-bottom waters may be a useful indicator of trophic state and could potentially be used as a monitoring tool to rapidly assess changes in trophic state in stratified lakes or in lakes not routinely monitoured.

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# PREFACE

This thesis is comprised of seven chapters, which describe the results obtained during the course of 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 fieldwork and laboratory work, data analysis, interpretation and writing was produced from my own ideas, undertaken while under the supervision of Associate Professor Chris Hendy and Professor David Hamilton (University of Waikato).

Co-authors of the papers listed below have contributed with supporting data, discussions and revisions of the manuscript. In Chapter 2, Warwick Silvester came up with the concept method for extracting dinitrogen gas. In Chapter 3, Chris McBride provided the data for the 11 lake $^{15}$N series and Denise Bruesewitz provided the denitrification potentials for the Rotorua lakes. In Chapter 5, Rachel Picket provided the piston core data for the Lake Rotorua sediment lead record. In Chapter 6, Chris Hendy developed the silicon transport model.

Chapter 2 has been published in Aquatic Geochemistry under the tile 'Nitrogen-15 isotope enrichment in benthic boundary layer gases of a stratified eutrophic iron and manganese rich lake' by L. K. Pearson, C. H. Hendy, D. P. Hamilton and W. B. Silvester (doi: 10.1007/s10498-011-9143-2).

Chapter 3 has been submitted to Hydrobiologia under the tile 'Nitrogen-15 isotope enrichment in lake bottom waters is related to trophic status and hypolimnetic oxygen demand' by L. K. Pearson, C. H. Hendy, D. P. Hamilton, C. G. McBride and D. A. Bruesewitz.

Chapter 4 will likely be submitted to a geochemical journal under the title 'Sediment-pore water geochemistry and diffusive fluxes of elements in selected lakes of the Taupo Volcanic Zone, New Zealand' by L. K. Pearson, C. H. Hendy and D. P. Hamilton.

Chapter 5 has been published in Earth and Planetary Science Letters under the title ‘Natural and anthropogenic lead in sediments of the Rotorua lakes, New Zealand’ by L. K. Pearson, C. H. Hendy, D. P. Hamilton and R. C. Pickett (doi: 10.1016.j.epsl.2010.07.005).

Chapter 6 is under review in Inland Waters under the title ‘Dynamics of silicon in lakes of the Taupo Volcanic Zone, New Zealand, and implications for diatom growth’ by L.K. Pearson, C.H. Hendy and D.P. Hamilton.

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# CHAPTER 1: INTRODUCTION

## 1.1 MOTIVATION

The Taupo Volcanic Zone (TVZ), in the North Island of New Zealand, contains many lakes of volcanic origin which differ greatly in their trophic status and limnological characteristics (McColl, 1977; Burns et al., 1997). In some, such as Rotorua and Rotoiti, there are problems with eutrophication, resulting in algal blooms and deoxygenation of bottom waters, which cause serious concerns for public health and lake ecosystem health. In others, such as Lake Taupo the threat of increasing eutrophication may result in major and potentially costly land use changes for land owners in this catchment. The intense public pressure brought to bear on regional authorities increases potential for impulsive actions before there is a thorough understanding of the processes currently affecting nutrient (especially nitrogen) behaviour within the lakes. Waikato Regional Council (formerly Environment Waikato) has a proposed 20% reduction in nitrogen loads to Lake Taupo from manageable sources, with the aim of protecting the lake (Environment Waikato, 2003). In 2005, the Bay of Plenty Regional Council (formerly Environment Bay of Plenty) introduced “Rule 11” to the Regional Land and Water Plan, which puts a nutrient cap on rural properties over 0.4 ha in catchments of lakes with degraded and/or declining water quality (Environment Bay of Plenty, 2004; 2008). The intent of Rule 11 is to cap nitrogen and phosphorus losses from the property to no more than the annual average loss that occurred during the benchmark period between July 2001 and June 2004. However, without increased knowledge of nutrient cycling in the lakes it is not possible to determine how effective the regional authorities’ plans are.

Nitrogen (N) and phosphorus (P) enter lakes in the Taupo Volcanic Zone largely as a result of leaching (as nitrate) and weathering (as particulate phosphorus). These lakes have had historically low levels of atmospheric N deposition and little urban development in their lake catchments. Groundwater, which is the dominant inflow to the lakes, is naturally high in P from edaphic sources (tephras) and ignimbrite aquifers (White, 1983). Analyses of N:P ratios (White, 1983; White et al., 1985; Elser et al. 1990; Koszelnik et al. 2007, Abell et al., 2010) and bioassays (Priscu et al., 1986; Downes, 1988; Downs et al., 2008) indicate that nitrogen (N) may limit primary productivity in many lakes in New Zealand, as well as globally and nitrogen limitation appears fairly widespread amongst lakes in the Taupo Volcanic Zone.

### 1.1.1 Nutrient Cycling

Studies of nutrient cycling in lakes, particularly in the Northern Hemisphere, emphasise understanding of phosphorus dynamics as it has a strong impact on the production of phytoplankton as the lakes are mostly P-limited (Søndergaard et al., 2003; Zhou, 2000; Van der Molen et al., 1998; Kleeberg & Kozerski, 1997). Nitrogen plays a fundamental role in eutrophication, however, because it is quite often a limiting nutrient in aquatic ecosystems, especially where there is a low N:P ratio (Koszelnik et al. 2007; Elser et al. 1990). Globally, there is increasing awareness of the need to reduce nitrogen inputs to aquatic ecosystems if water quality is to be improved (Vitousek et al., 1997; Galloway et al., 2003; Harrison et al., 2009; Gardner and McCarthy, 2009; Vanni, 2010), though the basis for N reductions to assist with eutrophication control remains the subject of ongoing debate (Schindler et al., 2008; Conley et al., 2009).

Intensification of land use in the TVZ is increasing the concentration of nitrate in groundwater discharging into many of these lakes via tributary streams arising in close proximity to the lakes (Morgenstern et al., 2004). However observations of concentrations of total nitrogen in the hypolimnia of seasonally stratified lakes do not show increases that might be expected from these increasing loads of nitrate entering the lakes. A significant lag time is recognised in nutrient stream and groundwater inflows and recent land use intensification is only partially expressed (Hamilton, 2005).

Lake sediments play an important role in nutrient dynamics and eutrophication because recycling of nutrients can markedly increase the total nutrient load to a lake (Søndergaard et al., 2003; Burger et al., 2007). Recent studies at the University of Waikato, investigating the behaviour of nutrients within TVZ lakes, especially Lake Rotorua, have shown that much of the phosphorus entering the lakes is retained within the lake system, often recycling many times between sediment and water column before being either discharged or incorporated into immobile phases within the sediment (Untaru, 2005; Burger, 2006; Motion, 2007; Pearson, 2007). Burger (2006) calculated the cycling of phosphorus and nitrogen from the sediments in Lake Rotorua and found that release rates varied with season and with sample water depth, with the highest release rates coinciding with periods of stratification and associated decline in dissolved oxygen in the hypolimnion in the deepest sample sites. Sediment re-suspension is also an important process in Lake Rotorua, and was estimated by to contribute up to 71% of the sedimenting total particulate matter (Burger, 2006). The Lake Rotorua nutrient budget indicated that internal nutrient sources derived from benthic fluxes are far more important than external nutrient sources to the lake, thus increasing the rate of eutrophication over what might be expected on the basis of external loads alone (Burger, 2006).

The removal of nitrogen in lakes is dominated by denitrification, the microbial reduction of nitrate ($NO_3^-$) to molecular nitrogen ($N_2$) under low-oxygen conditions (dissolved oxygen (DO) $< 0.2$ mg $L^{-1}$ (Seitzinger et al. 2006)). Denitrification is controlled primarily by the availability of carbon, nitrate, and levels of dissolved oxygen (Seitzinger 1988; Tomaszek 1995; Hellström 1996; Saunders and Kalff 2001). Conditions in the surficial bottom sediments of lakes favour denitrification due to high organic matter inputs from the overlying water column and strong DO gradients (Pina-Ochoa and Álvarez-Cobelas 2006; Seitzinger et al. 2006). Therefore, denitrification can remove a large fraction of the nitrogen originally sourced from lake catchments and the atmosphere (Seitzinger 1988). Bruesewitz (2011) measured denitrification enzyme activity (DEA) to assess the sediment denitrification potential of 10 Rotorua lakes ranging in the proportion of agriculture from 3 to 96% in the lake catchment to determine if there is a link between agricultural land use and sediment denitrification potential. It was found that Lake Okaro, with 96% catchment agriculture, had approximately 15 times higher DEA than Lake Tikitapu, with 3% catchment agriculture (232.2 vs. 15.9 µg N $g^{-1}$ AFDM $h^{-1}$, respectively; AFDM, ash free dry matter). Therefore, lakes retain a high capacity to remove excess N via denitrification under increasing N loads from higher proportions of catchment agriculture.

If a substantial fraction of the nitrogen, carried from the water column to the sediments, is denitrified at the sediment-water interface or within the water column itself, the potential to reduce the rate of eutrophication associated with increasing nitrogen loads increases. Priscu et al. (1986) showed that during summer stratification the hypolimnion of Lake Rotoiti was always a sink for chlorophyll, particulate nitrogen, particulate phosphorus and dissolved oxygen, and a source for ammonium and dissolved reactive phosphorus. However, a 0.34 mg $m^{-2}$ $d^{-1}$ diffusion of dissolved inorganic nitrogen from the hypolimnion to the epilimnion during summer would alleviate the nitrogen deficiency in the lake (Priscu et al., 1986). McCarthy et al., (2007) measured sediment-water interface nitrogen transformation rates in Lake Rotoiti using continuous-flow benthic chambers and found denitrification is fuelled primarily from overlying water nitrate rather than nitrate from nitrification. The findings of McCarthy et al. (2007) suggest that dissimilatory nitrate reduction to ammonium (DNRA) (Rysgaard et al., 1996; An and Gardner, 2002) contributed to some of the accumulated ammonium in the hypoxic hypolimnion in Lake Rotoiti.

Biological denitrification is not the only mechanism for producing dinitrogen (Hulth et al. 2005). Dinitrogen could also be produced by the reduction of nitrate by dissolved manganese (chemo-denitrification) (Sørensen et al. 1987; Aller 1990; Schultz et al. 1994; Murray et al. 1995; Luther et al. 1997). Alternatively, ammonium ions can be oxidised under anaerobic conditions utilising nitrate as the electron acceptor (anaerobic ammonium oxidation; ‘Anammox’) (Mulder et al. 1995; Thamdrup and Dalsgaard 2002; Daslsgard et al. 2003; Kuypers et al. 2003; Schubert et al. 2006; Bartlett 2008; Mortimer et al. 2002; 2004; Luther and Popp 2002; Humbert et al. 2010) and ammonium and organic-N can also be oxidized by $MnO_2$ (Froelich et al. 1979; Luther et al. 1997) to produce dinitrogen gas. Iron oxides and sulfates are also capable of oxidising ammonia in ecosystems such as lakes where pH in hypolimnetic waters may be <6.5. An analogous catalytic cycle involving iron is more thermodynamically favourable than manganese (Postma 1990; Luther et al. 1997; Luther 2010).

Identifying when, where, and how much denitrification occurs from monitoring the $N_2$ end-product of this reaction is particularly challenging as naturally abundant atmospheric $N_2$ dissolved in water masks relatively small changes that may be induced by denitrification (Seitzinger et al., 2002; Van Breemen et al., 2002; Galloway et al., 2004; Boyer et al., 2006; Groffman et al., 2006). Analysis of stable isotopes provides a technique for discriminating different sources of N used in denitrification, as the process of denitrification results in more rapid utilization of nitrate containing the $^{14}N$ isotope than $^{15}N$, resulting in significant discrimination and enrichment of the substrate pool in $^{15}N$ (Brandes and Devol 1997; Granger et al. 2008). Changes in $\delta^{15}N$ [$N_2$] in different vertical compartments (e.g., epilimnion, hypolimnion and benthic boundary layer) of monomictic lakes could allow the environmental drivers and location of denitrification to be identified throughout the annual cycle of stratification and mixing.

Silicon (Si) has often been overlooked when determining nutrient limitation in lakes as most studies have focused on nitrogen (N), phosphorus (P), or both nutrient species (Schindler et al. 2008, Harrison et al. 2009, Conley et al. 2009, Abell et al. 2010). Silicon is required as a macronutrient for diatoms and is incorporated into the frustule, which is composed of opaline or biogenic silica ($SiO_2.nH_2O$) (Round 1990). The ratios of different nutrient species have been used to indicate nutrient limitation but silicon is often not considered in these assessments.

Phytoplankton growth may become limited when the mass ratio (by weight) of total nitrogen (TN) to total phosphorus (TP) deviates from the Redfield ratio of 7.2:1 (Redfield 1958). However, there is no sharp boundary between N and P limitation because not all phytoplankton require N and P in the proportions of the Redfield mass ratio, and measurements of TN and TP are not always representative of the available nutrient supply (Rhee 1982, White et al. 1985, Pridmore 1987). Earlier studies have concluded phytoplankton growth is dependent on N when TN:TP <10 and P when TN:TP >17 (Sakamoto 1966, Forsburg et al. 1978, OECD 1982). For New Zealand lakes, which contain a considerable proportion of TN in the form of dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP), which are generally not immediately assessible as nutrient sources, White et al. (1985) proposed that the following ratios be used instead: ((TN-DON)/(TP-DOP)) < 7 as indicative of N limitation and > 15 as indicative of potential P limitation (Pridmore 1987). Concentrations of dissolved inorganic nitrogen (DIN) and dissolved reactive phosphorus (DRP) have also been demonstrated to be effective for identification of the limiting nutrient, especially at low N levels (Morris and Lewis 1988).

Diatom growth may become Si-limited when the Si:DIN mass ratio decreases below 2:1 (Turner et al. 1998) or the Si:$PO_4$ ratio decreases below 9:1 (Dortch and Whitledge 1992, Hamilton et al. 2006). Therefore, Si limitation of diatoms plays a fundamental role in the succession of phytoplankton communities (Sommer and Stable 1983, Carlsson and Granéli 1999, Gobler et al. 2006). When silica concentrations reach levels that limit diatom growth, diatoms may be out-competed by other phytoplankton, including cyanobacteria, which can exploit the available nutrient supply (Justić et al. 1995, Rocha et al. 2002).

### 1.1.2 Sediment-pore water interactions

Sediments may act as both sources and sinks for nutrients and trace elements, thus potentially playing an important role in the dynamics of the overlying water column (Nürnberg, 1984; Peterson et al., 1995; Søndergaard et al., 2003). Internal processes which result in redistribution of trace elements within lakes include; incorporation of trace elements into organic tissue and diatom frustules, adsorption onto the surfaces of suspended organic, clastic or colloidal material, release as substrates are metabolized or resolubilized, and precipitation of, or adsorption onto, new diagenetic minerals. The physical limnology and trophic status of lakes are critical to these processes. Lakes which are deep compared to their surface area, wind fetch or water flow, stratify with colder denser waters forming a hypoliminion separated from the warmer epilimnion by a thermocline. In these lakes oxygen is generally only re-supplied to the hypolimnion when the water column turns over, for example for a brief period in winter in monomictic lakes.

Organic matter produced in or transported to the epilimnion sinks towards the lake bottom, producing a volumetric hypolimnetic oxygen demand (VHOD) within the water column and at the sediment-water interface. The hypolimion becomes anoxic when the VHOD results in complete consumption of oxygen in this layer and is associated with a decrease in redox potential (Eh) and progressive loss of other oxidized species (e.g., nitrate, manganese IV and iron III). Anoxia may occur even in lakes where thermal stratification is brief (e.g. polymictic lakes) or trophic status is low, so that anoxic conditions do not develop within the water column. In these cases, the settling organic debris can result in anoxia in a zone of restricted turnover close to the sediment-water interface, commonly referred to as a benthic boundary layer (BBL) (Gloor et al., 1994; Boudreau and Jørgensen, 2001) or benthic nepheloid layer (BNL) (Hawley, 2004). As not all of the organic debris is re-metabolised during its descent to the sediment, oxidation continues following burial so long as oxidised species (dissolved oxygen, sulfate, ferric ions, manganic ions, nitrate, etc.) can be made available. This results in critical redox boundaries developing at various depths above and below the sediment-water interface.

As organic matter accumulates within the BNL or sediment column aerobic and then anerobic metabolism produce significant chemical changes to the settling material. Phosphorus contained within organic matter is recycled to phosphate ions, nitrogen to nitrate, nitrite or ammonium ions, ferric is reduced to ferrous, manganic to manganous and sulfate to sulfide. In addition many trace elements are released to solution as their host particulates are metabolised. This process results in significant changes in the concentrations of many of the ions and the generation of concentration gradients within the sediment pore waters. Concentration gradients of dissolved substances then result in transport by molecular diffusion within pore water and across the sediment-water interface where turbulent diffusion will play an increasingly important role.

There are three fundamental processes that affect concentration profiles of substances in pore water; consumption of a reactant in pore water, release of a substance from the solid phase to the pore water and diffusion transport of dissolved substances in pore water and across the sediment-water interface (Schultz, 2006). Common pore water concentration profiles are shown in Figure 1.1 where the sediments were initially homogeneous. If a substance is not subjected to any early diagenetic processes then the concentration profile is the same as the overlying water (Figure 1.1a). This is typical of conservative elements such as Li, B and Na. The concentration profile of a substance consumed by early diagenesis in the near surface sediment is similar to Figure 1.1b. For example dissolved oxygen will have this type of profile. With increasing depth the concentration gradient and the diffusive material will decline until they reach zero. This point is known as the penetration depth of a substance (Schultz, 2006). The reverse of profile b) shows the release of a substance near the sediment surface. If this release is limited to one reactive layer then profile c) is formed. The reverse of profile c) is the consumption of a substance in one reactive layer. Within the reactive layer the dissolved substance reaches zero concentration by depletion. The presence of two reactive layers forms a peak in concentration just below the sediment-water interface (Figure 1.1d). This peak represents a substance that is diffusing in both upward and downward directions along the concentration gradient. The substance is released into the overlying water body and removed from the pore water by diagenetic reactions deeper in sediment. Phosphate often displays this profile as organic phosphorus is decomposed by bacteria in the upper layers of the sediment releasing dissolved phosphate in to the pore water which is simultaneously removed from the pore water by the precipitation of authigenic minerals, such as vivianite, deep in the sediment (Berner, 1980).

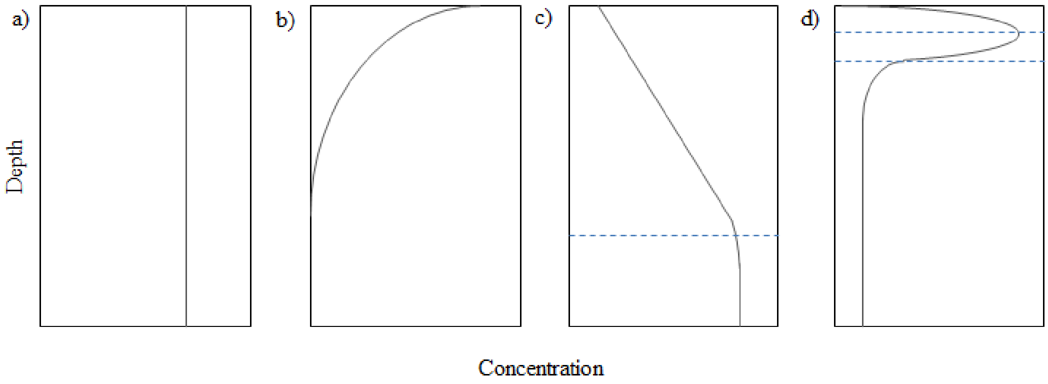

**Figure 1.1:** Common pore water concentration profiles showing a) a non-reacting substance, b) a substance that is depleted in the upper layers of the sediment, c) a substance being released into the pore water at depth and d) a substance being released into pore water near the sediment surface then removed from the sediment surface at depth (adapted from Schultz, 2006). The reactive layers are shown by dotted lines.

With advances in analytical techniques and improvements in the ionisation efficiency and sensitivity of inductively coupled plasma – mass spectrometry (ICP-MS) in recent years, environmental water samples are able to be analysed for a larger number of trace elements with much lower detection limits. This has also allowed the analysis of both major and a wide range of trace elements to be studied in smaller quantities of water to elucidate the diagenetic processes occurring at the sediment-water interface and within the surficial sediments. Although the lakes studied here are all of volcanic origin, the conclusions drawn are likely applicable to many other types of lakes in New Zealand and globally.

Determining deposition rates in most lakes is limited by the difficulty of determining the age of the sediment. Lakes in or close to the Taupo Volcanic Zone have had tephra deposits from a number of volcanic centres which provide a number of easily recognisable horizons of well-defined age. In the Rotorua lakes the two most commonly encountered tephras are the Tarawera Tephra of 10 June, 1886 and the Kaharoa Tephra of 1314 ± 12 AD, both of which erupted from the wider Okataina Volcanic Centre (Lowe and Green, 1992). For the purposes of this study, the Tarawera Tephra can be found within the top 20 cm of Lakes Tarawera, Okataina and approximately 30 cm from the sediment-water interface in Lake Rotoiti. The Rotomahana Mud (Tarawera Tephra) partially or totally sealed preexisting sediment at the time of the Tarawera eruption or shortly after during periods of extensive erosion (Adams, 1992).

The effectiveness of tephra as a dating tool can be applied to lakes where anthropogenic additions of a substance are preserved in the lake sediments. Lead is a good example of such a contaminant as it occurred naturally in the environment due to erosion of sediments and in association with weathering of catchment bedrock and soils (Renberg et al., 2002), as well as atmospheric inputs from volcanic eruptions (Graney et al., 1995). With increasing anthropogenic additions of lead to the natural environment it has been possible to distinguish anthropogenic sources from natural sources in lake sediments (Edgington and Robbins, 1976; Graney et al., 1995; Monna et al., 1999; Renberg et al., 2002). In New Zealand, the only significant, broadscale anthropogenic source of lead over the past century is from petroleum additives. In the absence of natural environmental fluctuations, variations in lead within recent lake sediments should reflect changes in anthropogenic sources, whilst variations amongst lakes may reflect complex interactions with the environmental conditions leading to net deposition to the sediments. The presence of tephras provides time markers from which age models can be used to determine the changing input rates of anthopogenic lead.

## 1.2 OVERVIEW OF TAUPO VOLCANIC ZONE LAKES

The TVZ is a long band of active volcanism caused by the oblique subduction of the Pacific tectonic plate beneath the Indo-Australian tectonic plate, to the east of the North Island, New Zealand (Cox, 1989). It is a NE-SW oriented zone of volcanic activity that extends from Ruapehu in the south to beyond White Island in the north. It has maximum dimensions of 300 km long x 60 km wide as defined by active volcanic centres (Wilson et al., 1995). Explosive rhyolitic eruptions have formed numerous calderas, hydrothermal explosion craters and associated pyroclastic flows have impeded drainage and subsequently formed lakes. Five

TVZ lakes were chosen as the focus of this study (Taupo, Tarawera, Okataina, Rotoiti and Ngapouri) and were used for comparison with other TVZ lakes.

New Zealand's largest lake, Taupo (area 616 $km^2$), is located near the centre of the North Island and was formed 27 097 ± 957 cal. yr BP from a super volcano (Oruanui eruption) and modified by subsequent eruptions of which the last was Taupo (1717 ± 13 cal. yr BP) (Lowe et al., 2008). The Rotorua Lakes District comprises more than 15 lakes of 0.3 to 80 $km^2$ which were formed up to 140 000 years ago by a series of volcanic eruptions that led to the formation of craters and damming of river valleys (Lowe and Green, 1992). Lakes Tarawera and Okataina formed as pyroclastic flows of the Te Rere phase of the Haroharo volcanic complex, dated by Nairn (1992) at 25 271 ± 779 cal. yr BP. Lake Rotoiti formed about 50 000 years ago from pyroclastic flows damming a river valley draining the Lake Rotorua caldera from the Haroharo volcanic complex (Lowe and Green, 1992). A caldera formed at the eastern end of the lake during this period of volcanism with depths mostly 60-80 m but with an active hydrothermal vent of 125 m within the caldera. Lake Ngapouri is a small eutrophic lake within a hydrothermal explosion crater formed as part of the Kaharoa eruption of 636 ± 12 cal. yr BP (Lowe et al., 2008).

Lake water quality monitoring has been undertaken in the Rotorua lakes since 1990 and in Lake Taupo since 1994, under the National Regional Monitoring Network (NERMN). The NERMN programme was established for general 'state of the environment' monitoring in which temperature, dissolved oxygen, conductivity and fluorescence are recorded with a profiler and water samples are collected at specific depths and analysed for nutrients (dissolved and total levels) and chlorophyll *a*, on a regular basis. The time series data for nutrients, transparency and algal biomass are synthesised using the Trophic Level Index (TLI) (Eq. 1.5) (Burns et al., 2000) to assess long term changes in water quality (Figure 1.2).

The TLI is calculated from the following equations:

Trophic Level for nitrogen (TLn) = -3.61 + 3.01 log(TN) (1.1)

Trophic Level for phosphorus (TLp) = 0.218+2.92 log(TP) (1.2)

Trophic Level for Secchi (TLs) = 5.10 + 2.27 log(1/SD – 1/40) (1.3)

Trophic Level for chlorophyll *a* (TLc) = 2.22 + 2.54 log(Chl*a*) (1.4)

TLI = (TLn + TLp + TLs + TLc)/4 (1.5)

Trophic level bands are grouped into trophic states for quantitative description, microtrophic to hypertrophic as shown in Table 1.1.

**Table 1.1:** Trophic level classification for New Zealand lakes and reserviours (Burns et al., 2000).

| Trophic state | Nutrient enrichment category | Trophic level | TP (mg/m$^3$) | TN (mg/m$^3$) | Chla (mg/m$^3$) | Secchi depth (m) |
|---|---|---|---|---|---|---|
| Ultramictrophic | Practically Pure | 0.0 to 1.0 | < 1.8 | < 34 | < 0.33 | >25 |
| Microtrophic | Very Low | 1.0 to 2.0 | 1.8 - 4.1 | 34 - 73 | 0.33 - 0.82 | 25 - 15 |
| Oligotrophic | Low | 2.0 to 3.0 | 4.1 - 9 | 73 - 157 | 0.82 - 2.0 | 15 - 7 |
| Mesotrophic | Medium | 3.0 to 4.0 | 9 - 20 | 157 - 337 | 2.0 - 5.0 | 7 - 2.8 |
| Eutrophic | High | 4.0 to 5.0 | 20 - 43 | 337 - 725 | 5.0 - 12.0 | 2.8 - 1.1 |
| Supertrophic | Very High | 5.0 to 6.0 | 43 - 96 | 725 - 1558 | 12.0 - 31.0 | 1.1 - 0.4 |
| Hypertrophic | Saturated | > 6.0 | > 96 | > 1558 | > 31 | < 0.4 |

Changes in trophic state can also be assessed by the rate of consumption of oxygen from the bottom waters of the lake, the volumetric hypolimnetic oxygen demand (VHOD). The VHOD is caused primarily by the decomposition of organic material in the hypolimnion and can be used as an integration of all biological processes (Burns, 1995).

The TLI of Lake Taupo shows a general increase in TLI (i.e. reduced water quality) from 1995 to present but net change is less than 0.5 of a TLI unit (Gibbs, 2011). The Rotorua lakes studied also showed a general increase in TLI from 1995 but in recent years there has been an indication of reducing TLI (Figure 1.2). Improvement in water quality may be due to remediation actions taken by the regional council. For example, in Lake Rotoiti a 1,275 m long diversion wall was constructed as a means to restore water quality in Lake Rotoiti by preventing incoming water originating from Lake Rotorua from entering the main body of the lake. This water is now diverted directly down the Kaituna River (Hamilton et al., 2009).

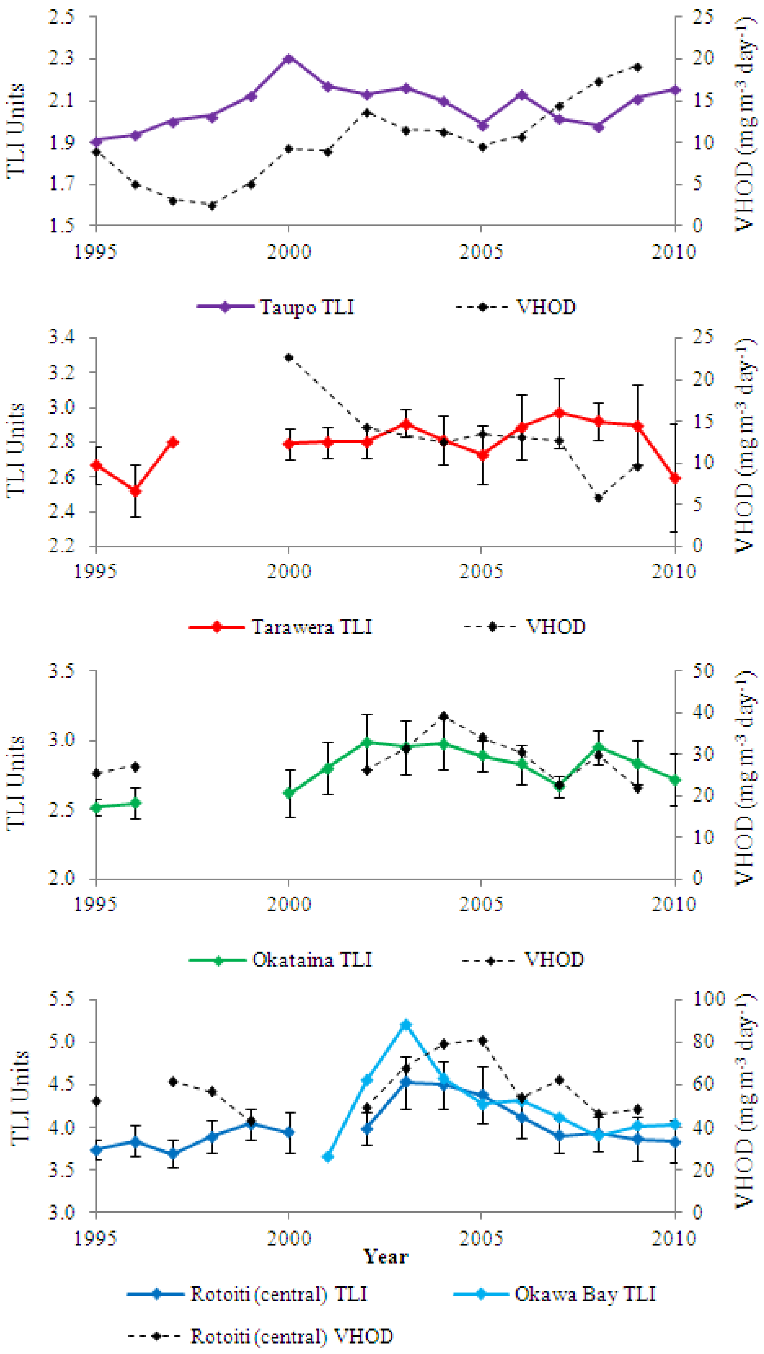

**Figure 1.2:** Average annual Trophic Level Index (TLI) (left axis) and volumetric hypolimnetic oxygen demand (VHOD) (right axis) for lakes Taupo, Tarawera, Okataina and Rotoiti. Error bars show standard error derived from monthly measurements. Figure produced from data provided by Scholes (2010) for the Rotorua lakes and Gibbs (2011) for Lake Taupo.

Lake Ngapouri is not incorporated in NERMN so there is no long-term data available for this lake. However, there is at least anecdotal evidence of a decline in water quality as Lake Ngapouri was reported as oligotrophic prior to 1962 (Fish 1970) and is presently eutrophic. The lake became increasingly eutrophied as native forest in the catchment was converted to pastoral farmland (beginning 1952; Fish 1970). Prior to 1962, the hypolimnion of Lake Ngapouri remained oxygenated throughout the year but by 1966 the hypolimnion had become anoxic (Fish 1970) and by 2007/08 it was anoxic for eight months of the year, with a high nutrient content and cyanobacteria biomass (Pearson 2012).

Phytoplankton assemblages in the TVZ lakes were assessed by Ryan et al. (2006), who examined the presence/absence of diatom and cyanobacteria genera (Table 1.1). It was found that in lakes that were polymictic and regularly fully mixed in summer, there was a greater variety of cyanobacteria genera than diatom genera compared with lakes that stratify in summer. Conversely, relatively high numbers of diatom to cyanobacteria genera were found in lakes that stratify seasonally compared with those that were regularly mixed. Mixing regime played a more important role in regulating phytoplankton composition than either nutrient status or light climate as eutrophic stratified Lake Okaro had a phytoplankton composition similar to that of the oligotrophic stratified lakes (e.g., Taupo) (Ryan et al., 2006). For full composition of algal population percentages for the Rotorua Lakes see Wilding (2000).

**Table 1.2:** Phytoplankton assemblages in Taupo Volcanic Zone lakes as shown by a shade matrix (adapted from Ryan et al., 2006). Lakes selected for this study are shown in red.

| | 2006 Trophic Level Index (TLI) | Mixing status (S= Stratified, P= Polymictic) | Diatoms | | | | | | | Cyanobacteria | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *Navicula* | *Asterionella* | *Cocconeis* | *Fragilaria* | *Cyclotella* | *Aulacoseira* | *Synedra* | *Anabena* | *Aphanizomenon* | *Oscillatoria* | *Microcystis* | *Coelosphaerium* |
| Taupo | 2.1 | S | | 🟥 | | 🟥 | 🟥 | 🟥 | | 🟥 | | | 🟥 | |
| Rotoma | 2.5 | S | ▨ | | | ▨ | ▨ | ▨ | | | | | | ▨ |
| Tarawera | 2.8 | S | | | | 🟥 | 🟥 | 🟥 | | | | | 🟥 | |
| Okataina | 2.9 | S | | | | 🟥 | 🟥 | | | 🟥 | | 🟥 | 🟥 | |
| Okareka | 3.3 | S | ▨ | | | | ▨ | | ▨ | | | | | |
| Rerewhakaaitu | 3.4 | P | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | | | | | |
| Rotomahana | 3.9 | S | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | ▨ | ▨ | | | ▨ |
| Rotoiti | 4.3 | S | | | | 🟥 | | 🟥 | 🟥 | 🟥 | 🟥 | | 🟥 | |
| Rotoehu | 4.5 | P | ▨ | | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | ▨ | ▨ |
| Rotorua | 4.9 | P | | | | ▨ | | ▨ | | ▨ | | | ▨ | ▨ |
| Okaro | 5.5 | S | ▨ | | | ▨ | ▨ | ▨ | | ▨ | ▨ | | ▨ | ▨ |

## 1.3 MAJOR OBJECTIVES

The purpose of this study is to develop an understanding of the sediment-pore water interactions over a range of trophic conditions and how the biogeochemical cycles influence the lake ecosystem and the implications that this has for management of the TVZ lakes.

The major objectives of my research were to:

1) Demonstrate the applicability of natural abundance nitrogen gas isotopic ratios for determining denitrification in lake and pore waters. This information can then be used to determine the extent of denitrification at the sediment/water interface and in the water column of lakes through an annual seasonal cycle in lakes of different trophic status.

2) Determine the concentration gradients across the sediment/water interface of selected TVZ lakes, and relate these observations to the internal loads of nutrients and elements through an annual seasonal cycle in lakes of different trophic status.

3) Investigate the sediment profiles of lead in selected lakes in the TVZ to assess the geochemical transitions in the lake sediments associated with different trophic status and exposure to both natural and anthropgenic sources of lead.

4) To understand the factors controlling the silicon concentration in pore waters and the flux to the overlying lake water. To determine the potential of Si to limit diatom productivity by assessing the temporal variation of Si, N, and P concentrations in the lake water of selected TVZ lakes and the effect Si limitation has on trophic status.

## 1.4 THESIS OVERVIEW

This thesis consists of five independent research chapters (Chapters 2-6) which have been written in the format of scientific papers. As a result of the format required to document the methods and study sites for these independent papers, there is some repetition to enable each chapter to stand as a single scientific paper. Chapter 7 concludes with a summary of the research and the implications for lake and catchment management.

In Chapter 2, temporal and spatial patterns of change in dissolved inorganic nitrogen (DIN) and $\delta^{15}N$ [$N_2$] in different vertical compartments of Lake Ngapouri were determined throughout its annual cycle of stratification and mixing. We hypothesised that the change in $\delta^{15}N$ [$N_2$] would allow the environmental drivers and location of denitrification to be identified. A method was thus developed that could quantitatively and efficiently sample the dissolved $N_2$ in lake water and make it readily available for isotopic analysis.

In Chapter 3, the objective was firstly to quantify $^{15}N$ [$N_2$] enrichment in surface (epilimnion), bottom (hypolimnion), and benthic boundary layer (BBL) waters, as well as in sediment pore waters, of 11 TVZ lakes and to test for relationships of enrichment to different environmental factors. Enrichment of $^{15}N$ [$N_2$] was measured monthly in the benthic boundary layer and sediment pore waters in five TVZ lakes, as well as in the hypolimnion and epilimnion, in order to provide a time series of $^{15}N$ [$N_2$] enrichment across lakes of varying trophic gradient. We ultimately test whether discrete samples of $\delta^{15}N$ [$N_2$] can be used as a management tool to monitor trophic status and denitrification in seasonally stratified temperate lakes.

Chapter 4 reports on several major processes observed in the pore water and sediments of five lakes in the Taupo Volcanic Zone. The objective of this part of the study was to elucidate the diagenetic processes that influence the availability of elements and nutrients operating across lakes of similar mixing regime but widely varying trophic state. The information is then used to estimate annual loads of trace elements and nutrients.

In Chapter 5, sediments from a diverse set of lakes within the Rotorua region of New Zealand were used to indicate rates of environmental inputs of lead whilst taking into account differences of trophic state and lead exposure between the lakes. The lakes investigated range in trophic status from oligotrophic to hypertrophic and also vary in their exposure to leaded petroleum emissions. The relatively isolated location and recent human settlement of New Zealand provided an opportunity to assess the geochemical transitions of lead in lake sediments associated with additions to petroleum.

In Chapter 6, pore waters from selected TVZ lakes ranging in trophic state from oligotrophic to eutrophic, were used to attempt to quantify the contribution of silicon from the sediments to the overlying lake water and the ability of diatoms to recycle this Si back to the sediments. Sediment pore water Si concentrations were measured in the lakes and a steady state model was developed to account for the pore water concentration gradients based. It was assumed in the model that dissolution of siliceous sediments would be a first order process. By evaluating the concentrations of biologically available nutrients (dissolved inorganic nitrogen, dissolved reactive phosphorus and dissolved silicon) in the surface waters, it was possible to determine which nutrients were likely to be limiting phytoplankton growth during stratified and mixed periods based on concentration thresholds.

Chapter 7 concludes with a summary of the research and the implications for lake and catchment management. These include the potential for an additional trophic state indicator using $^{15}N$ [$N_2$] enrichment, reassessment of nitrogen budgets based on the finding of unconventional denitrification parthways, using anthropogenic lead in combination with the depth to the Tarawera Tephra (a non-mobile marker) to assess sedimentation rates by dating the sediments, and using reactive silicon to promote diatom growth as a method of reducing nutrients in the water column. Recomendations are made for future research in this field.

## 1.5 REFERENCES

Abell, J. M., D. Özkundakci, and D. P. Hamilton. 2010. Nitrogen and Phosphorus Limitation of Phytoplankton Growth in New Zealand Lakes: Implications for Eutrophication Control. Ecosystems **13:** 966-977.

Adams, D. D. 1992. Sediment pore water geochemistry of Taupo volcanic zone lakes with special reference to carbon and nitrogen gases. Taupo Research Laboratory File Report 135. Taupo Research Laboratory DSIR.

Aller, R. 1990. Bioturbation and manganese cycling in hemipelagic sediments. Phil. Trans. Roy. Soc. London. **331:** 51-68.

An, S., and W. S. Gardner. 2002. Dissimilatory nitrate reduction to ammonium (DNRA) as a nitrogen link, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). Mar. Ecol. Prog. Ser. **237:** 41-50.

Bartlett, R., R. J. G. Mortimer, and K. Morris. 2008. Anoxic nitrification: evidence from Humber Estuary sediments (UK). Chem. Geol. **250:** 29-39.

Berner, R. A. 1980. Early Diagenesis: A theoretical approach. Princeton University Press, New Jersey.

Boudreau, B. P., and B. B. Jørgensen. 2001. The benthic boundary layer: Transport processes and biogeochemistry. Oxford University Press.

Boyer, E. W. and others 2006. Modelling denitrification in terrestrial and aquatic ecosystems at regional scales. Ecol. Appl. **16:** 2123-2142.

Brandes, J. A., and A. H. Devol. 1997. Isotopic fractionation of oxygen and nitrogen in coastal marine sediments. Geochim. Cosmochim. Acta. **61:** 1793-1801.

Bruesewitz, D. A., D. P. Hamilton, and L. A. Schipper. 2011. Denitrification potential in lake sediment increases across a gradient of catchment agriculture. Ecosystems **14:** 341-352.

Burger, D. F. 2006. Dynamics of internal nutrient loading in a eutrophic, polymictic lake (Lake Rotorua, New Zealand). Ph.D. Thesis. Department of Biological Sciences, University of Waikato.

Burger, D. F., D. P. Hamilton, C. A. Pilditch, and M. M. Gibbs. 2007. Benthic nutrient fluxes in a eutrophic, polymictic lake. Hydrobiologia **584:** 13-25.

Burns, N. M. 1995. Using hypolimnetic dissolved oxygen depletion rates for monitoring lakes. N. Z. J. Mar. Freshw. Res. **29:** 1-11.

Burns, N. M., G. Bryers, and E. Bowman. 2000. Protocol for monitoring trophic levels of New Zealand lakes and reservoirs. Ministry for the Environment, Wellington NZ.

Burns, N. M., J. Deely, J. Hall, and K. Safi. 1997. Comparing past and present trophic states of seven Central Volcanic Plateau lakes, New Zealand. N.Z. J. Mar. Freshw. Res. **31:** 71-87.

Carlsson, P., and E. Graneli. 1999. Effects of N: P: Si ratios and zooplankton grazing on phytoplankton communities in the northern Adriatic Sea. II. Phytoplankton species composition. Aquat. Microb. Ecol. **18:** 55-65.

Conley, D. J. and others 2009. Controlling eutrophication: nitrogen and phosphorus. Science **323:** 1014-1015.

Cox, G. J. 1989. Slumbering Giants: The Volcanoes and Thermal Regions of the Central North Island. William Collins Publishers LTD.

Dalsgaard, T., D. E. Canfield, J. Petersen, B. Thamdrup, and J. Acuña-González. 2003. $N_2$ production by the anammox reaction in the anoxic water column of Golfo Dulce, Costa Rica. Nature **422:** 606-608.

Dortch, Q., and T. E. Whitledge. 1992. Does nitrogen or silicon limit phytoplankton production in the Mississippi River plume and nearby regions? Cont. Shelf Res. **12:** 1293-1309.

Downes, M. T. 1988. Aquatic nitrogen transformations at low oxygen concentrations. Appl. Environ. Microb. **54:** 172-175.

Downs, T. M., M. Schallenberg, and C. W. Burns. 2008. Responses of lake phytoplankton to micronutrient enrichment: a study in two New Zealand lakes and an analysis of published data. Aquat. Sci. **70:** 347-360.

Edgington, D. N., and J. A. Robbins. 1976. Records of lead deposition in Lake Michigan sediments since 1880. Environ. Sci. Tech. **10:** 266-274.

Elser, J. J., E. R. Marzolf, and C. R. Goldman. 1990. Phosphorus and nitrogen limitation of phytoplankton growth in the freshwaters of North America: a review and critique of experimental enrichments. Can. J. Fish. Aquat. Sci. **47:** 1468-1477.

Environment Bay of Plenty. 2004. Proposed regional land and water plan: Version 8.0. Resource Planning Publication 2002/01. Environment Bay of Plenty.

Environment Bay of Plenty. 2008. Bay of Plenty Regional Water and Land Plan. Publication 2008/06. Environment Bay of Plenty.

Environment Waikato. 2003. Protecting Lake Taupo: A long-term strategic partnership, p. 27. Environment Waikato, Hamilton, NZ.

Fish, G. R. 1970. A limnological study of four lakes near Rotorua. N.Z. J. Mar. Freshwat. Res. **4:** 165-194.

Forsberg, C., S. O. Ryding, A. Claesson, and A. Forsberg. 1978. Water chemical analyses and/or algal assay? Sewage effluent and polluted lake water studies. Mitt. Int. Ver. Theor. Angew. Limnol. **21:** 352-363.

Froelich, P. and others 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta **43:** 1075-1090.

Galloway, J. and others 2004. Nitrogen cycles: past, present, and future. Biogeochem. **70:** 153-226.

Galloway, J. N. and others 2003. The nitrogen cascade. BioScience **53:** 341-356.

Gardner, W. S., and M. J. Mccarthy. 2009. Nitrogen dynamics at the sediment–water interface in shallow, sub-tropical Florida Bay: why denitrification efficiency may decrease with increased eutrophication. Biogeochem. **95:** 185-198.

Gibbs, M. 2011. Lake Taupo Long-term monitoring programme 2009-2010. Waikato Regional Council Technical Report 2011-12, Waikato Regional Council.

Gloor, M., A. Wüest, and M. Münnich. 1994. Benthic boundary mixing and resuspension induced by internal seiches. Hydrobiologia **284:** 59-68.

Gobler, C. J., N. J. Buck, M. E. Sieracki, and S. A. Sa Udo-Wilhelmy. 2006. Nitrogen and silicon limitation of phytoplankton communities across an urban estuary: The East River-Long Island Sound system. Estuar. Coast. Shelf Sci. **68:** 127-138.

Graney, J. R., A. N. Halliday, G. J. Keeler, J. O. Nriagu, J. A. Robbins, and S. A. Norton. 1995. Isotopic record of lead pollution in lake sediments from the northeastern United States. Geochim. Cosmochim. Acta **59:** 1715-1728.

Granger, J., D. M. Sigman, M. F. Lehmann, and P. D. Tortell. 2008. Nitrogen and oxygen isotope fractionation during dissimilatory nitrate reduction by denitrifying bacteria. Limnol. Oceanogr. **53:** 2533-2545.

Groffman, P. M. and others 2006. Methods for measuring denitrification: diverse approaches to a difficult problem. Ecol. Appl. **16:** 2091-2122.

Hamilton, D. P. 2005. Land use impacts on nutrient export in the Central Volcanic Plateau, North Island. N.Z. J. For. **49:** 27-31.

Hamilton, D. P., Paul, W., Mcbride, C. And Immenga, D. 2009. Water flow between Ohau Channel and Lake Rotoiti following implementation of a diversion wall. Centre for Biodiversity and Ecology Research, Report No. 96. Department of Biological Sciences, University of Waikato, Hamilton.

Hamilton, D. P., G. B. Douglas, J. A. Adeney, and L. C. Radke. 2006. Seasonal changes in major ions, nutrients and chlorophyll *a* at two sites in the Swan River estuary, Western Australia. Mar. Freshw. Res. **57:** 803-815.

Harrison, J. A. and others 2009. The regional and global significance of nitrogen removal in lakes and reservoirs. Biogeochem. **93:** 143-157.

Hawley, N. 2004. Response of the benthic nepheloid layer to near-inertial internal waves in southern Lake Michigan. J. Geophys. Res **109:** 1-14.

Hellstrom, T. 1996. An empirical study of nitrogen dynamics in lakes. Water Environ. Res. **68:** 55-65.

Hulth, S. and others 2005. Nitrogen removal in marine environments: recent findings and future research challenges. Mar. Chem. **94:** 125-145.

Humbert, S., S. Tarnawski, N. Fromin, M. P. Mallet, M. Aragno, and J. Zopfi. 2010. Molecular detection of anammox bacteria in terrestrial ecosystems: distribution and diversity. ISME **4:** 450-454.

Justić, D., N. N. Rabalais, and R. E. Turner. 1995. Stoichiometric nutrient balance and origin of coastal eutrophication. Mar. Pollut. Bull. **30:** 41-46.

Kleeberg, A., and H. P. Kozerski. 1997. Phosphorus release in Lake Groβer Müggelsee and its implications for lake restoration. Hydrobiologia **342:** 9-26.

Koszelnik, P., J. A. Tomaszek, and R. Gruca-Rokosz. 2007. The significance of denitrification in relation to external loading and nitrogen retention in a mountain reservoir. Mar. Freshwat. Res. **58:** 818-826.

Kuypers, M. M. M. and others 2003. Anaerobic ammonium oxidation by anammox bacteria in the Black Sea. Nature **422:** 608-611.

Lowe, D. J., and J. D. Green. 1992. Lakes, p. 107-143. *In* J. M. Soons and M. J. Selby [eds.], Landforms of New Zealand: Second Edition. Longman Paul.

Lowe, D. J., P. A. R. Shane, B. V. Alloway, and R. M. Newnham. 2008. Fingerprints and age models for widespread New Zealand tephra marker beds erupted since 30,000 years ago: a framework for NZ-INTIMATE. Quaternary Sci. Rev. **27:** 95-126.

Luther, G. W. 1997. Interactions of manganese with the nitrogen cycle: Alternative pathways to dinitrogen. Geochim. Cosmochim. Acta **61:** 4043-4052.

Luther, G. W. 2010. The role of one-and two-electron transfer reactions in forming thermodynamically unstable intermediates as barriers in multi-electron redox reactions. Aquat. Geochem. **16:** 395-420.

Luther, G. W., and J. I. Popp. 2002. Kinetics of the abiotic reduction of polymeric manganese dioxide by nitrite: an anaerobic nitrification reaction. Aquat. Geochem. **8:** 15-36.

McCarthy, M. J., D. F. Burger, D. P. Hamilton, C. H. Hendy, and W. S. Gardner. 2007. Sediment-water interface nitrogen transformations in Lakes Rotorua and Rotoiti (North Island, New Zealand): does dissimilatory nitrate reduction to ammonium (DNRA) contribute to water column ammonium accumulation? SIL Congress 2007, Montréal, QC, Canada.

McColl, R. H. S. 1977. Chemistry of sediments in relation to trophic condition of eight Rotorua lakes. N.Z. J. Mar. Freshw. Res. **11:** 509-523.

Monna, F., J. Dominik, J. L. Loizeau, M. Pardos, and P. Arpagaus. 1999. Origin and Evolution of Pb in Sediments of Lake Geneva (Switzerland- France). Establishing a Stable Pb Record. Environ. Sci. Technol **33:** 2850-2857.

Morgenstern, U., R. Reeves, C. Daughney, S. Cameron, and D. Gordon. 2004. Groundwater age and chemistry, and future nutrient load for selected Rotorua lakes catchments, p. 73. Institute of Geological and Nuclear Sciences, science report 2004/31, New Zealand.

Morris, D. P., and W. M. Lewis. 1988. Phytoplankton nutrient limitation in Colorado mountain lakes. Freshw Bio **20:** 315-327.

Mortimer, R. J. G. and others 2004. Anoxic nitrification in marine sediments. MEPS **276:** 37-51.

Mortimer, R. J. G. 2002. Evidence for suboxic nitrification in recent marine sediments. MEPS **236:** 31-35.

Motion, O. J. 2007. Early Digenesis in Lake Rotorua Sediment. M.Sc. Thesis. Department of Chemistry, University of Waikato.

Mulder, A., A. A. Van De Graaf, L. A. Robertson, and J. G. Kuenen. 1995. Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. FEMS Microbiol. Ecol. **16:** 177-184.

Murray, J. W., L. A. Codispoti, and G. E. Friederich. 1995. Oxidation-reduction environments: The suboxic zone in the Black Sea, p. 157-176. *In* C. P. Huang, C. R. O'Melia and J. J. Morgan [eds.], Aquatic Chemistry: Interfacial and Interspecies Processes. American Chemical Society.

Nairn, I. A. 1992. The Te Rere and Okareka eruptive episodes—Okataina Volcanic Centre, Taupo Volcanic Zone, New Zealand. N.Z. J. Geol. Geop. **35:** 93-108.

Nürnberg, G. K. 1984. The prediction of internal phosphorus load in lakes with anoxic hypolimnia. Limnol. Oceanogr. **29:** 111-124.

Organisation for Economic Co-Operation and Development. 1982. Eutrophication of waters: monitoring, assessment and control, p. 154. OECD, Paris.

Pearson, L. K. 2007. The nature, composition and distribution if sediment in Lake Rotorua, New Zealand. M.Sc. Thesis. Department of Chemistry, University of Waikato.

Pearson, L. K., C. H. Hendy, D. P. Hamilton, and W. B. Silvester. 2012. Nitrogen-15 isotope enrichment in benthic boundary layer gases of a stratified eutrophic iron and manganese rich lake. Aquat. Geochem. **18:** 1-19.

Petersen, W., K. Wallman, L. Pinglin, F. Schroeder, and H. D. Knauth. 1995. Exchange of trace elements at the sediment-water interface during early diagenesis processes. Mar. Freshw. Res. **46:** 19-26.

Pina-Ochoa, E., and M. Alvarez-Cobelas. 2006. Denitrification in aquatic environments: a cross-system analysis. Biogeochem. **81:** 111-130.

Postma, D. 1990. Kinetics of nitrate reduction by detrital Fe (II)-silicates. Geochim. Cosmochim. Acta **54:** 903-908.

Pridmore, R. D., and M. K. Etheredge. 1987. Planktonic cyanobacteria in New Zealand inland waters: distribution and population dynamics. N.Z. J. Mar. Freshw. Res. **21:** 491-502.

Priscu, J. C., R. H. Spigel, M. M. Gibbs, and M. T. Downes. 1986. A numerical analysis of hypolimnetic nitrogen and phosphorus transformations in Lake Rotoiti, New Zealand: A geothermally influenced lake. Limnol. Oceanogr. **31:** 812-831.

Redfield, A. C. 1958. The biological control of chemical factors in the environment. Am. Sci. **46:** 205-221.

Renberg, I., M. L. Brännvall, R. Bindler, and O. Emteryd. 2002. Stable lead isotopes and lake sediments--a useful combination for the study of atmospheric lead pollution history. Sci. Total Environ. **292:** 45-54.

Rhee, G. Y. 1982. Effects of environmental factors on phytoplankton growth, p. 33-74. *In* M. K.C. [ed.], Advances in microbial ecology. Plenum Press, New York.

Rocha, C., H. Galvao, and A. Barbosa. 2002. Role of transient silicon limitation in the development of cyanobacteria blooms in the Guadiana estuary, south-western Iberia. Mar. Ecol. Prog. Ser. **228:** 35-45.

Round, F. E., R. M. Crawford, and D. G. Mann. 1990. The Diatoms: biology & morphology of the genera. Cambridge University Press.

Ryan, E. F., I. C. Duggan, D. P. Hamilton, and D. F. Burger. 2006. Phytoplankton assemblages in North Island lakes of New Zealand: is trophic state, mixing, or light climate more important? N. Z. J. Mar. Freshw. Res. **40:** 389-398.

Rysgaard, S., N. Risgaard-Petersen, and N. P. Sloth. 1996. Nitrification, denitrification, and nitrate ammonification in sediments of two coastal lagoons in Southern France. Hydrobiologia **329:** 133-141.

Sakamoto, M. 1966. Primary production by phytoplankton community in some Japanese lakes and its dependence on lake depth. Arch. Hydrobiol. **62:** 1-28.

Saunders, D. L., and J. Kalff. 2001. Nitrogen retention in wetlands, lakes and rivers. Hydrobiologia **443:** 205-212.

Schindler, D. W. and others 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. PNAS **105:** 11254-11258.

Scholes, P. 2010. 2009/2010 Rotorua Lakes TLI Update. Environmental Publication 2010/8, Bay of Plenty Regional Council.

Schubert, C. J., E. Durisch-Kaiser, B. Wehrli, B. Thamdrup, P. Lam, and M. M. M. Kuypers. 2006. Anaerobic ammonium oxidation in a tropical freshwater system (Lake Tanganyika). Environ. Microbiol. **8:** 1857-1863.

Schulz, H. D. 2006. Quantification of early diagenesis: Dissolved constituents in marine pore water. *In* H. D. Schultz and M. Zabel [eds.], Marine Geochemistry. Springer, Berlin.

Schulz, H. D., A. Dahmke, U. Schinzel, K. Wallmann, and M. Zabel. 1994. Early diagenetic processes, fluxes, and reaction rates in sediments of the South Atlantic. Geochim. Cosmochim. Acta **58:** 2041-2060.

Seitzinger, S. P. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnol. Oceanogr. **33:** 702-724.

Seitzinger, S. P. and others. 2006. Denitrification across landscapes and waterscapes: A synthesis. Ecol. Appl. **16:** 2064-2090.

Seitzinger, S. P. and others. 2002. Nitrogen retention in rivers: model development and application to watersheds in the northeastern U.S.A. Biogeochem. **57:** 199-237.

Sommer, U., and H. H. Stabel. 1983. Silicon consumption and population density changes of dominant planktonic diatoms in Lake Constance. J. Ecol. **71:** 119-130.

Søndergaard, M., J. P. Jensen, and E. Jeppesen. 2003. Role of sediment and internal loading of phosphorus in shallow lakes. Hydrobiologia **506:** 135-145.

Sørensen, J., K. S. Jørgensen, S. Colley, D. J. Hydes, J. Thomson, and T. R. S. Wilson. 1987. Depth localization of denitrification in a deep-sea sediment from the Madeira Abyssal Plain. Limnol. Oceanogr. **32:** 758-762.

Thamdrup, B., and T. Dalsgaard. 2002. Production of $N_2$ through anaerobic ammonium oxidation coupled to nitrate reduction in marine sediments. Appl. Environ. Microbiol. **68:** 1312.

Tomaszek, J. A. 1995. Relationship between denitrification and redox potential in two sediment-water systems. Mar. Freshwat. Res. **46:** 27-31.

Turner, R. E. and others 1998. Fluctuating silicate: nitrate ratios and coastal plankton food webs. PNAS **95:** 13048.

Untaru, R. 2005. Geochemistry of trace elements in Lake Rotoiti, North Island, New Zealand. M.Sc Thesis. Chemistry Department, University of Waikato.

Van Breemen, N. and others 2002. Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern USA. Biogeochem. **57:** 267-293.

Van Der Molen, D. T., R. Portielje, P. C. M. Boers, and L. Lijklema. 1998. Changes in sediment phosphorus as a result of eutrophication and oligotrophication in Lake Veluwe, The Netherlands. Water Res. **32:** 3281-3288.

Vanni, M. J., W. H. Renwick, A. M. Bowling, M. J. Horgan, and A. D. Christian. 2010. Nutrient stoichiometry of linked catchment lake systems along a gradient of land use. Freshw. Bio. **56:** 791-811.

Vitousek, P. and others 1997. Human alteration of the global nitrogen cycle: sources and consequences. Ecol. Appl. **7:** 737-750.

White, E. 1983. Lake eutrophication in New Zealand—a comparison with other countries of the Organisation for Economic Co-operation and Development. N.Z. J. Mar. Freshw. Res. **17:** 437-444.

White, E., K. Law, G. Payne, and S. Pickmere. 1985. Nutrient demand and availability among planktonic communities—an attempt to assess nutrient limitation to plant growth in 12 central volcanic plateau lakes. N.Z. J. Mar. Freshwat. Res. **19:** 49-62.

Wilding, T. K. 2000. Rotorua Lakes Algae Report, p. 98. Bay of Plenty Regional Council, Technical Report 2000/06.

Wilson, C. J. N., B. F. Houghton, M. O. Mcwilliams, M. A. Lanphere, S. D. Weaver, and R. M. Briggs. 1995. Volcanic and structural evolution of Taupo Volcanic Zone, New Zealand: a review. J. Volcanol. Geoth. Res. **68:** 1-28.

Zhou, Q., C. E. Gibson, and R. H. Foy. 2000. Long-term changes of nitrogen and phosphorus loading to a large lake in north-west Ireland. Water Resour. **34:** 922-926.

# CHAPTER 2: NITROGEN-15 ISOTOPE ENRICHMENT IN BENTHIC NEPHELOID LAYER GASES OF A STRATIFIED EUTROPHIC IRON AND MANGANESE RICH LAKE

## 2.1 INTRODUCTION

The removal of nitrogen in lakes is dominated by denitrification, the microbial reduction of nitrate ($NO_3^-$) to gaseous nitrogen ($N_2$) under low-oxygen conditions (dissolved oxygen (DO) < 0.2 mg $L^{-1}$ (Seitzinger et al., 2006)). Denitrification is controlled primarily by the availability of carbon, nitrate and levels of dissolved oxygen (Seitzinger, 1988; Tomaszek, 1995; Hellström, 1996; Saunders and Kalff, 2001). At ecosystem scales, water residence time and N loading often constrain denitrification (Seitzinger et al., 2006). In lakes, relatively long residence times allow for a higher proportion of the N load to be denitrified as there is a greater potential for nutrient processing and sedimentation before N discharge via outflows (Saunders and Kalff, 2001; Bruesewitz et al., 2011). Conditions in the surficial bottom sediments of lakes favour denitrification due to high organic matter inputs from the overlying water column and strong DO gradients (Pina-Ochoa and Álvarez-Cobelas, 2006; Seitzinger et al., 2006). Therefore, denitrification can remove a large fraction of the nitrogen originally sourced from lake catchments and the atmosphere (Seitzinger, 1988).

In stratified lakes, nitrate from in situ production and from external inputs is distributed throughout the water column during the periods of vertical mixing. It is most likely to become available for denitrification when the lake stratifies and the bottom waters become anoxic (Priscu et al., 1986; Nishri and Hamilton, 2010). The primary zone of denitrification in stratified lakes is typically a thin layer of up to several millimetres, controlled by the position of the oxic-anoxic boundary. This in turn is controlled by the rate of oxygen supplied via hydrodynamic processes and the consumption of oxidants due to organic matter degradation. The thickness of the zone of denitification is balanced by concurrent processes of supply of inorganic electron donors (reducing agents) from below the active zone, sedimentation of organic matter and electron acceptors (oxidising agents) from above and the specific activity of nitrifiers and denitrifiers (Paerl and Pinckney, 1996; Seitzinger et al., 2006). The zone of denitrification may encompass the sediment-water interface at different stages of the seasonal cycle of mixing and stratification in deep lakes, due to respiratory oxygen depletion, exhaustion of reactive organic matter and fluctuations in dissolved oxygen concentrations in the water column, all of which are closely linked to mixing dynamics, respiration and primary production (Eckert et al., 2002).

Biological denitrification is not the only mechanism for producing dinitrogen (Hulth et al., 2005) and the rate of bacterial denitrification, frequently measured as the dinitrogen flux from sediments (Devol, 1991; Seitzinger, 1988), can be higher than that measured by acetylene inhibition or labelled $^{15}NO_3^-$ isotope dilution (Seitzinger et al., 1993). It has been shown that dinitrogen is also produced by the oxidation of ammonia and organic-N by $MnO_2$ (Froelich et al., 1979; Luther et al., 1997):

$$2\ NH_3 + 3\ MnO_2 + 6\ H^+ \longrightarrow 3\ Mn^{2+} + N_2 + 6\ H_2O \qquad (2.1)$$

Alternatively, dinitrogen may be produced when ammonium ions are oxidised under anaerobic conditions utilising nitrite as the terminal electron acceptor (anammox) (Mulder et al., 1995; Thamdrup and Dalsgaard, 2002; Dalsgaard et al., 2003; Kuypers et al., 2003; Schubert et al., 2006; Humbert et al., 2010) or by anoxic nitrification which uses manganese as the electron acceptor to form nitrate (Eq. 2.2) (Mortimer et al., 2002; 2004; Luther and Popp, 2002; Clément et al., 2005; Bartlett et al., 2008), which is then denitrified by biological denitrification or by the oxidation of $Mn^{2+}$ (chemo-denitrification) (Sørensen and Jørgensen, 1987; Aller, 1990; Schulz et al., 1994; Murray et al., 1995; Luther et al., 1997) (Eq. 2.3):

$$8\ MnO_2 + 2\ NH_4^+ + 12\ H^+ \longrightarrow 8\ Mn^{2+} + 2\ NO_3^- + 10\ H_2O \qquad (2.2)$$

$$5\ Mn^{2+} + 2\ NO_3^- + 4\ H_2O \longrightarrow 5\ MnO_2 + N_2 + 8\ H^+ \qquad (2.3)$$

Froelich et al. (1979) noted that iron oxides and sulfates are also capable of oxidising ammonia (as in equation 1), but are less efficient than manganese oxides or nitrate. Postma (1990) showed that small quantities of nitrate could be reduced by $Fe^{2+}$-bearing silicates (pH 2 to 7) as nitrate reduction is catalysed with the secondary products (FeOOH) of silicon dissolution in groundwater aquifers (Eq. 2.4 and 2.5). In ecosystems such as lakes where the pH in hypolimnetic waters may be < 6.5, an analogous catalytic cycle involving iron is more thermodynamically favourable than manganese if reactive oxide species are formed (Luther et al., 1997; Luther, 2010).

$$8\,FeOOH + NH_4^+ + 14\,H^+ \longrightarrow NO_3^- + 8\,Fe^{2+} + 13\,H_2O \qquad (2.4)$$

$$10\,Fe^{2+} + 2\,NO_3^- + 14\,H_2O \longrightarrow 2\,N_2 + 10\,FeOOH + 14\,H^+ \qquad (2.5)$$

The combination of these two processes yelds Eq. 2.6

$$2\,NH_4^+ + 6\,FeOOH + 10\,H^+ \longrightarrow 6\,Fe^{2+} + 12\,H_2O + N_2 \qquad (2.6)$$

Quantifying when, where and how much dinitrogen production occurs in an ecosystem is particularly challenging (Seitzinger et al., 2002; Van Breemen et al, 2002; Galloway et al., 2004; Groffman et al., 2006). Small changes in $N_2$, separate from the naturally abundant atmospheric concentrations, have been used to quantify denitrification rates but this method is often fraught with analytical difficulties. At present, there are no reliable methods for the direct measurement of denitrification rates at lake or catchment scale. At smaller scales, extrapolation of direct measurements of denitrification to system scales still remains questionable as data are often sparse, sometimes unreliable, and can have large spatial variations (Boyer et al., 2006; Groffman et al., 2006). Discerning the different reaction pathways of denitrification is also difficult in continually cycling environments, as ammonia is produced from the breakdown of organic matter and there can be multiple reductants (organic matter, manganese, iron and sulfide) together with cycling of solid oxides to aqueous species, that produce identical signals to those of conventional oxidation-reduction reactions (Hulth et al., 2005; Bartlett et al., 2008).

The process of denitrification results in more rapid utilisation of nitrate containing the $^{14}N$ isotope than $^{15}N$, resulting in significant discrimination and enrichment of the substrate pool by $^{15}N$ (Brandes and Devol, 1997; Granger et al., 2008). Lehmann et al. (2002, 2004) suggested that denitrification was responsible for an increase in $\delta^{15}N$ $[NO_3^-]$ from +8 ‰ to +27 ‰ in association with the development of anoxia in Lake Lugano, Switzerland. For $^{15}N$ $[NO_3^-]$ enrichment to occur as denitrification proceeds, the dinitrogen product must be depleted. If denitrification goes to completion, the $\delta^{15}N$ of the combined dinitrogen product will be identical to that of the initial nitrate substrate (Vogel et al., 1981). Previous studies of the isotopic abundance of N in lake waters have focused on the significance of external nitrogen loading (Ostrom et al., 1997; Teranes and Bernasconi, 2000) or fractionation from nitrate assimilation during denitrification (Hades et al., 2009). Little has been done to investigate $\delta^{15}N$ of $N_2$, the end product of denitrification.

Several approaches have been used to analyse the isotopic composition of dissolved nitrogen species, including evaporation or freeze-drying of filtered samples followed by combustion of the resulting solids in the presence of Cu, CuO and CaO to produce pure $N_2$ (Kendall and Grim, 1990), or the conversion of nitrate to ammonium by Kjeldahl digestion (Bremner, 1965; Bremner and Edwards, 1965). The ammonium can then be converted to $N_2$ gas by a number of different methods (Bremner, 1965; Bremner and Edwards, 1965; MacKown et al., 1987; Velinsky et al., 1989; Kendall and Grim, 1990; Sigman et al., 1997). These techniques require chilling, acidifying or poisoning of samples prior to analysis, as well as time-consuming processes such as distillation and freeze-drying of large volumes of water, which collectively increase the possibility of isotopic fractionation and contamination. Alternate methods have been developed using anion exchange resins to collect nitrate and pyrolytic methods to produce $N_2$ (Hoering, 1957; Garten, 1992; Wassenaar, 1995; Révész et al., 1997; Downs et al., 1999; Silva et al., 2000). These methods work effectively for lakes when nitrate concentrations are >1 mg N $L^{-1}$. McIlvin and Altabet (2005) developed a method suitable of converting $NO_x$ to $N_2O$ for the purpose of nitrogen isotope analysis for small water volumes (c. 50 mL); however, this procedure involves multiple, time-consuming steps that cannot be carried out quickly in the field.

The objective in this study was to determine temporal and spatial patterns of change in dissolved inorganic nitrogen (DIN) and $\delta^{15}$N [$N_2$] in different vertical compartments of a monomictic eutrophic lake throughout its annual cycle of stratification and mixing. We hypothesised that the change in $\delta^{15}$N [$N_2$] would allow the environmental drivers and location of denitrification to be identified. A method was thus developed that could quantitatively and efficiently sample the dissolved $N_2$ in lake water and make it readily available for isotopic analysis.

## 2.2 MATERIALS AND PROCEDURES

### 2.2.1 Study Site

Lake Ngapouri is approximately 24 km south of the city of Rotorua in the Central Volcanic Plateau, North Island, New Zealand. It has an area of 0.19 km$^2$, a maximum depth of 24.5m and was formed following volcanic activity approximately 950 yrs BP (Cross, 1963; Fish, 1970). Much of the catchment was converted from forest to pasture by 1956 (Forsyth, 1986) and > 90% of the catchment is currently in use as pastoral land, mostly for dairy farming. Nitrogen frequently limits primary productivity in many Taupo Volcanic Zone (TVZ) lakes (White et al., 1985) with ratios of total nitrogen to total phosphorus (TN:TP) that are low relative to the Redfield criterion. The lake is highly eutrophic and is thermally stratified for 9 months of the year (Forsyth, 1986). A sample site was selected in the deep central basin of the lake targeting the area conforming to a focal point for sediment accumulation (cf. Håkanson and Jansson, 1983).

### 2.2.2 Sampling and Field Methods

Water column and sediment core samples were taken monthly on Lake Ngapouri between November 2007 and November 2008. Lake water was collected using a Schindler-Patalas trap to capture water from the near-surface (1 m depth; ‘epilimnion’ and ‘hypolimnion’ (1 m above sediment-water interface). A 100 mL sample of the lake water was collected from within the Schindler-Patalas trap, avoiding contact with the air, for trace elements and nutrient analysis. A 'benthic nepheloid layer' (0.1 m above sediment-water interface) sample was taken from water overlying an intact sediment core for trace element, nutrient and gas analysis. The core was retained for pore water analyses. Eh and pH measurements were taken on the epilimnion, hypolimnion and benthic nepheloid layer water samples. Water samples for gas analysis were collected from the Schindler-Patellas trap with a submerged 60 ml syringe (BD Plastipak). The syringe had a three-way valve; one opening for the syringe tip, one stopped with a small rubber bung and one left open (Figure 2.1a). Any air space in the syringe was exhaled by inverting the syringe and compressing the piston, at the same time adjusting the water volume to 50 mL and closing the valve (Figure 2.1b). A vacuum was created within the syringe by applying strong back-pressure on the piston while also shaking the sample periodically over a period of three minutes (Figure 2.1c), after which time the gas volume was constant. The applied vacuum partitions gases between solution and the head space enabling a representative sample to be recovered. A 1 mL ultra-fine insulin syringe (BD Plastipak) was then inserted through the rubber stopper, and the gas drawn out of the syringe. Approximately 0.5 mL of gas was collected as well as sufficient water to 'seal' the gas in the syringe (~0.1 mL) (Figure 2.1d). The syringe was then removed from the stopper, inserted into a rubber bung and immersed fully in water to prevent penetration of air into the syringe (Figure 2.1e). Samples were collected in duplicate.

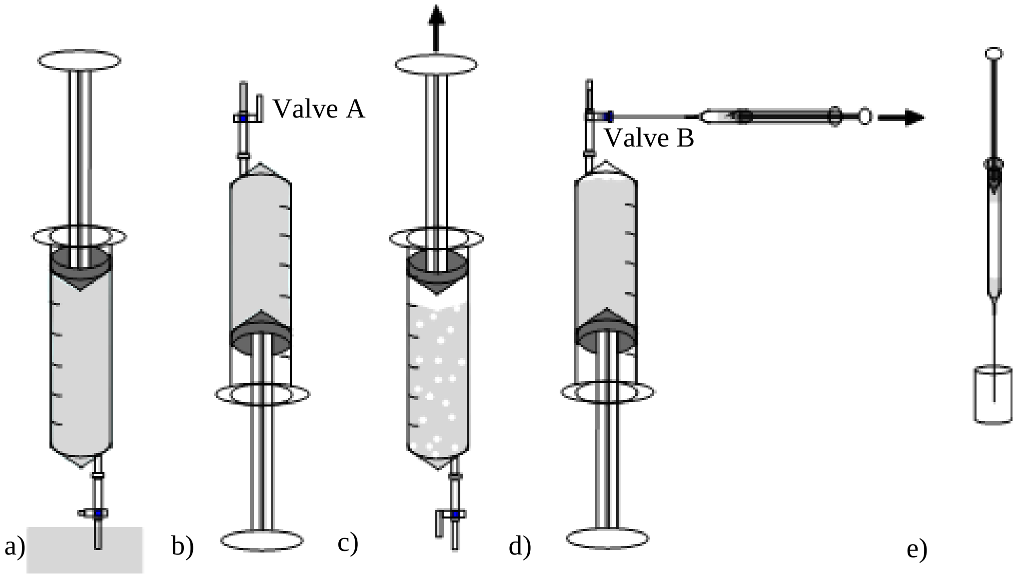

**Figure 2.1:** Gas extraction apparatus: a) collection of sample from Schindler-Patalas trap or intact sediment core, b) removal of excess air by inverting and closing 3-way valve (valve A), and adjustment of water volume to 50 ml, c) separation of gas from water by creating a vacuum from pulling piston in direction shown, and shaking, d) insertion of fine-needle syringe into valve bung (B) to extract gas into syringe with 0.1 ml of lake water either side of the gas sample to reduce the risk of gas exchange and e) the stored sample inserted into a rubber bung with water seals either side of the gas sample. The syringe was immersed in water until analysis.

Two sediment cores were taken in the central basin of Lake Ngapouri with a Swedish gravity corer (Pylonex HTH 70 mm) with a 60 x 600 mm Perspex (Plexiglas) core barrel to capture undisturbed sediments. The surface sediment was visually inspected with each core to determine if there was any disturbance at the sediment-water interface or in the sediment profile; the core was discarded and another one taken if there was any evidence of disturbance. A custom-made, gas-tight sampling chamber was fitted to the core barrel in order to minimise exposure of sediments to air (Pearson, 2007). The core was extruded by moving a piston upward from the base on the barrel. Excess supernatant water overflowed the top of the core before the sediment sample was collected. Samples were extruded in 2 cm vertical intervals and transferred into 50 mL polypropylene centrifuge tubes, which were purged of air with excess sediment and then sealed and placed on ice until return to the laboratory. The settling particulate organic matter (POM) was collected from the benthic nepheloid layer 2 cm above the sediment water interface inside one core barrel and dried for stable isotope analysis of particulate organic nitrogen (PON). The remaining duplicate core was kept intact, sealed and placed on ice for gas extraction from the core once it had been transferred to the laboratory.

A water column profile of temperature and dissolved oxygen at depth intervals of c. 0.02 m were measured on each sampling occasion with a conductivity-temperature-depth (CTD) profiler (Sea Bird Electronics, 19 plus SEACAT Profiler), fitted with a dissolved oxygen (DO, Seabird Electronics) sensor (detection limit of 0.1 mg $L^{-1}$). Data interpolation using Ocean Data View (http://odv.awi.de) allowed for the generation of isopleths of temperature and dissolved oxygen over the sampling period.

### 2.2.3 Laboratory Methods

The gravity core sediments were weighed for bulk density and separated from the pore water by centrifugation at 4000 rpm (2900 G) for 40 min. The pore water was filtered through 0.45 μm Millipore filters and kept frozen until subsequent analysis. Epilimnion, hypolimnion and benthic nepheloid layer water samples were filtered as above and separated for nutrient and trace element analysis. Nutrient samples were kept frozen until analysis, while trace elements samples were acidified with 2% $HNO_3$ and analysed immediately. The intact core was injected with 50 mL $CO_2$ through an air-tight valve in the top of the core (Figure 2.2a), at 5 cm intervals using a 60 mL syringe (BD Plastipak) modified with a stainless steel tube glued to the bottom. Simultaneously with $CO_2$ injection, gas was removed by a 60 mL syringe with a needle attached through another air-tight valve. The recaptured gas from the core was then injected into vials which were under vacuum and contained 5 mL NaOH to remove the $CO_2$ (Figure 2.2b). The process was repeated in successive 5 cm intervals in the core to a depth of 20 cm. The vials of sediment gas were analysed for $^{15}N$ along with the water column gas samples.

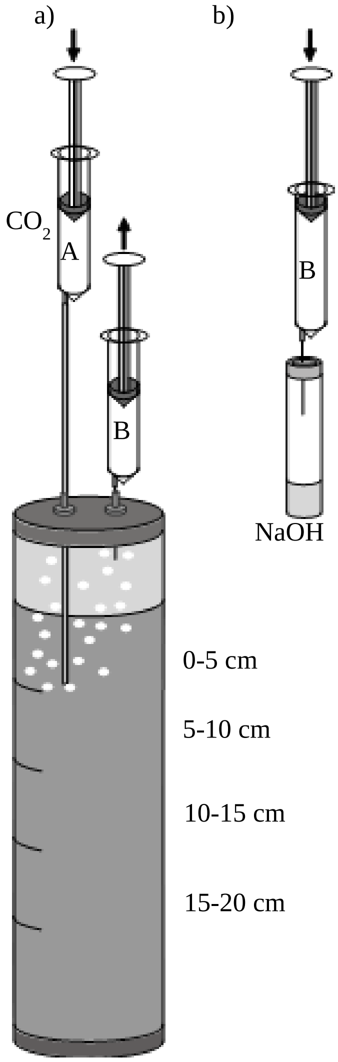

**Figure 2.2:** Apparatus for gas extraction from the sediment core: a) $CO_2$ injection into the core (syringe A) with simultaneous removal of the gas with syringe B and b) injection of syringe B through a rubber septum and gas transfer to a vial under vacuum and containing 5 mL NaOH.

### 2.2.4 Analytical Methods

Stable isotope analysis of $\delta^{15}N$ was undertaken by the Waikato Stable Isotope Unit, Waikato University. The $\delta^{15}N$ [$N_2$] was determined using a Dumas elemental analyser (Europa Scientific ANCA-SL) interfaced to an isotope mass spectrometer (Europa Scientific 20-20 Stable Isotope Analyser). The $\delta^{15}N$ of particulate organic nitrogen (PON) was determined using a LECO TruSpec CN Carbon/Nitrogen Determinator (LECO Corporation, 2006) interfaced to an isotope mass spectrometer (Europa Scientific 20-20 Stable Isotope Analyser). The nitrogen isotope ratio was expressed as per mill (‰) deviation from a laboratory reference (urea with a $\delta^{15}N$ standardised against a certified standard calibrated relative to atmospheric $N_2$) as defined by Mariotti (1983) (Eq. 2.6):

$$\delta^{15}N= [(^{15}N/^{14}N)_{sample} / \{(^{15}N/^{14}N)_{standard}-1\}] \times 1000 \qquad (2.6)$$

The analytical error of $\delta^{15}N$ determinations is within the range ±0.3‰. A standard error for $\delta^{15}N$ $[N_2]$ was calculated as the standard deviation between replicate samples divided by the square root of the number of samples. The average standard error for the technique was 0.24 ‰.

Analysis for $NH_4^+$, $NO_3^-$ and $NO_2^-$ was carried out spectrophotometrically on thawed lake water and pore water samples using a Lachat QuickChem® Flow Injection Analyser (FIA+ 8000 Series, Zellweger Analytics, Inc.). The detection limit was 0.001 mg $L^{-1}$.

Analysis for dissolved trace metals was carried out on acidified (2% $HNO_3$) lake and pore water samples by inductively coupled plasma mass spectrometry (ICP-MS model ELAN DRC II) using standard techniques. The detection limits were 0.0025 mg $L^{-1}$ and 0.00004 mg $L^{-1}$ for iron and manganese, respectively. Blanks determined on Type 1 water in identical sample containers and dosed with the same volume of nitric acid yielded < 0.01 mg $L^{-1}$ for Fe and Mn.

## 2.3 RESULTS

### 2.3.1 Temperature

Lake Ngapouri was strongly stratified at the time sampling commenced in November 2007 with a surface water temperature of 20 °C and a hypolimnion temperature of 11 °C (Figure 2.3a). A maximum surface water temperature of just above 21 °C occurred in February 2008. The depth to the thermocline was around 5 to 7 m. Stratification then became substantially weaker in May 2008 prior to turnover in June. From July to early September 2008, water temperature in Lake

Ngapouri was between 8 and 10 °C, with little or no vertical gradient. Seasonal thermal stratification commenced late in September 2008.

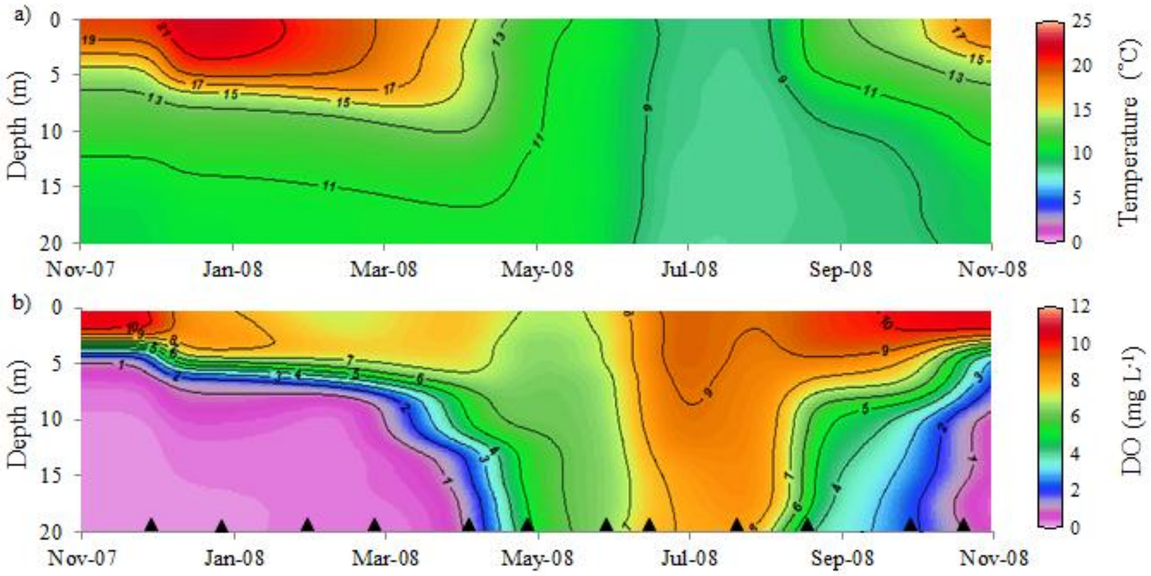

**Figure 2.3:** a) Temperature (°C) and b) dissolved oxygen (mg $L^{-1}$) in Lake Ngapouri over the twelve-month sampling period November 2007 to November 2008. Arrow heads on the horizontal axis indicate sampling times.

### 2.3.2 Dissolved oxygen

The hypolimnion of Lake Ngapouri was already strongly deoxygenated at the time that the sampling programme commenced in November 2007 and did not become well oxygenated until June 2008. Hypolimnetic dissolved oxygen concentrations decreased from 8.5 mg $L^{-1}$(c. 85 % of saturation for the corresponding water temperature) to below detection between July and December 2008 (Figure 2.3b). A volumetric hypolimnetic oxygen deficit (VHOD; Wetzel and Likens, 2000) of 0.125 g $m^{-3}$ $day^{-1}$ was calculated for a period of nearly linear decrease in dissolved oxygen concentrations (September – November 2008; Figure 2.4) though this value was based solely on measurements from 1 m above the sediment surface.

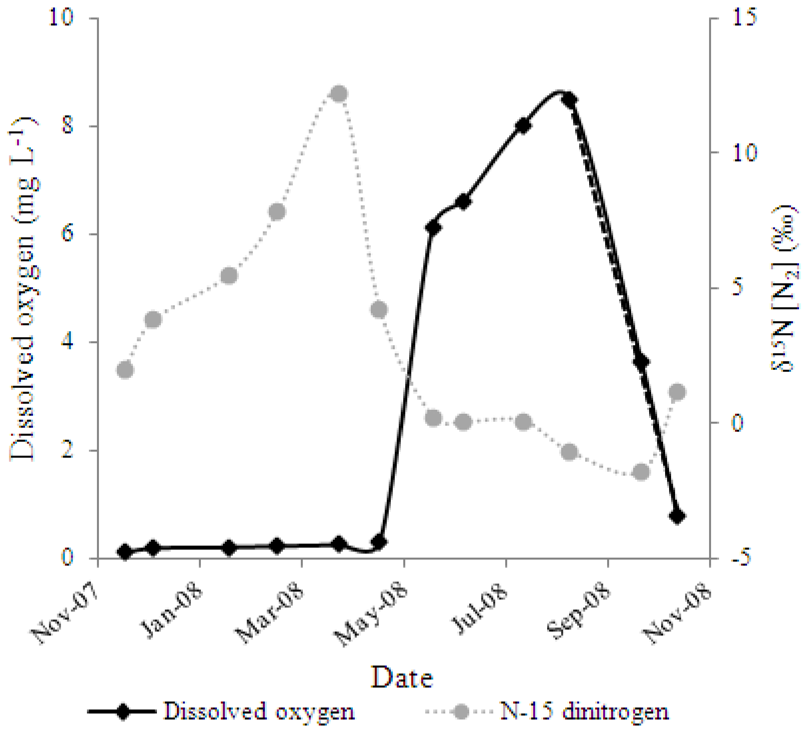

**Figure 2.4:** Hypolimnetic dissolved oxygen (measured 1 m above the sediment surface) (diamonds) (left axis) and average $\delta^{15}N$ [$N_2$] values for water samples 0.1 m above the sediment-water interface (circles) (right axis) from November 2007 to November 2008. The dashed line is a regression line fit to dissolved oxygen measurements taken on consecutive months from September to November 2008, given by the equation VHOD = -0.1257t + 8.54 where VHOD is the oxygen deficit (g $m^{-3}$ $d^{-1}$) and t is time in days after 29 September 2008.

### 2.3.3 Nutrient dynamics

For samples from 1 m below the surface and 1 m above the sediment, concentrations of $NH_4$-N were < 0.2 mg $L^{-1}$ at each of these depths throughout the sampling period and concentrations of $NO_3$-N were < 0.05 mg $L^{-1}$ from the commencement of sampling until water column turnover in June when they increased to 0.5 mg $L^{-1}$ (Figure 2.5b and c). The highest concentrations of dissolved inorganic nitrogen occurred 0.1 m above the sediment surface (benthic nepheloid layer) (Figure 2.5a). At this depth concentrations of $NH_4$-N reached a peak of 3.6 mg $L^{-1}$ in April, following a period of sustained increase after the initiation of sampling. Concentrations then generally declined and reached a minimum of 0.18 mg $L^{-1}$ in October, but remained above those of the other two depths on each sampling occasion. Concentrations of $NO_3$-N followed a similar trend to those of $NH_4$-N, reaching a maximum of 0.28 mg $L^{-1}$ in April, followed by a decline to 0.09 mg $L^{-1}$ by July before increasing rapidly to 0.56 mg $L^{-1}$ by October when $NH_4$-N was at a minimum. Concentrations of $NO_2$-N were negligible compared with the other two forms of dissolved inorganic forms at all sampling depths and times.

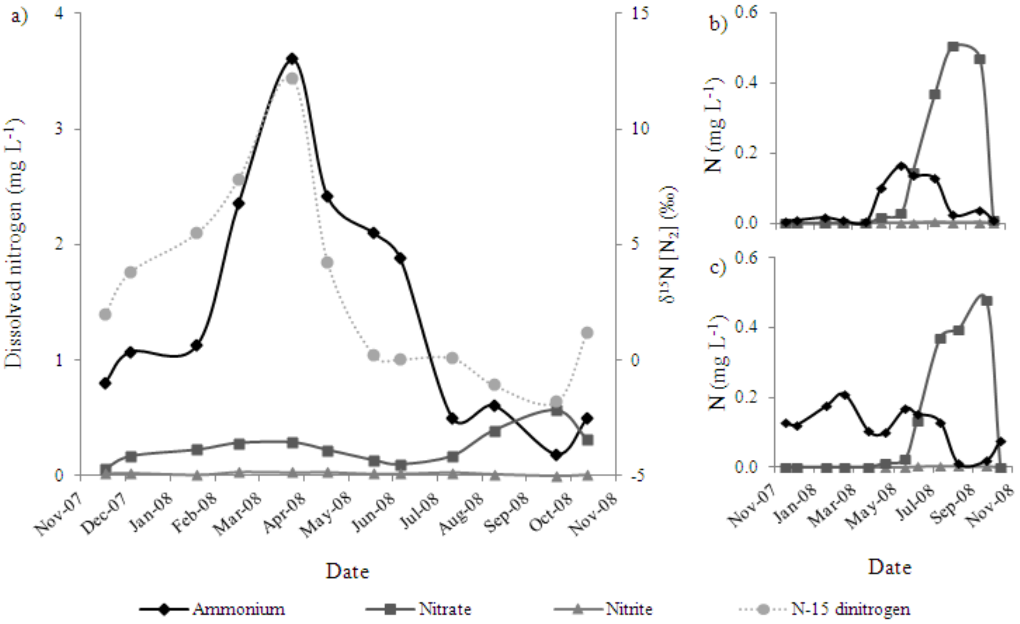

**Figure 2.5:** Concentrations of ammonium ($NH_4$-N), nitrate ($NO_3$-N) and nitrite ($NO_2$-N) (mg $L^{-1}$) in Lake Ngapouri from December 2007 to December 2008: a) benthic nepheloid layer including average $\delta^{15}N$ [$N_2$] values for these samples, b) hypolimnion and c) epilimnion.

Sediment pore water concentrations of $NH_4$-N increased with depth on each sampling occasion. There was a period of progressive increase in $NH_4$-N from the commencement of sampling until April 2008. The maximum concentration of $NH_4$-N of 15.5 mg $L^{-1}$ in sediment pore waters occurred at 15-20 cm depth in May (Figure 2.6). Concentrations of $NO_3$-N in sediment pore waters were at least an order of magnitude lower than those of $NH_4$-N and while they followed a similar temporal trend to $NH_4$-N concentrations, with a peak (0.25 mg $L^{-1}$) in April, they were largely invariant with depth. Pore water concentrations of $NO_2$-N were negligible.

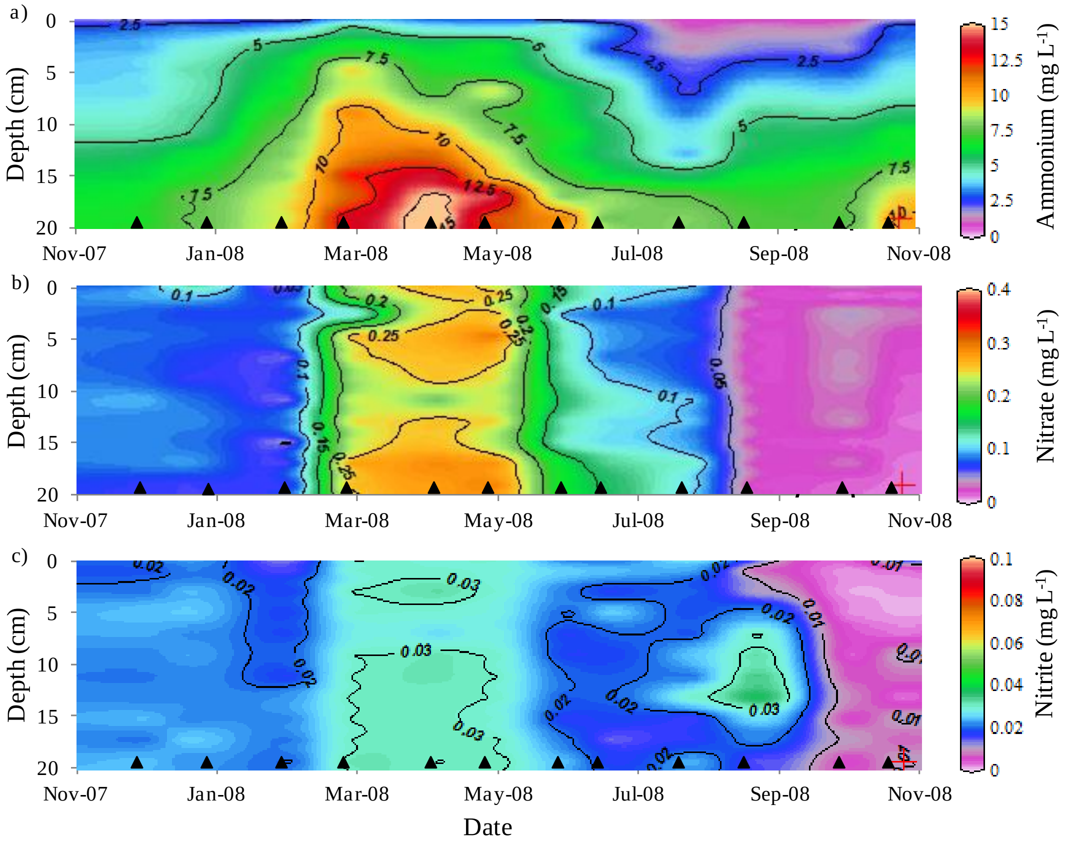

**Figure 2.6:** Sediment pore water concentrations of a) ammonium (NH$_4$-N), b) nitrate (NO$_3$-N) and c) nitrite (NO$_2$-N) (mg L$^{-1}$) in Lake Ngapouri sediments between November 2007 and November 2008. Arrow heads on the horizontal axis indicate sampling times. Note: Samples were not collected under anoxic conditions and the traces of NO$_3^-$ and NO$_2^-$ detected probably result from nitrification of NH$_4^+$ while briefly exposed to the atmosphere.

### 2.3.4 Isotopic values of nitrogen gas

Variations in average δ$^{15}$N [N$_2$] samples extracted from different water depths are shown in Figure 2.7 for the period of sampling. There was a slight seasonal trend and little variation (-1 ‰ while stratified to 0.29 ‰ while mixed) in samples taken from surface waters (epilimnion) of the lake, with δ$^{15}$N [N$_2$] remaining close to atmospheric levels. Water from the benthic nepheloid layer (0.1 m above the sediments) showed the largest variation in δ$^{15}$N [N$_2$] with a maximum of 12.2 ‰ in April and a minimum of -1.8 ‰ in October just prior to stratification. Samples from 1 m above the bottom sediment showed variations (-1.5 ‰ while mixed to 1.25 ‰ while stratified) that exceeded those of surface samples but were consistently lower than those 0.1 m above the sediments. Gas extracted from the sediment cores at depths of 0-5, 5-10, 10-15 and 15-20 cm showed smaller variations in $\delta^{15}N$ [$N_2$] than those from the water column 0.1 m above the sediments. The $\delta^{15}N$ [$N_2$] in the sediment pore waters reached a maximum of 3.8 ‰ in December 2007 at a depth of 5-10 cm when the lake was stratified and returned to close to zero after the lake mixed.

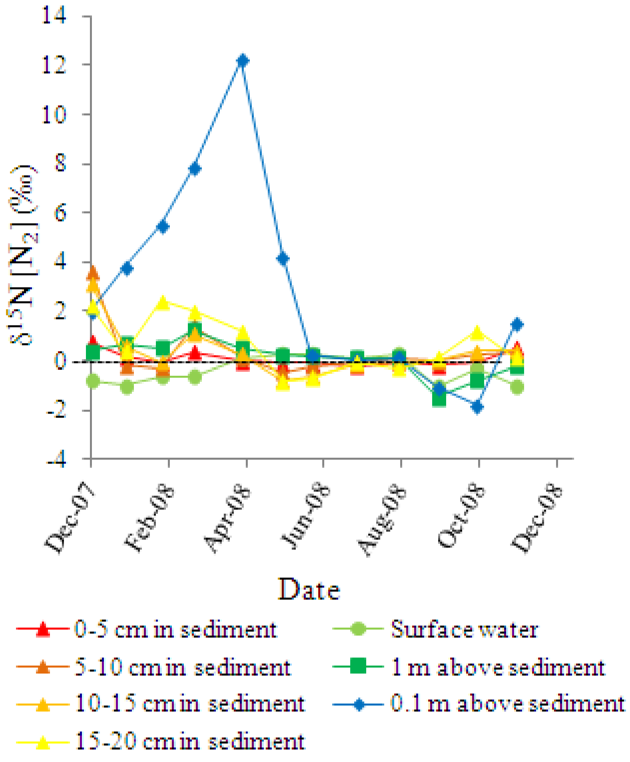

**Figure 2.7:** Annual variation in the $\delta^{15}N$ [$N_2$] in Lake Ngapouri water (diamonds) and sediment (triangles). The dashed line represents zero (i.e. equilibrium with the atmosphere).

While the lake remained fully mixed (June to September) $\delta^{15}N$ [$N_2$] of both water column and sediment pore waters remained close to isotopic equilibrium with the atmosphere. With the onset of stratification (September to November), the water column $N_2$ became briefly depleted in $^{15}N$ while deeper sediment pore waters became slightly enriched. With complete anoxia in the hypolimnion, the benthic nepheloid layer became progressively and strongly enriched in $^{15}N$ [$N_2$] whilst there was lesser enrichment of both sediment pore waters and of water from 1 m elevation in the hypolimnion. As stratification began to break down

(May), all sample sites showed a gradual return towards isotopic equilibrium with the atmosphere.

The settling PON collected 2 cm above the sediment-water interface in Lake Ngapouri had a $^{15}N$ value of 4.48 ‰.

### 2.3.5 Redox dynamics

In June to early September, when Lake Ngapouri was mixed, the pH of the epilimnion, hypolimnion and benthic nepheloid layer was around 6.5. There was an increase in pH of the epilimnion as the lake stratified to an average of 7. The pH of the hypolimnion remained about 6.5 during the stratified period. The pH of the benthic nepheloid layer decreased to an average of 6.25 when the lake was stratified (Figure 2.8).

The Eh of the epilimnion showed no consistent trend, reaching a maximum of 26 mV in December 2007 and a minimum of -63 mV prior to turn over in April 2007. When the epilimnion Eh was at a maximum, the hypolimnion and benthic nepheloid layer Eh values reached a minimum of -85 and -102 mV, respectively. This coincided with the development of hypolimnion anoxia (Figure 2.4). From December 2007, the Eh began to increase in the benthic nepheloid layer reaching a maximum of 20 mV when the lake was mixed in July 2008. Hypolimnion Eh measurements followed the same trend as the benthic nepheloid layer but with reduced range (maximum 2 mV). With the onset of stratification and developing anoxia, Eh declined sharply in the benthic nepheloid layer to -90 mV (Figure 2.8).

### 2.3.6 Iron and manganese dynamics

When Lake Ngapouri was mixed (June to early September) dissolved iron (0.5 mg $L^{-1}$) and manganese (0.2 mg $L^{-1}$) concentrations were uniform in the epilimnion and hypolimnion, and slightly elevated but declining in the benthic nepheloid layer (Figure 2.8). Following stratification, epilimnion concentrations of dissolved Fe and Mn decreased to near detection limits, while the hypolimnion concentrations increased as anoxia developed (Fe 1.7 mg $L^{-1}$ and Mn 0.35 mg $L^{-1}$). Once the hypolimnion became anoxic, Fe and Mn concentrations declined gradually until the onset of the next period of anoxia. Benthic nepheloid layer concentrations were out of phase with epilimnion concentrations, increasing markedly as anoxia developed (Fe 6.7 mg $L^{-1}$ and Mn 0.88 mg $L^{-1}$) and declining sharply following mixing (Fe 1.4 mg $L^{-1}$ and Mn 0.26 mg $L^{-1}$).

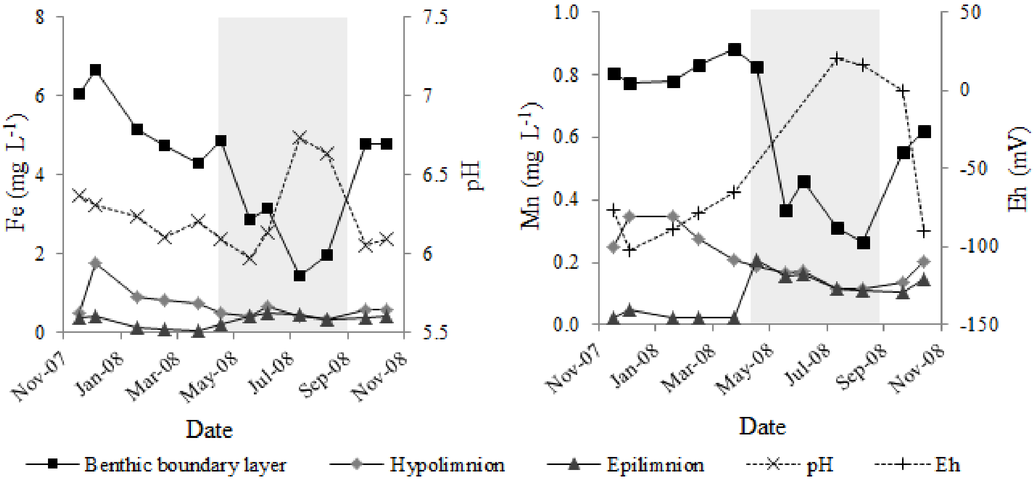

**Figure 2.8:** Monthly concentrations of a) iron and b) manganese (mg $L^{-1}$) in water from the epilimnion (1 m depth), hypolimnion (1 m above bottom) and benthic nepheloid layer (0.2 m above bottom) of Lake Ngapouri between November 2007 and November 2008 (Left axis). Right axis shows monthly benthic nepheloid layer a) pH and b) Eh (mV) values. Shading shows the period when the lake was mixed.

## 2.4 DISCUSSION

Nitrogen has previously been identified as the primary limiting nutrient in Lake Ngapouri (Fish, 1970; White, 1983; White et al., 1985) partly due to naturally high rates of phosphate input from weathering of the surrounding ignimbrite welded pyroclastics (Timperley, 1983; Froggatt and Rogers, 1990). Lake Ngapouri also has high concentrations of dissolved iron and manganese in the lake and sediment pore waters due to naturally high concentrations in the surrounding volcanic terrain. These concentrations are not atypical of compositions found in the Taupo Volcanic Zone lakes (McColl, 1972; Trolle et al., 2010).

The water column $^{15}N$:$^{14}N$ ratio, expressed as $\delta^{15}N$ [$N_2$], is dominated by atmospheric exchanges as there are only small fluctuations in $\delta^{15}N$ in surface waters (-1‰ while stratified to 0.29‰ while mixed) while the bottom waters show a small but reversed change with -1.5‰ while mixed to 1.25‰ while stratified. Fluxes of nitrogen isotopes that could lead to significant enrichment or depletion of N isotopic values in surface waters appear to show little departure from atmospheric equilibrium.

Dissolved inorganic nitrogen (DIN) concentrations were low in the water column (< 0.5 mg $L^{-1}$) compared with the concentration of dinitrogen (Adams, 1992); thus, $^{15}N$ enrichment of $N_2$ arising from denitrification would need to be substantial to raise $\delta^{15}N$ [$N_2$] to the levels observed in the benthic nepheloid layer. It is possible that $\delta^{15}N$ of DIN can be controlled by allochthonous sources and sinks of N, as well as internal cycling processes. Most allochthonous sources are usually in the form of fluvial inputs and include biological $N_2$ fixation, which would add relatively low $\delta^{15}N$ of between 0 and -2 ‰ (Brandes and Devol, 2002; Mahaffey et al., 2005). However, Lehmann et al. (2004) found no consistent relationship between the $\delta^{15}N$ of POM, $\delta^{15}N$ of DIN and nitrate concentration in surface waters of Lake Lugano, Italy. Thus neither PON generated in the epilimnion nor from allochthonous sources is likely to be sufficiently enriched in $^{15}N$ in Lake Ngapouri (4.48 ‰) to account for the observed values of $^{15}N$ [$N_2$].

In the relatively isolated lower water masses of the benthic nepheloid layer of Lake Ngapouri, the potential for isotopic enrichment is greatly enhanced by abundant PON as it settles out of the water column and accumulates in this thin dynamic water layer (Eckert et al., 2002). Adams (1992) found denitrification at the sediment-water interface of Lake Ngapouri resulted in elevated concentrations of nitrogen gas (18-27 ± 3 ml $L^{-1}$) near the sediment surface compared to nitrogen gas concentrations in the water column. We found high concentrations of dissolved inorganic nitrogen, mostly in the form of ammonium (up to 3.6 mg $L^{-1}$) in the benthic nepheloid layer, the presence of dissolved Fe and Mn oxides and anoxic conditions (DO <0.2 mg $L^{-1}$) during the mid to latter phase of seasonal stratification. Bioassay experiments in Lake Rotoiti (another TVZ lake) revealed that at DO between 1.0 and 0.2 mg $L^{-1}$ the primary sequence of nitrogen transformation was the conversion of $NH_4^+$ to $NO_2^-$ followed by reduction to $N_2O$ (Downes, 1988). While at lower oxygen concentrations, particularly <0.2 mg $L^{-1}$ complete reduction to $N_2$ gas dominated (Downes, 1988). A similar utilisation of $NH_4^+$ is likely occurring in Lake Ngapouri.

Nitrification and denitrification within the water column lead to N isotope fractionation (Mariotti et al., 1981; Lehmann et al., 2004; Hadas et al., 2009). Lehmann et al. (2004) noted $\delta^{15}N$ of bottom-water nitrate progressively increased from +8‰ to +27‰ as anaerobic conditions developed and nitrate concentrations decreased, suggesting active denitrification in the hypolimnion. As the $\delta^{15}N$ of the remaining nitrate increases with denitrification, the dinitrogen product must be depleted in $^{15}N$ and as the nitrate is progressively converted to dinitrogen, the product will eventually inherit the isotopic ratio of its nitrate substrate. In Lake Ngapouri, we found the opposite, with negligible nitrate and $\delta$ $^{15}N$ [$N_2$] starting near 0 ‰ and steadily increasing to 12.2 ‰ by the end of thermal stratification. With the onset of mixing the $\delta^{15}N$ values in the benthic nepheloid layer decreased as oxygen-rich water from the epilimnion, with $\delta^{15}N$ [$N_2$] close to zero, mixed into the hypolimnion and the nitrogen from the benthic nepheloid layer was exchanged with that in the overlying water.

Denitrification activity in groundwater has previously been interpreted from $\delta^{15}N$ [$N_2$] measurements which have shown an enrichment in the dinitrogen end-product (Groffman et al., 2006). Vogel et al. (1981) (reinterpreted by Böhlke et al., (2002)) showed that denitrification fractionated the nitrogen isotopes so that the $N_2$ product was enriched by about 20 ‰. The accumulated product became enriched through Rayleigh distillation (Mariotti et al., 1981) by about 10 ‰ after complete denitrification (Böhlke, 2002). This observation conflicts with that of Lehmann et al. (2004) who showed enrichment of $^{15}N$ in the nitrate pool. In Lake Ngapouri, the low concentrations of nitrate in the benthic nepheloid layer, and near absence of nitrate in the hypolimnion and sediment pore waters, suggest that if nitrate is the substrate for denitrification in this environment its existence is transitory, and its isotopic composition will be controlled by that of its precursors (benthic nepheloid layer PON), ammonification and nitrification. Gu (2009) showed that the $\delta^{15}N$ of POM in eutrophic lakes averaged +8 ‰ with a seasonal amplitude of 10.3 ‰. The $\delta^{15}N$ of POM is influenced by the isotopic composition of the DIN sources for phytoplankton, isotopic fractionation during partial utilisation of these sources and transfer to higher trophic levels (Altabet, 2006). If the $\delta^{15}N$ POM in Lake Ngapouri showed similar enrichment to the cases reviewed by Gu (2009), then progressive enrichment in $^{15}N$ [$N_2$] in the benthic nepheloid layer of Lake Ngapouri of up to 12.2 ‰ would not require any further isotopic fractionation. However, the $\delta^{15}N$ value of POM in Lake Ngapouri of 4.48 ‰ is not enough to produce $^{15}N$ [$N_2$] of up to 12.2 ‰ without additional enrichment.

Despite high concentrations of organic matter in the bottom sediment pore waters, it is unlikely that the sediments contribute substantially to the high $\delta^{15}N$ [$N_2$] in the benthic nepheloid layer. Sediment pore waters were only enriched only up to +3.8 ‰ (December 2007) and then decreased while the benthic nepheloid layer $\delta^{15}N$ [$N_2$] values increased (Figure 2.7). This demonstrates that the pore water nitrogen isotope ratio was not continuously linked with the nitrogen in the benthic nepheloid layer. Ammonium in the sediment pore waters increased to 10 mg $L^{-1}$ at 10 cm sediment depth and to more than 14 mg $L^{-1}$ at a depth of 15-20 cm under anoxic conditions (Figure 2.6). The minor increase in nitrate and nitrite shown in Figure 2.6 are most likely the result of contact with the atmosphere and nitrification of ammonium while handling the pore waters. These concentrations do not affect the denitrification argument presented in this study. When the lake mixed in June, concentrations of ammonium decreased to < 4 mg $L^{-1}$ at 10 cm to about 6 mg $L^{-1}$ at 15-20 cm in the sediments. The steep concentration gradients increase diffusion of ammonium from the pore waters to the benthic nepheloid layer while the lake is stratified. The significant exchange of pore water with overlying lake water during lake turnover and the rapid change in pore water chemistry following stratification show the sediment pore water system to be very dynamic. The low bulk density and high porosity of Lake Ngapouri sediment (0.02 g $cm^{-3}$ and 98 %, respectively at the sediment-water interface (Pearson, unpublished data)) allows for rapid penetration into surficial sediments when the lake mixes. In Lake Ngapouri, the benthic nepheloid layer separates the sediment from the overlying hypolimnion enabling the development of substantial concentration gradients when the lake stratifies, but when mixed it is insufficient to prevent interaction with the overlying water column.

The concentrations of $NO_3^-$ and $NO_2^-$ in the benthic nepheloid layer appear to be too low to provide significant $N_2$ product to influence the $\delta^{15}N$. Therefore, additions to the DIN pool (PON mineralisation), transformations within it (nitrification) and losses of DIN (denitrification) would need to be very high to produce sufficient $^{15}N$-enriched $N_2$ to substantially increase the $\delta^{15}N$ of the existing $N_2$ pool. Furthermore with concentrations of DIN (mainly $NH_4^+$) in the BNL of Lake Ngapouri (up to 4 mg $L^{-1}$) considerably higher than in the hypolimnion, the $\delta^{15}N$ and $NH_4^+$ would be continually diluted in the BNL due to diffusive exchanges with the hypolimnion. It appears, therefore, that the bulk of the enrichment may be due to ammonification of the settling PON followed by continuous denitrification to $N_2$, even under anoxic conditions. Any ammonium produced within the benthic nepheloid layer is likely augmented by diffusion from the pore waters. Burger (2006) measured a net sedimentation rate of 4,500 mg $m^{-2}$ $day^{-1}$ for total particulate matter and 103.7 mg $m^{-2}$ $day^{-1}$ for TN in eutrophic Lake Rotorua (another TVZ lake). If this material was to be metabolised completely within the BNL it would double the concentration of dinitrogen within 14 days. Thus, in eutrophic stratified lakes there would appear to be adequate capacity for PON to drive the observed enrichment of $\delta^{15}N$ [$N_2$]; an assertion that relies also on rapid transitions of N through the nitrate pool (explaining its low concentration) and a supply of electron acceptors for nitrification, even under anoxic conditions.

Iron and manganese are lost from the epilimnion as they are oxidised to insoluble and dense particulates. Simultaneously, concentrations of these ions increase in the benthic nepheloid layer suggesting that there is reduction of the descending particulates (Figure 2.8). The settling of oxidised particulates such as $MnO_2$ or $Fe(OH)_3$ could result in the oxidation ammonium to nitrate in the benthic nepheloid layer (chemo-denitrification (Sørensen et al., 1987; Luther et al., 1997: Luther, 2010)) which would subsequently be denitrified to dinitrogen, accounting for the progressive enrichment observed in the $\delta^{15}N$ [$N_2$]. Verification of this process could come from determination of $\delta^{15}N$ [$NH_4^+$] and $\delta^{15}N$ [$NO_3^-$], but was not done in this study. A similar process might also occur in confined groundwater aquifers accounting, for the enrichment of $^{15}N$ in dissolved dinitrogen (Van Hecke et al., 1990).

The observed enrichment of $\delta^{15}N$ $[N_2]$ and subsequent depletion in the benthic nepheloid layer are synchronous with the build up and decline in pore water ammonium concentrations as Lake Ngapouri stratifies and mixes (Figure 2.4 and 2.5a). Ammonium concentrations in the benthic nepheloid layer rise following the development of anoxia and decline when mixing reintroduces dissolved oxygen. Although our study has not identified the source of the $^{15}N$ depletion following re-oxygenation in the hypolimnion, the significant relationship ($r^2 = 0.59$, $p < 0.01$) between ammonium concentrations and $\delta^{15}N$ $[N_2]$ suggests an association with nitrification (Figure 2.5a). There was no correlation between $\delta^{15}N$ $[N_2]$ and the concentration of other nitrogen species.

Further study should be directed at identification of the $^{15}N$-depleted materials required to achieve isotopic mass balance in these water bodies. As ammonium concentrations were generally in phase with the observed $^{15}N$ enrichment of nitrogen gas, ammonium would be a potential candidate for $^{15}N$ measurements. A complete mass balance of $^{15}N$ in all of the nitrogen reservoirs is desirable to determine the processes involved.

## 2.5 REFERENCES

Adams, D. D. 1992. Sediment pore water geochemistry of Taupo Volcanic Zone lakes with special reference to carbon and nitrogen gases. File Report 135. Taupo Research Laboratory DSIR, Taupo, New Zealand.

Aller, R. 1990. Bioturbation and manganese cycling in hemipelagic sediments. Phil. Trans. Roy. Soc. London. **331:** 51-68.

Altabet, M. A. 2006. Isotopic traces of marine nitrogen cycle: present and past, p. 251-293. *In* J. K. Volkman [ed.], Marine organic matter: biomarkers, isotopes and DNA. Springer-Verlag.

Bartlett, R., R. J. G. Mortimer, and K. Morris. 2008. Anoxic nitrification: evidence from Humber Estuary sediments (UK). Chem. Geol. **250:** 29-39.

Böhlke, J.-K. 2002. Groundwater recharge and agricultural contamination. Hydrogeol. J. **10:** 153-179.

Boyer, E. W. and others 2006. Modelling denitrification in terrestrial and aquatic ecosystems at regional scales. Ecol. Appl. **16:** 2123-2142.

Brandes, J. A., and A. H. Devol. 2002. A global marine-fixed nitrogen isotopic budget: Implications for Holocene nitrogen cycling. Global Biogeochem. Cycles **16:** 1120.

Bremner, J. M. 1965. Isotope-ratio analysis of nitrogen in nitrogen-15 tracer investigations, p. 1256-1286. *In* C. A. Black et al. [eds.], Methods of Soil Analysis. Part 2, American Society of Agronomy, Madison, Wisconsin, USA.

Bremner, J. M., and A. P. Edwards. 1965. Determination and isotope-ratio analysis of different forms of nitrogen in soils: I. Apparatus and procedure for distillation and determination of ammonium. Soil Sci. Soc. Am. J. **29:** 504-507.

Bruesewitz, D. A., D. P. Hamilton, and L. A. Schipper. 2011. Denitrification potential in lake sediment increases across a gradient of catchment agriculture. Ecosystems **14:** 341-352.

Burger, D. F. 2006. Dynamics of internal nutrient loading in a eutrophic, polymictic lake (Lake Rotorua, New Zealand). Ph.D. Thesis. Department of Biological Sciences, University of Waikato.

Clément, J. C., J. Shrestha, J. G. Ehrenfeld, and P. R. Jaffé. 2005. Ammonium oxidation coupled to dissimilatory reduction of iron under anaerobic conditions in wetland soils. Soil Biol. Biochem. **37:** 2323-2328.

Cross, D. 1963. Soils and geology of some hydrothermal eruptions in the Waiotapu District. N. Z. J. Geol. Geop. **6:** 70-87.

Dalsgaard, T., D. E. Canfield, J. Petersen, B. Thamdrup, and J. Acuña-González. 2003. $N_2$ production by the anammox reaction in the anoxic water column of Golfo Dulce, Costa Rica. Nature **422:** 606-608.

Devol, A. H. 1991. Direct measurement of nitrogen gas fluxes from continental shelf sediments. Nature **349:** 319-321.

Downes, M. T. 1988. Aquatic nitrogen transformations at low oxygen concentrations. Appl. Environ. Microb. **54:** 172-175.

Downs, M. R., R. H. Michener, B. Fry, and K. J. Nadelhoffer. 1999. Routine measurement of dissolved organic $^{15}$N in precipitation and streamwater. Environ. Monit. Assess. **55:** 211-220.

Eckert, W., J. Imberger, and A. Saggio. 2002. Biogeochemical response to physical forcing in the water column of a warm monomictic lake. Biogeochem. **61:** 291-307.

Fish, G. R. 1970. A limnological study of four lakes near Rotorua. N.Z. J. Mar. Freshw. Res. **4:** 165-194.

Forsyth, D. J. 1986. Distribution and production of Chironomus in eutrophic Lake Ngapouri. N.Z. J. Mar. Freshw. Res. **20:** 47-54.

Froelich, P. and others 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta **43:** 1075-1090.

Froggatt, P. C., and G. M. Rogers. 1990. Tephrostratigraphy of high-altitude peat bogs along the axial ranges, North Island, New Zealand. N. Z. J. Geol. Geophys. **33:** 111-124.

Galloway, J. and others 2004. Nitrogen cycles: past, present, and future. Biogeochem. **70:** 153-226.

Garten, C. T. 1992. Nitrogen isotope composition of ammonium and nitrate in bulk precipitation and forest throughfall. Int. J. Environ. Anal. Chem **47:** 33-45.

Granger, J., D. M. Sigman, M. F. Lehmann, and P. D. Tortell. 2008. Nitrogen and oxygen isotope fractionation during dissimilatory nitrate reduction by denitrifying bacteria. Limnol. Oceanogr. **53:** 2533-2545.

Groffman, P. M. and others 2006. Methods for measuring denitrification: diverse approaches to a difficult problem. Ecol. Appl. **16:** 2091-2122.

Gu, B. 2009. Variations and controls of nitrogen stable isotopes in particulate organic matter of lakes. Oecologia **160:** 421-431.

Hadas, O., M. A. Altabet, and R. Agnihotri. 2009. Seasonally varying nitrogen isotope biogeochemistry of particulate organic matter in Lake Kinneret, Israel. Limnol. Oceanogr. **54:** 75-85.

Håkanson, L., and M. Jansson. 1983. Principles of Lake Sedimentology. 316.

Hellstrom, T. 1996. An empirical study of nitrogen dynamics in lakes. Water Environ. Res. **68:** 55-65.

Hoering, T. 1957. The isotopic composition of the ammonia and the nitrate ion in rain. Geochim. Cosmochim. Acta. **12:** 97-102.

Hulth, S. and others 2005. Nitrogen removal in marine environments: recent findings and future research challenges. Mar. Chem. **94:** 125-145.

Humbert, S., S. Tarnawski, N. Fromin, M. P. Mallet, M. Aragno, and J. Zopfi. 2010. Molecular detection of anammox bacteria in terrestrial ecosystems: distribution and diversity. ISME **4:** 450-454.

Kendall, C., and E. Grim. 1990. Combustion tube method for measurement of nitrogen isotope ratios using calcium oxide for total removal of carbon dioxide and water. Anal. Chem. **62:** 526-529.

Kuypers, M. M. M. and others 2003. Anaerobic ammonium oxidation by anammox bacteria in the Black Sea. Nature **422:** 608-611.

LECO Corporation. 2006. TruSpec CN Carbon/Nitrogen Determinator, Instruction Manual. LECO Corporation. United States.

Lehmann, M. F., S. M. Bernasconi, A. Barbieri, and J. A. Mckenzie. 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. Geochim. Cosmochim. Acta. **66:** 3573-3584.

Lehmann, M. F., S. M. Bernasconi, J. A. Mckenzie, A. Barbieri, M. Simona, and M. Veronesi. 2004. Seasonal variation of the δ13C and δ15N of particulate and dissolved carbon and nitrogen in Lake Lugano: constraints on biogeochemical cycling in a eutrophic lake. Limnol. Oceanogr. **49:** 415-429.

Luther, G. W. 1997. Interactions of manganese with the nitrogen cycle: Alternative pathways to dinitrogen. Geochim. Cosmochim. Acta **61:** 4043-4052.

Luther, G. W. 2010. The role of one-and two-electron transfer reactions in forming thermodynamically unstable intermediates as barriers in multi-electron redox reactions. Aquat. Geochem. **16:** 395-420.

Luther, G. W., and J. I. Popp. 2002. Kinetics of the abiotic reduction of polymeric manganese dioxide by nitrite: an anaerobic nitrification reaction. Aquat. Geochem. **8:** 15-36.

Mackown, C. T., P. D. Brooks, and M. S. Smith. 1987. Diffusion of nitrogen-15 Kjeldahl digests for isotope analysis. Soil Sci. Soc. Am. J. **51:** 87-90.

Mahaffey, C., A. F. Michaels, and D. G. Capone. 2005. The conundrum of marine $N_2$ fixation. Am. J. Sci. **305:** 546-595.

Mariotti, A. 1983. Atmospheric nitrogen is a reliable standard for natural 15N abundance measurements. Nature **303:** 685-687.

Mariotti, A. and others 1981. Experimental determination of nitrogen kinetic isotope fractionation: some principles; illustration for the denitrification and nitrification processes. Plant Soil **62:** 413-430.

McColl, R. H. S. 1972. Chemistry and trophic status of seven New Zealand lakes. N. Z. J. Mar. Freshw. Res. **6:** 399-447.

McIlvin, M. R., and M. A. Altabet. 2005. Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater. Anal. Chem **77:** 5589-5595.

Mortimer, R. J. G. and others. 2004. Anoxic nitrification in marine sediments. MEPS **276:** 37-51.

Mortimer, R. J. G. and others. 2002. Evidence for suboxic nitrification in recent marine sediments. MEPS **236:** 31-35.

Mulder, A., A. A. Van de Graaf, L. A. Robertson, and J. G. Kuenen. 1995. Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. FEMS Microbiol. Ecol. **16:** 177-184.

Murray, J. W., L. A. Codispoti, and G. E. Friederich. 1995. Oxidation-reduction environments: The suboxic zone in the Black Sea, p. 157-176. *In* C. P. Huang, C. R. O'Melia and J. J. Morgan [eds.], Aquatic Chemistry: Interfacial and Interspecies Processes. Am. Chem. Soc.

Nishri, A., and D. P. Hamilton. 2010. A mass balance evaluation of the ecological significance of historical nitrogen fluxes in Lake Kinneret. Hydrobiologia **655:** 109-119.Ostrom, N. E., S. A. Macko, D. Deibel, and R. J. Thompson. 1997. Seasonal variation in the stable carbon and nitrogen isotope biogeochemistry of a coastal cold ocean environment. Geochim. Cosmochim. Acta. **61:** 2929-2942.

Paerl, H. W., and J. L. Pinckney. 1996. A mini-review of microbial consortia: Their roles in aquatic production and biogeochemical cycling. Microb. Ecol. **31:** 225-247.

Pearson, L. K. 2007. The nature, composition and distribution of sediment in Lake Rotorua, New Zealand. M.Sc. Thesis. Department of Chemistry, University of Waikato.

Pina-Ochoa, E., and M. Alvarez-Cobelas. 2006. Denitrification in aquatic environments: a cross-system analysis. Biogeochem. **81:** 111-130.

Postma, D. 1990. Kinetics of nitrate reduction by detrital Fe (II)-silicates. Geochim. Cosmochim. Acta **54:** 903-908.

Priscu, J. C., R. H. Spigel, M. M. Gibbs, and M. T. Downes. 1986. A numerical analysis of hypolimnetic nitrogen and phosphorus transformations in Lake Rotoiti, New Zealand: A geothermally influenced lake. Limnol. Oceanogr. **31:** 812-831.

Révész, K., J. K. Böhlke, and T. Yoshinari. 1997. Determination of $\delta^{18}O$ and $\delta^{15}N$ in nitrate. Anal. Chem **69:** 4375-4380.

Saunders, D. L., and J. Kalff. 2001. Nitrogen retention in wetlands, lakes and rivers. Hydrobiologia **443:** 205-212.

Schubert, C. J., E. Durisch-Kaiser, B. Wehrli, B. Thamdrup, P. Lam, and M. M. M. Kuypers. 2006. Anaerobic ammonium oxidation in a tropical freshwater system (Lake Tanganyika). Environ. Microbiol. **8:** 1857-1863.

Schulz, H. D., A. Dahmke, U. Schinzel, K. Wallmann, and M. Zabel. 1994. Early diagenetic processes, fluxes, and reaction rates in sediments of the South Atlantic. Geochim. Cosmochim. Acta **58:** 2041-2060.

Seitzinger, S. P. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnol. Oceanogr. **33:** 702-724.

Seitzinger, S. P. and others 2006. Denitrification across landscapes and waterscapes: A synthesis. Ecol. Appl. **16:** 2064-2090.

Seitzinger, S. P., L. P. Nielsen, J. Caffrey, and P. B. Christensen. 1993. Denitrification measurements in aquatic sediments: a comparison of three methods. Biogeochem. **23:** 147-167.

Sigman, D. M., M. A. Altabet, R. H. Michener, D. C. McCorkle, B. Fry, and R. M. Holmes. 1997. Natural abundance-level measurement of the nitrogen isotopic composition of oceanic nitrate: an adaptation of the ammonia diffusion method. Marine Chem. **57:** 227-242.

Silva, S. R., C. Kendall, D. H. Wilkison, A. C. Ziegler, C. C. Y. Chang, and R. J. Avanzino. 2000. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. J. Hydrol. **228:** 22-36.

Sørensen J., Jørgensen K.S. 1987. Early diagenesis in sediments from Danish coastal waters: microbial activity and Mn-Fe-geochemistry. Geochim. Cosmochim. Acta **51:** 1583-1590.

Teranes, J. L., and S. M. Bernasconi. 2000. The record of nitrate utilization and productivity limitation provided by δ15N values in lake organic matter- A study of sediment trap and core sediments from Baldeggersee, Switzerland. Limnol. Oceanogr. **45:** 801-813.

Thamdrup, B., and T. Dalsgaard. 2002. Production of $N_2$ through anaerobic ammonium oxidation coupled to nitrate reduction in marine sediments. Appl. Environ. Microbiol. **68:** 1312.

Timperley, M. 1983. Phosphorus in spring waters of the Taupo volcanic zone, North Island, New Zealand. Chem. Geol. **38:** 287-306.

Tomaszek, J. A. 1995. Relationship between denitrification and redox potential in two sediment-water systems. Mar. Freshwat. Res. **46:** 27-31.

Trolle, D., D. P. Hamilton, and C. A. Pilditch. 2010. Evaluating the influence of lake morphology, trophic status and diagenesis on geochemical profiles in lake sediments. Appl. Geochem. **25:** 621-632.

Van Breemen, N. and others 2002. Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern USA. Biogeochem. **57:** 267-293.

Van Hecke, K., O. Van Cleemput, and L. Baert. 1990. Theoretical aspects on chemo-denitrification of nitrate in groundwater, p. 215-220. *In* R. Calvet [ed.], Nitrates-Agriculture-Water: International Symposium.

Velinsky, D. J., J. R. Pennock, J. H. Sharp, L. A. Cifuentes, and M. L. Fogel. 1989. Determination of the isotopic composition of ammonium-nitrogen at the natural abundance level from estuarine waters. Marine Chem. **26:** 351-361.

Vogel, J. C., A. S. Talma, and T. H. E. Heaton. 1981. Gaseous nitrogen as evidence for denitrification in groundwater. J. Hydrol. **50:** 191-200.

Wassenaar, L. I. 1995. Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of $^{15}N$ and $^{18}O$ in $NO_3^-$. Appl. Geochem. **10:** 391-405.

Wetzel, R. G., and G. E. Likens. 2000. Limnological Analyses, 3rd ed. Springer Verlag.

White, E. 1983. Lake eutrophication in New Zealand—a comparison with other countries of the Organisation for Economic Co-operation and Development. N. Z. J. Mar. Freshwat. Res. **17:** 437-444.

White, E., K. Law, G. Payne, and S. Pickmere. 1985. Nutrient demand and availability among planktonic communities—an attempt to assess nutrient limitation to plant growth in 12 central volcanic plateau lakes. N. Z. J. Mar. Freshwat. Res. **19:** 49-62.

# CHAPTER 3: NITROGEN-15 ISOTOPE ENRICHMENT IN BOTTOM WATERS AS A PROXY FOR TROPHIC STATUS AND HYPOLIMNETIC OXYGEN DEMAND

## 3.1 INTRODUCTION

There is increasing awareness globally of the need to reduce N inputs to aquatic ecosystems if lake water quality is to be improved (Vitousek et al., 1997; Galloway et al., 2003; Harrison et al., 2009; Gardner and McCarthy, 2009; Vanni, 2010), though the basis for N reductions to assist with eutrophication control remains the subject of ongoing debate (Schindler et al., 2008; Conley et al., 2009). Analyses of N:P ratios (White, 1983; White et al., 1985; Elser *et al.* 1990; Koszelnik *et al.* 2007, Abell et al., 2010) and bioassays (Priscu et al., 1986; Downes, 1988; Downs et al., 2008) indicate that nitrogen (N) may limit primary productivity in many lakes in NZ as well as globally. Lakes in the Taupo Volcanic Zone (TVZ), NZ, have had historically low levels of atmospheric N deposition, little urban development in lake catchments, and have naturally high phosphorus (P) inputs from edaphic sources (tephras) and ignimbrite aquifers that contribute groundwater that is the volumetrically dominant inflow to lakes in this region (White, 1983). Intensification of agriculture, particularly dairy farming, is associated with a growing dependence on N fertilizers in NZ (Richardson et al., 2004; MacLeod and Moller, 2006) and has resulted in increasing reactive N loads to TVZ lakes (Hamilton, 2005; Parfitt et al., 2006; Bruesewitz et al., 2011).

Identifying when, where, and how much denitrification occurs from monitoring the $N_2$ end-product of this reaction is particularly challenging as naturally abundant atmospheric $N_2$ dissolved in water masks relatively small changes that may be induced by denitrification (Seitzinger et al., 2002; Van Breemen et al., 2002; Galloway et al., 2004; Boyer et al., 2006; Groffman et al., 2006). Analysis of stable isotopes provides a technique for discriminating different sources of N used in denitrification. Previous studies aimed at understanding isotopic N composition in lakes have focused on external nitrogen loading (Ostrom et al., 1997; Teranes and Bernasconi, 2000) or fractionation during denitrification (Hadas et al., 2009) as this reaction rapidly utilizes $^{14}N$-nitrate ($NO_3^-$) rather than $^{15}N$-$NO_3^-$ resulting in significant enrichment of $^{15}N$ in the substrate pool (Brandes and Devol, 1997; Granger et al., 2008). As anoxia develops there is commensurate increase in denitrification which increases $\delta^{15}N$ [$NO_3^-$] in lake waters to values as high as +27 ‰ (Lehmann et al., 2002; 2004). Altabet (2006) has shown that the $\delta^{15}N$ of particulate organic matter (POM) in open waters is influenced mostly by the isotopic composition of the DIN sources for phytoplankton. These sources undergo fractionation during uptake and utilization by phytoplankton, as well as when phytoplankton are utilised as a food source for higher trophic levels. Although the isotopic composition of dinitrogen should reflect the above fractionation process, previous studies have focused on changes in $\delta^{15}N$ of the N substrate, $NO_3^-$, rather than the end production $\delta^{15}N$ [$N_2$].

In lakes that are N limited, low levels of nitrate generally preclude measurements of $\delta^{15}N$ [$NO_3^-$]. In the absence of $NO_3^-$ it would be assumed that dentirification would cease, precluding further changes in $\delta^{15}N$ [$N_2$]. However, Adams (1992) showed evidence of denitrification at the sediment-water interface (SWI) from measurements of dinitrogen in TVZ lakes despite minimal $NO_3^-$ concentrations. Pearson et al. (2011) have shown that iron and manganese hydroxides and oxides from material sedimenting out of the water column may have induced chemo-nitrification sufficient to oxidize ammonium in the anoxic benthic nepheloid layer. The nitrate formed would mostly be rapidly denitrified so that the $\delta^{15}N$ [$N_2$] would continue to become enriched during the presence of anoxia.

The objective of this paper was firstly to quantify $^{15}N$ [$N_2$] enrichment in surface (epilimnion), bottom (hypolimnion), and benthic nepheloid layer (BNL) waters, as well as in sediment pore waters, of 11 TVZ lakes and to test for relationships of enrichment to different environmental factors. Enrichment of $^{15}N$ [$N_2$] was measured monthly in the benthic nepheloid layer and sediment pore waters in five TVZ lakes, as well as in the hypolimnion and epilimnion, in order to provide a time series of $^{15}N$ [$N_2$] enrichment across lakes of varying trophic gradient. We ultimately test whether discrete samples of $\delta^{15}N$ [$N_2$] can be used as a management tool to monitor trophic status and denitrification in seasonally stratified temperate lakes.

## 3.2 METHODS

### 3.2.1 Study sites

The TVZ is in the Waikato and the Bay of Plenty regions of North Island of NZ. It contains many volcanic lakes which have diverse history, physiography, and limnology (Figure 1; Lowe and Green, 1987). The lakes vary in size (0.2 to > 600 km$^2$), mixing regime (monomictic and polymictic), and trophic status (oligotrophic to supertrophic) (Table 1). The lakes range in depth from 18 to 164 m. Oligotrophic Lake Taupo (area 616 km$^2$), the largest lake in NZ, is located near the centre of the North Island (Figure 1). Nitrogen has previously been identified as a limiting nutrient in many of the TVZ lakes (White et al., 1985; Burns, 1997; Schallenberg, 2004) partly due to naturally high rates of phosphate input from weathering of the surrounding ignimbrite (Timperley, 1983) and from welded pyroclastics (Froggatt and Rogers, 1990). The lakes are non-calcareous and have high concentrations of dissolved iron and manganese in water column and sediment pore waters due to naturally high concentrations found in surrounding volcanic terrain (McColl 1972; Trolle et al. 2010). The Rotorua Lakes District, north of Lake Taupo (Figure 1), has lakes of varying trophic status, some relatively unaffected by human activities and others heavily impacted by urbanisation and farming (McColl, 1972; Vincent et al., 1984; Hamilton, 2005; Bruesewitz et al., 2011).

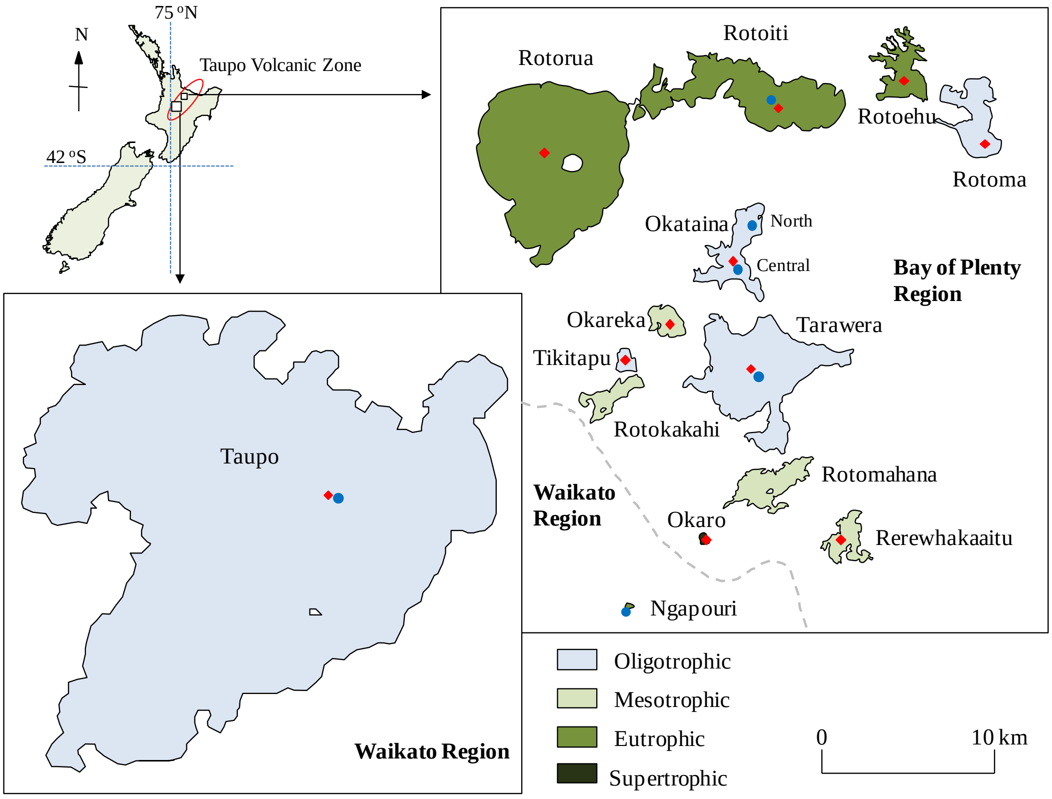

**Figure 3.1:** Location of Lake Taupo and the Rotorua lakes within the Taupo Volcanic Zone (circled top left), New Zealand. Sample sites on the lakes are marked by a red diamond for the lake survey and a blue circle for the times series study. Lake trophic status is identified by shading. Regional boundary indicated by dashed line.

### 3.2.2 Eleven-lake $^{15}$N [N$_2$] enrichment survey

Surface and bottom waters of eleven lakes in the TVZ were sampled for nutrients (Total N and dissolved inorganic nitrogen) and nitrogen stable isotope ratio of extracted N$_2$ gas between April and May 2007. The lakes covered a range of trophic states (oligotrophic to supertrophic) and mixing regimes (polymictic and monomictic). Sample collection was timed to coincide with the latter period of seasonal summer stratification in the monomictic lakes. Sites were selected to be in the deep central basin of each lake, with sampling targeting the area conforming to the accumulation bottom (cf. Håkanson and Jansson, 1983).

**Table 3.1:** Lake morphology, catchment area, nutrient concentrations (total nitrogen and total phosphorus), chlorophyll *a* concentration, Secchi depth, mixing regime and trophic state for the TVZ lakes studied. Water quality data are means from monthly values from Scholes and Bloxham (2007). Lake Ngapouri data is from McColl (1972).

| | Mean Depth (m) | Max. Depth (m) | Lake Area ($km^2$) | Catchment Area ($km^2$) | Total N (g $m^{-3}$) | Total P (g $m^{-3}$) | TN:TP | Chl $\alpha$ (μg $L^{-1}$) | Secchi depth (m) | Mixing Regime | Trophic State |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Taupo (Tp) | 100.0 | 162 | 620.0 | 2849.0 | 0.078 | 0.005 | 16.3 | 1.1 | 15.8 | Monomictic | Oligotrophic |
| Rotoma (Rm) | 37.0 | 83 | 11.1 | 28.1 | 0.146 | 0.005 | 30.2 | 1.4 | 12.1 | Monomictic | Oligotrophic |
| Okataina (Ot) | 39.4 | 79 | 11.0 | 56.8 | 0.145 | 0.009 | 16.7 | 2.1 | 9.4 | Monomictic | Oligotrophic |
| Tarawera (Tw) | 50.0 | 88 | 41.7 | 144.9** | 0.110 | 0.011 | 10.4 | 1.2 | 9.4 | Monomictic | Oligotrophic |
| Tikitapu (Ti) | 18.0 | 28 | 1.5 | 5.7 | 0.211 | 0.007 | 28.8 | 2.1 | 6.3 | Monomictic | Mesotrophic |
| Okareka (Oe) | 20.0 | 34 | 3.4 | 19.8 | 0.195 | 0.008 | 25.1 | 2.9 | 7.0 | Monomictic | Mesotrophic |
| Rerewhakaaitu (Rw) | 7.0 | 15 | 5.8 | 38.0 | 0.339 | 0.012 | 28.9 | 3.4 | 5.5 | Polymictic | Mesotrophic |
| Rotoiti (Ri) | 31.5 | 124 | 34.6 | 124.6** | 0.378 | 0.037 | 10.3 | 8.4 | 4.7 | Monomictic | Eutrophic |
| Rotoehu (Re) | 8.0 | 13 | 8.0 | 57.0 | 0.423 | 0.040 | 10.6 | 13.6 | 2.8 | Polymictic | Eutrophic |
| Rotorua (Rr) | 11.0 | 45 | 80.6 | 500.6 | 0.453 | 0.036 | 12.7 | 19.9 | 2.3 | Polymictic | Eutrophic |
| Ngapouri (Np) | 12.1 | 24 | 0.2 | 4.8 | * | 0.091 | * | 45.0 | 1.6 | Monomictic | Eutrophic |
| Okaro (Ok) | 12.5 | 18 | 0.3 | 3.7 | 1.267 | 0.090 | 14.0 | 77.2 | 1.4 | Monomictic | Supertrophic |

* No data

** Does not include catchments from upstream lakes

Lake water was collected using a Schindler-Patalas trap to capture near-surface (epilimnion, 1 m depth) and bottom waters (hypolimnion, 1 m from sediment-water interface). Gas was extracted and collected from the water sample using the method described by Pearson et al. (2012). Briefly, lake water was siphoned into a 60 mL syringe (BD Plastipak) fitted with a three-way valve; one opening for the syringe tip, one stopped with a small rubber bung, and one left open. Any air space in the syringe was exhaled by inverting the syringe and compressing the piston, at the same time adjusting the water volume to 50 mL and closing the valve. A vacuum was created within the syringe by applying strong back-pressure on the piston while also shaking the sample periodically over a period of three minutes, after which time the gas volume was constant. The applied vacuum partitions gasses between solution and the head space enabling a representative isotopic sample to be recovered. A 1 ml ultra-fine insulin syringe (BD Plastipak) was then inserted through the rubber stopper, and the gas drawn out of the syringe. Approximately 0.5 ml of gas was collected as well as sufficient water to “seal” the gas in the syringe (~0.1 ml). The syringe was then removed from the stopper, inserted into a rubber bung and immersed fully in water to prevent penetration of air into the syringe. Samples were collected in duplicate.

Depth–referenced (0.02 m) temperature and dissolved oxygen profiles were measured on each sampling occasion with a conductivity-temperature-depth (CTD) profiler (Sea Bird Electronics 19 plus SEACAT Profiler), fitted with a dissolved oxygen (DO, Seabird Electronics) sensor. Both the conductivity and DO sensors were flushed continuously with sample water by a pump attached to, and powered by, the CTD. Profiles at each station were conducted from the lake surface to the lake bottom.

### 3.2.3 Temporal changes in $^{15}N$ [$N_2$] enrichment in five lakes

Sites in the deep central basin of Lakes Taupo, Tarawera, Okataina, Rotoiti and Ngapouri were sampled monthly for up to one year between November 2007 and November 2008. Two sample sites were selected in Lake Okataina; north and central basins separated by a shallower ridge, whilst central stations were used in the other lakes. Water column CTD casts were taken monthly at each site as described above.

A Schindler-Patalas trap was used to capture near-surface (1 m depth) and bottom water (1 m from sediment-water interface) samples. Gas was extracted and collected from the water sample as above. An undisturbed sediment core with at least 5 cm of overlying lake water was taken with a Swedish gravity corer (Pylonex HTH 70 mm) with a 60 mm x 600 mm Perspex (Plexiglas) core barrel. The surface sediment was visually inspected and the core was discarded if there was any disturbance at the sediment-water interface or within the sediment profile. A water sample was collected 0-2 cm above the sediment-water interface (herewith referred to as the benthic nepheloid layer; BNL) with a 60 mL syringe and gas was extracted as soon as they were collceted from the lake. During the first site visit only, water samples of the 0-2 cm above the sediment-water interface (BNL) and top 0-2 cm of sediment were collected from an intact sediment core and stored in 50 mL centrifuge containers. The water and sediment was centrifuged, decanted and the POM dried and sampled for $^{15}N$ to test for enrichment of recently-sedimented particulate material.

An additional core, containing at least 25 cm of overlying lake water was collected for gas analysis each month. The undisturbed cores were kept intact and sealed with a rubber bung at the bottom and top. The latter bung had two airtight valves to allow for gas sampling (Pearson et al., 2012). The cores were kept on ice and transferred to the laboratory until gas extraction within 24 h. The procedure for capturing gas in sediment pore waters involved injecting 50 mL $CO_2$ at 5 cm depth in the core, using one valve in the top bung with a modified 60 mL syringe whilst removing gas with a 60 mL syringe (DB Plastipak) through the remaining valve (Pearson et al., 2012). The recaptured gas in the syringe was then injected into evacuated vials containing 5 mL NaOH solution (2 M) to remove $CO_2$. The process was repeated by increasing the injection depth in the sediment by successive 5 cm intervals to a depth of 20 cm. The vials of sediment gas were analysed for $^{15}N$ along with the surface, bottom and BNL water column gas samples.

### 3.2.4 Analytical methods

Stable isotope analysis of $\delta^{15}N$ was undertaken by the Waikato Stable Isotope Unit, Waikato University. The $\delta^{15}N$ [$N_2$] was determined using a Dumas elemental analyser (Europa Scientific ANCA-SL) interfaced to an isotope mass spectrometer (Europa Scientific 20-20 Stable Isotope Analyser). The $\delta^{15}N$ of particulate organic nitrogen (PON) was determined using a LECO TruSpec CN Carbon/Nitrogen Determinator (LECO Corporation, 2006) interfaced to an isotope mass spectrometer (Europa Scientific 20-20 Stable Isotope Analyser). The nitrogen isotope ratio was expressed as per mill (‰) deviation from a laboratory reference (urea with a $\delta^{15}N$ standardised against a certified standard calibrated relative to atmospheric $N_2$) as defined by Mariotti (1983) (Eq 3.1):

$$\delta^{15}N= [\{(^{15}N/^{14}N)_{sample} / (^{15}N/^{14}N)_{standard}\}-1] \times 1000 \qquad (3.1)$$

The analytical error of $\delta^{15}N$ determinations was within the range ± 0.3 ‰. The standard error involved in determining $\delta^{15}N$ [$N_2$] was calculated by the standard deviation between replicate samples divided by the square root of the number of samples. The average standard error for the technique was 0.24‰.

Analysis for concentrations of ammonium ($NH_4^+$), nitrite ($NO_2^-$) and total oxidised nitrogen ($NO_x$), was carried out spectrophotometrically on lake water and pore water samples using a Lachat QuickChem® Flow Injection Analyser (FIA+ 8000 Series, Zellweger Analytics, Inc.). Nitrate ($NO_3^-$) was calculated as the residual of $NO_x$ - $NO_2^-$. The analytical error was 0.001 mg $L^{-1}$. Total nitrogen (TN) was obtained by a potassium persulfate digestion which was put in an autoclave for 1 hour at 121 °C and analysed for nitrate as above.

### 3.2.5 Statistical analyses

We used several variables to define trophic condition, including total N (TN), total phosphorus (TP), chlorophyll *a* (Chl *a*), Secchi depth (SD), and volumetric hypolimnetic oxygen depletion rate (VHOD). Measurements of TN, TP and Chl *a* were from water samples integrated through the surface mixed layer provided by Bay of Plenty Regional Council (Scholes and Bloxham, 2007) for Rotorua lakes and Environment Waikato for Lake Taupo, based on routine monitoring data from the respective agencies. Measurements of TP, Chl *a* and Secchi disk depth for Lake Ngapouri was taken from McColl (1972). A Trophic Level Index (TLI) was used to integrate four of the variables (TN, TP, Chl *a*, and SD) (Burns et al., 1999). Values of TLI range from <2 (‘microtrophic’) to >5 (‘supertrophic’). No TLI value is given for Lake Ngapouri as this lake is not part of a routine monitoring program.

After satisfying the Kolmogorov-Smirnov test for normality ($P > 0.2$), linear regression (STATISTICA; www.statsoft.com) was used to test for relationships between maximum $\delta^{15}N$ [$N_2$] values in bottom waters and at the BNL of all lakes studied with several environmental parameters including volumetric hypolimnetic oxygen demand (VHOD), N loads and denitrification potential. Trophic level index was correlated with maximum $\delta^{15}N$ [$N_2$] using an exponential fit as TLI is itself represents log-transformed values of its individual components (Burns et al. 1999). The component variables of TLI were log transformed to approximate a normal distribution and correlated by linear regression with maximum $\delta^{15}N$ [$N_2$]

values to assess whether a single $\delta^{15}N$ sample could be used to determine or monitor trophic changes occurring in the lakes.

The VHOD was calculated from monthly CTD casts (Sea-Bird Electronics Inc., Washington) taken by us for Lakes Taupo, Tarawera, Okataina, Rotoiti and Ngapouri or by the regional environmental management agency Bay of Plenty Regional Council for Lakes Rotoma, Tikitapu, Okareka and Okaro. VHOD was calculated from the linear portion of the oxygen decrease observed at 1 m above the sediment-water interface from October 2007 until the hypolimnion was either strongly depleted in DO (c. 1 mg $L^{-1}$) or just prior turnover in lakes with well-oxygenated hypolimnia. As Lake Ngapouri was already anoxic at the time the monthly sampling programme was initiated, VHOD was calculated for the period after turnover when the lake began to restratify (between August 2008 and October 2008).

Nitrogen loads to the lakes are summarized in Bruesewitz et al. (2011) except for Lake Taupo, which was provided by the relevant management agency, Environment Waikato (http://www.ew.govt.nz), and Lake Ngapouri, which was derived from the Ministry of Agriculture and Forestry’s Catchment Land Use for Environmental Sustainability (CLUES) model (Elliott et al., 2008). Lake and catchment areas were taken from the Landcare Research Land Resource Inventory (www.landcareresearch.co.nz/databases/nzlri.asp). Total N loads to each lake were divided by lake area to obtain an aerial loading rate. Denitrification potential was taken from denitrification enzyme activity (DEA) assays of bottom sediments for all lakes except Taupo and Ngapouri (Bruesewitz et al. 2011). Rates are expressed relative to dry mass (DM) or ash-free dry mass (AFDM) of sediment (µg N g DM $h^{-1}$ or µg N g AFDM $h^{-1}$) to normalise for sediment organic matter content (Bruesewitz et al., 2011).

## 3.3 RESULTS

### 3.3.1 Eleven-lake $^{15}N$ [$N_2$] enrichment survey

All lakes showed vertical thermal gradients, taken here to be ≥0.2 °C between surface and bottom waters (Figure 3.2a). Lakes Rotorua, Rotoehu and Rerewhakaaitu, all of which have mean water depth ≤11 m, are polymictic (Table 3.1). At the time of sampling dissolved oxygen (DO) varied little with depth in these lakes, indicating occurrence of a recent mixing event penetrating the entire water depth. The eight monomictic lakes had not undergone winter mixing at the time of sampling as there were strong vertical gradients in both temperature and dissolved oxygen (Figure 3.2). All of the stratified lakes followed a clinograde oxygen profile as some degree of oxygen depletion was observed, with the more eutrophic lakes tending towards complete anoxia (DO <0.2 mg $L^{-1}$) in the bottom waters (Figure 3.2b). Lake Tarawera had a negative heterograde oxygen profile (Wetzel, 2001), possibly due to presence of a deep chlorophyll maximum (Hamilton et al. 2010).

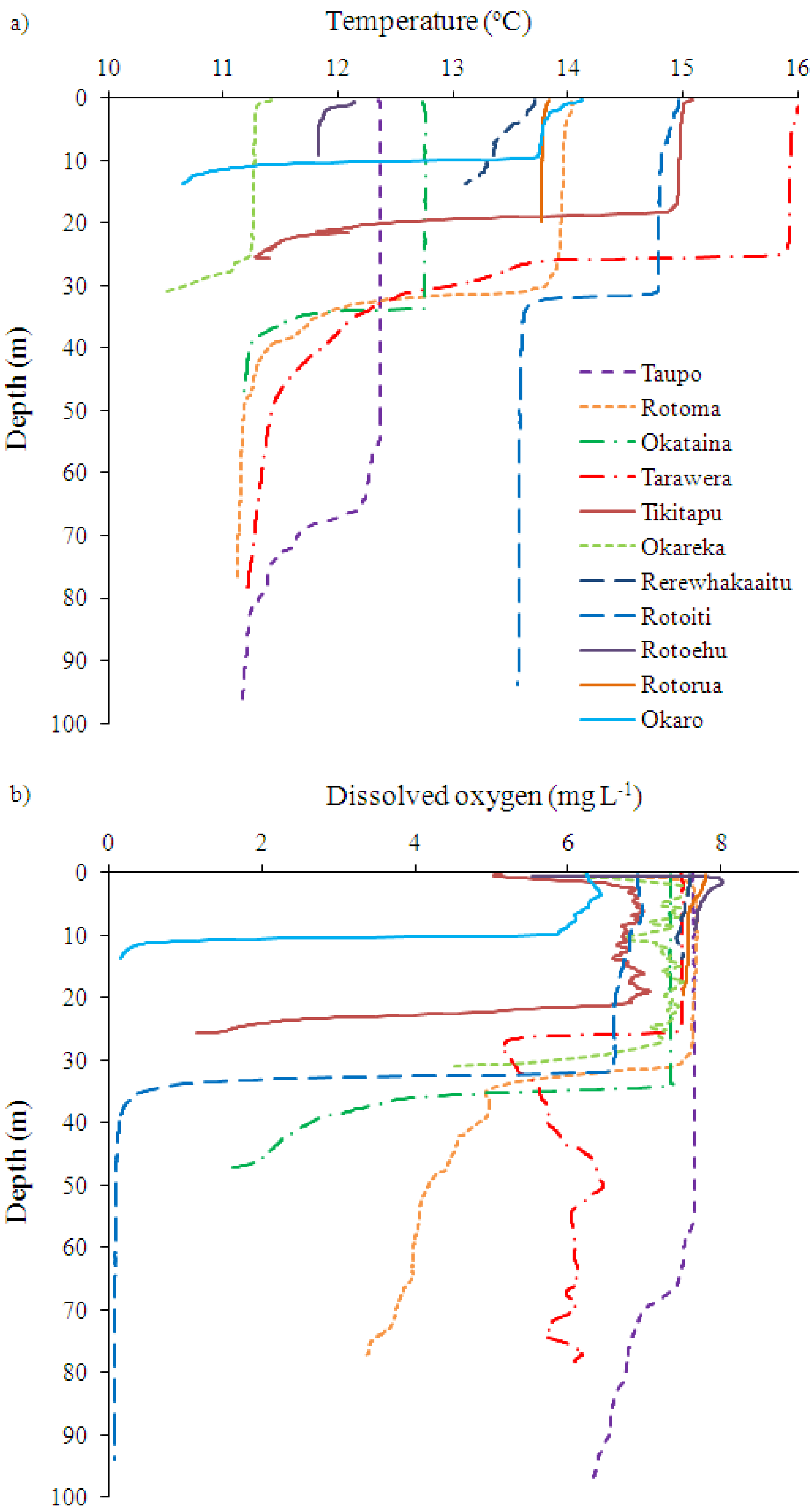

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**Figure 3.2:** Water column profiles in May – June 2007 of the 11 lakes for a) temperature and b) dissolved oxygen showing well developed stratification in the monomictic lakes.

Surface-water dissolved inorganic nitrogen (DIN) concentrations were less than 0.1 mg $L^{-1}$ in all lakes (Figure 3.3a). In Lakes Rotoma, Tarawera and Tikitapu the DIN in surface waters was dominated by nitrate whereas ammonium was dominant in the other lakes. Bottom-water DIN concentrations were higher than those of surface waters, and a maximum of 2.7 mg $L^{-1}$ occurred in Lake Okaro (Figure 3.3b). The dominant contributor to DIN in bottom waters was ammonium, except in Lakes Taupo, Rotoma and Tarawera where DO was >5 mg $L^{-1}$ throughout the hypolimnion. These oligotrophic lakes (Table 3.1), had very low DIN concentrations of around 0.01 mg $L^{-1}$ in surface and bottom waters. Concentrations of DIN in surface and bottom waters of meso- and eutrophic lakes (Table 3.1) ranged from 0.01 to 2.7 mg $L^{-1}$ for ammonium and from 0.001 to 0.08 mg $L^{-1}$ for nitrate. As the trophic status of the stratified lakes increased the ratio of ammonium to nitrate in the bottom waters also increased. Nitrite concentrations were all < 0.0015 mg $L^{-1}$ in the surface and < 0.01 mg $L^{-1}$ in the bottom waters. Overall, DIN made up only a small proportion of total N. Total N was low (≤ 0.13 mg $L^{-1}$) in bottom waters of oligotrophic Lakes Taupo, Rotoma, Tarawera and Okataina compared with the meso- and eutrophic lakes (Table 3.1) which had TN in the range 0.28 – 3.2 mg $L^{-1}$).

Mean surface-water $\delta^{15}N$ [$N_2$] values for each site ranged from -1.5 to -0.7‰ and in bottom waters from -1.42 to 20.20‰ (Table 3.2). The difference in $\delta^{15}N$ [$N_2$] between surface and bottom waters (Table 3.2) increased with lake trophic state (Table 3.1). There was no significant difference ($p < 0.05$) in $\delta^{15}N$ [$N_2$] between the surface and bottom waters of the non-stratified lakes (Rotorua, Rotoehu and Rerewhakaaitu).

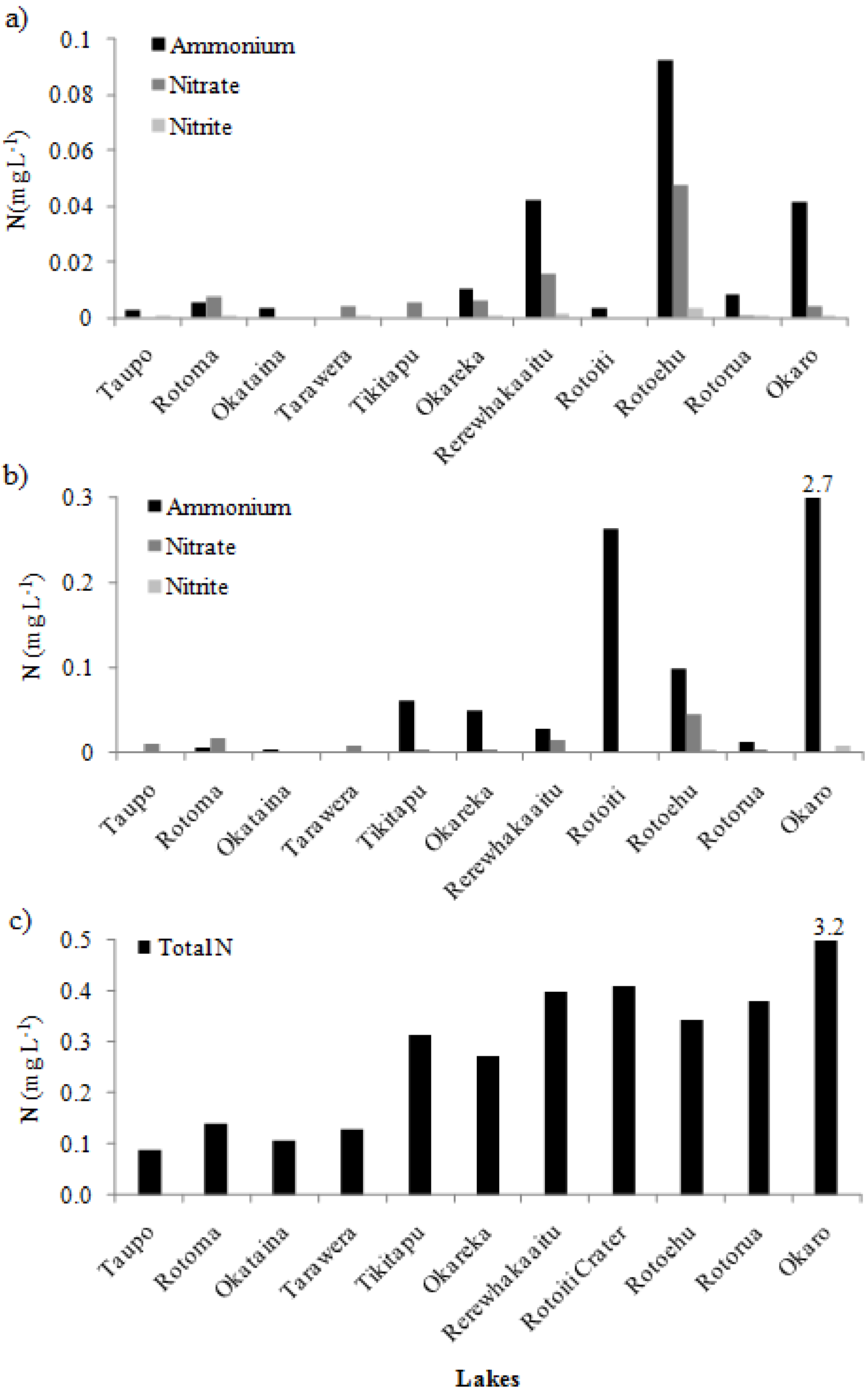

**Figure 3.3:** Dissolved ammonium, nitrate and nitrite in the a) epilimnion and b) hypolimnion and c) total nitrogen concentrations in the epilimnion of the selected TVZ lakes. Concentrations for Lake Okaro exceeding the vertical scale are shown above the bar.

**Table 3.2:** Nitrogen isotope analysis of gas extracted from the surface and hypolimnion (within 1 m of sediment-water interface) between May and June 2007. Samples are the average of duplicate samples ±1 standard deviation.

| | Sample depths (m) | Surface $\delta^{15}$N (‰) | Bottom $\delta^{15}$N (‰) | $\Delta\ \delta^{15}$N (‰) (Bottom-Surface) |
|---|---|---|---|---|
| *Stratified* | | | | |
| Taupo (Tp) | 0, 100 | -1.26 ± 0.10 | -1.13 ± 0.04 | 0.13 |
| Rotoma (Rm) | 0, 80 | -1.37 ± 0.13 | -0.67 ± 0.00 | 0.70 |
| Okataina (Ot) | 0, 50 | -1.04 ± 0.02 | 0.72 ± 0.16 | 1.75 |
| Tarawera (Tw) | 0, 75 | -1.28 ± 0.42 | -0.92 ± 0.05 | 0.36 |
| Tikitapu (Ti) | 0, 27 | -1.54 ± 0.02 | 2.12 ± 0.20 | 3.66 |
| Okareka (Oe) | 0, 30 | -1.03 ± 0.13 | 2.03 ± 0.03 | 3.06 |
| Rotoiti (Ri) | 0, 100 | -1.00 ± 0.05 | 2.30 ± 0.41 | 3.30 |
| Okaro (Ok) | 0, 14 | -0.84 ± 0.06 | 20.20 ± 4.89 | 21.04 |
| *Non-stratified* | | | | |
| Rerewhakaaitu (Rw) | 0, 10 | -0.92 ± 0.15 | -1.13 ± 0.07 | -0.21 |
| Rotoehu (Re) | 0, 10 | -1.42 ± 0.24 | -1.20 ± 0.20 | 0.22 |
| Rotorua (Rr) | 0, 20 | -1.19 ± 0.07 | -1.42 ± 0.02 | -0.23 |

### 3.3.2 Temporal changes in $^{15}$N [$N_2$] enrichment

There was little, if any, vertical gradient in water temperature during winter (June or July through August or September) in the five lakes, with values of just below 11°C in Lakes Taupo, Tarawera, Okataina and Rotoiti but < 9°C in smaller Lake Ngapouri (Figure 3.4). The onset of mixing also reflected variations in lake size, occurring in June in Lake Ngapouri but not until late July in Lake Taupo (Figure 3.4). Interestingly, however, mixing occurred slightly earlier in Lake Rotoiti than in the other lakes, likely influenced by weaker stratification from geothermal heating of bottom waters (Priscu et al., 1986; Gibbs, 1992). We interpret the progressive warming of hypolimnetic waters until turnover (Figure 3.4) as evidence of this geothermal heating. Vertical temperature stratification re-established around September in the five lakes. The magnitude and timing of peak surface water temperatures was similar amongst lakes (20-21°C in January or February) whilst surface mixed layer depth varied with lake size, from c. 33m in Lake Taupo to c. 11m in Lake Ngapouri at the time of maximum surface water temperature.

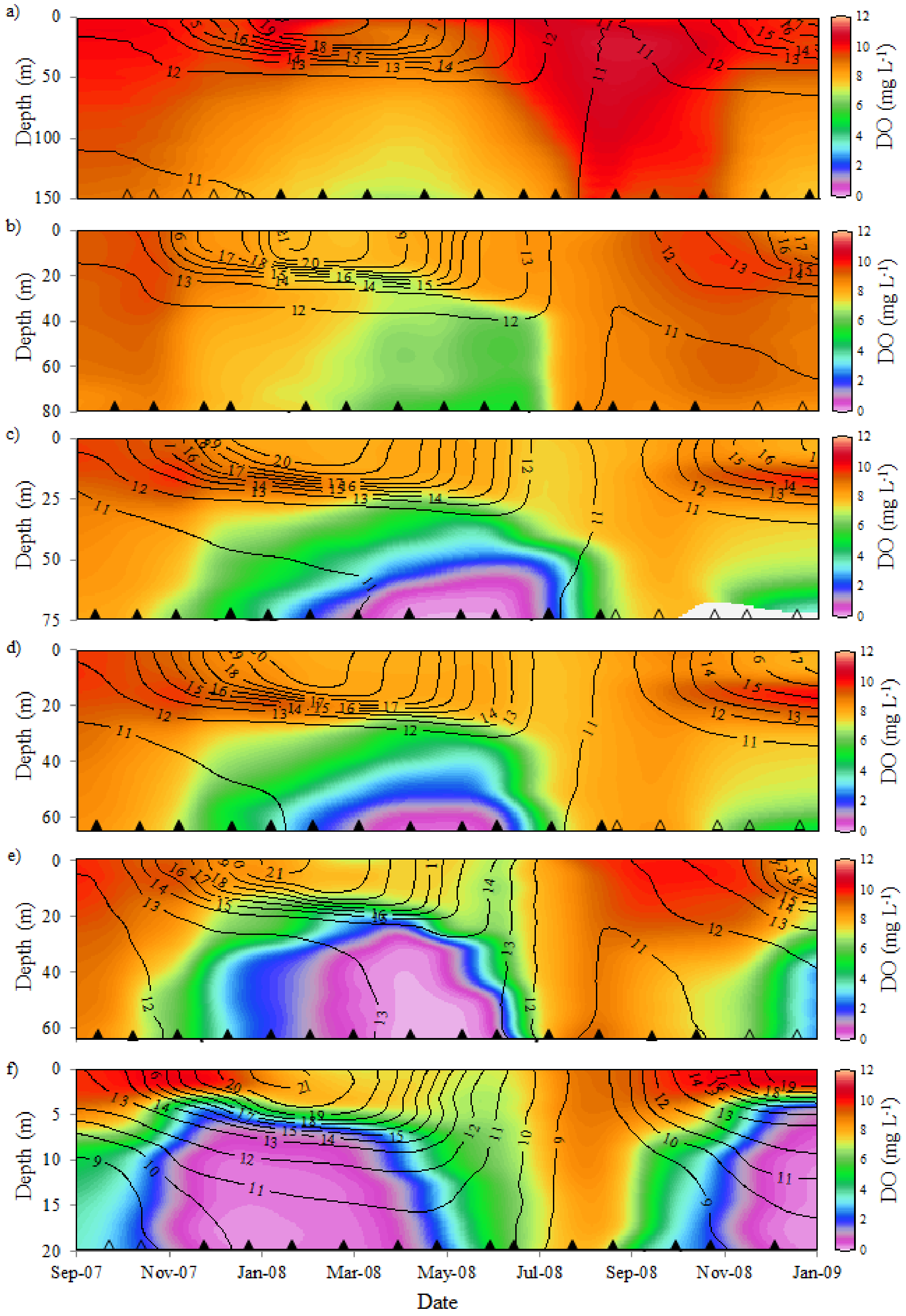

**Figure 3.4:** Temperature (°C) (black contour) and dissolved oxygen concentration (mg $L^{-1}$) (colour plot) in Lakes a) Taupo, b) Tarawera, c) Okataina (Central basin), d) Okataina (North basin), e) Rotoiti and f) Ngapouri. Solid arrows indicate sampling dates. Supplementary data was provided by Bay of Plenty Regional Council and NIWA to extend the series beyond the sampling dates of this study (hollow arrows).

During winter mixing concentrations of DO were vertically homogenous in the range 7 to 12 mg L$^{-1}$. The period of vertical homogeneity of DO was relatively short (>1 month) for Lakes Ngapouri and Rotoiti but up to 3 months for Lakes Taupo, Tarawera and Okataina. Lake Taupo was supersaturated in DO in its surface waters from late winter to early spring (August-October) possibly as snow melt adds cold saturated waters through the lake (Spigel et al., 2005) and productivity is maximal in winter (Vincent, 1981). Over the period of strong thermal stratification (c. 8-9 months) oligotrophic Lake Taupo consumed about one-half of the dissolved oxygen initially present in the hypolimnion (VHOD = 0.015 g m$^{-3}$ day$^{-1}$), whereas in Lake Ngapouri, all of the oxygen in the hypolimnion was largely consumed within the one-month sampling period following onset of stratification (VHOD = 0.116 g m$^{-3}$ day$^{-1}$) (Table 3.3). For Lake Okataina a mean VHOD of 0.051 g m$^{-3}$ day$^{-1}$ was derived from measurements in the central and northern basin sampling sites (0.049 and 0.053 g m$^{-3}$ day$^{-1}$, respectively).

**Table 3.3:** Lake trophic level index, oxygen demand based on measurements at 1 m from the lake bottom (VHOD), total nitrogen load (N load), denitrification potential (DEA) and maximum $\delta^{15}$N [N$_2$] and $\delta^{15}$N [PON] for the monomictic stratified TVZ lakes.

| Stratified Lakes | Trophic Level Index (TLI) (2008) | VHOD (g m$^{-3}$day$^{-1}$) | N Load to lake (kg yr$^{-1}$) | N Load (kg yr$^{-1}$ km$^{2}$) | Total N (g m$^{-3}$) | DEA (ug N g AFDM$^{-1}$ h$^{-1}$) | DEA (ug N m$^{-2}$ h$^{-1}$) | $\delta^{15}$N [N$_2$] max (‰) | $\delta^{15}$N [Phyto] (‰) | $\delta^{15}$N [PON] max (‰) |
|---|---|---|---|---|---|---|---|---|---|---|
| Taupo (Tp) | 2.20 | 0.015 | 1140000 | 1839 | 0.088 | * | * | 0.4 | * | 1.52 |
| Rotoma (Rm) | 2.44 | 0.019 | 16680 | 1503 | 0.138 | 3.14 | 61.84 | -0.7 | 2.6 | * |
| Okataina (Ot) | 2.83 | 0.051 | 22294 | 2027 | 0.107 | 71.28 | 842.97 | 5.3 | 4.3 | 2.79 |
| Tarawera (Tw) | 2.91 | 0.024 | 50431 | 1209 | 0.130 | 1.03 | 36.39 | 1.3 | 2.0 | 3.31 |
| Tikitapu (Ti) | 3.11 | 0.036 | 2406 | 1064 | 0.312 | 15.87 | 364.13 | 2.1 | 0.9 | * |
| Okareka (Oe) | 3.17 | 0.032 | 10542 | 3100 | 0.272 | 164.23 | 2463.80 | 2.0 | 3.5 | * |
| Rotoiti (Ri) | 4.00 | 0.060 | 127000 | 3671 | 0.411 | 30.14 | 316.69 | 6.4 | 4.5 | 3.74 |
| Ngapouri (Np) | * | 0.116 | 2000 | 10000 | 0.523 | * | * | 12.2 | 5.9 | 4.48 |
| Okaro (Ok) | 5.61 | 0.121 | 2714 | 9047 | 3.200 | 232.23 | 1646.04 | 20.2 | 7.0 | * |

* Data not available. TLI values and N load to lake are provided by the Regional Councils; Environment Bay of Plenty and Environment Waikato. VHOD values for Lakes Taupo, Tarawera, Okataina (2 site average), Rotoiti and Ngapouri were calculated from this study and values for Lakes Rotoma, Tikitapu, Okareka and Okaro were provided by Environment Bay of Plenty. Total N, $\delta^{15}$N [N$_2$] and $\delta^{15}$N [PON] is measured during this study. Denitrification potential is from Bruesewitz et al. (2010).

Concentrations of DIN were less than 0.1 mg $L^{-1}$ during the 2007-2008 annual cycle in the hypolimnion of the five lakes with time series measurements, although Lake Rotoiti reached 0.26 mg $L^{-1}$ during the previous year (Figure 3.3). By contrast DIN concentrations were very high in the BNL, contributed mostly by ammonium which reached maxima ranging from 0.18 mg $L^{-1}$ in Lake Taupo to 3.6 mg $l^{-1}$ in Lake Ngapouri during stratification (Figure 3.5). In most lakes nitrate concentrations in the BNL were maximal during turnover, but still remained lower than ammonium concentrations. Ammonium also tended to be at elevated levels at the onset of seasonal stratification.

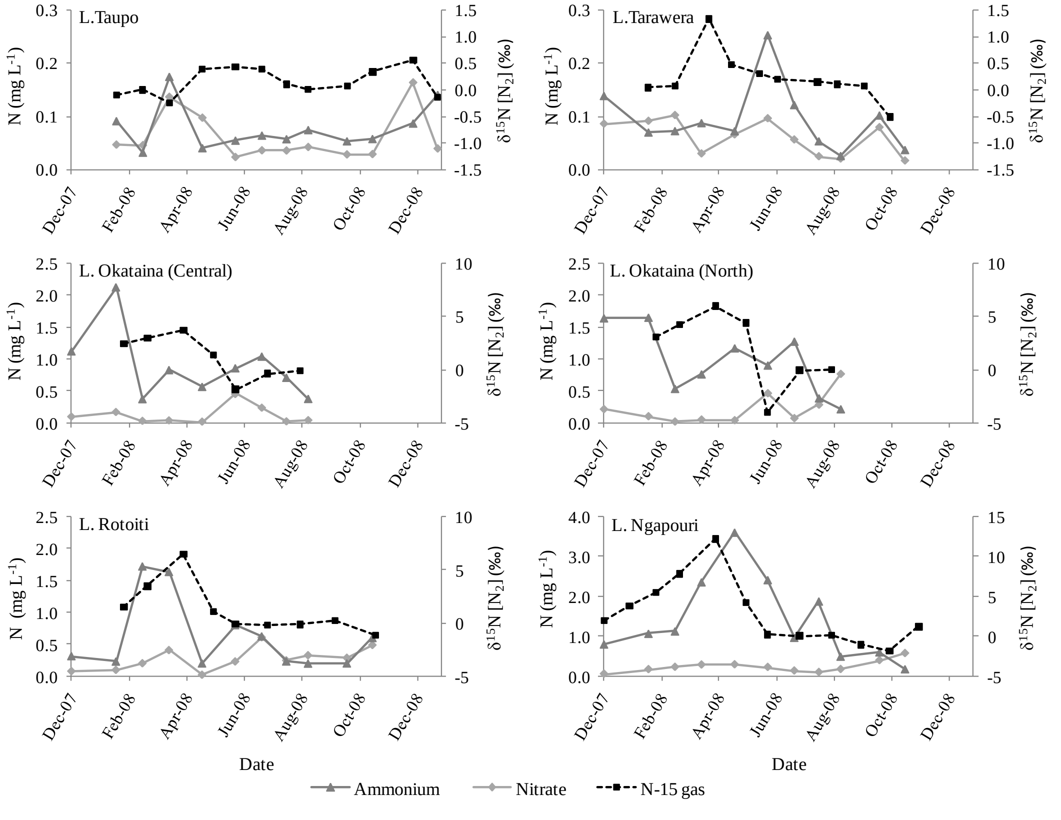

**Figure 3.5:** Ammonium and nitrate concentrations (mg $L^{-1}$) and $\delta^{15}N$ [$N_2$] (‰) in the benthic nepheloid layer (0.1 m above the sediment-water interface) at monthly intervals. Note the different scales used for N species and $\delta^{15}N$.

The $\delta^{15}N$ values in the gas extracted from water samples at the surface, hypolimnion, bottom (~1 m above lake bed), BNL (0.1 m above the sediment-water interface), and within the sediment at 0-5, 5-10, 10-15 and 15-20 cm intervals showed large variations in time and over depth within and between lakes (Figure 3.6). There was no seasonal trend in samples from surface waters of the lakes, with $\delta^{15}N$ [$N_2$] around 0‰ in magnitude. The bottom waters showed some seasonal variation (up to 1.2‰), with enrichment occurring towards the end of stratification. The most highly enriched $\delta^{15}N$ [$N_2$] water was at the BNL, with maximum $\delta^{15}N$ [$N_2$] of 0.4‰ for Lake Taupo, 1.3‰ for Lake Tarawera, 5.3‰ for Lake Okataina, 6.4‰ in Lake Rotoiti and 12.2‰ in Lake Ngapouri occurring near the end of stratification (Table 3.3). There was little change in $\delta^{15}N$ [$N_2$] in sediment pore waters, except in Lake Rotoiti where enrichment (up to 8.3‰) occurred between September and January at 10-20 cm below the sediment-water interface due to geothermal discharge through the lake bed.

Surface sediment and settling POM collected from the BNL during the first month of sampling produced $\delta^{15}N$ values of 1.52 ‰ for Lake Taupo, 3.31 ‰ for Lake Tarawera, 2.79 ‰ for Lake Okataina, 3.74 ‰ in Lake Rotoiti and 4.48 ‰ in Lake Ngapouri (Table 3.3). In Lakes Okataina, Rotoiti and Ngapouri the $\delta^{15}N$ values of POM were less enriched than those in water collected from the BNL.

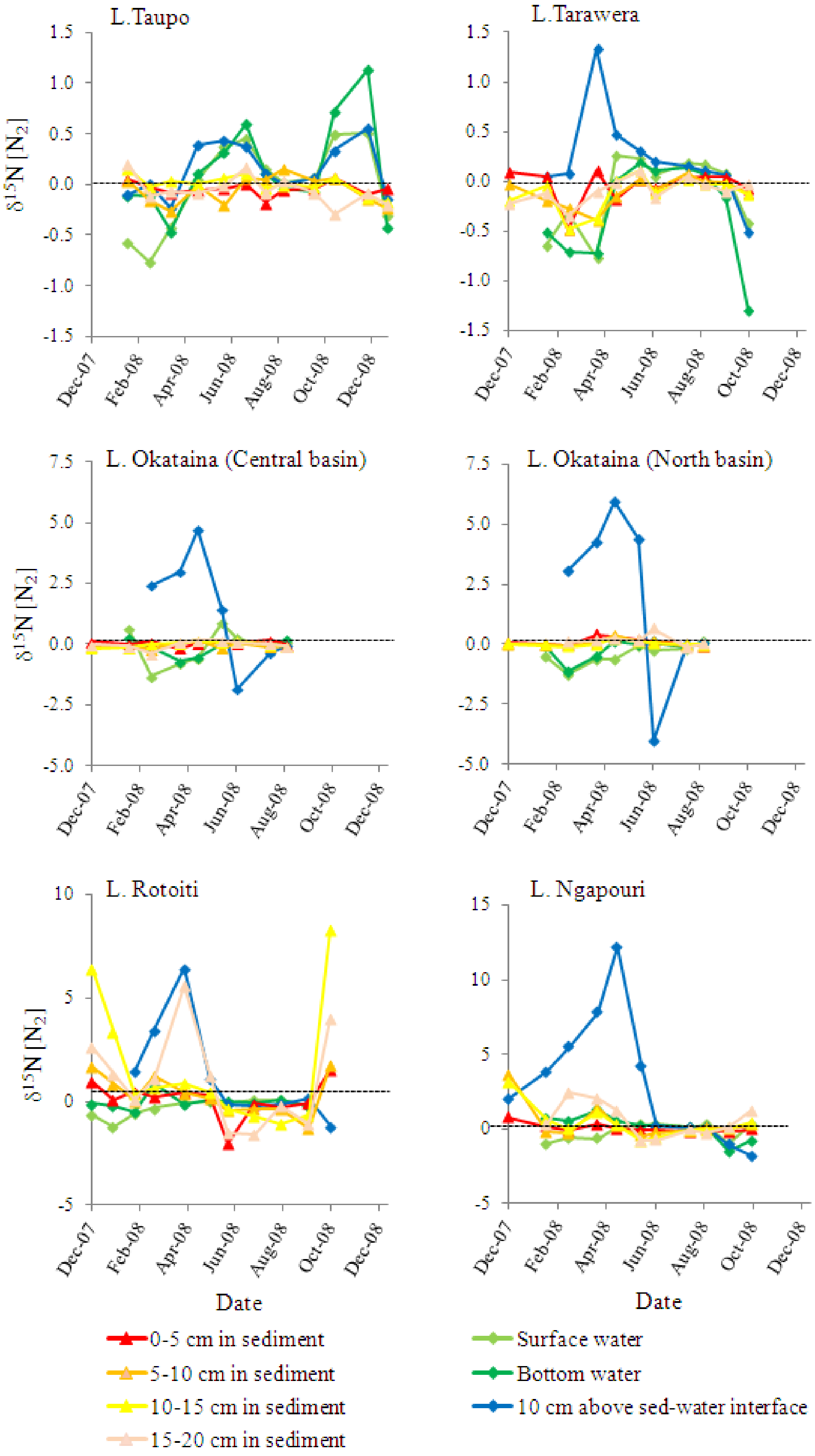

**Figure 3.6:** Variation in $\delta^{15}N$ [$N_2$] in the lake water (diamonds) and sediment (triangles) for monthly samples. Note the different scales for $\delta^{15}N$.

### 3.3.3 Relationships of $^{15}$N [N$_2$] to environmental variables

Values of $\delta^{15}$N [N$_2$] for the monomictic lakes were positively related by linear regression to each of the environmental parameters tested; VHOD, nitrogen load and sediment denitrification potential normalised for organic matter content and by exponential regression for TLI (Figure 3.7, Table 3.3). The percentage variation in $\delta^{15}$N [N$_2$] explained by these variables ranged from 92% for VHOD, ($P < 0.001$) to 59% ($P < 0.05$) for denitrification potential, though the latter relationship may have been affected by the outlier in denitrification potential contributed by Lake Okareka (discussed further below). Log transformed values of TLI components (TN, TP, Secchi disk depth and Chl *a*) explained 84 to 93% of the variation in $\delta^{15}$N [N$_2$] for the monomictic lakes, Figure 3.8).

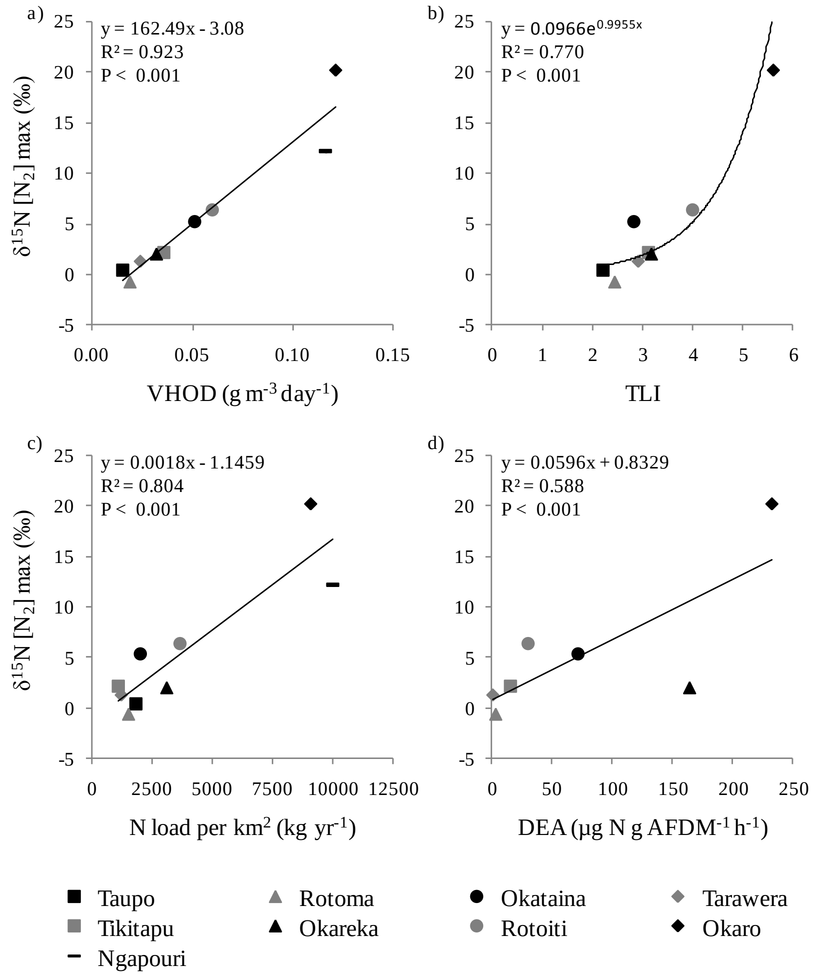

**Figure 3.7:** Relationships between maximum $\delta^{15}$N [N$_2$] in the bottom waters of monomictic TVZ lakes between a) volumetric hypolimnetic oxygen demand, b) trophic level index, c) nitrogen load to the lake and d) denitrification potential.

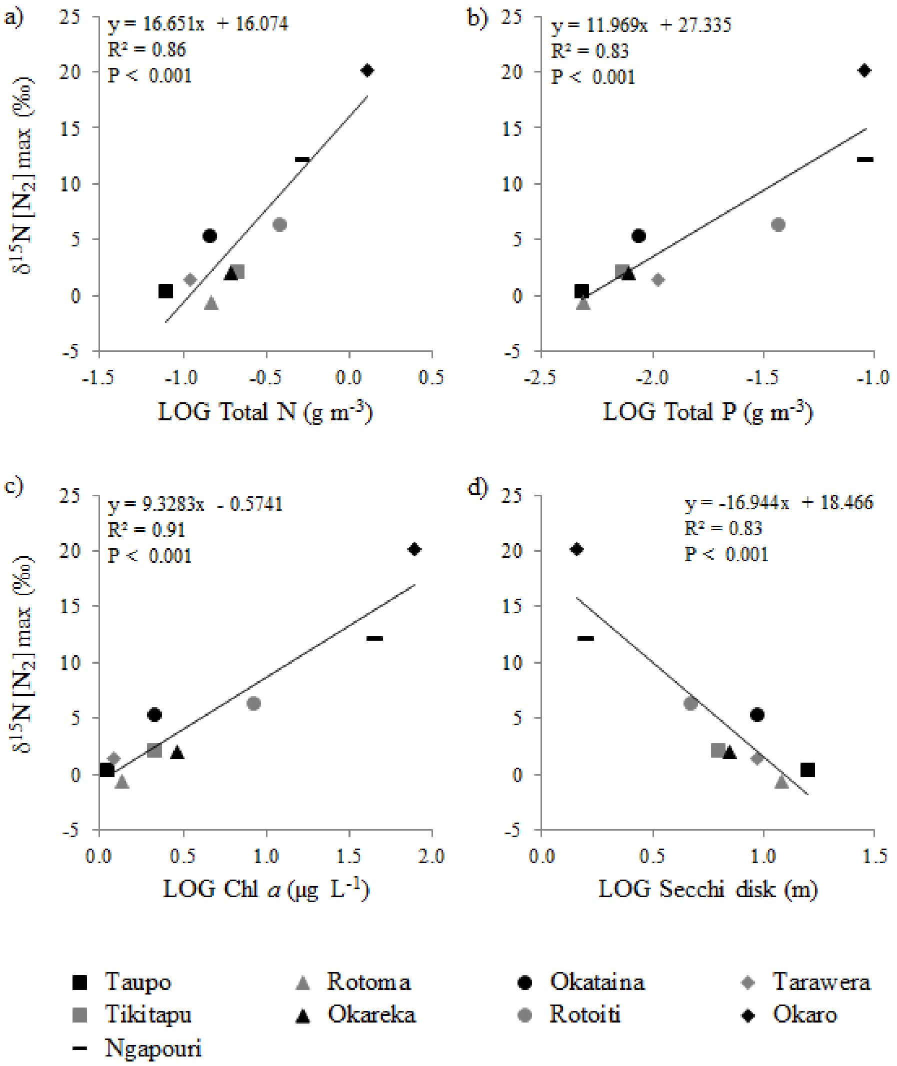

**Figure 3.8:** Correlation between TLI parameters a) TN, b) TP, c) Chl *a* and d) Secchi disk depth with maximum $\delta^{15}N$ [$N_2$] in the bottom waters of selected monomictic TVZ lakes. TLI parameters have been log transformed to approximate normality. TLI parameter data is from Scholes and Bloxham (2007) for the Rotorua lakes and NIWA for Lake Taupo. Lake Ngapouri TN was obtained from this study while TP, Chl *a* and Secchi disk data is from McColl (1972).

## 3.4 DISCUSSION

### 3.4.1 Factors controlling $^{15}N$ [$N_2$] in lake waters

Enrichment in $^{15}N$ [$N_2$] occurred in the bottom waters of all lakes that underwent seasonal thermal stratification. In polymictic lakes Rotorua and Rerewhakaaitu, gas exchange with the atmosphere occurs intermittently throughout the year and appears to be of sufficient duration to prevent significant departures of $\delta^{15}N$ [$N_2$] from 0‰, at least under the mixed conditions when these lakes were sampled. Polymictic Lake Rotoehu was stratified at the time of sampling and showed slight enrichment in the bottom water (0.2‰), but as stratification occurs only for limited duration (< ~1-2 weeks; Trolle et al. 2011) the time period for $^{15}N$ [$N_2$] enrichment is limited. Seasonally-stratified lakes in which the hypolimnion became anoxic showed greater enrichment in $^{15}N$ [$N_2$] than those in which the hypolimnion remained oxic. The time series analysis showed that the enrichment was progressive, increasing with duration of stratification. Atmospheric contamination during sampling and subsequent handling is clearly limited as there was excellent reproducibility amongst replicate samples as well as consistent seasonal changes.

Metabolism of organic matter descending through the water column does not occur at a uniform rate within the hypolimnion, but is most pronounced at the SWI where an organic-rich benthic nepheloid layer forms (Eckert et al., 2002). Sedimentation of POM is a source of nitrogen to the BNL and surficial sediments that may ultimately contribute to $N_2$ through a sequential process of mineralisation, nitrification and denitrification in the oxidised environment present at the onset of seasonal stratification. Internal cycling processes that have been shown to produce N isotope fractionation include nitrification and denitrification (Mariotti et al., 1981; Lehmann et al., 2004; Hadas et al., 2009). Fractionation is possible in the transformation of PON to $NH_4^+$ via mineralisation, so that the $\delta^{15}N$ [$NH_4^+$] will be equal to $\delta^{15}N$ [PON] plus a fractionation constant. Likewise, fractionation is possible in the transformation via nitrification of $NH_4^+$ to $NO_2^-$ and $NO_3^-$, however, as $NO_2^-$ and $NO_3^-$ disappear with concurrent denitrification (including possible anaerobic ammonium oxidation; ‘Anammox’ (Mulder et al., 1995)) and the hindrance of nitrification in a reducing environment, the $\delta^{15}N$ [$N_2$] signal should be that of the $NH_4^+$ plus the fractionation in N due to nitrification. With $\delta^{15}N$ [PON] values from 1.5 and 4.5 ‰ in our study lakes, and $\delta^{15}N$ [$N_2$] values up to 20 ‰, the combined fractionation of $\delta^{15}N$ could be as high as c. 15 ‰.

At the start of stratification $^{15}N$ [$N_2$] through the water column will be dominated by atmospheric N but there will be progressive enrichment as the hypolimnion forms and POM (and PON) is added to this layer, reaching maximum values just prior to turnover (Figure 6). We cannot explain with conventional nitrogen transformation processes the ongoing enrichment in $\delta^{15}N$ [$N_2$] that occurs after the hypolimnion becomes anoxic and there is little or no detectable $NO_3^-$. Pearson (2012) hypothesised that an alternative electron acceptor besides oxygen is required to support the nitrification needed for production of nitrate. Iron and manganese hydroxides and oxides from material sedimenting out of the water column may have induced chemo-nitrification sufficient to oxidize ammonium in the anoxic benthic nepheloid layer. The nitrate formed would mostly be rapidly denitrified so that the $\delta^{15}N$ [$N_2$] would continue to become enriched during the presence of anoxia, as observed in hypolimnion and benthic nepheloid layer of Lake Ngapouri (Pearson, 2012). The bottom waters of Lake Okaro, which have the greatest enrichment in $^{15}N$ [$N_2$], have very little $NO_3^-$ and its TN is dominated by $NH_4^+$ (86 % of TN) when the lake is stratified (Özkundakci, 2011). The continued increase of $\delta^{15}N$ [$N_2$] in eutrophic lakes despite the exhaustion of DO is testimony to the importation of an alternate electron acceptor, such as iron and manganese oxides/hydroxides, to the hypolimnion and BNL (Pearson et al., 2012).

The N supply to the BNL is dependent mostly on supply of POM to this layer which is influenced by both morphology and trophic status of a lake (Trolle et al., 2008). Since POM drives the VHOD (Schallenberg, 2004) a close correlation between VHOD and $\delta^{15}N$ [$N_2$] would be anticipated (Figure 7a). We observed in waters overlying our sediment cores that the BNLs were slightly turbid, particularly in eutrophic lakes, but were overlain by relatively clear hypolimnia. This turbidity was likely contributed in part by high concentrations of POM that create a redox microzones enabling mineralization, nitrification and denitrification to proceed in close proximity even though these processes have contrasting partial pressures of oxygen ($P_{O_2}$), energetic and thermodynamic demands (Paerl and Pickney, 1996). We consider that these processes are continuous in the BNL of all lakes, supported by diffusion of oxygen from the hypolimnion into the BNL in oligotrophic lakes and settling of oxidised minerals in eutrophic lakes, resulting in on-going dinitrogen production. Adams (1992) found concentrations of dissolved nitrogen in the hypolimnion of TVZ lakes were close to saturation with the atmosphere, but in sediment pore waters they were typically up to two-fold higher than saturation, which he attributed to increased denitrification within the sediments. We have shown that the $^{15}N$ [$N_2$] within the sediment pore waters is enriched but still significantly lower than in the BNL, suggesting that the BNL is where the majority of N fractionation occurs.

Although we have not attempted to determine a complete isotopic budget in this study, we hypothesise that the enriched $\delta^{15}N$ [$N_2$] in the benthic nepheloid layer must have originated from a particulate N source. Gu (2009) has reviewed variations in $^{15}N$ enrichment of POM and showed that in eutrophic lakes the seasonal amplitude of $\delta^{15}N$ [POM] is higher in eutrophic lakes than in oligotrophic lakes (10.3‰ vs. 4.2‰). The $\delta^{15}N$ of phytoplankton ($\delta^{15}N$ [Phyto]) in the epilimnion of the Rotorua lakes is also related to trophic status (McBride (2005); Table 3). In oligotrophic lakes, the $\delta^{15}N$ [Phyto] is close to atmospheric nitrogen values and with increasing lake trophic status $^{15}N$ of phytoplankton becomes increasingly enriched (McBride 2005). We observed that $\delta^{15}N$ [$N_2$] follows the pattern of $\delta^{15}N$ [Phyto] but becomes even more enriched than the range observed in the most eutrophic stratified lakes. The level of enrichment of settling POM (Table 3) is insufficient to cause the enrichment in $^{15}N$ [$N_2$] without additional fractionation through coupled processes of mineralisation, nitrification and denitrification.

We observed in Lake Taupo that for approximately two months following the onset of stratification there was $^{15}N$ [$N_2$] enrichment in the epilimnion, hypolimnion and BNL. This lake has a winter maximum in phytoplankton biomass and productivity that is followed by a period of sedimentation of heavy silicified diatoms sediment out of the water column (Vincent, 1983), with increased $NH_4^+$ concentrations as the associated PON is metabolised. As this PON is depleted it is likely that denitrification of nitrate dominates N transformations, resulting in negative $\delta^{15}N$ [$N_2$] in early summer.

In order to change the isotopic composition of dissolved nitrogen gas, which has a concentration c. 18 mg $L^{-1}$ when saturated by atmospheric nitrogen at typical lake water temperatures, similar quantities of enriched nitrogen gas would be required. In TVZ lakes, DIN concentrations are low in the hypolimnion (typically < 0.5 mg $L^{-1}$). Therefore additions to the DIN pool (PON mineralisation), transformations within it (nitrification, DNRA) and losses of DIN (denitrification, annamox) would need to be very high to produce sufficient $^{15}N$-enriched $N_2$ to substantially increase the $\delta^{15}N$ of the existing $N_2$ pool (Figure 3). Furthermore with concentrations of DIN (mainly $NH_4^+$) in the BNL of TVZ lakes (up to 4 mg $L^{-1}$ in Lake Ngapouri) considerably higher than in the hypolimnion the $\delta^{15}N$ and $NH_4^+$ would be continually diluted in the BNL due to diffusive exchanges with the hypolimnion. It appears, therefore, that the bulk of the enrichment may be due to ammonification of the settling PON followed by coupled conversion to $N_2$ by denitrification or anammox, even under anoxic conditions (Pearson, 2011). Burger (2006) measured a net sedimentation rate of 4,500 mg $m^{-2}$ $day^{-1}$ for total particulate matter and 103.7 mg $m^{-2}$ $day^{-1}$ for TN in eutrophic Lake Rotorua. If this material was to be metabolised completely within the BNL it would double the concentration of dinitrogen within 14 days. Thus in eutrophic stratified lakes there would appear to be adequate capacity for PON to drive the observed enrichment of $\delta^{15}N$ [$N_2$]; an assertion that relies also on rapid transitions of N through the nitrate pool (explaining its low concentration) as well as supply of electron acceptors for nitrification, even under anoxic conditions.

A mass balance of $^{15}N$ in all of the nitrogen reservoirs of the actively denitrifying zones is desirable to evaluate the relative fluxes that contribute as sources and sinks for the DIN and $N_2$ pools. This could be achieved by obtaining direct measurements of $\delta^{15}N$ in selected substrates (PON, $NO_3^-$, and $NH_4^+$). Since metabolism of the POM produces $N_2$ and $CO_2$ as its terminal products, quantifying these fluxes could be done by determining the increase in partial pressure of dissolved $N_2$ ($P_{N_2}$), and the increase in $\Sigma CO_2$ ($CO_2$ + $HCO_3^-$ and $CO_3^2$). The use of $\delta^{13}C$ [$CO_2$] as well as $\delta^{15}N$ [$N_2$] will distinguish the terminal products from the original pool of N and $CO_2$ in the water, enabling confirmation of the link between carbon and nitrogen fluxes.

### 3.4.2 Correlations between $\delta^{15}N$ [$N_2$] and environmental parameters

Lake trophic status may be expressed in several ways (e.g., TLI and its constituents). There are also strong inter-correlations amongst these trophic status variables and other environmental variables (e.g., VHOD, N load and DEA) for which process-based explanatory relationships have been proposed (e.g. Inwood et al., 2005; Fraterrigo and Downing, 2008; Bruesewitz, 2010). The strong correlation between maximum $\delta^{15}N$ [$N_2$] and VHOD (Figure 7a) likely comes about because VHOD is critically influenced by POM deposition into the hypolimnion (and thus the BNL) (Schallenberg, 2004) and $\delta^{15}N$ [$N_2$] in the BNL is therefore likely to reflect both $\delta^{15}N$ [POM ] and the rate of sedimentation of nitrogen in POM entering the BNL.

There was also a close relationship of both DEA and nitrogen load with maximum BNL $\delta^{15}N$ [$N_2$] in the lakes. The relationship between $\delta^{15}N$ [$N_2$] and DEA suggests that denitrification is significant to producing the $^{15}N_2$ enrichment. Compared with the regression line prediction the DEA of Lake Okareka was high (164 ug N g AFDM$^{-1}$ h$^{-1}$) relative to the maximum $\delta^{15}N$ [$N_2$] value of 2‰. Bruesewitz et al. (2011) similarly found that Lake Okareka had very high DEA compared with predictions based on regressions against the proportion of agriculture in the catchment and the ratio of catchment agricultural area to lake area. We have no other supporting evidence to suggest that the DEA value for Lake Okareka was anomalous but we note that when Lake Okareka data was removed the percentage of variation in maximum $\delta^{15}N$ [$N_2$] explained by DEA increased from 58 to 95% ($P < 0.001$).

The TLI represents log-transformed values of its individual components (TN, TP, SD and Chl *a*). Log transformations of these components showed strong correlations with $\delta^{15}N$ [$N_2$] despite the shallow eutrophic lakes being excluded in this analysis as they are polymictic with $\delta^{15}N$ [$N_2$] dominated by atmospheric exchange. Such polymictic lakes will still be expected to produce enriched $^{15}N$ [$N_2$] in the BNL, however, $^{15}N$ [$N_2$] may accumulate during episodic stratification intervals at rates which would be expected to be dependent on VHOD. This enrichment could be utilised as a proxy for trophic status indicators if the rate of increase in $\delta^{15}N$ [$N_2$] was determined during these temporary stratification events.

In the case of Lake Rotorua, which has a VHOD of about 1.5 g $m^{-3}$ $day^{-1}$ (Özkundakci, pers. com.) each day of stratification should increase $\delta^{15}N$ [$N_2$] in the BNL by about 1.2‰.

Our results indicate that $\delta^{15}N$ of dinitrogen gas can be used as a simple, one-off monitoring tool for Rotorua lakes that stratify on a seasonal basis. Polymictic lakes (e.g. Lake Rotorua; see Read et al., 2011) require high-frequency monitoring to enable VHOD determination and for these lakes it may also be possible to use $\delta^{15}N$ measurements at different stages of a stratification-destratification cycle as an indicator of not only trophic state but also denitrification potential. Our results so far pertain only to a subset of lakes within the Taupo Volcanic Zone but there is no reason why the methodology should not be trialled and likely proven effective as a monitoring tool for a far wider set of lakes, ultimately providing a 'snapshot' of trophic state in lakes where it may not be possible to set up routine (e.g. monthly) monitoring programmes. In the case of Lake Ngapouri, for example, which is not included in a regular monitoring programme, the $\delta^{15}N$ [$N_2$] values correspond to a TLI value of 4.44 in which case the lake would be eutrophic, as noted from previous observations by McColl (1972). Future study to confirm relationships between $\delta^{15}N$ [$N_2$] and trophic status should be directed at obtaining samples from multiple years and making direct comparisons with measured TN, TP, Chl *a*, Secchi disk and VHOD measurements over a wider geographical range of lakes.

## 3.5 REFERENCES

Abell, J. M., D. Özkundakci, and D. P. Hamilton. 2010. Nitrogen and Phosphorus Limitation of Phytoplankton Growth in New Zealand Lakes: Implications for Eutrophication Control. Ecosystems **13:** 966-977.

Adams, D. D. 1992. Sediment pore water geochemistry of Taupo volcanic zone lakes with special reference to carbon and nitrogen gases. Taupo Research Laboratory File Report 135. Taupo Research Laboratory DSIR

Altabet, M. A. 2006. Isotopic traces of marine nitrogen cycle: present and past, p. 251-293. In J. K. Volkman [ed.], Marine organic matter: biomarkers, isotopes and DNA. Springer-Verlag.

Boyer, E. W. and others 2006. Modelling denitrification in terrestrial and aquatic ecosystems at regional scales. Ecol. Appl. **16:** 2123-2142.

Brandes, J. A., and A. H. Devol. 1997. Isotopic fractionation of oxygen and nitrogen in coastal marine sediments. Geochim. Cosmochim. Acta. **61:** 1793-1801.

Bruesewitz, D. A., D. P. Hamilton, and L. A. Schipper. 2011. Denitrification potential in lake sediment increases across a gradient of catchment agriculture. Ecosystems **14:** 341-352.

Burger, D.F. 2006. Dynamics of internal nutrient loading in a eutrophic, polymictic lake (Lake Rotorua, New Zealand). Ph.D. thesis. Univ. of Waikato.

Burns, N., J. Rutherford, and J. Clayton. 1999. A monitoring and classification system for New Zealand lakes and reservoirs. Lake Reserv. Manage. **15:** 255-271.

Burns, N. M., J. Deely, J. Hall, and K. Safi. 1997. Comparing past and present trophic states of seven Central Volcanic Plateau lakes, New Zealand. N.Z. J. Mar. Freshw. Res. **31:** 71-87.

Conley, D. J. and others 2009. Controlling eutrophication: nitrogen and phosphorus. Science **323:** 1014-1015.

Downes, M. T. 1988. Aquatic nitrogen transformations at low oxygen concentrations. Appl. Environ. Microb. **54:** 172-175.

Downs, T. M., M. Schallenberg, and C. W. Burns. 2008. Responses of lake phytoplankton to micronutrient enrichment: a study in two New Zealand lakes and an analysis of published data. Aquat. Sci. **70:** 347-360.

Eckert, W., J. Imberger, and A. Saggio. 2002. Biogeochemical response to physical forcing in the water column of a warm monomictic lake. Biogeochem. **61:** 291-307.

Elliott, S. and others 2008. CLUES Spatial DSS: From farm-scale leaching models to regional decision support, p. 592-599. In M. Sànchez-Marrè, J. Béjar, J. Comas, A. E. Rizzoli and G. Guariso [eds.], Proceedings of the iEMSs Forth Biennial Meeting: International Congress on Environmental Modelling Software (iEMSs 2008)

Elser, J. J., E. R. Marzolf, and C. R. Goldman. 1990. Phosphorus and nitrogen limitation of phytoplankton growth in the freshwaters of North America: a review and critique of experimental enrichments. Can. J. Fish. Aquat. Sci. **47:** 1468-1477.

Fraterrigo, J.M., and J.A. Downing. 2008. The influence of land use on lake nutrients varies with watershed transport capacity. Ecosystems **11:** 1021-1034.

Froggatt, P. C., and G. M. Rogers. 1990. Tephrostratigraphy of high-altitude peat bogs along the axial ranges, North Island, New Zealand. N. Z. J. Geol. Geophys. **33:** 111-124.

Galloway, J. and others 2004. Nitrogen cycles: past, present, and future. Biogeochem. **70:** 153-226.

Galloway, J. N. and others 2003. The nitrogen cascade. BioScience **53:** 341-356.

Gardner, W. S., and M. J. McCarthy. 2009. Nitrogen dynamics at the sediment–water interface in shallow, sub-tropical Florida Bay: why denitrification efficiency may decrease with increased eutrophication. Biogeochem. **95:** 185-198.

Gibbs, M. M. 1992. Influence of hypolimnetic stirring and underflow on the limnology if Lake Rotoiti, New Zealand. N.Z. J. Mar. Freshw. Res. **26:** 453-463.

Granger, J., D. M. Sigman, M. F. Lehmann, and P. D. Tortell. 2008. Nitrogen and oxygen isotope fractionation during dissimilatory nitrate reduction by denitrifying bacteria. Limnol. Oceanogr. **53:** 2533-2545.

Groffman, P. M. and others 2006. Methods for measuring denitrification: diverse approaches to a difficult problem. Ecol. Appl. **16:** 2091-2122.

Gu, B. 2009. Variations and controls of nitrogen stable isotopes in particulate organic matter of lakes. Oecologia **160:** 421-431.

Hadas, O., M. A. Altabet, and R. Agnihotri. 2009. Seasonally varying nitrogen isotope biogeochemistry of particulate organic matter in Lake Kinneret, Israel. Limnol. Oceanogr. **54:** 75-85.

Håkanson, L., and M. Jansson. 1983. Principles of Lake Sedimentology. 316.

Hamilton, D. P. 2005. Land use impacts on nutrient export in the Central Volcanic Plateau, North Island. N.Z. J. For. **49:** 27-31.

Hamilton, D. P., K. R. O’Brien, M. A. Burford, J. D. Brookes, and C. G. McBride. 2010. Vertical distributions of chlorophyll in deep, warm monomictic lakes. Aquat. Sci. **72:** 295-307.

Harrison, J. A. and others 2009. The regional and global significance of nitrogen removal in lakes and reservoirs. Biogeochem. **93:** 143-157.

Inwood, S.E, J.L. Tank, and M.J. Bernot. 2005. Patterns of denitrification associated with land use in 9 midwestern headwater streams. J. N. Am. Benthol. Soc. **24:** 227-245.

Irwin, J. 1968. Observations of temperatures in some Rotorua district lakes. N.Z. J. Mar. Freshw. Res. **2:** 591-605.

Koszelnik, P., J. A. Tomaszek, and R. Gruca-Rokosz. 2007. The significance of denitrification in relation to external loading and nitrogen retention in a mountain reservoir. Mar. Freshwat. Res. **58:** 818-826.

LECO Corporation. 2006. TruSpec CN Carbon/Nitrogen Determinator, Instruction Manual. LECO Corporation. United States.

Lehmann, M. F., S. M. Bernasconi, A. Barbieri, and J. A. Mckenzie. 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. Geochim. Cosmochim. Acta. **66:** 3573-3584.

Lehmann, M. F., S. M. Bernasconi, J. A. Mckenzie, A. Barbieri, M. Simona, and M. Veronesi. 2004. Seasonal variation of the δ13C and δ15N of particulate and dissolved carbon and nitrogen in Lake Lugano: constraints on biogeochemical cycling in a eutrophic lake. Limnol. Oceanogr. **49:** 415-429.

Lowe, D. J., and J. D. Green. 1987. Origins and development of the lakes, p. 64. In A. B. Viner [ed.], Inland waters of New Zealand. DSIR Bulletin 241. DSIR Science Information Publishing Centre.

Macleod, C. J., and H. Moller. 2006. Intensification and diversification of New Zealand agriculture since 1960: an evaluation of current indicators of land use change. Agric. Ecosyst. Environ. **115:** 201-218.

Mariotti, A. 1983. Atmospheric nitrogen is a reliable standard for natural 15N abundance measurements. Nature **303:** 685-687.

Mariotti, A. and others 1981. Experimental determination of nitrogen kinetic isotope fractionation: some principles; illustration for the denitrification and nitrification processes. Plant Soil **62:** 413-430.

McBride, C. G. 2005. Stable isotopes in the Rotorua lakes: Food web structures and relationships to lake morphology and limnology. M.Sc. thesis. Univ. of Waikato.

McColl, R. H. S. 1972. Chemistry and trophic status of seven New Zealand lakes. N. Z. J. Mar. Freshw. Res. **6:** 399-447.

Mulder A, A.A. van de Graaf, L.A. Robertson and J.G. Kuenen. 1995. Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. FEMS Microbiol Ecol **16:**177-184.

Ostrom, N. E., S. A. Macko, D. Deibel, and R. J. Thompson. 1997. Seasonal variation in the stable carbon and nitrogen isotope biogeochemistry of a coastal cold ocean environment. Geochim. Cosmochim. Acta. **61:** 2929-2942.

Özkundakci, D., D. P. Hamilton, and M. M. Gibbs. 2010. Hypolimnetic phosphorus and nitrogen dynamics in a small, eutrophic lake with a seasonally anoxic hypolimnion. Hydrobiologia **661:** 5-20.

Paerl, H. W., and J. L. Pinckney. 1996. A mini-review of microbial consortia: Their roles in aquatic production and biogeochemical cycling. Microb. Ecol. **31:** 225-247.

Parfitt, R. L., L. A. Schipper, W. T. Baisden, and A. H. Elliott. 2006. Nitrogen inputs and outputs for New Zealand in 2001 at national and regional scales. Biogeochem. **80:** 71-88.

Pearson, L.K., C.H. Hendy, D.P., Hamilton and W.B. Silvester. 2012. Nitrogen-15 isotope enrichment in the benthic boundary layer gases of a stratified eutrophic iron and manganese rich lake. Aquat. Geochem. **18:** 1-19.

Priscu, J. C., R. H. Spigel, M. M. Gibbs, and M. T. Downes. 1986. A numerical analysis of hypolimnetic nitrogen and phosphorus transformations in Lake Rotoiti, New Zealand: A geothermally influenced lake. Limnol. Oceanogr. **31:** 812-831.

Read, J. and others 2011. Derivation of lake mixing and stratification indices from high-resolution lake buoy data using “Lake Analyser”. Environ. Modell. Softw. doi: 10.1016/j.envsoft.2011.1005.1006.

Richardson, P., K. Botherway, R. Cooper, P. L. Couteur, N. Potter, and J. M. Williams. 2004. Growing for good: Intensive farming, sustainability and New

Zealand's environment. Parliamentary Commissioner for the Environment, Wellington.

Schallenberg, M. 2004. Primary production in the open water. *In* J. Harding, P. Mosley, C. Pearson and B. Sorrell [eds.], Freshwaters of New Zealand. New Zealand Hydrological Society Inc.

Schindler, D. W. and others 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. PNAS **105:** 11254-11258.

Scholes, P., and M. Bloxham. 2007. Rotorua lakes water quality 2006 report, Environmental Publication 2007/12. Environment Bay of Plenty, Whakatane, New Zealand.

Seitzinger, S. P. and others 2002. Nitrogen retention in rivers: model development and application to watersheds in the northeastern U.S.A. Biogeochem. **57:** 199-237.

Spigel, R. H., C. Howard-Williams, M. Gibbs, S. Stephens, and B. Waugh. 2005. Field calibration of a formula for entrance mixing of river inflows to lakes: Lake Taupo, North Island, New Zealand. N.Z. J. Mar. Freshw. Res. **39:** 785-802.

Teranes, J. L., and S. M. Bernasconi. 2000. The record of nitrate utilization and productivity limitation provided by δ15N values in lake organic matter- A study of sediment trap and core sediments from Baldeggersee, Switzerland. Limnol. Oceanogr. **45:** 801-813.

Timperley, M. 1983. Phosphorus in spring waters of the Taupo Volcanic Zone, North Island, New Zealand. Chem. Geol. **38:** 287-306.

Trolle, D., D. P. Hamilton, C. H. Hendy, and C. Pilditch. 2008. Sediment and nutrient accumulation rates in sediments of twelve New Zealand lakes: influence of lake morphology, catchment characteristics and trophic state. Mar. Freshwat. Res. **59:** 1067-1078.

Trolle, D., D. P. Hamilton, and C. A. Pilditch. 2010. Evaluating the influence of lake morphology, trophic status and diagenesis on geochemical profiles in lake sediments. Appl. Geochem. **25:** 621-632.

Trolle, D., D. P. Hamilton, C.A. Pilditch, I.C. Duggan and E. Jeppesen. 2011. Predicting the effects of climate change on trophic status of three morphologically varying lakes: implications for lake restoration and management. Environ. Modell. Softw. **26:** 354-370.

Van Breemen, N. and others 2002. Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern USA. Biogeochem. **57:** 267-293.

Vanni, M. J., W. H. Renwick, A. M. Bowling, M. J. Horgan, and A. D. Christian. 2010. Nutrient stoichiometry of linked catchment lake systems along a gradient of land use. Freshw. Bio. **56:** 791-811.

Vincent, W., M. Gibbs, and S. Dryden. 1984. Accelerated eutrophication in a New Zealand lake: Lake Rotoiti, central North Island. N.Z. J. Mar. Freshwat. Res. **18:** 431-440.

Vincent, W.F. 1983. Phytoplankton production and winter mixing: Contrasting effects in two oligotrophic lakes. J. Ecol. **71:** 1-20.

Vincent, W. F. 1981. Production strategies in Antarctic inland waters: phytoplankton eco-physiology in a permanently ice-covered lake. Ecology **62:** 1215-1224.

Vitousek, P. and others 1997. Human alteration of the global nitrogen cycle: sources and consequences. Ecol. Appl. **7:** 737-750.

Vogel, J. C., A. S. Talma, and T. H. E. Heaton. 1981. Gaseous nitrogen as evidence for denitrification in groundwater. J. Hydrol. **50:** 191-200.

Wassenaar, L. I. 1995. Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of 15N and 18O in NO3-. Appl. Geochem. **10:** 391-405.

White, E. 1983. Lake eutrophication in New Zealand—a comparison with other countries of the Organisation for Economic Co-operation and Development. N. Z. J. Mar. Freshwat. Res. **17:** 437-444.

White, E., K. Law, G. Payne, and S. Pickmere. 1985. Nutrient demand and availability among planktonic communities—an attempt to assess nutrient limitation to plant growth in 12 central volcanic plateau lakes. N. Z. J. Mar. Freshwat. Res. **19:** 49-62.

# CHAPTER 4: SEDIMENT-PORE WATER GEOCHEMISTRY AND DIFFUSIVE FLUXES OF ELEMENTS IN SELECTED LAKES OF THE TAUPO VOLCANIC ZONE, NEW ZEALAND

## 4.1 INTRODUCTION

Sediments have the potential to influence and strongly regulate the trophic state of lakes (Håkanson and Jansson, 1983; Maassen et al., 2003; Trolle et al., 2008). They may act as both sources and sinks for elements, thus they potentially have an important role in the dynamics of the overlying water column (Nürnberg, 1984a; Peterson et al., 1995; Søndergaard et al., 2003). Changes in element distributions within lake sediments have tended to be regarded as indicative of changes in loads of these elements from the connected catchment (Mosello et al., 2001; Eckert et al., 2003) but internal processes can markedly affect element distributions at seasonal and inter-annual time scales (Sinke et al., 1990; Sherman et al., 1994).

Whilst concentrations of most dissolved species in near-surface bottom sediments are low compared with concentrations in the solid phase (Søndergaard et al., 2003), the relatively large pore water volume and seasonally-induced changes in sediment redox potential (Sinke et al., 1990; Sherman et al., 1994) can change the mobility and bioavailability of nutrients and metals, both in the water column as well as in the sediments (Bortleson and Lee, 1974; McKee et al., 1989). For example, within the bottom sediments a concave concentration profile is interpreted as depletion of a substance from pore water and a convex profile as a release of a substance into the pore water (Schultz, 2006). Dissolved substances are then transported by molecular diffusion within pore water and across the sediment-water interface (SWI) whilst also being affected by processes such as bioturbation (Svensson and Leonardson, 1996; Meysman et al., 2005), resuspension (Pierson and Weyhenmeyer, 1994; Weyhenmeyer et al., 1995), gas ebullition (Boudreau et al., 2001; Ostrovsky, 2003; Brennwald et al., 2005) and sub-lacustrine inputs (Priscu et al., 1986; Granina et al., 2007). Transformations of elements also occur in the bottom sediments due to mineralisation and metabolism of organic matter, sediment diagenesis and biogenic sedimentation (Meyers and Ishiwatari, 1993).

Lakes which are deep compared to their surface area may stratify permanently or seasonally, with cold denser waters forming a hypoliminion separated from an upper epilimnion by a thermocline (Wetzel, 2001). In these lakes oxygen is generally only re-supplied to the hypolimnion when the water column turns over, for example, for a period in winter in warm monomictic lakes. Organic matter produced in, or transported to, the epilimnion sinks; producing a volumetric hypolimnetic oxygen demand (VHOD) contributed from within the hypolimnetic water and at the sediment-water interface (Wetzel, 2001). Following seasonal formation of the hypolimnion, there is generally a progressive decrease in redox potential (Eh) and there may be a loss of oxidized species (e.g., nitrate, ferric ions and manganic ions), particularly if the hypolimnion becomes anoxic with complete consumption of oxygen in this layer. In other cases anoxia may be confined to microzones or the benthic boundary layer (BBL) (Boudreau and Jørgensen, 2001), depending on interactions amongst inputs of sedimenting detritus and the spatial and temporal occurrence of thermal stratification. As not all of the organic debris is re-metabolised during its descent to the sediment, oxidation continues following burial so long as oxidised species (e.g., dissolved oxygen, sulfate, ferric ions, manganic ions, nitrate, etc.) are available. The outcome of reductive processes is the development of critical redox boundaries at various depths above and below the SWI (Canfield and Thamdrup, 2009).

With advances in analytical techniques, particularly recent improvements in the ionisation efficiency and sensitivity of inductively coupled plasma – mass spectrometry (ICP-MS) operation, it is possible to analyse pore water concentrations of a large number of elements with higher precision on small-quantity water samples. This advance has allowed comparison between elements with similar chemistry but with concentration ranges over 2-3 orders of magnitude.

Here we report on several major chemical species and processes observed in the sediments and pore waters of five lakes in the Taupo Volcanic Zone, North Island, New Zealand. Central basin sediments in the Taupo Volcanic Zone (TVZ) lakes comprise of mostly fine diatomaceous material with little evidence of reworking; tephras from previous volcanic eruptions remain highly intact as horizontal horizons within the central lake basin (Trolle et al., 2008; Pearson et al., 2010). The objective of this study was to elucidate the diagenetic processes that influence the availability of major and trace elements and nutrients across lakes of similar mixing regime but widely varying trophic state. This information is used to estimate internal fluxes of elements and nutrients over one year based on monthly measurements of pore water concentrations.

## 4.2 MATERIALS AND METHODS

### 4.2.1 Site description

The TVZ is a complex tectonic depression which is the source of Quaternary volcanism in the Central North Island of New Zealand and has been active since 2 Ma (Wilson et al., 1984). Most of the volcanism is concentrated in an area of 7500 km$^2$ which is occupied by six major caldera volcanoes, Rotorua, Okataina, Kapenga, Mangakino, Maroa and Taupo. The TVZ contains many lakes of volcanic origin with diverse history, physiography, and limnology (McColl, 1977; Burns et al., 1997) (Figure 4.1). The majority of these lakes are associated with rhyolitic volcanic events and pyroclastics in the form of extensive ignimbrite sheets. Tepheric cover beads dominate the surface geology within the region.

Five lakes were chosen for the present study: Taupo, Tarawera, Okataina, Rotoiti and Ngapouri. The lakes were formed from activity associated with the Okataina caldera (Okataina, Tarawera, Ngapouri and Rotoiti) and Taupo caldera (Taupo). General morphological features and catchment characteristics for the lakes are presented in Table 4.1. These lakes are all monomictic, mixing for c. 3

months each year, but vary widely in trophic status. Lakes Taupo, Tarawera and Okataina are considered to be oligotrophic and lakes Rotoiti and Ngapouri are eutrophic.

**Table 4.1:** General catchment and lake characteristics for the study sites (from Fish, 1970; Trolle et al., 2008 and Bruesewitz et al., 2011).

| | Elevation above sea level (m) | Mean depth (m) | Max. depth (m) | Lake area ($km^2$) | Catchment area ($km^2$) | Catchment agriculture (%) | Catchment forest (%) | Catchment urban (%) | Water residence time (m) | Trophic State |
|---|---|---|---|---|---|---|---|---|---|---|
| Taupo (Tp) | 384 | 100.0 | 164 | 620.0 | 2849.0 | 21.6 | 77.4 | 1.0 | 126.0 | Oligotrophic |
| Tarawera (Tw) | 298 | 50.0 | 88 | 41.7 | 144.9** | 21.1 | 62.4 | 0.7 | 41.0 | Oligotrophic |
| Okataina (Ot) | 311 | 39.4 | 79 | 11.0 | 56.8 | 9.6 | 84.6 | 0.0 | 44.6 | Oligotrophic |
| Rotoiti (Ri) | 279 | 31.5 | 124 | 34.6 | 124.6** | 23.9 | 42.9 | 1.1 | 21.5 | Eutrophic |
| Ngapouri (Np) | 451 | 12.1 | 24 | 0.2 | 4.8 | 99.0 | 1.0 | 0.0 | * | Eutrophic |

* Data unavailable

** Does not include catchments from upstream lakes draining to lake of interest.

New Zealand's largest lake, Taupo (area 616 $km^2$), is located near the centre of the North Island and was formed up to 26 500 years B.P. as a result of a super volcano. This lake was sampled in the Waitahanui Basin, 165 m water depth, at the location of a national water quality monitoring site (Figure 4.1). The Rotorua Lakes District comprises more than 15 lakes (area 0.3 to 80 $km^2$) which were formed up to 140 000 years ago by a series of volcanic eruptions that led to the formation of craters and damming of river valleys (Lowe and Green, 1992). Lakes Tarawera and Okataina formed as pyroclastic flows of the Te Rere phase of the Haroharo volcanic complex, which is dated by Nairn (1992) at between 18 and 22 ka. Lake Rotoiti formed about 50,000 years ago from pyroclastic flows damming a river valley draining the Lake Rotorua caldera from the Haroharo volcanic complex (Lowe and Green, 1992). A caldera formed at the eastern end of the lake producing basin depths of 60-80 m, but with an active hydrothermal vent of 125 m within the caldera. Lake Ngapouri is small and positioned within a hydrothermal explosion crater, which formed as part of the Kaharoa eruption of 1314 ± 12 AD.

Lakes in the TVZ have all been associated with some form of volcanism in the past, with varying types of geothermal discharges to the lakes (Timperley and Vigor-Brown, 1986). Lakes Taupo, Tarawera and Rotoiti have direct geothermal discharges through the sediments of each lake. Although submerged and shoreline geothermal discharges are known for lakes Tarawera and Taupo (Hedenquist, 1986; Bibby et al., 1994), hypolimnetic temperature remains largely invariant seasonally. The hypolimnion of Lake Rotoiti, however, shows increasing concentrations of anions and cations, as well as temperature, which are consistent with a significant submerged geothermal field (Priscu et al., 1986; Gibbs, 1992; Pickrill, 1993). The sampling site in Lake Rotoiti chosen for this study has localised geothermal fluid flow, which was not detectable at any other lake.

Sample sites were selected near the deepest part of the central basin in each lake, targeting areas of sediment accumulation (cf. Håkanson and Jansson, 1983; Hilton, 1985; Nürnburg, 1991). Two sites were selected in Lake Okataina, central (75 m) and north basin (65 m) (Figure 4.1), to assess variability of sediment pore waters in two basins of the lake connected by a 50 m deep ridge (Irwin, 1968).

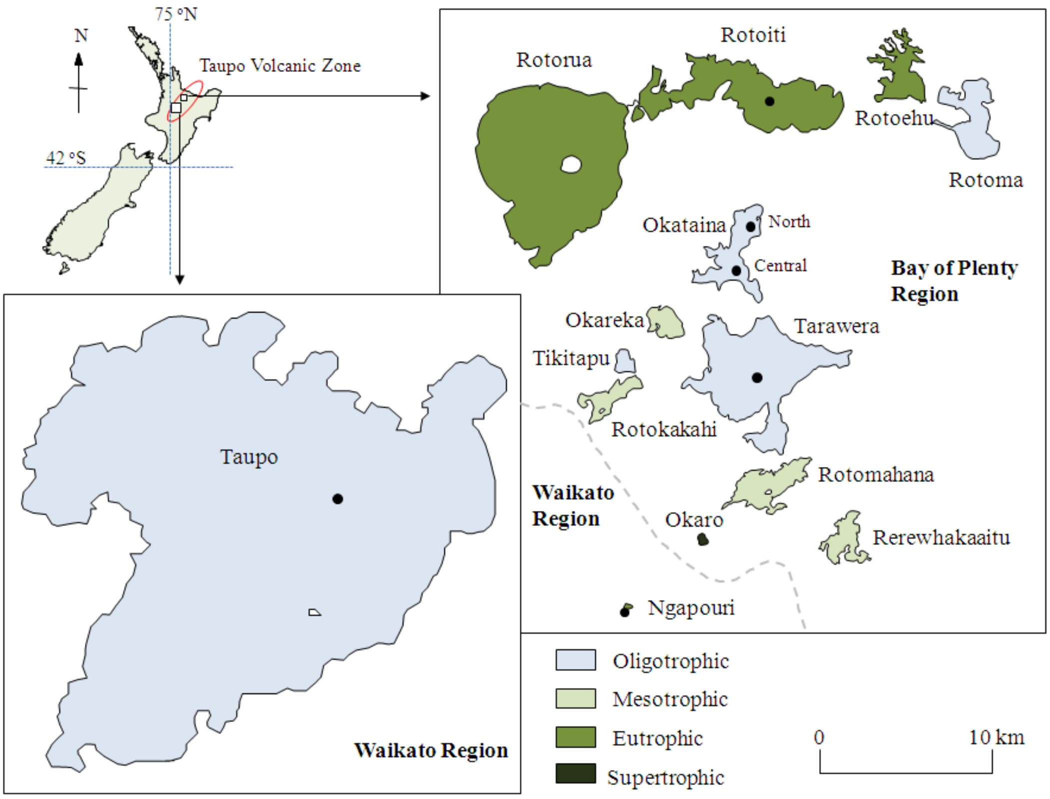

**Figure 4.1:** Location and trophic state of Lake Taupo and the Rotorua lakes within the Taupo Volcanic Zone (inset, circled), New Zealand. Sample sites on the lakes are marked with a • and lake trophic status is identified by shading. The lakes belong to two regional boundaries: Rotorua District (Bay of Plenty Region) and Waikato Region.

### 4.2.2 Sampling and field methods

Monthly sampling was undertaken between September 2007 and December 2008. On each occasion, at each sampling site, a water column profile of temperature, dissolved oxygen, conductivity and depth was taken with a Sea Bird Electronics 19 plus SEACAT Profiler (CTD, Sea-Bird Electronics Inc., Washington), fitted with a dissolved oxygen sensor (DO, Seabird Electronics; detection limit 0.1 mg $L^{-1}$). The CTD probe was lowered slowly while sampling at a frequency of 4 Hz to provide a vertical resolution of the order of c. 0.02 m. Data interpolation using Ocean Data View (http://odv.awi.de) allowed for generation of isopleths of temperature and dissolved oxygen with depth over the sampling period. Lake water was collected using a Schindler-Patalas trap to capture the bottom water (1 m from SWI) for elemental analysis.

Duplicate sediment cores were taken at each site with a Swedish gravity corer (Pylonex HTH 70 mm) with a 60 x 600 mm Perspex (Plexiglas) core barrel to capture undisturbed sediments along with c. 20 cm of the overlying water. The surface sediment was visually inspected in each core to determine if there was any disturbance at the SWI or in the sediment profile; the core was discarded and another one taken when sediments had been disturbed. Once the core was retrieved, a custom-made, gas-tight sampling chamber, designed to minimise exposure of potentially anoxic sediment to the air, was fitted to the core barrel and the core was extruded by a piston from the base of the core. Excess supernatant water overflowed the top of the core upon extrusion until 2 cm of water was overlying the SWI. This water was collected in a 50 mL polypropylene centrifuge tube and herewith is termed the benthic nepheloid layer (BNL) sample. Sediment samples were extruded at 2 cm vertical intervals and transferred into 50 mL polypropylene centrifuge tubes; the sediment completely filled the tubes and small amounts of residual sediment were discarded. Eh (Platinum Mettler ToLedo InLab Redox, Electrolyte 3 mol/L KCl) and pH (EDT BA350 pH meter, EDT direct-ion electrode) of the sediment and water samples were measured in the field before the tubes were capped and placed on ice until return to the laboratory. Eh has been calibrated according to the following: $Eh = E_{(measured)} + Eh_{(Zoebells\ theoretical)}$

- $E_{(\text{Zoebells measured})}$ (Patnaik, 2010) . Zoebells theoretical was 234 mV and measured 225 mV.

### 4.2.3 Analytical methods

In the laboratory, the gravity core sediments were weighed to determine bulk density ($\rho_b$) before pore waters were separated by centrifugation at 4000 rpm (2900 G) for 40 min. All sediments were dried at 105 °C for 48 h and ground lightly using a mortar and pestle. The pore water was filtered through a 0.45 µm Millipore filter and split into two polypropylene vials; one vial was acidified with nitric acid (2%) and the other was frozen immediately. Trace element concentrations of the sediment were determined on one core each month. The sediments were dried and lightly ground and digested with reverse Aqua Regia (3 $HNO_3$ : 1 HCL) at 50 °C for one hour based on a modified standard procedure (Martin et al., 1994; Trolle et al., 2008). The resulting digest along with the acidified pore water was analysed using inductively coupled plasma mass spectrometry (ICP-MS model ELAN DRC II; Perkin-Elmer SCIEX). Analysis for concentrations of ammonium ($NH_4$-N), nitrite ($NO_2$-N), total oxidised nitrogen ($NO_x$-N) and phosphate ($PO_4$-P) were carried out spectrophotometrically on thawed lake water and pore water samples using a Lachat QuickChem® Flow Injection Analyser (FIA+ 8000 Series, Zellweger Analytics, Inc.). Nitrate was calculated as the residual of $NO_x$ - $NO_2^-$. The sediment dry weight fraction was determined by weighing solid samples before and after drying, and taking into account pore water mass. Loss on ignition (LOI) was determined on a 2 g sample of the dried sediment. To approximate carbon content in these sediments, which have low carbonate content (McColl, 1972), samples from one core were analysed by both LOI and an elemental analyser in which the $CO_2$ produced by combustion was determined my mass spectrometory. A correlation factor for percentage carbon of 0.54 times percentage LOI was determined with a coefficencent of variance of 0.92.

### 4.2.4 Data analysis

The concentrations of elements in the sediment were averaged from digests of one of the cores sampled each month. Pore water concentrations of each element were averaged over the 12 month sampling period, except for elements which showed strong seasonal variations. For these elements averages were taken for two time periods; when the lake had been stratified for some time and when it was mixed (based on assessment of mixing status from temperature profiles). For lakes Taupo, Tarawera and Okataina, the stratified period average was determined with data from the months April to June, Lake Rotoiti from March to May, and Lake Ngapouri from January to March. The mixed period average was taken from August to October in lakes Taupo and Tarawera, September to November in Lake Okataina, August to October in Lake Rotoiti and July to September in Lake Ngapouri.

After satisfying the Kolmogorov-Smirnov test for normality ($P > 0.2$), a Pearson correlation coefficient (r) was used to test for relationships between average species concentrations at each 2-cm depth separation. From this analysis a correlation matrix was produced to show the significance (p-value) using STATISTICA software (www.statsoft.com).

### 4.2.5 Calculation of diffusive flux

Two diffusive flux (J) values were calculated for nutrient and element transfers between sediments and lake water based on annual average pore water concentrations for two sediment layers; between BNL and the 0-2 cm sediment section, and between the 0-2 cm and 2-4 cm depth core sections. The diffusive flux was calculated using Ficks first law (Eq. 4.1) where D is the diffusion coefficient (Table 4.2, Supplementary data A) and dc is the change in concentration over the change in distance dx (2 cm) (Table 4.3, Supplementary data A):

$$J = -D(dc/dx) \qquad (4.1)$$

The diffusion coefficient was reduced by the square of the tortuosity (Eq. 4.2) to account for longer diffusive paths in fine-grained unlithified sediments (Boudreau, 1996) (Table 4.3, Supplementary data A). Values of tortuosity ($\theta$) were related to porosity ($\varepsilon$) values as:

$$\theta^2 = 1\text{-}\ln(\varepsilon^2) \qquad (4.2)$$

Porosity was in turn calculated assuming a particle density ($\rho_d$) of 2.09 g $cm^{-3}$, which approximates to silicon-dominated sediments (Round et al., 1990):

$$\varepsilon = 1 - (\rho_b/\rho_d) \qquad (4.3)$$

where bulk density ($\rho_b$) is the is the average of the respective sediment layers. A positive diffusive flux for the BNL to 0-2 cm section is indicative of an increase in concentration of the overlying lake water and vice-versa for a negative flux. A positive diffusive flux for the 0-2 cm to 2-4 cm section indicates an increase concentration in the 0-2 cm pore water layer whilst a negative flux would indicate a loss of the element to the deeper layer in the sediment.

## 4.3 RESULTS

### 4.3.1 Stratification regime

There was little, if any, vertical gradient in water temperature during winter (June or July through August or September) in the five lakes. Temperatures were slightly < 11 $^{o}$C in lakes Taupo, Tarawera, Okataina and Rotoiti but < 9 $^{o}$C in Lake Ngapouri (Figure 4.2). The onset of mixing reflected variations in lake size, occurring in late July in Lake Taupo but in June in the smaller Lake Ngapouri (Figure 4.2a and f). Interestingly, however, mixing occurred slightly earlier in Lake Rotoiti than in the other lakes. We interpret the progressive warming of hypolimnetic waters until turnover in this lake (Figure 4.2e) as evidence of the geothermal heating (Priscu et al., 1986; Gibbs, 1992), with a reduced vertical density gradient leading to earlier mixing. Vertical temperature stratification re-established around September in the five lakes. The magnitude and timing of peak surface-water temperatures were similar amongst lakes (20-21 $^{o}$C in Jan. or Feb.) whilst surface mixed layer depth varied with lake size, from c. 33 m in Lake

Taupo to c. 11 m in Lake Ngapouri at the time of maximum surface water temperature.

During the period of winter mixing, concentrations of DO were vertically homogenous in the range 7 to 12 mg $L^{-1}$ (Figure 4.2). The period of vertical homogeneity of DO was relatively short (<1 month) for lakes Ngapouri and Rotoiti and up to 3 months for lakes Taupo, Tarawera and Okataina. Lake Taupo was supersaturated in DO in its surface waters from late winter to early spring (August-October). Whilst snow melt adds cold saturated waters through the lake (Spigel et al., 2005) it is likely that the winter period of peak phytoplankton productivity due to high diatom biomass in this lake (Vincent, 1983), is responsible for the observed supersaturation. It was evident in the five lakes that DO is consumed both within the hypolimnion and at the SWI.

Values of VHOD were estimated as the rate of oxygen decline at 1 m above the SWI from October 2007 until the hypolimnion was strongly depleted in DO (c. 1 mg $L^{-1}$) or for lakes with well-oxygenated hypolimnia, the last sample before turnover. As Lake Ngapouri was already anoxic at the time the monthly sampling programme was initiated, VHOD was calculated for the period after turnover when the lake began to re-stratify (between August 2008 and October 2008). VHOD increased with trophic state. Over the period of strong thermal stratification (c. 8-9 months), oligotrophic Lake Taupo consumed about one-half of the dissolved oxygen initially present in the hypolimnion (VHOD = 0.015 g $m^{-3}$ $day^{-1}$) whereas in Lake Ngapouri all of the oxygen in the hypolimnion was consumed within the one-month sampling period following onset of stratification (VHOD ~ 0.116 g $m^{-3}$ $day^{-1}$). For Lake Okataina a mean VHOD of 0.051 g $m^{-3}$ $day^{-1}$ was derived from measurements in the central and northern basin sampling sites (0.049 and 0.053 g $m^{-3}$ $day^{-1}$, respectively). Lakes Tarawera and Rotoiti had a VHOD of 0.024 and 0.06 g $m^{-3}$ $day^{-1}$, respectively.

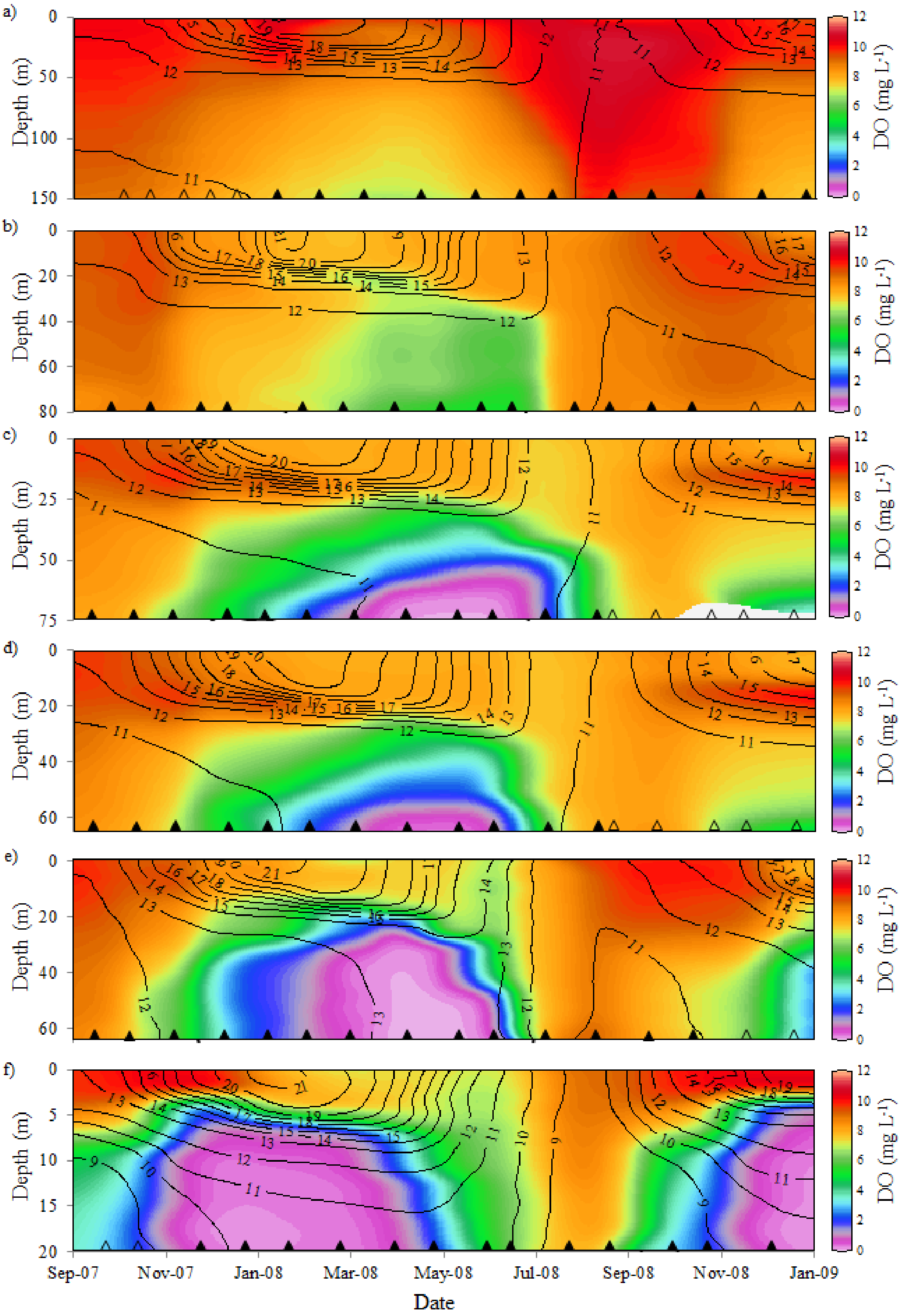

**Figure 4.2:** Temperature (°C) (black contour) and dissolved oxygen concentration (mg L$^{-1}$) (colour contour) in lakes a) Taupo, b) Tarawera, c) Okataina (central) d) Okataina (north) e) Rotoiti and f) Ngapouri. Solid arrows indicate sampling dates of this study. Temperature and dissolved oxygen data were provided from routine monitoring by the regional authorities to interpolate when no data from this study were available (hollow arrows).

### 4.3.2 Sediment characteristics

Sediments of the TVZ consist primarily of diatomaceous materials with layers of volcanic materials deposited from recent eruptions. Ejecta from the Tarawera eruption (1886 AD) were observed in the lakes Tarawera, Okataina and Rotoiti core samples between depths of 18 to 30 cm in the sediment (Figure 4.3). Sediment bulk density increased with depth (Figure 4.4a) with the densest sediment in Lake Taupo (up to 0.29 g cm$^{-3}$ at 20 cm depth). Lake Rotoiti had the lowest bulk density, as low as 0.15 g cm$^{-3}$ at 20 cm depth. The porosity of the sediments in all the lakes reduced from about 98 to 88% by 20 cm sediment depth (Figure 4.4b). Loss on ignition of surface sediment samples showed the percentage of organic carbon decreased with depth in all lakes (Figure 4.4c). The most eutrophic lake, Ngapouri, had the highest carbon content in the surface sediments at 13% and oligotrophic Lake Okataina had the lowest values; 6.8% in the central basin and 4.4% in the north basin.

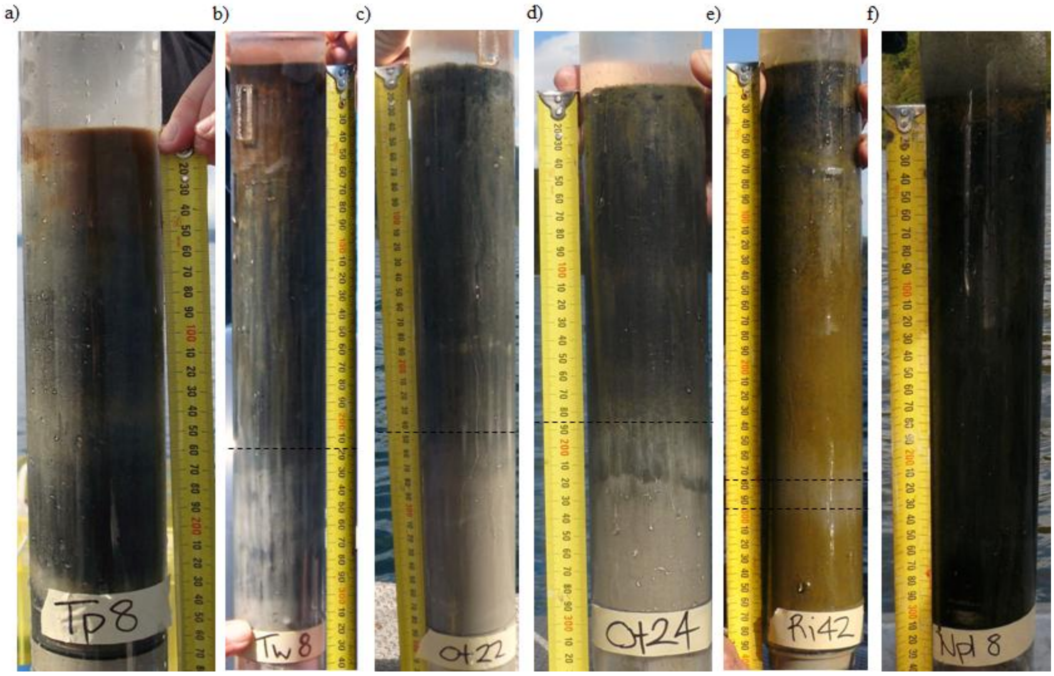

**Figure 4.3:** Sediment cores from lakes a) Taupo (155 m) b) Tarawera (82 m) c) Okataina (Site 1) (75 m) d) Okataina (Site 2) (65 m) e) Rotoiti (64 m) and f) Ngapouri (25 m). The Tarawera tephra is indicated with a dashed line. This tephra extends to the base of the core unless the base of the tephra is above the base of the core in which case a second dashed line is shown. Note the high-turbidity water above the sediment in Lake Ngapouri is typical of the benthic nepheloid layer in that lake and was not associated with resuspension of surficial sediments.

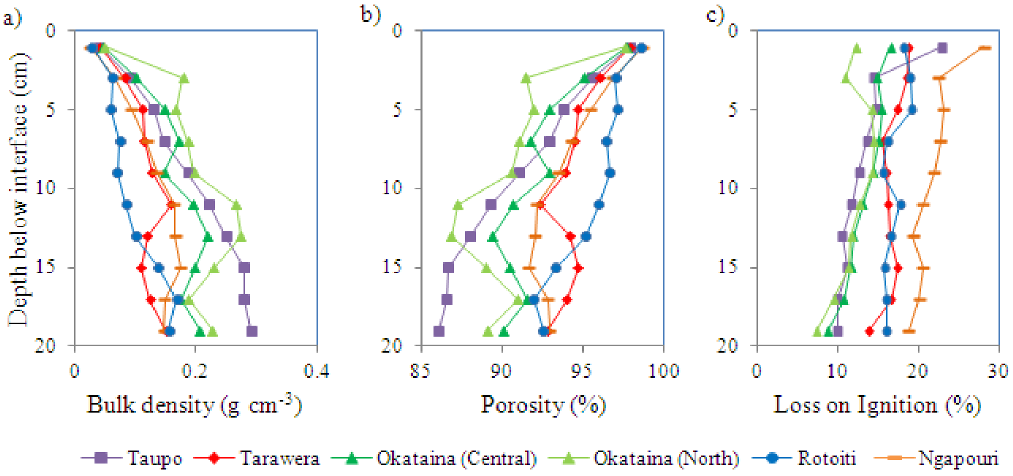

**Figure 4.4:** a) Bulk density b) porosity and c) loss on ignition of bottom sediments (as depth below the sediment-water interface) in the five study lakes.

## 4.3.3 Sediment-pore water chemistry

### 4.3.3.1 pH and Eh

The oligotrophic lakes had an average pH between 6.4 and 6.1 in the sediment pore water and the eutrophic lakes had an average pH between 6.4 and 5.8 (Figure 4.5). The Eh remained somewhat higher in the oligotrophic lakes (between 100 and -180 mV) than the eutrophic lakes (between 30 and -220 mV) (Figure 4.5). With the exception of Lake Rotoiti, the Eh of all pore waters decreased with sediment depth. The Eh of Lake Rotoiti pore water remained constant with depth below the SWI. An Eh-pH diagram for the iron and sulfur system shows the annual average pore water at each 2 cm sampling depth for the five lakes mostly lie close to the boundaries between ferrous ions, iron oxide/hydroxides and pyrite (Figure 4.6).

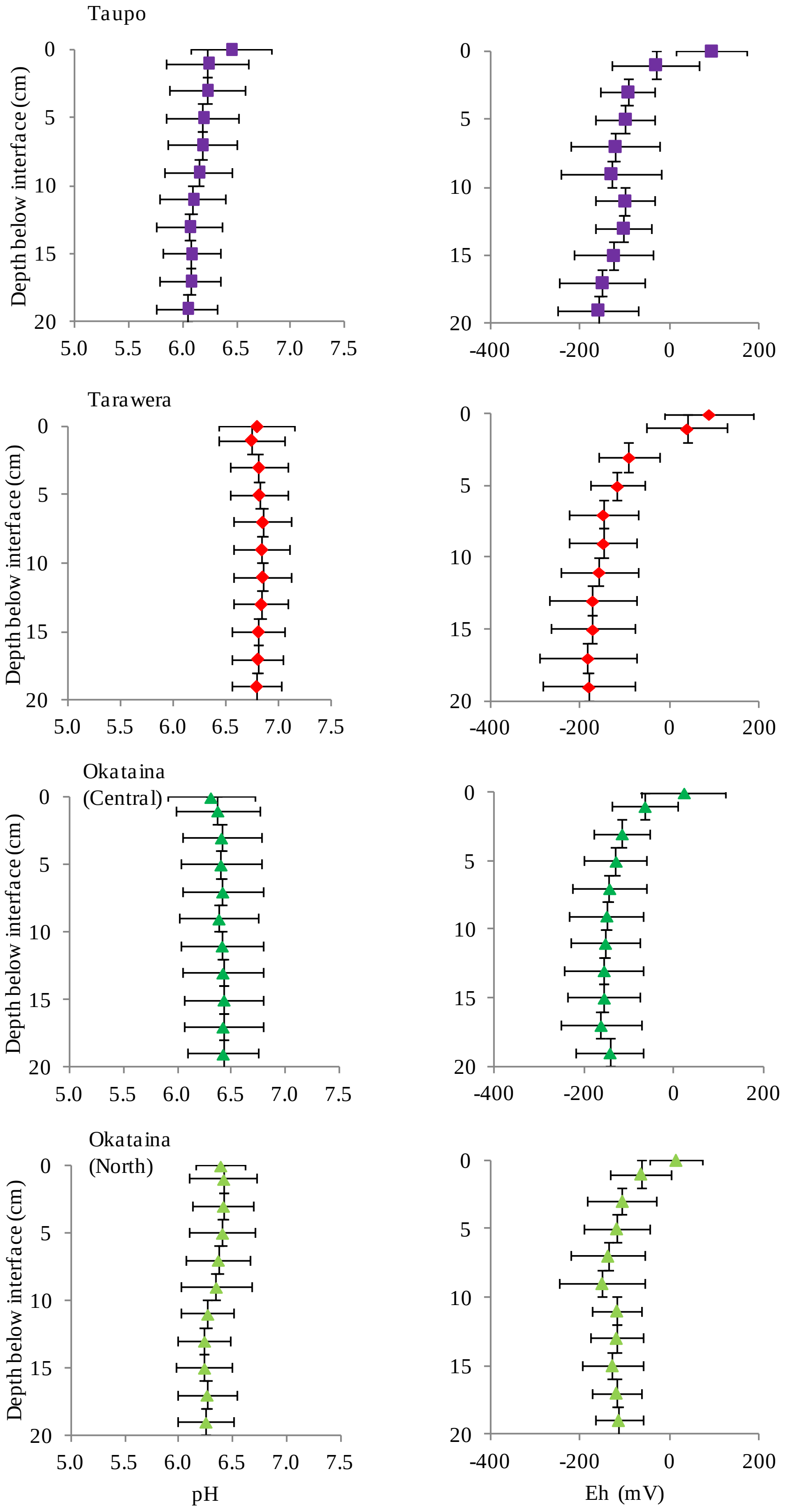

**Figure 4.5:** Average pH and Eh for oligotrophic Lakes Taupo, Tarawera and Okataina calculated from two sediment cores collected for 12 months. Vertical error bars show depth range and horizontal error bars represent standard deviation.

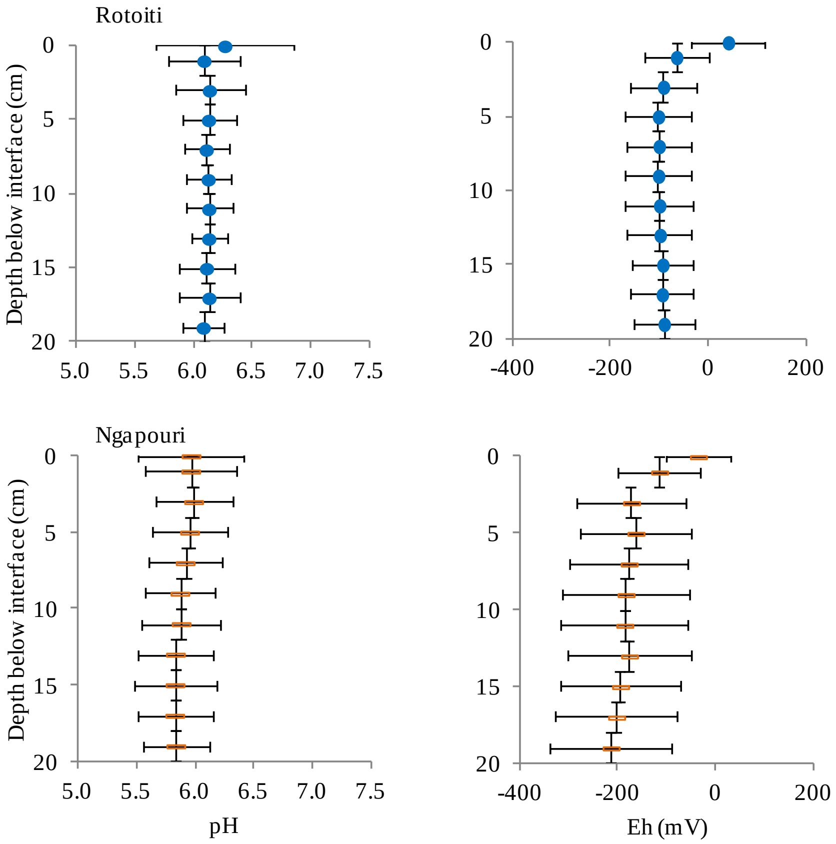

**Figure 4.5 continued:** Average pH and Eh for eutrophic Lakes Rotoiti and Ngapouri calculated from two sediment cores collected for 12 months. Vertical error bars show depth range and horizontal error bars represent standard deviation.

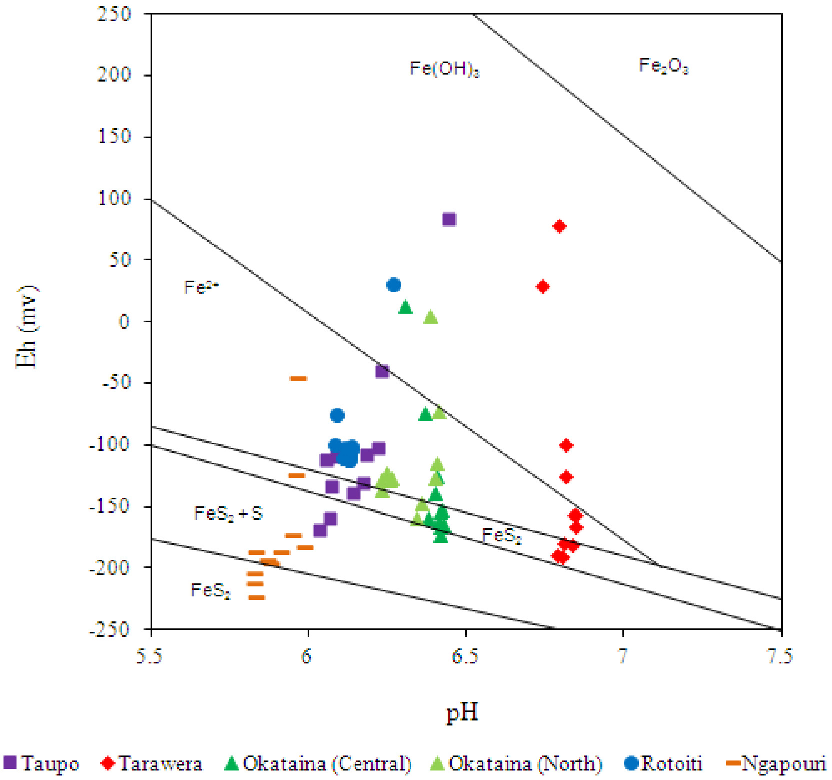

**Figure 4.6:** Eh-pH diagram of Fe and S stability at concentrations of $10^{-6}$ M showing annual average pore water data at 2 cm depth intervals from lakes Taupo, Tarawera, Okataina, Rotoiti and Ngapouri. The lines represent the boundaries between the stability fields of the chemical species as labelled.

### 4.3.3.2 Iron, Manganese and Sulfur

Pore water concentrations of iron increased down core in the study lakes with typical values ranging between 1 mg $L^{-1}$ in Lake Taupo and 8 mg $L^{-1}$ in Lake Okataina (Figure 4.7a). Lake Ngapouri had the highest concentrations of Fe, with a maximum up to 48 mg $L^{-1}$ at 20 cm depth when the lake was stratified. Manganese concentrations in the pore waters were at a maximum in the surface sediments (0-2 cm section), with the exception of Lake Tarawera which had maximum concentration in the 2-4 cm section, and Lake Ngapouri which had increasing concentration with sediment depth (Figure 4.7b). Sulfur concentrations in the pore water were maximal at the SWI or overlying hypolimnion in lakes Rotoiti and Ngapouri (Figure 4.7c). Sulfur declined rapidly in the pore water to concentrations < 2.5 mgL$^{-1}$ at 20 cm depth in all lakes. Maximum pore water concentrations were found during the stratified period for Mn and during the mixed period for Fe and S.

In the sediments the concentrations of Fe and Mn were highest in Lake Tarawera, up to 80500 µg g$^{-1}$ and 42000 µg g$^{-1}$, respectively (Figure 4.7d and e). Lowest concentrations of Fe and Mn occurred in Lake Rotoiti, up to 10500 and 760 µg g$^{-1}$, respectively. In the sediment, S typically displayed a convex curve with typical concentrations of 2000 µg g$^{-1}$, with the exception of Lake Ngapouri which had maximum concentrations in the surface sediments of 30000 µg g$^{-1}$ (Figure 4.7f).

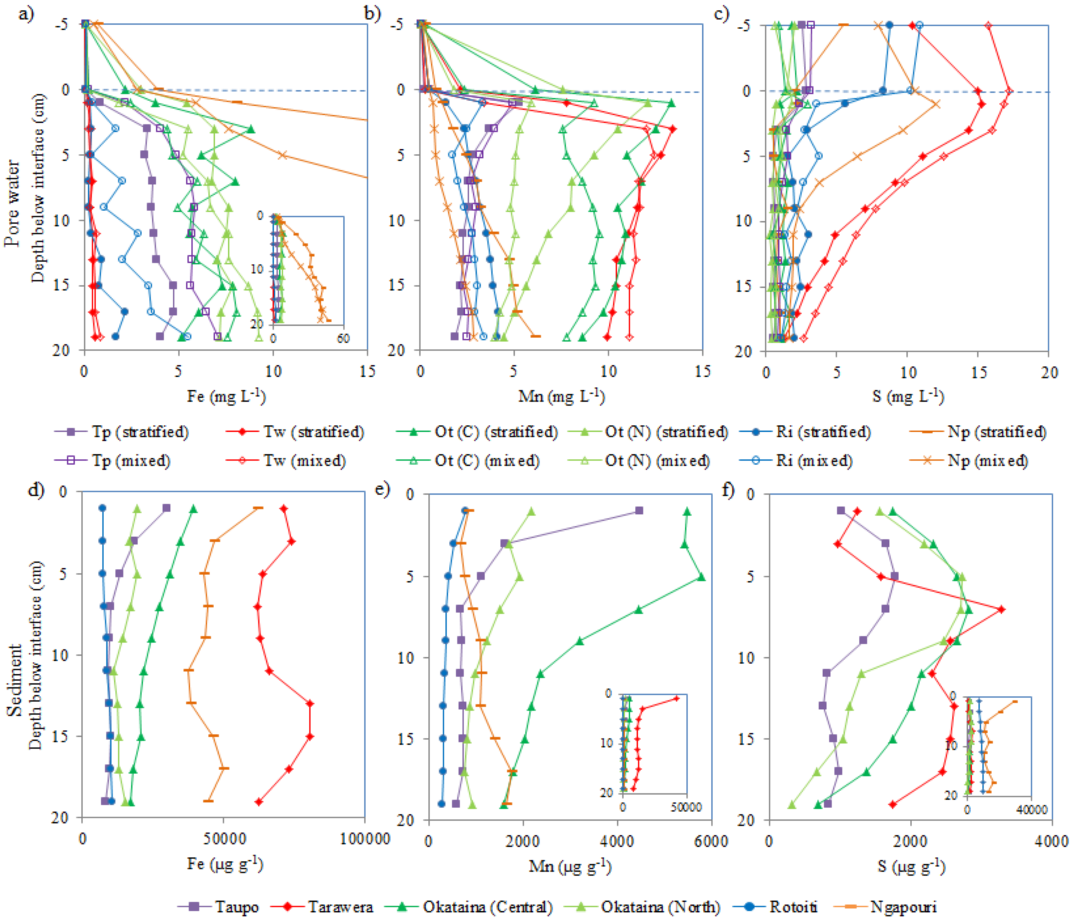

**Figure 4.7:** Average concentration of Fe, Mn and S in sediment pore water for stratified (solid symbol) and mixed water column (open symbol) (a-c) and average lake sediment concentrations (d-f) for the five study lakes. Average concentrations were calculated from 2 cm depth sections of duplicate cores sampled monthly for 12 months. Insets show pore water or sediment concentration when values far exceeded concentrations found in the other study lakes.

### 4.3.3.3 Silicon, Aluminium and Uranium

Pore water silicon concentrations in the TVZ lakes investigated typically ranged from 20 to 30 mg L$^{-1}$ at 20 cm sediment depth and decreased along diffusion gradients towards the SWI, where concentrations ranged between 0.3 to 20.5 mg L$^{-1}$ (Figure 4.8a). The oligotrophic lakes had Si concentrations ranging between 11 to 20.5 mg L$^{-1}$ at the SWI. Lake Rotoiti had much lower Si concentrations at the SWI (1.8 mg L$^{-1}$). Lake Ngapouri was similar in concentration to the oligotrophic lakes at 15.6 mg L$^{-1}$. The pore water profile in Lake Ngapouri did not exhibit a monotonic curve as in the other lakes but was more representative of a mixing line (Figure 4.8a). Silicon in the sediment was unable to be determined using the aqua regia digestion as not all silicon is digested.

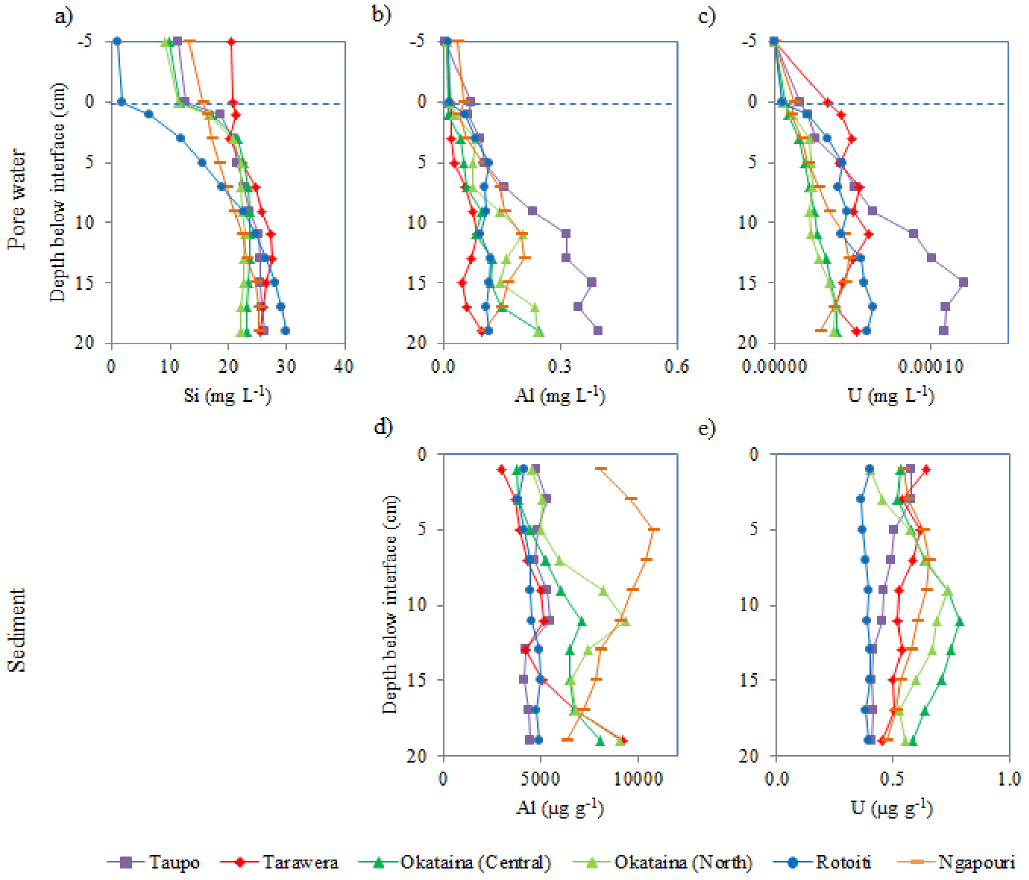

**Figure 4.8:** Average concentration of Si, Al and U in pore water (a-c) and lake sediment (d-e) for the five study lakes. Average concentrations were calculated from 2 cm depth sections of duplicate cores sampled monthly for 12 months. Silicon was not analysed for the sediments as not all Si is digested using Aqua Regia.

Aluminium concentrations were generally very low in lake waters (0.004 mg $L^{-1}$ in Lake Taupo to 0.03 mg $L^{-1}$ in Lake Ngapouri) but pore water concentrations increased with sediment depth (up to 0.4 mg $L^{-1}$ in Lake Taupo at 20 cm depth) (Figure 4.8b). With the exception of Lake Ngapouri, aluminium concentrations in the sediments were uniform (c. 5000 µg $g^{-1}$). Lakes Tarawera and Okataina showed increases up to >9000 µg $g^{-1}$ immediately below 18-20 cm depth (Figure 4.8d) where the Tarawera tephra occurred. In Lake Ngapouri the maximum aluminium concentration of 10800 µg $g^{-1}$ occurred at 4-6 cm.

Pore water concentrations of uranium showed a similar pattern to those of aluminium, ranging from 5 x $10^{-6}$ mg $L^{-1}$ (Okataina) to 34 x $10^{-6}$ mg $L^{-1}$ (Tarawera) at the SWI, and increasing with depth to range from 38 x $10^{-6}$ mg $L^{-1}$ (Okataina) to 122 x $10^{-6}$ mg $L^{-1}$ (Taupo) at 20 cm sediment depth (Figure 4.8c). Concentrations of uranium in the TVZ lake sediments were typically c. 0.5 µg $g^{-1}$, with only small variations with depth (Figure 4.8e).

#### 4.3.3.4 Phosphorus and Arsenic

Total dissolved phosphorus (TDP) concentrations in the sediment pore waters of TVZ lakes were typically less than 0.8 mg $L^{-1}$, except in Lake Rotoiti where TDP was significantly higher, up to 4.5 mg $L^{-1}$ at 20 cm depth when the lake was stratified (Figure 4.9a). Sediment concentrations were typically 2000 µg $g^{-1}$ and declined with depth from the SWI to about 500 µg $g^{-1}$ (Figure 4.9c). The most eutrophic lake, Ngapouri, had significantly higher TDP concentrations than the other TVZ lakes studied, with a maximum of 3400 µg $g^{-1}$ and declining to 2400 µg $g^{-1}$ by 20 cm sediment depth.

Arsenic concentrations in the pore waters of the study lakes were typically less than 0.4 mg $L^{-1}$ and increased with depth, except in Lake Okataina which achieved maximum concentrations at depth 2-4 cm (redox boundary) (Figure 4.9b). Lake Tarawera had a maximum arsenic concentration of 1.1 mg $L^{-1}$ at 12 cm sediment depth, well below the redox boundary. Arsenic concentrations in Lake Rotoiti slightly increased with depth throughout the 20 cm sample depth, reaching a maximum of 0.7 mg $L^{-1}$ at 20 cm. Sediment arsenic concentrations were typically < 200 µg $g^{-1}$ but increased towards the sediment surface, reaching a maximum in Lake Tarawera of 5650 µg $g^{-1}$ in the uppermost layer (Figure 4.9d). In Lake Rotoiti, however, concentrations tended to increase with depth in the sediment.

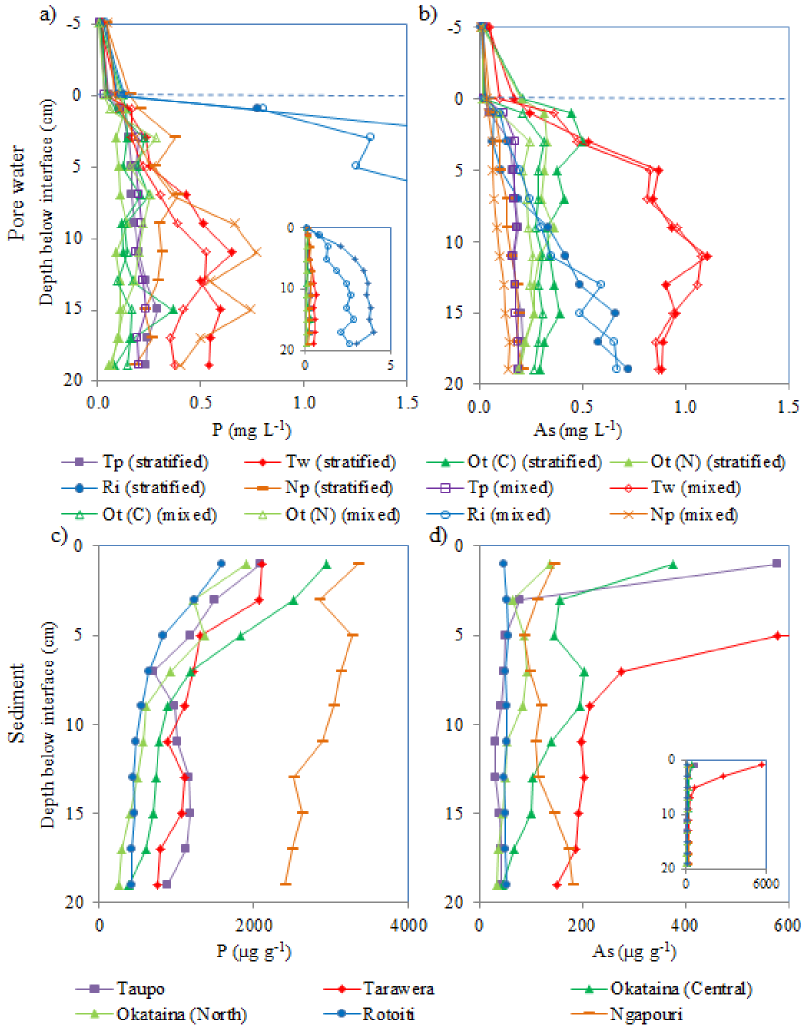

**Figure 4.9:** Average concentration of P (as total dissolved phosphorus) and As in pore water when under stratified (solid symbol) and mixed conditions (hollow symbol) (a-b) and average lake sediment concentration (c-d) for the five TVZ lakes studied. Average concentrations were calculated from 2 cm depth sections of duplicate cores sampled monthly for 12 months. Insets show pore water or sediment concentration when values far exceeded concentrations found in the other study lakes.

### 4.3.3.5 Ammonium, Nitrate and Phosphate

In the TVZ lakes, the concentration of ammonium (as $NH_4$-N) in the pore water was much higher in the eutrophic lakes (up to 12 mg $L^{-1}$) than in the oligotrophic lakes (< 3 mg $L^{-1}$) (Figure 4.10a). In all lakes the ammonium concentrations increased down-core; although in some lakes it reached a maximum within the top 20 cm and decreased slightly in concentration at greater depths. Nitrate (as $NO_3$-N) concentration gradients showed a contrasting pattern to ammonium with maxima (0.06 to 0.8 mg $L^{-1}$) occurring in the BNL and concentrations at greater depths in the sediment generally lower (0.02 – 0.5 mg $L^{-1}$, Figure 4.10b).

Dissolved reactive phosphate (DRP) concentrations were reasonably uniform over the 20 cm core depth in pore waters from Lake Taupo and Okataina, at around 0.02 and 0.03 mg $L^{-1}$, respectively (Figure 4.10c). In Lake Tarawera DRP concentrations were maximal (c. 0.2 mg $L^{-1}$) at 10 cm depth and declined to c. 0.05 mg $L^{-1}$ at the SWI. Lake Rotoiti also exhibited maximum DRP concentration (0.93 mg $L^{-1}$) below the sediment surface, at a depth of 6-8 cm and had relatively low concentrations (0.05 mg $L^{-1}$) at the SWI.

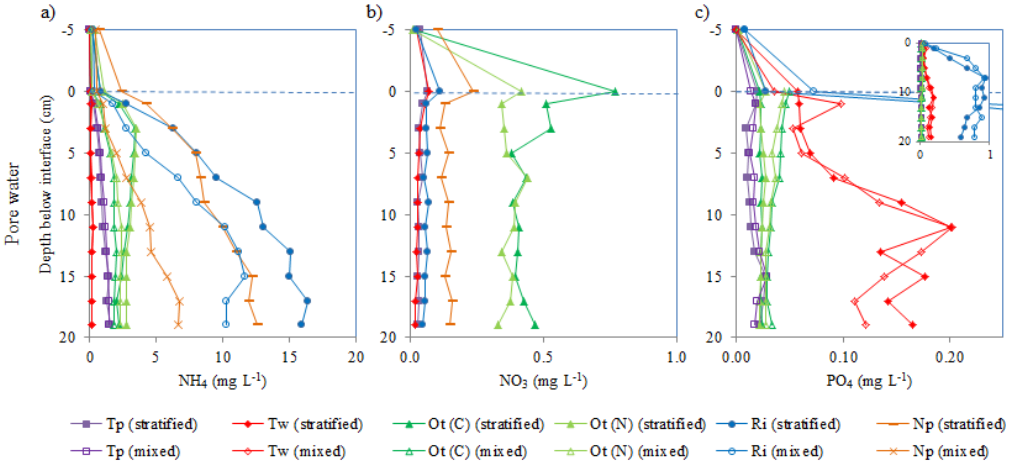

**Figure 4.10:** Average concentrations of a) $NH_4$-N b) $NO_3$-N and c) $PO_4$-P (as DRP) in the sediment pore water. Average concentrations were calculated from 2 cm depth sections of duplicate cores sampled monthly for 12 months. Where it was possible to distinguish seasonal variations in concentration these have been plotted as solid symbols for the stratified period and open symbols for the mixed period. No $PO_4$ data was available for Lake Ngapouri. Inset shows pore water concentration when values far exceed concentrations found in the other study lakes.

#### 4.3.3.6 Lithium, Boron, Sodium and Potassium

The concentration of lithium, boron and sodium in the pore water was uniform with depth in lakes Taupo (0.05, 0.2 and 15 mg L$^{-1}$), Okataina (0.06, 0.05 and 17 mg L$^{-1}$) and Ngapouri (0.01, 0.02 and 10 mg L$^{-1}$) (Figure 4.11 a-c). Lake Tarawera typically had concentrations c. ten-fold larger than the other lakes (0.5, 0.7 and 85 mg L$^{-1}$ respectively). Potassium in the pore water reached a maximum at the SWI, with concentrations up to 10 mg L$^{-1}$ in Lake Tarawera (Figure 4.11 d). The pore water profile of Li, B, Na and K in Lake Rotoiti was typical of a mixing gradient associated with concentrated geothermal fluids found at depth to the lower concentrations in overlying lake water (Figure 4.11 a-d). Concentrations in Lake Rotoiti far exceeded those found in the pore waters of the other study lakes.

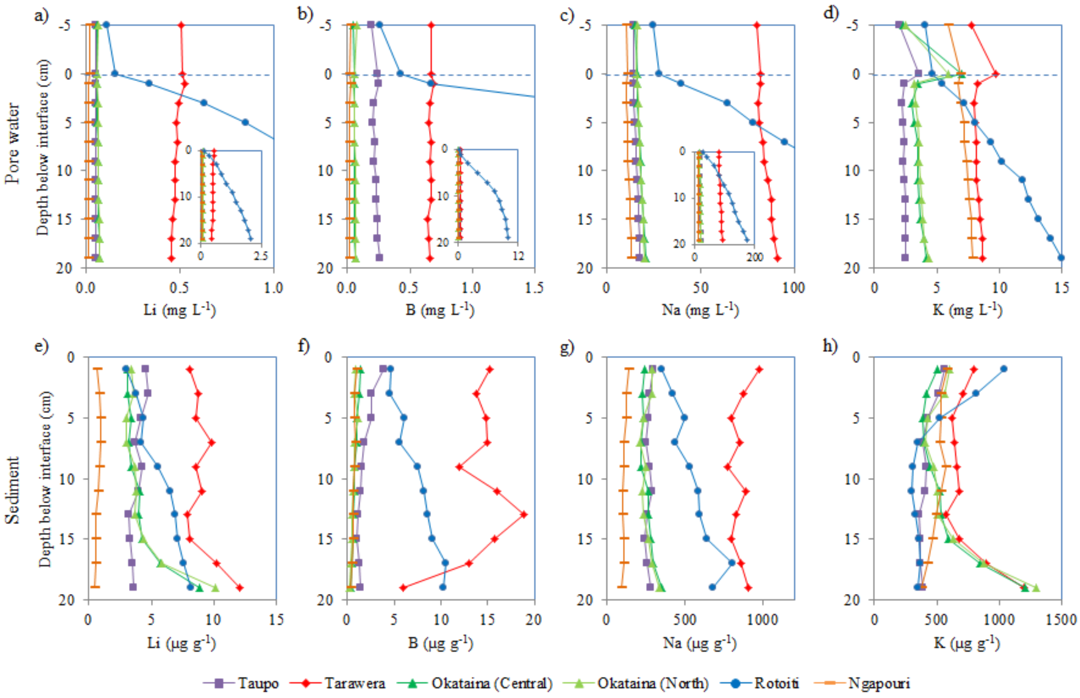

**Figure 4.11:** Average concentration of Li, B, Na and K in pore water (a-d) and lake sediment (e-h) of the five TVZ study lakes. Average concentrations were calculated from 2 cm depth sections of duplicate cores sampled monthly for 12 months. Insets show pore water concentrations when values far exceeded concentrations found in the other study lakes.

The sediments also displayed fairly uniform concentrations down-core amongst the lakes (Figure 4.11 e-h). Lake Tarawera had increased concentrations of the conservative metals in the sediment compared with the other lakes. Lakes Tarawera and Okataina exhibited an increase in Li, K and, to a lesser extent, Na at 16-20 cm where the Tarawera Tephra was located. A decrease in B occurred in Lake Tarawera within the Tarawera Tephra. The conservative elements in Lake Rotoiti sediments all increased towards the SWI.

#### 4.3.3.7 Magnesium, Calcium, Strontium and Barium

Concentrations of magnesium, calcium and strontium in the pore waters showed similar trends, increasing with depth and always exceeding the concentration of the overlying lake waters. Concentrations typically reached about two times the concentration of the lake water by 20 cm depth (Figure 4.12 a-c). Pore water concentrations of barium increased with depth in lakes Taupo, Rotoiti and Ngapouri but declined with depth in lakes Okataina and Tarawera after reaching a maximum close to the SWI (0-2 cm in Okataina and 4-6 cm in Tarawera) (Figure 4.12 d).

In the sediments, concentrations of Mg, Ca, Sr and Ba were fairly uniform, with increases at the SWI (Figure 4.12 e-h). Lakes Tarawera and Okataina showed higher concentrations of all alkaline earth metals at 16-20 cm sediment depth which corresponded to the location of the Tarawera tephra.

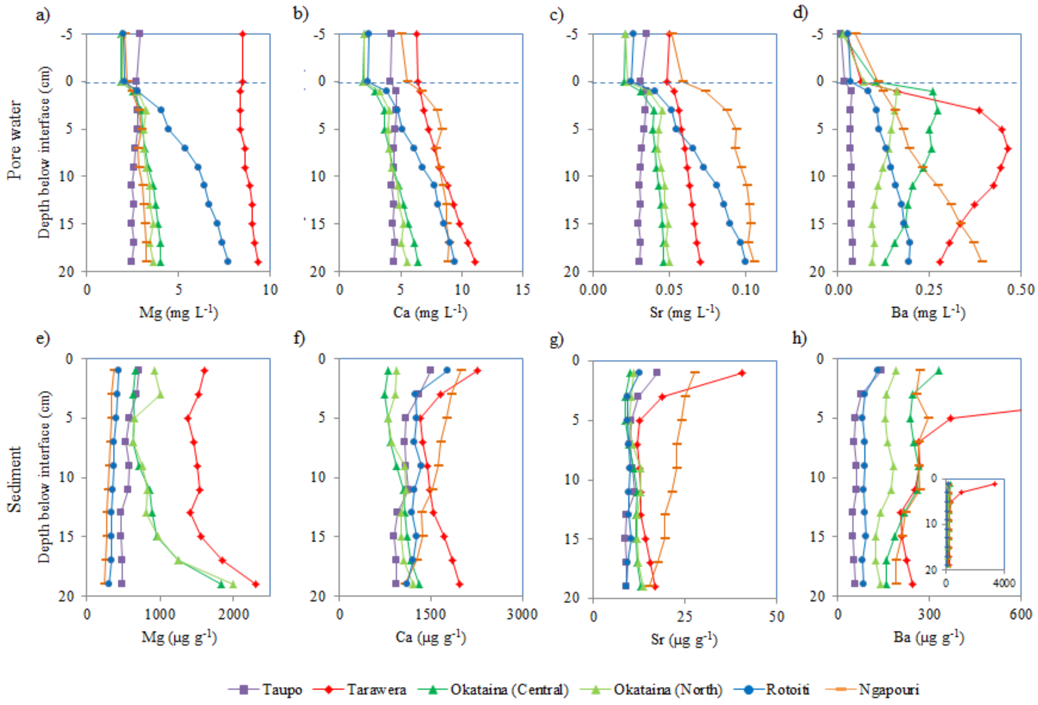

**Figure 4.12:** Average concentrations of Mg, Ca, Sr and Ba in pore water (a-d) and lake sediment (e-h) of the five TVZ study lakes. Average concentrations were calculated from 2 cm depth sections of duplicate cores sampled monthly for 12 months. Inset shows sediment concentrations when values far exceeded concentrations found in the other study lakes.

### 4.3.3.8 Copper, Zinc, Lead and Mercury

Concentrations of copper and zinc in the lake sediment were fairly uniform throughout the profile (Figure 4.13 e-f). Lake Taupo was the only lake where copper could be considered to be above background levels in both pore water (up to 0.0045 mg L$^{-1}$) and sediments (> 10 µg g$^{-1}$). Lake Ngapouri also had copper concentrations of >10 µg g$^{-1}$ in the sediments, but unlike Lake Taupo, had pore water concentrations close to detection limits (0.001 mg L$^{-1}$). Highest zinc concentrations were found in the overlying lake water, with the exception of Lake Taupo. Zinc concentrations in the pore water ranged between 0.005 and 0.012 mg L$^{-1}$ and were typically between 10 and 60 µg g$^{-1}$ in the lake sediments (Figure 4.13 b and f). Lake Ngapouri had the highest concentration of zinc in the sediments (up to 200 µg g$^{-1}$).

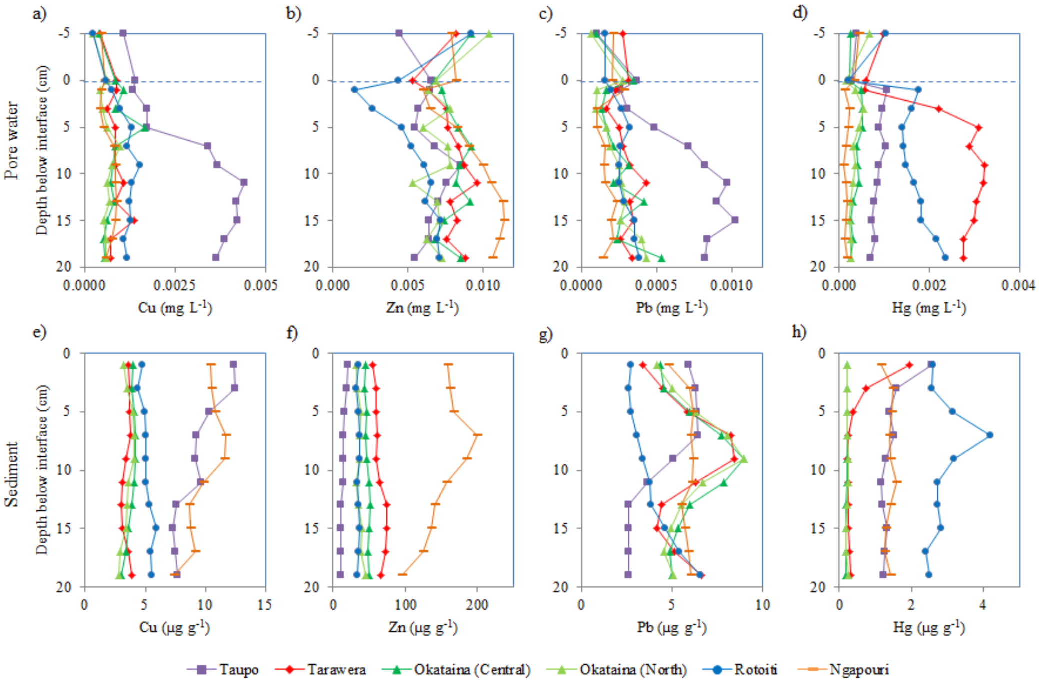

**Figure 4.13:** Average concentration of Cu, Zn, Pb and Hg in pore water (a-d) and lake sediment (e-h) of five TVZ study lakes. Average concentrations were calculated from 2 cm depth sections of duplicate cores sampled monthly for 12 months.

Pore water concentrations of lead were typically between 0.0001 and 0.0004 mg $L^{-1}$, except for Lake Taupo where concentrations were up to 0.001 mg $L^{-1}$ below the sulfate reduction zone (Figure 4.13 c). A peak in lead concentration in the sediments was clearly defined in the oligotrophic lakes, Tarawera and Okataina, from 5 µg $g^{-1}$ at 20 cm sediment depth, increasing to 8 µg $g^{-1}$ at 10 cm depth and returning to < 5 µg $g^{-1}$ at the SWI. Lake Taupo had a maximum lead concentration of 6.5 µg $g^{-1}$ at 6 cm and declined above and below this depth. Lakes Rotoiti and Ngapouri had maximum concentrations of lead at depths exceeding 20 cm (Figure 4.13 g).

Mercury concentrations in the pore waters were lowest at the SWI and increased with depth. Lakes Rotoiti and Tarawera had the highest concentrations, reaching up to 0.003 mg $L^{-1}$ in Lake Tarawera. The highest concentrations of Hg in the sediments were found in Lake Rotoiti (up to 4 ug $g^{-1}$) (Figure 4.13 h).

## 4.4 DISCUSSION

### 4.4.1 Sediment composition

TVZ lake sediments are predominantly made up of the remains of diatoms; unicellular algae in in the size range 2-200 µm. They persist due to limited degradation of the frustule, which is composed of opaline or biogenic silica ($SiO_2.nH_2O$; Round, 1990). Diatom frustules may comprise the bulk of the sediment in these lakes (see also McColl, 1972; Pickrill, 1991; Nelson and Lister, 1995; Burns et al., 1997; Pearson, 2007; Trolle et al., 2008; 2010). Sedimentation arising from cyanobacteria and other phytoplankton appears to contribute relatively small amounts of residual material to the bottom sediments, but diatom frustules remain largely intact and dominate the finer, low-density component of the sediments. Diatom productivity is dependent on season, and highest water column concentrations are commonly found in autumn through to early spring (Cassie-Cooper, 1996), often associated with water column turnover and mixing (Vincent et al. 1984). Dissolution of diatom frustules in the TVZ lakes appears to have been limited by moderate levels of silicic acid arising from volcanic material deposited in the TVZ lakes, the discharge of silica-laden geothermal waters and ignimbrite aquifers that contribute groundwater with high silica concentrations (Rawlence, 1984; 1985).

Organic matter commonly constitutes a minor but important fraction of lake sediments (Meyers and Ishiwatari, 1993). It originates from the complex mixture of lipids, carbohydrates, proteins, and other substances produced by organisms resident in the lakes, as well as the material brought into the lakes from their catchments (Meyers and Lallier-Verges, 1999). Loss on ignition of surface sediment samples from each of the TVZ lakes produced a carbon content c. 5% for the oligotrophic lakes and up 13% in the most eutrophic lake, Ngapouri (Figure 4.4c). Carbonates have little or no contribution to the loss on ignition due to the dominance of rhyolitic volcanics in the TVZ, resulting in low levels of calcium in the lake water ($< 8.3$ mg $L^{-1}$) (McColl, 1972).

Ejecta from the Tarawera eruption (1886 AD) were clearly observed in the Lake Tarawera, Okataina and Rotoiti core samples. The Tarawera Tephra is evident as a grey layer of volcanic mud. It is often observed as two distinct layers; an upper mud layer of Rotomahana Mud (1886) which covered the landscape as superheated sediment was forced from Lake Rotomahana during the eruption, and a thinner, gritty, black basaltic scoria along the base of the Rotomahana Mud known as Tarawera Ash (Pullar and Kennedy, 1981). The Tarawera Tephra was typically 2-10 cm thick and found 16 to 20 cm below the SWI of lakes Tarawera, Okataina and at 30 cm depth in Lake Rotoiti (Figure 4.3).

### 4.4.2 Sediment-pore water interactions

Lakes are very dynamic systems, where inputs, mixing and removal processes can vary substantially on different time scales. There are a variety of competing scavenging phases (detrital particles, phytoplankton and authigenic precipitates) as well as variations in the chemical composition of the lake water. The SWI is characterised by a substantial increase in particle concentration and a decrease in transport rates compared with the overlying lake water. The SWI sits within the BNL and the bottom sediments where the rates of a number of processes are elevated and result in high spatial variability including oxidation of organic matter and consequential reduction of electron acceptors ($Fe^{3+}$, $Mn^{4+}$, $SO_4^{2-}$), changes in sulfide concentrations affecting the stability of chalcophiles (Cu, Zn, Pb, Hg), changes in pH specifically affecting the stability of hydroxides, changes in $P_{CO_2}$, and kinetically-limited reactions. It is generally difficult to distinguish between diffusion across the SWI and dissolution of settling particles as the source of increases in concentrations of trace elements within the BNL (Hamilton-Taylor and Davison, 1995). In addition to sediment diagenesis there may be advection and mixing of waters of markedly different composition associated with inputs such as geothermal fluids, groundwater and lake water.

#### 4.4.2.1 Oxidation and reduction of Fe, Mn and S

The redox behaviour of iron and manganese in lakes has been comprehensively reviewed (e.g., Davison, 1993; Hamilton-Taylor and Davison, 1995) along with the role of iron (Davison and De Vitre, 1992) and manganese (De Vitre and Davison, 1993) particulates in freshwater and the mechanisms of iron redox transformations (Stumm and Sulzberger, 1992). Iron and manganese, in well-oxygenated water, are present as stable hydrolysed oxide colloids or particulates, and are found in their higher oxidation state ($Fe^{3+}$ and $Mn^{3+/4+}$). In the absence of oxygen, lower redox states occur ($Fe^{2+}$ and $Mn^{2+}$) (Bortleson and Lee, 1974; Hamilton-Taylor and Davison, 1995). Sulfate, which is present at moderate concentrations in waters of many of the lakes, is reduced to sulfide which strongly affects the speciation and solubility of numerous trace elements, the most significant of which is Fe.

There appear to be two phases of iron formation in the sediment; an oxide/hydroxide phase in the oxygenated sediments and a sulfide phase deeper within the sediments where the sediments are anoxic (Figure 4.6). It would be anticipated that development of an anoxic hypolimnion or BNL would result in significant seasonal changes in Eh and pH in the upper sediment pore waters near the SWI. With the loss of dissolved oxygen, Eh would be expected to become more negative and the increased $P_{CO_2}$ would result in a reduction in pH.

The Eh of Lake Rotoiti pore water showed little variation with depth, reflecting the predominance of geothermal fluids advected through the sediment from beneath the lake, which maintain a controlling influence on the redox chemistry until close to the SWI. In eutrophic lakes where bottom waters became anoxic (Ngapouri and Rotoiti), the onset of stratification was generally associated with a decrease in pH in the pore waters but an increase in Eh in deeper pore waters, although remaining within the $Fe^{2+}$ field of the Eh pH diagram (Figure 4.6), whilst both pH and Eh in the overlying water (1 m above the SWI) increased. In Okataina, where anoxia occurred in the bottom waters at the end of stratification, both pH and Eh decreased with anoxia, taking the waters from the $Fe(OH)_3$ to the $Fe^{2+}$ field (Figure 4.6). In the oligotrophic lakes, where the hypolimnion remained oxygenated (Taupo and Tarawera), Eh varied little at the

SWI but in deeper pore waters it became more positive, similar to the lakes where hypolimnetic deoxygenation was observed.

In the oligotrophic TVZ lakes, Taupo and Tarawera, oxygen diffuses several cm into the sediments from the overlying water column. Organic matter incorporated into the sediments is first metabolised utilizing dissolved oxygen, when present, followed by a succession of electron acceptors. Reduction of nitrate and sedimentary manganese then takes place followed by iron and sulfate (Canfield and Thamdrup, 2009). As sulfide is produced within the pore waters it reacts with ferrous ions and likely precipitates as pyrite, preventing increases in iron concentrations that would normally be associated with iron reduction (Figure 4.6 and 4.7). Manganese II oxidizes on contact with oxygenated pore waters and precipitates, and strongly absorbs negatively-charged phosphate and arsenate (discussed further in section 4.2.3). Both iron and manganese can be lost from solution to re-oxidation near the SWI while the hypolimnion is oxic, generating the upper light-brown layer visible in cores from lakes Taupo and Tarawera (Figure 4.3a and b). Lakes Okataina, Rotoiti and Ngapouri are sufficiently eutrophic that the hypolimnion becomes seasonally anoxic, allowing significant quantities of manganese and iron to be recycled seasonally into the water column during stratification, with reprecipitation back to the sediments as these elements are re-oxidised during winter mixing.

Reduction to sulfide, within the sediments, removes sulfur from the pore waters and is partially replaced by sulfate diffusing from the overlying hypolimnion or generated from metabolism of particulates at the SWI, resulting in decreasing pore water concentrations with depth (Holmer and Storkholm, 2001). In our study lakes, pore water concentrations of S often decreased to close to detection limits (0.1 mg $L^{-1}$) with increasing depth. The availability of sulfur is strongly dependent on discharges into the lakes. Acid sulfate geothermal springs are common in several of the TVZ lake catchments (e.g., Tarawera, Rotoiti and Ngapouri) (Timperley and Vigor-Brown, 1986). The concentration of sulfate in the near-surface pore waters often exceeds that of the overlying lake water, indicating that some sulfur is introduced into the sediment as particulates and is subsequently released through diagenesis. Sulfur concentrations in both pore waters and the hypolimnion are significantly higher when the hypolimnion is oxic than when it is anoxic (Figure 4.7c), indicating that sulfate reduction takes place in both the hypolimnion and in the sediments. Eutrophic Lake Ngapouri, where there is an extended period of hypolimnetic anoxia, showed marked increases in sulfur concentrations in sediment pore waters and in the hypolimnion during mixed conditions. The precipitation of sulfide from the pore waters in the other lakes increases sediment concentrations of sulphur below the zone of sulfate reduction (Figure 4.7f).

Reduction of ferric and manganic species in the sediments results in increasing concentrations of ferrous and manganous ions in pore waters near the SWI (Figure 4.7). Ferrous ion concentrations are moderated by sulfide precipitation in lakes where there are high sulfate concentrations in pore water. Thus, there is an increase in concentrations of iron and sulfur in the sediments several cm below the SWI, and often very low concentrations of iron in the pore waters, e.g., lakes Tarawera and Rotoiti (Figure 4.7). In lakes where the hypolimnion is anoxic, sulfate reduction may continue in the water column and result in precipitation of sulfides (Davison et al., 1992). In lakes where sulfate concentrations are low and ferrous iron production exceeds sulfide production, the behaviour of iron is dominated by the precipitation of oxides and hydroxides. For example, in pore waters of lakes Taupo and Okataina ferrous ion concentrations in the pore waters are high except near the SWI where they can decrease abruptly when there is overlying oxygenated water (Figure 4.7). As manganese sulfide is considerably more soluble than pyrite (Davison, 1991; Davison, 1993), ferrous ions tend to consume all of the sulfide produced, allowing manganous to diffuse towards the SWI where it is oxidised and precipitates as oxides/hydroxides. With the exception of Lake Ngapouri, manganese concentrations in pore waters are high until contact with oxidised upper sediment layers whereupon they decrease rapidly. By contrast, concentrations in the sediments are maximal at or near the sediment surface (Figure 4.7) due to net upward movement of manganese within the sediment pore waters. Manganous ions produced under anoxic conditions in the pore waters may be oxidised and precipitate as manganic oxides/hydroxides at higher levels when the overlying water is sufficiently well oxygenated. Lake Ngapouri differs from the other lakes in that Mn concentrations are very low, and the transport of manganese through the sediments appears to be dominated by a source below the depth cored rather than through recycling within the upper sediment layers. Thus Mn concentrations in sediment and pore water increase with depth.

#### 4.4.2.2 Weathering of Si, Al and U

Soils in the Rotorua region are predominantly amorphous aluminosilicate glass (from the rhyolitic tephra), which is readily weathered and contributes large silicon loads to the lakes (McColl, 1972). Concentrations of silicon in streams draining into the region's largest lake, Rotorua, range between 23 and 43 mg Si $L^{-1}$ (Morgenstern et al., 2005), and similar concentrations would be expected in streams draining other TVZ lakes. Geothermal fluids in the TVZ region have considerably higher silicon concentrations, typically > 200 mg Si $L^{-1}$ (Giggenbach and Glover, 1992). In the lakes, Si is consumed by diatoms which subsequently sediment out, resulting in lower concentrations in lake waters than in the stream inflows.

Dissolved silicon was abundant in the study lakes (9 - 20.5 mg $L^{-1}$), except Lake Rotoiti (0.3 mg $L^{-1}$). Rotoiti received (prior to construction of a diversion wall in 2008; Hamilton et al., 2009) about half of its water from Lake Rotorua where concentrations of Si are c. 0.5 mg $L^{-1}$ (L. Pearson, unpublished data). As a result, Lake Rotoiti inherited both a high nutrient (nitrogen and phosphorus) load but Si levels that may have been sufficiently low to limit diatom productivity (Redfield, 1958). In Lake Ngapouri, the hypolimnion silicon concentration has increased from < 2 mg $L^{-1}$ in 1970-71 (McColl, 1972) to 13.25 mg $L^{-1}$ in 2008 (this study). This change appears to be associated with increasing eutrophication and dominance by cyanobacteria, likely displacing diatoms. In oligotrophic lakes where there is a significant external silicon source contributed by geothermal discharges, but insufficient phosphorus and nitrogen to promote substantial diatom growth, silicon concentrations can remain high within the water column, as observed in our study in lakes Taupo, Tarawera and Okataina.

The weathering of alumnosilicate glass, from tephric deposits in the catchment or from direct air fall of tephric sediments will be associated with inputs of aluminium to lakes. Analysis of the sediments in this study, including diatomaceous oozes, show the presence of aluminium in all facies supporting the hypothesis that aluminium is closely involved in biogochemical cycles (Exley, 2003). Diagenesis of the diatomaceous oozes probably also releases aluminium to the pore waters but little remains in solution as most species are insoluble, especially oxides and hydroxides at near-neutral pH. The concentrations found in TVZ lakes exceed the solubility product of gibbsite ($Al(OH)_3$) as Al concentrations are at least 100 times greater than saturation at these pH levels (May et al., 1979) , and indicate that the majority of the aluminium is present as colloids. It is likely that most of the aluminium precipitates near the SWI probably as aluminosilicates, as suggested by the close relationship between Al and Si ($r = 0.69\text{-}0.98$, $p<0.01$; Supplementary data B).

The increase in uranium pore water concentrations with depth suggests a dissolution process from the sediments. The near-constant concentrations in the sediment show the dissolution process is insufficient to alter its bulk composition. Similar concentrations of uranium have been reported by Nagao et al. (2002) who found pore water concentrations of $69\text{-}145 \times 10^{-6}$ mg $L^{-1}$ and sediment concentrations between 0.5 and 4 µg $g^{-1}$ in a number of Japanese lakes. Chappaz et al. (2010) reported that once uranium is released to the pore water, it is associated with the remobilisation and recycling of iron oxyhydroxides from the sediments to the overlying water column. With reoxidation of iron following winter mixing the uranium is recycled to the sediments. Our finding of significant correlations of uranium with aluminium ($r = 0.83\text{-}0.99$, $p<0.001$ except in Lake Tarawera; Supplementary data B) suggests that uranium is also sourced from the weathering of the volcanic glass and is removed from the pore waters along with aluminium, iron ($r = 0.71\text{-}0.90$, $p<0.01$ except in Lake Tarawera; Supplementary data B) and manganese ($r = -0.88$ to $-0.95$, $p<0.001$ in oligotrophic lakes and $r = 0.83$, $p<0.01$ in eutrophic lakes; Supplementary data B).

#### 4.3.2.3 Absorbable polyoxides of P and As

Lakes in the TVZ receive naturally high phosphorus inputs from edaphic sources (tephras) and ignimbrite aquifers that contribute groundwater, the volumetrically dominant inflow in this region (White, 1983). The behaviour of P is complicated in lakes as it is both transported from the epilimnion to the sediments by settling particulates from organic and inorganic sources, and released back into solution as particulate organic matter (POM) undergoes diagenesis (Meyers and Ishiwatari, 1993) or with dissolution from inorganic sediments (Søndergaard et al., 2003). Oxy-hydroxides can remove P from the water column by adsorbing it onto inorganic particle surfaces coated with Fe, Mn and Al. Reducing conditions within the sediments and in anoxic hypolimnia can result in Fe and Mn remobilization followed by reprecipitation at the oxic boundary (Søndergaard et al., 2003). When the Fe or Mn is remobilized P is also returned to an aqueous state. A particular difficulty with interpreting the behaviour of P is its tendency to be associated with Fe, Mn and Al colloids which pass through standard filters used to analytically differentiate ‘dissolved’ and ‘particulate’ species (e.g. a 0.45 μm glass fibre filter) (Sheldon, 1972; Town and Filella, 2002; Kammer et al., 2003).

Concentrations of TDP in the TVZ lake sediments are similar to (Trolle et al. 2008; 2010), or lower than those of many other lakes (e.g., Bortleson and Lee, 1974; Sondergaard et al., 2003), which may reflect the diluting effect brought about by abundant diatom frustules within the sediments. Deeper within the sediments formation of authigenic minerals, such as vivianite ($Fe_3(PO_4)_2$), can remove phosphate from solution. Vivianite formation may occur in anoxic lake sediments when there is insufficient sulfate for pyrite formation but when decomposition of organic matter continues to liberate ferrous iron. The formation of vivianite in Lake Greifensee, Switzerland has been well documented by Emerson and Widmer (1978). The net result of the competing sources and sinks of phosphate are pore water total phosphorus concentrations that vary considerably with depth in individual lakes as well as amongst lakes (Figure 4.9a). Maxima of pore water TDP may occur at depths >10 cm; by contrast TDP concentrations in the sediments are often maximal at the SWI. With continued sedimentation much of the newly buried phosphorus has its iron or manganese oxide binders reduced to soluble forms that are then remobilised and move towards the SWI to be either recycled or to diffuse down their respective concentration gradients.

In the TVZ lake sediments both the TDP and the organic carbon content decrease with depth (Figures 4.9c and 4.4c), but phosphorus decreases to a greater extent than carbon suggesting that part of the phosphorus source is organic and partly adsorbed onto mineral surfaces. The pore water concentrations increase with depth, indicating upward mobility as phosphorus is recycled back to the lake. The most eutrophic lake, Ngapouri, had the highest sediment phosphorus concentration, whereas Rotoiti, which is also eutrophic, had the lowest concentration in the sediment. However, the pore water phosphorus concentration in Lake Rotoiti far exceeded that of any other lakes studied. The difference between Lake Ngapouri and Lake Rotoiti appears to be related to the respective ferrous ion concentrations in the pore waters, with vivianite precipitation a likely sink for phosphorus in Lake Ngapouri.

Arsenic commonly occurs in two oxidation states, $As^{3+}$ and $As^{5+}$, whose presence in lakes is commonly regulated by the biogeochemical cycling coupled to that of Fe, S and organic carbon (McCreadie et al., 2000; Couture et al., 2010). Aggett et al. (1985; 1986; 1988) have examined the biogeochemical cycling of arsenic based mostly on observations at Lake Ohakuri, New Zealand, a seasonally anoxic lake receiving high arsenic inputs from geothermal sources. The behaviour of As in this lake was found to be closely linked to that of iron and manganese oxides and hydroxides, in a similar process to phosphorus. Arsenic can also be mobilised microbiologically (Cullen and Reimer, 1989). In manganese-rich lakes, redox cycling of arsenic occurs where the redox boundary lies within the sediment column, in association with the reductive dissolution and re-precipitation of oxides (Farmer and Lovell, 1986; Anderson and Bruland, 1991). The strong correlations between arsenic concentrations and iron ($r = 0.81$ to $0.97$, $p<0.01$ except in Lake Okataina; Supplementary data 1) and manganese ($r = -0.92$, $p<0.001$ in Taupo, $r = 0.98$ and $0.97$, $p<0.001$ in lakes Rotoiti and Ngapouri, respectively; Supplementary data B) in the TVZ lake pore waters indicate that arsenic may be sorbed to iron and manganese oxy-hydroxides and subsequently released. As has been observed in many other lakes, iron and manganese are remobilized by chemical reduction (Aggett and O’Brien, 1985; Aggett and Kriegman, 1988; Cullen and Reiner, 1989; Anderson and Bruland, 1991; McCreadie et al., 2000). Lake Rotoiti is an exception in that the flow of geothermal fluids from beneath the sediment resulted in As concentrations that were a good fit to a mixing line.

#### 4.3.2.4 Remineralisation of $NH_4$, $NO_3$ and $PO_4$

Vertical profiles of C, N and P in lake sediments showed that concentrations were generally higher in the uppermost recently-deposited sediment strata (Figure 4.4c and 4.10), driven largely by natural diagenetic processes such as the flux of organic matter, burial, breakdown of organic matter and bioturbation, rather than eutrophication alone (Trolle et al., 2010). The source of the ammonium is nitrogen contained in organic matter, which is remineralised in the sediments and migrates along concentration gradients. The concentrations observed depend on the ratio of deposition of organic matter to that of inorganic sediment (clastics, diatom frustules, etc.) and the diffusion of the remineralised ammonium along its concentration gradient. If organic sedimentation rates increase, ammonium production rates in surficial sediments will also increase and some of the remineralised ammonium will diffuse, both downwards into deeper pore waters as well as upwards to the overlying lake water. Therefore, internal nutrient loading from the remineralisation of organic matter directly affects lake water nutrient concentrations (Marsden, 1989; Søndergard et al., 2003; Jeppesen et al., 2005). The presence of nitrate is reliant on sufficiently well-oxidised conditions to allow sufficient formation of nitrate from ammonium through nitrification to prevent nitrate reduction resulting from denitrification.

Ammonium concentrations in pore waters showed strong seasonal changes which were greatest in the most eutrophic lake (Ngapouri). In Lake Ngapouri, concentrations during the stratified period (with an anoxic hypolimnion) were approximately twice those of the mixed period (with oxygen present through the depth profile; Figure 4.2). This lake shows large changes in Eh between stratified and mixed periods. We hypothesise that advection of cold, dense bottom waters into the sediment in winter may displace the existing reduced pore waters, leading to lower ammonium concentrations in the sediment pore waters.

Phosphorus concentrations in the sediments decrease with depth but at a far greater rate than those of organic carbon (Figure 4.9c and 4.4c), suggesting that phosphorus is being accumulated in the near-surface sediments from processes other than sedimentation of particulate organic matter. Concentrations of TDP and DRP in the pore water increase with depth but the proportion of non-reactive P (i.e. TDP - DRP) increases with depth, with DRP constituting between 38-75% of the TDP in the BNL to 11-50% at depths greater than 4 cm (Figure 4.14a). The increasing proportion of non-reactive P (Figure 4.14b) indicates that most of the remobilised phosphorus is in the form of colloids, polyphosphates or organic phosphates (McKelvie et al., 1995). Some of the remobilised P diffuses into the overlying lake water but most is reincorporated into the upper few cm of the sediment column.

In anoxic waters, which are typically rich in ferrous ion, it is difficult to manipulate samples without causing precipitation of ferric oxides and hydroxides, which results in loss of DRP. This underestimation of reactive P has been shown to be as high as 40% within 2 h of sample aeration (Nürnberg, 1984b). It was observed that an iron hydroxide floc developed in the Lake Ngapouri pore water samples during freezing for storage prior to nutrient analysis. Iron precipitated from these solutions likely removed phosphate from solution and consequently these samples were not analysed for DRP. Total dissolved phosphorus analysed by ICP-MS was not affected as the samples were acidified immediately after filtering.

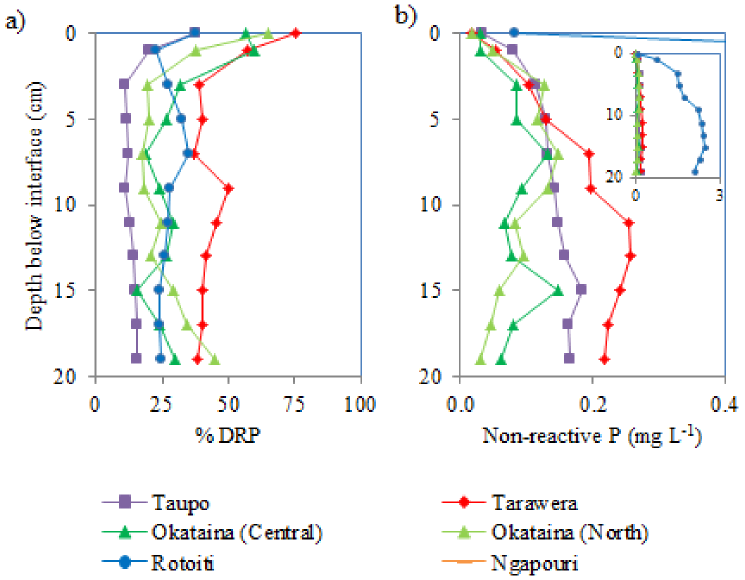

**Figure 4.14:** a) Average percentage of dissolved reactive phosphorus of total dissolved phosphorus and b) average non-reactive P (mg $L^{-1}$) in the pore waters of selected TVZ lakes. Average concentrations were calculated from 2 cm depth sections of duplicate cores sampled monthly for 12 months. Non-reactive P was calculated from TDP-DRP. Insets show pore water when values far exceed concentrations found in the other study lakes.

### 4.4.2.5 Conservative elements (Li, B, Na, K)

The alkali elements (Li, Na and K) and B are generally found in volcanic-derived rocks, sediments and in tephra. Their origin in lakes is likely to be from weathering in the surrounding catchment, although high concentrations of these elements also occur in geothermal waters. Timperley and Vigor-Brown (1985) found that in Lake Taupo large fluxes of sodium were derived from pumice. Volcanic glass, particularly rhyolite, has a tendency to hydrolyse in the presence of water. Hence it is probable that pumice from the surrounding ignimbrites and other pyroclastic material undergo some degree of dissolution by weathering, leading to slight increases in concentration of the conservative elements with depth in the sediment. In lakes which have significant geothermal discharges within the catchment, such as Lake Tarawera, the concentrations of conservative elements tended to be high in the water column and the underlying pore waters. A change in the ratio of geothermal inflows to other inflows would likely produce a break in the slope of the vertical pore water concentration gradients. A small change in slope in the Li, B and Si pore water gradients indicates that a recent increase in geothermal inputs relative to other discharges may have occurred in Lake Tarawera. The direct discharge of geothermal fluids through the sediments, as is the case in Lake Rotoiti, results in a continuous increase in concentration with depth to produce gradients that lie along a mixing line between the overlying lake water and the geothermal source (Figure 4.11). Potassium is an exception to this generalisation of conservative element behaviour, with maximum pore water concentrations at the SWI, except where geothermal fluid flow dominates (Lake Rotoiti) (Figure 4.11d). Surficial sediments are also enriched in potassium suggesting that it is being weathered from particulates supplied to the BNL. Catchment erosion of the Tarawera Tephra, which contains much higher K concentrations than the bulk of the sediment, could be the source of the additional K. The remainder of the conservative elements (Li, B and Na) generally showed little change in concentration through the sediment profile and the pore waters showed similar concentrations to the overlying lake water. This suggests a continuous supply to the lakes, with little diagenesis.

#### 4.4.2.6 Alkaline earth metals (Mg, Ca, Sr, Ba)

The alkaline earth elements Mg, Ca, Sr, Ba are constituents of silicate minerals and typically have low concentrations in geothermal waters. As the Taupo Volcanic Zone is almost devoid of calcareous minerals, the concentrations of calcium in these lakes are low compared to lakes in most other parts of the world (e.g. Faure et al., 1967). Alkaline earth elements may be stripped from the water column by settling particulates. Biogenic material may also be an important influence on Ca cycling; for example, ostracod species with calcareous carapaces are common in New Zealand lakes (Chapman, 1963; Barclay, 1968; Chapman et al., 1985), and molluscs and fish otoliths also contain Ca (Farrell and Campana, 1996). Calcareous materials incorporate Mg and Sr along with Ca. As a result when calcareous particles, which are especially prone to protonation from carbon dioxide produced within the sediments during diagenesis (Stumm and Morgan, 1981), dissolve, they release Ca, Mg and Sr into the pore waters (Figure 4.12). Strong correlations occur between Ca, Mg and Sr in all lakes, with r values between 0.8 and 1 ($p<0.01$) (Supplementary data B). With increasing eutrophication the ratio of Sr to Ca increases as Ca is preferentially removed from the water column through biogenic uptake.

Although Ba is also an alkaline earth element its diagenetic behaviour differs from that of Mg, Ca and Sr (Figure 4.12d). Barium concentrations are much greater at the sediment surface than deeper within the sediments. Pore water concentrations increase markedly with depth. The pattern of this increase is dependent on the chemistry of the overlying lake water, suggesting that the Ba is transported to the sediments as barite and dissolved once reduction of pore water sulfate has reduced the sulfate ion activity to below the solubility product of barite. The solubilised Ba can either diffuse back into the overlying lake water or be incorporated into new mineral phases at greater depth. As a result Ba is recycled back into the lake waters more efficiently than other alkaline earth elements.

#### 4.4.2.7 Sulfide-controlled elements (Cu, Zn, Pb, Hg)

The occurrence of sulfide strongly affects the speciation and solubility of numerous trace elements including Cu, Zn, Pb and Hg. Chalcophile elements are likely bound to algal material (and other mineral components of SPM) in the epilimnion due to both uptake and adsorption, and may be transported to the sediments as the biogenic matter dies and sediments out. The combination of sulfate in the lake water and abundant organic carbon in the sediments leads to sulfate reduction in upper sediment layers with subsequent precipitation of insoluble sulfides. This limits the concentration of chalcophile elements in pore waters until the sulfide is removed, resulting in pore water concentrations being controlled by the water chemistry and not by the concentration of the element in the sediment (Figure 4.13). It is likely that chalcophilic elements undergo some degree of redox cycling, either directly or indirectly (Sigg et al., 1987; Hamilton-Taylor and Davison, 1995). Sigg et al. (1987) demonstrated the importance of binding of chalcophilic elements to settling material in Lake Zurich, where the precipitation of manganese oxides within the hypolimnion at the end of stratification provided additional sedimenting material to which chalcophilic elements were bound.

Concentrations of copper and zinc in the lake sediment are fairly uniform (Figure 4.13 e-f). Lake Taupo is the only lake where copper concentrations are elevated in both pore water (up to 0.0045 mg $L^{-1}$) and sediments (> 10 µg $g^{-1}$) relative to other lakes. Copper in the pore water in Lake Taupo is negatively correlated with sulfur ($r= -0.71$, $p <0.05$, Supplementary data B), and peak Cu (0.045 mg $L^{-1}$) occurs at a point where sulfur concentrations have decreased to near detection limits (0.7 mg $L^{-1}$). Lake Ngapouri also has Cu concentrations >10 µg $g^{-1}$ in the sediments, but unlike Lake Taupo, its pore water concentrations are close to detection limits (0.001 mg $L^{-1}$). The difference between Lake Ngapouri and Lake Taupo is the depth to which sulfides are generated in the pore waters (4 cm in Lake Taupo and >20 cm in Lake Ngapouri, Figure 4.7c). Above these depths any Cu released from particulates will be reprecipitated as copper sulfides.

Lake Ngapouri, with its catchment dominated by pastoral farming, displayed the highest concentration of zinc in the sediments (up to 200 µg $g^{-1}$) (Figure 4.13f). A significant anthropogenic addition of Zn to the lake catchment may occur through the use of zinc oxide to mitigate the effects of facial eczema in grazing animals and through the oxidation of galvanised metal structures such as fencing. Zinc is also found in pesticides and fertilizers and may be a significant component of the Zn flux to the lake (Pickrill et al., 1991). There is little change in zinc concentrations with depth in the pore waters but all lakes show a minimum in the near-surface sediments, with zinc migrating from both below and above, as zinc concentrations in the water column are generally greater than in the pore waters immediately below the SWI (Figure 4.13b). Like Cu, Zn is probably transported from the epilimnion within particulates and released within the BNL. The Zn concentrations are an order of magnitude higher than Cu in the pore water. Sulfide precipitation within the upper few cm of the sediment column removes Zn, resulting in concentration minima between 0-4 cm (Figure 4.13b). With increasing depth in the sediment sulfide generation ceases and Zn pore water concentrations increase again. Insufficient Zn is mobilised in the BNL or precipitated near the SWI to produce measurable changes of Zn in the sediment.

Natural lead concentrations in the sediments are similar to those of Cu, however the lead profile of TVZ lakes has been influenced by the addition of anthropogenic lead from the use of leaded petroleum, which reached a peak in the 1980s before being completely removed by 1996. The sediments now exhibit lead profiles dependent to a large extent on the inputs of leaded petroleum within the lakes and catchments (Pearson et al., 2010). The trophic state and redox status of the lower water layers alter sedimentation rates and vertical transport of lead in the sediments. Diagenesis results in some redistribution of lead as iron and manganese are mobilised through oxidation and are immobilised by sulfate reduction to insoluble sulfides (Pearson et al., 2010). Eutrophic lakes Rotoiti and Ngapouri have high sedimentation rates and therefore the 20 cm depth of the core was not sufficient to capture the peak in lead concentration. Pearson et al. (2010) captured a maximum lead concentration at a depth of 22 cm in Lake Rotoiti.

Mercury is widely distributed in the environment and is present naturally in aquatic ecosystems (Ullrich et al., 2001; He et al., 2007; Ethier et al., 2010; Feyte et al., 2011). The TVZ lakes have elevated concentrations of Hg in the sediment (up to 4 $\mu g\ g^{-1}$) compared with background levels, due to the elevated Hg levels in geothermal inputs. Lake Rotoiti, which discharges geothermal fluid through the sediment, has increasing pore water concentrations of Hg down-core (up 0.0025 $mg\ L^{-1}$). Lowest concentrations of pore water Hg are found at the SWI where sulfide production is highest. Concentrations of Hg in lakes Tarawera and Taupo pore water increase down-core in a similar fashion to Mn suggesting that Hg is influenced indirectly by redox cycling through adsorption onto manganese oxides ($r = 0.82$, $p < 0.01$, Supplementary data B). As a result of this, sediment concentrations of Hg peak together with Mn at the SWI in lakes where Mn is a major component of the sediment.

### 4.4.3 Diagenesis and nutrient/trace element diffusive transfers

Diffusive flux values were calculated for nutrient and element transfers between sediments and lake water based on the annual average pore water concentrations for two sediment layers; between the BNL and the 0-2 cm sediment section, and between the 0-2 cm and 2-4 cm depth core sections. A positive diffusive flux for the BNL to 0-2 cm section is indicative of an increase in concentration of the overlying lake water and vice-versa for a negative flux. A positive diffusive flux for the 0-2 cm to 2-4 cm section indicates an increase concentration in the 0-2 cm pore water layer whilst a negative flux would indicate a loss of the element to the deeper layer in the sediment.

Analysis of the elemental fluxes show four patterns of transport between the sediment and overlying lake water (Figure 4.15) and within the upper layers of the sediment (Figure 4.16). These processes are 1) transport to the lake from beneath the sediment 2) release to pore waters from within the sediment 3) redistribution within the sediment and 4) transport from the lake water above.

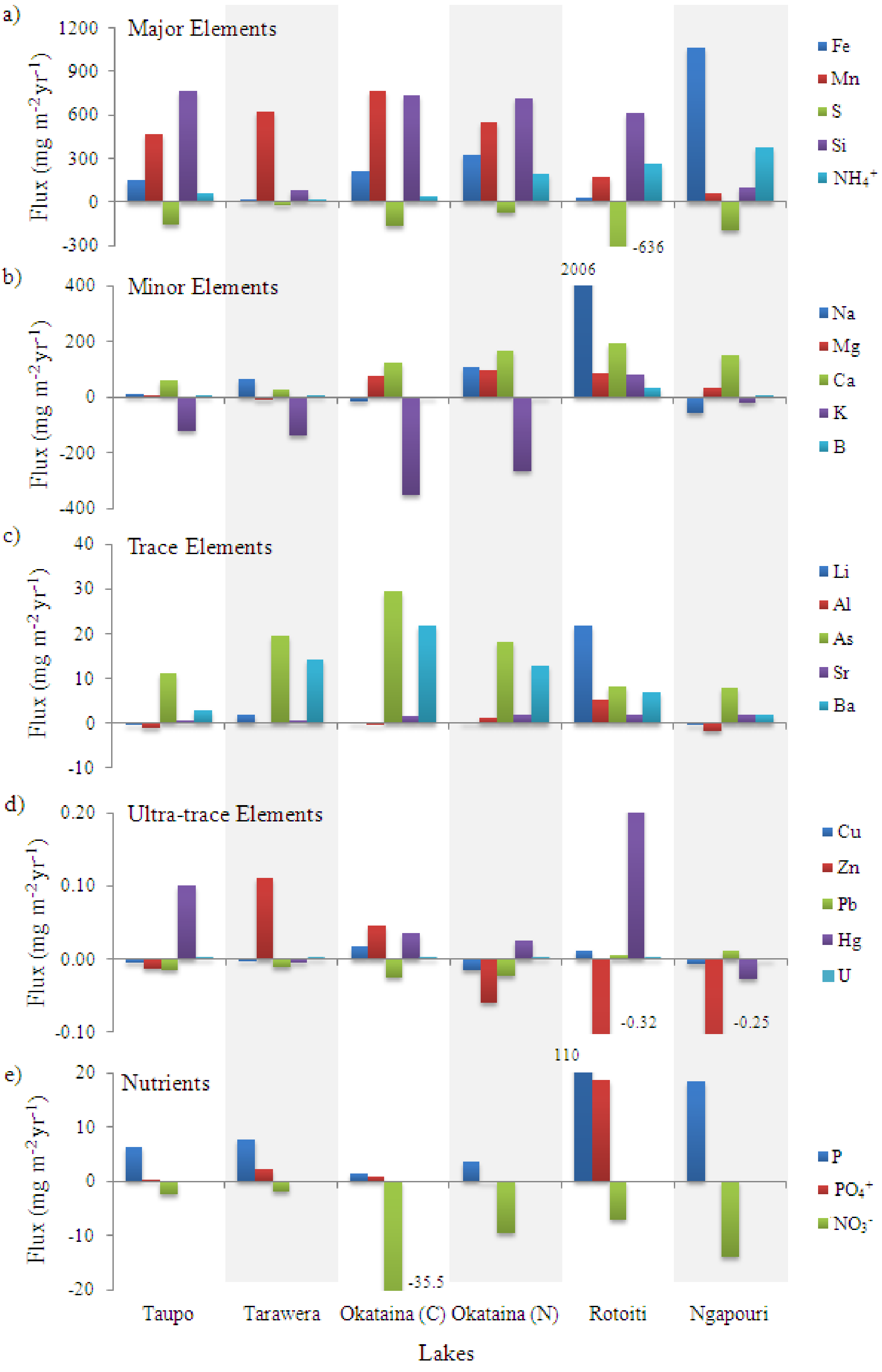

**Figure 4.15:** Diffusive fluxes from the 0-2 cm sediment section to the benthic nepheloid layer (positive) or from the BNL to 0-2cm sediments (negative) for a) major elements, b) minor elements, c) trace elements, d) ultra-trace elements and e) nutrients in the five TVZ study lakes. Note ammonium is considered a major element due to the magnitude of the diffusive flux. Phosphate in Lake Ngapouri was not measured.

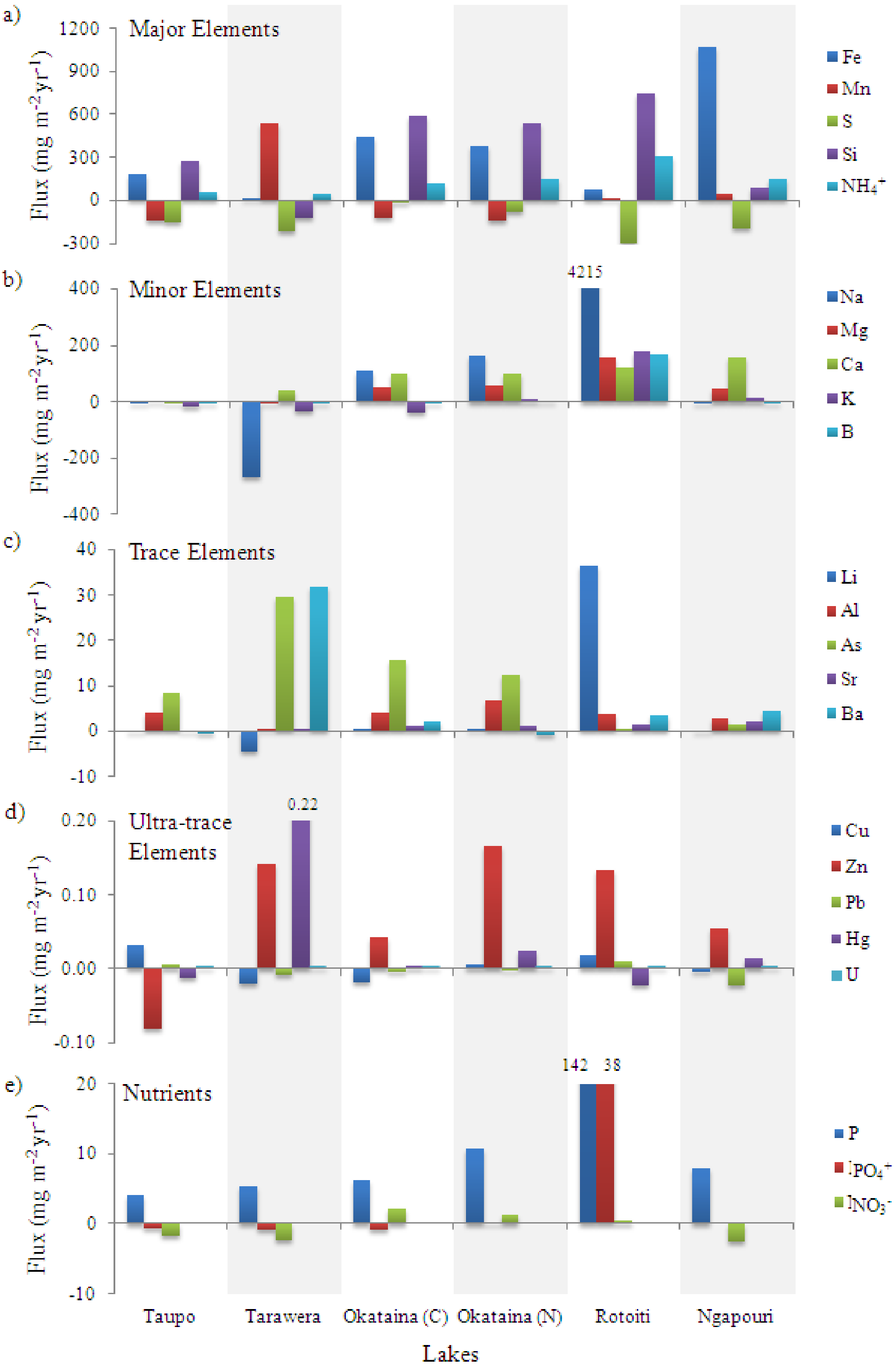

**Figure 4.16:** Diffusive flux from the 2-4 cm sediment section to the 0-2 cm sediment section (positive) or from the 0-2 cm sediment section to the 2-4 cm sediment (negative) for a) major elements, b) minor elements, c) trace elements, d) ultra-trace elements and e) nutrients in the TVZ lakes studied. Note ammonium is considered a major element due to the magnitude of the diffusive flux. Phosphate in Lake Ngapouri was not measured.

#### 4.4.3.1 Transport to the lake from beneath the sediment

The largest flux of any element was that of sodium in Lake Rotoiti associated with the transport of geothermal fluids through the bottom sediments (Figure 4.15b and 4.16b). The geothermal fluid also transports other conservative (K, B and Li) and non-conservative species (Mg, and As) to the lake as these are neither adsorbed nor generated by the sediments to any significant degree but are present at elevated concentrations in geothermal fields (Timperley and Vigor-Brown, 1986).

#### 4.4.3.2 Release to pore waters from within the sediment

Diagenesis within the sediments releases many species into the pore waters and these species then diffuse back into the overlying lake water. This is particularly evident in the case of ammonium generated from the anaerobic metabolism of organic matter and silicon generated from the dissolution of diatom frustules and rhyolitic glass shards (Figure 4.15 and 4.16). The ammonium flux is lowest in Lake Tarawera (16.5 mg $m^{-2}$ $yr^{-1}$) and increases to 377 mg $m^{-2}$ $yr^{-1}$ in the most eutrophic lake, Ngapouri. The silicon flux is controlled largely by the Si concentration of the overlying lake water, with the most oligotrophic lakes having the highest fluxes. Thus the flux is highest in Lake Taupo (768 mg $m^{-2}$ $yr^{-1}$) then lakes Okataina and Rotoiti (733 and 611 mg $m^{-2}$ $yr^{-1}$, respectively) but is much lower in Ngapouri (96 mg $m^{-2}$ $yr^{-1}$). In Lake Tarawera, diatom production is low in this nutrient-depauperate lake and, with geothermal springs discharging silicon rich waters, the Si concentrations exceed that of pore waters below 4 cm, which we interpret as the result of a recent increase in the proportion of geothermal fluid in inflows to Lake Tarawera. Diagenesis of diatom frustules results in both recycling of Si back to the overlying lake water (80 mg $m^{-2}$ $yr^{-1}$, Figure 4.15) and a calculated transient diffusive loss to the underlying sediments of 126 mg $m^{-2}$ $yr^{-1}$ to accommodate the changing lake concentration (Figure 4.16). Lake Ngapouri has the lowest Si flux due to apparent increasing eutrophication which appears to have changed the phytoplankton assemblage from one dominated by diatoms to greater prevalence of cyanobacteria (McColl, 1972). With the reduced demand from diatom growth, Si concentrations in the overlying lake water have increased from < 2.5 mg $L^{-1}$ in 1970/71 (McColl, 1972) to 12.5 mg $L^{-1}$ in this study. The pore water concentrations have also responded to the change in Si demand with reduced recycling and a change in the slope of the gradient from diffusion (as seen in Lake Rotoiti) to a linear mixing profile (Figure 4.8a).

Barium appears to be generated at different depths in the lakes (Figure 4.15 and 4.16) and is controlled mostly by the pore water sulfate concentrations. It is likely that the barium is transported to the sediments from the overlying lake water as barite. As reduction removes sulfate from the pore waters the barium/sulfate ion product falls below the barite solubility product, resulting in barium released to the pore waters. Diffusion recycles Ba to the lake which reacts with sulfate in the water column to repeat the process. This is most significant in lakes Tarawera and Ngapouri where the ion activity products of barium and sulfate are typically $2x10^{-10}$. In Lake Okataina, which has much lower sulfate concentrations, the peak barium pore water concentrations occur within the upper few cm of the sediment as sulfate is reduced, resulting in the greatest flux (22 mg Ba $m^{-2}$ $yr^{-1}$) to the water of any of the lakes.

The association between aluminium and uranium, as noted in Section 4.2.2, results in the transport of ~400 times as much aluminium as uranium throughout the sediment columns of all lakes, except Tarawera. As the aluminium concentrations exceed the solubility product for aluminium hydroxide, aluminium is likely to be in colloidal form. Except for Lake Rotoiti, where geothermal discharge probably influences the recycling of aluminium to the overlying lake water (5.1 mg $m^{-2}$ $yr^{-1}$), most of the aluminium generated within the sediments is lost to the 0-2 cm layer (Figure 4.16c).

The strong correlation between calcium and strontium in the pore waters, both of which appear to be generated within the sediments, suggests a common source. The fluxes of Ca and Sr and the Ca:Sr ratio increases with lake trophic status. The fluxes of calcium, from the 0-2 cm section to the BNL, range between 29 (Tarawera) to 195 mg $m^{-2}$ $yr^{-1}$ (Rotoiti) and, for strontium, between 0.6 (Taupo) to 2 mg $m^{-2}$ $yr^{-1}$ (Rotoiti). Lake Taupo, which has the lowest trophic status, has very low fluxes of both calcium and strontium. It is possible that the source of the calcium and strontium is carbonate generated biologically within the water column. The pattern of magnesium fluxes from the lake sediments is similar to that of Ca and Sr, with the largest fluxes from the more eutrophic lakes, with typically 75 mg $m^{-2}$ $yr^{-1}$ being recycled to the overlying water in lakes which have seasonally anoxic hypolimnia.

The conservative elements lithium and boron show little to no movement in the sediment pore waters in all the lakes, except for Rotoiti, as discussed in Section 4.3.3.1. Sodium behaves similarly to lithium and boron, except that in Lake Tarawera it is lost from the surface sediment to both the overlying lake water (68 mg $m^{-2}$ $yr^{-1}$) and to deeper in the sediments (268 mg $m^{-2}$ $yr^{-1}$) (Figure 4.15 and 4.16). This is considered to be a response to a changing proportion of external geothermal discharge into the lake waters.

#### 4.4.3.3 Redistribution within the sediment

The fluxes of redox-sensitive species (iron and manganese) and the associated elements (phosphorus, arsenic and heavy metals) are dictated mostly by the depth at which reduction of the iron and manganese takes place and the depths at which re-precipitation occurs. These depths change when hypolimnetic waters become anoxic, and may also be affected by loading of organic matter in the BNL, which in turn is affected mostly by rates of deposition of algal detritus.

In lakes Tarawera and Rotoiti, fluxes of iron to the overlying lake water show little seasonal variation (Figure 4.17a) and are less than 50 mg $m^{-2}$ $yr^{-1}$ despite the high concentrations of iron in the sediments, notably in Lake Tarawera (>50000 µg $g^{-1}$). The low fluxes of iron appear to be due to high rates of sulfate reduction. In Lake Taupo, iron is generated below 4 cm depth in the sediment and is transported to the overlying lake water when the lake is mixed. When the lake is stratified, however, fluxes are impeded in the 0-2 cm sediment layer by sulfide precipitation. The annual recycling rate to the overlying lake water is 156 mg $m^{-2}$ $yr^{-1}$ in Lake Taupo. The two basins of Lake Okataina (central and north) show similar iron recycling rates to the lake (218 and 324 mg $m^{-2}$ $yr^{-1}$, respectively; Figure 4.17a) with the difference reflecting the depths to which the redox boundary descends when the hypolimnion becomes anoxic (Figure 4.2c and d). Lake Ngapouri shows a greater release of iron to the overlying lake water when the lake is stratified and anoxic (552 mg $m^{-2}$ $yr^{-1}$) compared to the mixed period (421 mg $m^{-2}$ $yr^{-1}$). The largest change in the flux occurs from the 2-4 cm layer to the 0-2 cm sediment layer when this lake is stratified (1380 mg $m^{-2}$ $yr^{-1}$) compared to when it is mixed (228 mg $m^{-2}$ $yr^{-1}$; Figure 4.17a). The Eh-pH diagram indicates that pyrite should be precipitating in the sediment (Figure 4.6). For each mg of Fe removed to pyrite, 1.14 mg of S will also be removed; however, the upward flux of Fe exceeds the downward flux of S by a factor of 5, necessitating an additional sink for Fe.

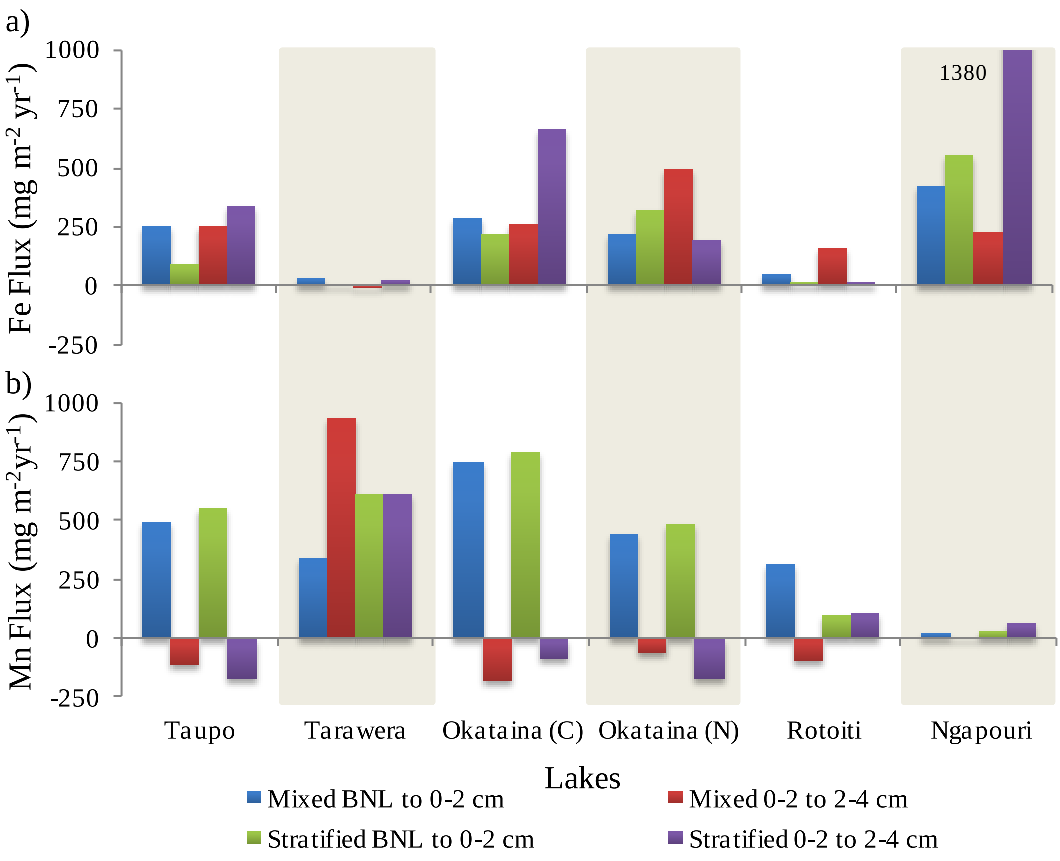

**Figure 4.17:** a) Iron and b) manganese fluxes from the BNL to 0-2 cm sediment section and the 0-2 cm to 2-4 cm sediment section, with separation into mixed and stratified periods.

The pattern of manganese transport shows broad similarities between oligotrophic lakes Taupo, Tarawera and Okataina, with fluxes from the sediment to the overlying lake water between 465 and 767 mg $m^{-2}$ $yr^{-1}$ (Figure 4.15). Lakes Rotoiti and Ngapouri, which have relatively low abundance of manganese in the bottom sediments (380 and 915 µg $g^{-1}$ respectively), have low manganese pore water concentrations and hence low fluxes to the overlying lake water (177 and 59 mg $m^{-2}$ $yr^{-1}$, respectively). Unlike iron, manganese does not show significant differences between stratified and mixed periods (Figure 4.17), but does show loss from the 0-2 cm section to the 2-4 cm sediments, except for Lake Tarawera where the Mn maxima occurs at a slightly greater depth. Manganese is strongly mobilised from the 0-2 cm layer and migrates into the overlying BNL but is subsequently precipitated and reincorporated into the sediments.

The flux of phosphorus from the sediments to the overlying lake water is far greater in Lake Rotoiti than in any of the other lakes studied (110 mg $m^{-2}$ $yr^{-1}$, Figure 4.14e). Only 20 % (18.5 mg $m^{-2}$ $yr^{-1}$) of this is reactive phosphorus. The majority is likely to be attached to colloids (linked to iron, manganese or aluminium), and is probably transported by geothermal fluid flow. The phosphorus flux from the sediments to the overlying lake water in lakes Taupo, Tarawera and Ngapouri increases with trophic status of the lake (6.2, 7.8 and 19 mg $m^{-2}$ $yr^{-1}$ respectively). However, Lake Okataina has the smallest phosphorus flux from the sediments to the water column (1.4 and 5.6 mg $m^{-2}$ $yr^{-1}$ for the central and north basins), with the largest flux within its sediments from the 2-4 cm to the 0-2 cm sediment layer, but small (6.2 and 10.7 mg $m^{-2}$ $yr^{-1}$, respectively) in comparison with the other TVZ lakes studied.

Arsenic fluxes are from the surface sediment to the overlying lake water in all lakes. Fluxes are 7.8, 8.1, 11.2 and 19.5 mg $m^{-2}$ $yr^{-1}$ in lakes Ngapouri, Rotoiti, Taupo and Tarawera, respectively. The largest flux occurs in Lake Okataina central basin (29.5 mg $m^{-2}$ $yr^{-1}$), well above that of the northern basin (18.3 mg $m^{-2}$ $yr^{-1}$). The depth within the sediments from which arsenic is mobilised varies between lakes. In lakes Taupo, Okataina and Ngapouri, remobilisation occurs close to the sediment surface, to a depth c. 4 cm. In lakes Tarawera and Rotoiti, arsenic is remobilised much deeper in the sediments and is likely associated with tephra layers and geothermal fluid movement.

The ultra-trace heavy metals (Cu, Zn, Pb, Hg and U) have fluxes to and from the lake water < 0.3 mg $m^{-2}$ $yr^{-1}$ reflecting their low abundance in the lake waters and sediments. Uranium has the lowest flux of any element and is transported to the overlying lake water at a rate of about 1 µg $m^{-2}$ $yr^{-1}$.

#### 4.4.3.4 Transport from the lake water above

Sulfur is transported from the water into the sediments in all the lakes, driven by sulfate reduction once dissolved oxygen and other reducible species are consumed. The fluxes of sulfate into the sediments from the BNL are weakly correlated, or not at all, with the sulfate concentration, and are likely driven by the oxygen demand and resulting redox potential within the sediments. Typical sulfate fluxes to the sediments range between 22.8 mg $m^{-2}$ $yr^{-1}$ (Tarawera) and 636 mg $m^{-2}$ $yr^{-1}$ (Rotoiti) (Figure 4.15a).

Potassium is also transported from the BNL into the 0-2 cm layer of sediments in the lakes, except in Lake Rotoiti where it is transported from the sediments into the overlying lake water (82 mg $m^{-2}$ $yr^{-1}$), likely in association with the upward geothermal flow in the sediments of this lake. The fluxes of K in to the sediment range from 19.1 mg $m^{-2}$ $yr^{-1}$ in Lake Ngapouri to 349 mg $m^{-2}$ $yr^{-1}$ in Lake Okataina. As these lakes receive some geothermal water, either directly from surface springs or indirectly as groundwater, potassium is absorbed into the sediment from the lake. The fluxes from the 0-2 to 2-4 cm section suggest there is some degree of remobilisation in the surface sediments (Figure 4.16b).

Fluxes of nitrate from overlying water to the sediment are approximately 2-2.5 mg $m^{-2}$ $yr^{-1}$ for lakes Taupo and Tarawera, 7 mg $m^{-2}$ $yr^{-1}$ for Lake Rotoiti and 13.9 mg $m^{-2}$ $yr^{-1}$ for Lake Ngapouri (Figure 4.15e). Lake Okataina had the largest fluxes, with 33.8 mg $m^{-2}$ $yr^{-1}$ in the central basin and 9.45 mg $m^{-2}$ $yr^{-1}$ in the north basin. Sediments provide a sink for nitrate and the flux to the sediments will depend on the availability of nitrate in the hypolimnion. In eutrophic, stratified lakes this is limited by the availability of oxygen, for example in Lake Okataina, where there is a longer period of anoxia in the central basin than the north basin at the end of the stratification period. The extended period of anoxia increases the capacity for the upper few cm of the sediment to take up nitrate during the rest of the year (Figure 4.10b).

## 4.5 SUMMARY

Sediment core samples, collected monthly from the central basins of five monomictic TVZ lakes of varying trophic state, were separated into sediment and pore water fractions and analysed to elucidate the diagenetic processes that influence the availability of major, trace elements and nutrients. The sediments consisted of fine diatomaceous ooze, although rhyolitic tephras are also present in some of the lakes.

The most obvious diagenetic process is reduction of oxidised species within the sediment as organic matter is metabolised and dissolved oxygen depleted. As sediments generally became more reducing at greater depth, the zones in which individual species were reduced varied from species to species, from lake to lake, and seasonally. Nitrogen compounds were reduced early to ammonium, which diffused to the overlying lake. Manganese often diffused to the SWI before being reoxidised, where it acted as a co-precipitator for many other trace species. Ferric iron was reduced to ferrous, which then precipitated with sulfides if there was sufficient sulfate at that depth, with the sulfate source initially from the overlying lake water. When ferrous iron production exceeded sulfate reduction, ferrous iron also diffused to the SWI before being re-oxidised. As the hypolimnion chemistry changed with stratification, the pore water chemistry showed seasonal changes, especially for redox-driven Fe, Mn, $NH_{4,}$ $SO_4$ and associated species such as $PO_4$. Following the development of hypolimnetic anoxia the concentrations of Fe, Mn and $NH_4$ in upper pore waters increased markedly and $SO_4$ concentrations decreased. The reduction of sulfate in the sediments limited chalcophile element (Cu, Zn, Pb, Hg) pore water concentrations until the sulfide was removed.

Polyoxides ($PO_4$ and $AsO_4$) adsorbed onto settling particulates and were released back into solution as particulate organic matter underwent diagenesis or with dissolution of the inorganic particulates (Fe, Mn and Al oxyhydroxides). The ubiquitous presence of readily soluble siliceous material resulted in the release of silicon to the pore waters and subsequent diffusion to overlying lake waters. The extent of the flux of silicon was controlled largely by the trophic status of the lake, being greatest in lakes where high concentrations of diatoms could reduce epilimnetic silicon concentrations to $< 1$ mg $L^{-1}$. The weathering of alumnosilicate glass, from tephric deposits in the catchment or from direct air fall of tephra, also released silicon along with aluminium and uranium, to the pore waters. As the concentration of aluminium exceeded the stability for aluminium hydroxide, it is likely that the majority of the pore water aluminium was present as colloids. Such colloids are strong absorbers of polyoxides and are likely to be aggregated at the SWI as the aluminium concentration in overlying waters was very low. The alkaline earth elements (Ca, Mg and Sr) all increased in concentration in the upper pore waters, suggesting dissolution of these elements and that planktonic calcifiers (eg. ostracods), fish otoliths or mollusc exoskeletons would dissolve in the $CO_2$-rich environment. Barium exhibited a different behaviour, with pore water concentrations increasing at greater depths in the sediment, suggesting transport from the water column as barite ($BaSO_4$) and subsequent solution as sulfate was reduced to sulfide. Conservative elements (Li, B, Na, K) showed little change in pore water concentrations except where geothermal fluids moved vertically up through the bottom sediments, as was the case for Lake Rotoiti.

Fluxes of nutrient species to the overlying lake water, calculated from the near-surface diffusion gradients, were in the range 16.5 to 377 mg $m^{-2}$ $yr^{-1}$ for ammonium, 1.3 mg $m^{-2}$ $yr^{-1}$ to 110 mg $m^{-2}$ $yr^{-1}$ for phosporus, and 79 to 768 mg $m^{-2}$ $yr^{-1}$ for silicon (except for Lake Tarawera where the water column was a source of Si for the bottom sediments). These values are of use for modelling lake productivity when combined with the external import and export nutrient budgets. It should be noted however, that this study has focused on central basin sediments, which are likely to have far greater fluxes than those in the littoral zone.

## 4.6 REFERENCES

Aggett, J. and Kriegman, M. R., 1988. The extent of formation of arsenic (III) in sediment interstitial waters and its release to hypolimnetic waters in Lake Ohakuri. Water Res. **22**, 407-411.

Aggett, J. and O'Brien, G. A., 1985. Detailed model for the mobility of arsenic in lacustrine sediments based on measurements in Lake Ohakuri. Environ. Sci. Technol. **19**, 231-238.

Aggett, J. and Roberts, L. S., 1986. Insight into the mechanism of accumulation of arsenate and phosphate in hydro lake sediments by measuring the rate of dissolution with ethylenediaminetetraacetic acid. Environ. Sci. Technol. **20**, 183-186.

Anderson, L. C. D. and Bruland, K. W., 1991. Biogeochemistry of arsenic in natural waters: The importance of methylated species. Environ. Sci. Technol. **25**, 420-427.

Barclay, M. H., 1968. Additions to the freshwater ostracod fauna of New Zealand. N.Z. J. Mar. Freshw. Res. **2**, 67-80.

Bibby, H. M., Bennie, S. L., Stagpoole, V. M., and Caldwell, T. G., 1994. Resistivity structure of the Waimangu, Waiotapu, Waikite and Reporoa geothermal areas, New Zealand. Geothermics **23**, 445-471.

Bortleson, G. C. and Lee, G. F., 1974. Phosphorus, iron, and manganese distribution in sediment cores of six Wisconsin lakes. Limnol. Oceanogr., 794-801.

Boudreau, B. P., 1996. A method-of-lines code for carbon and nutrient diagenesis in aquatic sediments. Comput. Geosci. **22**, 479-496.

Boudreau, B. P., Gardiner, B. S., and Johnson, B. D., 2001. Rate of growth of isolated bubbles in sediments with a diagenetic source of methane. Limnol. Oceanogr. **46**, 616-622.

Boudreau, B. P. and Jørgensen, B. B., 2001. The benthic boundary layer: Transport processes and biogeochemistry. Oxford University Press.

Brennwald, M. S., Kipfer, R., and Imboden, D. M., 2005. Release of gas bubbles from lake sediment traced by noble gas isotopes in the sediment pore water. Earth Planet. Sci. Lett. **235**, 31-44.

Bruesewitz, D. A., Hamilton, D. P., and Schipper, L. A., 2011. Denitrification potential in lake sediment increases across a gradient of catchment agriculture. Ecosystems **14**, 341-352.

Burns, N., McIntosh, J., and Scholes, P., 2009. Managing the lakes of the Rotorua District, New Zealand. Lake Reservoir Manage. **25**, 284-296.

Canfield, D. E. and Thamdrup, B., 2009. Towards a consistent classification scheme for geochemical environments, or, why we wish the term 'suboxic'would go away. Geobiology **7**, 385-392.

Cassie-Cooper, V., 1996. Microalgae: microscopic marvels. Riverside Books, Hamilton, New Zealand.

Chapman, M. A., 1963. A review of the freshwater ostracods of New Zealand. Hydrobiologia **22**, 1-40.

Chapman, M. A., Green, J. D., and Jolly, V. H., 1985. Relationships between zooplankton abundance and trophic state in seven New Zealand lakes. Hydrobiologia **123**, 119-136.

Chappaz, A., Gobeil, C., and Tessier, A., 2010. Controls on uranium distribution in lake sediments. Geochim. Cosmochim. Acta **74**, 203-214.

Couture, R. M., Gobeil, C., and Tessier, A., 2010. Arsenic, iron and sulfur co-diagenesis in lake sediments. Geochim. Cosmochim. Acta **74**, 1238-1255.

Cullen, W. R. and Reimer, K. J., 1989. Arsenic speciation in the environment. Chem. Rev. **89**, 713-764.

Davison, W., 1991. The solubility of iron sulphides in synthetic and natural waters at ambient temperature. Aquatic Sciences-Research Across Boundaries **53**, 309-329.

Davison, W., 1993. Iron and manganese in lakes. Earth-Sci. Rev. **34**, 119-163.

Davison, W. and De Vitre, R., 1992. Iron particles in freshwater. Environmental particles **1**, 315.

Davison, W., Grime, G. W., and Woof, C., 1992. Characterization of lacustrine iron sulfide particles with proton-induced X-ray emission. Limnol. Oceanogr., 1770-1777.

De Vitre, R. and Davison, W., 1993. Manganese particles in freshwater. Environmental particles **2**, 317–352.

Eckert, W., Didenko, J., Uri, E., and Eldar, D., 2003. Spatial and temporal variability of particulate phosphorus fractions in seston and sediments of Lake Kinneret under changing loading scenario. Hydrobiologia **494**, 223-229.

Emerson, S. and Widmer, G., 1978. Early diagenesis in anaerobic lake sediments--II. Thermodynamic and kinetic factors controlling the formation of iron phosphate. Geochim. Cosmochim. Acta **42**, 1307-1316.

Ethier, A. L. M., Scheuhammer, A. M., Blais, J. M., Paterson, A. M., Mierle, G., Ingram, R., and Lean, D. R. S., 2010. Mercury empirical relationships in sediments from three Ontario lakes. Sci. Total Environ. **408**, 2087-2095.

Exley, C., 2003. A biogeochemical cycle for aluminium? J. Inorg. Biochem. **97**, 1-7.

Farmer, J. G. and Lovell, M. A., 1986. Natural enrichment of arsenic in Loch Lomond sediments. Geochim. Cosmochim. Acta **50**, 2059-2067.

Farrell, J. and Campana, S. E., 1996. Regulation of calcium and strontium deposition on the otoliths of juvenile tilapia, Oreochromis niloticus. Comp. Biochem. Phys. A. **115**, 103-109.

Faure, G., Crocket, J. H., and Hueley, P. M., 1967. Some aspects of the geochemistry of strontium and calcium in the Hudson Bay and the Great Lakes. Geochim. Cosmochim. Acta **31**, 451-461.

Feyte, S., Gobeil, C., Tessier, A., and Cossa, D., 2011. Mercury dynamics in lake sediments. Geochim. Cosmochim. Acta **doi: 10.1016/j.gca.2011.02.007**.

Fish, G. R., 1970. A limnological study of four lakes near Rotorua. N.Z. J. Mar. Freshwat. Res. **4**, 165-194.

Gibbs, M. M., 1992. Influence of hypolimnetic stirring and underflow on the limnology if Lake Rotoiti, New Zealand. N.Z. J. Mar. Freshw. Res. **26**, 453-463.

Giggenbach, W. F. and Glover, R. B., 1992. Tectonic regime and major processes governing the chemistry of water and gas discharges from the Rotorua geothermal field, New Zealand. Geothermics **21**, 121-140.

Granina, L. Z., Klerkx, J., Callender, E., Leermakers, M., and Golobokova, L. P., 2007. Bottom sediments and pore waters near a hydrothermal vent in Lake Baikal (Frolikha Bay). Russ. Geol. Geophys. **48**, 237-246.

Håkanson, L. and Jansson, M., 1983. Principles of Lake Sedimentology. The Blackburn Press, New Jersey.

Hamilton, D. P., Paul, W., McBride, C. and Immenga, D., 2009. Water flow between Ohau Channel and Lake Rotoiti following implementation of a diversion wall. Centre for Biodiversity and Ecology Research, Report No. 96. Department of Biological Sciences, University of Waikato, Hamilton.

Hamilton-Taylor, J. and Davison, W., 1995. Redox-Driven Cycling of Trace Elements in Lakes. Springer-Verlag.

He, T., Lu, J., Yang, F., and Feng, X., 2007. Horizontal and vertical variability of mercury species in pore water and sediments in small lakes in Ontario. Sci. Total Environ. **386**, 53-64.

Hedenquist, J. W., 1986. Geothermal systems in the Taupo Volcanic Zone: their characteristics and relation to volcanism and mineralisation. Late Cenozoic volcanism in New Zealand: Royal Society of New Zealand Bulletin **23**, 134-168.

Hilton, J., 1985. A conceptual framework for predicting the occurrence of sediment focusing and sediment redistribution in small lakes. Limnol. Oceanogr., 1131-1143.

Holmer, M. and Storkholm, P., 2001. Sulfate reduction and sulphur cycling in lake sediments: a review. Freshwater Biol. **46**, 431-451.

Irwin, J., 1968. Observations of temperatures in some Rotorua district lakes. N.Z. J. Mar. Freshw. Res. **2**, 591-605.

Jeppesen, E., Soendergaard, M., Jensen, J. P., Havens, K. E., Anneville, O., Carvalho, L., Coveney, M. F., Deneke, R., Dokulil, M. T., and Foy, B. O. B., 2005. Lake responses to reduced nutrient loading–an analysis of contemporary long term data from 35 case studies. Freshwater Biol. **50**, 1747-1771.

Kammer, F., Baborowski, M., Tadjiki, S., and Tuempling Jr, W., 2003. Colloidal particles in sediment pore waters: Particle size distributions and associated element size distribution in anoxic and re-oxidized samples, obtained by FFF-ICP-MS coupling. Acta hydrochim. hydrobiol. **31**, 400-410.

Lobo, V. M. M., 1993. Mutual diffusion coefficients in aqueous electrolyte solutions. Pure & Appl. Chem **65**, 2613-2613.

Lowe, D. J. and Green, J. D., 1992. Lakes. In: Soons, J. M. and Selby, M. J. Eds.), Landforms of New Zealand: Second Edition. Longman Paul, Auckland.

Maassen, S., Röske, I., and Uhlmann, D., 2003. Chemical and microbial composition of sediments in reservoirs with different trophic state. Int. Rev. Hydrobiol. **88**, 508-518.

Marsden, M. W., 1989. Lake restoration by reducing external phosphorus loading: the influence of sediment phosphorus release. Freshwater Biol. **21**, 139-162.

Martin, T. D., Creed, J. T., and Brockhoff, C. A., 1994. Method 200.2 (Revision 2.8): Sample preparation procedure for spectrochemical determination of total recoverable elements. In: USEPA (Ed.), Methods for the Determination of Metals in Environmental Samples, Cincinnati, OH.

May, H. M., P. A. Helmke, and M. L. Jackson. 1979. Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25 C. Geochim. Cosmochim. Acta **43:** 861-868.

McColl, R. H. S., 1972. Chemistry and trophic status of seven New Zealand lakes. N.Z. J. Mar. Freshw. Res. **6**, 399-447.

McColl, R. H. S., 1977. Chemistry of sediments in relation to trophic condition of eight Rotorua lakes. N.Z. J. Mar. Freshw. Res. **11**, 509-523.

McCreadie, H., Blowes, D. W., Ptacek, C. J., and Jambor, J. L., 2000. Influence of reduction reactions and solid-phase composition on porewater concentrations of arsenic. Environ. Sci. Technol. **34**, 3159-3166.

McKee, J. D., Wilson, T. P., Long, D. T., and Owen, R. M., 1989. Pore water profiles and early diagenesis of Mn, Cu, and Pb in sediments from large lakes. J. Great Lakes Res. **15**, 68-83.

McKelvie, I. D., Peat, D. M. W., and Worsfold, P. J., 1995. Techniques for the quantification and speciation of phosphorus in natural waters. Anal. Proc. **32**, 437-445.

Meyers, P. A. and Ishiwatari, R., 1993. Lacustrine organic geochemistry--an overview of indicators of organic matter sources and diagenesis in lake sediments. Org. Geochem. **20**, 867-900.

Meyers, P. A. and Lallier-Vergès, E., 1999. Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. J. Paleolimnol. **21**, 345-372.

Meysman, F. J. R., Boudreau, B. P., and Middelburg, J. J., 2005. Modeling reactive transport in sediments subject to bioturbation and compaction. Geochim. Cosmochim. Acta **69**, 3601-3617.

Morgenstern, U., Reeves, R., Daughney, C., Cameron, S., and Gordon, D., 2005. Groundwater Age and Chemistry, and Future Nutrient Loads for Selected Rotorua Lakes Catchments. Institute of Geological & Nuclear Sciences, Lower Hutt, New Zealand.

Mosello, R., Barbieri, A., Brizzio, M. C., Calderoni, A., Marchetto, A., Passera, S., Rogora, M., and Tartari, G., 2001. Nitrogen budget of Lago Maggiore: the relative importance of atmospheric deposition and catchment sources. J. Limnol. **60**, 27-40.

Nagao, S., Yanase, N., Yamamoto, M., Kofuji, H., Sohrin, Y., and Amano, H., 2002. The geochemistry of uranium in pore waters from lake sediments. J. Radioanal. Nucl. Ch. **252**, 225-232.

Nairn, I. A., 1992. The Te Rere and Okareka eruptive episodes—Okataina Volcanic Centre, Taupo Volcanic Zone, New Zealand. N.Z. J. Geol. Geop. **35**, 93-108.

Nelson, C. S. and Lister, G. S., 1995. Surficial bottom sediments of Lake Taupo, New Zealand: texture, composition, provenance, and sedimentation rates. N.Z. J. Geol. Geop. **38**, 61-79.

Nürnberg, G. K., 1984a. The prediction of internal phosphorus load in lakes with anoxic hypolimnia. Limnol. Oceanogr. **29**, 111-124.

Nürnberg, G. K., 1984b. Iron and hydrogen sulfide interference in the analysis of soluble reasctive phosphorus in anoxic waters. Water Res. **18**, 369-377.

Nürnberg, G. K., 1991. Phosphorus from internal sources in the Laurentian Great Lakes, and the concept of threshold external load. J. Great Lakes Res. **17**, 132-140.

Ostrovsky, I., 2003. Methane bubbles in Lake Kinneret: Quantification and temporal and spatial heterogeneity. Limnol. Oceanogr. **48**, 1030-1036.

Patnaik, P. 2010. Handbook of environmental analysis: chemical pollutants in air, water, soil, and solid wastes, 2nd ed. CRC Press.

Pearson, L. K., 2007. The nature, composition and distribution if sediment in Lake Rotorua, New Zealand, M.Sc. Thesis. Department of Chemistry, University of Waikato.

Pearson, L. K., Hendy, C. H., Hamilton, D. P., and Pickett, R. C., 2010. Natural and anthropogenic lead in sediments of the Rotorua lakes, New Zealand. Earth Planet. Sci. Lett. **297**, 536-544.

Petersen, W., Wallman, K., Pinglin, L., Schroeder, F., and Knauth, H. D., 1995. Exchange of trace elements at the sediment-water interface during early diagenesis processes. Mar. Freshw. Res. **46**, 19-26.

Pickrill, R. A., 1993. Shallow seismic stratigraphy and pockmarks of a hydrothermally influenced lake, Lake Rotoiti, New Zealand. Sedimentology **40**, 813-828.

Pickrill, R. A., Nelson, C. S., Stoffers, P., and Craig, G. G. P., 1991. Influence of late holocene pyroclastic eruptions on the sedimentary geochemistry of Lake Rotoiti, North Island, New Zealand. J. Paleolimnol. **6**, 173-192.

Pierson, D. C. and Weyhenmeyer, G. A., 1994. High resolution measurements of sediment resuspension above an accumulation bottom in a stratified lake. Hydrobiologia **284**, 43-57.

Priscu, J. C., Spigel, R. H., Gibbs, M. M., and Downes, M. T., 1986. A numerical analysis of hypolimnetic nitrogen and phosphorus transformations in Lake Rotoiti, New Zealand: A geothermally influenced lake. Limnol. Oceanogr. **31**, 812-831.

Pullar, W. A. and Kennedy, N. M., 1981. Tephra deposits in the Rotorua Lakes District. In: Chapman, V. J. (Ed.), Handbook of the Rotorua Lakes District. The Guardians of the Rotorua Lakes, Rotorua, New Zealand.

Rawlence, D. J., 1984. A study of pigment and diatoms in a core from Lake Rotorua, North Island, New Zealand, with emphasis on recent history. J. Roy. Soc. New Zeal. **14**, 119-132.

Rawlence, D. J., 1985. Post-Tarawera eruption (AD 1886) diatom stratigraphy of Lake Rotoiti, North Island, New Zealand. N.Z. J. Mar. Freshw. Res. **19**, 391-397.

Redfield, A. C., 1958. The biological control of chemical factors in the environment. Am. Sci. **46**, 205-221.

Round, F. E., Crawford, R. M., and Mann, D. G., 1990. The Diatoms: biology & morphology of the genera. Cambridge University Press, UK.

Schulz, H. D., 2006. Quantification of early diagenesis: Dissolved constituents in marine pore water. In: Schultz, H. D. and Zabel, M. Eds.), Marine Geochemistry. Springer, Berlin.

Sheldon, R. W., 1972. Size separation of marine seston by membrane and glass-fiber filters. Limnol. Oceanogr. **17**, 494-498.

Sherman, L. A., Baker, L. A., Weir, E. P., and Brezonik, P. L., 1994. Sediment pore-water dynamics of Little Rock Lake, Wisconsin: Geochemical processes and seasonal and spatial variability. Limnol. Oceanogr. **39**, 1155-1171.

Sigg, L., Sturm, M., and Kistler, D., 1987. Vertical transport of heavy metals by settling particles in Lake Zurich. Limnol. Oceanogr. **32**, 112-130.

Sinke, A. J. C., Cornelese, A. D. I. A., Keizer, P., Tongeren, O. F. R., and Cappenberg, T. E., 1990. Mineralization, pore water chemistry and phosphorus release from peaty sediments in the eutrophic Loosdrecht lakes, The Netherlands. Freshwater Biol. **23**, 587-599.

Søndergaard, M., Jensen, J. P., and Jeppesen, E., 2003. Role of sediment and internal loading of phosphorus in shallow lakes. Hydrobiologia **506**, 135-145.

Spigel, R. H., Howard-Williams, C., Gibbs, M., Stephens, S., and Waugh, B., 2005. Field calibration of a formula for entrance mixing of river inflows to lakes: Lake Taupo, North Island, New Zealand. N.Z. J. Mar. Freshw. Res. **39**, 785-802.

Stumm, W. and Morgan, J. J., 1981. Aquatic chemistry: Chemical Equilibria and Rates in Natural Waters. Wiley New York.

Stumm, W. and Sulzberger, B., 1992. The cycling of iron in natural environments: Considerations based on laboratory studies of heterogeneous redox processes. Geochim. Cosmochim. Acta **56**, 3233-3257.

Svensson, J. and Leonardson, L., 1996. Effects of bioturbation by tube dwelling chironomid larvae on oxygen uptake and denitrification in eutrophic lake sediments. Freshwater Biol. **35**, 289-300.

Timperley, M. H. and Vigor-Brown, R. J., 1986. Water chemistry of lakes in the Taupo volcanic zone, New Zealand. N.Z. J. Mar. Freshw. Res. **20**, 173-183.

Town, R. M. and Filella, M., 2002. Size fractionation of trace metal species in freshwaters: implications for understanding their behaviour and fate. Rev. Environ. Sci. Biotechnol. **1**, 277-297.

Trolle, D., Hamilton, D. P., Hendy, C. H., and Pilditch, C., 2008. Sediment and nutrient accumulation rates in sediments of twelve New Zealand lakes: influence of lake morphology, catchment characteristics and trophic state. Mar. Freshwat. Res. **59**, 1067-1078.

Trolle, D., Hamilton, D. P., and Pilditch, C. A., 2010. Evaluating the influence of lake morphology, trophic status and diagenesis on geochemical profiles in lake sediments. Appl. Geochem. **25**, 621-632.

Ullrich, S. M., Tanton, T. W., and Abdrashitova, S. A., 2001. Mercury in the aquatic environment: a review of factors affecting methylation. Crit. Rev. Env. Sci. Tec. **31**, 241-293.

Vincent, W., Gibbs, M., and Dryden, S., 1984. Accelerated eutrophication in a New Zealand lake: Lake Rotoiti, central North Island. N.Z. J. Mar. Freshwat. Res. **18**, 431-440.

Vincent, W. F., 1983. Phytoplankton production and winter mixing: contrasting effects in two oligotrophic lakes. J. Ecol. **71**, 1-20.

Wetzel, R. G., 2001. Limnology: lake and river ecosystems. Academic press San Diego, California.

Weyhenmeyer, G. A., Meili, M., and Pierson, D. C., 1995. A simple method to quantify sources of settling particles in lakes: resuspension versus new sedimentation of material from planktonic production. Mar. Freshwat. Res. **46**, 223-231.

White, E., 1983. Lake eutrophication in New Zealand—a comparison with other countries of the Organisation for Economic Co-operation and Development. N.Z. J. Mar. Freshw. Res. **17**, 437-444.

Wilson, C. J. N., Rogan, A. M., Smith, I. E. M., Northey, D. J., Nairn, I. A., and Houghton, B. F., 1984. Caldera volcanoes of the Taupo volcanic zone, New Zealand. J. Geophys. Res. **89**, 8463-8484.

# SUPPLEMENTARY DATA A: FLUX CALCULATION VARIABLES

**Table 4.1:** Diffusion coefficient at 11˚C from Lobo (1993).

| Element | Diffusion Coefficient ($cm^2$ $sec^{-1}$ $x10^{-6}$) | Diffusion Coefficient reduced by $\theta^2$ |
|---|---|---|
| Li | 8.156 | 7.773 |
| B | 8.797* | 8.384 |
| $NH_4$ | 13.058 | 12.445 |
| $NO_3$ | 8.797* | 8.384 |
| Na | 11.268 | 10.739 |
| Mg | 8.117 | 7.736 |
| Al | 8.797* | 8.384 |
| Si | 8.797* | 8.384 |
| P | 8.797* | 8.384 |
| $PO_4$ | 7.396 | 7.049 |
| S | 9.023 | 8.599 |
| K | 6.565 | 6.257 |
| Ca | 8.554 | 8.152 |
| Fe | 8.797* | 8.384 |
| Mn | 7.198 | 6.860 |
| Cu | 5.310 | 5.061 |
| Zn | 7.325 | 6.981 |
| As | 8.797* | 8.384 |
| Sr | 9.002 | 8.579 |
| Ba | 9.463 | 9.019 |
| Hg | 8.797* | 8.384 |
| Pb | 8.797* | 8.384 |
| U | 8.797* | 8.384 |

* Value estimated from average of published diffusion coefficients.

**Table 4.2:** Bulk density, porosity and element gradients for the BBL to 0-2 cm and 0-2 cm to 2-4 cm sediment sections used to calculate the diffusive flux for the respective depth and lake (* Not measured).

| | Taupo | | Tarawera | | Okataina (central) | | Okataina (north) | | Rotoiti | | Ngapouri | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | BBL to 0-2cm | 0-2cm to 2-4cm | BBL to 0-2cm | 0-2cm to 2-4cm | BBL to 0-2cm | 0-2cm to 2-4cm | BBL to 0-2cm | 0-2cm to 2-4cm | BBL to 0-2cm | 0-2cm to 2-4cm | BBL to 0-2cm | 0-2cm to 2-4cm |
| Bulk density (g cm$^{3}$) | 0.055 | 0.075 | 0.056 | 0.068 | 0.042 | 0.084 | 0.062 | 0.084 | 0.023 | 0.051 | 0.022 | 0.055 |
| Porosity (%) | 97.192 | 96.426 | 97.187 | 96.764 | 96.829 | 95.998 | 97.030 | 95.987 | 98.707 | 97.543 | 98.930 | 97.385 |
| Gradient | | | | | | | | | | | | |
| Li | -9.83E-07 | -7.12E-07 | 7.56E-06 | -1.80E-05 | 7.20E-07 | 1.44E-07 | 1.34E-06 | 1.17E-06 | 8.93E-05 | 1.49E-04 | -1.20E-06 | -2.94E-07 |
| B | 1.78E-06 | -1.95E-05 | 8.97E-06 | -1.62E-05 | -1.92E-06 | -3.98E-07 | -7.45E-07 | 6.39E-07 | 1.19E-04 | 6.29E-04 | 1.06E-06 | -1.64E-06 |
| $NH_4$ | 1.52E-04 | 1.50E-04 | 4.21E-05 | 1.13E-04 | 9.51E-05 | 2.99E-04 | 4.85E-04 | 3.74E-04 | 6.69E-04 | 7.85E-04 | 9.59E-04 | 3.78E-04 |
| $NO_3$ | -9.09E-06 | -6.59E-06 | -7.56E-06 | -9.10E-06 | -1.28E-04 | 8.24E-06 | -3.57E-05 | 4.54E-06 | -2.67E-05 | 1.40E-06 | -5.25E-05 | -9.53E-06 |
| Na | 3.60E-05 | -1.37E-05 | 2.00E-04 | -7.89E-04 | -4.03E-05 | 3.22E-04 | 3.17E-04 | 4.83E-04 | 5.92E-03 | 1.24E-02 | -1.72E-04 | -2.06E-05 |
| Mg | 1.30E-05 | 2.14E-05 | -4.61E-05 | -1.27E-05 | 3.11E-04 | 2.17E-04 | 4.05E-04 | 2.39E-04 | 3.63E-04 | 6.42E-04 | 1.46E-04 | 1.90E-04 |
| Al | -4.03E-06 | 1.56E-05 | 1.50E-06 | 1.26E-06 | -5.91E-07 | 1.55E-05 | 4.66E-06 | 2.60E-05 | 1.94E-05 | 1.41E-05 | -6.96E-06 | 1.09E-05 |
| Si | 2.90E-03 | 1.04E-03 | 3.01E-04 | -4.76E-04 | 2.77E-03 | 2.24E-03 | 2.71E-03 | 2.01E-03 | 2.31E-03 | 2.80E-03 | 3.62E-04 | 3.43E-04 |
| P | 2.37E-05 | 1.49E-05 | 2.94E-05 | 2.04E-05 | 5.10E-06 | 2.34E-05 | 1.36E-05 | 4.03E-05 | 4.18E-04 | 5.38E-04 | 6.98E-05 | 3.01E-05 |
| $PO_4$ | 1.93E-07 | -2.91E-06 | 1.05E-05 | -3.80E-06 | 4.21E-06 | -3.54E-06 | -1.60E-06 | 7.42E-07 | 8.34E-05 | 1.69E-04 | * | * |
| S | -5.76E-04 | -5.59E-04 | -8.43E-05 | -7.83E-04 | -6.23E-04 | -4.99E-05 | -2.56E-04 | -2.80E-04 | -2.34E-03 | -1.12E-03 | -7.24E-04 | -7.13E-04 |
| K | -6.03E-04 | -9.66E-05 | -7.02E-04 | -1.63E-04 | -1.77E-03 | -2.06E-04 | -1.35E-03 | 4.80E-05 | 4.19E-04 | 8.98E-04 | -9.69E-05 | 8.26E-05 |
| Ca | 2.28E-04 | -2.46E-06 | 1.13E-04 | 1.49E-04 | 4.78E-04 | 3.94E-04 | 6.40E-04 | 3.87E-04 | 7.60E-04 | 4.61E-04 | 5.77E-04 | 6.23E-04 |
| Fe | 5.89E-04 | 6.93E-04 | 5.82E-05 | 4.59E-05 | 8.24E-04 | 1.69E-03 | 1.22E-03 | 1.43E-03 | 1.13E-04 | 2.95E-04 | 4.01E-03 | 4.04E-03 |
| Mn | 2.15E-03 | -6.48E-04 | 2.86E-03 | 2.47E-03 | 3.54E-03 | -5.44E-04 | 2.52E-03 | -6.56E-04 | 8.18E-04 | 6.40E-05 | 2.73E-04 | 2.15E-04 |
| Cu | -3.28E-08 | 1.98E-07 | -1.28E-08 | -1.32E-07 | 1.14E-07 | -1.23E-07 | -9.33E-08 | 4.20E-08 | 7.64E-08 | 1.09E-07 | -4.17E-08 | -2.31E-08 |
| Zn | -5.97E-08 | -3.68E-07 | 5.03E-07 | 6.42E-07 | 2.12E-07 | 1.94E-07 | -2.73E-07 | 7.52E-07 | -1.48E-06 | 6.06E-07 | -1.11E-06 | 2.44E-07 |
| As | 4.23E-05 | 3.17E-05 | 7.36E-05 | 1.12E-04 | 1.11E-04 | 5.98E-05 | 6.92E-05 | 4.68E-05 | 3.06E-05 | 2.00E-06 | 2.98E-05 | 5.09E-06 |
| Sr | 2.02E-06 | -6.77E-07 | 2.44E-06 | 1.70E-06 | 5.67E-06 | 4.26E-06 | 6.90E-06 | 4.23E-06 | 7.52E-06 | 5.70E-06 | 7.34E-06 | 7.30E-06 |
| Ba | 9.86E-06 | -2.01E-06 | 4.95E-05 | 1.12E-04 | 7.72E-05 | 7.32E-06 | 4.54E-05 | -3.33E-06 | 2.43E-05 | 1.17E-05 | 6.75E-06 | 1.60E-05 |
| Hg | 3.83E-07 | -4.99E-08 | -1.89E-08 | 8.28E-07 | 1.36E-07 | 1.49E-08 | 1.01E-07 | 9.15E-08 | 7.85E-07 | -8.57E-08 | -1.04E-07 | 5.39E-08 |
| Pb | -5.38E-08 | 2.46E-08 | -4.40E-08 | -2.95E-08 | -9.19E-08 | -1.48E-08 | -8.88E-08 | -2.66E-09 | 1.95E-08 | 3.63E-08 | 3.96E-08 | -8.89E-08 |
| U | 2.22E-09 | 2.44E-09 | 4.11E-09 | 3.46E-09 | 1.05E-09 | 3.17E-09 | 2.98E-09 | 5.40E-09 | 8.20E-09 | 6.64E-09 | -5.96E-10 | 3.07E-09 |

# SUPPLEMENTARY DATA B: CORRELATION TABLES

**Table 4.3:** Pearson correlation coefficients for each element studied in Lake Taupo (n=10). The element concentration is the average of the 24 cores at each depth interval.

| | Mn | S | Si | Al | U | P | As | $NH_4$ | $NO_3$ | $PO_4$ | Li | B | Na | K | Mg | Ca | Sr | Ba | Cu | Zn | Pb | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Fe** | -0.98 | -0.83 | 0.96 | 0.90 | 0.90 | 0.94 | 0.94 | 0.99 | -0.76 | 0.61 | 0.65 | 0.19 | 0.86 | 0.50 | -0.76 | -0.56 | -0.91 | 0.43 | 0.86 | 0.10 | 0.89 | -0.81 |
| **Mn** | | 0.84 | -0.95 | -0.88 | -0.90 | -0.95 | -0.92 | -0.98 | 0.73 | -0.61 | -0.66 | -0.15 | -0.84 | -0.49 | 0.76 | 0.61 | 0.92 | -0.37 | -0.84 | -0.08 | -0.90 | 0.82 |
| **S** | | | -0.74 | -0.61 | -0.60 | -0.68 | -0.91 | -0.77 | 0.69 | -0.13 | -0.24 | 0.30 | -0.46 | -0.02 | 0.51 | 0.59 | 0.75 | 0.08 | -0.71 | -0.22 | -0.72 | 0.54 |
| **Si** | | | | 0.98 | 0.97 | 0.96 | 0.82 | 0.99 | -0.74 | 0.74 | 0.69 | 0.36 | 0.93 | 0.61 | -0.86 | -0.60 | -0.95 | 0.60 | 0.92 | 0.18 | 0.93 | -0.87 |
| **Al** | | | | | 0.99 | 0.95 | 0.72 | 0.95 | -0.72 | 0.83 | 0.70 | 0.51 | 0.95 | 0.69 | -0.92 | -0.61 | -0.94 | 0.71 | 0.91 | 0.20 | 0.92 | -0.87 |
| **U** | | | | | | 0.97 | 0.71 | 0.95 | -0.67 | 0.86 | 0.77 | 0.48 | 0.96 | 0.73 | -0.90 | -0.60 | -0.93 | 0.70 | 0.90 | 0.15 | 0.92 | -0.88 |
| **P** | | | | | | | 0.82 | 0.97 | -0.73 | 0.79 | 0.75 | 0.34 | 0.92 | 0.63 | -0.83 | -0.57 | -0.92 | 0.57 | 0.85 | 0.05 | 0.90 | -0.90 |
| **As** | | | | | | | | 0.88 | -0.76 | 0.33 | 0.45 | -0.12 | 0.65 | 0.24 | -0.56 | -0.49 | -0.80 | 0.14 | 0.75 | 0.14 | 0.78 | -0.66 |
| **$NH_4$** | | | | | | | | | -0.76 | 0.71 | 0.71 | 0.30 | 0.92 | 0.59 | -0.81 | -0.56 | -0.93 | 0.53 | 0.88 | 0.10 | 0.91 | -0.88 |
| **$NO_3$** | | | | | | | | | | -0.38 | -0.17 | -0.06 | -0.61 | -0.11 | 0.57 | 0.36 | 0.72 | -0.29 | -0.59 | -0.15 | -0.64 | 0.82 |
| **$PO_4$** | | | | | | | | | | | 0.85 | 0.80 | 0.91 | 0.89 | -0.77 | -0.33 | -0.67 | 0.89 | 0.62 | -0.11 | 0.65 | -0.78 |
| **Li** | | | | | | | | | | | | 0.59 | 0.85 | 0.92 | -0.61 | -0.26 | -0.58 | 0.69 | 0.60 | -0.18 | 0.62 | -0.62 |
| **B** | | | | | | | | | | | | | 0.62 | 0.79 | -0.57 | -0.09 | -0.32 | 0.88 | 0.28 | -0.16 | 0.25 | -0.43 |
| **Na** | | | | | | | | | | | | | | 0.82 | -0.82 | -0.39 | -0.83 | 0.81 | 0.79 | -0.01 | 0.81 | -0.87 |
| **K** | | | | | | | | | | | | | | | -0.67 | -0.26 | -0.54 | 0.86 | 0.59 | 0.02 | 0.59 | -0.54 |
| **Mg** | | | | | | | | | | | | | | | | 0.80 | 0.94 | -0.64 | -0.88 | -0.28 | -0.90 | 0.73 |
| **Ca** | | | | | | | | | | | | | | | | | 0.80 | -0.12 | -0.77 | -0.49 | -0.80 | 0.34 |
| **Sr** | | | | | | | | | | | | | | | | | | -0.49 | -0.94 | -0.29 | -0.96 | 0.78 |
| **Ba** | | | | | | | | | | | | | | | | | | | 0.53 | 0.07 | 0.49 | -0.60 |
| **Cu** | | | | | | | | | | | | | | | | | | | | 0.50 | 0.97 | -0.64 |
| **Zn** | | | | | | | | | | | | | | | | | | | | | 0.43 | 0.14 |
| **Pb** | | | | | | | | | | | | | | | | | | | | | | -0.71 |

░ Significant at $p < 0.05$
▒ Significant at $p < 0.01$
▓ Significant at $p < 0.001$

**Table 4.4:** Pearson correlation coefficients for each element studied in Lake Tarawera (n=10). The element concentration is the average of the 24 cores at each depth interval.

| | Mn | S | Si | Al | U | P | As | $NH_4$ | $NO_3$ | $PO_4$ | Li | B | Na | K | Mg | Ca | Sr | Ba | Cu | Zn | Pb | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Fe** | 0.20 | -0.96 | 0.81 | 0.91 | 0.32 | 0.84 | 0.81 | 0.88 | -0.88 | 0.74 | -0.91 | -0.46 | 0.89 | 0.69 | 0.93 | 0.94 | 0.97 | 0.17 | 0.17 | 0.74 | 0.73 | 0.66 |
| **Mn** | | -0.08 | 0.11 | 0.18 | 0.30 | 0.30 | 0.55 | 0.55 | -0.45 | 0.15 | -0.43 | -0.67 | -0.17 | -0.41 | -0.09 | 0.01 | 0.16 | 0.93 | -0.15 | 0.54 | 0.03 | 0.82 |
| **S** | | | -0.84 | -0.83 | -0.08 | -0.84 | -0.79 | -0.86 | 0.87 | -0.73 | 0.91 | 0.48 | -0.96 | -0.81 | -0.97 | -0.99 | -0.99 | -0.05 | -0.23 | -0.56 | -0.68 | -0.59 |
| **Si** | | | | 0.86 | 0.32 | 0.98 | 0.87 | 0.82 | -0.72 | 0.95 | -0.68 | -0.24 | 0.76 | 0.53 | 0.78 | 0.77 | 0.80 | 0.27 | 0.48 | 0.65 | 0.88 | 0.63 |
| **Al** | | | | | 0.55 | 0.89 | 0.82 | 0.81 | -0.80 | 0.85 | -0.73 | -0.17 | 0.75 | 0.51 | 0.80 | 0.78 | 0.82 | 0.27 | 0.14 | 0.81 | 0.82 | 0.63 |
| **U** | | | | | | 0.40 | 0.32 | 0.26 | -0.21 | 0.40 | -0.05 | 0.24 | 0.02 | -0.26 | 0.13 | 0.04 | 0.11 | 0.44 | 0.03 | 0.72 | 0.48 | 0.33 |
| **P** | | | | | | | 0.93 | 0.90 | -0.79 | 0.96 | -0.76 | -0.37 | 0.71 | 0.43 | 0.75 | 0.76 | 0.82 | 0.42 | 0.41 | 0.76 | 0.85 | 0.76 |
| **As** | | | | | | | | 0.97 | -0.85 | 0.83 | -0.84 | -0.58 | 0.61 | 0.34 | 0.65 | 0.71 | 0.80 | 0.61 | 0.31 | 0.79 | 0.75 | 0.92 |
| **$NH_4$** | | | | | | | | | -0.92 | 0.76 | -0.93 | -0.68 | 0.69 | 0.44 | 0.73 | 0.80 | 0.89 | 0.54 | 0.23 | 0.76 | 0.66 | 0.92 |
| **$NO_3$** | | | | | | | | | | -0.62 | 0.92 | 0.57 | -0.76 | -0.57 | -0.80 | -0.85 | -0.91 | -0.38 | 0.10 | -0.60 | -0.47 | -0.78 |
| **$PO_4$** | | | | | | | | | | | -0.60 | -0.19 | 0.63 | 0.35 | 0.65 | 0.64 | 0.69 | 0.33 | 0.46 | 0.71 | 0.88 | 0.63 |
| **Li** | | | | | | | | | | | | 0.75 | -0.79 | -0.61 | -0.82 | -0.89 | -0.95 | -0.31 | -0.07 | -0.63 | -0.51 | -0.78 |
| **B** | | | | | | | | | | | | | -0.28 | -0.17 | -0.30 | -0.45 | -0.53 | -0.49 | -0.13 | -0.36 | -0.08 | -0.73 |
| **Na** | | | | | | | | | | | | | | 0.92 | 0.99 | 0.98 | 0.94 | -0.22 | 0.18 | 0.38 | 0.61 | 0.34 |
| **K** | | | | | | | | | | | | | | | 0.88 | 0.86 | 0.78 | -0.49 | 0.12 | 0.06 | 0.38 | 0.05 |
| **Mg** | | | | | | | | | | | | | | | | 0.98 | 0.96 | -0.14 | 0.17 | 0.47 | 0.64 | 0.41 |
| **Ca** | | | | | | | | | | | | | | | | | 0.99 | -0.06 | 0.16 | 0.49 | 0.61 | 0.50 |
| **Sr** | | | | | | | | | | | | | | | | | | 0.10 | 0.16 | 0.59 | 0.64 | 0.63 |
| **Ba** | | | | | | | | | | | | | | | | | | | 0.05 | 0.62 | 0.22 | 0.82 |
| **Cu** | | | | | | | | | | | | | | | | | | | | 0.27 | 0.62 | 0.15 |
| **Zn** | | | | | | | | | | | | | | | | | | | | | 0.75 | 0.78 |
| **Pb** | | | | | | | | | | | | | | | | | | | | | | 0.52 |

░ Significant at $p < 0.05$

▒ Significant at $p < 0.01$

▓ Significant at $p < 0.001$

**Table 4.5:** Pearson correlation coefficients for each element studied in Lake Okataina (Central basin) (n=10). The element concentration is the average of the 24 cores at each depth interval.

| | **Mn** | **S** | **Si** | **Al** | **U** | **P** | **As** | **NH$_4$** | **NO$_3$** | **PO$_4$** | **Li** | **B** | **Na** | **K** | **Mg** | **Ca** | **Sr** | **Ba** | **Cu** | **Zn** | **Pb** | **Hg** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Fe** | -0.64 | -0.38 | 0.93 | 0.64 | 0.71 | 0.55 | 0.02 | 0.84 | -0.41 | -0.56 | 0.47 | 0.17 | 0.57 | 0.16 | 0.69 | 0.64 | 0.86 | -0.36 | -0.42 | 0.31 | 0.31 | -0.45 |
| **Mn** | | 0.62 | -0.64 | -0.95 | -0.88 | -0.01 | 0.57 | -0.44 | 0.26 | 0.13 | -0.91 | -0.81 | -0.91 | -0.75 | -0.86 | -0.90 | -0.84 | 0.87 | 0.55 | -0.09 | -0.71 | 0.72 |
| **S** | | | -0.50 | -0.66 | -0.59 | -0.02 | 0.39 | -0.36 | 0.47 | 0.07 | -0.56 | -0.54 | -0.56 | -0.35 | -0.59 | -0.59 | -0.58 | 0.57 | 0.19 | -0.24 | -0.63 | 0.47 |
| **Si** | | | | 0.69 | 0.78 | 0.45 | -0.20 | 0.94 | -0.66 | -0.68 | 0.52 | 0.22 | 0.62 | 0.24 | 0.75 | 0.68 | 0.88 | -0.42 | -0.37 | 0.44 | 0.44 | -0.48 |
| **Al** | | | | | 0.94 | 0.01 | -0.65 | 0.46 | -0.33 | -0.23 | 0.95 | 0.68 | 0.96 | 0.79 | 0.94 | 0.96 | 0.90 | -0.91 | -0.68 | 0.16 | 0.84 | -0.83 |
| **U** | | | | | | 0.17 | -0.63 | 0.56 | -0.50 | -0.51 | 0.93 | 0.52 | 0.97 | 0.75 | 0.99 | 0.98 | 0.96 | -0.88 | -0.67 | 0.09 | 0.70 | -0.87 |
| **P** | | | | | | | 0.27 | 0.51 | -0.34 | -0.48 | -0.09 | -0.39 | -0.01 | -0.21 | 0.12 | 0.04 | 0.27 | 0.23 | -0.05 | 0.16 | -0.18 | -0.22 |
| **As** | | | | | | | | -0.08 | 0.36 | 0.10 | -0.75 | -0.57 | -0.72 | -0.90 | -0.61 | -0.64 | -0.40 | 0.77 | 0.46 | -0.07 | -0.73 | 0.70 |
| **NH$_4$** | | | | | | | | | -0.71 | -0.69 | 0.26 | 0.08 | 0.37 | 0.03 | 0.52 | 0.42 | 0.68 | -0.14 | -0.14 | 0.59 | 0.29 | -0.25 |
| **NO$_3$** | | | | | | | | | | 0.79 | -0.27 | -0.12 | -0.33 | -0.11 | -0.44 | -0.34 | -0.47 | 0.20 | -0.10 | -0.32 | -0.25 | 0.29 |
| **PO$_4$** | | | | | | | | | | | -0.22 | 0.22 | -0.31 | -0.01 | -0.48 | -0.36 | -0.55 | 0.12 | 0.14 | -0.07 | 0.03 | 0.29 |
| **Li** | | | | | | | | | | | | 0.69 | 0.99 | 0.90 | 0.94 | 0.97 | 0.82 | -0.98 | -0.72 | -0.10 | 0.74 | -0.87 |
| **B** | | | | | | | | | | | | | 0.62 | 0.64 | 0.49 | 0.57 | 0.40 | -0.71 | -0.11 | 0.04 | 0.60 | -0.38 |
| **Na** | | | | | | | | | | | | | | 0.87 | 0.97 | 0.99 | 0.89 | -0.96 | -0.75 | -0.01 | 0.75 | -0.89 |
| **K** | | | | | | | | | | | | | | | 0.75 | 0.81 | 0.56 | -0.91 | -0.69 | -0.08 | 0.74 | -0.83 |
| **Mg** | | | | | | | | | | | | | | | | 0.99 | 0.96 | -0.89 | -0.73 | 0.05 | 0.70 | -0.87 |
| **Ca** | | | | | | | | | | | | | | | | | 0.93 | -0.94 | -0.76 | -0.01 | 0.72 | -0.88 |
| **Sr** | | | | | | | | | | | | | | | | | | -0.75 | -0.66 | 0.14 | 0.60 | -0.76 |
| **Ba** | | | | | | | | | | | | | | | | | | | 0.69 | 0.11 | -0.76 | 0.84 |
| **Cu** | | | | | | | | | | | | | | | | | | | | 0.19 | -0.51 | 0.73 |
| **Zn** | | | | | | | | | | | | | | | | | | | | | 0.44 | -0.03 |
| **Pb** | | | | | | | | | | | | | | | | | | | | | | -0.73 |

| | |
|---|---|
| ░ | Significant at $p < 0.05$ |
| ▒ | Significant at $p < 0.01$ |
| ▓ | Significant at $p < 0.001$ |

**Table 4.6:** Pearson correlation coefficients for each element studied in Lake Okataina (North basin) (n=10). The element concentration is the average of the 24 cores at each depth interval.

| | **Mn** | **S** | **Si** | **Al** | **U** | **P** | **As** | **NH$_4$** | **NO$_3$** | **PO$_4$** | **Li** | **B** | **Na** | **K** | **Mg** | **Ca** | **Sr** | **Ba** | **Cu** | **Zn** | **Pb** | **Hg** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Fe** | -0.87 | -0.96 | 0.96 | 0.80 | 0.87 | 0.05 | 0.14 | 0.96 | 0.20 | -0.40 | 0.77 | 0.82 | 0.83 | 0.73 | 0.88 | 0.84 | 0.91 | -0.75 | 0.47 | 0.15 | 0.73 | -0.43 |
| **Mn** | | 0.88 | -0.75 | -0.93 | -0.95 | 0.40 | 0.34 | -0.79 | -0.02 | 0.71 | -0.96 | -0.90 | -0.98 | -0.95 | -0.90 | -0.95 | -0.89 | 0.94 | -0.26 | -0.02 | -0.96 | 0.75 |
| **S** | | | -0.94 | -0.88 | -0.85 | 0.06 | -0.09 | -0.94 | -0.22 | 0.51 | -0.78 | -0.87 | -0.85 | -0.73 | -0.91 | -0.87 | -0.91 | 0.83 | -0.38 | 0.05 | -0.77 | 0.52 |
| **Si** | | | | 0.71 | 0.73 | 0.24 | 0.34 | 0.99 | 0.35 | -0.26 | 0.61 | 0.81 | 0.70 | 0.56 | 0.78 | 0.71 | 0.80 | -0.66 | 0.59 | 0.06 | 0.62 | -0.35 |
| **Al** | | | | | 0.83 | -0.42 | -0.28 | 0.76 | -0.08 | -0.73 | 0.86 | 0.87 | 0.91 | 0.87 | 0.89 | 0.92 | 0.88 | -0.91 | 0.11 | -0.13 | 0.93 | -0.63 |
| **U** | | | | | | -0.36 | -0.29 | 0.75 | -0.01 | -0.66 | 0.94 | 0.75 | 0.94 | 0.89 | 0.90 | 0.93 | 0.91 | -0.84 | 0.16 | 0.10 | 0.84 | -0.61 |
| **P** | | | | | | | 0.90 | 0.20 | 0.56 | 0.79 | -0.56 | -0.20 | -0.49 | -0.59 | -0.34 | -0.47 | -0.28 | 0.50 | 0.64 | 0.36 | -0.51 | 0.58 |
| **As** | | | | | | | | 0.26 | 0.46 | 0.59 | -0.47 | -0.11 | -0.37 | -0.55 | -0.12 | -0.30 | -0.08 | 0.35 | 0.41 | 0.24 | -0.49 | 0.56 |
| **NH$_4$** | | | | | | | | | 0.36 | -0.27 | 0.64 | 0.84 | 0.72 | 0.62 | 0.77 | 0.72 | 0.79 | -0.68 | 0.61 | 0.06 | 0.68 | -0.37 |
| **NO$_3$** | | | | | | | | | | 0.44 | -0.15 | 0.16 | -0.07 | -0.16 | -0.07 | -0.12 | -0.10 | 0.05 | 0.69 | 0.10 | -0.06 | -0.07 |
| **PO$_4$** | | | | | | | | | | | -0.78 | -0.62 | -0.78 | -0.73 | -0.70 | -0.78 | -0.66 | 0.85 | 0.39 | 0.30 | -0.74 | 0.75 |
| **Li** | | | | | | | | | | | | 0.78 | 0.99 | 0.98 | 0.91 | 0.97 | 0.90 | -0.92 | 0.05 | 0.03 | 0.90 | -0.75 |
| **B** | | | | | | | | | | | | | 0.86 | 0.78 | 0.80 | 0.83 | 0.78 | -0.92 | 0.43 | -0.07 | 0.89 | -0.77 |
| **Na** | | | | | | | | | | | | | | 0.96 | 0.94 | 0.99 | 0.92 | -0.96 | 0.13 | 0.02 | 0.92 | -0.77 |
| **K** | | | | | | | | | | | | | | | 0.85 | 0.93 | 0.83 | -0.88 | 0.10 | 0.01 | 0.94 | -0.75 |
| **Mg** | | | | | | | | | | | | | | | | 0.98 | 0.99 | -0.89 | 0.07 | 0.04 | 0.78 | -0.57 |
| **Ca** | | | | | | | | | | | | | | | | | 0.96 | -0.95 | 0.05 | 0.02 | 0.88 | -0.69 |
| **Sr** | | | | | | | | | | | | | | | | | | -0.86 | 0.09 | 0.10 | 0.77 | -0.50 |
| **Ba** | | | | | | | | | | | | | | | | | | | -0.10 | 0.09 | -0.92 | 0.85 |
| **Cu** | | | | | | | | | | | | | | | | | | | | 0.29 | 0.21 | -0.14 |
| **Zn** | | | | | | | | | | | | | | | | | | | | | -0.11 | 0.16 |
| **Pb** | | | | | | | | | | | | | | | | | | | | | | -0.80 |

░ Significant at $p < 0.05$

▒ Significant at $p < 0.01$

▓ Significant at $p < 0.001$

**Table 4.7:** Pearson correlation coefficients for each element studied in Lake Rotoiti (n=10). The element concentration is the average of the 24 cores at each depth interval.

| | **Mn** | **S** | **Si** | **Al** | **U** | **P** | **As** | **$NH_4$** | **$NO_3$** | **$PO_4$** | **Li** | **B** | **Na** | **K** | **Mg** | **Ca** | **Sr** | **Ba** | **Cu** | **Zn** | **Pb** | **Hg** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Fe** | 0.95 | -0.92 | 0.93 | 0.66 | 0.86 | 0.78 | 0.94 | 0.90 | -0.45 | 0.56 | 0.95 | 0.91 | 0.96 | 0.97 | 0.95 | 0.97 | 0.97 | 0.96 | 0.39 | 0.86 | 0.70 | 0.68 |
| **Mn** | | -0.85 | 0.90 | 0.57 | 0.83 | 0.71 | 0.98 | 0.89 | -0.33 | 0.40 | 0.93 | 0.87 | 0.93 | 0.95 | 0.92 | 0.97 | 0.96 | 0.96 | 0.32 | 0.80 | 0.66 | 0.76 |
| **S** | | | -0.97 | -0.84 | -0.94 | -0.92 | -0.86 | -0.94 | 0.19 | -0.76 | -0.96 | -0.95 | -0.96 | -0.95 | -0.97 | -0.94 | -0.94 | -0.94 | -0.65 | -0.94 | -0.77 | -0.44 |
| **Si** | | | | 0.84 | 0.95 | 0.93 | 0.92 | 0.99 | -0.21 | 0.75 | 0.99 | 0.99 | 0.99 | 0.98 | 1.00 | 0.98 | 0.98 | 0.98 | 0.65 | 0.98 | 0.73 | 0.46 |
| **Al** | | | | | 0.91 | 0.87 | 0.66 | 0.81 | -0.05 | 0.85 | 0.81 | 0.85 | 0.80 | 0.76 | 0.81 | 0.74 | 0.75 | 0.76 | 0.76 | 0.88 | 0.78 | 0.13 |
| **U** | | | | | | 0.87 | 0.89 | 0.92 | -0.16 | 0.70 | 0.95 | 0.93 | 0.95 | 0.93 | 0.94 | 0.92 | 0.93 | 0.94 | 0.60 | 0.93 | 0.86 | 0.48 |
| **P** | | | | | | | 0.71 | 0.93 | 0.01 | 0.92 | 0.87 | 0.93 | 0.86 | 0.84 | 0.91 | 0.84 | 0.84 | 0.85 | 0.81 | 0.95 | 0.58 | 0.12 |
| **As** | | | | | | | | 0.90 | -0.34 | 0.44 | 0.96 | 0.90 | 0.96 | 0.97 | 0.93 | 0.98 | 0.97 | 0.97 | 0.36 | 0.84 | 0.74 | 0.75 |
| **$NH_4$** | | | | | | | | | -0.16 | 0.75 | 0.98 | 0.99 | 0.97 | 0.96 | 0.98 | 0.97 | 0.97 | 0.97 | 0.66 | 0.97 | 0.64 | 0.42 |
| **$NO_3$** | | | | | | | | | | 0.02 | -0.26 | -0.20 | -0.30 | -0.32 | -0.25 | -0.31 | -0.31 | -0.28 | 0.32 | -0.17 | -0.37 | -0.51 |
| **$PO_4$** | | | | | | | | | | | 0.67 | 0.78 | 0.66 | 0.62 | 0.72 | 0.60 | 0.62 | 0.62 | 0.85 | 0.83 | 0.43 | -0.20 |
| **Li** | | | | | | | | | | | | 0.98 | 1.00 | 1.00 | 1.00 | 0.99 | 0.99 | 0.99 | 0.57 | 0.95 | 0.76 | 0.57 |
| **B** | | | | | | | | | | | | | 0.97 | 0.96 | 0.99 | 0.96 | 0.96 | 0.96 | 0.69 | 0.99 | 0.68 | 0.41 |
| **Na** | | | | | | | | | | | | | | 1.00 | 0.99 | 0.99 | 0.99 | 0.99 | 0.56 | 0.95 | 0.77 | 0.58 |
| **K** | | | | | | | | | | | | | | | 0.99 | 1.00 | 1.00 | 1.00 | 0.51 | 0.93 | 0.76 | 0.62 |
| **Mg** | | | | | | | | | | | | | | | | 0.99 | 0.99 | 0.99 | 0.61 | 0.97 | 0.73 | 0.51 |
| **Ca** | | | | | | | | | | | | | | | | | 1.00 | 1.00 | 0.50 | 0.92 | 0.72 | 0.63 |
| **Sr** | | | | | | | | | | | | | | | | | | 1.00 | 0.50 | 0.93 | 0.73 | 0.62 |
| **Ba** | | | | | | | | | | | | | | | | | | | 0.50 | 0.93 | 0.74 | 0.62 |
| **Cu** | | | | | | | | | | | | | | | | | | | | 0.76 | 0.34 | -0.28 |
| **Zn** | | | | | | | | | | | | | | | | | | | | | 0.70 | 0.31 |
| **Pb** | | | | | | | | | | | | | | | | | | | | | | 0.55 |

░ Significant at $p < 0.05$
▒ Significant at $p < 0.01$
▓ Significant at $p < 0.001$

**Table 4.8:** Pearson correlation coefficients for each element studied in Lake Ngapouri (n=10). The element concentration is the average of the 24 cores at each depth interval.

| | **Mn** | **S** | **Si** | **Al** | **U** | **P** | **As** | **$NH_4$** | **$NO_3$** | **$PO_4$** | **Li** | **B** | **Na** | **K** | **Mg** | **Ca** | **Sr** | **Ba** | **Cu** | **Zn** | **Pb** | **Hg** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Fe** | 0.98 | -0.96 | 0.95 | 0.77 | 0.86 | 0.84 | 0.97 | 0.99 | -0.42 | | -0.95 | -0.67 | 0.80 | 0.90 | 0.97 | 0.96 | 0.97 | 0.95 | 0.62 | 0.79 | -0.14 | -0.58 |
| **Mn** | | -0.94 | 0.99 | 0.71 | 0.83 | 0.74 | 0.97 | 0.99 | -0.29 | | -0.91 | -0.71 | 0.91 | 0.96 | 0.94 | 0.89 | 0.91 | 0.99 | 0.59 | 0.83 | -0.03 | -0.51 |
| **S** | | | -0.95 | -0.89 | -0.94 | -0.87 | -0.89 | -0.94 | 0.33 | | 0.95 | 0.65 | -0.77 | -0.91 | -0.89 | -0.89 | -0.93 | -0.92 | -0.79 | -0.88 | 0.08 | 0.59 |
| **Si** | | | | 0.76 | 0.88 | 0.73 | 0.92 | 0.96 | -0.18 | | -0.91 | -0.73 | 0.93 | 0.98 | 0.89 | 0.83 | 0.86 | 0.99 | 0.69 | 0.90 | 0.05 | -0.50 |
| **Al** | | | | | 0.96 | 0.83 | 0.63 | 0.72 | -0.21 | | -0.78 | -0.49 | 0.54 | 0.73 | 0.69 | 0.73 | 0.78 | 0.71 | 0.93 | 0.86 | -0.03 | -0.44 |
| **U** | | | | | | 0.86 | 0.77 | 0.83 | -0.23 | | -0.87 | -0.62 | 0.69 | 0.84 | 0.79 | 0.80 | 0.84 | 0.84 | 0.89 | 0.91 | 0.02 | -0.47 |
| **P** | | | | | | | 0.77 | 0.81 | -0.63 | | -0.89 | -0.46 | 0.44 | 0.63 | 0.81 | 0.87 | 0.89 | 0.68 | 0.70 | 0.62 | -0.18 | -0.71 |
| **As** | | | | | | | | 0.98 | -0.44 | | -0.92 | -0.61 | 0.82 | 0.86 | 0.95 | 0.92 | 0.92 | 0.94 | 0.47 | 0.68 | -0.02 | -0.60 |
| **$NH_4$** | | | | | | | | | -0.41 | | -0.95 | -0.67 | 0.84 | 0.91 | 0.96 | 0.93 | 0.95 | 0.96 | 0.59 | 0.77 | -0.06 | -0.61 |
| **$NO_3$** | | | | | | | | | | | 0.50 | -0.01 | 0.11 | -0.03 | -0.48 | -0.58 | -0.56 | -0.17 | -0.06 | 0.12 | 0.31 | 0.56 |
| **$PO_4$** | | | | | | | | | | | | | | | | | | | | | | |
| **Li** | | | | | | | | | | | | 0.63 | -0.71 | -0.82 | -0.87 | -0.89 | -0.92 | -0.88 | -0.70 | -0.74 | 0.00 | 0.72 |
| **B** | | | | | | | | | | | | | -0.72 | -0.78 | -0.66 | -0.61 | -0.59 | -0.74 | -0.43 | -0.69 | 0.20 | 0.21 |
| **Na** | | | | | | | | | | | | | | 0.95 | 0.75 | 0.64 | 0.66 | 0.95 | 0.49 | 0.84 | 0.16 | -0.28 |
| **K** | | | | | | | | | | | | | | | 0.84 | 0.77 | 0.80 | 0.98 | 0.66 | 0.93 | -0.01 | -0.37 |
| **Mg** | | | | | | | | | | | | | | | | 0.98 | 0.97 | 0.90 | 0.48 | 0.69 | -0.25 | -0.48 |
| **Ca** | | | | | | | | | | | | | | | | | 0.99 | 0.84 | 0.50 | 0.64 | -0.30 | -0.54 |
| **Sr** | | | | | | | | | | | | | | | | | | 0.86 | 0.58 | 0.70 | -0.28 | -0.57 |
| **Ba** | | | | | | | | | | | | | | | | | | | 0.61 | 0.87 | 0.01 | -0.44 |
| **Cu** | | | | | | | | | | | | | | | | | | | | 0.85 | 0.21 | -0.47 |
| **Zn** | | | | | | | | | | | | | | | | | | | | | 0.07 | -0.29 |
| **Pb** | | | | | | | | | | | | | | | | | | | | | | -0.23 |

░ Significant at $p < 0.05$
▒ Significant at $p < 0.01$
▓ Significant at $p < 0.001$

Note: $PO_4$ not measured.

# CHAPTER 5: NATURAL AND ANTHROPOGENIC LEAD IN THE SEDIMENTS OF THE ROTORUA LAKES, NEW ZEALAND

## 5.1 INTRODUCTION

Lead has a long residence time in the environment compared with most other pollutants (Davies, 1990; Nriagu, 1998). Natural sources of lead include particulates transported to lake sediments directly from erosion of sediments in the catchment, mobilisation of lead from the weathering of catchment bedrock and soils (Renberg et al., 2002), and atmospheric inputs from volcanic eruptions (Graney et al., 1995). Historically, the natural airborne lead fraction has been insignificant compared with supply from catchments (Bindler et al., 2001). With increasing anthropogenic additions of lead to the natural environment it has been possible to distinguish anthropogenic sources in disparate environments such as the Arctic (Sturges and Barrie, 1989), Pacific Ocean atmosphere (Settle and Patterson, 1982), Antarctic and Greenland ice (Murozumi et al., 1969; Rosman et al., 1993; Hong et al., 1994), peat bogs (Shotyk et al., 1998), Alantic and Pacific Ocean corals (Shen and Boyle, 1987), coastal marine sediments (Chow et al., 1973; Veron et al., 1987) and lake sediments (Edgington and Robbins, 1976; Graney et al., 1995; Monna et al., 1999; Renberg et al., 2002). In these studies, isotopic ratios and/or changes in concentrations of lead have been used to infer a variety of different sources. Local emissions from industrial and urban sources dominate the lead found in lake sediments (Monna et al., 1999; Harrison and Laxen, 1984). In New Zealand, the only significant, broadscale anthropogenic source of lead is from petroleum additives. In the absence of natural environmental fluctuations, variations in lead within recent lake sediments should reflect changes in anthropogenic sources, whilst variations amongst lakes may reflect complex interactions with the environmental conditions leading to net deposition to the sediments.

In New Zealand lead alkyls were first added to petroleum in the 1920s as a cheap and convenient method of boosting octane ratings and reducing uneven ignition (“knocking”) in combustion engines. When leaded petroleum is combusted in a motor vehicle engine, > 75% of lead is emitted from the exhaust as large particles which fall rapidly to the ground, while finer particles stay airborne for considerably longer periods of time (Eisenreich et al., 1986). By contrast, the exhaust from the predominantly two-stroke motor boat fleet is generally discharged directly to water. Prior to 1986, New Zealand had one of the highest levels of lead in petrol (0.84 g $L^{-1}$) of any nation (Taylor, 1998). Despite a reduction in 1986 to 0.45 g $L^{-1}$, levels were still high compared with elsewhere. For example, most of Europe, including Britain, had reduced lead additives by 1986 to 0.15 g $L^{-1}$ and the limit for the United States was 0.026 g $L^{-1}$ (Taylor, 1998). A transition from leaded to unleaded petroleum took place in New Zealand between 1987 and 1996, resulting in almost complete elimination of airborne lead from the New Zealand environment (Wilson and Horrocks, 2008) . In summary, except for a brief interruption in the 1940s, lead alkyl consumption in New Zealand increased steadily from the 1930s, plateaued between 1975 and 1986, and then decreased rapidly (Figure 5.1).

Once lead has entered a lake, both specific adsorption and ion exchange mechanisms operate to transfer lead onto suspended sediments. The most significant sink for heavy metals in aerobic waters is scavenging by colloidal hydrous ferric and manganese oxides ($Fe(OH)_3$ and $MnO_2$) (Harrison and Laxen, 1981). The sorption process is rapid and mostly irreversible, especially if the metal is incorporated with the hydrous oxide as it is precipitated. However, the adsorption is strongly pH dependent, increasing with an increase in pH. Hydrous ferric and manganese oxides are readily reduced and become soluble under anaerobic conditions, and may release their associated metals. In eutrophic lakes the sediments, may be anoxic for long periods, with sulfate (if sufficent is present) being reduced to sulfide, which removes any lead from the soluble phase via transformation to highly insoluble lead sulfide (Harrison and Laxen, 1981). In oligotrophic lakes the sediments may still be anoxic, but generally for brief periods of time and at much greater depth below the sediment-water interface, so that diagenetic immobilisation of lead will occur only deeper in the bottom sediments.

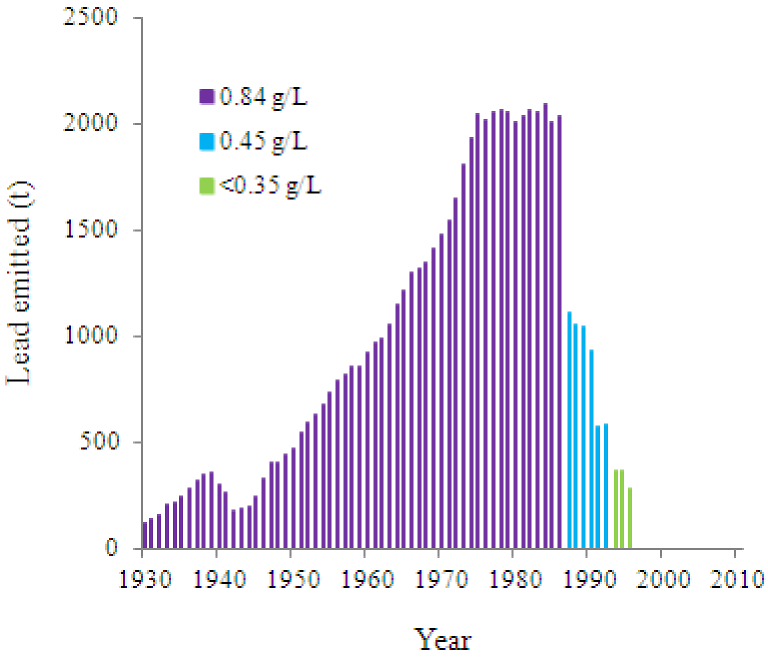

**Figure 5.1:** Total amount of lead entering the New Zealand environment from petroleum consumption calculated by the total amount of petroleum consumed multiplied by the reported percentage of lead additive. Data from Statistics New Zealand (1960; L. Mackie, personal communication, February 17, 2009) and Ministry of Commerce (1996).

The aim of our study was to use sediments from a diverse set of lakes within the Rotorua region of New Zealand to indicate rates of environmental inputs of lead whilst taking into account differences of trophic state and lead exposure between the lakes. The lakes investigated range in trophic status from oligotrophic to highly eutrophic and also vary in exposure to leaded petroleum emissions (Table 5.1). The relatively isolated location and recent human settlement of New Zealand provided an opportunity to assess the geochemical transitions of lead in lake sediments associated with additions to petroleum.

## 5.2 MATERIALS AND METHODS

### 5.2.1 Study sites

The Rotorua lakes have been formed up to 140 000 years ago from a series of volcanic eruptions that characterise the Taupo Volcanic Zone (TVZ) (Figure 5.2) and have provided a series of stratigraphic markers for dating lake sediments (Lowe and Green, 1987). The most recent, the Tarawera tephra (arising from 10 June, 1886) is very distinctive in the sediment and can be easily distinguished visually within the top metre of sediment in all of the Rotorua Lakes. The tephra is described by Pullar and Kennedy (1981) as comprising of Tarawera scoria, a loose scoriaceous dark coloured coarse material underlying the Rotomahana mud, a grey to olive grey sandy to silty material. It is this upper extent of the Rotomahana mud layer that we term the ‘depth to the Tarawera tephra’. The Rotorua District is still geothermically active, with lakes Rotorua, Rotoiti, Tarawera, Rotomahana and Rotoehu influenced by geothermal inflows (Vincent and Forsyth, 1987), which contribute significant sulfate to these lakes (Timperly and Vigor-Brown, 1986).

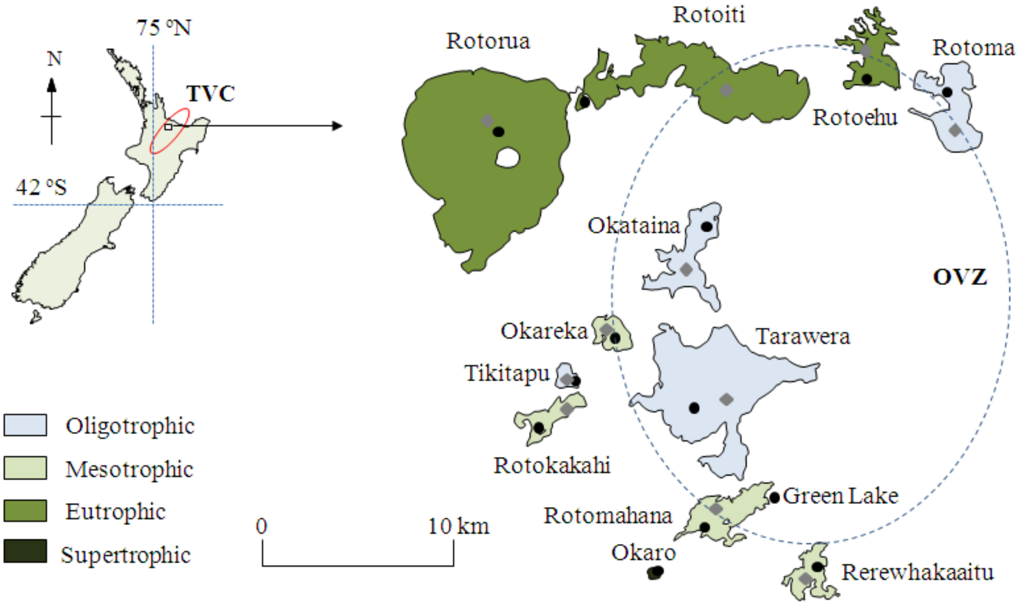

**Figure 5.2:** Location of the Rotorua lakes, showing sample sites (marked with a ● for core 1 and a ◆ for core 2) and trophic status (shaded) of Rotorua lakes, within the Taupo Volcanic Centre (TVC) (solid line), New Zealand. The Okataina Volcanic Centre (OVC) is located in the Rotorua

region and is shown by the dashed line. It is these volcanic centeres that are the source of the tephra layers used to date the sediment. Note only one core was collected in Green Lake.

The Rotorua lakes vary widely in trophic status (oligotrophic to highly eutrophic) and have two predominant mixing regimes; monomictic and polymictic (Table 5.1) (McColl, 1977; Burns et al., 1997; Trolle et al., 2008). Lake trophic status and silica availability are important controls on sedimentation rates (mainly diatom frustules where there is sufficient silica) and the extent of chemical reduction within the sediments (Trolle et al., 2008). A detailed chemical composition for the Rotorua lakes is given in Timperley and Vigor-Brown (1986). Sedimentation rates for the lakes are quoted from Trolle et al. (2008) who determined the depth to the Tarawera tephra in multiple cores taken from central deep basin of each of the lakes. They assumed a constant sedimentation rate since 1886. Where lakes have become more eutrophic subsequently, sedimentation rates can also be expected to increase, especially where diatoms predominate (Fish, 1969; Flint, 1977).

**Table 5.1:** Physical characteristics of the Rotorua Lakes (McColl, 1975; Timperley, 1975; Burns et al., 1997; Trolle et al., 2008).

| Lake | Mean depth (m) | Max. depth (m) | Lake area (ha) | Catchment area (ha) | Sedimentation rate (1886-2006) (mm $y^{-1}$) | Trophic state | Mixing Regime | Potential Lead Input |
|---|---|---|---|---|---|---|---|---|
| Rotoma | 36.9 | 83.0 | 1104 | 2914 | 1.4 (0.9-1.8) | Oligotrophic | M | Moderate |
| Tarawera | 50.0 | 87.5 | 4165 | 14 494 | 2.2 (2.1-2.3) | Oligotrophic | M | Moderate |
| Okataina | 39.4 | 78.5 | 1104 | 5676 | 1.4 (1.4-1.4) | Oligotrophic | M | Low |
| Tikitapu | 18.0 | 27.5 | 146 | 567 | 0.6 (0.6-0.6) | Oligotrophic | M | High |
| Rotokakahi | 17.5 | 32.0 | 452 | 1872 | 1.0 (0.3-1.4) | Mesotrophic | M | Moderate |
| Okareka | 20.0 | 33.5 | 342 | 1958 | 1.4 (1.3-1.5) | Mesotrophic | M | Moderate |
| Rerewhakaaitu | 7.0 | 15.8 | 579 | 3816 | 1.7 (1.6-1.8) | Mesotrophic | P | Low |
| Rotomahana | 60.0 | 125.0 | 897 | 7994 | 0.8 (0.75-0.9) | Mesotrophic | M | Low |
| Rotoiti | 31.5 | 124.0 | 3460 | 12 462 | 1.7 (1.7-1.7) | Eutrophic | M | High |
| Rotoehu | 8.2 | 13.5 | 795 | 5673 | 2.6 (2.6-2.6) | Eutrophic | P | Moderate |
| Rotorua | 11.0 | 44.8 | 8079 | 52 346 | 3.0 (3.0-3.0) | Eutrophic | P | High |
| Okaro | 12.5 | 18.0 | 32 | 407 | 2.3 (1.5-2.8) | Highly Eutrophic | M | Moderate |
| Green Lake | * - | 26.2 | 1.12 | 2.16 | * - | Highly Eutrophic | M | Very Low |

* Some variables for Green Lake have not been determined.

Note: Physical characteristics of the lakes from McColl (1975); Timperley (1975) and Burns et al. (1997). Sedimentation rate from Trolle et al. (2008) showing the mean value and range in parentheses. Trophic state is evaluated by Environment Bay of Plenty using the Trophic Level

Index (TLI) (Burns et al., 2009). Potential lead exposure is rated by usage of the lake by motorised vessels, proximity to major roads and urban runoff. High input has been assigned to Lakes Rotorua and Rotoiti because of the density of settlement, extent of major roads and high usage by motor vessels. Tikitapu is a small lake used intensively for motorised water sports. Lakes Okataina, Rotomahana and Rerewhakaaitu have limited access, negligible urbanisation and motorised vessels are only occasionally encountered; they have been assigned low input.

### 5.2.2 Sampling methods

Sediments from thirteen Rotorua lakes; Rotoma, Tarawera, Okataina, Tikitapu, Okareka, Rotokakahi, Rerewhakaaitu, Rotomahana, Rotoiti, Rotoehu, Rotorua, Okaro and Green Lake, were sampled between March 2006 and January 2007. Two cores separated by a few metres were taken at a site near the deepest part of the central basin in each lake (Figure 5.2; Table 5.2), targeting areas conforming to accumulation bottoms (cf. Håkanson and Jansson, 1983). Cores were taken with a Swedish gravity corer (Pylonex HTH 70 mm) with a 60 x 600 mm Perspex (Plexiglas) core barrel to capture undisturbed sediments. The gravity corer penetrated to a depth between c. 16 and 30 cm depending on the density of the sediment. The surface sediment was visually inspected in each core to determine if there was any disturbance at the sediment-water interface or in the sediment profile; the core was discarded and another core taken if the core was considered to have been disturbed during coring. A description of the core was recorded, including the depth to the Tarawera tephra. A custom made gas-tight sampling chamber, designed to minimise exposure of potentially anoxic sediment to the air, was fitted to the core barrel and, following retrieval, the core was extruded by a piston from the base of the core. Excess supernatant water overflowed the top of the core before the sediment sample was collected. Samples were extruded in 2 cm intervals and transferred into 50 mL polypropylene centrifuge tubes which were then sealed and placed on ice until return to the laboratory.

**Table 5.2:** Details of sediment cores taken for this study.

| Lake | Core no. | Water depth of sample site (m) | Depth to Tarawera tephra (mm) | Core sedimentation rate (mm y$^{-1}$) |
|---|---|---|---|---|
| Rotoma | 1 | 81.7 | 200 | 1.7 |
| | 2 | 35.6 | 180 | 1.5 |
| Tarawera | 1 | 82.2 | 260 | 2.2 |
| | 2 | 83.5 | 240 | 2.0 |
| Okataina | 1 | 69.1 | 160 | 1.3 |
| | 2 | 68.1 | 160 | 1.3 |
| Tikitapu | 1 | 25.2 | 90 | 0.8 |
| | 2 | 25.4 | 90 | 0.8 |
| Rotokakahi | 1 | 28.7 | 130 | 1.1 |
| | 2 | 28.6 | 130 | 1.1 |
| Okareka | 1 | 28.5 | 180 | 1.5 |
| | 2 | 24.8 | 140 | 1.2 |
| Rerewhakaaitu | 1 | 13.7 | 220 | 1.8 |
| | 2 | 10.0 | 260 | 2.2 |
| Rotomahana | 1 | 74.0 | 90 | 0.8 |
| | 2 | 74.0 | 120 | 1.0 |
| Rotoiti | 1 | 64.9 | 300 | 2.5 |
| | 2 | 4.8 | 170 | 1.4 |
| Rotorua | 1 | 18.4 | 460 | 3.8 |
| | 2 | 18.4 | 460 | 3.8 |
| Rotoehu | 1 | 9.8 | 300 | 2.5 |
| | 2 | 9.6 | 300 | 2.5 |
| Okaro | 1 | 15.0 | 300 | 2.5 |
| | 2 | 17.0 | 320 | 2.7 |
| Green Lake | 1 | 10.2 | 300 + | < 2.5 |

Sedimentation rates calculated from depth to Tarawera tephra in the captured core.

In March 2007, a piston core was taken through progressively deeper sediments in Lake Rotorua to a depth of 8 m below the sediment surface in a water depth of 18.4 m. The core was taken using a 3 m modified Livingstone piston coring system fed through a 15 cm diameter PVC pipe to guide the piston core to the same location on the lake bed for each successive core (Pickett, 2008). Sequential 3 m piston cores were extracted into longitudinally sectioned PVC tubes of the same diameter as the core barrel. As the piston coring method fails to capture the upper few cm of sediment an additional gravity core was collected adjacent to the piston core, and processed in the same way as the gravity cores from other lakes. This allowed the interpolation of the sediment record to the sediment-water interface. In the laboratory, the piston core was split using a wire cutter and the exposed core surface cleaned by scraping back to a uniform flat surface to ensure any sedimentary or structural features became evident and distinguishable from any features originating from the core splitting process. The core was then described and photographed (Pickett, 2008). Sediment samples of approximately 0.5 cm were cut from the core at 1 cm intervals to achieve a high-resolution sediment record. Tephra horizons were recognised by textural and colour changes (white to pale grey), within the olive diatomaceous lake sediment (Table 5.3) and confirmed by x-ray imaging. The majority of the tephra layers exhibited primary depositional features with a sharp base that readily enabled recognition of the tephra extent and depth.

**Table 5.3:** Details of tephra located in the Lake Rotorua core.

| Tephra Name | Source | Age (Cal. yrs B.P.) | Year | Depth in sed. (mm) | Inferred sedimentation rate (mm $yr^{-1}$) | Tephra Pb conc. ($\mu g\ g^{-1}$) |
|---|---|---|---|---|---|---|
| Tarawera | OVC | 64 | 1886 AD | 360-450 | 3.3 | 8.80 |
| Reworked 1 | - | | | 2110-2126 | | 3.40 |
| TgVC ash | TVC | | | 2190-2200 | | 1.99 |
| Reworked 2 | - | | | 3880-3900 | | 1.94 |
| Reworked 3 | - | | | 5010-5020 | | 2.79 |
| Kaharoa | OVC | 636 ± 12 | 1314 ± 12 AD | 5040-5130 | 3.45 | 2.40 |
| Taupo (Unit Y) | TVC | 1717 ± 13 | 233 ± 13 AD | 5670-5690 | 0.48 | 1.63 |
| Waimihia (Unit S) + secondary Whakaipo tephra (Unit V) | TVC | 3410 ± 40 | 1460 BC | 6730-6750 | 0.61 | 2.79 |
| Whakatane + secondary Unit K | OVC | 5530 ± 60 | 3580 BC | 6950- | 0.12 | 0.84 |

Tephras were identified by on the basis of field appearance, stratigraphic position, ferromagnesian mineralogy, and major element glass chemistry (Pickett, 2008). Source shows the origin of tephra (Okataina Volcanic Centre, Taupo Volcanic Centre (Figure 5.2)). Age (Cal yrs. B.P) is the radiocarbon date with before present (B.P. 1950) taken from Lowe et al. (2008). Inferred sedimentation rate shows the rate of sediment accumulation between the tephra and the next overlying dated tephra. The Tarawera tephra shows the sedimentation rate for sediment accumulated since the eruption. The rate is calculated from comparison between both piston and gravity cores. The tephra lead concentration shows the maximum lead value present in the samples taken from the tephra layer.

### 5.2.3 Analytical methods

In the laboratory, the gravity core sediments were weighed to determine bulk density before porewaters were separated by centrifugation at 4000 rpm for 40 min. All sediments were dried at 50 °C for 48 h and ground using a mortar and pestle. Lead content of the sediment was determined after the solids had been digested with reverse Aqua Regia at 50 °C for one hour based on a modified standard procedure (Martin et al., 1994; Pearson, 2007). The resulting digest was analysed using inductively coupled plasma mass spectrometry (ICP-MS model ELAN DRC II). The sediment dry weight fraction was determined by weighing solid samples before and after drying, and taking into account porewater mass. The pore water was filtered through a 0.45 µm Millipore filter and acidified with nitric acid before analysis on ICP-MS as above. Scanning electron microscope (SEM) images were taken of the dried Lake Rotorua sediment before it was ground to assess the nature of the sediment. A detailed analysis of the composition of the sediment under SEM can be found in Pearson (2007) and Pickett (2008) (see also Figure 5.7).

## 5.3 RESULTS AND DISCUSSION

### 5.3.1 Preindustrial lead

An age model to identify pre-industrial sediment deposition in the Rotorua core was created from the thicknesses of biogenic material between tephras of known age (Whakatane (5530 ± 60 cal. BP), Waimihia (3410 ± 20 cal. BP), Taupo (1717 ± 13 cal. BP), Kaharoa (c. AD 1314 ± 12) and the Tarawera eruption (AD 1886) (Balance, 1981; Newnham et al., 1998; Hogg et al., 2003; Lowe et al., 2008)) assuming constant sedimentation rates between eruption events. Tephra layers recorded as ‘reworked’ were not included in the age model as they are inferred to be caused by the reworking of coarse-grained tephra in shallower water, with these sediments deposited in the deeper lake basin during large storm events (c. 1300, 520 and 220 cal years B.P) (Pickett, 2008). The thickness of the reworked layers was accounted for in the determination of the sedimentation rate as these sediments are not biogenic material.

Lake Rotorua is antipodal to the preindustrial sources of atmospheric lead but still shows increases in lead concentrations from < 2 up to 3.5 µg $g^{-1}$ between the Whakatane eruption (5530 ± 60 cal. yrs BP) and the Tarawera eruption (Figure 5.3). These changes parallel the trend of increases in lead observed in European and American lake sediments (Renberg et al., 1994; Graney et al., 1995; Monna et al, 1999; Renberg et al., 2002), but at much lower levels. Settle and Patterson (1980) concluded that because the residence time of atmospheric aerosols is an order of magnitude less than the inter-hemispheric exchange time, the impact in the Southern hemisphere from Northern hemisphere sources would be about one-tenth of that in the Northern Hemisphere; similar to fraction of lead in Lake Rotorua relation to the Northern Hemisphere lakes.

Concentrations of lead in the Rotorua core have local maxima centred around the tephra layers in pre-industrial sediments. Lead concentrations increase (> 2 µg Pb $g^{-1}$) in the core commencing soon after deposition of the Tongariro tephra (age unknown but approximately 1700 AD), which may be related to a global increase in atmospheric lead levels (Settle and Patterson, 1980; Renberg et al., 1994) as there was no significant source of lead in New Zealand at this time of early Polynesian settlement. Globally, lead production has continued to increase since 5000 years BP and the concentration of lead in the sediments of Lake Rotorua mimics this global production trend (Figure 5.3). An increase in lead concentrations, well above background levels or those of any of the tephras, occurred at a depth of 10 cm below the top of the core, where the peak is 14.1 µg Pb $g^{-1}$ in the year 1982 (Figure 5.3). We attribute this peak to an increase in anthopogenic lead sources (Figure 5.1).

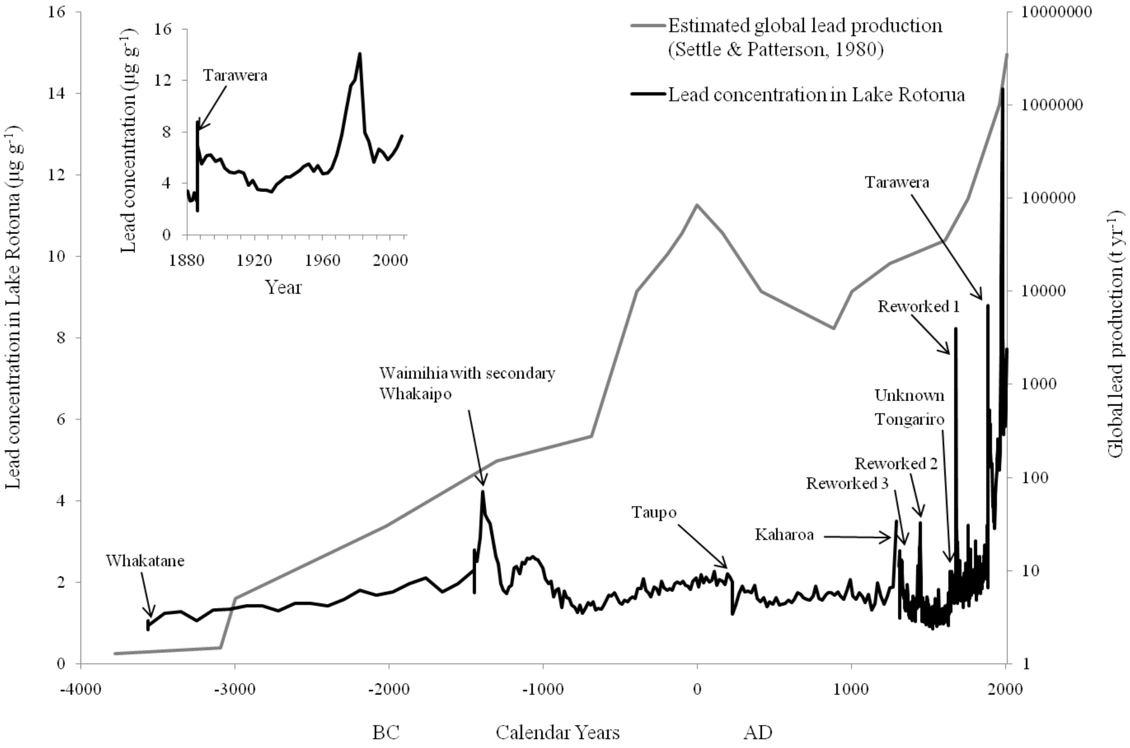

**Figure 5.3:** Lead concentration in a Lake Rotorua sediment core with depositional age in excess of 5500 years on the left vertical axis. Global lead production for the same time period on the right vertical axis (Settle and Patterson, 1980). Annotations show volcanic events. Insert graph shows the lead concentration in Lake Rotorua for the period 1880 to present.

### 5.3.2 Anthropogenic lead

Identification of sediments likely to be impacted by local anthropogenic emissions is facilitated by the presence of the Tarawera tephra, which occurs in all of the Rotorua lakes. Sources of anthropogenic lead in the Rotorua lakes were negligible before the 1950s, peaked in the 1980s and declined during the 1990s, as lead was withdrawn from petroleum (Statistics New Zealand, 1960; L. Mackie, personal communication, February 17, 2009). Sediment profiles of the lead concentration in the Rotorua lakes all show a subsurface peak above the Tarawera tephra, with the exception of Green Lake (Figure 5.4). The spatial variation between the sampling sites in the lakes is not significant with both profiles exhibiting similar results. Figure 5.5 shows a sediment profile of lead concentrations based on proportional age assuming a steady sedimentation rate since the Tarawera eruption (1886). The concentration and pattern of distribution of lead in the sediments of the Rotorua lakes show differences consistent with trophic status. Oligotrophic lakes (Figure 5.5a) show a steady increase in lead concentrations since the Tarawera tephra, with a peak between 7 and 12 µg $g^{-1}$ between 1950 and 1970, followed by a decline towards the sediment-water interface. Mesotrophic lakes (Figure 5.4b) show a higher peak lead concentration (12-15 µg $g^{-1}$) between sediments aged 1970 and 1990, while eutrophic lakes, Rotoehu, Okaro and Rotoiti (Figure 5.4c), show a peak in lead concentration up to 25 µg $g^{-1}$ between 1920 and 1950, followed by a steady decline towards the sediment-water interface. Lakes with the lowest sedimentation rates (Tikitapu and Rotomahana; see Table 5.1) both have peak lead concentrations very close to the sediment surface. Peak concentrations of lead appear in sediments older than those corresponding to the peak discharge of lead to the environment. The extent of the displacement appears to be closely related to lake trophic status with the greatest displacement in the most eutrophic lakes.

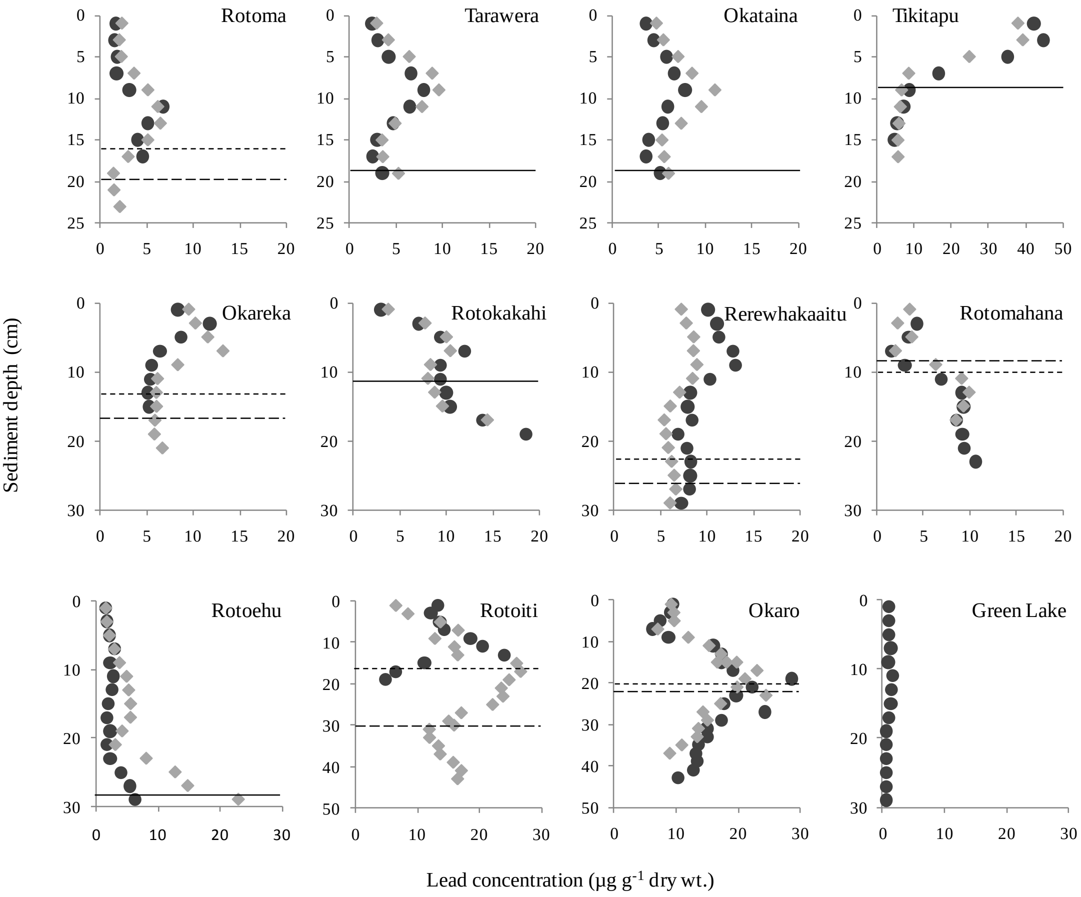

**Figure 5.4:** Sediment concentration profiles of lead in the Rotorua lakes. Two cores (marked with a ●and ◆) were collected from the 13 lakes. Plots are arranged from oligotrophic to eutrophic (from left to right and top to bottom). If present in the core, the start of the Tarawera tephra layer, a layer of ash deposited during the 1886 AD eruption, has been highlighted (marked with - - - - for sites represented by ●, — — for sites represented by ◆, and —— where the tephra layer was present at the same vertical depth for both sites. The y-axis represents depth below the sediment-water interface (cm) and the x-axis represents the lead concentration (µg g$^{-1}$ dry wt.). Note the different scales for both axes.

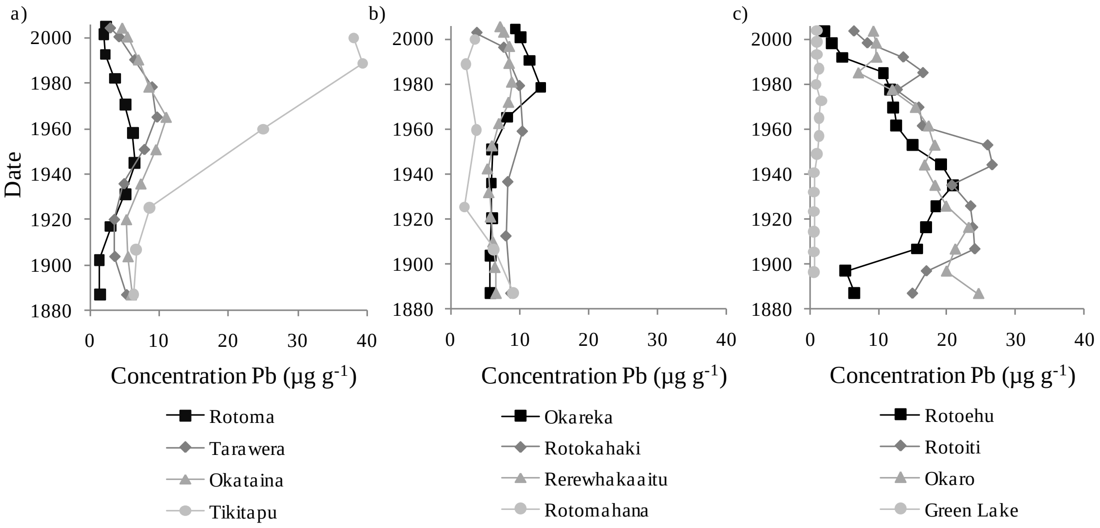

**Figure 5.5:** Concentration of lead in sediment of a) oligotrophic lakes b) mesotrophic lakes and c) eutrophic lakes versus the sediment age calculated by the accumulation rate (mg cm$^{-2}$ yr$^{-1}$ from bulk density) to the Tarawera tephra. Each data point represents a 2 cm slice of core.

### 5.3.3 Redistribution of lead and diagenesis within lake sediments

Lakes Rotorua, Rotoehu, Rotoiti and Okaro have become significantly eutrophied in recent decades (Burns et al., 2009), resulting in high rates of organic matter deposition (Trolle et al., 2009) and a peak lead concentration that is deeper in the sediment. In these lakes there is a broad distribution of elevated lead concentrations across the depth profile as a result of diagenesis and re-precipitation. Analyses of pore waters in these lakes typically show increasing concentrations of iron and manganese and decreasing concentrations of sulfur with depth below the sediment-water interface (Figure 5.6). In many of the lake sediments, iron concentrations in the pore waters remain low and do not display systematic changes until sulfur concentrations are low. Scanning Electron Microscope (SEM) images of dried sediments from Lake Rotorua produced high densities of small framboidal clusters of pyrite that we suggest are indicative of super-saturation and precipitation of iron sulfides (Figure 5.7). Energy dispersive x-ray fluorescence (XRF) analysis of the framboidal pyrite detected significant fluorescence’s for sulphur, iron and minor fluorescence for lead. Lead is most likely bound to inorganic particle surfaces by iron or manganese hydroxides and oxy-hydroxides, as indicated by a high covariance between lead and iron ($r^2$=0.98 p<0.01), and lead and manganese ($r^2$=0.93 p<0.01) in the top 20 cm of sediment (Pearson, 2007). While the sediments remain oxidised, iron and manganese adsorption can be expected to maintain the lead in a particulate, immobile form (Sigg, 1985). With burial, the sediments of all of the lakes will become anoxic, which will induce reduction of manganese and iron, and mobilization of the lead. This effect is most pronounced in eutrophic lakes, with seasonally anoxic hypolimnia where sulfide generation in the sediments results in precipitation of lead sulfide, limiting the concentration of lead in the pore waters (Schindler, 1985). As sulfate reduction tends to occur deeper in the sediment than iron or manganese reduction, this process tends to redistribute lead from deeper in the sediments, reducing peak concentrations and smearing distributions across the depth profile as observed in Figure 5.5.

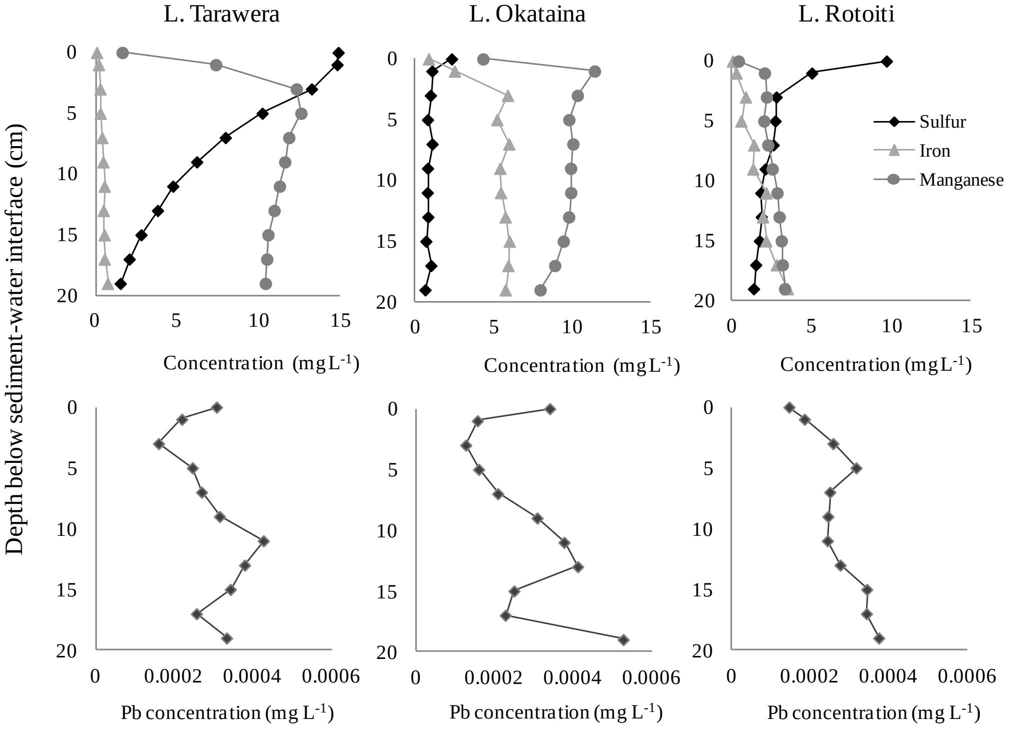

**Figure 5.6:** Mean annual concentrations of sulfur, iron, manganese and lead in pore waters of selected Rotorua Lakes. In a) Lake Tarawera the hypolimnion remains oxygenated the whole year, whereas in b) Lake Okataina the hypolimnion experiences seasonal anoxia during summer stratification (3 months) and in c) Lake Rotoiti the hypolimnion remains anoxic for half of the year (c. 6 months).

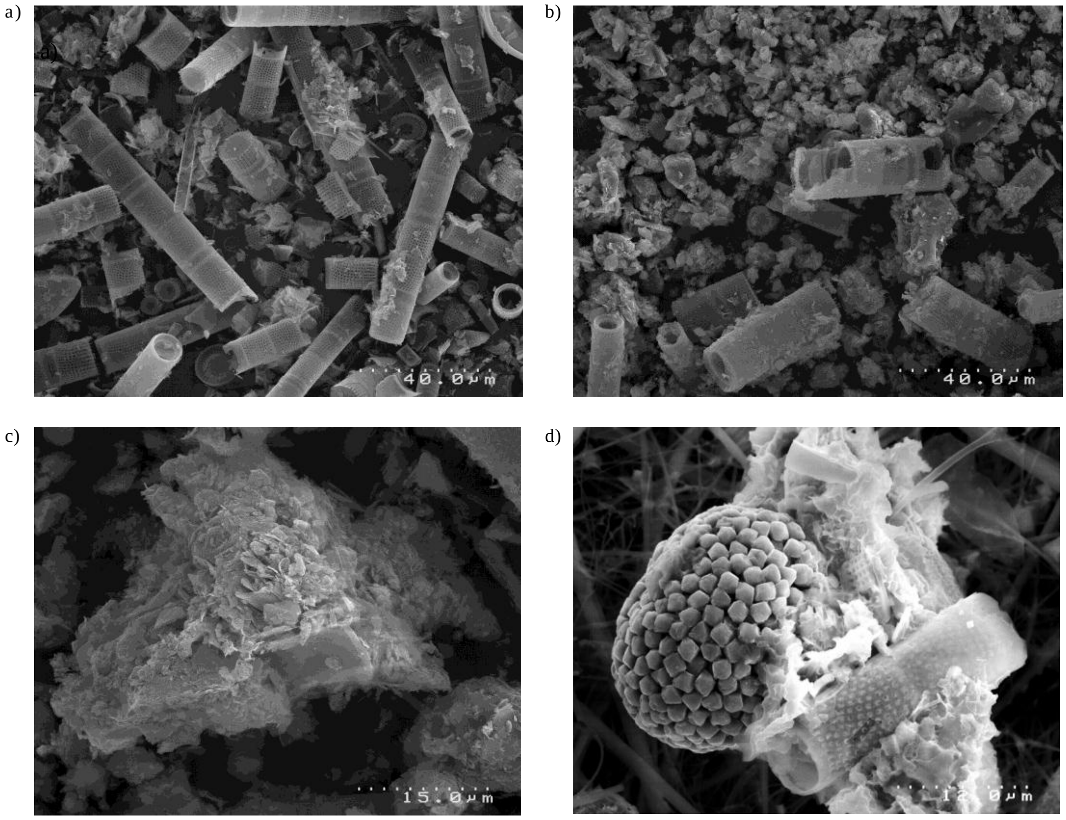

**Figure 5.7:** Scanning Electron Microscope image of Lake Rotorua sediment showing a) the dominance of *Aulacoseira granulata* (diatom) frustules (cylindrical shape) over other diatom species and mineral particles, b) Rotomahana mud (Tarawera Tephra) erupted from Lake Rotomahana during the Tarawera eruption), c) increased magnification of Rotomahama mud layer showing the presence of diatoms within the mud layer and d) framboidal pyrite (upper left of foreground) and *Aulacoseira granulata* frustules (Pearson, 2007).

### 5.3.4 Lake Outliers

Lakes Tikitapu, Rotomahana and Green Lake are outliers to the general pattern in other Rotorua lakes of occurrence of peak lead at a depth dependent on trophic status (Figures 5.4 and 5.5). Lake Tikitapu has a low concentration of reactive silicate (0.01-0.30 mg Si $L^{-1}$) (McColl, 1972), resulting in negligible representation of diatoms amongst the phytoplankton assemblage of this lake (Ryan, 2006). This lake has a correspondingly very low sedimentation rate (0.6 mm $yr^{-1}$; Trolle, 2008) and the lead peak is not resolved as a sub-surface peak at the 2 cm vertical sampling resolution used in this study. Modern Lake Rotomahana was created by the 1886 Tarawera eruption (Balance, 1981). It has a low sedimentation rate (0.8 mm $yr^{-1}$; Trolle et al., 2008, and 1 mm $yr^{-1}$ estimated from our study) and is inaccessible to the general public, limiting its exposure to anthropogenic lead sources. The accumulation of lead in Lake Rotomahana sediment is therefore likely to be largely through catchment erosion, dominated by the Rotomahana Mud unit of the Tarawera eruption, and atmospheric aerosols. The lake has high sulfate concentrations from geothermal inputs which are reduced in the sediment pore waters to sulfide, preventing mobilisation of iron and lead through precipitation of pyrite and galena. The third outlier is Green Lake, which is a very small, highly eutrophic lake located 10 m from the shore of Lake Rotomahana. It was formed as an explosion crater during the Tarawera eruption (1886). The lake is totally inaccessible to motor boats and has negligible external catchment; groundwater and rainfall may contribute a substantial fraction of the total hydraulic load to the lake.  Lead concentrations in the sediments of this lake are very low (< 2 µg Pb $g^{-1}$) and comparable to prehistoric concentrations in Swedish lake sediments (Renburg et al., 1994), further suggesting that atmospheric deposition is the only source of lead to the lake.

## 5.4 SUMMARY

Sediment profiles of lead from selected lakes in the TVZ were used to assess the exposure of the lakes to both natural and anthropgenic sources of lead as well as the diagenetic processes that also influenced its distribution. Despite the phasing out of lead in petroleum completely by 1996, lead is still widely distributed in the environment, having accumulated in depositional areas such as lake sediments, where it can provide an historical marker of human use. In New Zealand, after accounting for diagenetic processes, it is possible to track the depositional history of petroleum based lead inputs to lakes through sediment depositional layers. For sediments of the Rotorua lakes corresponding to those deposited within the 18th century, there are low lead concentrations. In sediments above the Tarawera tephra layer, deposited in 1886, there is a clearly identifiable stratum corresponding to anthropogenic lead from petroleum products. Variations between lakes are a function of exposure to leaded petroleum within the catchment and lake, as well as lake trophic state and redox status in lower water layers, which alters sedimentation rates and vertical transport of lead in the sediments. Diagenesis results in some redistribution of lead as iron and manganese are mobilised through oxidation and they are in turn are immobilised by sulfate reduction to produce insoluble sulfides. The anthropogenic lead peak from lead alkyl petroleum additives can be expected to be buried rapidly, and is unlikely to affect the aquatic system unless sediments are significantly disturbed.

## 5.5 REFERENCES

Balance, P. F. 1981. Geology and Landforms of the Rotorua Lakes Area, p. 14-19. *In* V. J. Chapman [ed.], Handbook of the Rotorua Lakes District: The Guardians of the Rotorua Lakes.

Bindler, R., I. Renberg, M. L. Brännvall, O. Emteryd, and F. El-Daoushy. 2001. A whole-basin study of sediment accumulation using stable lead isotopes and flyash particles in an acidified lake, Sweden. Limnol. Oceanogr. **46:** 178-188.

Burns, N., J. McIntosh, and P. Scholes. 2009. Managing the lakes of the Rotorua District, New Zealand. Lake Reservoir Manage. **25:** 284-296.

Burns, N. M., J. Deely, J. Hall, and K. Safi. 1997. Comparing past and present trophic states of seven Central Volcanic Plateau lakes, New Zealand. N.Z. J. Mar. Freshw. Res. **31:** 71-87.

Chow, T. J., K. W. Bruland, K. Bertine, A. Soutar, M. Koide, and E. D. Goldberg. 1973. Lead pollution: records in southern California coastal sediments. Science **181:** 551.

Davies, B. E. 1990. Lead, p. 117-194. *In* B. Alloway [ed.], Heavy metals in soils. Blackie and Sons Ltd.

Edgington, D. N., and J. A. Robbins. 1976. Records of lead deposition in Lake Michigan sediments since 1880. Environ. Sci. Tech. **10:** 266-274.

Eisenreich, S. J., N. A. Metzer, N. R. Urban, and J. A. Robbins. 1986. Response of atmospheric lead to decreased use of lead in gasoline. Environ. Sci. Tech. **20:** 171-174.

Fish, G. R. 1968. The oxygen content of some New Zealand lakes. Verh. Internat. Verein. Theor. Angew. Limnol. **1969:** 392-403.

Flint, E. A. 1977. Phytoplankton in seven monomictic lakes near Rotorua, New Zealand. N.Z. J. Bot. **15:** 197-208.

Graney, J. R., A. N. Halliday, G. J. Keeler, J. O. Nriagu, J. A. Robbins, and S. A. Norton. 1995. Isotopic record of lead pollution in lake sediments from the northeastern United States. Geochim. Cosmochim. Acta **59:** 1715-1728.

Håkanson, L., and M. Jansson. 1983. Principles of Lake Sedimentology. 316.

Harrison, R. M., and D. P. H. Laxen. 1984. Lead pollution: causes and control. Chapman and Hall Ltd.

Hogg, A. G., T. F. G. Higham, D. J. Lowe, J. G. Palmer, P. J. Reimer, and R. M. Newnham. 2003. A wiggle-match date for Polynesian settlement of New Zealand. Antiquity **77:** 116-125.

Hong, S., J. P. Candelone, C. C. Patterson, and C. F. Boutron. 1994. Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman civilizations. Science **265:** 1841.

Lowe, D. J., and J. D. Green. 1987. Origins and development of the lakes, p. 64. *In* A. B. Viner [ed.], Inland waters of New Zealand. DSIR Bulletin 241. DSIR Science Information Publishing Centre.

Lowe, D. J., P. A. R. Shane, B. V. Alloway, and R. M. Newnham. 2008. Fingerprints and age models for widespread New Zealand tephra marker beds erupted since 30,000 years ago: a framework for NZ-INTIMATE. Quaternary Sci. Rev. **27:** 95-126.

Martin, T. D., J. T. Creed, and C. A. Brockhoff. 1994. Method 200.2 (Revision 2.8): Sample preparation procedure for spectrochemical determination of total recoverable elements, p. 15–24. *In* USEPA [ed.], Methods for the Determination of Metals in Environmental Samples.

McColl, R. H. S. 1972. Chemistry and trophic status of seven New Zealand lakes. N. Z. J. Mar. Freshw. Res. **6:** 399-447.

McColl, R. H. S. 1975. Chemical and biological conditions in lakes of the volcanic plateau, p. 123-139. *In* V. H. Jolly and J. M. A. Brown [eds.], New Zealand Lakes. Auckland University Press.

McColl, R. H. S. 1977. Chemistry of sediments in relation to trophic condition of eight Rotorua lakes. N. Z. J. Mar. Freshw. Res. **11:** 509-523.

Ministry of Commerce. 1996. Premium unleaded petrol: Detailed report on investigations into reported fuel system failures following the introduction of premium unleaded petrol. Ministry of Commerce.

Monna, F., J. Dominik, J. L. Loizeau, M. Pardos, and P. Arpagaus. 1999. Origin and Evolution of Pb in Sediments of Lake Geneva (Switzerland- France). Establishing a Stable Pb Record. Environ. Sci. Technol. **33:** 2850-2857.

Murozumi, M., T. J. Chow, and C. C. Patterson. 1969. Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. Geochim. Cosmochim. Acta **33:** 1247-1294.

Newnham, R. M., D. J. Lowe, M. S. McGlone, J. M. Wilmshurst, and T. F. G. Higham. 1998. The Kaharoa Tephra as a Critical Datum for Earliest Human Impact in Northern New Zealand* 1. J. Archaeol. Sci. **25:** 533-544.

Nriagu, J. O. 1998. Paleoenvironmental research: Tales told in lead. Science **281:** 1622-1623.

Pearson, L. K. 2007. The nature, composition and distribution of sediment in Lake Rotorua, New Zealand. M.Sc. Thesis. Department of Chemistry, University of Waikato.

Pickett, R. C. 2008. A tephra-dated record of palaeoenvironmental change since ~ 5,500 years ago from Lake Rotorua, North Island, New Zealand. M.Sc. Thesis. Department of Earth and Ocean Sciences, University of Waikato.

Pullar, W. A., and N. M. Kennedy. 1981. Tephra deposits in the Rotorua Lakes District, p. 23-25. *In* V. J. Chapman [ed.], Handbook of the Rotorua Lakes District. The Guardians of the Rotorua Lakes.

Renberg, I., M. L. Brännvall, R. Bindler, and O. Emteryd. 2002. Stable lead isotopes and lake sediments--a useful combination for the study of atmospheric lead pollution history. Sci. Total Environ. **292:** 45-54.

Renberg, I., M. W. Persson, and O. Emteryd. 1994. Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. Nature **368:** 323-326.

Rosman, K. J. R., W. Chisholm, C. F. Boutron, J. P. Candelone, and U. Görlach. 1993. Isotopic evidence for the source of lead in Greenland snows since the late 1960s. Nature **362:** 333-335.

Ryan, E. F. 2006. Phytoplankton dynamics in North Island lakes, New Zealand. University of Waikato.

Schindler, D. W. 1985. The Coupling of Elemental Cycles by Organisms: Evidence from Whole-Lake Chemical Perturbations, p. 225-250. *In* W. Stumm [ed.], Chemical Processes in Lakes John Wiley and Sons, New York

Settle, D. M., and C. C. Patterson. 1980. Lead in albacore: guide to lead pollution in Americans. Science **207:** 1167.

Settle, D. M., and C. C. Patterson. 1982. Magnitudes and sources of precipitation and dry deposition fluxes of industrial and natural leads to the North Pacific at Enewetak. J. Geophys. Res. **87:** 8857-8869.

Shen, G. T., and E. A. Boyle. 1987. Lead in corals: reconstruction of historical industrial fluxes to the surface ocean. Earth Planet. Sci. Lett. **82:** 289-304.

Shotyk, W. and others 1998. History of atmospheric lead deposition since 12,370 $^{14}$C yr BP from a peat bog, Jura Mountains, Switzerland. Science **281:** 1635-1640.

Sigg, L. 1985. Metal transfer mechanisms in lakes: the role of settling particles, p. 283-310. *In* W. Stumm [ed.], Chemical Processes in Lakes. John Wiley, New York.

Statistics New Zealand. 1960. New Zealand Official Yearbook. Department of Statistics, R.E Owen, Government Printer, Wellington, New Zealand.

Sturges, W. T., and L. A. Barrie. 1989. Stable lead isotope ratios in Arctic aerosols: evidence for the origin of Arctic air pollution. Atmos. Environ. **23:** 2513-2519.

Taylor, B. 1988. Lead in Petrol, p. 80-89. *In* J. E. Hay and S. J. de Mora [eds.], Lead in the New Zealand Environment: Proceedings of a Conference at the University of Auckland, August 12, 1988. Environmental Science Occasional Publication No. 9, Environmental Science, Auckland.

Timperley, M. H. 1987. Regional influences on lake water chemistry, p. 97-111. *In* A. B. Viner [ed.], Inland waters of New Zealand. DSIR Bulletin 241. DSIR Science Information Publishing Centre.

Timperley, M. H., and R. J. Vigor-Brown. 1986. Water chemistry of lakes in the Taupo volcanic zone, New Zealand. N.Z. J. Mar. Freshw. Res. **20:** 173-183.

Trolle, D., D. P. Hamilton, C. H. Hendy, and C. Pilditch. 2008. Sediment and nutrient accumulation rates in sediments of twelve New Zealand lakes: influence of lake morphology, catchment characteristics and trophic state. Mar. Freshwat. Res. **59:** 1067-1078.

Veron, A., C. E. Lambert, A. Isley, P. Linet, and F. Grousset. 1987. Evidence of recent lead pollution in deep north-east Atlantic sediments. Nature **326:** 278-281.

Vincent, W. F., and D. J. Forsyth. 1987. Geothermally influenced waters, p. 349-377. *In* A. B. Viner [ed.], Inland waters of New Zealand. DSIR Bulletin 241. DSIR Science Information Publishing Centre.

Wilson, N., and J. Horrocks. 2008. Lessons from the removal of lead from gasoline for controlling other environmental pollutants: A case study from New Zealand. Environ. Health **7:** 1-10.

# CHAPTER 6: DYNAMICS OF SILICON IN LAKES OF THE TAUPO VOLCANIC ZONE, NEW ZEALAND, AND IMPLICATIONS FOR DIATOM GROWTH

## 6.1 INTRODUCTION

Silicon (Si) is often overlooked when considering nutrient limitation in lakes as most studies focus on nitrogen (N), phosphorus (P), or both nutrient species (Schindler et al. 2008, Harrison et al. 2009, Conley et al. 2009, Abell et al. 2010). It is required as a macronutrient for diatoms and is incorporated into the diatom frustule, which is comprised of opaline or biogenic silica ($SiO_2.nH_2O$) (Round 1990). Silicon therefore plays a key role in the succession of phytoplankton communities (Sommer and Stable 1983, Carlsson and Granéli 1999, Gobler et al. 2006). When silica concentrations are reduced to critical levels, diatom growth will be reduced, potentially increasing opportunities for other phytoplankton, including cyanobacteria, to exploit the available nutrient supply (Justić et al. 1995, Rocha et al. 2002).

The silicon cycle in lakes is dominated by biological uptake and regeneration, and about 80 % of the Si taken up by diatoms may be recycled (Willén 1991). The Si concentration in lake water is strongly dependent on the proportion and abundance of diatoms amongst the phytoplankton community, the Si requirements of the dominant diatom species, the dissolution of diatom frustules following sedimentation and the Si load (Martin-Jézéquel et al. 2000). Concentrations of Si in sediment pore waters are affected by pore water pH, sediment mineralogy, sesquioxide content (oxides and oxyhydroxides of Fe, Mn and Al), and organic acids (Koski-Vähälä et al. 2001). These factors are all dependent on the physical and chemical properties of the water body. Dissolution of diatom frustules in lakes in the Taupo Volcanic Zone (TVZ) of New Zealand appears to have been limited by moderate levels of silicic acid arising from the high abundance of Si-rich volcanic substrate. Discharges from Si-laden geothermal waters and ignimbrite aquifers also contribute groundwaters with high silicon concentrations (Rawlence 1984, 1985).

Diatom productivity tends to be highly seasonal and highest biomass often occurs under conditions of low temperature and light, high turbulence and high nutrient concentrations (Reynolds 1984, Cassie-Cooper 1996). Diatom blooms in dimictic lakes have been associated with mixing events (Kingston et al. 1983, Werner and Smol 2005) whilst diatom populations may peak during annual winter mixing in monomictic lakes (Vincent 1984, Ryan et al. 2006). If nutrients are replete and there is sufficient light, then high rates of diatom production may adequately offset losses due to high rates of sinking, leading to rapid increases in diatom biomass (Viner and Kemp 1983). Dissolved Si concentrations are also spatially variable and higher concentrations generally occur in the hypolimnion of stratified lakes where regeneration of biogenic Si and weathering of mineral silicates from the sediment surface dominate over the uptake that is mostly confined to epilimnetic waters (Aston 1983).

In this study sediment pore waters were sampled from selected TVZ lakes ranging in trophic state from oligotrophic to eutrophic, and together with overlying water column measurements, were used to quantify the contribution of Si transferred from the sediments to the overlying lake water and the ability of diatoms to recycle Si back to the sediments via sedimentation. Sediment pore water Si concentrations were measured in the lakes and a steady state model was developed to account for the pore water concentration gradients. It was assumed in the model that dissolution of siliceous sediments would be a first order process. By evaluating the relative and absolute concentrations of bioavailable nutrients (equivalent analytically to dissolved inorganic nitrogen, dissolved reactive phosphorus and dissolved silicon) in the surface waters, we made inference to the nutrient limiting phytoplankton growth for periods of stratification and mixing.

## 6.2 STUDY SITE

The TVZ is in the Waikato and Bay of Plenty regions of the North Island of New Zealand (NZ) (Figure 6.1). It contains many volcanic lakes which have diverse history, physiography, and limnology (Lowe and Green 1987). The lakes vary in size (0.2 to > 600 km$^2$), mixing regime (monomictic and polymictic), trophic status (oligotrophic to highly eutrophic) and depth (up to 164 max. depth; Lake Taupo) (Table 6.1). Oligotrophic Lake Taupo is the largest lake by area (616 km$^2$) in NZ. The Rotorua Lakes District, north of Lake Taupo, has lakes of varying trophic status, some relatively unaffected by human activities and others heavily impacted by urbanisation and farming (McColl 1972, Vincent et al. 1984, Hamilton 2005, Bruesewitz et al. 2011).

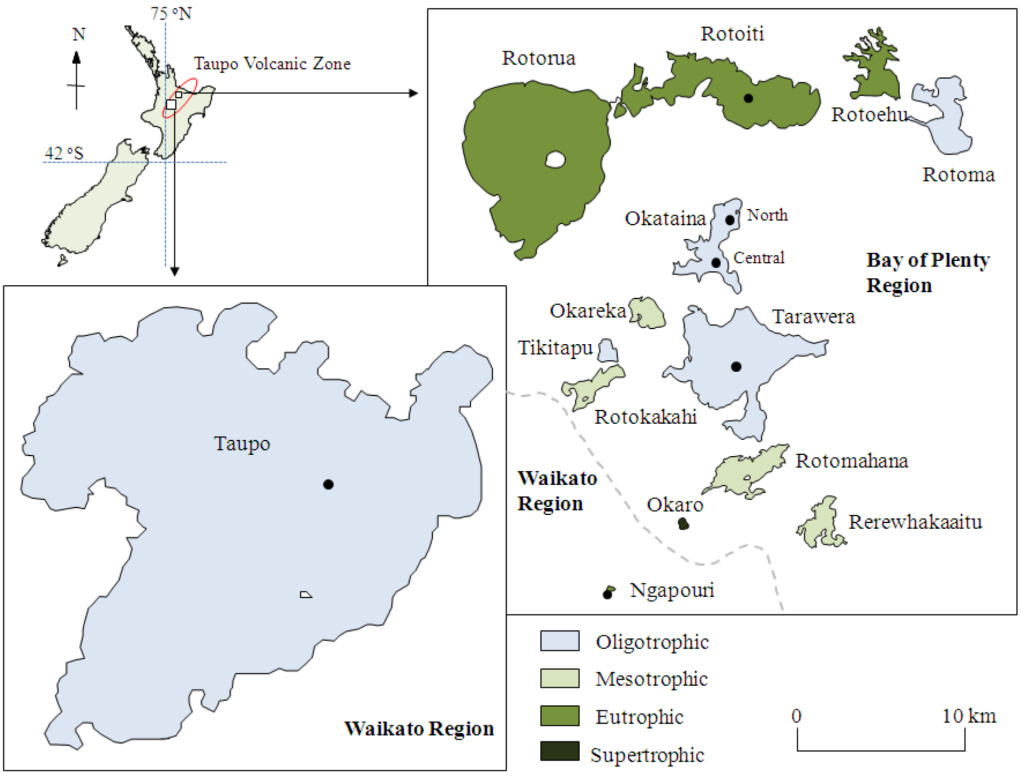

**Figure 6.1:** Location and trophic state of Lake Taupo and the Rotorua lakes within the Taupo Volcanic Zone (inset, circled), New Zealand. Sample sites on the lakes are marked with a • and lake trophic status is identified by shading. The lakes belong to two regional boundaries: Rotorua District (Bay of Plenty Region) and Waikato Region.

Nine lakes were selected for this study: Taupo, Tarawera, Okataina, Rotokawau, Tikitapu, Rotoiti, Rotorua, Ngapouri and Okaro (Table 6.1). Sites were selected to be in the deep central basin of each lake, with sampling targeting areas of sediment accumulation (cf. Håkanson and Jansson 1983) except for three lakes where sites were selected to allow comparison of (i) two distinct basins within a lake (central and north basins of Lake Okataina), (ii) a deep central basin with a shallow bay (Lake Rotoiti) and the (iii) north and south ends of a single basin (Lake Okaro).

**Table 6.1:** General catchment and lake characteristics for the study sites (Timperley, 1987; Trolle et al., 2008; Bruesewitz et al., 2011, Freshwater Environments New Zealand database (FWENZ)).

| | Elevation above sea level (m) | Mean depth (m) | Max. depth (m) | Lake area ($km^2$) | Catchment area ($km^2$) | Catchment agriculture (%) | Catchment forest (%) | Catchment urban (%) | Water residence time (yr) | Mixing regime | Trophic State |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Taupo | 384 | 100.0 | 164 | 620.0 | 2849.0 | 21.6 | 77.4 | 1.0 | 126.0 | Monomictic | Oligotrophic |
| Tarawera | 298 | 50.0 | 88 | 41.7 | 144.9** | 21.1 | 62.4 | 0.7 | 41.0 | Monomictic | Oligotrophic |
| Okataina | 311 | 39.4 | 79 | 11.0 | 56.8 | 9.6 | 84.6 | 0.0 | 44.6 | Monomictic | Oligotrophic |
| Rotokawau | 335 | 44.2 | * | 0.5 | 3.0 | 29.5 | 65.0 | 0.0 | * | Monomictic | Oligotrophic |
| Tikitapu | 415 | 18.0 | 28 | 1.5 | 5.7 | 3.0 | 79.2 | 0.0 | 44.3 | Monomictic | Oligotrophic |
| Rotoiti | 279 | 31.5 | 124 | 34.6 | 124.6** | 23.9 | 42.9 | 1.1 | 21.5 | Monomictic | Eutrophic |
| Rotorua | 280 | 11.0 | 45 | 80.6 | 500.6 | 51.8 | 25.1 | 8.1 | 17.5 | Polymictic | Eutrophic |
| Ngapouri | 451 | 12.1 | 24 | 0.2 | 4.8 | 99.0 | 1.0 | 0.0 | * | Monomictic | Eutrophic |
| Okaro | 419 | 12.5 | 18 | 0.3 | 3.7 | 95.7 | 3.6 | 0.0 | 5.6 | Monomictic | Supertrophic |

* Data unavailable

** Does not include catchments from upstream lakes draining to lake of interest

The geology of the region is predominantly Mamaku ignimbrite and rhyolitic pyroclastics (Forsyth et al. 1972), resulting in ground water which is high in silicon. Lake Tikitapu is surrounded by a rhyolite lava flow, which weathers considerably slower than ignimbrites, and highly fragmented pyroclastics (Forsyth et al. 1972). Soils in the TVZ contain predominantly amorphous aluminosilicate glass (from the rhyolitic tephra), which is readily weathered and contributes large silicon loads to the lakes (McColl 1972). Concentrations of Si monitored in stream inflows to Lake Rotorua range between 23 and 43 mg Si $L^{-1}$ (Morgenstern et al. 2005) and similar concentrations would be expected in stream inflows to other TVZ lakes, with the exception of Lake Tikitapu. Geothermal fluids have considerably higher Si concentrations, typically > 200 mg Si $L^{-1}$ (Giggenbach and Glover 1992).

The bulk of the sediment in these lakes is comprised of fine, low-density, siliceous material accumulated from the decomposition of biota (McColl 1972, Pickrill 1991, Nelson and Lister 1995, Burns et al. 1997, Pearson 2007, Trolle et al. 2008, 2010). The concentration of Si in lake bottom sediments was not determined in this study but scanning electron microscopy (SEM) of Lake Rotorua sediments has shown that *Aulacoseira granulata* frustules comprise approximately 97% by volume of the sediment (Figure 6.2 a) (Pearson 2007, 2010). Rawlence and Reay (1976) also found the sediments of Lake Taupo were dominated by diatom frustules, predominantly *Aulacoseira granulata* and to a lesser extent *Cyclotella stelliger*. However, Lake Tikitapu is an exception to the frustule-dominated sediment of TVZ lakes, and here clastic volcanic glasses dominate (Figure 6.2 b) (A.M. Carter, University of Waikato, unpubl. data).

Ejecta from recent eruptions can be found as distinct tephra layers in the lake sediments and can be used to date the subsequent sediment deposition (Trolle et al. 2008, Pearson 2010). These tephra also provide a source of silicon to the lakes. The Tarawera Tephra, arising from an eruption of Mt Tarawera in June 1886, is evident as a grey layer of volcanic mud in lakes Rotokawau, Tarawera, Okataina, Tikitapu, Rotoiti, Rotorua and Okaro. The tephra often comprises two distinct layers; an upper layer of Rotomahana Mud which covered the landscape as superheated sediment was forced from Lake Rotomahana during the Tarawera eruption, and a thinner, gritty, black basaltic scoria along the base of the Rotomahana Mud known as Tarawera Ash. The Tarawera Tephra is typically 2-10 cm thick and found 0.1 to >1 m below the sediment-water interface amongst different lakes (Trolle et al. 2008). Lake Rotokawau also has a 0.5 cm-thick, grey ash layer visible at 3.5 cm sediment depth, which is due to the Ruapehu eruption (17 June 1996), which deposited ash over parts of the Rotorua region (Hurst and Turner 1999).

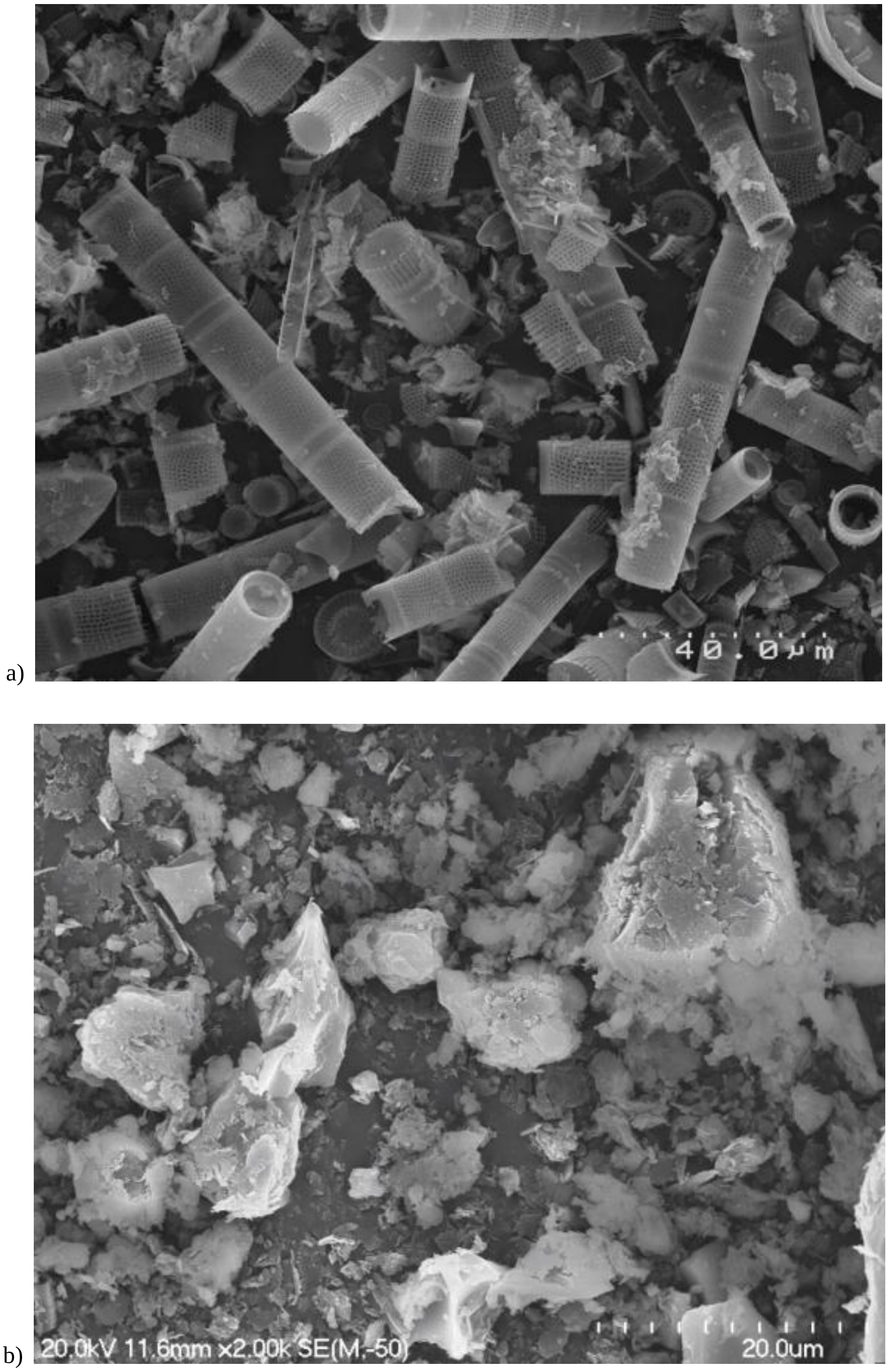

**Figure 6.2:** Scanning electron microscope image of a) Lake Rotorua sediment showing dominance of *Aulacoseira granulata* and b) Lake Tikitapu sediment showing the dominance of clastic volcanic glass particles.

## 6.3 METHODS

### 6.3.1 Sampling and field methods

Sediment cores were collected on the nine selected TVZ lakes using a Swedish gravity corer (Pylonex HTH 70 mm) with a 60 x 600 mm Perspex (Plexiglas) core barrel to capture undisturbed sediments along with a c. 20 cm layer of the overlying water. The surface sediment was visually inspected in each core to determine if there had been any disturbance at the sediment-water interface or in the sediment profile; the core was discarded and another one taken when sediments had been disturbed. Once the core was retrieved, a custom-made gas-tight sampling chamber was fitted to the core barrel and the core was extruded by pushing a piston upward from the base of the core. Excess supernatant water was allowed to overflow the top of the core upon extrusion until 2 cm of water was overlying the sediment-water interface. This water was collected in a 50 mL polypropylene centrifuge tube. Sediment samples were then extruded at 2 cm intervals and transferred into 50 mL polypropylene centrifuge tubes; the sediment completely filled the tubes and small amounts of residual sediment were discarded. The tubes were capped and placed on ice until return to the laboratory.

To assess the temporal variability of potentially limiting nutrients (Si, N and P), surface water samples were collected monthly from five of the study lakes; oligotrophic lakes Taupo, Tarawera and Okataina as well as eutrophic lakes Rotoiti and Ngapouri. Lake water was collected using a Schindler-Patalas trap to capture near-surface (epilimnion; 1 m depth) and bottom-water (hypolimnion; 1 m from sediment-water interface) samples at each sample site between September 2007 and December 2008. For four other lakes surface water samples were collected on one day only; oligotrophic lakes Tikitapu and Rotokawau and eutrophic lakes Rotorua and Okaro. Water samples were stored in 100 mL polyethylene bottles and kept on ice untill return to the laboratory. Chlorophyll *a* (chl *a*) concentrations, calculated from a 10-m intergrated surface water sample, were provided by the Bay of Plenty Regional Council (BoPRC) from their monthy monitoring on the Rotorua lakes over the same sampling period. Chlorophyll *a* was analysed by filtering whole water samples through GC-50 filters (Advantec, nominal pore size 0.5 μm), freezing and then solvent extraction and fluorometric analysis with correction for phaoepigments (Arar & Collins, 1997).

At the time of sampling a water column profile of temperature and dissolved oxygen at depth intervals of c. 0.02 m were measured on each sampling occasion with a conductivity-temperature-depth (CTD) profiler (Sea Bird Electronics 19 plus SEACAT Profiler), fitted with a dissolved oxygen (DO, Seabird Electronics) sensor (detection limit of 0.1 mg $L^{-1}$) to determine the thermal gradient of the lake.

### 6.3.2 Analytical methods

In the laboratory, the pore waters were separated from the sediments by centrifugation at 4000 rpm (2900 x g) for 40 min. The pore water and lake water samples were filtered through a 0.45 μm membrane filter (Millipore Corp., Bedford, MA) and split into two 15 ml polypropylene vials. One vial was acidified with nitric acid (2 %) and the other was frozen immediately. Silicon concentrations of the pore water were analysed using inductively coupled plasma mass spectrometry (ICP-MS model ELAN DRC II, Perkin-Elmer SCIEX) on the acidified vial. Ammonium ($NH_4$-N), total oxidised nitrogen ($NO_x$-N) and dissolved reactive phosphorus (DRP) were analysed spectrophotometrically on the non-acidified samples of lake water and pore water using a Lachat QuickChem® Flow Injection Analyser (FIA+ 8000 Series, Zellweger Analytics, Inc.). Concentrations of DIN were calculated as the sum of the ammonium ($NH_4$-N) and total oxidised nitrogen ($NO_x$-N) concentrations. The detection limit was 0.001 mg $L^{-1}$.

### 6.3.3 Mathematical silicon transport model and flux

The upward diffusion of Si in the sediments, together with any dissolution of diatom frustules through diagenesis, can be modelled mathematically as follows. Consider the flow of silicon into and out of the pore water in a layer of sediment at depth z (cm) and with a thickness (δz) (Figure 6.3). Let the rate of production of silicon ($Si_{dis}$) from dissolution of the sediment within this layer be proportional to the difference in the concentration of Si at depth z ($c_z$ in units g $m^{-3}$) and the concentration of Si at a hypothetical infinite depth ($c_\infty$) (i.e., the steady state value):

$Si_{dis}=k(c_\infty-c_z)$ (6.1)

where k is the rate constant for the dissolution of silicon from the sediment and has units of g $s^{-1}$. The gain of silicon ($Si_{(z+1)}$) from below z is related to the concentration gradient below:

$Si_{(z+1)}=D(c_{(z+1)}-c_z)/\delta z$, (6.2)

and the loss of silicon to the layer above ($Si_{(z-1)}$) is proportional to the concentration gradient above:

$Si_{(z-1)}=D(c_z-c_{(z-1)})/\delta z$, (6.3)

where D is the diffusion coefficient reduced by the square of the tortuosity (Boudreau 1996) and has units of $m^2$ $s^{-1}$. In time δt, the movement of silicon in and out of the layer will be:

$\delta c/\delta t=[k(c_\infty-c_z)+D(c_{(z+1)}+c_{(z-1)}-2c_z)]/\delta z$ (6.4)

Considering the concentrations of silicon to be at steady state, i.e., $\delta c/\delta t = 0$, we get

$k(c_\infty-c_z)= -D(c_{(z+1)}+c_{(z-1)}-2c_z)/\delta z$ (6.5)

Integrating Eq. 6.5 gives

$c_z=Ae^{(z\sqrt{k/D})}+Be^{(-z\sqrt{(k/D)})}+c_\infty$ (6.6)

Since c goes to $c_\infty$ at $z = \infty$, and since $c_\infty$ is a finite number, A must equal 0. Further, $c = c_0$ when $z = 0$, and $B = c_0 - c_\infty$, which gives:

$c_z=c_\infty+ (c_0-c_\infty)\exp(-z\sqrt{(k/D)})$ (6.7)

Curves were generated from Eq. 6.7 using values for $c_0$ derived from the Si concentration in the overlying hypolimnion (Figures 6.4 and 6.5) using $c_\infty$ as the estimated steady state maximum concentration of pore water Si concentration observed at depth in the sediments and k/D values as specified in Table 6.2. Values of k/D were trialled to obtain a best fit of $c_z$ based on measured $c_0$ and $c_\infty$ from the sediment cores.

The flux of Si back to the overlying lake water can be calculated using Ficks first law where D is the diffusion coefficient and dc is the change in concentration over the change in elevation dz (0.02 m):

$$J = -D(dc/dz) \qquad (6.8)$$

The change in concentration was calculated from the 0-0.02 m and 0.02-0.04 m sediment sections from measured pore water concentrations.

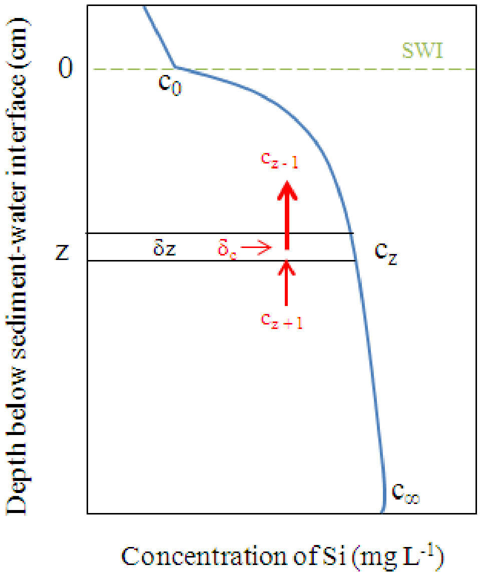

**Figure 6.3:** Conceptual model of silicon transport through lake sediments during steady state. Arrows indicate the upward transport of Si towards the sediment water interface (SWI) from depth z.

### 6.3.4 Estimates of potential nutrient limitation

Estimates of potential nutrient limitation were based on concentration thresholds, defined below, from the surface waters of the five lakes sampled monthly (Taupo, Tarawera, Okataina, Rotoiti and Ngapouri) and four spot samples on other lakes in the TVZ (Tikitapu, Rotokawau, Rotorua and Okaro). The lakes are assessed based on stratified and homothermal conditions in Figure 6.6.

Several studies have shown that phytoplankton maintain maximum or near-maximum rates of growth down to external concentrations of 0.003-0.006 mg P L$^{-}$

$^{1}$ and 0.08-0.1 mg N L$^{-1}$ (Reynolds 1990, Egge and Aksnes 1992, Reynolds 1997, Reynolds 1998). Diatoms can continue to utilise silicon down to concentrations as low as 0.12 mg Si L$^{-1}$ provided there is adequate supply of nitrogen and phosphorus (Reynolds 1997). As nutrient supply becomes growth-rate limiting before the nutrient supply is exhausted and there is no recognised definitive concentration for limitation, potential growth-rate limitation was assumed when N reached < 0.08 mg L$^{-1}$, P < 0.003 mg L$^{-1}$ and Si < 0.12 mg L$^{-1}$ (Reynolds et al. 2001 and references therein). These growth-rate thresholds are indicated in Figure 6.6 by horizontal and vertical lines at these concentrations. Thus there are four boxes delineated in each of the plots given in Fig. 6; one for no limitation, one for co-limitation and one each for limitation by the two nutrients represented in the axis labels. White et al. (1985) specified that when concentrations of DIN or DRP were less than 0.0015 mg N L$^{-1}$ and 0.001 mg P L$^{-1}$, there was strong evidence of N or P limitation, respectively, in TVZ lakes. Reynolds (1973) showed that growth in the diatoms *Asterionella* and *Fragilaria* ceased at concentrations of Si of 0.04 mg L$^{-1}$. In Figure 6.6 these lower-concentration nutrient limitation criteria are indicated with darker shading between the prescribed limitation value and the horizontal or vertical axis used for each nutrient plot. The degree of shading was considered the best way in which to indicate severity of potential limitation as well as to indicate that there is no single definitive concentration for limitation by N,P and Si. Nutrient mass ratios that delineated potential limitation were N:P=7.2:1, Si:P=9:1 and Si:N=2:1 (Redfield 1958, White et al. 1985, Pridmore 1987, Hamilton et al. 2006) and are represented by dashed lines in Fig. 6. Our analysis did not consider other potential influences on phytoplankton growth limitation such as light, temperature, or trace elements.

## 6.4 RESULTS

### 6.4.1 Pore water silicon profile

Sediment pore water Si concentrations at 20 cm depth in the nine TVZ lakes generally ranged from 20 to 30 mg L$^{-1}$ and decreased vertically upward along diffusion gradients to where concentrations were 0.2 to 20.5 mg L$^{-1}$ at the sediment-water interface (Figure 6.4). The oligotrophic lakes, with the exception of Lake Tikitapu, had Si concentrations ranging from 11 to 20.5 mg L$^{-1}$ at the sediment-water interface. Lake Tikitapu had the lowest Si pore water concentrations, which ranged from 12.8 mg L$^{-1}$ at 20 cm depth to 0.5 mg L$^{-1}$ at the sediment-water interface. The eutrophic lakes, Rotorua, Rotoiti and Okaro, had much lower Si concentrations at the sediment-water interface, from 1.7 to 3.6 mg L$^{-1}$, but in highly eutrophic Lake Ngapouri, concentrations at this location were 15.6 mg L$^{-1}$. The pore water profile in Lake Ngapouri showed a linear change in Si concentration with depth, rather than the monotonic curve, and had a $c_\infty$ value of 26 and $c_0$ value of 15.6 mg L$^{-1}$ (Figure 6.5).

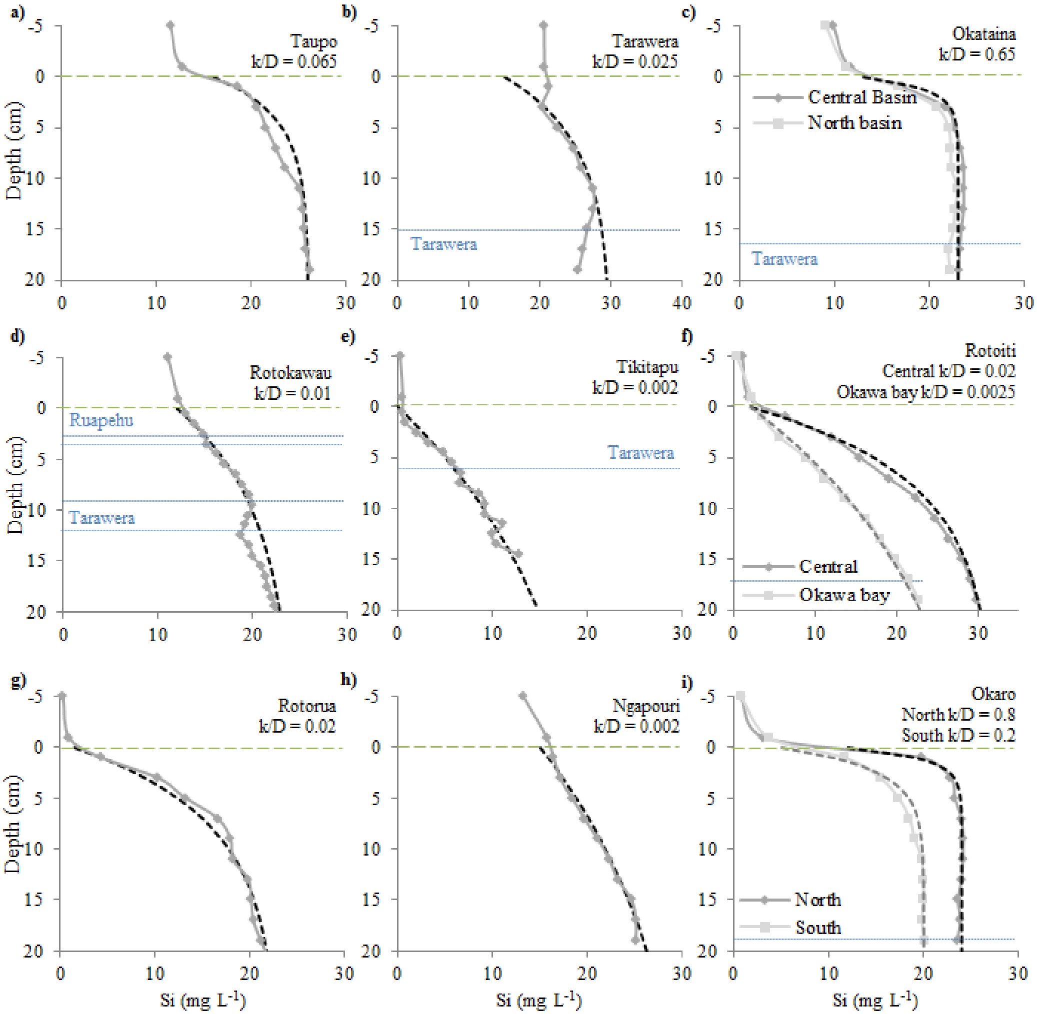

**Figure 6.4:** Measured pore water silicon concentrations (mg L$^{-1}$) in the nine TVZ lakes studied. Modelled Si profiles are shown by thick dashed line. The sediment-water interface is marked with a thin dashed line. If present, the start of tephra layer is marked with a solid line which continues to the base of the core unless succeeded by another solid line to indicate the base of the tephra layer as shown for Lake Rotokawau.

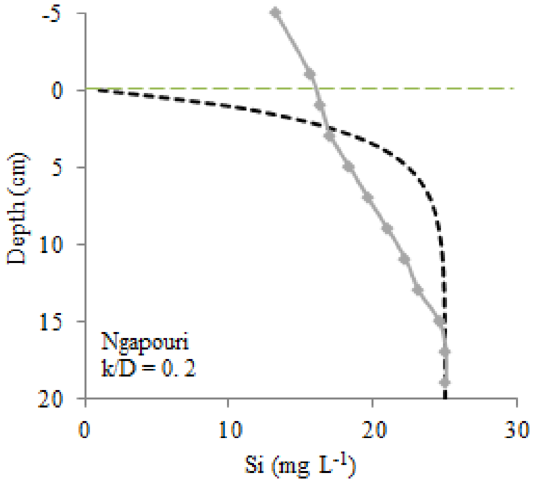

**Figure 6.5:** Model simulation of likely Si profile in Lake Ngapouri in 1970 (dashed line) compared to pore water profile in 2008 (diamonds, solid line).

### 6.4.2 Silicon transport model and flux

The silicon transport equation (Eq. 6.7) was used to fit a sediment pore water profile to each lake, based on input data of hypolimnion silicon concentration ($c_0$), a steady state pore water concentration value ($c_\infty$) and an estimated Si dissolution/diffusion rate (k/D) (Table 6.2). The pore water Si concentrations modelled in this way explained > 95% of the variance ($p < 0.01$) in measured Si concentrations through the profile in each lake except where there was a thick tephra layer, such as in Lake Rotokawau, or geothermal inputs, such as in Lake Tarawera. Modelled Si profiles in these two lakes accounted for 83.9 and 80.5% of the Si variance observed, respectively ($p < 0.01$).

The flux of Si from the sediments to the overlying lake water was calculated from Ficks Law (Eq. 6.8) using the difference between the measured pore water Si concentration at 0-2 cm and 2-4 cm. Values ranged between 0.09 g $cm^{-2}$ $yr^{-1}$ in Lake Tikitapu and 0.83 g $cm^{-2}$ $yr^{-1}$ in Lake Rotorua except for Lake Tarawera where there was a negative flux (-0.13 g $cm^{-2}$ $yr^{-1}$) which reflected higher lake water concentrations than sediment pore water concentrations (Table 6.2).

**Table 6.2:** Flux of Si to the overlying lake water from the 2-4 cm sediment section, input values of $c_0$ and $c_\infty$ for sediment model and coefficient of variance between modelled and measured pore water Si concentrations.

| | Flux of silicon ($g\ cm^{-2} yr^{-1}$) | $c_0$ ($g\ cm^3$) | $c_\infty$ ($g\ cm^3$) | k/D ($g\ m^2$) | $R^2$ |
|---|---|---|---|---|---|
| Taupo | 0.29 | 15.5 | 26.0 | 0.065 | 0.94 |
| Tarawera | -0.13 | 15.0 | 30.0 | 0.025 | 0.80 |
| Okataina (Central) | 0.62 | 13.0 | 23.0 | 0.650 | 0.98 |
| Okataina (North) | 0.56 | 13.0 | 23.0 | 0.650 | 0.98 |
| Rotokawau | 0.09 | 12.5 | 24.5 | 0.010 | 0.83 |
| Tikitapu | 0.58 | 0.1 | 25.0 | 0.002 | 0.97 |
| Rotoiti (Central basin) | 0.83 | 2.0 | 32.0 | 0.020 | 0.99 |
| Rotoiti (Okawa Bay) | 0.78 | 2.0 | 35.0 | 0.003 | 0.99 |
| Rotorua | 0.31 | 1.5 | 23.0 | 0.020 | 0.98 |
| Ngapouri | 0.41 | 15.0 | 34.0 | 0.002 | 0.99 |
| Okaro (North) | 0.52 | 11.0 | 24.0 | 0.800 | 0.95 |
| Okaro (South) | 0.10 | 5.0 | 20.0 | 0.200 | 0.98 |

### 6.4.3 Nutrient limitation potential

Based on the growth rate-limiting thresholds of N < 0.08 mg $L^{-1}$, P < 0.003 mg $L^{-1}$ and Si < 0.12 mg $L^{-1}$, phytoplankton growth in the oligotrophic lakes (Taupo, Tarawera and Okataina) was predominantly co-limited by N and P (Figure 6.6 a) or N limited in Lake Okataina when the lake was homothermal (Figure 6.6 b). The single samples for oligotrophic Lake Rotokawau and Lake Tikitapu collected in July (homothermal) and April (stratified), respectively, indicated N-limitation in Lake Rotokawau and strong co-limitation by N, P and Si in Lake Tikitapu. Phytoplankton growth in eutrophic Lake Rotoiti was predominantly N limited over the annual cycle and co-limited with Si during the end of homothermy (Figure 6.6 b and c). According to our criteria for growth limitation, phytoplankton growth in Lake Ngapouri was not nutrient-limited during homothermy but showed N limitation or co-limitation of N and P during stratification. The single samples for eutrophic lakes Rotorua and Okaro, collected in July when the lakes were homothermal, showed no limitation of phytoplankton growth by N, P or Si (Figure 6.6 b). For these lakes mass ratios of Si:N and Si:P were close to 2:1 and 9:1, respectively, indicating a nearly balanced supply of N, P and Si in these lakes.

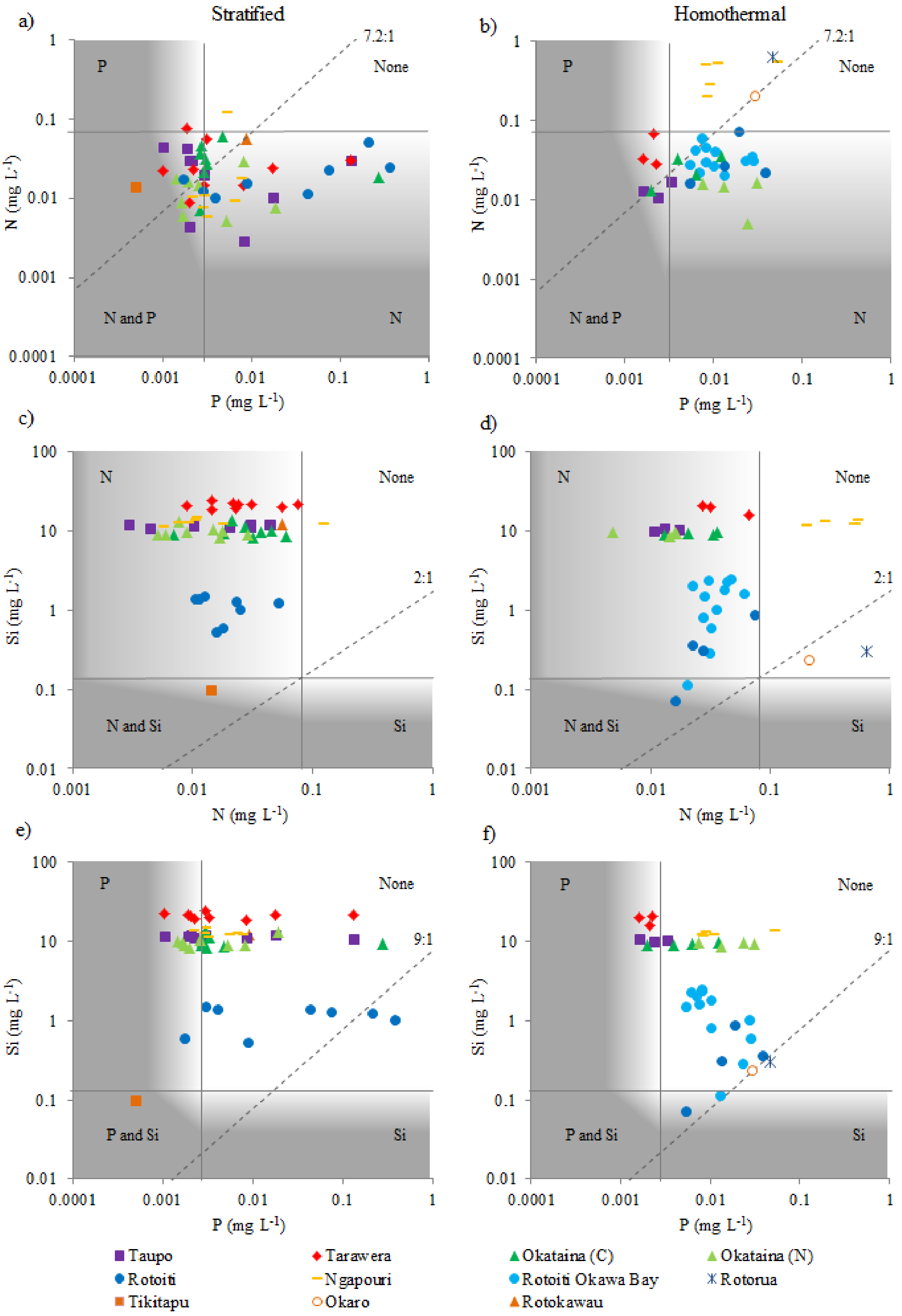

**Figure 6.6:** Concentrations of N (DIN), P (DRP) and dissolved Si for stratified (right) and mixed (left) surface waters of selected TVZ lakes. Dashed lines represent mass ratios for balanced growth (N:P = 7.2:1, Si:N = 2:1 and Si:P = 9:1) and increasing shading represents growth limiting concentration limits beginning at 0.08 mg L$^{-1}$ for N, 0.003 mg L$^{-1}$ for P and 0.12 mg L$^{-1}$ for Si. Where there is potential for growth limitation shading is used to show the severity of the limitation and the limiting nutrient in the quadrant is defined.

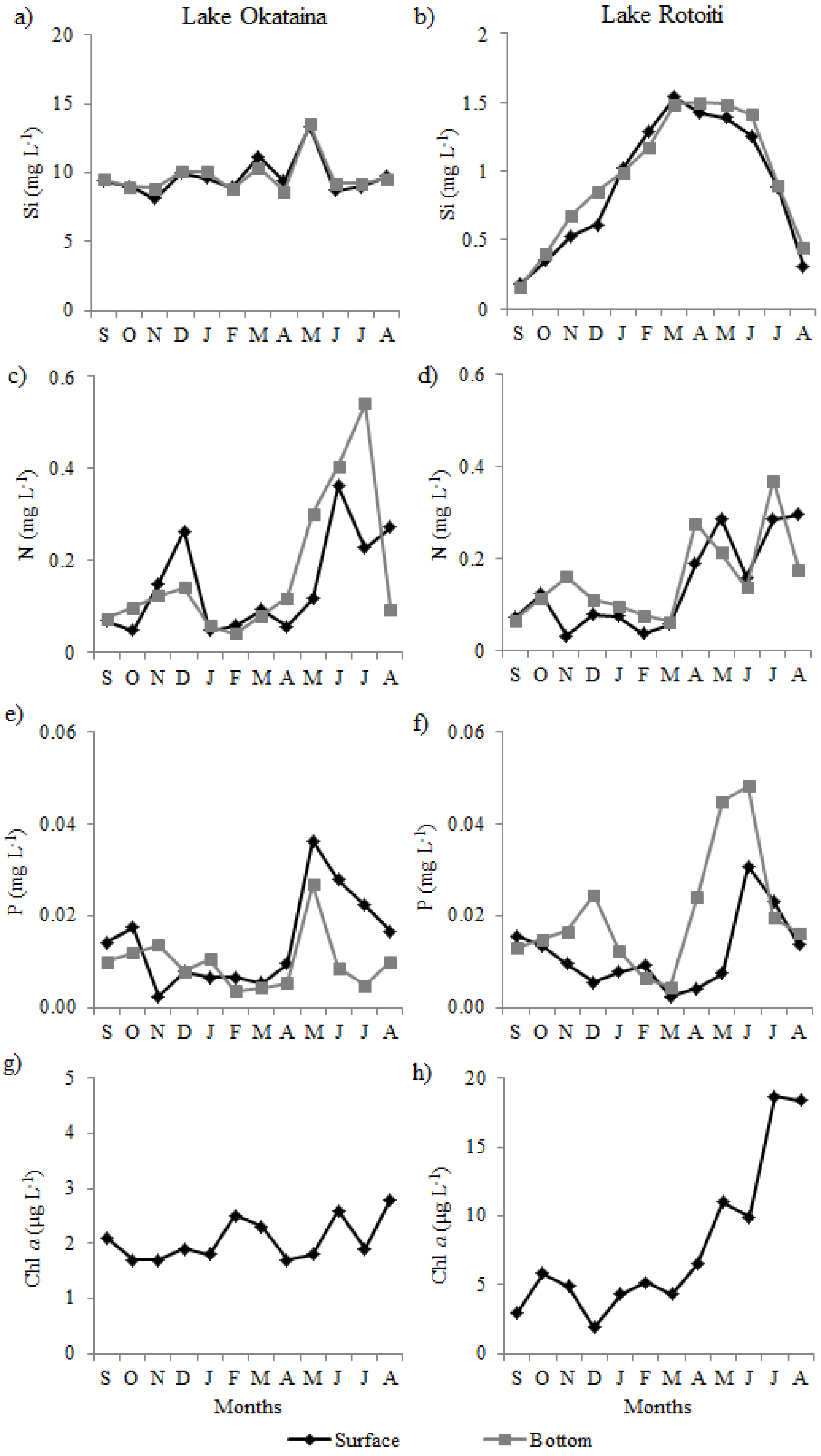

**Figure 6.7:** Dissolved silicon, dissolved inorganic nitrogen and dissolved reactive phosphorus (mg L$^{-1}$) in surface and bottom waters of Lake Okataina (a, c and e, respectively) and Lake Rotoiti (b, d and f respectively). Chl *a* concentration (µg L$^{-1}$) in the surface waters of g) Lake Okataina and h) Lake Rotoiti was provided by Bay of Plenty Regional Council for the same time period.

## 6.5 DISCUSSION

The lack of abrupt transition of silicon concentrations between the bottom waters and pore waters in TVZ lakes likely reflects the upward diffusion of silicon from deeper within the sediments, as well as dissolution of diatom frustules through diagenesis. Volcanic eruptions have deposited rhyolitic tephras which punctuate the diatomaceous sediments in the lake sediments. The resulting tephra layer creates a barrier to diffusion of Si through changing the porosity of the sediments, but can also alter the rate of Si dissolution directly. Thus, the profile of Si is less monotonic in the sediment pore waters, as is evident in lakes Tarawera, Okataina, Rotokawau and Tikitapu (Figure 6.4). Releases of silicon to pore waters occur with weathering of alumnosilicate glass within the sediments as well as from dissolution of diatom frustules.

Lakes in which there was a poor fit to the steady state Si model, received high proportions of geothermal water or had thick tephra deposits in the sediment. Geothermal discharge occurs around Lake Tarawera producing higher Si concentrations in the hypolimnion of this lake than in the sediment pore waters (Figure 6.4 b). Thus, the direction of Si diffusion is reversed, and there is a gain to the sediment from the overlying lake water (0.13 g cm$^{-2}$ yr$^{-1}$), at least to a depth of 4 cm in the sediments, before diffusion from the dissolution of diatoms appears to re-establish the typical monotically increasing Si profile with depth, similar to the Si profiles shown in Figure 6.4. Clastic materials, such as the aluminosilicates of the Rotomahana mud (Tarawera Tephra), which make up the bulk of the sediment in Lake Tikitapu (Figure 6.2 b), appear to have lower dissolution rates than diatom frustules, and could even be a net sink for silicon. The rarity of intact diatom frustules in SEM images suggests that diatom growth is likely to be Si-limited though it is possible that there are higher rates of diatom frustule decomposition compared with the other lakes sampled. Lake Tikitapu also has low concentrations of inorganic N and P, which is likely to impose strong nutrient limitation on phytoplankton in this lake.

The variability of sediment pore waters associated with multiple basins, large bays and a single basin were assessed from additional sediment coring sites chosen on Lake Okataina (a central and north basin), Lake Rotoiti (a central basin and a bay at the western end of the lake) and Lake Okaro (north and south side of a single basin). Sediment pore water concentrations were similar in the two separate basin sites selected in Lake Okataina (Figure 6.4 c). Lake Okaro, a small eutrophic lake, had higher pore water Si concentrations on the north side of the lake than the south (Figure 6.4 i), possibly due to clastic sediment entering from the only surface inflow on the south side of the lake, and increasing the sedimentation rate of slow-dissolving aluminosilicates. In Lake Rotoiti, sediment pore water Si concentrations were substantially higher in the central lake basin than in Okawa Bay. As noted by von Westernhagen (2010) in comparisons of primary productivity between Okawa Bay and the central basin, our study also indicates that shallow (depth 5 m) Okawa Bay is quite different from the main basin as it is almost continuously homothermal and has frequent cyanobacteria blooms. We found low Si concentrations ($< 2.5$ mg $L^{-1}$) in Lake Rotoiti compared with most other lakes sampled, and in the main basin minimum concentrations occurred in October (0.12 mg $L^{-1}$), likely following an autumn-winter peak of diatoms (Vincent et al. 1984, von Westernhagen et al. 2010). Up until July 2008, water from Lake Rotorua discharged into Lake Rotoiti via the Ohau Channel (Hamilton et al. 2009). The likelihood of Si limitation in Lake Rotoiti was exacerbated by initial depletion in Lake Rotorua compared with most of the other Rotorua lakes, where Si concentrations remain relatively constant c. 10 mg $L^{-1}$. The inflow from Rotorua was previously the dominant inflow to Lake Rotoiti. The completion of a diversion wall in August 2008, which directs most of the Ohau Channel water from Lake Rotorua directly to the Kaituna River outflow rather than into Lake Rotoiti, has removed a major source of water, low in Si and high in N and P, from Lake Rotoiti. We would expect to see a change in the ratios of Si:N:P in the water column in time due to the removal of the Rotorua waters.

Where a lake has had significant change in trophic status, the Si concentrations in the overlying waters will change, affecting diffusion rates from from the sediment pore waters. A good example of this is Lake Ngapouri, which became increasingly eutrophic as native forest in the catchment was converted to pastoral farmland beginning in 1952 (Fish 1970). Prior to 1962, the lake was oligotrophic and its hypolimnion remained oxygenated throughout the year but by

1966 the hypolimnion had become anoxic (Fish 1970) and by 2007/08 the lake was highly eutrophic with an anoxic hypolimnion for 8 months of the year (Pearson et al. 2012). McColl (1972) found that Si declined from 2.5 mg $L^{-1}$ during homothermy in June, to a minimum of 0.25 mg $L^{-1}$ (surface) and 0.8 mg $L^{-1}$ (bottom) by October, during sampling between April 1970 and April 1971. The rapid decline in Si coincided with chlorophyll *a* concentrations increasing as high as 109 µg $L^{-1}$. Increasing eutrophication appeared to have changed the phytoplankton assemblage from one dominated by diatoms to greater prevalence of cyanobacteria. The reduction in Si demand by diatoms likely resulted in an increase in the annual average Si concentrations to 12.5 mg $L^{-1}$ in the surface and 15.1 mg $L^{-1}$ in the bottom waters by 2008. These changes have resulted in a change in the diffusion gradient of Si from the sediment to the water column (Figure 6.5). The diffusion gradient during the 1970s has been estimated using the Si transport model (Eq. 6.7) assuming a similar k/D value to Lake Okaro (a lake of similar size and trophic state, where k/D ~ 0.02 g $m^{-2}$) (Figure 6.5). In contrast the observed 2008 profile of Si in the pore waters of Lake Ngapouri lies on a mixing line between the lake water and the sediment pore waters at 15 cm depth. With sufficient time a new steady state ($c_\infty$) is likely to occur and a monotonic curve re-established.

The flux of Si from the sediments to the overlying lake water is controlled mostly by the rate of dissolution in the sediments into pore waters and the concentration of Si in the overlying water. Most of the lake sediments are dominated by diatomaceous material and will have similar rates of dissolution (Figure 6.2 a). In eutrophic lakes where diatom productivity is sufficiently high to keep the concentrations of Si < 2 mg $L^{-1}$ recycling rates are very high (Lakes Rotorua (0.83 g $cm^{-2}$ $yr^{-1}$), Rotoiti (0.78 g $cm^{-2}$ $yr^{-1}$) and Okaro (0.41-0.52 g $cm^{-2}$ $yr^{-1}$)). With increasing nutrient loads prompting elevated trophic status, cyanobacteria can dominate, reducing the ability of diatoms to utilise the available Si and resulting in a reduction in the flux from the sediments (e.g. Lake Ngapouri where this flux was only 0.1 g $cm^{-2}$ $yr^{-1}$).

Phosphorus most commonly limits primary production in freshwater systems (Sterner 2008), however, White et al. (1985) and Abell et al. (2010) found a higher prevalence of lakes in the TVZ where productivity was limited by N or co-limited by N and P. Nitrogen limitation may favour the development of cyanobacteria which are more competitive for N than other phytoplankton species, such as diatoms (Downing et al. 2001, Havens et al. 2003). Furthermore heterocystous species of cyanobacteria may overcome periods of nitrogen limitation by using nitrogenase to fix atmospheric N dissolved in the water column (e.g., Wood et al. 2010). A feature of the eutrophic lakes of this study (Rotoiti, Rotorua, Ngapouri and Okaro) is a high prevalence of species known to produce heterocysts (Vincent et al. 1984, Pridmore and Etheredge 1987, Hamilton 2003) but there have been no direct measurements of N-fixation nor any indirect measurements of N-fixation based on heterocyst density in the lakes. Differences in prevalence of different diatom species may also reflect lake trophic state. *Cyclotella* sp. is more common in oligotrophic lakes, while *Aulacoseira* and *Stephanodiscus* species tend to be prominent in eutrophic lakes (Hutchinson 1967). As different diatom species have varying Si requirements, some species will dominate over others depending on the concentration of Si in the water column and the rate of supply. For example Reynolds (1990) found that *C. meneghiniana* became limited at 0.04 mg Si $L^{-1}$ while *A. formosa* became limited at 0.1 mg Si $L^{-1}$. Without specific information on the limiting Si concentrations for the species present in TVZ lakes we have assumed values of 0.1 mg $L^{-1}$ to 0.04 mg $L^{-1}$ as the band within which diatom growth limitation was likely to occur (Figure 6.6).

Based on nutrient concentrations in the epilimnion of the stratified lakes (Figure 6.6) nitrogen limitation or co-limitation by nitrogen and phosphorus was most likely to occur in the oligotrophic lakes, while eutrophic lakes were more likely to be N-limited. These findings are consistent with White et al. (1985) who found there was a strong seasonality of N and P limitation in 12 TVZ lakes based on bioassay experiments. Co-limitation occurs when algal communities contain species with different nutrient requirements resulting in high responsiveness to multiple nutrient enrichments. Our study showed that, with the exception of Lake Tikitapu, all lakes sampled had concentrations of N and P much higher than the limiting concentrations specified by White et al. (1985) (Figure 6.6 a and b). Potential silicon limitation of diatom productivity was found in lakes Rotoiti (central basin) and Tikitapu prior to homothermy (Figure 6.6 c-f). In Lake Rotoiti there was a rapid decrease in Si concentrations associated with a rapid increase in chlorophyll *a* over the months of July to August when the lake was homothermal (Figure 6.7 h).

Observations of phytoplankton species composition in the TVZ lakes (e.g. Vincent et al. 1984, Cassie-Cooper 1996, Ryan et al. 2006) consistently demonstrate that diatoms dominate during holothermy in winter, under conditions of low temperature, low light, high turbulence and elevated nutrient concentrations. Trolle et al. (2011) predicted that a reduced period of winter mixing would occur in a stratified TVZ lake under a future warming climate, together with reductions in the proportion of negatively buoyant diatom populations compared with buoyant cyanoabacteria. Decreases in diatom productivity with a warming climate may be reflected in increasing concentrations of Si in the water column (e.g. Lake Ngapouri) but these changes will be difficult to distinguish in lakes which have been subject to N and P enrichment.

It has been hypothesised (Paerl 1997) that increases in N and P associated with anthropogenic eutrophication may stimulate higher productivity by non-siliceous over siliceous phytoplankton, as silicon concentrations remain largely unaffected by eutrophication. Regeneration of silicon from bottom sediments occurs at significantly lower rates than N and P, relative to diatom requirements. With increasing internal nutrient loads associated with eutrophication and onset of anoxia (Burger et al. 2007, Trolle et al. 2008) it is likely that the occurrence of Si limitation will increase. The prediction of Trolle et al. (2011) of reduced periods of turbulent mixing in winter resulting from a warming climate (Salinger 1995, Easterling et al. 1997) would reduce the period in the year that is conducive to rapid diatom growth. Under this scenario of greater internal loads and a warming climate, buoyant bloom-forming species, such as cyanobacteria, would be likely to increase in abundance compared with diatoms (Reynolds et al. 1987).

Our observation of rapid depletion in Si in some TVZ lakes suggests there is potential for the use of reactive silicon as a remediation method. It is likely that additions of reactive Si to the water column during times when diatoms are naturally dominant (June to August) may extend periods of diatom dominance and result in sedimentation removing significant quantities of reactive N and P from the water column. The removal of substantial reactive N and P will likely reduce the potential for harmful cyanobacterial blooms which could otherwise dominate in the summer months, provided there is not greater regeneration of N and P from the bottom sediments.

## 6.6 SUMMARY

In summary our Si transport model calculates steady state concentration profiles of pore water concentrations with coefficients of variance between 80 and 99%, assuming uniform boundary conditions. Deviation between modelled concentrations and actual concentrations will occur when these conditions are not met. One such change in boundary condition occurs when the trophic status of the lake is altered, resulting in a change in the hypolimenetic Si concentration. The Si model is useful to lake management by providing evidence of such changes. Similarly inhomogeneous in the sediment column, such as tephra or lenses of clastic material (storm events, land slips etc.), will alter the values of both k and D, resulting in a change in slope of the pore water profile. Despite relatively high rates of regeneration of Si from the sediment, Si has been shown to be a limiting nutrient in some lakes, while N limits in others and co-limitation of at least two of N, P and Si occurs in others. The Si concentration in the water column is most likely to reach limiting concentrations during homothermy when other lakes are often at high or maximum concentrations in the annual cycle.

## 6.7 REFERENCES

Abell, J. M., D. Özkundakci, and D. P. Hamilton. 2010. Nitrogen and Phosphorus Limitation of Phytoplankton Growth in New Zealand Lakes: Implications for Eutrophication Control. Ecosystems **13:** 966-977.

Arar, E. J., and G. B. Collins. 1997. Method 445.0, *In vitro* determination of chlorophyll *a* and pheophytin *a* in marine and freshwater algae by fluorescence. Methods for the determination of chemical substances in marine and estuarine environmental matrices. National Exposure Research Laboratory, Office f research and development, USEPA, Ohio.

Aston, S. R. 1983. Natural water and atmospheric chemistry of silicon, p. 77-100. *In* S. R. Aston [ed.], Silicon Geochemistry and Biogeochemistry. Academic Press: London.

Boudreau, B. P. 1996. The diffusive tortuosity of fine-grained unlithified sediments. Geochim. Cosmochim. Acta **60:** 3139-3142.

Bruesewitz, D. A., D. P. Hamilton, and L. A. Schipper. 2011. Denitrification potential in lake sediment increases across a gradient of catchment agriculture. Ecosystems **14:** 341-352.

Burger, D. F., D. P. Hamilton, C. A. Pilditch, and M. M. Gibbs. 2007. Benthic nutrient fluxes in a eutrophic, polymictic lake. Hydrobiologia **584:** 13-25.

Burns, N. M., J. Deely, J. Hall, and K. Safi. 1997. Comparing past and present trophic states of seven Central Volcanic Plateau lakes, New Zealand. N.Z. J. Mar. Freshw. Res. **31:** 71-87.

Carlsson, P., and E. Graneli. 1999. Effects of N: P: Si ratios and zooplankton grazing on phytoplankton communities in the northern Adriatic Sea. II. Phytoplankton species composition. Aquat. Microb. Ecol. **18:** 55-65.

Cassie-Cooper, V. 1996. Microalgae: microscopic marvels. Riverside Books.

Conley, D. J. and others 2009. Controlling eutrophication: nitrogen and phosphorus. Science **323:** 1014-1015.

Downing, J. A., S. B. Watson, and E. Mccauley. 2001. Predicting cyanobacteria dominance in lakes. Can. J. Fish. Aquat. Sci. **58:** 1905-1908.

Easterling, D. R. and others 1997. Maximum and minimum temperature trends for the globe. Science **277:** 364.

Egge, J. K., and D. L. Aksnes. 1992. Silicate as regulating nutrient in phytoplankton competition. Mar. Ecol. Prog. Ser. **83:** 281-289.

Fish, G. R. 1970. A limnological study of four lakes near Rotorua. N.Z. J. Mar. Freshwat. Res. **4:** 165-194.

Forsyth, J., B. S. Lyttle, and B. Morrison. 1972. Geological map of New Zealand. Institute of Geological & Nuclear Sciences.

Giggenbach, W. F., and R. B. Glover. 1992. Tectonic regime and major processes governing the chemistry of water and gas discharges from the Rotorua geothermal field, New Zealand. Geothermics **21:** 121-140.

Gobler, C. J., N. J. Buck, M. E. Sieracki, and S. A. Sa Udo-Wilhelmy. 2006. Nitrogen and silicon limitation of phytoplankton communities across an urban estuary: The East River-Long Island Sound system. Estuar. Coast. Shelf Sci. **68:** 127-138.

Håkanson, L., and M. Jansson. 1983. Principles of Lake Sedimentology, 2nd ed. The Blackburn Press.

Hamilton, D. P. 2003. An historical and contemporary review of water quality in the Rotorua lakes., p. 3-15. Proceedings Rotorua Lakes. Proceedings Rotorua Lakes.

Hamilton, D. P. 2005. Land use impacts on nutrient export in the Central Volcanic Plateau, North Island. N.Z. J. For. **49:** 27-31.

Hamilton, D. P., G. B. Douglas, J. A. Adeney, and L. C. Radke. 2006. Seasonal changes in major ions, nutrients and chlorophyll *a* at two sites in the Swan River estuary, Western Australia. Mar. Freshw. Res. **57:** 803-815.

Hamilton, D. P., W. Paul, C. Mcbride, and D. Immenga. 2009. Water flow between Ohau Channel and Lake Rotoiti following implementation of a diversion wall. CBER Contract Report No. 96. Centre for Biodiversity and Ecology Research, Department of Biological Sciences, University of Waikato.

Harrison, J. A. and others 2009. The regional and global significance of nitrogen removal in lakes and reservoirs. Biogeochem. **93:** 143-157.

Havens, K. E., R. T. James, T. L. East, and V. H. Smith. 2003. N: P ratios, light limitation, and cyanobacterial dominance in a subtropical lake impacted by non-point source nutrient pollution. Environ. Pollut. **122:** 379-390.

Hurst, A. W., and R. Turner. 1999. Performance of the program ASHFALL for forecasting ashfall during the 1995 and 1996 eruptions of Ruapehu volcano. N.Z. J. Geol. Geop. **42:** 615-622.

Hutchinson, G. E. 1967. A treatise on limnology: Introduction to lake biology and the limnoplankton. Wiley & Sons, New York.

Justić, D., N. N. Rabalais, and R. E. Turner. 1995. Stoichiometric nutrient balance and origin of coastal eutrophication. Mar. Pollut. Bull. **30:** 41-46.

Kingston, J. C., R. L. Lowe, E. F. Stoermer, and T. B. Ladewski. 1983. Spatial and temporal distribution of benthic diatoms in northern Lake Michigan. Ecology **64:** 1566-1580.

Koski-Vähälä, J. H., H. Hartikainen, and P. Tallberg. 2001. Phosphorus mobilization from various sediment pools in response to increased pH and silicate concentration. J. Environ. Qual. **30:** 546-552.

Lowe, D. J., and J. D. Green. 1987. Origins and development of the lakes, p. 64. *In* A. B. Viner [ed.], Inland waters of New Zealand. DSIR Bulletin 241. DSIR Science Information Publishing Centre.

Martin-Jézéquel, V., M. Hildebrand, and M. A. Brzezinski. 2000. Silicon metabolism in diatoms: implications for growth. J. Phycol. **36:** 821-840.

Mccoll, R. H. S. 1972. Chemistry and trophic status of seven New Zealand lakes. N.Z. J. Mar. Freshw. Res. **6:** 399-447.

Morgenstern, U., R. Reeves, C. Daughney, S. Cameron, and D. Gordon. 2005. Groundwater Age and Chemistry, and Future Nutrient Loads for Selected Rotorua Lakes Catchments, p. 73. Institute of Geological & Nuclear Sciences.

Nelson, C. S., and G. S. Lister. 1995. Surficial bottom sediments of Lake Taupo, New Zealand: texture, composition, provenance, and sedimentation rates. N.Z. J. of Geol. Geop. **38:** 61-79.

Paerl, H. W. 1997. Coastal eutrophication and harmful algal blooms: Importance of atmospheric deposition and groundwater as" new" nitrogen and other nutrient sources. Limnol. Oceanogr. **42:** 1154-1165.

Pearson, L. K. 2007. The nature, composition and distribution if sediment in Lake Rotorua, New Zealand.  M.Sc. Thesis. Department of Chemistry, University of Waikato.

Pearson, L. K., C. H. Hendy, D. P. Hamilton, and R. C. Pickett. 2010. Natural and anthropogenic lead in sediments of the Rotorua lakes, New Zealand. Earth Planet. Sci. Lett. **297:** 536-544.

Pearson, L. K., C. H. Hendy, D. P. Hamilton, and W. B. Silvester. 2012. Nitrogen-15 isotope enrichment in benthic boundary layer gases of a stratified eutrophic iron and manganese rich lake. Aquat Geochem **18:** 1-19.

Pickrill, R. A., C. S. Nelson, P. Stoffers, and G. G. P. Craig. 1991. Influence of late holocene pyroclastic eruptions on the sedimentary geochemistry of Lake Rotoiti, North Island, New Zealand. J. Paleolimnol. **6:** 173-192.

Pridmore, R. D. 1987. Phytoplankton responce to changed nutrient concentrations, p. 183-194. *In* W. N. Vant [ed.], Lake Managers Handbook. National Water and Soil Conservation Authority, Publication No.103.

Pridmore, R. D., and M. K. Etheredge. 1987. Planktonic cyanobacteria in New Zealand inland waters: distribution and population dynamics. N.Z. J. Mar. Freshw. Res. **21:** 491-502.

Rawlence, D. J. 1984. A study of pigment and diatoms in a core from Lake Rotorua, North Island, New Zealand, with emphasis on recent history. J. Roy. Soc. New Zeal. **14:** 119-132.

Rawlence, D. J. 1985. Post-Tarawera eruption (AD 1886) diatom stratigraphy of Lake Rotoiti, North Island, New Zealand. N.Z. J. Mar. Freshw. Res. **19:** 391-397.

Rawlence, D. J., and P. F. Reay. 1976. Diatom numbers and phosphorus levels in deepwater sediment from Lake Taupo, New Zealand. N.Z. J. Mar. Freshw. Res. **10:** 589-595.

Redfield, A. C. 1958. The biological control of chemical factors in the environment. Am. Sci. **46:** 205-221.

Reynolds, C. S. 1984. The ecology of freshwater phytoplankton. Cambridge Univ Pr.

Reynolds, C. S. 1990. Temporal scales of variability in pelagic environments and the response of phytoplankton. Freshw. Bio. **23:** 25-53.

Reynolds, C. S., R. L. Oliver, and A. E. Walsby. 1987. Cyanobacterial dominance: the role of buoyancy regulation in dynamic lake environments. N.Z. J. Mar. Freshw. Res. **21:** 379-390.

Rocha, C., H. Galvao, and A. Barbosa. 2002. Role of transient silicon limitation in the development of cyanobacteria blooms in the Guadiana estuary, south-western Iberia. Mar. Ecol. Prog. Ser. **228:** 35-45.

Round, F. E., R. M. Crawford, and D. G. Mann. 1990. The Diatoms: biology & morphology of the genera. Cambridge University Press.

Ryan, E. F., I. C. Duggan, D. P. Hamilton, and D. Burger. 2006. Phytoplankton community composition in North Island lakes of New Zealand: is trophic state, mixing, or light climate more important. NZ J Mar Freshw Res **40:** 389-398.

Salinger, M. J. 1995. Southwest Pacific temperatures: trends in maximum and minimum temperatures. Atmos Res **37:** 87-99.

Schindler, D. W. and others 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. PNAS **105:** 11254-11258.

Sommer, U., and H. H. Stabel. 1983. Silicon consumption and population density changes of dominant planktonic diatoms in Lake Constance. J. Ecol. **71:** 119-130.

Sterner, R. W. 2008. On the phosphorus limitation paradigm for lakes. Int. Rev. Hydrobiol. **93:** 433-445.

Timperley, M. H. 1987. Regional influences on lake water chemistry, p. 97-111. *In* A. B. Viner [ed.], Inland waters of New Zealand. DSIR Science Infrmation Publishing Centre.

Trolle, D., D. P. Hamilton, C. H. Hendy, and C. Pilditch. 2008. Sediment and nutrient accumulation rates in sediments of twelve New Zealand lakes: influence of lake morphology, catchment characteristics and trophic state. Mar. Freshwat. Res. **59:** 1067-1078.

Trolle, D., D. P. Hamilton, and C. A. Pilditch. 2010. Evaluating the influence of lake morphology, trophic status and diagenesis on geochemical profiles in lake sediments. Appl. Geochem. **25:** 621-632.

Trolle, D., D. P. Hamilton, C. A. Pilditch, I. C. Duggan, and E. Jeppesen. 2011. Predicting the effects of climate change on trophic status of three morphologically varying lakes: Implications for lake restoration and management. Environ. Modell. Softw. **26:** 354-370.

Vincent, W., M. Gibbs, and S. Dryden. 1984. Accelerated eutrophication in a New Zealand lake: Lake Rotoiti, central North Island. N.Z. J. Mar. Freshwat. Res. **18:** 431-440.

Viner, A. B., and L. Kemp. 1983. The effect of vertical mixing on the phytoplankton of Lake Rotongaio (July 1979 January 1981). N.Z. J. Mar. Freshw. Res. **17:** 407-422.

Von Westernhagen, N., D. P. Hamilton, and C. A. Pilditch. 2010. Temporal and spatial variations in phytoplankton productivity in surface waters of a warm-temperate, monomictic lake in New Zealand. Hydrobiologia **652:** 57-70.

Werner, P., and J. P. Smol. 2005. Diatom–environmental relationships and nutrient transfer functions from contrasting shallow and deep limestone lakes in Ontario, Canada. Hydrobiologia **533:** 145-173.

White, E., K. Law, G. Payne, and S. Pickmere. 1985. Nutrient demand and availability among planktonic communities—an attempt to assess nutrient limitation to plant growth in 12 central volcanic plateau lakes. N.Z. J. Mar. Freshwat. Res. **19:** 49-62.

Wilding, T. K. 2000. Rotorua Lakes Algae Report, p. 98. Bay of Plenty Regional Council, Technical Report 2000/06.

Willén, E. 1991. Planktonic diatoms-an ecological review. Algological Studies **62:** 69-106.

Wood, S. A., M. J. Prentice, K. Smith, and D. P. Hamilton. 2010. Low dissolved inorganic nitrogen and increased heterocyte frequency: precursors to Anabaena planktonica blooms in a temperate, eutrophic reservoir. J Plankton Res **32:** 1315.

# CHAPTER 7: RESEARCH CONCLUSIONS

## 7.1 RESEARCH SUMMARY

Globally, cultural eutrophication has become the most widespread problem affecting surface water quality (Smith and Schindler, 2009). Eutrophication in New Zealand is increasingly becoming an issue, where it is estimated that 30% of lakes greater than one hectare in area have very poor to extremely poor water quality as a result of cultural eutrophication (Ministry for the Environment, 2007). In order to reduce eutrophication it is generally accepted that a decrease in the nutrient loads entering a water body is required, whether that nutrient be nitrogen (N), phosphorus (P) or both species (Sterner, 2008; Schindler et al., 2008; Conley et al., 2009; Abell et al., 2010).

Lakes in the Taupo Volcanic Zone (TVZ) tend to have naturally high phosphorus concentrations from weathering and desorption from ignimbrite that constitutes much of the aquifer bedrock of this region (White, 1983). Phytoplankton in these lakes have been identified as more likely to be N-limited or co-limited (White, 1983; Abell et al., 2010) than is commonly been documented elsewhere around the world (Schindler, 1997; Schindler et al., 2008; Guildford and Hecky, 2000).

Intensification of agriculture, particularly dairy farming, is associated with a growing dependence on N fertilizers (Richardson et al., 2004; MacLeod and Moller, 2006) and has resulted in increasing reactive N loads to TVZ lakes (Hamilton, 2005; Parfitt et al., 2006; Bruesewitz et al., 2011). Regional authorities have implemented nutrient reduction targets to deal specifically with the reduction of N (Environment Waikato, 2003; Burns et al., 2009). However, the reduction of external loading does not always produce the desired improvement in water quality as internal cycling from bottom sediments can have a significant impact. Constructing a budget for internal recycling of reactive nitrogen is complicated by the loss through denitrification of some of the nitrogen transported to the bottom sediments (Bruesewitz et al., 2011). Various techniques have been developed for determining denitrification rates but are fraught by analytical difficulties and often underestimate the amount of N lost via denitrification (Seitzinger et al., 2002; Van Breemen et al., 2002; Galloway et al., 2004; Boyer et al., 2006; Groffman et al., 2006).

In Chapter 2, a method was developed to capture quantitatively and efficiently dissolved $N_2$ in lake water and make it readily available for isotopic analysis without the need for further sample manipulation. Water samples were collected from the epilimnion, hypolimnion, benthic nepheloid layer (BNL) and at 5-cm intervals from the sediment pore waters at monthly intervals in Lake Ngapouri for one year. The water column $\delta^{15}N$ in surface waters was dominated by atmospheric exchanges as there were only small fluctuations in $\delta^{15}N$ in surface waters (-1‰ while stratified to 0.29‰ while mixed). The bottom waters showed a small but reversed change, from -1.5‰ while mixed to 1.25‰ while stratified. Fluxes of nitrogen isotopes in surface waters, and to a lesser extent in bottom waters, appear to show little departure from atmospheric equilibrium. However, significant increases in $^{15}N$-enriched dinitrogen take place in the benthic nepheloid layer (up to 12.2 ‰) during periods of anoxia. This may be related to abundant $^{15}N$-enriched ammonium substrate (up to 3.6 mg $L^{-1}$) supporting nitrification, with the nitrate subsequently mostly denitrified. Nitrate concentrations remained low (< 0.5 mg $L^{-1}$ with increasing duration of anoxia) requiring an alternative electron acceptor, besides oxygen, to support the nitrification-denitrification coupling that was needed to obtain the observed level of $^{15}N$ enrichment in the BNL. It is thermodynamically favourable for iron and manganese hydroxides and oxides to induce sufficient nitrification to oxidize ammonium in the anoxic BNL (Luther et al., 1997). Both dissolved iron and manganese concentrations in the BNL rose markedly during anoxia (Fe 1.7 mg $L^{-1}$ and Mn 0.35 mg $L^{-1}$). The nitrate formed would mostly be rapidly denitrified to di-nitrogen which would continue to become enriched in $^{15}N$ during anoxia, as observed in the hypolimnion and, to a greater extent, the BNL of Lake Ngapouri.

In Chapter 3, the $\delta^{15}N$ [$N_2$] study was extended further to TVZ lakes of varying trophic status (oligotrophic to hypertrophic) and in mixing regime (polymictic and monomictic). The $\delta^{15}N$ [$N_2$] was determined for water samples from the epilimnion and hypolimnion of 11 TVZ lakes at the end of the stratification cycle. Polymictic lakes showed no $^{15}N$ enrichment in the bottom waters and $\delta^{15}N$ was approximately zero, i.e., at atmospheric levels. The monomictic stratified lakes showed enrichment of $\delta^{15}N$ [$N_2$] in the hypolimnion of up to 20.2‰. Following a once-off survey of 11 lakes a subset of five lakes was sampled monthly over one year. Water samples were taken from the epilimnion, hypolimnion and 0.1 m above the sediment-water interface (benthic nepheloid layer), and from within the sediment at 5-cm depth intervals. Gas extracted from the surface waters of all lakes was close to equilibrium with the atmosphere (around 0‰) throughout the year. The hypolimnion showed some enrichment in autumn (up to 1.2‰), whilst samples from the BNL were strongly enriched in $^{15}N$. Maximum BNL values of $^{15}N$ [$N_2$] were 0.4‰ for Lake Taupo, 1.3‰ for Lake Tarawera, 5.3‰ for Lake Okataina, 6.4‰ in Lake Rotoiti and 12.2‰ in Lake Ngapouri. Enrichment of $^{15}N$ [$N_2$] within the BNL was greatest in lakes of highest trophic status which had anoxic hypolimnia, suggesting enrichment via diagenesis of particulate organic matter (POM) to ammonium, which was subsequently denitrified.

The potential use of $\delta^{15}N$ [$N_2$] extracted from the BNL or near-bottom waters could potentially be used as a monitoring tool to rapidly assess changes in trophic state in stratified lakes on a seasonal basis or with high-frequency monitoring in polymictic lakes where anoxia occurs in the hypolimnion in response to temporary stratification (Chapter 3). Strong correlations were found with a number of key environmental parameters (volumetric hypolimnetic oxygen demand (VHOD), N load, denitrification enzyme activity (DEA), trophic level index (TLI) and the parameters constituting the TLI (TP, TN, Secchi, Chl *a*). Lakes increase their capacity to remove oxidized inorganic nitrogen via denitrification under increasing nitrogen loads. For selected Rotorua Lakes (Rotoma, Okataina, Tarawera, Tikitapu, Rotoiti and Okaro), $\delta^{15}N$ [$N_2$] explained 95% of the sediment denitrification potential after the removal of Lake Okareka which was an outlier in the study by Bruesewitz et al. (2011) based on regressions against the proportion of agriculture in the catchment and the ratio of catchment agricultural area to lake area. Given the close relationship of $\delta^{15}N$ [$N_2$] in the BNL with a range of general environmental indicators of trophic status, the greatest value of its application could be as an indicator of trophic status in stratified lakes not routinely monitored.

Chapter 4 presents an attempt to understand the diagenetic processes taking place in siliceous lake sediments. Sediment core samples were collected monthly from the central basins of five monomictic TVZ lakes of varying trophic state, and separated into sediment and pore water fractions. The sediments consisted of fine diatomaceous ooze, although rhyolitic tephras are also present in some of the lakes.

The major diagenetic process is reduction of oxidised species within the sediment as organic matter is metabolised and dissolved oxygen depleted. As sediments generally became more reducing at greater depth, the zones in which individual species were reduced varied amongst chemical species, lakes and seasons. Nitrogen compounds were reduced early to ammonium which diffused back to the overlying lake water. Manganese often diffused to the SWI before being re-oxidised, where it acted as a co-precipitator for many other trace species. Ferric ions reduced to ferrous ions, which then precipitated with sulfides if there was sufficient sulfate at that depth, with the sulfate sourced initially from the overlying lake water and transported by diffusion to reducing zones in the sediment. When ferrous ion production exceeded sulfate reduction, ferrous ions also diffused to the SWI before being re-oxidised. As the hypolimnion chemistry changed with stratification, the pore water chemistry also showed seasonal changes, especially for redox-driven Fe, Mn, $NH_4$, $SO_4$ and associated species such as $PO_4$. Following the development of hypolimnetic anoxia concentrations of Fe, Mn and $NH_4$ in upper pore waters increased markedly and $SO_4$ concentrations decreased. The reduction of sulfate in the sediments prevented build up of chalcophile element (Cu, Zn, Pb, Hg) pore water concentrations until the sulfide was removed.

Other processes occurring in the sediments are adsorption and ion exchange, hydrolysis of silicates, protination, solution and remineralisation. Polyoxides ($PO_4$ and $AsO_4$) were adsorbed onto settling particulates and released back into solution as particulate organic matter underwent diagenesis or with dissolution of the inorganic particulates (Fe, Mn and Al oxyhydroxides). The ubiquitous presence of readily soluble siliceous material resulted in the release of silicon to the pore waters and subsequent diffusion to overlying lake waters. The extent of the flux of silicon was controlled largely by the trophic status of the lake, and was greatest in lakes where high concentrations of diatoms reduced epilimnetic silicon concentrations to $< 1$ mg $L^{-1}$. The weathering of alumnosilicate glass, from tephric deposits in the catchment or from direct air fall of tephra, also released silicon along with aluminium and uranium, to the pore waters. As the concentration of aluminium exceeded the stability for aluminium hydroxide, it is likely that the majority of the pore water aluminium was present as hydroxy-colloids. Such colloids strongly absorb polyoxides and appeared to coalesce at the SWI as the aluminium concentration in overlying waters was very low. The alkaline earth elements (Ca, Mg and Sr) all increased in concentration in the upper pore waters, suggesting dissolution of these elements from planktonic calcifiers (e.g. ostracods), fish otoliths or mollusc exoskeletons dissolving in the $CO_2$-rich environment. Barium exhibited a different behaviour, with pore water concentrations increasing at greater depths in the sediment, suggesting transport from the water column as barite ($BaSO_4$) and subsequent reduction of sulfates to sulfides. Conservative elements (Li, B, Na, K) showed little change in pore water concentrations except where geothermal fluids moved vertically through the bottom sediments, as was the case for Lake Rotoiti. In this case, pore water concentrations increased monotonically down-core according to a mixing curve between geothermal waters and the overlying lake water.

From the near-surface pore water concentration gradients, obtained in Chapter 4, the diffusion equation has been used to calculate fluxes of soluble species. Diffusive fluxes of nutrient species were in the range 16.5 to 377 mg $m^{-2}$ $yr^{-1}$ for ammonium, 1.3 to 110 mg $m^{-2}$ $yr^{-1}$ for total dissolved phosphorus, 0.05 to 18.5 mg $m^{-2}$ $yr^{-1}$ for reactive phosphate species and 80 to 767 mg $m^{-2}$ $yr^{-1}$ for silicon (except for Lake Tarawera where the water column was a source of Si for the bottom sediments). These values are of use for modelling lake productivity when combined with the external nutrient budgets, although this task was beyond the scope of the current study. It should be noted however, that the present study has focused on central basin sediments, which are likely to have far greater fluxes than those in the littoral zone.

In Chapter 5, sediment profiles of lead from selected lakes in the TVZ were used to assess the exposure of the lakes to both natural and anthropogenic sources of lead as well as the diagenetic processes that also influence its distribution. Despite the removal of all lead in New Zealand petroleum by 1996, lead is still widely distributed in the environment, having accumulated in depositional areas such as lake sediments, where it can provide an historical marker of human use. In New Zealand, after accounting for diagenetic processes, it is possible to track the depositional history of petroleum-based lead inputs to lakes through sediment depositional layers. For sediments of the Rotorua lakes corresponding to those deposited within the 18th century, there are low lead concentrations. In sediments above the Tarawera tephra layer, deposited in 1886, there is a clearly identifiable stratum corresponding to anthropogenic lead from petroleum products. Variations between lakes are a function of exposure to leaded petroleum within the catchment and lake, as well as lake trophic state and redox status in lower water layers, which alter sedimentation rates and vertical transport of lead in the sediments. Diagenesis results in some redistribution of lead as iron and manganese are mobilised through oxidation and they are in turn are immobilised by sulfate reduction to produce insoluble sulfides. The anthropogenic lead peak from lead alkyl petroleum additives can be expected to be buried rapidly, and is unlikely to affect the aquatic system unless sediments are significantly disturbed.

A silicon transport model was developed in Chapter 6 from the gradients of the pore water concentration of silicon measured in 9 lakes ranging in trophic state from oligotrophic to supertrophic. The model simulated the Si transport gradient with high precision ($r^2 > 0.95$, $p < 0.01$) in lakes with no volcanic tephra layers or significant geothermal discharges to the lake water. The ubiquitous presence of readily soluble diatom frustules in the sediment resulted in the release of silicon to the pore waters and subsequent diffusion to overlying lake waters. The extent of the flux of silicon was found to be controlled by the trophic status of the lake, being greatest in eutrophic lakes where diatom populations were able to reduce epilimnetic silicon concentrations to $< 1$ mg $L^{-1}$. Temporal variations in the concentrations and mass ratios of Si, N, and P suggest that over most of the year diatom growth in the oligotrophic lakes is limited by nitrogen, or co-limited by nitrogen and phosphorus, whilst in eutrophic lakes, silicon may limit diatom growth during winter and phosphorus and/or nitrogen limits in summer. With increasing Si-limitation it is likely that phytoplankton blooms will increase with increasing dominance of non-siliceous flagellated species, such as cyanobacteria.

## 7.2 IMPLICATIONS FOR LAKE AND CATCHMENT MANAGEMENT

The challenge facing lake managers is that there is not one single factor that controls water quality. Biogeochemical cycles controlling the availability and cycling of nutrients cannot be separated from those processes controlling other chemical species. Conservative components are needed to compare, contrast and understand non-conservative transitions. Small changes in climate, nutrient loading, land use or other factors all may affect water quality but may not cause a significant decline in water quality until certain thresholds are reached which can be difficult to reverse (Scheffer et al., 2001; Scheffer and Carpenter, 2003). Such a change occurs when hypolimnia become anoxic, resulting in potentially massive releases of nutrients to the water column.

Trophic level index (TLI) is used to assess changes in water quality in New Zealand lakes based on parameters of TN, TP, Secchi depth and Chl *a*. The sensitivity of this monitoring method is often reduced as a significant change in one parameter may be offset by other parameters constituting the TLI value. For example, Lakes Tarawera and Okataina are both classified as oligotrophic with similar TLI values of 2.91 and 2.83, respectively. The benthic nepheloid layer $\delta^{15}N$ [$N_2$] values, however, were quite different at 1.3‰ for Lake Tarawera and 5.3‰ for Lake Okataina. Anoxia develops in the hypolimnion of Lake Okataina during stratification whereas c. 50% of dissolved oxygen present at the start of stratification is lost by the end of stratification in Lake Tarawera. Thus, the sediments remain oxic immediately below the sediment-water interface and the flux of nutrients (especially N) in Lake Tarawera (17 mg $NH_4$-N $m^{-2}$ $yr^{-1}$, 2.5 mg $PO_4$-P $m^{-2}$ $yr^{-1}$) is significantly lower than in Lake Okataina (39-200 mg $NH_4$-N

$m^{-2}$ $yr^{-1}$, 1 mg $PO_4$-P $m^{-2}$ $yr^{-1}$). It is possible that the $\delta^{15}N$ [$N_2$] may be a more sensitive indicator of potential for internal nutrient loading and subsequent increase in the TLI when comparing these two lakes. Based on the close relationship of $\delta^{15}N$ [$N_2$] in the BNL with a range of general environmental indicators of trophic status (VHOD, TP, TN, Secchi, Chl *a*), the greatest value of its application could be as an indicator of trophic status in stratified lakes not routinely monitored.

Significant increases in $^{15}N$-enriched $N_2$ take place in the hypolimnion and BNL that cannot be explained by conventional denitrification processes. The enrichment occurs while lakes are stratified and is most pronounced when the hypolimnia become anoxic. The enrichment may be related to abundant $^{15}N$-enriched ammonium substrate supporting nitrification, which is followed by denitrification. However, nitrate concentrations remain too low to produce the observed $^{15}N$ enrichment requiring an alternative electron acceptor, besides oxygen, to support the nitrification-denitrification coupling. It is thermodynamically favourable for iron and manganese hydroxides and oxides to induce sufficient nitrification to oxidize ammonium in the anoxic benthic nepheloid layer (Luther et al., 1997). The nitrate formed appears to be rapidly denitrified to di-nitrogen. This unexpected denitrification pathway needs to be considered by lake managers when assessing the nutrient budgets of lakes and catchment systems, as this process may remove more nitrogen than would otherwise have been estimated.

There are several processes within lake sediments which affect their nutrient budgets. These processes include: permanent sequestration of elements in the sediment from burial by accumulating particulate matter; metabolism of organic matter releasing ammonium into the sediment pore water; reduction of iron and manganese which releases phosphate into the sediment pore water; re-oxidation of ferrous and manganous which binds phosphorus back to iron and manganese; reduction of sulfate to sulfide which removes iron in the form of pyrite; dissolution of diatoms which recycles silicon back to the lake water; and the flow of geothermal and other groundwaters carrying solutes (e.g. Na, Si, $PO_4$) into the lake water. The overall budget of the lake cannot be fully understood without including these processes. An interesting example of this is lead in lake sediments. Anthropogenic inputs of lead greatly exceed natural inputs. They peaked in the 1980s, providing a distinct anthropogenic marker. Diagenetic processes mobilised the lead by solubilising the iron and manganese binding lead to particulates and re-precipitating lead as sulfides following reduction of sulfate. As a consequence the lead concentration peaks in the sediments are of a different age to that where the input peak occurred. The extent of the offset is closely related to the trophic state of the lake. The same processes will affect the distribution of other trace elements. Where lead has not been significantly remobilised (oligotrophic lakes) its peak concentration relative to the depth to the Tarawera Tephra (a non-mobile marker) can be used to assess sedimentation rates. Özkundakci et al. (In press) used this approach to parameterise sediment geochemistry for simulating water quality responses to long-term catchment and climate changes.

Measurements of the concentration of Si available for diatom consumption in the water column have not been considered important for routine monitoring by managers of the TVZ lakes. It has been assumed that competition for nutrients and light between cyanobacteria and other phytoplankton control the succession of species within and amongst these groups. This study has shown that Si is recycled from the sediments at rates which are dependent on the nature of the sediment and the concentration of Si in the water column. The settling of diatoms enriches Si in the sediments and as lakes become more eutrophic this process results in reduction of Si concentrations to low levels ($< 0.1$ mg $L^{-1}$, for example, Lake Rotoiti). However, with increasing eutrophication algal assemblages can be dominated by buoyant groups, such as cyanobacteria, reducing diatom productivity and demand on Si and allowing concentrations to rise in the water column (for example, Lake Ngapouri). This in turn alters the rate of diffusion of Si from the bottom sediments to the water column. Analysis of pore waters can be used to identify these types of recent changes in the trophic status of a lake. Routine analysis of Si in the water column could provide early warning of such changes in algal succession and it has been recommended to the Bay of Plenty Regional Council that silicon become part of the routine monitoring programme, with concentrations recorded on a monthly basis.

The observation of rapid depletion in silicon in some TVZ lakes suggests there is potential for the use of reactive silicon as a remediation method. It is likely that additions of reactive Si to the water column during times when diatoms are naturally dominant (June to August) may extend periods of diatom dominance and result in diatom sedimentation removing significant quantities of reactive N and P from the water column during spring stratification. The removal of substantial reactive N and P could reduce the potential for harmful cyanobacterial blooms which could otherwise dominate in the summer months provided there is not greater regeneration of N and P from the bottom sediments. This has been suggested for Lake Michigan (Committee on Restoration of Aquatic Ecosystems, 1992) but rejected due to the scale and cost associated with a lake of this size, however a smaller lake in which sediments are focused could be a much more attractive proposition. With a Si to P ratio of 9:1, an addition of 400 t of sodium silicate during June/July should remove 10 t of phosphorus at a cost of $100 000 from a lake such as Rotoiti.

Lake managers seek to control the trophic status of lakes so that blooms do not occur and the water quality remains high for both recreation and maintenance of the natural ecosystem. Knowledge of the biogeochemical processes occurring that affect trophic status is therefore of critical importance. The timing and magnitude of nutrient exchanges at the SWI are a key link to lake trophic status. Nutrients are released from settling organic matter as its passes into anoxic zones, either within the hypolimnion or following burial. In monomictic lakes, in which hypolimnia become anoxic during stratification, or in polymictic lakes which can stratify and bottom waters become anoxic for short periods of time, nutrients released from the sediment pore waters are recycled when the lake mixes. An indicator of pending nutrient release is a decline in the concentration of dissolved oxygen in the water column. Under anoxia, iron and manganese are mobilised, releasing adsorbed phosphate. Historically lake managers have utilised a number of remediation actions to reduce this nutrient recycling process. Chemical dosing has been undertaken in high-risk lakes using a number of different products either individually or in combination (e.g. at Lake Okaro with alum and zeolite (McIntosh, 2004; Özkundakci, 2010; Gibbs and Özkundakci, 2011), at Lake Okareka with Phoslock (McIntosh, 2007), and with stream inflows into Lake

Rotorua with alum (Bay of Plenty Regional Council, 2012)). These interventions tend to be very expensive. Understanding the lake-specific sediment diagenetic processes, coupled with ecological modelling, should enable remediation strategies to be better targeted.

Lake managers in the TVZ currently monitor temperature, dissolved oxygen, conductivity and fluorescence by monthly profiles; however the frequency of these profiles may be too low to show de-oxygenation events, especially in polymictic lakes. Real time monitoring buoys, which transmit meteorological and water quality data continuously at high frequency, have been deployed in a number of TVZ lakes (Taupo, Tarawera, Rotoiti, Rotorua and Rotoehu). Water quality variables transmitted include surface and bottom dissolved oxygen, chlorophyll fluorescence and phycocyanin (indicative of cyanobacteria biomass), water temperature, pH, light and nitrate. As deoxygenation is proven to have a significant impact on sediment nutrient release, destratification of the water column is to be trialled in polymictic Lake Rotoehu. Two oxygenation systems will be deployed in the lake and will pump water from the epilimnion to the hypolimnion during periods of stratification to prevent deoxygenation of the bottom waters and subsequent nutrient release (Andy Bruere, Bay of Plenty Regional Council, pers. comm.). The real time monitoring buoy will provide alerts to potential stratification events and enable the destratification system. Prior to the deoxygenation devices installation, a sediment survey will be undertaken to assess the composition of both sediments and pore waters. Comparison with the geochemical data obtained during this extensive study can provide valuable information about the sediment-pore water interactions occurring in Lake Rotoehu. By understanding the processes leading up to nutrient release from the sediment and innovative remediation stratigies, lake manages can have an active role in controlling lake water quality. However, missing from the current monitoring is analysis of the silicon available for diatom growth, thus potentially leaving lake managers unable to monitor the growth requirements of this important group of algae which might otherwise remove nutrients from the water column.

## 7.3 RECOMMENDATIONS FOR FUTURE WORK

Further study should be directed at identification of the $^{15}$N-depleted materials required to achieve isotopic mass balance in the TVZ lakes. As ammonium concentrations were generally in phase with the observed $^{15}$N enrichment of nitrogen gas, ammonium would be a potential candidate for $^{15}$N measurements as nitrate concentrations are often negligible when anoxia occurs in bottom waters. Within the benthic nepheloid layer it would be useful to know the dynamics of POM and ammonium in particular, and further study should be directed at obtaining direct measurements of $\delta^{15}$N in selected substrates (PON, $NO_2^-$ and $NO_3^-$ (when possible), as well as $NH_4^+$). The relationship between increase in the partial pressure of dissolved $N_2$ ($P_{N_2}$), change in $\delta^{13}$C [$CO_2$] and the increase in $\delta^{15}$N [$N_2$] should be evaluated in the denitrifying layer to confirm the link between carbon and nitrogen fluxes. A complete mass balance of $^{15}$N may ultimately be possible in all of the nitrogen reservoirs of actively denitrifying zones allowing for determination of all of the relevant processes involved.

If $\delta^{15}$N [$N_2$] was to be used as a monitoring tool, future study should be directed at improving the relationships between $\delta^{15}$N [$N_2$] and trophic status by obtaining samples from multiple years and comparing with measured TN, TP, Chl *a*, Secchi disk and VHOD measurements. It would also be beneficial to extend the study to a wider set of lakes including within New Zealand and globally, to test for the generality of relationships developed for the TVZ lakes, especially for lakes which may be less strongly N-limited.

The data collected in the sediment pore water study (Chapters 4-6) can be used to parameterise ecological models for the large volcanic lakes in this study and to provide a whole lake perspective on the influence of denitrification and sediment-water exchanges on the dynamics of the lakes. DYRESM-CAEDYM, a coupled one-dimensional hydrodynamic-ecological model used for vertical resolution of temperature and ecological variables, and ELCOM-CAEDYM, a three-dimensional hydrodynamic model that is coupled to the same ecological model as the one-dimensional DYRESM model, could be applied to help better understand the basin scale fluxes and assist with the mass balance calculations mentioned above. Processes of specific interest for modelling include nitrogen dynamics (specifically nitrogen fixation and denitrification), benthic-pelagic coupling, bloom-forming algae and the trophic cascade. The CAEDYM model also includes a dynamic sediment model which incorporates CANDI (carbon and nutrient diagenesis; Boudreau, 1996) and WEB-PHREEQ sediment models. The sediment model tracks changes in bottom sediment composition with changes in redox status and associated sediment diagenesis. It is capable of calculating transient or steady-state diagenesis of organic matter, nutrients ($NH_4^+$, $NO_3^-$, $PO_4^{3-}$), oxidants ($O_2$, $NO_3^-$, $MnO_2$, $Fe^{3+}$ and $SO_4^-$), reduced by-products ($Mn^{2+}$, $Fe^{2+}$, $NH_4^+$, $H_2S$, $CH_4$ and FeS), acid base speciation (carbonate, ammonia, sulfide and phosphate species) and pH in aqueous sediments. It can simulate a wide range of burial velocities and depth dependent transport processes and properties, such as bio-diffusivities that decrease with depth. The sediment nutrients and trace element data from this study, as well as the inferred processes such as denitrification, provide ideal data with which to test the algorithms in the dynamic sediment model and to calibrate the associated parameters. Both Trolle et al. (2011) and Özkundakci et al. (2011) recognised the need to include the dynamic response of sediment nutrient releases in the DYRESM-CAEDYM model, to better understand the temporal variability of sediment nutrient releases in response to changes in external loading and climate change.

## 7.4 REFERENCES

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

Bay of Plenty Regional Council. 2012. Improving water quality in Lake Rotorua: Information on the way land is used. Strategic Policy Publication 2012/03, Bay of Plenty Regional Council.

Boudreau, B. P. 1996. A method-of-lines code for carbon and nutrient diagenesis in aquatic sediments. Comput. Geosci. **22:** 479-496.

Boyer, E. W. and others 2006. Modelling denitrification in terrestrial and aquatic ecosystems at regional scales. Ecol. Appl. **16:** 2123-2142.

Bruesewitz, D. A., D. P. Hamilton, and L. A. Schipper. 2011. Denitrification potential in lake sediment increases across a gradient of catchment agriculture. Ecosystems **14:** 341-352.

Burns, N., J. Mcintosh, and P. Scholes. 2009. Managing the lakes of the Rotorua district, New Zealand. Lake Reserv. Manag. **25:** 284-296.

Committee on Restoration of Aquatic Ecosystems. 1992. Restoration of Aquatic Ecosystems: Science, Technology and Public Policy. National Academy Press, Washington, D.C.

Conley, D. J. and others 2009. Controlling eutrophication: nitrogen and phosphorus. Science **323:** 1014-1015.

Environment Waikato. 2003. Protecting Lake Taupo: A long-term strategic partnership, p. 27. Environment Waikato, Hamilton, NZ.

Galloway, J. and others 2004. Nitrogen cycles: past, present, and future. Biogeochem. **70:** 153-226.

Gibbs, M., and D. Özkundakci. 2011. Effects of a modified zeolite on P and N processes and fluxes across the lake sediment-water interface using core incubations. Hydrobiologia **661:** 21-35.

Guildford, S. J., and R. E. Hecky. 2000. Total nitrogen, total phosphorus, and nutrient limitation in lakes and oceans: Is there a common relationship? Limnol. Oceanogr. **45:** 1213-1223.

Groffman, P. M. and others 2006. Methods for measuring denitrification: diverse approaches to a difficult problem. Ecol. Appl. **16:** 2091-2122.

Hamilton, D. P. 2005. Land use impacts on nutrient export in the Central Volcanic Plateau, North Island. N.Z. J. For. **49:** 27-31.

Luther, G. W. 1997. Interactions of manganese with the nitrogen cycle: Alternative pathways to dinitrogen. Geochim. Cosmochim. Acta **61:** 4043-4052.

MacLeod, C. J., and H. Moller. 2006. Intensification and diversification of New Zealand agriculture since 1960: an evaluation of current indicators of land use change. Agric. Ecosyst. Environ. **115:** 201-218.

McIntosh, J. 2004. Lake Okaro Alum treatment. Technical Report 040405, Environment Bay of Plenty.

McIntosh, J. 2007. Phoslock application – Lake Okareka final report. Environment Bay of Plenty Environmental Publication 2007/23, Environment Bay of Plenty.

Ministry for the Environment. 2007. Lake water quality in New Zealand: status in 2006 and recent trends 1990-2006. Ministry for the Environment. Wellington, New Zealand. Publication No. ME 832.

Özkundakci, D. 2010. Speciation and dynamics of phosphorus in relation to lake restoration methods. Ph.D. Thesis. University of Waikato.

Özkundakci, D., D. P. Hamilton, and D. Trolle. Modelling the response of a highly eutrophic lake to reductions in external and internal nutrient loading. N. Z. J. Mar. Freshwat. Res. **45:** 165-185.

Özkundakci, D., C. G. McBride and D. P. Hamilton. In press. Parameterisation of sediment geochemistry for simulating water quality responses to long-term catchment and climate changes in polymictic, eutrophic Lake Rotorua, New Zealand. CMEM.

Parfitt, R. L., L. A. Schipper, W. T. Baisden, and A. H. Elliott. 2006. Nitrogen inputs and outputs for New Zealand in 2001 at national and regional scales. Biogeochem. **80:** 71-88.

Richardson, P., K. Botherway, R. Cooper, P. L. Couteur, N. Potter, and J. M. Williams. 2004. Growing for good: Intensive farming, sustainability and New

Zealand’s environment. Parliamentary Commissioner for the Environment, Wellington, New Zealand.

Schindler, D. W. 1977. Evolution of phosphorus limitation in lakes. Science **195:** 260-262.

Schindler, D. W. and others 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. PNAS **105:** 11254-11258.

Seitzinger, S. P. and others 2002. Nitrogen retention in rivers: model development and application to watersheds in the northeastern U.S.A. Biogeochem. **57:** 199-237.

Smith, V. H., and D. W. Schindler. 2009. Eutrophication science: where do we go from here? Trends Ecol. Evol. **24:** 201-207.

Sterner, R. W. 2008. On the phosphorus limitation paradigm for lakes. Int. Rev. Hydrobiol. **93:** 433-445.

Trolle, D., D. P. Hamilton, C. A. Pilditch, I. C. Duggan, and E. Jeppesen. 2011. Predicting the effects of climate change on trophic status of three morphologically varying lakes: Implications for lake restoration and management. Environ. Modell. Softw. **26:** 354-370.

Van Breemen, N. and others 2002. Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern USA. Biogeochem. **57:** 267-293.

White, E. 1983. Lake eutrophication in New Zealand - a comparison with other countries of the Organisation for Economic Co-operation and Development. N. Z. J. Mar. Freshwat. Res. **17:** 437-444.