Temporal variability in the water quality of a deep temperate oligotrophic lake

A thesis
submitted in fulfilment
of the requirements for the degree of
Doctor of Philosophy in the School of Science
at
The University of Waikato
by

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University of Waikato

2016

Abstract

Lakes change over time in response to climate and catchment disturbance, even in the absence of anthropogenic stressors. This temporal change may impact the setting of reference conditions for lakes. Many sources of information including monitoring data, historical information, modelling and paleolimnology can be used to understand temporal dynamics of lakes. In this thesis, the contribution of catchment disturbance by volcanic eruptions, introduction and proliferation of invasive mammals, and climate variability, to temporal variability in lake reference conditions was studied in a deep lake (Lake Okataina) in the Central North Island in New Zealand that is close to reference state. The lake and its catchment have been subject to anthropogenic and natural biotic and abiotic disturbances during the last millennium. Polynesian settlements were thought to have been established in and around the lake catchment in the early 14th century following the Kaharoa eruption of AD 1314 ± 12. Mt Tarawera erupted 10 June 1886 and damaged large tracts of vegetation in the Okataina catchment. Following European settlements around the catchment in the early 20th century, mammals which were hitherto not present, were liberated into the forest and rainbow trout (*Oncorhynchus mykiss*) were released into the lake. Large populations of the dama wallaby (*Macropus eugenii*), wild boar (*Sus scrofa*), red deer (*Cervus elaphus*) and the Australian brushtail possum (*Trichosurus vulpecula*) exist in the catchment. These mammals have become the "new normal" in many New Zealand catchments.

To understand the role of volcanic eruptions and invasive mammals in shifting baseline conditions of lakes, two 49 cm cores were retrieved from a central deep location at Lake Okataina. The core was sliced at 1 cm intervals and slices dated using ^{210}Pb, with the tephra from the Kaharoa and Tarawera eruptions used to validate the dates and benchmark events. Dating indicated the length of the core encompassed the period between the Kaharoa eruption of AD 1314 ± 12 and 2009. Various inorganic and organic geochemical proxies in the sediment core slices were analysed to determine: changes in catchment erosion, phosphorus speciation, phytoplankton community assemblage, primary productivity, sources of organic matter loading, redox potential, and internal phosphorus loading to the lake.

A suite of statistical techniques, including structural equation modelling (SEM), general linear modelling (GLM), nonmetric multidimensional scaling (NMDS) and correlation analysis was used to interpret vertical changes in the composition of the core slices and relationships amongst analytes. SEM was used to compare the relative importance of climate and catchment disturbance in changing the primary productivity of Lake Okataina after the Tarawera eruption (1886) and European settlement (1900). Changes in historical primary productivity inferred from total organic carbon in sediment core slices were modelled as a function of geochemical proxies for erosion (Al and Ti) and records of climate variability (Southern Oscillation Index and Temperature Anomaly). The results of this study showed that erosion is the main driver of changes in primary productivity although climate contributes substantially to the variations, and also contributes to changes in erosion itself.

The relationship between phosphorus speciation and algal community dynamics in the lake over the past ~ 700 years was established by applying NMDS and GLM to sequentially extracted phosphorus species and algal pigments from the sediment core. Pigments representing diatoms, cyanobacteria, chlorophytes and chryptophytes were measured vertically through the core at 1 cm intervals, as well as phosphorus associated with apatite and $CaCO_3$, Fe and Mn (oxy) hydroxides, Al (oxy) hydroxides and labile phosphorus. Highly significant correlations were established amongst the algal groups and the phosphorus fractions. The NMDS showed diatoms were strongly correlated with phosphorus fractions associated with permanent burial (apatite and $CaCO_3$ and Al (oxy) hydroxides), while cyanobacteria and chlorophytes were correlated with potentially bioavailable phosphorus (Fe and Mn (oxy) hydroxides and labile phosphorus). Chlorophytes, cyanobacteria and chryptophytes co-dominated when diatom populations were reduced, and *vice versa*. Using GLM, phosphorus fractions could be used to hindcast historical variations in the composition of algal communities (as inferred from pigments), with the exception of alloxanthin (representative of chryptophytes).

Long-term changes in the water quality of Lake Okataina were inferred from sediments deposited from 1836 to 2009, during which time the forested catchment was disturbed by both a pyroclastic volcanic eruption (Tarawera 1886) and invasive mammals (commencing c. 1900). Multiple sediment geochemical proxies were analysed stratigraphically to ascertain trends in organic matter loading (TOC, TN, $\delta^{13}C$ and $\delta\ ^{15}N$ and TOC/TN ratio), primary productivity (Ni, Cu), redox potential (U, V and Mo) and phosphorus retention capacity (Al/Fe and Al/P ratios) of the lake. The chronosequence of the proxies showed that the main source of organic matter loading to the lake is algae although terrestrial loading was increased immediately after the eruption of 1886. Erosion of inorganic materials was relatively high after the eruption but decreased after about twenty years, possibly linked to vegetation regrowth. After 1920 there was a sustained increase in the terrestrial flux of inorganic material. The redox potential of the lake also changed substantially from about 1930, suggesting a reduced degree of bottom water oxygenation. Primary productivity increased considerably after about 1960, while the phosphorus retention capacity of the lake has substantially decreased over the last 50 years.

Using eleven years (2003 to 2013) of contemporary monthly monitoring data, I tested for patterns of temporal coherence in three deep oligotrophic lakes of the Rotorua region, which have similar catchment geology, trophic state and morphometry. Variables measured in the upper 1 m and bottom 2 m of the lakes, or variables calculated from depth profiles, as well as water level, were included in the coherence analysis. The directly measured variables included temperature, dissolved oxygen, nutrients and chlorophyll *a*, and the calculated variables were depths of the thermocline, deep chlorophyll maximum and euphotic zone, as well as Schmidt stability. Temporal coherence was calculated for each of variable using Pearson correlation coefficient values after LOESS decomposition. The average temporal coherence for the lake pairs was high ($r=0.65$) indicating that the variability in most lake water quality properties is not lake-specific, but instead responds strongly to regional climate. Surface variables were more coherent than those at depth. Physical variables were more coherent than chemical variables, and the variables derived from the depth profiles were less coherent than directly measured variables. Our results indicate the strong influence of regional climate on physical variables in particular, which propagates into progressively reducing influence on chemical and biological variables. The effects of climate are progressively filtered from physical to chemical and biological variables. Coherence analysis is a useful tool to tease apart the relative influence of climate change on these variables and provides a contemporary context for lake behaviour in response to climate forcing, rather than using specific lakes which are benchmarked to a pre-anthropogenic era.

The results of this thesis show that while the effect of eruptions is catastrophic, it is also relatively transient compared with the recent impacts of invasive mammals and climate warming, which are more continuous perturbations to the lake and landscape dynamics. Climate variability and invasive mammals tended to act synergistically to increase catchment loads of sediment and nutrients to the lake, effectively creating a shifting reference condition for a lake that would otherwise be considered relatively stable. With current climate change scenarios for New Zealand showing increasing temperatures, and without significant control of exotic mammals, recent trends in phytoplankton assemblages observed in this study, towards domination by cyanobacteria and chlorophytes, may be expected to be reinforced, and bottom-water oxygen levels may decline further. In setting targets for lake restoration goals, management of populations of invasive mammals should be included where there are substantial areas of native forest, because of the potential for these species to reduce vegetative cover, increase loads of sediment and nutrients to lakes, and negatively impact water quality.

Acknowledgements

Thank you Jesus, for your grace and mercy, and for seeing me through this study successfully. It is your doing and it is marvellous in my sight. You brought the right people at the right time to help me through this study.

I am deeply indebted to my chief supervisor Professor David P. Hamilton for his guidance, support and the opportunity to be tutored by him. I am particularly grateful for his painstaking review and very constructive critique of all manuscripts. I am also grateful to my co-supervisors, Dr Adam Hartland, Dr Christopher H. Lusk and Dr Daniel C. Laughlin for providing prompt and useful comments. Your inputs have greatly enhanced my scientific writing style and statistical inquiries.

This study wouldn't have come to fruition without the PhD scholarship offered me by the Bay of Plenty Regional Council through the University of Waikato Chair in Lake Restoration. I particularly want to say thank you to Andy Bruere for his support. I acknowledge the support of the ministry of Business Innovation and Employment (MBIE) (Contract UOX1503) in funding part of the field work and conference attendance. The Global Lake Ecological Observatory Network (GLEON) also supported me with travel grant to GLEON 16 conference in Quebec, Canada, while the international association of limnogeology and the University of Waikato funded my trip to the 6th Limnogeology Conference in Reno, USA. I am grateful to all these organisations. Anthea Kivell, thank you so much for handling all my financial requirements towards this study with apt and tact.

I am grateful for the tremendous technical support I received from Joseph Butterworth, Annie Barker, Annette Rogers, Helen Turner and Steve Cameron. Professor David Lowe, thank you for the advice on dating the cores and sharing your expertise on tephrochronology. Arianto Santoso, you were not only an office mate but a friend I could easily discuss my work with. We discussed and shared *R* codes. It was great knowing you. To my other office colleagues, Wang Me, Kohji Muraoka, Mat Allan, Simon Stewart, Hannah Muller and Katie Noakes, thank you so much for your friendship. Chris McBride and Richard Lamont you offered me advice at one point or another regarding this study. Thank you. I am also grateful to Dr Christopher Dada and Dr Moritz Lehmann for their support in discussing some of the ideas in this study. Chris, you also proof read some of my manuscripts. Dr Piet Verburg (NIWA), your valuable review of the third chapter of this thesis is much appreciated.

To my family, words alone cannot say how grateful I am to you. Rita, you abandoned your successful budding career to follow me to pursue this study. For a long period, you were a stay home mum. I know how challenging that was to you. May God exceedingly bless you. My children, Nichole, Nikao, Nanetta and Zane-Immanuel, you tolerated my absence from home and understood when I said I have to stay long hours in the office because I need to finish quite soon. I couldn't have asked for better children. You are fantastic. To my mum Theodora and dad Alfred, you laid the foundation for this work. Thank you.

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Preface

This thesis consists of six chapters. Chapters 2 to 5 have been written in a format intended for publication in peer-reviewed scientific journals. Except where referenced, the content of this thesis is my own contribution, including field and laboratory analysis, statistical analysis and interpretation. It has been conceived, birthed and nurtured under the supervision Professor David Hamilton, Dr Adam Hartland, Dr Christopher Lusk and Dr Daniel Laughlin. Co-authors of the papers have contributed with discussion and revisions prior to submission. As a result of the format used, some overlap and repetition is necessary as each chapter equates to a stand-alone scientific paper.

Chapter 2 has been prepared as a research brief for submission to *Inland waters* under the title "Erosion and climate variability as drivers of post-European settlement changes in primary production in a deep temperate oligotrophic lake". Authors are Alfred Theodore N.K Kpodonu, David P. Hamilton, Adam Hartland, Daniel C. Laughlin and Christopher H. Lusk.

Chapter 3 has been published in *Biogeochemistry* as Kpodonu A.T.N.K, D.P. Hamilton, A. Hartland, D.C. Laughlin, and Lusk C.H 2016. Coupled use of sediment phosphorus speciation and pigment composition to infer 700-year phytoplankton phenology in a deep oligotrophic lake Biogeochemistry **129 (1)**: 181-196.

Chapter 4 has been prepared for submission to the *Journal of Paleolimnology* as "Recent changes in the water quality of a deep temperate oligotrophic lake linked to invasive mammals". Authors are Alfred Theodore N.K Kpodonu, David P. Hamilton, Adam Hartland, Daniel C. Laughlin, Christopher H. Lusk and Piet Verburg.

Chapter 5 has the title "Climate-driven synchronicity of water quality in three deep, temperate, oligotrophic lakes" by Theodore N.K Kpodonu, David P. Hamilton, Adam Hartland, Daniel C. Laughlin and Christopher H. Lusk. It has been submitted for publication in the journal *Aquatic Sciences*.

In chapter 1, the objectives for the study are laid out while in chapter 6 a brief discussion of each chapter is presented and an overarching perspective of the thesis is given.

1 Introduction

1.1 General background

1.1.1 Variability in lake ecosystems

Successfully developing lake management plans requires an understanding of variation in natural conditions in space and time, and the drivers of this variation (Smol 1992, Landres et al. 1999). In the field of limnology, variations in water quality conditions prevailing prior to human disturbance are known as temporal natural variability (Stoddard et al. 2006, Bennion et al. 2011) and used in informing reference conditions and/or restoration targets. However, the concept of "naturalness" is problematic (Willis and Birks 2006) as anthropogenic markers have been recorded even in remote landscapes and lakes (Catalan et al. 2013). This influence of anthropogenic disturbance extends back several centuries in some parts of the world (Dearing et al. 2008). Also, ecosystems generally, are now viewed as being in a state of non-equilibrium (Michaelian 2005). Therefore, reference state conditions are themselves in a constant state of variability, but the non-anthropogenic drivers of this variability are rarely studied (Erlandsson et al. 2008). Variability is a product of disturbance, hydrology and climate, and is important in maintaining heterogeneity and diversity in ecosystems through space and time (White 1979). Natural disturbances are important in shaping and structuring ecosystems. By releasing resources and creating habitat heterogeneity, disturbances can maintain, or even increase species diversity (Sousa 2001). The impacts of disturbances are, however, strongly scale-dependent. Ultimately, the effects of disturbance will depend the disturbance characteristics and on the size of the systems' stability domain (Scheffer et al. 2001). Importantly, stability domains can be variable and adaptive and change in the face of disturbances, and resilience cannot be considered as a fixed property of an ecosystem (Gunderson 2000, Scheffer et al. 2001).

1.1.2 Sources of temporal variability

The "state" of lakes is a reflection of properties of the catchment. Climate, hydrology, catchment vegetation and soils combine to shape chemical and biological variables of lakes over timescales ranging of 10 to 1,000 years (Fritz and

Anderson 2013). Confounding the natural lake developmental processes are anthropogenic forces (Elser et al. 2007, Blais et al. 2015, Rosen, 2015). However, the difference between natural and anthropogenic drivers of change is not always clear, and the interaction of these drivers in defining current water quality is difficult to determine (Anderson 2014). Anthropogenic modification of lakes can occur through direct inputs into lakes (e.g., sewerage, industrial waste), or indirectly through modification of catchment vegetation and soils, as well as anthropogenic climate change. Eutrophication of New Zealand lakes for instance, has been attributed mostly to human modifications of their catchments (Hamilton 2005). While there is a large body of literature on cultural modifications of lakes through agricultural development (Bachmann et al. 2013), industrial activities (Erlandsson et al. 2007) and urban expansion, little is known about the impact on lakes of non-indigenous mammals. The proliferation of these mammals is known to modify vegetation cover and hydrological and depositional patterns from changes in catchment soils (Bardgett et al. 1998, Blick et al. 2008). This source of disturbance in catchments can be difficult to distinguish from other sources of variability in lake reference conditions. Because invasive mammals have become part of many natural ecosystems in New Zealand, they have the potential to be part of the “new normal” and therefore to be perceived to contribute to natural temporal variability.

Also important in modifying catchments are discrete disturbance events such as volcanic eruptions and earthquakes. These are known to have immediate and direct “pulse” effects, as well as longer-term indirect changes in lake water quality (Anderson 2014). The impacts of volcanic eruptions on lake catchments include vegetation destruction, landslides and alteration of catchment soils (Foster et al. 1998). The result is the alteration of particulate rates and patterns of solute entry into lakes, thereby modifying reference conditions (Bain et al. 2012).

Variability in lake conditions is also caused by changes in climate, either directly or indirectly. Climate can influence lake dynamics on intra- and inter-annual timescales, and impact biogeochemical fluxes, water residence times and hydrological pathways (Bouwman et al. 2013). The shift in algal composition of temperate lakes towards cyanobacteria dominance has been associated with changes in thermal regimes of lakes due to regional warming (Posh et al., 2012). Weathering of underlying rocks, soil development, microbial activity, fire and vegetation development in a lake catchment are controlled by climate and this ultimately controls the flux of solutes and particulates into lakes (Battarbee 2000).

The lack of long-term monitoring time-series for most lakes makes it difficult to separate natural and anthropogenic impacts on water quality (Clerk et al. 2000, Quinlan et al. 2008). A long temporal resolution capturing pre-disturbance conditions would be ideal to separate natural and anthropogenic impacts but direct measurements are rare as anthropogenic disturbance has usually pre-dated quantitative measurements of water quality. Long-term trends can, however, be inferred using paleolimnological techniques based on sediment cores (Smol 1992, Bennion et al. 2011), providing an opportunity to disentangle natural and anthropogenic sources of variability in water quality. There are a number of proxies that are used in paleolimnology to identify physical, chemical and biological changes in variables of lakes (Meyers 1997, Cohen 2012). These proxies can be used to identify the source of variability in lakes as well as catchment development history (Cohen 2000). These proxies include isotopic, elemental, molecular and biological constituents of lakes. The use of lacustrine fossils has been the main paleolimnological tool of choice for many years and has provided comprehensive insights into changes that have occurred in lakes and their catchment through time (Smol, 1992). Their use in paleolimnology is based on inferences derived from correlations between modern and historical analogues of fossils, coupled with understanding of their taphonomy. Their use recently in paleolimnology has declined due to the difficulty in finding corresponding modern and historical analogues in the same lake sediment, correctly identifying the organisms, understanding ecological causality and scale, taphonomy and time-averaging, historical contingency and evolutionary processes (Cohen 2000, Juggins 2013).

Lake sediment geochemistry is determined by the interactions between external inputs from catchment geology, hydrology, soils, vegetation, airshed and internal processes (Cohen 2000, Rosen 2015). However, these sources of input are influenced by climate and anthropogenic forces making their interpretation complex. The use of multi-proxy geochemical indices enhances the accuracy of the interpretation. Bioturbation and diagenesis also affect the geochemical archives of lakes. While the effect of diagenesis can be minimised by the choice of appropriate proxies, the effect of bioturbation is more complex to remove with mathematical modelling suggested as a possible tool to do so (Matisoff, 1982, Robbins, 1986).

The impact of climate on temporal variability can also be inferred using paleolimnology. However, climate signals in sediments are often confounded when there is anthropogenic nutrient enrichment in lakes (George 2007). Separating climate effects and nutrient enrichment in sediment cores is challenging. Temporal coherence provides an alternate means of assessing the role of climate variability on lake dynamics. Within a defined area climate exerts a largely uniform, dominant control on limnological variables of lakes (Palmer et al. 2014). The degree to which lakes in a defined region have similar temporal responses to climate forcing factors has been described as temporal coherence or lake synchrony (Magnuson et al. 1990). Coherence is expected to be greatest when the climate signal has marked inter-annual variation but limited spatial variation (Magnuson et al. 1990, Kratz et al. 1998). It can be measured either as the mean coefficient of determination calculated between all possible lake pairs used in the analysis, as the mean coefficient of determination calculated between each lake and the mean time-series of all other lakes (Livingstone and Dokulil, 2001), or as an intraclass correlation coefficient (Rusak et al., 1999).

1.1.3 Temporal variability in Lake Okataina: A research priority

Lake Okataina (38°07′S; 176°25′E) was chosen as the site for this PhD study and forms the focus of chapters 2-5. It was originally an arm of Lake Tarawera, but was impounded about 7,000 years ago as a result of a volcanic eruption. It is a large (10.8 km^2), deep lake (Z_{mean} = 39 m) with 62% deeper than 40 m, and is situated 311 m above mean sea level. Amongst the New Zealand North Island lakes, Lake Okataina is close to a “reference state” due to low-level anthropogenic activities in the lake and its catchment in the past century. It is also of cultural significance to Te Arawa the tribe of the Māori settlers around the lake, who are the legal owners of the lake bed.

Lake Okataina is oligotrophic and the trophic Lake Index (TLI) (Burns et al. 1999) in the last two decades has fluctuated between 2.5 and 3.0. The TLI is a nationwide lake monitoring, classification and decision making tool adopted by regional councils in New Zealand to detect changes in trophic state of lakes. The calculation of the TLI is based on Secchi depth and the concentrations of total phosphorus, total nitrogen, and chlorophyll *a* at a selected central location in a lakes. Over the last decade the total phosphorus concentration in Lake Okataina has increased slightly, while the total nitrogen concentration has decreased (Scholes and Bloxham 2007). These changes have occurred despite no obvious change in the land use in the last century. The only major perturbation in the lake catchment during this period has been the establishment of large populations of the dama wallaby (*Macropus eugenii*), wild boar (*Sus scrofa*), red deer (*Cervus elaphus*) and the Australian brushtail possum (*Trichosurus vulpecula*). Rainbow trout (*Oncorhynchus mykiss*) were also released into the lake around 1904. Prior to human settlements in New Zealand, flora, fauna and soils evolved without competition from terrestrial mammals, and plants are generally not adapted to mammalian herbivory (Harada and Glasby 2000). The rainbow trout and the brushtail possum were liberated into the lake and the catchment, respectively, by the European settlers around 1904, while wallaby populations were established by 1942 (Veblen and Stewart 1982). The red deer was released into the forest in and around the catchment in 1916 with large populations recorded by 1942. The lake management plan for the lake (as part of the Water and Land Plan for the Bay of Plenty Regional Council) prescribes a TLI value of 2.6. The choice of TLI 2.6 is based on the 1994 value; the lowest (i.e., high water quality) since monitoring began on the lake. However, to achieve this, there is a need to understand the source of recent change.

The New Zealand National Policy Statement for Freshwater Management (NPS-FM 2014) prescribes strategies for managing freshwater in New Zealand to acceptable levels. The policy sets out objectives that guide regional councils to manage water in an integrated and sustainable way, while providing for economic growth within set water quantity and quality limits. The policy requires that sources of contaminants are identified although the emphasis is on anthropogenic sources of eutrophication. There are compulsory national bottom lines for two values; ecosystem health and human health for recreation, and minimum acceptable states based on other national values. However, the NPS-FM 2014 does not consider potential sources of temporal and spatial variability in setting the bottom lines. The prescription of “minimum acceptable states” is also subjective and without regard to any benchmark that might relate to variability amongst lakes. The need to understand the sources of temporal variability in New Zealand lakes and integrate them into management decisions arises because of the occurrence of disturbances such as volcanic eruptions and earthquakes, and the "new normal" resulting from the impact of invasive mammals. The predominance of indigenous natural vegetation in Lake Okataina's catchment, effectively making it close to a reference condition lake, provided an ideal opportunity through this study to examine natural temporal variability and attempt to decipher the more recent direct and indirect changes.

1.2 Main objectives

The overall aim of this PhD was to identify the causes of long-term trends in the water quality of Lake Okataina (Central North Island, New Zealand), by combining analyses from paleolimnological sampling of sediment cores and contemporary water column monitoring data. The study included a detailed geochemical analysis of a sediment core retrieved from the lakebed, the length of which covered a period of 700 years. Various statistical techniques were used to interpret the geochemical proxies in discrete vertical layers of the core in order to infer changes in catchment erosion, phytoplankton phenology, primary productivity, redox potential and phosphorus speciation and retention capacity. Additionally, a coherence analysis was performed on an eleven-year monthly monitoring data set for the water column of three lakes in close proximity and similar morphological and trophic status, one of which was Lake Okataina, to understand the influence of climate variability. Based on the aim of this study, four main hypotheses were formulated:

1. That persistent catchment disturbance rather than short-lived climate variability is the main driver of increases in primary productivity.
2. That the phenology of major phytoplankton groups varies with the availability phosphorus species.
3. That the synergistic effect of the Tarawera volcanic eruption and increasing mammal numbers in the Lake Okataina catchment would result in sustained increases in inorganic and organic material loading to the lake.
4. That physical, chemical and biological components of proximal lakes are altered in a coherent manner by climate.

1.1 Thesis overview

This thesis comprises four main research chapters (Chapters 2-5) which have been prepared for, or already submitted to, peer-reviewed journals. As a result of the format used, some overlap and repetition are necessary as each chapter equates to a stand-alone scientific paper.

Chapter 2 compares the relative importance of catchment disturbance and climate variability in defining primary productivity in Lake Okataina. Structural Equation Modelling (SEM), a hitherto unused statistical technique in paleolimnology was employed as a common platform to compare catchment disturbance and climate variability.

Chapter 3 focuses on natural variability in phosphorus species as a consequence of volcanic eruptions and invasive mammals, as well as climate, in shaping the phytoplankton phenology of Lake Okataina over a c.700 y period. Multivariate regression and non-dimensional scaling were used to establish the relationship between phosphorus species and algal pigments extracted from the sediment core.

In Chapter 4, the chronosequence in a sediment core retrieved for Lake Okataina was examined for variability in the source of organic matter to the lake, changes in phosphorus retention in the lake, and changes in redox potential and primary productivity as a result of the Tarawera eruption of 1886 in the antecedent period which included the introduction of exotic mammals to the catchment and trout in the lake around 1900 AD.

In Chapter 5, coherence analysis was used to examine the impact of climate on physical, chemical and biological variables in Lake Okataina in a contemporary study. To achieve this, synchrony was evaluated in the monitored variables of the three lakes of similar size and depth, trophic status and land-use.

In the final chapter (Chapter 6), the research is summarised and an overarching perspective discussed based on the results of Chapters 2-5.

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2 Erosion and climate variability as drivers of post-European settlement changes in primary production in a deep temperate oligotrophic lake

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Abstract

Lakes may change over time in response to climate and catchment disturbance. Effective management of lakes requires an improved understanding of how these stressors combine to influence lake water quality. In this study, sediment core proxies for erosion (Al and Ti) were combined with recorded indices of climate variability (Southern Oscillation Index and Temperature Anomaly) to determine the relative importance of climate variability and catchment erosion on primary productivity (total organic carbon from sediment core) of a deep temperate oligotrophic lake using Structural Equation Modelling (SEM). SEM is a multivariate statistical technique that combines factor and path analysis .The core was dated to include a period of approximately 123 years (1886-2009) which included a volcanic eruption in 1886 and the introduction of invasive mammals commencing around 1900s. The SEM model explained 68% of the variation in the total organic carbon concentration in the lake sediment core. The standardised path coefficient showed that erosion (standardised path coefficient = 0.80) was more important in influencing the primary productivity of the lake than climate variability (0.60). Climate variability, however, also contributed to the variation in erosion (0.64), thereby making an additional, indirect contribution to the variation in primary productivity (TOC) of the lake.

2.1 Introduction

Lake ecosystems globally are under threat from catchment modification and climate variability and change (Fritz and Anderson 2013). Catchment disturbance, whether from natural or anthropogenic causes, results in increased delivery of sediment and nutrients to lakes, and is likely to increase primary productivity, although in some cases the increased sediment loading might lead to high rates of sedimentation and disappearance of lakes (Rosen, 2015). For instance, in rural areas of the English Lake District, increased livestock movement was associated with increased sediment and nutrient delivery to the lakes, contributing to eutrophication of some lakes (Van der Post et al. 1997). Extreme climate events have also been reported to account for increases in the primary productivity in lakes by modifying the nutrient load delivered from catchments (Dokulil et al., 2006). Extremely high rainfall has been shown to increase nutrient loading to Canadian lakes, which has led to increased primary productivity (Hall and Smol 1996). Apart from the catchment mediated impact of climate variability on lake primary production, climate is also known to directly impact cycling of nutrients in lakes, thereby altering their trophic state (Fritz and Anderson 2013). In Lake Tanganyika, for example, regional warming patterns commencing in the twentieth century have given rise to increased surface-water temperature and greater stability of the water column (O’Reilly et al. 2013). Combined with a regional decrease in wind velocity, this has reduced water column mixing and decreased deep-water nutrient upwelling and entrainment into surface waters, which in turn has led to a decline in primary productivity (O'Reilly et al. 2003). The response of lakes to catchment disturbance and climate variability depends on the nature of the disturbance, its intensity and duration, coupled with the vulnerability of the system (Cohen 2003). Hence identifying pathways through which disturbance is translated to changes in lake ecosystem dynamics is important in the development of management regimes for lakes.

The effect of catchment modification and climate on the mass accumulation rates of nutrients and trophic status in lakes strongly overlap, making it difficult to separate their impact on lake ecosystems (Cohen 2003). For example, increasing water temperature produced conditions identical to those created by cultural eutrophication, such as increased primary productivity, increased hypolimnetic oxygen stress and accelerated nutrient re-cycling (Moss et al. 2011), while climate mediated changes in catchment run-off and soil biogeochemistry can enhance nutrient loading (Blenckner et al. 2007). The absence of long-term monitoring data for most lakes also adds to the complexity of isolating climate signatures from those due to land-use change. However, by combining paleolimnological and climate data, or neolimnological data, it is possible to identify the dominant pathways determining the primary productivity of lakes (Battarbee et al. 2005).

A number of inorganic and organic geochemical archives of sediments are associated with catchment disturbance and erosion, and can therefore be used to reconstruct primary productivity and catchment erosion. Anderson et al. (2012) used aluminium (Al) and titanium (Ti) fluxes in sediment cores retrieved from lakes in the Kangerlussuaq area of southwest Greenland, as proxies for paleo-erosion. The utility of these metals as erosion proxies for catchment disturbance is because they are insoluble in water at circum-neutral pH. Therefore catchment derived Al and Ti remain buried in lake sediments and changes in their concentration or fluxes largely reflect changes in catchment erosion (Magyari et al. 2009). Al and Ti also remain immobile during diagenesis (Piper and Perkins 2004). Total organic carbon (TOC) on the other hand, has been used in many paleolimnological studies as a proxy for primary productivity (Beuning et al. 2011, Platt 2012). The utility of TOC in paleolimnology as a productivity proxy depends on the dominant source of organic matter and conditions for the preservation of organic carbon in lake sediments (Meyers and Ishiwatari 1993). The ratio of TOC to total nitrogen (TN) is used as an indicator of the provenance of organic material, with molar values < 10 generally described as being autochthonous (Meyers 1997).

The Southern Oscillation Index (SOI) and Temperature Anomaly (Temp) are used as measures of climate variability in studies examining variability on lakes (MacIntyre 2012). Around 30-40% of year-to-year variability in climate especially rainfall, is attributable to the El Niño-Southern Oscillation (ENSO) (Salinger et al. 2001). Where the period of lake sediment archives overlaps with contemporary SOI and Temp data, it may be possible to disentangle the effects of climate and catchment modification on lakes (Battarbee et al. 2005).

Most studies on the impact of catchment disturbance and climate variability on lakes have established bivariate relationships between catchment and climate variables, but these models generally do not integrate multiple pathways of climate and catchment disturbance (Downes et al. 2002) and do not address underlying mechanisms that generate the observed responses (Burcher et al. 2007). To elucidate the causal pathways between erosion and climatic impact on primary productivity and account for the interdependence between the proxies, Structural Equation Modelling (SEM) is used in this study. SEM is a multivariate statistical technique that combines factor and path analysis (Pugesek et al. 2003). Unlike multivariate regression, SEM can be explicitly used to test indirect relationships between two variables, where the effect between the two can be mediated by an intermediary variable (Tabri and Elliott 2012, Bollen 2014). SEM incorporates *a priori* scientific knowledge into model formulation, allowing for the testing of specific hypotheses. It can therefore test for conceptual variables that are not directly measured and also allows for the testing of the overall model along with significant tests for individual parameters of the model (McCune et al. 2002). Covariance structure created by the *a priori* model, is tested against a covariance matrix of the observed data. Unlike conventional statistical models where the rejection of the null hypothesis is sought, the objective of SEM is the acceptance of the null hypothesis, which implies that the proposed model is supported by the observed data. In this study, we used sediment inorganic and organic geochemical proxies and meteorological data to test the hypothesis that erosion would be more important in altering the primary productivity of a deep temperate oligotrophic lake than climate variability.

2.2 Methods

2.2.1 Sampling site

Lake Okataina (38°07′S; 176°25′E) (Fig. 2.1), which was originally an arm of Lake Tarawera, was impounded about 7,000 years before present as a result of a volcanic eruption. Together with 11 other lakes it constitutes a family of lakes in the Okataina Volcanic Caldera (OVC) in the central North Island of New Zealand. The lake has a surface area of 10.8 km^2, a maximum depth of 80 m, a mean depth of 39 m, and surface water level is c. 311 m above mean sea level. The lake is fed by two streams with irregular flow, with stormflows and groundwater likely making up the remainder of catchment hydrological inputs (McColl 1972). The lake has no known surface outlet but drains underground to Lake Tarawera (McColl 1972).

More than 80% of the catchment area of Lake Okataina's (62.9 km^2) is steep, and prone to landslides and bank erosion (McColl 1972). Surface soils are loose allophanic and pumice mineralogy of recent volcanic origin (Cooper and Thomsen 1988), rich in Al and Si (Parfitt 1990). There has been little forest clearance in the catchment since 1886, and only localized timber extraction. Native forest covers about 81% of the catchment area, 8% is exotic pine (*Pinus radiata*) plantations, 10% is dry-stock farming and the remainder (1%) is made up of roads, car parks and buildings (Scholes and Bloxham 2007).

Based on the Trophic Level Index (TLI) classification (Burns et al. 1999), Lake Okataina is oligotrophic (TLI 2.5). Chlorophyll *a* concentrations range from 4 to 8 $\mu g\ L^{-1}$ over an annual cycle, with the highest concentrations occurring in August, in the last month of the austral winter (Fish 1970). The lake undergoes uninterrupted thermal stratification for nine months, with vertical mixing between June and August. Prior to 1980, the hypolimnion of the lake had been reported to be well oxygenated, even during thermally stratified periods (Jolly 1968, Fish 1970, McColl 1972), but in the last decade a large proportion of the hypolimnion has become anoxic during the stratified period (Pearson et al. 2010).

There have been anthropogenic, biotic and abiotic perturbations to the catchment during the last millennium. Polynesian settlements were thought to have been established in and around the catchment of the lake in the early 14th century following the Kaharoa eruption of AD 1314 ± 12 (Hogg et al. 2003). Fire was used as a tool for forest clearance and some timber was logged in the late 19th century for Māori canoes (Stafford 1967). Mt Tarawera erupted 10 June 1886 and damaged large tracts of vegetation in the catchment (Clarkson and Clarkson 1983). Following European settlements around the catchment in the late 19th and early 20th century, mammals were liberated into the forest and rainbow trout (*Oncorhynchus mykiss*) released into the lake. Populations of the dama wallaby (*Macropus eugenii*), wild boar (*Sus scrofa*), red deer (*Cervus elaphus*) and the Australian brushtail possum (*Trichosurus vulpecula*) are currently widespread in the catchment.

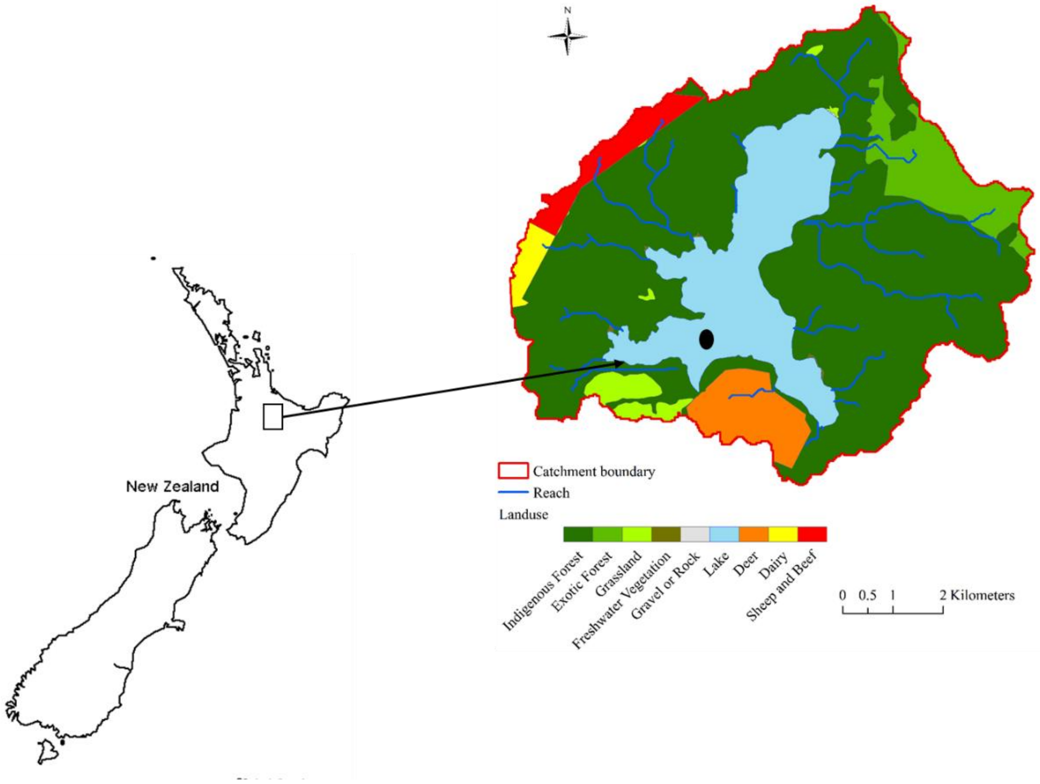

Figure 2.1 Land use map of Lake Okataina with black dot depicting where the sediment core was retrieved from.

2.2.2 Core retrieval

A 23 cm sediment core was retrieved from the deepest basin of Lake Okataina in February 2014 using a Swedish gravity corer (Pylonex HTH 70 mm) with a 60 x 600 mm Plexiglas core barrel. A distinctly grey coloured tephra was identified near the base of the core, corresponding to the Tarawera (1886) eruption. The section of the core above the Tarawera tephra was sliced horizontally at a vertical resolution of 1 cm and transferred into separate 50 ml labelled polypropylene centrifuge tubes. The sediment samples were put in cold storage (4 °C) prior to analysis.

Approximately 1 g of dried sediment sample from each 1 cm layer was submitted to the Radiocarbon Unit (University of Waikato, New Zealand), for determination of ^{210}Pb and ^{137}Cs activity. The ^{210}Pb gamma-ray activity was counted at 46.52 keV emission for 43,200 to 259,200 s using a Canberra germanium well detector (1 x 4 cm), (Meriden, USA) with 22.5% efficiency for ^{60}Co. The 1886 tephra served as a control date for the ^{210}Pb activity. The constant rate of supply (CRS) model (Appleby 2002) was applied to the profiles using a modified method in which the activity of the lowermost sample was calculated on the basis of a regression of unsupported ^{210}Pb (Bq kg^{-1}) versus accumulated dry density (kg m^{-2}).

2.2.3 Laboratory analytical techniques and data sourcing

Dry weight of the sediment overlying the Tarawera tephra was determined by oven drying the sliced samples at 105 °C until no weight change was recorded. Bulk dried sediment densities were also determined. Sediment samples were digested using reverse *aqua regia*. Approximately 0.1 g of dried sediment was weighed out and placed in a pre-weighed 50 ml centrifuge tube. The samples were placed in a digestion block and reverse *aqua regia* solution (0.6 ml of HNO_3 and 0.2 ml of HCl) was added to each tube. The centrifuge tubes were left to stand overnight, to enable the removal of organic matter. The following day samples were heated in the digestion block at 50 °C for 1 h, after which time the samples were removed from the block and allowed to cool. Thirty ml of Type 1 water (ultra-purified) was added (the amount of water depends on the amount of nitric acid added), capped, mixed and left to settle. Once the samples had settled they were placed in a centrifuge for 15 minutes at 4000 rpm to separate the residue from the liquid sample. A 10 ml sample of the centrifuged mixture was pipetted into a 15 ml tube for analysis. A suite of trace elements was analysed using Perkin-Elmer (Massachusetts, USA) SCIEX ELAN DRC II inductively coupled plasma mass spectrometer (ICP-MS). For this study we used concentration of Ti and Al. A blank reagent and quality assurance solution were run with each of the sample batches. For total organic carbon (TOC) and total nitrogen (TN) analyses, approximately 0.1 g of the dried pulverised sediment samples was placed in tin foil using a LECO TruSpec (Michigan, USA) CN Carbon/Nitrogen analyser.

2.2.4 Structural equation modelling

Prior to the structural equation modelling, bivariate relationships between Al, Ti, TOC and SOI were examined. The plots enabled checks to be made for the presence of outliers and evidence of linearity. An autoregressive temporal autocorrelation model was also fitted to the variables and residuals were examined to assess autocorrelation of the time component. A conceptual diagram of the structural equation model is shown in Figure 2.2. The SOI and Temperature Anomaly data were downloaded from https://data.mfe.govt.nz and in this study were aligned with the ^{210}Pb dating of slices and the tephra from 1886 Tarawera eruption for the purpose of SEM. Variables associated with erosion (Al, Ti) and climate (SOI, Temp) were included in the model. The model represented what was considered to be the most plausible structural relationships based on *a priori* knowledge and literature. Structural equation models can be quite complex and incorporate both latent factors and observed variables with either directed or undirected paths as illustrated in the *a priori* model of Fig 2.2.A chi-square maximum likelihood test was used to evaluate the performance of the model. The model-implied covariance structure was compared with the covariance structure of the observed data. Good-fitting models yield low chi-square statistics because the difference between the observed and the model-implied covariance is not significant ($P > 0.05$) (Grace 2006). The overall model fit was also assessed using the comparative fit index (CFI) and the standardised root mean square residual (SRMR). The comparative fit index (CFI) analyses a model fit by examining the discrepancy between the data and the hypothesized model, while adjusting for the issues of sample size inherent in the chi-squared test of model fit, and the normed fit index (Grace 2006). A CFI value of .90 or larger is generally considered to indicate acceptable model fit. The SRMR is an absolute measure of fit and is defined as the standardized difference between the observed correlation and the predicted correlation (Grace 2006). A value less than .01 is generally considered a good fit. Good-fitting SEMs do not prove causal relationships, but inferences based on sound scientific knowledge aids in the interpretation of the signs and strength of the directional paths (Grace 2006). SEM analyses were carried out using the *LAVAAN* package (Rosseel 2012) in the R program (Version 3.1.3) (R Development Core Team 2015).

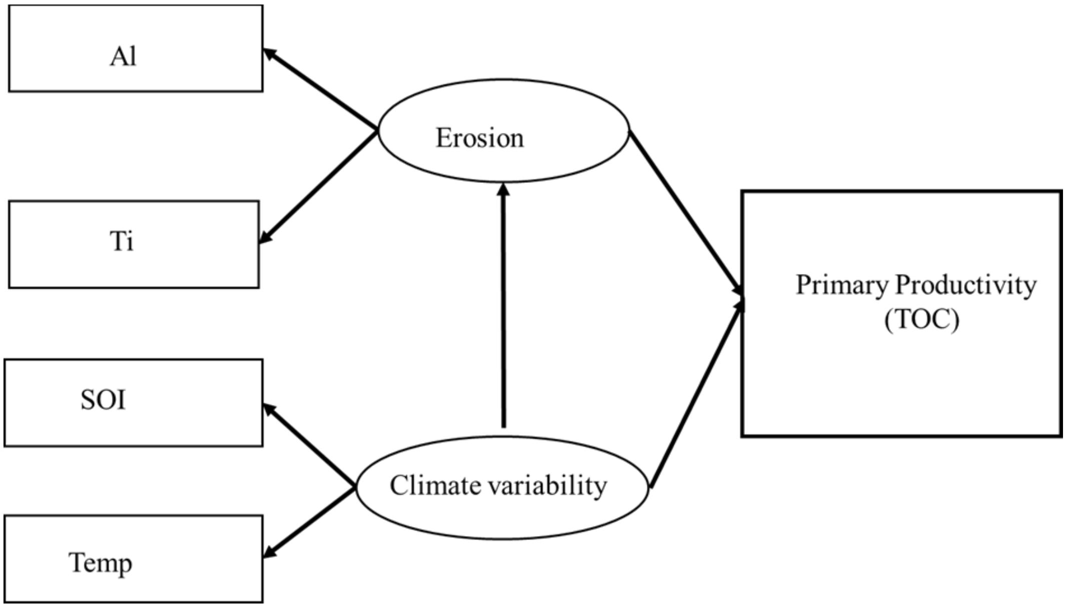

Figure 2.2. The specified *a priori* model for primary productivity (TOC) showing causal path directions in solid arrows. Climate variability and erosion represent latent variables and Al, Ti, SOI and Temp are observed variables. Primary productivity is the primary variable. The latent variables are linked by a regression model and assumed to have an impact on primary productivity.

2.3 Results

2.3.1 Bivariate correlations

Pearson-Moment correlations show Al, Ti, SOI, temperature anomaly (Temp) and TOC are positively correlated with Al, Ti and TOC ($P < 0.01$). SOI and Temp are also strongly positively correlated ($P < 0.01$). Ti is correlated strongly with SOI and Temp (Figure 2.3). There was no indication of outliers in any of the variables.

2.3.2 Structural Equation model

There were no discrepancies between the data and the *a priori* model as indicated by $P > 0.05$, CFI > 0.90 and SRMR < 0.1 ($P = 0.76$, $\chi^2=0.71$, $df=6$, CFI = 0.97, SRMR = 0.09), suggesting the model was efficient in explaining the data (Fig. 2.3). The model explained 68% of the variation in primary productivity (TOC). Erosion had the strongest effect on primary productivity with a standardised path coefficient of 0.80 (Fig. 2.4) and the climate variability pathway was significant (0.60) in defining both TOC and erosion (0.64).

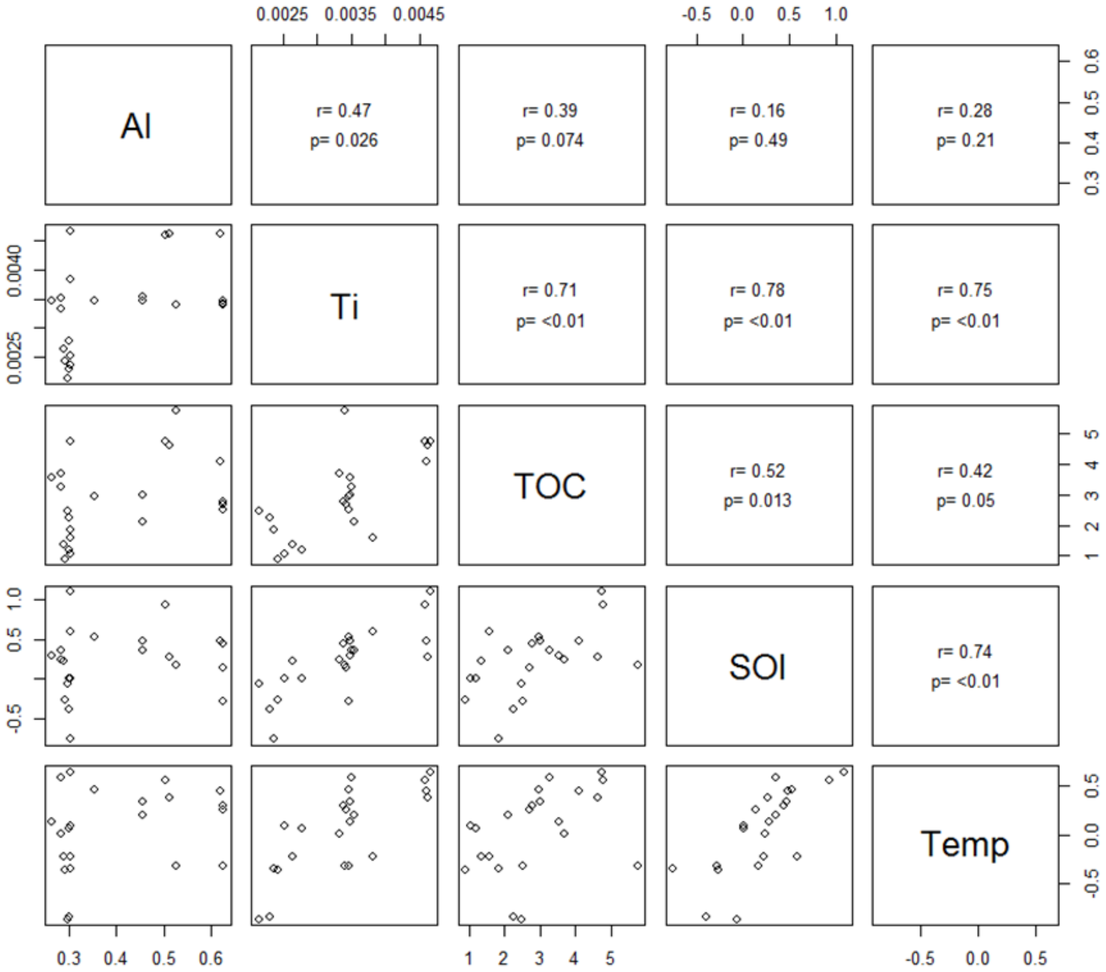

Figure 2.3. Correlation matrix of Al, Ti, Southern Oscillation Index (SOI), temperature anomaly (Temp) and total organic carbon (TOC) for Lake Okataina, with corresponding Pearson coefficients of correlation and levels of significance

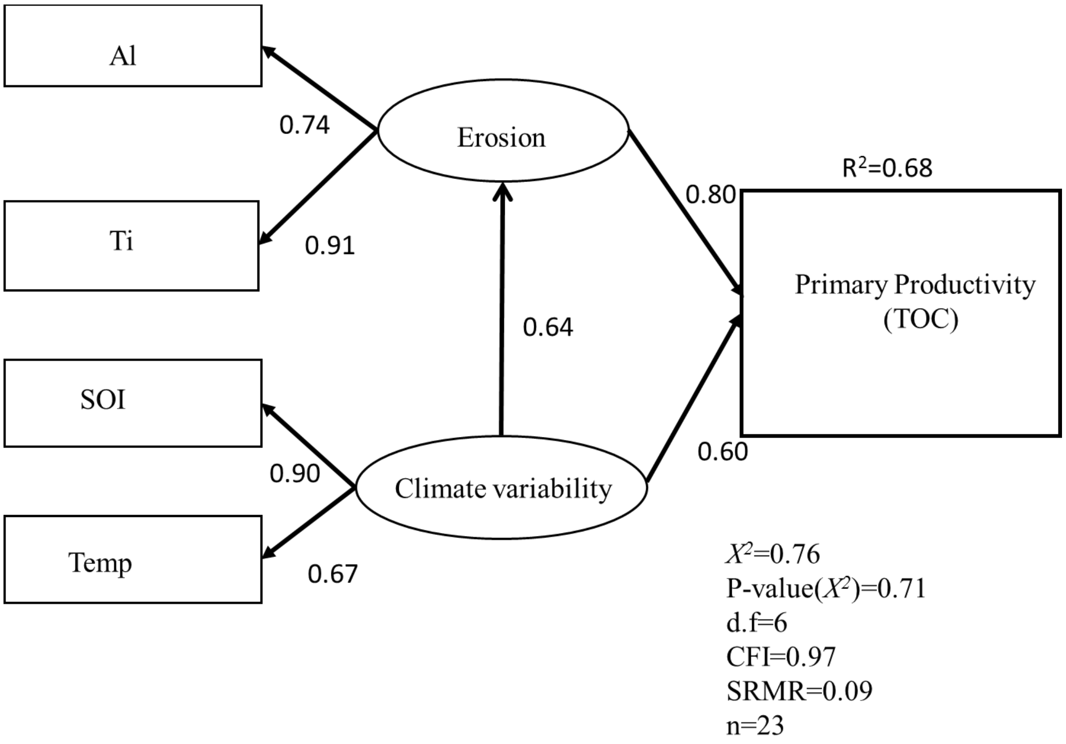

Figure 2.4 Structural equation model results for the effect of erosion and climate variability on the primary productivity of Lake Okataina. Values next to arrows represent the standardised path coefficients (range from -1 to +1). Other statistical indices for the SEM are at bottom right (see text for acronyms).

2.4 Discussion

The implications of erosion and climate variability combining to affect the primary productivity of Lake Okataina, are far reaching because eroding materials have long been known to be sources of phosphorus to lakes (Kerr et al. 2011) and can therefore alter primary productivity, while climate variability accounts for both seasonal and long-term dynamics in primary productivity. Phosphorus is a key limiting nutrient for primary productivity in lakes (Schindler, 2012) and catchment erosion has been identified as a major source of non-point source of phosphorus inputs to lakes (Schindler, 2012). The eutrophication of Lake Pepin on the Upper Mississippi river (USA) since 1850, has been linked to inorganic phosphorus associated with catchment erosion (Grundtner et al., 2014), while over 90% of the total phosphorus (TP) load to Lake Champlain has recently been identified to be from bank erosion (Smeltzer et al., 2009).

Eroding materials not only contribute external nutrients but also lead to increased rates of sedimentation, and may increase sediment oxygen demand, leading to anoxia of hypolimnetic waters (Loh et al. 2013). Anoxia occurs concomitantly with reductions in redox potential in the hypolimnion, which is associated with internal phosphorus loading, and therefore it has far-reachng impacts on primary productivity (Nurnberg 2009). Internal loading of phosphorus as a consequence of increased sedimentation has, for example, been reported to be responsible for the eutrophication of Lake Sæbyvannet in Norway (Łukawska-Matuszewska et al., 2013).

The relationship between vegetation cover, physical weathering and erosion is well established and therefore factors that disturb catchment vegetation and soils increase erosion rates. The current study showed that catchment disturbance would invariably lead to increases in primary productivity. Lake Okataina is located in landscapes with steep slopes characterised by landslides. Landslides are a major source of allochthonous sediment for lakes in the Central North Island of New Zealand (Page et al. 1994) although the contribution of these landslides to lake water quality has not been quantified. Landslides and bank erosion have been noted elsewhere to be a major source of inorganic phosphorus (e.g., Lake Chaplain, USA; Ishee et al., 2015).

Volcanic eruptions also constitute a source of erosion in the Central North Island of New Zealand (Crozier 1997). Catchment soils and vegetation of the lakes in this region have been modified by numerous volcanic eruptions, with the most recent major eruption in 1886. Eruptions partially account for high rates of erosion from New Zealand catchments (McGlone, 1989) and erosion accompanying eruptions is known to have resulted in algal blooms in some lakes (Anderson 2014). For example, eroding materials as a consequence of volcanic eruptions resulted in "pulses" of primary productivity in a Tanzanian crater lake (Barker et al 2000).

The significance of the direct climate variability pathway on the primary productivity of Lake Okataina is not unexpected. Climate is a major driver of the thermodynamics of lakes. Mixing regimes in lakes, which contribute to variations in the vertical distribution of nutrients and primary productivity, depend predominantly on wind and air temperature, and interactions with lake morphology.

In New Zealand, downscaled general circulation models indicate an estimated 3.5 °C increase in atmospheric temperature and greater dominance of strong westerly and south-westerly winds, with less precipitation in the Central North Island of New Zealand by 2100 (Salinger et al. 2001). Lake Okataina is a monomictic lake and a warmer climate could be expected to produce longer stratification periods, while stronger winds would act to counter this effect. Climate is known to modify hydrological pathways and thus affect the amount and patterns of material deposited in lakes (Anderson 2013). Based on the paleolimnological record of Lake Tutira in the Hawkes Bay, North Island, New Zealand, it is possible infer that climate variability (i.e., infrequent enormous storms) has been responsible for a disproportionate amount of deposition of bottom sediment (Page et al. 1994, Orpin et al. 2010).

This is the first time SEM has been used as a tool to demonstrate the inter-relationships between catchment erosion, climate variability and primary productivity of lakes in a paleolimnology study. The model supported theory to show that eroding materials can stimulate primary productivity in lakes as they are conduits for the transmission of catchment nutrients. Climate can both directly and indirectly control primary productivity of lakes through the modification of thermal regimes in lakes and hydrological pathways of catchments. Our approach provides a single platform for comparing the direct and indirect impact of catchment disturbance and climate on lake water quality.

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3 Coupled use of sediment phosphorus speciation and pigment composition to infer phytoplankton phenology over 700 years in a deep oligotrophic lake

Abstract

Restoration and management of lake ecosystems require an understanding of natural variability in primary productivity and the factors that drive change. To understand long-term changes in, and relationships amongst phosphorus species and phytoplankton groups, a sediment core was retrieved from Lake Okataina in the central North Island of New Zealand. The core was dated to include a period of approximately 700 years, from pre-human settlement to its current state, close to natural reference conditions. Pigments representing different planktonic groups were measured vertically through the core at 1cm intervals, as well as phosphorus fractions associated with apatite and $CaCO_3$, Fe and Mn (oxy) hydroxides, Al (oxy) hydroxides and labile phosphorus. Highly significant correlations were established amongst the algal groups and the phosphorus species. Diatoms were strongly correlated with phosphorus fractions associated with permanent burial, while cyanobacteria and green algae were correlated with potentially bioavailable phosphorus. Green algae, cyanobacteria and chryptophytes co-dominated when diatom populations were reduced, and *vice versa*. Using multivariate linear regression, phosphorus fractions could be used to hindcast historical variations in the composition of algal communities (as inferred from pigments), with the exception of alloxanthin (representative of chryptophytes). Our approach provides a technique for rapid assessment of long-term changes in the major phytoplankton groups in lakes and may be used to infer natural variability in the reference state as well as partitioning the extent of alteration of phytoplankton community composition between human and natural disturbances.

3.1 Introduction

Phosphorus (P) has long been known as an important nutrient and is integral to ecosystem structure and productivity (Elser et al. 2007). It is the nutrient that most commonly limits phytoplankton growth in lake ecosystems and also influences the composition of phytoplankton communities (Carpenter et al. 1998, Schindler 2012). The relationship between total phosphorus (TP) and phytoplankton biomass measured as chlorophyll *a* has been found to be either positively linear (Jones and Bachmann 1976) or curvilinear (Hoyer and Jones 1983) across a wide range of total phosphorus (TP) concentrations. This relationship is also a foundation in paleolimnology for the use of diatom-inferred P as a measure of historic productivity (Hall and Smol 1996, Augustinus et al. 2012). While there is a wealth of information on the relationship between phosphorus and aquatic primary productivity, much less is known about the relationship between terrestrial and aquatic P pools and how they influence phytoplankton dynamics in lakes. This distinction is important because managing lakes demands an understanding of within-lake and whole-catchment nutrient dynamics. Furthermore, while many studies have focused on how P from anthropogenic sources affects lake ecosystems (Bouwman et al. 2013), the links between natural changes in catchment P pools and variations in lake ecosystem productivity have received much less attention.

Phosphorus enters lake ecosystems in either particulate or dissolved forms, with most dissolved P directly bioavailable to algae (Carey and Rydin 2011). While the bioavailability of particulate P in lakes has received some attention, its implications for primary productivity are still unclear (Boström et al. 1988, Abell and Hamilton 2013). In the water column, dissolved P becomes incorporated into particulate material (e.g., by adsorption, biological assimilation) and together with particulate P from in-lake and catchment sources, settles out of the water column. This particulate P is in inorganic and organic forms (Psenner and Pucsko 1988, Søndergaard et al. 1996). The inorganic P is sorbed by various chemical species, yielding different properties and behavior (Hupfer et al. 1995, Fytianos and Kotzakioti 2005). Understanding sedimentary P speciation is critical to explaining the contribution of different P species to lake primary productivity because a fraction of the P can re-enter the water column. Processes that return P to the water column include bioturbation (Adámek and Maršálek 2013, Bajer and Sorensen

2015), resuspension (Horppila and Nurminen 2003, Burger et al. 2007) and diagenesis (Nurnberg 2009, Loh et al. 2013). However, changes in sedimentary P speciation have not previously been related to long-term dynamics of phytoplankton communities.

Several lake sediment studies have focused on the role of internal loading of P to the water column (Wilson et al. 2010, Homyak 2012) and the loss of P through sedimentation and burial (Kopacek et al. 2005, Norton et al. 2008). They have provided valuable information on P dynamics in the short to medium term under varying water column and sediment pore water conditions (Kerr et al. 2011). However, sediment composition and chemical fluxes vary over multiple time scales in response to changes in temperature, redox potential, and sedimentation rates (Burdige 2006). Sediments are also derived from terrestrial soils (Kerr et al. 2011) and therefore the proportions of the various species of P in lake sediments will depend on the balance of P from both autochthonous and allochthonous sources (Kerr et al. 2011). Because different species of phytoplankton vary in their demand for P, the speciation of P could in turn impact the structure of algal communities in lakes. Photosynthetic pigments in lake sediments can be used to provide essential diagnostic information on changes in the community structure of primary producers (Lizotte and Priscu 1998, Waters et al. 2013). An array of algal pigments has been used to provide knowledge of changes in community composition (Tani et al. 2009, Romero-Viana et al. 2010, Ohtsuki et al. 2015), with insights gained from analysis of specific photosynthetic pigments (Pinckney et al. 2001, Paerl et al. 2003). Derivation of relationships between P species and algal pigments over long time scales may help to better define “reference conditions” for phytoplankton communities and improve predictions of changes in phytoplankton diversity.

Several paleolimnological methods have been used to describe the reference condition of lakes (Bennion et al. 2011) but the most common is diatom-inferred “transfer functions” (Smol 1992, Reid 2005). Despite the usefulness of this technique, transfer functions are often specific to lake districts and demand knowledge of diatom taxonomy, availability of recent analogues for fossil diatoms, and adequate time for diatom identification (Juggins 2013). In this study we use a complementary approach to determine the reference conditions of a lake based on relationships between P species and algal pigments.

The aim of this study was to understand long-term (ca. 700 year) changes in sediment P species using sequential extraction, and examine relationships to lake phytoplankton community composition derived from sediment algal pigment analysis. We chose a deep oligotrophic lake as a study site because it may be considered as a proxy for a natural reference site, with minimal anthropogenic influence. Specifically, we used a dated sediment core to determine the dominant P and phytoplankton species in the lake between AD 1314 (Kaharoa eruption) and AD 2009, and to infer some of the historical drivers of changes in phytoplankton phenology.

3.2 Methods

3.2.1 Study site

The study site was Lake Okataina (38°07′S; 176°25′E), one of the lakes in the Okataina Volcanic caldera (OVC) in the central North Island of New Zealand (Fig. 3.1). Amongst New Zealand lakes, Okataina may be considered close to a natural reference state. The lake was initially an arm of the nearby Lake Tarawera but was impounded about 7,000 years ago as a result of a volcanic eruption. It is 311 m above mean sea level, has a surface area of 10.8 km^2, a maximum depth of 80 m and a mean depth of 39 m. Lake Okataina has no surface outlet but drains underground toward Lake Tarawera. The lake is fed by two small permanent streams, with stormflows and groundwater contributing most of the direct inflow to the lake (McColl 1972).

The catchment area of Lake Okataina is 62.9 km^2 and is steep and prone to landslides and bank erosion (McColl 1972). Surface soils in the catchment are free-draining and mostly of recent volcanic origin, dominated by allophanic material rich in Al and Si (Parfitt 1990). Eighty-one percent of the catchment area is native forest, 10% is used for dry-stock farming, 8% is exotic pine (*Pinus radiata*) plantations and the remaining 1% includes roads, car parks and buildings (Scholes and Bloxham 2007). Around 19% of the catchment area, including the area of dry-stock farming, exotic forest and settlements, has at one time been logged (Stafford 1967).

Lake Okataina currently has a Trophic Level Index (TLI) (Burns et al. 1999) of approximately 2.5, indicative of oligotrophic status. It is continuously thermally stratified about nine months in each hydrological year and vertically mixed between the austral winter months of June and August. The chlorophyll *a* concentration varies between 4 and 8 µg L^{-1} over an annual cycle, with highest levels recorded during the period of mixing in August (Jolly 1968). Although records of dissolved oxygen prior to 1980 showed the lake hypolimnion remained oxygenated throughout stratification (Jolly 1968, Fish 1970, McColl 1972), records over the past 10 years indicate anoxia of a large proportion of the hypolimnion volume (Pearson et al. 2010).

Lake Okataina catchment has been affected by disturbances of anthropogenic and natural origin during the last millennium. Polynesians are thought to have settled in and around the Okataina catchment between the late 13th and early 14th century following the Kaharoa eruption of AD 1314 ± 12 (Hogg et al. 2003). Early Polynesian settlers used fire to clear forest while some logging took place in the late 19th century mainly for the production of Māori canoes (Stafford 1967). On 10 June 1886, Mt Tarawera erupted and damaged large tracts of vegetation in the catchment (Clarkson and Clarkson 1983). Europeans first settled in and around the catchment in the early 20th century and introduced mammals into the forest as well as rainbow trout (*Oncorhynchus mykiss*) to the lake. Currently, there are known populations of the dama wallaby (*Macropus eugenii*), wild boar (*Sus scrofa*) and red deer (*Cervus elaphus*) in the catchment, and the Australian brushtail possum (*Trichosurus vulpecula*) is widespread. These populations have opened up the forest canopy, exposing soils to increased run-off (Allen et al. 1984, Bardgett et al. 1998, Wardle et al. 2001).

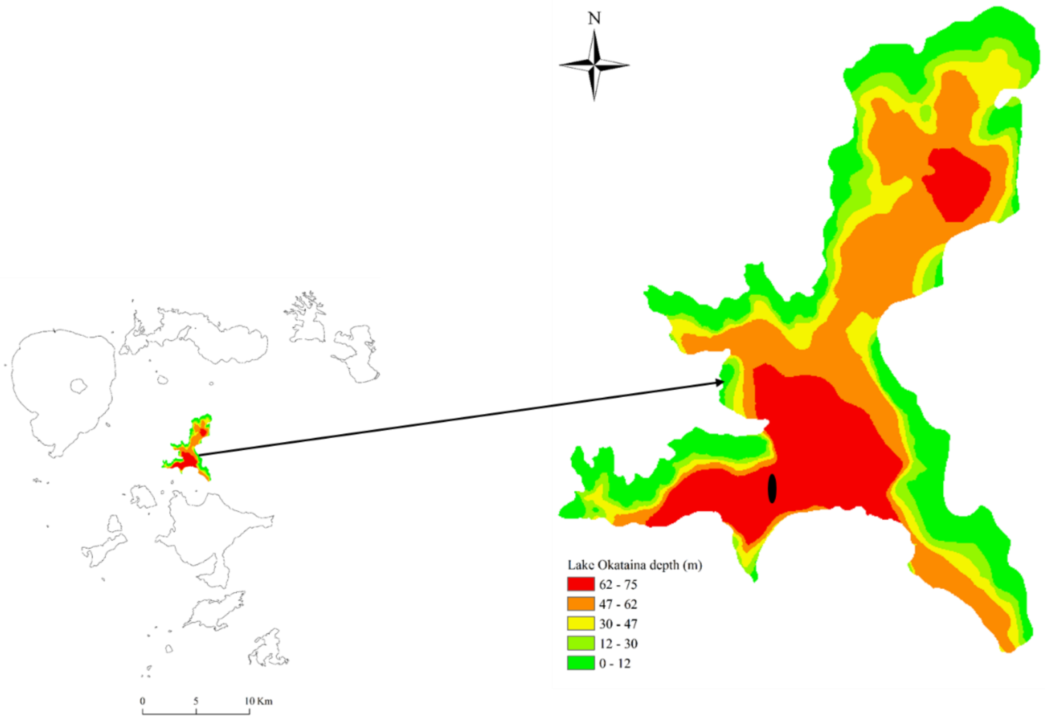

Figure 3.1 Bathymetric map of Lake Okataina with depth contours mapped by colours and juxtaposed amongst other lakes of the Rotorua region. The black dot is the sampling point.

3.2.2 Core retrieval

A 48 cm sediment core was retrieved from Lake Okataina using a Swedish gravity corer (Pylonex HTH 70 mm) with a 60 x 600 mm Plexiglas core barrel. Two tephras were identified as white and grey coloured layers in the sediment core. The depth at which they occurred in the cores was recorded (40 and 48 cm down the core barrel respectively). The core was extruded and separated into 50 ml polypropylene centrifuge tubes at 1cm vertical intervals. The extruded sediment samples were transported on ice in a dark chamber to the laboratory for subsequent analysis.

3.2.3 Extraction and analyses of algal pigments and phosphorus species

Algal pigments (Table 3.1), proxies of past variation in the taxonomic composition of algal communities, were extracted from core sediments. The pigments were extracted on the same day the core was collected, immediately upon its arrival at the laboratory. Extraction followed methods previously described by Leavitt et al. (1989). Fifty mg of wet sediment from each depth was soaked in 6 mL of a solvent mixture of acetone, methanol and deionised water (85:15:5) and allowed to sit for 24 h in the dark. The supernatants were centrifuged and syringe-filtered using a

0.22 µm membrane (Sigma-Aldrich, St Louis, USA). Pigments were separated and quantified using a Dionex Ultimate 3000 HPLC with a photo diode array detector and a Sigma-Aldrich (St Louis, USA) C18 reverse column (300A pore size, 5 µm particle size, 4.6 mm ID x 250 mm). The mobile phase gradients consisted of a mixture of methanol and 0.5 M ammonium acetate (80:20 v:v) as solvent A and a mixture of methanol and acetone (70:30 v:v) as solvent B. A combined gradient and isocratic elution technique was used for the analytical separation. An injection volume of 1 µl was used at an initial flow rate of 0.1 ml/min and flow rate was increased from 0.1 ml/min until a final flow rate of 1.5 ml/min was attained. Pigments were identified using retention times of known authentic standards (canthaxanthin, myxoxanthophyll, alloxanthin, diatoxanthin, lutein and chlorophyll *b* and *a*) (Sigma-Aldrich, St Louis, USA). Pigment concentrations were calculated by comparing spectral peaks to the peaks of standards of known concentration, and expressed as µgg^{-1} wet sediment.

Phosphorus species from each layer in the core were determined by sequential extraction following a modification of the method of Psenner and Pucsko (1988). One gram aliquots of the wet sediment sample from each depth were dispensed into 50 mL centrifuge tubes and thereafter subjected to the following sequential extraction procedure:

1. 1 M NH_4Cl (pH 7 at 25 °C) was added and the mixture was left for 1 h and homogenised to obtain loosely adsorbed, exchangeable and pore water fractions of P.

2. 0.1 M of $NaHCO_3$-buffered 0.1 M $Na_2S_2O_4$ (bicarbonate-dithionite, BD) at 40 °C was added and the mixture was left for 30 min to extract reducible fractions of P associated with (oxy) hydroxides of Fe and Mn.

3. 0.1 M NaOH at 25 °C was added and the mixture was left for 16 h to release fractions associated with Al (oxy) hydroxides as well as some organic and biogenic P.

4. 0.5 M HCl at 25 °C was added and the mixture was left for 16 h to dissolve fractions associated with apatite and $CaCO_3$.

5. 1 M NaOH at 85 °C was added and the mixture was left for 24 h to solubilize residual material and release recalcitrant fractions.

Table 3.1 Primary producer groups represented by specific algal pigments.

Algal group	**Pigment**
Total algal abundance	Chlorophyll *a*
Chlorophytes + macrophytes	Chlorophyll *b*
Diatoms	Diatoxanthin
Chryptophytes	Alloxanthin
Attached cyanobacteria	Canthaxanthin
Colonial cyanobacteria	Myxoxanthophyll
Chlorophytes	Lutein

The 50 mL centrifuge tubes containing the sediment and the extraction solution were capped and shaken in a water bath at the required temperatures for the period specified in each step. The tubes were then centrifuged at ~7000 rpm for 20 min, the supernatant collected and the sediment rinsed with the extraction solution, centrifuged and decanted a second time. Concentrations of Al, Fe and fractions associated with (oxy) hydroxides of Fe and Mn, Al (oxy) hydroxides, apatite and $CaCO_3$, and refractory fractions were analysed on a Perkin-Elmer (Massachusetts, USA) SCIEX ELAN DRC II inductively-coupled plasma mass spectrometer (ICP-MS). The labile fractions were also analysed using ICP-MS while the fraction associated with (oxy) hydroxides of Fe and Mn was again measured using the molybdate-blue method to determine the reactive component of P. The difference between the ICP-MS concentration and the molybdate-blue method was taken to be the non-reactive (organic P) component. Table 3.2 summarises the methods and the associated fractionation steps used for P speciation.

Table 3.2 Phosphorus fractions recovered in the different sequential analytical steps and the solvents used in their recovery

Step	Solvent	P form
1	NH_4Cl	Labile P
2	Bicarbonate-dithionite (BD) at 40 °C	Redox sensitive P (Fe-P)
3	NaOH at 25 °C	Al bound P (Al-P)
4	HCl at 25 °C	Apatite bound P (Ca-P)
5	NaOH 85 °C	Organic refractory P (Re-P)
6	Molybdate blue TP – step 2	Organic P (Org-P)
7	Step 1 to 5	Total extractable P (TEP)

3.2.4 Core dating

The presence of two clearly identifiable and dated tephra layers in the sediment core was useful for cross-validation of the dates determined from ^{210}Pb analysis. The extracted tephra were identified and dated based on the depths that they were extruded from (Hogg et al. 2003, Lowe et al. 2013). Dried sediment samples from each depth were also submitted to the Radiocarbon Unit (University of Waikato, New Zealand), for the determination of ^{210}Pb and ^{137}Cs activity (see appendix 1). The ^{210}Pb gamma-ray activity was counted under 46.52 keV emission for 43,200 to 259,200 s using a Canberra germanium well detector (1 x 4 cm), (Meriden, USA) with 22.5% efficiency for ^{60}Co. The unsupported ^{210}Pb activity was estimated by subtracting the constant background ^{210}Pb activity from the total ^{210}Pb. Ages of the samples were calculated based on the constant rate of supply model developed by Appleby and Oldfield (1978). Ages older than ~150 years were extrapolated assuming that sedimentation rate was constant. Visual evidence of tephra was confirmed from their mineralogy and major element glass chemistry, as the Tarawera and Kaharoa eruptions have previously been aged at AD 1886 and 1314±12, respectively, using wiggle matching and radiometric techniques (Lowe et al. 2013). Considering that the Kaharoa core has a ±12 y uncertainty and ^{210}Pb calibration of the modern sediments ±0.1 y, our earliest dating has an error of ±13 y.

3.2.5 Flux calculation

Concentrations of pigments and P species were converted to fluxes using mass accumulation rates (*MAR*) instead of sediment accumulation rates. While sediment accumulation rate is an important tool in characterising changes to sediment loads and compaction of sediments, its use in paleolimnology is complicated since the observed changes are a consequence of compaction and/or diagenesis (Stephens et al. 2012). The use of *MAR* is therefore essential to remove concentration and early diagenesis effects (Street-Perrott et al. 2007). Using the concentrations of the pigments and P species, we calculated *MAR* (kg m^{-2} y^{-1}) as:

$$MAR = \rho_{dry} \times SAR$$

where ρ_{dry} (kg m^{-3})is the dry sediment density,

SAR (m y^{-1}) is the sediment accumulation rate calculated as:

$$SAR = \frac{\Delta z}{\Delta t}$$

where Δz is the total length of the sediment core (m), and Δt is the total time span corresponding to the length of the sediment core (y).

The fluxes of each P fraction were calculated as a percentage of total extractable phosphorus (TEP). Similarly, for pigments, concentrations were calculated as a percentage of chlorophyll *a* per year. Core stratigraphies were constructed based on the percentage change in the P fractions and pigments.

3.2.6 Statistical techniques

Pearson moment correlation was used to determine the relationship between the P species and phytoplankton pigments. Nonmetric multidimensional scaling (NMDS) with the *vegan package* (Oksanen et al. 2013) was used to project the distribution of P species on the clustering of algal pigments.

To further determine whether phytoplankton groups could be defined by multiple P species, we employed generalized additive models (GAMs) in time series mode (Zuur et al. 2007). Smoothed functions were used in GAMs to describe both linear and non-linear relationships between the predictor variables (P species) and the response variables (algal pigments). A stepwise approach was used and the most parsimonious models were selected based on Akaike Information Criterion (AIC) and fed into a generalised linear model (GLM) to create predictive models. GAMs were used in preference to other parametric techniques to account for temporal autocorrelation of model residuals, a characteristic of time series data which leads to the violation of the independence criteria on which regression modelling is based. All statistical analysis was completed in R version 3.1.0 (R Development Core Team 2013) with GAMs done using the *mgcv package* (Wood 2011).

3.3 Results

3.3.1 Phosphorus species in the sediment core (AD1314 – AD2009)

Phosphorus speciation in the sediments can be used to delineate between refractory and bioavailable forms of phosphorus. In the Okataina core, ca. 80% of P fractions can be considered refractory (i.e., Ca-P, Al-P and Re-P), with the remaining 20% in labile and Fe-P fractions that are considered to be potentially bioavailable. As a mean percentage obtained through the 1cm interval core profile, P bound to Al (oxy) hydroxides was most abundant (39% TEP), while the labile component was the least abundant (2%).

The P fractions varied through the sediment core profile, however, corresponding to the dated periods of 1314 and 2009 AD (Fig. 3.2). Labile P constituted about 3% of the TEP at the base of core (i.e., 1314), and gradually declined to about 0.5% of TEP by 1680. Between 1680 and 1870, labile P increased from 0.5 to 2.8%, decreased to about 1.4% between 1870 and 1900, then increased rapidly from 1.4 to 3.8% between 1900 and 2009. Species bound to (oxy) hydroxides of iron (Fe-P) ranged between 4 and 12% of TEP between 1314 and 1800 but increased to 18% of TEP by 1820, then decreased to 8% of TEP by 1900. This was followed by a sharp increase to about 25% by 1950 after which time the fraction remained reasonably constant until 2009 (i.e., to the top of the core). Aluminium-bound P was the dominant species between 1314 and 1886, but was less prominent after 1886. It ranged between 25 and 55% of TEP, but decreased drastically from around 50% in 1886 to < 10% by 2009. The Ca-P species oscillated strongly between 30% of TEP (1314) and 2.5% (1700) after which time levels were relatively stable and at the lower end of the range. However there was a sharp increase to about 15% by 1920. Refractory organic P oscillated around 30% of TEP between 1314 and 1886 then increased rapidly after 1886 to 60% of TEP by 2009. Thus Re-P was the dominant P species in the most recently deposited sediments. The most stable component of the P species through the core was the organic fraction. It averaged about 8% of TEP through the core profile but there were spikes of up to 14% around 1400, 1550, 1800 and 1900.

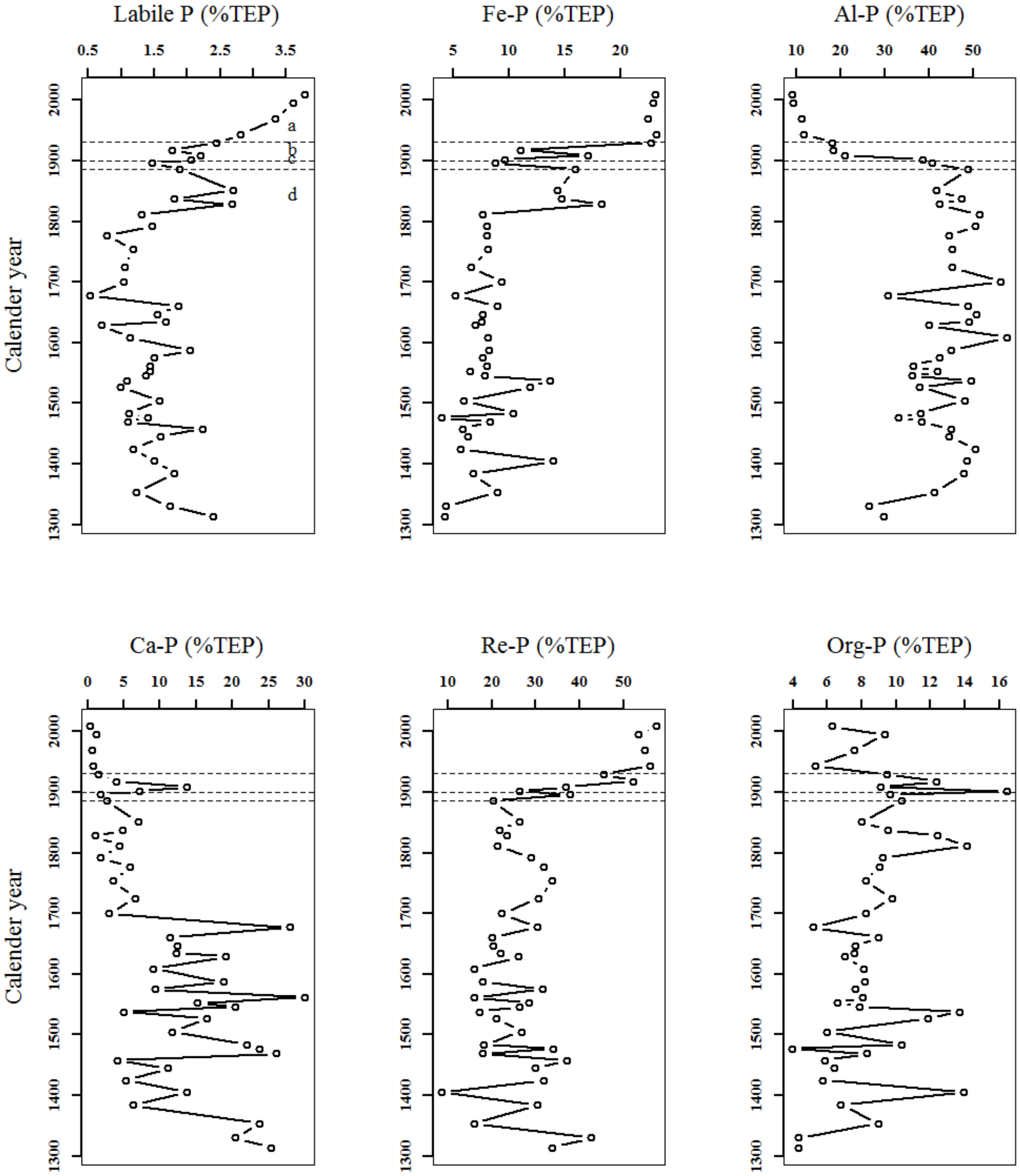

Figure 3.2 Relative change of the different P fractions as a percentage of the total extractable P pool in the Lake Okataina core between c. 1314 and 2009. Letters represent periods associated with: (a) increasing populations of the dama wallaby, deer and the Australian brushtail possum commencing c. 1920, (b) era of European settlement around c.1900, (c) post-Tarawera eruption of 1886, and (d) = post-Kaharoa eruption of c. 1314 and subsequent Polynesian settlement.

3.3.2 Phytoplankton community dynamics in the sediment core (AD1314 – AD2009)

Changes in phytoplankton phenology of Lake Okataina were inferred from variations in pigment composition of the dated 1cm slices (48) of the sediment core. Diatoxanthin, representing diatoms, was the dominant pigment, representing 59% of chlorophyll *a* on average for the 48 core slices. It was strongly dominant between 1314 and 1810 (up to 80% of chlorophyll *a*), decreased to about 10% by 1810, increased to 40% between 1900 and 1932, and decreased again to about 10% of chlorophyll *a* by 2009 (Fig. 3.3).

Canthaxanthin, representing attached cyanobacteria, ranged between 0.9 and 15% of chlorophyll *a* between 1320 and 1410, increased sharply to about 25% by 1840, then decreased to 15% soon after 1886 (coinciding with the Tarawera eruption). It was highest in most recently deposited sediment, at ca. 28% of chlorophyll *a* in 2009. Myxoxanthophyll, representing colonial cyanobacteria, was relatively stable at about 0.9% of chlorophyll *a* until 1890, then increased rapidly to about 15% by 1910. This was followed by a sharp decrease to about 5% by 1920 before increasing again to be 10% by 2009. Alloxanthin, representing chryptophytes, varied between 1 and 2% of chlorophyll *a* during the entire period except between 1890 and 1932, when a major spike up to 20% was observed.

The lutein pigment is confined to chlorophytes, and can be expected to indicate chlorophyte presence similar to chlorophyll *b* except that the latter pigment also includes macrophytes. The lutein and chlorophyll *b* pigments showed a similar pattern through the core until about 1950. Based on lutein, chlorophytes increased gradually from about 2% of chlorophyll *a* in 1314 to nearly 25% between 1890 and 1920, with levels remaining elevated (12-20%) through to 2009. Chlorophyll *b* constituted about 15% of chlorophyll *a* until about 1800, increased rapidly to 70% by 1950 and remained somewhat elevated (>35%) to 2009.

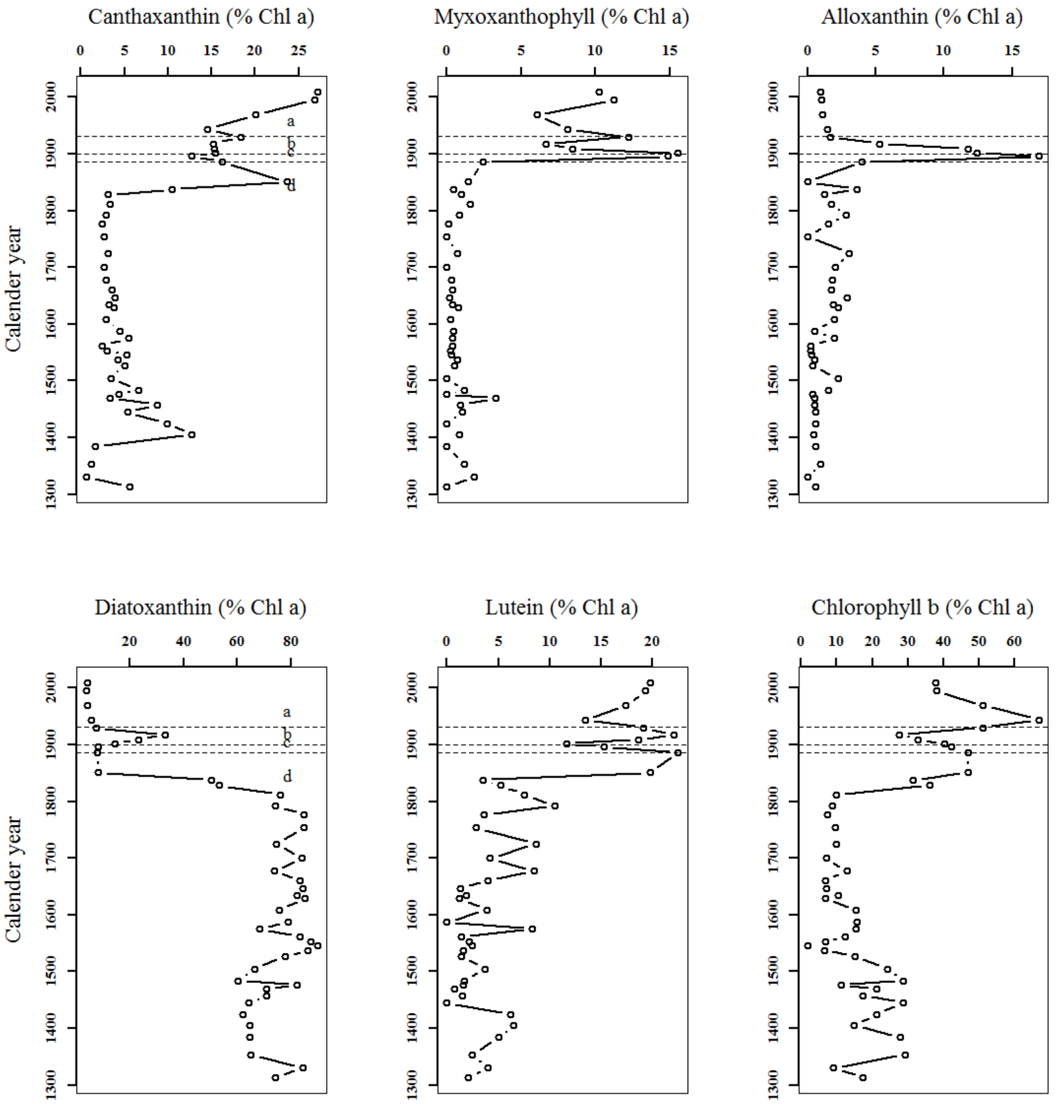

Figure 3.3 Change of different algal pigments as a percentage of chlorophyll a in the Lake Okataina core between c. 1314 and 2009. Letters represent periods associated with: a = increasing populations of the dama wallaby, deer and the Australian brushtail possum commencing c. 1920, b = era of European settlement around c. 1900, c = post-Tarawera eruption of 1886, and d = post-Kaharoa eruption of c. 1314 and subsequent Polynesian settlement.

3.3.3 Relationship between P species dynamics and phytoplankton phenology

Nonmetric multidimensional scaling was used to examine the clustering patterns of the pigments and P species (Fig. 3.4), with Pearson correlation used to examine the bivariate relationship between them. There was a negative gradient between diatoxanthin and the other algal pigments and a close clustering of lutein and canthaxanthin, while myxoxanthophyll and alloxanthin also showed some association. Chlorophyll *b* and diatoxanthin clustered separately from other pigments and P species. The NMDS also showed that lutein and canthaxanthin were associated with labile P and Re-P while alloxanthin and myxoxanthophyll clustered with Fe-P and Org-P. Diatoxanthin clustered with Al-P and chlorophyll *b* with Ca-P.

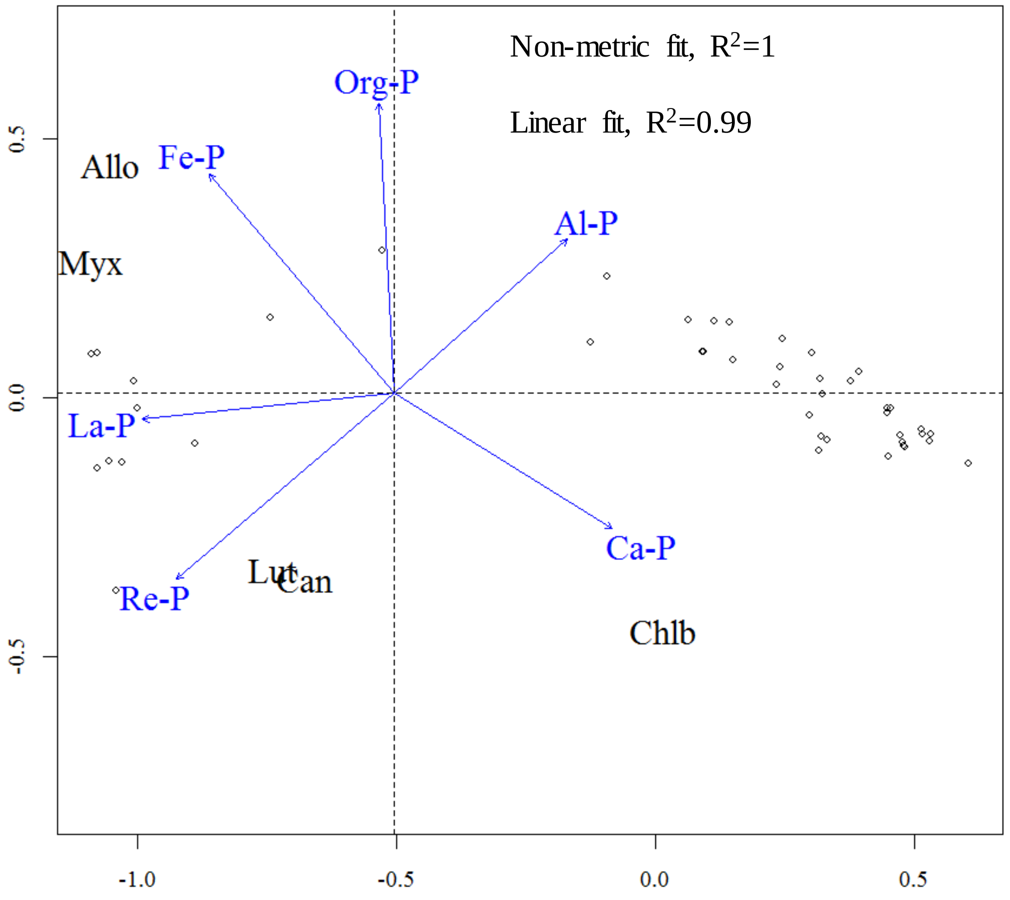

Figure 3.4 NMDS of Bray–Curtis similarity matrix for alloxanthin (Allo), myxoxanthophyll (myx), lutein (Lut), canthaxanthin (Can) diatoxanthin (Dia) and chlorophyll b (Chlb) as a percentage of chlorophyll *a*. Phosphorus species as a percentage of (TEP) (blue) were projected as vectors on the ordinated pigments. Open spheres represent the calendar years.

Pigments representing green algae and cyanobacteria, tended to be highly positively correlated ($p<0.001$) with potentially bioavailable P species and strongly negatively correlated with refractory species (Table 3.3). Relationships between P species and diatoms (diatoxanthin) were contrary to those found between P-species and cyanobacteria, green algae and chlorophytes and macrophytes. Chryptophytes (alloxanthin) did not correlate with any P species apart from the weak positively correlation with organic P species (r=0.36, p<0.05).

Table 3.3 Pearson-Moment correlation of phosphorus species (as a percentage of TEP) with algal pigment (as a percentage of chlorophyll a) based on 1 cm slices (n=48) of core retrieved from Lake Okataina.

	Canthaxanthin	Myxoxanthophyll	Alloxanthin	Diatoxanthin	Lutein	Chlorophyll *b*
Labile-P	0.76***	0.53***	0.01	-0.72***	0.59***	0.67***
Fe-P	0.77***	0.58***	0.06	-0.77***	0.67***	0.73***
Al-P	-0.64***	-0.62***	-0.06	0.61***	-0.57***	-0.54***
Ca-P	-0.48**	-0.39**	-0.22	0.52***	-0.55***	-0.43**
Re-P	0.59***	0.58***	0.11	-0.58***	0.61***	0.49***
Org-P	0.14	0.28	0.36*	-0.17	0.2	0.08

*** p<0.001, ** p<0.01 and * p<0.05.

3.3.4 Relationships amongst algal pigments and phosphorus species

Correlations amongst the algal pigments in the sediment core are shown in Fig. 3.5. The pigment proxies for cyanobacteria (i.e., canthaxanthin and myxoxanthophyll) were strongly positively correlated (p<0.01) with those for chlorophytes (i.e., lutein and chlorophyll *b*) but strongly negatively correlated with proxies for diatoms and chryptophytes.

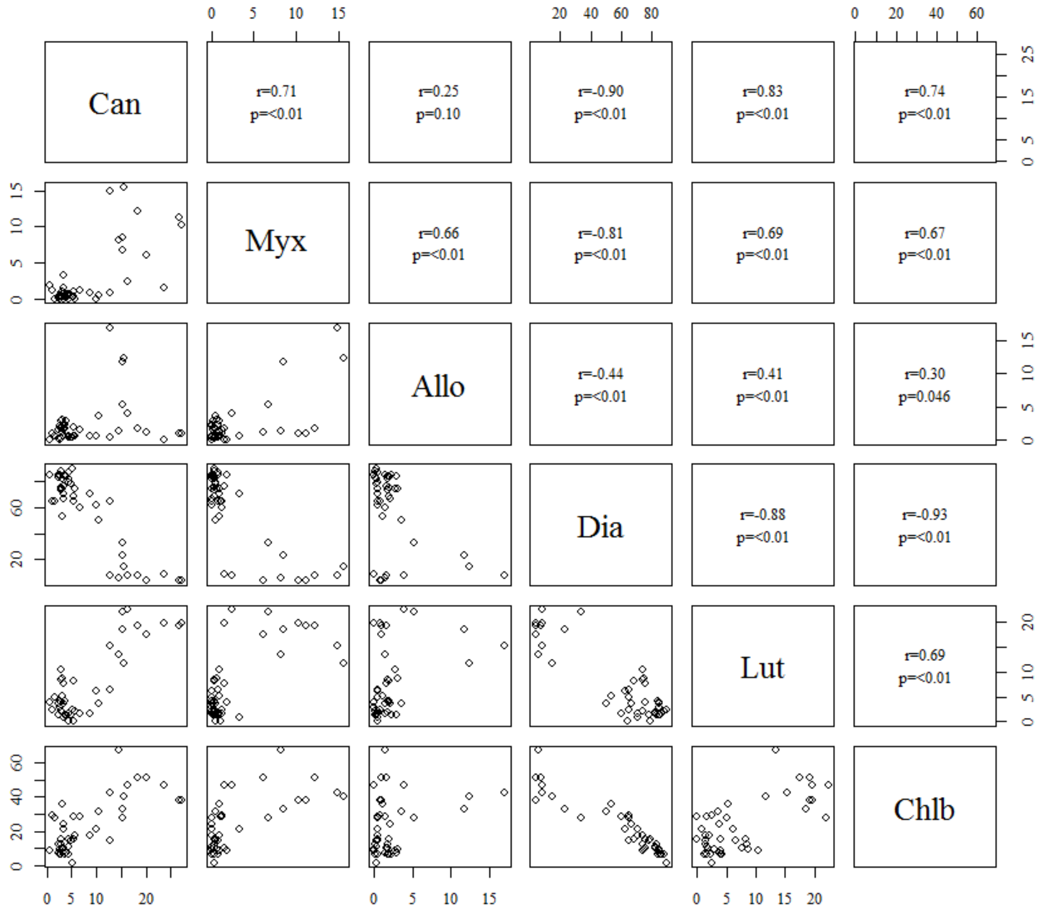

Figure 3.5 Correlation matrix of the phosphorus species. Coefficients of correlation and levels of significance are given in diagonal mirror.

All the phosphorus species except Org-P were correlated strongly amongst each other as shown in Fig. 3.6. Potentially bioavailable P species (i.e., labile P and Fe-P) were strongly positively correlated ($p<0.01$) but each was strongly negatively correlated ($p<0.01$) with species associated with permanent burial (Al-P and Ca-P).

3.3.5 General linear model

A GLM was used to predict phytoplankton dynamics from phosphorus species. Each of the algal species could be predicted to an acceptable level of significance ($p<0.05$) from various combinations of P species. Labile P, Al-P and Ca-P were included as independent variables in multiple regressions that explained 71, 62 and 61% of the variation in canthaxanthin, diatoxanthin and lutein, respectively (Table 3.4), while the relationship for Fe-P and alloxanthin was not significant ($p>0.05$),. For myxoxanthophyll an additional phosphorus variable of Re-P was included in the multiple regression, while for chlorophyll *b*, only labile P and Fe-P were included.

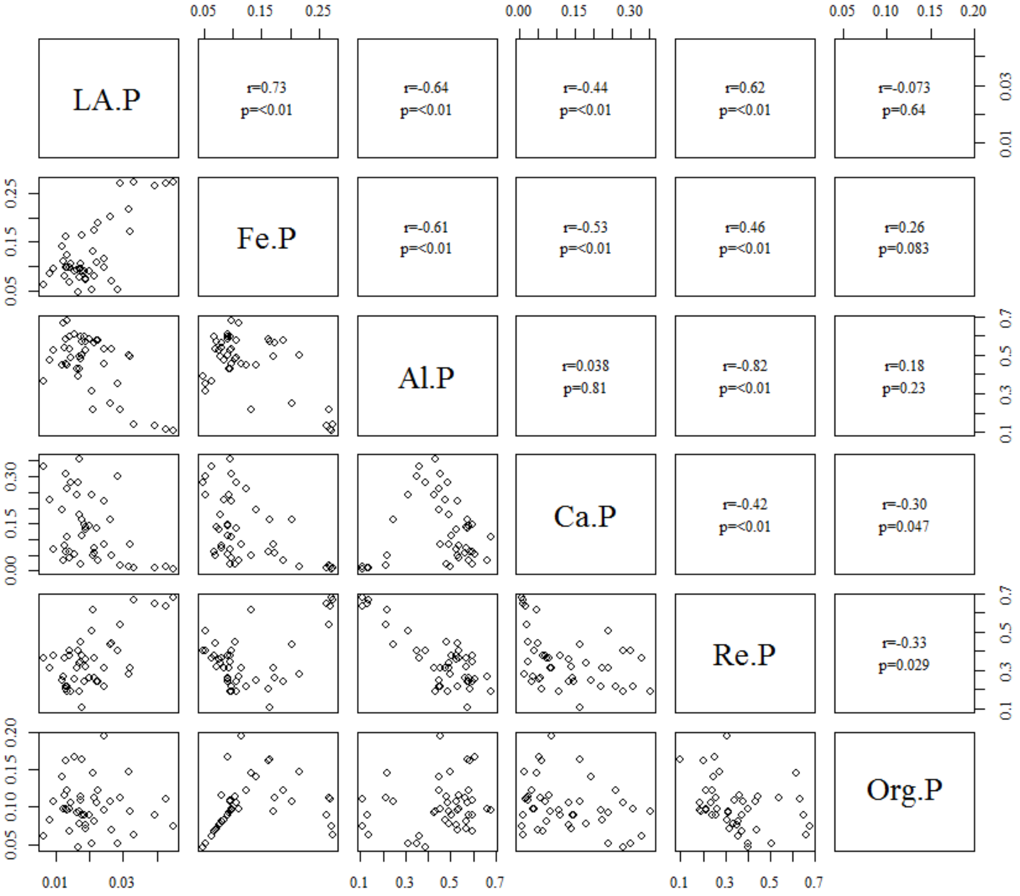

Figure 3.6 Correlation matrix of the phosphorus species and corresponding coefficients of correlation and levels of significance.

Table 3.4 Multiple regression models to explain algal pigments from P species.

Response variable	Equation	R^2	p
Canthaxanthin	5.25+ 254.79LA-P +33.57Fe-P – 11.30Al-P -11.73Ca-P	0.71	<0.001
Myxoxanthophyll	71.53+ 2.64LA-P -67.88Fe-P – 73.71Al-P -65.49Ca-P-52.29Re-P	0.62	<0.001
Alloxanthin	9.72-93.20LA-P -7.58Fe-P -6.48Al-P -13.15Ca-P	0.10	0.42
Diatoxanthin	58.21-684.53LA-P -150.82Fe-P +53.28Al-P +70.48Ca-P	0.69	<0.001
Lutein	19.48-31.21LA-P +18.27Fe-P – 21.72Al-P -30.79Ca-P	0.61	<0.001
Chlorophyll *b*	-3.53+ 529.04LA-P +121.58Fe-P	0.58	<0.001

3.4 Discussion

In this study, changes in the phytoplankton phenology were reconstructed for Lake Okataina, New Zealand, in response to phosphorus speciation in lake sediments. Most phytoplankton groups delineated by pigment analysis had a strong statistical relationship to one or more of the P species analyzed. There was a shift from a diatom dominated community to a cyanobacteria and chlorophyte community (early 1900) which was related to a change from phosphorus species associated with permanent burial (i.e., Ca-P and Al-P) to potentially bioavailable species (labile P and Fe-P). Below, we discuss phosphorus speciation in relation to catchment disturbance and consider the resultant impacts on the lake phytoplankton communities inferred from sediment pigment analysis. We also discuss the application of our methodology in derivation of reference conditions for lakes in light of changes observed through the core time sequence (of ca. 700 years), including the role of changes in water levels, climate, invasive mammals and natural disasters.

The time period encompassed by our sediment core represents an era of pre-human settlement punctuated by abrupt events such as volcanic eruptions and earthquakes, which have been shown in other lakes to contribute to natural variability over time scales of 10 to 1000 years (Leavitt et al. 2009, Anderson 2014). Changes in P species in catchment soils could result from either paedogenesis (Walker and Syers 1976), anthropogenic factors (Kerr et al. 2011) or natural disasters (Fritz and Anderson 2013), ultimately affecting P loads and lake water quality. In Europe, reference conditions are benchmarked to pre 1850 when cultural eutrophication was considered to have started as a consequence of the agricultural revolution (Battarbee 2000, Bennion et al. 2011), although eutrophication in some lakes was reported prior to 1850 (Guilizzoni and Lami 2001). Variability in P species and phytoplankton pigments in our core took place long before the expansion of agriculture in New Zealand, which occurred mostly after 1870 in the North Island, with use of chemical fertilizers reported to have started in the early 20th century (McLintock 1966). Therefore the sustained increase in the proportion of labile P in Lake Okataina sediments between 1800 and 1886, following negligible variation between 1314 and 1800, is not due to agricultural intensification although we cannot rule out impacts from some small amount of land clearance in the catchment for agricultural production More recent and sustained increases in the proportion of labile P are of concern given the relationship to increasing proportions of cyanobacteria pigments in lake sediments. The cause of this recent increase in labile P is not obvious from the catchment disturbance history. Increasing numbers of free-ranging deer populations in the catchment, first introduced in the late 1800s, may, be a source of labile phosphorus as deer are known to facilitate erosion by removing forest understory and trampling soils (McDowell and Paton 2004). Similar potential effects from other invasive mammal introductions are discussed below. In-lake changes in food web trophic structure could also influence both phosphorus and pigment deposition. For example, introduction of exotic rainbow trout (*Onchorynchus mykiss*), introduced into Lake Okataina in 1906, have been reported elsewhere to remove top herbivorous zooplankton and macroinvertebrates, resulting in a shift towards less efficient grazers and enhanced nutrient cycling which together promote higher algal productivity (Knapp et al. 2001, Parker and Schindler 2006).

The higher proportions and considerable variability of Ca-P between ~1480 and 1700 is puzzling. A component of the variability could be associated with vegetation clearance by early Polynesian settlers who used fire as a tool for land clearance (McGlone 1989). Increases in the proportion of Ca-P in lake sediments have been associated with land clearance (Filippelli et al. 2010) and pools of Ca-P in catchments are generally associated with weathering of apatite-bearing rocks and are related to erosion and run-off (Armengol and Vidal 1988, Filippelli et al. 2010). A spike in the proportion of Ca-P was noted following the Tarawera eruption of 1886 and Ca-P was also very high in the bottom slices of the core, which is a period following the Kaharoa eruption of AD 1314 ± 12. There is evidence to suggest large-scale destruction of catchment vegetation during the 1886 Tarawera eruption (Clarkson and Clarkson 1983, McGlone 1989). Vegetation regeneration and canopy closure following the eruption took about 27 years (Timmins 1983) but the intervening period might be expected to yield higher erosion rates and therefore more Ca-P as a fraction of TEP.

The marked increase in the Re-P component after 1886 may be attributable to the Tarawera eruption in 1886 and subsequent landslides. This pool is considered to be inert and associated with soils, terrestrial plant parts and dust entering lakes via inflows, wind and precipitation (Psenner and Pucsko 1988). The destruction of catchment vegetation during the 1886 Tarawera eruption might have introduced large amounts of Re-P-species into the lake. In 1906, 20 years after the Tarawera eruption, Re-P was about 40% of the TEP pool. Similarly, the Re-P pool represented about 40% of TEP in 1334, some 20 years after the Kaharoa eruption. Eruptions result in large additions to the sediment pool of terrestrial plant materials which are high in Re-P. The proportion of Re-P continued to increase almost for 100 years, however, following the Tarawera eruption and despite the vegetation largely recovering after 27 years (Timmins 1983). Other natural changes may be relevant to consideration of the recent sustained increase in the proportion of Re-P. For example, water levels, recorded since early 1920s rose by 10 m in 1931 and 3 m in 1962 and 1971 (McColl 1972). These increases resulted in extensive destruction of riparian vegetation, which may have contributed additional Re-P that ultimately deposited to the lake sediments. Bank/shoreline erosion is also a common feature on the shores of the lake, a consequence of steep slopes, loose pumice soils and heavy rainfall (Cooper and Thomsen 1988). Possums, deer and wallabies, all introduced into the catchment of Lake Okataina over the past 150 years, decrease plant canopy cover, reduce the understory and in some cases cause tree dieback (Bellingham and Allan 2003). They may therefore reduce forest rainfall interception and evapotranspiration, invariably leading to increased run-off and erosion (Wardle et al. 2001), including increased Re-P loads. The impacts of vegetation clearance by invasive mammals on sediment erosion in a catchment characterized by steep slopes, heavy rainfall and wind storms (Hicks 1989) is likely to be substantial.

Burrows (1979) has indicated that annual mean air temperature from 1000 to 1900 AD has not varied by more than 0.5 °C in the Southern Hemisphere, which suggests that climate is unlikely to have driven some of the changes observed in the core prior to 1000 AD. By contrast, Cook et al. (2002), reported a 1.5 °C increase in air temperature in the last 200 years, immediately followed the Little Ice Age in New Zealand. Concomitantly there were increases in canthaxanthin, lutein and chlorophyll *b*, and reduction in diatoxanthin in Lake Okataina sediments from the past 200 years, coincided with a period in the past 200 years when air temperature has increased. In laboratory experiments. Lürling et al. (2013) and Schabhüttl et al.

(2013) showed that rapid increases in temperature altered phytoplankton community composition, favoring proliferation of cyanobacteria and chlorophytes. They postulated that diatoms, which are better adapted to cooler temperatures, may be outcompeted by cyanobacteria and chlorophytes at higher temperatures. Field experiments in a series of lakes spanning the whole of continental America have also shown a positive relationship between temperature and chlorophyte and cyanobacteria concentrations (Beaulieu et al. 2013).

The period encompassed by the core and prior to the Tarawera eruption was characterized by low to moderate variability in the proportions of phytoplankton pigments and phosphorus species, but abrupt changes associated with the eruption and then more sustained changes occurring following the eruption and through to present. Some changes may be associated with a period of warming following the Tarawera eruption but invasive mammal introductions and their proliferation appear to pose the most immediate threat to the quality of lake water as they serve as potential vectors for transferring easily erodible sediments to the lake from the catchment and could potentially facilitate landslides in this steep catchment. The effects of catchment erosion and phosphorus inputs may potentially be acting synergistically with impacts from trout on the trophic structure of the lake, increasing the cycling of nutrients and inducing changes in P species and phytoplankton pigments that are similar to low to moderate levels of nutrient enrichment. This study indicates that lakes are highly dynamic even under apparently low to moderate levels of natural perturbation, and that derivation of reference conditions should therefore reflect an inherent variability to allow better understanding of anthropogenic impacts.

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4 Recent changes in the water quality of a deep temperate oligotrophic lake

Abstract

This study explored long-term changes in water quality of Lake Okataina inferred from sediments deposited between from 1836 to 2009, during which time the forested catchment has been disturbed by both a pyroclastic volcanic eruption (Tarawera 1886) and more recently by invasive mammals. Multiple geochemical proxies were analysed stratigraphically to ascertain changes in trends in organic matter loading, primary productivity, redox potential and phosphorus retention capacity of the lake. The chronosequence of the proxies showed that the main source of organic matter loading to the lake is algae although there was terrestrial loading immediately after the volcanic eruption of 1886. Erosion of inorganic materials was relatively high after the eruption but the flux decreased after about twenty years, possibly linked to vegetation regrowth. Following 1920, however there was a sustained increase in inorganic erosion flux. The redox potential of the lake also changed substantially from about 1930 suggesting a reduced degree of bottom water oxygenation. Primary productivity increased considerably after about 1960, but has remained relatively unchanged since that time, while the phosphorus retention capacity of the lake substantially decreased over the last 50 years. Our results suggest that while the changes that followed the volcanic eruption were transient, lasting a few decades, recent changes in the lake chemistry appear to be more pervasive.

4.1 Introduction

Lake water quality is intrinsically linked to its catchment. Catchment vegetation, land use, hydrology, soils and geology combine with other factors such as climate to determine the quality of lakes (Anderson 2014). As a result, the quality of lakes differs between land-use types, with lakes in forested catchments reported to have the highest water quality (Foley et al. 2005). Forests moderate catchment hydrology through interception and evapotranspiration processes while their soils and root networks facilitate water filtration, contaminant removal and nutrient recycling (Baillie and Neary 2015). Landscape disturbance results in significant changes to water quality with cultural eutrophication associated with anthropogenic land use change. The deterioration in the water quality of lakes in the North Island of New Zealand for instance, has been linked to anthropogenic modification of their catchments (Hamilton 2005) and the current state of most European and American lakes is considered to be influenced by urbanisation and the "agricultural revolution" (Carpenter et al. 1998, George et al. 2000, May et al. 2012), although Bachmann et al. (2013) argued that most of the eutrophic American lakes existed prior to human settlement.

In catchments with minimal human activities, natural events such as volcanic eruptions and earthquakes can disturb catchment vegetation and catchment processes. Widespread destruction of vegetation has been reported as a consequence of the 1886 Tarawera eruption in New Zealand (Clarkson and Clarkson 1983), and tree mortality of up to 25% was reported in some New Zealand forests after an earthquake in the Southern Alps in 1994, with a further 22% of trees suffering damage (Allen et al. 1999). The modification of forested catchments as a consequence of these natural disasters erodes their capacity to maintain high water quality in lakes. Forested catchment modifications have induced changes in erosional, geomorphic and hydrologic responses (Sahin and Hall 1996, Moore and Allard 2011), with important consequences for the water quality of rivers and lakes (Lee et al. 2009). Other sources of perturbations in forested catchments could include invasive mammals which are known to modify both above- and below-ground components of forests, thereby interfering with hydrological and erosional processes (Bardgett et al. 1998).

Catchment disturbances trigger a series of geochemical processes in lakes that may be identifiable in the sediment record. Lake sediments are archives of environmental conditions in catchments and lakes at the time of deposition (Meyers 1997, Cohen 2012). Geochemical signatures in lake sediments from different sources of disturbance can be deciphered in lake sediment cores and used to infer paleoenvironmental history of lakes (Smol 1992, Meyers and Ishiwatari 1993). In particular, periods of high lacustrine primary productivity preserve evidence of processes that affect organic matter delivery and burial in sediments (Routh et al. 2004). The response of lakes to catchment disturbance and climate variability depends on the nature of the disturbance, its intensity and duration, coupled with the vulnerability of the system (Cohen 2003). In this study, it was contended that the impact of invasive mammals in the lake catchment resulted in a long lasting negative effect on the lake water quality while the impact of volcanic eruptions was massive but short-lived. Here I used a multiproxy approach to understand the impacts of catchment disturbances during the last 170+ years on the sediment geochemistry of Lake Okataina, a deep temperate oligotrophic lake in the North Island of New Zealand. Specifically, we compared changes in the source of organic matter to the lake, phosphorus retention capacity of the lake, changes in redox and primary productivity post Tarawera eruption of 1886 to post introduction of invasive mammals to the catchment around 1900 AD.

4.2 Methods

4.2.1 Site description

Lake Okataina (38°07′S; 176°25′E) (Fig. 4.1) which was originally an arm of Lake Tarawera, was impounded about 7,000 years ago as a result of a volcanic eruption. Together with 11 other lakes they constitute a family of lakes in the Okataina Volcanic Caldera (OVC) in the central North Island of New Zealand. Okataina has a surface area of 10.8 km^2, a maximum depth of 80 m, a mean depth of 39 m, and is situated 311 m above mean sea level. The lake is fed by two streams with irregular flow and is therefore considered to be fed mostly by stormflows and groundwater (McColl 1972). The lake has no known surface outlet but drains underground to Lake Tarawera (McColl 1972).

More than 80% of Lake Okataina’s 62.9 km^2 catchment is steep, and prone to landslide and bank erosion (McColl 1972). Surface soils are loose allophanic and pumice of recent volcanic origin (Cooper and Thomsen 1988), rich in Al and Si (Parfitt 1990). There has been little forest clearance in the catchment since 1886, and only localized timber extraction. Native forest covers about 81% of the catchment area, 8% in is exotic pine (*Pinus radiata*) plantations, 10% under dry-stock farming with the remainder (1%) made up of roads, car parks and buildings (Scholes and Bloxham 2007).

Based on the Trophic Level Index (Burns et al. 1999) classification, Lake Okataina is oligotrophic (TLI 2.5). Chlorophyll *a* concentrations range from 4 to 8 $\mu g\ L^{-1}$ over an annual cycle, with the highest concentrations occurring in August, the peak of the austral winter (Fish 1970). The lake undergoes uninterrupted thermal stratification for nine months, with vertical mixing between June and August, the austral winter months. Prior to 1980, the hypolimnion of the lake had been reported to be completely oxygenated even during thermally stratified periods (Jolly 1968, Fish 1970, McColl 1972) but in the last decade, a large proportion of the hypolimnion has reportedly become anoxic during the stratified period (Pearson et al. 2010).

There have been anthropogenic, biotic and abiotic perturbations to the catchment during the last millennium. Polynesian settlements were thought to have been established in and around the lake's catchment in the early 14th century following the Kaharoa eruption of AD 1314 ± 12 (Hogg et al. 2003). Fire was used as a tool for forest clearance and some timber was logged in the late 19th century for Māori canoes (Stafford 1967). Mt Tarawera erupted on the 10th of June 1886 and damaged large tracts of vegetation in the catchment (Clarkson and Clarkson 1983). Following European settlements around the catchment in the early 20th century, mammals were liberated into the forest and the rainbow trout (*Oncorhynchus mykiss*) released into the lake. Large populations of the dama wallaby (*Macropus eugenii*), wild boar (*Sus scrofa*), red deer (*Cervus elaphus*) and the Australian brushtail possum (*Trichosurus vulpecula*) are currently widespread in the catchment.

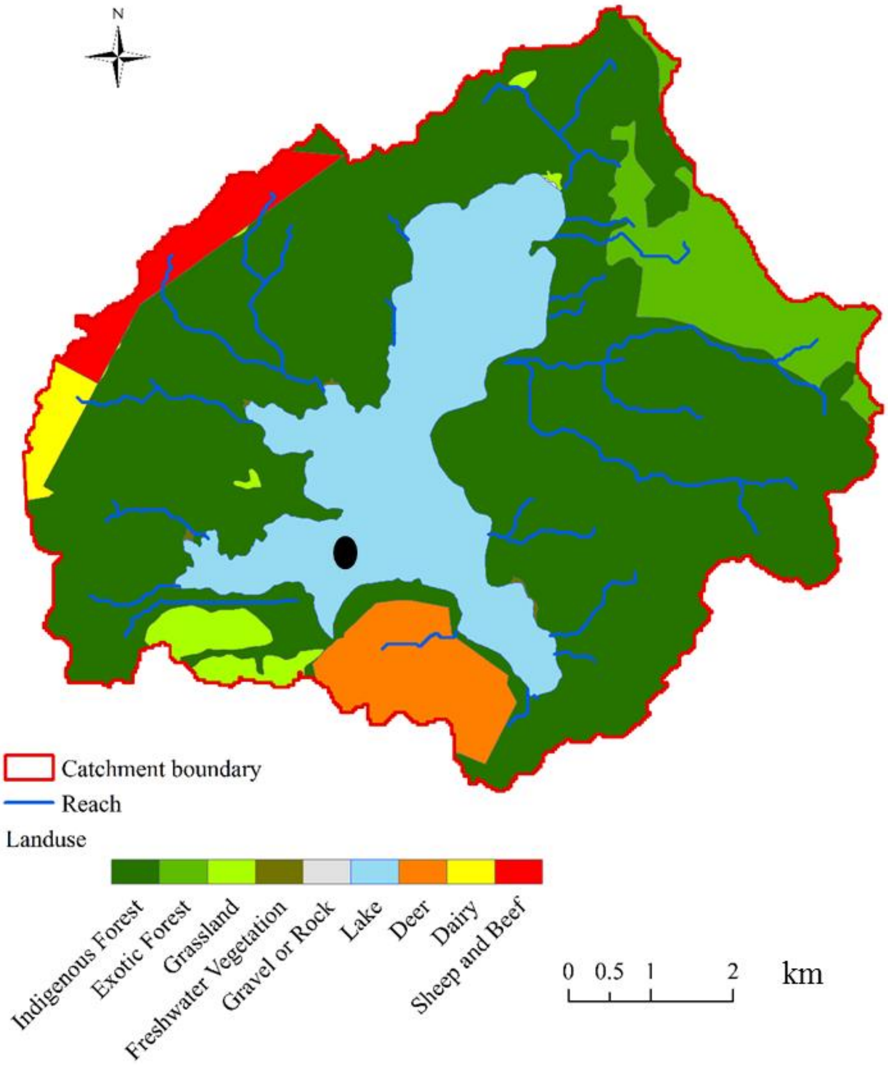

Figure 4.1 Map of Lake Okataina showing the land use categories in its catchment and the reaches of the lake with the sampling point in black.

4.2.2 *Sediment coring and dating*

A 26 cm sediment core was retrieved from the deepest basin of Lake Okataina in February 2014 using a Swedish gravity corer (Pylonex HTH 70 mm) with a 60 x 600 mm Plexiglas core barrel. A distinctly grey coloured tephra layer was identified in core as the Tarawera (1886) eruption 30 mm above the base of the core. The section of the core above the Tarawera tephra was sliced at 10 mm vertical intervals and separated into 50 ml polypropylene centrifuge tubes. The sediment samples were put in cold storage (4 °C) prior to analyses. Sediment samples dated from fifty years prior to the Tarawera eruption and included the Tarawera tephra to present-day sediments.

Sediment samples were dated using ^{210}Pb activity (see appendix 1) with the 1886 tephra serving as a control date. Approximately 1 g of dried sediment sample from each 10 mm layer was submitted to the Radiocarbon Unit (University of Waikato, New Zealand), for determination of ^{210}Pb and ^{137}Cs activity. The ^{210}Pb gamma-ray activity was counted at 46.52 keV emission for 43,200 to 259,200 s using a Canberra germanium well detector (1 x 4 cm), (Meriden, USA) with 22.5% efficiency for ^{60}Co. The constant rate of supply (CRS) model (Appleby 2002) was applied to the profiles using a modified method in which the activity of the lowermost sample was calculated on the basis of a regression of unsupported ^{210}Pb (Bq kg^{-1}) versus accumulated dry density (kg m^{-2}).

4.2.3 Proxies and laboratory analytical approach

4.2.3.1 Source organic matter

Total organic carbon (TOC) and total nitrogen (TN) together with stable isotopic signatures of organic carbon and nitrogen (δ^{13}C and δ^{15}N) were used to determine the source and route of delivery of OM to lake sediments. The TOC/TN ratio is also a useful proxy for OM sources in lake sediment. Molar ratios <10 are indicative of autochthonous production while >10 indicate allochthonous delivery of OM (Meyers and Ishiwatari 1993).

Organic carbon and nitrogen were analysed as percentage dry weight after acidification of ~2 g of sediment samples from each layer. The Isoprime 100 elemental analyser (EA) at the University of Waikato, New Zealand was used for the analysis.

Bulk OM δ^{13}C and total δ^{15}N analyses were conducted at the University of Waikato, New Zealand (Waikato Stable Isotope Unit). Analysis was conducted using an online Elemental Analyser (EA) coupled to a Continuous Flow-Isotope Ratio Mass Spectrometer (CF-IRMS) (Europa Scientific 20-20 Stable Isotope Analyser, Cheshire, UK). Data was reported as per mil (‰) deviation from a standard ratio (Vienna PeeDee Belemnite limestone standard, VPDB for δ^{13}C and atmospheric N_2 for δ^{15}N). The analytical uncertainty was ± 0.5 ‰ for δ^{13}C and ± 1.0 ‰ for δ^{15}N. We used the algorithm of Verburg (2007) to account for the Suess effect on δ^{13}C in organic sediment, resulting from the anthropogenic decrease in atmospheric δ^{13}C.

4.2.3.2 Internal phosphorus loading

Changes in phosphorus retention capacity of the lake sediment was determined as Al:Fe ratios and Al:P ratios during the sequential extraction of phosphorus (P) (Kopacek et al. 2005). We also used regression equations involving labile phosphorus to describe changes in release rate (RR) (Nürnberg 1988). Negative RR values mean the lake serves as a P sink while positive values make the lake a P source. In this study, we followed the Psenner and Pucsko (1988) fractionation method in sequentially extracting P, Al, and Fe. The concentrations associated with each step were analysed using a Perkin-Elmer (Massachusetts, USA) SCIEX ELAN DRC II inductively coupled plasma mass spectrometer (ICP-MS) at the University of Waikato.

4.2.3.3 Changes in Redox and primary productivity

Changes in the flux of Uranium (U), vanadium (V) and molybdenum (Mo) were used to infer changes in redox conditions of lakes (Wirth et al. 2013), while nickel (Ni) and copper (Cu) were used as surrogates of paleo-productivity because they are often sediment out in association with organic matter and are subsequently retained in sediment in association with pyrite after organic matter decomposition (Tribovillard et al. 2006). Trace elements were analysed using X-ray fluorescence (XRF) spectrometry (Boyle 2000) (Spectro X- Lab 200 X- ray spectrometer, Kleve, Germany). The analytical recovery was ensured by including subsamples of certified reference material in the run. The precision was evaluated from replicates, which were prepared for every tenth sample. All samples were submitted to the laboratory in randomized order. Only the elements with concentrations well above the detection limit and with a satisfactory replicate match were included in further analysis (40 elements). The mean concentrations of these elements were in most cases more than 20 times the detection limit, and the analytical precision was within ±12.5%.

4.2.3.4 Catchment disturbance

Zirconium (Zr) and titanium (Ti) were used as proxies for erosion because they are strongly resistant to diagenesis and therefore remain immobile during diagenesis (Piper and Perkins 2004).

4.3 Results

4.3.1 *Catchment disturbance*

Fluxes of Zr and Ti remained relatively unchanged prior to the Tarawera eruption (Fig. 4.2). The baseline in both fluxes shifted (increased) after the eruption. After 1925, flux of Zr returned to conditions close to the pre eruption era, but began to increase after about 1940 and through to the top of the profile. The flux in Ti only decreased after 1964 but never returned to pre-eruption rates.

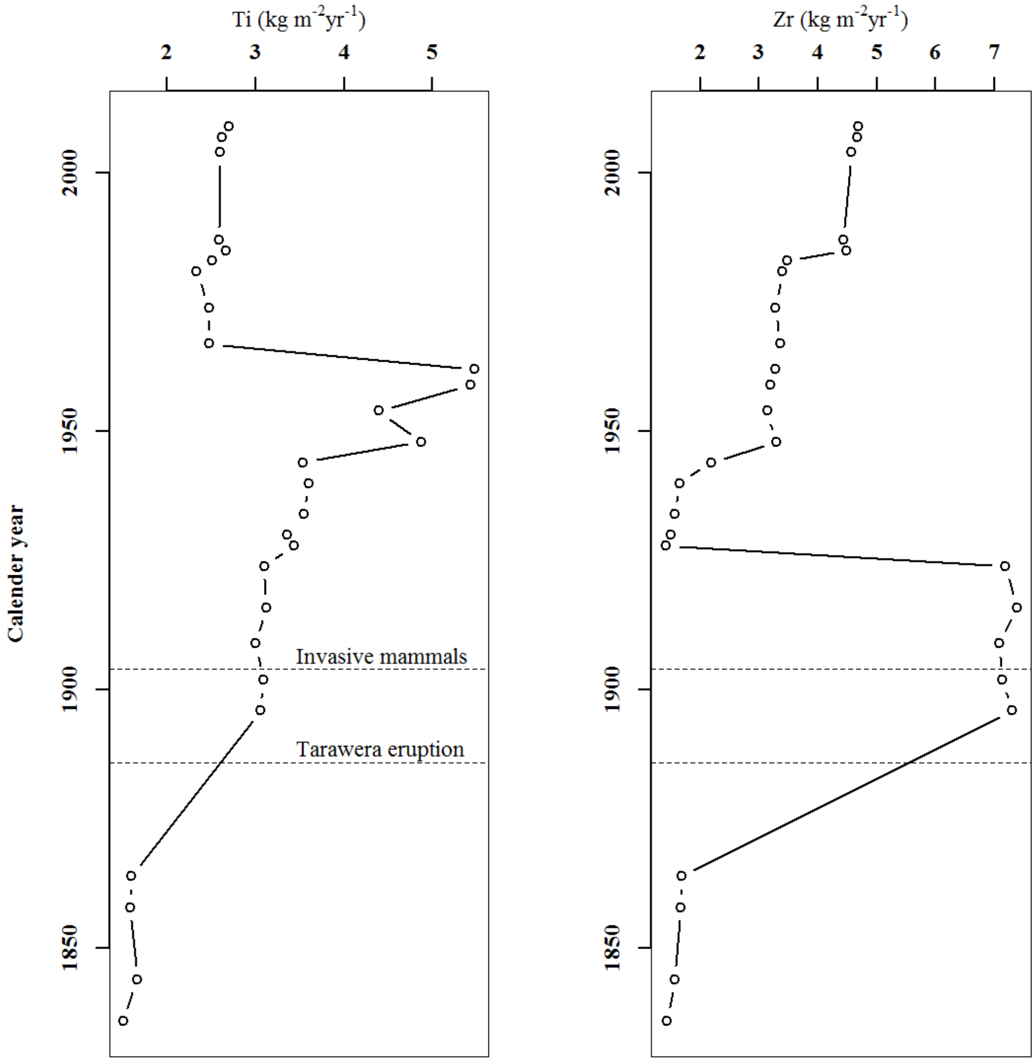

Figure 4.2 Ti and Zr fluxes in the sediment core of Lake Okataina plotted against calendar year. Dates of significant events are denoted (Tarawera eruption and commencement of proliferation of invasive mammals).

4.3.2 Source of organic matter in the lake sediment

The concentration of TOC and TN in the core was relatively constant prior to the Tarawera eruption but increased substantially after the eruption (Fig. 4.3). It then decreased so that in 1904 it was close to pre-eruption concentrations but subsequently began a sustained increase after 1916 until about 1955. While TN concentration decreased substantially after c. 1960, TOC concentration only decreased slightly in the same period. The concentration of both TOC and TN increased again after c. 1970.

The Suess-corrected δ^{13}C values ranged between -29.3 and -25.8‰. Prior to 1960, the values were relatively stable, ranging between -29.3 and -28.0‰. Values increased after about 1960, to a range of 25.8 and 26.5 (1960-2000). Between 1836 and 1920, δ^{15}N values ranged between 0.35 and 0.38‰. Values then increased rapidly to be in the range 6.6 and 8.98‰ between 1930 and 2009.

The atomic TOC/TN ratios (Fig. 4.4) in the sediment core ranged between 3.37 and 12.94. The TOC/TN ratio decreased rapidly between 1896 and 1916 and then began a steady rise until 1980 after which time there were slight reductions in the ratio.

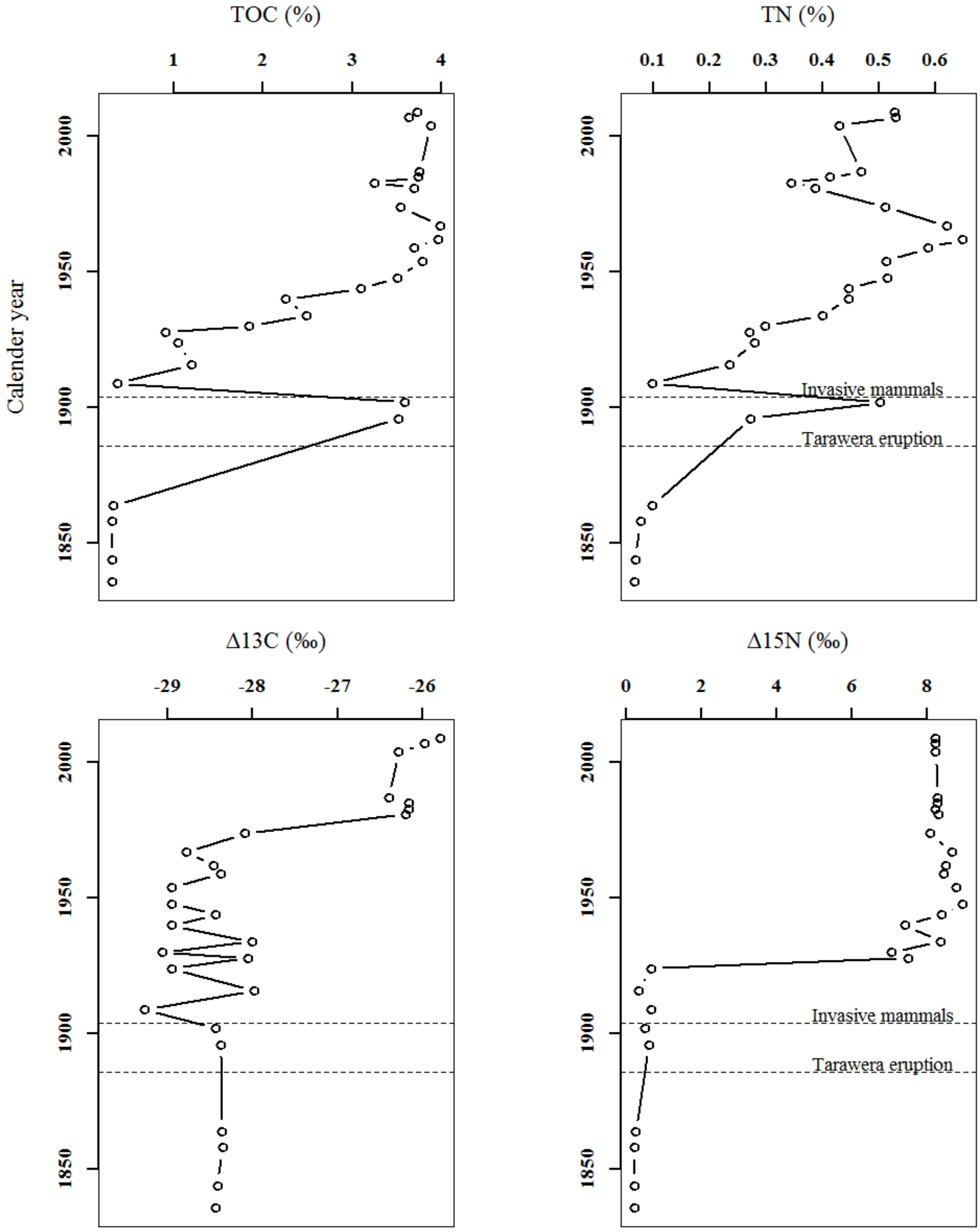

Figure 4.3 Records of TOC, TN, Suess-corrected δ13C, and δ15N plotted against calendar year. Dates of significant events are denoted (Tarawera eruption and commencement of proliferation of invasive mammals).

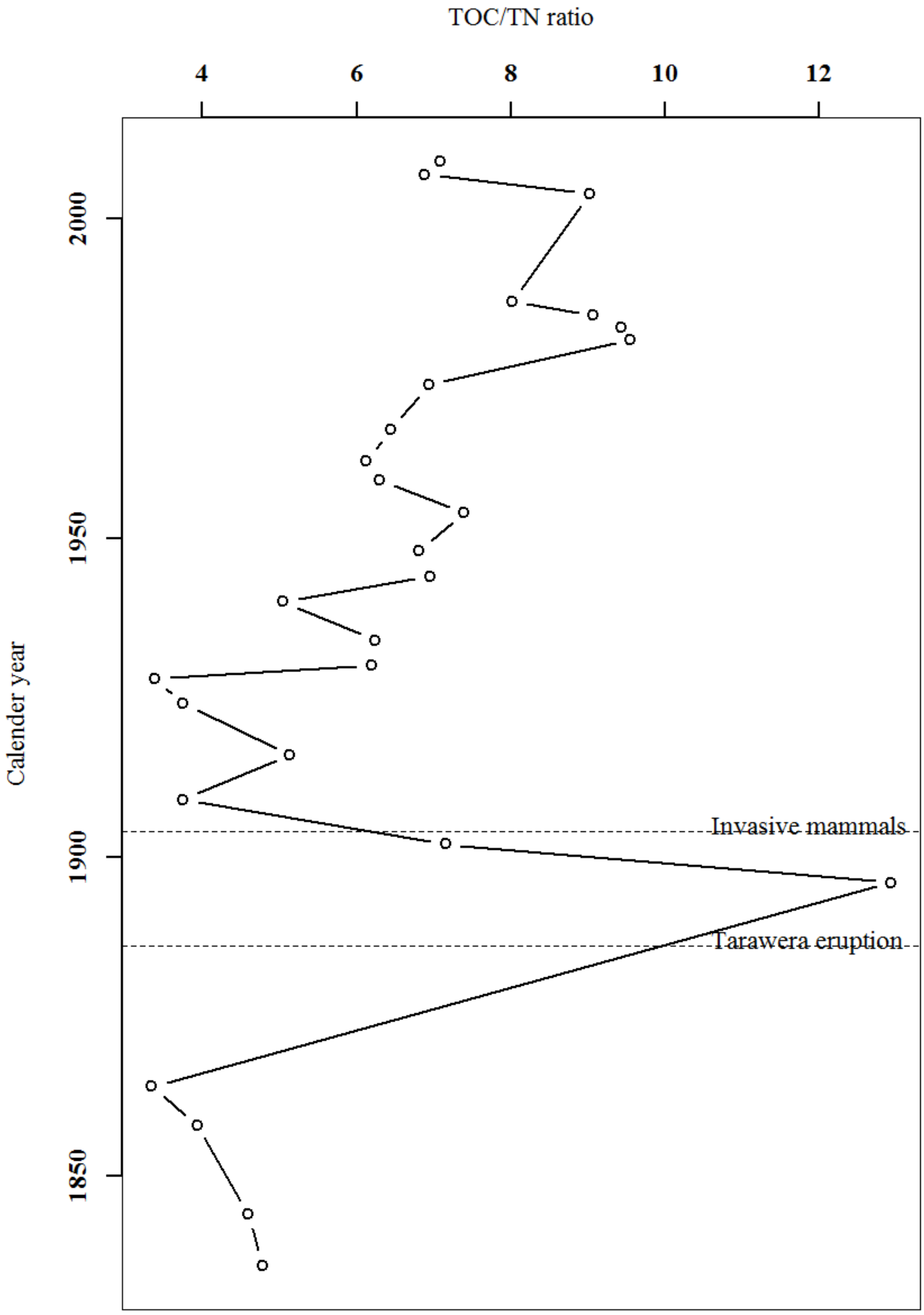

Figure 4.4 Molar TOC/TN ratio of the sediment profile of Lake Okataina plotted against calendar years. Dates of significant events are denoted (Tarawera eruption and commencement of proliferation of invasive mammals).

4.3.3 Phosphorus retention capacity of the sediment

The three proxies used to represent phosphorus retention capacity (Fig. 4.5) indicate that the lake was a net sink for phosphorus over most of the study period, because the values were below the threshold required for P loading. The proxy for release rate (RR) suggested that from about 1987, P was being released (positive flux) to the water column at a rate less than 0.1 mg m^{-2} yr^{-1}. From about 1916, the retention ability of the lake sediment, as indicated by Al:Fe and Al:P ratios, began to decline although the ratios still remained above the threshold (>3 and >25, respectively) at which the sediment would be expected to act as a source of P to the lake (Kopacek et al. 2005).

4.3.4 Changes in Redox

The increase in flux of U started around 1910, that of V started around 1940 and Mo around 1950. The proxies for redox conditions (Fig. 4.6) showed similar patterns with slight differences in the onset of changes in their flux rates.

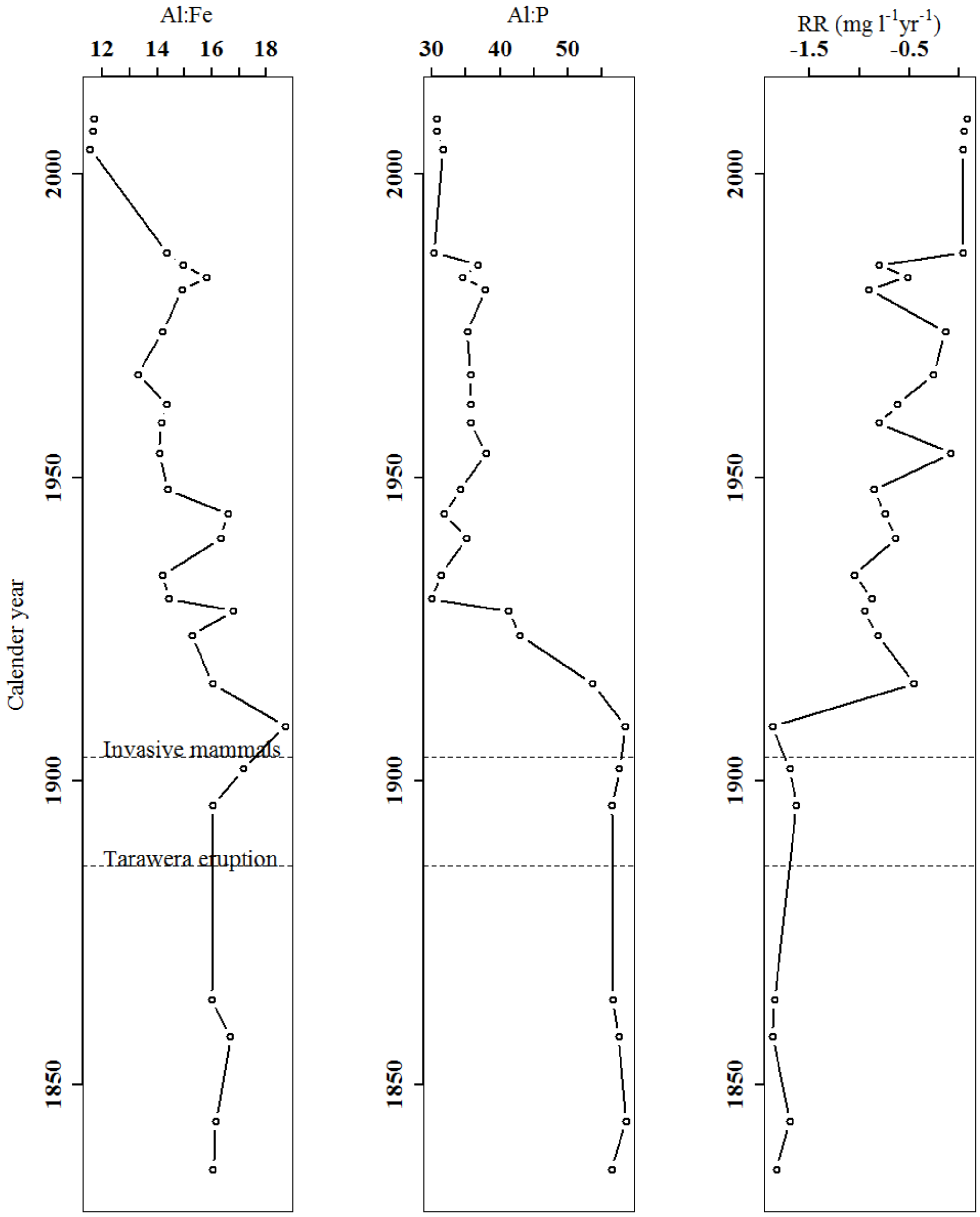

Figure 4.5 Changes in the Al:Fe, Al:P and release rate (RR) in the sediment profile of Lake Okataina plotted against calendar year. Dates of significant events are denoted (Tarawera eruption and commencement of proliferation of invasive mammals).

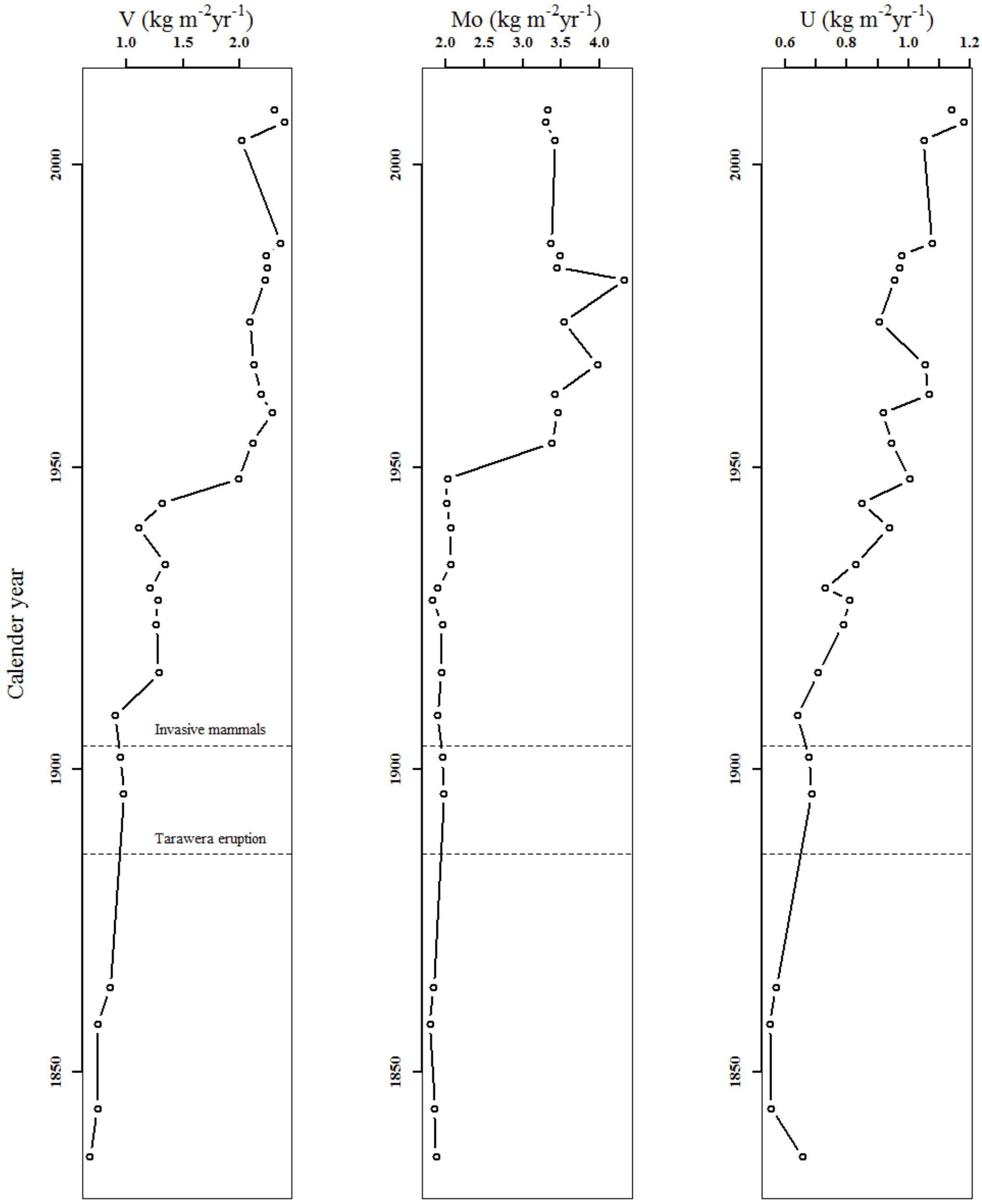

Figure 4.6 Changes in the flux of V, Mo and U in the sediment profile of Lake Okataina plotted against calendar years. Dates of significant events are denoted (Tarawera eruption and commencement of proliferation of invasive mammals).

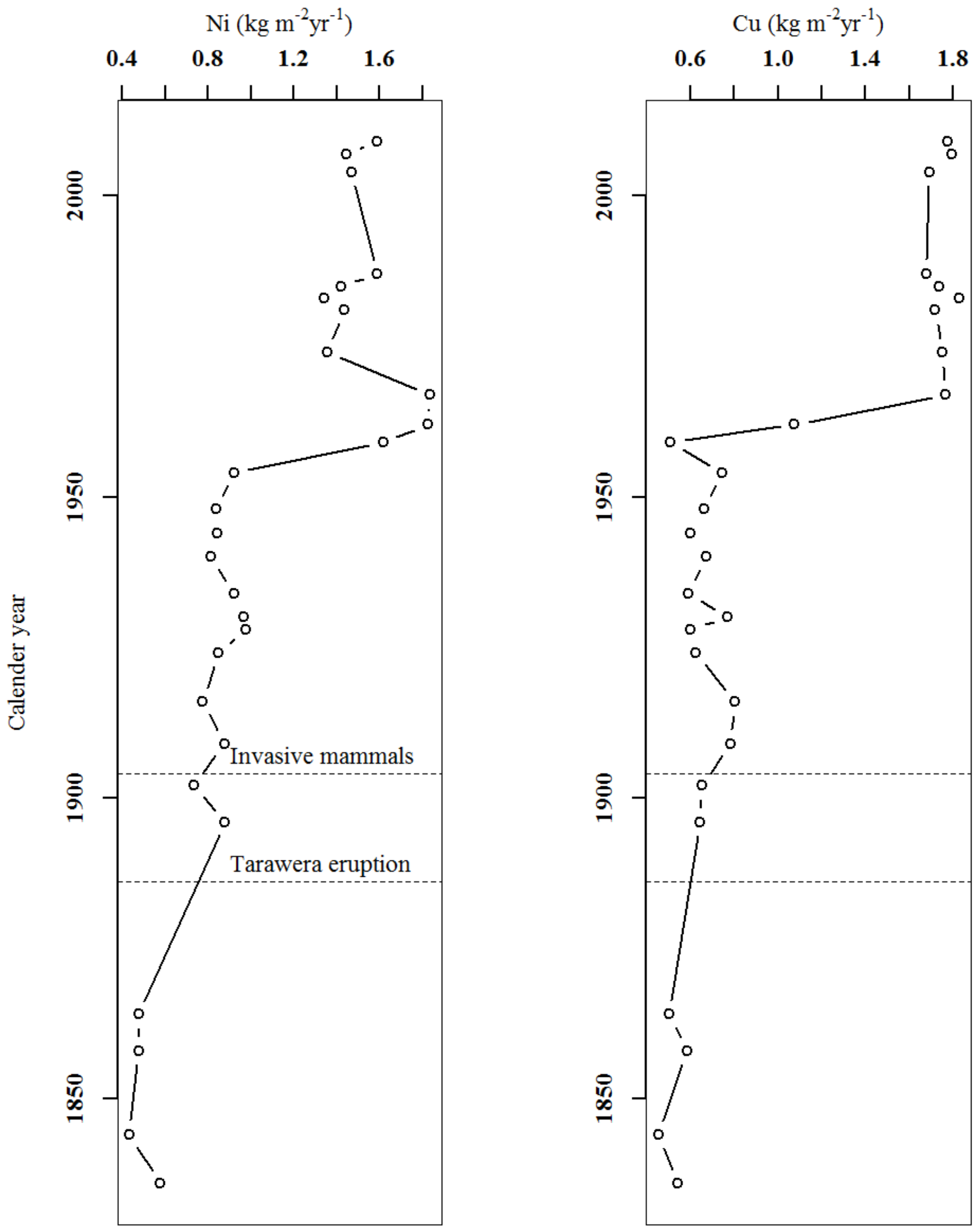

Figure 4.7 Changes in the flux of Ni and Cu in the sediment profile of Lake Okataina plotted against calendar year. Dates of significant events are denoted (Tarawera eruption and commencement of proliferation of invasive mammals).

4.4 Discussion

The general trends exhibited by most of the proxies in the sediment core profile suggest that the variability in water quality of Lake Okataina over ~170 years was largely a product of vegetation disturbance as a result of the Tarawera eruption of 1886 and invasive mammals introduced into the lake catchment around 1900. The high Zr flux in the lake sediment after the Tarawera eruption is indicative of increased erosion as a consequence of vegetation destruction during the eruption. The eruption was known to have destroyed forests close to the eruptive centre, and caused widespread forest damage throughout the Okataina catchment (Clarkson and Clarkson 1983). The resulting reduction in forest cover is likely to have exposed the soils to erosion, including both the mineral and organic components of the soil. The elements Zr and Ti are used as measures of grain size associated with catchment erosion. Zr denotes silt particles and Ti corresponds to clay and fine silt (Koinig et al. 2003, Augustsson et al. 2013). The reduction in the Zr component after 1920 could be the result of regeneration of vegetation which resulted in reduced in-wash of catchment soils into the lake. Vegetation recovery with canopy closure was reported to have taken about twenty-seven years after the Tarawera eruption (Timmins 1983), corresponding closely to the duration of the period of high Zr flux.

The gradual increase in the flux of Zr after 1940 is indicative of increasing and sustained levels of disturbance in the catchment. The most likely cause of this disturbance is the expanding populations of invasive mammals (dama wallaby, wild boar, red deer and Australian brushtail possum) introduced into the area at the start of the twentieth century. These mammals can cause rapid depletion of understorey trees and shrubs which have large, soft leaves, such as Patē or Seven-finger (*Schefflera digitatax*), ‘Puahou’ or 'Whauwhaupaku' *(Pseudopanax arboreus)*, māhoe or whiteywood (*Melicytus ramiflorus)* and kanono or raurekau (*Coprosma grandifolia)* (Forsyth et al. 2002) and possums have also been implicated in increased mortality of the overstorey species Northern rātā *(Metrosideros robusta)* and kāmahi (*Weinmannia racemose)* (Allen et al. 1997). Although browsing may result in competitive release of less palatable trees and shrubs (often species with small and/or tough leaves), the net impact of intense browsing is likely to be a decline in vegetation density (Wardle et al. 2001, Blick et al. 2008). The relationship between vegetation cover, physical weathering and erosion is well established: a reduction in vegetation cover leads to increased weathering and erosion (Kauppila and Salonen 1997), and the steep slopes and friable young volcanic soils of the catchment may have made the area particularly vulnerable to increased erosion.

Organic matter loading to the lake appeared to be strongly influenced by disturbance in the catchment from the Tarawera eruption. The high TOC/TN ratio around 1900 is consistent with large inputs of terrestrial organic matter from the catchment after the destruction of vegetation by the 1886 eruption (cf. Meyers and Ishiwatari 1993). By 1910 the TOC/TN ratio was lower, likely reflecting stabilization of soils by vegetation recovery (Timmins et al. 1983), and a consequent return of sediment composition to reflect dominance by autochthonous production.

Sustained gradual increases in the concentrations of TOC and TN over most of the 20th century probably reflect increasing autochthonous primary productivity, rather than an influx of terrestrial OM. The carbon and nitrogen isotopic signatures of the bulk OM were indicative of in-lake sources of OM. Stratigraphic fluctuations in the ∂^{13}C and ∂^{15}N values of Lake Okataina sediment OM probably reflect a combination of factors, including a shift in relative contribution of autochthonous/allochthonous OM, and changing autochthonous primary productivity (Torres et al. 2011). Oligotrophic lakes might be expected to have relatively high proportions of allochthonous C contribution to sediment OM (Gu et al. 1996). Terrestrial C_3 plants discriminate against ^{13}C, and organic matter derived from these plants typically has ∂^{13}C values between -27 and -29% (Meyers 1997). Hammarlund et al. (1997) related progressive depletion of ^{13}C in Lake Tibetanus (Sweden) to increases in the input of OM from surrounding vegetation. Also, phytoplankton discriminates against ^{13}C in the water column. Consequently, autochthonous OM in Lake Okataina might also be expected to show low ∂^{13}C values. The δ^{13}C signature of lacustrine phytoplankton cannot be distinguished from C_3 vascular plants (Meyers 2003) and therefore must be interpreted with caution. In New Zealand there are only indigenous C_3 vascular plants and therefore the signature could represent both terrestrial plants and lacustrine algae. Ratios of TOC/TN provide a more useful interpretation of the source of OM in the lake. Increases in organic matter in the sediment after 1910, may be linked to forest disturbance as a result of invasive mammals and associated erosion. However, while the concentrations of TOC and TN increased profoundly during the 20th century, the source of organic matter was mainly autochthonous. This conclusion was supported by TOC/TN ratio values <10 (Fig. 4.4). Erosional material may have been low in organic matter while increased nutrient loading from the catchment caused by erosion (e.g., Fraterrigo and Downing 2008) led to the increased production of algae in the lake. The change in δ^{15}N values to those associated with algal use of dissolved inorganic nitrogen also lends credence to the interpretation that the dominant source of organic matter deposition changed from terrestrial to in-lake production around 1900. The δ^{15}N values for lacustrine algae are close to 8.5‰ although this varies depending on the dominant algal group (Teranes and Bernasconi 2000). Plants discriminate against ^{15}N during inorganic N uptake (Inglett and Reddy 2006). Allochthonous OM derived from C_3 terrestrial plants generally has a ∂^{15}N value of about 0.4% (Peterson and Howarth 1987). Autochthonous OM in aquatic ecosystems also typically has higher ∂^{15}N signatures, whereas N-fixing algae possess values near that of atmospheric N_2, i.e. 0% (Peterson and Howarth 1987). The increase in autochthonous organic matter is reflected in the metal proxies of primary productivity and the δ^{13}C values, which indicate increased primary productivity.

The high phosphorus retention capacity of lake sediments immediately after the eruption reflects the high concentration of Al typical of rhyolitic eruptions. Correspondingly high ratios of Al:Fe and Al:P are observed in the sediment during this era. The Tarawera eruption was pyroclastic and high in Al and Si concentrations (Parfitt 1990, Pickrill et al. 1991). Gibbsite ($Al(OH)_3$) binds phosphorus strongly and phosphorus is only released when the ambient pH exceeds the point of zero charge, often above neutral (Gächter and Müller 2003). The high P retention capacity during this period was likely due to its proximity and association with sediments deposited from the eruption, resulting in the lake being a net sink for phosphorus.

Increased fluxes in the redox proxies suggest a diminishment in bottom water aeration. The sediment oxygen demand appears not to have been affected greatly by increased erosion associated with the eruption of 1886 but subsequent events in the lake could have stimulated the DO reduction. Redox potential of the lake changed in response to an increase in organic matter deposition to the sediment after 1900 or a change in the quality of the organic matter. Accumulation of organic matter is known to produce hypoxic or anoxic conditions in the hypolimnion of lakes, thus altering the redox potential (Gächter and Müller 2003).

Increases in primary productivity occurred following apparent reductions in the phosphorus retention capacity of the lake sediment and the decline in bottom water aeration. This suggests that catchment and in-lake processes prior to 1960 might have contributed to an increase in primary productivity, possibly implying a degree of hysteresis in the response of the lake to disturbance. The relative stability of primary productivity after 1960 may therefore not be sustained in the long-term, as contemporary catchment and in lake processes may trigger changes in the current status. Also, while there was increased erosion into the lake after 1960, the lake water may have remained low in nutrients, because phosphorus would likely have been bound to the sediment. Pumice soils are the predominant source of nutrients to the lake, but are deficient in most nutrients (Cooper and Thomsen 1988, del Moral and Grishin 1999) and are therefore unlikely to stimulate high rates of production by algae. However, increased organic matter delivery to the lake sediment over time could change the redox potential of the hypolimnion of the lake, resulting in an increase in the internal loading of nutrients. The stable primary productivity proxies (Ni and Cu) at the base of the core profile also support the attribution of high TOC, around 1900, to terrestrial inputs rather than increased algal production.

The increase in the primary productivity of the lake might also have been the result of rainbow trout introduced post 1900. Introduced trout can alter nutrient cycling, as well as algal production and standing crop in previously fishless lakes (Leavitt et al 1994). Primary production can increase when size-selective predation by fish on large herbivorous zooplankton reduces grazing on phytoplankton communities (Carpenter and Kitchell 1993). However, several studies have shown that overall lake production may be more strongly limited by nutrient supply than by the intensity of herbivory, particularly in oligotrophic systems (Neill and Peacock 1980; Elser et al 1990). In these systems, introduced trout may stimulate algal production by regenerating benthic and terrestrial nutrients, thereby increasing pelagic nutrient supply for phytoplankton growth. The magnitude of the response by lake primary producers to introduced fish depends on the source of nutrients that fish regenerate. Predation by fish on zooplankton regenerates pelagic nutrients (for example, P and N) within the water column, but pelagic regeneration does not constitute a new source of nutrients for phytoplankton.

Another potential cause of increased productivity after 1960 could be the lag effect of the 10 m rise in water level in 1931. Variability in lake hydrology, resulting in fluctuations in the water level, is a key factor affecting the functioning of lake ecosystems (Coops et al. 2003; Beklioglu et al. 2007; Jeppesen et al. 2014). Various processes related to water level fluctuation may also lead to changes in diapycnal and boundary mixing and therefore affect the upward flux of hypolimnetic nutrients and their supply into overlying waters. This happens at extreme water level drawdown or full mixing events (Naselli-Flores 2003, Baldwin et al. 2008) resulting in the uplifting and mixing of the hypolimnion by large cold inflows that plunge under an existing hypolimnion (Vilhena et al. 2010). Also, basin scale internal waves are a known feature of many stratified lakes, especially large ones. Internal waves occur at the depth of the thermocline as a consequence of water level fluctuations and when they hit the sloping boundary of a lakebed they can break, causing turbulent mixing and sediment resuspension (Gloor et al. 1994, Ostrovsky and Yacobi 1999), and thus entrainment of nutrients contained in the uppermost sediment layer and the interstitial water. The turbulent mixing sets up horizontal intrusions of water of intermediate density into the lake interior (Imberger and Patterson 1989).

The use of multiple proxies to infer changes in the water quality of Lake Okataina showed that both the Tarawera eruption and the introduction of invasive mammals in the catchment have had a marked influence on the composition of the lake water. However, while recent trends in lake conditions can be attributed to the introduced mammalian populations in the catchment and other perturbations such as lake level rises in 1931 and 1970 as the effects of the Tarawera eruption on lake processes appear to have been more transient, lasting only a few decades. Intense browsing by invasive mammals and the 10 m rise in lake level in the early 1931 are likely to be responsible for increased erosion post c. 1940, through a reduction in vegetation density, and this appears to be exerting a sustained but somewhat unpredictable negative impact on the lake water quality.

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5 Climate-driven synchronicity of water quality in three deep, temperate, oligotrophic lakes

Abstract

The objective of this study was to test for patterns of temporal coherence in three deep oligotrophic lakes in a region with similar catchment geology, trophic state and morphometry. Variables measured in the upper 1 m and bottom 2 m of the lakes, or variables calculated from depth profiles, as well as water level, were included in the coherence analysis. The directly measured variables included temperature, dissolved oxygen, nutrients and chlorophyll *a*, and the calculated variables were depths of the thermocline, deep chlorophyll maximum and euphotic zone, as well as Schmidt stability. Temporal coherence was calculated for each of variable using Pearson correlation coefficient values after LOESS decomposition. The average temporal coherence for the lake pairs was high (r=0.65) indicating that the variability in most variables is not lake-specific, but instead responds strongly to regional climate. Surface variables were more coherent than those at depth. Physical variables were more coherent than chemical variables and the variables derived from the depth profiles were less coherent than the directly measured variables. Our results indicate the strong influence of regional climate on physical variables in particular, which propagates into progressively reducing influence on chemical and biological variables. The effects of climate will be progressively filtered from physical to chemical and biological variables, and coherence analysis may provide a tool to tease apart the relative influence of climate change on these variables.

5.1 Introduction

Lake dynamics and responses to anthropogenic pressures are critically dependent on the balance of external forcing factors such as climate and the quantity and quality of inflows, as well as intrinsic factors such as internal nutrient loading and trophic structure (Schindler 2009). Climate variables such as wind, precipitation, air temperature, and solar radiation are components of the extrinsic climate forcing that affects lake dynamics (Diaz 2001, Arhonditsis et al. 2004, and Williamson et al. 2008). Within a defined area climate exerts a largely uniform, dominant control on limnological variables of lakes (Shimoda et al. 2011, Luoto and Nevalainen 2013, Palmer et al. 2014), except where intrinsic factors such as internal nutrient cycling or biotic interactions dominate (Magnuson et al. 1990). Under these conditions inter-annual variations due to climate are likely to be dampened (Magnuson et al. 1990, Modenutti et al. 2013, Lottig et al. 2014) and relationships to external forcing factors will be weaker.

Climate can influence lake dynamics on intra- and inter-annual timescales, and impact biogeochemical fluxes, water residence times and hydrological pathways (Schindler 2009, Bouwman et al. 2013). Climate change is predicted to influence lake ecosystems through modification of trophic state, hydrology and temperature (Rosenzweig et al. 2007, O'Reilly et al. 2015). It is also expected to increase climate variability and may be associated with an increased frequency of El Niño events (Urban et al. 2000). A critical challenge to water quality management is therefore to understand how these climatic changes induce departures from lake reference conditions, and thus impact upon setting targets for managing water quality and trophic status of lakes.

The degree to which lakes in a defined region have similar temporal responses to external forcing factors has been described as temporal coherence or lake synchrony (Magnuson et al. 1990). It is typically measured as the correlation between concurrent time series of a measured variable in lake pairs (Baines et al. 2000, Magnuson et al. 2006). Correlation coefficients are usually calculated using annual or seasonal mean values for each variable within a lake-by-year matrix. Temporal coherence provides an alternate means of assessing the role of extrinsic factors such as climate change and other regional drivers, such as acid rain, on lake dynamics. Coherence is expected to be greatest when the climate signal has marked inter-annual variation but limited spatial variation (Kling et al. 2000, Lenters et al. 2005). It also varies with mechanisms that link limnological variables to climate, the number of nested processes affecting the dynamics of the variable of interest, and the sensitivity of the variable to locally unique conditions (Kratz et al. 1998). Near-perfect coherence can therefore be attained in proximal lakes which respond directly to external forcing factors (Folster et al. 2005). However, different properties of a catchment, including soils, vegetation, local weather and hydrology, and intrinsic factors such as lake morphology, water residence time and trophic status, combine to alter or reduce the amplitude of the climate signal in lakes, thereby reducing coherence (Palmer et al. 2014). Lakes with greatest synchrony in a landscape will therefore be expected to have similar catchment type, trophic state and morphometry.

Coherence has been used as a means to identify the influence of climate change on lake ecosystems (Straile 2000, Seebens et al. 2007, Straile et al. 2007, Ghanbari and Bravo 2008). However, attributing high coherence to climate change or variability alone is often problematic because of the additional influence of regional drivers (Baines et al. 2000, Hessen et al. 2009). To account for these confounding factors, de-trending or high-pass filtering methods have been used to constrain the influence of climate variability (George et al. 2000, Blenckner et al. 2007, Seebens et al. 2007, Weyhenmeyer et al. 2007).

We contend that lakes of similar origin and with minimal human disturbance may provide valuable proxies for the influence of climate variability, and hence, climate change, on lakes. New Zealand lakes have been minimally affected by atmospheric contaminants (e.g., nitrogen, sulphur and heavy metal deposition) (Holden and Clarkson 1986, Pearson et al. 2010) that affect the trophic status and condition of lakes in the Northern Hemisphere, where most studies on reference conditions have been focused. Subsets of some New Zealand lakes, with common origins have also been minimally impacted by human land use activities (Newnham et al. 1998). These lakes may therefore serve as ideal model systems for understanding the influence of climate on lake dynamics in a contemporary context rather than using specific lakes which are benchmarked to a pre-anthropogenic era.

Most of the research on coherence has tended to focus on a small number of lake variables amongst a large array of lakes positioned within a region or between regions (Livingstone and Dokulil 2001, Anneville et al. 2002, Livingstone 2003, Dokulil et al. 2006), leading to potential for over-generalization of the external controls on lakes. Furthermore, inferences on the coherence between lakes in a landscape typically depend on the variables that are analysed. For instance, physical variables such as surface temperature and ice-out dates have been reported to be highly synchronous (Kratz et al. 1998, Benson et al. 2000, Livingstone 2008), whereas biological and chemical variables are less synchronous (Webster et al. 2000). Furthermore, thermally mediated variables such as thermocline depth have been shown to exhibit only moderate synchrony within lake districts (Kratz et al. 1998, Benson et al. 2000). The combination of physical, chemical and biological variables, as well as derived variables such as thermocline depth, is most likely to provide an integrated assessment of the extrinsic factors that control lake dynamics.

In this study we focus on three deep oligotrophic lakes in the same region and of common volcanic origin, with similar soil type and hydrology, which may be considered reference lakes. Large, deep lakes provide an exceptional resource for studying the interaction between the atmosphere, land surface, hydrology, and aquatic ecosystem responses (Williamson et al. 2008). Their large volume can be expected to integrate the complexities of short-term variability in local climate, increasing the ability to interpret the effects of global climate change on lake processes. In this study, we elucidate the influence of climate on a large number of lake variables in order to predict the regional effects of climate variability. Six directly-measured variables (chlorophyll *a*, dissolved inorganic nitrogen (DIN), dissolved reactive phosphorus (DRP), dissolved oxygen (DO), water temperature (T) and water level (LL) and four derived variables (deep chlorophyll maximum depth (DCM), thermocline depth (Epi), euphotic zone depth (Zeu) and Schmidt stability (St)) were used for the coherence analysis. The chosen variables not only represent a mix of physical, biological and chemical variables, but also include ecologically important proxies that can also be expected to be influenced by climate in different ways. For the three lakes we used an 11-year data set to determine the rate of monthly and/or seasonal cycling for the chosen variables, and the synchronicity of long-term and seasonal trends amongst variables and lakes

5.2 Methods

5.2.1 Description of study sites

The three lakes in this study are located in the central North Island of New Zealand (Fig. 5.1) in a region known as the Okataina Volcanic Caldera (OVC). Some characteristics of the lakes and land use in their catchment are summarised in Table 1. The lakes are monomictic and thermally stratify for 9-10 months of the year and mix during winter (July-August). They are deep but vary in their morphometry and hydrology. Lake Okataina has a smaller hypolimnion to epilimnion volume ratio than lakes Tarawera and Rotoma (Jolly and Chapman 1977). The soils in the catchment of the three lakes have a high content of light pumice originating from the Kaharoa and Tarawera eruptions of AD1314 and 1886, respectively (Lloyd 1959). Lake Tarawera receives water from seven other lakes in the OVC while water discharge to Lake Okataina is reported to occur through sub-surface seepage via porous pumice, and Lake Rotoma is fed by streams and springs (McColl 1972). Lake Tarawera drains into the Tarawera River but Okataina and Rotoma have no known surface outlets. They drain underground, at an annual discharge rate reported to average 7% of the lake volume (McColl 1972). Water level fluctuations in lakes Okataina and Rotoma have been linked to fault lines in their basin inducing periodic rapid water losses, and complicate the interpretation of seasonal patterns in water level (Clayton et al. 1981).

Table 5.1 Characteristics of the three lakes and their catchment, culled from (McColl, 1977; Scholes & Bloxham, 2007)

					Catchment land-use		
Lake	Lake area (km^2)	Maximum depth (m)	Trophic state	Catchment size (km^2)	Indigenous forest (%)	Pasture (%)	Exotic forest (%)
Okataina	10.8	78.5	Oligotrophic	62.9	84.1	10.7	5.2
Rotoma	11.1	83.0	Oligotrophic	28.1	46	23.4	26.7
Tarawera	41.3	87.5	Oligotrophic	145.2	62.4	19.7	16.0

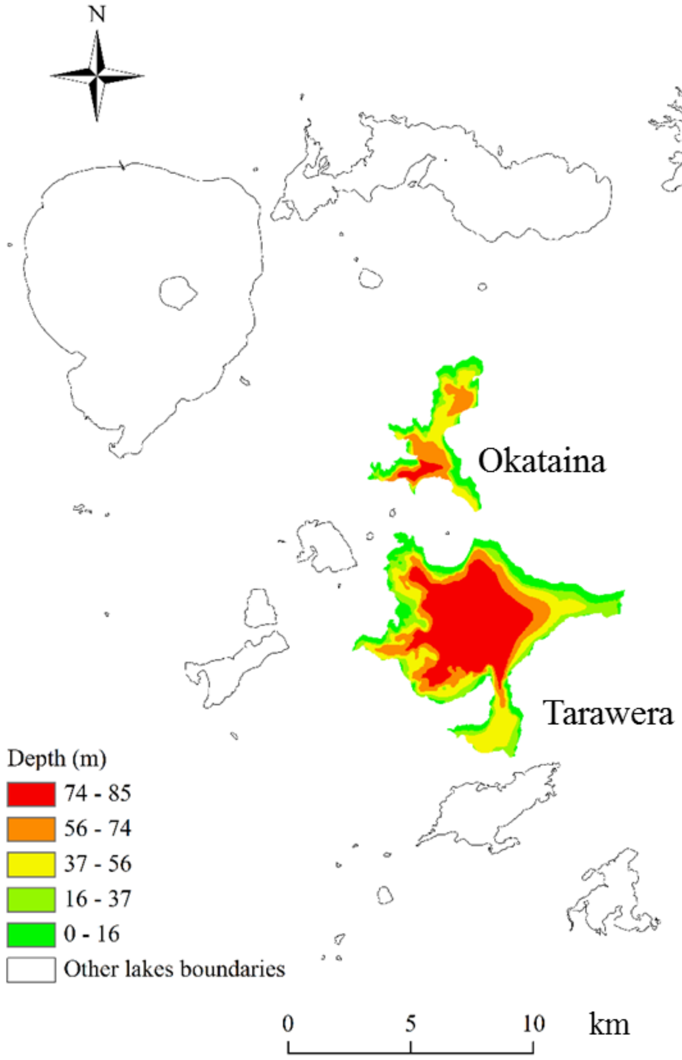

Figure 5.1 Bathymetric map of Lakes Okataina, Rotoma and Tarawera with depth contours mapped by colours. Locations are shown relative to other lakes of the Rotorua region.

5.2.2 *Sampling and data analysis*

Sampling was carried out monthly in the lakes at a central station, from 2002 to 2013 (11- years). Water samples were collected with an integrated tube from a central station in each lake for subsequent analysis of chlorophyll *a* and nutrient concentrations. Known volumes of sample water were syringe-filtered (0.45 µm GF/C), and filters and water samples were then placed on ice in the dark before freezing on return to the laboratory later the same day. Thawed water samples were analysed with a Lachat QuickChem® Flow Injection Analyser (FIA+ 8000 Series, Zellweger Analytics, Inc.) for ammonium (NH_4-N), dissolved reactive phosphorus

(DRP) and oxidized nitrogen species (NO_X-N, NO_2-N) (Lachat QuickChem® Methods 10-107-06-2-C, 10-115-01-1-A and 10-107-04-1-A, respectively). Concentrations of NO_3-N were determined by subtracting NO_2-N from NO_X-N. Chlorophyll *a* concentrations were determined spectrofluorometrically following thawing of filters and pigment extraction in 90% acetone. Samples were then acidified to correct for phaeopigments (Arar and Collins 1997).

Water column profiles of temperature and dissolved oxygen were taken with a Sea-Bird Electronics 19 plus SEACAT Profiler (CTD; Sea-Bird Electronics Inc., Washington, USA) and additional mounted sensors for down-welling broadband photosynthetically active radiation [E_d(PAR)] (Licor Inc., Nebraska, USA) and chlorophyll fluorescence (Chelsea Instruments Ltd, Surrey, UK). The depth of the thermocline was determined from the minimum (i.e. negative) value of the temperature (T) depth gradient, dT/dz where z is water depth defined positive downward from the temperature profile. Chlorophyll fluorescence data in each profile were normalised to values between 0 and 1 based on assigning a value of 1 to the maximum value in the depth profile. This method avoided attempting to compare fluorescence values across different dates. The depth of the DCM was where there was a normalised chlorophyll fluorescence value of 1 at least 15 m below the surface, taking care that effects of surface non-photochemical quenching did not create an artificial DCM (Hamilton et al. 2010). Euphotic depth was calculated as the depth where PAR was 1% of the upper sub-surface value. Schmidt stability was calculated from the water temperature profile using the lake analysis tool *rlakeanalyser* (Winslow et al. 2015).

5.2.3 Seasonal and inter-annual variability

Monthly mean values of directly-measured variables (chlorophyll *a*, DIN, DRP, DO, water temperature and water level) and the derived variables (Schmidt stability, thermocline depth, euphotic depth and DCM depth) were calculated for the whole 11-year period and for the four individual seasons over the 11 years. Seasons in this paper refer to austral seasons defined as summer (December-February), autumn (March-May), winter (June-August) and spring (September-November). Directly measured variables were divided into surface and bottom samples (except water level and chlorophyll *a*). Surface/epilimnetic variables were taken as the monthly mean (over the 11-year cycle) of the upper 1 m of water column while bottom/hypolimnetic variables were from the last 2 m of the water column.

To constrain our study to climate, long-term trends, seasonal and residual fluctuations in all directly-measured and derived variables were determined using seasonal and trend decomposition based on loess fit to the data (STL) (Cleveland and Grosse 1991). The seasonal cycle which represents the climate component of the variable, was used in the coherence analysis. The non-parametric seasonal Kendall and Mann-Kendall tests (Hirsch and Slack 1984), which account for serial correlation, were used to determine the significance in the rate of change of each parameter per year (α=0.05). All statistical analysis was done using R version 3.1.3 (R Development Core Team 2013). The R *forecast* package was used for STL (de Livera et al. 2011) and the R *Kendall* package was used to test the significance of the trends (McLeod 2005).

5.2.4 Temporal coherence analysis

We adopted the method of Kratz et al. (1998) to determine temporal coherence. Pearson product-moment correlations for each decomposed variable (long-term and individual seasons) were calculated for all lake pairs. For the 11-year decomposed data, long-term coherence was calculated as the average of all the correlation values for the lake pairs. To compare coherence for each variable between the lake pairs, the mean correlation of the variable of choice in the lake pairs was taken. We followed Kratz et al. (1998) in interpreting strong coherence to be $r \geq 0.5$ and weak coherence $r<0.5$.

5.1 Results

5.1.1 Seasonal dynamics in directly measured lake metrics

The epilimnetic temperature followed a predictable seasonal pattern in the three lakes (Fig. 5.2) whereas hypolimnetic temperatures varied little (Fig. 5.3). The monthly maximum was about 22.2 °C in February and the minimum about 10.1 °C in August (late winter). Between February (late summer) and July, the monthly mean epilimnetic temperature in Lakes Rotoma (red line) and Tarawera (blue line) were almost identical and slightly less (~0.1 °C) than the temperature in Lake Okataina (black line). However, between August and December, the epilimnetic temperature in Lake Rotoma was about 1 and 2 °C higher than in Tarawera and

Okataina respectively. In the bottom waters (Fig. 5.3), the mean monthly temperature in Lakes Rotoma and Okataina reached an annual maximum of 11.2 °C in May (i.e., at the end of autumn) while a maximum of 11.4 °C was recorded for Lake Tarawera. The lowest mean temperature recorded in the bottom of all three lakes occurred in August.

Little seasonality of DRP was apparent, and concentrations were higher in Tarawera than in the other two lakes throughout most of the year. The highest mean monthly concentration of DRP in the epilimnion was recorded in Lake Tarawera (7.83 µg/l) followed by Lake Okataina (3.81 µg/l) and Lake Rotoma (2.77 µg/l). On a monthly basis, two peaks of 13.2 and 13.8 µg/l were recorded in July and September, respectively, for Lake Tarawera while the monthly peak of 3.1 µg/l occurred in June in Lake Rotoma. In Lake Okataina, DRP was around 4 µg/l from January to March and again from July to August. Mean annual DRP concentrations in the bottom waters were 15.4 µg/l in Lake Tarawera, 5.64 µg/l in Lake Okataina and 3.41 µg/l in Lake Rotoma. The highest monthly mean concentration in Lake Tarawera was 23.8 µg/l and the lowest was 9 µg/l in both May and August. The maximum of the monthly mean DRP in Lake Okataina was 9.9 µg/l in March and the minimum was 3.4 µg/l in September. In Lake Rotoma, the maximum of the monthly mean concentration was 5 µg/l in January and the minimum was 2.82 µg/l in May and November.

Monthly mean concentrations of DIN showed seasonal variation in all three lakes, especially in the hypolimnion (Fig. 5.2-5.3). A peak of 14.8 µg/l occurred in June and July for Lakes Tarawera and Rotoma, respectively. In Lake Okataina, a peak of 14.8 µg/l persisted through the months of May, June and July. The lowest monthly mean DIN values occurred in November in Lakes Tarawera and Rotoma, and in both April and September in Lake Okataina. In the bottom waters of the lakes, the highest monthly mean DIN concentrations were 46.1 µg/l in Lake Tarawera in May, 40.2 µg/l in Lake Rotoma in May and 34.7 µg/l in Lake Okataina in March. The corresponding lowest mean values were 4.86 µg/l in August in Lake Tarawera, 9.36 µg/l in September in Lake Rotoma and 6.36 µg/l in September in Lake Okataina.

The mean epilimnetic DO concentration in the three lakes rose steadily from January and peaked in either August or October in all three lakes. The highest monthly mean concentrations were 9.7 mg/l in Lake Okataina, 9.7 mg/l in Lake Rotoma and 9.7 mg/l in Lake Tarawera and the lowest were 8.6, 8.5 and 8.4 mg/l in Lakes Okataina, Rotoma and Tarawera, respectively. Concentrations of DO remained elevated from January through May in Lake Tarawera, at a time when concentrations in Lake Okataina were low compared with other times of the year in that lake. The highest monthly mean concentrations in bottom waters occurred in August and were 9.4 mg/l in Lake Okataina, 9.7 mg/l in Lake Rotoma and 9.7 mg/l in Lake Tarawera, and the lowest were 0.6 mg/l in May in Lake Okataina, 6.1 mg/l in April in Lake Rotoma and 3.9 mg/l in May in Lake Tarawera.

Monthly mean concentrations of chlorophyll *a* in the epilimnion were consistently higher in Okataina than in the other two lakes. Maxima occurred in August (late winter) in Lakes Okataina (4.0 µg/l) and Rotoma (2.2 µg/l) and in Lake Tarawera the lowest concentration (0.8 µg/l) occurred in November.

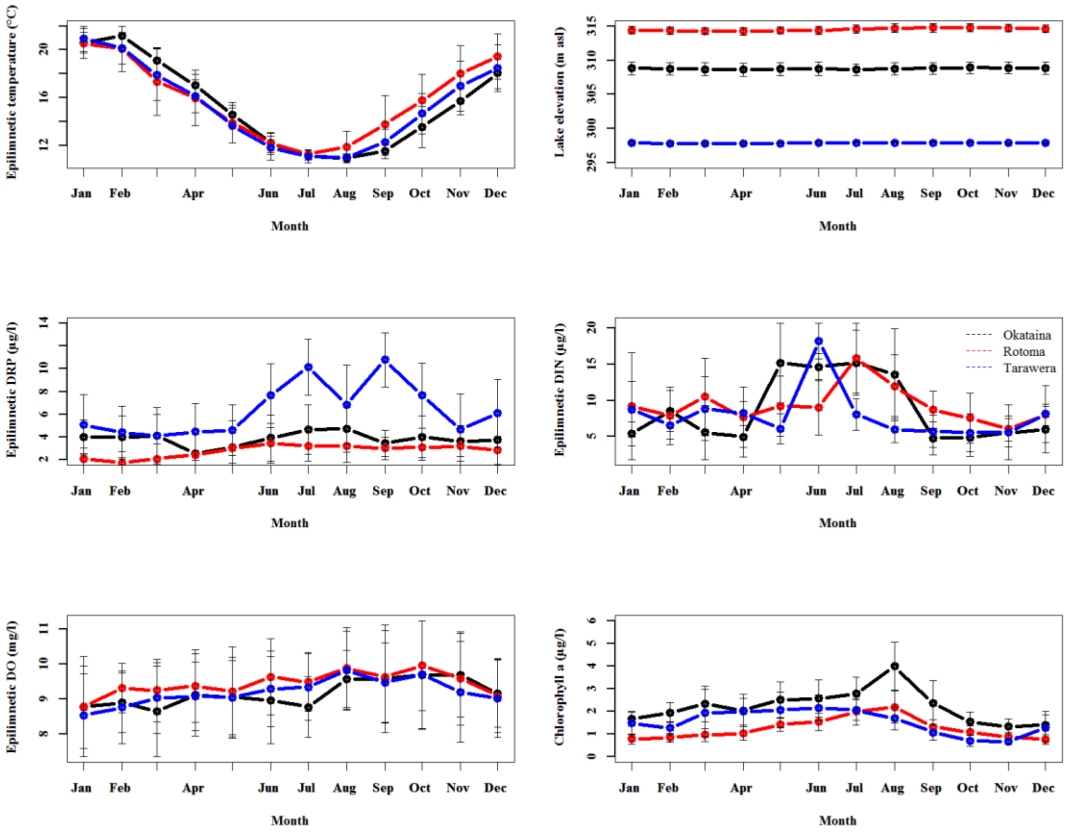

Figure 5.2 Annual mean (2003-2013) values of temperature, DRP, DIN, DO and chlorophyll a in the upper 1 m of the water column in the three study lakes

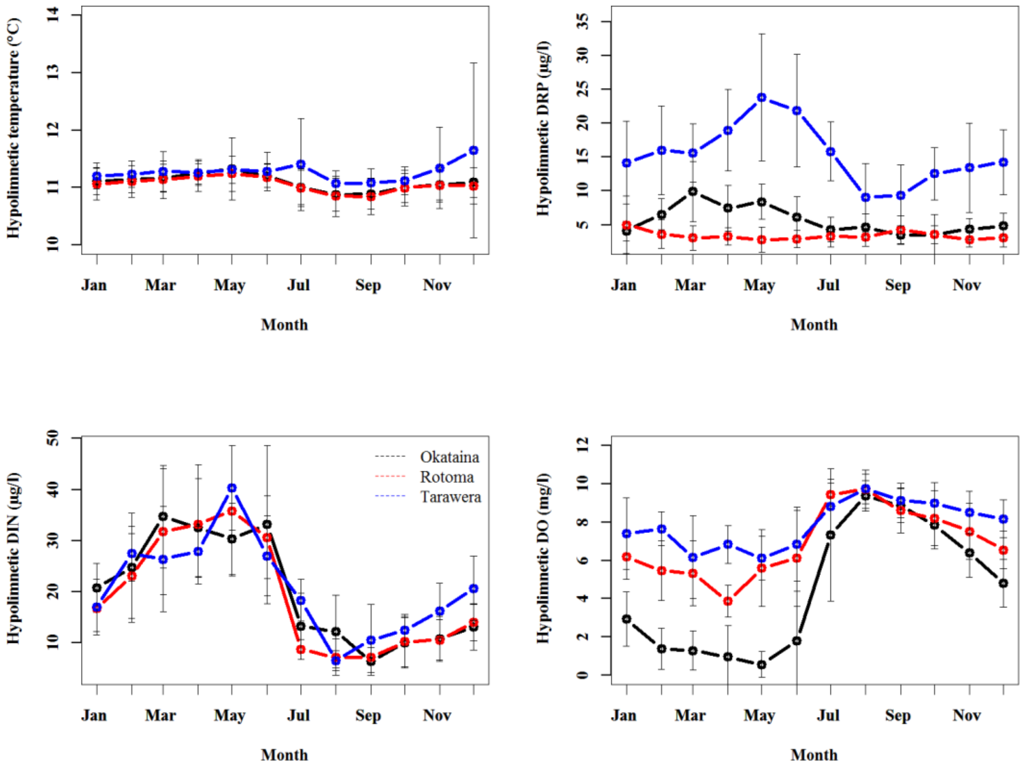

Figure 5.3 Annual mean (2003-2013) values of temperature, DRP, DIN and DO in the bottom 2 m of the water column in the three study lakes

5.1.2 Month-by-month changes in lake variables

Little difference existed in the monthly rate of change in water temperature in the three lakes (Fig 5.4). The change in surface water temperature was about ±1.5 °C/month except between March and June when it decreased to about 0.8 °C/month. However, the error bars (standard deviation) show there was considerable inter-annual variability (~2.0 °C/month). The monthly mean change in the bottom temperature was about ±0.1 °C/month in all of the lakes.

Fluctuations in monthly mean water level in all three lakes were generally small (< 0.01 m/month). However, between June and August, water level increased by about 0.2 m/month in Lakes Rotoma and Okataina, with large standard deviations of water level (0.62 m/month and 0.75 m/month, respectively).

The monthly rate of change of chlorophyll *a* in Lakes Okataina and Rotoma was similar but differed slightly from that of Lake Tarawera. The change in chlorophyll *a* was mostly around ±0.1 µg/l/month in Lake Rotoma except in August when the range was up to around ±1 µg/l/month. In Lake Okataina, the monthly mean rate fluctuated between ±0.1 and 0.4 µg/l/month until July when it increased to ±1 µg/l/month and reached ±2 µg/l/month in August after which it returned to the ±0.1 to 0.4 µg/l/month range. The mean monthly change in chlorophyll *a* concentration in Lake Tarawera was about ±0.1 µg/l/month throughout the year except between February and March when it reached ±0.6 µg/l/month.

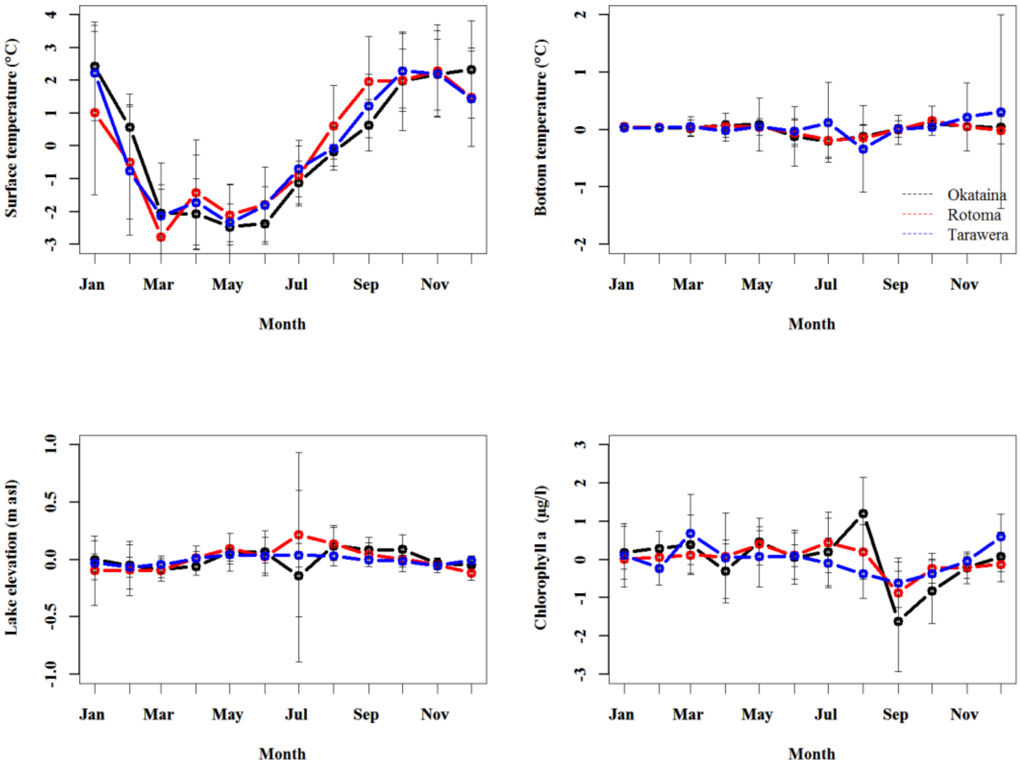

Figure 5.4 Monthly mean rate of change (2003-2013) in values of surface water temperature, water level and chlorophyll *a* of the three study lakes. Error bars are the standard deviations of the mean.

5.1.3 *Seasonal and monthly dynamics in derived lake metrics*

The lakes were stratified between January and June and fully mixed (taken to be a vertical temperature gradient < 0.1 °C) for about one month between July and

August. Temperatures in winters of 2004, 2008 and 2009 were relatively cold (<10 °C throughout the water column) (Fig. 5.5).

There was a clear seasonal pattern in the chlorophyll fluorescence of the lakes, with a water column maximum in the austral winter and a mid-column peak for much of the remainder of the year when the lakes were thermally stratified (Fig. 5.5). This mid-column peak (a 'deep chlorophyll maximum') (DCM) was closely associated with the thermocline depth (Fig. 5.6). Mean DCM depth was 25 m in Lake Okataina, 28 m in Lake Rotoma and 22 m in Lake Tarawera.

There was an austral winter low (July and August) in the euphotic depth of the three lakes (Fig. 5.7), then a fairly long period (c. 6 months) of progressive increase in clarity in all three lakes. There was high interannual variability in euphotic depth, indicated by the wide error bars in the monthly means.

Schmidt stability values indicated Lake Tarawera was the most thermally stable and Lake Okataina was the least stable. The lakes were most stable in either January or February (i.e., the end of summer), with Lake Okataina reaching a peak Schmidt stability of 4000 J/m^2, Lake Rotoma 4800 J/m^2 and Lake Tarawera 6,500 J/m^2. The mean Schmidt stability in July was similar (500 J/m^2) in all three lakes. The standard deviation was high (c. 500 J/m^2) in all three lakes outside of the austral winter when values of Schmidt stability values were very low.

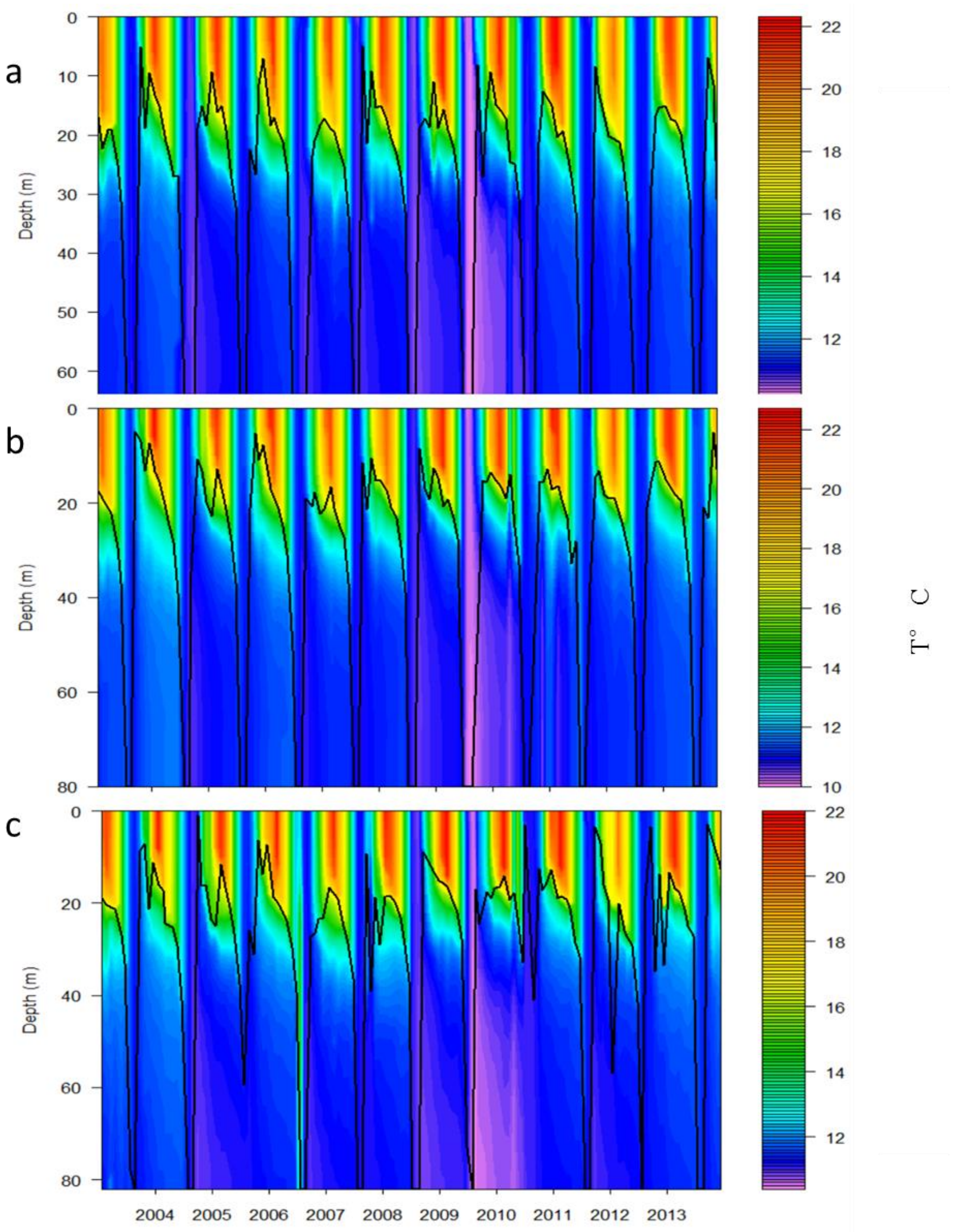

Figure 5.5 Heat maps of depth and time distributions of temperature in (a) Lake Okataina (b) Lake Rotoma and (c) Lake Tarawera from January 2003 to December 2013. The dark line represents the thermocline depth.

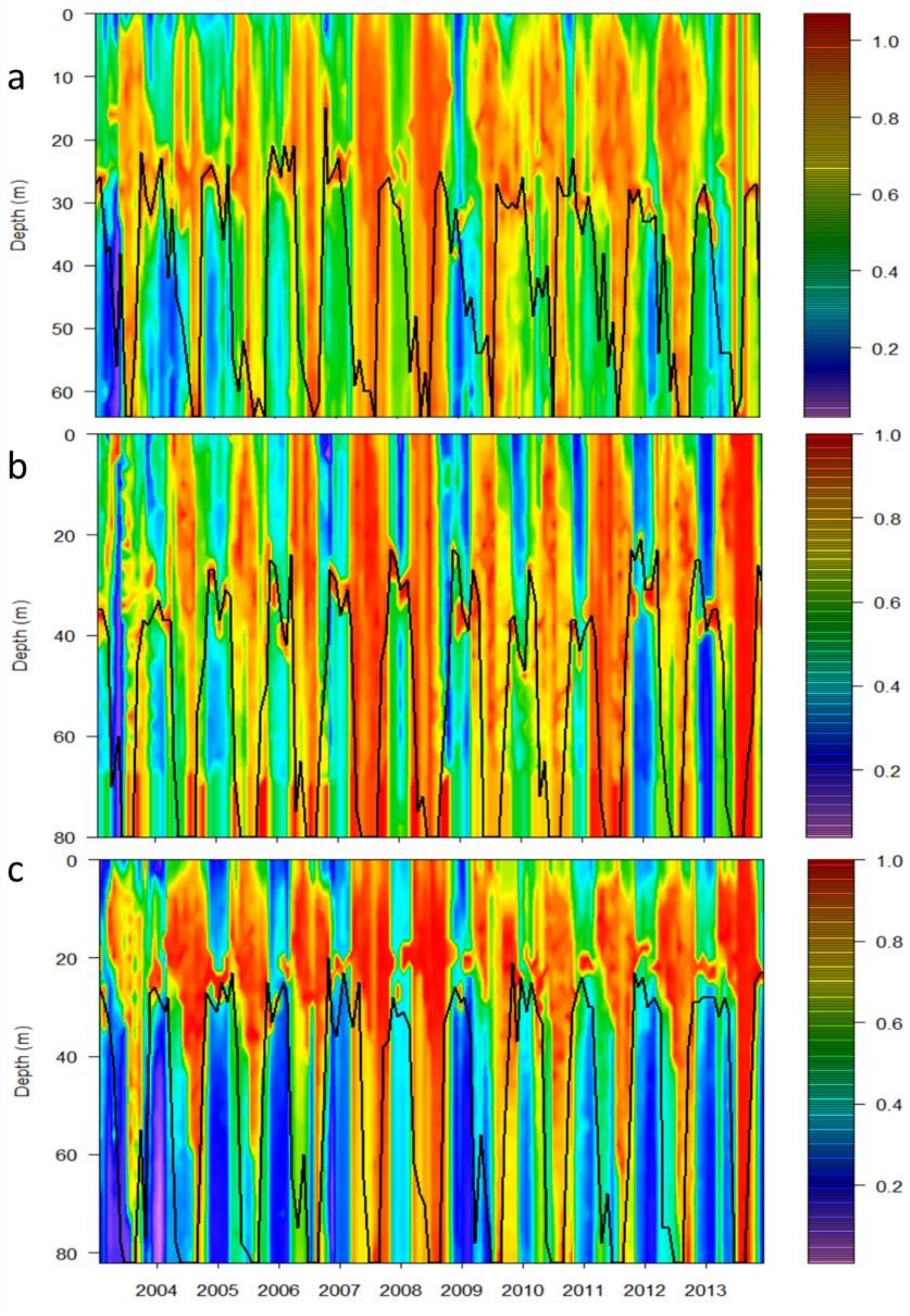

Figure 5.6 Heat maps of depth and time distributions of chlorophyll fluorescence in (a) Lake Okataina, (b) Lake Rotoma and (c) Lake Tarawera from January 2003 to December 2013. The dark line represents the DCM depth

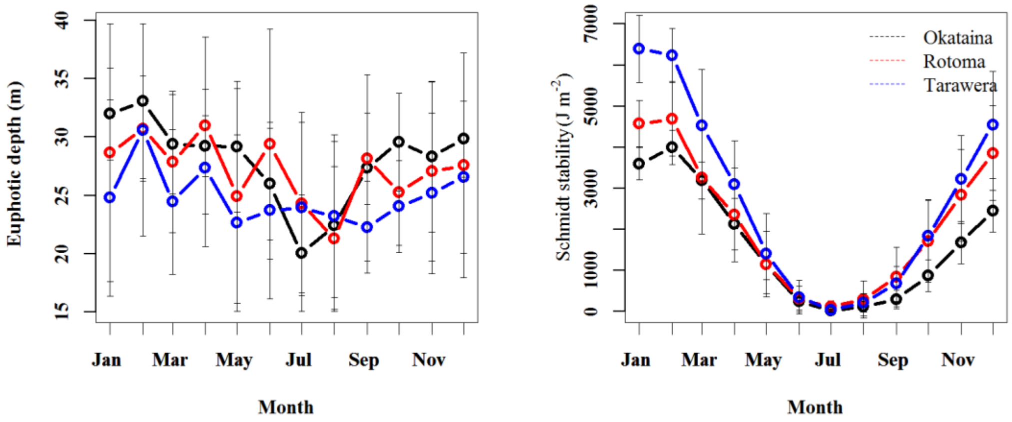

Figure 5.7 Monthly mean (2003-2013) euphotic zone depth and Schmidt stability of the three study lakes.

5.1.4 Synchrony in decomposed long-term and seasonal trends

Measurements in surface waters of the three lakes were generally more synchronous than corresponding measurements in the bottom waters for the corresponding variable (Table 5.2). For example, temperature, DO, DIN and DRP in surface waters had r values of 0.98, 0.97, 0.64 and 0.56, respectively, compared to 0.90, 0.62, 0.40 and 0.23 for bottom waters. Most derived variables were more strongly synchronous, with r values of 0.90 for Schmidt stability, 0.65 for epilimnion depth and 0.64 for DCM depth. Chlorophyll *a* and lake heights were also strongly coherent (r=0.51 and 0.76). The only exception, with weak coherence, was euphotic depth (r=0.34).

Averaged synchrony (2003-2013) was higher across the long-term (inter-annual) decomposed variables (r=0.65) compared to specific seasons of summer (r=0.52), autumn (0.45), winter (0.47) and spring (0.48). The coherence between the lake pairs was similar: Okataina–Rotoma and Okataina–Tarawera were 0.66 and Rotoma–Tarawera was 0.64 (Table 5.3).

The coherence in the individual variables per lake pair is summarised in Table 5.4. The coherence between the lake pairs Okataina-Rotoma and Okataina-Tarawera was generally slightly higher than coherence in the lake pair Rotoma-Tarawera. However, coherence in the depth at which DCM is formed, surface and bottom DIN, and euphotic depth, were more coherent in the lake pair Rotoma-Tarawera.

Table 5.2 Temporal coherence of the three lakes (as mean Pearson correlation coefficient values) of the long-term and seasonal data (2003-2013) of the directly measured and derived variables.

	Period				
Variable	Long-term	Summer	Autumn	Winter	Spring
Chlorophyll *a*	0.51	0.25	0.37	0.14	0.68
Deep chlorophyll maxima (depth)	0.64	0.54	0.23		0.25
Surface dissolved inorganic nitrogen	0.61	0.52	0.22	0.51	0.21
Bottom dissolved inorganic nitrogen	0.40	0.35	0.21	0.67	0.44
Surface dissolved reactive phosphorus	0.56	0.41	0.37	0.32	0.38
Bottom dissolved reactive phosphorus	0.23	0.16	0.15	0.12	0.15
Surface dissolved oxygen	0.97	0.78	0.72	0.73	0.74
Bottom dissolved oxygen	0.62	0.53	0.51	0.56	0.56
Euphotic zone depth	0.34	0.44	0.21	0.18	0.09
Thermocline depth	0.65	0.58	0.53	0.42	0.47
Surface water temperature	0.98	0.71	0.72	0.75	0.76
Bottom water temperature	0.90	0.76	0.71	0.58	0.74
Schmidt stability	0.90	0.65	0.70	0.72	0.69
Water level	0.76	0.68	0.58	0.41	0.59
Mean coherence	0.65	0.52	0.45	0.47	0.48

Table 5.3 Temporal coherence between the lake pairs (as mean Pearson correlation coefficient values) of the long-term and seasonal data (2003-2013).

Period					
Lake pairs	Long-term	Summer	Autumn	Winter	Spring
Okataina vs Rotoma	0.66	0.55	0.48	0.59	0.52
Okataina vs Tarawera	0.66	0.54	0.45	0.43	0.47
Rotoma vs Tarawera	0.64	0.53	0.42	0.40	0.44
Mean	0.65	0.53	0.45	0.47	0.48

Table 5.4 Temporal coherence between the lake pairs for the long-term (2003-2013) data for the directly measured and derived variables.

	Lake Pairs		
Variable	Okataina vs Rotoma	Okataina vs Tarawera	Rotoma vs Tarawera
Chlorophyll *a*	0.63	0.37	0.32
Deep chlorophyll maxima	0.78	0.59	0.55
Surface dissolved inorganic nitrogen	0.55	0.63	0.66
Bottom dissolved inorganic nitrogen	0.31	0.43	0.45
Surface dissolved reactive phosphorus	0.65	0.78	0.25
Bottom dissolved reactive phosphorus	0.20	0.27	0.21
Surface dissolved oxygen	0.99	0.96	0.96
Bottom dissolved oxygen	0.51	0.64	0.7
Surface water temperature	0.98	0.98	0.98
Bottom water temperature	0.98	0.89	0.84
Thermocline depth	0.65	0.58	0.73
Euphotic depth	0.35	0.18	0.48
Schmidt stability	0.87	0.92	0.92
Water level	0.77	0.79	0.72

5.2 Discussion

The lakes in our study were selected to have similar catchment, hydrological and morphological properties, thereby providing an opportunity to better quantify responses to climate variability. The relatively high coherence (r =0.65) between lake pairs and all lake variables suggests that the three lakes respond strongly to regional drivers. Climate induced synchronicity impacts on lake quality and management through nested feedback processes. Increases in temperature and changes in precipitation alter thermal regimes and hydrology, which propagate through to changes in chemical and biological processes. The sensitivity of the responses to regional climate drivers observed in this study can also be related to the similarities of trophic state, hydrological pathways, catchment soils and land use amongst the lakes. Differences in catchment soils, vegetation and hydrology, and intrinsic factors such as lake morphology, water residence time, and trophic status, combine to alter or reduce the amplitude of the climate signal, thereby reducing coherence amongst lakes (Palmer et al. 2014). Climate driven synchronicity is expected to be more apparent in lake pairs with minimal altitudinal difference (Kratz et al. 1998). The three lakes in this study have a difference in altitude <100 m.

Climate change, which will affect hydrological cycles, can be expected to also cause a shift in the rates and quantity of delivery of sediment and nutrients to the lakes, thereby altering biogeochemical processes and possibly the trophic status of the lakes. Climate change is also likely to be associated with increased frequency of ENSO (Urban et al. 2000). The high coherence exhibited by our chosen variables makes them good proxies or sentinels for climate change (Williamson et al. 2008). The criteria for choosing variables and lakes for climate change studies is largely dependent on their level of coherence, ease of measurement and ecosystem functions (Adrian et al. 2009).

Coherence is known to vary with mechanisms that link limnological variables to climate, the number of nested processes affecting the dynamics of the variable of interest, and the sensitivity of the variable to locally unique conditions (Kratz et al. 1998). As expected from studies from Europe (e.g., Weyhenmeyer 2008) and North America (e.g., Kratz et al. 1998), the physical variables in my study were more coherent than the chemical and biological variables. If coherence of physical variables only was considered, the mean coherence would have been 0.90, considerably larger than the value of 0.65 recorded for all variables in this study. The coherence in the physical variables measured in the bottom of the lakes were generally substantially higher than coherence in the chemical variables in both the surface and the bottom of the lakes, suggesting that physical variables in lakes are more sensitive the effects of climate than chemical variables. The high coherence detected in the depth derived variables (Schmidt stability, thermocline depth and deep chlorophyll maxima) might be because their calculation and annual cycle is closely tied to water temperature. The lack of a direct relationship between water temperature and euphotic depth might have accounted for the low coherence in this variable.

The high coherence (r=0.98) in surface water temperature recorded in this study is comparable to that reported in studies elsewhere (e.g., George et al. 2000). High coherence was also observed in thermocline depth and Schmidt stability in the three study lakes and provides evidence that changes in climate will impact not only surface water temperature but also mixing and stratification dynamics, as well as thermocline depth. Surface water temperature responds directly to climate forcing and has been shown to be highly correlated with atmospheric temperature (O’Reilly et al. 2003). Hence recent studies have shown a general trend of warming in lakes across the globe in response to warming air temperature, but with greater consistency of response for lakes within specific regions or latitudinal bands (Sharma et al. 2015, O’Reilly et al. 2016). The strength of regional climatic drivers on lake dynamics is reinforced in the current study by the strong coherence of each of the physical variables amongst the lakes.

Temporal coherence values for epilimnetic DIN (0.61) and DRP (0.56) between the three study lakes can be considered to be elevated relative to other studies (e.g., George et al 2000). The relatively high coherence might be related to the similarity in the sources of the nutrients. Nutrient concentrations in lakes are related to mineral weathering rates and soil nutrient concentrations, which are influenced by the amount and intensity of precipitation and the resultant run-off (Wilhelm and Adrian 2008). The catchments of the three lakes are predominantly forested and the soils are loose pumice. Furthermore there are marked changes in the nutrient composition of runoff which occur with transition of forested to pastoral areas in this region (Dons 1987). The relatively high percentage of catchment land under indigenous forestry (Table 5.1) might have accounted for the high coherence in the dissolved nutrients.

Internal processes associated with thermal gradients and/or primary productivity, can also account for altered nutrient concentration in lakes (Bergström and Jansson 2006, Boisvenue and Running 2006). The monthly cycling of the dissolved nutrients in the study lakes followed the thermal gradients observed in the lakes and therefore could account for the relatively high coherence in the dissolved nutrients. The level of coherence might however, be affected by the differences in the concentration of oxygen in the lakes during thermal stratification. Whereas the concentration of DO in the bottom of Lake Okataina is completely depleted during thermal stratification, the concentration in both Lakes Tarawera and Rotoma get reduced but not depleted. Elevated dissolved nutrient concentrations occur when DO concentrations reduced in the bottom of the lakes reduce hence this differences could be a source of reduction in the coherence of the nutrients. The high coherence in the DIN between the lake pairs was unexpected but the limited literature on nutrient coherence suggests that nitrogen species are generally more coherent than phosphorus species (George et al. 2000, Kling et al. 2000, and Webster et al. 2000); a pattern also observed in the three study lakes.

Compared to temporal coherence values for chlorophyll *a* in lakes from other regions around the globe, our value (r=0.51, Table 1) for surface waters in the three lakes is high. For example, Kratz et al. (1998) reported r=0.07 coherence for summer chlorophyll *a* in Wisconsin lakes and George et al. (2000) reported r=0.15 for lakes in the English Lake District. Chlorophyll *a* and algal biomass tend to be most temporally coherent in lakes with clearly defined seasonal patterns (Kasprzak et al. 2000); an observation in this study too.

A potential source of dampening in the coherence values for chlorophyll *a* could related to different seasonal patterns of phytoplankton succession and dominance amongst the lakes. Chlorophyll *a* was highly coherent between Lakes Okataina and Rotoma but average between Okataina and Tarawera or Rotoma and Tarawera. Lakes Okataina and Rotoma exhibit similar seasonal patterns of relatively low concentrations of chlorophyll *a* between January and July but a peak in August and a decline again in September. This pattern differed in Lake Tarawera where there was no distinct peak but slightly elevated concentrations though the months of March to July. These differences are likely to be related to the dominant phytoplankton groups found in each lakes. The phytoplankton community in Lakes Okataina and Rotoma is dominated by Bacillariophyta and Chlorophyta while Lake Tarawera has more Chrysophyta and Cyanoprokaryota (Paul et al. 2012). In discussing the seasonal succession of phytoplankton groups of some the lakes in the Central North Island of New Zealand, Vincent (1983) indicated that Bacillariophyta are abundant in the winter and spring while Chrysophyta and Cyanoprokaryota become increasingly dominant in summer and autumn. Dominant phytoplankton species in lakes were found to impinge on the coherence of chlorophyll *a* in the three Gorges reservoir in China (Xu et al., 2009)

Changes in thermal regimes also affect the distribution of nutrients and dissolved oxygen concentrations as well and the vertical distribution of organisms in the three lakes. The depth at which the DCM formed was highly coherent, implying that climate change and its variability influence the depth distribution of phytoplankton in the studied lakes. Several studies have established relationships between the depth of the DCM and thermocline depth (e.g. Hamilton et al., 2010). Hamilton et al (2010) also found the dominant phytoplankton group in the DCM of Lakes Tarawera and Rotoma was diatom, which could account for the high coherence in the depth at which the DCM formed although organisms associated with the DCM in Lake Okataina have not been studied.

Lake management plans are mainly lake specific and targeted at predictable variables that degrade water quality. However, the existence of coherence in many of the variables studied for the three lakes showed that lakes would respond to changes in climate. Temporal variability in lakes variables would therefore not be only an index of catchment factors only but also climate variability.

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6 General discussion and recommendations

6.1 Overview

The current debate on climate change and anthropogenic impacts on lake ecosystems, and the concomitant demand for lake management policies, have increased the need for knowledge of long-term changes in lakes and their catchments, *vis-à-vis* natural variability. Using a suite of statistical techniques, this study has contributed knowledge of how lake ecosystems change as a consequence of volcanic eruptions and invasive mammals, with the latter being a "new normal" in most New Zealand catchments. The remainder of this chapter discusses the main findings of each research chapter.

6.2 Erosion and climate variability as drivers of primary productivity in Lake Okataina

This study represents the first use of Structural Equation Modelling (SEM) to quantify the relative importance of climate variability and erosion in altering the lake primary productivity. SEM has wide use in ecology, for example to understand how the effects of mineral soil properties on understorey plant species richness are propagated through a network of processes involving the forest canopy, soil organic matter, soil nitrogen, and understory plant abundance (Laughlin et al. 2007). In limnology, Arhonditsis et al. (2006) compared the efficacy of SEM to Bayesian analysis in delineating the role of abiotic conditions and biological interactions in regulating phytoplankton dynamics and water clarity during the summer-stratified period in Lakes Washington and Mendota, USA.

In this study, the modelling supported theory in demonstrating that catchment disturbance and both direct and indirect effects of climate variability have important influences on primary productivity, with erosion the most important but itself also substantially influenced by climate variability. Catchment erosion serves as a medium to transfer nutrients to lakes and is therefore an indirect trigger for increased primary production in lakes (Fraterrigo and Downing 2008). Increased catchment erosion has also been shown to increase primary productivity of small lakes on the Alaskan tundra-taiga boundary (Medeiros et al. 2014) and the eutrophication of the Alexander Lake in the South Island of New Zealand has been linked to high rates of sediment erosion after the clearance of the forest in the catchment around 1950. On the other hand very high levels of mineral turbidity can reduce primary productivity when they decrease euphotic depth in artificial lakes with high rates of through-flow (Jones and Knowles 1995).

Soil erosion in catchments worldwide is becoming one of the most significant geomorphic processes acting at the Earth's surface (Pimentel 2006) and therefore constitutes a threat to lake ecosystems across the globe. Increased rates of erosion can be associated with altered frequency and intensity of precipitation (Boardman and Poesen 2006), and deforestation, grazing and cultivation (Augustsson et al. 2013). Natural catchment disturbances such as earthquakes, volcanic activities and wildfires can yield areal rates of sediment erosion that are comparable to those associated with anthropogenic forest clearance (Owens et al. 2010). Compared with other countries, sediment erosion rates in New Zealand are very high, with about 200 x 10^6 t y^{-1} of sediment delivered to the ocean (Hicks et al. 2011). Steep slopes, high rates of seismicity and volcanism, high rainfall and high-intensity rainstorms contribute to high rates of erosion, and these factors can be related to a high-energy geomorphic environment from New Zealand's location at an active plate boundary in the mid-latitude zone where there are strong westerly winds (Basher 2013). With this study showing erosion being linked to primary productivity of a large lake, it follows that factors that trigger erosion could serve as underlying causes of changes in algal production in lakes. Naturally high rates of erosion in many New Zealand catchments have also been accelerated in the last century as a result of converting large areas of forest to pastures for grazing (Glade 2003). In addition to increased erosion from pastures, large amounts of nitrogen and phosphorus have been added to the soil (Scott et al. 2015) and also increase the risk of eutrophication of lakes. Nutrient exports from pastures have been found to account for the eutrophication of most New Zealand lakes (Abell et al. 2011).

Lakes are used as climate change sentinels because they are sensitive to temperature changes and good integrators of catchment properties and climate forcing (Adrian et al. 2009). Eutrophication in lakes is generally expected to increase with climate warming (Moss et al. 2011). Climate controls the thermal and hydrologic budgets in lakes, thereby influencing the biogeochemistry and biota of the water column (Fritz and Anderson 2013). Mixing regimes in lakes, which strongly affect the vertical distribution of nutrients and primary productivity in lakes, depend primarily on wind conditions and air temperature. In New Zealand, downscaled general circulation models indicate that global climate change is expected to result in increased El Niño-like weather conditions, with an estimated 3.5 °C increase in atmospheric temperature by 2100 (Salinger et al. 2001). This would result in dominance by westerly and south-westerly winds and less precipitation in the Central North Island of New Zealand. The increased temperature could be expected to result in longer periods of thermal stratification, while at the same time higher intensity westerly winds may counter this effect (Hamilton et al. 2013). If the net effect is an increase in the duration and intensity of stratification, then there may be increased duration of anoxia in bottom waters, which has the potential to increase inputs of nutrients to hypolimnetic waters from bottom sediments, ultimately leading to increased primary productivity.

New Zealand is mountainous, with 60% of the land being above 300 m elevation and 70% having a slope of between 12 and 25°, but little is known about the temporal trends in erosion rate (Basher 2013). Because of this natural predisposition of exposure of lakes to erosion, land use change has increased potential to lead to an eutrophication. Furthermore the effects of climate change and erosion on lakes may act synergistically, as demonstrated in this study. Increasing temperatures and more intense storms expected to accompany climate change will also accelerate mineralization of nutrients from catchment soils and increase soil erosion (Jones and Brett 2014). Whereas catchment disturbance can be managed, lake managers have no control over climate. Erosion management from lake catchments might therefore be an effective tool in managing eutrophication of lakes.

6.3 Sediment phosphorus speciation and pigment composition to infer historical lake phytoplankton phenology

This chapter explored the impact of catchment disturbance as a consequence of two volcanic eruptions, introductions of invasive mammals, and climate on the speciation of phosphorus and algal pigments in a sediment core retrieved from Lake Okataina. The length of the core encompassed the period between AD 1314 ± 12 and 2009. Sequentially extracted phosphorus species (Homyak et al. 2014) and algal pigments (Waters et al. 2005) in the sediment have previously been used in isolation in various sedimentary biogeochemical studies to understand changes in reference conditions, but have never been coupled to understand how changes in phosphorus species impact phytoplankton dynamics of lakes. Hitherto, total phosphorus (TP) extracted from lake sediments was coupled with total carotenoids (TC) to understand phytoplankton biomass response to total phosphorus dynamics (Guilizzoni et al. 1983) or spectrometrically-determined TC used to hindcast historical concentrations of TP in lakes (Guilizzoni et al. 2011). The results of this PhD study can be used to infer ecological shifts in the primary producer community structure as a consequence of changes in the total phosphorus pool. Shifts in phytoplankton diversity are likely to have important and profound consequences for ecosystem structure and functioning (Levin et al. 2001). A major consequence of phytoplankton species loss in lakes may be a change in, or loss of, important ecosystem processes (Naeem and Wright 2003), hence understanding how historical changes in nutrient cycling in lakes impact biodiversity of the primary producer pool of lakes is important in developing current and future management tools.

Nutrient availability, amongst other factors, accounts for shifts in primary producer communities in lakes (Jeppesen et al. 2003). The relative proliferation of different algal groups depends strongly on the amount of bioavailable phosphorus in lakes. Releases from lake sediments contribute to this phosphorus pool and depend on the different forms of phosphorus present in the sediments and physicochemical properties at the sediment-water interface (Ruban et al. 2001). Source material (i.e., phosphorus from the lake catchment; Bouwman et al. 2013), in addition to physical, chemical and biological processes in the water column, determine the phosphorus species that deposit to the lake bottom (Kerr et al. 2011).

Based on the sediment core from Lake Okataina, different species of phosphorus dominated when there were specific events in the catchment that altered the composition of soil pools of phosphorus. For example, phosphorus species associated with permanent burial (i.e., Ca-P and Al-P) were prevalent after the Kaharoa and Tarawera eruptions of AD 1314±12 and 1886, respectively. The eruptions were pyroclastic and high in Al and Si minerals (Parfitt 1990, Pickrill et al. 1991). Oxides of Al such as gibbsite $Al(OH)_3$ bind phosphorus strongly and only release it when the ambient pH exceeds the point of zero charge, often above neutral (Gächter and Müller 2003). Phosphorus bound to Ca is also associated with weathered terrestrial soils and high fluxes to lake sediments are likely to be related to erosion of these soils. After the eruptions, the rate of erosion may have increased as a consequence of the destruction of catchment vegetation (Clarkson and Clarkson 1983) which acted to bind and protect soils in the catchment. The core stratigraphy showed that phosphorus species changed markedly around 1900, from those associated with permanent burial (i.e., Ca-P and Al-P) to potentially bioavailable species (labile P and Fe-P). This period coincides with when invasive mammals were first introduced into the catchment. Large animal populations in catchments have been known to contribute to nutrient loading to lakes through trampling and vegetation destruction that lead to increased rates of erosion. For example, increases in nutrient loading to some New Zealand lakes and rivers have been attributed to forest understory removal and soil trampling by deer (McDowell and Paton 2004). The period of increasing potentially bioavailable phosphorus also coincided with the introduction of rainbow trout into the lake. Rainbow trout have been reported elsewhere to remove top herbivorous zooplankton and macroinvertebrates, resulting in a shift towards less efficient grazers and enhanced nutrient cycling which together promote higher algal productivity (Knapp et al. 2001, Parker and Schindler 2006).

In the sediment core of Lake Okataina, which represented a period of ~700 years, diatoms were dominant in the water column between 1314 and early 1800, but cyanobacteria and green algae appeared to become increasingly prominent in recent times (last 200 years) when potentially available phosphorus species dominated. Nonmetric multidimensional scaling (NMDS) and general linear modelling (GLM) of sedimentary phosphorus species and algal pigments extracted from the sediment core showed strong statistical relationships of cyanobacteria and green algae to labile and iron bound phosphorus, while pigments representative of diatoms were strongly related to aluminium and calcium bound phosphorus. The increasing dominance of cyanobacteria and green algae as invasive mammals increased in the lake catchment may be relevant to future lake management. A precautionary approach would suggest that mammal populations should be reduced and managed to reduce eutrophication-like changes in algal biomass and species composition in Lake Okataina.

Climate change could also be a potential driver of the switch to green algae and cyanobacteria. Air temperature in New Zealand has increased by 1.5 °C in the last

200 years (Cook et al. 2002). Green algae and cyanobacteria may be favoured by such increases in temperature (Jones and Brett 2014) and cyanobacteria have a number of pysiological adaptations that mean that they are selectively advantaged by temperature increases. With projected acceleration of atmospheric warming (IPCC, 2007), green algae and cyanobacteria may increasingly dominate the phytoplankton assemblage and measures to control external nutrient loads (e.g., control of invasive mammals) may become increasingly important.

6.4 Changes in water quality and invasive mammal populations in the catchment of Lake Okataina

To decipher the impact of invasive mammals and volcanic eruptions, this chapter was focused on the last ~170-year period of deposited sediments sampled from a core in the deep basin of the lake; a period that encompassed the Tarawera eruption of 1886 and the introduction of invasive mammals a few years after the eruption. Inorganic and organic geochemical proxies in the sediment core were used to determine changes in the source of organic matter to the lake, its phosphorus retention capacity, and changes in redox and primary productivity. Inorganic geochemical proxies in lake sediments are important tools in identifying historic catchment disturbance and its concomitant impact of various components of lake water quality. For example, Burden et al. (1986) used the elements Na, Mg, Ba, Al, Ti and Dy to identify erosion signals in lake sediments as a consequence of deforestation in Awenda Provincial Park, in Ontario, Canada. Tribovillard et al. (2006) have reviewed the use of trace metals as paleoredox and paleoproductivity proxies in lake sediments and found Ni and Cu to be good proxies of primary productivity, while V, Mo and U enrichment are good archives for paleoredox. Organic proxies such as total organic carbon, total nitrogen and their isotopic signatures have also been used to identify events in catchment and changes in lake water quality (Meyers 1997, Bragée et al. 2013).

Major disturbances in lake catchments result in higher than normal water column sedimentation rates which may not necessarily return to baseline conditions prior to the disturbance (Cohen 2003). A pulsed increase in erosion in the catchment of Lake Okataina was indicated by increased fluxes of Ti and Zr to lake sediments after the Tarawera eruption of 1886. Fluxes decreased over the following 20 to 30 years but did not return to levels prior to the eruption. Moreover, erosion fluxes have undergone a gradual but sustained increase in the last ~80 years, likely due to increased populations of deer, wallabies and possums. Subsequently, proxies for redox potential suggest a reduction in bottom-water oxygenation. Increased erosion and sedimentation rates have been linked to anoxia in the hypolimnion of lakes elsewhere (Loh et al. 2013). While catchment erosion appears to have increased over the past century, the sediment core composition indicates that the dominant source of organic matter input to lake sediments (indicated by concentrations of TOC, TN, $\delta^{13}C$, $\delta^{15}N$, and TOC/TN ratios) is associated with phytoplankton, except for the period just after the Tarawera eruption.

The ability of the lake to retain phosphorus in bottom sediments, indicated by Al:Fe and Al:P ratios, weakened in the last ~50 years, possibly due to increasing organic carbon deposition to bottom sediments and higher rates of mineralisation. These conditions predispose lakes to increased internal phosphorus loading (Gächter and Müller 2003). Interestingly, the reduction in phosphorus retention capacity occurred a few decades after the initial increase in erosion flux to the lake c 1900.

After 1960, there appeared to be a substantial increase in primary productivity (indicated by increases in $\delta^{13}C$, Ni, Cu through the core stratigraphy), which may have been related to reduced bottom-water oxygenation and sediment phosphorus retention capacity, and greater internal phosphorus loading.

6.5 Climate-driven synchronicity of water quality in three deep, temperate, oligotrophic lakes

This chapter shifted the focus from the role of catchment disturbance to that of climate in influencing the natural variability of three large lakes in the Rotorua region. The three lakes, Okataina, Rotoma and Tarawera, have similar lake to catchment area ratios, land use and hydrological connectivity, and are located in the Okataina Volcanic Caldera (OVC). Fluctuations in limnological variables were analysed to determine the synchronicity of responses of the lakes to climate. Recent studies have shown that limnological variables of lakes within a defined geographical area show similar patterns in response to regional forcing factors, mainly climate; a phenomenon referred to as synchrony (Kratz et al. 1998) or temporal coherence (Magnuson et al. 1990). Temporal coherence is therefore an effective tool to identify the role of climate in shifting baselines of limnological parameters in lakes over time (Ghanbari and Bravo 2008). Attributing synchronous responses to climate alone can be problematic, because of other regional drivers, such as atmospheric deposition of nutrients or acid rain. In New Zealand, however, there are low rates of atmospheric deposition of nutrients or acid rain (Holden and Clarkson 1986, Pearson et al. 2010). Furthermore the three lakes in this study had similar catchment soils, vegetation and hydrology, as well as intrinsic factors such as morphology, water residence time, and trophic status, leading to an expectation of high levels of coherence (Palmer et al. 2014). LOESS detrending was also used to remove low frequency fluctuations in the time series data. Other studies have used detrending (George et al. 2000, Seebens et al. 2007), or high-pass filters (Weyhenmeyer et al. 2007) to remove regional factors that may confound evaluation of synchronicity due to climate forcing.

The high temporal coherence of the three lakes in this study reflects their similar morphometry and catchment land use and soils. Climate has a tendency to synchronise seasonal and interannual cycles in physical (Baines et al. 2000), chemical (Pham et al. 2008) and biological (Yan et al. 2008) variables in proximal lakes. It tends to be relatively uniform over large geographical areas (Dröscher et al. 2009). The high levels of temporal coherence recorded in the three lakes of this study have long term implications for the water quality of the lakes. With anticipated global warming, it is expected that the baselines of most limnological variables in lakes will change due to their sensitivity to climate, as shown in this study. Climate is the main factor which regulates physical, chemical and biological processes in lakes over long time periods in the absence of pervasive human influences (Hughes 2000). Temperature and Schmidt stability were the variables most strongly related to atmospheric temperature hence global warming could impact the timing and duration of phytoplankton blooms and nutrient cycling in the lakes.

6.6 Overarching Perspectives

The aim of this study was to identify the causes of temporal variability in a range of limnological variables in a largely undisturbed lake. Inorganic and organic geochemical archives were examined from a sediment core extracted from the deep central basin of the lake. Using tephrochronology and ^{210}Pb dating, it was determined that the length of the core encompassed the period AD1314 ±12 to 2009

(~700 years). To complement the information extracted from the core, an eleven year monthly monitoring dataset was also analysed to understand the role of climate in the contemporary variability of the lake ecosystem. Volcanic eruptions, invasive mammals and climate were identified as the main drivers of change in the natural baseline of many of the limnological variables. Volcanic eruptions represent a pulse disturbance while invasive mammals and climate can be regarded as pressure disturbances. The effects of the volcanic eruption on the lake were found to be transmitted mostly through catchment disturbance. The eruption delivered mostly refractory organic matter from the catchment to the lake, and also increased fluxes of minerals from the catchment. Based on erosion and organic matter cycling, it was inferred that this effect was relatively short-lived (~ 25 years). Although the eruptions started as a pulse disturbance, they triggered a series of processes in the catchment that served as pressured disturbances. The processes triggered by the eruptions likely created lag effects which fed into the processes induced by the introduction of mammals. The synergistic effect of the pulse and pressure disturbance resulted in the sustained increased loading of OM and sediment to the lake. Volcanic eruptions and the presence of invasive mammals were also found to have accounted for changes in the phosphorus pool in the lake sediment. This change appeared to be associated with alterations to the composition of phytoplankton groups in the lake. The combined effect of eruptions and invasive mammals in the catchment was shown in the study to have contributed to increased erosion into the lake. Related to the increased erosion rates are contemporary (within three or four decades from present) reductions in dissolved oxygen in bottom waters and increased internal loading of phosphorus. The marked increase in primary productivity in Lake Okataina about 1960 followed the reduction in hypolimnetic oxygen and the onset of reduced capacity of bottom sediments to retain phosphorus.

The effects on lake productivity of climate and invasive mammals have been shown to be pervasive in this study. These mammals are the “new normal” in many New Zealand catchments. Their role as conduits for transfer of soil and nutrients from catchments to lakes has been demonstrated. To manage lakes effectively in New Zealand under the NPS-FM, will require that stressors are identified and removed or managed. Identifying, enumerating and managing invasive mammals in the catchment of lakes could reduce the rate of transfer of sediment and nutrients to lakes, thereby maintaining the integrity of these ecosystems. The direct impact of climate on lakes cannot be managed but its indirect effects on catchment erosion and landslides that accompany rainstorms may at least by partly mitigated through careful management and planting of riparian areas, slope stabilization and wise choices about the suitability of different land uses.

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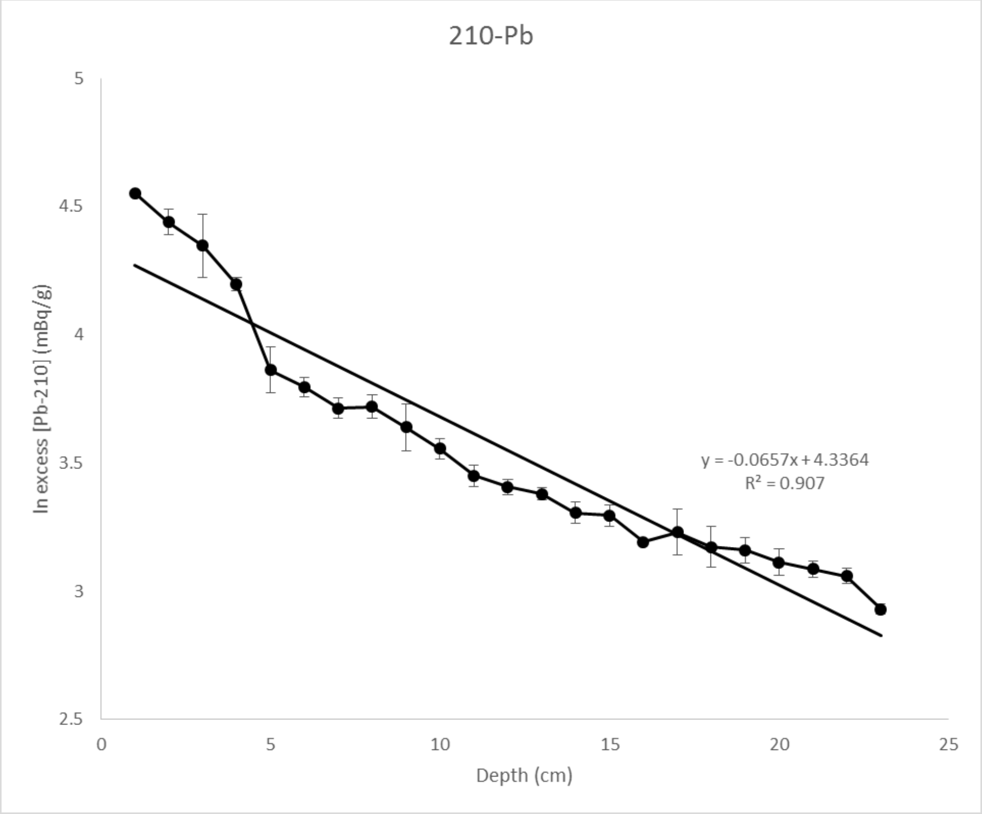
Appendices

Appendix 1



Unsupported ^{210}Pb activity concentration *versus* layer depth from the core (sedimentation rate: 0.15 cm y^{-1}).

Appendix 2

Flux (mg m^{-2} yr^{-1}) of sedimentary algal pigment and phosphorus species used in Chapter 3 of the thesis

Year	Can	Myx	Allo	Dia	Lut	Chlb	LA-P	Fe-P	Al-P	Ca-P	Re-P	Org-P
2009	27.12377	10.25739	0.92944	4.064598	19.73178	37.89303	0.044762	0.272423	0.108055	0.004749	0.678326	0.073938
1995	26.8189	11.23844	0.999643	3.642832	19.31097	37.98921	0.042681	0.270244	0.111344	0.015303	0.631959	0.110723
1969	20.03464	6.046383	1.066965	4.273857	17.40434	51.17381	0.039408	0.265047	0.131947	0.007963	0.648226	0.089662
1944	14.53206	8.141283	1.427856	5.646293	13.44689	66.80561	0.033254	0.27376	0.138745	0.010097	0.663454	0.062943
1930	18.39179	12.20786	1.641644	7.462018	19.12217	51.17452	0.028931	0.268935	0.215932	0.018074	0.538647	0.111735
1918	15.23155	6.678726	5.24602	33.28509	22.09841	27.4602	0.020938	0.131031	0.218583	0.047763	0.617883	0.146056
1909	15.35906	8.434331	11.7487	23.08517	18.60005	32.77269	0.026114	0.202203	0.247716	0.162418	0.435946	0.107857
1902	15.42475	15.55855	12.44684	14.52132	11.65854	40.39	0.024248	0.113973	0.454407	0.085383	0.309738	0.194504
1896	12.67391	14.88406	16.97305	8.042615	15.28097	42.14539	0.017425	0.103489	0.479562	0.021735	0.445624	0.114418
1886	16.22318	2.452483	3.985285	7.97057	22.46475	46.90374	0.022342	0.188682	0.576972	0.031336	0.24051	0.122411
1851	23.6458	1.447702	0	8.203643	19.72494	46.97792	0.031887	0.16993	0.491782	0.082784	0.311148	0.094722
1838	10.50101	0.421727	3.584683	50.4386	3.550945	31.50304	0.021336	0.173392	0.56061	0.057902	0.256676	0.112338
1828	3.118104	0.959417	1.199271	53.34357	5.228821	36.15082	0.031738	0.216552	0.499749	0.011939	0.275902	0.146375
1812	3.32989	1.571165	1.712515	75.83995	7.556812	9.989671	0.015406	0.090173	0.605684	0.052318	0.251702	0.16697
1792	2.870749	0.851834	2.84392	74.31753	10.46348	8.652492	0.017417	0.095379	0.596702	0.022069	0.341742	0.108945
1777	2.434054	0.135854	1.52836	84.90886	3.656742	7.336126	0.00934	0.094443	0.524815	0.069637	0.377356	0.106663
1754	2.711263	0	0	84.75865	2.875966	9.654124	0.013949	0.096162	0.533916	0.041091	0.400025	0.09711
1725	3.149002	0.691244	3.072197	74.50077	8.678955	9.907834	0.012537	0.07864	0.535357	0.07864	0.361491	0.115589
1700	2.693952	0	2.020464	84.05647	4.196348	7.032768	0.01227	0.110443	0.663783	0.034634	0.263978	0.097146
1677	2.846452	0.307363	1.804089	73.76721	8.445811	12.82908	0.006321	0.061529	0.362933	0.330609	0.359333	0.061529
1661	3.520747	0.377223	1.760374	83.52793	4.023711	6.790013	0.022141	0.106419	0.576644	0.134136	0.236494	0.106419

Year	Can	Myx	Allo	Dia	Lut	Chlb	LA-P	Fe-P	Al-P	Re-P	Ca-P	Org-P
1647	3.957161	0.199673	2.886186	84.40733	1.361409	7.188237	0.018351	0.090054	0.59775	0.147235	0.238808	0.090054
1635	3.209913	0.373246	1.866229	82.11406	1.866229	10.57032	0.019767	0.089435	0.58026	0.144311	0.259044	0.089435
1629	3.756643	0.769654	2.253986	85.21165	1.246106	6.761957	0.008333	0.083187	0.473776	0.225327	0.308444	0.083187
1609	2.894955	0.248139	1.964433	75.4756	3.908189	15.50868	0.013416	0.096177	0.680178	0.10799	0.188315	0.096177
1587	4.433391	0.454152	0.540657	78.93599	0	15.63581	0.024212	0.096645	0.531446	0.221515	0.21179	0.096645
1575	5.498193	0.387197	1.935983	68.40475	8.286009	15.48787	0.017733	0.089971	0.501312	0.111049	0.372217	0.089971
1562	2.433351	0.375738	0.250492	83.19914	1.395598	12.34568	0.016905	0.095012	0.429616	0.355318	0.19039	0.095012
1552	2.978339	0.252708	0.234657	87.54513	2.220217	6.768953	0.017076	0.077538	0.494131	0.180126	0.335844	0.077538
1546	5.263158	0.344319	0.29513	89.76881	2.484014	1.844565	0.016165	0.093138	0.427378	0.241582	0.310851	0.093138
1538	4.269944	0.708186	0.520725	86.44032	1.624662	6.436159	0.012928	0.161925	0.583312	0.059783	0.202381	0.161925
1527	4.981378	0.488827	0.349162	77.74674	1.419926	15.01397	0.01175	0.140052	0.44698	0.195064	0.248355	0.140052
1505	3.423849	0	2.213695	66.41086	3.689492	24.2621	0.018767	0.070605	0.567783	0.138521	0.315971	0.070605
1484	6.597549	1.178134	1.508011	60.32045	1.696513	28.69934	0.013163	0.122374	0.449288	0.260463	0.214593	0.122374
1477	4.346302	0	0.350508	82.36944	1.577287	11.35647	0.016601	0.046769	0.390781	0.280641	0.400693	0.046769
1469	3.360791	3.294893	0.494234	70.8402	0.757825	21.25206	0.012943	0.097928	0.451905	0.308986	0.212565	0.097928
1458	8.727429	0.902837	0.515907	70.93723	1.504729	17.41187	0.026353	0.069277	0.530557	0.048995	0.437794	0.069277
1445	5.328597	1.065719	0.577265	64.38721	0	28.64121	0.018952	0.075403	0.526772	0.131774	0.35395	0.075403
1425	9.858551	0	0.557222	62.15174	6.215174	21.21732	0.014053	0.067513	0.595907	0.062584	0.374683	0.067513
1405	12.7401	0.823207	0.470404	64.68052	6.468052	14.81772	0.017809	0.164521	0.572518	0.162364	0.100521	0.164521
1384	1.691094	0	0.563698	64.82525	5.016911	27.90304	0.021369	0.080392	0.566094	0.074238	0.359769	0.080392
1354	1.160991	1.160991	0.928793	65.01548	2.47678	29.25697	0.014587	0.105998	0.487722	0.280134	0.187815	0.105998
1330	0.578035	1.867497	0	84.48199	4.001779	9.070698	0.020526	0.051401	0.313163	0.242028	0.503734	0.051401
1314	5.596802	0	0.571102	74.24329	2.113078	17.47573	0.028374	0.050992	0.352507	0.299327	0.400062	0.050992

Appendix 3

Flux (mg m^{-2} yr^{-1}) of organic and inorganic proxies used in Chapter 4 of the thesis

Year	Ti	Zr	V	Mo	U	Ni	Cu	Al:Fe	Al:P	RR	C	N	ratio	15N	13C
2009	2.70	4.69	2.30	3.33	1.14	1.59	1.78	11.69	30.66	0.08	3.74	0.53	7.08	8.21	-25.79
2007	2.62	4.68	2.39	3.30	1.18	1.45	1.79	11.68	30.74	0.05	3.64	0.53	6.88	8.21	-25.98
2004	2.60	4.58	2.02	3.41	1.05	1.47	1.69	11.56	31.65	0.03	3.89	0.43	9.03	8.22	-26.29
1987	2.59	4.44	2.36	3.37	1.08	1.59	1.68	14.37	30.31	0.04	3.76	0.47	8.02	8.27	-26.40
1985	2.66	4.49	2.23	3.48	0.98	1.42	1.74	14.94	36.71	-0.81	3.74	0.41	9.08	8.28	-26.16
1983	2.51	3.48	2.24	3.44	0.97	1.34	1.83	15.81	34.55	-0.52	3.25	0.34	9.43	8.22	-26.16
1981	2.33	3.40	2.22	4.32	0.96	1.44	1.72	14.92	37.82	-0.91	3.70	0.39	9.56	8.31	-26.20
1974	2.48	3.28	2.09	3.53	0.90	1.36	1.75	14.20	35.18	-0.14	3.55	0.51	6.94	8.08	-28.09
1967	2.48	3.36	2.12	3.97	1.05	1.84	1.77	13.30	35.67	-0.26	3.99	0.62	6.45	8.65	-28.78
1962	5.47	3.29	2.18	3.42	1.07	1.83	1.08	14.36	35.67	-0.62	3.97	0.65	6.13	8.49	-28.46
1959	5.43	3.20	2.28	3.45	0.92	1.62	0.51	14.15	35.64	-0.81	3.70	0.59	6.30	8.45	-28.38
1954	4.40	3.14	2.11	3.37	0.94	0.92	0.75	14.08	37.99	-0.08	3.79	0.51	7.40	8.78	-28.95
1948	4.87	3.29	1.99	2.02	1.01	0.84	0.66	14.39	34.14	-0.86	3.51	0.52	6.81	8.94	-28.95
1944	3.54	2.19	1.32	2.01	0.85	0.84	0.60	16.60	31.73	-0.75	3.10	0.45	6.95	8.37	-28.43
1940	3.60	1.65	1.10	2.06	0.94	0.82	0.67	16.33	35.08	-0.64	2.25	0.45	5.05	7.41	-28.95
1934	3.54	1.57	1.34	2.07	0.83	0.92	0.59	14.20	31.29	-1.06	2.49	0.40	6.24	8.36	-28.01
1930	3.36	1.50	1.20	1.90	0.73	0.97	0.77	14.43	29.88	-0.88	1.85	0.30	6.20	7.04	-29.06
1928	3.43	1.42	1.28	1.83	0.81	0.98	0.60	16.78	41.22	-0.95	0.91	0.27	3.38	7.49	-28.06
1924	3.10	7.19	1.26	1.95	0.79	0.85	0.63	15.27	42.95	-0.82	1.05	0.28	3.75	0.67	-28.95

Year	Ti	Zr	V	Mo	U	Ni	Cu	Al:Fe	Al:P	RR	C	N	ratio	15N	13C
1906	3.12	7.38	1.29	1.94	0.71	0.78	0.8	16.04	53.63	-0.46	1.21	0.23	5.14	0.35	-27.98
1909	3	7.08	0.9	1.9	0.64	0.88	0.78	18.69	58.49	-1.88	0.37	0.1	3.75	0.66	-29.26
1902	3.09	7.14	0.94	1.96	0.68	0.73	0.66	17.15	57.63	-1.7	3.59	0.5	7.16	0.51	-28.43
1896	3.06	7.29	0.97	1.98	0.69	0.88	0.64	16.05	56.45	-1.64	3.53	0.27	12.94	0.61	-28.37
1864	1.6	1.69	0.85	1.84	0.57	0.48	0.5	16	56.63	-1.86	0.33	0.1	3.34	0.26	-28.36
1858	1.59	1.68	0.74	1.8	0.55	0.48	0.58	16.69	57.49	-1.88	0.31	0.08	3.93	0.21	-28.35
1844	1.66	1.58	0.74	1.86	0.56	0.43	0.46	16.15	58.63	-1.7	0.31	0.07	4.59	0.23	-28.41
1836	1.51	1.44	0.67	1.88	0.66	0.58	0.54	16.05	56.45	-1.84	0.32	0.07	4.78	0.21	-28.44