THE INFLUENCE OF SEDIMENT NUTRIENT DYNAMICS ON THE RESPONSE OF LAKE ECOSYSTEMS TO RESTORATION AND CLIMATE CHANGE

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Abstract

Human activities such as urban settlement, farming, forestry and recreation, have caused deterioration of water quality in many freshwater lakes worldwide. Apart from anthropogenic impacts, it is also recognized that climate has a direct influence on lake water temperature, nutrient loads, phytoplankton abundance and chemistry. However, little is known about the potential effects of future climate change on lake water quality. Understanding the dynamics, abundance and availability of nutrient pools in lake bottom sediments is fundamentally important for predicting how, and over what time-scales, lake ecosystems will respond to future scenarios such as climate change, in-lake restoration or altered external nutrient loading. Through a sediment field study on 14 different lakes, and applications of complex lake ecosystem models to three New Zealand lakes, this study examined the spatial and temporal dynamics of sediment nutrient concentrations, and made considerations of the effects of restoration measures and future climate change on lake water quality.

To gain insight into processes influencing the dynamics of horizontal and vertical gradients of sediment nutrient concentrations, intact sediment cores were collected from twelve lakes within the Bay of Plenty province, North Island of New Zealand. In addition, intact sediment cores were collected from shallow Lake Te Waihora (Ellesmere) in the Canterbury province, South Island of New Zealand and shallow Lake Taihu in the Jaingsu province, China. The observed vertical concentration profiles of total phosphorus (TP) in the sediments revealed that the shape of these profiles can be similar across gradients of widely differing trophic status. Empirical and mechanistic steady state profile models were derived to describe the vertical distribution of total carbon (TC), total nitrogen (TN) and TP concentrations in the sediments. These models revealed that density-driven burial and biodiffusive mixing, which in the models also includes effects of redox-driven gradients, are strongly correlated with vertical gradients of sediment TC, TN and TP content, whereas lake trophic status was not.

Despite enhancing knowledge of the processes influencing vertical gradients of sediment nutrient concentrations, little is known about the rates at which sediment nutrient concentrations may change as a response to changes in external loading or climate. Studies into the composition of bottom sediments have been undertaken intermittently over the past three decades for the 12 lakes in the Bay of Plenty. These studies, together with the data collected in this study, were used to quantify temporal changes in sediment chemistry across the lakes. Comparison of the data collected in this study with results from a survey in 1995 showed that surficial sediment (0-2 cm) TP concentrations have increased in three of the 12 lakes, at rates ranging from 27.5 to 114.4 mg P kg^{-1} dry wt yr^{-1}. TN concentrations in surficial sediments have increased in nine of the 12 lakes at rates ranging from 51.8 to 869.2 mg N kg^{-1} dry wt yr^{-1}. A correlation analysis revealed that temporal changes in sediment TP and TN concentrations were not significantly linearly related ($p > 0.05$) to catchment area or temporal changes of different water column indices considered to reflect lake trophic state, including annual mean water column concentrations of TP, TN or chlorophyll a (Chl a).

While vertical profiles of sediment nutrient concentrations can be used to provide information about historical changes of trophic status in lakes, little is known about horizontal variability of sediment nutrient concentrations, including possibly relationships with horizontal variations in water column variables. In the large, shallow and eutrophic Lake Taihu, China, there are distinct horizontal water column concentration gradients of nutrients and Chl a. Concentrations are generally high in the north, where some of the major polluted tributaries enter the lake, and relatively low in the south, where macrophytes generally are abundant. To test whether these water column concentration gradients are similarly reflected in spatial heterogeneity of nutrient concentrations within the bottom sediments of Lake Taihu, I examined correlations between concentrations of TP and TN in surficial sediments (0-2 cm) and TP, TN and Chl a concentrations in water column samples determined for 32 sites in 2005. Linear correlation analysis revealed that surficial sediment TP concentrations across the 32 stations were related significantly, though weakly, to annual mean water column concentrations of TP and TN as well as Chl a. Correlations of surficial sediment TN with water column variables were, however, not significant ($p > 0.05$).

To better understand the effects of future climate change on lakes of different trophic status, I applied the one-dimensional lake ecosystem model, DYRESM-CAEDYM, to oligo-mesotrophic Lake Okareka, eutrophic Lake Rotoehu and highly eutrophic Lake Te Waihora. All three models were calibrated based on a three-year period (July 2002 - June 2005) and validated on a separate two-year period (July 2005 - June 2007). The model simulations generally showed good agreement with observed data for temperature, dissolved oxygen (DO), and total nutrient and Chl *a* concentrations. To represent a possible future climate of 2100, temperature predictions were derived from the regional climate model, DARLAM, based on the Intergovernmental Panel on Climate Change (IPCC) 'A2' scenario, which suggests that air temperatures by the year 2100 will increase by an average of 2.5 ºC and 2.7 ºC for the Bay of Plenty and the Canterbury province, respectively, relative to the base scenario (years 2002-2007). Model simulations of the future climate scenarios indicate that climatic changes generally will lead to a degradation of lake water quality in all three lakes, especially during summer months, and further suggest that the effects on annual mean surface concentrations of TP, TN and Chl *a* will be equivalent to an increase in external TN and TP loading by 25-50%. Simulations for Lake Rotoehu, where diatoms and cyanophytes were represented in the conceptual model, further suggest that cyanophytes will be more abundant in the future, increasing by >15% in annual mean biomass. Although the effects of climate change may be delayed or slightly mediated by the chemical resilience of the sediment nutrient pools, the effects of climate change on lake water quality in the New Zealand lakes will be of a magnitude that should be considered as management strategies are planned and implemented, thus increasing the probability of successful preservation or improvement in water quality in future decades.

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Acknowledgements

Preface

The main body of the thesis is comprised of four chapters (Chapters 2-5), which have each been submitted to peer-reviewed journals as separate manuscripts for publication. Except where referenced, the content of this thesis, including field and laboratory data, statistical analysis, interpretations and writing, is based on my own ideas and work, undertaken while under the supervision of Prof. David Hamilton, Dr. Conrad Pilditch, Associate Prof. Chris Hendy (The University of Waikato, New Zealand) and Prof. Erik Jeppesen (The National Environmental Research Institute, Denmark). Co-authors of the papers listed below have contributed with discussions and revisions to the manuscripts prior to submission.

Chapter 2 has been submitted to *Applied Geochemistry* as "Evaluating the influence of lake morphology, trophic status and diagenesis on geochemical profiles in lake sediments", by Trolle, D., D.P. Hamilton and C. Pilditch.

Chapter 3 has been published as "Trolle, D., D.P. Hamilton, C. Hendy and C. Pilditch. 2008. Sediment and nutrient accumulation rates in sediments of twelve New Zealand lakes: influence of lake morphology, catchment characteristics and trophic state. *Marine and Freshwater Research*, 59: 1067-1078".

Chapter 4 has been published as "Trolle, D., G. Zhu, D.P. Hamilton, L. Luo, C. McBride and L. Zhang. 2009. The influence of water quality and sediment geochemistry on the horizontal and vertical distribution of phosphorus and nitrogen in sediments of a large, shallow lake. *Hydrobiologia*, 627: 31-44".

Chapter 5 has been submitted to *Ecological Applications* as "Predicting the effects of climate change on ecosystem dynamics in three New Zealand lakes using the DYRESM-CAEDYM model – implications for lake restoration and management", by Trolle, D., D.P. Hamilton, C. Pilditch, I.C. Duggan and E. Jeppesen.

Chapter 1: General introduction

1.1 Motivation

The deterioration of water quality in freshwater lakes, due to human activities such as urban settlement, farming, forestry and recreation, has focused worldwide attention on the sustainability of lake environments (Wetzel 1992). Today, great efforts are made to improve water quality using different lake restoration approaches (Jeppesen et al. 2005). Apart from anthropogenic impacts, it is widely recognized that climate also has a direct influence on lake temperature distribution, nutrient loadings, phytoplankton abundance and lake chemistry (Straile et al. 2003; Jeppesen et al. 2005). However, little effort has been made to elucidate and quantify the effects of climate change on lakes (Blenckner 2005). With the expectation of a significant climate change in the future (IPCC 2007) research into this area is highly relevant, to adapt restoration alongside these changes in climate. For example, Jeppesen et al. (2007) consider that within the next century, or perhaps even within decades, climatic changes may cause a further deterioration of lake water quality, thereby rendering the present time-consuming and costly restoration efforts less productive. Concurrently, internal nutrient loading from lake sediments is known to affect lake trophic status and can substantially delay the recovery of lake ecosystems to reduced external loading (Marsden 1989; Søndergaard et al. 2003; Jeppesen et al. 2005). Understanding the size and availability of the nutrient pools in the sediments is therefore of critical importance in predicting how and when lake ecosystems will respond to changes in external loading (Nürnberg 1984; Van der Molen et al. 1998) or changes in climate (Jeppesen et al. 2007).

1.2 Main objectives

The overall aim of this Ph.D. study was to examine possible drivers of spatial heterogeneity and temporal dynamics of nutrients in bottom sediments across a wide range of lake trophic states. An additional objective was to predict the effects of future climate change on lake water quality in a range of New Zealand

lakes, by application of complex process-based ecological models. The principal work conducted for this thesis includes a comprehensive sediment field study and a computer based modelling study.

1.2.1 Field study

As bottom sediments in lakes are major accumulation zones for nutrients and contaminants, and can provide a record of past historical events, they are often a focus of limnological research. A key factor for understanding how and at what time-scales lake ecosystems will respond to the influences of in-lake restoration, changes in external loading or changes in climate, is the dynamics, abundance and availability of the nutrient pool in the bottom sediments (Søndergaard et al. 2003; Jeppesen et al. 2007). However, little is known about long-term changes (years to decades) of these nutrient pools, and how these may be interrelated with overlying lake water quality across a range of different lakes (Trolle et al. 2008a). In this thesis, field and laboratory work sought to address this knowledge gap with measurements of the distribution of nutrients in lake sediments and quantification of rates at which sediment nutrient concentrations may change through time in response to changes in environmental drivers such as the external nutrient load.

Variation in sedimentation patterns (Blais and Kalff 1995) and diagenetic processes can confound within- and among-lake comparisons of sediment nutrient properties and, as a consequence no quantitative generality for sediment nutrient dynamics across a wide range of lakes has emerged. A considerable part of within- and among lake variation in sediment composition is caused by morphology and catchment characteristics (Kalff 2002) that influence the exposure (or lake surface area) and sedimentation patterns within lakes (Rowan et al. 1992). Sediment focusing, first expressed by Likens and Davis (1975), describes the resuspension of sediments in shallow zones caused by waves and currents, and the subsequent transport and settling of the suspended sediments to deeper zones of lakes. Based on this observation, Håkanson and Jansson (1983) divided lake bottoms into three zones, based on differences in patterns of resuspension and sediment movement. These zones are (1) the erosional zone, which is influenced by the exposure and is characterised by coarse-grained,

noncohesive sediments, (2) a transportation zone, where discontinuous sedimentation and occasional resuspension and transport of sediments occurs, and (3) an accumulation zone. The influence of sediment focussing within individual lakes may be expressed by the area of sediment accumulation relative to the total surface area (Blais and Kalff 1995).

In this study, sediments from twelve lakes were sampled within the Bay of Plenty province, North Island of New Zealand. In addition, shallow Lake Te Waihora (Lake Ellesmere) in the Canterbury province, South Island of New Zealand, and shallow Lake Taihu in the Jaingsu province, China, were sampled. In attempting to achieve a clear separation in comparisons of sediment nutrient properties between lakes, sampling sites were selected within the deepest basins of these lakes, thus targeting accumulation zones and minimising effects of sediment focusing and within-lake variability. Together, the 14 lakes form an excellent basis for a comparative study of sediment geochemical properties within lakes of a wide variety of depths and trophic states, ranging from oligotrophic to highly eutrophic, and mixing regimes ranging from monomictic to polymictic.

1.2.2 Model applications

Three New Zealand lakes were selected for ecological model applications to simulate the effects of a future climate on these ecosystems; lakes Okareka, Rotoehu and Te Waihora. These lakes range in depth from shallow to deep and in trophic state from oligo-mesotrophic to highly eutrophic. Setting up models for these three lakes provides an excellent opportunity to evaluate the capacity of complex ecological models to predict changes in lake ecosystem functioning under different environmental conditions and in lakes with different morphological characteristics.

Model applications were based on the one-dimensional lake ecosystem model DYRESM-CAEDYM (DYCD), which has been developed at the Centre for Water Research, The University of Western Australia. DYCD is a highly complex one-dimensional lake ecosystem model, and several successful applications of the model to a range of different lakes have been published (e.g., Schladow and

Hamilton 1997; Bruce et al. 2006; Burger et al. 2007; Trolle et al. 2008b). Previous studies have also used complex ecosystem models to predict effects of climate change on lake water quality (e.g., Komatsu et al. 2007; Mooij et al. 2007). However, the models applied in these studies were largely un-calibrated, and consequently their predictions should be viewed as qualitative rather than quantitative, and may only be indicative of possible trends in the water quality in response to different lake management strategies and climate change. Hence, this study is the first to use intensively calibrated models for quantifying the effects of future climate change on lake water quality.

1.3 Thesis overview

This thesis is based on four main research chapters (Chapters 2-5) which have been prepared for, or published in, peer-reviewed scientific journals. The present chapter (Chapter 1) gives a brief overview of the study, and places each of the four main chapters in the context of the general objectives of my Ph.D. thesis. Chapter 6 contains a brief summary of main conclusions derived from Chapters 2-5.

In Chapter 2, the appearance of vertical sediment concentration profiles of dry/wet weight fraction, total phosphorus (TP), total nitrogen (TN), total carbon (TC), iron (Fe) and manganese (Mn) were quantified for sediment cores collected from the deep basins of all 14 study lakes. The importance of a range of environmental factors on these vertical concentration profiles, including physical and morphological variables (net sedimentation rates, lake mean depth and lake surface area), diagenetic parameters (burial, biodiffusion and organic matter degradation) as well as biological and chemical water column variables (annual mean TP, TN, chlorophyll *a* and Secchi depth), were examined by applying an empirical model concurrently with a mechanistic diagenetic model to describe the observed vertical profiles.

In Chapter 3, the effects of morphological features and lake trophic state on net sedimentation rates and sediment nutrient concentrations were examined for the 12 lakes in the Bay of Plenty province. Multiple linear regression was used to

examine how the variation in net sedimentation rates across the 12 lakes could be explained by lake trophic state and catchment size. Surficial sediment concentrations of TP, TN and TC from the field study in 2006 were compared with those obtained from earlier sediment surveys, in 1995 and 1972, to quantify rates of change in sediment nutrient concentrations on a time scale extending some decades.

In Chapter 4, horizontal and vertical geochemical gradients in sediments of large and shallow Lake Taihu, China, were quantified based on surficial sediments sampled at 32 sites and with vertical sections at 2 cm intervals to a sediment depth of approximately 0.2 m at 8 sites. Surficial sediment samples were analysed for TP, TN and fraction of organic matter (represented by loss on ignition, LOI), and vertical profiles for TP, TN, TC, Fe, Mn and calcium (Ca). Variability in surficial sediment chemistry was examined in relation to annual mean water column concentrations of TP, TN and chlorophyll *a* (Chl *a*).

In Chapter 5, the latest stable release of the DYCD model (V5.0.0-35) was applied to lakes Okareka, Rotoehu and Te Waihora. A range of nutrient loading and climate change scenarios were simulated for each of these lakes to quantify the implications of future climate change (represented by increases in air temperature) for lake restoration (represented by various alterations in nutrient loading).

This Ph.D. study provides a fundamental understanding of the main processes influencing spatial heterogeneity in sediment nutrient concentrations, and contributes knowledge that is essential to interpret the information provided by vertical nutrient concentration profiles. It also provides the first quantitative assessment of the effects of climate change on lake water quality, derived from calibrated deterministic ecological models.

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Chapter 2: Influence of lake morphology, trophic status and diagenesis on geochemical profiles in lake sediments

2.1 Introduction

Internal nutrient loading can directly affect lake trophic status and substantially delay lake ecosystem responses to reduced external loading (Marsden 1989; Søndergaard et al. 2003; Jeppesen et al. 2005). The size and availability of the nutrient pool in the bottom sediments are therefore of critical importance in understanding how lake ecosystems will respond to changes in external loading (Nürnberg 1984; Van der Molen et al. 1998; Spears et al. 2007) or changes in climate (Jeppesen et al. 2007).

Recognizing that lake sediments can provide information about historical changes in lakes, the vertical distribution of nutrients in lake sediments is often used to describe how lake trophic state may have changed through geological time and from recent human activities (Selig et al. 2007). Hence, several studies have used observed profiles of phosphorus and organic nitrogen and carbon to quantify temporal variations in sediment nutrient accumulation rates, and infer changes in lake trophic status (Schelske and Hodell 1995; Hambright et al. 2004; Smoak and Swarzenski 2004). Only a few studies, however, have compared sediment geochemical profiles collected from a range of lakes of different trophic states (Bortleson and Lee 1974; Søndergaard et al. 1996). These studies have focused on shallow lakes and did not examine relationships between vertical geochemical profiles and lake trophic state. Concurrently, both laboratory and field studies have indicated that various phosphorus species are able to migrate vertically through the sediments (Carignan and Flett 1981; Søndergaard et al. 1996). It is also well known that organic species of phosphorus, nitrogen and carbon will undergo a natural decay with time (Reitzel et al. 2007), thereby generating naturally lower concentrations in the deeper and older sediments. These observations should be accounted for in relationships of nutrient concentration

profiles in the sediments and historical changes in lake trophic state. In addition, several studies have shown that that the surficial sediment concentrations of both phosphorus and nitrogen cannot readily be related to lake trophic state (McColl 1977; Håkanson 1984; Trolle et al. 2008). Consequently, there is a large degree of uncertainty as to whether, or how strongly, specific profile properties (i.e., the shape of the vertical profiles) are related to lake trophic state. Therefore recent geochemical studies are marked by confusion in their evaluation of factors that influence the vertical distribution of phosphorus, nitrogen and carbon in lake sediments, thereby leading to misinterpretations of the information provided by the concentration profiles of these elements.

Diagenetic models that describe the vertical distribution of various geochemical elements may help to quantify the importance of factors such as trophic state, lake morphology and various diagenetic processes. Both two-layer oxic/anoxic sediment diagenesis models (e.g. Wang et al. 2003a, b) as well as more complex one-dimensional multi-layer sediment diagenesis models (e.g. Jørgensen et al. 1982; Boudreau 1996) have been used to describe the vertical distribution of nutrients in sediments as well as fluxes from the sediments to the water column, which may strongly influence lake water quality. However, these models have typically only been applied to sediment cores collected from a single lake (e.g. Van Rees et al. 1996; Schauser et al. 2004).

The main objective of the present study was to quantify the influence of lake trophic state and morphology, and diagenetic processes on vertical profiles of total phosphorus (TP), total nitrogen (TN) and total carbon (TC) in sediments of a wide variety of lakes, by concurrently applying an empirical and a mechanistic model. Sediment cores were collected from 14 different lakes (Table 2.1), ranging from shallow to deep, and from oligotrophic to highly eutrophic. I derived both an empirical and a mechanistic model to describe the vertical concentration profiles observed in these sediment cores. Model parameters, obtained by fitting the empirical and mechanistic models to observed vertical profiles of TP, TN and TC, could then be examined for correlations with trophic status attributes, lake morphology and a range of diagenetic parameters.

Table 2.1. Morphological properties and trophic status of the 14 study lakes (after Taylor et al. 1996; Hamilton and Mitchell 1997; Trolle et al. 2008; Trolle et al. 2009).

	Mean depth (m)	Max depth (m)	Lake area (ha)	Catchment area (ha)	Lake trophic status	Latitude (N) Longitude (E)
Te Waihora (Ellesmere)	1.3	2.5	18,200	256,000	Highly eutrophic	43º 47'00 N 172º16'00 E
Taihu	1.9	3.0	233,800	3,690,000	Highly eutrophic	31º11'00 N 120º08'00 E
Okaro	12.5	18.0	32	407	Highly eutrophic	38º17'55 N 176º23'40 E
Rotorua	11.0	44.8	8,079	52,346	Eutrophic	38º04'50 N 176º16'00 E
Rotoehu	8.2	13.5	795	5,673	Eutrophic	38º01'10 N 176º31'50 E
Rotoiti	31.5	93.5	3,460	12,462	Eutrophic	38º02'30 N 176º26'00 E
Rotomahana	60.0	125	897	7,994	Mesotrophic	38º16'00 N 176º26'00 E
Rerewhakaaitu	7.0	15.8	579	3,816	Mesotrophic	38º17'40 N 176º30'00 E
Okareka	20.0	33.5	342	1,958	Mesotrophic	38º10'15 N 176º21'45 E
Rotokakahi	17.5	32.0	452	1,872	Mesotrophic	38º13'00 N 176º19'15 E
Tikitapu	18.0	27.5	146	567	Oligotrophic	38º11'45 N 176º19'50 E
Okataina	39.4	78.5	1,104	5,676	Oligotrophic	38º07'50 N 176º24'30 E
Tarawera	50.0	87.5	4,165	14,494	Oligotrophic	38º12'00 N 176º25'00 E
Rotoma	36.9	83.0	1,104	2,914	Oligotrophic	38º02'50 N 176º35'00 E

2.2 Methods

2.2.1 Sampling sites

Two intact sediment cores were collected from the deep basins in each of the 14 lakes, targeting areas conforming to accumulation bottoms (c.f. Håkanson and Jansson 1983). The two cores were collected at similar depths, but at two different sites within the deep basin of each lake, in order to capture some of the spatial variability within the basins. Twelve lakes (the Rotorua lakes) were within the Bay of Plenty Province, North Island of New Zealand. The other two lakes were

shallow and included Lake Te Waihora (Lake Ellesmere) in the Canterbury Province, South Island of New Zealand, and Lake Taihu in the Jaingsu Province, China.

2.2.2 Sampling methods

Sampling was conducted in all 14 lakes during the period March 2006 to January 2007. The sediment cores were collected using a cylindrical gravity or piston corer, which was designed to leave cores intact. The surface sediment was visually inspected in each core, and if there was any evidence of disturbance at the sediment-water interface or in the core profile, the core was discarded and another one taken. Samples of the sediment were collected from each core at intervals of 2 cm to a vertical depth that varied from 8 to 38 cm, using a custom-made slicing chamber. Each sample was transferred to 50 mL Vulcan™ centrifuge tubes, which were sealed and placed on ice until return to the laboratory, where pore-waters were immediately separated by centrifugation at 4000 rpm for 40 min. For Lake Taihu, samples were collected in air-tight plastic bags, and pore-waters were not separated from solids. The resulting sub-samples of pore-waters and sediment solids from each lake were stored frozen (-18 ℃) before further analysis.

2.2.3 Analytical methods

Sediment dry weight fraction was determined by weighing solid samples before and after drying at 105 ℃ for 24 h, and also taking into account pore-water mass. Subsequently, sediment wet weight was determined as the difference between the bulk weight (total weight including both solids and pore-water) and the sediment dry weight.

Total phosphorus (TP), *iron* (Fe) and *manganese* (Mn) content in the dry sediment was determined after the solids had been ground with mortar and pestle, and approximately 0.5 g of each sample had been digested with Aqua Regia (3:1 v:v of 1:5 conc. hydrochloric acid solution and 1:2 conc. nitric acid solution), based on a modified standard procedure (Martin et al. 1994). Liquid from the digested solid samples and from pore-water samples was acidified with two drops

of conc. hydrochloric acid, and then analyzed for TP, Fe and Mn on an ICP-MS (model ELAN DRC II).

Total carbon (TC) and *nitrogen* (TN) content in sediment solids was determined by sub-sampling approximately 0.25 g of the dry sediment solids and analyzing by combustion (LECO TruSpec model CN Determinator). Most of the study lakes have non-calcareous sediments with total carbon content closely related to the sediment organic content (McColl 1977). Concentrations of TC and TN were determined for every second vertical sub-sample in 20 out of the 28 cores; for the remaining cores only the surficial sediments were analyzed.

Total nitrogen in pore-waters was analyzed spectrophotometrically with a Lachat Instruments flow injection analyzer (model QuikChem 8000 FIA+) following persulphate digestion (Ebina et al. 1983).

2.2.4 Mathematical methods

The concentration of TP, TN, TC, Fe and Mn in the dried sediment was calculated for each 2 cm interval in each individual core. The pore-water fraction was excluded from further statistical analysis as this fraction was found to be negligible relative to the total mass of elements in the sediments (e.g., pore-waters accounted for an average < 1% of the TP concentration across all samples collected). Most vertical profiles of the measured elements showed exponentially decreasing concentrations with depth in the sediments (as demonstrated by TP concentration profiles in Fig. 2.1). An empirical exponential model was therefore set up to reproduce the vertical distribution of TP, TN, TC, Fe and Mn in (mg kg^{-1} dry wt), and to quantify three characteristic profile parameters: the profile surface concentration ($\beta + \gamma$) at the sediment-water interface, the background concentration (γ) and the vertical decay coefficient α (cm^{-1}):

$$C_i(z) = \gamma + \beta \cdot \exp(-\alpha \cdot z) \qquad (1)$$

where $C_i(z)$ is the concentration of TP, TN, TC, Fe or Mn at vertical depth z (cm) in the sediment (mg kg^{-1} dry wt). Values of γ, β and α were calculated for each individual sediment core and for each element (TP, TN, TC, Fe and Mn) using equation (1) to fit the observed geochemical profiles. Goodness of fit of models was tested using Root-Mean-Square-Error (RMSE) values and Pearson correlation coefficients (r). The RMSE value for each profile was minimized by calibrating γ, β and α using *Solver* in Microsoft Excel, after which Pearson correlation coefficients were calculated. Solver uses a generalized reduced gradient non-linear optimization code to minimize model error (thereby searching for and converging on a minimum in the RMSE value space). In order to evaluate the influence of sediment compaction on vertical profiles of TP, TN, TC, Fe and Mn, γ, β and α values were also calculated for wet weight profiles. Each of these three empirical parameters could then be examined for correlations with trophic status attributes, lake morphology and a range of diagenetic parameters.

To interpret the three parameters given by the empirical exponential model from a diagenetic perspective, and to quantify the influence of a range of diagenetic processes on these parameters, one must first consider the general diagenetic advection-diffusion-reaction (ADR) equation (Berner 1980; Boudreau 1997) for the mass balance of solid organic matter (OM), where burial and biodiffusive mixing are the transport processes, and OM decays with a first order kinetic rate:

$$\frac{\partial C_{OM}}{\partial t} = D_b \cdot \frac{\partial^2 C_{OM}}{\partial z^2} - w \cdot \frac{\partial C_{OM}}{\partial z} + k \cdot C_{OM} \qquad (2)$$

where C_{OM} is the concentration of organic matter in mg kg^{-1} dry wt, D_b is the biodiffusion coefficient in cm^2 yr^{-1}, w is the advective velocity for solids (also referred to as a burial rate, net sedimentation rate or sediment accumulation rate) in cm yr^{-1} and k is a first order kinetic rate coefficient in yr^{-1} for the breakdown of OM. If steady state mass-conservation is assumed, equation (2) simplifies to:

$$D_b \cdot \frac{\partial^2 C_{OM}}{\partial z^2} - w \cdot \frac{\partial C_{OM}}{\partial z} + k \cdot C_{OM} = 0 \qquad (3)$$

Equation (3) can be solved as a second order ODE (Boudreau 1997; DiToro 2001; Meysman et al. 2005), given a constant flux boundary at the sediment-water interface:

$$F_{OM}^0 = \rho \cdot (1-\phi) \cdot \left[-D_b \cdot \frac{\partial C_{OM}}{\partial z} + w \cdot C_{OM} \right]_{z=0} \tag{4}$$

where F_{OM}^0 is the constant flux of OM to the sediment-water interface in $\mu g\ cm^{-2}$ yr^{-1}, ρ is the solid sediment density in $g\ cm^{-3}$ and ϕ the porosity; and a zero-gradient boundary in the deep sediments:

$$\left[\frac{\partial C_{OM}}{\partial z} \right]_{z \to \infty} = 0 \tag{5}$$

The analytical solution to equation (3) then becomes:

$$C_{OM}(z) = \frac{1}{\rho \cdot (1-\phi)} \cdot \frac{2 \cdot F_{OM}^0}{\left[w + \sqrt{w^2 + 4 \cdot D_b \cdot k} \right]} \cdot \exp\left(\frac{w - \sqrt{w^2 + 4 \cdot D_b \cdot k}}{2 \cdot D_b} \cdot z \right) \tag{6}$$

Finally, assuming that OM can be divided into a labile and a refractory fraction (where k ~ 0 for refractory OM) the steady state concentration profile becomes:

$$C_{OM,total}(z) = \frac{1}{\rho \cdot (1-\phi)} \cdot \left[\frac{F_R}{w} + \frac{2 \cdot F_L}{\left[w + \sqrt{w^2 + 4 \cdot D_b \cdot k} \right]} \cdot \exp\left(\frac{w - \sqrt{w^2 + 4 \cdot D_b \cdot k}}{2 \cdot D_b} \cdot z \right) \right] \tag{7}$$

where F_R and F_L are a constant flux of refractory and labile OM to the sediment-water interface, respectively. It is now apparent that equation (7) is equivalent to the empirical expression in equation (1).

To determine how the diagenetic parameters of equation (7) influence the vertical concentration profiles of TP, TN and TC, and how they may be related to environmental variables (water quality, lake depth, etc.), I applied equation (7) to

the observed concentration profiles of TP, TN and TC. When calibrating the diagenetic parameters I assumed a constant porosity (ϕ, estimated to 0.46-0.92 from water content in each individual sediment core) and a constant sediment solids density (ρ) of 2.5 g cm^{-3}. To estimate burial rates (w) I recorded the depth to a tephra layer, which was present at a depth between 7 and 31 cm below the sediment-water interface in most sediment cores collected from the Rotorua Lakes, New Zealand. The tephra is comprised of ash and mud which were dispersed over an area > 200 km^2 over North Island of New Zealand during the volcanic eruption of Mount Tarawera in 1886 (White et al. 1997). For sediment cores where no tephra was present, I used net sedimentation data from Trolle et al. (2008) for Rotorua lakes and from Wang et al. (2001) for Lake Taihu. As no burial rate data was available for Lake Te Waihora, I initially assumed that this large and shallow eutrophic lake had a burial rate similar to that of Lake Taihu. The parameters F_R and F_L were initially fitted by assuming a constant mid-range biodiffusion coefficient (Meysman et al. 2003) (D_b) of 0.5 cm^2 yr^{-1} and a first order kinetic rate coefficient (k) for moderately labile organic matter (Luff et al. 2000) of 0.4 yr^{-1}. Goodness of fit of models was again tested using RMSE values and Pearson correlation coefficients. From equation (7) it is evident that the value of F_R during initial model calibration (converging on a minimum of the RMSE value space) will be adjusted relative to the observed background concentrations. Following the initial calibration step, I performed a second calibration of parameters F_R, F_L, D_b and k. For the second calibration-step of the diagenetic parameters for the Lake Te Waihora profiles I also included the burial rate (w).

The three parameters given by the empirical model (equation 1) were then examined for statistically significant linear relationships with the diagenetic parameters given by the mechanistic model (equation 7), and subsequently all parameters from the two models were used to test for relationships with lake trophic state (represented by biological and chemical water column attributes) and a selection of morphological variables across all the lakes. The trophic state was estimated from annual average (based on years 2005-2006) concentrations of TP, TN and chlorophyll a (Chl a) and Secchi depths for the water column of each lake from monthly samples, which were representative of the current trophic state of each individual lake.

2.3 Results

2.3.1 Observed geochemical profiles of TP, TN, TC, Fe and Mn

The concentration profiles of TP (Fig. 2.1), TN, TC, Fe and Mn, derived from each of two sediment cores collected from within the deep basin of each lake, generally showed a similar pattern in the deep lakes.
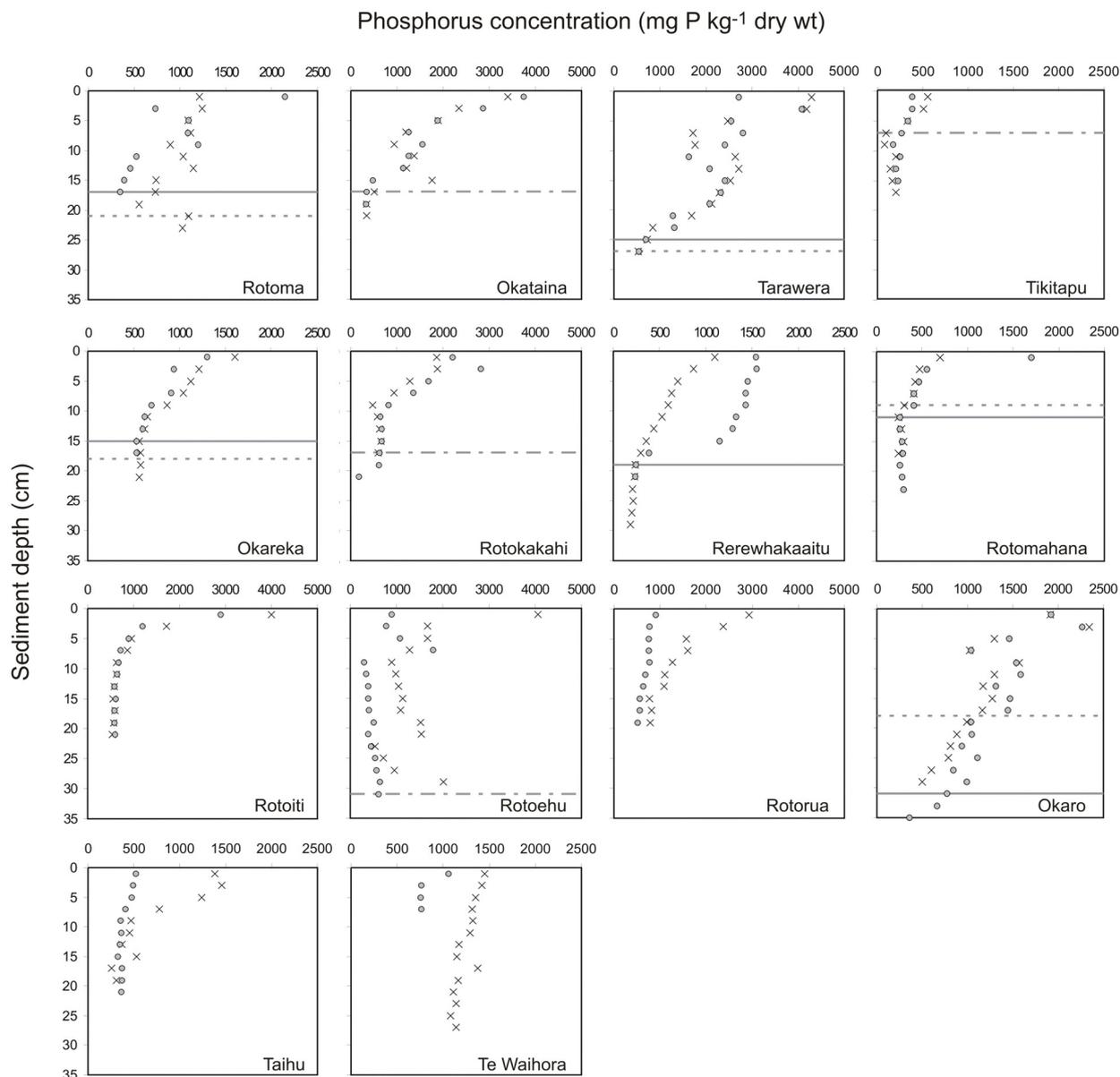
Figure 2.1. Sediment concentration profiles of TP in 14 different lakes. Two cores (marked × and ◎) were collected from each of the 14 lakes. Plots are arranged from oligotrophic to eutrophic lakes (from left to right and top to bottom). If present in the vertical cores, the start of the Tarawera tephra layer has been highlighted (marked with ▬ for sites represented by ◎, ▪ ▪ ▪ for sites represented by ×, and ▬▪▬ where the tephra layer was present at the same vertical sediment depth at both sites). The y-axis represents depth below the sediment-water interface (cm) and the x-axis represents the TP concentration (mg P kg^{-1} dry wt); note different scales for x axis.

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The variability between the two cores collected from within the same basin was, however, typically quite high for the shallower lakes (e.g. Rerewhakaaitu, Rotoehu, Rotorua, Taihu and Te Waihora), even though sampling site depths differed by < 1 m within the individual lakes.

The surficial sediment concentrations, represented by the first discrete horizontal sediment sample slice (0-2 cm) from each sediment core, ranged between 400 and 4,300 mg P kg^{-1} dry wt for TP; 1,400 and 19,900 mg N kg^{-1} dry wt for TN; 7,000 and 136,400 mg C kg^{-1} dry wt for TC; 7,000 and 57,600 mg Fe kg^{-1} dry wt for Fe and 140 and 28,800 mg Mn kg^{-1} dry wt for Mn. For most of these elements the concentration decreased exponentially with sediment depth, until it became somewhat constant, typically around 15 cm into the sediments. The depth at which TP concentrations reached the background level tended to be deeper into the sediments for some of the deep oligo-mesotrophic lakes, e.g., Lake Okareka at 15-17 cm compared with deep eutrophic Lake Rotoiti (7-9 cm). The range in background concentrations was generally smaller than that observed in surface sediment samples, and was between 200 and 1,300 mg P kg^{-1} dry wt for TP; 800 and 9,200 mg N kg^{-1} dry wt for TN; 4,400 and 80,600 mg C kg^{-1} dry wt for TC; 7,500 and 37,700 mg Fe kg^{-1} dry wt for Fe and 180 and 9,100 mg Mn kg^{-1} dry wt for Mn.

The tephra layers appeared to influence the various geochemical profiles; dry matter content increased in the tephra, while TN and TC concentrations decreased. The TP, Fe and Mn concentrations in the tephra layers were, however, generally similar to those found in the overlying lacustrine sediment.

In examining the concentration profiles of TP (Fig. 2.1), there was no clear separation between oligotrophic and eutrophic lakes. For example, the TP profiles in sediment cores collected from deep, oligotrophic Lake Okataina, where anthropogenic impacts are still negligible, showed a similar vertical distribution to TP profiles from sediments in deep, eutrophic, Lake Rotoiti, which has undergone a period of severe eutrophication during the 1970s (Vincent et al. 1984) and has since remained eutrophic (Hamilton et al. 2006).

2.3.2 Model predictions of sediment geochemical profiles

The empirical model used to describe the vertical decay of TP, TN, TC, Fe, Mn and wet weight with sediment depth, as well as the diagenetic model for profiles of TP, TN and TC, generally produced close fits to observed geochemical profiles across the 14 lakes (Table 2.2), though some cores showed a somewhat irregular concentration profile of various elements (e.g., Lake Tarawera; Fig. 2.2). In sediment cores that extended into the Tarawera tephra, the tephra values were omitted from the model fit. Because of the similarity of the empirical and the mechanistic models the best fit to the exponential decrease of elemental concentrations with sediment depth explained the same relative amount of variability in the concentration profiles of TP, TN and TC (Table 2.2). The models explained between 51 and 100% of the variability in the vertical profiles of TP, TN and TC across the 14 lakes. Concentration profiles which were relatively uniformly or linearly distributed through the sediments (mostly for Fe and Mn) were also reproduced satisfactorily by the empirical model, but with the vertical decay coefficient (α) for these profiles equal to zero (Table 2.2).
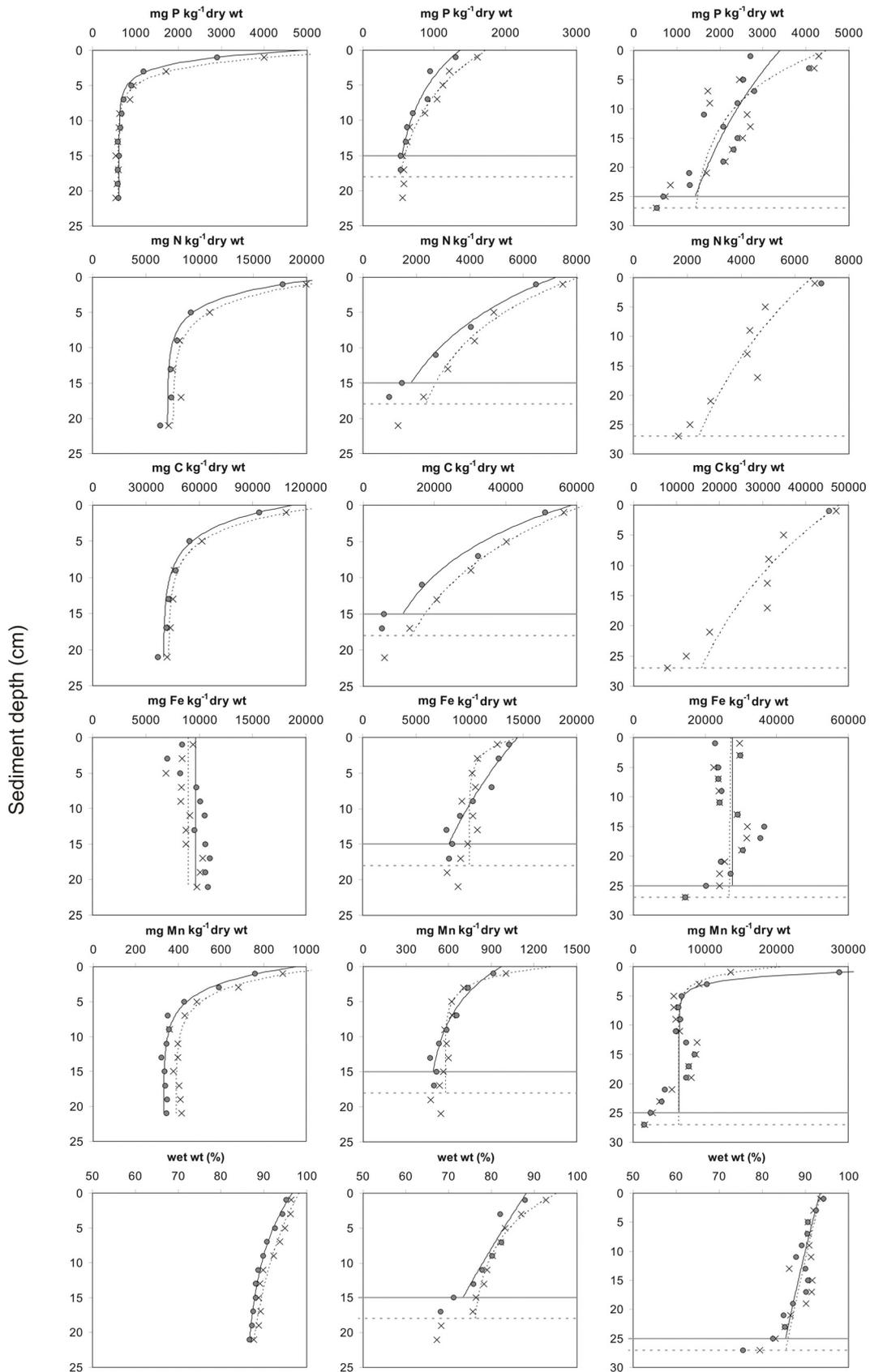
Figure 2.2. Examples of vertical profiles of TP, TN, TC, Fe and Mn concentrations and wet weight in lakes Rotoiti, Okareka and Tarawera. Two cores (marked with ✕ and ⦾ respectively) were collected from eutrophic Lake Rotoiti (left), mesotrophic Lake Okareka (middle) and oligotrophic Lake Tarawera (right). If present in the vertical cores, the start of the Tarawera tephra layer has been highlighted (marked with ▬ for sites represented by ⦾ and ▪ ▪ ▪ for sites represented by ✕). Lines represent modeled profiles (the empirical model plot is equivalent to the mechanistic model plot for TP, TN and TC profiles).

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Table 2.2. Average background concentration (γ) in mg kg^{-1} dry wt, surface concentration ($\gamma + \beta$) in mg kg^{-1} dry wt and exponential vertical decay coefficient (α) in cm^{-1} as determined by the empirical expression (equation 1), with variation explained denoted by r^2_{exp}, and average flux of refractory (F_R) and labile (F_L) organic matter in μg (TP, TN or TC) cm^{-2} yr^{-1}, burial rates (w) in cm yr^{-1}, biodiffusion coefficients (D_b) in cm^2 yr^{-1} as determined by the diagenetic steady state equation (equation 7), with variation explained denoted by r^2_{mech}; average values based on model fits to two cores collected from the deep basin in each of the 14 study lakes. *** = significant at $p < 0.001$, ** = significant at $p < 0.01$ and * = significant at $p < 0.05$.

Rotoma

	TP	TN	TC	Fe	Mn	Wet wt
γ	392	373	0	0	0	80
$\gamma+\beta$	13084	8570	57963	28541	8140	97
α	1.45	0.056	0.053	0.018	0.043	0.25
r^2_{exp}	0.71**	1**	0.97*	0.21	0.22	0.87***
F_R	11.8	13.8	3681			
F_L	890	581				
w	0.16	0.18	0.14			
D_b	15.1	0.35	0.34			
k	0.055	0.15	0.14			
r^2_{mech}	0.71**	1**	0.97*			

Okataina

	TP	TN	TC	Fe	Mn	Wet wt
γ	869	939	0	6716	1326	84
$\gamma+\beta$	4398	7580	50622	30127	2747	95
α	0.26	0.076	0.061	0.012	0.34	0.40
r^2_{exp}	0.89***	0.84**	0.90*	0.30	0.34	0.79***
F_R	46.2	49.0	6824			
F_L	663	1004				
w	0.14	0.14	0.14			
D_b	0.76	0.28	0.27			
k	0.26	0.39	0.30			
r^2_{mech}	0.89***	0.84**	0.90*			

Tikitapu

	TP	TN	TC	Fe	Mn	Wet wt
γ	0	2746	28523	3648	98	0
$\gamma+\beta$	573	5489	57042	7289	188	92
α	0.12	0.18	0.26	0	0	0.034
r^2_{exp}	0.82	N/A	N/A	N/A	N/A	0.98*
F_R	0	110.4	948.5			
F_L	149	789	9520			
w	0.058	0.058	0.058			
D_b	0.37	0.50	0.50			
k	0.31	0.40	0.40			
r^2_{mech}	0.82	N/A	N/A			

Tarawera

	TP	TN	TC	Fe	Mn	Wet wt
γ	641	0	0	13688	6351	53
$\gamma+\beta$	3929	6594	47683	27354	40830	93
α	0.074	0.037	0.041	0.001	0.77	0.009
r^2_{exp}	0.61**	0.84**	0.86**	0.001	0.76**	0.65**
F_R	74.4	0	9582			
F_L	786	1298				
w	0.22	0.23	0.23			
D_b	0.28	0.24	0.25			
k	0.45	0.25	0.26			
r^2_{mech}	0.61**	0.84**	0.86**			

Rerewhakaaitu

	TP	TN	TC	Fe	Mn	Wet wt
γ	54	8595	78710	16280	296	31
$\gamma+\beta$	1388	11907	91178	48684	966	97
α	0.057	0.21	0.30	0.28	0.57	0.014
r^2_{exp}	0.94***	1***	0.82	0.95***	0.88***	0.95***
F_R	3.6	441.9	4046.9			
F_L	191	580	2134			
w	0.16	0.16	0.16			
D_b	0.21	0.54	0.82			
k	0.52	0.38	0.23			
r^2_{mech}	0.94***	1***	0.82			

Rotomahana

	TP	TN	TC	Fe	Mn	Wet wt
γ	342	0	29042	8684	254	15
$\gamma+\beta$	2288	8422	59423	17356	8196	96
α	0.63	0.031	0.91	0	0.62	0.012
r^2_{exp}	0.97**	0.77	1***	N/A	0.99***	0.60
F_R	8.1	0	522.1			
F_L	136	324	2371			
w	0.084	0.092	0.092			
D_b	3.35	0.30	2.97			
k	0.15	0.07	0.04			
r^2_{mech}	0.97**	0.77	1***			

Rotorua

	TP	TN	TC	Fe	Mn	Wet wt
γ	344	0	0	6832	174	57
$\gamma+\beta$	2127	7559	49517	10282	544	96
α	0.10	0.008	0.013	0.10	0.023	0.01
r^2_{exp}	0.94***	0.70***	0.79***	0.13	0.60*	0.82**
F_R	24.2	0	0			
F_L	240	457	3120			
w	0.3	0.3	0.3			
D_b	0.42	0.36	0.37			
k	0.25	0.02	0.03			
r^2_{mech}	0.94***	0.70***	0.79***			

Okaro

	TP	TN	TC	Fe	Mn	Wet wt
γ	809	3534	25829	9381	243	31
$\gamma+\beta$	2165	16575	130542	18738	461	99
α	0.12	0.079	0.050	0.10	0	0.01
r^2_{exp}	0.62*	0.91**	0.81**	N/A	N/A	0.88***
F_R	32.7	112.4	821.2			
F_L	154	1331	9108			
w	0.20	0.20	0.20			
D_b	0.37	0.29	0.28			
k	0.46	0.40	0.24			
r^2_{mech}	0.62*	0.91**	0.81*			

Okareka

	TP	TN	TC	Fe	Mn	Wet wt
γ	372	699	0	4961	505	37
$\gamma+\beta$	1541	7621	60179	14469	1143	92
α	0.12	0.10	0.098	0.29	0.35	0.084
r^2_{exp}	0.95***	0.98**	0.975*	0.84**	0.97***	0.94***
F_R	25.0	45.6	13426			
F_L	277	1530				
w	0.14	0.14	0.14			
D_b	0.34	0.32	0.31			
k	0.50	0.44	0.45			
r^2_{mech}	0.95***	0.98**	0.975*			

Rotokakahi

	TP	TN	TC	Fe	Mn	Wet wt
γ	157	2116	6439	8774	378	77
$\gamma+\beta$	2646	16185	108195	17530	742	100
α	0.14	0.20	0.16	0	0	0.17
r^2_{exp}	0.85**	1***	1***	N/A	N/A	0.97***
F_R	12.4	143.3	435.9			
F_L	628	3537	24726			
w	0.14	0.14	0.14			
D_b	0.38	0.53	0.44			
k	0.47	0.38	0.42			
r^2_{mech}	0.85**	1***	1***			

Rotoiti

	TP	TN	TC	Fe	Mn	Wet wt
γ	604	7247	41195	4662	359	85
$\gamma+\beta$	5656	23757	123230	9302	1045	97
α	0.59	0.35	0.31	0.01	0.36	0.081
r^2_{exp}	1***	0.99***	0.99***	N/A	0.98***	0.97***
F_R	67.6	812.8	4620.2			
F_L	1171	5114	26465			
w	0.17	0.17	0.17			
D_b	3.29	1.19	0.98			
k	0.02	0.12	0.16			
r^2_{mech}	1***	0.99***	0.99***			

Rotoehu

	TP	TN	TC	Fe	Mn	Wet wt
γ	779	3991	9200	4583	371	40
$\gamma+\beta$	4115	14182	79195	30293	3842	98
α	0.41	0.095	0.049	0.15	0.007	0.045
r^2_{exp}	0.53*	0.90***	0.93***	0.42	0.02	0.94***
F_R	124.2	612.7	1662.9			
F_L	742	2988	16760			
w	0.26	0.26	0.26			
D_b	5.77	0.30	0.23			
k	0.15	0.62	0.43			
r^2_{mech}	0.53*	0.90***	0.93***			

Taihu

	TP	TN	TC	Fe	Mn	Wet wt
γ	182	1182	7371	5796	250	39
$\gamma+\beta$	1151	7504	24171	27646	1308	92
α	0.14	1.17	0.89	0.01	0.089	0.69
r^2_{exp}	0.88***	0.83**	0.39	0.35	0.96***	0.95***
F_R	1.58	10.8	22.5			
F_L	398	774	4047			
w	0.01	0.01	0.01			
D_b	0.33	10.7	0.83			
k	0.62	0.33	0.13			
r^2_{mech}	0.88***	0.83**	0.51			

Te Waihora (Ellesmere)

	TP	TN	TC	Fe	Mn	Wet wt
γ	867	1388	6150	20196	319	37
$\gamma+\beta$	2283	2841	12504	133799	2538	100
α	1.05	0.89	0.25	1.59	1.73	1.81
r^2_{exp}	0.87***	0.56	0.88***	0.88	0.92*	0.63
F_R	5.02	6.78	30.1			
F_L	389	324	2709			
w	0.005	0.005	0.005			
D_b	5.62	3.98	0.59			
k	0.52	0.013	0.32			
r^2_{mech}	0.87***	0.56	0.88***			

2.3.3 Geochemical profiles related to diagenetic parameters

I found a strong and significant correlation between the sediment background concentrations (γ) and the flux of refractory matter (F_R) of TP, TN and TC (Table 2.3), whereas the surface concentrations ($\gamma+\beta$) of TP, TN and TC were more closely related to the flux of labile matter (F_L). The vertical decay coefficients (α) for TP, TN and TC profiles were most strongly related to the biodiffusion coefficients (D_b), while the vertical decay coefficients for TN and TC profiles, but not TP profiles, were also significantly and inversely correlated with the burial rates (w). The vertical decay coefficients for TP were also significantly, though weakly, related to the vertical decay coefficients for Fe ($r = 0.47$, $p < 0.05$, $n = 28$), Mn ($r = 0.46$, $p < 0.05$, $n = 28$) and wet weight ($r = 0.50$, $p < 0.01$, $n = 28$). However, the correlation between the vertical decay coefficients for TP and the Fe and Mn profiles cannot be justified as causation, as the vertical decay coefficients for the Fe and Mn profiles were also strongly inter-correlated with the vertical decay coefficients for wet weight profiles ($p < 0.001$). Vertical decay coefficients for wet weight profiles were also strongly correlated with the vertical decay coefficients for TN and TC profiles. The first order kinetic rate coefficients (k) were not significantly correlated with any of the parameters given by the empirical model for TN and TC profiles, but were significantly related to both the surface concentrations and the vertical decay coefficients for the TP profiles (Table 2.3).

Table 2.3. Pearson correlation coefficients between model-predicted parameters for TP, TN, TC and wet weight profiles, $(\gamma + \beta)$, γ, α, F_R, F_L, D_b, k, w and a range of morphological, chemical and biological variables (n = 26-28). *** = significant at $p < 0.001$, ** = significant at $p < 0.01$ and * = significant at $p < 0.05$.

TP

	$F_{R(TP)}$	$F_{L(TP)}$	$D_{b(TP)}$	$k_{(TP)}$	w	$(\gamma+\beta)_{TP}$	$(\gamma)_{TP}$	$(\alpha)_{TP}$	$(\gamma+\beta)_{Wet}$	$(\gamma)_{Wet}$	$(\alpha)_{Wet}$	site/mean depth ratio	[TP] water	[TN] water	[Chl a] water	Secchi depth
$F_{R(TP)}$	-	0.57**	0.19	-0.16	0.45*	0.26	0.70***	0.08	0.16	0.32	-0.15	0.06	-0.15	-0.21	-0.12	0.06
$F_{L(TP)}$		-	0.66***	-0.31	0.15	0.78***	0.44*	0.58**	0.28	0.58**	0.13	0.00	-0.14	-0.14	-0.13	0.28
$D_{b(TP)}$			-	-0.46*	-0.04	0.91***	0.32	0.94***	0.17	0.21	0.28	-0.38*	0.04	-0.06	0.07	0.20
$k_{(TP)}$				-	-0.23	-0.38*	-0.02	-0.50*	-0.43*	-0.29	-0.13	-0.20	0.26	0.37	0.19	-0.24
w					-	0.12	0.12	-0.19	0.44*	0.25	-0.46*	0.49**	-0.44*	-0.54**	-0.26	0.20
$(\gamma+\beta)_{TP}$						-	0.37	0.81***	0.18	0.40*	0.03	-0.14	-0.161	-0.20	-0.13	0.40*
$(\gamma)_{TP}$							-	0.32	-0.10	0.29	0.13	-0.31	0.29	0.01	0.32	-0.04
$(\alpha)_{TP}$								-	0.20	0.15	0.50**	-0.46*	0.18	0.01	0.22	0.11

TN

	$F_{R(TN)}$	$F_{L(TN)}$	$D_{b(TN)}$	$k_{(TN)}$	w	$(\gamma+\beta)_{TN}$	$(\gamma)_{TN}$	$(\alpha)_{TN}$	$(\gamma+\beta)_{Wet}$	$(\gamma)_{Wet}$	$(\alpha)_{Wet}$	site/mean depth ratio	[TP] water	[TN] water	[Chl a] water	Secchi depth
$F_{R(TN)}$	-	0.79***	-0.14	0.13	0.31	0.69**	0.82***	-0.06	0.27	0.48*	-0.23	0.36	-0.20	-0.26	-0.16	-0.10
$F_{L(TN)}$		-	-0.09	0.05	0.31	0.82***	0.53*	-0.02	0.36	0.37	-0.16	0.44	-0.27	-0.30	-0.24	-0.03
$D_{b(TN)}$			-	-0.42	-0.45*	0.04	-0.02	0.97***	0.04	-0.08	0.91***	-0.34	0.40	0.66**	0.15	-0.37
$k_{(TN)}$				-	0.20	-0.06	0.14	-0.45	-0.02	-0.12	-0.34	-0.03	-0.22	-0.04	-0.33	-0.02
w					-	0.36	0.11	-0.56**	0.44*	0.25	-0.46*	0.49**	-0.44*	-0.54**	-0.26	0.20
$(\gamma+\beta)_{TN}$						-	0.67**	0.06	0.63**	0.27	-0.11	0.33	-0.21	-0.26	-0.25	-0.10
$(\gamma)_{TN}$							-	-0.01	0.22	0.43	-0.19	0.34	-0.07	-0.13	-0.08	-0.14
$(\alpha)_{TN}$								-	-0.08	-0.01	0.89***	-0.33	0.49*	0.67**	0.27	-0.43

TC

	$F_{R(TC)}$	$F_{L(TC)}$	$D_{b(TC)}$	$k_{(TC)}$	w	$(\gamma+\beta)_{TC}$	$(\gamma)_{TC}$	$(\alpha)_{TC}$	$(\gamma+\beta)_{Wet}$	$(\gamma)_{Wet}$	$(\alpha)_{Wet}$	site/mean depth ratio	[TP] water	[TN] water	[Chl a] water	Secchi depth
$F_{R(TC)}$	-	0.52*	0.17	0.02	0.18	0.56*	0.81***	0.01	0.24	0.46	-0.25	0.49*	-0.19	-0.24	-0.15	-0.05
$F_{L(TC)}$		-	-0.16	0.39	0.33	0.62**	0.07	-0.23	0.33	0.32	-0.23	0.45	-0.32	-0.36	-0.26	0.04
$D_{b(TC)}$			-	-0.52*	-0.29	-0.08	0.33	0.52*	-0.16	-0.29	-0.15	-0.09	0.09	0.12	0.00	-0.20
$k_{(TC)}$				-	0.10	0.07	-0.12	-0.39	-0.02	0.12	-0.06	0.05	-0.14	-0.25	-0.02	0.10
w					-	0.50*	-0.04	-0.65**	0.44*	0.25	-0.46*	0.49**	-0.44*	-0.54**	-0.26	0.20
$(\gamma+\beta)_{TC}$						-	0.49*	-0.29	0.62**	0.15	-0.43	0.37	-0.28	-0.45	-0.27	0.04
$(\gamma)_{TC}$							-	0.18	0.20	0.21	-0.21	0.33	-0.07	-0.11	-0.10	-0.11
$(\alpha)_{TC}$								-	-0.01	-0.24	0.66**	-0.25	0.27	0.59*	-0.04	-0.38
$(\gamma+\beta)_{Wet}$									-	0.15	0.13	0.20	-0.40*	-0.41*	-0.36	0.20
$(\gamma)_{Wet}$										-	-0.01	0.39*	-0.16	-0.16	-0.10	0.33
$(\alpha)_{Wet}$											-	-0.52**	0.63***	0.47*	0.62***	-0.29
site/mean depth ratio												-	-0.72***	-0.62***	-0.56**	0.58**
[TP] water													-	0.76***	0.91***	-0.73***
[TN] water														-	0.48*	-0.69***
[Chl a] water															-	-0.61**
Secchi depth																-

2.3.4 Geochemical profiles related to morphological, chemical and biological variables

I generally found no or only weak correlations between the parameters given by the two models and lake water quality data, represented by annual mean TP, TN, Chl *a* concentrations and Secchi depth (Table 2.3). Correlations between the biodiffusion coefficients and vertical decay coefficients of TN profiles and water column TN concentrations were, however, sufficiently strong to suggest causation, whereby the biodiffusion coefficients tended to increase with increasing water column TN. The coring site depth, lake mean depth, surface area and catchment area were generally not significantly correlated with any of the parameters given by the two models ($p > 0.05$). However, the coring site depth to lake mean depth ratio was significantly correlated with the burial rates and the flux of refractory TC (Table 2.3), and also inversely correlated with the vertical decay coefficients for wet weight profiles. The vertical decay coefficients for wet weight profiles were also significantly related to annual mean TP, TN, Chl *a* concentrations in the water column. However, this correlation can also be induced by the coring site to lake mean depth ratio, which was also significantly correlated with these water quality attributes.

2.4 Discussion

2.4.1 Model applications and constraints

While the calibration routine for the empirical model always converged on distinct model parameter values in a global minimum of the RMSE value space, the mechanistic model, which contains five parameters, could reproduce the same vertical profiles based on different parameter value combinations. I was able to accurately estimate and fix the burial rates (*w*) in the mechanistic model, but had to fit the parameters F_R, F_L, D_b and k by initially assuming fixed midrange values for D_b and k, so that F_R and F_L were close to the background and surface concentrations, respectively. The biodiffusion coefficients can be estimated more accurately based on the vertical distribution of tracer elements (e.g., ^{137}Cs and ^{210}Pb) that decay with known first order kinetic rate coefficients (Mulsow et al.

1998; Henderson et al. 1999; Meysman et al. 2005). This could lead to more accurate estimates of the first order kinetic rate coefficients for the decay of organic matter. Tracer data was not available for the 14 lakes in this study, however, and the parameter fit produced the best possible alternative approach to estimate the diagenetic parameters.

The empirical model, which was readily calibrated, may also be used as a tool in comparative studies where the discrete sectioning depth differs. For example, Bortleson and Lee (1970) described the vertical distribution of TP in sediments of six Wisconsin lakes, which ranged from oligotrophic to eutrophic. They sectioned sediment cores into 5 cm vertical intervals, however, and the concentrations in their surface samples are thus not directly comparable to the 2 cm vertical intervals used in this study. However, an empirical model fit to the TP profiles found in their six lakes provides estimates of the surficial sediment concentrations for each of their study lakes.

2.4.2 Vertical irregular profiles driven by redox-processes and variability in timescales

Most vertical profiles of TP, TN, TC, Fe, Mn and wet weight, showed high concentrations near the sediment-water interface and a relatively smooth trend of exponential decrease with sediment depth. Some geochemical profiles, however, especially from the deep oligotrophic lakes (e.g. Rotoma, Okataina and Tarawera), had irregular vertical concentration distributions, especially for TP, Fe and Mn. The vertical profiles of TP tend to follow a Gaussian shape (c.f. Davison 1993) in these lakes, where a subsurface maximum of sediment TP concentrations appears at a depth of approximately 5-13 cm in the sediments. This sub-surface peak of TP generally coincides with the location of peaks in Fe and Mn (e.g. Fig. 2.2, Lake Tarawera). The Gaussian-shaped profiles have previously been described for sediments in the deep, oligotrophic, Lake Baikal in Russia (Müller et al. 2002), which has long hydraulic retention time (~19 years) and low sedimentation rates (Edgington et al. 1991), and where oxygen is known to penetrate more than 2 cm into the sediments (Martin et al. 1993) as opposed to more eutrophic lakes, where oxygen penetrates no further than a few mm into the

sediments (Sweerts et al. 1991). The penetration of oxygen is strongly related to the organic content of the sediments (House 2003), and in deep oligotrophic lakes, with a relatively low organic content in the sediments, oxygen can penetrate deep into the sediments thereby extending the redox boundary, at which iron and manganese precipitate and where phosphorus species are adsorbed, deeper into the sediments, and thus creating these Gaussian shaped profiles with sub-surface peaks of TP, Fe and Mn (Davison 1985). The relatively simple empirical and mechanistic models presented in this study are generally less successful at reproducing the vertical concentration profiles of TP in these deep oligotrophic lakes. Nevertheless, the models still captured between 61 and 89% of the variation of TP in the sediments of lakes Rotoma, Okataina and Tarawera.

In applying steady state models to sediment profiles, I had to assume that the vertical concentration profiles (and model parameters) are at equilibrium with the given boundary conditions. However, the models were set up based on data from sediment deposited during the past 120 years, and only some of the lakes have remained relatively undisturbed during this period, and several of the lakes have become increasingly eutrophic, driven mostly by anthropogenic activities (Hamilton et al. 2006). Subsequently, sediment profiles from some of the lakes may not yet be at equilibrium with the current external nutrient load, which may render the correlations between current lake water quality data across all 14 lakes and the observed vertical sediment profiles less significant.

2.4.3 Understanding the vertical distribution of TP, TN and TC in lake sediments

The results presented in this study attest that the appearance of vertical profiles of sediment TP, TN and TC concentrations is not attributable to lake trophic status (or eutrophication) alone. Thus, studies that use these vertical geochemical profiles in lake sediments as evidence of anthropogenic effects (Smoak and Swarzenski 2004; Vreca and Muri 2006) should first account for the natural drivers of these vertical gradients. The correlation analysis revealed that the fluxes of refractory and labile components and the biodiffusive mixing may have a strong influence on the vertical distributions of TP, TN and TC across the 14

lakes. The flux of the labile component of TP, for example, had the greatest influence on the surface TP concentration (Fig. 2.3a), while the flux of refractory component of TP (Fig. 2.3b) and the burial rate (Fig. 2.3c) had the greatest influence on the background TP concentration. One might expect that the flux of labile TP would be related to lake productivity (and thereby trophic state) and depth.
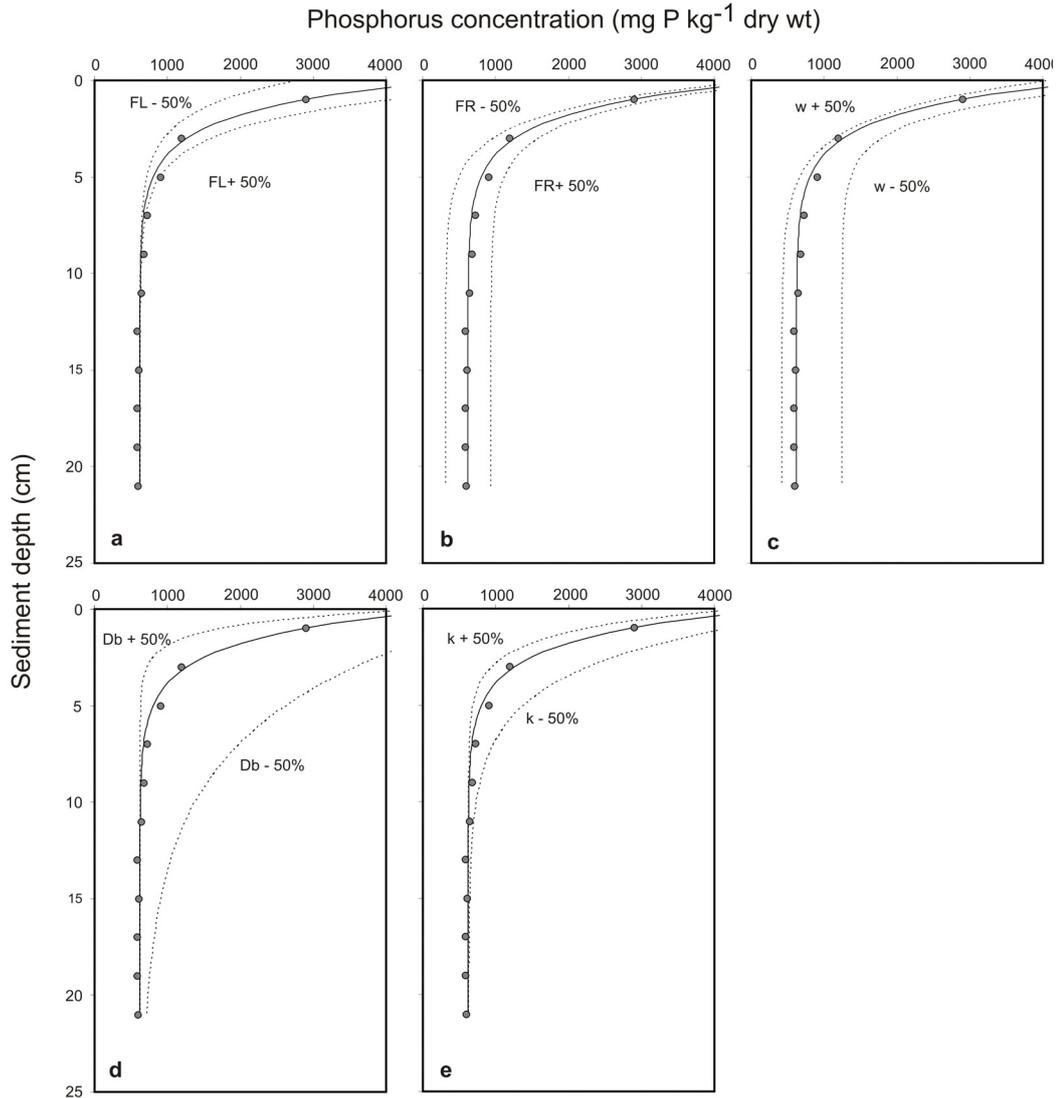
Figure 2.3. Application of the steady state diagenetic model to a sediment core from Lake Rototi. The influence of the flux of labile (a) and refractory (b) component of TP, burial rate (c), biodiffusion coefficient (d) and first order kinetic rate coefficient (e) on the vertical steady state distribution of TP concentrations.

However, across the 14 lakes there was no significant correlation between the flux of labile TP and any of the water quality attributes. The biodiffusive mixing generally showed a higher sensitivity towards the vertical decay of TP than the kinetic rate coefficient (Fig. 2.3d, Fig. 2.3e). In this context it should be noted that the biodiffusion coefficients for TP profiles generally were higher than those derived from TN and TC profiles. This may reflect the influence of the inorganic fraction of TP that can be strongly linked to the mineral composition of the sediments (e.g. Fe concentrations), causing some phosphorus species to be adsorbed to, for example, iron-oxyhydroxide complexes above certain redox boundaries in the sediments, enhancing vertical gradients of TP. As the mechanistic model used in this study did not distinguish between organic and inorganic phosphorus species (and did not include any adsorption processes), the assigned biodiffusion coefficients for TP will compensate for this, causing D_b to increase in order to reproduce the observed profiles. By contrast, the biodiffusion coefficients derived from the TN and TC profiles can be expected to better represent the actual biodiffusive mixing in the sediments, as there is not the same confounding effect of inorganic material.

When considering the transport process and the reactions described by the mechanistic diagenetic equation, it appears that physical compaction alone cannot be responsible for generating vertical concentration gradients in sediments. Nevertheless, the vertical decay coefficients for the wet weight profiles, which were effectively representing compaction, was the only single parameter that was significantly correlated with all other vertical decay coefficients (including those for TP, TN, TN, Fe and Mn). It is important to acknowledge that lake sediments are not, as I assumed in the mechanistic model, a homogenous mass of constant porosity and density. If one instead assumes that the sediments are comprised of high density material with low TP content (e.g., inorganic material) and low density material with high TP content (e.g., organic material), a density driven compaction may cause denser material to sink faster and deeper into the sediments relative to lighter material, as observed in tephra studies where relatively dense tephra sink several centimetres into lighter organic lake sediments (Beierle and Bond 2002). The correlation analysis suggests that this density driven compaction may be at least partly responsible for creating vertical concentration gradients in

natural lake sediments. The correlation analysis also revealed that the vertical decay coefficients for wet weight profiles were inversely correlated with site to mean depth ratios, which essentially demonstrates that the vertical profiles of sediment density are more uniformly distributed in shallower lakes/regions, presumably caused by resuspension that may intermittently mix and rework the surficial sediments in these lakes/regions (Håkanson and Jansson 1983).

In summary, this study shows that factors influencing vertical gradients in sediment geochemical profiles are multiple and complex but that the flux of refractory and labile matter, and biodiffusive mixing, may be the most important parameters influencing the observed geochemical gradients of TP, TN and TC in lake sediments. Physical compaction of the sediments may also be partly responsible for creating these gradients, presumably by causing denser material (with lower TP, TN and TC concentrations relative to lighter organic material) to sink faster into the sediments. Therefore, when evaluating the effects of anthropogenic activities on, for example, vertical profiles of sediment TP concentrations one must consider natural drivers of these vertical profiles, which readily can be done by applying the models presented in this study.

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Chapter 3: Sediment and nutrient accumulation rates in sediments of twelve New Zealand lakes: Influence of lake morphology, catchment characteristics and trophic state

3.1 Introduction

Internal nutrient loading can directly influence lake trophic state and substantially delay lake ecosystem responses to reduced external loading (Marsden 1989; Søndergaard et al. 2003; Jeppesen et al. 2005). Knowledge of nutrient dynamics associated with bottom sediments is therefore of critical importance in understanding and predicting whether a lake ecosystem is in equilibrium with its external nutrient load (Vollenweider 1970), and the duration of the delay that occurs in response to changes in external loading (Søndergaard et al. 2003). Sediment nutrient concentrations alone have been shown not to be an especially useful indicator of lake trophic status over a range of different lake ecosystems (Bortelson and Lee 1974; McColl 1977; Håkanson 1984). Temporal changes in sediment nutrient concentrations in individual lakes, however, may indicate changes in external loading (Eckert et al. 2003; Van der Molen et al. 1998), with causal activities linked to increasing agricultural land use or clearing of native forest (e.g. Schleske and Hodell 1995; Smoak and Swarzenski 2004). Studies of changes in sediment nutrient concentrations have tended to focus on individual lakes (e.g. Goedkoop and Pettersson 2000; Hambright et al. 2004) and there are no simple empirical models that relate sediment and nutrient accumulation rates to specific morphological features and land use activities over a series of lakes of widely varying trophic states.

The first objective of the present study was therefore to quantify net sedimentation rates and temporal changes in sediment nutrient concentrations in lakes ranging in trophic state from oligotrophic to highly eutrophic. A second objective was to test for relationships of net sedimentation rates and temporal changes in sediment

nutrient concentrations to chemical, biological and morphological variables across the lakes, using multiple linear regressions.

Studies into the composition of bottom sediments in several lakes in the Rotorua District, New Zealand, have been undertaken intermittently over the past three decades (e.g., McColl 1977; Stoffers et al. 1983; Pearson 2007). These studies form an excellent basis for a comparative study of temporal changes in sediment chemistry across these lakes. Furthermore, the presence of distinct tephra layers in the lake sediments as a result of periodic volcanic eruptions (Lowe and Green 1987) provides a valuable historical marker for undertaking comparative studies of net sedimentation rates. In the present study several intact sediment cores were collected and analyzed from within the deepest basins of 12 lakes in the Rotorua District and temporal changes in sediment nutrient chemistry were assessed by comparing data from the present study with that obtained by McColl (1977), Fish and Andrew (1980) and Blomkvist and Lundstedt (1995).

3.2 Materials and methods

3.2.1 Sampling sites

The Rotorua lakes (Fig. 3.1) were formed up to 140,000 years B.P. by a series of volcanic eruptions which led to formation of craters and damming of river valleys (Lowe and Green 1987). The geological area in and around the Rotorua District is still geothermally active, and lakes Rotorua, Tarawera, Rotomahana and Rotoehu are influenced by geothermally heated surface inflows, which can be naturally high in concentrations of phosphorus and a range of metals (Vincent and Forsyth 1987). Some of the lakes in the Rotorua District have been increasingly affected by human activities such as urbanization and farming, resulting in eutrophication, while others have been more or less unaffected (McColl 1972; Vincent et al. 1984; Hamilton 2004). The present Rotorua lakes have trophic states ranging from oligotrophic to highly eutrophic and mixing regimes from monomictic to polymictic, and provide an ideal opportunity to conduct comparative studies across various gradients of lake and catchment sizes and environmental stressors (Table 3.1).
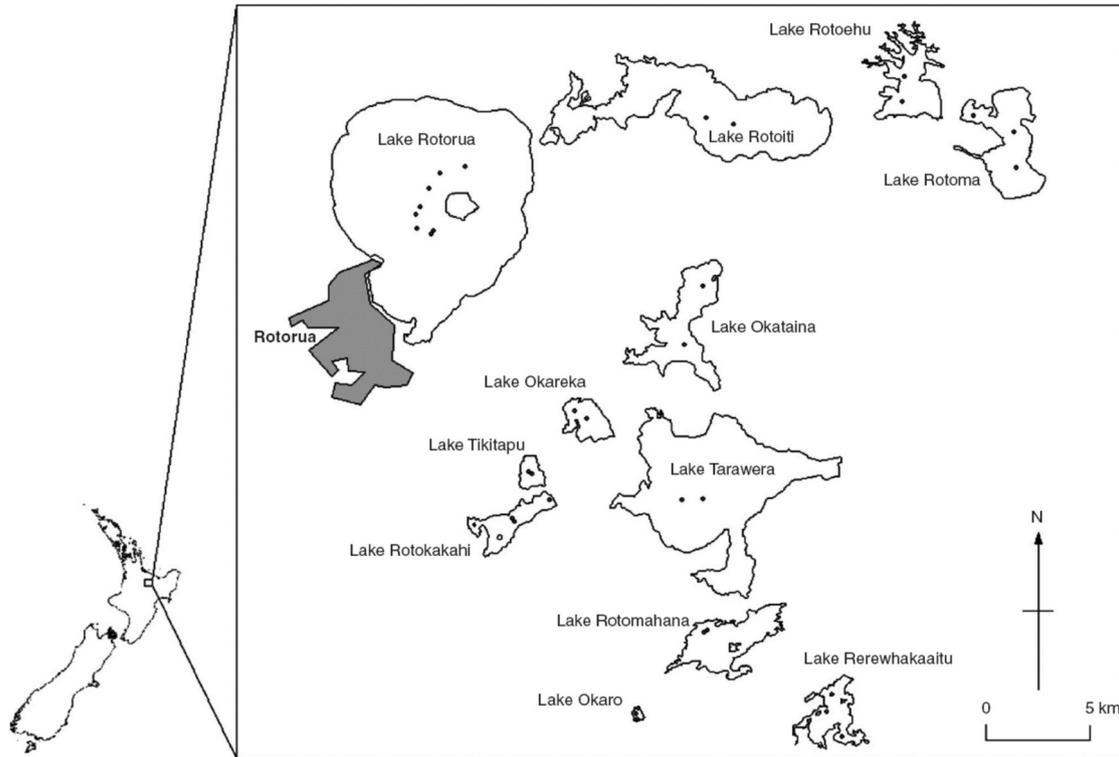
Figure 3.1. Locality map of the 12 study lakes in the Rotorua District and sampling sites (black dots).

Table 3.1. Characteristics of the Rotorua Lakes, from McColl (1975), Timperley (1987) and Scholes and Bloxham (2007). Trophic state is based on values of the Trophic Level Index (Burns et al. 2000). TN, TP and chlorophyll *a* figures from Lake Rotokakahi after 2000 are based on outflow data.

	Mean depth (m)	Max depth (m)	Lake area (ha)	Catchment area (ha)	1995-2006 average (mg m^{-3})			Trophic state
					TN	TP	Chl *a*	
Okaro	12.5	18.0	32	407	1220	117	40.0	Highly eutrophic
Rotorua	11.0	44.8	8,079	52,346	449	38	18.2	Eutrophic
Rotoehu	8.2	13.5	795	5,673	447	34	11.7	Eutrophic
Rotoiti	31.5	124.0	3,460	12,462	307	27	8.8	Eutrophic
Rotomahana	60.0	125.0	897	7,994	215	22	5.0	Mesotrophic
Rerewhakaaitu	7.0	15.8	579	3,816	400	8	5.9	Mesotrophic
Okareka	20.0	33.5	342	1,958	221	7	4.8	Mesotrophic
Rotokakahi	17.5	32.0	452	1,872	219	11	4.2	Mesotrophic
Tikitapu	18.0	27.5	146	567	215	6	2.0	Oligotrophic
Okataina	39.4	78.5	1,104	5,676	129	7	2.5	Oligotrophic
Tarawera	50.0	87.5	4,165	14,494	117	8	1.6	Oligotrophic
Rotoma	36.9	83.0	1,104	2,914	142	4	1.4	Oligotrophic

Water quality in 12 lakes in the Rotorua District has been monitored routinely since 1990 by Environment Bay of Plenty (EBOP) (Scholes and Bloxham 2007). The chemical composition of sediments is not part of the routine monitoring program, however, surface sediment samples (0-2 cm) were analysed in the 12 lakes in 1995 (Blomkvist and Lundstedt 1995). Furthermore, sediment samples were collected from six of the lakes in 1972 (McColl 1977) and from Lake Rotorua in 1976-79 (Fish and Andrew 1980). In these previous studies, most of the coring was in the deepest basins of the lakes (Table 3.2), hence areas conforming to accumulation bottoms (cf. Håkanson and Jansson 1983). In this study, sediment cores were collected from a further one to seven other sites within the deep basins, to estimate spatial variability in the deep basin in each of the 12 lakes (Fig. 3.1).

Table 3.2. Number of sediment cores taken and average depth of sampling sites in four studies selected for comparative analysis of sediment TP, TN and TC concentrations.

	Present study (2006)		Blomkvist and Lundstedt (1995)		Fish and Andrew (1979)		McColl (1972)	
	No. cores	Average site depth (m)	No. cores	Average site depth (m)	No. cores	Average site depth (m)	No. cores	Average site depth (m)
Okaro	3	14.7	3	15.0			4	15.0
Rotorua	8	20.9	9	19.7	1	19.0		
Rotoehu	3	10.2	3	9.5				
Rotoiti	2	57.2	6	63.0				
Rotomahana	2	74.0	3	94.3				
Rerewhakaaitu	4	11.9	3	13.0				
Okareka	2	30.4	3	32.1			2	30.0
Rotokakahi	3	23.8	3	23.2			3	19.3
Tikitapu	2	25.3	3	26.3			9	22.8
Okataina	2	66.4	3	64.4			4	60.0
Tarawera	2	82.9	3	72.9				
Rotoma	3	63.2	3	71.2			10	65.0

3.2.2 Sampling methods

Sampling took place between March 2006 and January 2007. Cores were collected with a cylindrical gravity corer that was designed to leave the core intact. The surface sediment was visually inspected in each core, and when there was any evidence of disturbance at the sediment-water interface or in the core profile, the core was discarded and another one taken.

The volcanic eruption of Mt Tarawera in 1886 dispersed tephra over an area >200 km^2 including much of the Rotorua District (White et al. 1997). Lake Rotomahana, which was near the centre of the eruption site, was the lake most affected by the eruption, changing from a small shallow crater lake to the deepest of all of the Rotorua lakes (z_{max}= 125 m). Remains of Tarawera tephra are evident in bottom sediments of all of the 12 sampled lakes, and depth was measured from the sediment-water interface to the Tarawera tephra by viewing through the transparent core barrel as cores were collected. Using this tephra depth, an annual mean net sedimentation rate was calculated for the period 1886-2006.

Samples of the surficial sediment (0-2 cm) were collected from each core using a custom-made slicing chamber. A 50 mL Vulcan™ centrifuge tube was filled completely with the surficial sediments, sealed with a cap to be airtight, and placed on ice until return to the laboratory, where porewaters were immediately separated by centrifugation at 4000 rpm for 40 min. The resulting sub-samples of both porewaters and sediment solids were stored frozen (-18 ºC) before further analysis. The remaining sediment layers above the Tarawera tephra were stored for dry weight analysis.

3.2.3 Analytical methods

Sediment dry weight fraction was determined by weighing solid samples of surficial sediments before and after drying at 105 ºC for 24 hours, and also taking into account the porewater fraction. Dry weight of the remaining sediment overlying the Tarawera tephra was also determined to quantify average net sedimentation rates (kg m^{-2} yr^{-1}).

Total phosphorus (TP) and *iron* (Fe) content in the dried surficial sediments was determined after the dried solids had been ground with mortar and pestle, and approximately 0.5 (±0.1) g of each sample had been digested with Aqua Regia (3:1 v:v of 1:5 conc. hydrochloric acid solution and 1:2 conc. nitric acid solution), based on a modified standard procedure (Martin et al. 1994). Liquid from the digested solid samples, and from porewater samples acidified with two drops of conc. hydrochloric acid, was then analyzed for phosphorus and iron by Induced Coupled Plasma Mass Spectrometry (ICP-MS model ELAN DRC II).

Total carbon (TC) and *nitrogen* (TN) content in sediment solids were determined by sub-sampling approximately 0.25 (±0.06) g of the dry sediment solids and analyzing by combustion (LECO TruSpec model CN Determinator). The lakes have non-calcareous sediments with total carbon content closely related to the sediment organic content (McColl, 1977). Carbon content analysis was not conducted in the survey by Blomkvist and Lundstedt (1995).

Total nitrogen in porewaters was analyzed spectrophotometrically as for nitrate with a Lachat Instruments flow injection analyzer (model QuikChem 8000 FIA+) after a preliminary persulphate digestion (Ebina et al. 1983).

3.2.4 Mathematical and statistical methods

Comparison of results from the present study with those of previous studies (McColl 1977; Fish and Andrew 1980; Blomkvist and Lundstedt 1995) was based on TP, TN and TC concentrations in the top 2 cm of the sediment, combining the concentrations from dry sediment solids and sediment porewaters. The temporal changes in sediment nutrient concentrations referred to in this study, are thus based on a change in mean concentrations of sediment phosphorus, nitrogen and carbon from two separate sampling years (1995 and 2006 for phosphorus and nitrogen, and 1972 and 2006 for carbon), whereas net sedimentation rates are based on sediment accumulated between 1886 and 2006. As the number of cores taken in each individual study was limited to between two and ten per lake, a range of concentrations is presented, to best represent the variability for sediments of each individual lake basin.

Statistical relationships of mean rates of net sedimentation were tested against readily quantifiable lake variables (e.g. water depth at coring sites, mean and max. lake depth, lake volume, catchment area, percentage of pasture in catchment, annual mean TP, TN and chlorophyll *a* concentrations in the water column and mean lake trophic state during the period 1995-2006), using multiple stepwise linear regression. In this context the Trophic Level Index (TLI) was used, as an indicator of trophic state of the lakes (Burns et al. 2000). The TLI values are calculated from annual means of water column TP, TN, chlorophyll *a* and Secchi depth and generally range between two (oligotrophic) and six (highly eutrophic) for the Rotorua lakes (Burns et al. 2000).

Using multiple stepwise linear regression, Søndergaard et al. (1996) showed that the TP concentrations of surface sediment in shallow Danish lakes can be described by the external load, sediment iron concentration, sediment organic content (represented by loss on ignition) and mean lake depth ($r^2 = 0.91$, $p < 0.0001$, $n = 21$). Vollenweider (1976) showed that the water column TP concentration will equilibrate with the external load at a rate dependent on the inflow TP concentration and the hydraulic residence time. Thus, a given change in the external load is also assumed implicitly to drive a temporal change in the sediment TP concentrations. Pearson correlation coefficients were calculated to test for correlations between temporal changes of nutrients in the sediment and temporal changes of nutrients in the water column of the 12 lakes within the Rotorua district.

Goodness of fit of the multiple regression models was tested using Root-Mean-Square-Error (RMSE) values and Pearson correlation coefficients (r). The RMSE value for each empirical model was minimized by calibrating the empirical parameters using *Solver* in Microsoft Excel, after which the Pearson correlation coefficients were calculated. Solver uses a generalized, reduced gradient, non-linear optimization code to minimize model error. Since Lake Rotomahana has been in a transitional state with increasing water levels following the 1886 Mt Tarawera eruption, data from this lake were discarded from the statistical analysis.

3.3 Results

3.3.1 Net sedimentation rates

The depth to the Tarawera tephra varied from 7 to 36 cm below the surface of the sediments in the deep basins across the 12 lakes, giving a range of mean net sedimentation rates in the lakes of 0.6 to 3.0 mm yr^{-1} (Table 3.3). Lakes with very deep basins and lakes with high TLI values tended to have the highest net sedimentation rates, e.g., oligotrophic Lake Tarawera (mean depth, $\bar{z}$ = 50 m) and eutrophic Lake Rotoehu ($\bar{z}$ = 8.2 m) with net sedimentation rates of 2.2 and 2.6 mm yr^{-1}, respectively. Not surprisingly, the net sedimentation rates expressed in mm yr^{-1} were strongly correlated (r = 0.82, p < 0.01, n = 12) with net sedimentation rates (dry weight) expressed in kg m^{-2} yr^{-1}.

Table 3.3. Net sedimentation rates in the deepest basins and annual mean Trophic Level Index (TLI) values (Burns et al. 2000) for the period 1995-2006. Sediment cores that did not extend to the tephra layers have been disregarded in calculations of net sedimentation rates. Hence, mean depth of sampling sites may differ slightly from that presented in Table 3.2.

Lake	Mean and range (in parentheses) of net sedimentation rate for 1886-2006 (mm · yr^{-1})	Mean and range (in parentheses) of net sedimentation rate for 1886-2006 (kg · m^{-2} · yr^{-1})	Net sedimentation rate (Lowe and Green 1987) (mm · yr^{-1})	Mean site depth (m)	Mean TLI
Okaro	2.3 (1.5-2.8)	0.21 (0.12-0.29)		14.7	5.7
Rotorua	3.0 (3.0-3.0)	0.35 (0.35-0.35)	0.4-0.7	21.4	4.7
Rotoehu	2.6 (2.6-2.6)	0.36 (0.34-0.37)		10.4	4.6
Rotoiti	1.7 (1.7-1.7)	0.20 (0.20-0.20)	1.0-2.3	45.3	4.1
Rotomahana	0.8 (0.75-0.9)	0.08 (0.07-0.09)		74.0	3.8
Rerewhakaaitu	1.7 (1.6-1.8)	0.21 (0.20-0.22)		13.8	3.6
Okareka	1.4 (1.3-1.5)	0.26 (0.26-0.26)		30.4	3.3
Rotokakahi	1.0 (0.3-1.4)	0.16 (0.05-0.21)		23.8	3.4
Tikitapu	0.6 (0.6-0.6)	0.11 (0.11-0.12)		25.3	3.0
Okataina	1.4 (1.4-1.4)	0.21 (0.19-0.23)		66.4	2.8
Tarawera	2.2 (2.1-2.3)	0.21 (0.21-0.21)		82.9	2.8
Rotoma	1.4 (0.9-1.8)	0.27 (0.18-0.36)	0.2-1.7	63.2	2.4

3.3.2 Sediment TP, TN and TC concentrations

The mean TP concentration increased in surficial sediments in seven of the 12 lakes in the period 1995-2006 though the data from the present study also show a large range in concentration within the deep basins of individual lakes (Fig. 3.2). However, in sediments of the deep basins in lakes Rotoiti, Rotokakahi and Okareka, the minimum TP concentration in cores from our study exceeds the highest concentration recorded in 1995. The average rate of increase in TP concentrations in the sediments of these three lakes ranged between 27.5 and 114.4 mg P kg^{-1} dry wt yr^{-1}. Lake Rotoiti ($\bar{z}$ = 31.5 m) showed an increase of more than 55 % in mean TP concentration in surficial sediments, from 2,200 to 3,460 mg P kg^{-1} dry wt, between 1995 and 2006. Three lakes also showed a decrease in mean surficial sediment TP concentration, most notably Lake Rotorua ($\bar{z}$ = 11m) where the concentration between 1995 and 2006 decreased by 40 %, from 1,740 to 1,040 mg P kg^{-1} dry wt.
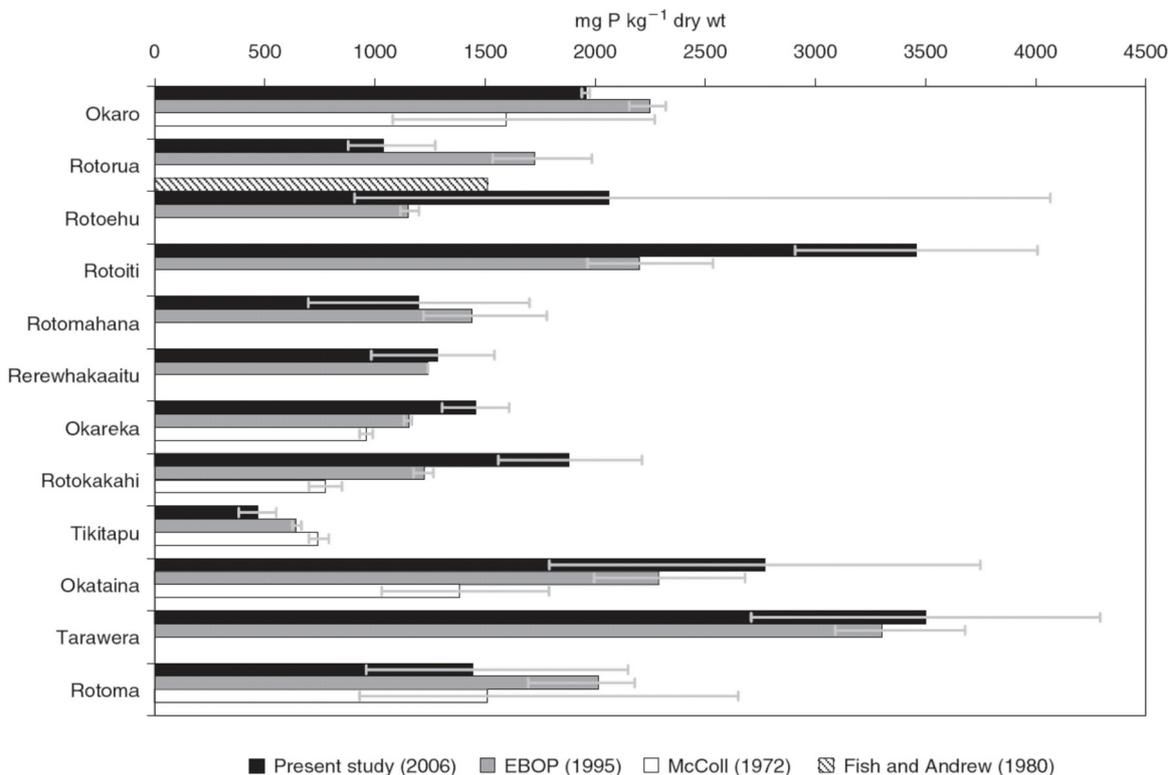
Figure 3.2. Mean TP concentration in surficial sediments (0-2 cm) in deep basins of the 12 lakes (see Table 3.2) at present (2006) and compared with earlier studies. Sampling dates are presented in parentheses. Error bars represent ranges.

The mean TN concentration in surficial sediments increased in 11 of the 12 lakes during the period 1995-2006 (Fig. 3.3). The TN concentration range is relatively small for cores from individual lakes, thus the maximum TN concentration found in 1995 is less than the minimum concentration found in 2006 in 9 of the 12 lakes (Fig. 3.3), and average rates of increase in TN concentrations ranged between 51.8 and 869.2 mg N kg^{-1} dry wt yr^{-1}. Highest concentrations of sediment TN generally occur in the shallower, eutrophic lakes, e.g., Lake Rotoehu ($\bar{z}$ = 8.2 m) and Lake Okaro ($\bar{z}$ = 12.5 m). However, relatively deep Lake Rotoiti ($\bar{z}$ = 31.5 m) has the highest sediment TN concentrations, and also shows the largest rate of increase, from 9,400 to 18,900 mg N · kg^{-1} dry wt; an increase of nearly 100 % between 1995 and 2006. Only Lake Rotorua shows evidence of a decrease in sediment TN concentrations, with a reduction of 30 % from 10,000 to 6,800 mg N kg^{-1} dry wt.
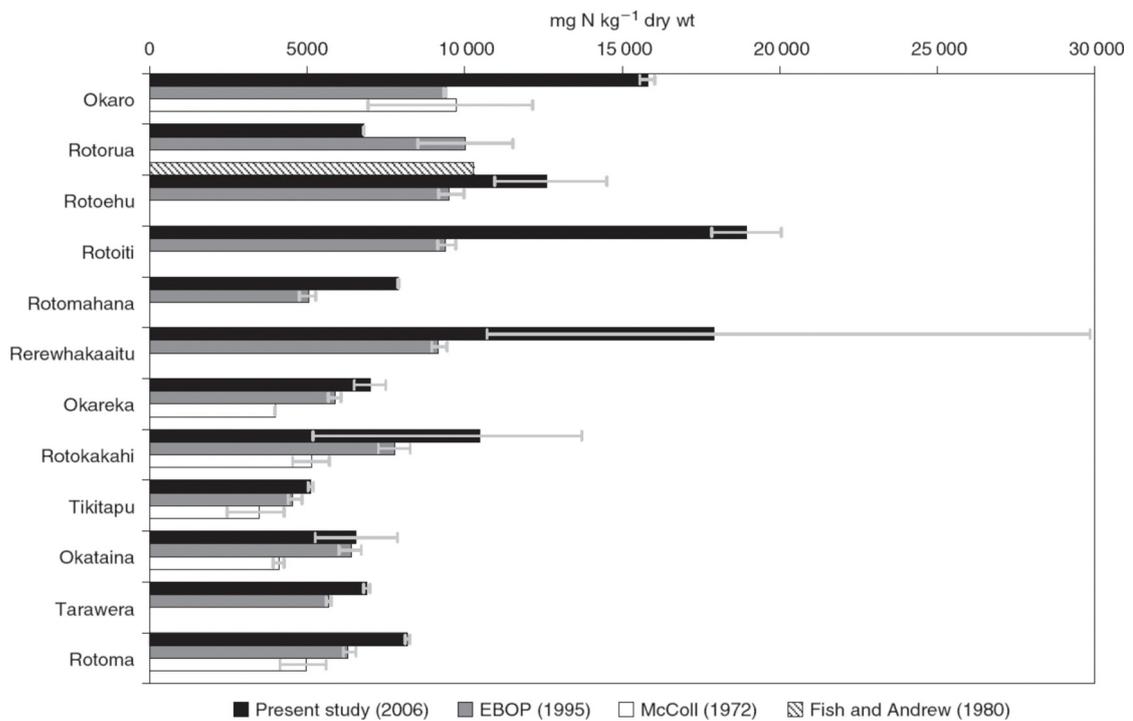
Figure 3.3. Mean TN concentrations in surficial sediments (0-2 cm) in deep basins of the 12 lakes (see Table 3.2) at present (2006) and compared with previous studies. Sampling dates are presented in parentheses. Error bars represent ranges.

For four of the six lakes analyzed in 1972 by McColl (1977) minimum TC concentrations found in the survey from 2006 exceed the highest concentration recorded in 1972 (Fig. 3.4). The average rate of increase of TC concentrations ranged between 426.7 and 1313.8 mg C kg^{-1} dry wt yr^{-1}. As for TN, the highest TC concentration tends to occur in the sediments of shallow or eutrophic lakes. For example, the mean concentration of TC in surficial sediments was highest in shallow Lake Rerewhakaaitu ($\bar{z}$ = 7 m) though concentrations of TC were highly variable in this lake, however, similar to results for TN.
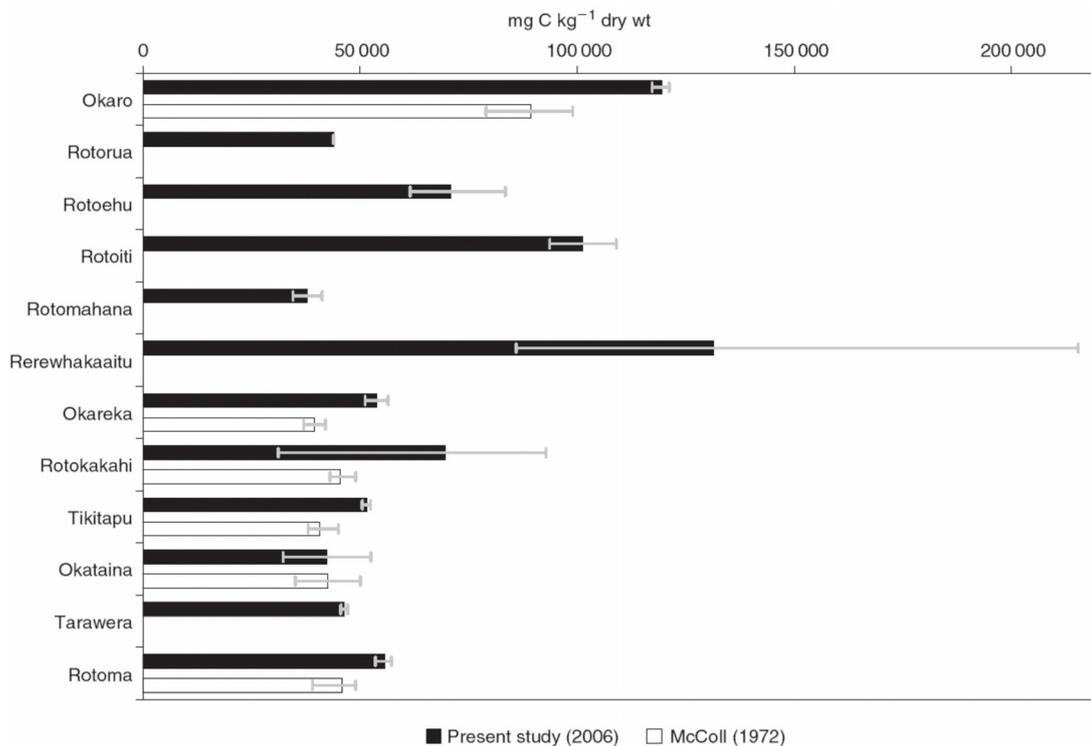
Figure 3.4. Mean TC concentrations in surficial sediments (0-2 cm) in deep basins of the 12 lakes (see Table 3.2) at present (2006) and compared with earlier studies. Sampling dates are presented in parentheses. Error bars represent ranges.

3.3.3 Correlation analysis – net sedimentation rates

Through linear regression analysis I found a significant correlation between net sedimentation rates (expressed here in mm yr^{-1}) and the average TLI for the period 1995-2006 (r = 0.66, p < 0.05, n = 11) as well as the catchment area (r = 0.65, p < 0.05, n = 11) (Table 3.4). The average TLI and the catchment area explained more

than 67% of the variability in net sedimentation rates by multiple linear regression (Table 3.4). Variables such as site depth, lake volume, or catchment area to lake volume ratio were not significantly correlated (p > 0.05) with net sedimentation rates.

Table 3.4. Empirical linear regression models describing net sedimentation rates (S_{mean}; mm yr^{-1}). Input variables for the empirical models include TLI (based on an average of annual TLIs in the period 1995 to 2006) and catchment area/watershed size (WS_{size}; km^2) for all individual lakes excluding Lake Rotomahana (n = 11). RMSE values are in mm yr^{-1}.

	Variables	RMSE	r	p-value
S_{mean}	= 1.45 + 0.00310 x WS_{size}	0.51	0.65	< 0.05
S_{mean}	= 0.023 + 0.47 x TLI	0.51	0.66	< 0.05
S_{mean}	= 0.167 + 0.366 x TLI + 0.00243 x WS_{size}	0.38	0.82	< 0.01

3.3.4 Correlation analysis – sediment TP, TN and TC concentrations

Correlations were examined amongst mean concentrations of TC, TN and TP of surficial sediments from the 2006 survey of the 11 lakes (Table 3.5). Sediment TC concentrations were strongly linearly correlated with sediment TN concentrations (r = 0.93, p < 0.01, n = 11), but not with sediment TP concentrations, nor was there a correlation between sediment TN and TP concentrations (Table 3.5). The current TLI (based on annual averages from July 2005 to June 2006) and mean sediment concentrations of TP, TN and TC were also not significantly correlated (Table 3.5). Concentrations of TP, TN and TC expressed per unit area in the surficial 2 cm sediment (i.e., mg m^{-2}) were also not significantly related to any water quality indices (p > 0.05). When accounting for between-lake differences in sediment focusing, by normalizing TP, TN and TC concentrations by the area of sediment accumulation relative to total lake surface area, as described by Blais and Kalff (1995), I also found no significant correlations with water quality indices.

Table 3.5. Correlation matrix (excluding data from Lake Rotomahana, n = 11) between average site depth (m), TLI based on the year 2005/2006, surficial sediment concentrations of TP, TN and TC (based on survey from 2006), and sediment ratios as well as water column ratios of N:P, C:P and C:N. ** = significant at $p < 0.01$ and * = significant at $p < 0.05$.

	TP sediment	TN sediment	TC sediment	N:P sediment	C:P sediment	C:N sediment	N:P water	C:P water	C:N water	TLI water	Average site depth (m)
TP sediment	-	0.28	0.05	-0.66*	-0.72*	-0.66*	-0.62*	-0.48	0.05	-0.04	0.66*
TN sediment		-	0.93**	0.41	0.18	-0.40	-0.03	-0.25	-0.11	0.49	-0.30
TC sediment			-	0.62*	0.44	-0.08	0.20	-0.19	-0.25	0.45	-0.44
N:P sediment				-	0.95**	0.51	0.72*	0.14	-0.29	0.19	-0.69*
C:P sediment					-	0.74*	0.77**	0.11	-0.38	0.04	-0.60
C:N sediment						-	0.64*	0.13	-0.41	-0.27	-0.24
N:P water							-	0.30	-0.57	-0.48	-0.25
C:P water								-	0.51	0.07	-0.29
C:N water									-	0.58	-0.09
TLI water										-	-0.61*
Average site depth (m)											-

Sediment ratios (Table 3.6) of C:N were significantly correlated with sediment ratios of C:P (r = 0.74, p < 0.05, n = 11) but not ratios of N:P (Table 3.5). The sediment N:P ratios were, however, strongly correlated with sediment C:P ratios (r = 0.95, p < 0.01, n =11). Water column ratios of N:P (based on annual average TN and TP from July 2005 to June 2006) were significantly correlated with sediment ratios of C:N (r = 0.64, p < 0.05, n = 11), C:P (r = 0.77, p < 0.01, n = 11) and N:P (r = 0.72, p < 0.05, n = 11). However, water column ratios of C:N or C:P (where carbon content in water column is estimated by a chlorophyll *a* conversion factor of 50 mg C mg^{-1} Chl *a*) showed no statistical relationship with sediment C:N, C:P and N:P ratios (p > 0.05). I also found that TLI (July 2005 to June 2006) produced no statistical relationship with sediment ratios of C:N, C:P or N:P (Table 3.5). The site depth was, however, significantly correlated with the sediment N:P ratio (r = -0.69, p < 0.05, n = 11) but not the N:P and C:N ratios (Table 3.5). Hence, sediment N:P ratios showed a significant decrease with increasing site depth, but depth still explained less than 50% of variation in the sediment nutrient ratios across the lakes.

Table 3.6. Mean mass ratios of C:N, C:P and N:P in surficial sediments. Ranges are denoted in parentheses.

Lake	C:N	C:P	N:P
Okaro	7.6 (7.3-7.8)	61.0 (59.3-62.5)	8.1 (7.9-8.3)
Rotorua	6.5 (6.5-6.5)	42.3 (34.5-50.0)	6.6 (5.3-7.7)
Rotoehu	5.6 (4.2-7.6)	34.3 (15.1-92.0)	6.1 (2.7-16.0)
Rotoiti	5.3 (4.7-6.1)	29.3 (23.4-37.5)	5.5 (4.4-6.9)
Rotomahana	4.8 (4.4-5.2)	31.6 (20.3-59.2)	6.6 (4.6-11.4)
Rerewhakaaitu	7.3 (2.9-20.1)	102.4 (55.7-219.1)	13.9 (6.9-30.4)
Okareka	7.7 (6.8-8.7)	36.9 (31.8-43.2)	4.8 (4.0-5.7)
Rotokakahi	6.7 (2.3-17.9)	37.1 (14.1-59.5)	5.6 (2.3-8.8)
Tikitapu	10.1 (9.7-10.4)	110.3 (91.5-137.3)	11.0 (9.1-13.6)
Okataina	6.5 (4.1-10.0)	15.3 (8.6-29.3)	2.4 (1.4-4.4)
Tarawera	6.7 (6.5-6.9)	13.2 (10.6-17.4)	2.0 (1.6-2.6)
Rotoma	6.8 (6.5-7.1)	38.6 (24.9-59.6)	5.7 (3.8-8.6)

3.3.5 Correlation analysis – temporal changes of sediment TP, TN and TC concentrations

There was high variability in the rates of accumulation or loss of sediment TP and TN based on differences between samples taken from the 12 lakes in 1995 and in 2006, and in surficial sediment TC concentrations based on 1972 and 2006 samples (Fig. 3.5).
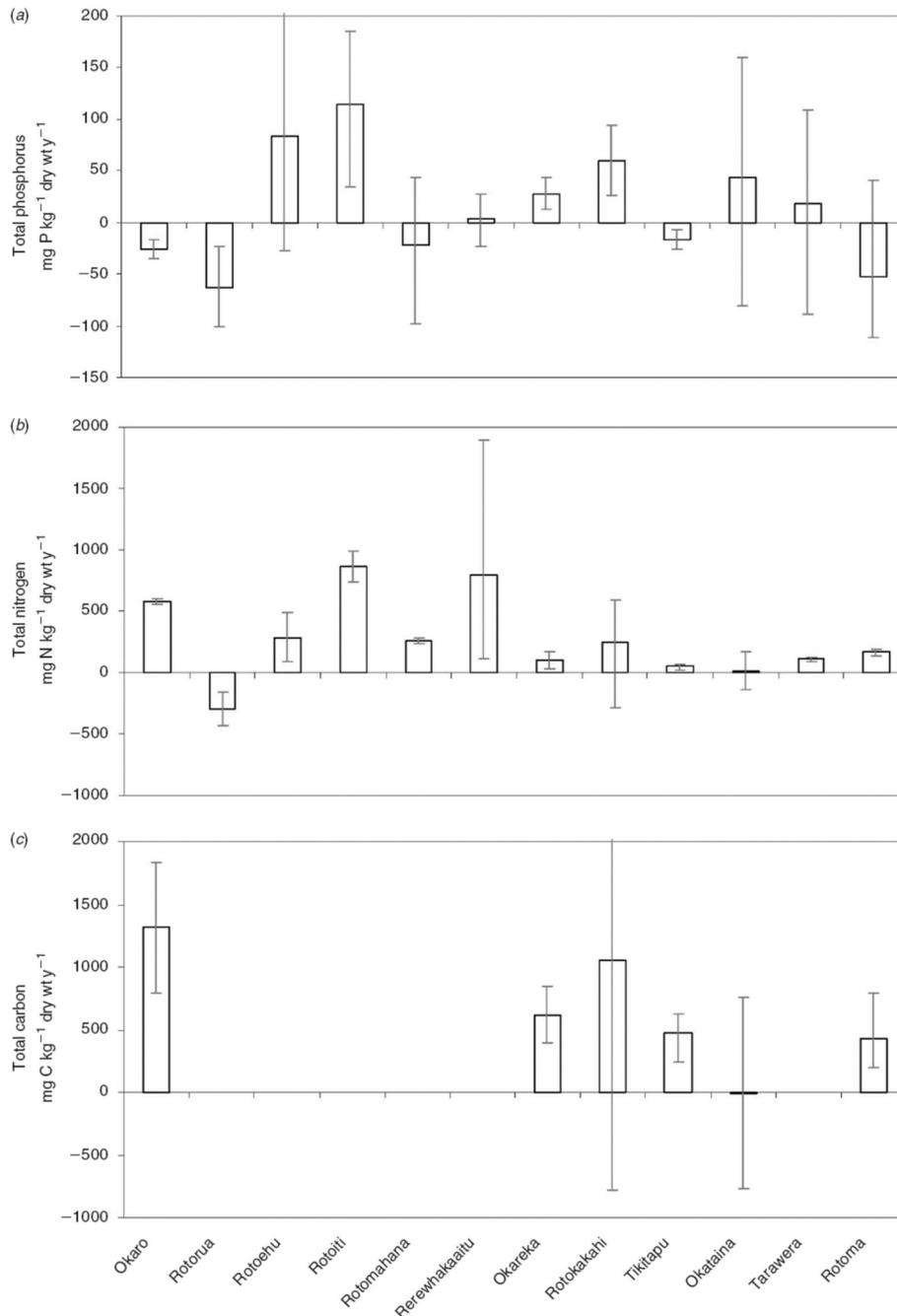
Figure 3.5. Mean temporal changes in TP, TN and TC concentrations in the surficial sediments (0-2 cm) in the deep basins of the 12 lakes. Error bars represent range between sites. TP and TN changes are based on the period 1995-2006, whereas TC changes, available for only six lakes, are based on the period 1972-2006. The mean change of TC concentrations in Lake Okataina is close to zero.

A selection of lake water column variables (including annual mean TP, TN, and Chl *a* concentrations as well as temporal trends of water column TP, TN and Chl *a* concentrations for the period 1995-2006) did not yield statistically significant relationships (p = 0.16-0.93) with temporal changes in mean sediment TP, TN and TC concentrations in the lakes. Similarly, physical and morphological variables (including net sedimentation rates, catchment area, lake mean depth, site depth and percentage of pasture in the catchment were not significantly related to temporal changes in sediment TP, TN and TC concentrations (p = 0.13-0.97).

3.4 Discussion

3.4.1 Trends in net sedimentation rates

Several complex interacting factors are known to influence sedimentation rates in lakes, including sediment focusing (Blais and Kalff 1995) external allochthonous load, autochthonous productivity and sediment resuspension (Håkanson 1995). Nonetheless I derived a simple empirical model that produced a strong correlation with the observed net sedimentation rates in lakes in the Rotorua district, based only on lake trophic state and catchment area (Table 3.4). These variables equate roughly to autochthonous productivity and to the external load of allochthonous material, respectively. For example, predictions of sedimentation rate for Lake Rotoiti (estimated to be 2.0 mm yr^{-1} from the model) would vary from 1.4 to 2.6 mm yr^{-1} if the lake was to have a TLI ranging from the most oligotrophic (TLI = 2.5, Lake Rotoma) to the most eutrophic (TLI = 5.7, Lake Okaro) of the Rotorua lakes, respectively.

The observed net sedimentation rates found in the 12 New Zealand lakes in our study are similar to those reported by Kumar et al. (2007) for eight North Indian lakes. The North Indian lakes have also been subjected to varying anthropogenic influences in recent decades (Kumar et al. 2007). The observed net sedimentation rates, which are used to derive our empirical regression model, are based on the depth to the Tarawera tephra, and therefore represent averages for the period 1886-2006, but the TLI values which are used in the correlation analysis are based on the most recent decade (corresponding to the data available to the author).

Changes in trophic state will contribute to variations in the mean net sedimentation rate within the period 1886-2006, and it is notable in this context that several of the lakes have become eutrophic in recent decades. TLI values based only on data from the period 1995-2006, however, still produced a significant correlation with the observed net sedimentation rates. Compared with earlier sedimentation data from Lowe and Green (1987) some of the Rotorua lakes now appear to have higher sedimentation rates (Table 3.3). Lake Rotorua in particular, has a current net sedimentation rate most likely > 3 mm yr^{-1} though there is no evidence of a change in sedimentation rates in Lake Rotoiti and Lake Rotoma.

3.4.2 Sediment TP, TN and TC concentrations – comparative studies

As net sedimentation rates clearly differ between lakes in this study, the surficial 0-2 cm of sediment may represent different time scales of deposited material (ranging 7-30 years). Therefore, one could assume that sediment sampling taking into account the net sedimentation rates of each individual lake, so that the discrete sediment sampling depth represents the same integrated time interval, is a prerequisite for making comparisons of sediment nutrient concentrations between lakes. However, in this context it is important to also acknowledge that some nitrogen and phosphorus species undergo diagenetic transformations and can be mobile in lake sediments, and therefore migrate vertically (Carignan and Flett 1981), resulting in formation of vertical concentration profiles (Søndergaard et al. 1996) under a sediment-water interface concentration boundary and a zero flux boundary deeper in the sediments. Bioturbation may also affect the vertical concentration profiles as well as the nutrient fluxes at the sediment-water interface. A practical issue to consider when sampling lake sediments is that considerable quantities of sediment are required for analytical purposes. In practise this means that vertical sections of 1-5 cm of sediment have been sampled in most studies. Therefore, to overcome these sampling issues, comparative lake sediment studies (e.g. Håkanson 1984; Søndergaard et al. 1996) have traditionally considered a fixed sediment depth interval where nutrient concentrations may change as a response to changes in boundary conditions at the sediment-water interface.

Important prerequisites to ensure direct comparison of various geochemical concentrations found in different lake sediment studies are that seasonal variation is negligible and that analytical methods are equivalent. Seasonal variations may be observed in the surface 0-0.5 cm sediment (Goedkoop and Pettersson 2000) but in the present study involving sampling of the surface 2 cm of sediment, including both dissolved and particulate fractions, reduces seasonal variability, and changes in sediment TP, TN and TC concentrations should only be evident on a time scale of several years. Analytical methods for determining nutrient concentrations in the sediment differ slightly between the present and previous studies from which temporal changes were derived. For example, the studies of both Blomkvist and Lundstedt (1995) and McColl (1977) to determine TP used a sulphuric acid digestion procedure which could have slightly different extraction capabilities from the Aqua Regia digestion, though this may typically account for < 1% of the variation (Gasparatos and Haidouti 2001). By comparison, the standard deviation of sediment phosphorus concentrations in eight cores collected from the same deep basin in Lake Rotorua and at similar depths (20.4 m to 21.6 m) exceeded 20 % of the mean concentration. For TN concentrations, Blomkvist and Lundstedt (1995) analysed for total Kjeldahl nitrogen (TKN), which may yield nitrogen concentrations slighter higher (0-10%) than those obtained from the dry combustion used in our study (Kowalenko 2001), while McColl (1977) also used combustion analysis to determine both sediment TN and TC concentrations. Hence, analytical differences between studies cannot explain the relatively large increase of TP and, in particular, TN concentrations in the sediments of some Rotorua lakes between 1995 and 2006 (Fig. 3.5). The increasing sediment TP and TN concentrations are therefore likely linked to the eutrophication of some of the Rotorua lakes. In Lake Rotoiti, for example, annual average TP concentrations in the epilimnion have increased from 20 μg P L^{-1} to more than 30 μg P L^{-1} between 1995 and 2006, and concurrently the average surficial sediment TP concentration has changed from 2200 to 3460 mg P kg^{-1} dry wt.

Several lake studies which have used similar analytical methods to describe phosphorus, nitrogen and carbon concentrations in surficial sediments (e.g., Konrad et al. 1970; Bortleson and Lee 1974; Håkanson 1984; Maassen et al.

2005) have been based on vertical depth intervals of 1 to 5 cm. Søndergaard et al. (1996) studied surficial sediments of 32 relatively shallow Danish lakes and sampled using same vertical depth intervals as in this study (0-2 cm), and Reitzel et al. (2007) quantified TP concentrations at various sediment depth intervals (including 0-1 and 1-2 cm) in mesotrophic Lake Erken, Sweden. The mean concentration of TP in the surficial sediments of the 12 lakes in our study (450-3,500 mg P kg^{-1} dry wt) is relatively low compared to concentrations found by Søndergaard et al. (1996) and Reitzel et al. (2007) (200-8,500 mg P kg^{-1} dry wt). Compared with the Rotorua lakes, the Danish lakes were generally of higher trophic state (mesotrophic to highly eutrophic). The mean concentration of TP exceeded 2,000 mg P kg^{-1} dry wt in surficial sediments of only 4 out of 12 (33 %) of the New Zealand lakes compared with c. 50 % of the 32 Danish lakes while Lake Erken had a concentration of 2,200 mg P kg^{-1} dry wt.

Mean concentrations of TN and TC in the surficial sediments of the 12 New Zealand lakes are also generally low compared to those recorded by Vreca and Muri (2006), who analyzed organic carbon (OC) and TN in surficial sediments (0-2cm) of an oligotrophic and a eutrophic Slovenian lake. The mean TN and TC concentration from the 12 New Zealand lakes ranged between 5,000-19,000 mg N kg^{-1} dry wt and 40,000-130,000 mg C kg^{-1} dry wt, whereas Vreca and Muri (2006) found ranges of 17,500-19,000 mg N kg^{-1} dry wt and 146,000-159,000 mg OC kg^{-1} dry wt in the two Slovenian lakes.

3.4.3 Patterns of change in sediment TP, TN and TC

Although sediment TP, TN and TC concentrations found in our Rotorua lakes survey from 2006 generally appear to be lower than for lakes of central and northern Europe (represented by Slovenian and Danish lakes respectively), it is evident that concentrations in most Rotorua lakes are increasing. The magnitude of the increases in sediment TP in some of the lakes suggests that, for example, within a decade or so concentrations may be similar to the more eutrophic lakes of Denmark. This does not necessarily mean that the lakes in New Zealand also will reach a trophic state that is similar to the lakes in Denmark, as I found no significant correlation between sediment concentrations of TP, TN and TC and

lake trophic state. Lakes in the Rotorua District are generally deeper than the Danish lakes, which cause the surficial sediments in these lakes to be relatively enriched with TP even though these New Zealand lakes are generally of lower trophic status.

No other studies have yet described temporal trends of surficial sediment TP, TN and TC concentrations across lakes of different trophic states, though there is evidence of trends for individual lakes. Eckert et al. (2003) described a trend of decreasing surficial sediment TP concentrations at two different sites in mesotrophic/eutrophic Lake Kinneret, Israel, during the period 1997-2000. Annual mean sediment TP concentration decreased by 146-147 mg P kg^{-1} dry wt yr^{-1} in the surficial sediments at the two sites during this time. This rate of decrease exceeds the highest rate of decrease observed in the lakes from my study, which occurred in Lake Rotorua (63 mg P kg^{-1} dry wt yr^{-1}). The decrease of sediment TP concentrations in Lake Kinneret was, however, associated with a sequence of drought years (Eckert et al. 2003). Another case study from Lake Veluwe, The Netherlands, suggests that TP concentrations have doubled in the surface sediments during a period of eutrophication, between 1956 and 1979 (Van der Molen et al. 1998), which is a change similar to that observed in sediment TP concentrations in Lake Rotoiti during the period 1995-2006.

None of the variables included in the linear correlation analysis, including in-lake water quality variables (such as annual mean water column TP concentrations or temporal trends of water column TP concentrations based on the period 1995-2006) as well as properties of the lake catchment and morphometry, produced statistically significant correlations with temporal changes of sediment TP, TN and TC concentrations in the Rotorua lakes. In-lake variability of sediment TP concentrations in particular, but also TN and TC concentrations, was generally high and confounded statistical relationships. Between lake variations in sediment mineral composition (e.g., iron and manganese concentrations) as well as redox conditions (i.e. lakes with or without seasonal anoxic hypolimnia) will also influence retention and release rates of phosphorus and nitrogen species in the sediments. Therefore, the sediment nutrient composition across the 12 lakes may respond differently to for example a change in water column productivity – even

if the change of water column productivity is of similar magnitude in all lakes. Variations in concentrations of surficial sediment total iron (Fe) clearly demonstrate the geochemical diversity between the lakes (Fig. 3.6), and the sediment Fe:TP ratios also varied substantially between lakes (from 3 to 29 by weight). Although I found no significant linear correlation between Fe and TP in surficial sediments across all the lakes ($p > 0.05$), high Fe concentrations in sediments of oligotrophic Lake Okataina and Lake Tarawera may be related to the high TP content of these lake sediments.
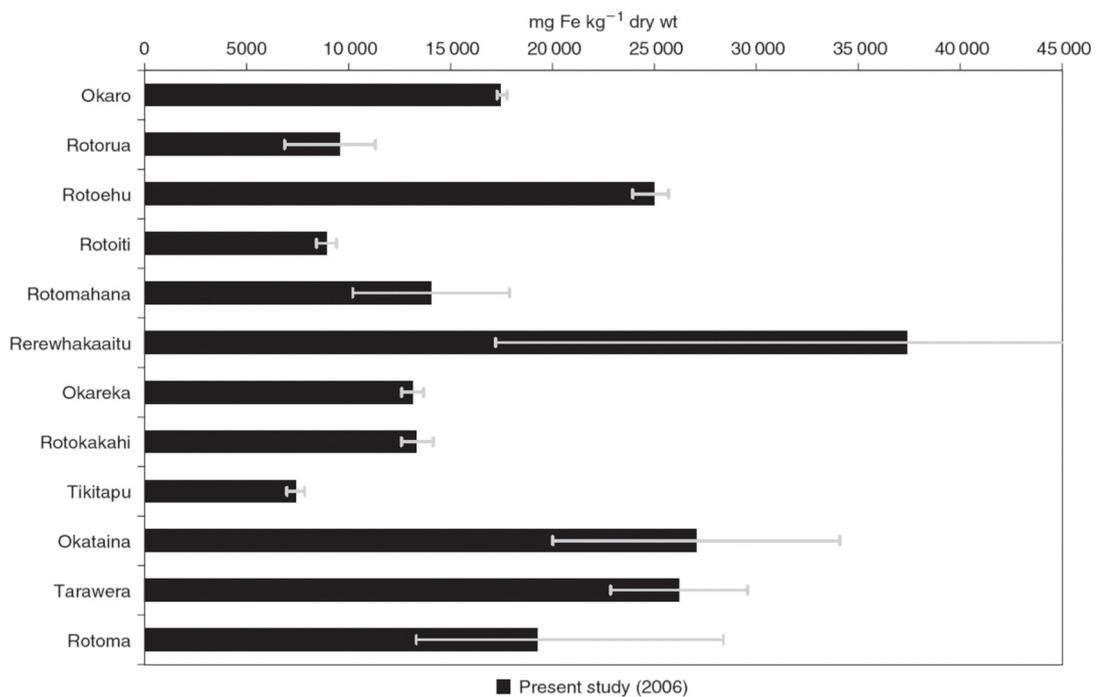
Figure 3.6. Mean Fe concentrations in surficial sediments (0-2 cm) in deep basins of the 12 lakes (see table 2) at present (2006). Error bars represent ranges.

In summary, I found that a multiple linear regression model, accounting for catchment area and lake trophic state, explained the majority of the variation in net sedimentation rates across the study lakes. Linear regression models, also including catchment area and lake trophic state as well as temporal changes of water column TP, TN and Chl *a* concentrations, were, however, not able to explain the temporal changes of sediment TP, TN and TC concentrations.

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Chapter 4: The influence of water quality and sediment geochemistry on the horizontal and vertical distribution of phosphorus and nitrogen in sediments of a large, shallow lake

4.1 Introduction

It has long been recognized that bottom sediments play an important role in lake ecosystem dynamics, both as a sink and source of nutrients, thereby strongly influencing lake trophic status and biodiversity (Nürnberg 1984; Søndergaard et al. 2003). Knowledge of sediment nutrient abundance and availability in lake bottom sediments is therefore of critical importance for understanding and predicting whether a lake ecosystem is in equilibrium with its external nutrient load (Vollenweider 1970), and the duration of the delay that may occur in response to changes in external loading (Søndergaard et al. 2003). Studies into the composition of lake sediments have traditionally focussed on either horizontal distributions of nutrients and metals in surficial sediments (e.g. Håkanson 1984; Nõges and Kisand 1999; Eckert et al. 2003) or vertical distributions (e.g. Konrad et al. 1970; Søndergaard et al. 1996; Jinglu et al. 2007). Spears et al. (2006), for example, found that horizontal variations of sediment phosphorus species were linked to benthic algae abundance in surficial sediments of shallow lake Loch Leven, Scotland, but they did not consider variations in the vertical sediment profile. Conversely, Vreca and Muri (2006) related the vertical distribution of organic carbon and total nitrogen in sediment cores collected from two Slovenian lakes to changes in accumulation rates of these variables during the prior decade, but did not consider horizontal variations within the individual lakes.

Vertical and horizontal distributions of nutrients and metals in sediments have been described separately for individual lakes; however, these distributions are very rarely quantified concurrently. An integrated approach considering all dimensions could improve understanding of the role of tributary loadings, water

column productivity, advection and mixing, and diagenesis in contributing to spatial variability of sediment nutrient concentrations. In the present study I examine sediment phosphorus and nitrogen concentrations in both horizontal and vertical dimensions in large (area 2,338 km^2), shallow (max. depth 3.0 m, mean depth 1.9 m) Lake Taihu, China, which is subject to sediment resuspension events (Qin et al. 2004), rapid eutrophication (Zhu 2008) and in summer 2007, an exceptional bloom of toxin producing cyanobacteria (Guo 2007).

It has previously been demonstrated that surficial sediment nutrient concentrations are not readily related to trophic status across a series of different lakes (McColl 1977). However, distinct horizontal water column concentration gradients occur in Lake Taihu (Chen et al. 2003a; Wang and Liu 2005), from high nutrient and chlorophyll *a* concentrations in the water column in the north, where some of the major polluted tributaries enter the lake, towards relatively low concentrations in the south, where macrophytes generally are abundant. I hypothesise that the surface sediment nutrient concentrations of Lake Taihu may be closely related to the spatial variability of water column variables. The main objective of this study was to test whether the horizontal distribution of surficial sediment phosphorus and nitrogen concentrations are related to the distinct spatial heterogeneity observed in the water column of Lake Taihu. A further objective was to quantify how phosphorus concentrations in surficial sediments relate to those obtained deeper in the sediments, from vertical sections. This information sets a basis for evaluating the influence of processes that may lead to spatial heterogeneity in sediment concentrations, such as known temporal trends of enrichment in tributaries entering northern bays of Lake Taihu (Qin et al. 2007b) or the effects of wave induced turbulence and horizontal transport of resuspended sediments across the lake (Qin et al. 2004).

The internal phosphorus loading from sediments of Lake Taihu, and the influence of wind-wave disturbance, have been the focus of several studies (e.g. Fan et al. 2004a; Qin et al. 2004; Luo et al. 2006). In order to control internal loading of phosphorus in the north-east area of the lake, 0.5 m of the surface sediments were dredged from Wuli Lake, which is situated in the northern part of Meiliang Bay (Fig. 4.1) (Jin et al. 2006). Dredging of other bays has not yet been carried out,

however, because the merits of dredging the lake sediments have not been clearly established, both from scientific and economic viewpoints (Fan et al. 2004b; Cao et al. 2007; Zhong et al. 2008). Thus, information about both the horizontal and vertical distribution of phosphorus in the sediments of Lake Taihu is highly pertinent to considerations of future management of the lake. An additional objective of this study was therefore to use a large number of sampling stations of relatively uniform depth to evaluate both the horizontal and the vertical variability of total phosphorus, total nitrogen and organic content in the sediments of Lake Taihu, in order to identify whether there are regions where sediment nutrients are differentially concentrated.
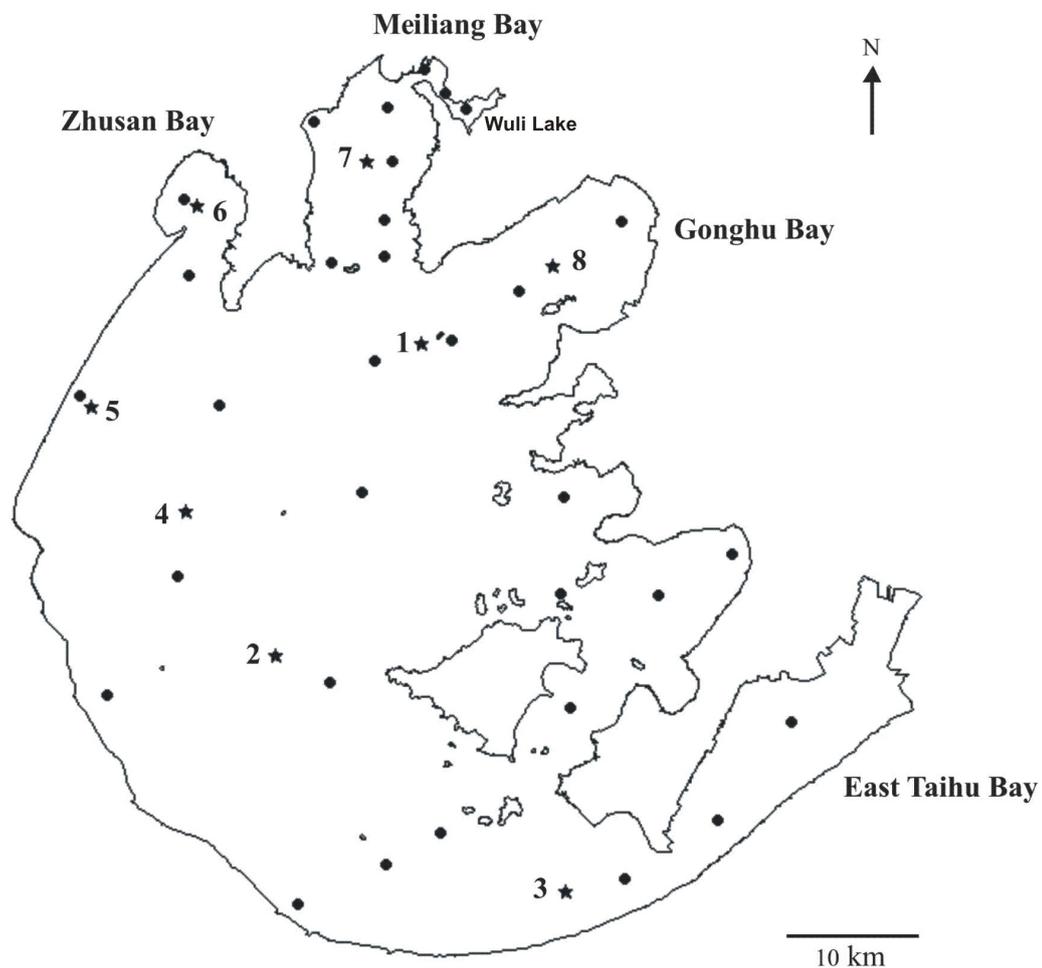
Figure 4.1. Distribution of sampling sites in Lake Taihu, China. Water column and surficial sediments were sampled at sites marked with the symbol (●) during 2005 and vertical sediment cores were collected at sites marked with the symbol (★) in 2006.

4.2 Materials and methods

4.2.1 Study site

Lake Taihu is the third largest freshwater lake in China and is located in the southern Changjiang River Delta (Qin et al. 2007a). The lake is in a subtropical region strongly influenced by monsoons. Between 1991 and 1999 water temperature varied from 1.5 to 32.5 ^{o}C, with a mean of 17.6 ^{o}C (Chen et al. 2003a). The Lake Taihu catchment (36,900 km^2) is densely populated (37 million inhabitants in 2000), with land use predominantly for rice and wheat cultivation. The lake is an important source of drinking water and fishery, and is also used extensively for navigation, transportation and recreation. Lake Taihu is prone to blooms of toxin producing cyanobacteria, and since the 1980s *Microcystis* spp. blooms have occurred each summer and have spread progressively south from the northern end of the lake (Qin et al. 2007a).

4.2.2 Sampling

Thirty-two widely distributed sites in Lake Taihu (Fig. 4.1) were sampled by the Taihu Laboratory for Lake Ecosystem Research, to quantify the horizontal variability of both water column and surficial sediment variables, thus obtaining one sampling point for every ~3% of the lake surface area. Surface water samples were taken monthly from 14 of the 32 sites and the remaining 18 sites were sampled seasonally during 2005. Water samples were divided into two subsamples, with one subsample immediately filtered (GF/C filter) for chlorophyll *a* analysis. The filter was placed on ice together with the remainder of the water sample and both were deep frozen immediately upon return to the laboratory. Sediment samples were collected using a piston corer from the 32 water sampling sites on one occasion in May 2005. Only surficial sediments (0-2 cm) were sampled, using a custom-made slicing disk to separate the upper sediment. I conducted an additional sediment survey in October 2006, when sediment cores were collected from eight sites (Fig. 4.1). Each of these eight cores was divided into vertical sections at 2 cm intervals down to a sediment depth of approx 20 cm. Sediment samples from the 2005 survey were air dried in the laboratory to constant weight over at least 3 days, while the eight cores in 2006 were oven dried

(103-105 ^{o}C) in the laboratory to constant weight over approximately 24 hours. Dry matter content was calculated by weighing samples before and after drying.

4.2.3 Analysis of water samples and surficial sediments collected from 32 sites in 2005

Total phosphorus (TP) and *total nitrogen* (TN) concentrations in *water column* samples were analyzed following thawing, using a combined persulphate digestion (Ebina et al. 1983) followed by spectrophotometric analysis as for phosphate and nitrate (Qian and Fu 1987).

Chlorophyll a (Chl *a*) was determined spectrophotometrically for water samples using ethanol extraction from thawed filters (Jespersen and Christoffersen, 1987). The Chl *a* concentration was calculated based on measurements of absorbance at wavelengths 665 and 750 nm (Chen et al. 2006).

Sediment loss on ignition (LOI) was determined by weighing a dried sediment sub-sample before and after ignition in a muffle furnace at 550 ºC for 4 hours.

Total phosphorus and *total nitrogen* in surficial *sediments* were determined by sub-sampling c. 30 mg of the dried sediment from each site, grinding with mortar and pestle, weighing, adding 25 mL of distilled water, and then analysis as for TP and TN in water samples.

4.2.4 Analysis of vertical sediments cores collected from 8 sites in 2006

Total phosphorus (TP), *total iron* (Fe), *total manganese* (Mn) and *total calcium* (Ca) content of sediment cores collected in October 2006 were determined on dried sediments that had been ground with a mortar and pestle. Approximately 0.5 g of each sample was digested with Aqua Regia (3:1 v:v of 1:5 conc. hydrochloric acid solution and 1:2 conc. nitric acid solution), based on a modified standard procedure (Martin et al. 1994). Liquid from the digested solid samples was then analyzed for TP, Fe, Mn and Ca by Induced Coupled Plasma Mass Spectrometry (ICP-MS, model ELAN DRC II).

Total carbon (TC) and *total nitrogen* (TN) content in dried sediment was determined by sub-sampling approx 0.25 g and analyzing by combustion (LECO TruSpec model CN Determinator). Concentrations of TC and TN were determined for every second vertical sub-sample in each core.

4.3 Results

4.3.1 Surficial sediment chemistry and water column concentrations

The coverage from 32 stations was used to produce a contour plot of sediment and water column concentrations across the lake basin, based on surficial sediment data from the 2005 survey and water column data constituted as a mean of the monthly or seasonal surface water samples in 2005 (Fig. 4.2). Concentrations of TP and TN in surficial sediments of Lake Taihu generally varied between 330 and 1,030 mg P kg dry wt^{-1} and 380 and 2,370 mg N kg dry wt^{-1}, respectively (Fig. 4.2), and LOI varied between 1.68 and 9.38 % of dry wt. The horizontal distribution of annual mean TP and TN concentrations in the water column varied from 0.036 to 0.25 mg P L^{-1} and 1.00 to 8.43 mg N L^{-1}, respectively (Fig. 4.2), and the annual mean concentration of Chl *a* in the water column varied between 3.4 and 38.6 μg L^{-1}. While some isolated stations deviated in concentration substantially from the relatively uniform distribution across adjacent stations, there were clear spatial trends on a basin scale. For example, TP concentrations in surficial sediments were strongly elevated above those of the main lake basin in Zhushan, Meiliang and Gonghu bays. Similarly, water column TP concentrations were high in Zhushan and Meiliang bays, but tended to be slightly lower in Gonghu Bay. The relative variation across the lake tended to be higher for water column TP than for sediment TP.
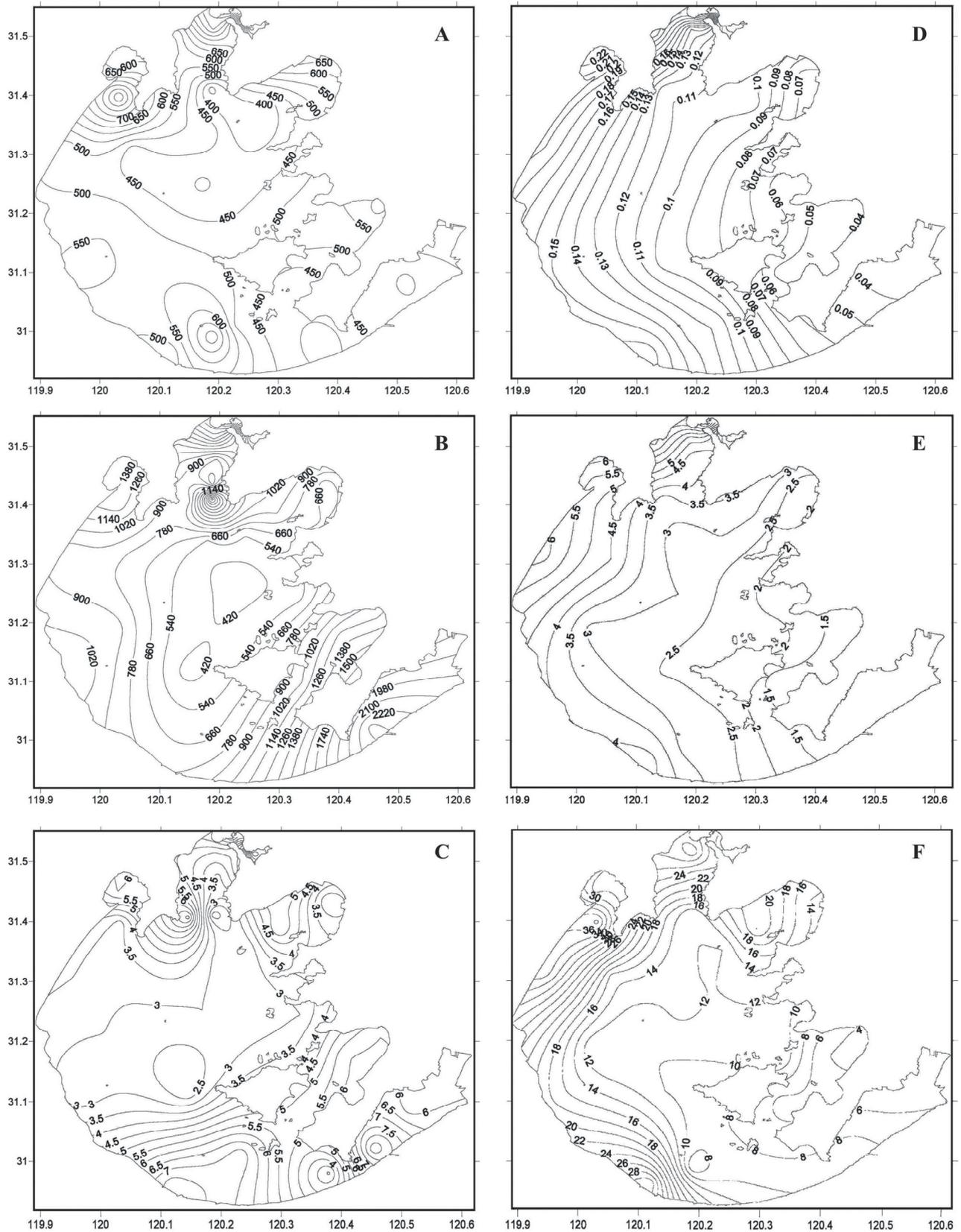
Figure 4.2. Contour plots of surficial sediment concentrations of A. total phosphorus (mg P kg dry wt^{-1}), B. total nitrogen (mg N kg dry wt^{-1}) and C. organic content (% LOI) and 2005 average water column concentrations of D. total phosphorus (mg P L^{-1}), E. total nitrogen (mg N L^{-1}) and F. chlorophyll *a* (µg Chl a L^{-1}). Contour lines were produced by the Surfer Mapping System v8.00 software using Kriging interpolation between sites surveyed in 2005. X-axis and y-axis are latitude and longitude respectively.

The surficial sediment TP concentrations were significantly correlated with water column TP concentrations ($r = 0.45$, $p < 0.05$, $n = 32$) as well as TN ($r = 0.54$, $p < 0.01$, $n = 32$) and Chl *a* concentrations ($r = 0.46$, $p < 0.01$, $n = 32$) (Table 4.1) but generally with low Pearson correlation coefficient values. Correlations for relationships of sediment TN to water column variables were generally not significant ($p > 0.05$) and only sediment LOI produced a weak but significant correlation with sediment TN ($r = 0.37$, $p < 0.05$, $n = 32$). Sediment TN tended to be more horizontally uniformly distributed over the lake than sediment TP, but for the water column there was a clear gradient of increasing TN towards the north-western area of the lake, similar to water column TP concentrations, and reflected in the high correlation coefficient between water column TN and TP ($r = 0.93$, $p < 0.001$, $n = 32$).

Table 4.1. Correlation matrix ($n = 32$) of surficial sediment (0-2 cm) TP, TN and LOI with annual mean water column TP, TN and Chl *a* based on 32 sites sampled in 2005. ** = significant at $p < 0.01$ and * = significant at $p < 0.05$.

	TP sediment	TN sediment	LOI sediment	TP water	TN water	Chl *a* water
TP sediment	-	$r = 0.31$	$r = 0.35$	$r = 0.45*$	$r = 0.54**$	$r = 0.46**$
TN sediment		-	$r = 0.37*$	$r = 0.09$	$r = 0.17$	$r = 0.06$
LOI sediment			-	$r = 0.10$	$r = 0.10$	$r = 0.05$
TP water				-	$r = 0.93**$	$r = 0.78**$
TN water					-	$r = 0.81**$
Chl *a* water						-

Not surprisingly, Chl *a* concentrations were closely correlated with both TP ($r = 0.78$, $p < 0.001$, $n = 32$) and TN ($r = 0.81$, $p < 0.001$, $n = 32$) in the water column, but of the sediment variables there was only a weak correlation with TP (Table 4.1). Both water Chl *a* and sediment LOI had lower values in the middle of the main lake basin. For LOI there was a strong decreasing gradient from both the north and south towards the centre of the lake compared with Chl *a* for which the gradient was skewed much more towards high levels in the north-western part of the lake, particularly in Zhushan Bay and to a lesser extent Meiliang Bay.

Mean water column ratios of TN:TP for the 32 stations (Table 4.2) indicate that primary producers in Lake Taihu are more likely to be phosphorus rather than nitrogen limited, with an annual average TN:TP mass ratio in the water column of 29.7:1 during the 2005 survey. By contrast the TN:TP mass ratio in the surficial sediments sampled at these stations in 2005 was only 2.1:1. The average TC:TN mass ratio (5.3:1) in the surficial sediments was relatively close to the Redfield ratio (5.7:1), whereas the average TC:TP mass ratio in the surficial sediments (13.7:1) was much lower than the Redfield ratio (41.1:1).

Table 4.2. Annual average TN:TP ratios (± SD) in water column and surficial sediments sampled at 32 stations in 2005, average TN:TP ratio in inflows and outflows of Lake Taihu based on the hydrological year of 2001-2002 (from Xu and Qin 2005) and average TN:TP ratio of nutrients derived from atmospheric wet deposition (from Luo et al. 2007). The ratios of TC:TN and TC:TP are based on data from surficial sediments sampled at 8 stations in 2006.

	TN:TP ratio (wt:wt)	TC:TN ratio (wt:wt)	TC:TP ratio (wt:wt)
Water column	29.7 (± 5.0)		
Sediment	2.1 (± 1.3)	5.3 (± 1.1)	13.7 (± 4.5)
Inflows	27.8		
Outflows	21.8		
Atmospheric wet deposition	56.3		

4.3.2 Vertical geochemical profiles

With the exception of site 6 from Zhusan Bay, which had a relatively high surficial sediment TP concentration of 1,380 mg P kg dry wt^{-1} and TN concentration of 2,600 mg N kg dry wt^{-1}, surficial sediments from the eight core sites in 2006 all had TP concentrations within the range 450-580 mg P kg dry wt^{-1} and TN in the range 1,150-1,800 mg N kg dry wt^{-1} (Fig. 4.3, Fig. 4.4 and Fig. 4.5). Some cores (sites 1-5) had relatively low TP concentrations at the surface and increasing concentrations with sediment depth (Fig. 4.3, Fig. 4.4 and Fig. 4.5). However, profiles from the northern bays of Lake Taihu (sites 6, 7 and 8) generally had high TP concentrations in the uppermost sediment layers, and decreasing concentrations with sediment depth. Even though vertical TP concentration profiles appear to be quite variable between the eight cores, the TP

variation in individual cores was strongly related to variations in TC, Fe and Mn (Fig. 4.3, Fig. 4.4 and Fig. 4.5).
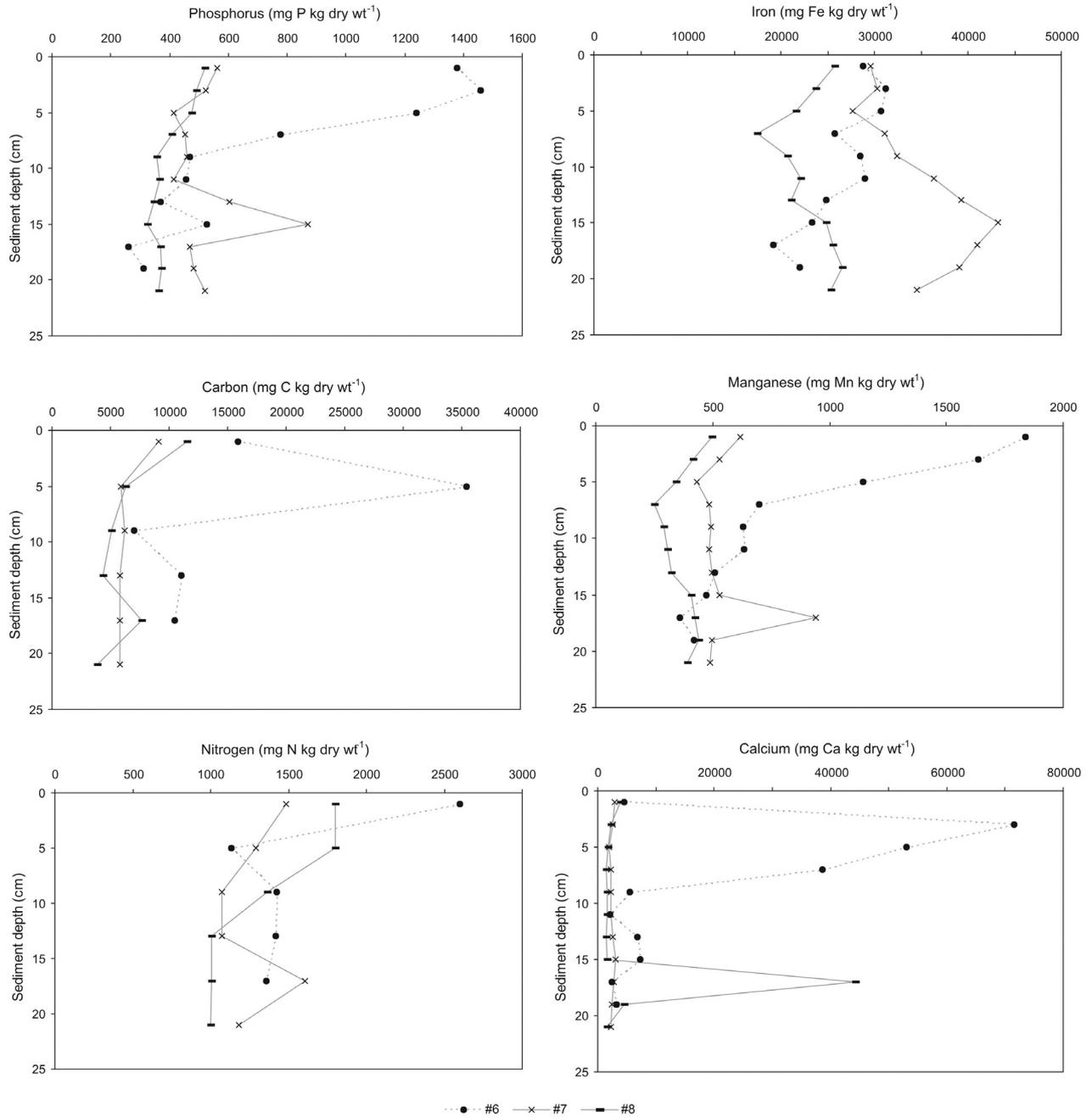
Figure 4.3. Vertical profiles of sediment total phosphorus (mg P kg dry wt[-1]), total nitrogen (mg N kg dry wt[-1]), total carbon (mg C kg dry wt[-1]), iron (mg Fe kg dry wt[-1]), manganese (mg Mn kg dry wt[-1]) and calcium (mg Ca kg dry wt[-1]) based on 2006 survey from the three most northern sampling sites (sites #6, #7 and #8 as located in Fig. 4.1).
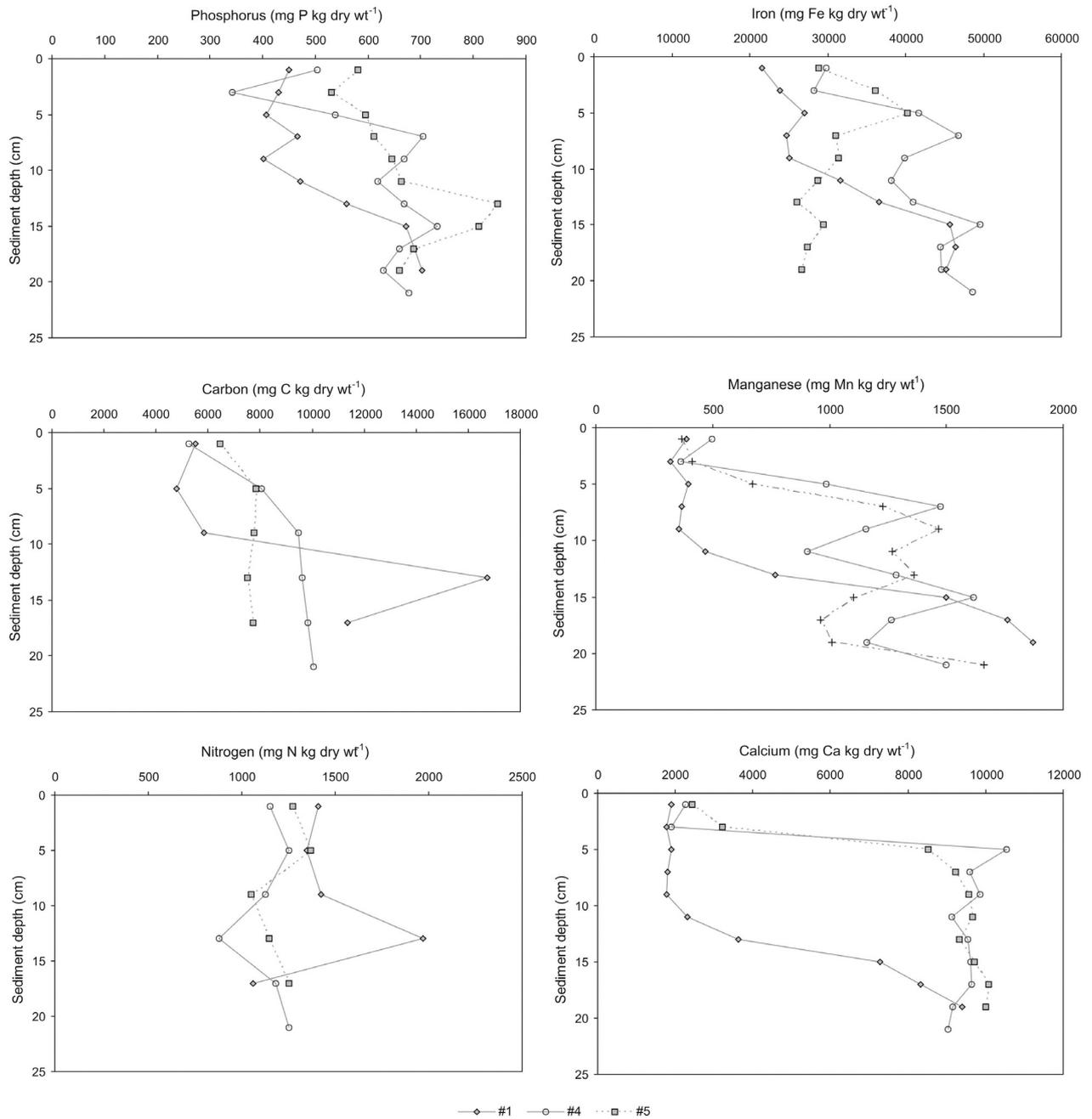
Figure 4.4. Vertical profiles of sediment total phosphorus (mg P kg dry wt[-1]), total nitrogen (mg N kg dry wt[-1]), total carbon (mg C kg dry wt[-1]), iron (mg Fe kg dry wt[-1]), manganese (mg Mn kg dry wt[-1]) and calcium (mg Ca kg dry wt[-1]) based on 2006 survey from the three north-centre sampling sites (sites #1, #4 and #5 as located in Fig. 4.1).
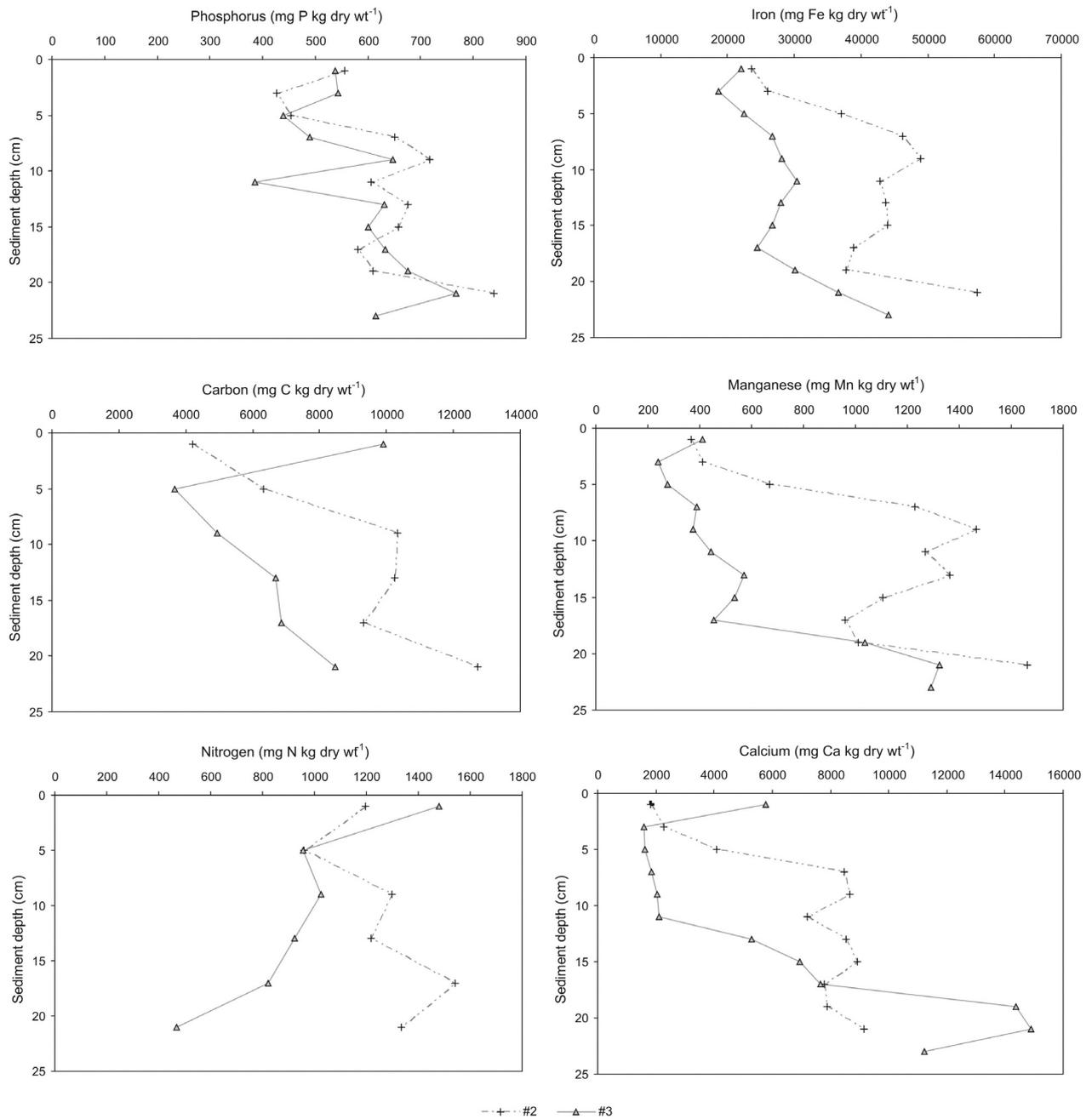
Figure 4.5. Vertical profiles of sediment total phosphorus (mg P kg dry wt[-1]), total nitrogen (mg N kg dry wt[-1]), total carbon (mg C kg dry wt[-1]), iron (mg Fe kg dry wt[-1]), manganese (mg Mn kg dry wt[-1]) and calcium (mg Ca kg dry wt[-1]) based on 2006 survey from the two centre-south sampling sites (sites #2 and #3 as located in Fig. 4.1).

The TP concentration in the vertical profiles was significantly linearly correlated with TC (r = 0.67, p < 0.001, n = 45), Fe (r = 0.36, p < 0.05, n = 45) and Mn (r = 0.72, p < 0.001, n = 45) (Table 4.3). There was no significant correlation, however, between TP and TN in the vertical profiles (r = 0.21, p = 0.17, n = 45). Total nitrogen was also not significantly correlated with TC (r = 0.25, p = 0.09, n = 45), whereas TC was significantly correlated with sediment Ca (r = 0.67, p < 0.001, n = 45), suggesting that calcium carbonate could be a significant component of the total sediment carbon content.

Table 4.3. Correlation matrix (n = 45) between sediment TP, TN, TC, Fe, Mn and Ca in vertical profiles based on eight sediment cores collected in 2006. ** = significant at p < 0.01 and * = significant at p < 0.05.

	TP sediment	TN sediment	TC sediment	Fe sediment	Mn sediment	Ca sediment
TP sediment	-	r = 0.21	r = 0.67**	r = 0.36*	r = 0.72**	r = 0.42**
TN sediment		-	r = 0.25	r = -0.08	r = 0.12	r = -0.21
TC sediment			-	r = 0.23	r = 0.48**	r = 0.67**
Fe sediment				-	r = 0.79**	r = 0.12
Mn sediment					-	r = 0.27
Ca sediment						-

4.3.3 Coupling horizontal and vertical variability

Multiple stepwise linear regression was used to examine relationships of sediment TP to other sediment constituents that were measured in the eight cores collected in 2006, with horizontal and vertical dimensions combined, and extending the statistical analysis beyond single independent variables (Table 4.3). For the surficial sediments, Mn and TC explained 91 % of the variation in TP (Fig. 4.6), however with Mn and TC weakly inter-correlated (r = 0.48, p < 0.01, n = 45). Concentrations of Mn and TC explained 65 % (p < 0.01) of the vertical variation in TP across all cores (Fig. 4.6). Hence, Mn and TC concentrations, which are presumably representative of inorganic and organic fractions of TP, respectively, have a close relationship with sediment TP concentrations in both the horizontal and the vertical dimension.
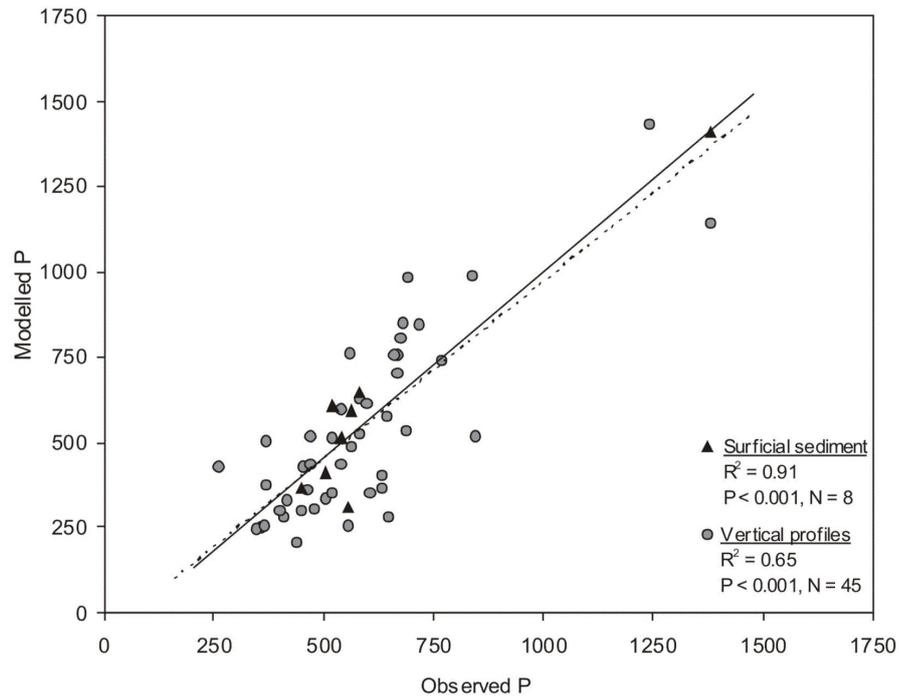
Figure 4.6. Modelled sediment phosphorus concentrations, derived from multiple linear regression, versus observed sediment phosphorus concentrations (mg P kg dry wt^{-1}) for surficial samples and vertical profiles from the eight sites sampled in 2006. Regression model for surficial sediment TP concentrations (solid regression line): TP = 0.032 x TC + 0.49 x Mn and for vertical profiles of sediment TP concentrations (dashed regression line): TP = 0.028 x TC + 0.37 x Mn.

4.4 Discussion

4.4.1 Surficial sediment chemistry of Lake Taihu

Using a large number of sampling sites, it has previously been shown that horizontal nutrient concentration gradients can be present in surface sediments of shallow lakes, induced by high external nutrient loadings and often associated with elevated sediment nutrient concentrations near river mouths (e.g. Xu et al. 2003). Although a large number of sampling sites were also used in this study, Lake Taihu comprise a formidable surface area, and each sampling site therefore represented a relatively large area ($\sim$ 70 km^2), which may render the Kriging interpolation used for contour plots (Fig. 4.2) less successful. However, I was able to achieve a horizontal distribution of Chl *a*, that was remarkably similar to that

found by Wang and Liu (2005), who sampled 75 sites for Chl *a* in Lake Taihu during 1999, and also used Kriging interpolation to generate a contour plot. It is therefore reasonable to assume that the horizontal distributions of sediment and water column variables presented in Fig. 4.2 give a realistic representation of the actual horizontal distributions in Lake Taihu. From the horizontal distributions of surficial sediment TP in Lake Taihu, based on data from 32 sites sampled in 2005, it is evident that highest concentrations occur in the northern regions of Lake Taihu, where some of the major inflows and sources of external phosphorus enter the lake. The northern part of the lake is subject to severe seasonal algal blooms and TP concentrations in the water column are also elevated in this region.

Concentrations of TP in the surficial sediments of Lake Taihu are similar to those found in shallow eutrophic Lake Chao, China (Xu et al. 2003), whereas TN concentrations tend to be higher in sediments of Lake Taihu. However, compared with other studies, including shallow eutrophic lakes in northern Europe (e.g. Håkanson 1984; Søndergaard et al. 1996), New Zealand (Hamilton and Mitchell, 1997) and Estonia and Russia (Nõges et al. 2007), TP, TN and LOI are generally at low levels in sediments of Lake Taihu, i.e., the sediments have a higher relative abundance of inorganic material. This may be attributed in part to the exceptionally large surface area of Lake Taihu, which effectively means that fetch is not limiting wave generation at the selected stations, regardless of wind direction, and this energy is available for mixing and resuspension. Hence, fine organic particles, which have high phosphorus and nitrogen content, may be almost continuously resuspended (at least to a greater degree than in shallow lakes with smaller surface area), and partly mineralised in the water column rather than buried in the sediments.

The average TN:TP ratios in the water column of Lake Taihu are similar to those of the inflows and outflows, but an order of magnitude higher than TN:TP ratios found in the surficial sediments (Table 4.2). This difference between water column and sediment TN:TP ratios suggests that up to ~90 % of the nitrogen that reaches the sediments is 'lost' through denitrification in the sediments. This figure is much higher than those reported in a microcosm study from Lake Taihu (Wang et al. 2007), where the total nitrogen loss in the sediments (without adding

additional electron donors) was estimated to ~22 %. However, the difference between water column and sediment TN:TP ratios in Lake Taihu is similar to that found in shallow eutrophic Lake Ellesmere (area = 182 km^2), New Zealand (Hamilton and Mitchell 1997). Furthermore, a Lake Taihu nutrient budget for the hydrological year 2001-2002 (Xu and Qin 2005), which was subsequently updated to include atmospheric wet deposition (Luo et al. 2007), suggests that around 60 % of the nitrogen that enters the lake cannot be accounted for, presumably as a result of denitrification. The TC:TN ratios in the surficial sediments, based on the data collected in 2006, are similar to the Redfield ratio, suggesting that the vast majority of nitrogen in the sediments is associated with organic material. Conversely, the TC:TP ratios in the surficial sediments are approximately three times lower than the Redfield ratio, which suggest that a considerable portion of the phosphorus in the sediments is associated with inorganic material.

4.4.2 Horizontal variability in sediment TP concentrations

A study by Nõges and Kisand (1999) of shallow eutrophic Lake Võrtsjärv, Estonia, suggests that dry matter content may explain the majority (72-96 %) of the horizontal variation of various phosphorus fractions in the surface 10 cm of sediment. Nõges and Kisand (1999) also showed that the effective fetch and prevailing wind direction accounted for most (87 %) of the variability in the sediment dry matter content. Hence the physical properties (fetch and wind direction) explained the vast majority of the horizontal variability of TP in the surficial sediments of Lake Võrtsjärv. This strong link between physical properties and horizontal distribution of sediment TP concentrations is not apparent in Lake Taihu, however, as I found the correlation between sediment dry matter content, which according to Nõges and Kisand (1999) is driven largely by fetch and prevailing wind direction, and surficial sediment TP concentrations to be weak and not significant (r = -0.39, p > 0.05, n = 8). The main drivers of the horizontal variations of sediment TP concentrations in Lake Taihu appear to be more closely linked to the strong water column gradients of nutrients (i.e., TP and TN concentrations) and biological variables (i.e., Chl *a*) that are associated with a trend of increasing trophic status from south to north, driven by large external

nutrient loads entering in the north (Wang and Liu 2005; Qin et al. 2007b). Although studies have shown that surficial sediment nutrient concentrations are generally not significantly correlated with lake water quality (represented by water column concentrations of TP, TN and Chl *a*) across a range of lakes with a wide variety of trophic states (McColl 1977; Trolle et al. 2008), this study showed that within Lake Taihu, surficial sediment TP concentrations are in fact significantly correlated with water column concentrations of TP, TN and Chl *a* (Table 4.1).

4.4.3 Vertical distribution of sediment TP concentrations

The vertical distribution of sediment TP in the northern region of Lake Taihu was similar to that observed in other lakes (e.g. Bortleson and Lee 1974; Søndergaard et al. 1996), with a general exponential decrease of TP concentrations with sediment depth. Vertical profiles of TP in other regions of the lake, however, were either relatively uniform or increased slightly with sediment depth. This pattern was also found in Lake Taihu by Kelderman et al. (2005) who suggested that the elevated TP concentrations in the uppermost sediment layers of the northern regions of the lake were due to greater localized external loading. However, the elevated TP concentrations in the surficial sediments of these northern regions may not necessarily be attributed to eutrophication alone, as evidence suggests that phosphorus is mobile in lake sediments (Carignan and Flett 1981), and profiles with exponentially decreasing TP concentrations can form naturally in lakes that have not undergone eutrophication. Whether some phosphorus forms are available for release from deeper sediment layers, for example followed by dredging and subsequently exposing these deeper sediment layers to the water column, has not been investigated but would be highly relevant to consideration of removal of the upper sediment layers by dredging. Until more information on the origin, age and properties of these sediments is established, dredging to mitigate internal loads would best be confined to the northern basins of Lake Taihu, where surficial sediment TP concentrations, at least to a depth of 10 cm, tend to be elevated relative to deeper layers. Clearly, however, it is essential to first of all address the driver of the enrichment of surficial sediments in the northern basin; the high external nutrient loads.

4.4.4 Linking horizontal and vertical distribution of sediment TP

It is evident, that the factors influencing both horizontal and vertical variability of sediment TP concentrations are complex and can also be expected to vary between lakes. Some of the variation between sediment nutrient surveys between 2005 and 2006 may also be attributable to different analytical techniques, however, the results for both surficial sediment TP and TN concentrations were generally similar and differences were of a magnitude similar to the standard deviation of the analytical techniques used for determination of sediment TP and TN concentrations in 2006 ($\pm$5-15%).

I previously hypothesized that the chemical and biological gradients in the water column may have a strong influence on the TP concentration of the surficial sediments in Lake Taihu. Therefore it was unexpected that there was no significant correlation between surficial sediment TP concentrations and sediment LOI (Table 4.1), as the organic carbon content of the sediment presumably will increase with increased water column productivity. However, there was a significant correlation between sediment TC and TP concentrations ($r = 0.67$, $p < 0.01$, $n = 45$) (Table 4.3) in the vertical profiles. I analysed the sediments for total carbon (TC), however, which may also include inorganic species of carbon (for example carbonates), but concurrently I found that the TC concentrations from this study were similar to the total organic carbon (TOC) content found by Jinglu et al. (2007) and Huang et al. (2005) in the sediments of Lake Taihu. Furthermore, a sediment study by Zhu et al. (2006) describing various fractions of phosphorus forms in sediments of Lake Taihu, showed that calcium-bound phosphorus generally amounted to < 4% of sediment TP, whereas organically associated phosphorus and iron-bound phosphorus were the most abundant forms at levels 4-5 times greater than calcium-bound phosphorus. Therefore, it is reasonable to conclude that sediment TP concentrations are significantly related to the organic content of the sediments, in this case represented by TC concentrations. I also found a significant correlation between sediment TP and Mn ($r = 0.72$, $p < 0.01$, $n = 45$), which was stronger than that between sediment TP and Fe ($r = 0.36$, $p < 0.05$, $n = 45$). This does not mean, however, that phosphorus is predominantly associated with Mn mineral complexes in the sediments of Lake Taihu, as many

factors influence on the final distribution of Fe and Mn in the sediments, such as the relative supply rates of these minerals to the sediments and also the migration of Fe and Mn as influenced by pH and redox conditions (Davison 1993). The latter influence can cause total Fe to vary independently of the final TP concentration to a greater extent than for Mn (Bortleson and Lee 1974).

In summary, this study revealed that within large and shallow Lake Taihu, in-lake variability of surficial sediment TP concentrations, but not sediment TN concentrations, is significantly correlated with in-lake variability of water column concentrations of TP, TN and Chl *a*. The study also revealed that the mineral/inorganic content of the sediments (represented by the Mn concentration) and the organic content (represented by the TC concentration) are responsible for the majority (91 %) of horizontal variability in TP concentrations in sediments of Lake Taihu, and that this relationship can be expanded to the vertical dimension, where Mn and TC concentrations explain 65 % of the variability in TP. Thus, both inorganic and organic components of the sediments have a strong influence on TP in the bottom sediments of Lake Taihu, and are presumably strongly inter-connected with lake water quality through regular sediment resuspension events. The delineation of the horizontal as well as the vertical distribution of phosphorus in sediments of Lake Taihu suggests that dredging to mitigate internal loads would best be confined to the northern basins of Lake Taihu, where surficial sediment TP concentrations, at least to a depth of 10 cm, are generally elevated relative to deeper layers. However, it is essential to first of all address the driver of the enrichment of surficial sediments in the northern basin; the high external nutrient loads.

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Chapter 5: Predicting the effects of climate change on ecosystem dynamics in three New Zealand lakes using the DYRESM-CAEDYM model – implications for lake restoration

5.1 Introduction

Deteriorating water quality in lakes, due to human activities such as urban settlement, farming, forestry and recreation, has focused attention worldwide on the sustainability of lake environments (Wetzel 1992). Today, great efforts are being made to improve water quality using different lake restoration approaches (Jeppesen et al. 2005). Apart from anthropogenic impacts, it is widely recognized that climate also has a direct influence on lake temperature distributions, nutrient loadings, phytoplankton abundance and lake water chemistry (Straile et al. 2003; Jeppesen et al. 2005). However, little effort has been made to elucidate and quantify the effects of climate change on lakes (Blenckner 2005). With the expectation of a significant climate change in the future (IPCC 2007), research into this area is highly relevant. Within the next century, or perhaps within only decades, climatic changes may cause a further deterioration of lake water quality, thereby rendering the present time-consuming and costly restoration efforts less productive or insufficiently effective (Jeppesen et al. 2007).

The main objective of this study was to predict effects of future climate change on lake water quality and the implications for lake restoration, by applying complex lake ecosystem models to three New Zealand lakes. The one-dimensional DYRESM-CAEDYM model was applied to deep Lake Okareka, moderately shallow Lake Rotoehu and shallow Lake Te Waihora (Lake Ellesmere), and a series of climate change and nutrient loading scenarios were simulated. The lakes range from deep to shallow, and from monomictic to polymictic, thus allowing evaluation of the impacts of climate change on lakes with various mixing regimes. The lakes also range from oligo-mesotrophic to highly eutrophic, thereby

allowing a comparison of climate change effects across lakes with a range of trophic states.

5.1.1 Study sites

Lake Okareka is a deep, oligo-mesotrophic, monomictic lake (Table 5.1), in the Bay of Plenty province, North Island of New Zealand. In-lake water quality variables, including concentrations of phosphorus and nitrogen species, chlorophyll *a* (Chl *a*), dissolved oxygen (DO) and temperature at various depths in the water column, have been monitored on a monthly basis since 1992. Inflow and outflow volumes and nutrient concentrations in inflows have been monitored on a monthly basis since mid 2002.

Table 5.1. Morphological properties and trophic status of lakes Okareka, Rotoehu and Te Waihora.

Lake	Mean depth (m)	Max depth (m)	Lake area (ha)	Catchment area (ha)	Lake trophic status
Okareka	20.0	33.5	342	1,960	Oligo-mesotrophic
Rotoehu	8.2	13.5	795	5,670	Eutrophic
Te Waihora (Ellesmere)	1.3	2.5	18,200	256,000	Highly eutrophic

Lake Rotoehu is a moderately shallow, eutrophic lake (Table 5.1), also in the Bay of Plenty province. For this lake, the same suite of in-lake water quality variables as for Lake Okareka has been monitored on a monthly basis since 1993, and inflow volumes and nutrient concentrations in inflows have been monitored on a monthly basis since mid 2002. For both Lake Okareka and Lake Rotoehu, biomass of the most abundant zooplankton taxa was recorded on a monthly basis for the year May 2006 – April 2007. The third lake, Te Waihora, is shallow and highly eutrophic (Table 5.1), situated in the Canterbury province, South Island of New Zealand. In-lake water quality variables have been monitored on a monthly basis since 1992, and the main inflow volumes and nutrient concentrations in inflows have been monitored either continuously (for flow) or on a monthly basis since 1993. Surface samples, as referred to in this study, are represented by integrated samples at 0-10 and 0-9 m for lakes Okareka and Rotoehu, respectively, while samples from Lake Te Waihora are actual discrete surface

samples. Bottom samples from lakes Okareka and Rotoehu are represented by discrete samples collected at 26 and 9 m depth, respectively. Zooplankton biomass data were not available from Lake Te Waihora at regular intervals.

5.2 Methods

5.2.1 Model description

The one-dimensional water quality model DYRESM-CAEDYM (DYCD), was developed at Centre for Water Research at The University of Western Australia, and has undergone continuous development during the last two decades. The model consists of two main components: a one-dimensional hydrodynamic model (DYRESM - Dynamic Reservoir Simulation Model), which resolves the vertical distribution of temperature, salinity and density in a lake/reservoir, and an aquatic ecosystem model (CAEDYM - Computational Aquatic Ecosystem Dynamics Model), which simulates a range of biological, chemical and physical processes, essentially expressing the variables that are commonly associated with water quality (such as TP, TN, phytoplankton biomass, zooplankton biomass etc.). More detail on the theoretical background for DYCD can be found in Hamilton and Schladow (1997), Hipsey et al. (2006) and Imerito (2007). Today, DYCD is a highly complex one-dimensional lake ecosystem model, and several successful applications of the model to a range of different lakes have been published (e.g., Bruce et al. 2006; Burger et al. 2007; Trolle et al. 2008a).

5.2.2 Conceptual models for each lake

The conceptual lake ecosystem described by DYCD can be made more or less complex depending on the purpose of the model and the availability of data. Simulations can, for example, include up to seven different phytoplankton groups, five zooplankton groups, fish and submerged vegetation. In this study, the conceptual biota model for Lake Okareka included only chlorophytes and diatoms as phytoplankton groups, and these are used to represent the dominant phytoplankton taxa in the lake (Wilding 2000), and cladocerans, which generally dominate the zooplankton biomass, and in the model can graze on both

phytoplankton groups. For Lake Rotoehu, the conceptual biota model included cyanophytes (blue-green algae) and diatoms (Wilding 2000), and cladocerans, which in the model were calibrated to graze predominantly on diatoms. As no data for zooplankton biomass were available for Lake Te Waihora, the conceptual biota model for this lake included only chlorophytes and diatoms, which tend to be the dominant phytoplankton taxa (Taylor et al. 1996). As Lake Te Waihora is shallow and has a large surface area it is prone to full water column mixing and sediment resuspension. Resuspension events can supply nutrients to the water column and also increase turbidity, and may therefore influence growth of phytoplankton through light limitation and/or the supply of nutrients. Therefore, inorganic suspended sediments were included in the conceptual model for Lake Te Waihora, with these sediments able to settle out or be resuspended from the bottom sediments. The physical, chemical and biological components of the conceptual models, and the interactions between these, influence the cycling of phosphorus and nitrogen in the models (Fig. 5.1). The water temperature has a central role in determining the magnitude of many of the processes described by the model, including phytoplankton growth rates, zooplankton grazing rates, decomposition/mineralisation rates of particulate organic matter (POM) to dissolved organic matter (DOM) and then to inorganic nutrients (PO_4 and NH_4), as well as sediment nutrient release rates. A gradual, prolonged increase in water temperature may therefore change the balance between the various ecosystem components.

5.2.3 Model input

To calculate the vertical distribution of temperature and the resultant stratification (or mixing) between layers, DYCD requires daily average input data for six meteorological variables including air temperature (ºC), shortwave radiation (W m^{-2}), cloud cover (fraction of whole sky) or longwave radiation (W m^{-2}), vapour pressure (hPa), wind speed (m s^{-1}) and rainfall (m). These data were acquired from meteorological stations in close proximity to the lakes; at the Rotorua Airport for lakes Okareka and Rotoehu, and at Lincoln (Broadfield), Christchurch, for Lake Te Waihora. Daily inflow and outflow data are also required as boundary conditions to produce an accurate water and nutrient balance in the models. Where

continuous flow data were not available, linear interpolation between monthly samples for flow and nutrient concentrations was used to derive daily values. Residual inflow and/or outflow were derived from a daily water balance for each individual lake.
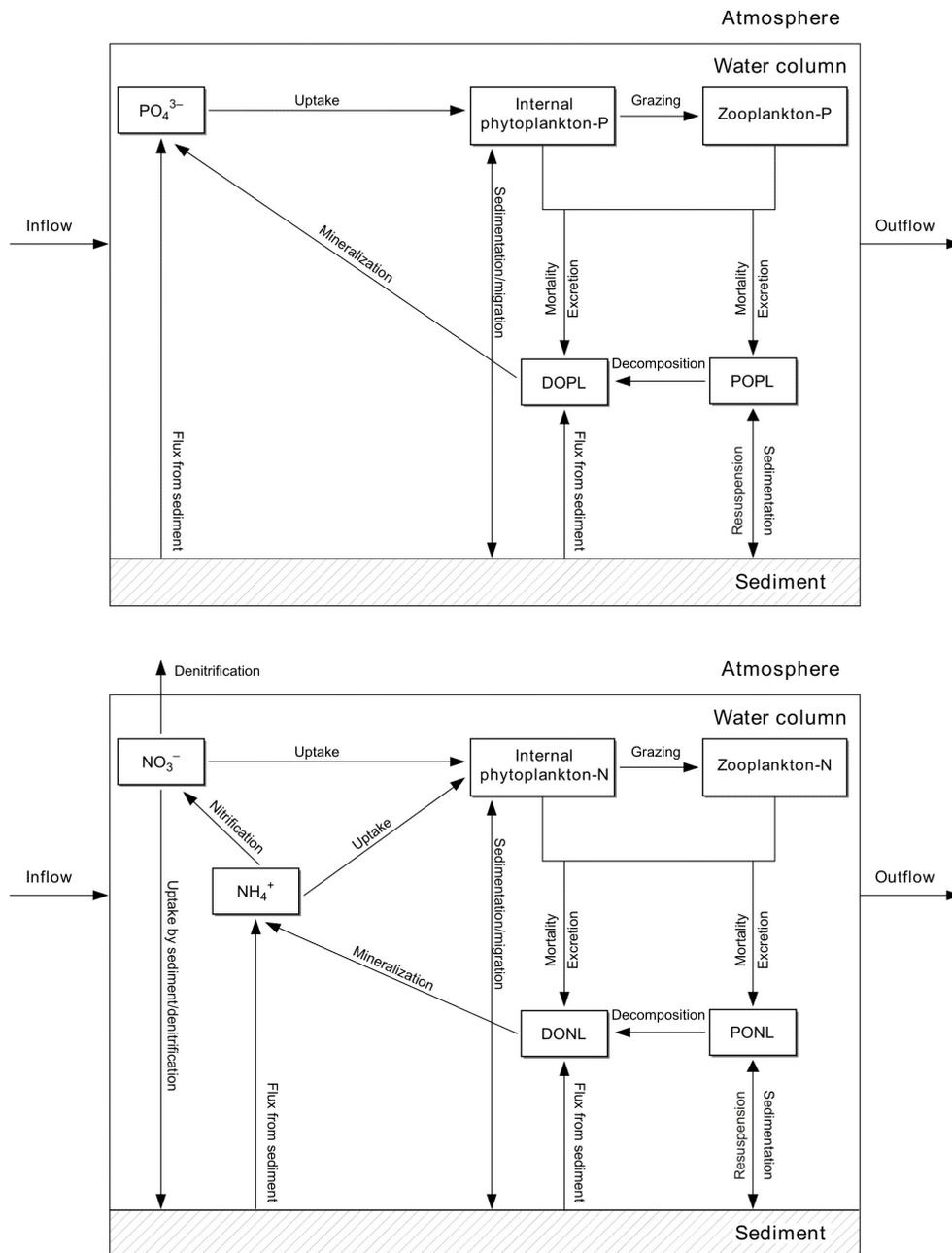
Fig. 5.1. Conceptual diagram of the phosphorus (top) and nitrogen (bottom) cycle in the DYRESM-CAEDYM model after Trolle et al. (2008a, b). Resuspension is only active for Lake Te Waihora, for which zooplankton dynamics were not included. POPL and PONL represent particulate labile organic phosphorus and nitrogen, respectively, and DOPL and DONL represent dissolved labile organic phosphorus and nitrogen, respectively.

The water balance included observed data for lake heights adjusted to volume from surface area, inflows, outflows, rainfall and theoretical evaporation. Evaporation was derived from estimation of the evaporative heat flux (Fischer et al. 1979) and the saturated vapour pressure (Wunderlich 1972). Nutrient concentrations in residual inflows were estimated based on volume-weighted averages of observed inflow concentrations.

5.2.4 Model calibration and validation procedure

To achieve a basis for comparisons between lakes, all models were calibrated based on a three year period (July 2002 – June 2005), and validated on a separate two year period (July 2005 – June 2007).

When calibrating the models I initially used predefined values for model parameters based on typical literature values (e.g., Schladow and Hamilton 1997). Model parameters were manually adjusted in a stepwise fashion within intervals for the various parameters derived from literature (e.g., Schladow and Hamilton 1997). After each simulation/calibration step, the model error was calculated, which was represented by a normalised root-mean-square-error (NRMSE, derived by dividing root-mean-square error values with the mean value of observations) for each output variable (temperature, DO, TP, PO_4, TN, NH_4, NO_3 and Chl a) for surface samples (top) and bottom samples (bottom) for lakes Okareka and Rotoehu, and surface samples for Lake Te Waihora. As Te Waihora is prone to full water column mixing it was assumed to be vertically homogeneous for the purpose of the model comparisons. The stepwise manual calibration continued until the model errors could no longer be appreciably minimised for the various output variables. To gain further insight into the performance of the models, Pearson correlation coefficients (r) between model output and observed data were calculated for all output variables.

5.2.5 Future climate change and nutrient loading scenarios

For predictions of future climate, I used the regional climate model "Division of Atmospheric Research Limited Area Model" (DARLAM), developed by the

Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Australia (McGregor and Walsh 1993). In recent years, the observed global temperatures tend to follow the projections of the A2 scenario by the Intergovernmental Panel on Climate Change (IPCC), which describes a future scenario with "a heterogeneous world" and a continuously increasing global population. I therefore applied the A2 scenario to the DARLAM model using the CLIMPACTS software, developed by the International Global Change Institute (IGCI), the University of Waikato, to obtain projections of future climate for the Bay of Plenty and Canterbury provinces, and the corresponding locations of the lakes. As there are still considerable uncertainties relating to various climate model predictions of meteorological variables such as wind speed and rainfall, I altered only air temperature in the forcing data for the model scenarios of future climate. The years 2002-2007 were used as a base scenario and the air temperature predicted for 2100 was used as a future climate scenario. According to the DARLAM model and the IPCC A2 scenario, air temperatures will increase by an average of 2.5 ºC and 2.7 ºC for the Bay of Plenty and the Canterbury provinces (at the locations of the lakes), respectively, in the future scenarios (year 2100) relative to the base scenarios (years 2002-2007). In order to quantify the implications of future climate change for lake restoration - and lake water quality in general - a series of nutrient loading scenarios were also set up, where the external loading of both phosphorus and nitrogen were decreased (to represent lake restoration scenarios) or increased (to represent possible effects of land-use intensification or increased run-off) by 10, 25, and 50% in the both the base climate and future climate scenarios.

5.3 Results

5.3.1 Calibration and validation

Lake Okareka

The simulations of temperature and DO in both the surface and bottom waters (represented by 26 m depth) of Lake Okareka generally showed good agreement with observed data during the calibration period (Table 5.2). Furthermore, the

ability of the model to reproduce observed temperature and DO data was generally similar between the calibration and the validation periods (Fig. 5.2).

As the bottom waters become anoxic, phosphate (PO_4) tends to build up in bottom waters of Lake Okareka. The model was generally able to reproduce the timing and magnitude of this build up (Fig. 5.2) and correspondingly showed good agreement with observed data for total phosphorus (TP), which was present predominantly as PO_4 in the bottom waters. Similar to the inorganic phosphorus cycle, ammonium (NH_4) can build up in bottom waters, which was also captured in the model simulations (Fig. 5.3). The model also captured the small build up of nitrate (NO_3) in the bottom waters, which likely originates from ammonium that is nitrified during the early period of stratification while DO is still present in the hypolimnion. For the calibrated model the nitrification rate was adjusted to a relatively high value to reproduce this quite rapid NO_3 build-up in the hypolimnion. The conceptual seasonal succession of phytoplankton, with a winter bloom of diatoms that in the model will settle out of the water column at onset of stratification, and a summer bloom of chlorophytes, was accurately reproduced by the model, and thus the modelled total Chl *a* concentration also showed good agreement with observed data (Fig. 5.4). The modelled peak of zooplankton biomass generally followed the modelled winter bloom of diatoms, and the modelled zooplankton biomass was generally within the range of observations. The timing of the zooplankton biomass peaks was, however, slightly offset and generally occurred earlier than in the observed data from 2006-2007.

Table 5.2. Normalised root-mean-square-error values (NRMSE) and Pearson correlation coefficients (r) between modelled output and observations for the surface and bottom waters of Lake Okareka.

	Surface waters (top)				Bottom waters			
	NRMSE		r		NRMSE		r	
	Calib.	Valid.	Calib.	Valid.	Calib.	Valid.	Calib.	Valid.
Temperature	0.048	0.045	0.99	0.99	0.053	0.10	0.81	0.17
DO	0.10	0.072	0.51	0.76	0.32	0.12	0.89	0.99
TP	0.40	0.55	0.0065	-0.023	0.77	0.98	0.28	0.049
PO_4	1.15	1.19	-0.068	-0.069	1.079	1.028	0.81	0.54
TN	0.23	0.24	-0.0068	-0.25	0.49	0.37	-0.19	0.54
NO_3	1.20	1.080	-0.088	-0.28	1.83	1.43	0.31	-0.21
NH_4	1.55	1.25	0.12	0.090	1.00	1.16	0.65	0.05
Chl *a*	0.75	0.37	0.23	0.67	-	-	-	-
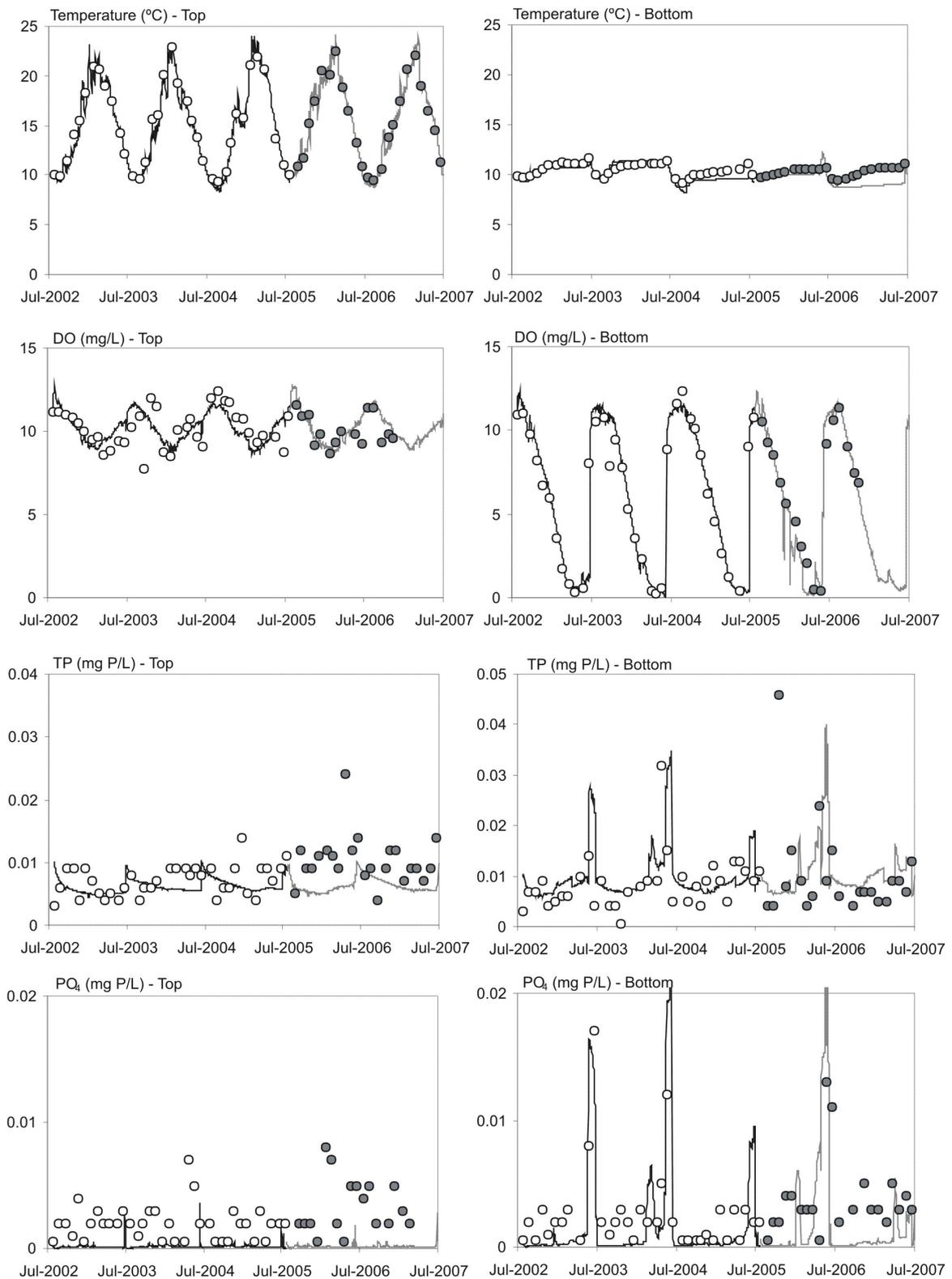
Fig. 5.2. Simulated (line plots) and observed values (circles) for temperature, DO, TP and PO$_4$ in the surface and bottom waters of Lake Okareka during the calibration (black lines and open circles) and validation periods (grey lines and full circles).
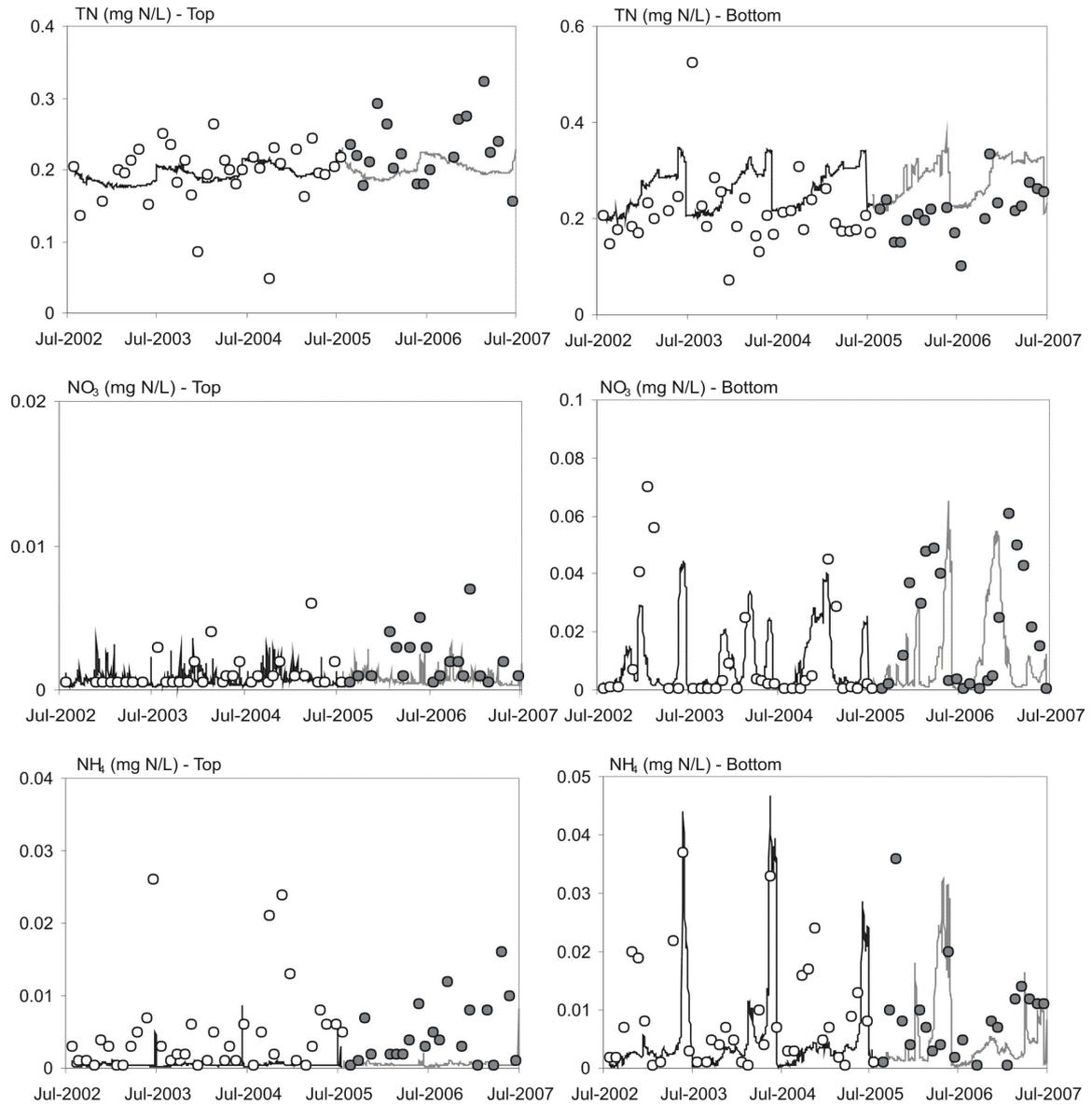
Fig. 5.3. Simulated (line plots) and observed values (circles) for TN, NO_3 and NH_4 in the surface and bottom waters of Lake Okareka during the calibration (black lines and open circles) and validation periods (grey lines and full circles).
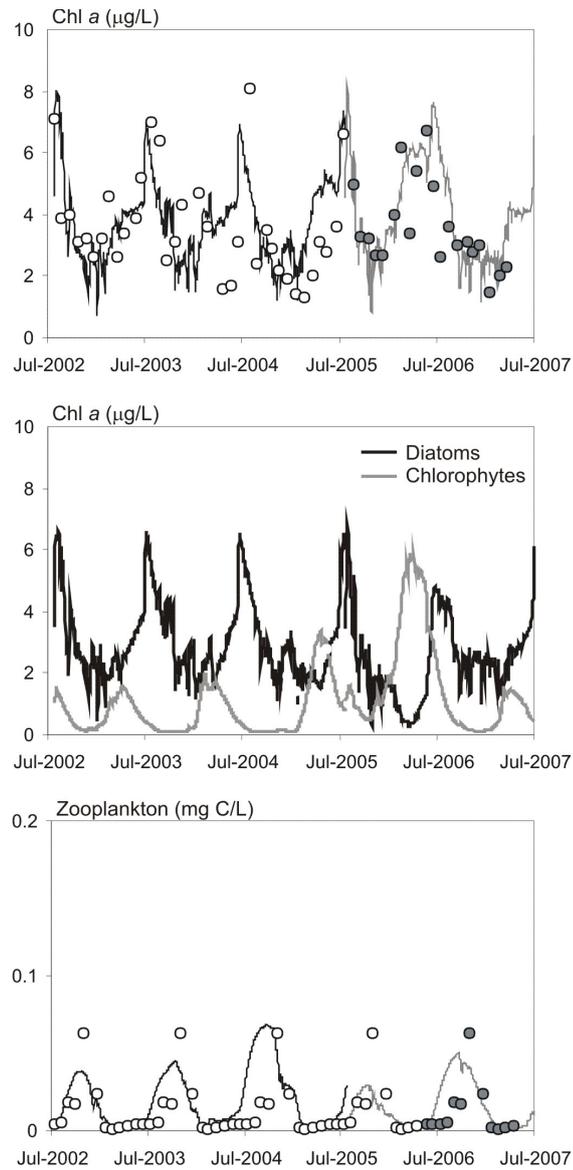
Fig. 5.4. Simulated (line plots) and observed values (circles) for Chl *a* and zooplankton biomass in the surface waters of Lake Okareka during the calibration (black lines and open circles) and validation periods (grey lines and full circles); and the simulated contribution of diatoms and chlorophytes to the total Chl *a* biomass. Zooplankton biomass data are only available for the period July 2006 – July 2007, and data from this year have been assigned to all others years only to give an approximation of levels and timing of zooplankton biomass.

Lake Rotoehu

The model simulation for Lake Rotoehu generally captured the dynamics of temperature and DO in both the surface and bottom waters (represented by 9 m depth) in both the calibration and the validation periods (Table 5.3).

Table 5.3. Normalised root-mean-square-error values (NRMSE) and Pearson correlation coefficients (r) between modelled output and observations for the surface and bottom waters of Lake Rotoehu.

	Surface waters (top)				Bottom waters			
	NRMSE		**r**		**NRMSE**		**r**	
	Calib.	Valid.	Calib.	Valid.	Calib.	Valid.	Calib.	Valid.
Temperature	0.089	0.061	0.99	0.99	0.086	0.072	0.99	0.99
DO	0.16	0.16	0.52	0.44	0.21	0.17	0.84	0.91
TP	0.42	0.52	0.44	0.68	0.45	0.40	0.73	0.74
PO_4	0.98	1.16	0.60	0.67	1.050	1.22	0.75	0.65
TN	0.27	0.44	0.60	0.44	0.23	0.26	0.74	0.59
NO_3	1.64	2.010	0.13	-0.14	1.63	1.38	0.28	-0.11
NH_4	1.42	1.11	-0.11	0.47	2.040	0.96	0.34	0.53
Chl *a*	0.92	0.69	-0.06	0.015	-	-	-	-

During summer, when the water column stratifies intermittently, the observed DO concentrations in bottom waters (9 m) show fluctuations, occasionally increasing in association with brief periods of mixing. The model was able to capture the alternation of weak mixing and stratification events, exemplified by the summer 2005/2006 (Dec-Feb), and also the build up of PO_4 (Fig. 5.5) and NH_4 (Fig. 5.6) in the bottom waters. The model simulations generally showed good agreement with observed data for both TP and TN concentrations, although simulations tended to underestimate TN concentrations at the surface during summer. The model simulations also reproduced the conceptual seasonal succession of phytoplankton, with a winter increase of diatom biomass and a summer bloom of cyanophytes, and as a result there was good agreement between observed and simulated data for total Chl *a*. The modelled zooplankton biomass, which approximately follows the biomass of diatoms, generally peaked during early summer (December) but tended to overestimate observed data, though there were no data with which to verify the simulated peaks for December 2006.
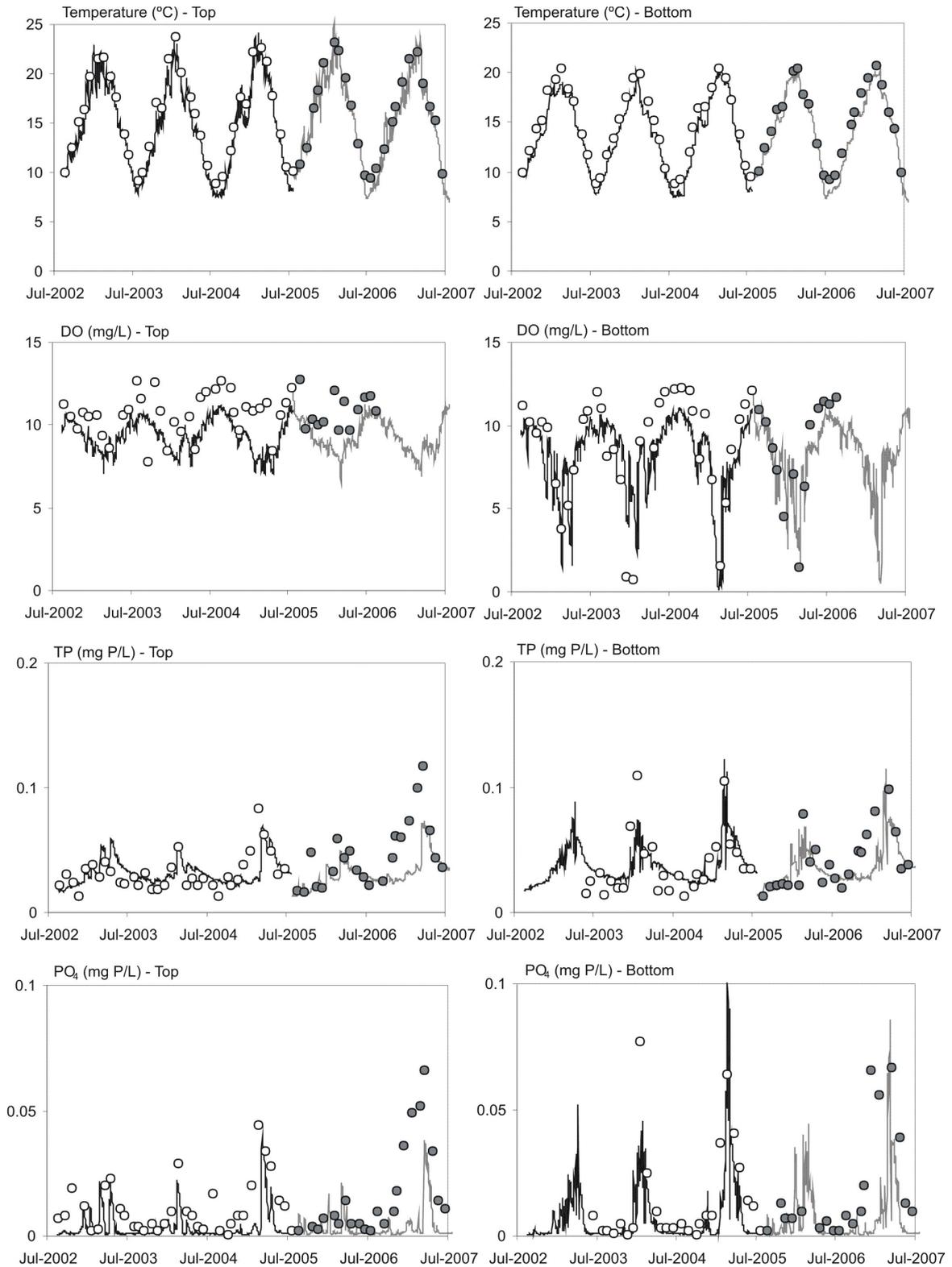
Fig. 5.5. Simulated (line plots) and observed values (circles) for temperature, DO, TP and PO₄ in the surface and bottom waters of Lake Rotoehu during the calibration (black lines and open circles) and validation periods (grey lines and full circles).
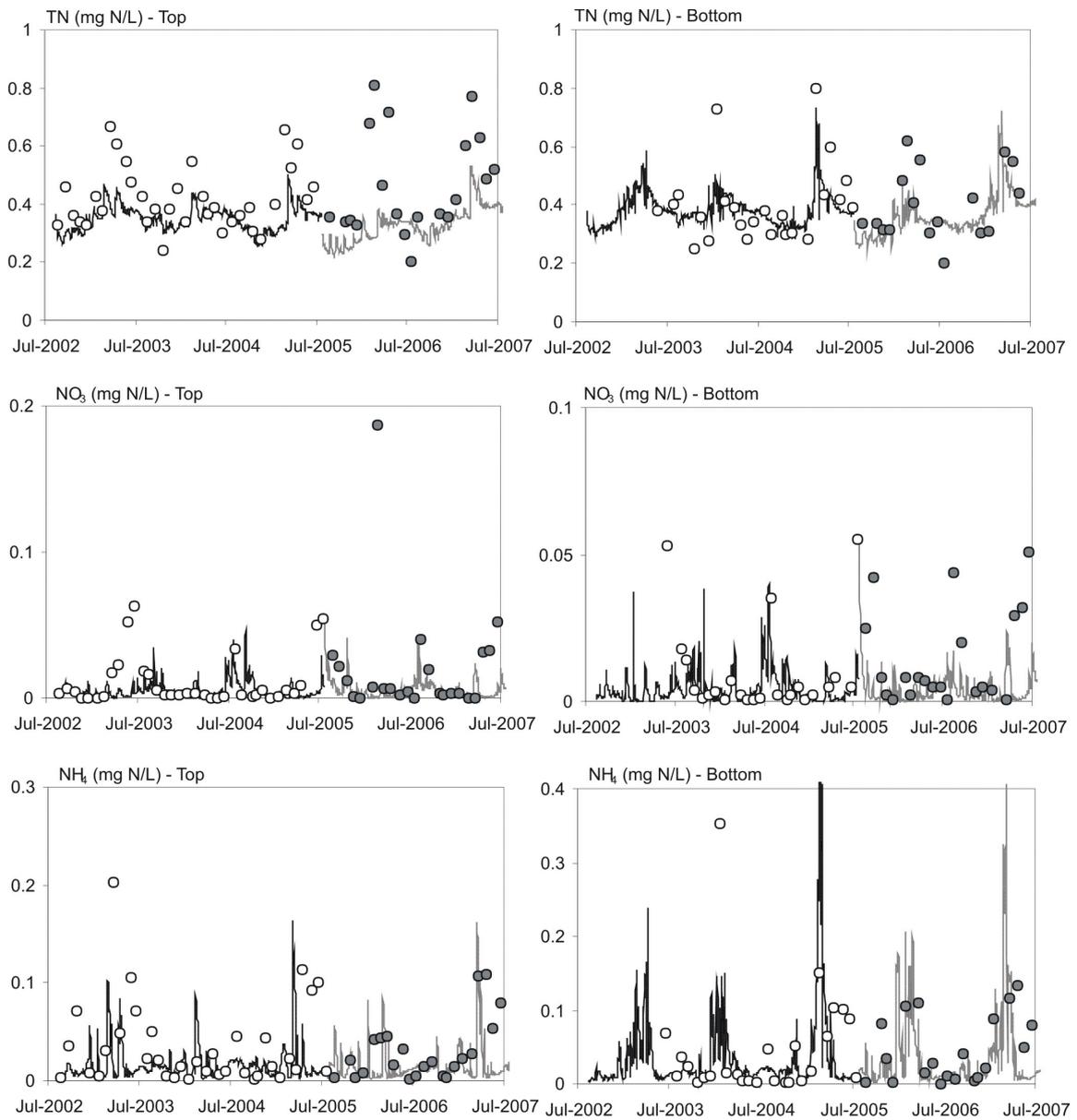
Fig. 5.6. Simulated (line plots) and observed values (circles) for TN, NO_3 and NH_4 in the surface and bottom waters of Lake Rotoehu during the calibration (black lines and open circles) and validation periods (grey lines and full circles).
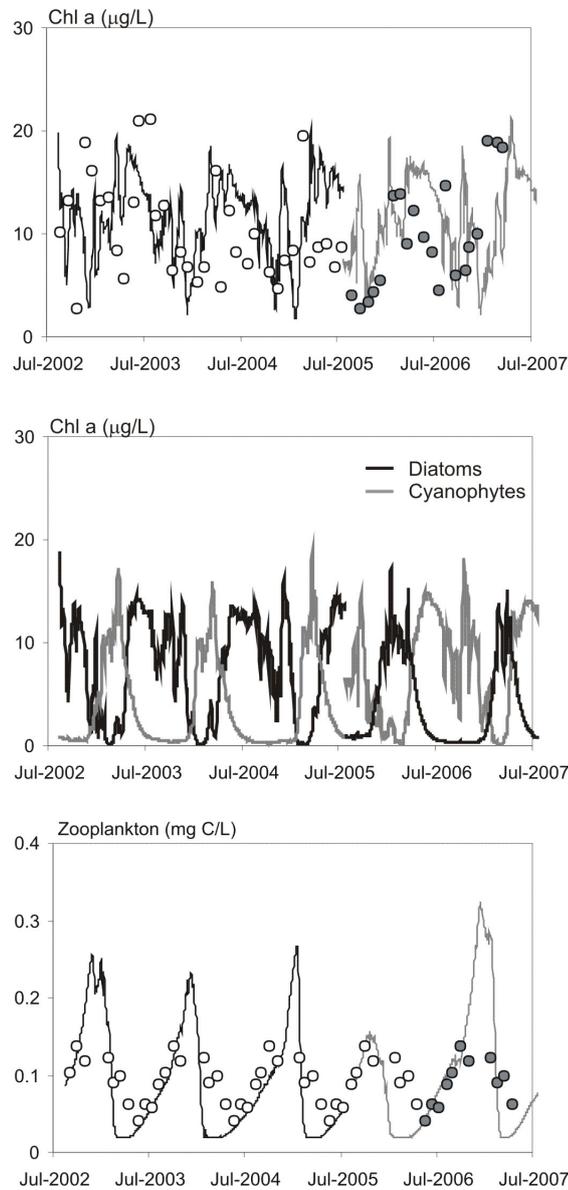
Fig. 5.7. Simulated (line plots) and observed values (circles) for Chl *a* and zooplankton biomass in the surface waters of Lake Rotoehu during the calibration (black lines and open circles) and validation periods (grey lines and full circles); and the simulated contribution of diatoms and cyanophytes to the total Chl *a* biomass. Zooplankton biomass data are only available for the period July 2006 – July 2007, and data from this year have been assigned to all others years only to give an approximation of levels and timing of zooplankton biomass.

Lake Te Waihora

The calibration and validation of the model for Lake Te Waihora surface waters generally showed good agreement with observed data for temperature, DO and total nutrients (Fig. 5.8). The model captured the conceptual seasonal succession of Chl *a*, represented by winter blooms of diatoms and summer blooms of chlorophytes, although the Chl *a* biomass was underestimated during an exceptionally severe bloom recorded in the spring-summer of 2006-2007. As Lake Te Waihora does not stratify over prolonged periods like lakes Okareka and Rotoehu, the modelled annual succession of diatoms and chlorophytes for Te Waihora is driven mostly by differences in growth relating to light and temperature functions in the model, rather than assigned sedimentation rates for diatoms. Resuspension events were generally also captured by the model based on outputs of the concentration of inorganic suspended solids (inorganic SS) (Fig. 5.9), which is the main constituent of suspended sediments in Lake Te Waihora (Hamilton and Mitchell 1996). The modelled inorganic SS should therefore be expected to be slightly lower than observations, as the observation data are based on determination of total SS and therefore also include organic material. The ability of the model to reproduce the dynamics of the observed data did not show any evident decline when comparing the NRMSE and r-values of the calibration and validation periods (Table 5.4).

Table 5.4. Normalised root-mean-square-error values (NRMSE) and Pearson correlation coefficients (r) between modelled output and observations for the surface waters of Lake Te Waihora.

	NRMSE		**r**	
	Calib.	Valid.	Calib.	Valid.
Temperature	0.14	0.15	0.98	0.97
DO	0.091	0.098	0.88	0.83
TP	0.29	0.31	0.64	0.56
PO_4	1.12	1.63	0.28	-0.13
TN	0.21	0.19	0.52	0.38
NO_3	1.14	1.36	0.32	0.98
NH_4	1.39	1.06	0.35	-0.16
Chl *a*	0.39	0.71	0.31	0.43

Regular sediment resuspension events in Lake Te Waihora (Fig. 5.9) cause the light availability throughout the majority of the water column to be limiting for primary production. Hence, the average euphotic depth during the calibration period was ~90 cm and minimum euphotic depth was < 20 cm, based on the integrated water column light extinction coefficient and assuming compensatory irradiance levels at a 1% light level relative to surface irradiance. Almost all macrophyte beds have been lost from Lake Te Waihora since the Wahine storm in 1968 (Gerbeaux and Ward 1991), and the model simulations are a testament to the great difficulties of re-establishing macrophyte communities, as light levels are not sufficient (i.e. < 1% of surface irradiance) for primary production at 1.5 m depth, for example, for >88% of days that were simulated.
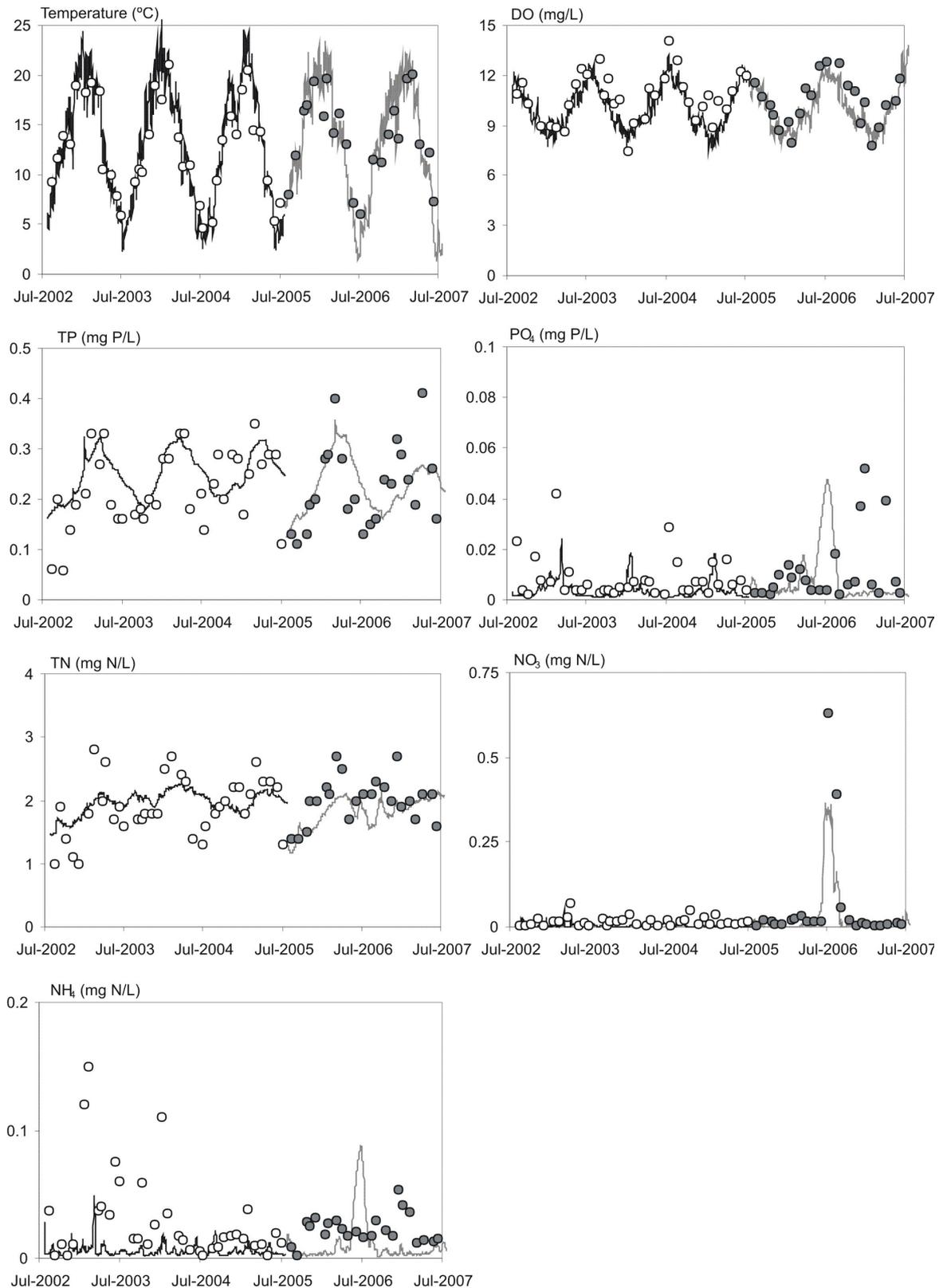
Fig. 5.8. Simulated (line plots) and observed values (circles) for temperature, DO, TP, PO₄, TN, NO₃ and NH₄ in the surface waters of Lake Te Waihora during the calibration (black lines and open circles) and validation periods (grey lines and full circles).
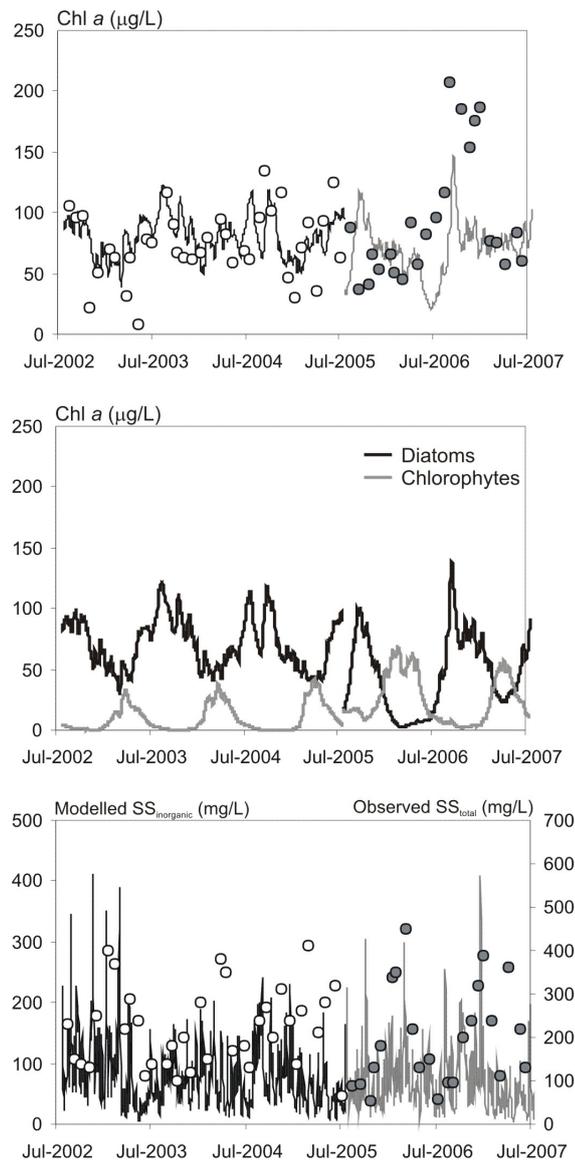
Fig. 5.9. Simulated (line plots) and observed values (circles) for Chl *a* and suspended solids (SS) in the surface waters of Lake Te Waihora during the calibration (black lines and open circles) and validation periods (grey lines and full circles); and the simulated contribution of diatoms and chlorophytes to the total Chl *a* biomass.

Sensitive model parameters

In summary, the model simulations generally reproduced the seasonal dynamics of the observed physical, chemical and biological variables in lakes Okareka, Rotoehu and Te Waihora, by using parameter values, of which the most sensitive are presented in Table 5.5, that are within ranges observed in literature (e.g. Schladow and Hamilton 1997) or other model studies (e.g., Arhonditsis and Brett 2005; Burger et al. 2007; Trolle et al. 2008a).

Table 5.5. Assigned values for sensitive parameters used in the calibration of DYRESM-CAEDYM for lakes Okareka, Rotoehu and Te Waihora.

Parameter	Unit	Okareka	Rotoehu	Te Waihora
Sediment parameters				
Sediment DO demand	g m^{-2} d^{-1}	0.92	4.4	1.65
Maximum potential PO$_4$ release rate	g m^{-2} d^{-1}	0.005	0.035	0.026
Maximum potential NH$_4$ release rate	g m^{-2} d^{-1}	0.016	0.17	0.080
Nutrient parameters				
Mineralization rate of DOPL to PO$_4$	d^{-1}	0.0075	0.007	0.005
Mineralization rate of DONL to NH$_4$	d^{-1}	0.003	0.007	0.009
Nitrification rate	d^{-1}	0.29	0.05	0.04
Denitrification rate	d^{-1}	0.11	0.65	0.75
Phytoplankton parameters		diatoms, chlorophytes	diatoms, cyanophytes	diatoms, chlorophytes
Maximum potential growth rate	d^{-1}	2.2, 1.6	1.1, 0.7	1.2, 1.0
Half-saturation constant for P uptake	mg L^{-1}	0.0010, 0.0020	0.0028, 0.0035	0.0040, 0.0031
Half-saturation constant for N uptake	mg L^{-1}	0.0060, 0.010	0.021, 0.020	0.019, 0.018
Minimum internal P concentration	mg P (mg Chl *a*)$^{-1}$	0.09, 0.12	0.25, 0.23	0.22, 0.21
Maximum internal P concentration	mg P (mg Chl *a*)$^{-1}$	1.9, 1.9	2.0, 2.4	2.0, 2.1
Maximum rate of P uptake	mg P (mg Chl *a*)$^{-1}$ d^{-1}	0.50, 0.40	0.25, 0.28	0.24, 0.22
Minimum internal N concentration	mg N (mg Chl *a*)$^{-1}$	3.4, 3.1	3.5, 4.0	3.4, 3.1
Maximum internal N concentration	mg N (mg Chl *a*)$^{-1}$	9.0, 9.0	9.0, 11.0	10.2, 11.5
Maximum rate of N uptake	mg N (mg Chl *a*)$^{-1}$ d^{-1}	4.0, 3.0	3.5, 4.2	3.3, 3.8
Respiration rate coefficient	d^{-1}	0.06, 0.06	0.09, 0.12	0.16, 0.135
Zooplankton parameters				
Maximum potential grazing rate	(g phyto C L^{-1})/(g zoo C L^{-1})/day	0.34	0.16	-
Half-saturation constant for grazing	mg C L^{-1}	0.14	0.10	-
Respiration rate coefficient	d^{-1}	0.13	0.09	-
Suspended solids parameters				
Density	kg m^{-3}	-	-	2,650
Diameter	m	-	-	3·10^{-6}
Critical shear stress	N m^{-2}	-	-	0.05

The parameter values calibrated for the three lakes also reflect the trophic status and morphology of theses lakes. Hence, the assigned sediment oxygen demand was higher in eutrophic lakes Rotoehu and Te Waihora relative to oligo-mesotrophic Lake Okareka. Similarly, the assigned sediment nutrient release rates, which influence strongly the supply of nutrients to the water column, were also higher for lakes Rotoehu and Te Waihora.

5.3.2 Effects of future climate change and nutrient loads on lake water quality

Simulations for each of the lakes with increasing air temperatures, as predicted for the IPCC A2 scenario for the year 2100, have a strong effect on lake water quality indices, represented here by annual mean surface TP, TN and Chl *a* concentrations, when compared against the base climate scenario (years 2002-2007) (Fig. 5.10).
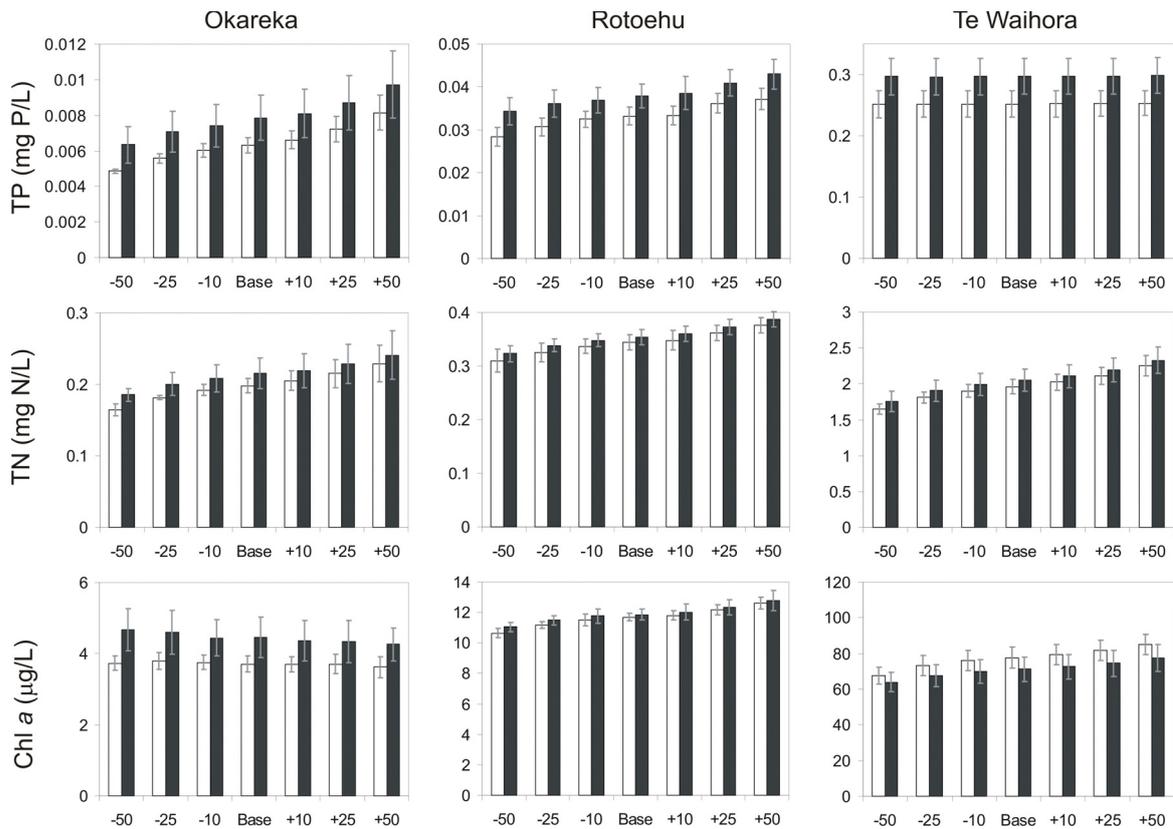
Fig. 5.10. Simulated responses of annual average TP, TN and Chl *a* concentrations in the surface waters of lakes Okareka, Rotoehu and Te Waihora, to present climate of 2002-2007 (white bars), future climate of 2100 (black bars), and loading scenarios ranging from a 50% reduction (-50) to a 50% increase (+50) in the external load of TP and TN. Error bars represent standard deviation of five years of simulation.

In most cases, the effects of present nutrient load but future climate change are similar to the effects of increasing the external load by 25-50% relative to the base climate scenario. Correspondingly, the simulations suggest that the external nutrient load should be reduced by c. 25-50% if the lakes are to retain their current trophic status by 2100. One exception is the annual average Chl *a* concentrations of Lake Te Waihora, which decrease, while TP and TN concentrations increase in the future scenarios. In this lake there were progressively more severe summer blooms in the future scenarios, and average summer (December-February) Chl *a* concentration, which is represented mostly by chlorophyte biomass, increased by 39% in the simulations. The winter 'bloom' (June-August), however, represented mostly by diatom biomass, decreased by 37% in the simulations. Over the entire five-year simulation, the annual average Chl *a* concentration is slightly reduced in the future climate scenario for Lake Te Waihora. As the chlorophytes can obtain a higher TP:Chl *a* and TN:Chl *a* biomass ratio relative to diatoms (Table 5.5), the net effect of the future climate is increasing TP and TN concentrations, despite a slight decrease in annual average Chl *a* concentrations.

Future climate simulations for lakes Okareka and Rotoehu show a somewhat similar pattern, with summer average Chl *a* concentrations increasing by 27 and 10%, respectively, over the base case. However, simulations also show a negligible or slight increase in winter-averaged Chl *a* biomass, by 9 and 0.1% for Lake Okareka and Lake Rotoehu, respectively.

Simulations for Lake Rotoehu, where diatoms and cyanophytes were included in the conceptual model, further indicate that cyanophytes will be increasingly prevalent in the future scenario. Thus, with the base loading (based on observation data from 2002-2007), the simulated annual average biomass of cyanophytes increased by 16%, and the relative abundance of cyanophytes increased from 32% to 36% of annual average total Chl *a* in the future climate scenario relative to the base scenario.

The deterioration of water quality induced by climate change seems to be most severe for oligo-mesotrophic Lake Okareka, when comparing relative changes in

TP, TN and Chl *a* concentrations (Fig. 5.11), all of which increase most in Lake Okareka relative to lakes Rotoehu and Te Waihora.
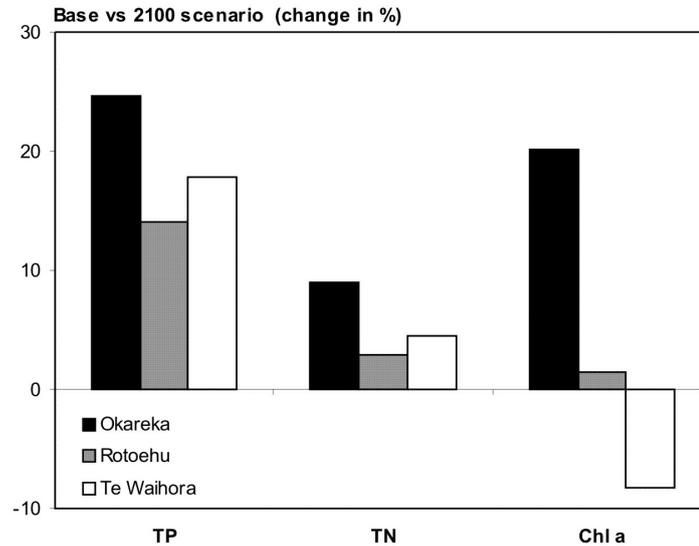
Fig. 5.11. The relative change of annual average TP, TN and Chl *a* concentrations in surface waters of lakes Okareka, Rotoehu and Te Waihora, as a response to future climate relative to the simulated base scenario.

When examining loading scenarios for the base climate scenario (Fig. 5.12), there is also a clear tendency for the two eutrophic lakes to be less sensitive to changes in the external loading, and changes in the external load of ±50% had only a minor effect on the modelled water quality in Lake Te Waihora (±5-10%).
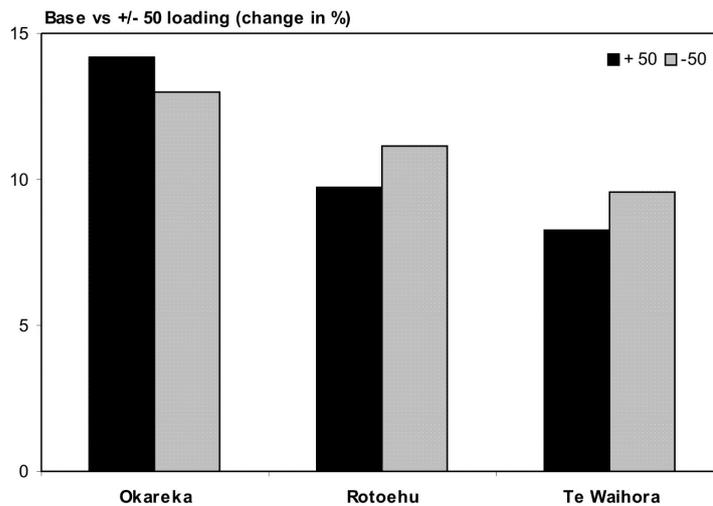
Fig. 5.12. The mean relative absolute change of annual average TP, TN and Chl *a* concentrations in surface waters of lakes Okareka, Rotoehu and Te Waihora, as a response to a 50% reduction (-50) and 50% increase (+50) in the external TP and TN load.

5.4 Discussion

5.4.1 Model constraints

The DYCD models calibrated for lakes Okareka, Rotoehu and Te Waihora generally showed good agreement with observed seasonal dynamics of physical, chemical and biological variables in all three lakes (Table 5.2-5.4). Surprisingly, when considering the immense differences in trophic status and mixing dynamics, NRMSE values were generally similar across the lakes. The Pearson correlation coefficients were overall similar to those obtained in other studies (e.g., Arhonditsis and Brett 2005; Burger et al. 2007). Nevertheless, both the NRMSE and r values showed that a considerable component of the variability, in particular for inorganic nutrient species (PO_4, NO_3 and NH_4), was not captured by the DYCD model simulations (Table 5.2-5.4).

Pearson correlation coefficients between modelled and observed data for the inorganic nutrients for Lake Okareka, in particular, were low (or even slightly negative in the case of, for example, surface water PO_4 and NO_3). This can be at least partially explained by the very low concentrations of these nutrients in this lake, which for the majority of time were below or marginally above the nominal detection limit for flow injection analysis (that is used by the regional councils) of 0.005 mg/L (Müller et al. 1991). As a result the variance/range in the observed data for inorganic nutrients is very low, which naturally leads to a low co-variance between observed and modelled data, and subsequently low Pearson correlation coefficients. Although the calibration period demonstrated a high correspondence between modelled and observed data for temperature in the hypolimnion of Lake Okareka, the model underestimated temperature during the last year of the validation period, which suggests that the transfer of heat through the thermocline and hypolimnion mixing may not be fully represented. The model did, however, accurately capture the volumetric hypolimnetic oxygen demand (VHOD) and the yearly anoxia occurring in bottom waters of Lake Okareka, as well as the abrupt peaks of TP and PO_4 that occurred concurrently with periods of anoxia and just before water column mixing in winter.

The model simulations for Lake Rotoehu generally showed good agreement with observed data for temperature, DO, TN and TP in both surface and bottom waters. However, the modelled TP and PO_4, in particular, were underestimated in surface waters during the final year of the validation period. The observed data for this last year may have been influenced by a weed harvesting trial, as Environment Bay of Plenty commissioned a two-week trial of hornwort (*Ceratophyllum demersum*) harvesting in Lake Rotoehu during April 2006 (to remove plants but also the associated nutrients from the lake). Unlike many other macrophytes, *Ceratophyllum demersum* absorbs nutrients from the water column rather than the sediments, and partial removal of these macrophytes from the lake may therefore cause increased dissolved nutrient concentrations in the water column, at least in the short-term, which could readily enhance phytoplankton growth. This external influence was not accounted for in the model simulations for Lake Rotoehu. The weed harvesting trials are now planned as annual events for the next ten years (Cronin et al. 2007), and once observation data become available for upcoming years, the model calibration for Lake Rotoehu may need to be adjusted or specific process representations used, to better reflect the complexities of the ecosystem dynamics and management interventions.

Unlike lakes Okareka and Rotoehu, where annual anoxic events in bottom waters drive a seasonal response of inorganic nutrient release from the sediments, observed data for inorganic nutrients in Lake Te Waihora showed no clear seasonal patterns. However, one event during the first year of validation was associated with an exceptional peak of NO_3 concentrations during winter, and the model simulation was able to reproduce this event. The model simulations showed that DO concentrations were close to saturation throughout the water column during this time, and therefore suggest that this NO_3 peak was not caused by an abrupt internal load driven by a single anoxic event that could potentially release NH_4, which would be nitrified to NO_3. Instead, this event is driven largely by a high winter run-off event which was reflected in the inflow file to DYCD as a peak in the loading of both TN and TP during mid June 2006.

In summary, all three models were generally good at reproducing TP, TN and total Chl *a* concentrations, which were the key water quality indices used to

interpret the effects of future climate change and changing nutrient loadings on lake water quality. It is therefore reasonable to assume that the results presented in this study provide a realistic representation of the future effects of climate change on lake water quality.

It is well known, that the amount and availability of nutrient pools in lake sediments can strongly influence lake water quality (Søndergaard et al. 2003), and can even prevent or delay the response of lake water quality to changes in external loading (Jeppesen et al. 2005). The effects of temporal changes in sediment nutrient releases as a response to changes in external loading and/or climate change were not included in the DYCD model version used in this study, however, and the model scenarios may therefore slightly underestimate the extent of the ecosystem responses. Using ecosystem models that include a dynamic response of sediment nutrient releases to changes in external loading and climate may help to better capture the dynamic influence of sediments in contributing to the resilience of water quality responses to climatic changes and could also be valuable in examining the time scales of the response, as opposed to the equilibrium condition (Fig. 5.13).
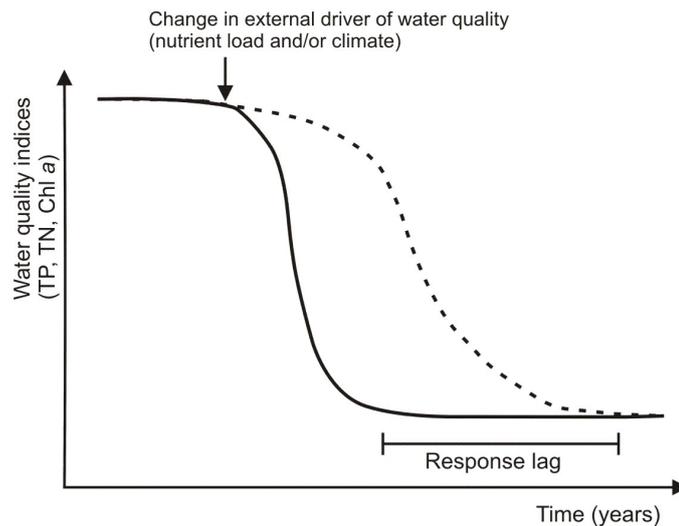
Fig. 5.13. Hypothetical model of response of water quality indices to reduction in external loading and/or changes in climate, using a static sediment model (solid line) and a dynamic sediment model (dashed line).

5.4.2 Validity of future climate change scenarios

Although the model simulations in this study generally reproduced the seasonal ecological dynamics of the three New Zealand lakes, the accuracy of the future predictions made by the models is irrevocably linked to the accuracy of the boundary forcing data, such as meteorological variables and nutrient loadings, for which scenarios were set up to represent future conditions. I included only changes in air temperature to represent future meteorological conditions, as this variable is arguably the most influential of those that will respond to a changing climate. One must also acknowledge the potential effects of other variables and processes, however, which were not accounted for in the simulations presented in this study. Most obvious is the possible change of other meteorological variables that influence the heat budget and thermal structure of lakes (Yeates and Imberger 2003); including, for example, cloud cover or atmospheric turbidity due to air pollution that could affect both long-wave and short-wave radiation impinging on the lake, relative humidity that influences the exchange of latent heat, and wind speed that influences mixing and the exchange of both latent and sensible heat at the water surface (Livingstone 2003). The regional climate models suggest that rainfall, for example, may increase slightly in the Bay of Plenty and Canterbury provinces. However, at present, these models are not able to reproduce the observed patterns of these additional meteorological variables with sufficient accuracy and confidence that they should be applied as input data in an additional predictive lake model such as DYCD (Rivington et al. 2008). Therefore I assumed that changing air temperatures will be the most important factor influencing water quality in the future scenario, and that other meteorological variables will remain similar to the base scenario.

Changes in meteorological variables, including air temperature, will not only influence the thermal dynamics of lakes and the balance of evaporation and rainfall at the water surface, but also catchment scale run-off, and thereby the external nutrient loading to lakes. Recent model studies from regions with temperate climate in the northern hemisphere (e.g., Barlage et al. 2002; Andersen et al. 2006), where climate change also is expected to cause an increase in annual mean precipitation, suggest that catchment run-off and nutrient export from river

basins (represented in this case by TN) may increase by 5-10% in these regions during the next century. Therefore, the most realistic scenario of the simulations for 2100 presented in this study may well be the combination of future air temperatures and an increased nutrient loading of 10% (Fig. 5.10).

5.4.3 Complex response patterns to climate change across a range of lake ecosystems

The effects of climate change on the physical and ecological dynamics in lakes are generally diverse, and individual lakes may respond very differently to climatic changes (Mooij et al. 2005). Climate change, and global warming in particular, is known to influence water temperature and the thermal properties of water bodies. Long-term datasets have shown how increasing surface water temperature increases the stability of stratification in some lakes (e.g., Livingstone 2003). However, a study by Tanentzap et al. (2008) has also shown evidence of water column cooling with changes in wind speed and coloured dissolved organic matter concentrations, despite increasing air temperature. Depending on the seasonal distribution of heat and the energy available for mixing and the water depth and light attenuation, bottom waters may receive more heat with climatic warming, resulting in reduced density gradients between the epilimnion and hypoliminon during stratification events.

Generally, it is expected that climate change, and in particular increasing water temperature, will increase lake productivity and favour the occurrence of cyanophyte blooms in lakes (Paerl and Huisman 2008), and also invoke a shift in the timing of seasonal phytoplankton and zooplankton biomass peaks (Gerten and Adrian 2000). However, for individual lakes, like the deep Lake Tanganyika, East Africa, which is permanently anoxic in the bottom waters, climatically induced increases in water column stability and decreased nutrient upwelling from deeper waters, can also cause a decrease in ecosystem productivity (O'Reilly et al. 2003). The simulations presented in this study reflect this complex nature of the response of lake water quality to climate change. Hence, the model simulations suggest that annual average productivity, represented in this case by total Chl *a* biomass, will increase in lakes Okareka and Rotoehu, but decrease in Lake Te Waihora as a

response to climate change (and increased air temperature). The effects of climate change on shallow New Zealand lakes that, unlike Lake Te Waihora, have a healthy and abundant macrophyte community (e.g. Lake Rerewhakaaitu, Bay of Plenty) may be different to those predicted for Lake Te Waihora, as the macrophyte communities can cause these lakes to be more resilient to climate change (Moss et al. 2003). For all three lakes in this study, there was a clear general pattern of degrading water quality, induced by climate change, however, suggesting that productivity in a future warming climate will be higher during summer months in particular, and that cyanophytes, which were represented in the simulations for Lake Rotoehu, will be more dominant in the future. This increasing dominance of cyanophytes was also found in a modelling study by Elliot et al. (2006), who used the phytoplankton community model PROTECH to simulate the importance of temperature and nutrient loading for phytoplankton community structure in Bassenthwaite Lake, England.

5.4.4 The implications of climate change for lake restoration and management

Previous studies have used complex ecosystem models to predict effects of climate change on lake water quality (e.g. Komatsu et al. 2007; Mooij et al. 2007) and these studies also suggest that climate change will cause water quality to degrade. However, the models applied in these studies were largely un-calibrated, and consequently their predictions should be viewed as qualitative rather than quantitative, and will only be indicative of possible trends in the responses of lake water quality to different management strategies and climate change. Hence, this study is the first to use intensively calibrated models for predicting the effects of future climate change on lake water quality. The three models applied in this study suggest that the future climate of 2100 will cause annual average TP concentrations across the three lakes to increase 14-25%, TN concentrations to increase 3-9% and Chl *a* concentrations to increase 2-20% in two of the lakes, but to decrease (-8%) in Te Waihora as a result of extended predominance of summer blooms, represented by increased chlorophyte biomass, which reduces the duration of diatom dominance during winter. As the chlorophytes in the Te Waihora model are represented with a higher TP:Chl *a* and TN:Chl *a* ratio relative

to diatoms, the net effect of the future climate is increasing annual average TP and TN concentrations. The simulations presented in this study further suggest that the effects of climate change by 2100 generally will be equivalent to considerable increases in the external nutrient loading (25-50%), particularly when added to the likely changes in catchment runoff and nutrient loading, and the changes to lake water quality induced by climatic changes are clearly of a magnitude that should be incorporated into long-term management strategies for the New Zealand lakes. For example, if the New Zealand regional councils, responsible for managing water quality in the three New Zealand lakes, are planning to restore lake water quality by reducing the external nutrient loading to the lakes by less than 25%, the beneficial effects of this reduction will likely be overwhelmed within the next century by a warming climate.

Although the predicted effects of climate change for the three New Zealand lakes may seem severe, the relative changes in water quality indices such as TP and TN concentrations are still considerably lower than the extreme changes observed in Antarctic lakes, where nutrient concentrations in some lakes are currently changing an order of a magnitude per decade (Quayle et al. 2002). Nonetheless, the effects of climate change on lake water quality in the New Zealand lakes should be considered when management strategies are planned and implemented, thus successfully preserving or improving water quality in future decades.

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Chapter 6: Conclusions

6.1 Research summary

It is not a question if, but rather a question of when and by how much climatic changes will affect the ecological quality of lakes across the world. The magnitude and timescales on which lake ecosystems will respond to steadily increasing air and water temperatures depend strongly on the ecological resilience of the lakes, and the associated dynamics, abundance and availability of sediment nutrient pools. Deterministic lake ecosystem models, like the one-dimensional DYRESM-CAEDYM (DYCD) model, are currently being developed to include complex sediment diagenetic processes, with the ultimate goal of being able to predict not only the ecosystem effects of climate change or lake restoration, but also the lag-time (which can range from years to several decades) before the full ecosystem response to, for example, changes in climate or external loading is achieved. The new diagenesis module developed for DYCD adds a high degree of parameter complexity to an already complex water column model, however, and following the statute that "*all models are wrong but some are useful*" (George Box 1979, Professor in Statistics at the University of Wisconsin), extensive testing of the model performance, as well as a fundamental understanding of essential diagenetic drivers, are required before the predictions of the model can be fully trusted and could henceforth be useful for research and management purposes. Through a comprehensive field study and a computer-based modelling study, this thesis provides a fundamental understanding of the diagenetic drivers that control the nutrient distribution and cycling in lake sediments, of which many are parameterised and included in dynamic sediment diagenesis models. The results presented in this thesis also provide the first estimates of the effects of future climate change on water quality in New Zealand lakes, and therefore have important implications for the management of lakes in New Zealand generally.

The aim of Chapter 2 was to provide a fundamental understanding of the processes influencing vertical concentration profiles in lake sediments, based on sediment cores collected from 14 different lakes, including 12 lakes within the

Bay of Plenty province, North Island of New Zealand, shallow Lake Te Waihora (Lake Ellesmere) in the Canterbury province, South Island of New Zealand, and shallow Lake Taihu in the Jaingsu province, China. The observed vertical concentration profiles of total phosphorus (TP), total nitrogen (TN) and total carbon (TC) revealed that the profile distributions can be similar in sediments across gradients of widely differing trophic status between the lakes. Empirical and mechanistic steady state profile models were derived to describe the vertical distributions of TP, TN and TC concentrations in the sediments. These models revealed that density-driven burial and biodiffusive mixing, which in the models also include effects of redox-driven gradients, are strongly correlated with vertical gradients of sediment TC, TN and TP content, whereas lake trophic status is not. The knowledge gained in this study provides a strong basis for interpreting the historical information provided by vertical concentration profiles in lake sediments, and will be useful, in particular, for diagenetic modellers, when calibrating the parameters that influence these vertical profiles. The findings also have major implications for sediment dating techniques which assume that diagenetic effects (including biodiffusion) are negligible. This is clearly not the case, and to obtain more accurate estimates of sediment age, future studies involving sediment dating techniques (e.g., Pb^{210}) must employ profile models that also account for diagenesis, as is the case for the model presented in this chapter.

While the results presented in Chapter 2 are based on empirical and mechanistic steady state models, i.e., assuming that current geochemical sediment profiles are at steady state with the current trophic status of the lakes, it is evident that sediment nutrient concentrations can change in response to temporal changes in environmental drivers such as the external nutrient loading. In Chapter 3, the temporal rates at which sediment TP, TN and TC may change through a decadal timescale were quantified by comparing data obtained in this study with those of previous sediment studies that have been undertaken intermittently over the past three decades for the 12 lakes in the Bay of Plenty, of which some have undergone eutrophication during recent decades. The calculated temporal changes in surficial (0-2 cm) sediment TP and TN concentrations ranged from 27.5 to 114.4 mg P kg^{-1} dry wt yr^{-1} and 51.8 to 869.2 mg N kg^{-1} dry wt yr^{-1}, respectively,

and were not significantly linearly related to catchment area or temporal changes of different water column indices considered to reflect lake trophic state, including annual mean water column concentrations of TP, TN or chlorophyll *a* (Chl *a*). Hence, between-lake variations in sediment TP and TN concentrations are influenced by a range of complex, interacting factors, such as sediment focusing, sediment redox conditions (and periodic anoxia in the hypolimnion of some lakes), and variations in sediment mineral composition (that influences retention and release of various sediment phosphorus and nitrogen species), and these factors cause sediment TP and TN concentrations across the 12 lakes to respond differently to temporal changes in water column TP and TN concentrations. The rates of temporal changes in sediment nutrient concentrations, as presented in this chapter, are of fundamental importance in the calibration of diagenetic models, and provide a dataset that enables evaluation of long-term (years to decades) diagenetic model simulations.

The knowledge gained from chapters 2 and 3 provide an excellent basis for calibrating and evaluating one-dimensional diagenesis models. However, these models may not accurately capture the sediment nutrient dynamics and the interactions with the water column, if considerable horizontal variability of nutrient concentrations exists in the sediments and/or the water column. It is unclear, however, if distinct spatial gradients of nutrient concentrations in the water column are also reflected in spatial gradients in the bottom sediments. In Chapter 4, interrelations between spatial variability in water column and sediment TP and TN concentrations were examined for the large, shallow and highly eutrophic Lake Taihu, where distinct horizontal water column concentration gradients of TP, TN and Chl *a* have been shown to occur. The concentration of TP and TN in surficial sediments (0-2 cm) and TP, TN and Chl *a* concentrations in water column samples from Lake Taihu, have been determined from 32 sites in 2005, and in this study sediment TP, TN, TC, iron (Fe) and manganese (Mn) concentrations were measured vertically at 2 cm intervals, extending to a depth of approximately 20 cm, at an additional 8 sites in 2006. Linear correlation analysis revealed that surficial sediment TP concentrations across the 32 stations were related significantly, though weakly, to the annual mean water column concentrations of TP and TN as well as Chl *a*. Correlations of surficial sediment

TN with water column variables were, however, not significant. Amongst the geochemical variables tested, the vertical variability of sediment TP concentrations was most strongly related to sediment Mn and TC concentrations. A multiple stepwise linear regression revealed that the combination of sediment Mn and TC concentrations explained 91% of the horizontal variability in sediment TP concentrations and 65% of the vertical variability. The knowledge gained in this chapter provides an insight into within-lake variability of sediment nutrient concentrations, which is superior to previous knowledge and understanding, and demonstrate how spatial heterogeneity in water column productivity, and not just external suspended sediment and nutrient point sources, may influence sediment nutrient properties.

As clearly demonstrated by the results presented in Chapter 4, a one-dimensional vertically resolved water column and/or sediment model, would not be able to capture the distinct horizontal gradients occurring in both the water column and sediments of large, shallow Lake Taihu. However, one-dimensional lake ecosystem models, which yield long-term simulations (several years to decades), have been able to capture the seasonal nutrient and phytoplankton dynamics in lakes with a less formidable surface area than Taihu. In Chapter 5, the latest release of the DYCD model (not yet including a stable diagenesis module) was applied to three lakes, including oligo-mesotrophic Lake Okareka, eutrophic Lake Rotoehu and highly eutrophic Lake Te Waihora. All three models were calibrated based on a three year period (July 2002 - June 2005) and validated on a separate two year period (July 2005 - June 2007). The models generally showed good agreement with observed data for temperature, dissolved oxygen, TP and TN during both the calibration and the validation periods. The models were also able to capture the seasonal fluctuations of phytoplankton biomass, represented by total Chl *a* concentrations. Normalised root-mean-square-errors (NRMSE) and Pearson correlation coefficients (r) were used for model calibration, and these values were generally similar for the calibration and validation periods. The predictions of the regional climate model, DARLAM, and the IPCC A2 scenario, used to represent the future climate of 2100, suggest that air temperature will increase by an average of 2.5 ºC and 2.7 ºC for the Bay of Plenty and the Canterbury provinces, respectively, relative to the base scenario (years 2002-

2007). A series of nutrient loading regimes, where the external loading of both phosphorus and nitrogen were decreased (to represent lake restoration scenarios) or increased (to represent possible effects of land-use intensification or increased run-off) by 10, 25, and 50% in the base and future climate scenarios, were set up in order to quantify the implications of future climate change for lake restoration – and lake water quality in general. Model simulations of the future climate scenarios indicate that climatic changes, represented here by increasing air temperature, are likely to lead to varying levels of degradation of water quality in all three lakes, in particular during summer months, and suggest that the effects on annual mean surface concentrations of TP, TN and Chl *a* will generally be equivalent to the effects of increasing the external nutrient loading of both TP and TN by 25-50%. Simulations for Lake Rotoehu, where diatoms and cyanophytes were represented in the conceptual model, further suggested that cyanophytes will be more abundant in the future, increasing by >15% in annual mean biomass despite little change in the annual average levels of Chl *a*. The effects of climate change may be delayed, however, by the resilience of the bottom sediments. As demonstrated in Chapter 3, during a single decade, the TP concentration of surface sediments can increase or decrease by up to 55% and 40%, respectively, as a response to changes in external loading. Nevertheless, the insights provided by this chapter should no be ignored, and the effects of climate change on lake water quality in the New Zealand lakes will be of a magnitude that should be considered when management strategies are planned and implemented, thus being able to successfully preserve or improve water quality in the future. If left ignored, and no management actions taken, the most likely future scenario presented in this chapter (increased air temperatures concurrently with a 10% increase in external nutrient loading) suggests that Lake Okareka, the most oligotrophic of the lakes in this study, will shift from an oligo-mesotrophic to a eutrophic state, while lakes Rotoehu and Te Waihora will become increasingly eutrophic and subject to more frequent harmful algal blooms.

6.2 Recommendations for future work

During this study I tested the fully coupled dynamic sediment diagenesis and water column modules implemented in a new version of DYCD, however, this new diagenesis module was not applied in Chapter 5, as the stability of the new FORTRAN code is still not sufficient to carry out repeated long-term (multiple-year) simulations. The evaluation of the performance of this coupled model is still in its early stages, however, and further testing is required before simulations are stable and can be fully trusted. Future research should therefore include further model development and testing of the diagenetic module in DYCD. An applicable model test can be divided into a short- and a long-term evaluation, where annual or decadal rates of change in sediment nutrient concentrations, such as those presented in Chapter 3, can be used for long-term evaluation of the ability of the model to reproduce key water quality indicators and ecosystem dynamics generally. The ability of the model to reproduce long-term changes could be evaluated by comparing rates of change of sediment nutrient concentrations predicted by the model to those observed in the field. Understanding the importance of some of the essential diagenetic processes, including those examined in Chapter 2, may also help to narrow the focus to a limited range of processes described by the diagenetic module. If the diagenetic module is able to reproduce the long-term dynamics of the sediment nutrient releases, it may eventually be possible to simulate not only the ecosystem effects of lake restoration and/or climate change, but also the lag-time (which can range from years to several decades) before the ecosystem approaches an equilibrium associated with the prevailing change in the forcing data (as also discussed in Chapter 5).

A short-term evaluation of the diagenetic module's ability to reproduce seasonal sediment dynamics will require further field studies with at least a frequency of monthly sampling, in which vertical profiles of both sediment solids and porewaters are analysed for the most important chemical species, similar to the variables measured in this study. A sampling technique, where vertical profiles were resolved in 2 cm intervals, will not suffice for porewaters of eutrophic lakes, however, where the oxic layer in the sediments that strongly influences the

organic matter decomposition and also nutrient sorption/desorption, may be only a few millimetres thick. The use of micro-profilers combined with vertical sediment peepers (in situ porewater sampling technique) would therefore provide a dataset more suitable for calibration and validation of seasonal sediment porewater dynamics at suitably resolved vertical scales.

As demonstrated in Chapter 5, the model performance of DYCD, based on the statistical parameters used for model evaluation (NRMSE and r), was generally similar to that obtained in other studies. Nevertheless, the Pearson correlation coefficients between modelled and observed data showed that a considerable part of the variability, in particular for inorganic nutrients, was not explained by the DYCD model simulations. For lakes Rotoehu and Te Waihora, this may at least partly be caused by the one-dimensional assumption of DYCD, as these lakes are likely to have large horizontal concentration gradients, which do not exist conceptually in DYCD. For Lake Rotoehu, nutrient gradients are likely to be associated with a geothermal inflow (Soda springs) entering in the south-east, which is generally high in phosphorus concentrations. For Lake Te Waihora, horizontal gradients of salinity, and most likely also nutrients, are driven by artificial openings, tidal incursions and over-topping of the gravel spit that separates the southern part of the lake from the Pacific Ocean, as well as a major river inflow (the Selwyn River) that enters in the northern part of the lake. Whether these horizontal gradients are largely constant or highly seasonal is, however, not fully understood. Future research should therefore include applications of three-dimensional hydrodynamic and ecological models (like ELCOM-CAEDYM, and associated with additional horizontally resolved sampling, which may help to quantify the magnitude and fluctuations of concentrations across lakes Rotoehu and Te Waihora.