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Variability in nutrient loading to lake ecosystems and associated impacts on water quality

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View eastwards over Lake Rotorua at dawn, January 2012

Abstract

Globally, the accelerated eutrophication of lake ecosystems due to excess inputs of nitrogen (N) and phosphorus (P) is a significant problem. The rate of loading of N and P to lakes varies both in space and time; consequently, developing good understanding of such spatial and temporal variability is critical for developing integrated approaches to managing lake water quality. This study aimed to improve understanding of spatial and temporal variations in N and P loading to lakes, and, to examine how this variability affects water quality. The topic was considered at global, national and catchment scales.

Analysis of an extensive global dataset was undertaken to examine relationships between N, P and chlorophyll *a* (chl *a*) in lakes along a gradient of latitude inclusive of tropical, temperate and polar regions. The ratio of total nitrogen (TN) to total phosphorus (TP) was positively correlated with latitude, reflecting global-scale variation in nutrient cycling processes and/or nutrient sources. Relative to temperate lakes, the statistical capability of concentrations of TN and TP to predict chl *a* concentration (i.e. indicating bottom-up control by nutrients) was shown to be poor for both tropical and polar lakes. These differences reflected latitudinal variation in lake ecosystem functioning, and highlighted the potential unsuitability of applying relationships derived for temperate lakes elsewhere. Quantile regression was used to derive theoretical chl *a* near-maxima as a function of either TN or TP concentrations. Consequently, chl *a*:TN and chl *a*:TP yields (by mass) of 0.046:1 and 0.87:1 were determined to approximate the maximum possible yields of chl *a* under optimal conditions as a proxy for phytoplankton biomass potential.

Nationally-significant relationships between landscape characteristics and in-lake TN and TP concentrations were quantified for a representative sample of 101 lakes in New Zealand. Geographical Information Systems were used to analyse data from a range of sources that related to both lake-specific and wider landscape characteristics. Inferential statistical methods were then used to quantify relationships between in-lake nutrients and both land use and naturally-occurring soil P. National-scale variability in mean catchment soil P was found to be unrelated to in-lake TP concentrations, reflecting the dominant influence of human-related sources of P on TP concentrations in New Zealand lakes. The

extent of intensive pastoral agriculture was the best land use predictor of TN and TP concentrations, accounting for 38.6% and 41.0% of variation respectively. Exotic forestry accounted for a further 18.8% of variation in TP concentrations. A sub-sample of lakes for which intensive pastoral agriculture was the dominant catchment land use was then considered to test hypotheses regarding potential interactive effects of eight landscape characteristics on the positive relationship between intensively managed pasture and in-lake nutrient concentrations. Both maximum lake depth and the ratio of catchment to lake area had significant interactive effects, exerting a negative and a positive influence, respectively. In addition, an indicator of hydrological connectivity (lake order) also had a positive interactive effect on the relationship between this land use type and in lake TP (but not TN) concentrations.

To examine these broad relationships at finer spatial resolution, and also to quantify temporal variations in nutrient loading, an extensive field programme was conducted in the catchment of Lake Rotorua (Bay of Plenty, New Zealand); a large (80.5 km²), relatively shallow ($z_{\text{mean}} = 10.8$ m) lake that has experienced eutrophication. The Ngongotaha and Puarenga streams are two major inflows to the lake that were sampled at high frequency throughout a wide range of stream discharge coinciding with rainfall events. Both streams had different catchment characteristics (e.g. land use and hydrogeomorphology) which enabled spatial variations in nutrient loading between sub-catchments located upstream of a common lake ecosystem to be examined. Streams were sampled during a total of 17 hydrological events, including three during which both streams were simultaneously sampled to compare differences in pollutant transport between the streams during similar hydrological conditions. Relationships between nutrient concentrations and stream discharge were broadly similar for the two catchments, and quantification of relationships permitted nutrient loading to be estimated continuously over annual periods. Key findings included the dominance of event loads by dissolved inorganic N and the strong positive correlation between discharge and particulate P concentrations. Quantification of hysteresis in relationships between nutrient concentrations and discharge provided information about the relative importance of near- versus far-channel sources during individual events. For example, elevated concentrations of dissolved inorganic N during recessing hydrograph limbs for the Puarenga Stream suggested diffuse delivery of N from an upstream source. Temporal inequality in estimated loading

over a two-year period was high for TP as, for example, 50% of estimated cumulative two-year loads of TP were calculated to have been transported during 10–17% of the two-year time period.

The effects of storm flow discharges on water quality in Lake Rotorua were studied at fine spatial and temporal resolution for a five-day period with high rainfall in summer. An intensive programme of lake and stream sampling was paired with application of a three-dimensional hydrodynamic-ecological model (ELCOM-CAEDYM) to specifically study how dynamic fluxes in water, sediment, N and P transport in the Ngongotaha Stream inflow influenced water quality and phytoplankton nutrient limitation in the transition zone present where the stream enters the lake. Wind-driven basin-scale horizontal circulations in the lake caused deflection of the inflowing stream which strongly influenced water quality in the littoral zone for a distance of up to 1 km from the stream mouth, thus highlighting the potential importance of basin-scale horizontal transport processes in mediating the effects of storm flow discharges on lake water quality. The nutrient limitation status of phytoplankton varied both spatially and temporally within the lake in relation to nutrient transport processes, emphasising the relatively fine spatial and temporal scales at which key processes that affect phytoplankton ecology can occur. Dilution of lake water by the stream inflow strongly affected the spatial distribution of chl *a*, although the highly spatially resolved sampling identified ‘hot spots’ within the nutrient-rich plume which contributed to fine scale (≈ 10 –30 m) patchiness in the transition zone. The results of nutrient enrichment experiments indicated that such patchiness was consistent with a scenario of relative stimulation in the growth of lentic phytoplankton due to high nutrient availability in the spreading plume.

To further examine the issue of nutrient bioavailability, chemical fractionation techniques and batch culture experiments were conducted to investigate spatial (between streams) and temporal (between periods of varying stream discharge) variations in the bioavailability of particulate P transported in storm flow for the two study streams. Bicarbonate-dithionate extraction indicated that 25–100% of particulate P transported in stream water samples collected during storm flow was potentially bioavailable if exposed to anoxia, e.g. in the lake hypolimnion during calm summer periods. Somewhat paradoxically though, bioassays indicated that, under oxic conditions in the laboratory, bioavailable P was actually higher in filtered samples (particulate P removed) than in unfiltered

samples (higher TP concentrations, particulate P present). This result was attributed to net adsorption of dissolved inorganic P to the sediments present in the unfiltered treatments, and therefore highlights the importance of considering physicochemical characteristics of receiving environments when assessing bioavailability of P sorbed to sediments.

Hence, by examining a range of spatial scales and integrating understanding gained using a range of research methods, this study has provided knowledge of underlying drivers of spatial and temporal variability in nutrient loading to lake ecosystems at scales ranging from global to a few metres. Furthermore, it has provided insight into how such variability can affect lake water quality. This knowledge can guide actions that are increasingly required to safeguard the services provided by lake ecosystems in a future with increasing global and local pressures on freshwaters.

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Preface

The main body of this thesis comprises seven chapters, of which Chapters 2–6 are individual research chapters. Each research chapter is in the style of a separate scientific paper that has been prepared for, or published in, a peer-reviewed scientific journal. This format means that there is some minor repetition of methodological details and referencing styles vary between chapters.

Together, these chapters form a coherent portfolio of work that makes an original contribution to my chosen thesis topic. Additional relevant published work that has been completed during my PhD candidature also contributes to Chapter 1, and forms the content of Appendix 1. Except where stated otherwise, the work in this thesis, including study design, field and laboratory work, data analyses and writing, was undertaken by me while under the supervision of Professor David Hamilton (University of Waikato) and Dr J. C. Rutherford (National Institute of Water and Atmospheric Research).

Co-authors for each chapter are listed below. All co-authors reviewed relevant chapters and provided advice where necessary.

Chapter 2 has been published as: Abell JM, Özkundakci D, Hamilton DP, Jones JR (2012) Latitudinal variation in nutrient stoichiometry and chlorophyll–nutrient relationships in lakes: A global study. *Fundamental and Applied Limnology* **181**, 1–14.

Chapter 3 has been published as: Abell JM, Özkundakci D, Hamilton DP, Miller SD (2011) Relationships between land use and nitrogen and phosphorus in New Zealand lakes. *Marine and Freshwater Research* **62**, 162–175.

Chapter 4 is currently in press (DOI: 10.1039/c3em00083d) and will be published in *Environmental Science: Processes and Impacts*. Co-authors are David P. Hamilton and J. C. Rutherford.

Chapter 5 has been submitted to *Ecohydrology*. My co-author is David P. Hamilton.

Chapter 6 is currently in press and will be published in abridged form in the *New Zealand Journal of Marine and Freshwater Research*. My co–author is David P. Hamilton.

Appendix 1 has been published as: Abell JM, Hamilton DP, Paterson J (2011) Reducing the external environmental costs of pastoral farming in New Zealand: Experiences from the Te Arawa lakes, Rotorua. *Australasian Journal of Environmental Management* **18**, 139–154.

Appendix 2 presents photographs of study sites and some sampling instruments that were used.

1 Introduction

1.1 General background

1.1.1 *Variability in lake ecosystems*

Ecosystems are in a state of non–equilibrium (Michaelian, 2005). Thus, they are characterised by concentration gradients in both space and time which interact dynamically as gradients continually establish and dissipate (Müller, 1998; Jørgensen and Marques, 2001). Such a conceptual framework is particularly pertinent for lake ecosystems due to high heterogeneity (Kratz et al., 2005) and sensitivity to fine–scale perturbations as a result of the distorted temporal and spatial scales that planktonic organisms inhabit relative to terrestrial ecosystems (Reynolds, 1995). Hence, while isolated measurement along spatial and temporal gradients can provide insight into the state and structure of lake ecosystems, investigation of gradient dynamics is necessary to gain good understanding of how lake ecosystems function (Müller, 1998).

1.1.2 *Linking lakes and landscapes*

Historically, there has been tendency for limnologists to consider individual lakes as isolated units of study (Johnes, 1999). In recent decades, however, the importance of considering the continuity between lakes and their wider catchments (including overlying atmosphere) has been widely recognised (e.g. Bormann and Likens, 1967; Odum, 1969; Baron et al. 2002). This holistic perspective, in conjunction with increased availability and extent of spatially–resolved data, has promoted study at the landscape–scale that has highlighted the close coupling between many fundamental components of lake ecosystems and processes that operate at landscape–scales (Johnson and Host, 2010). Recognising continuity between lakes and the surrounding landscape is particularly important when considering biogeochemical cycling, as lake water chemistry is intrinsically related to wider catchment characteristics (e.g. Håkanson, 2005, Martin and Soranno, 2006). Consequently, the emerging field of landscape limnology has developed in recent years; involving application of statistical techniques with increasingly large datasets to allow the spatially–explicit study of lakes and interactions with surrounding landscapes (Soranno et al., 2010). Hydrological processes have a fundamental role in controlling the transport of materials from

terrestrial environments to receiving lake ecosystems. Such processes therefore mediate how other landscape characteristics affect lake water quality, and impose temporal variations to material fluxes to lakes due to the episodic nature of hydrological transport processes such as stream flow (e.g. Yahdjian & Sala, 2010). Comprehensive understanding of the fundamental interactions between biogeochemical and hydrological systems is, however, currently lacking, and further investigation of these linkages has been identified as a priority for further research (Burt & Pinay, 2005; Lohse et al. 2009; Green & Finlay, 2010).

1.1.3 Nutrient loading and eutrophication

Understanding the factors that regulate inputs of nitrogen (N) and phosphorus (P) to lakes has long been of particular interest to limnologists. Nitrogen and P are required in relatively large quantities to support a range of essential cell physiological functions (Maathuis, 2009) and, although micronutrients such as iron and zinc can limit phytoplankton growth in some unproductive lakes (Goldman, 1960, Downs et al., 2008), N and P have been shown to most frequently limit primary production in freshwaters (Vollenweider, 1968, Hecky and Kilham, 1988, Elser, 2007). There are a range of fractions of N and P present in freshwaters, with the total pool of N and P comprising a particulate and a dissolved fraction that is typically operationally defined by filtration (reviewed by Worsfold et al., 2008). The extent to which nutrients can be assimilated by living organisms (bioavailability) varies between fractions, the most bioavailable being the inorganic dissolved component which comprises the fully dissociated orthophosphate ions (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}) in the case of P (Reynolds and Davies, 2001) and nitrite (NO_2^-), nitrate (NO_3^-) and ammonium (NH_4^+) ions in the case of N (Rabalais, 2002). In waters of natural lakes that are pristine or little disturbed by human activities, tightly-coupled cycling between landscapes and freshwaters means that bioavailable N and P are continually scarce, maintaining both low overall primary productivity, and, a natural tendency for N and P to be equally influential in bottom-up control of phytoplankton (i.e. co-limitation) (Moss et al., 2012). In undisturbed ecosystems, and over seasonal timescales, the relative abundance of these two nutrients (i.e. stoichiometry) in pelagic surface waters of a lake may therefore be expected to approximate the ‘Redfield ratio’ of 7.2 N:1 P by mass (Redfield et al., 1963). Such a ratio has been shown to approximate the average of species-specific biochemical optima (Klausmeier et

al., 2004) which reflect homeostasis in the synthesis of ribosomal RNAs and proteins (Loladze and Elser, 2011). In many catchments, however, failure to adequately treat pollution from human sources such as sewage and agricultural emissions has now resulted in freshwaters becoming analogous to a “waste bin” (Moss, 2008). Variation in N:P between sources of nutrient pollution has resulted in an increased range of N:P in lake water, secondary to a general trend of nutrient enrichment (Downing & McCauley 1992, Moss et al. 2012). Consequently, anthropogenically–accelerated eutrophication has now become a widespread problem for lake ecosystems, resulting in major ecological, social and economic impacts that include: de–oxygenation, fish kills, loss of biodiversity, decreased water potability and proliferation of potentially toxic algal blooms (Carpenter et al., 1998, Schindler and Vallentyne, 2008).

1.1.4 Controlling eutrophication in New Zealand

The need to limit loading of N and P to lakes to control eutrophication has been widely recognised (e.g. Conley et al., 2009), although some researchers advocate that a policy of P–only control should be adopted; an argument supported by ecosystem–scale experiments conducted in the Canadian Experimental Lakes Area which showed that N controls were offset by increased N₂ fixation by heterocystous cyanobacteria (Schindler et al., 2008). Despite this, P–only control is not, however, generally recommended to control eutrophication in New Zealand catchments. In an extension of a study by White (1983), Abell et al. (2010) compared multi–annual median ratios of total nitrogen (TN) to total phosphorus (TP) concentrations for 121 lakes in New Zealand, with those for 689 lakes in 15 European Union countries. The study showed that median TN:TP was significantly lower for the New Zealand dataset for each of the five categories of trophic state that were considered¹(Figure 1.1a). These systematic differences were attributed primarily to relatively lower N concentrations in unproductive New Zealand lakes (Figure 1.1b), and to relatively higher P concentrations in more eutrophic lakes (Figure 1.1c).

¹ Trophic state was defined on the basis of chlorophyll *a* concentrations defined by the OECD (1982) fixed–boundary system.

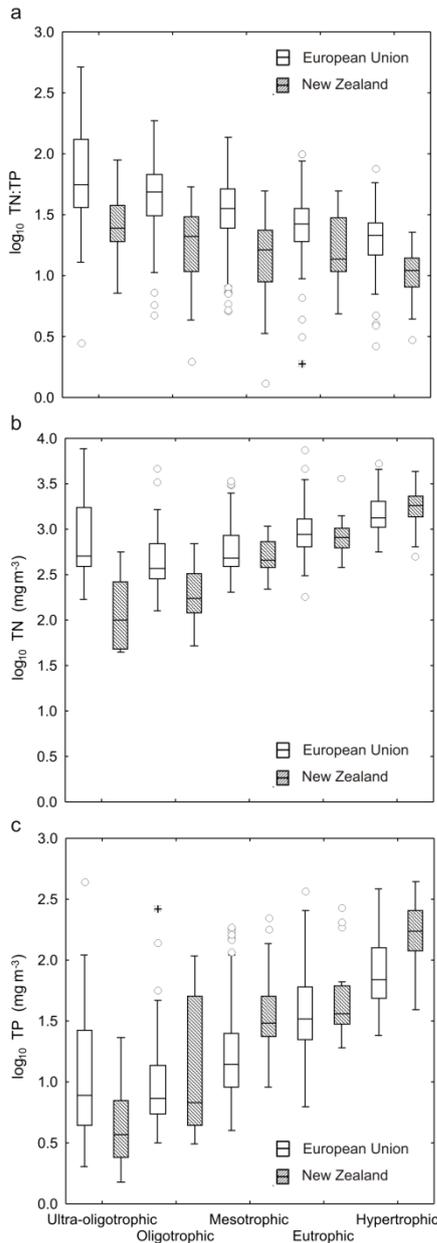


Figure 1.1 Median mass ratios of total nitrogen (TN) to total phosphorus (TP) (a), TN (b), and TP (c) concentrations for 121 New Zealand lakes and 689 lakes in European Union countries, by five categories of trophic status. Data are \log_{10} transformed. The whiskers represent the non-outlier range, the outer edges of the boxes represent the 25th and 75th percentiles, the lines within the boxes represent the median, circles represent outliers, and crosses represent extreme data points.

The near-pristine concentrations of N present in ultra-oligotrophic and oligotrophic New Zealand lakes, in conjunction with the high relative importance of N in limiting phytoplankton biomass (implicit in low observed TN:TP), therefore means that failure to control N loads to New Zealand lakes has the potential to cause eutrophication. Hence, although conclusions about strategies to reverse eutrophication cannot be solely made on the basis of knowledge about current nutrient limitation (due to hysteretic effects; Schindler, 2012), the potential for further ecological decline if N is not controlled warrants the need to control N pollution in New Zealand. The rationale for dual control of N and P is further supported by New Zealand’s island status which means that there is

frequently high connectivity between freshwater and marine ecosystems, for which sensitivity to N-enrichment is well established (cf. Paerl, 2009).

1.1.5 Quantifying spatial and temporal variations in nutrient loading to Lake Rotorua: A research priority

Lake Rotorua (Bay of Plenty, New Zealand) and its surrounding catchment was the study site chosen for the programme of field and laboratory work that forms the focus of chapters 4–6. It is a large (80.5 km²), relatively shallow ($z_{\text{mean}} = 10.8$ m) and polymictic lake that was volcanically-formed. The lake is nationally iconic and of particular cultural significance to Te Arawa who are the legal owners of the lake bed.

Lake Rotorua has experienced eutrophication and associated water quality decline over recent decades. Rutherford (1984) analysed trends in lake water quality from 1966–1983 and identified water quality decline during the periods 1967–1970 and 1978–1983. These periods of deterioration were attributed primarily to meteorological conditions that favoured stratification (and hence internal nutrient loading) and inputs from sewage effluent respectively. Rutherford et al. (1989) later analysed trends in lake water quality and nutrient inputs over one decade (1976–1986) and recommended that both N and P inputs from sewage be removed from the lake. Sewage inputs were diverted from the lake in 1991 and wastewater was instead discharged into the Whakarewarewa forest in the Puarenga Stream sub-catchment to the south of the lake (Tomer et al., 2000). This action was supported by implementation of the Upper Kaituna Catchment Control Scheme which comprised a range of comprehensive diffuse pollution control measures such as riparian planting and hillside stabilization that were implemented throughout the 1980s (Williamson et al., 1996). Despite these actions, and other measures (see Abell et al., 2011, Appendix 1), Lake Rotorua remains eutrophic and, as recently as 2009, no long-term improvement in water quality had yet been recognised (based on analysis of monthly monitoring data over c. 13 years; Burns et al., 2009). Most recent data do, however, exhibit evidence of a slight reduction in trophic status between 2001 and 2012, with surface water TP concentrations in particular exhibiting a decreasing trend (Abell et al. 2012).

In response to public dissatisfaction with water quality, Lake Rotorua was identified as a priority for restoration (Parliamentary Commissioner for the

Environment, 2006) and national and regional government funds were designated to support this (Her Majesty the Queen et al., 2008). It is recognised that continuing research is required to guide the long-term changes to both land use and land management that are necessary as part of an integrated catchment management approach to achieve restoration objectives (Parliamentary Commissioner for the Environment, 2006). Specifically, improved quantification of nutrient loading to the lake during episodic storm flow periods has been identified as a research priority by separate studies (Rotorua Lakes Strategy Group, 2000; Hamilton, 2003). Recently, the rationale for developing good understanding of spatial and temporal variations in nutrient loading to the lake has been strengthened following use of dynamic process-based models to inform decision-making (e.g. Burger et al., 2008), and the consequent need for accurate and suitably resolved input data.

1.2 Objectives

The overarching objective of this thesis was to improve understanding of spatial and temporal variations in N and P loading to lakes, and, to examine how these variations affect water quality. Accordingly, research was conducted at a range of spatial and temporal scales to develop broad and integrated understanding. Research comprised: collation and critical analysis of existing datasets from a range of sources; an extensive programme of field work conducted in the catchment of Lake Rotorua during different hydrological conditions; configuration and application of a coupled ecological-hydrodynamic model, and; developing and undertaking laboratory-based experiments.

1.3 Thesis overview

This thesis comprises five main research chapters (Chapters 2–6) which have been prepared for, or published in, peer-reviewed scientific journals. These chapters are presented in order of decreasing spatial scale at which the research was conducted. Consequently, Chapter 2 has global focus, Chapter 3 has a national-scale focus and Chapters 4–6 concern specific research relating to Lake Rotorua (see Section 1.1.5). Chapter 7 provides an overview of the main conclusions of the research chapters, and also provides ideas for how the research could be further advanced.

Chapter 2 presents analysis of global latitudinal variations in relationships between phytoplankton biomass (inferred from chlorophyll *a* concentration), and N and P concentrations, using an extensive sample of lakes. This chapter describes previously unreported systematic global-scale variation in the relative abundance of TN and TP in lakes, and, quantifies latitudinal variations in relationships between nutrients and phytoplankton biomass that reflect latitudinal variations in lake ecosystem functioning.

Chapter 3 describes a study that used Geographical Information Systems to compile and analyse data relating to land use and catchment characteristics for 101 lakes throughout New Zealand. Inferential statistical techniques were used to analyse relationships between land use and multi-annual mean in-lake TN and TP concentrations, to provide national-scale understanding of linkages between landscape factors and lake water quality.

Chapter 4 presents the results of an extensive field study involving high-frequency water sampling of surface stream inflows to Lake Rotorua. The aim of the research was to quantify both temporal (with sub-catchment) and spatial (between sub-catchment) variations in loads of both N and P transported to the lake, with particular emphasis on high-discharge periods that are typically not included in routine sampling. A range of different nutrient fractions was considered to provide insight into how the relative composition of total nutrient loads can vary during different hydrological conditions. Loads of suspended sediment were also quantified, reflecting the association between sediments and particulate nutrients, in addition to the status of this potential pollutant as an important determinant of water quality in its own right.

Chapter 5 describes an integrated study of fine-scale spatial and temporal variations in the water quality of Lake Rotorua throughout a meteorologically dynamic period during early summer. The study extends the topic of temporal variability in nutrient and sediment loading that is introduced in Chapter 4 by examining the resulting effects of such variability on water quality. Specifically, the study focused on biogeochemical processes in the transition zone present at the interface between a stream inflow and the littoral zone of the lake. The study involved: sampling lake and stream water; analysis of high-frequency data collected using *in situ* sensors; configuration and validation of a three-dimensional coupled ecological-hydrodynamic computer model, and; laboratory-

based nutrient enrichment experiments to determine the nutrient limitation status of phytoplankton communities.

Chapter 6 addresses uncertainties raised in Chapters 4 and 5 by examining the bioavailability of particulate P transported in stream storm flow. The chapter presents results of chemical analyses to quantify potential desorption of dissolved inorganic P under anoxic conditions. In addition, results are presented of an experiment designed to examine whether phytoplankton isolated from the lake can utilise particulate P. Briefly, the experiment involved measuring the growth rate and maximum biomass of initially P-limited phytoplankton cultures added to stream waters that had been: filtered (no particulate P) or unfiltered (particulate P present), and also, exposed to a reducing agent (particulate P and dissolved redox-sensitive P present).

Appendix 1 is an article that critically examines policy and restoration approaches for managing water quality in the Te Arawa lakes (which include Lake Rotorua) in New Zealand. The article specifically focuses on the control of nutrient pollution from agricultural sources and discusses potential ways to address the issue at the national-scale.

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2 Latitudinal variation in nutrient stoichiometry and chlorophyll-nutrient relationships in lakes: A global study

2.1 Introduction

As primary producers, phytoplankton are a fundamental component of lake ecosystems, occupying a pivotal role in the global carbon cycle and providing resources to support higher trophic levels (Reynolds 2006). Following anthropogenic perturbation, however, phytoplankton can become excessively abundant, resulting in adverse ecological and economic impacts (Smith 2003). Resource limitation theory states that the yield of phytoplankton biomass is controlled by the availability of the factor (e.g. an essential macronutrient) most deficient in relation to algal growth requirements (von Liebig 1885; Klausmeier et al. 2004). This theory forms the basis of bottom–up models that have been used for decades to quantitatively predict phytoplankton biomass (usually inferred from chlorophyll *a* (chl *a*) concentration), based on the abundance of the essential nutrients nitrogen (N) and phosphorus (P) (e.g. Sakamoto 1966; Canfield & Bachmann, 1981; OECD 1982; Phillips et al. 2008). Researchers typically focus on the mean response of dependent variables in such models, although in common with many other ecological data, the law of limiting factors (von Liebig 1885) imposes a ‘factor ceiling’ to data distributions (Thomson et al. 1996). Examining other portions of data distributions can therefore also provide insight to ecological relationships (Scharf et al. 1998); however, such an approach has so far been applied sparingly to limnological datasets (e.g. Kaiser et al. 1994; Jones et al. 2011).

Understanding how variation in nutrient abundance affects phytoplankton biomass has relevance to applied ecology and recent debate has focused on the relative importance of N and P in limiting phytoplankton biomass and the subsequent implications for developing effective policies to control eutrophication (Moss et al. 2012). As in this study, applied scientists are typically concerned with understanding the factors that regulate phytoplankton standing crop, as opposed to the factors that limit the instantaneous growth rate of individual species which may vary within a single assemblage (Hecky & Kilham 1988; Reynolds 2006). To

date, empirical analyses of chl *a*–nutrient relationships have predominantly (and often exclusively) considered lakes at northern temperate latitudes (e.g. OECD 1982). These analyses frequently show P to be a better predictor of chl *a* than N, supporting the view that P is the principal nutrient that limits the production of phytoplankton biomass in lakes, with N occupying a secondary role (Sterner 2008). This view is divergent from the results of a large–scale meta–analysis of nutrient enrichment experiments which found that phytoplankton in lakes are equally responsive to N and P additions (Elser 2007).

Results of enrichment experiments suggest that there may be a latitudinal influence on chl *a*–nutrient relationships, as bioassays suggest that N limitation may be more prevalent in tropical than temperate lakes (Hecky & Kilham 1988; Elser et al. 2007). Several hypotheses have been suggested to explain why chl *a*–nutrient relationships might vary with latitude, including correlation between latitude and: nutrient inputs (Schindler 1978); light limitation (Canfield & Bachmann 1981); temperature–dependent metabolic enzyme activity (Markager et al. 1999); denitrification rate (Lewis 1996; 2002); rate of phosphorus weathering (Lewis 1996); stratification processes (Lewis 1990) and top–down control (Flanagan et al. 2003). Despite this, only a small number of studies have explicitly compared chl *a*–nutrient relationships between temperate and non–temperate lakes (e.g. Jones et al. 2000; Flanagan et al. 2003; Huszar et al. 2006). Such comparisons have yielded discordant results, for example; Jones et al. (2000) showed that the chl *a*–total phosphorus (TP) relationship in 13 reservoirs in Thailand (c. 13–16 °N) matches that of temperate systems, a finding that is contrary to that of Huszar et al. (2006) who studied 192 tropical lakes and found the chl *a*–TP relationship to be markedly poorer compared to typical temperate models. Evidently, understanding of how phytoplankton biomass–nutrient relationships vary with latitude is lacking, and as yet, no study has sought to determine how latitude influences chl *a*–nutrient relationships in lakes along a global latitudinal gradient.

This study investigates relationships between latitude, chl *a*, total nitrogen (TN) and TP using data from a large sample of lakes. To the best of my knowledge, the sample is the largest used to date to examine these relationships and comprises lakes situated along a latitudinal gradient that includes tropical, temperate and polar regions. As is inevitable with such a broad–scale study, individual measurements may not necessarily be representative of lakes within a

specific latitudinal range. However, by examining relationships *between* variables along a global latitudinal cline, this study seeks to address the following research questions:

- 1) Does relative nutrient abundance (TN:TP) in lakes vary with latitude?
- 2) How do phytoplankton biomass–nutrient relationships differ between latitudinal zones?
- 3) Is there evidence of latitudinal variation in nutrient limitation of phytoplankton biomass in lakes?

2.2 Methods

2.2.1 Data collection

The study focused analysis on latitudinal variation in three empirical measures of either phytoplankton nutrient limitation or nutrient assimilation (Table 2.1). Matched concentrations (mg m^{-3}) of chl *a*, TN and TP were obtained for unfiltered water samples taken from 1317 lakes. Data were obtained for lakes in over 30 countries, situated from 69.5 °S – 83.0 °N. In addition, latitude (to the nearest 0.1 degree) and data for lake depth (z_{max} or z_{mean}) were obtained for each of the lakes in the sample. Where possible, mean concentrations relating to a number of samples collected over several years were obtained for trophic state variables, however, in some instances values related to one or more samples taken during a single day. This is particularly the case for polar lakes, many of which are difficult to access and only ice-free for a short period of the year. Data sources comprised published papers as well as national or regional databases of lake monitoring data (Table 2.2).

Table 2.1 Summary of empirical measures used in this study to quantify nutrient limitation of phytoplankton biomass and/or chlorophyll *a* (chl *a*)–nutrient relationships in lakes

| Empirical measure | Variable | Rationale |
|--|--|---|
| Mass ratio of total nitrogen (TN) to total phosphorus (TP) | TN:TP | An indicator of the relative availability of each respective nutrient, widely used to infer whether the accumulation of phytoplankton biomass in a lake is likely to be limited by N or P, or, whether the stoichiometry of the two nutrients is broadly consistent with phytoplankton growth requirements (Hecky & Kilham 1988). The predictive power of this indicator is moderate and strongly dependent on the refractory portion of the TN pool (Ptacnik et al. 2010). |
| Proportion of variation in mean chl <i>a</i> attributed to variation in TN or TP | Standardised regression coefficients (β^*) | Linear regression statistics are widely used to describe the relationship between algal biomass and nutrient concentrations (Kaiser et al. 1994). Critical interpretation of relationships is necessary due to frequent covariation between N and P and non-independence of variables (Lewis & Wurtsbaugh 2008). |
| Yield of chl <i>a</i> per mass unit of TN or TP | chl <i>a</i> :TN, chl <i>a</i> :TP | Chl <i>a</i> yield is used as an indicator of nutrient assimilation by phytoplankton, reflecting both bottom–up and top–down processes (Stauffer 1993). |

Table 2.2 Data sources used in the study

| Geographic region / country | n | Details | Data source |
|---|-----|--|------------------------------------|
| Antarctica | 2 | Mean of two samples collected from the centre of the lakes at mid depth in December 2003 (on ice cover) and January 2004 (after ice cover had completely disappeared). | Kudoh et al. (2009) |
| Brazil | 20 | Mean of depth integrated samples from the euphotic zone collected in Nov 1999, Dec 1999 and Jan 2000. | Trevisan & Forsberg (2007) |
| Canada | 29 | Depth integrated sample collected from the euphotic zone in summer 2007. | Murphy et al. (2010) |
| Canada | 54 | One sample collected in July 2003 from 0.15 m depth. | Keatley et al. (2007) |
| Canada | 38 | One sample collected in July 1998. | Michelutti et al. (2002) |
| Canada | 22 | One sample collected in July 2000 from 0.30 m depth. | Lim & Douglas (2003) |
| Central and South America (Argentina, Brazil, Columbia, Ecuador, Mexico, Venezuela, Puerto Rico, USA (n=1)) | 22 | Mean of samples collected monthly over at least a year in the 1970s and 1980s. | Salas & Martino (1991) |
| Europe – Belgium | 3 | Mean data from 1965 – 2007. Only data that does not violate European Environment Agency Quality Assurance checks chosen. | European Environment Agency (2009) |
| Europe – Croatia | 6 | | |
| Europe – Denmark | 20 | | |
| Europe – Estonia | 8 | | |
| Europe – Finland | 188 | | |
| Europe – France | 4 | | |
| Europe – Germany | 19 | | |
| Europe – Great Britain | 1 | | |
| Europe – Hungary | 8 | | |
| Europe – Iceland | 1 | | |
| Europe – Ireland | 3 | | |
| Europe – Italy | 109 | | |
| Europe – Latvia | 39 | | |
| Europe – Lithuania | 27 | | |

| Geographic region / country | n | Details | Data source |
|--|-----|--|--|
| Europe – Netherlands | 4 | | |
| Europe – Slovenia | 5 | | |
| Europe – Sweden | 154 | | |
| Europe – Switzerland | 9 | | |
| Europe – The former Yugoslav Republic of Macedonia | 2 | | |
| Japan | 3 | Mean concentrations of samples taken from 13 – 15 locations in each lake on one occasion at a depth of 0.5 m. | Takamura et al. (2003) |
| New Zealand | 121 | Samples collected either from the lake surface, or from integrated depths in the surface mixed layer, at monthly or quarterly intervals during the period of 2004 to 2006. | New Zealand Ministry for the Environment and Regional Councils (pers. comm.) |
| South America (Brazil, Argentina, Uruguay) | 83 | Sampled once between November 2004 and March 2006 by the same team who collected integrated water samples at 20 random points in each lake. Two L of each integrated sample were gathered in a bulk sample totalling 40 L. | Kosten et al. (2009) |
| Sri Lanka | 25 | One sample collected during January – February 1997. | Silva & Schiemer (2000) |
| Thailand | 13 | Mean concentrations from samples collected in the monsoon season of 1988 and the pre monsoon season of 1991. Samples from < 4 m depth. | Jones et al. (2000) |
| USA (Alaska) | 13 | Summer means from 1992, 1993 and 1995. Samples taken from 2 m depth. | Laperriere et al. (2003a) |
| USA (Alaska) | 15 | Mean of three samples collected over summer (May – September) 1993 – 1994. Samples were depth integrated to a depth of twice the Secchi depth or to within 1 m of the bottom in shallow, clear lakes. | Laperriere et al. (2003b) |
| USA (Iowa, Kansas, Missouri, Nebraska) | 247 | Summer median values. | Central Plains Center for BioAssessment. |

2.2.2 Lake classification

Lakes were assigned to four latitudinal categories: tropical (0 – 23.5° N/S), low–temperate (22.6 – 44.5° N/S), high–temperate (44.6 – 66.5° N/S) and polar (66.5 – 90° N/S). Boundaries of ‘tropical’ and ‘polar’ categories reflect the approximate axial tilt of the Earth, while the temperate zone was sub–divided to ensure that the four categories were approximately equal in °N/S. Lakes were also assigned to two categories based on depth: deep and shallow. For 1202 (91%) lakes in the sample, the criterion of $z_{\text{mean}} \leq 3.0$ m was used to define shallow lakes (see Padisák & Reynolds 2003), or when z_{mean} was unknown, lakes with $z_{\text{max}} \leq 10$ m were defined as shallow. Data for the remaining 114 lakes (9%) were obtained from several studies of ‘ponds’ and ‘lakes’ undertaken in the Arctic. ‘Ponds’ were defined as sites which completely froze to the bottom in winter whereas ‘lakes’ did not (e.g. see Michelutti et al. 2002). For the purpose of this study, ‘ponds’ were defined as shallow and ‘lakes’ as deep. Lakes were assigned to the following trophic state categories based on chl *a* concentration (mg m^{-3}) defined in the OECD (1982) fixed boundary system: ultra–oligotrophic ($\text{chl } a \leq 1.0$), oligotrophic ($1.0 < \text{chl } a \leq 2.5$), mesotrophic ($2.5 < \text{chl } a \leq 8.0$), eutrophic ($8.0 < \text{chl } a \leq 25.0$) and hypertrophic ($\text{chl } a > 25.0$). Only one polar lake was in the eutrophic category and no polar lake was classified as hypertrophic.

2.2.3 Data analysis

The combined dataset was checked for outliers and one lake with an anomalously high TP concentration ($> 9000 \text{ mg m}^{-3}$) was removed, resulting in a total sample size of 1316 lakes. Data for all trophic state parameters were logarithmically (base 10) transformed to achieve normal distributions prior to analysis using parametric tests. To conform with typical analytical detection limits, minimum chl *a*, TP and TN concentrations were set at 0.1, 0.1 and 1.0 mg m^{-3} , respectively, and all concentrations below these values were therefore adjusted to the respective minima prior to transformation. The distribution of in–lake TN:TP displayed high kurtosis and was skewed to the right, so consequently, this variable was \log_{10} transformed to achieve normal distribution. Least squares linear regression was then used to analyse the relationship between \log_{10} (TN:TP) and latitude. As TN:TP has been shown to negatively correlate with trophic state (Downing & McCauley 1992) and can be influenced by lake depth (Hamilton & Mitchell 1997), residuals in the regression of \log_{10} (TN:TP) on latitude were analysed and

also factorial Analysis of Variance (ANOVA) was also used to quantify the potentially interactive effects of latitude, lake depth and trophic state on TN:TP. Eutrophic and hypertrophic lakes were not included in the ANOVA because both deep and shallow polar lakes were not represented in these trophic state categories. Least squares linear regression was used to quantify linear variation in standardised TN and TP data (z scores) along the latitudinal gradient. The z scores were calculated by subtracting the mean and dividing by the standard deviation to generate descriptors with a common scale, thereby permitting direct comparison of regression slopes.

The effect of latitude on chl *a*–nutrient relationships was investigated by using linear least squares regression to examine the relationship between \log_{10} chl *a* and both \log_{10} TN and \log_{10} TP in each of the four latitudinal categories. As chl *a*–nutrient relationships can vary between deep and shallow lakes due to variation in the water column light climate (Nixdorf & Deneke 1997), separate models were derived for deep and shallow lakes, as well as for the combined (deep and shallow) sample. For each regression, the standardised regression coefficient was calculated which is the regression slope obtained when variables have been standardised. Standardised coefficients are numerically equivalent to a Pearson's correlation coefficient (r) and provide a measure of the magnitude of variance in the dependent variable (i.e. \log_{10} chl *a*) that is described by the independent variable (i.e. \log_{10} TN or \log_{10} TP).

The bivariate distributions of chl *a* and both TN and TP data displayed distinct upper boundaries, typical of 'factor ceiling' distributions characteristic of ecological datasets in which the dependent variable is subject to limitation by the independent variable (Thomson et al. 1996). The upper boundaries were interpreted to represent conditional chl *a* maxima at a given TN or TP concentration, under conditions whereby phytoplankton biomass accumulation is solely limited by N or P abundance, respectively. Consequently, the slopes of the upper boundaries are an approximation of the maximum mass of chl *a* per mass unit of TN or TP observed in the global dataset. Conditional maxima in the chl *a* = $f(\text{TN})$ and chl *a* = $f(\text{TP})$ relationships were estimated using quantile regression (Koenker & Basset 1978). Quantile regression is a semi-parametric technique that can be used to estimate rates of change in *all* parts of the distribution of a dependent variable, unlike ordinary least squares regression which estimates variation only in the mean of a dependent variable (y), conditional on values of an

independent variable (x) (Cade & Noon 2003). Accordingly, conditional maxima were estimated by using the linear equation for the 95th quantile of observed chl *a*, calculated by minimisation of the following quantity (Scharf et al. 1998):

$$\sum_i |y_i - \beta_j x_{ij} + c| h_i \quad (1)$$

with

$$h_i = \begin{cases} \tau, & [y_i - (\beta_j x_{ij}) + c] \geq \tau \\ (\tau - 1), & [y_i - (\beta_j x_{ij}) + c] < \tau \end{cases}$$

where y is chl *a* concentration (mg m^{-3}) in a given lake i , β_j is the coefficient of the x term (TN or TP), x_{ij} is TN or TP concentration (mg m^{-3}), c is a constant and τ is the quantile value (0.95). Minimisation was performed using the Solver add-in to Microsoft Excel 2007. All other statistical analyses were undertaken using Statistica (Version 8.0; Statsoft, Tulsa, USA) and a significance level of $p \leq 0.05$ was assumed for all tests.

2.3 Results

2.3.1 Latitudinal variation in TN:TP

The magnitude of trophic state variables varied markedly between the four latitudinal categories. Median concentrations of TN, TP and chl *a* were all lowest in the polar category and highest in the low-temperate category (Table 2.3). Regression of \log_{10} (TN:TP) on latitude ($^{\circ}$ N/S) yielded a significant positive relationship between the two variables ($r^2 = 0.34$, $p < 0.001$) (Fig. 2.1a). The relationship was also significant when only northern hemisphere ($n = 1076$, $r^2 = 0.33$, $p < 0.001$) or southern hemisphere lakes ($n = 240$, $r^2 = 0.05$, $p < 0.001$) were analysed, and was also significant when only temperate lakes were included in the regression ($n = 1054$, $r^2 = 0.19$, $p < 0.001$). Regression analyses of \log_{10} transformed and standardised TN and TP on latitude showed that latitudinal variation in \log_{10} (TN:TP) is a function of a proportionally greater decreasing trend in TP, relative to that for TN (Fig. 2.1b, 2.1c).

Table 2.3 Summary statistics for the lakes included in this study. Median values of variables are presented with interquartile range as a percentage of the median in parentheses. See text for definition of depth and latitude categories.

| Lake group | n | Deep (n) | Shallow (n) | Chl <i>a</i> (mg m ⁻³) | TN (mg m ⁻³) | TP (mg m ⁻³) | TN:TP (mass) | Chl <i>a</i> :TN (mass) | Chl <i>a</i> :TP (mass) |
|----------------|------|----------|-------------|---------------------------------------|-----------------------------|-----------------------------|-----------------|----------------------------|----------------------------|
| Entire dataset | 1316 | 802 | 514 | 5.9 (244) | 620.5 (150) | 27.1 (246) | 24.9 (109) | 0.010 (138) | 0.26 (117) |
| olar | 144 | 78 | 66 | 0.6 (139) | 232.0 (142) | 4.8 (128) | 52.9 (136) | 0.009 (202) | 0.32 (180) |
| High–temperate | 616 | 450 | 166 | 5.1 (161) | 567.5 (115) | 18.7 (159) | 31.6 (76) | 0.009 (108) | 0.31 (93) |
| Low–temperate | 438 | 207 | 231 | 13.2 (230) | 1148.0 (147) | 81.9 (154) | 15.5 (108) | 0.014 (132) | 0.21 (123) |
| Tropical | 118 | 67 | 51 | 12.8 (171) | 462.5 (164) | 42.3 (161) | 9.8 (133) | 0.024 (175) | 0.28 (151) |

Table 2.4 Summary of factorial ANOVA to examine the higher order interactive effects of lake depth (deep or shallow), trophic state (ultra-oligotrophic, oligotrophic and mesotrophic) and latitude (tropical, low–temperate, high–temperate and polar) on log₁₀ (TN:TP) in 768 lakes. Significant ($p \leq 0.05$) p –values are shown in bold. Note that eutrophic and hypertrophic lakes are excluded from the ANOVA because not all categorical variables are represented at these trophic states. See text for definition of categorical variables.

| | Sum of squares | d.f | Mean of squares | <i>F</i> | <i>p</i> |
|----------------------------------|----------------|-----|-----------------|----------|----------------|
| Depth | 0.0001 | 1 | 0.001 | 0.01 | 0.93 |
| Latitude | 22.75 | 3 | 7.58 | 64.08 | < 0.001 |
| Trophic state | 0.05 | 2 | 0.25 | 0.21 | 0.81 |
| Depth × latitude | 6.39 | 3 | 2.13 | 18.01 | < 0.001 |
| Depth × trophic state | 0.25 | 2 | 0.13 | 1.07 | 0.35 |
| Latitude × trophic state | 2.40 | 6 | 0.40 | 3.38 | < 0.01 |
| Depth × latitude × trophic state | 1.96 | 6 | 0.33 | 2.76 | 0.01 |

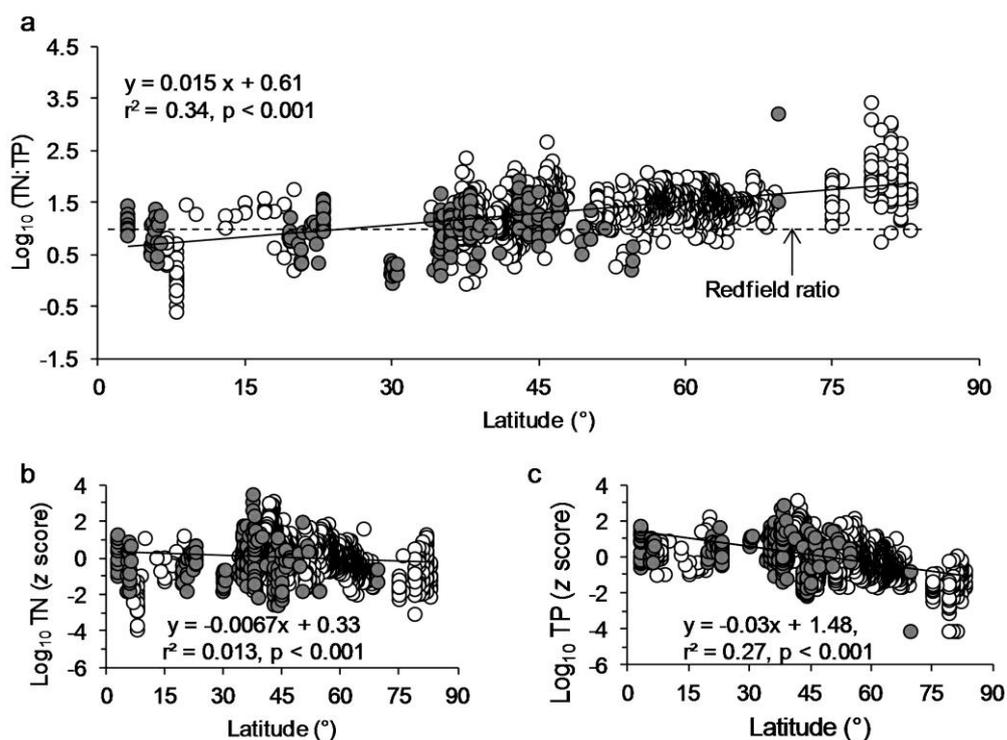


Figure 2.1 Relationships between latitude and (a) TN:TP (by mass), (b) TN and (c) TP for 1316 lakes. Standardised TN and TP observations (*z* scores) are presented to allow comparison of slopes. The linear equation, r^2 and p statistics relate to the average trend in the data shown by the solid line. Open circles denote northern hemisphere lakes; shaded circles denote southern hemisphere lakes. Dependent variables are \log_{10} transformed.

To test whether the relationship between TN:TP and latitude was a spurious result of co-variation between latitude and trophic state (i.e. proportionally more oligotrophic lakes at higher latitudes and more eutrophic lakes at lower latitudes), the residuals from the regression of \log_{10} (TN:TP) on \log_{10} chl *a* (slope = -0.28 , $r^2 = 0.18$, $p < 0.001$) were regressed against latitude ($^{\circ}$ N/S). There was a highly significant positive relationship between the two variables in the latter regression ($r^2 = 0.19$, $p < 0.001$) indicating that the relationship between TN:TP and latitude does not simply reflect underlying variation in lake trophic state (Downing & McCauley 1992).

The results of a multi-factorial ANOVA of the effect of latitude, depth and trophic state on TN:TP supported this conclusion (Table 2.4). Differences in mean TN:TP were highly significant between latitudinal categories but not

between categories based on depth or trophic state, and furthermore, interaction effects between latitude and the other categorical variables were significant (Table 2.4). Although eutrophic and hypertrophic lakes could not be included in the ANOVA due to inadequate representation of polar lakes at these trophic states, mean TN:TP followed the same general trend at these trophic states: lowest in tropical lakes and highest in high–temperate lakes (Fig. 2.2).

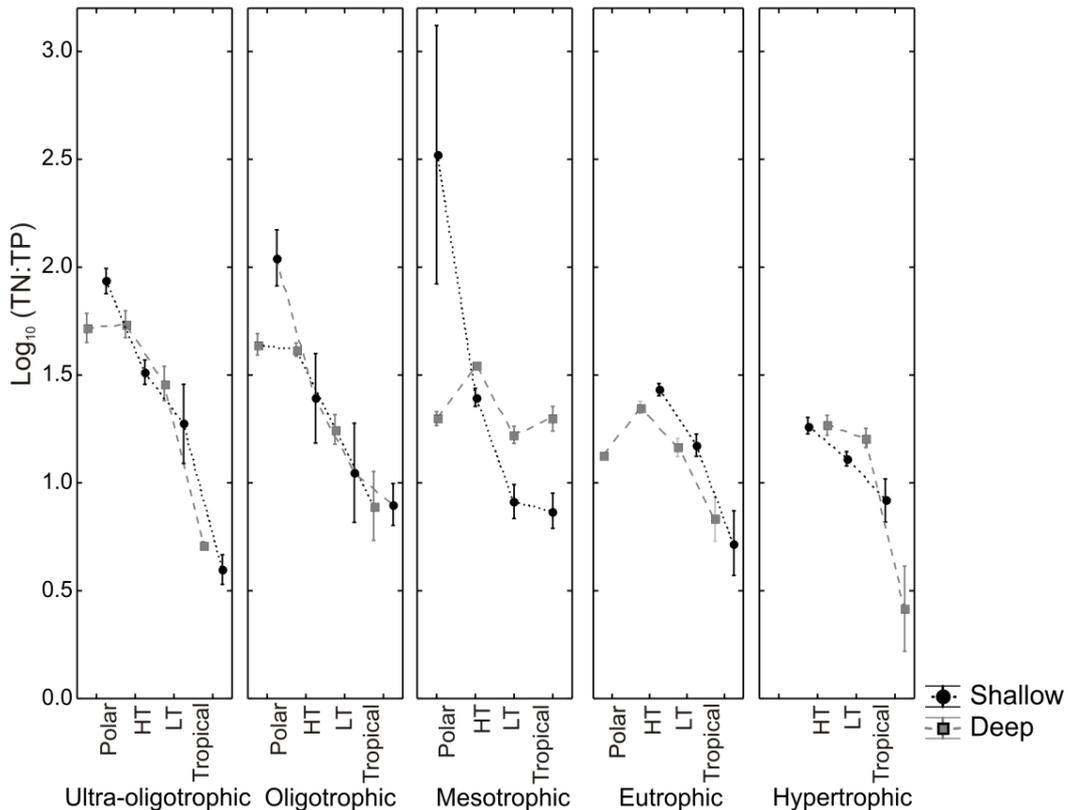


Figure 2.2 Interactive effects of the categorical variables depth, trophic state and latitude on $\text{log}_{10}(\text{TN:TP})$ (by mass) in 1316 lakes. Vertical bars denote standard error, except where $n = 1$ (deep polar eutrophic). Temperate lakes were classified as either ‘high–temperate’ (HT) or ‘low–temperate’ (LT). See text for definition of categorical variables.

2.3.2 Latitudinal variation in chl *a*–nutrient relationships

Standardised coefficients (β^*) of regression models to predict chl *a* from TN or TP varied with latitude (Fig. 2.3). The coefficients were highest for temperate lake categories ($\beta^* = 0.58 - 0.76$), indicating that both N and P concentrations explained more variation in chl *a* concentration at temperate latitudes than at tropical or polar latitudes. Temperate lake models subsequently had higher

coefficients of determination (r^2) (Table 2.5), as well as lower standard error (Fig. 2.3), than those for either tropical or polar lakes. Regression of \log_{10} chl *a* on \log_{10} TN was not significant for the combined dataset of deep and shallow lakes in both tropical and polar regions and, furthermore, regressions of \log_{10} chl *a* on either \log_{10} TN or \log_{10} TP were not significant for both deep tropical lakes and shallow polar lakes. Where significant relationships were established, standardised coefficients of regression models to predict chl *a* from TP were higher than for those to predict chl *a* from TN, with the sole exception of shallow low–temperate lakes, where the standardised coefficient for the chl *a* = f (TN) regression was higher than for the chl *a* = f (TP) regression (but within the range of standard error).

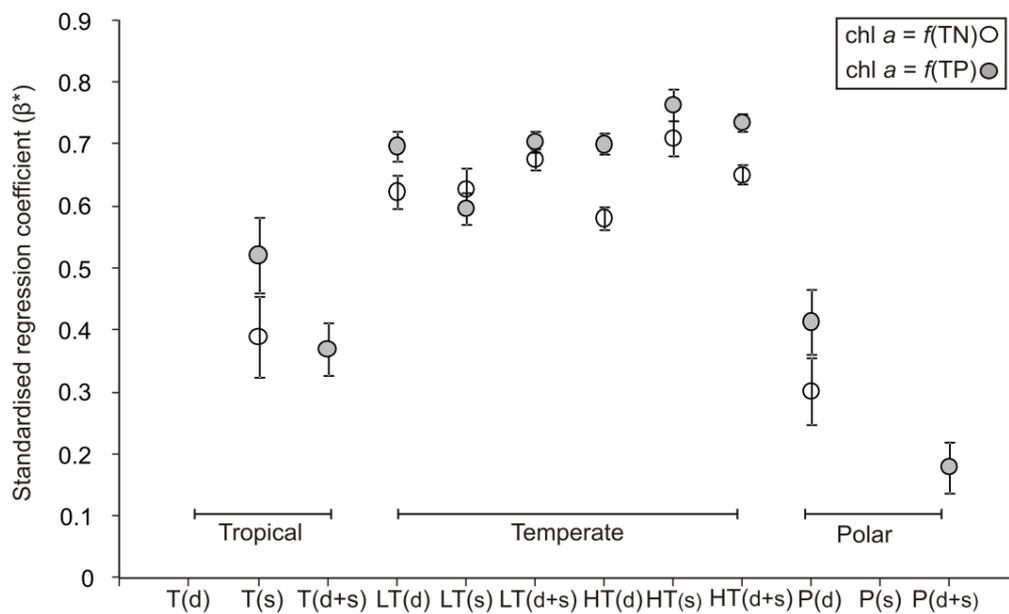


Figure 2.3 Standardised coefficients of linear regression models to predict chlorophyll *a* (chl *a*) from TN and TP concentrations in tropical (T), low–temperate (LT), high–temperate (HT) and polar (P) lakes. Separate coefficients are calculated for deep (d), shallow (s) and combined deep and shallow (d + s) lakes and only coefficients for regressions that are statistically significant ($p \leq 0.05$) are presented. Vertical lines denote standard error. See text for definition of categorical variables.

Table 2.5 Linear regression equations to predict chlorophyll *a* (chl *a*) concentration from TN and TP concentrations for selected categories of lakes in the sample of 1316 lakes. Regressions which are not statistically significant ($p > 0.05$) are denoted by ‘n.s.’. Definitions of lake categories are provided in the text.

| Lake category | | Log ₁₀ chl <i>a</i> on log ₁₀ TN | | | Log ₁₀ chl <i>a</i> on log ₁₀ TP | | |
|----------------|---------|--|-----------|-------|--|-----------|-------|
| Latitude | Depth | Slope | Intercept | r^2 | Slope | Intercept | r^2 |
| Tropical | Deep | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. |
| | Shallow | 0.45 | -0.16 | 0.14 | 1.01 | -0.80 | 0.26 |
| | All | n.s. | n.s. | n.s. | 0.52 | 0.12 | 0.13 |
| Low–temperate | Deep | 0.71 | -1.20 | 0.39 | 0.72 | -0.34 | 0.48 |
| | Shallow | 0.80 | -1.20 | 0.39 | 0.79 | -0.32 | 0.35 |
| | All | 0.84 | -1.45 | 0.46 | 0.81 | -0.42 | 0.50 |
| High–temperate | Deep | 0.90 | -1.81 | 0.34 | 0.74 | -0.26 | 0.49 |
| | Shallow | 1.25 | -2.68 | 0.50 | 1.09 | -0.72 | 0.58 |
| | All | 1.06 | -2.24 | 0.42 | 0.86 | -0.39 | 0.54 |
| Polar | Deep | 0.60 | -1.58 | .09 | 0.48 | -0.51 | 0.17 |
| | Shallow | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. |
| | All | n.s. | n.s. | n.s. | 0.17 | -0.34 | 0.03 |

Approximated conditional maxima (defined as ‘near–maxima’) in the chl *a*–TN (chl $a_{\approx\max}(\text{TN})$) and chl *a*–TP (chl $a_{\approx\max}(\text{TP})$) relationships were determined using Equations 2 and 3 respectively, derived using quantile regression ($\tau = 0.95$) (Fig. 2.4):

$$\text{chl } a_{\approx\max}(\text{TN}) = 0.046 \text{ TN} + 4.14 \quad (2)$$

$$\text{chl } a_{\approx\max}(\text{TP}) = 0.87 \text{ TP} - 0.42 \quad (3)$$

Maximum yields of chl *a* to TN [(chl *a*:TN) _{$\tau=0.95$}] and chl *a* to TP [(chl *a*:TP) _{$\tau=0.95$}] were therefore approximated as 0.046:1 and 0.87:1 respectively. Regression of log₁₀ (chl *a*:TN) on latitude yielded a significant negative relationship ($r^2 = 0.18$, $p < 0.001$; Fig. 2.5a), regression of log₁₀ (chl *a*:TP) on latitude did not yield a significant relationship (Fig. 2.5b).

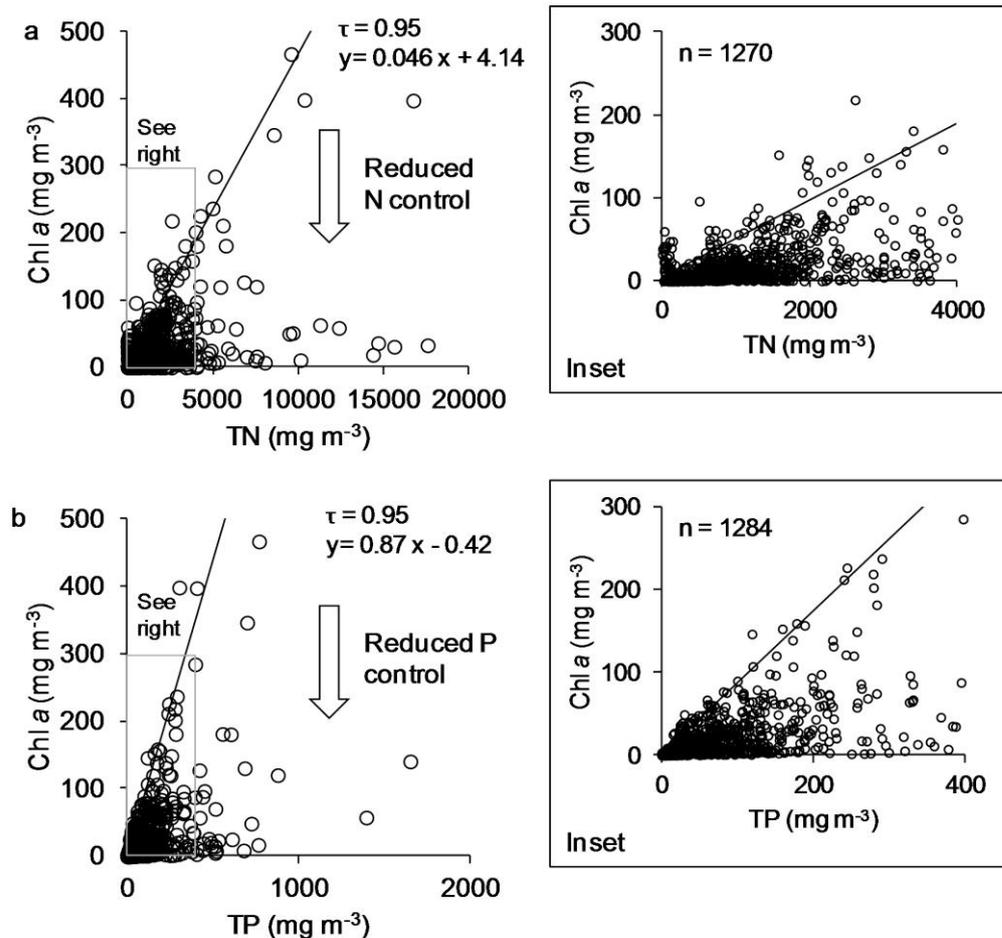


Figure 2.4 Relationships between concentrations of chlorophyll *a* (chl *a*) and TN (a) and TP (b) for 1316 lakes. The upper boundary of chl *a* concentration conditional on N or P abundance is estimated using quantile regression ($\tau = 0.95$; solid line). Resource limitation theory implies that other unquantified factors contribute to limiting phytoplankton biomass accumulation in lakes represented by data points that lie below these conditional near-maxima. For clarity, one extreme data point (chl *a* > 1000 mg m⁻³) is omitted from the plots but was included in the regression analysis.

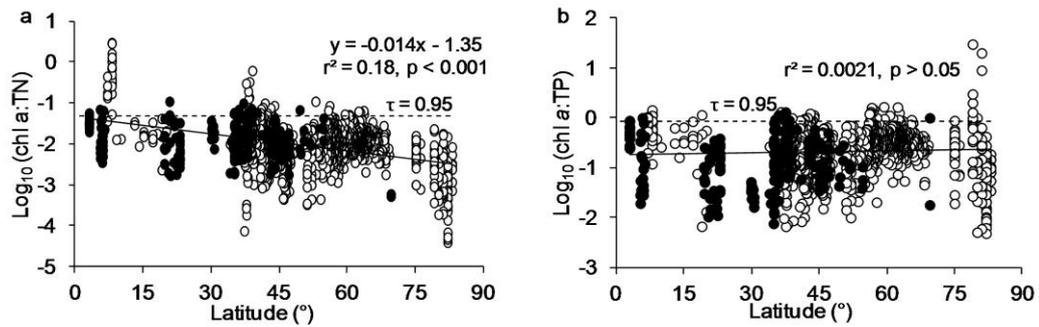


Figure 2.5 Relationships between latitude and the ratio of chlorophyll *a* (chl *a*) concentration to TN (a) and TP (b) respectively for 1316 lakes. The linear equation, r^2 and p statistic relate to the average trend in the data shown by the solid line. The dashed line indicates approximate maximum yields of chl *a* per mass unit of TN [(chl *a*:TN) $_{\tau=0.95}$] and per mass unit of TP [(chl *a*:TP) $_{\tau=0.95}$] estimated from quantile regression (see Fig. 2.4). Open circles denote northern hemisphere lakes; shaded circles denote southern hemisphere lakes. Dependent variables are \log_{10} transformed.

2.4 Discussion

2.4.1 *N and P stoichiometry*

This analysis shows that in-lake TN:TP increases with increasing distance from the equator, providing the most extensive example to date of “big-scale stoichiometry” (cf. Sterner & Elser 2002) along a spatial gradient in lentic ecosystems. This trend is independent of underlying co-variation between latitude and either trophic state or lake depth in the sample. Although the wide distribution of observed \log_{10} (TN:TP) around the regression line (Fig. 2.1a) indicates that factors other than latitude exert a strong influence on nutrient stoichiometry in lakes (i.e. local lake and catchment characteristics) (Downing & McCauley 1992; Hessen et al. 2009; Kosten et al. 2009), the latitudinal trend reported here mandates consideration of wider-scale drivers of nutrient stoichiometry in lakes.

The findings provide evidence for global-scale latitudinal variation in nutrient cycling processes and/or nutrient sources; either one or both of these factors could account for the latitudinal trend in TN:TP. With respect to nutrient cycling, a number of hypotheses can be proposed to explain why various processes (e.g. denitrification, N fixation, P resuspension, P weathering) might vary with latitude. Of these, latitudinal variation in denitrification is likely the best

developed, and modelling of hypothetical lakes has shown that there is a steep latitudinal gradient in the denitrification potential of lake hypolimnia driven by variation in hypolimnetic oxygen–holding capacity (Lewis 1996; 2002). Thus, more frequent de–oxygenation of bottom waters, in association with higher temperatures, may result in relatively higher denitrification rates in tropical lakes, thereby potentially causing the latitudinal trend in TN:TP observed. High abundance of leguminous terrestrial vegetation and N–fixing trees (e.g. *Alnus*) in both taiga and tundra biomes has also been linked to relative increased TN (and thus increased TN:TP) in high–latitude lakes (Laperriere et al. 2003a).

It is also possible that latitudinal variation in nutrient sources could explain or at least partially account for the observed variation in TN:TP. Lake nutrient sources can vary widely in N:P (Downing & McCauley 1992) and therefore latitudinal variation in such sources could cause a commensurate trend in in–lake TN:TP. On average, TP concentrations in the sample decrease at a greater rate with increasing latitude than TN concentrations (Fig. 2.1b, 2.1c); therefore, the occurrence of either relatively higher TP loads to lakes at low latitudes or relatively higher TN loads at high latitudes (or a combination of both) could at least partly explain the global trend in TN:TP. Nitrogen enrichment due to relatively higher levels of atmospheric N deposition at high latitudes in the Northern Hemisphere is one hypothesis that warrants particular consideration, as spatial variation in this N source has been shown to influence geographic patterns of nutrient limitation (Bergström & Jansson 2006; Elser et al. 2009), and northern hemisphere lakes are disproportionately represented in the dataset (although not necessarily when the global distribution of lakes is considered) (Downing et al. 2006; Lewis 2011). Furthermore, the fact that the trend is strongest when only northern hemisphere lakes are analysed lends support to this hypothesis, although the existence of a significant (yet much weaker) positive relationship between latitude and TN:TP in southern hemisphere lakes implies that other mechanisms at least contribute to the trend. Other potential source–related explanations for the trend observed include latitudinal differences in: natural soil phosphorus abundance (Walker & Syers 1976); the relative proportions of arable versus pastoral agriculture (Arbuckle & Downing 2001); and, inputs of excreta and vegetation clearance rates (Moss et al. 2012).

Characterising the main drivers of this variation presents a challenge to researchers. Greater application of global–scale process–based modelling

approaches (e.g. Lewis 2011) could potentially help to address this by elucidating how variables relating to physical factors (e.g. climate, geology, soils, altitude), anthropogenic pressures (e.g. agricultural land use) and ecosystem structure (e.g. piscivore abundance) interact to influence nutrient cycling and lake trophic state across large spatial scales. Such an approach could provide broad-scale understanding detached from any bias resulting from collation and analysis of uncoordinated datasets which predominantly relate to anthropogenically disturbed systems.

2.4.2 *Chl a–nutrient relationships*

The marked latitudinal variation in chl *a*–nutrient relationships highlights broad disparities in both ecosystem structure and function between lakes at different latitudes. The weak relationships between nutrients and chl *a* in tropical, relative to temperate lakes (Table 2.5; Fig. 2.3), implies that factors other than N or P are relatively more important in controlling lentic phytoplankton productivity at tropical latitudes. This finding is in accordance with Huszar et al. (2006) who similarly found that TP was a poorer predictor of chl *a* in tropical regions than in temperate regions, a result that they attributed to either greater prevalence of light limitation in tropical lakes or differences in food web interactions (*not* greater prevalence of N limitation). Certainly, higher turbidity in tropical lakes could at least partly explain this variation; it is well established that elevated inorganic suspended sediment concentration can decouple chl *a*–nutrient relationships (Schindler 1978; Canfield & Bachmann, 1981) and elevated turbidity can occur in tropical lakes both due to enhanced erosion during the wet season (e.g. McCullough & Barber 2007) and following water loss in the dry season (e.g. Dejenie et al. 2008).

Chlorophyll *a*–nutrient relationships are also markedly weaker in polar lakes compared to those in temperate lakes. It is noted, however, that the weaker relationships are likely to partly reflect the very low trophic status of the polar lakes; the small gradients in TN and TP that are present when concentrations of determinands are at or close to detection limits are not conducive to establishing strong relationships with chl *a* (Michelutti et al. 2002). Similarly, unusually high chl *a*:TP in lakes situated at 80–81° N (Fig. 2.5b) is likely an artefact of very low (<1 mg m⁻³) TP. Nevertheless, more substantive explanations may account for relatively weak chl *a*–nutrient relationships in polar lakes. Firstly, light limitation

is discounted as all data for polar lakes are based on samples collected during summer months, when photosynthetically active radiation flux is comparable to other latitudes (Campbell & Aarup 1989). There are, however, numerous structural characteristics of polar lake ecosystems that may decouple water column chl *a*–nutrient relationships. Notably, these include: strong top–down controls due to relatively high abundance of herbivorous zooplankton (e.g. Christoffersen et al. 2008); frequent occurrence of dominance by benthic, rather than pelagic, primary producers due to often high abundance of benthic algal mats in polar lakes (*ibid*); and, potentially, frequent macrophyte dominance (Teissier et al. 2012) in shallow unproductive polar lakes during summer. Low temperatures may also constrain phytoplankton biomass accumulation at high latitudes as phytoplankton primary productivity correlates positively with water temperature (Faithfull et al. 2011). Variation in ecosystem structure and temperature limitation could therefore account for the weaker chl *a*–nutrient relationships for polar lakes compared to temperate lakes.

Other studies have highlighted the existence of upper asymptotes in chl *a*–nutrient scatterplots due to reduction of euphotic depth at high chl *a* concentration (Schindler 1978; Phillips et al, 2008; Jones et al. 2011). Fig. 2.4 highlights that there is little evidence, however, that such asymptotes are absolute. Phillips et al. (2008) report inflection points at TP = 100 mg m⁻³ and TN = 1700 mg m⁻³, and although there seems to be a reduction in slope at these points, exceedances of chl *a* near–maxima at twice these concentrations reflect the extreme chl *a* concentrations that are possible, presumably in the presence of dense buoyant algal scums. Also, the results emphasise that chl *a* seldom reaches near–maxima conditional on N and P abundance. The near–maxima are interpreted as representing chl *a* concentrations achieved during phytoplankton blooms; blooms typically arise only when a phytoplankton assemblage comprises certain species, and, regulating factors such as temperature and light intensity are present at demand–saturating levels over timescales that correspond to multiple generation times (Reynolds 2006). Clearly, such conditions are the exception. Furthermore, Jones et al. (2011) have highlighted significant regional differences in TP–conditional chl *a* maxima which they attributed to differences in climate and mineral turbidity. Variability in nutrient bioavailability between lakes would also influence lake–specific chl *a* near–maxima and therefore the near–maxima are

interpreted as indicative of potential limits that will likely not be reached in many lakes.

Also of note, is that some data points in Fig. 2.4 exceed the near–maxima, reflecting use of the 95th percentile as a compromise between identifying the uppermost boundary and minimising any bias that may result due to analytical error present in the data. Approximately, 4% of lakes exceed the near–maxima in Fig. 2.4 and, in particular, measured chl *a* in a number of lakes substantially exceeds chl $a_{\sim\max}$ (TN). The average ratio of observed chl *a* (chl a_{obs}) to chl $a_{\sim\max}$ (TN) is 2.82 in lakes where this ratio > 1, whereas average chl $a_{\text{obs}}:\text{chl } a_{\sim\max}$ (TP) is 1.45 in lakes where the ratio > 1. Interestingly, a substantial portion (43%) of the 53 lakes for which chl $a_{\text{obs}}:\text{chl } a_{\sim\max}$ (TN) > 1 comprises a group of reservoirs in Sri Lanka. Amongst these reservoirs there is the largest chl $a_{\text{obs}}:\text{chl } a_{\sim\max}$ (TN) (10.18) and they cluster in the upper left–hand portion of Fig. 2.5a at 7–8° latitude. These reservoirs are characterised by low dissolved inorganic N (typically < 100 mg m³), very low TN:TP (mean = 1.9:1), extremely high chl *a*:TN and dominance of the diatom *Aulacoseira granulata* (Silva & Schiemer, 2000). *A. granulata* is a bloom–forming species that readily forms aggregates (Reynolds 2006) and has been determined to have an atypically low ratio of carbon to chl *a* (mean = 26:1, range 10:1 – 57:1; Yacobi & Zohary, 2010). Thus, it seems that observations may significantly exceed the empirical maxima under exceptional conditions and, in particular, some variability in chl *a*–nutrient relationships reflects imprecision of chl *a* as a surrogate for phytoplankton biomass due to influence by factors such as light intensity and the presence of accessory pigments (Reynolds, 2006).

2.4.3 *N and P limitation*

The Redfield ratio of 7.2:1 by mass (16:1 by moles) is widely used as an indicator of the N:P ratio below which N is likely to limit phytoplankton biomass accumulation (rather than P alone or both N and P together) (Redfield et al. 1963; Klausmeier et al. 2004; Ptacnik et al. 2010). Based on the equation for the linear trend in the data (Fig. 2.1a), average TN:TP is predicted to be below this threshold at latitudes of approximately < 16 °N/S which correspond to the mid–tropics. This latitudinal trend in TN:TP is commensurate with the observed increase in chl *a*:TN towards the equator and tendency towards the chl *a*:TN near–maximum in the tropics (Fig. 2.5a).

Together, the latitudinal trends in TN:TP and chl *a*:TN suggest that N limitation will be more prevalent in lakes at low than at high latitudes, consistent with experimental observations (Hecky & Kilham 1988; Elser et al. 2007). This conclusion cannot, however, be readily reconciled with the results of regression analysis between chl *a* and nutrients for the different latitudinal categories of lakes (Table 2.5; Fig. 2.3). Although there are contradictions between substantive theory of limiting factors and the use of standard regression techniques to characterise nutrient limitation (Kaiser et al. 1994), the finding that TN was markedly inferior as a predictor of chl *a* in tropical lakes compared to temperate lakes (Fig. 2.3) is inconsistent with that expected if N were more often a limiting nutrient in the tropics than at temperate latitudes. The results therefore suggest that, while N is less abundant relative to phytoplankton growth requirements at lower latitudes, macronutrient limitation of phytoplankton biomass (by N or P) is less prevalent in the tropics overall (relative to temperate lakes) due to decoupling of chl *a*–nutrient relationships by factors not quantified.

This last conclusion differs from those made in studies that analysed results of nutrient enrichment experiments and found that N limitation is more prevalent overall in tropical than temperate lakes (Hecky & Kilham 1988; Elser et al. 2007). To potentially explain this disparity, it is noted that the overwhelming majority of nutrient enrichment experiments are undertaken at the sub–ecosystem scale, i.e. using mesocosms or laboratory culture vessels. Such designs invariably simplify natural systems (Hecky & Kilham, 1988) and potentially reduce the likelihood of limitation by factors other than nutrients, e.g. due to exclusion of zooplankton or maintenance of artificially high ambient light levels. Thus, it is possible that relative deficiency in N at low latitudes means that nutrient enrichment experiments using tropical lake waters have an enhanced likelihood of yielding significant growth responses to added N, even though nutrient limitation of phytoplankton biomass in natural systems over longer time scales is secondary to other forms of limitation that are otherwise suppressed under typical experimental conditions.

An important caveat concerns the use of total nutrient pools (rather than the more labile dissolved fraction) in the analysis. The bioavailability of TN in particular is uncertain; it comprises both labile inorganic N forms, as well as organic forms which have been shown to vary in bioavailability depending on their source (Seitzinger et al. 2002). Any latitudinal bias in TN composition in the

sample could therefore compromise the utility of empirical parameters derived using TN for assessing broad spatial trends in phytoplankton nutrient limitation (Ptacnik et al. 2010). Clearly, analysis of only three trophic state variables cannot provide comprehensive understanding of how lake ecosystems function, and, while this study has highlighted global–scale latitudinal trends in the stoichiometry of lentic ecosystems, more work is necessary to develop better understanding of the causes and ecological implications of these trends.

In general, the analysis supports the view that P is more likely than N to limit phytoplankton biomass in lakes (Schindler 1977). Regressions to predict chl *a* from TP were significant for more of the lake categories than those with TN as the predictor variable. Furthermore, the models based on TP generally had higher standardised coefficients than those based on TN (Fig. 2.3), indicating that TP usually accounted for a greater proportion of the variation in chl *a* concentration than TN. Shallow low–temperate lakes were an exception to this, however, as the standardised coefficient for the chl *a* = $f(\text{TN})$ regression was marginally higher (but within the distribution of standard error) than for the chl *a* = $f(\text{TP})$ regression. This may reflect the fact that this category contained 24% of lakes from New Zealand where lacustrine N limitation has been shown to be more prevalent than in northern temperate regions (Abell et al. 2010). The majority (57%) of the lakes in this category were in the southern USA, however, and this propensity for geographic variation in chl *a*–nutrient relationships highlights the importance of exercising caution when applying relationships established in one locality to lakes elsewhere, particularly in the presence of latitudinal gradients. In particular, it should not be assumed that chl *a*–nutrient models developed using temperate datasets will be applicable to tropical lakes and the relative paucity of observations and increasing anthropogenic pressures on water resources in the tropics necessitates enhanced research efforts focused on these systems.

As Moss et al. (2012) note, the concept that there is one predominant limiting nutrient in undisturbed lakes is likely invalid, as evolution would redress any such imbalance in selection pressure. The greater relative tendency for P limitation implied by the analysis may therefore reflect proportionally greater prevalence of N pollution in anthropogenically disturbed ecosystems and is not necessarily a fundamental reflection of natural systems.

2.5 References

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3 Relationships between land use and nitrogen and phosphorus in New Zealand lakes

3.1 Introduction

Excess inputs of nitrogen (N) and phosphorus (P) to lakes can cause eutrophication and the associated decline of water quality and ecological integrity (Vollenweider 1968; Smith 2003). Natural sources of these nutrients to freshwaters include: organic matter derived from natural senescence processes in intact ecosystems which undergo mineralisation; atmospheric di-nitrogen fixed by heterocystous phytoplankton species, and; P associated with apatite bearing minerals (Newman 1995; Rabalais 2002). Inputs from anthropogenic sources are, however, increasing in many parts of the world and loading associated with pollution now greatly exceeds natural N and P loads to many lakes (Smith 2003).

Lake managers require an understanding of nutrient sources and the processes that drive lake productivity before developing plans to improve water quality in eutrophied lakes (Moss 2007). Although limnologists have traditionally focussed on the study of in-lake processes (Johnes 1999), there is now widespread understanding that the successful control of nutrient pollution and its associated problems is contingent on developing a holistic and integrated understanding of lakes in the context of their wider catchments (Ferrier and Jenkins 2010). While there is limited scope to adopt an experimental approach to investigate how natural and anthropogenic factors influence nutrient loading to lakes, the empirical analysis of relationships between lake and catchment variables across different scales can advance mechanistic understanding. Geographical Information Systems (GIS) can provide a platform for the collation and integration of data relating to a wide range of bio-physical parameters at a catchment scale (Macleod *et al.* 2007; Johnson and Host 2010) and numerous studies have used GIS to investigate relationships between catchment characteristics and water quality (e.g. Arbuckle and Downing 2001; Lee *et al.* 2009; Roberts and Prince 2010).

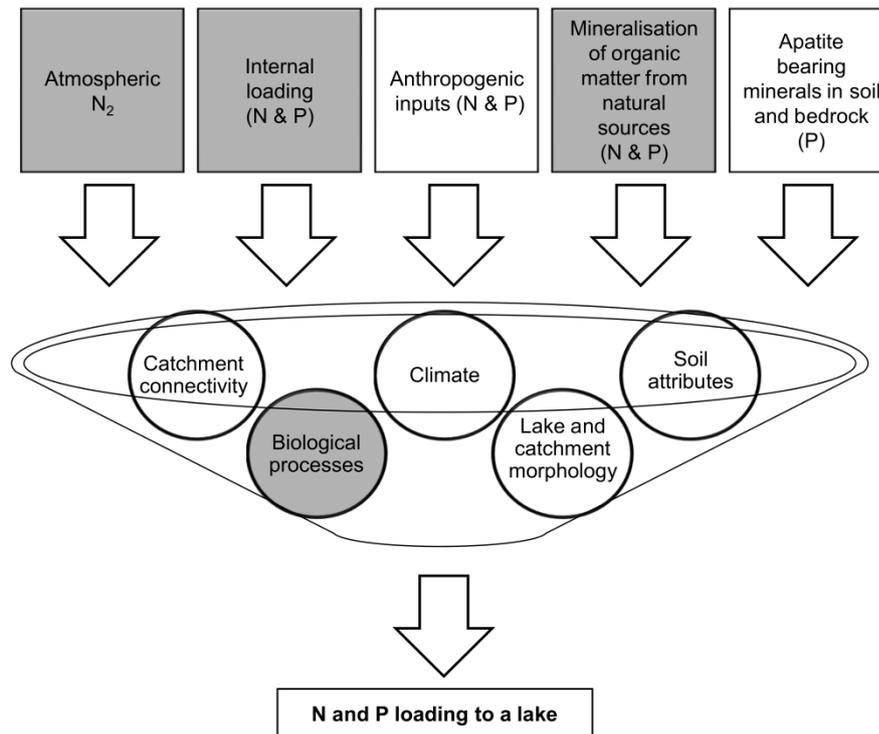


Figure 3.1 Conceptual diagram showing hypothetical relationships between sources of nitrogen (N) and phosphorus (P) in a lake catchment (rectangles) and factors that may mediate the relationship between sources and nutrient loading (circles). Sources and factors shaded grey were not examined in this study.

When empirically investigating how catchment characteristics interact to influence nutrient loading to a lake, it is useful to distinguish between characteristics that are nutrient sources (or direct proxies for specific sources) and characteristics that do not represent sources yet mediate the pathway between the nutrient source and the lake (Figure 3.1). For example, the proportion of farmland in a catchment is a direct indicator of the amount of nutrients from agricultural sources available for export to a lake, whereas average catchment slope is an indicator of the gravitational energy available for the transfer of those nutrients via mechanisms such as overland flow. A failure to make this distinction can lead to confounding conclusions regarding the likely contribution of various nutrient sources to external lake nutrient loads. This is also complicated by covariation of natural and anthropogenic factors (e.g. land use and soil type) which is frequently encountered in landscape ecology and can make it problematic to determine whether a relationship is causal or spurious (Van Sickle 2003; Allan 2004; Daniel

et al. 2010). For example, Liu *et al.* (2010) studied 103 lakes across China and found that natural factors, specifically variables relating to geographic location, lake morphology and climate, accounted for 13.3 – 57.5% of the variance in eutrophication parameters. As the authors concede, however, the reason why some ‘natural’ factors such as longitude and altitude partly determine trophic state is because these factors are probably co-related with human development and therefore anthropogenic nutrient pollution; a factor not represented in their study.

Eutrophication is a significant problem affecting freshwaters in New Zealand where an estimated 32% of lakes greater than 1 ha in area ($n > 1000$) are classified as eutrophic or hypertrophic and consequently have very poor water quality (Ministry for the Environment 2010). Empirical studies and experiments have shown that both N- and P-limitation of phytoplankton growth occurs widely in New Zealand lakes and this, in addition to frequent high connectivity between freshwater and marine ecosystems, supports the need for dual control of N and P export from New Zealand lake catchments (Abell *et al.* 2010). Intensification of land use resulting in increased external nutrient loads has become an increasing concern for resource managers and policy makers (Hamilton 2005; Edgar 2009). In particular, nutrient export from New Zealand’s increasingly intensive agricultural land has been subject to scrutiny (Parliamentary Commissioner for the Environment 2004) and the presence of pastoral land in a catchment has been shown to correlate with the occurrence of a shift from a clear to a de-vegetated, turbid state in lakes (Schallenberg and Sorrell 2009). While the relationship between catchment land use and water quality has been investigated for streams and rivers in New Zealand (Close and Davies Colley 1990; Larned *et al.* 2004; McDowell *et al.* 2009), the contribution of catchment land use to in-lake nutrient concentrations has not been quantified at a national scale. This study investigated how catchment characteristics relate to in-lake concentrations of total phosphorus (TP), total nitrogen (TN) and chlorophyll *a* for 101 lakes distributed throughout New Zealand. By differentiating between variables that are direct proxies for nutrient sources and those that represent other factors, the study sought to highlight relationships that are significant at the national scale. The research questions were: (1) to what extent do anthropogenic land uses explain variation in TN and TP concentrations? and (2) is the relationship between land use and in-lake nutrient concentrations influenced by other catchment and lake characteristics?

3.2 Methods

3.2.1 Data collection

3.2.1.1 Lake water quality data

Mean data relating to the trophic status parameters total phosphorus (TP), total nitrogen (TN) and chlorophyll *a* (chl *a*) were obtained from New Zealand regional councils for 101 lakes located throughout New Zealand (Figure 3.2). The data related to samples collected by regional environmental managers, either from the lake surface, or from integrated depths in the surface mixed layer, at monthly or quarterly intervals during 2004 – 2006 (Ministry for the Environment 2006). All samples were analysed using standard methods based on APHA (1998) and described by Burns *et al.* (2000). Each mean datum is therefore representative of at least 12 samples taken over a three-year period.

3.2.1.2 Extracting lake catchment data

A GIS map layer comprising delineated catchment boundaries in polygon format was created for the 101 lakes using ArcGIS (ESRI, version 9.3.1), based on a digital map layer of lake catchment boundaries that was provided by the New Zealand Department of Conservation. Lake catchment boundaries were originally defined by the National Institute of Water and Atmospheric Research (NIWA) as part of the development of the River Environmental Classification (REC) system. The REC system is based on a digital elevation model using a 30 m pixel size with 20 m contour data (Ministry for the Environment and NIWA 2004).

3.2.1.3 Catchment connectivity and morphology data

The following ‘connectivity’ parameters were calculated for each catchment: average catchment slope (in degrees), stream length (m) relative to area (km²) of non-lake catchment and lake order. Average catchment slope was calculated using the ‘slope’ tool within ArcGIS which was applied to a 25 m resolution topographic raster map. Stream length was calculated using the REC line feature stream map. Lake order was defined in accordance with Martin and Soranno (2006) as the highest Strahler stream order of a lake inflow. The ratio of catchment area to lake area ($A_c:A_l$) was calculated for each lake and maximum depth (z_{max}) and lake altitude were obtained from Ministry for the Environment (2006).

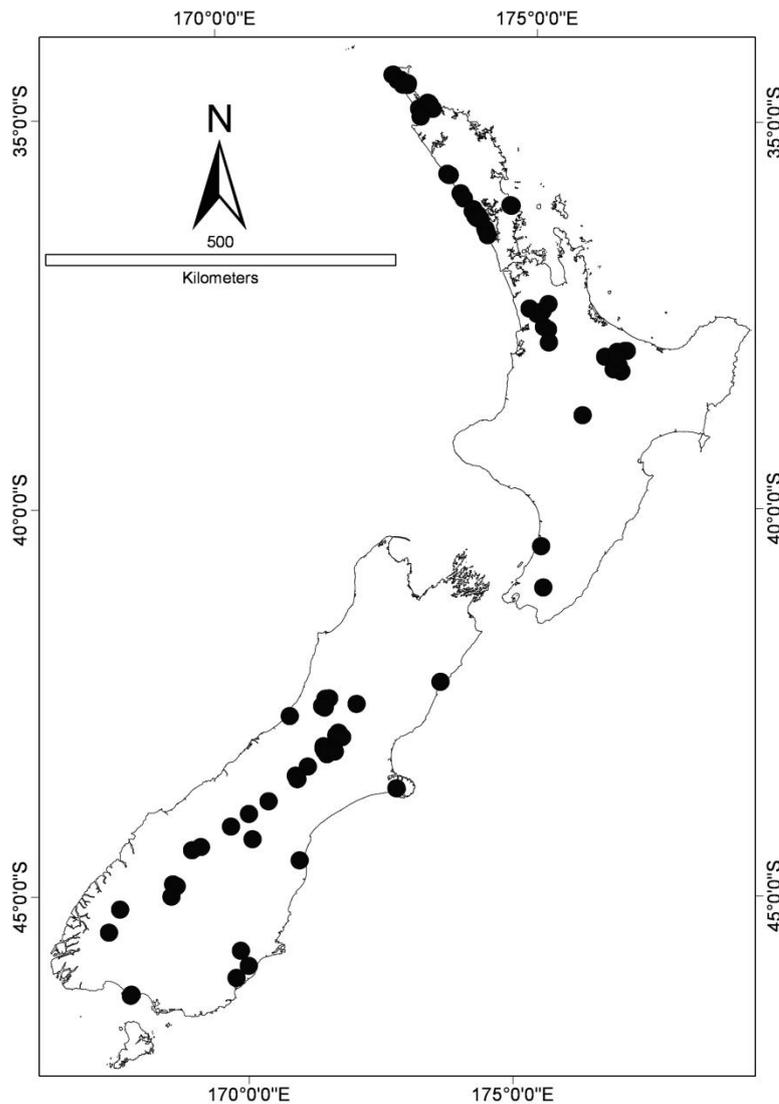


Figure 3.2 Location of the 101 lakes included in the study.

3.2.1.4 Land use data

The area of individual land use/ land cover (hereafter ‘land use’) categories in each lake catchment was calculated using the New Zealand Land Cover Database version 2 (LCDB2). The LCDB2 is a GIS map layer in polygon format that has a 15 m resolution and describes the spatial distribution of 43 land use types based on Landsat 7 ETM+ imagery acquired in 2000–2001 (Ministry for the Environment 2004). Areas of the following land uses were calculated for each catchment: ‘built up area’ (built up area), ‘exotic forest’ (exotic), ‘arable cultivation’ (crop), ‘native forest’ (native), ‘high-producing grassland’ (high prod. grass), and ‘low-producing grassland’ (low prod. grass). Areas were then converted into percent coverage of non-lake catchment. The area of exotic forest was calculated by taking the sum of the six LCDB2 ‘planted forest’ land use

categories (see Ministry for the Environment 2004) while the area of native forest was defined as the sum of the ‘indigenous forest’ and ‘broadleaved indigenous hardwoods’ categories. The area of ‘arable cultivation’ was calculated by taking the sum of the ‘short rotation cropland’, ‘orchard and other perennial crops’ and ‘vineyard’ categories. The remaining three categories correspond to single LCDB2 categories. ‘Low-producing grassland’ comprises both native and exotic grasses that display relatively low plant vigour indicative of low soil fertility, short growing season and/or minimal fertiliser application. It is typically managed as pasture for low densities of sheep or beef cattle. ‘High-producing grassland’ comprises exotic grasses that are intensively managed as pasture for livestock production and receive fertiliser application.

3.2.1.5 Soil data

Area-weighted catchment mean values of soil cation exchange capacity (CEC) and drainage were calculated using digital soil fundamental data layers (FDLs). FDLs contain data for 16 key soil attributes (polygon format) for all New Zealand soils derived from stereo aerial photograph interpretation, field verification and single factor soil surveys undertaken as part of the 1:63 360/1:50 000 scale New Zealand Land Resource Inventory (NZLRI) survey (Newsome *et al.* 2000). Data are not available for soils that are permanently submerged or in urban areas. In most areas only the soil record (i.e. soil type) has been mapped in the field and data for other parameters are derived from established correlations with the mapped soil (Newsome *et al.* 2000). Mean values for CEC and drainage were calculated for 99 of the 101 catchments as two catchments had no exposed soil as they comprised urban land or exposed bedrock. The NZLRI maintains a record of data for each attribute in the form of discrete rating categories, as described in Table 3.1. An area-weighted mean value was calculated for the P content of the soil in each catchment using the Land Environment New Zealand (LENZ) acid soluble phosphorus data layer (polygon format). This parameter provides a measure of the natural abundance of P in the soil and does not reflect P from anthropogenic sources such as fertiliser. Soil fertility data included in the LENZ database have been developed by grouping soils together based on the nutrient status of 129 classes of parent material (Leathwick *et al.* 2002a). Each group has been assigned a rating based on acid soluble P concentration, ranging from 1 (very low) to 5 (very high) (Table 3.1).

Table 3.1 Description of soil attributes considered in the study. Cation exchange capacity (CEC) and drainage description from Newsome et al. (2000). Acid soluble P content description from Leathwick et al. (2002a).

| Soil parameter | CEC (0 – 0.6 m) | Drainage | Acid soluble P content |
|----------------|---------------------------|-----------------|---------------------------|
| Unit | meq (100 g) ⁻¹ | Class | mg (100 g) ⁻¹ |
| Rating | | | |
| 1 | > 40 | Very poor | 0–7 |
| 2 | 25 – 39.9 | Poor | 7–15 |
| 3 | 12 – 24.9 | Imperfect | 15–30 |
| 4 | 6 – 11.9 | Moderately well | 30–60 |
| 5 | < 5.9 | Well | 60–100 |

For each catchment, an area-weighted mean value was calculated for each of the three soil attributes using the median value of each rating category present in the catchment. For CEC, soils with a rating of 1 were assumed to have a CEC of 40 meq (100 g)⁻¹ while soils with a rating of 5 were assumed to have a CEC of 5.9 meq (100 g)⁻¹.

3.2.1.6 Rainfall data

Annual mean rainfall was calculated for each catchment using monthly GIS raster layers that have been developed by Landcare Research using data collected by the New Zealand Meteorological Service from 2202 monitoring stations during 1951 – 1980 (Leathwick *et al.* 2002b).

3.2.2 Statistical analysis

All statistical analyses were undertaken using Statistica (version 8.0; Statsoft, Tulsa, USA) and a significance level of $p \leq 0.05$ was adopted in all tests. Probability plots and histograms were inspected before analysis and most variables were transformed to improve normality and homogeneity of variances. Land cover percentages were converted to a proportion and then arcsine square-root transformed. The remaining variables were log₁₀ transformed with the exception of ‘length of stream per km²’ which was normally distributed. Data were reduced to a common scale by subtracting the mean and dividing by the standard deviation to produce standardised descriptors that allow for the calculation of meaningful covariances (Legendre and Legendre 1998).

Standardised data were then used during initial data exploration and to address the first research question.

The data were initially explored by constructing a Pearson correlation matrix and then by undertaking principal component analysis (PCA) (see Figure 3.3 for an overview of analytical methods). PCA can be applied to multivariate data to identify a small number of transformed variables that describe most of the variation in the data. Analysis of a projection of the two principal components allowed the main relationships between lake and catchment variables to be visualised.

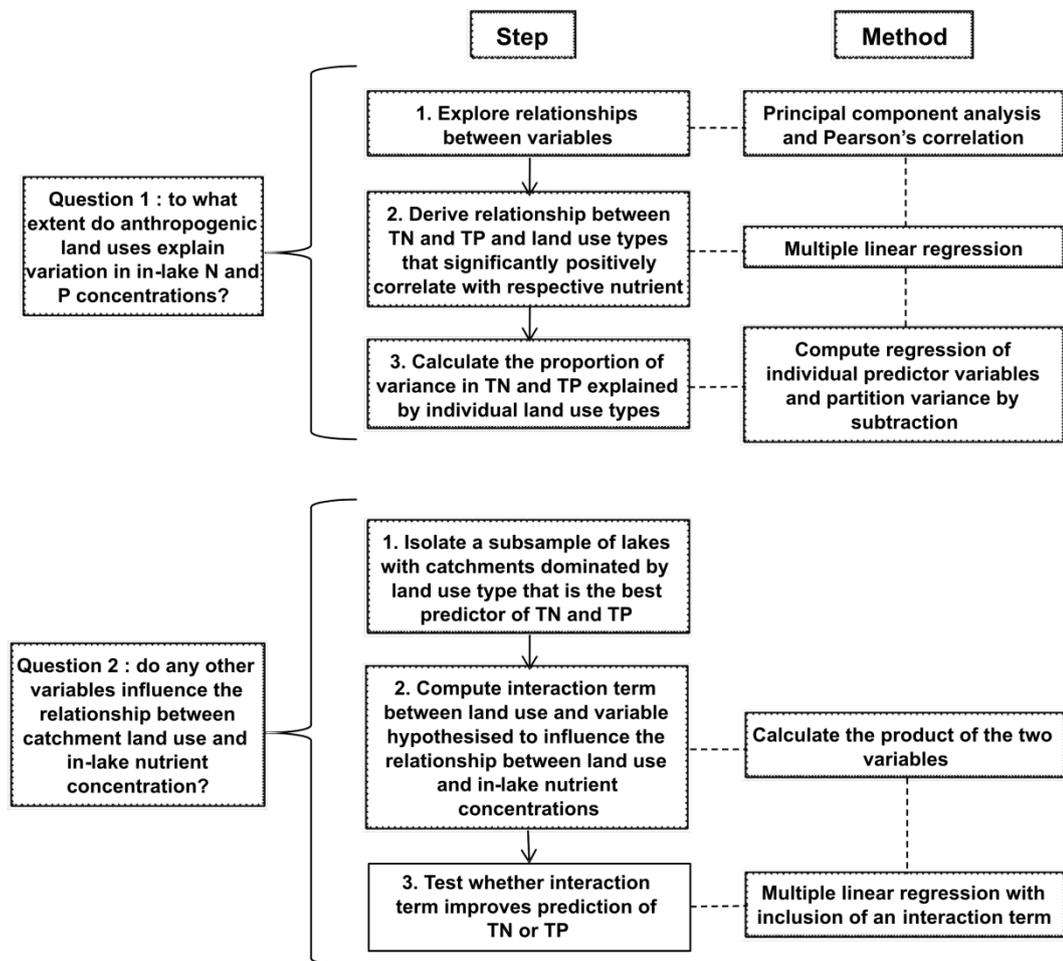


Figure 3.3 Conceptual diagram outlining analytical methods used to address research questions. Detailed descriptions of individual analytical methods are given in the text.

Linear regression analysis was then used to identify the variance in TN and TP explained by nutrient sources. Subsequently, the method for selecting predictor (independent) variables reflects this aim. Predictor variables for regression analysis were chosen by selecting variables that: (1) represent nutrient sources (anthropogenic land use proportions or soil P content) and (2) significantly positively correlate with lake TN or TP. Separate multiple linear regression functions to predict both TN and TP were developed using the chosen predictor variables. To identify the variance in TN and TP solely explained by each predictor variable, partial linear regressions were computed with and without the variable(s) of interest and variance partitioned using the method described by Legendre and Legendre (1998) and adopted in a similar study by Goldstein *et al.* (2007). Briefly, this method separates the variance in a dependent variable explained by a particular predictor variable (or set of predictor variables) (R_a^2) from the variance explained by another predictor variable (or set of predictor variables) (R_b^2) included within a multiple linear regression model that can explain variance R_{abc}^2 , where R_c^2 is the combined variance explained by variables a and b . Therefore, $R_a^2 = (R_{abc}^2) - (R_b^2)$. This method thus allowed quantification of the degree to which each predictor variable in the regression functions explained the variation in in-lake TN or TP by removing the effect of covariation with other predictor variables included in the regression model.

To address the second research question, a sub-sample ($n = 43$) of lakes was isolated that had catchments dominated by the land use type that best correlated with lake TN and TP. Based on *a priori* hypotheses (Table 3.2), eight variables were then tested to identify whether they influenced the relationship between land use and in-lake nutrient concentrations in the national-scale sample. To test hypotheses, multiple linear regression was used to quantify whether the inclusion of a term to represent interaction between the land use variable and the variable of interest significantly improved the prediction of \log_{10} TN or \log_{10} TP. The form of the linear model was:

$$\text{NUTRIENTS} = a + (\beta_1 \times \text{LAND USE}) + (\beta_2 \times (\text{LAND USE} \times \text{VARIABLE})) + \varepsilon$$

where NUTRIENTS = transformed TN or TP concentrations; a = intercept, LAND USE = transformed land use proportion; VARIABLE = catchment characteristic variable hypothesised to mediate the relationship between land use and in-lake nutrient concentrations; ε = error term; β_1 and β_2 are

regression coefficients. Separate multiple linear regression models were developed to predict both TN and TP based on land use and each of the eight variables being tested. It was concluded that the relationship between in-lake nutrient concentrations and the land use variable was influenced by a catchment characteristic if inclusion of the interaction term made a significant improvement to the model prediction. Variables used in the analysis were transformed as previously described to achieve normality, which was then confirmed using a Kolmogorov Smirnov test ($p < 0.05$). Data were not standardised for this analysis.

Table 3.2 Summary of the hypothesised interactions of catchment characteristics on the relationship between anthropogenic land use and in-lake nutrient concentrations.

| Catchment characteristic | Variable analysed | Hypothesised influence on the relationship between anthropogenic land use and in-lake nutrient concentrations | Reason (hypothesised) |
|---------------------------|---|---|---|
| Lake/catchment morphology | Catchment to lake area ratio | Positive | High catchment to lake ratio will yield a high nutrient load per unit of lake area. Shallow lakes less able to buffer nutrient inputs than deep lakes. Rate of nutrient flux associated with hydrological flows (e.g. overland flow) will be higher in steeper catchments due to higher gravitational energy. |
| | Maximum lake depth | Negative | |
| | Average catchment slope | Positive | |
| Catchment connectivity | Stream length per km ² catchment | Positive | More hydrologically connected catchments have greater capacity to transport nutrients. More hydrologically connected catchments have greater capacity to transport nutrients. |
| | Lake order | Positive | |
| Soil attributes | Cation exchange capacity (CEC) | Negative | Greater mobility of mineral nutrients with decreasing soil CEC. Rate of nutrient flux associated with hydrological flows will be higher in well drained catchments. |
| | Drainage | Positive | |
| Climate | Mean rainfall | Positive | Rate of nutrient flux associated with hydrological flows (e.g. throughflow) will be higher in wetter catchments. |

3.3 Results

3.3.1 Data exploration

The sample of 101 lakes included a diverse range of lakes from a broad geographic range within New Zealand (see Table 3.3 and Figure 3.2). Lake area ranged from 0.03 – 612.6 km², the largest lake being Lake Taupo which is the largest lake in New Zealand. Maximum lake depth ranged from 1 – 444 m. Eighty-seven of the lakes had been categorized into broad groups based on lake formation mechanism (see Ministry for the Environment 2006), including: dune (n = 32), glacial (n = 20), volcanic (n = 14), riverine (n = 8), peat (n = 5), lagoon (n = 3), reservoir (n = 3) and landslide (n = 1). The origin of 14 lakes was undetermined. Lake trophic state varied from microtrophic to hypertrophic (see Burns *et al.* 2000 for definitions), with concomitant wide variations in the trophic status parameters TN (44.5 – 4247.5 mg m⁻³), TP (1.5 – 440.0 mg m⁻³) and chl *a* (0.3 – 149.0 mg m⁻³) (Table 3.3). The land use composition of the lake catchments was broadly representative of the overall land use composition of New Zealand (Table 3.4).

Significant ($p \leq 0.05$) Pearson's correlation coefficients (Table 3.5) show that as expected, the parameters TN, TP and chl *a* were highly positively inter-correlated. Total nitrogen provided a better predictor of chl *a* ($r = 0.85$, $p < 0.001$) than TP ($r = 0.80$, $p < 0.001$). Comparison of correlations between catchment land use and lake eutrophication parameters showed that TN was positively correlated with % high prod. grass ($r = 0.60$, $p \leq 0.001$) and weakly positively correlated with % built up area ($r = 0.20$, $p \leq 0.05$). Total phosphorus was positively correlated with % high prod. grass ($r = 0.57$, $p < 0.001$) and % exotic forest ($r = 0.32$, $p \leq 0.001$). There was a significant ($p \leq 0.05$) negative correlation between % low prod. grass and both TN ($r = -0.43$) and TP ($r = -0.55$) and % native also correlated negatively with both TN ($r = -0.36$) and TP ($r = -0.31$). Chlorophyll *a* was positively correlated with % high prod. grass ($r = 0.62$) and % built up area ($r = 0.20$), while it correlated negatively with % low prod. grass ($r = -0.46$) and % native ($r = -0.20$). Catchment soil P correlated negatively with in-lake TP ($r = -0.52$) and also TN ($r = -0.48$). Chlorophyll *a* declined both with increasing lake altitude ($r = -0.60$) and maximum depth (Z_{\max} , $r = -0.57$), both of which were positively correlated ($r = 0.66$).

Table 3.3 Descriptive statistics for lake and catchment variables

| Characteristic | Variable | N | Unit | Abbreviation | Range | Mean |
|---------------------------|---|-----|---------------------------|--------------------|----------------|--------|
| Trophic status parameters | Total nitrogen | 101 | mg m ⁻³ | TN | 44.5 – 4247.5 | 687.1 |
| | Total phosphorus | 101 | mg m ⁻³ | TP | 1.5 – 440.0 | 64.3 |
| | Chlorophyll <i>a</i> | 101 | mg m ⁻³ | Chl <i>a</i> | 0.3 – 149.0 | 17.7 |
| Land use | % low producing grassland | 101 | % | % low prod. grass | 0.0 – 90.0 | 9.4 |
| | % high producing grassland | 101 | % | % high prod. grass | 0.0 – 99.8 | 33.1 |
| | % built up area | 101 | % | % built up area | 0.0 – 73.8 | 2.3 |
| | % arable cultivation | 101 | % | % crops | 0.0 – 19.8 | 0.4 |
| | % exotic forestry | 101 | % | % exotic | 0.0 – 98.3 | 15.1 |
| | % native forest | 101 | % | % native | 0.0 – 80.0 | 13.3 |
| Lake/catchment morphology | Max lake depth | 101 | m | Z_{\max} | 1 – 444 | 44.1 |
| | Lake area | 101 | km ² | A_l | 0.02 - 612.6 | 26.2 |
| | Catchment area (m ²) to lake area (m ²) ratio | 101 | - | $A_c:A_l$ | 1.5 - 451.3 | 28.4 |
| | Altitude | 101 | m a.s.l | Alt | 1.26 - 826.0 | 200.0 |
| | Average catchment slope | 101 | Degrees | Slope | 0.4 – 32.2 | 10.8 |
| Catchment connectivity | Lake order | 101 | - | LO | 0 - 7 | 2.8 |
| | Stream (m) per km ² of catchment | 101 | m | Str. length | 225.6 – 3015.0 | 1245.3 |
| Catchment soil attributes | Cation exchange capacity | 99 | meq (100 g) ⁻¹ | Soil CEC | 4.9 – 40.0 | 15.1 |
| | Acid soluble phosphorus content of the soil | 101 | mg (100 g) ⁻¹ | Soil P | 4.0 – 47.1 | 16.6 |
| | Drainage score (1 = very poor, 5 = well drained) | 99 | Nominal score | Drainage | 1.3 – 5.0 | 4.1 |
| Climate | Mean annual rainfall | 101 | cm | Mean rain | 53.2 – 355.9 | 128.5 |

Table 3.4 Mean proportion of Land Cover Database (LCDB) version 2 land use classes in the 101 lake catchments included in the study compared to the overall proportions for New Zealand (Ministry for the Environment 2009). Note that ‘arable cultivation’ refers to the sum of ‘short rotation cropland’, ‘vineyard’ and ‘orchard and other perennial crops’.

| LCDB 2 Land use type | High producing grassland | Exotic forest | Native forest | Low producing grassland | Built up area | Arable cultivation |
|--|--------------------------------|------------------|------------------|-------------------------------|------------------|-----------------------|
| Mean proportion in 101 catchments studied (%) | 33.1 | 15.1 | 13.3 | 9.4 | 2.3 | 0.4 |
| Proportion in New Zealand (%) | 33.1 | 7.3 | 26.1 | 6.2 | 0.6 | 1.5 |

The results of PCA (Figure 3.4) helped to characterise the inter–relations between lake and catchment variables. The Eigenvalues of the two principal components were 3.86 and 2.17 respectively and cumulatively they accounted for 40.2 % of the variance in the lake and catchment variables that were analysed. The first component, represented on the horizontal axis of the ordination diagram, is most strongly loaded with the variables of slope (-0.42), soil P (-0.39), z_{\max} (-0.35), lake order (-0.34) and % high prod. grass (0.29). The second component is represented on the vertical axis and is most strongly loaded with the variables mean annual rainfall (0.45), $A_c:A_1$ (-0.44), % native (0.38) and % low prod. grass (-0.34). Different lake types are relatively evenly distributed along both axes, however glacial lakes are predominantly in the negative sector of the horizontal axis whereas dune lakes are predominantly in the positive sector of the horizontal axis.

Table 3.5 Pearson correlation matrix of lake and catchment variables. Significant correlations are shown in bold ($p \leq 0.05$). Data have been transformed prior to analysis.

| | TN | TP | Chl <i>a</i> | Alt | z_{\max} | $A_c:A_l$ | Str. length | Slope | % low prod. grass | % high prod. grass | % built up area | % crop | % exotic | % native | Soil CEC | Soil P | Drain -age | Mean rain |
|-----------------------|----|------------|-----------------|--------------|--------------|------------|----------------|--------------|-------------------------|--------------------------|--------------------------|-----------|--------------|--------------|--------------|--------------|---------------|--------------|
| TN | - | .87 | .85 | -0.71 | -0.76 | .11 | .01 | -0.62 | -0.43 | .60 | .20 | .12 | .11 | -0.36 | -.16 | -0.48 | -0.31 | -0.45 |
| TP | | - | .80 | -0.75 | -0.64 | .21 | .09 | -0.56 | -0.55 | .57 | .09 | .19 | .32 | -0.31 | -0.21 | -0.52 | -0.29 | -0.40 |
| Chl <i>a</i> | | | - | -0.60 | -0.57 | .17 | .13 | -0.46 | -0.45 | .60 | .20 | .18 | .06 | -0.20 | -.09 | -0.39 | -0.27 | -0.28 |
| Alt | | | | - | .66 | -.15 | -.01 | .59 | .53 | -0.44 | -.15 | -.16 | -0.22 | .17 | .11 | .44 | .35 | .28 |
| z_{\max} | | | | | - | -.19 | .03 | .48 | .15 | -0.43 | -.03 | -.11 | -.12 | .43 | .07 | .32 | .28 | .56 |
| $A_c:A_l$ | | | | | | - | .27 | .09 | .12 | -.02 | -0.25 | .12 | .07 | -.17 | -.01 | .07 | .19 | -0.22 |
| Stream length | | | | | | | - | -.02 | .03 | .09 | -0.24 | .14 | -.07 | .04 | .18 | .07 | .03 | -.02 |
| Slope | | | | | | | | - | .40 | -0.36 | -0.29 | -.07 | -0.30 | .42 | .16 | .60 | .43 | .33 |
| % low prod. grass | | | | | | | | | - | -0.50 | -.20 | 0.01 | -0.27 | -0.22 | .14 | .55 | .31 | -0.20 |
| % high prod. grass | | | | | | | | | | - | .01 | .14 | -.18 | -.14 | -.07 | -0.36 | -0.50 | -0.22 |
| % built up | | | | | | | | | | | - | .11 | -.17 | .06 | .40 | .06 | -.06 | -.02 |
| % crop | | | | | | | | | | | | - | -.03 | -.08 | .09 | .05 | -.05 | -0.24 |
| % exotic | | | | | | | | | | | | | - | -.17 | -0.39 | -0.49 | .16 | -.14 |
| % native | | | | | | | | | | | | | | | .11 | .29 | .18 | .60 |
| Soil CEC | | | | | | | | | | | | | | | - | .36 | .18 | .12 |
| Soil P | | | | | | | | | | | | | | | | - | .37 | .13 |
| Drainage | | | | | | | | | | | | | | | | | - | .11 |
| Mean rain | | | | | | | | | | | | | | | | | | - |

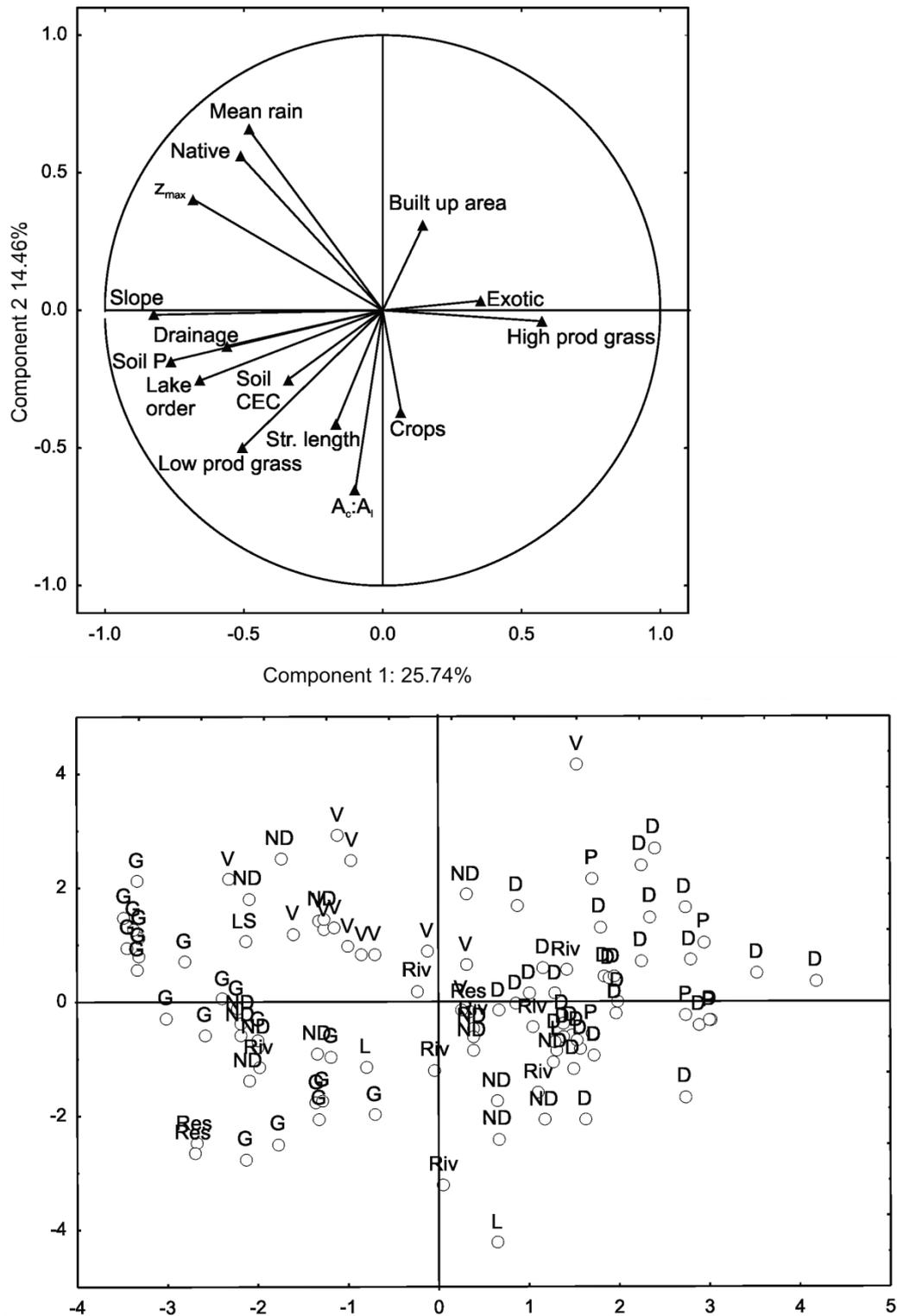


Figure 3.4 Projection of lake and catchment variables (see Table 3.3) on the factor plane and associated ordination diagram for the principal components analysis (PCA). The text labels on the ordination diagram specify lake formation type, where: D is dune; G is glacial; L is landslide; R is riverine; Res is reservoir; U is unknown and V is volcanic.

3.3.2 Quantifying land use effects

To address the first question (to what extent do anthropogenic land uses explain variation in TN and TP concentrations?), separate linear regression models for TN and TP were computed using predictor variables that represented nutrient sources and significantly positively correlated with lake TN or TP, respectively. Individual predictor variables were not inter-correlated (Table 3.6).

A multiple linear regression model to predict TN from % high prod. grass and % built up area was highly significant ($p < 0.001$, $SE = 0.77$). Following partitioning of variance by subtraction, % high prod. grass accounted for 38.6% of the variation in in-lake TN while % built up area accounted for 3.7% of the variation in in-lake TN.

A multiple linear regression model to predict TP from % high prod. grass and % exotic was also highly significant ($p < 0.001$, $SE = 0.70$). Following partitioning of variance by subtraction, % high prod. grass and % exotic accounted for 41.0% and 18.8%, respectively, of the variation in in-lake TP.

Table 3.6 Summary of linear regression analyses. All data were standardised and nutrient data were \log_{10} transformed and land use data were arcsine square-root transformed prior to analysis. The variance column denotes the proportion of variance in the dependent variable explained by each land use type after a correction has been made to account for covariation between predictor variables.

| Dependent variable | Predictor variable | β | r^2 | Standard error of estimate | p | Variance (%) |
|--------------------|-------------------------------------|------------|-------|----------------------------|--------|--------------|
| TN | % high prod. grass | 0.62 | 0.39 | 0.79 | <0.001 | 38.6 |
| | % built up area | 0.20 | 0.04 | 0.99 | 0.05 | 3.7 |
| | % high prod. grass, % built up area | 0.62, 0.19 | 0.42 | 0.77 | <0.001 | - |
| TP | % high prod. grass | 0.57 | 0.33 | 0.79 | <0.001 | 41.0 |
| | % exotic | 0.32 | 0.11 | 0.95 | <0.001 | 18.8 |
| | % high prod. grass, % exotic | 0.65, 0.44 | 0.52 | 0.70 | <0.001 | - |

3.3.3 *The effect of catchment characteristics on the relationship between land use and in-lake nutrients*

To address the second question (is the relationship between land use and in-lake nutrient concentrations influenced by other catchment and lake characteristics?), analysis focused on catchments comprising high prod. grass as the dominant land use, i.e. catchments where the proportion of high prod. grass in the non-lake area of the catchment was greater than the proportion of any of the other 40 LCDB2 land use types present in the sample. Accordingly, a sub-sample of 43 lakes was identified with catchments comprising 28.7% – 99.8% high prod. grass. These lakes were distributed throughout New Zealand with North Island lakes (69.8 % of the sub-sample) being marginally better represented than in the whole sample (65.2%).

Regression of TN on % high prod. grass yielded a significant function ($p < 0.001$, $r^2 = 0.27$, $SE = 0.31$). This regression model was significantly improved by the addition of interaction terms that included the product of % high prod. grass and $A_c:A_1$ and z_{max} (Table 3.7). The addition of an interaction term to represent the influence of z_{max} yielded the greatest improvement to the predictive power of the model ($r^2 = 0.43$) and the standardised regression coefficient for this term had a negative value, while the coefficient for the interaction term to represent the influence of $A_c:A_1$ was positive.

Regression of TP on % high prod. grass also yielded a significant function ($p < 0.01$, $r^2 = 0.16$, $SE = 0.43$). Like TN, this regression model was significantly improved by the addition of interaction terms to represent the influence of $A_c:A_1$ and z_{max} with the terms having a positive and a negative coefficient respectively (Table 3.7). The addition of an interaction term to represent the influence of lake order also significantly improved the regression model and this term had a positive coefficient.

Table 3.7 Multiple linear regression models to predict in-lake total nitrogen (TN) and total phosphorus (TP) concentrations from the percentage of high producing grassland in a lake catchment (% high prod. grass) and an interaction term that represents the hypothesised interaction between the land use variable and other catchment characteristics. a = intercept; ε = error; β_1 and β_2 are regression coefficients. Model statistics are only reported in cases where the interaction term (β_2) is statistically significant ($p \leq 0.05$). Variable abbreviations are defined in Table 3.3.

| Dependent variable | Model | p-value of interaction (β_2) | β_2 (standardised) | r^2 |
|--------------------|--|--------------------------------------|--------------------------|-------|
| TN | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{mean rain}) + \varepsilon$ | > 0.05 | - | - |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * A_c:A_1) + \varepsilon$ | < 0.05 | 0.41 | 0.38 |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * Z_{\text{max}}) + \varepsilon$ | < 0.01 | - 0.41 | 0.43 |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{slope}) + \varepsilon$ | > 0.05 | - | - |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{CEC}) + \varepsilon$ | > 0.05 | - | - |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{drainage}) + \varepsilon$ | > 0.05 | - | - |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{stream length}) + \varepsilon$ | > 0.05 | - | - |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{LO}) + \varepsilon$ | > 0.05 | - | - |
| TP | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{mean rain}) + \varepsilon$ | > 0.05 | - | - |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * A_c:A_1) + \varepsilon$ | < 0.01 | 0.49 | 0.31 |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * Z_{\text{max}}) + \varepsilon$ | < 0.05 | - 0.36 | 0.28 |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{slope}) + \varepsilon$ | > 0.05 | - | - |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{CEC}) + \varepsilon$ | > 0.05 | - | - |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{drainage}) + \varepsilon$ | > 0.05 | - | - |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{stream length}) + \varepsilon$ | > 0.05 | - | - |
| | $a + \beta_1 * \% \text{ high prod. grass} + \beta_2 * (\% \text{ high prod. grass} * \text{LO}) + \varepsilon$ | < 0.01 | 0.39 | 0.30 |

3.4 Discussion

This study sought to quantify the relationship between anthropogenic land use and in-lake N and P concentrations at the national scale in New Zealand. It was shown that, following correction for the effect of co-variation between land use types, the proportion of high intensity pasture in a lake catchment accounted for more variation in the national dataset than any other land use, explaining 38.6% of the variation in TN and 41.0 % of the variation in TP. The proportion of exotic forestry explained 18.8% of the variation in TP and the proportion of built up (urban) area explained 3.7% of the variation in TN. To qualify whether a range of catchment characteristics influence the relationship between anthropogenic land use and in-lake nutrient concentrations, the study then focused on lakes where high production grassland was the dominant land use type in the catchments. For this sub-sample, it was shown that lake and catchment morphology variables ($A_c:A_l$ and z_{max}) and a catchment connectivity variable (lake order in the TP model) influenced the relationship between the proportion of high intensity grassland in a lake catchment and in-lake nutrient concentrations. Increasing maximum lake depth (z_{max}) reduced the influence of high intensity grassland on in-lake TN and TP concentrations while increasing catchment area to lake area ratio ($A_c:A_l$) had the opposite effect. Lake order (LO) had a positive interactive effect indicating that increasing lake order resulted in an increasingly positive relationship between high intensity grassland and in-lake TP concentrations.

3.4.1 Land use effects at the national scale

A positive relationship between pastoral agriculture and nutrient concentrations in freshwaters has generally been established in New Zealand (McCull 1972; Larned *et al.* 2004; Parliamentary Commissioner for the Environment 2004; Galbraith and Burns 2007; McDowell 2009). Larned *et al.* (2004) analysed data for 229 stream sites throughout New Zealand and found that median dissolved reactive P and dissolved N concentrations from pastoral sites exceeded recommended guidelines in all stream orders sampled, and concentrations of these nutrients were significantly higher in samples obtained from pastoral sites than in those from native and exotic forest sites. Likewise, Galbraith and Burns (2007) found that the proportion of pasture in a catchment was positively related to TN and TP in 45 water bodies in the Otago region. Elsewhere, other landscape-scale studies have established links between agricultural land use and elevated nutrients in

freshwaters. For example Hooda *et al.* (1997) attributed elevated P in streams in the west of Scotland to intensive dairy farming in the catchments and Tong and Chen (2002) concluded that N and P losses from agriculture in Ohio watersheds were seven and six times higher, respectively, than the second-most polluting land use (impervious urban).

The strength of the positive relationship between high producing grassland and in-lake TN and TP concentrations is particularly significant given the scale of the study. Goldstein *et al.* (2007) found that the relationship between land use and physical stream habitat condition characteristics became weaker with increasing spatial scale from regional to national level. By distinguishing between low and high producing grassland, it has been shown that the intensity of pastoral land use has a significant bearing on the magnitude of nutrient losses to lakes. The major pastoral-related nutrient sources are urine and N fertiliser in the case of N, and faeces and superphosphate fertiliser in the case of P (Monaghan *et al.* 2007). The magnitude of nutrient loss is broadly related to stocking rate (*ibid.*) and therefore increasing intensity results in greater nutrient loss. Whilst research into management options to mitigate nutrient losses from pasture has been an active field (see Cherry *et al.* 2008), it is clear that a significant change in practices is required if productivity is to be decoupled from nutrient loss. The contrast in nutrient losses between low and high productivity grassland is further emphasised by the fact that even though low intensity pasture and mean catchment soil P content were positively correlated (see Figure 3.4 and Table 3.5), both correlated negatively with in-lake P due to the opposing influence of high producing grassland. Although estimates of mean acid-soluble P content for catchment soils are derived from relatively broad categories, a positive relationship between soil P and in-lake TP concentrations was expected, especially given the range in the soil P values (4.0 – 47.1 mg (100 g)⁻¹) and the fact that unusually high concentrations of P in igneous rocks in New Zealand have been shown to be associated with elevated P concentrations in freshwaters at a regional scale (Timperley 1983) and a local scale (Quinn and Stroud 2002). The fact that results are contrary to this expectation indicates that, at the national scale, anthropogenic sources of P exert a greater influence on in-lake TP concentrations than naturally occurring edaphic sources.

The magnitude of variance (18.8%) in in-lake TP explained by the proportion of exotic forestry in a catchment was appreciably high. Exotic forests

in New Zealand comprise 90% radiata pine (*Pinus radiata* Dons) (Fahey *et al.* 2004) and, while it has been noted that pine plantations have the potential to export P at a greater rate than native forests in New Zealand (Hamilton 2005), a knowledge gap exists regarding nutrient export from plantation forests (Drewry 2006). Intriguingly, export coefficients used to estimate P loss from exotic forests in New Zealand can be less than those for native forests (Ministry for the Environment 2002), however, these are based on a limited number of studies. Cooper and Thomsen (1988) estimated TP export from pine-forested catchments at $9.5 \text{ kg km}^{-2} \text{ yr}^{-1}$; lower than their estimate for either native forest ($12 \text{ kg km}^{-2} \text{ yr}^{-1}$) or pasture ($167 \text{ kg km}^{-2} \text{ yr}^{-1}$). Similarly, Quinn and Stroud (2002) compared a stream draining pine forest with two streams draining native forest and found that average dissolved reactive P concentrations were significantly lower in the stream draining pine forest. Analysis of land use effects in the previously cited study was based, however, on monthly sampling; a frequency that may not be sufficient to derive precise estimates of P export due a failure to obtain accurate data for P loss during high-flow events (Johnes 2007). Studies have shown that TP exported from plantation forest catchments predominantly comprises particulate phosphorus (PP) (Zhang *et al.* 2007; Luz Rodriguez-Blanco *et al.* 2009) which can be higher in storm flow than in base flow by a factor of ten (Ellison and Brett 2006). The export of PP from sources in exotic forests such as exposed soil in clear-felled areas and logging roads may therefore be underestimated due to the spatial heterogeneity of such critical source areas and the temporally variable nature of losses from these sources. Although PP that enters streams draining exotic forest may not be immediately available for plant uptake (and thus would appear not to promote eutrophication), for example due to pH constraints (McDowell *et al.* 2004), PP which enters downstream lentic receiving systems may become available following early diagenesis processes at the sediment-water boundary (Pacini and Gachter 1999; Søndergaard *et al.* 2003). Sediment flux (but not necessarily P export) has been shown to be greatest following initial native forest clearance and to then steadily diminish following afforestation (Kasai *et al.* 2005). It is therefore possible that P in lakes that have catchments containing substantial proportions of exotic forest is in part a legacy of PP export during historic land clearance and not associated *per se* with ongoing forestry operations. Clearly, the finding that a substantial proportion of the variance in in-lake TP can be attributed to the extent of exotic forest in a

catchment elicits the need for further research to quantify P export from this source, and, underlines the importance of considering the potential for P loss when making decisions regarding aspects of forestry management such as felling regimes and the maintenance of riparian buffers within the forested hydrological landscape (Quinn 2005).

The relatively small proportion of the variance in in-lake TN explained by the proportion of built up area (3.7%) is indicative of the predominantly rural nature of the lake catchments (and therefore New Zealand as a nation); only 2.3% of the lake catchments on average comprised this land use (Table 3.3). High rates of N export from urban land (for example in storm drainage), are well established (e.g. Line *et al.* 2002; Allan 2004; Dietz and Clausen 2008) and therefore urbanization in a catchment has the potential to greatly increase nutrient loads to lakes that are hydrologically connected.

3.4.2 Factors that mediate the relationship between land use and in-lake nutrients

Our finding that lake and catchment morphology variables mediate the relationship between pastoral land use and in-lake nutrients is consistent with other studies. Deeper lakes have greater volume relative to their area than shallow lakes and, therefore, lake depth has been shown to have a buffering effect on nutrient inputs (Nixdorf and Deneke 1997; Nõges 2009; Liu *et al.* 2010). Furthermore, both wind driven resuspension of sediment (Hamilton and Mitchell 1997) and internal loading of P (Søndergaard *et al.* 2003) are more prevalent in shallow lakes than in deep lakes, thereby providing mechanisms for nutrients in lake sediments that originate from agricultural sources to be recycled in the water column. The positive interactive effect of the catchment to lake area ratio is in accord with empirical analysis undertaken by Håkanson (2005) which showed that TP was significantly related to this variable. This result reflects the fact that external N and P loads to lakes will typically be greater in a lake with a relatively large catchment compared to a lake with a relatively small catchment but the same proportion of land use (Nõges 2009).

Although intuitive, there is limited precedent in the literature for the finding that a variable (lake order) related to hydrologic connectivity in catchments mediates the relationship between land use and in-lake nutrient P concentrations. Fraterrigo and Downing (2008) used temporal variation in in-lake

TN and TP concentrations as a proxy for ‘watershed transport capacity’ which is equivalent to ‘catchment connectivity’ referred to in this study. Using an equivalent sample size (101) to this study, these authors established that the influence of land use on in-lake nutrient concentrations varied with watershed transport capacity, with near-shore land use being more influential in determining nutrient concentrations in lakes with low watershed transport capacity than in lakes with high transport capacity where nutrient concentrations were more closely related to land use throughout the whole catchment. Buck *et al.* (2004) obtained a similar result for streams, finding that the proportion of pasture in a catchment related better to water quality in fourth order than in second order streams. The finding that lake order has a positive interaction on the relationship between land use and TP, but not TN concentrations, is likely to be a reflection of the variation in the transport mechanisms of the two nutrients. Relative to P, surface transport of N in stream channels accounts for a lower proportion of total nutrient flux in many catchments due to the high mobility of nitrate which results in a high proportion of N-transport via subsurface hydrological pathways (Petry *et al.* 2002).

3.4.3 Implications for lake water quality policy

It is reasonable to conclude that the results provide an approximation of the relative contribution made by major land uses to explaining variation in nutrients in New Zealand lakes, given the range of lake types and the representative land use composition of the catchments included in this study (Table 3.4). Also, the sample size would seem appropriate for a national scale study; Liu *et al.* (2010) analysed 103 lakes to characterise relationships amongst lake and catchment variables at the national scale in China and Van Sickle (2003) notes that watershed studies rarely have a sample size exceeding 50 and a sample of 20–30 is common. The findings therefore provide an evidence base to guide water quality policy at the national level. On this basis, results indicate that actions are required to reduce nutrient pollution from intensive pastoral farms to mitigate lake eutrophication in New Zealand. Furthermore, by highlighting the potential for significant interactive effects, this study emphasises the importance of considering individual lake and catchment characteristics when assessing the likely vulnerability of lake ecosystems to land use change.

Following free market reforms, agricultural productivity has increased markedly in New Zealand in recent decades, however, this expansion has had an associated environmental cost (Parliamentary Commissioner for the Environment 2004; Barnett and Pauling 2005). Further development of the industry requires that these costs be explicitly recognized and mitigated, if this development is to be sustainable. The analysis indicates that land use effects on lake nutrients may be non-linear (note use of log-transformed nutrient concentrations in linear models), thus suggesting that the relationship with in-lake nutrient concentrations may exhibit a threshold response (Gergel *et al.* 2002), possibly in relation to the observed propensity for lakes to shift from clear water to turbid equilibria (Schallenberg and Sorrell 2009). This possibility mandates a precautionary approach to agricultural expansion in the catchments of lakes with significant ecological value and warrants further research into the form of the relationship between agricultural land use and lake water quality. The results also highlight the potential for P export from plantation forests to contribute to eutrophication in lakes and this issue is recommended as the focus of further research. Finally, the results indicate that lake and catchment morphology, and catchment connectivity need to be considered when strategically assessing and planning for the potential impact of land use on lake water quality.

Given the national scale of this study, care should be taken when extrapolating the results to smaller scales. The results reflect the subset of New Zealand lakes included and, while the range of lakes in the sample is broadly representative of those in New Zealand, it would clearly not be appropriate to apply the empirical relationships that have been derived at the scale of individual lakes. In particular, it is noted that the inverse correlation between z_{\max} and high prod. grass in the sample (Figure 3.4; Table 3.5) may cause the variance in the nutrient concentrations attributed to high prod. grass to be greater than would be obtained at a scale where this correlation is not present. The aim when using regression analysis to address the first of the two questions was to seek explanatory insight, as opposed to predictive power which is a disparate objective of environmental modelling (Mac Nally 2000; Beven 2001). It is likely therefore that the inclusion of more predictor variables in the regression models would have yielded higher predictive power, however, this gain would be at the expense of understanding the relative contribution of anthropogenic land uses. For example, including variables which were also *negatively* correlated with lake nutrient

concentrations (e.g. ‘% native’) may have resulted in better predictive power (e.g. higher r^2) but less explanatory depth due to the opposing influences of natural and anthropogenic land uses in determining lake nutrient concentrations. It is also acknowledged that lake nutrient concentrations are a function of both historic and contemporary catchment land use (Johnes 1999) and therefore the respective land use proportions that have been calculated for each catchment are a simplification of land use pressures on lake water quality as historic land use was not accounted for, nor was land use change that may have occurred between 2000–2001 (land use imagery acquisition) and 2004–2006 (water sampling). Similarly, the analysis of factors that potentially mediate the land use – water quality relationship was undertaken at a broad spatial scale and several studies have highlighted the importance of aligning the scale at which relationships between catchment variables are analysed to the scale of the study (Buck *et al.* 2004; Daniel *et al.* 2010). For instance, it is possible that analysis at finer spatial scales would yield significant relationships between the effect of land use on lake nutrients and variables such as slope, as have been established in other studies (Kamenik *et al.* 2001; Chang *et al.* 2008). A worthwhile subject for further research is to undertake finer scale spatial analysis to better define relationships between land use and nutrients in New Zealand lakes, and to investigate how factors such as the spatial configuration of land use (Lee *et al.* 2009), biological diversity and abundance (e.g. macrophyte coverage), lake mixing status, historic land use and future climate scenarios mediate this relationship. Finally, future studies with larger sample sizes may wish to investigate higher (second and greater) order interactions between variables to provide greater insight into catchment interactions.

3.5 References

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4 Spatial and temporal variations in sediment, nitrogen and phosphorus transport in stream inflows to a eutrophic New Zealand lake

4.1 Introduction

Excess sediment and nutrient loading can have major adverse ecological impacts on receiving aquatic ecosystems (Donohue & Molinos 2009, Vollenweider 1968). Characterising spatial and temporal variations in fluxes of these potential pollutants through hydrological landscapes is therefore necessary to inform the implementation of actions (e.g. best agricultural management practices) designed to mitigate water pollution (Mainstone et al. 2008). Additionally, resource managers require precise estimates of sediment and nutrient loads to receiving waters to monitor compliance with water quality standards, as well as to provide robust input data for water quality models that are increasingly used to help to understand ecosystem processes (Burger et al. 2008, Collins & McGonigle 2008).

Quantifying pollutant flux in surface streams requires knowledge of both discharge (Q) and determinand concentration, with the latter typically measured at lower frequency. Although infrequent (e.g. monthly) measurements may suffice for reasonable estimation of sediment and nutrient loads during base flow conditions (but see Jordan et al. 2005 for discussion of variable base flow loading), the potential for high temporal variation in determinand concentrations following rain events necessitates high-frequency sampling to accurately estimate loads conveyed in storm flow, particularly in low-order streams that respond quickly to rainfall (Chiwa et al. 2010, Johnes 2007, Lim 2003). In addition to informing load estimation, determinand concentration– Q relationships derived using high-frequency sampling can provide insight into the dominant sources and transport mechanisms of sediments and nutrients in catchments. This ability reflects the role of a catchment as a filter which mediates the downstream transport of pollutants, and, consequently, temporal variations in concentration during storm flows provide a signature that integrates the effects of complex upstream hydrological and biogeochemical interactions (Guan et al. 2011, Kirchner et al. 2000, Lewis & Grimm 2007).

Suspended sediment concentration typically increases in storm flow due to erosive processes, while nutrient concentrations may either increase or decrease due, for example, to flushing from critical source areas, mobilisation of channel-bed stores or dilution by rainwater respectively (e.g. Kato et al. 2009, Salvia-Castellví et al. 2005, Zhang et al. 2010). In addition to Q, concentration may also vary in association with other hydrological variables that influence catchment transport processes such as soil moisture content (Rozemeijer et al. 2010). Furthermore, when there is a relationship between concentration and Q, it may be non-monotonic, i.e. there may be hysteresis related to differences in concentration at particular Q depending on whether Q is increasing or receding (Bowes et al. 2005, House & Warwick 1998). The occurrence of a concentration peak before maximum Q (Q_{\max}) during a hydrological event suggests a ‘first flush’ effect, attributed to mobilisation of sediments or nutrients accumulated in critical source areas on land or channel bed stores since a prior event (e.g. Zhang et al. 2010), assuming that the flushing process is source and not Q-limited (Burns 2005). Alternatively, the occurrence of a concentration peak during the recessing limb of the hydrograph has been interpreted to indicate slow diffuse delivery of pollutant to the channel (e.g. Bowes et al. 2005). The potential for determinand concentrations to correlate positively with Q can contribute to temporal inequality in pollutant loading, i.e. a proportion of the cumulative load for a time period may be transported in a disproportionately short period of time. Such inequality can be quantified using Lorenz curves. Lorenz curves are typically used to describe the cumulative distribution function of economic variables (Atkinson 1970) but have recently been used to quantify temporal inequality in both Q and daily nutrient loads estimated from monthly samples (Jawitz & Mitchell, 2011).

The concentration–Q relationship may vary between catchments depending on individual characteristics such as land use. For example, Siwek et al. (2011) found that nitrate (NO_3^-) concentration was positively correlated with Q in a woodland catchment (attributed to entrainment of NO_3^- in soil by surface runoff), whereas the relationship was negative in an agricultural catchment (attributed to dilution of polluted stream water by rainwater). Improving understanding of how landscape characteristics such as land use and hydrogeomorphology interact to influence sediment and nutrient transport has been identified as a research priority (Collins & McGonigle 2008, Lohse et al. 2009) and is important to aid development of models of pollutant transport in catchments, calibration of which

is frequently constrained by lack of data relating to pollutant concentrations at high Q (Letcher et al. 2002). In the case of nutrients, there is specific need to consider variations related to individual fractions (e.g. dissolved and particulate) due to the differing bioavailability of various nitrogen and phosphorus forms and their subsequent discrepant potential to contribute to eutrophication in downstream waters (Boström et al. 1988, Bronk et al. 2007).

This study focuses on two stream inflows to a large eutrophic lake and examines temporal variations in suspended sediment, nitrogen and phosphorus loading during a range of Q. High frequency event-based sampling was conducted over an extended period (2+ years) which included concurrent sampling of both streams in order to investigate spatial variations in pollutant transport between the two catchments during similar hydrological conditions. The objectives were: (1) to quantify temporal (within-catchment) variations in suspended sediment and nutrient concentration in both base and storm flow; (2) to investigate how temporal changes in concentration-Q relationships can vary spatially (between sub-catchments upstream of a common lake ecosystem); and (3) to improve understanding of the potential for nutrients conveyed in storm flow to promote downstream eutrophication.

4.2 Methods

4.2.1 Study catchments

Event-based water sampling was undertaken of two stream inflows (Fig. 4.1) to Lake Rotorua, a large (81 km²), eutrophic and polymictic lake in the Bay of Plenty Region of New Zealand. The local igneous geology is complex with a series of large aquifers that are distinct from surface water catchments (Morgenstern et al. 2005). Soils comprise deep, porous sands or loams that are high in allophane (Newsome et al. 2000). Water quality in Lake Rotorua has declined since at least the 1960s due to excess nutrient loading and, as a result, the lake is eutrophic, experiences undesirable algal blooms and is now a priority for remediation (Parliamentary Commissioner for the Environment 2006, Rutherford 1984). The lake has nine major stream inflows which supply approximately 66% of the total input of water (Hoare 1980). Of these, the Ngongotaha and Puarenga streams have the two largest surface sub-catchments and the fourth and second greatest mean Q respectively (*ibid*). Both streams are estimated to convey a high proportion of water in storm flow: 44% and 36% respectively (Rutherford &

Timpany 2008). Median discharge (Q_{50}) is similar in the two streams (Ngongotaha = $1.90 \text{ m}^3 \text{ s}^{-1}$, Puarenga = $1.92 \text{ m}^3 \text{ s}^{-1}$; May 2010 – August 2012), although base flow is typically lower in the Ngongotaha Stream which has a more elongated catchment with lower drainage density than the Puarenga Stream catchment (Fig. 4.1). The Ngongotaha Stream catchment predominantly comprises pastoral agriculture with forested areas on steeper slopes. A sampling site was located upstream of the township of Ngongotaha. The dominant land use in the Puarenga Stream catchment is exotic coniferous forest comprising mostly *Pinus radiata*, although there is some pastoral agriculture (drystock and dairy farms), and suburban land use immediately upstream of the sampling location (Fig. 4.1). The Rotorua Wastewater Treatment Plant (Fig. 4.1) is situated downstream of the Puarenga sampling location although treated sewage from the plant is discharged to land upstream of the sampling location at the Rotorua Land Treatment System where effluent has been spray-irrigated over a 193 ha forested area since 1991 (Tomer et al. 2000). The Whakarewarewa geothermal area is immediately upstream of the sampling location.

4.2.2 Sampling methods

The Ngongotaha Stream was sampled 2.5 km from the lake and Q was recorded at a permanent gauge sited 80 m further upstream. Precipitation (mm; hereafter ‘rainfall’) was measured at a permanent gauge sited at Upper Oturoa Road, 9 km to the north-west (Fig. 4.1). The Puarenga Stream was sampled 2.1 km from the lake and Q was recorded at a permanent gauge sited 800 m downstream. Rainfall was measured at a permanent gauge sited 3 km to the south-east (Whakarewarewa; Fig. 4.1). Discharge was measured every 15–60 minutes and rainfall every hour. Soil moisture was measured using an *in situ* dielectric probe situated at the rain gauge site north of Ngongotaha Stream catchment (Fig 4.1).

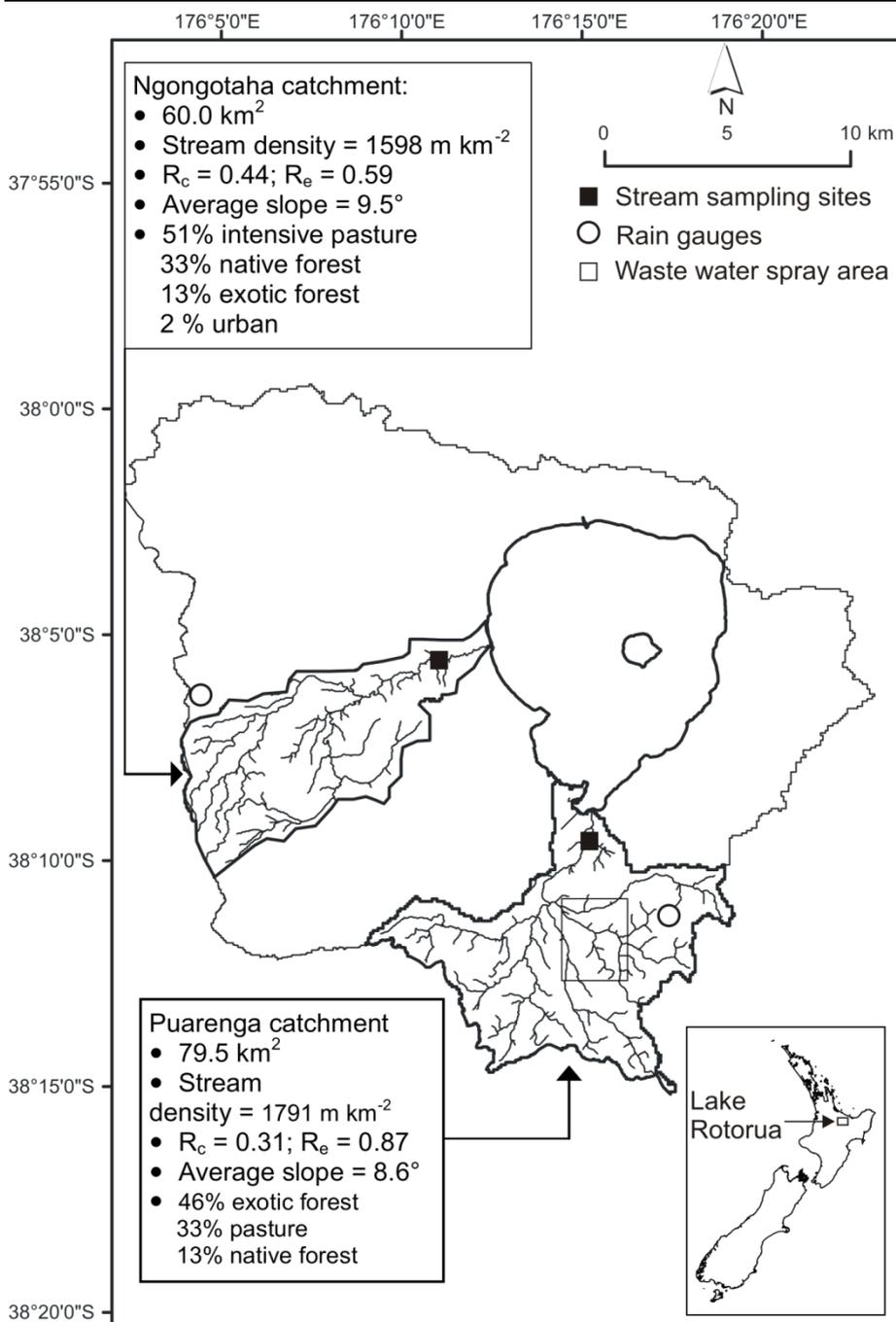


Figure 4.1 Location of Lake Rotorua catchment, study stream surface catchments, monitoring locations and rain gauges. Catchment boundaries are from Rutherford et al. (2011) and land use statistics are derived from the Land Cover Database 2 (Ministry for the Environment 2004). R_c, circularity ratio; R_e, elongation ratio.

Stream water at both sites was sampled at high frequency over 1–5 day periods coinciding with forecasted rainfall during different seasons between May 2010 and July 2012. The objective was to sample during pre–event base flow and throughout the rising and recessing limbs of the hydrograph. Stream water (0.5–1.0 L) was sampled from mid base flow water depth using automatic samplers (Manning VST portable) programmed to sample at 1–2 h frequency over the duration of each sampling period. A small number of supplementary samples were also collected manually from the same sites (< 5 % of samples). Sample bottles and hoses were acid–washed (10% HCl) and triple–rinsed with analytical grade deionised water (Millipore Co.) prior to deployment during each sampling period. Samplers were filled with ice and samples retrieved daily before the ice melted. Sub–samples for dissolved nutrient analysis were taken by filtration in the field (0.5 μm , Advantec GF GC-50) using acid–washed syringes during daily retrieval. Filtered and unfiltered sub–samples for nutrient analysis were stored in acid–washed polypropylene tubes and preserved at ≤ 4 °C during transport to the laboratory where they were frozen. Sub–samples for determination of suspended sediment concentration (not all events for Puarenga Stream, Table 4.1) were collected in clean plastic bottles and analysed on return to the laboratory or refrigerated for up to five days.

A total of six separate periods were sampled for the Ngongotaha Stream and 13 for the Puarenga Stream (Fig 4.2). Two distinct Q peaks were sampled during Puarenga Stream sampling of 11–15 May 2010 (event # 1 and # 2, Fig 4.2), hence, a total of 14 separate events were sampled on this stream. During three events, both streams were sampled simultaneously (two in late Austral summer, one in winter; Fig. 4.2) to specifically study how pollutant transport varied between the two streams during similar hydrological conditions. In total, there were three gaps > 3 h during sampling due to sampler malfunction or maintenance periods, none of which occurred during Q_{max} (Table 4.1). Two grab samples (in duplicate) were also collected during a large event in August 2012 (Ngongotaha Stream $Q = 22.0 \text{ m}^3 \text{ s}^{-1}$, Puarenga Stream $Q = 10.8 \text{ m}^3 \text{ s}^{-1}$) and data (TN, TP and TSS concentrations) were used in derivation of regression models (see below).

Table 4.1 Characteristics of sampling periods for the Ngongotaha (Ngo) and Puarenga streams (Pua; Fig. 4.2). h, duration of sampling period in hours; Q_{\max} , maximum discharge ($\text{m}^3 \text{s}^{-1}$) sampled; 24-h EMC, event mean concentration based on 24-h continuously-sampled period when discharge was greatest; Q_{avg} ; average hourly discharge during 24-h continuously-sampled period when discharge was greatest ($\text{m}^3 \text{s}^{-1}$); TN, total nitrogen; TP, total phosphorus; TSS, total suspended sediments; VSS, volatile suspended sediments. ‘–’ indicates that determinand was not measured.

| Stream | # | Date | Sampling frequency (h) | h | Q_{\max} | 24-h EMC (mg L^{-1}) | | | | | | Q_{avg} | Notes | |
|--------|----|------------------|------------------------|--------|------------|---------------------------------|-------|------------------------|------------------------|------------------------|--------|------------------|-------|---|
| | | | | | | TN | TP | $\text{NO}_3\text{-N}$ | $\text{NH}_4\text{-N}$ | $\text{PO}_4\text{-P}$ | TSS | | | VSS |
| Ngo. | 1 | 16–18 Dec ‘10 | 2.0 | 46.00 | 1.5 | 1.03 | 0.055 | 0.84 | 0.016 | 0.034 | 4.80 | – | 1.4 | |
| | 2† | 21–24 March ‘11 | 1.0 | 74.25 | 2.7 | 0.93 | 0.076 | 0.79 | 0.027 | 0.050 | 14.42 | 3.51 | 2.2 | |
| | 3 | 12–16 Dec ‘11 | 1.5–2.0 | 121.50 | 3.1 | 1.26 | 0.083 | 0.85 | 0.043 | 0.044 | 22.56 | 8.04 | 2.6 | One gap of 3.75 h |
| | 4 | 7–8 Jan ‘12 | 1.0 | 25.00 | 18.0 | 1.63 | 0.237 | 0.70 | 0.056 | 0.043 | 170.71 | 31.82 | 6.0 | |
| | 5* | 02–04 March 2012 | 1.0 | 47.50 | 2.4 | 1.03 | 0.085 | 0.85 | 0.011 | 0.028 | 8.47 | 5.83 | 2.3 | Falling limb not fully sampled |
| | 6‡ | 15–17 July 2012 | 1.0 | 50.50 | 13.1 | 1.66 | 0.235 | 0.68 | 0.035 | 0.029 | 198.10 | 41.37 | 7.5 | One gap of 7 h during rising limb. |
| Pua. | 1 | 11–13 May ‘10 | 1.0–2.0 | 24.00 | 3.8 | 1.34 | 0.127 | 0.81 | 0.072 | 0.033 | – | – | 2.5 | One gap of 12 h during pre-event base flow. 5 h overlap between # 1 and # 2 |
| | 2 | 13–15 May ‘10 | 1.0 | 24.00 | 6.5 | 1.54 | 0.172 | 0.80 | 0.077 | 0.026 | – | – | 2.6 | |
| | 3 | 24–27 May ‘10 | 2.0 | 67.00 | 15.6 | 2.54 | 0.316 | 0.96 | 0.498 | 0.056 | – | – | 10.2 | |

Chapter 4 – Spatial and temporal variations in nutrient transport in two streams

| Stream | # | Date | Sampling frequency (h) | h | Q _{max} | 24-h EMC (mg L ⁻¹) | | | | | | Q _{avg} | Notes | |
|--------|-----|--------------------|------------------------|-------|------------------|--------------------------------|-------|--------------------|--------------------|--------------------|--------|------------------|-------|-------------------------------|
| | | | | | | TN | TP | NO ₃ -N | NH ₄ -N | PO ₄ -P | TSS | | | VSS |
| | 4 | 01–04 Aug '10 | 1.0 | 71.50 | 5.0 | 1.53 | 0.194 | 0.79 | 0.084 | 0.021 | – | – | 3.7 | Rising limb not fully sampled |
| | 5 | 25–27 Aug '10 | 1.0 | 47.50 | 2.9 | 1.38 | 0.075 | 0.91 | 0.076 | 0.031 | 13.85 | – | 2.5 | |
| | 6 | 18–21 Jan '11 | 1.0 | 73.25 | 2.6 | 1.13 | 0.156 | 0.87 | 0.053 | 0.037 | 39.59 | – | 2.2 | |
| | 7† | 21–24 March '11 | 1.0 | 71.50 | 4.8 | 1.27 | 0.135 | 0.86 | 0.060 | 0.075 | 55.98 | 14.35 | 3.7 | |
| | 8 | 10–13 Aug '11 | 1.0 | 70.00 | 3.4 | 1.30 | 0.130 | 0.89 | 0.067 | 0.053 | 35.67 | – | 2.9 | |
| | 9 | 03–05 Oct '11 | 1.0 | 50.25 | 4.7 | 1.41 | 0.184 | 0.80 | 0.088 | 0.028 | 93.18 | – | 3.8 | |
| | 10 | 10–13 Oct '11 | 1.0 | 71.00 | 8.3 | 1.49 | 0.225 | 0.76 | 0.106 | 0.031 | 128.14 | – | 6.8 | |
| | 11 | 08–09 Jan '12 | 1.0 | 27.25 | 7.4 | 1.44 | 0.097 | 0.80 | 0.126 | 0.021 | 37.73 | 8.61 | 5.1 | |
| | 12 | 12–13 Jan '12 | 1.0 | 26.00 | 5.3 | 1.20 | 0.109 | 0.85 | 0.076 | 0.053 | – | – | 4.4 | Rising limb not fully sampled |
| | 13* | 02–04 March '12 | 1.0 | 48.00 | 3.7 | 1.18 | 0.141 | 0.74 | 0.055 | 0.026 | 31.20 | 10.45 | 2.9 | |
| | 14‡ | 15–17 July '12 | 1.0 | 48.00 | 6.5 | 1.37 | 0.201 | 0.75 | 0.111 | 0.027 | 112.88 | 27.13 | 4.7 | |

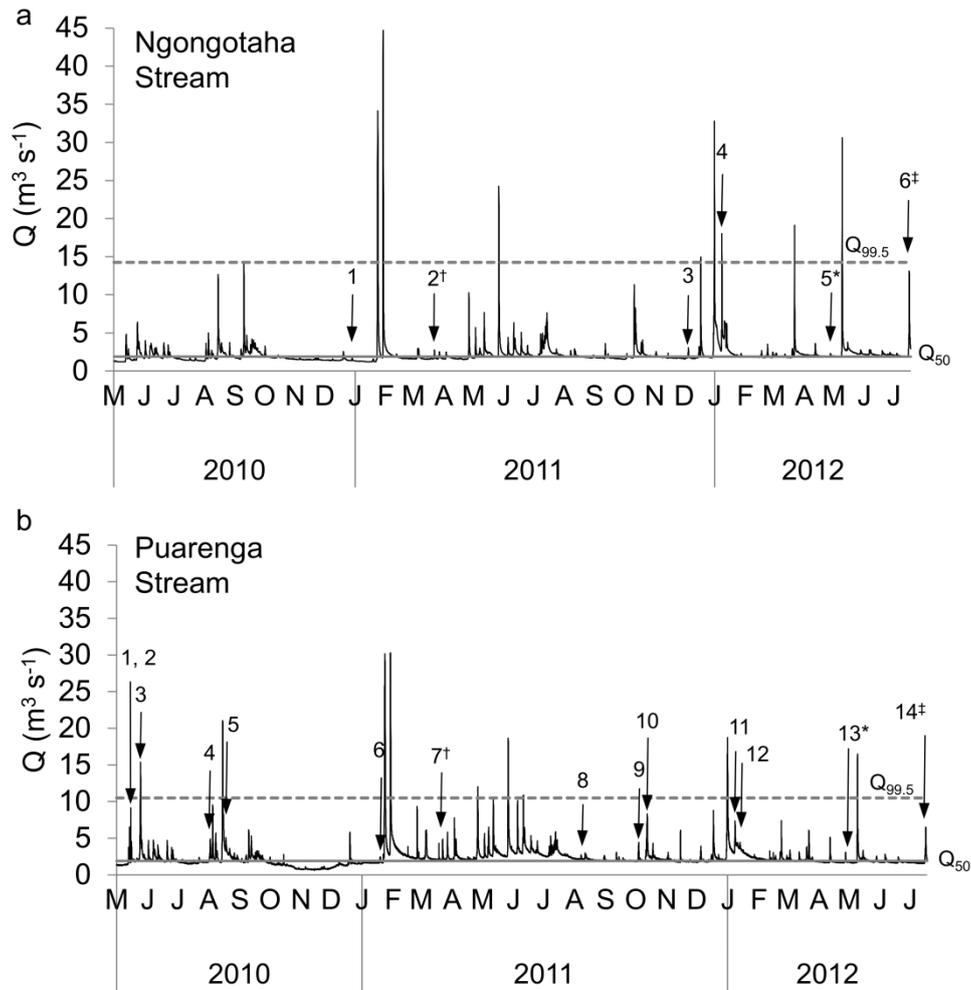


Figure 4.2 Hourly measured discharge (Q) in the Ngongotaha (a) and Puarenga (b) streams during May 2010 – August 2012. Solid horizontal line denotes median discharge (Q_{50}) and dashed line denotes the 99.5 discharge percentile ($Q_{99.5}$). Numbers denote sampling periods (Table 4.1), superscript symbols denote events for which both streams were simultaneously sampled.

4.2.3 Water quality analysis

Sediment concentrations were determined by filtering 65 – 500 mL of stream water through pre-combusted (550°C for 3 h) and pre-weighed glass fibre filters ($0.5\ \mu\text{m}$, Advantec GF GC-50). Total suspended sediment (TSS) concentrations were determined gravimetrically following drying (105°C for 8 h) and volatile suspended sediment (VSS) concentrations were then determined by weight difference following subsequent ashing (550°C for 3 h). Dissolved nutrients (NH_4^+ , NO_2^- , NO_3^- , PO_4^{3-}) were measured with an Aquakem 200 discrete analyser (Thermo Fisher) using standard colorimetric methods (APHA 1998). Limits of detection were $0.001\ \text{mg N L}^{-1}$ for NO_2^- , NO_3^- , $0.002\ \text{mg N L}^{-1}$ for NH_4^+ and

0.001 mg P L⁻¹ for PO₄³⁻. Total nitrogen (TN) and total phosphorus (TP) concentrations were determined following combined persulphate digestion (APHA 1998) of an unfiltered sample and subsequent colorimetric analysis for NO₃⁻ and PO₄³⁻ respectively, using a Lachat QuickChem flow injection analyser (Zellweger Analytics Inc.). A range of check standards was analysed in concert to confirm analytical detection limits. Total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) concentrations were determined as for TN and TP respectively but using the field-filtered sample (0.5 µm, Advantec GF GC-50). These last two analyses were only undertaken for the three events when both streams were simultaneously sampled.

4.2.4 Data treatment and measured load calculation

Dissolved organic nitrogen (DON) concentration was determined as TDN minus the sum of NH₄-N, NO₂-N and NO₃-N; dissolved organic phosphorus (DOP) was determined as TDP minus PO₄-P. A value of zero was assigned when concentrations of DON and DOP were below the limit of detection. A small number (< 5%) of concentration data were disregarded due to suspected contamination arising from sampling or measurement error (e.g. when PO₄-P > TP). For load calculations, disregarded concentration values were replaced with the mean of the two hourly measurements immediately before and after the anomalous result. Such estimated values are not reported

Daily loads of determinands during each storm event were calculated using samples collected during the 24-h period of maximum Q that was continuously sampled. The approximate duration of events was one day and loads were calculated for standard 24-h periods (rather than the duration of individual events) primarily to aid comparison between both stream and events. It also negated the need to fill gaps in concentration data for the minority of events which were not completely sampled or for which there were breaks in sampling. Observed 24-h loads were calculated as:

$$L = \sum_{i=1}^n \left(\frac{C_i + C_{i-1}}{2} \right) \left(\frac{Q_i + Q_{i-1}}{2} \right) \quad (1)$$

where L is the calculated 24-h load (kg day⁻¹), n is the number of samples collected during the 24-h period and C_i and Q_i are determinand concentration and discharge respectively at time i.

Consequently, event mean concentration (24-h EMC) of determinands was calculated as:

$$24-h EMC = \frac{24-h load}{\sum_{i=1}^n \left(\frac{Q_i + Q_{i-1}}{2} \right)} \quad (2)$$

4.2.5 Quantifying hysteresis in concentration–discharge relationships

Scatterplots of relationships between determinand concentration and Q for each event (typically the entirety of the sampling period) were inspected to identify hysteresis that reflected consistent difference in concentration between the rising and recessing limbs of the hydrograph. Observed hysteresis was subsequently characterised for all sampling periods that included at least five samples collected during both the rising and recessing limbs of the hydrograph. Hysteresis was quantified by fitting two parameters (p and g) to the following model proposed by Bowes et al. (2005) after House & Warwick (1998).

$$\hat{C}_i = C_{base} + p \left(\frac{Q_i - Q_{i-1}}{dt} \right) + \frac{(g(Q_i - Q_{base}))}{Q_i Q_{base}} \quad (3)$$

where \hat{C}_i is estimated determinand concentration (mg L^{-1}) at time i , C_{base} is the mean determinand concentration (mg L^{-1}) measured in samples collected during the sampling period prior to the onset of the hydrograph rising limb, dt is time elapsed (s) between times i and $i-1$ and Q_{base} is the mean discharge ($\text{m}^3 \text{s}^{-1}$) during the sampling period prior to the onset of the hydrograph rising limb. Parameter p is a response factor ($\text{g m}^{-6} \text{h}^2$) that quantifies the magnitude of the hysteresis loop, as well as the direction, i.e. clockwise ($p > 0$, concentration higher during rising limb than the recessing limb) or anti-clockwise ($p < 0$, *vice versa*). Parameter g is a loop gradient term (g s^{-1}) that is related to the size of the hydrograph peak and is normalised with respect to Q. Both p and g were determined by iteration using the Solver add-in to Microsoft Excel 2007 with the objective to minimise the root mean squared error between measured (C_i) and estimated concentration (\hat{C}_i) during the sampling period

4.2.6 Comparison of load estimation methods

The extensive dataset collected during this study provided an opportunity to compare the accuracy of a range of commonly used methods for estimating pollutant loads. Observed 24-h loads of TN, TP and TSS were compared to estimates derived using the following three main methods of load estimation (Preston et al. 1989): averaging, ratio estimation and regression approaches.

Averaging approaches are frequently used when few concentration data are available. The Bay of Plenty Regional Council conduct routine (monthly) monitoring, which furnishes a time series of monthly concentrations. An important question is whether event loads can be estimated accurately as the product of Q measured continuously during a storm event and the mean concentration of samples collected during routine monitoring. Event pollutant loads were thus estimated from the product of Q measured hourly during a storm event and the mean concentration of routine samples:

$$L_{avg} = \bar{C}_{monthly} \times \sum_{i=1}^n Q_i \quad (4)$$

where L_{avg} is the estimated 24-h event load and $\bar{C}_{monthly}$ is the mean concentration of 20–25 grab samples collected at approximately 4-week intervals by the regional council between May 2010 and July 2012 as part of a routine monitoring programme. The Ngongotaha Stream site was ≈ 1 km downstream from the event sampling site and the Puarenga Stream sites were at the same location.

Ratio estimation methods assume correlation between concentration and an auxiliary variable which is more frequently sampled (typically Q) (Preston et al. 1989). Instantaneous load estimates are consequently proportionally adjusted with reference to the auxiliary variable to derive a load for longer time periods, e.g. greater weighting is apportioned to concentration measurements taken when Q is high. To reflect correlation between concentration and Q , the Q -weighted mean concentrations were calculated using data collected in this study, and used in place of the arithmetic means of Eq. 4. To maintain independence, Q -weighted mean concentrations were calculated separately for each load calculation using only data for other events.

$$C_{QWM} = \frac{\sum_{j=1}^N C_j Q_j}{\sum_{j=1}^N Q_j} \quad (5)$$

where C_{QWM} is the discharge-weighted mean concentration, N is the number of samples and C_j and Q_j are determinand concentration and discharge respectively measured during sampling periods at time j . Then:

$$L_{ratio} = C_{QWM} \times \sum_{i=1}^n Q_i \quad (6)$$

where L_{ratio} is the estimated 24-h event load.

Regression can be used to estimate concentration based on Q (rating curves) where a defined relationship exists between the two variables and when data relating to a sufficiently wide range of Q are available (Johnes 2007). Log_{10} –

\log_{10} rating curves were constructed using ordinary least squares linear regression and loads estimated as:

$$L_{rating} = \sum_{i=1}^n \left(\frac{\hat{C}_i + \hat{C}_{i-1}}{2} \right) \left(\frac{Q_i + Q_{i-1}}{2} \right) \quad (7)$$

where L_{rating} is the estimated 24-h load and \hat{C}_i is concentration at time i estimated with a rating curve constructed using only data measured during other sampling periods. All dependent variables used in regression models were \log_{10} -transformed and untransformed estimators were derived by calculating the antilogarithm and multiplying by the following bias correction factor proposed by Ferguson (1986):

$$BCF = e^{2.65\sigma^2} \quad (8)$$

where σ^2 is the model variance.

In addition to Q, other hydrological variables that affect pollutant transport have been shown to explain additional variation in concentration measurements (Rozemeijer et al. 2010). Regression models were trialled that used the following independent variables to predict measured concentration: $\frac{Q_i}{Q_{i-xh}}$ where Q_{i-xh} is discharge x -h prior to sampling (values for x of 1, 1.5, 2 and 3 were considered); the sum of rainfall measured in preceding 1, 3 and 6 hours, and soil moisture (%) at the time when the sample was collected. Linear interpolation of hourly measurements was used to derive sub-hourly estimates of independent variables.

Additional hydrological variables aside from Q were only used to improve prediction of TN and TP concentrations for the Puarenga Stream, as datasets for this stream were the most extensive, and included events during different seasons with a range of different characteristics. The aim when trialling regression models was to seek parsimonious compromise between maximising model performance (r^2) and minimising the number of independent variables. Where necessary, variables were transformed to improve normality and ensure linearity of relationships. Residual plots were visually inspected for normal distributions. The predictive power of the TN model for the Puarenga Stream was improved with the addition as an independent variable of the ratio of Q at the time of sampling to Q 3-h previously (Q_i/Q_{i-3h}):

$$\widehat{TN}_{hydrolog} = (\beta_1 \times \log_{10} Q_i) - (\beta_2 \times \left(\frac{Q_i}{Q_{i-3h}} \right)) + c_1 \quad (9)$$

where $\widehat{TN}_{hydrolog}$ is estimated \log_{10} transformed TN concentration, β_1 and β_2 are regression coefficients (both > 0) and c_1 is the y intercept of the regression line.

The predictive power of the TP model for the Puarenga Stream was improved with the addition of the following independent variables: the ratio of Q at the time of sampling to Q 1.5 h previously ($Q_i/Q_{i-1.5\text{ h}}$); the sum of rainfall (mm) in the preceding 6-h ($\log_{10} + 1$ transformed; $rain_6$), and soil moisture (%) at the time of sampling (square-root transformed; $soil$):

$$\widehat{TP}_{hydro} = (\beta_3 \times \log_{10} Q_i) - [\beta_4 \times (\frac{Q_i}{Q_{i-1.5\text{ h}}})] + (\beta_5 \times rain_6) - (\beta_6 \times soil) + c_2 \quad (10)$$

where \widehat{TP}_{hydro} is estimated \log_{10} transformed TP concentration, $\beta_3, \beta_4, \beta_5$, and β_6 are regression coefficients (all > 0) and c_2 is the y intercept of the regression line.

Regression coefficients and y intercept values were determined using ordinary least squares linear regression. To maintain independence, values for these parameters were determined individually for each event using only measured data for all *other* events.

Consequently, estimated loads (L_{hydro}) were calculated using Eq. 1 with substitution of C_i for concentration estimated using regression models described above that included two or more hydrological variables as predictors.

4.2.7 Quantifying temporal inequality in pollutant transport

In order to compare how determinand loading varied temporally between the two streams over longer time periods, regression models fitted to measured data (see above) were used to estimate the average hourly concentration of TN, TP and TSS in each stream over the two-year period of May 2010–May 2012 (soil moisture probe malfunctioned in June 2012). Root mean squared error statistics were calculated for models using a bootstrapped sample drawn from measured data (sample with replacement; $n = 10000$). Lorenz curves were then constructed to examine how the cumulative proportion of the total estimated two-year load (x) varied with respect to the cumulative proportion of time (y). The Gini coefficient (G) was calculated to quantify temporal inequality in loading; this parameter equals the ratio of the area enclosed by the Lorenz curve and the 1:1 line, to the area under the 1:1 line (Fig. 4.3). The parameter therefore equals a value between 0 (loading is equal at all times) and 1 (all loading occurs in an infinitesimally small period). For constructed Lorenz curves, G was calculated as:

$$G = 1 - 2 \int_0^1 Y(X)dX \quad (11)$$

with integration performed numerically.

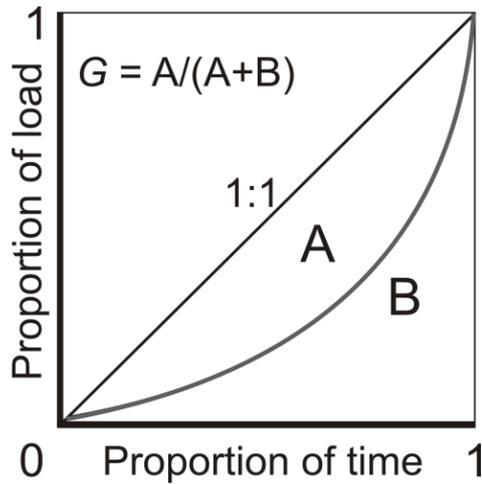


Figure 4.3 Example of Lorenz curve used to examine the relationship between the proportion of a total load transported and the proportion of time elapsed during a defined period. The Gini coefficient (G) quantifies temporal inequality in loading from a scale of 0–1, where 0 implies that loading occurs at a constant rate and 1 implies that all loading occurs during the shortest time step.

4.3 Results

4.3.1 Hydrology

The sampling periods spanned a wide range of Q (Fig. 4.2). Although median Q was very similar in the two streams ($\approx 1.9 \text{ m}^3 \text{ s}^{-1}$) the hydrograph for the Puarenga Stream (highest circularity ratio and drainage density) was the flashier of the two, with more peaks and steeper base flow recession. By contrast, the Ngongotaha Stream hydrograph displayed fewer peaks but higher Q_{\max} during large storms (e.g. $Q_{99.5}$ was highest in the Ngongotaha Stream, Fig. 4.2). Discharge during the study period exceeded the range of sampled Q for 0.35% of the total time for the Puarenga Stream and for 0.25% of the time for the Ngongotaha Stream. Rainfall was above average during the sampling period; e.g., total rainfall for Rotorua city was 6% above the 1981–2010 average in 2010 (1436 mm) and 47% above average in 2011 (1997 mm) (NIWA 2011–2012). In particular, uncharacteristically high rainfall occurred during both Austral summers and two very large floods occurred in January 2011 following passage of tropical anticyclones, although these were not sampled. Hourly Q_{\max} in the Ngongotaha stream during the largest flood was the highest measured for 15 years (NIWA 2012; long-term continuous monitoring data not available for the Puarenga Stream).

4.3.2 Relationships between concentration and discharge

Data for the three events during which both streams were sampled illustrate typical relationships between determinand concentration and Q (Figs. 4.4–4.6). Suspended sediment concentrations were highly positively correlated with Q in both streams (e.g. Fig 4.4b, f). Suspended sediments were predominantly inorganic; on average VSS comprised 32% of TSS sampled in the Puarenga stream and 42% in the Ngongotaha stream. The proportion of TSS comprising VSS varied widely between events at base flows, although it was typically $\approx 20\%$ during storm flow in both streams indicating relatively higher flux of inorganic sediments during storm events.

Concentrations of NO_3^- typically exhibited a weak dilution effect in both streams and declined during the period of Q_{max} (e.g. Figs 4.5c, d). Consequently, the lowest $\text{NO}_3\text{-N}$ 24-h EMCs measured in the Ngongotaha Stream occurred during the largest events (events # 4 and # 6; Table 4.1). During the recessing limb of the hydrograph, an increase in $\text{NO}_3\text{-N}$ concentrations to above pre-event base flow was observed in several events sampled in the Puarenga Stream (e.g. Fig. 4.5g). Total nitrogen concentrations were positively correlated with Q in both streams although this determinand was invariant during smaller events as a result of minor increases in concentrations of DON and particulate N being balanced by reduced $\text{NO}_3\text{-N}$ concentrations (e.g. Fig. 4.4c). Concentrations of $\text{NH}_4\text{-N}$ typically comprised only a small proportion of TN concentrations (Ngongotaha Stream mean = 2%; Puarenga Stream mean = 9%) and generally showed no clear relationship with Q, although highest concentrations were measured during the largest events in both streams. Concentrations of $\text{NO}_2\text{-N}$ were less than detection limits ($< 0.001 \text{ mg L}^{-1}$) in all samples and are not presented.

Concentrations of PO_4^{3-} were highly variable; coefficients of variation for this determinand in the streams were 43% (Ngongotaha) and 56% (Puarenga). Typically, concentrations of $\text{PO}_4\text{-P}$ were a minor component of TP concentrations and unrelated to Q, although the March 2011 event (medium-sized event in late summer) during which both streams were sampled was an exception as $\text{PO}_4\text{-P}$ concentrations displayed peaks after and before Q_{max} respectively in the Ngongotaha and Puarenga streams (Fig. 4.4d, h). Total P concentrations exhibited positive correlation with Q in both streams (e.g. Figs. 4.5d and 4.5h). The relative rate at which concentrations of TP increased with Q was typically greater than for TN, hence, mass ratios of TN:TP generally decreased during

storm flow (Fig 4.7). Dissolved organic P was a minor component of the TP pool in the three events for which it was measured (Figs. 4.4d, 4.4h, 4.5d, 4.5h, 4.6d, 4.6h) and the positive correlation between TP concentrations and Q therefore overwhelmingly reflects mobilisation of particulate P during elevated Q.

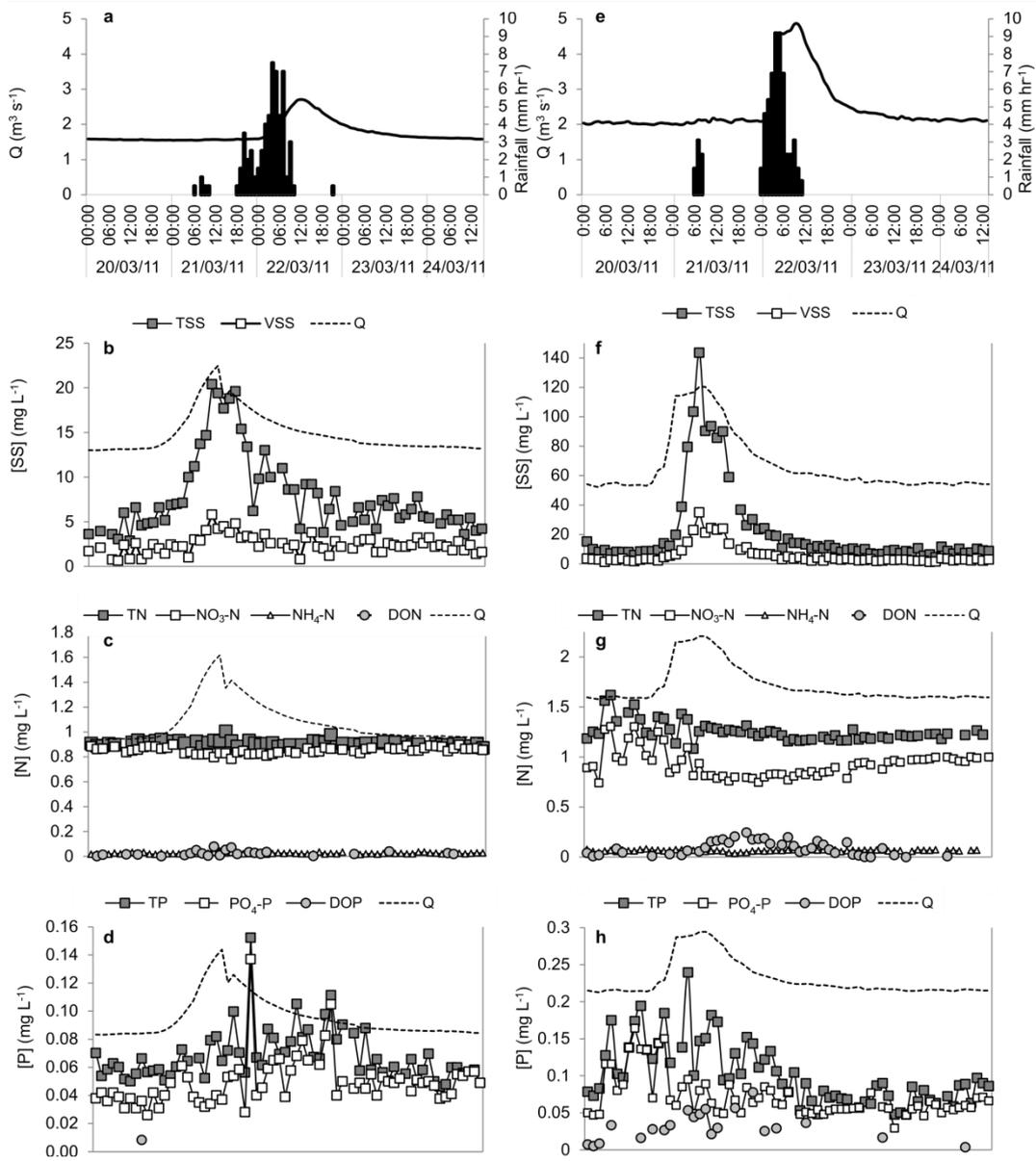


Figure 4.4 Temporal variations in measurements for the Ngongotaha Stream (left panels, a–d) and the Puarenga Stream (right panels, e–h) during simultaneous sampling of both streams in March 2011 (event # 2 and #7 respectively; Fig. 4.2). Scale for discharge (Q) data not shown on concentration plots.

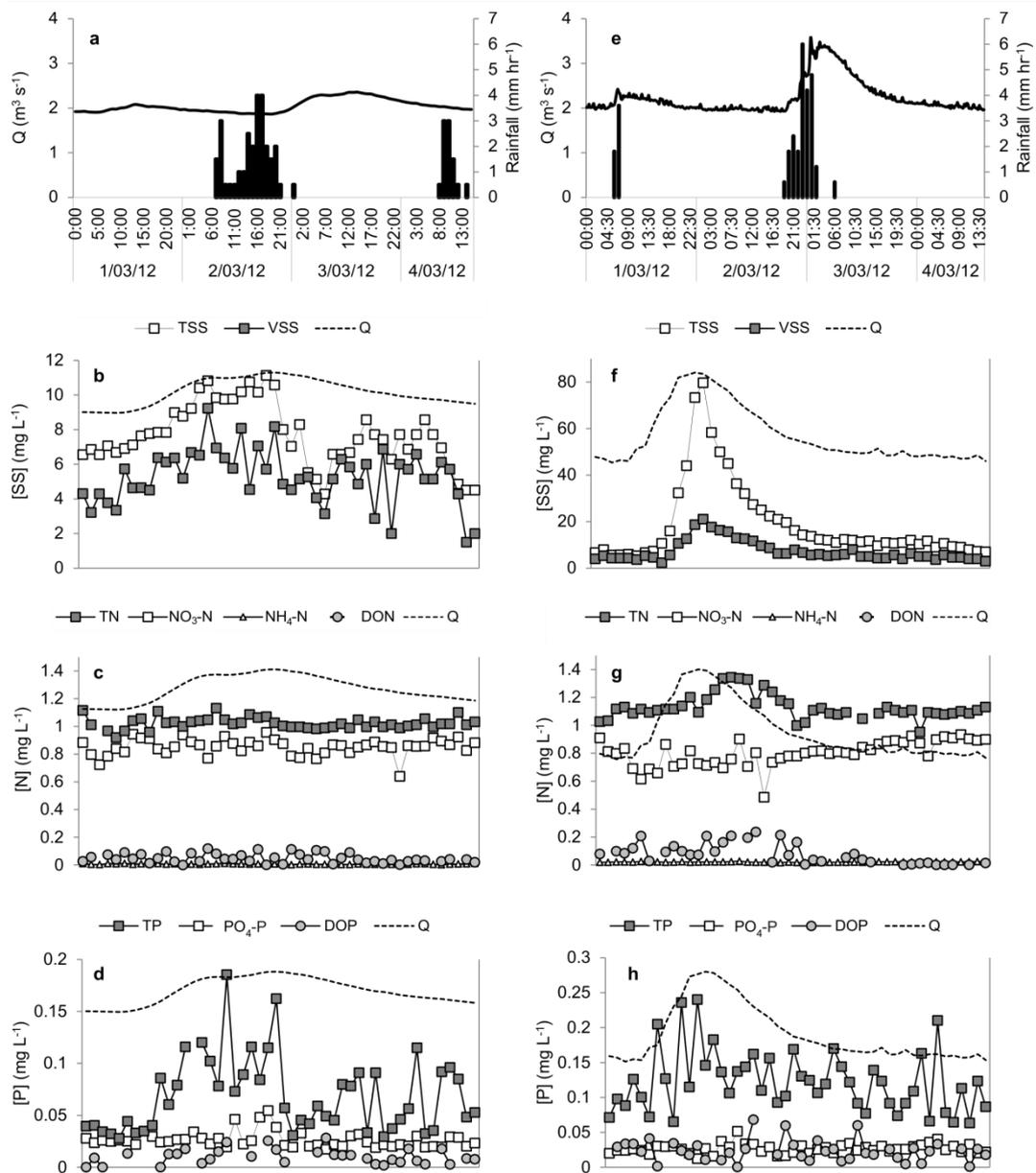


Figure 4.5 Temporal variations in measurements for the Ngongotaha Stream (left panels, a–d) and the Puarenga Stream (right panels, e–h) during simultaneous sampling of both streams in March 2012 (event # 5 and #13 respectively; Fig. 4.2). Scale for discharge (Q) data not shown on concentration plots.

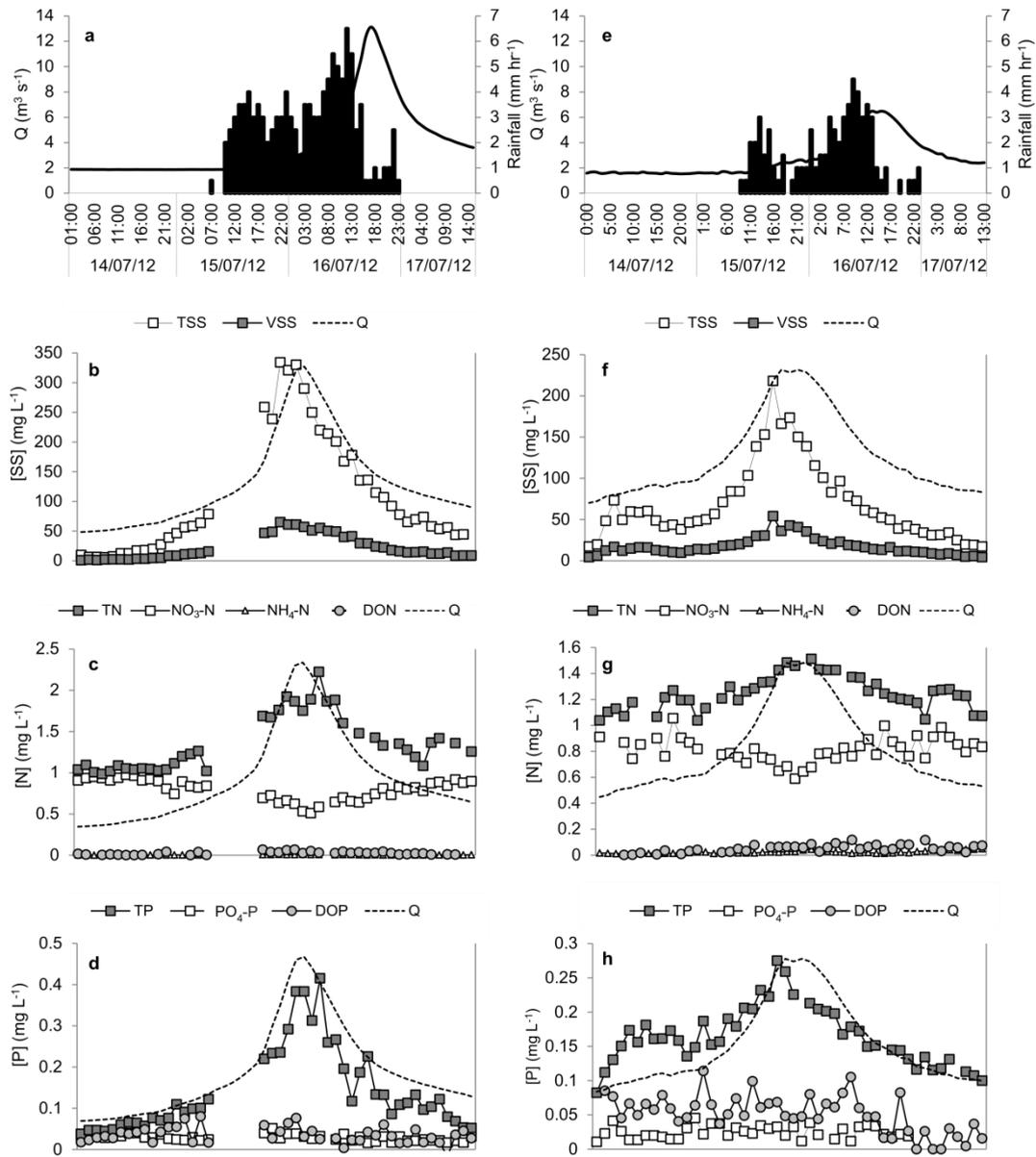


Figure 4.6 Temporal variations in measurements for the Ngongotaha Stream (left panels, a–d) and the Puarenga Stream (right panels, e–h) during simultaneous sampling of both streams in July 2012 (event # 6 and #14 respectively; Fig. 4.2). Scale for discharge (Q) data not shown on concentration plots. There was a 7–hour break in sampling (sampler malfunction) during the rising limb for Ngongotaha Stream data.

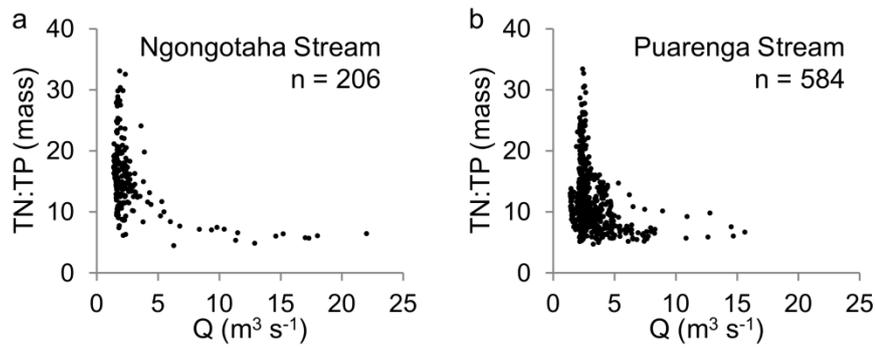


Figure 4.7 Relationships between measured TN:TP and discharge (Q) for the Ngongotaha (a) and Puarenga (b) streams.

4.3.3 Hysteresis in concentration–discharge relationships

Temporal trends in determinand concentration during events were not always aligned with variations in Q . For example, marked increases in concentrations of TN and TP in the Puarenga Stream (due to peaks in NO_3^- and PO_4^{3-} respectively) observed at the start of event # 7 occurred following very light rainfall that had negligible influence on Q , thereby suggesting flushing of local pollution sources (Figs. 4.4g and 4.4h). Similarly, TP concentrations in the Puarenga Stream display a distinct local peak during event # 14 approximately 16-h before Q_{\max} (Fig. 4.6h), consistent with apparent flushing of TSS (Fig. 4.6f).

Calculation of the response factor (p) and loop gradient term (g) allowed such hysteretic behaviour in concentration– Q relationships to be quantified (Table 4.2). Figure 4.8 shows examples of observed hysteresis in four determinands and illustrates relative differences between hysteresis loops with various values for p and g . Observed hysteresis in TN in the Puarenga Stream was always anticlockwise (i.e. $p < 0$; Fig. 4.8a) indicating relatively elevated concentrations during the recessing limb, an occurrence that usually reflected elevated $\text{NO}_3\text{-N}$ measured post Q_{\max} as recessing Q approached pre-event levels. Of the two examples of hysteresis in TN observed in the Ngongotaha Stream, one was small ($g = 2.97 \text{ g s}^{-1}$) and clockwise ($p > 0$; Fig. 4.8a), the other anticlockwise. Both clockwise and anticlockwise hysteresis in TP was observed in the Puarenga Stream and the largest TP hysteresis loops ($g = 0.51\text{--}0.97 \text{ g s}^{-1}$) observed in the Puarenga Stream were anticlockwise (e.g. Fig. 4.8b). Various hysteresis patterns were observed for TSS during all three events when both streams were concurrently sampled. For example, anticlockwise hysteresis was observed in both streams in the March 2011 event (medium-sized event in late summer; Figs.

4.4b, f), whereas clockwise hysteresis was observed for TSS in both streams during the July 2012 event (larger event in winter; Figs. 4.6b, 4.6f and 4.7c).

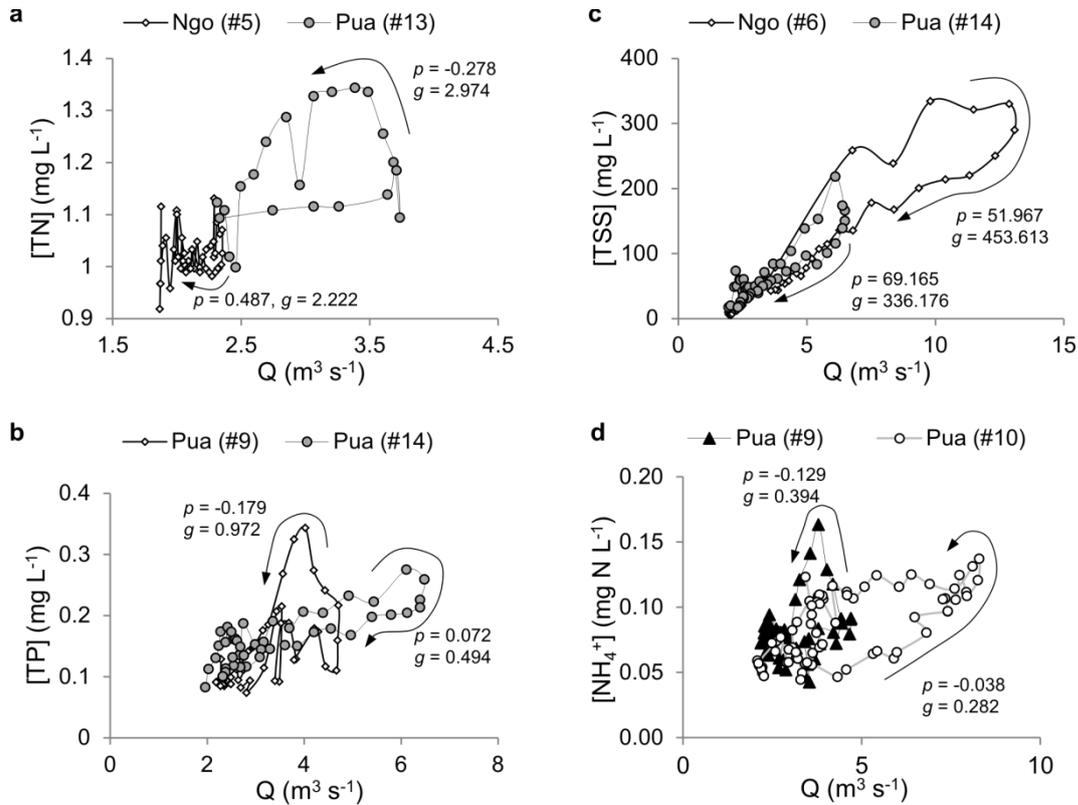


Figure 4.8 Examples of hysteresis loops in measured concentrations of total nitrogen (TN), total phosphorus (TP), total suspended sediments (TSS) and ammonium (NH_4^+) for the Ngongotaha (Ngo) and Puarenga (Pua) streams. Parameter p is a response factor ($\text{g m}^{-6} \text{h}^2$) that quantifies the magnitude of the hysteresis loop, as well as the direction, i.e. clockwise ($p > 0$, concentration higher during rising limb than the recessing limb) or anti-clockwise ($p < 0$, *vice versa*). Parameter g is a loop gradient term (g s^{-1}) that is related to the size of the loop.

Table 4.2 Characteristics of observed hysteresis loops in concentration–discharge data for the Ngongotaha (Ngo) and Puarenga streams (Pua). Parameter p is a response factor ($\text{g m}^{-6} \text{h}^2$) that quantifies the magnitude and direction of the hysteresis loop and g is a loop gradient term (g s^{-1}) (see Fig. 4.8). Numbered events shown in Fig. 4.2, symbols denote events for which both streams were simultaneously sampled. ‘×’ indicates that no hysteresis was evident from visual inspection of scatterplots. Time, length of sampling period; Q_{base} , mean discharge for samples collected prior to rising limb; Q_{max} , maximum discharge sampled; TN, total nitrogen; TP, total phosphorus; TSS, total suspended sediments.

| Stream | Event # | Time (h) | Q_{base} (n) ($\text{m}^3 \text{s}^{-1}$) | Q_{max} ($\text{m}^3 \text{s}^{-1}$) | TN | | NO ₃ -N | | NH ₄ -N | | TP | | PO ₄ -P | | TSS | |
|--------|---------|----------|---|--|-------|------|--------------------|------|--------------------|------|-------|------|--------------------|------|--------|--------|
| | | | | | P | g | p | g | p | g | p | g | p | g | p | g |
| Ngo. | 2† | 72.75 | 1.6 (11) | 2.7 | × | × | × | × | × | × | × | × | × | × | -3.62 | 57.34 |
| | 3 | 84.25 | 1.7 (9) | 3.1 | -1.74 | 2.95 | 0.03 | 1.55 | -0.10 | 0.16 | -0.13 | 0.22 | -0.02 | 0.08 | × | × |
| | 5* | 47.50 | 1.9 (6) | 2.4 | 0.49 | 2.22 | 0.64 | 2.07 | × | × | 0.42 | 0.59 | × | × | 36.97 | 29.64 |
| | 6‡ | 50.50 | 2.0 (3) | 13.1 | × | × | 0.01 | 1.23 | × | × | × | × | 0.01 | 0.04 | 51.97 | 453.61 |
| Pua. | 4 | 71.00 | 1.9(2) | 5.0 | -0.21 | 2.90 | -0.03 | 1.22 | -0.02 | 0.22 | × | × | × | × | - | - |
| | 5 | 47.50 | 2.2 (5) | 2.9 | × | × | × | × | × | × | × | × | × | × | × | × |
| | 6 | 73.25 | 1.8 (5) | 2.6 | × | × | × | × | × | × | × | × | × | × | × | × |
| | 7† | 71.50 | 2.2 (11) | 4.8 | × | × | 0.20 | 1.11 | 0.01 | 0.12 | 0.02 | 0.47 | 0.01 | 0.23 | -34.15 | 273.23 |
| | 8 | 35.0 | 2.2 (16) | 3.4 | × | × | × | × | × | × | -0.04 | 0.51 | 0.03 | 0.06 | -34.00 | 309.30 |
| | 9 | 49.25 | 2.7 (1) | 4.7 | -0.89 | 5.36 | -0.08 | 1.69 | -0.13 | 0.39 | -0.18 | 0.97 | × | × | -34.48 | 632.62 |
| | 10 | 71.00 | 2.2 (7) | 8.3 | -0.23 | 3.62 | -0.13 | 1.72 | -0.04 | 0.28 | -0.01 | 0.57 | × | × | × | × |
| | 13* | 48.00 | 2.1 (5) | 3.7 | -0.28 | 2.97 | × | × | × | × | × | × | -0.01 | 0.07 | -37.43 | 198.50 |
| | 14‡ | 48.00 | 2.0 (2) | 6.5 | -0.04 | 2.51 | × | × | -0.04 | 0.31 | 0.07 | 0.49 | × | × | 69.16 | 336.18 |

4.3.4 Storm load size and composition

During similar Q, TN, TP and TSS concentrations were typically lower in the Ngongotaha Stream (e.g. see 24-h EMCs in Table 4.1) and therefore loads during similar-sized events were lower than in the Puarenga Stream. Comparison of 24-h loads highlights large disparities between events of different magnitude that result from the positive correlation between determinand concentration and Q (Fig. 4.9). The largest measured 24-h loads of TN, TP and TSS for the Ngongotaha Stream were, respectively 9, 23 and 220 times greater than the smallest loads. For the Puarenga Stream, the largest measured 24-h loads of TN, TP and TSS were, respectively, 10, 9 and 10 times greater than the smallest loads.

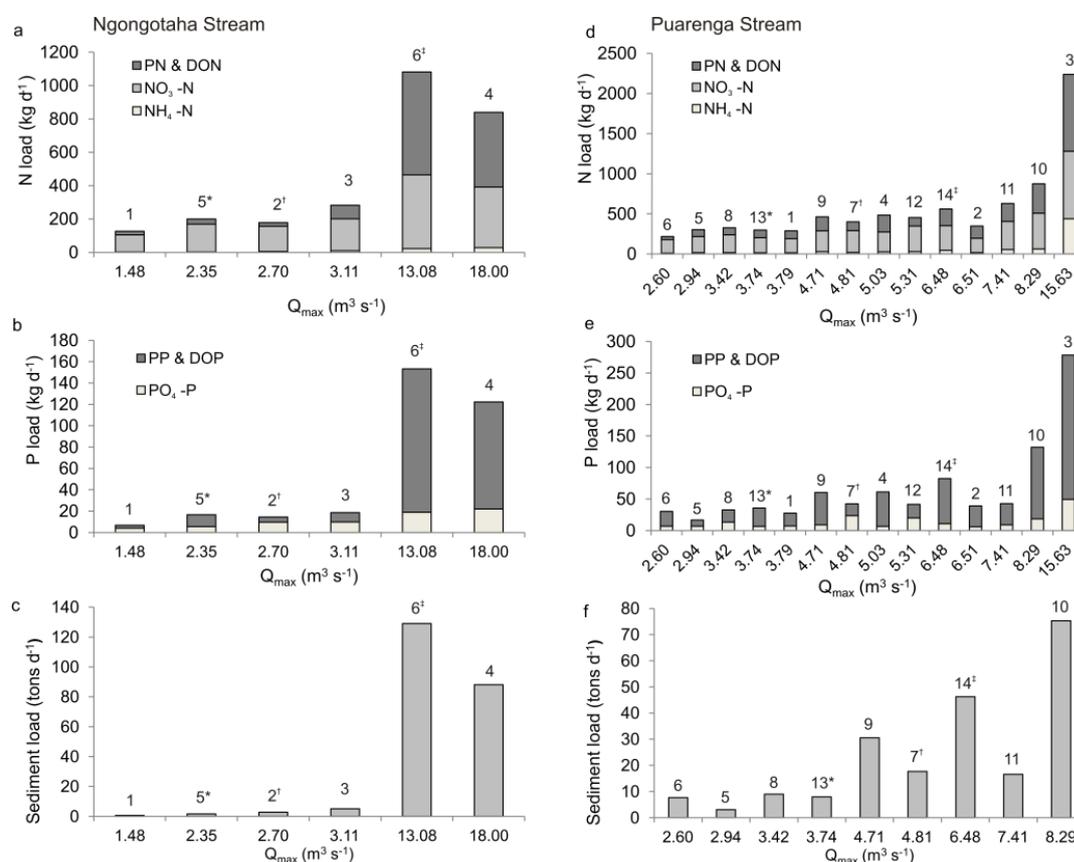


Figure 4.9 Measured 24-h loads of nutrients and suspended sediments conveyed in the Ngongotaha (a–c) and Puarenga (d–f) streams. PN, particulate nitrogen; DON, dissolved organic nitrogen; PP, particulate phosphorus; DOP, dissolved organic phosphorus; Q, discharge. Numbers above bars denote event numbers in Fig. 4.2, superscript symbols denote events for which both streams were simultaneously sampled.

Measured 24-h loads in the Ngongotaha Stream were higher for event #6 ($Q_{\max} = 13.1 \text{ m}^3 \text{ s}^{-1}$) than event #4 ($Q_{\max} = 18.0 \text{ m}^3 \text{ s}^{-1}$) because, despite higher Q_{\max} , the cumulative Q was 21% lower for event #4 during which only the rising limb and peak of the hydrograph were sampled (sampler was removed shortly after Q_{\max} to remove risk of damage to the instrument).

The relative contribution of dissolved inorganic nutrients to TN and TP loads decreased with increasing Q (Figs. 4.9a, b, d, e). This was particularly the case for TP; the contribution of $\text{PO}_4\text{-P}$ to measured 24-h loads of TP varied from 12% ($Q_{\max} = 13.1 \text{ m}^3 \text{ s}^{-1}$) to 66% ($Q_{\max} = 2.7 \text{ m}^3 \text{ s}^{-1}$) in the Ngongotaha Stream and from 11% ($Q_{\max} = 5.0 \text{ m}^3 \text{ s}^{-1}$) to 55% ($Q_{\max} = 4.8 \text{ m}^3 \text{ s}^{-1}$) in the Puarenga Stream. The majority of measured 24-h TN loads comprised predominantly dissolved inorganic N (Ngongotaha Stream range = 43–89%; Puarenga Stream range 57–82%), and the contribution of dissolved inorganic N to 24-h TN loads was less than 50% in only the two largest events sampled on the Ngongotaha Stream. Loads of $\text{NH}_4\text{-N}$ were typically minor compared to $\text{NO}_3\text{-N}$ loads although event # 3 for Puarenga Stream (autumn event with highest stream Q_{\max} sampled) was an exception: approximately 20% of the 24-h TN load comprised $\text{NH}_4\text{-N}$ (Fig. 4.9d) and $\text{NH}_4\text{-N}$ 24-h EMC (0.498 mg L^{-1} ; Table 4.1) was approximately an order of magnitude greater than for other events sampled. Measurements of DON (Figs. 4.4c, g; 4.5c, g; 4.6c, g) indicated that this fraction comprised a larger proportion of the TN in event loads transported in the Puarenga Stream (largely forested catchment) than in the Ngongotaha Stream. Loads of DON in the Puarenga Stream, expressed as a proportion of the 24-h TN loads, were 9% (event # 7), 27% (event # 13) and 20% (event # 14), whereas for the Ngongotaha Stream, DON comprised 3% (event # 2), 9% (event # 5) and 11% (event # 6) of the 24-h TN loads. Similarly, the relative contribution of DOP to 24-h TP loads was also highest in the Puarenga Stream. Proportions in the Puarenga Stream were 24% (event # 7), 17% (event # 13) and 30% (event # 14), compared to 0%, 14% and 15% in the Ngongotaha Stream.

Suspended sediment loads during events predominantly comprised inorganic sediments (e.g. Figs. 4.4b, f). The relative contribution of VSS to 24-h TSS loads was similar in both streams ($\approx 15\text{--}30\%$), although an atypically large proportion of the 24-h TSS load comprised VSS (69%) for Ngongotaha Stream event # 5, suggesting flushing of organic material accreted during the dry period prior to this very small event during late summer.

4.3.5 Comparison of load estimation methods

Table 4.3 presents comparison between estimated and measured 24-h loads. Measured loads are calculated using Eq. 1. Estimated loads are calculated using one averaging method (L_{avg} ; Eq. 4), one ratio method (L_{ratio} ; Eq. 6) and two regression methods (L_{rating} ; Eq. 7 and L_{hydro}).

The averaging method (that used mean concentrations of samples collected during routine monthly monitoring) substantially underestimated measured 24-h loads for TP, TN and TSS, as routine monitoring was typically conducted during base flow when TP, TN and TSS concentrations were lower than during storm events.

The ratio estimation method yielded imprecise loads (e.g. -61% to +183% error for TP loads). However, it generally yielded more accurate 24-h TN loads than the averaging method for the largest events. Of the regression methods, L_{hydro} was generally more accurate than L_{rating} , reflecting the inclusion of more independent variables (and subsequent higher predictive power) in models used to derive concentration estimates for L_{hydro} calculations. Differences between TN L_{hydro} and TN L_{rating} were, however, minor.

Table 4.3 Error in estimated 24-h loads of total nitrogen (TN) total phosphorus (TP) and total suspended sediment (TSS; not measured in all events) relative to measured loads conveyed in the Ngongotaha (Ngo) and Puarenga streams (Pua) during events shown in Fig. 4.2. Symbols denote events for which both streams were simultaneously sampled. Loads were derived using measured discharge (Q) and concentration data, estimated using regression models that incorporate discharge and other hydrological variables (L_{hydrol} ; Puarenga Stream TN and TP only), concentration–Q rating curves (L_{rating}), event mean concentrations calculated using data for other events (L_{ratio}) and mean values for samples collected during a routine monthly monitoring programme (L_{avg}). Q_{max} , maximum discharge sampled. Q_{avg} ; average hourly discharge during 24-h period ($\text{m}^3 \text{s}^{-1}$). Calculated TP L_{hydrol} was not derived for Puarenga event # 14 due to soil moisture probe malfunction.

| Stream | # | Q_{max} ($\text{m}^3 \text{s}^{-1}$) | Q_{avg} ($\text{m}^3 \text{s}^{-1}$) | TN load error | | | | TP load error | | | | TSS load error | | | |
|--------|-----|--|--|---------------------|---------------------|--------------------|------------------|---------------------|---------------------|--------------------|------------------|---------------------|---------------------|--------------------|------------------|
| | | | | L_{hydrol} | L_{rating} | L_{ratio} | L_{avg} | L_{hydrol} | L_{rating} | L_{ratio} | L_{avg} | L_{hydrol} | L_{rating} | L_{ratio} | L_{avg} |
| Ngo. | 1 | 1.5 | 1.4 | | -9% | 32% | -5% | | 90% | 183% | 7% | | -6% | 2446% | 99% |
| | 2† | 2.7 | 2.2 | | 16% | 53% | 5% | | -11% | 119% | -23% | | -17% | 737% | -34% |
| | 3 | 3.1 | 2.6 | | -14% | 12% | -22% | | 2% | 82% | -29% | | -29% | 441% | -58% |
| | 4 | 18.0 | 6.0 | | 5% | -21% | -40% | | 6% | -45% | -75% | | 197% | -49% | -94% |
| | 5* | 2.4 | 2.3 | | 6% | 40% | -5% | | -15% | 92% | -31% | | 50% | 1302% | 13% |
| | 6‡ | 13.1 | 7.5 | | -5% | -23% | -41% | | -15% | -45% | -75% | | -37% | -61% | -95% |
| Pua. | 1 | 3.8 | 2.5 | -7% | -3% | 8% | -7% | -7% | -16% | 13% | -43% | | | | |
| | 2 | 6.5 | 2.6 | -24% | -20% | -10% | -32% | -23% | -35% | -16% | -50% | | | | |
| | 3 | 15.6 | 10.2 | -39% | -50% | -47% | -57% | -16% | -31% | -61% | -75% | | | | |
| | 4 | 5.0 | 3.7 | -12% | -34% | -7% | -28% | -29% | -30% | -25% | -56% | | | | |
| | 5 | 2.9 | 2.5 | -10% | -8% | -1% | -20% | 37% | 52% | 99% | 14% | 58% | 271% | -10% | |
| | 6 | 2.6 | 2.2 | 14% | 14% | 24% | -2% | -18% | -37% | -8% | -45% | -63% | 30% | -68% | |
| | 7† | 4.8 | 3.7 | 12% | 14% | 16% | -13% | 21% | 6% | 8% | -37% | -9% | -3% | -78% | |
| | 8 | 3.4 | 2.9 | -17% | 5% | 11% | -15% | 5% | -3% | 12% | -34% | -4% | 50% | -65% | |
| | 9 | 4.7 | 3.8 | -19% | 2% | 1% | -22% | -27% | -23% | -24% | -54% | -49% | -46% | -87% | |
| | 10 | 8.3 | 6.8 | 16% | 16% | -3% | -26% | -16% | -15% | -38% | -62% | 33% | -66% | -90% | |
| | 11 | 7.4 | 5.1 | 2% | 8% | 1% | -23% | 83% | 85% | 51% | -12% | 200% | 40% | -67% | |
| | 12 | 5.3 | 4.4 | -3% | 21% | 21% | -8% | 33% | 36% | 29% | -22% | | | | |
| | 13* | 3.7 | 2.9 | 17% | 16% | 25% | -6% | -15% | -12% | 4% | -39% | 0% | 73% | -60% | |
| | 14‡ | 6.5 | 4.7 | 12% | 12% | 6% | -19% | | -21% | -29% | -57% | -28% | -58% | -89% | |

4.3.6 Temporal inequality in sediment and nutrient loading

Regression models fitted to measured hydrological variables and concentrations of TN, TP and TSS (Table 4.4) were used to estimate cumulative hourly loads over the two-year period of May 2010–May 2012. All models included Q as an independent variable with positive coefficient, reflecting the positive correlation between the three determinands and Q . Equations 9 and 10 were used to estimate concentrations of TN and TP respectively in the Puarenga stream, as the inclusion in these models of hydrological variables in addition to Q_i improved predictive power. Regression coefficients and y intercept values for these equations were fitted using all measured data (see Table 4.4 for full equations). Given the high number of independent variables in the TP model, there was uncertainty about the validity of extrapolating to periods when antecedent hydrological characteristics deviated markedly from those during sampling. Consequently, a linear \log_{10} – \log_{10} rating curve was used to estimate TP concentration based on Q_i for periods when estimated TP concentration exceeded the maximum that was measured (0.543 mg L^{-1} ; 4% of time period). Linear \log_{10} – \log_{10} rating curves with high r^2 values (0.72 and 0.68 respectively) were used to estimate measured TN and TP concentration for the Ngongotaha stream. A linear \log_{10} – \log_{10} rating curve was used to estimate TSS concentration in the Puarenga Stream although a marginally poorer-fitting power function (exponent < 1) was used to estimate TSS concentration when Q exceeded the Q_{\max} during TSS sampling ($10.81 \text{ m}^3 \text{ s}^{-1}$; 0.6% of time period) in order to minimise likelihood of over-estimating concentration during high Q periods which contribute disproportionately to cumulative load. Similarly, a power function with exponent < 1 provided good approximation of measured TSS concentration in Ngongotaha Stream samples and was applied to the measured Q range. Maximum estimated concentrations (mg L^{-1}) of TN, TP and TSS, relative to maximum measured concentrations (in parentheses), for the two-year period were 2.78 (2.75), 0.788 (0.427) and 2250 (510.46) respectively in the Ngongotaha Stream and 2.58 (3.096), 0.542 (0.543) and 682.46 (462.54) respectively in the Puarenga Stream.

Table 4.4 Summary of regression models used to estimate the concentration of total nitrogen (TN), total phosphorus (TP) and total suspended sediment (TSS) in the Ngongotaha and Puarenga streams over a two year period. Q_i , discharge ($\text{m}^3 \text{s}^{-1}$) at time i ; rain_6 , sum of rainfall (mm) in the previous 6 h ($\log_{10} + 1$ transformed); soil, soil moisture (%) (square-root transformed). Root mean squared error of estimates was calculated for a bootstrapped sample ($n = 10000$) drawn from measured data. α denotes statistical significance.

| Stream | Dependent variable (mg L^{-1}) | Regression model | n | r^2 | RMSE (untransformed units; mg L^{-1}) | α |
|------------|--|--|-----|-------|--|----------|
| Ngongotaha | \log_{10} TN | $0.321 \times \log_{10} Q_i - 0.090$ | 247 | 0.72 | 0.13 | <0.001 |
| | \log_{10} TP | $0.801 \times \log_{10} Q_i - 1.666$ | 260 | 0.68 | 0.027 | <0.001 |
| | \log_{10} TSS | $2.296 \times (\log_{10} Q_i)^{0.740}$ | 256 | 0.85 | 38.49 | <0.001 |
| Puarenga | \log_{10} TN | $0.239 \times \log_{10} Q_i - [0.096 \times (Q_i/Q_{i-3 \text{ h}})] + 0.108$ | 581 | 0.23 | 0.27 | <0.001 |
| | \log_{10} TP | $0.632 \times \log_{10} Q_i - [2.01 \times (Q_i/Q_{i-1.5 \text{ h}})] + 0.018 \times \text{rain}_6 - 0.096 \times \text{soil} - 0.397$ | 608 | 0.39 | 0.042 | <0.001 |
| | \log_{10} TP | $0.5549 \times \log_{10} Q_i - 1.193$ | 654 | 0.30 | 0.045 | <0.001 |
| | \log_{10} TSS | $2.018 \times \log_{10} Q_i + 0.437$ | 507 | 0.65 | 24.81 | <0.001 |
| | | $2.161 \times (\log_{10} Q_i)^{0.626}$ | 507 | 0.60 | 27.64 | <0.001 |

Plotting cumulative estimated loads as a function of cumulative time allowed temporal inequality in pollutant loading over the two-year period (May 2010–May 2012) to be examined (Fig 4.10). Gini coefficients for individual determinands were ordered as follows in both streams: $TN < TP < TSS$. Temporal inequality in loading was therefore lowest for TN and highest for TSS, i.e. a given proportion of the TSS total load was transported to the lake in a shorter time than the same proportion of the TN load when estimated hourly loads are arranged in order of increasing magnitude and the largest loads are considered. The value of G for TN was the same in both streams (0.312) indicating, for example, that 50% of the TN load in both streams was transported in approximately 28% of the time (expressed as days in Table 4.5; minor difference between catchments reflects rounding of G). Gini coefficients for TP and TSS were highest for estimates of loads conveyed in the Ngongotaha Stream; 50% of estimated TP loading occurred for 10% of time for the Ngongotaha Stream ($G = 0.511$), compared to 17% of time for the Puarenga Stream ($G = 0.455$). Extremely high inequality for TSS load estimates implies that 50% of the total TSS load over the two-year period was estimated to have been transported in a cumulative time equivalent to approximately just 1 day for the Ngongotaha Stream ($G = 0.909$) and 7.5 days for the Puarenga Stream ($G = 0.793$). Expressing G in terms of days aids interpretation although it is important to note that one ‘day’ may, for example, comprise 24 separate 1-h periods during Q_{\max} of 24 events.

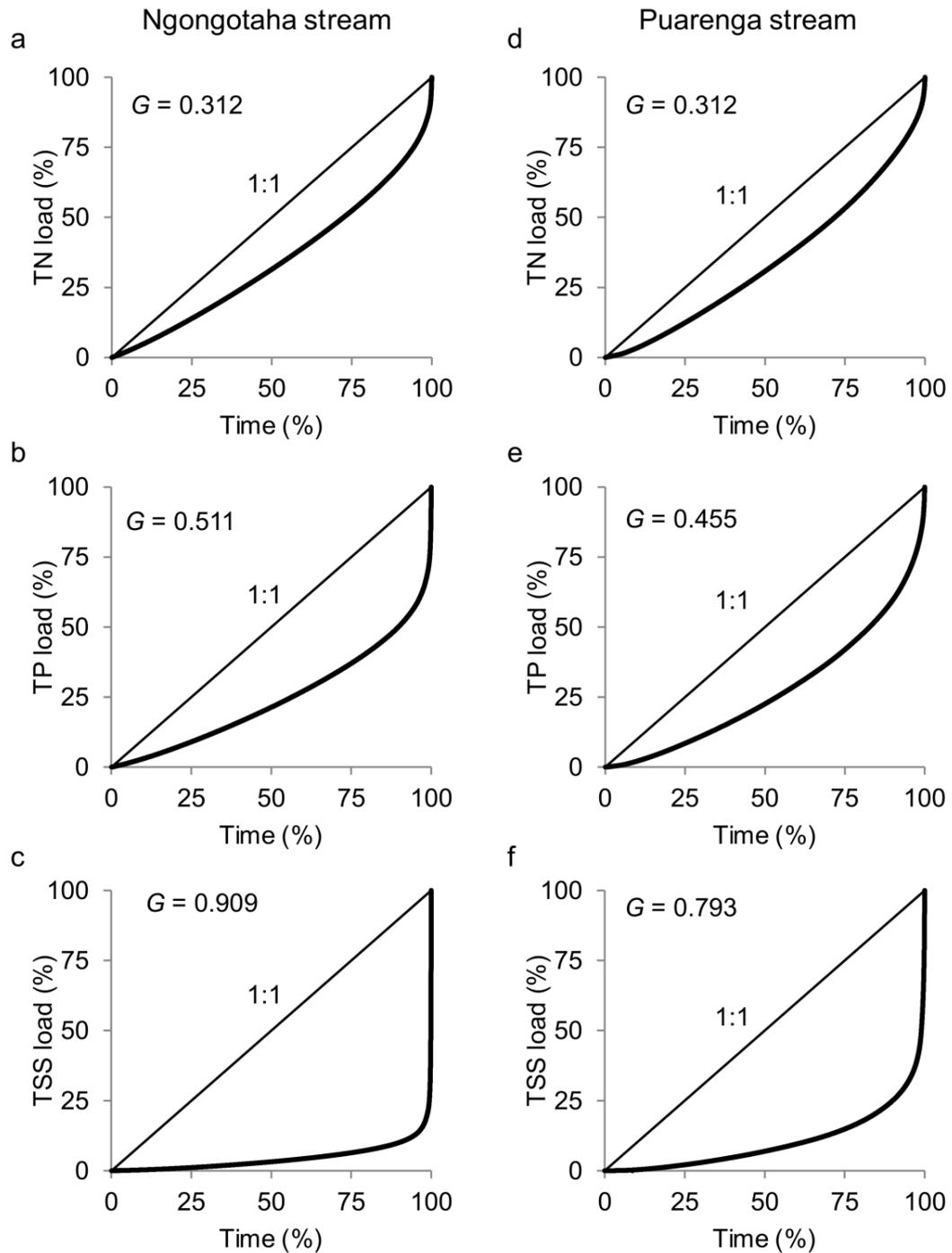


Figure 4.10 Lorenz curves describing the relationship between cumulative proportion of estimated hourly loads during two–years (May 2010–May 2012) and cumulative proportion of time for the Ngongotaha (a–c) and the Puarenga (d–f) streams. Gini coefficients (G) quantify temporal inequality in loading (see Fig. 4.3 for calculation method). TN, total nitrogen; TP, total phosphorus; TSS, total suspended sediments.

Table 4.5 Estimated shortest time (nearest 0.5 d) during which 25% and 50% of the total loads of total nitrogen (TN) total phosphorus (TP) and total suspended sediment (TSS) were conveyed in the Ngongotaha and Puarenga streams during a two–year period (May 2012– May 2012). Estimates are based on modelled hourly loads and ‘days’ do not necessarily comprise consecutive hours.

| Proportion of cumulative load | Time (d) | | | | | |
|----------------------------------|-------------------|------|-----|-----------------|-------|-----|
| | Ngongotaha Stream | | | Puarenga Stream | | |
| | TN | TP | TSS | TN | TP | TSS |
| 50% | 201.5 | 75.5 | 1.0 | 206.5 | 126.0 | 7.5 |
| 25% | 41.5 | 3.5 | 0.5 | 57.5 | 23.0 | 1.5 |

4.3.7 Yield estimates

Two–year load estimates derived using regression models to estimate concentration (see above) were used to estimate yields of TN, TP and TSS from each stream surface catchment on a per unit area basis (Table 4.6). Estimated yields of TN were very similar for the catchments ($\approx 12.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$) while TP yield was approximately 30% higher in the Puarenga stream catchment ($1.34 \text{ kg ha}^{-1} \text{ yr}^{-1}$) compared to the Ngongotaha stream catchment ($1.01 \text{ kg ha}^{-1} \text{ yr}^{-1}$). Estimated yield of TSS was markedly greater in the Ngongotaha Stream catchment ($741 \text{ kg ha}^{-1} \text{ yr}^{-1}$) compared to the Puarenga Stream catchment ($479 \text{ kg ha}^{-1} \text{ yr}^{-1}$). This difference can, however, be attributed largely to the occurrence of larger peak Q during the two flood events in January 2011; TSS yield estimates made without inclusion of the flood peaks (substitution of Q_{50} for the nine–day period) are comparable for the two catchments ($\approx 350 \text{ kg ha}^{-1} \text{ yr}^{-1}$). These large events were not sampled and, consequently, contribute considerable uncertainty to load estimates.

Table 4.6 Estimated yields of total nitrogen (TN), total phosphorus (TP) and total suspended sediment (TSS) from the Ngongotaha and Puarenga surface stream catchments. Yields are based on estimated loads during May 2010–May 2012. Yields are calculated with and without (discharge during 23/01 – 01/02 replaced with median values) inclusion of the two large floods in January 2011 (see Fig. 4.2).

| Stream catchment | Jan 2011 storms included? | Yield (kg ha ⁻¹ yr ⁻¹) | | |
|------------------|---------------------------|---|------|-----|
| | | TN | TP | TSS |
| Ngongotaha | Y | 12.73 | 1.01 | 741 |
| | N | 11.90 | 0.90 | 359 |
| Puarenga | Y | 12.71 | 1.34 | 479 |
| | N | 12.00 | 1.22 | 330 |

4.4 Discussion

4.4.1 Summary

By analysing data for > 900 samples collected during 17 hydrological events, this study provides insight into how hydrological and catchment characteristics interact to influence sediment and nutrient transport across landscapes. High-frequency sampling during a wide range of discharge (Q) enabled relationships between Q and concentrations of various suspended sediment and nutrient fractions to be determined. Quantification of hysteretic behaviour in these relationships provided information about likely relative importance of far- versus near-channel sources during individual events. Lastly, quantification of temporal inequality in loading highlighted the importance of considering storm flow processes in loading estimates and emphasised the potentially highly disproportionate contribution of individual flood peaks to estimates of annual-scale loads to a nationally iconic lake.

4.4.2 Temporal variations in nutrient and suspended sediment concentration during events

The relationships between concentration and Q for individual determinands were broadly similar between the two streams. The observed decreases in NO₃-N concentration during storm flow can be attributed to dilution by rainfall of steady inputs to the stream channels from groundwater sources high in NO₃⁻. Studies

elsewhere have similarly reported dilution of NO_3^- following onset of storm flow, typically followed by increases in NO_3^- to above pre-event concentrations (Salvia–Castellví et al. 2005, Vanni et al. 2001, Zhu et al. 2011), as was frequently observed in data for the Puarenga Stream. In general though, maximum observed post-event increases in NO_3^- were relatively modest (e.g. $\approx 25\%$ above pre-event $\text{NO}_3\text{-N}$ for Puarenga Stream event # 10); by contrast, Vanni et al. (2001) report up to five-fold increases in $\text{NO}_3\text{-N}$ concentrations for the recessing limb in a stream draining a predominantly arable catchment, while Oeurng et al. (2010) report increases in NO_3^- from approximately 8 mg N L^{-1} to $> 30 \text{ mg N L}^{-1}$ in a large French river, even after small events. Such behaviour likely reflects diffuse delivery of NO_3^- to the stream channel by throughflow processes and accounts for the anticlockwise hysteresis in NO_3^- observed during several events for the Puarenga Stream (but not the Ngongotaha Stream) (Table 4.2). This result also accounts for the significance of $Q_i/Q_{i-3 \text{ h}}$ as an independent variable (negative coefficient) in the regression model used to predict TN concentrations for the Puarenga Stream.

The lack of relationship between concentrations of $\text{PO}_4\text{-P}$ and Q that was generally observed conforms to the ‘Type 1’ classification proposed by Haygarth et al. (2004) who note that such behaviour likely reflects occurrence of steady state between the dissolution kinetics of the soil and stream water. The coarse volcanic soils in the lake catchment are high in allophanic clays which have high capacity to adsorb P (Parfitt 1990) and, therefore, stream sediments likely buffer PO_4^{3-} in stream water via either adsorption or desorption processes (Mayer & Gloss 1980). When either peaks or hystereses in $\text{PO}_4\text{-P}$ were apparent, they were typically during small events (e.g. Table 4.2, Fig. 4.4d) or outside of the period of storm flow (e.g. Fig. 4h). It is possible, therefore, that ratios of TSS to $\text{PO}_4\text{-P}$ were insufficient during these periods to readily buffer elevated $\text{PO}_4\text{-P}$ arising from flushing processes.

While concentrations of TP may be unrelated to Q in some catchments (e.g. in intensively farmed catchments where P delivery is highly influenced by temporal variability in sources; see McDowell and Wilcock 2007), the strong positive relationship between concentrations of TP and Q has been observed elsewhere (e.g. Drewry et al. 2009, Salvia–Castellví et al. 2005, Stutter et al. 2008) and generally reflected mobilisation of inorganic particulate phosphorus (PP) by erosive processes during storm flow. Consequently, concentrations of

TSS and TP were highly correlated (e.g. compare Fig 4.6f and 4.6h) and, where observed, the direction of hysteresis with Q tended to be the same for both determinands suggesting similarity of sources. The importance of erosive processes in determining TP variations is reflected in the inclusion of both rainfall and soil moisture content (positive coefficients) as independent variables in the regression model used to predict TP concentrations for the Puarenga Stream; both these variables directly influence overland flow, which is the dominant transport mechanism for PP across landscapes (McDowell et al. 2004). The strong correlation between TP and Q accounted for the frequent large underestimations in TP loads (more so than for TN) when using averaging methods based on samples predominantly collected during base flow periods (L_{avg} ; Table 4.3).

Concentrations of suspended sediments consistently increased with Q although some occurrence of hysteretic behaviour implied that variability in supply processes affected the linearity of this relationship (Burns 2005). Specifically, occurrence of clockwise hysteresis during larger events (e.g. Ngongotaha Stream event # 6; Fig. 4.8c) indicated depletion of within- or near-channel sediment sources (these two source areas cannot be distinguished), while anticlockwise hysteresis indicated delayed delivery of sediments from far-channel sources to the stream channel. (e.g. Puarenga Stream events # 7, # 8, # 9 and # 13; Table 4.2)

4.4.3 Variations in nutrient and suspended sediment transport between catchments

Given the predominant land use in the two catchments, it is interesting to note that base flow concentrations of all N and P fractions were typically greater (although marginally so for PO_4^{3-}) in the Puarenga Stream (mixed land use but predominantly forested) than in the Ngongotaha Stream (pasture dominated) since, relative to forested catchments, the occurrence of high nutrient concentrations in streams draining agricultural land is well established in New Zealand (Larned et al. 2004) and elsewhere (Allan 2004). In the case of N, it is noted that NO_3-N was the main component of TN which, as discussed above, originates from groundwater sources. Therefore, due to discontinuity between surface and groundwater catchments that is present in the Lake Rotorua catchment (Morgenstern et al. 2005), groundwater chemistry does not necessarily reflect overlying land use. Furthermore, the large storage capacity of local aquifers

means that mean residence time for nutrients in groundwater is in the order of decades (e.g. 16 years for the Ngongotaha Stream catchment; *ibid*) and, therefore, the effects of current catchment land use are yet to be fully realised given the short time elapsed since agricultural intensification began in the lake catchment (i.e. mainly post-1940; Rutherford et al. 2011). There is, however, evidence that recent nutrient-enrichment of the Ngongotaha Stream has occurred in conjunction with land use intensification; concentrations of $\text{NO}_3\text{-N}$ measured when Q was below the median for the study period (0.84 mg L^{-1} , $n = 110$) were 60% higher than mean base flow $\text{NO}_3\text{-N}$ reported by Hoare (1982) for 1975–1978 (0.53 mg L^{-1}), a period since which substantial agricultural intensification has occurred in the stream catchment (Rutherford et al. 2011). In addition, it is noted that there are numerous potential N sources in the Puarenga catchment, including naturally NH_4 -enriched geothermal springs (Morgenstern et al. 2005), suburban land, farmland, and a waste water application area where N-enriched treated effluent is spray irrigated. Owing to the local free-draining soils, dissolved N in treated effluent has been shown to readily leach from experimental plots in the Puarenga catchment (Magesan et al. 1998) and data following hydrological events do exhibit evidence of flushing in the catchment of both $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ that could potentially have originated from effluent sources (e.g. note unusually high $\text{NH}_4\text{-N}$ 24-EMC following event # 3 and anticlockwise hysteresis for both determinands; Tables 4.1 and 4.2). Methods used in this study cannot, however, be used to isolate the influence of individual sources, although data collected provide a comprehensive baseline to examine future trends and further assess potential environmental impacts of land management practices.

The higher TP concentrations generally measured in the Puarenga Stream reflect the typically higher TSS concentrations which, as discussed above, are a strong determinant of PP, which was the dominant P fraction in samples. The relatively high TSS in the Puarenga Stream likely reflects the predominance of exotic forestry which has been shown to be related to elevated TSS in New Zealand streams; e.g. Quinn & Stroud (2002) found that median TSS concentration (18.1 mg L^{-1}) in a stream draining a pine-forested catchment was the highest of seven sites with contrasting land use. Association between elevated TSS and exotic forestry can be attributed to the general lack of ground cover vegetation under plantation trees which promotes the formation of gully networks, the connectivity of which is a critical factor in influencing sediment transport in

larger catchments (>10 km²) where sediment flux tends to be transport– rather than supply–limited (de Vente & Poesen 2005). Plantation forest can also be associated with critical source areas such as unsealed logging roads which can represent disproportionately large sources of sediment (Lane & Sheridan 2002). In addition, the ability of the Puarenga Stream to transport TSS (and hence PP) during its typical range of Q, is likely to be higher due to the high drainage density of the catchment and short distances between headwaters and sampling location (Fig. 4.1).

Despite generally higher base flow concentrations for nutrient and suspended sediment fractions, estimated yields of TN and TSS were, respectively, either comparable or lower for the Puarenga Stream compared to the Ngongotaha Stream (Table 4.6). This partly reflects difference in area but also differences in hydrology between the two catchments, as, due to the disproportionate influence of large storm flows on loading (Fig. 4.10; Table 4.5), the occurrence of larger storm flow peaks (reflecting local variation in rainfall between the catchments and, potentially, variability in water yield related to land use differences) compensated for lower loading rates during base flows. Given the unusually high rainfall during the study period, particularly in January of 2011 and 2012, yields calculated in this study are not necessarily representative of longer–term loading for the two catchments. Higher estimated TP yields for the Puarenga Stream catchment reflect the relatively much higher TP concentrations for base flow conditions in this stream and the TP yields are an order of magnitude higher than in another study that estimated TP yield from a pine forested catchment in New Zealand (Cooper & Thomsen 1988).

4.4.4 Implications for lake water quality and management

Nutrient enrichment experiments have demonstrated both N– and P– limitation of phytoplankton biomass in Lake Rotorua (Burger et al. 2007a); consequently, excess addition of either nutrient has the potential to promote undesirable phytoplankton growth. The relatively high contribution of dissolved inorganic nutrients to TN in event loads means rain events have the potential to cause delivery of high loads of labile N to Lake Rotorua over short periods. The implications of this for water quality will depend on ambient physical, chemical and biological conditions; the mechanisms by which storm events mediate phytoplankton resource limitation in lakes are complex, and include enhanced

light limitation and increased flushing, in addition to relaxation of nutrient limitation (Vanni et al. 2006).

By contrast, the extent to which TP transported during hydrological events can be utilised by primary producers downstream is less certain, owing to the high proportion of PP present in TP event loads (Fig. 4.9b). The short-term bioavailability of PP in storm flow has been shown to vary from 25–75% for a hardwater catchment with loamy brown earth soils (Pacini & Gachter 1999), although Hatch et al. (1999) observed no stimulation of phytoplankton growth following addition of PP associated with particles $> 0.45 \mu\text{m}$ sourced from the Lake Tahoe (California, USA) catchment. Due to the lower bioavailability of mineral PP relative to dissolved P, Lewis et al. (2011) propose that it may be preferable to use only dissolved P (i.e. $\text{PO}_4\text{-P}$) as a basis for assigning loading limits for lakes. Such a policy cannot, however, be endorsed for Lake Rotorua as previous work has highlighted the significance of benthic releases of PO_4^{3-} that occur when low oxygen conditions prevail in the hypolimnion (e.g. during summer stratification) (Burger et al. 2007b). Although the chemical composition of PP was not examined in this study, allophanic sediments from the central North Island region of New Zealand can be high in Fe which can form redox-sensitive complexes with $\text{PO}_4\text{-P}$ (Evans et al. 2004, Parfitt 1990). Therefore, although stream-borne PP may not be immediately bioavailable in the receiving lake environment, the disproportionately high loading of PP to the lake during high Q that is typically unaccounted during routine monthly monitoring, should be an important consideration for lake managers, given the known status of sediments as the largest source of $\text{PO}_4\text{-P}$ to the lake over annual periods (Burger et al. 2007b). Further investigation of P-sorption characteristics (e.g. water-soluble P and equilibrium P concentrations) of TSS and potential sediment sources such as stream banks, channel beds and gully slopes could help to better quantify the potential for PP originated from eroded material to contribute to eutrophication in Lake Rotorua (Pothig et al. 2010).

The potential for few large events to account for the majority of TSS and TP loading has been observed elsewhere. For example, Salvia-Castellví et al. (2005) note that annual TP loads in a rural stream are dominated by TP transported during the rising limb of only a small number of storm events each year. Empirical approaches to load estimation that fail to consider the strong relationship between TP and Q will substantially underestimate TP loads to the

lake (Table 4.3), while inter-annual variation in the size and frequency of floods means that error may be large if static nutrient export coefficients based only on land use are used to estimate nutrient transport in a particular year. A more sophisticated approach to export coefficient modelling that estimates nutrient yields as a function of land management and inter annual variability in hydrological factors (in addition to solely land use; see Johnes 1996) could potentially reduce error in load estimation. Adoption of such an approach is currently hindered, however, by lack of fine-scale data regarding land management. Also, the temporal scale of load estimates provided by such approaches (i.e. typically annual) is too coarse for modelling downstream effects on water quality using dynamic ecosystem models which require daily or sub-daily resolution forcing data. For this application, regression or ratio estimation approaches that reflect concentration-Q relationships are therefore preferable, and, in the case of ratio estimators, a stratified approach based on Q_{\max} could be used to improve precision. Such techniques are dependent, however, on the availability of catchment-specific event-based samples which are costly and laborious to collect. Moreover, they require periodic review and modification to account for temporal variability in empirical relationships which arise due to changes in factors such as land management and climate that can alter the underlying processes that regulate pollutant transport in catchments. Dynamic process-based models could potentially resolve issues around accounting for temporal (e.g. due to land use change) and spatial differences in transport processes between sub-catchments and, consequently, aid estimation of pollutant flux where fewer data are available (Wade et al. 2008). Such an approach would still though require catchment-specific field data for calibration/validation, and the complex groundwater interactions in the lake catchment also present a challenge to adoption of more mechanistic models.

High temporal inequality in loading shown in this study underlines the importance of best management practices designed to minimise erosion (e.g. see McDowell & Nash 2012) for controlling sediment-associated pollutant loads to the lake. Although implementation of many such actions has already occurred in parts of the lake catchment (Williamson et al. 1996), the predicted increase in the frequency and magnitude of extreme rainfall events for New Zealand (IPCC 2007) enhances the importance of widely adopting sustainable land management practices. Increased predicted climatic variability will also likely make it more

difficult to characterise trends in lake water quality, i.e. the disproportionate significance of individual high Q events for nutrient loading means that it will be an increasing challenge for lake managers to distinguish changes in lake water quality due to specific management actions from those due to fluctuation in wider hydrological factors.

4.5 References

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5 Biogeochemical processes and phytoplankton nutrient limitation in the inflow transition zone of a large eutrophic lake during stream storm flow

5.1 Introduction

Ecosystems can be considered to comprise concentration gradients in space and time (Muller, 1998). Such an approach is particularly pertinent for lakes, owing to their pronounced spatial and temporal heterogeneity (Kratz et al., 2005). At a fundamental level, the distribution of phytoplankton biomass in a lake is regulated both stoichiometrically by available nutrients, and also by ‘processing fluxes’ which relate to photosynthetic active radiation (PAR), carbon and oxidation (Reynolds, 2002).

Vertical variation is a well-recognised trait of lake ecosystems; examples include: attenuation of downwelling photosynthetically active radiation (PAR) and differences in nutrient abundance between the hypolimnion and the surface mixed layer that arise in association with seasonal cycles of stratification (Lewis, 1983; Kratz et al., 2005). Such vertical variations can result in concomitant gradients in the density of primary producers (Hamilton et al., 2010), which, in the case of phytoplankton, may be mediated by behavioural traits (e.g. motility) that assist in aggregation. In contrast, horizontal heterogeneity in lakes has been far less studied; programmes to monitor water quality in many lakes frequently ignore horizontal differences by assuming that a single sampling location is representative of an entire lake. Despite this, numerous studies have highlighted the potential for horizontal heterogeneity (‘patchiness’) within lakes, reporting marked variation in biogeochemical parameters such as nutrient concentrations or phytoplankton biomass metrics over scales of 10^3 – 10^5 m (e.g. Hillmer et al., 2008; Scott et al., 2009; von Westernhagen et al., 2010; Sorokovikova et al., 2012), 10 – 10^3 m (e.g. Mackay et al., 2011a; Mackay et al., 2011b) and 10^{-3} – 10^{-1} m (Barker et al., 2010).

Chemical, physical and biological gradients can be particularly pronounced at the lotic–lentic transition where a stream enters a lake (Izydorczyk et al., 2008; Scott et al., 2009; Mackay et al., 2011a). Stream inflows provide a variable source of dissolved nutrients which may either undergo active

transformation (e.g. adsorption, biological assimilation, redox reactions) in the receiving lake environment or disperse conservatively (Mackay et al., 2011a). Similarly, entrained sediments may settle at the mouth of the inflow or be transported elsewhere in the lake, depending on particle characteristics, as well as turbulent mixing and advective processes in the transition zone (Fischer et al., 1979). Propagation of a stream inflow is influenced by differences in density between the stream and the lake that can arise due to discontinuity in temperature, salinity and particulate matter composition (Imberger & Patterson, 1990). A stream inflow that is positively buoyant will overflow the surface of the lake (Na & Park, 2006), while a relatively dense stream flowing into a lake basin will plunge, and, depending on the vertical density profile of the lake, either intrude horizontally into the water column at a lower depth (Marti et al., 2011), or spread across the bed as an underflow (Romero & Imberger, 2003). The horizontal trajectory of an inflow will vary depending on several factors, including: lake–bed topography (Rueda & MacIntyre, 2010), ambient wind forcing (*ibid*), geostrophic forcing arising from Earth’s circulation (Csanady, 1977), the occurrence of dynamic interaction with the shoreline (Jones et al., 2007) and the internal wave field (Fischer & Smith, 1983; Laborde et al., 2010). The propagation characteristics of a lake inflow have important implications for ecosystem functioning. For example, intrusion of turbid inflows into the photic zone can induce light limitation (Schallenberg et al., 1999) or alleviate nutrient limitation through enhanced nutrient loading (Na & Park, 2006; Vidal et al., 2012). Alternatively, particulate forms of nutrients that are otherwise refractory could become labile if entrained in negatively buoyant inflows and transported to anoxic hypolimnetic waters (Burger et al., 2007a).

Spatial and temporal gradients in the vicinity of stream inflows can become more pronounced following changes to prevailing weather conditions that may occur over time scales of hours to days. In particular, rainfall in the upstream catchment will affect biogeochemical characteristics of an inflow–lake transition zone by causing elevated stream discharge, increased sediment loading and altered nutrient flux as a consequence of either concentration or dilution processes (Petry et al., 2002). Similarly, variability in wind direction and increased wind speed associated with low–pressure frontal systems may affect the pathway of lake inflows (Morillo et al., 2008) and also enhance resuspension of sediments and associated nutrients by increasing benthic shear stress (Hamilton & Mitchell,

1997). Few studies have sought to explicitly examine how changes in the surrounding catchment influence fine-scale spatial-temporal variability in linked freshwater systems, and improving the presently-limited understanding of linkages between hydrology and biogeochemistry constitutes a “grand challenge” for researchers (Lohse et al., 2009).

High-frequency sampling is necessary to characterise biogeochemical gradients and physical processes that occur in the vicinity of a lake inflow under variable forcing conditions. Ecosystem modelling can augment understanding derived from field observations to provide further insight, although a relatively sophisticated three dimensional (3-D) modelling approach employing fine temporal resolution forcing data is necessary to resolve such a spatially and temporally dynamic domain. Simpler and less computationally demanding one dimensional models can also be useful, however, to aid model calibration and bound suitable values for biogeochemical parameters (Romero et al., 2004).

This study was undertaken in a large polymictic lake that was sampled during a five-day period when high rainfall associated with a passing frontal system occurred during early Austral summer. The study focussed on spatial and temporal gradients in water quality where a stream enters the lake. The aim was to better understand physical and biogeochemical processes in the transition zone and surrounding waters proximal to a major stream inflow during dynamic hydrological and meteorological forcing conditions. Analysis of high-frequency field data collected from the stream inflow and the lake was supported by a 3-D coupled hydrodynamic-ecological model application.

5.2 Methods

5.2.1 Study site: Lake Rotorua

Lake Rotorua (38.1 °S, 176.3 °E) is a large (80.5 km²), volcanically-formed lake in central North Island, New Zealand (Fig. 5.1). The lake contains localised deep holes ($z_{\max} \approx 53$ m) but is predominantly shallow ($z_{\text{mean}} = 10.8$ m) with an extensive littoral area (see 3 m contour in Fig. 5.1). Lake Rotorua is eutrophic and there are occasional cyanobacterial blooms. It is polymictic and stratifies for periods of up to 3–4 weeks in summer. During stratification, the hypolimnion can become anoxic, which enhances benthic release rates of phosphate and ammonium, with the result that internal nutrient releases exceed external loads to the lake over annual time scales (Burger et al., 2007a). The lake catchment is

approximately 500 km² and water input to the lake is dominated by surface inflows; Hoare (1980) estimated that discharge (Q) from nine major streams ($Q_{\text{mean}} = 0.4 - 3.1 \text{ m}^3 \text{ s}^{-1}$) accounts for 66% of input to the lake, with minor streams accounting for 2% of total water input.

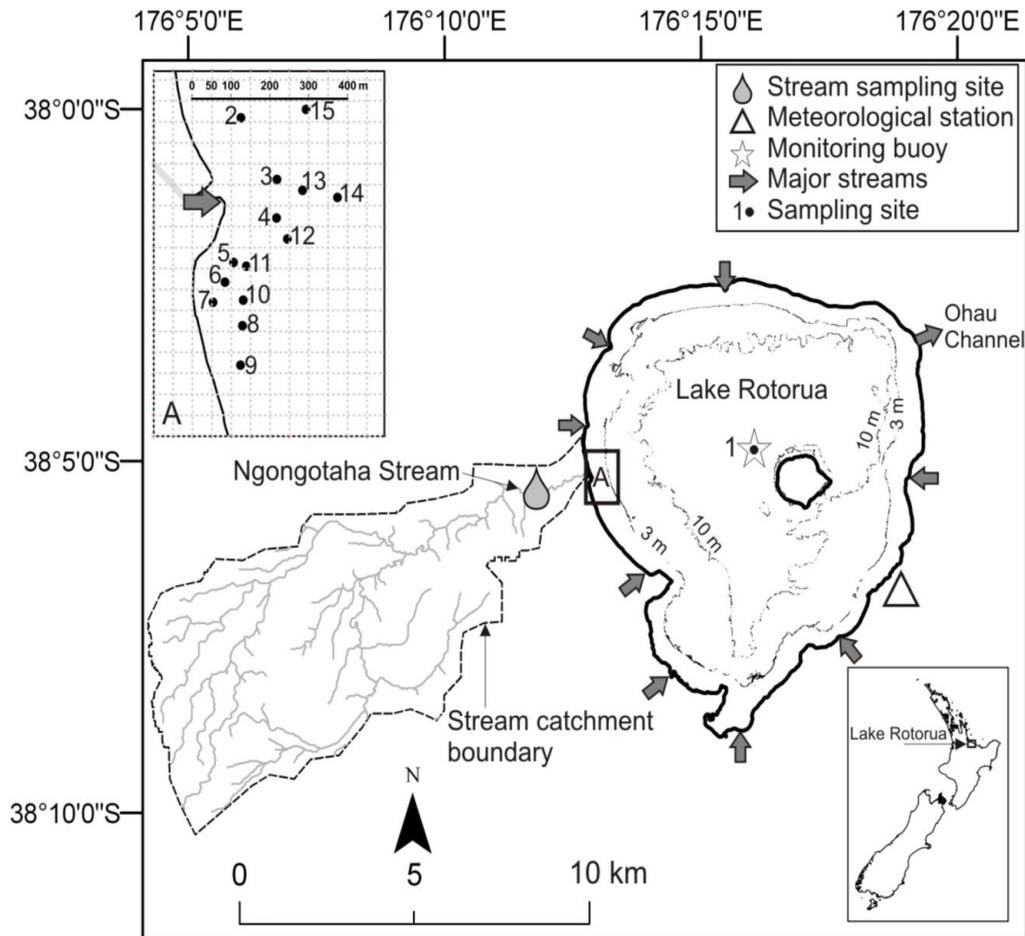


Figure 5.1 Location of the Ngongotaha Stream sub-catchment and Lake Rotorua, New Zealand. Inset (A) shows sampling sites in transition zone.

5.2.2 Study site: Ngongotaha Stream

The Ngongotaha Stream ('the stream') flows into the western side of Lake Rotorua (Fig. 5.1) and drains a catchment of approximately 62.5 km², predominantly comprising intensive pastoral agriculture (51% of catchment; mainly dairy) (Ministry for the Environment, 2004). The stream bed is sandy and banks mainly comprise light and coarse-textured pumicious soils. Base flow is approximately 1.7 m³ s⁻¹ and the stream conveys a larger proportion of water as storm flow (44 %) than any other major inflow (Rutherford and Timpany, 2008).

5.2.3 Field sampling

5.2.3.1 Stream sampling

The field study spanned a five-day period of 12–17 December 2011, commencing and ending at midday. Hourly rainfall measured at a permanent gauge (Upper Oturoa Road) sited 2 km from the northern edge of the stream catchment was assumed equal to rainfall in the stream catchment. Measured discharge (Q) for the stream was obtained at 15-minute intervals from a discharge gauge sited 2.5 km upstream of Lake Rotorua. Water for determination of concentrations of nutrients, total suspended sediment (TSS) and volatile suspended sediment (VSS) was sampled immediately downstream of the gauge using an automatic sampler (Manning VST portable). One-litre samples were collected every 2 h for the first three days and every 1.5 h thereafter, yielding 65 samples in total. Sampler hose and bottles were acid-washed (10% HCl) and triple-rinsed with analytical grade deionised water prior to initial deployment. Once emptied, sampler bottles were again triple-rinsed with deionised water before redeployment. Samples were stored on ice immediately following sampling and were retrieved before the ice melted. Sub-samples for dissolved nutrient determination were taken by filtration in the field with acid-washed syringes (0.5 µm, Advantec GF GC-50) following retrieval. Filtered and unfiltered sub-samples for nutrient determination were stored in acid-washed polypropylene tubes and preserved at ≤ 4 °C during transport to the laboratory where they were frozen before analysis.

Dissolved nutrients (NH₄⁺, NO₂⁻, NO₃⁻, PO₄³⁻) were measured with an Aquakem 200 discrete analyser (Thermo Fisher, Scoresby, Australia) using standard colorimetric methods (APHA, 1998). Limits of detection were 0.001 mg N L⁻¹ for NO₂⁻, NO₃⁻, 0.002 mg N L⁻¹ for NH₄⁺ and 0.001 mg P L⁻¹ for PO₄³⁻. Total nitrogen (TN) and total phosphorus (TP) concentrations were determined

following combined persulphate digestion (APHA, 1998) of an unfiltered sample and subsequent colorimetric analysis for NO_3^- and PO_4^{3-} respectively, using a Lachat QuickChem flow injection analyser (Zellweger Analytics Inc.). A range of check standards was analysed in concert to confirm analytical detection limits.

Suspended sediment concentrations were determined by filtering 250 – 900 mL of water through pre-combusted (550 °C for 3 h) and pre-weighed glass fibre filters (0.5 μm , Advantec GF GC-50). Total suspended sediment concentrations were determined gravimetrically following drying (105 °C for 8 h) and VSS concentrations were then determined by weight difference following subsequent ashing (550 °C for 3 h). Inorganic suspended sediment (ISS) concentration was determined as the difference of TSS and VSS.

Determinand load (L) was calculated as:

$$L = \sum_i^{n=65} \left(\frac{C_{i-1} + C_i}{2} \right) \left(\frac{Q_{i-1} + Q_i}{2} \right) \quad (1)$$

where C_i and Q_i are the determinand concentration and discharge respectively at time i and n is the number of samples. Relationships between Q and determinand concentrations were analysed using Pearson correlation analysis, with \log_{10} transformation of non-normally distributed variables (Q , TSS, ISS; Kolmogorov–Smirnov test). All statistical tests (except geographically-weighted regression; see below) were undertaken using Statistica (version 9.1, Statsoft, Tulsa, USA) and assuming a significance criterion of $p \leq 0.05$.

5.2.3.2 Lake water sampling

Lake water was sampled on three of the five days: day 1 (pre-rainfall), day 2 (post light rainfall) and day 5 (post heavy rainfall) (Fig. 5.2). Surface water samples were collected for determination of concentrations of nutrients, TSS and VSS from a central lake site by a monitoring buoy (site 1; depth, $z = 21$ m) and 12–14 sites ($z = 0.71$ – 1.34 m) located approximately 4 km from the confluence of the stream and Lake Rotorua (sites 7 and 12 were not sampled on days 2 and 5; see Fig. 5.1 for sampling locations). Protocols for filtering, storing and analysing samples for nutrient and suspended sediment concentration analysis were as for stream sampling. Filters from sites at the stream mouth were retained and frozen for up to two weeks before determination of chlorophyll a (chl a) concentration by extraction from thawed filters using 90% acetone and measuring fluorescence of the extract with a 10-AU Fluorometer (Turner Designs), with correction for phaeophytin using HCl (Arar & Collins, 1997).

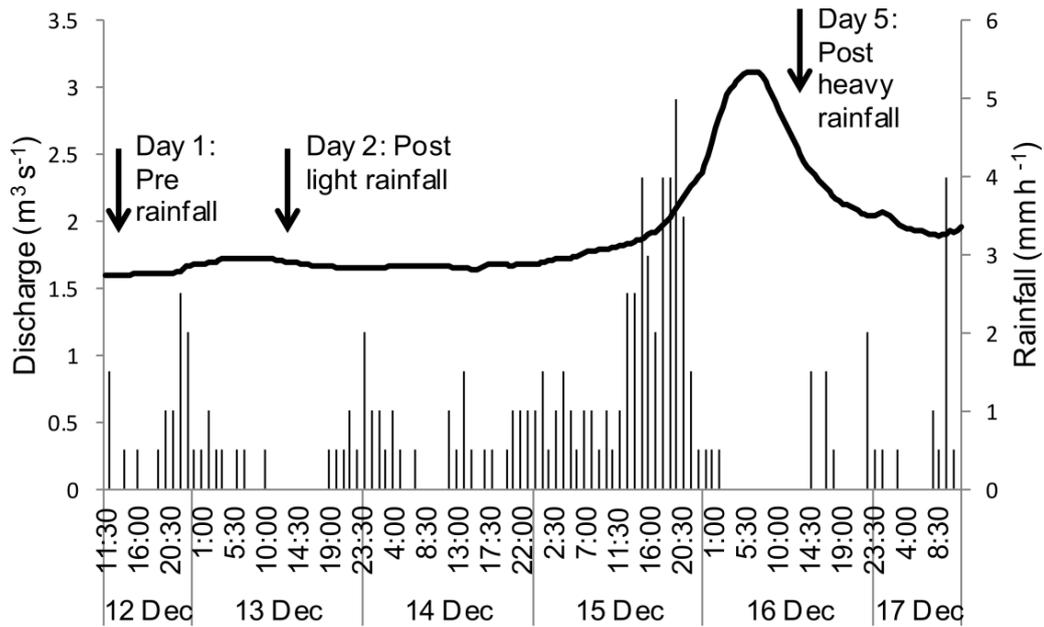


Figure 5.2 Discharge (Q) of the Ngongotaha Stream and rainfall at Upper Otoroa Road gauge during the five-day study period. Arrows denote occasions when the lake was sampled.

Nutrient enrichment experiments were undertaken on each day of lake sampling to examine N- and P-limitation of phytoplankton communities in both the transition zone and the main body of the lake. Each day, 1–L samples were collected in acid-washed containers from two sites: site 1 (‘pelagic zone’ site) and site 5, the closest site to the stream inflow (‘transition zone’ site). Samples were kept in the dark on ice before commencing experiments on return to the laboratory. Experiments were undertaken in loosely-stoppered, acid-washed, 100-mL glass tubes. Three nutrient addition treatments (+N, +P, +N+P) and one control (no added nutrients) were established in triplicate. Nitrogen enrichment comprised addition of NH_4Cl to increase N concentration by 1 mg N L^{-1} and P enrichment comprised addition of KH_2PO_4 to increase P concentration by 0.01 mg P L^{-1} . Nutrient stock solutions were prepared using analytical grade chemicals (BDH Laboratory Reagents) and analytical grade deionised water. Tubes were incubated at constant light level ($47 \mu\text{mol m}^{-2} \text{ s}^{-1} \mu\text{A}^{-1}$) in a temperature-controlled room set to $16 \text{ }^\circ\text{C}$ (average surface temperature across transition zone $\pm 2 \text{ }^\circ\text{C}$). Incubation time was set to 24 h as a compromise between ensuring sufficient time for cells to potentially respond to treatments and minimising possibility of ‘bottle effects’ (Beardall et al., 2001). Following incubation, growth

response in each tube was determined by measuring *in vivo* fluorescence (day 1 and 2) with a 10–AU Fluorometer or determination of extracted chl *a* concentration (day 5; method as above). Phytoplankton community–level nutrient limitation was examined by analysing mean treatment growth response (normalised to mean growth response of daily triplicate controls) using a one–way ANOVA with Fisher’s LSD post–hoc test.

A BioFish robotic system (ADM–Elektronik) with several built–in sensors was towed behind the survey vessel at the lake surface (depth sampled ≈ 0.3 m) to obtain highly spatially–resolved water quality data in the vicinity of the transition zone. This method was used to collect temperature (ADM–Elektronik), specific conductance (SpC; ADM–Elektronik), beam transmission (ADM–Elektronik) and chlorophyll fluorescence (Dr. Haardt Optik Mikroelektronik miniBackScat I) data which were geo–referenced using a GPS (Garmin GPSMAP 168 Sounding). BioFish data were processed with Ocean Data View (Schlitzer, 2011) to interpolate measurements into isopleths over the survey area. Surface water chl *a* concentration was estimated from a linear regression of measured extracted chl *a* concentration ($\mu\text{g L}^{-1}$) at each sampling site on *in situ* chlorophyll fluorescence (relative fluorescence units) measured from the BioFish sensor ($r^2 = 0.77$, $n = 37$, measured range = $0.12 - 21.11 \mu\text{g L}^{-1}$).

Specific conductance measurements were used to map the propagation of stream water in the lake (cf. Atkinson & Mabe, 2006; Mackay et al., 2011a). Specific conductance was assumed to behave as a conservative tracer and, subsequently, the proportion of stream water in the lake at each measurement location ($S_{\%}$) was calculated as:

$$S_{\%} = 100 \left(\frac{SpC_i - SpC_L}{SpC_S - SpC_L} \right) \quad (2)$$

where SpC_i is measured SpC, SpC_L is SpC of the lake (assumed to be the maximum SpC measured on each day) and SpC_S is SpC of the stream (assumed to be the minimum SpC measured on each day).

Estimated $S_{\%}$ was used to infer a concentration (\hat{C}) of TSS, DIN (= $\text{NH}_4\text{-N} + \text{NO}_3\text{-N} + \text{NO}_2\text{-N}$) and $\text{PO}_4\text{-P}$ based on linear conservative mixing between stream and lake water, and, assuming that samples collected from the stream and the lake monitoring buoy (site 1; Fig. 5.1) were wholly representative of stream and lake water quality respectively. Thus:

$$\hat{C}_i = \frac{S_{\%} S_i}{100} + \left(1 - \frac{S_{\%}}{100} \right) L_i \quad (3)$$

where S_i is the measured determinand concentration in the stream sample collected at the time (nearest 0.75 h) when the site was sampled and L_i is the measured determinand concentration in the sample collected at the lake buoy (< 2 h) prior to sampling. The ratio of measured determinand concentration (C_i) to \hat{C}_i (i.e. $C_i:\hat{C}_i$) thus provides a measure of the relative extent to which C_i is likely to be influenced by processes that cause net accumulation (e.g. resuspension for TSS) or net loss (e.g. uptake by biota for DIN and $\text{PO}_4\text{-P}$). Thus, if $C_i:\hat{C}_i$ is centred on zero (by subtracting one) then positive values indicate net accumulation and negative values indicate net loss in the water column. Values were calculated for eleven sites as day 2 sample for site 4 was lost.

Lake water temperature was measured at ten depths between 0.5 m and 20.5 m inclusive every 15 minutes at the monitoring buoy at site 1 (Fig. 5.1). Temperature and bathymetry data were used to calculate Schmidt Stability (Schmidt, 1928) every 15 minutes. This index provides a measure of the strength of thermal stratification by quantifying the mechanical mixing required to establish vertically uniform density. Schmidt Stability was calculated using Lake Analyzer (Read et al., 2011) which uses Idso's (1973) formulation of the concept:

$$\text{Schmidt Stability} = \frac{g}{A_s} \int_0^{z_D} (z - z_v) \rho_z A_z \partial z \quad (4)$$

where g is the acceleration due to gravity, A_s is the surface area of the lake, A_z is the area of the lake at depth z , z_D is the maximum depth of the lake, and z_v is the depth to the centre of volume of the lake.

Hourly lake water level was obtained from a recorder sited by the southern shore of the lake, operated by the Bay of Plenty Regional Council (BoPRC).

5.2.3.3 Sediment traps

Sediment traps were deployed in the lake at sites 2–15 (Fig. 5.1) to measure gross deposition in the transition zone. Traps were deployed on the first day of lake sampling and retrieved after 96 h during the final day of lake sampling. During this period, 76 mm of rain was recorded and maximum Q (Q_{\max}) was recorded approximately 8 h prior to trap retrieval. In accordance with criteria defined by Håkanson et al. (1989), traps were cylindrical (height = 53 cm), with diameter > 4 cm (7 cm), aspect ratio > 3 (7.6) and were deployed without chemical preservatives. Traps were secured on the lake bed in an upright position using marked stakes. Traps at sites 2, 4 and 12 deviated from an upright position due to wave action and were subsequently excluded from the study. Remaining traps

were retrieved whilst wading by lifting them directly upwards to prevent loss of deposited material. Supernatant water was siphoned off using a manual pump and remaining trap contents (~ 1 L) were transferred to a clean sample bottle and placed on ice. Trap contents were dried in aluminium trays (60 °C for 24 h) and weighed to determine the mass of accumulated sediment. Dried sediment was then ashed (550 °C for 3 h) to determine the mass of organic material. Sediment accumulation rates ($\text{g m}^{-2} \text{d}^{-1}$) were not normalised for variation in depth of overlying water to aid comparison with other studies.

5.2.4 Modelling

5.2.4.1 Model description

The Estuary and Lake and Coastal Ocean Model (ELCOM; v. 2.2, Perth, Australia) was used as a 3-D hydrodynamic driver for the dynamically coupled Computational Aquatic Ecosystem DYnamics Model (CAEDYM; v. 3.3, Perth, Australia) which simulated water quality. Overview of these models is provided by Hodges & Dallimore (2011) and Hipsey et al. (2011), respectively. Model application required simplifying lake morphology by discretizing the water column into 3-D cells with dimensions: $x = 50 \text{ m}$, $y = 50 \text{ m}$ and $z = 0.5 - 2 \text{ m}$. Water column z_{mean} was determined by interpolation using a bathymetry map with 5-m horizontal resolution. ‘Flow’ boundary conditions were specified at the lake-bottom and sidewalls.

5.2.4.2 Meteorological data

Hourly-average measured wind speed, wind direction, air temperature, solar radiation, atmospheric pressure, cloud cover and total rainfall data (Fig. 5.3) were obtained from a meteorological station at Rotorua Airport on the south-east shore of the lake (Fig. 5.1). Data were assumed representative of conditions across the lake.

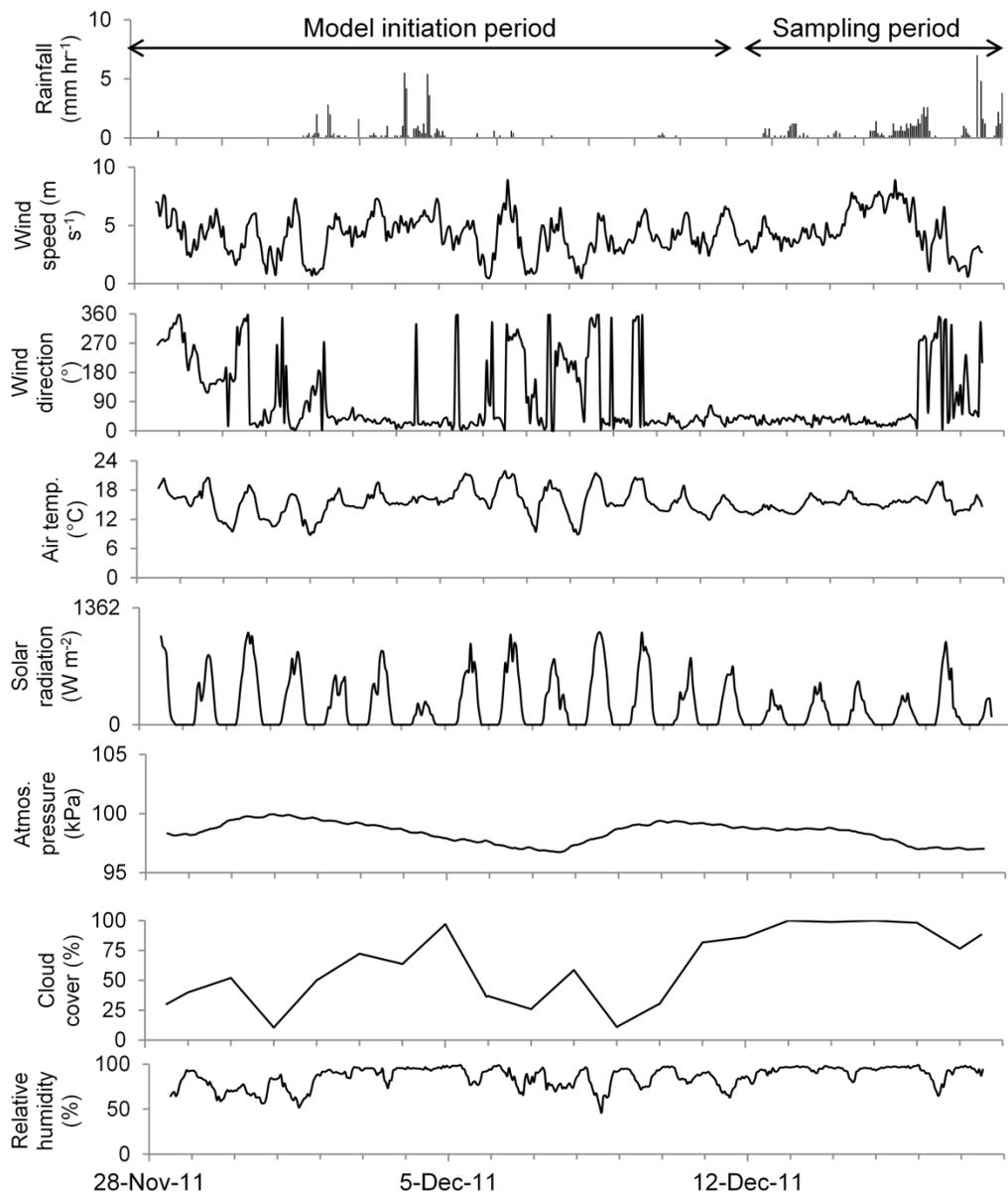


Figure 5.3 Meteorological data measured at Rotorua Airport during the modelling period.

5.2.4.3 Water balance

Hourly Q ($\text{m}^3 \text{s}^{-1}$) data were used to quantify surface stream inflow in the model (Tables 5.1 and 5.2). Discharge data were assigned based on either measured (four major streams; 20.1% of inflow during study period) or estimated Q (22.6 % of inflow during study period; see Table 5.1 for a summary of the water balance).

Table 5.1 Water fluxes simulated in ELCOM–CAEDYM during five–day study period. Stream inflows and outflow are described in Table 5.2. *Groundwater* equals the residual term to close a water balance and thus includes all unaccounted flows.

| | | Mean flow rate (m ³ s ⁻¹) | Proportion of total inflows/outflows (%) |
|---------|--------------------------------|--|--|
| Inflow | Ngongotaha (study stream) | 1.92 | 6.4 |
| | Other major stream inflows (8) | 10.93 | 36.3 |
| | Rainfall | 10.31 | 34.2 |
| | Groundwater | 6.71 | 22.4 |
| | Minor stream inflows (6) | 0.28 | 0.9 |
| Outflow | Ohau channel | 17.92 | 59.4 |
| | Δ storage | 11.28 | 37.4 |
| | Evaporation | 0.95 | 3.2 |

Hourly mean evaporation rate (E ; m³ s⁻¹) was calculated using the method used in ELCOM, based on Fischer et al. (1979):

$$E = \frac{A \left(\frac{-0.622 C_L \rho_a L_E U (e_a - e_s)(T_{0.5})}{P} \right)}{L_v} \quad (5)$$

where A is the area of the lake (m²; assumed static), C_L is the latent heat transfer coefficient for wind speed (0.0013), ρ_a is air density (kg m⁻³), L_E is the latent heat of evaporation of water (2453000 J kg⁻¹), U is measured wind speed (m s⁻¹), e_a is the vapour pressure of the air (Pa), e_s is the saturated vapour pressure of the air (Pa) corresponding to the lake water surface temperature (°C) measured at the monitoring buoy, P is the atmospheric pressure (Pa), L_v is the latent heat of vaporisation (2260000 J kg⁻¹) and $T_{0.5}$ is the water temperature (°C) measured at the monitoring buoy ($z = 0.5$ m). A value of 0 was substituted where $E < 0$ as ELCOM does not simulate condensation effects (Hodges & Dallimore, 2011).

e_s was calculated by the Magus–Tetens formula used in ELCOM:

$$e_s(T_{0.5}) = 100 \exp \left[2.3026 \left(\frac{7.5 T_{0.5}}{T_{0.5} + 237.3} \right) + 0.758 \right] \quad (6)$$

Water input that was in addition to rainfall and the simulated stream inflows was assumed to comprise groundwater entering the lake via the bed (Table 5.1). This input was assumed equal to the residual quantity necessary to close the water balance and was thus calculated as:

$$\textit{Groundwater} = (Q_{Ohau} + E + \Delta S) - (Q_{inflow} + \textit{rainfall}) \quad (7)$$

where *Groundwater* is mean hourly groundwater input (m³ s⁻¹), Q_{Ohau} is mean hourly discharge of the only lake surface outflow (m³ s⁻¹), ΔS is mean hourly rate

of change in lake storage ($\text{m}^3 \text{s}^{-1}$) due to water level change and assuming constant lake area, Q_{inflow} is mean hourly total stream discharge ($\text{m}^3 \text{s}^{-1}$) and rainfall is mean hourly precipitation input ($\text{m}^3 \text{s}^{-1}$) assuming a constant lake area.

5.2.4.4 Temperature

Hourly mean temperature ($^{\circ}\text{C}$) of surface inflows (T_s ; Table 5.2) was estimated using an empirical model described by Mohseni et al. (1998):

$$T_s = \frac{\alpha}{1 + e^{\gamma(\beta - T_a)}} \quad (8)$$

where T_a is the average measured air temperature for the prior five days ($^{\circ}\text{C}$), α is the maximum measured stream temperature ($^{\circ}\text{C}$) and both γ and β are dimensionless parameters. Parameters γ and β were determined by fitting the model to historic spot measurements of stream temperature provided by BoPRC ($n = 65 - 96$) and minimising root mean squared error using the Solver add-in to Microsoft Excel 2007. Measured data were not available for most minor streams and subsequently T_s for one stream (Lynmore) was assigned to five minor streams. This approach estimates only seasonal variation in T_s and diurnal variation was not considered.

5.2.4.5 CAEDYM configuration

CAEDYM has a modular structure which allows a range of ecosystem components and processes to be simulated (Hamilton & Schladow, 1997). In this study, CAEDYM was configured to simulate three groups of phytoplankton which broadly related to non N-fixing Cyanoprokaryota, Chlorophyta and Bacillariophyta. Three forms of dissolved nitrogen (NO_3^- , NH_4^+ and labile organic) and one particulate form (labile organic) were simulated. For phosphorus, two dissolved forms (PO_4^{3-} and labile organic) and two particulate forms (labile organic and labile inorganic) were simulated. The following processes were simulated to regulate the concentration of the different N and P pools in the water column: water inflow and outflow; phytoplankton mortality, excretion and uptake; sedimentation and sediment releases; decomposition and mineralisation; and denitrification in the case of N. Effects on these pools by fauna or higher plants were not considered.

Table 5.2 Summary of discharge (Q) and temperature (T) assigned to 19 inflows and one outflow simulated in ELCOM–CAEDYM application. T was derived empirically (see text) unless stated otherwise. BoPRC, Bay of Plenty Regional Council; NIWA, National Institute of Water and Atmospheric Research.

| Inflow (I)/outflow (O) | Q (m ³ s ⁻¹) | T (° C) | Notes |
|---------------------------------------|-------------------------------------|------------------|---|
| Hamurana (I) | 2.70 | 12.74–13.06 | Q from Pang et al. (1996) and assumed constant (groundwater spring). |
| Puarenga (I) | 1.75–4.57 | 16.89–17.69 | Q measured hourly at BoPRC gauge. |
| Utuhina (I) | 1.60–4.40 | 14.41–14.89 | Q measured hourly at BoPRC gauge. |
| Ngongotaha (I) | 1.53–3.11 | 13.27–14.01 | Q measured hourly at NIWA gauge. |
| Awahou (I) | 1.35–2.76 | 12.75–12.95 | Initial base flow Q from Hoare (1980), linearly correlated to Ngongotaha Q thereafter. |
| Waiteti (I) | 1.01–2.24 | 13.08–13.14 | As for Awahou. |
| Waiowhero (I) | 0.32–0.66 | 13.70–14.03 | As for Awahou. |
| Waiohewa (I) | 0.29–0.60 | 15.31–16.00 | As for Awahou. |
| Waingaehe (I) | 0.25–0.37 | 16.34–16.66 | Q measured hourly at BoPRC gauge. |
| Minor streams (6; I) | 0.002–0.10 | 13.70–16.20 | Each stream represented as individual inflow. Initial base flow Q from BoPRC, linearly correlated to Waingaehe Q thereafter. |
| Groundwater seeps at lake edge (3; I) | 0.02–0.04 | 17.11–35.00 | Each seep represented as individual inflow. Q from BoPRC, assumed constant. T for geothermal seep from Wood (1992), otherwise set to measured T (0.5 m) at monitoring buoy. |
| Groundwater at lake bed (I) | 5.04 | 16.46 – 18.59 | Q derived from residual term in water balance calculation and assumed constant. Inflow assigned to 24.65 km ² area. T set to measured T (20.5 m) at monitoring buoy. |
| Ohau Channel (O) | 15.69– 20.42 | Not assigned | Hourly Q derived from linear interpolation of daily measured Q at NIWA gauge. T calculated by ELCOM–CAEDYM. |

This study used CAEDYM parameter values assigned in a separate study that used a one-dimensional hydrodynamic driver (DYRESM) with CAEDYM to simulate water quality in Lake Rotorua over decadal timescales (Hamilton et al., 2012). The cited study used a four-year period to calibrate DYRESM–CAEDYM using monthly field data pertaining to temperature, dissolved oxygen (DO) and nutrient concentrations at three depths in the lake, as well as chl *a* concentrations at the lake surface. Model performance was generally satisfactory with good agreement between measured and simulated data for both temperature and DO during the four-year validation period. Measures of model performance (Pearson’s *r* and root mean square error (RMSE)) were weaker for simulated nutrient concentrations. Comparison of measured and simulated chl *a* concentration during validation yielded *r* of 0.11 and RMSE of 16.0 µg L⁻¹.

5.2.4.6 Biochemical state variables

Nutrient concentrations in inflows were estimated based on samples collected and analysed using methods described above, or using concentrations measured by BoPRC as part of routine sampling during 2000–2010, in accordance with methods prescribed by Burns et al. (2000). Table 5.3 describes how biochemical state variables were assigned to inflows.

Table 5.3 Summary of biochemical state variables (all as concentration or mass units) assigned to inflows in ELCOM–CAEDYM application. Abbreviations: BoPRC, Bay of Plenty Regional Council; DIC, dissolved inorganic carbon; DIN, dissolved inorganic nitrogen; DO, dissolved oxygen; DOCL, labile dissolved organic carbon; PIP, particulate inorganic phosphorus; POCL, labile particulate organic carbon; PON, particulate organic nitrogen; PIN, particulate inorganic nitrogen; Q, stream discharge; SSol, inorganic suspended sediment ; TN, total nitrogen; TP, total phosphorus; TSS, total suspended sediment; VSS, volatile suspended sediment.

| Simulated inflow | State variable | Notes |
|------------------|----------------|--|
| All | PON | Estimated as TN – DIN |
| | PIP, POP | Assumed all particulate P was mineral associated, thus: PIP = TP - PO ₄ -P and POP = 0. |
| | POCL | Estimated as DON x 7.29 based on C:N reported by Sterner et al. (2008). |
| | DOCL | Estimated as DIN x 7.29 based on C:N reported by Sterner et al. (2008). |

| Simulated inflow | State variable | Notes |
|------------------------------------|--|---|
| All cont. | SiO ₂ | Set to constant values based on concentrations of single samples measured by Morgenstern et al. (2005). |
| Ngongotaha (study stream) | NO ₃ ⁻ , NH ₄ ⁺ , PO ₄ ³⁻ , PIP, PON DO, pH SSol | Measured field data used during study period. Values for initiation period derived as per other major streams. As per other major streams. Measured field data used during study period (1.5 – 2 h frequency). Values for initiation period derived using a log ₁₀ Q–log ₁₀ SSol rating curve relating to measured range of Q with correction for transformation bias (Ferguson, 1986). Curve was defined using TSS and VSS concentrations measured in 2010–2012 using methods as per this study (n = 143). Assumed that SSol = TSS - VSS. |
| Other major streams (8) | DO, NO ₃ ⁻ , NH ₄ ⁺ , pH, PO ₄ ³⁻ , PON PIP SSol | Set to mean values measured in each stream by BoPRC (n = 80 – 128). For Ngongotaha initiation period, Utuhina and Puarenga (large streams, not groundwater dominated): derived using a log ₁₀ Q–log ₁₀ PIP rating curve relating to measured range of Q with correction for transformation bias (Ferguson, 1986). For Ngongotaha and Puarenga, curve was defined using PIP concentrations measured in 2010–2012 using methods as per this study (n = 128 and 371, respectively). For Utuhina, curve was defined using values measured by BoPRC (n = 32). Set to mean of values measured by BoPRC for other streams (n = 84 – 127). For Utuhina and Puarenga (large streams, not groundwater dominated): derived using a log ₁₀ Q–log ₁₀ SSol rating curve relating to measured range of Q with correction for transformation bias (Ferguson, 1986). For Puarenga, curve was defined using TSS and VSS concentrations measured in 2010–2012 using methods per this study (n = 164). Assumed that SSol = TSS - VSS. For Utuhina, the Ngongotaha rating curve (see above) was used for storm flow periods. For other streams and Utuhina baseflow periods, mean adjusted (× 0.55) TSS concentrations provided by BoPRC and specific to each stream were used. |
| Minor surface streams (6) | DO, NO ₃ ⁻ , NH ₄ ⁺ , pH, PO ₄ ³⁻ , PIP, PON SSol | Set to median concentration of samples collected by BoPRC from either Lynmore Stream (one urban stream, n = 99 – 115) or Hauraki Stream (five rural streams, n = 18 – 20). Set to discharge–weighted average TSS concentration of samples collected from Lynmore Stream by BoPRC (n = 25). |
| Groundwater seeps at lake edge (3) | DO, NO ₃ ⁻ , NH ₄ ⁺ , pH, PO ₄ ³⁻ , PIP, PON SSol | Set to volumetric mean concentration of samples collected by BoPRC from six lake–edge springs (n = 195). Assumed zero. |
| Groundwater to lake bed | DO, NO ₃ ⁻ , NH ₄ ⁺ , pH, PO ₄ ³⁻ , PIP, PON, SiO ₂ | Set to volumetric averages of values for Awahou, Hamurana and Waiteti (groundwater dominated) streams. |

5.2.4.7 Initialisation

Measured water column temperature at the monitoring buoy was used to assign the initial vertical temperature profile of the lake. Water column nutrient and chl *a* concentrations and pH were initialised using a piecewise linear distribution method to reflect stratified conditions present at the start of the modelling period. Concentrations at the surface and 20 m were assigned based on mean or median (depending on frequency distribution characteristics) concentrations of samples collected by BoPRC (n = 35 – 67) from the lake in November and December during 2000–2010 from the surface and at $z \geq 15$ m during stratified periods, respectively. The initial chl *a* concentration was subdivided between the three simulated groups of phytoplankton in accordance with relative abundance data for Lake Rotorua measured by Paul et al. (2012). Assigned horizontal conditions were initially uniform. Model time step was 120 s and a 14-day ‘spin up’ or initiation period was simulated prior to the five-day study period.

5.2.4.8 Modelled nitrogen and phosphorus limitation

Phytoplankton internal N and P stores were dynamically simulated within CAEDYM. Subsequently, CAEDYM calculates values (0–1) of N and P limitation functions ($f(N)$ and $f(P)$ respectively) which, in addition to the levels of light, temperature, carbon and silica (Bacillariophyta only), determine the maximum growth rate of each phytoplankton group. $f(N)$ and $f(P)$ are calculated as (Hamilton & Schladow, 1997; Hipsey et al., 2011):

$$f(N/P) = \frac{AI(N/P)max_a}{AI(N/P)max_a - AI(N/P)min_a} \left[1 - \frac{AI(N/P)min_a}{AI(N/P)_a} \right] \quad (9)$$

where $f(N/P)$ is $f(N)$ or $f(P)$, $AI(N/P)max$ and $AI(N/P)min$ are defined limits of internal N or P concentration, $AI(N/P)$ is internal N or P concentration and *a* denotes the phytoplankton group. Values of $AI(N/P)$ are a function of temperature, in addition to dissolved inorganic nutrient concentrations (DIN and PO_4-P respectively) and dissolved nutrient uptake rates dependent on group-specific half saturation constants. Nutrient limitation functions subsequently reflect both ambient conditions and recent phytoplankton environmental histories.

5.2.4.9 Model validation: Hydrodynamic processes

Modelled water column temperature was validated by comparing hourly simulated and measured temperatures at ten depths at the monitoring buoy site. Simulated propagation of a conservative tracer added to the stream inflow was

compared to calculated $S_{\%}$ (Eq. 2) to validate how well the model reproduced the horizontal trajectory of the stream inflow observed during lake sampling.

5.2.4.10 Model validation: Ecology

Modelled surface ($z = 0 - 0.5$ m; single layer) chl a concentration in the vicinity of the transition zone was compared with chl a concentration measured with the BioFish. Mean measured concentrations were calculated for $50 \text{ m} \times 50 \text{ m}$ grid cells ($n = 103 - 153$) corresponding to model cells to permit spatially contiguous comparisons. Model performance was assessed by comparing measured (no interpolation) and modelled values by calculating root mean square error (RMSE) and the coefficient of determination (r^2) for geographically-weighted linear regressions (SAM v.4.0; Rangel et al., 2010). Simulated $f(\text{N})$ and $f(\text{P})$ values were output for the surface layers of the grid cells containing the ‘transition zone’ and ‘pelagic zone’ sampling sites used for nutrient enrichment experiments. Overall assemblage values of $f(\text{N})$ and $f(\text{P})$ were calculated by weighting each phytoplankton group-specific value based on the relative contribution of each group to overall chl a concentration. This allowed for comparison between nutrient enrichment experiment results and corresponding simulated $f(\text{N})$ and $f(\text{P})$.

5.3 Results

5.3.1 Event characteristics

A total of 83 mm of rain was recorded over the five-day study period (Fig. 5.2): approximately 73% of the monthly average rainfall for Rotorua in December (NIWA, 2010). Light rainfall (12.5 mm) was recorded between lake sampling on day 1 and 2 which had minor effect on stream Q (Fig. 5.2). Most of the rainfall (53 mm) was on days 3 and 4 and was of low to moderate intensity ($0.5 - 5 \text{ mm h}^{-1}$). Subsequently, Q_{max} ($3.12 \text{ m}^3 \text{ s}^{-1}$) occurred at 0700 h on day 5 and was ≈ 1.95 times the pre-event Q .

Throughout the study period, wind was of moderate speed (mean = 3.2 m s^{-1} , maximum hourly mean = 8.1 m s^{-1}) and mostly from a north to north-east direction (Fig. 5.3). Schmidt stability declined throughout day 2 coincident with light rainfall, reaching $< 10 \text{ J m}^{-2}$ on day 3 (Fig. 5.4) when wind speed was elevated ($> 5 \text{ m s}^{-1}$) and the water column was isothermal at the monitoring buoy (Fig. 5.5a).

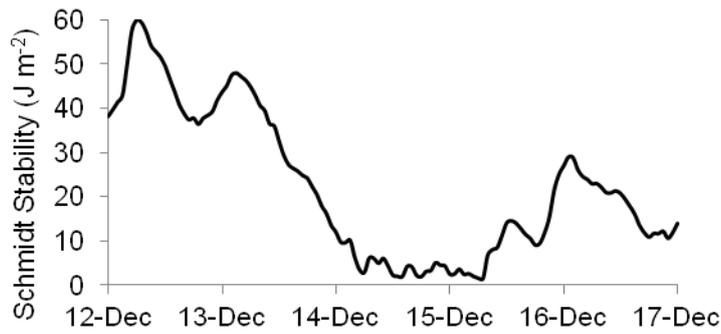


Figure 5.4 Schmidt Stability for Lake Rotorua during the five-day study period. Index was calculated using temperature measured at the monitoring buoy (Fig. 5.1) at depths 0.5 – 20.5 m.

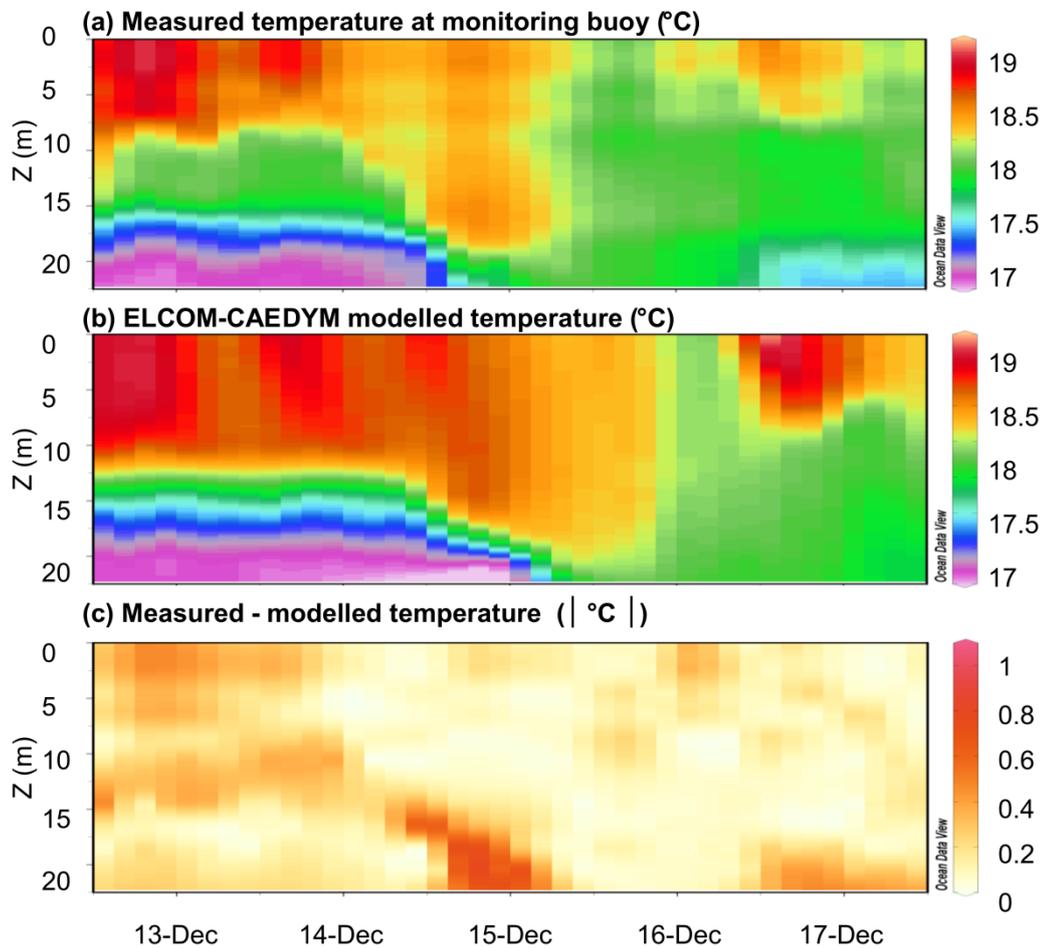


Figure 5.5 Comparison between (a) hourly temperature of Lake Rotorua measured at the monitoring buoy, and (b) temperature simulated using ELCOM–CAEDYM. Absolute error is shown in (c).

5.3.2 Stream water quality

Stream suspended sediment concentrations displayed a typical concentration response to elevated Q (Fig. 5.6a); TSS was highly correlated with Q ($r = 0.96$). During the five-day period, 44% of the total measured TSS load (8601 kg) comprised VSS and 37% of the TSS load was conveyed during the 12 h period coinciding with Q_{\max} .

Total nitrogen concentration also increased in response to elevated Q (Fig. 5.6b), principally due to variation in PN which was correlated with both VSS and ISS concentrations ($r = 0.54$ and 0.62 , respectively). Concentrations of $\text{NO}_3\text{-N}$ were relatively constant throughout (mean = 0.85 mg N L^{-1} , C.V. = 5.2%) and $\text{NH}_4\text{-N}$ was weakly positively correlated with Q ($r = 0.37$) although this determinand only comprised a small ($\approx 2.5\%$) proportion of the TN load.

Concentrations of $\text{PO}_4\text{-P}$ were variable throughout the study period (mean = $0.034 \text{ mg P L}^{-1}$, C.V. = 43%) and were uncorrelated with Q (Fig. 5.6c). Total phosphorus concentrations were positively correlated with Q ($r = 0.74$) and both VSS and ISS concentrations ($r = 0.57$ and 0.64 , respectively).

5.3.3 Lake water sampling

Measured temperature, specific conductance and beam transmittance were higher in the main body of the lake than in the vicinity of the stream inflow (Fig. 5.7). Chlorophyll *a* concentration was typically lowest in the vicinity of the stream inflow although pronounced patchiness was observed on day 5. The influence of stream water on lake water quality was most apparent during sampling on days 2 and 5, following light and heavy rainfall, respectively. On these days, measurements indicated that the inflowing stream was deflected to the right and subsequently flowed southwards adjacent to the shoreline, influencing lake water quality up to 1 km from the mouth. Beam transmittance in the transition zone was lowest on day 5 reflecting the influence of elevated stream TSS concentrations ($\approx 20 \text{ mg L}^{-1}$; Fig. 5.6a), although the linear relationship between beam transmittance and suspended sediment concentration was considered too weak to permit use of beam transmittance as a reliable proxy of suspended sediment concentration (Fig. 5.8). In particular, beam transmission at four sites (5, 6, 7 and 9) sampled on day 5 was markedly lower than that predicted by the linear relationship with TSS concentration (see points circled in Fig. 5.8a). In general, sampled VSS had a greater negative influence on water clarity (i.e. beam

transmittance) than ISS, as indicated by the slope of the regression lines in Figs 5.8b and c.

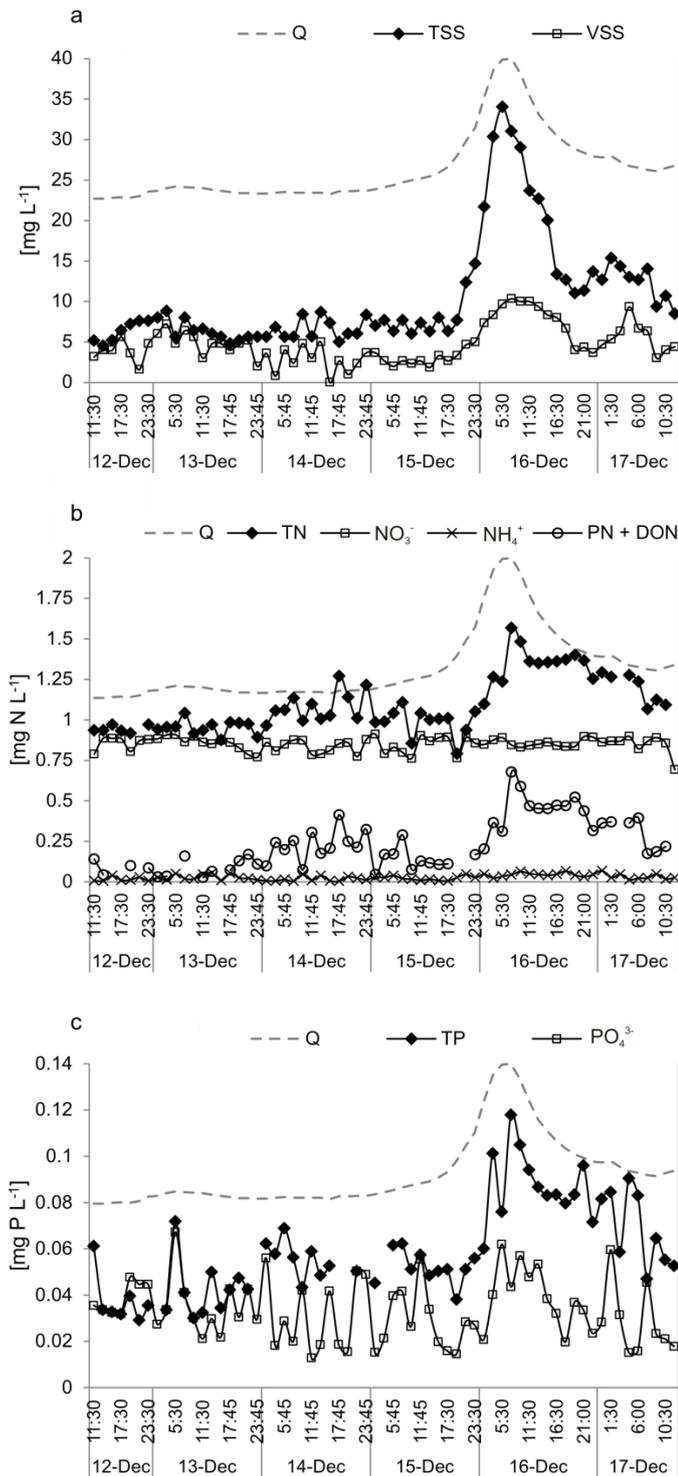


Figure 5.6 Temporal variations in concentrations of (a) suspended sediments, (b) nitrogen and (c) phosphorus in the Ngongotaha Stream during the five-day study period. TSS, total suspended sediment; VSS, volatile suspended sediment; TN, total nitrogen; PN, particulate nitrogen; DON, dissolved organic nitrogen; TP, total phosphorus; Q, discharge (see Fig. 5.2 for scale).

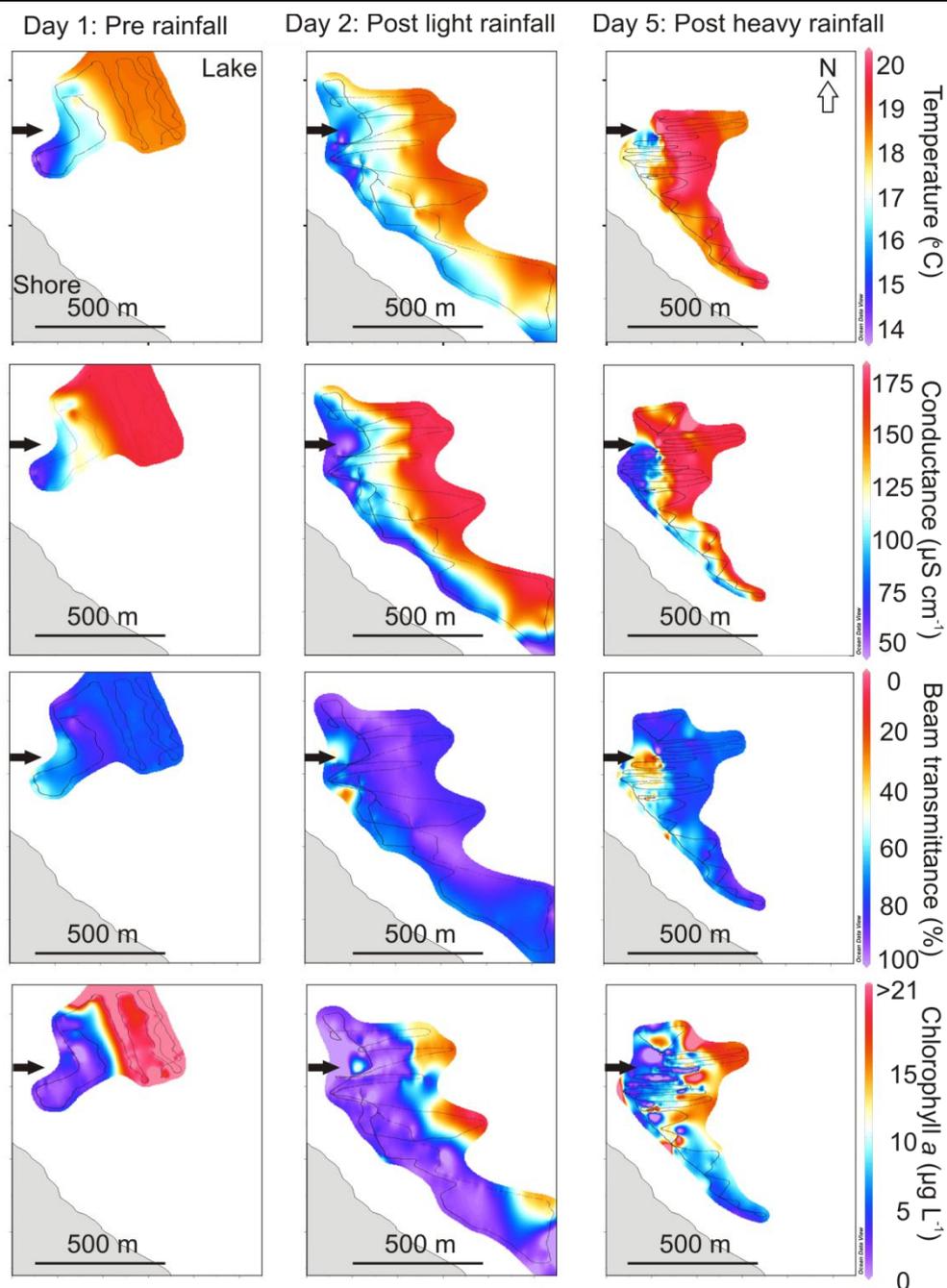


Figure 5.7 Surface temperature, specific conductance, beam transmission and chlorophyll *a* concentration measured on three days in the vicinity of the transition zone where the Ngongotaha Stream inflows to Lake Rotorua. Measurements were made using sensors attached to a towed BioFish system (see Methods). Chlorophyll *a* was calculated from a linear relationship between fluorescence measured at the BioFish and chlorophyll *a* concentration determined from grab samples ($n = 37$, $r^2 = 0.77$, range = $0.12 - 21.11 \mu\text{g L}^{-1}$). Measurements are interpolated; line shows path of survey vessel. Arrows denote location of stream inflow.

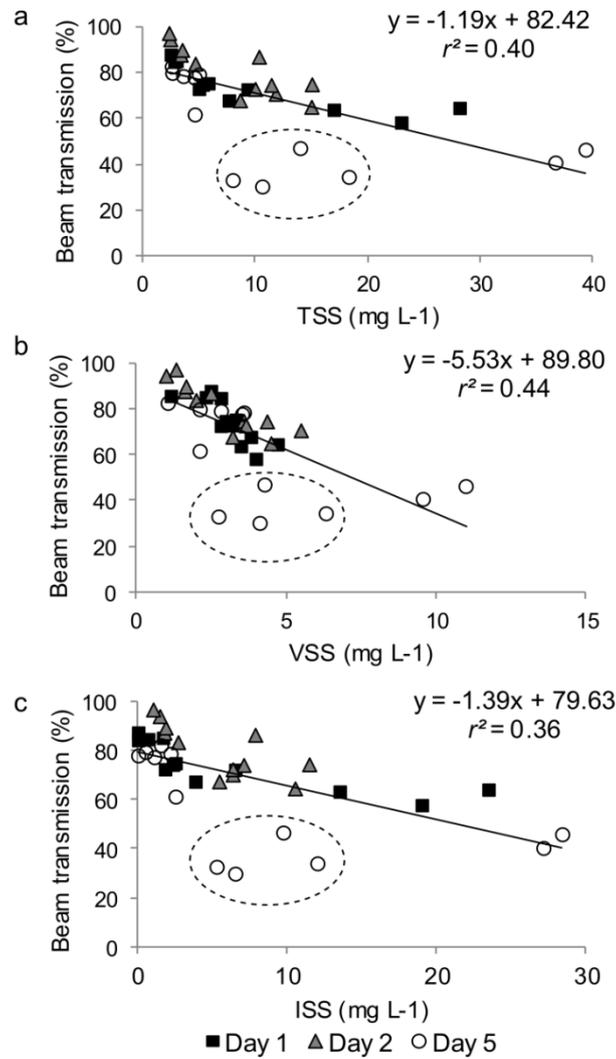


Figure 5.8 Relationships between measured beam transmission and concentrations of (a) total suspended sediment (TSS), (b) volatile suspended sediments (VSS), and (c) inorganic suspended sediments (ISS) on three days in the vicinity of the transition zone where the Ngongotaha Stream inflows to Lake Rotorua. Circled sites were in the main path of the stream inflow (see text) and are included in the regression analysis.

Nutrient and TSS concentrations were higher in the stream than at the pelagic zone site during lake sampling. On days 1 and 2, TSS sampled at the pelagic zone site wholly comprised VSS (3.83 and 4.17 mg L⁻¹ respectively) whereas on day 5 (post heavy rainfall) VSS comprised only 36 % of measured TSS (4.89 mg L⁻¹). Zero-centred values of $C_i:\hat{C}_i$ (hereafter ‘mixing ratios’; see Methods) for DIN, PO₄-P and TSS vary between both sites and sampling occasions, indicating occurrence of non-conservative processes that caused both accumulation and removal of these determinands in the transition zone (Fig. 5.9). On day 1, DIN mixing ratios (Fig. 5.9a) are close to zero at most sites, with moderately negative values (suggesting active removal) at the three sites furthest from the shore (13, 14, 15) and values > 0.4 at sites 8 and 9. Dissolved inorganic nitrogen mixing ratios are predominantly positive (suggesting active accumulation) on day 2 and predominantly negative on day 5, with particularly low values (-6.0 and -1.14) calculated for sites closest to the stream inflow.

Mixing ratios for PO₄-P (Fig. 5.9b) were predominantly negative on day 1 and all positive on day 2. On day 3, PO₄-P mixing ratios were predominantly negative in the path of the inflow. Mixing ratios for TSS (Fig. 5.9c) were predominantly positive and typically large (mean = 1.34) on day 1 although negative ratios (< 0.5) were calculated for sites furthest to the shore and to the north of the inflow. On day 2, mixing ratios for TSS were close to zero at most sites. Ratios on day 5 were predominantly negative although positive values were calculated for three sites (8, 10, 11) in the inflow path where water velocity is expected to have been highest.

5.3.4 Nutrient enrichment experiments

On all days, there was no significant difference in growth response between treatments and the control for the nutrient enrichment experiments conducted using water sampled from the transition zone (Fig. 5.10), thereby indicating that the phytoplankton communities sampled in the transition zone were not nutrient limited. In contrast, results of experiments conducted using water sampled from the pelagic zone varied between days: a significant response was measured to both +N and +N+P addition on day 1 (indicating N limitation of the sampled phytoplankton community; Fig. 5.10a); no difference between treatments and control was measured on day 2 (indicating no limitation by N or P; Fig 5.10b); and, a significant response was measured all treatments (+N, +P, +N+P) on day 5 (indicating co-limitation of the phytoplankton community by both N and P on this day; Fig. 5.10c).

5.3.5 Sediment trap accumulation rates

Sediment accumulation rate measured in the eleven traps over the 4-d deployment period ranged from 493 g m⁻² d⁻¹ to 2074 g m⁻² d⁻¹ (Fig. 5.11). The lowest rate was measured to the north of the stream inflow (site 15) and the highest rate at a site located approximately 300 m perpendicular to the inflow location on the lake shoreline (site 14). Accumulated sediments were predominantly inorganic (90.0 – 97.1% of mass in each trap).

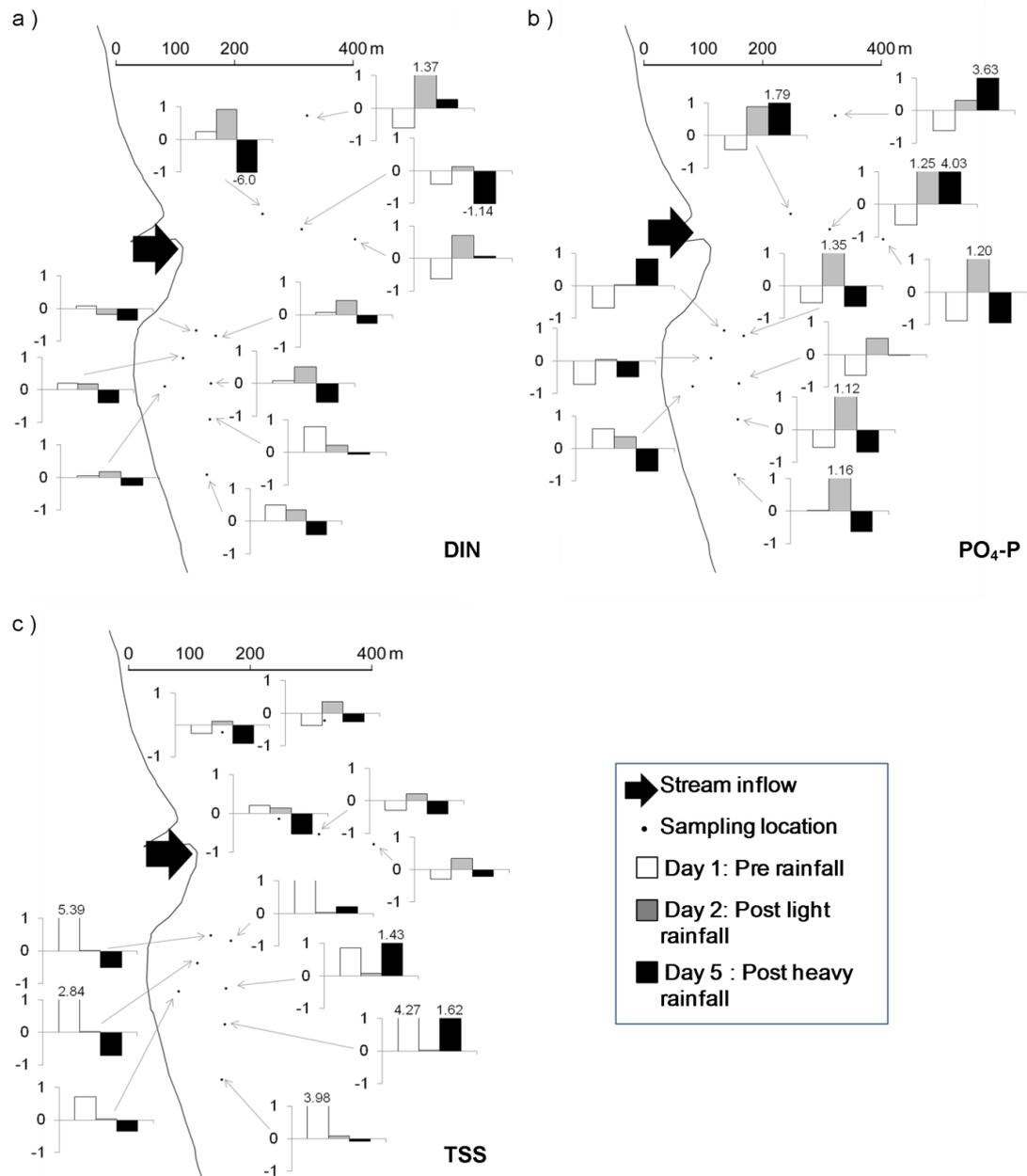


Figure 5.9 Zero-centred mixing ratios for (a) dissolved inorganic nitrogen (DIN), (b) PO₄-P, and (c) total suspended sediment (TSS) during three sampling occasions (see Fig. 5.2) in the vicinity of the transition zone where the Ngongotaha Stream inflows to Lake Rotorua. Mixing ratios are calculated as the ratio of measured concentration to concentrations estimated by assuming conservative mixing between stream and lake water (see Methods). Positive values therefore indicate net accumulation while negative values indicate net loss, as a result of the occurrence of non-conservative processes in the water column. Numbers refer to ratios that are outside the range of the scale (-1 to 1).

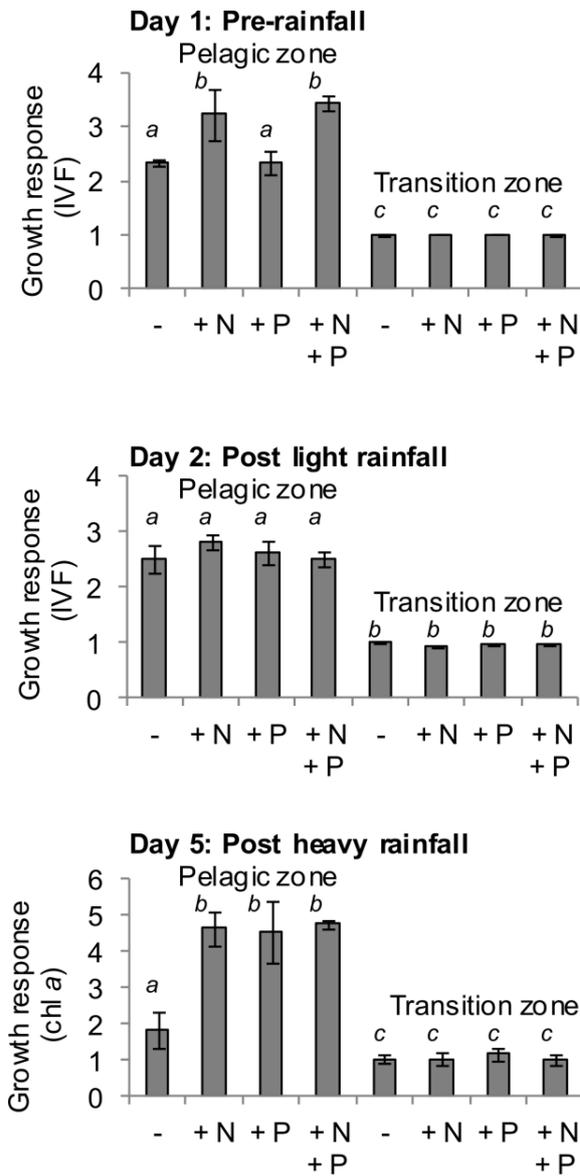


Figure 5.10 Results of nutrient enrichment experiments undertaken on three days using lake water obtained from a central pelagic site in Lake Rotorua (site 1, Fig. 5.1) and a site in the transition zone near the Ngongotaha Stream inflow (site 5, Fig. 5.1). Bars denote mean growth response of treatments relative to the control (no added nutrients) for the transition zone sample ± 1 standard error. Growth response was measured using *in vivo* fluorescence (IVF) or by measuring chlorophyll *a* (chl *a*) concentration. Different letters (*a*, *b*, *c*) denote significant ($p \leq 0.05$) differences between treatments.

5.3.6 Model performance and validation

There was good agreement between modelled and observed temperature at the lake monitoring buoy (RMSE = 0.21 °C, $r = 0.90$) (Fig. 5.5). Simulating propagation of a conservative tracer from the stream to the lake indicated that the model successfully reproduced the observed deflected trajectory of the stream inflow along the shoreline to the south (Fig. 5.12).

Overall, the model simulated variation in measured chl *a* concentration in the vicinity of the transition zone well ($r^2 = 0.71-0.90$), capturing the transition in chl *a* concentration from relatively low in the littoral to relatively high towards the pelagic region of the lake on days 1 and 2 (Fig. 5.13). In addition, the model simulated to some extent the increased horizontal heterogeneity observed on day 5, although the horizontal resolution (50 × 50 m) exceeded dimensions of fine-scale ($\approx 10 - 30$ m) patchiness observed in chl *a* concentration on that day (Fig.

5.7). Simulated chl *a* concentration was higher than measured data close to shore ($\approx 8 \mu\text{g L}^{-1}$ compared to $\approx 2 \mu\text{g L}^{-1}$) resulting in a relatively large RMSE of $9.19 \mu\text{g L}^{-1}$ on day 1, although RMSE was lower on days 2 and 5 (6.6 and $3.3 \mu\text{g L}^{-1}$ respectively).

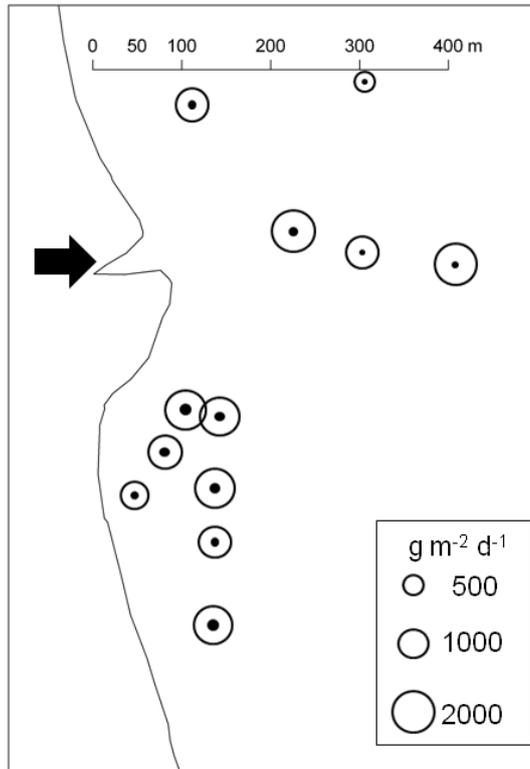


Figure 5.11 Sediment trap accumulation rates measured in the transition zone where the Ngongotaha Stream inflows to Lake Rotorua, 12–16 December 2011. Circled area is proportional to rate (see scale). Outer circles denote total sediment; inner black circles denote the organic fraction. Arrow denotes location of stream inflow.

Relative variations in simulated $f(\text{N})$ and $f(\text{P})$ (Fig. 5.14) corresponded broadly to the results of nutrient enrichment experiments (Fig. 5.10). Both $f(\text{N})$ and $f(\text{P})$ were high (i.e. reduced nutrient limitation) in the transition zone compared to the pelagic zone site during the three sampling occasions, which concurs with the lack of growth response observed in the experiments conducted with transition zone waters. Simulated $f(\text{N})$ in the pelagic zone was highest during day 2 sampling which was the only day when N-limitation was not measured. Likewise, $f(\text{P})$ was lowest during day 5 sampling (although this index was relatively invariant overall) which was the only day when P-limitation was measured. Of note is that both $f(\text{N})$ and $f(\text{P})$ were still relatively high (> 0.7) on the occasions when nutrient limitation was determined experimentally, and $f(\text{P})$ in particular remained high throughout the study period with only very minor fluctuations.

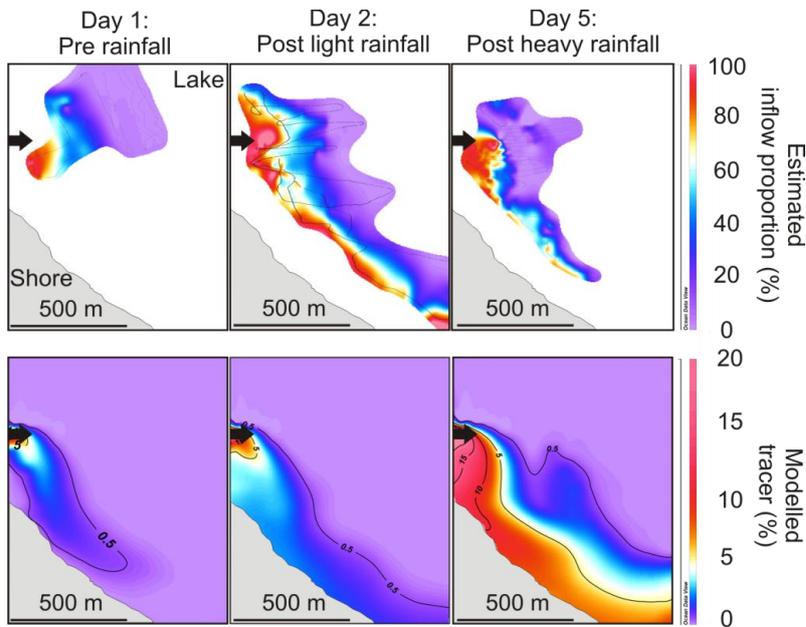


Figure 5.12 Proportion of Ngongotaha Stream water entrained in lake water estimated using measured specific conductance and assuming conservative mixing (top panels) compared to simulated concentration of stream tracer in ELCOM–CAEDYM (bottom panels) on three sampling days.

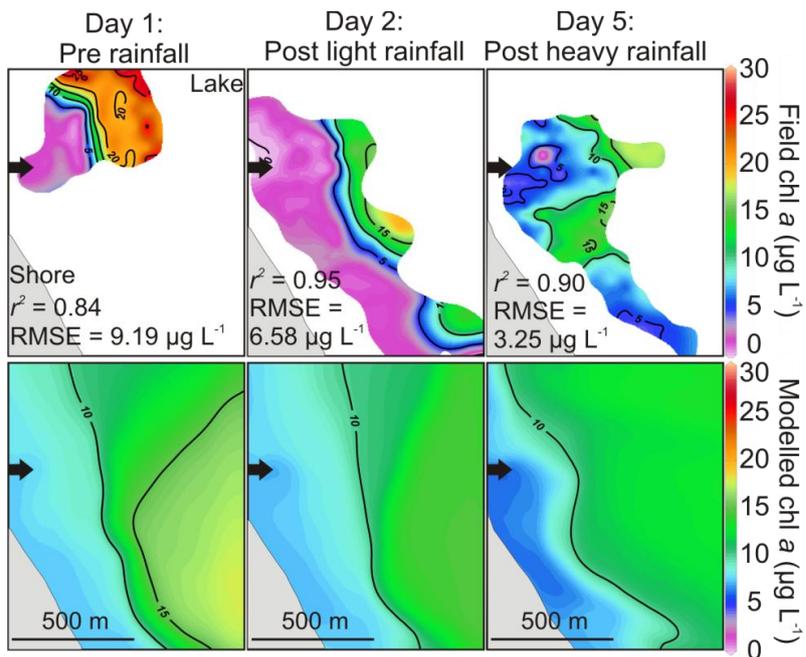


Figure 5.13 Measured chlorophyll a (chl a) concentration in the vicinity of the transition zone where the Ngongotaha Stream inflows to Lake Rotorua (top panels) compared to ELCOM–CAEDYM simulated surface chl a concentration (bottom panels) on three sampling days. Measured field data are averaged over 50 m × 50 m grid cells that correspond to modelled cells. Coefficients of determination (r^2) relate to geographically–weighted linear regressions (measured data not interpolated).

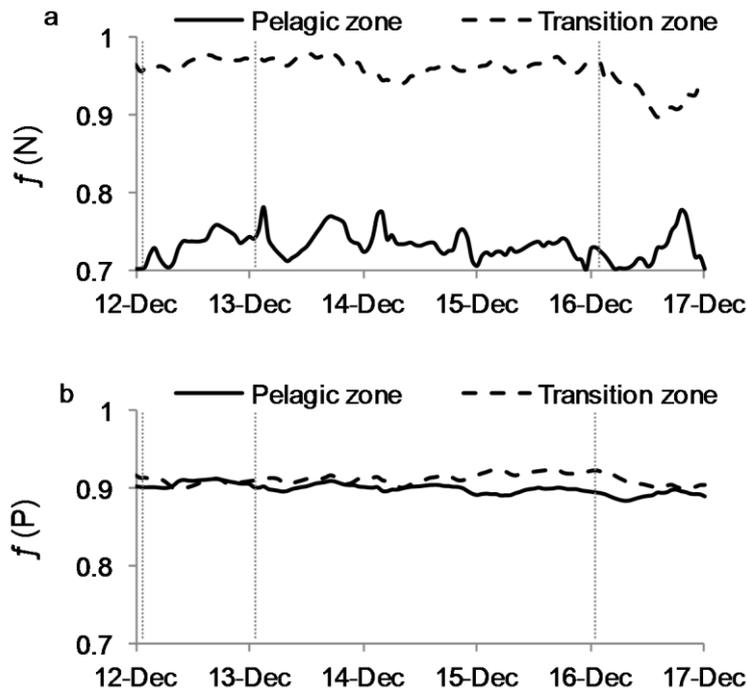


Figure 5.14 ELCOM–CAEDYM surface layer output for a central pelagic site (site 1, Fig. 5.1) and a site in the transition zone where the Ngongotaha Stream inflows to Lake Rotorua (site 5, Fig. 5.1) during the five–day study period. Plots show assemblage–weighted (a) nitrogen and (b) phosphorus limitation functions (see Methods). Dashed vertical lines denote when lake sampling was conducted (see Fig 5.10).

5.3.7 Hydrodynamic simulations

Simulated depth–averaged velocity indicated the presence of a double gyre pattern of basin–scale horizontal circulation within the lake during the study period (Fig. 5.15). This feature comprised southward currents along both west and east shorelines of Lake Rotorua, and, northward redistribution of water into the centre of the lake from the south. Water velocity was greatest on 15 Dec (days 3–4) of the study period) coinciding with peak wind speeds (daily average = 7.12 m s^{-1} ; Fig. 5.3) and destratification (Fig. 5.5). Simulation of horizontal and vertical propagation of the stream inflow (Fig. 5.16) indicates that maximum lateral extent of the inflow was reached approximately 6 h after maximum stream Q (Fig. 5.2), approximately corresponding to when lake sampling was undertaken on day 5. Throughout the five–day study period, the stream water was predominantly confined to within 500 m of the shore in the littoral zone, with only a maximum of approximately 1% of stream water reaching a depth of $> 3 \text{ m}$.

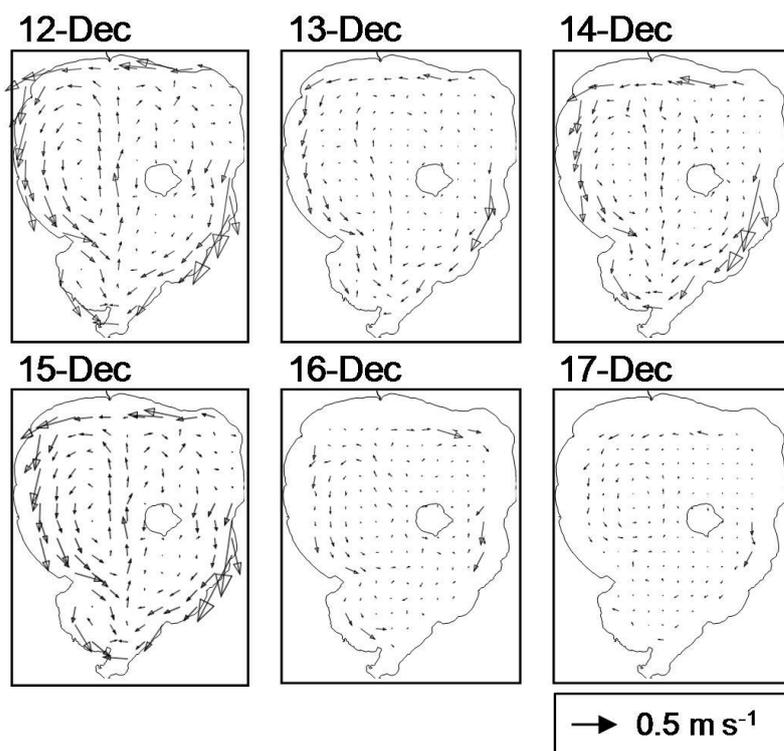


Figure 5.15 ELCOM–CAEDYM simulated depth-averaged velocity vectors at 1200 h on each calendar day during the study period, highlighting southward currents along the western shoreline that comprise part of the larger basin-scale double gyre circulation pattern.

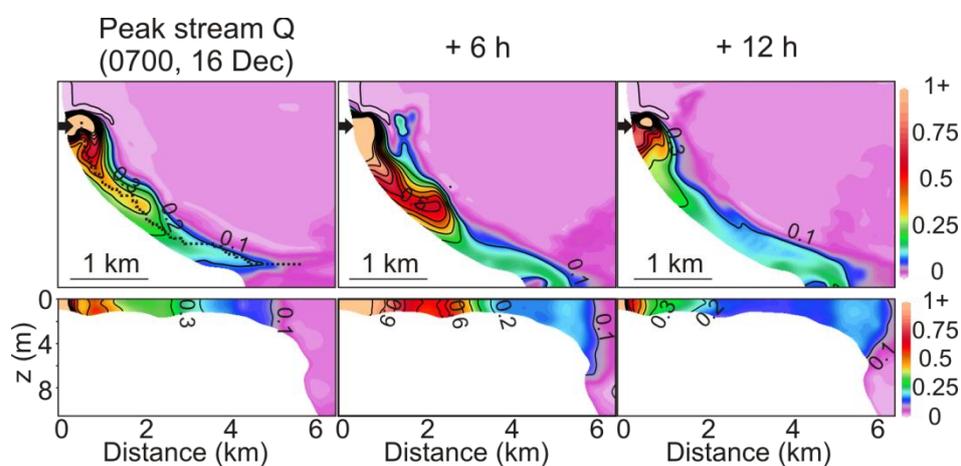


Figure 5.16 ELCOM–CAEDYM simulated horizontal (plan view; top panels) and vertical (section view; bottom panels) propagation of the Ngongotaha Stream inflow (arrows) into Lake Rotorua during and after the time of peak discharge (Q) measured during the study period. The section shown in bottom panels corresponds to a curtain through the plume, denoted by the dashed line in the top left panel. Colour scale represents concentration of a modelled conservative tracer (simulated concentration in the stream water = 10 nominal units).

5.4 Discussion

5.4.1 Inflow dynamics

Modelled basin-scale circulation, which was validated at a local scale by the field data, had a major influence on how the inflow affected biogeochemical processes in the pelagic zone of the lake and the extent of lateral transport to deeper waters of the main basin. The double gyre circulation pattern that was simulated has been previously noted in Lake Erie where it has been associated with uniform wind fields during winter when winds are strongest (Beletsky et al., 1999). In this study, the simulated horizontal circulation reflects the relatively consistent north-east direction wind forcing in the days prior to and throughout the majority of the study period (Fig. 5.3). Given that the stream was colder than the lake (as are other surface streams that enter the western side of the lake and were likely to be entrained in the current), presence of the southward current along the western shoreline helps to explain why the littoral zone was cooler than the main body of the lake; an otherwise surprising result given that sampling was conducted around midday in summer.

Propagation of the inflow may best be classified as a ‘wall jet’ which Jones et al. (2007) define as a “*weakly deflected jet... discharged in a coflow (or nearly so) along the bank*”. Dynamic attachment with the shoreline can occur in highly deflected inflows (Imberger & Patterson, 1990) although mixing ratios for TSS on day 5 when Q was greatest (Fig 5.16c) suggest that water velocity was lower close (< 100m) to the shoreline relative to further offshore (≈150 m). That is to say, the ratios indicate that the three sites closest to the shoreline to the south of the inflow (5, 6, 7) were depositional environments, whereas the three adjacent sites further from shore (8, 10, 11) were accumulation environments (i.e. sediment entrainment due to higher water velocity). Plunging of relatively cool stream inflows on entry to a lake is well recognised (e.g. Schallenberg et al., 1999; Marti et al., 2011), however in this case, confinement of the stream inflow to the littoral zone by the prevailing horizontal current prevented transport into the main body of the lake and promoted turbulent mixing in shallow waters.

5.4.2 Phytoplankton productivity in the transition zone

Dilution of lake water by the stream inflow was the dominant factor influencing chl *a* distribution in the transition zone, resulting in a zone of relatively low chl *a* concentration extending 200 – 500 m perpendicular from the shoreline. Mackay et

al. (2011a) similarly found dilution by a stream inflow to be the dominant contributor to observed increases in lake chl *a* concentration with distance from a stream mouth. The zone of dilution was least apparent on day 5 (post heavy rainfall) when pronounced patchiness was measured in the transition zone. The extent to which this patchiness reflects hydrological or ecological processes is uncertain. The boundary of the propagating inflow was somewhat less distinct on day 5 (Fig. 5.12), potentially due to the reduced southwards-oriented velocity along the western shore of the lake compared with days 1 and 2, according to model simulations (Fig. 5.15). Thus, reduced velocity of the entraining current and, potentially, fluctuations in wind direction (Fig. 5.3) could have caused intrusion of parcels of lake water with relatively high chl *a* concentration into the zone of stream water, thereby contributing to the occurrence of the chl *a* ‘hot spots’ that were observed within the transition zone on day 5. Of note, however, is that fluorescence (and thus estimated chl *a*; Fig. 5.7) measured in such patches was markedly greater than the relatively constant measurements made furthest offshore, outside the extent of stream water. For example, measured fluorescence along small (≈ 10 m) sections of the survey transect in the transition zone 300 m south of the mouth corresponded to chl *a* concentrations of $22.7 - 63.9 \mu\text{g L}^{-1}$ whereas estimated chl *a* concentrations outside the transition zone were $16.0 - 19.4 \mu\text{g L}^{-1}$. Thus, although there is uncertainty associated with the higher chl *a* concentrations as they exceed the upper range of the *in situ* fluorescence calibration, their relatively high magnitude, in addition to the consistency of specific conductivity and temperature measurements with adjacent water of lower chl *a* concentration, suggests that these ‘hot spots’ may instead reflect localised regions of enhanced phytoplankton productivity that have developed in specific response to high nutrient abundance in the inflow–lake transition zone. Stormwater plumes have been shown to promote localised phytoplankton productivity in receiving nutrient–poor marine waters (Corcoran et al., 2010). However, although relatively high phytoplankton productivity in a transition zone has been attributed to locally elevated TP concentrations (Izydorczyk et al., 2008), such pronounced patchiness in a lake transition zone is not well–recognised.

5.4.3 *Phytoplankton nutrient limitation*

The marked spatial and temporal variations in phytoplankton community nutrient limitation status that were observed underline the dynamic nature of lentic algal communities and the factors that regulate them (Reynolds, 1995; Davies et al., 2010). The consistent lack of growth response to added nutrients in the transition zone enrichment experiments (Fig. 5.10) reflects the high concentrations of dissolved nutrients (Fig. 5.6) and low phytoplankton biomass present in the stream relative to the lake, resulting in nutrient replete conditions in the transition zone. Similarly, Vanni et al. (2006) found that the severity of nutrient limitation in a reservoir increased with distance from an inflow towards the dam.

Relaxation on day 2 of prior N-limitation (Fig. 5.10) may reflect enhanced external N-loading following light rainfall between sampling on day 1 and day 2 (Fig. 5.2). The results of the nutrient enrichment experiments conducted for the pelagic site on day 5 indicate the presence of reciprocal limitation, i.e. co-limitation whereby some species in the assemblage are limited by N and some by P as a result of variation in species' physiological requirements (Morris & Lewis, 1988). Previous experimental work in Lake Rotorua has identified species-specific variation in growth responses to N and P additions, likewise suggesting that co-limitation was present in the phytoplankton assemblage (Burger et al., 2007b). The shift from no nutrient limitation on day 2 (post light rainfall) to co-limitation on day 5 (post high rainfall) was an unexpected result, given the elevated external nutrient loading following high rainfall (e.g. Fig. 5.6) and mobilisation of hypolimnetic nutrients that would have occurred following lake mixing on day 3 (cf. Burger et al., 2007a). Several possible explanations can potentially explain this result. Firstly, it is notable that this result is consistent with relative changes in simulated $f(N)$ and $f(P)$, and model results also suggest that the rate of horizontal transport in the lake was lower on day 5 than on day 2 (compare 13 and 16 Dec. plots in Fig. 5.15), consistent with reduced wind speeds (Fig. 5.3). Thus, despite presumably higher nutrient loading to the lake on day 5, the rate of nutrient transport to the pelagic zone may have been insufficient to alleviate nutrient limitation. In addition, it has been shown that summer rain events can rapidly alter phytoplankton community composition (Znavor et al., 2008), and Barbiero et al. (1999) note the occurrence of short term (< 1 week) increases in phytoplankton species richness following storm events due to temporary increases in abundance of previously rare species that possess high

rates of both growth and nutrient uptake. It is possible, therefore, that prevalence of such species on day 5 may also have contributed to the reciprocal limitation that was observed. Furthermore, it is notable that measured solar irradiance on 16 Dec (day 5 lake sampling) was higher than any other day in the study period; maximum solar radiation on 13 Dec (day 2 of lake sampling) was nearly half that on day 5 (503 compared to 964 W m⁻²; Fig. 5.3). High irradiance may therefore have caused relative stimulation of phytoplankton growth on day 5, contributing to the observed nutrient limitation.

5.4.4 Sediment and nutrient fluxes in the transition zone

Measurements of beam transmittance generally allowed the spatial distribution of sediments entrained in the inflow to be characterised continuously throughout the study area, although measured beam transmission did not fully account for variations in TSS concentration (Fig. 5.8a). The four sites circled in Figs. 5.8a–c that displayed the highest deviation from the general relationship between beam transmittance and suspended sediment concentrations were located in the main path of the deflected inflowing stream. The unusually low beam transmittance (relative to TSS concentration) measured at these sites therefore indicates that sediments transported to the lake during this period of high Q had markedly different optical characteristics compared with other sediments that were sampled. Light attenuation is strongly dependent on particle size; attenuation per unit of sediment mass peaks at an intermediate particle size that approximately corresponds to silt (Davies–Colley & Smith, 2001). A change in particle size characteristics of TSS during high discharge in the sediment plume, for example due to relative increase in the contribution of silt-sized particles (i.e. 3.9 – 62.5 µm; Wentworth, 1922), is therefore likely to account for these data points that deviate from the overall relationship between beam transmittance and suspended sediment concentration.

Comparison of measured dissolved nutrient and TSS concentrations with estimated concentrations (\hat{C}_i) based only on assumed dilution effects helped to quantify the occurrence of dynamic processes in the lake. Similar methods have been used previously to study transition zone processes (e.g. Mackay et al., 2011a; Sorokovikova et al., 2012) and the approach is particularly suitable for cases such as this study where there was a marked difference between stream and lake concentrations. Given the likely heterogeneity in chemical composition of pelagic

waters, however, it is appropriate to be cautious about attributing high significance to individual mixing ratio values due to uncertainty in whether samples collected at the monitoring buoy are truly representative of 'lake' water and, also, potential in-lake variation in tracer values (SpC), e.g. due to the influence of other entrained stream waters. Nonetheless, high (e.g. > 1) and low (e.g. < -1) mixing ratios suggest occurrence of both dynamic loss and accumulation processes in the transition zone (Fig. 5.9).

Overall, there is congruence between the results of nutrient enrichment experiments and mixing ratios calculated for dissolved nutrient concentrations. On day 1, negative DIN mixing ratios at three sites furthest from the shore (i.e. least influenced by stream water; Fig. 5.9a) are consistent with N-limitation measured at the pelagic site, suggesting active DIN uptake by N-deficient phytoplankton at the periphery of the transition zone. Likewise, predominance of negative DIN mixing ratios on day 5 is also consistent with measurement of N-limitation at the pelagic site on that day, again suggesting active uptake by phytoplankton. These results contrast with day 2 when DIN mixing ratios were predominantly positive and N-limitation was not measured in the lake. Day 5 was the only day when pelagic nutrient enrichment experiments yielded a positive growth response to added P and, accordingly, the majority of mixing ratios are negative (suggesting active biotic uptake) although high (> 1.5) values at the three northern-most sites disaffirm the trend (Fig. 5.9b). Overall, DIN mixing ratios were less variable and were closer to zero than those for $\text{PO}_4\text{-P}$ and TSS. While the occurrence of negative mixing ratios is consistent with a hypothesis of DIN uptake by nitrogen-limited phytoplankton, an explanation for the occurrence of positive ratios is less apparent. Desorption of $\text{NH}_4\text{-N}$ from stream-borne suspended sediments is discounted as a major cause because $\text{NH}_4\text{-N}$ was a minor component of DIN. It is possible therefore that the positive DIN mixing ratios (most apparent for day 2 data to the north of the stream confluence) may reflect the influence of DIN sourced from other lake inflows and transported in the southwards orientated current.

High (e.g. > 0.5) $\text{PO}_4\text{-P}$ mixing ratios are interpreted as indicative of PO_4^{3-} desorption from suspended sediments. Sediment resuspension can markedly increase water column PO_4^{3-} concentrations (SanClements et al., 2009), however, there is no correlation between TSS and $\text{PO}_4\text{-P}$ mixing ratios on any of the three days, as would be expected if areas of active resuspension (i.e. positive TSS

mixing ratios) were also associated with net PO_4^{3-} accumulation due to desorption from re-suspended material. Instead, it is therefore plausible that particulate phosphorus associated with stream-borne sediments provided a net source of desorbed PO_4^{3-} at some sites. Up to 70% of catchment-derived particulate phosphorus transported following rainfall has been shown to be potentially bioavailable in receiving waters in the short-term (Pacini & Gächter, 1999) although the bioavailability of particulate phosphorus can vary widely depending sediment characteristics (e.g. Fe abundance; Evans et al., 2004). The composition of the particulate phosphorus transported in the stream during the study period is unknown, for example, the relative contribution of loosely bound forms compared to more refractory apatite-associated forms was not quantified. Of particular note is that, although nutrient enrichment experiments indicated absence of P-limitation on both days 1 and 2 (Fig. 5.10), $\text{PO}_4\text{-P}$ mixing ratios were predominantly negative on day 1 and were all positive on day 2. The concentration of TSS can affect the equilibrium PO_4^{3-} concentration of associated water, thus controlling whether or not reversibly-adsorbed particulate phosphorus contributes to water column PO_4^{3-} concentration (Uusitalo et al., 2000). One explanation for this result, therefore, is that elevated stream TSS concentrations on day 2 (Fig. 5.6) were associated with a shift from sediments being a sink of PO_4^{3-} (i.e. net adsorption) to a net source (net desorption) due to altered PO_4^{3-} equilibrium state.

Sediment trap accumulation rates measured in this study integrate deposition of stream-borne sediments, resuspension of sediments from the lake bed and settling of lake seston. Sediment accumulation rate has previously been measured over 4–5 day periods at a deeper site (5 m) approximately 1 km offshore from the stream mouth during 2003 (Burger, 2006). Gross sediment accumulation rates measured in the cited study ($6 - 12.5 \text{ g m}^{-2} \text{ d}^{-1}$) were approximately more than two orders of magnitude lower than in this study, reflecting the high rate of the sediment depositional processes occurring in the transition zone during the study period. This is further emphasised by noting that the depth of the water overlying the traps (mean = 0.33 m, range 0.18–0.81 m) was typically less than half the total water depth at individual sites. The proportion of accumulated material that was organic (25–40%) measured by Burger (2006) was higher than in this study, likely reflecting lower relative contribution of lake-derived organic seston to sediments in this study. In a study specifically addressing transient

sedimentation conditions, Effler et al. (2006) measured sediment accumulation following rainfall in traps deployed in an elongated reservoir at a site approximately 3 km downstream of the inflow. Despite higher influent loads, measured sediment accumulation rates were typically lower than in this study, likely reflecting reduced contribution of re-suspended material due to the greater depth (≈ 15 m) and greater distance from the inflow. Their maximum accumulation rate measured over 8 d during the largest flood (return period = 1 yr, estimated maximum inflow TSS concentration > 1000 mg L⁻¹) was, however, comparable to the mean accumulation rate measured in this study (1211 g m⁻² d⁻¹ compared to 1485 g m⁻² d⁻¹).

There is little correspondence between spatial variation in sediment trap accumulation rates and the pathway of the southward-deflected stream inflow. Although the lowest accumulation rate was measured at a site to the north of the mouth (site 15), this was also the deepest site (1.34 m) and therefore the relatively low rate is likely to be at least partly due to reduced resuspension owing to the inverse relationship between depth and benthic shear stress (Hamilton & Mitchell, 1997). Highest accumulation measured at a site perpendicular to the mouth and approximately 400 m offshore likely reflects high potential for deposition in this area of the transition zone, due to high rate of sediment supply, yet low water velocity.

In conclusion, this study contributed to understanding how dynamic short-term (hours–days) variations in both meteorological forcing and the water quality of a stream draining a predominantly agricultural catchment can interact to influence water quality of a downstream lake. Rainfall in the stream catchment increased sediment and nutrient loads to the lake as a result of both increases in discharge and concentrations of suspended sediments and total nutrients. Wind-driven horizontal circulations in the lake caused deflection of the inflowing stream and the resulting pathway of the propagating inflow strongly influenced the spatial distributions of biogeochemical processes and water quality variables at distances up to 1 km from the stream mouth. Biogeochemical processes in the transition zone resulted in spatial–temporal variations in the occurrence of net loss and accumulation processes of both sediments and nutrients in the water column. Notably, there was correlation between apparent uptake of dissolved nutrients by primary producers within the plume of stream water and the nutrient limitation status of pelagic phytoplankton. Observed inflow dynamics and spatial variations

in chl *a* concentration were reproduced by a coupled hydrodynamic–water quality model which provided insight into hydrological and ecological processes that occurred in the lake beyond the temporal and spatial bounds of the sampling programme. The nutrient limitation status of phytoplankton varied spatially and temporally within the lake, reflecting transience of nutrient transport processes and, potentially, variation in assemblage composition and environmental history that confounded the link between external nutrient loading and nutrient limitation state. Dilution was the main process that influenced phytoplankton distribution in the transition zone although patchiness observed following high discharge may have reflected enhanced productivity of nutrient limited phytoplankton due to nutrient–rich conditions in the plume. This study highlights how characteristics of the coupled littoral–pelagic relationship can influence dynamic spatial and temporal variations in the water quality of large lakes during short time scales.

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6 Bioavailability of phosphorus transported during storm flow to a eutrophic, polymictic lake: Chemical and biological analyses of the bioavailability of phosphorus sampled from two stream inflows to Lake Rotorua

6.1 Introduction

Phosphorus (P) is a macronutrient that is essential for synthesis of organic compounds such as nucleic acids and ATP (Maathuis, 2009). It is frequently the limiting nutrient in freshwaters (Schindler, 1977, Elser, 2007), thus, reducing excess P loads from external sources such as farmland is important for improving water quality in lakes that exhibit nuisance excess growth of phytoplankton following anthropogenic eutrophication (Lewis et al., 2011, Schindler, 2012).

Phosphorus exists in freshwaters in numerous forms which vary widely in bioavailability to primary producers (Reynolds and Davies, 2001). Knowledge of how the relative composition of the P load to a lake varies in space and time is therefore useful to help lake managers to efficiently allocate efforts to control P inputs from catchments. With occasional exceptions (e.g. see Twinch and Breen, 1982), dissolved reactive phosphorus measured using the molybdenum–blue method (Murphy and Riley, 1962; hereafter ‘ $\text{PO}_4\text{-P}$ ’) represents the minimum concentration of P in a water sample that is immediately bioavailable (Reynolds and Davies, 2001, Auer et al., 1998). This fraction may be, however, only a minor component of the total phosphorus (TP) load transported in surface stream inflows to a lake, particularly during storm flow periods when TP can predominantly comprise particulate phosphorus (PP) bound to suspended sediments (e.g. Hoare, 1982, Hatch et al., 2001, Ellison and Brett, 2006). This PP can consist of a number of different fractions that range in bioavailability from loosely sorbed $\text{PO}_4\text{-P}$ that may be considered readily bioavailable, to P that is refractory as it is tightly bound in the lattice of apatite minerals (e.g. Boström et al., 1988, Machesky et al., 2010).

The composition of PP can be quantified using chemical extraction techniques that permit isolation of individual fractions (e.g. see Psenner et al.,

1998). Such extraction schemes allow individual PP fractions to be operationally defined, however, the biogeochemical origin of individual extracted fractions has not always been clear (Lukkari et al., 2007), and there is debate regarding the relative bioavailability of individual fractions to phytoplankton (Golterman, 2001). Such uncertainty partly reflects that the bioavailability of individual fractions is usually dependent on factors such as pH or redox potential. For example, the bioavailability to lentic phytoplankton of PP specifically extracted using a reducing agent is clearly dependent on the redox conditions that the PP is likely to be exposed to in the lake environment (Uusilato et al., 2003). Despite being less convenient, physiological assays that involve measuring the growth response of P-limited phytoplankton exposed to particular P fractions are therefore also useful to determine the relative bioavailability of a P source (Bostrom, 1988).

This study was undertaken in the catchment of Lake Rotorua; a large (80.5 km²), volcanically-formed lake in central North Island, New Zealand. The lake has undergone eutrophication and water quality now fails to meet community expectations (Parliamentary Commissioner for the Environment, 2006). Currently, the majority of the P load to the lake is from internal sources, i.e. derived from high benthic sediment release of PO₄³⁻ that reflects decades of high external loading and consequent P accumulation in the sediments (Burger et al., 2007). A non-statutory target to reduce the annual P load to the lake from the catchment by 10 tonnes, in addition to nitrogen load reduction, has been proposed to achieve desired water quality improvement (Bay of Plenty Regional Council et al., 2009). Loads of P from the surface catchment can comprise a high proportion of PP, particularly during storm flow in streams not dominated by groundwater input (Hoare, 1982). The bioavailability of this PP is currently uncertain, and hence, the aim of this study was to investigate the potential for catchment-derived PP to contribute to eutrophication of Lake Rotorua. Water samples were collected from two stream inflows during elevated discharge and results are presented of: i) quantitative chemical analyses of P fractionation and suspended sediment characteristics, and; ii) a bioassay conducted using P-limited phytoplankton.

6.2 Methods

6.2.1 Stream sampling

Water samples were collected from the Puarenga and Ngongotaha streams which are two of the nine major stream inflows to Lake Rotorua. Both streams are estimated to convey a high proportion of water in storm flow (Rutherford and Timpany, 2008) and TP loads transported in storm flow are dominated by PP in both streams (authors' unpublished data). Mean discharge in both streams is approximately $1.7 \text{ m}^3 \text{ s}^{-1}$ (Rutherford & Timpany, 2008).

Both streams were sampled during elevated discharge following two separate rain events in March and August 2012. The August event was particularly large, resulting in minor localised flooding of the Ngongotaha Stream (see Table 6.1 for event characteristics). Grab samples were collected in 5-L containers that had been acid washed (10% HCL) and rinsed with analytical grade deionised water (Millipore Co.). Samples were transported to the laboratory and refrigerated until analysis or experimental work commenced the following day.

Table 6.1 Characteristics of sampling events

| Stream | Date | Maximum discharge during event ($\text{m}^3 \text{ s}^{-1}$) | Discharge during sampling ($\text{m}^3 \text{ s}^{-1}$) | Stage of hydrograph during sampling |
|------------|----------------|--|---|-------------------------------------|
| Ngongotaha | 03 March 2012 | 3.7 | 2.3 | Falling |
| | 12 August 2012 | 47.0 | 22.0 | Falling |
| Puarenga | 03 March 2012 | 2.4 | 2.1 | Falling |
| | 12 August 2012 | 13.8 | 10.8 | Rising |

6.2.2 Water chemistry analysis

Suspended sediment concentrations were determined by filtering 65 – 500 mL of stream water through pre-combusted (550 °C for 3 h) and pre-weighed glass fibre filters (0.5 μm , Advantec GF GC-50). Total suspended sediment (TSS)

concentrations were determined gravimetrically following drying (105 °C for 8 h) and volatile suspended sediment (VSS) concentrations were then determined by weight difference following subsequent ashing (550 °C for 3 h). Particle size distribution of the grab samples was analysed using laser diffraction (Mastersizer 2000, Malvern Instruments) which quantified the volume of suspended sediment corresponding to 48 size classes in the range 0.05 – 2000 µm. For each grab sample, average results were recorded of analysis of three well-shaken sub-samples (250–400 mL) with no added dispersant.

Phosphate concentration was determined by analysis of a filtered sample (0.5 µm, Advantec GF GC-50) using a standard molybdenum–blue method (Murphy and Riley, 1962, APHA, 1998) with an Aquakem 200 discrete analyser (Thermo Fisher). A preliminary reducing step to prevent interference from arsenate and silicon (e.g. see Downes, 1978) was not undertaken and hence the potential for some overestimation of PO₄–P concentration due to the presence these constituents cannot be discounted. Total phosphorus and total dissolved phosphorus (TDP) were determined following acidic persulphate digestion (APHA, 1998) of an unfiltered and filtered (0.5 µm, Advantec GF GC-50) sample, respectively, followed by colorimetric analysis of PO₄–P using a standard molybdenum–blue method (Murphy and Riley, 1962, APHA, 1998) with a Lachat QuickChem flow injection analyser (Zellweger Analytics Inc.). In accordance with convention (e.g. Hatch et al., 2001), dissolved organic phosphorus (DOP) was calculated by subtraction of PO₄–P from TDP, although this fraction may also include PP associated with inorganic colloids not retained by the filter (i.e. < 0.5 µm). A range of check standards was analysed in concert to confirm analytical detection limits.

The bicarbonate–dithionate extraction developed by Uusitalo and Turtola (2003) was used to determine the concentration of redox–sensitive P. This method is based on the reductive extraction step described by Psenner (1998) and is designed to quantify potentially bioavailable P in waters that develop anoxia. Specifically, this reductive step selectively isolates P bound to reducible metals, principally oxidised forms of iron (Lukkari et al., 2007). To perform the extraction, 1 mL of 0.298 M NaHCO₃ and 1 mL of 0.574 M Na₂S₂O₄ (both prepared immediately prior to the procedure) were sequentially added to 40 mL of sample in a 50 mL capacity polypropylene centrifuge tube. Solutions were agitated using an orbital shaker (15 min, 120 rpm) and then filtered (0.5 µm,

Advantec GF GC-50) and frozen prior to analysis. The P concentration of solutions was subsequently determined as for TP, i.e. by colorimetric analysis of PO₄-P following digestion, with correction for dilution due to addition of salt solutions. The digestion step is necessary because interference of PO₄-P determination following Na₂S₂O₄ addition has been noted without digestion (Uusitalo and Turtola, 2003). Redox-sensitive P was then calculated by subtracting TDP concentration from the final P concentration of filtered water in the extraction step (a mean of duplicates was used).

6.2.3 Bioassays

Bioassays were conducted using water sampled from both streams during the March event. A comparable experiment was conducted for the August event but the results were discarded due to suspected interference from growth of non-inoculated phytoplankton. Bioassays (including all method development work; results not shown) were undertaken using a monoculture of a Chlorophyta species isolated from a water sample collected from Lake Rotorua. The species was identified using text of Brook (2002) as belonging to the genus *Closterium*, of which there are about 140 species (*ibid*). The species was chosen for its amenity to laboratory culture and distinctive form which aided accurate counting. A monoculture was used because variations between species in the relationship between P availability and cell chlorophyll *a* content (Chen et al., 2011) could otherwise confound results. Initial cell isolation was undertaken using a micromanipulator (Eppendorf Transfer Man NK2) in conjunction with an inverted microscope (Olympus IX71). Phytoplankton were cultured in Bold's Basal Medium (Nichols and Bold, 1965), prepared using stock solutions made with analytical grade chemicals (BDH Laboratory Reagents) and analytical grade deionised water (Millipore). This medium is designed to satisfy all nutritional requirements, however, soil solution prepared using local soil was also added (four drops per L) as a further precaution to prevent micro-nutrient limitation. Media were sterilised in an autoclave prior to use and cell transfers were undertaken in a laminar flow cabinet to minimise potential for contamination although, despite these precautions, cultures were assumed to be non-axenic. All glassware was acid washed (10% HCl) and cotton wool stoppers used to cover culture flasks were sterilised in an autoclave.

Prior to undertaking bioassays (before stream sampling), a subsample (2 mL) of monoculture was transferred to P-free medium (250 mL) that was prepared using the recipe for Bold's Basal Medium but without P-containing salts. This permitted a culture to be established which was considered after one week to be P-limited and which had visibly lower cell density than a control culture containing P. This P-limited culture was then used to inoculate (2 mL) water collected from both streams to permit investigation of P-utilisation. The following three experimental treatments (five replicates for each) were established using both stream water samples: unfiltered, filtered and anoxic (Table 6.2). These treatments were chosen to allow comparison of growth between phytoplankton with access to PP (unfiltered stream water), without access to PP retained by the filter (filtered stream water) and with initial (at least) access to redox-sensitive PP (Table 6.2). Phosphorus-deficient media and additional nitrogen (NH_4Cl added to increase concentration by 2.5 mg N L^{-1}) were added to each treatment (final volume = 51 mL) to eliminate potential for limitation by nutrients other than P.

Table 6.2 Description of the three experimental treatments used in the bioassays to investigate phosphorus bioavailability in stream water

| Experimental treatment | Details |
|------------------------|---|
| Unfiltered | Untreated stream water |
| Filtered | Filtered stream water (0.5 μm Advantec GF GC-50 filter) |
| Anoxic | Reducing agent (bicarbonate dithionate) added to stream water in the same proportion as used for extraction (see Methods) |

The experiments were conducted in glass tubes (Schott Duran), loosely covered with plastic film and maintained upright in metal racks placed on an orbital shaker plate (40 rpm). Treatments were incubated under artificial light ($47 \mu\text{mol m}^{-2} \text{ s}^{-1} \mu\text{A}^{-1}$) set to a 18-h light:6-h dark regime in a temperature-controlled room (16 °C). Tubes were randomly rearranged in the racks each day. Growth response was measured daily by *in vivo* fluorescence with a 10-AU fluorometer (Turner Designs) following onset of exponential growth and until the mortality phase. Tubes were placed in a vortex prior to determination of fluorescence to promote homogenisation of cells. Measured fluorescence was converted to cell density

using the equation for a linear regression ($r^2 = 0.90$, y intercept set to 0) of fluorescence (fluorescence units) on cell density (cells mL⁻¹) that was derived by undertaking cell counts ($n = 18$) for the range of measured fluorescence values. Cell counts were undertaken using Utermöhl settling chambers and an inverted microscope (Utermöhl, 1958). To account for fluorescence of photosynthetic pigments already present in the samples (e.g. associated with terrestrially-derived plant material or lotic phytoplankton), controls (in triplicate) were established that lacked inoculates (replaced with analytical grade deionised water) for each treatment for both streams. The mean fluorescence of treatment- and stream-specific controls was then subtracted from the growth response of experimental treatments to derive corrected cell density that accounted for the effect of background fluorescence. Blanks (five replicates) were also incubated to confirm presence of P-limitation. Blanks were prepared as for the unfiltered treatments except analytical grade deionised water was substituted for stream water. Once an apparent mortality phase was reached, a sub-sample of treatments was inspected with a microscope (Olympus IX71, 60 × magnification) to confirm absence of zooplankton or growth of phytoplankton species that differed from the species used as inoculates.

Growth rate (r) for individual replicates was quantified using the exponential increase constant which was assumed equal to the gradient of a linear regression of natural log-transformed cell density (cells mL⁻¹) on time (days) for the period of exponential growth (Reynolds, 2009). Two-way analysis of variance (ANOVA) and factorial ANOVA with Fisher's LSD post hoc tests were used to quantify significant ($p \leq 0.05$) differences in the mean of both r and maximum yield between blanks with no added P and treatments for both streams. Maximum yield was assumed equal to the maximum corrected cell density measured during the stationary phase following exponential growth. Identification of significant differences between treatment responses thus permitted qualitative comparison of the relative bioavailability of the P between treatments. Culture of P-limited cells with additions of PO₄-P standards of known concentration (range = 0.01–0.25 mg P L⁻¹, nine standards trialled in triplicate) confirmed that cell density typically increased with PO₄-P concentration, although attempts to quantify differences in cell density in terms of PO₄-P concentration was unsuccessful due to inconsistent variations in the response curve (data not presented). Non linearity in such relationships has been observed elsewhere for a Chlorophyta species (Sigeo et al.,

2007) and may reflect changes in intracellular carbon allocation with variations in resource availability or the interactive influence of other ions in the growth medium (Evens and Niedz, 2010).

6.3 Results

Suspended sediment and P characteristics were comparable between the two streams over individual events although they differed greatly between the two events (Figs. 6.1 and 6.2; Table 6.3). For each stream, concentrations of TSS and VSS were more than one order of magnitude greater for the August event than for the March event, reflecting the much higher discharge that was sampled. Despite the higher discharge (and therefore erosive energy), the median diameter of suspended sediments was much lower during the August event in both streams; median particle diameter in both streams corresponded to coarse sand in the March event compared to silt in the August event (based on classification of Wentworth, 1922). Total P concentrations for both streams were almost one order of magnitude greater in the August event, compared to the March event, although concentrations of $\text{PO}_4\text{-P}$ were very similar between streams and events (range = 0.035–0.038 mg L^{-1} ; Fig. 6.1). Concentrations of DOP were a minor component of TP (range = 0–9%) and hence PP was the dominant fraction of TP (52–55% for March event, 91–93% for August event). All of the non- $\text{PO}_4\text{-P}$ in both stream samples was redox-sensitive for the March event, whereas only 23% (Ngongotaha Stream) and 28% (Puarenga Stream) of the non- $\text{PO}_4\text{-P}$ was redox-sensitive for the August event (Fig 6.2).

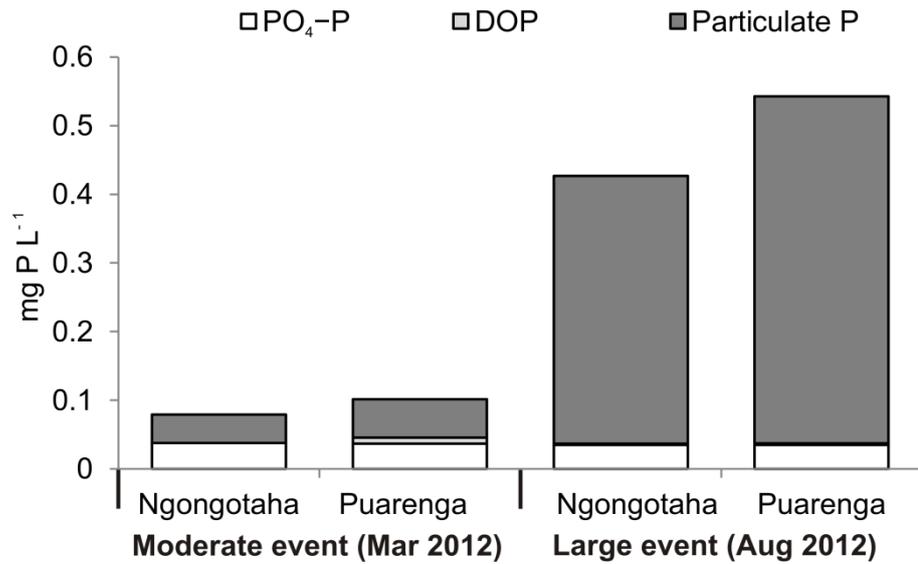


Figure 6.1 Proportion of total phosphorus constituents in stream water samples comprising dissolved inorganic phosphorus (PO₄-P), operationally defined dissolved organic phosphorus (DOP) and particulate phosphorus.

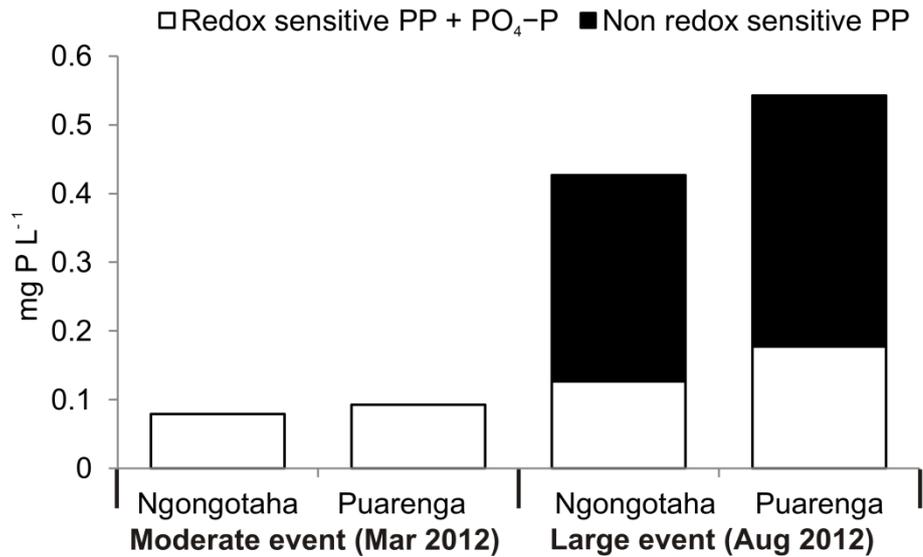


Figure 6.2 Proportion of total phosphorus constituents in stream water samples comprising the sum of dissolved inorganic phosphorus (PO₄-P) and redox sensitive particulate phosphorus (PP) determined using bicarbonate dithionate extraction.

Table 6.3 Summary of suspended sediment and redox-sensitive phosphorus analyses. Q, discharge; Ngo., Ngongotaha; Pua., Puarenga; TP, total phosphorus; TSS, total suspended sediments; VSS, volatile suspended sediments.

| Stream | Event (2012) | Q (m ³ s ⁻¹) | TSS (mg L ⁻¹) | VSS (mg L ⁻¹) | Median (by volume) particle diameter (µm) | % of TP comprising PO ₄ -P or redox sensitive P |
|--------|--------------|-------------------------------------|---------------------------|---------------------------|---|--|
| Ngo. | March | 2.3 | 11.2 | 3.0 | 1239 | 100 |
| | Aug. | 22.0 | 462.5 | 82.8 | 59 | 30 |
| Pua. | March | 2.1 | 20.0 | 5.4 | 997 | 100 |
| | Aug. | 10.8 | 510.5 | 101.0 | 29 | 33 |

Bioassays were undertaken over 12 days (Fig. 6.3). Typical sigmoid growth was observed for both the filtered and unfiltered treatments although no growth response was observed for both streams for one of the five replicates of the filtered treatment. This lack of growth was attributed to initial inoculates being unviable and data for these replicates were consequently omitted from analysis. No growth was observed in reduced treatments for either stream. Some growth was observed for the blanks which did not contain added P, likely indicating either utilisation of intracellular P stores or background P contamination from an unknown source. Both these factors were assumed to be equal for all treatments and hence measured growth response for treatments that was significantly greater than the response measured in the blanks was assumed to indicate relatively higher P availability.

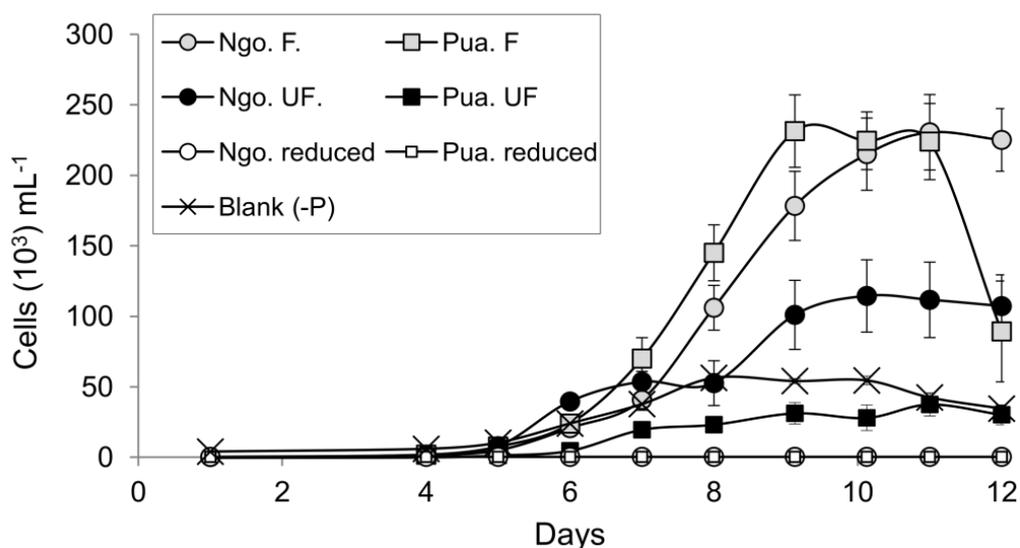


Figure 6.3 Measured cell density for treatments and blanks (no stream water and no added P) during the bioassay conducted with samples collected from the Ngongotaha (Ngo) and Puarenga (Pua) streams during the March event (see Tables 6.1 and 6.3). Measurements have been corrected for potential interference by photosynthetic pigments present in the stream water prior to inoculation (see Methods). Symbols denote the mean and bars denote ± 1 standard error. F, filtered treatment; UF, unfiltered treatment.

Mean growth rate was significantly higher in the filtered compared to the unfiltered treatments ($F = 33.63$; d.f. = 1; $p < 0.001$) but there was no significant difference between the two streams (Fig. 6.4a). There was no significant difference in mean growth rate between the unfiltered treatments and the blanks that did not contain added P. Similarly, comparison of measurements on day 11 (stationary phase of growth) indicated that corrected cell density was significantly higher in the filtered than in the unfiltered treatments ($F = 22.57$; d.f. = 1; $p < 0.001$; Fig. 6.4b). Mean corrected cell density was significantly higher than the blanks for the filtered treatments for both streams and for the unfiltered treatment for the Ngongotaha Stream (d.f = 14; $p = 0.001 - 0.026$).

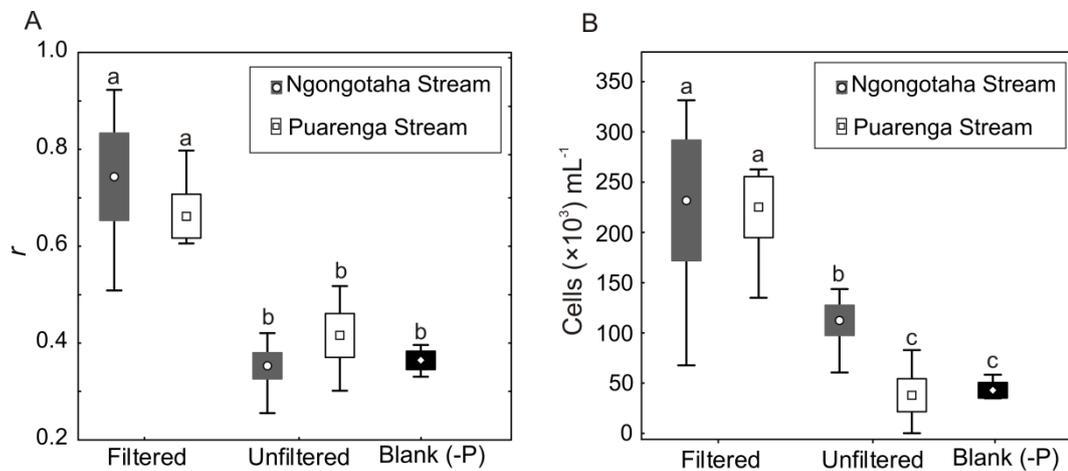


Figure 6.4 Box and whisker plots showing differences between blanks (no stream water and no added phosphorus) and filtered and unfiltered treatments in growth rate (r) during exponential phase (a) and cell density (b) measured on day 11 of the bioassay (Fig. 6.3). Whiskers denote the range, boxes denote ± 1 standard error and symbols in the boxes denote the mean. Different letters denote significant ($p \leq 0.05$) differences based on ANOVA.

6.4 Discussion

The similarities in P fractionation between catchments during individual events (Figs. 6.1 and 6.2) suggest that there may be potential to apply relationships between discharge and relative P composition to other stream catchments, although further analyses are required to confirm this. In particular, further investigation would be beneficial to confirm whether the P fractionation results in Fig. 6.2 for the March event samples are typical of TP transported during moderate events, i.e. that all the TP load is potentially bioavailable if exposed to anoxia. The coarse texture of sampled suspended sediment (Table 6.3), and the moderate magnitude of sampled discharge (implying limited contribution of PP transported in overland flow from far-channel sources), suggests that PP transported in the March event is likely to be associated with the pumiceous sands and loams that comprise the bed and bank sediments of the two streams. By contrast, the marked reduction in median particle diameter sampled during the August event suggests that finer, terrestrially-derived particles (predominantly silts) had a greater contribution to PP concentration. Analysis of sediments sampled from a range of potential source areas, each of which will vary in importance depending on event characteristics (Thompson et al. 2012), could therefore aid more general understanding of the composition of PP transported in storm flow throughout the wider lake catchment.

The finding that either all or a proportion of the PP was redox sensitive indicates that catchment-derived PP transported in storm flow can cause increase of water column $\text{PO}_4\text{-P}$ concentration in Lake Rotorua, given that this polymictic lake is known to develop anoxia in the hypolimnion during stratification periods of more than a few days (Burger et al., 2007). However, the implications of this for primary productivity are not clear. Okubo et al. (2012) concluded that *Microcystis aeruginosa* utilise redox-sensitive P, after observing slightly higher growth response in cultures exposed to soil that had undergone extraction (i.e. the fraction had been removed) with NH_4Cl (to remove P loosely adsorbed on surfaces of compounds such CaCO_3), relative to cultures exposed to soil that had undergone extraction with both NH_4Cl and a reducing agent. In a natural setting, however, Reynolds and Davies (2001) posit that P bound to metal hydroxides that is released during anoxia will quickly re-precipitate and have limited influence on primary productivity. Further investigation of the potential for this fraction to promote phytoplankton growth in the lake (e.g. using mesocosms) would be

beneficial. Also, quantification of other PP fractions in potential source sediments could be advantageous as several studies have found bioavailable P can be well quantified by determination of the NaOH-extractable PP fraction (Sharpley et al., 1991, Auer et al., 1998), assumed to represent organic P and the P associated with aluminium oxides and non-reducible iron oxides (Lukkari et al., 2007). The utility of considering non-redox sensitive fractions is supported by a previous study of benthic PO₄-P release in Lake Rotorua, which noted that PO₄-P release rates were largely independent of dissolved oxygen concentration (Burger et al., 2007). Although redox potential was not quantified in that study, their result suggests that factors aside from redox are important controls of P bioavailability in the lake (e.g. pH, see Hupfer and Lewandowski, 2008; Gao et al. 2012).

It was initially hypothesised that the differences in growth response measured during the bioassay would conform to the order: filtered < unfiltered < reduced, in accordance with predicted variations in bioavailable P concentration. The results were, however, contrary to this prediction. Absence of growth in the reduced treatments is not attributed to P-limitation; it more likely reflects otherwise unsuitable conditions caused by addition of the reductant, e.g. due to reduced pH (Uusitalo and Turtola, 2003) or sulphide evolution. Although somewhat void, the result highlights the constraints of laboratory-based physiological approaches to investigating the bioavailability of redox-sensitive PP. An option for future research, therefore, is to conduct similar experiments using larger volumes that permit the simulation of both oxic epilimnia and anoxic hypolimnia formation.

The significantly higher growth rate and yield measured in the filtered treatments is attributed to bioavailable P concentration being higher in the filtered samples, despite TP concentration being lower. Light limitation due to higher turbidity is discounted as the coarse nature of the suspended sediments in the samples (Table 6.3) meant that the sediments rapidly settled, minimising potential for differences in light attenuation. Mean cell density was lower than in the blanks for the Puarenga Stream unfiltered treatments during part of the bioassay period (Fig. 6.3), but, both growth rate and maximum yield for the unfiltered samples were either the same or higher than the blanks. This result is therefore interpreted as evidence of suspended sediments acting as a sink, not a source, of PO₄-P. Rapid decrease of PO₄-P concentration following increased suspended sediment concentration has previously been reported, and reflects buffering (i.e. adsorption

processes) that can occur in the space of a few hours in response to alteration of the ambient equilibrium $\text{PO}_4\text{-P}$ concentration (Mayer and Gloss, 1980, Wang and Li, 2010). Presumably, this result indicates that, despite higher TP concentrations, the immediate bioavailability of the P in March samples would actually have been *lower* in a downstream oxic environment than for base flow samples with comparable $\text{PO}_4\text{-P}$ concentration, yet lower PP (and thus TP) concentration. This is not necessarily the case, however, when considering longer term bioavailability (i.e. for time scales longer than hours), as such adsorbed $\text{PO}_4\text{-P}$ may be readily re-released back into the water column under altered ambient equilibrium $\text{PO}_4\text{-P}$ concentration, for example, following subsequent resuspension of sediments into overlying water with lower suspended sediment concentration (Wildman and Hering, 2012). Investigation of $\text{PO}_4\text{-P}$ adsorption kinetics for local sediments, for example by quantifying equilibrium $\text{PO}_4\text{-P}$ concentration (Mayer & Gloss, 1980) for various conditions, could help to improve understanding of how stream-derived sediments can influence $\text{PO}_4\text{-P}$ concentration in the lake. Even with further research, however, such understanding is likely to remain incomplete until wider scientific advances are made as, currently; there is “no general model” of whether lake sediments act as a net source or a sink of bioavailable phosphorus (Reynolds and Davies, 2001).

6.5 Conclusions

The bioavailability of P present in grab samples collected from two streams during two contrasting storm flow periods was investigated. Dissolved inorganic P concentrations were relatively invariant between samples, accounting for 40–48% of TP for samples collected during a moderate event and 6–8% of TP for a large event. Particulate phosphorus concentrations were an order of magnitude greater in samples collected during the large event. Determination of redox-sensitive P indicated that the entirety of this fraction was potentially bioavailable if exposed to anoxia for the samples collected during the small event, compared to approximately 25% for the large event. Despite the potential bioavailability of PP, a laboratory bioassay indicated that under oxic conditions, suspended sediments acted as a sink, rather than a source of bioavailable P to P-limited phytoplankton. This result highlights the importance of considering the nature of the receiving environment when assessing the bioavailability of P transported through hydrological landscapes.

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7 Conclusions

7.1 Overview

This thesis has examined the topic of spatial and temporal variations in nutrient loading to lake ecosystems, and, explored how such variations affect lake water quality, with specific focus on the related topics of phytoplankton nutrition and eutrophication. By combining both reductionist and more holistic multi-disciplinary approaches, the research has sought to develop broad understanding at spatial resolutions ranging from global to fine scales (e.g. 1–10 m). Where applicable, research findings have been placed in an applied context to guide actions necessary to address the significant problems related to eutrophication that have been identified at international (Millennium Ecosystem Assessment, 2005), national (Verburg et al., 2010) and regional (Parliamentary Commissioner for the Environment, 2006) levels. The remainder of this chapter summarises the main findings of each research chapter, and provides ideas for future research to extend knowledge derived from this study.

7.2 Key findings and recommendations for future research

Chapter 2 described and quantified global-scale trends in both nutrient stoichiometry in lake water and relationships between nutrient concentrations and phytoplankton biomass. The previously unreported global-scale positive correlation between latitude and the ratio of total nitrogen (TN) to total phosphorus (TP) described in Chapter 2 highlights the importance of considering lake spatial context beyond the local bounds of the immediate hydrological catchment when considering drivers of lake water quality. This is consistent with a wider shift towards a more global viewpoint within limnology (Walz and Adrian, 2008), as researchers increasingly seek global-scale biogeographic patterns in lake ecosystems (Elser et al., 2009; Gonzalez-Bergonzoni et al., 2012). Results demonstrated marked differences between latitudinal categories in the statistical power of empirical models to estimate chlorophyll *a* concentration based on TN and TP concentrations (i.e. bottom-up control by nutrients), highlighting systematic disparities in lake ecosystem functioning between latitudes. Various possible reasons for the observed differences were postulated, for example; weak relationships between nutrients and chlorophyll *a*

concentration in the tropics may be due to relatively greater influence of light limitation; whereas similarly weak relationships at polar latitudes may reflect greater influence of top down control by zooplankton grazing, or, greater relative contribution of benthic autotrophs to primary productivity. Testing these hypotheses, however, represents a challenge to future researchers and to do so experimentally would be a major task. It may be desirable, therefore, to adopt the approach of the “model experimentalist” (Mooij et al., 2010) by comparing individual aspects (i.e. parameter values) of well-calibrated lake ecosystem models across latitudinal gradients to elucidate systematic differences in the relative importance of key biogeochemical processes.

Chapter 3 then focussed on identifying relationships between in-lake concentrations of TN and TP, and individual catchment characteristics, which are statistically significant for a nationally-representative sample of lakes in New Zealand. The strong relationships between land use and in-lake nutrient concentrations that were identified support discussion points in Chapter 2 regarding the potential for latitudinal trends in TN:TP to reflect latitudinal gradients in the distribution of land uses. The results of Chapter 3 contribute to the knowledge-base necessary to guide national-level water quality policy, emphasising the dominant role of intensive pastoral agriculture in influencing eutrophication in New Zealand lakes, yet also providing insight into other factors such as hydrological connectivity that can mediate the effects of intensive pastoral agriculture in individual catchments. The applied issue of how to mitigate nutrient pollution from agricultural sources is the focus of Appendix 1, and this article seeks to highlight some of the major reforms that are necessary for the overall nutrient footprint of pastoral agriculture to be greatly reduced without compromising the status of this activity as a primary component of New Zealand’s economy. Chapter 3 also identified a positive correlation between exotic forestry and in-lake TP concentrations for New Zealand that was not well acknowledged in the literature. This finding warrants further research, for example by undertaking further detailed measurement of particulate P export from forested New Zealand catchments at different stages in the harvesting cycle and during varying discharge. Overall, this chapter demonstrated that anthropogenic factors are the dominant control on nutrient loading to New Zealand lakes, e.g. rather than variations in the distribution of naturally P-rich volcanic soils. Given the pervasive nature of human development, this fact invites further research to

determine reference water quality for different lake types which represents the states of lakes in the absence of anthropogenically–accelerated eutrophication. Such an exercise has been conducted elsewhere (e.g. Dodds et al., 2006) and would provide a benchmark against which current water quality could be judged, thus informing targets for lake restoration and providing guidance for the reform of water quality policy that is currently occurring in New Zealand (Land and Water Forum, 2012).

Chapter 4 extended the concept of spatial variations in nutrient transport between catchments by focussing in detail on two surface sub–catchments that drain into Lake Rotorua (Bay of Plenty, New Zealand). The chapter also introduced the topic of temporal variations in nutrient loading, by presenting analysis of high frequency (1–2 h) time series data relating to concentrations of fractions of N, P and suspended sediments that were measured during an intensive programme of field work. Concentrations of determinands were typically shown to vary predictably with stream discharge (Q), and relationships between Q and concentrations were broadly similar between the two catchments, although some differences occurred which could be attributed to variation in catchment characteristics such as potential nutrient sources and geomorphology. Empirical models were fitted to measured data to estimate continuous loading over a two year period and, in particular, the relatively high annual yield of TP estimated for the Puarenga Stream catchment (largely comprising exotic coniferous forestry) is consistent with the relationship described in Chapter 3 between plantation forestry and in–lake TP concentrations. Positive correlations between Q and concentrations of particulate nutrients, particularly particulate P, contribute to the propensity for temporal inequality in nutrient loading, reflecting that periods of elevated Q associated with storm events contribute disproportionately to annual nutrient loads. This highlights the importance of considering hydrologically–driven variations in concentration when estimating nutrient loads, and, in the case of Lake Rotorua, future research to develop process–based catchment models may be beneficial to aid load estimation and assess the likely impacts of land use/management changes. A practical solution to the problem of obtaining data relating to loading during high Q periods could be the installation of turbidity sensors in inflowing streams. With adequate calibration these sensors may provide high–frequency estimates of the dominant particulate P fraction of TP loads, with suitable accuracy and relatively minor financial outlay (cf. Jones et al., 2011).

Such data could also be an interesting subject for wavelet analysis to investigate the dynamics of different transport processes using a statistical tool that has so far had limited application to water quality concentration data (Guan et al., 2011). The propensity for temporal inequality in loading also further emphasises the need for further research to consider the likely effects of predicted future changes in the frequency and intensity of rainfall on lake water quality (IPCC, 2007).

Chapter 5 shifts focus from the surface catchment of Lake Rotorua towards the lake itself. This chapter highlighted the importance of horizontal transport processes in mediating the effects of storm flow discharges on lake water quality. This chapter also demonstrated the value of a three-dimensional coupled ecological-hydrodynamic computer model for interpreting field data and gaining insight into processes outside of the spatial and temporal bounds of sampling programmes. Future research could use the coupled model to focus on other events of different characteristics to improve understanding of transport of catchment-derived materials within the lake. For example, transport of stream water into the main body of the lake was very limited during the sampled event, hence it would be valuable to undertake further study to identify the conditions necessary for more direct transport of stream-derived sediments into the main basin. In particular, it is expected that events of larger magnitude (i.e. greater maximum discharge) would be associated with more pronounced horizontal transport and hence it would be interesting to contrast propagation characteristics between large summer and winter events during which the inflowing stream would be expected to be negatively and positively buoyant, respectively. Remotely-sensed data pertaining to suspended sediment concentration could be incorporated into future studies to quantify the location of storm flow-associated sediment plumes and thus validate model output. In addition, there is scope to apply the model to further broad understanding of dominant horizontal circulation processes that are active in the lake, as has been done elsewhere for large lakes (Beletsky et al., 1999). Data collected using *in situ* sensors to measure water velocity (including data that has been collected historically) would be useful to validate model performance during such a study. The spatial and temporal discontinuities in phytoplankton nutrient limitation status that are presented in this chapter emphasise the distorted spatial and temporal scales at which key processes that affect phytoplankton ecology can occur, and demonstrate lack of coherence between these scales and the typical resolution of sampling programmes. Further

investigation of the currently poorly-understood effects of meteorological disturbances on phytoplankton ecology, for example by examining species succession in the lake during a period coinciding with a large storm (cf. Znachnor et al. 2008), could be an interesting avenue for future research. In addition, more detailed statistical consideration of the phenomenon of patchiness described in this chapter could help to better quantify how representative of ‘average’ lake water quality individual grab samples are likely to be under different physical conditions.

Chapter 6 focused on the issue of particulate nutrient bioavailability that was a component of previous chapters, and, in particular, sought to address uncertainty regarding the potential contribution to eutrophication of particulate P that was shown in Chapters 4 and 5 to dominate TP loads during storm flow periods. Although a relatively small number of samples was analysed, the finding that as much as 100% of particulate P conveyed in storm flow can be released into the dissolved if exposed to anoxia has important implications for assessing the potential impact of this nutrient fraction on water quality of Lake Rotorua, as well as for other lakes in the Central Volcanic Plateau region of New Zealand that have similar catchment sediment characteristics. Whether or not lake hypolimnia become anoxic is therefore clearly an important determinant of the potential for particulate P transported in storm flow to contribute to elevated dissolved inorganic P concentrations and, therefore, maintenance of oxic hypolimnia should be an important objective for lake managers. The critical importance of oxic conditions was further emphasised by the somewhat paradoxical results of bioassays. These results highlighted that, in addition to biological uptake, dynamic physicochemical processes are critically important for regulating the availability of dissolved inorganic P in the water column. Further research relating to P sorption kinetics of sediments from a range of potential source areas should be undertaken to develop understanding of the potential for particulate P to contribute to eutrophication of Lake Rotorua. In a wider context, further examination of the short-term interactions between biological, physical and chemical processes (e.g. associated with pH effects) that regulate P bioavailability is an important and interesting topic for further study.

7.3 References

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Appendix 1 – Reducing the external environmental costs of pastoral farming in New Zealand: Experiences from the Te Arawa lakes, Rotorua

Abstract

Decades of nutrient pollution have caused water quality to decline in the nationally iconic Te Arawa (Rotorua) lakes in New Zealand. Pastoral agriculture is a major nutrient source and therefore this degradation represents an external environmental cost to intensive farming. This cost is borne by the wider community and a major publically-funded remediation programme is now underway. This article describes the range of actions being taken to reduce nutrient loads from internal (lake bed sediments) and external (primarily diffuse) sources in the lake catchments. The high economic cost and uncertain efficacy of engineering-based actions to reduce internal nutrient loads is highlighted. Major changes to land management practices to control diffuse nutrient pollution are required throughout New Zealand if the need for costly and lengthy remediation programmes elsewhere is to be avoided. More action to educate farmers and the public about eutrophication issues, development and enforcement of environmental standards, and further consideration of the use of market-based instruments are proposed as ways to correct the current market failure.

Introduction

New Zealand is renowned for being ‘clean and green’, a concept that is an important part of the country’s competitive advantage in several core industries and part of the national marketing strategy for tourism. The activities of the country’s largest primary industry, namely agriculture (New Zealand Treasury 2009), do not, however, always complement this reputation. Pastoral agriculture, particularly dairy farming, has intensified over the last few decades: the national dairy herd increased by approximately 82% between 1980 and 2009 to nearly six million cows (Figure 1). This intensification has contributed to the decline of several essential ecosystem services including the provision of good quality freshwater (PCE 2004; Baskaran et al. 2009). As a result, declining freshwater quality is now a critical issue in New Zealand (Land and Water Forum 2010); improving the management of the country’s water resources has become a government priority (MfE 2009).

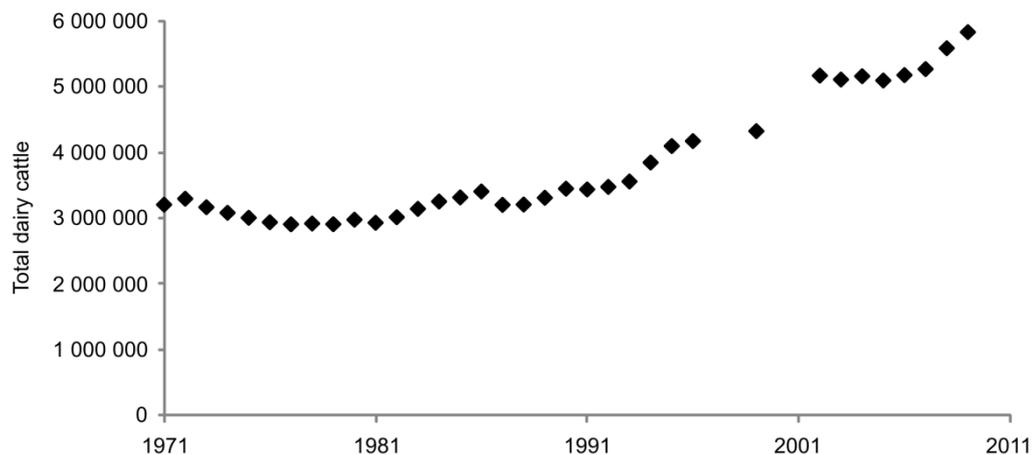


Figure 1 Total dairy cattle in New Zealand 1980–2009. Note that the calculation method was changed in 2002 (Statistics New Zealand, 2009).

A major cause of water quality decline in New Zealand is the anthropogenic eutrophication of streams and lakes caused by excess nutrient inputs, primarily nitrogen and phosphorus, from agricultural sources (PCE 2004; Abell et al. 2011). In this respect, the intensification of the dairy industry is of particular concern as median nutrient loads from dairy farms have been shown to be significantly higher than from other pastoral land uses such as sheep farming (McDowell & Wilcock 2008). The main sources of nutrients to waterbodies from New Zealand grazing systems are nitrate leached from animal excreta (particularly urine), while phosphorus is typically associated with eroded soil particles transported by

surface runoff (PCE 2004; McDowell & Wilcock 2008). Elevated nutrient concentrations in freshwaters can cause undesirable growth of algae, resulting in unsightly, odorous and potentially toxic blooms, along with an overall decline in ecological health (Smith et al. 1999). The challenges to maintaining and improving New Zealand's water quality represent a microcosm of the global situation, and predicted climate change is expected to result in both an increase in nutrient loads and an enhanced sensitivity of inland waters to nutrient pollution, thereby exacerbating the problem (Jeppesen et al. 2011).

The anthropogenic eutrophication in predominantly agricultural catchments in New Zealand is an archetypal example of the 'Tragedy of the Commons' (Hardin 1968). Hardin's original analogy focused on the inevitability of overgrazing to occur when herdsmen are allowed to graze their stock on common land. As he acknowledged, the concept applies equally to the pollution of common resources such as air, or in this case, freshwater, whereby polluters (e.g. farmers) are only burdened with an individual cost from polluting a common resource that is much smaller than the cost of adequately treating or eliminating their waste.

The developing field of ecological economics allows the degradation of common resources to be viewed in terms of a reduction to the value of ecosystem services as a result of the externalisation of environmental costs associated with production activities (Lant et al. 2008). Ecosystem services are derived from ecosystem functions and include climate regulation, soil formation and erosion control (Costanza et al. 1997). In this case, the common resource in question is fresh water and the external environmental costs of agricultural production include a decline in recreational opportunities, reduced landscape and visual values and the constraints on supply of, or additional treatment requirements for, drinking water. The cost is external because individual farmers usually bear only a small share of the costs (economic, social and environmental) that arise from the depletion of the ecosystem services caused by excess loss of nutrients from farmland. In other words, the polluter does not pay the full cost associated with the pollution they produce and instead, where there is an economic cost associated with the remediation of the pollution, it is often the wider community that pays the price by means of government instigated remediation funded by public taxes. This article examines the approach being taken to remediate diffuse pollution from agricultural sources in order to improve water quality in the Te Arawa lakes

in the Bay of Plenty region of New Zealand. It discusses some of the major (and often expensive) actions that now have to be taken to improve the water quality of several of the lakes. Water quality in the lakes has declined due to decades of excess nutrient input from sources that include, amongst others, agricultural activities. Options for future lake management policy are discussed with reference to how farming in this region, and throughout New Zealand, might become more sustainable by internalising its environmental costs.

Case study: the Te Arawa lakes

National policy context

To provide background to the regional case study, it is useful to first consider the national policy context. Following a major change in the early–mid 1980s, New Zealand farmers have operated in a competitive system characterised by a lack of subsidies (MacLeod & Moller 2006). There is no formal link between central government and the agricultural sector (e.g. unlike Europe) and regulation of agri–environmental performance is principally the role of regional councils, which vary widely in their capacity and commitment to enforcement (Jay 2007). Under the Resource Management Act 1991, regional and unitary councils are also responsible for managing water quality, and guidance on this issue was long lacking at the national level. This situation recently changed with a National Policy Statement (NPS) for Freshwater Management in May 2011 (New Zealand Government 2011). The NPS reflects recommendations made following an extensive ‘collaborative governance’ process undertaken by an independent group which engaged widely with stakeholders (Land and Water Forum 2010). In particular, the NPS requires councils to safeguard freshwater ecosystems by establishing and observing limits relating to water quality and flows (Policies A1–3, B1–2). The NPS also explicitly recognises the need to consider diffuse pollution in spatial plans (Policy A4) and mandates integrated catchment management that considers downstream water resources (Policy C1–2).

Regional overview

The Te Arawa lakes are situated on the central volcanic plateau in the Bay of Plenty region of New Zealand’s North Island (Figure 2). They are highly valued by the Te Arawa people who have a cultural relationship with the lakes and are the legal owners of the lake beds after Te Arawa signed a Deed of Settlement with

the Crown in 2004. The iconic lakes are also valued for their natural beauty and for recreational activities such as trout fishing which attract tourists to the region.

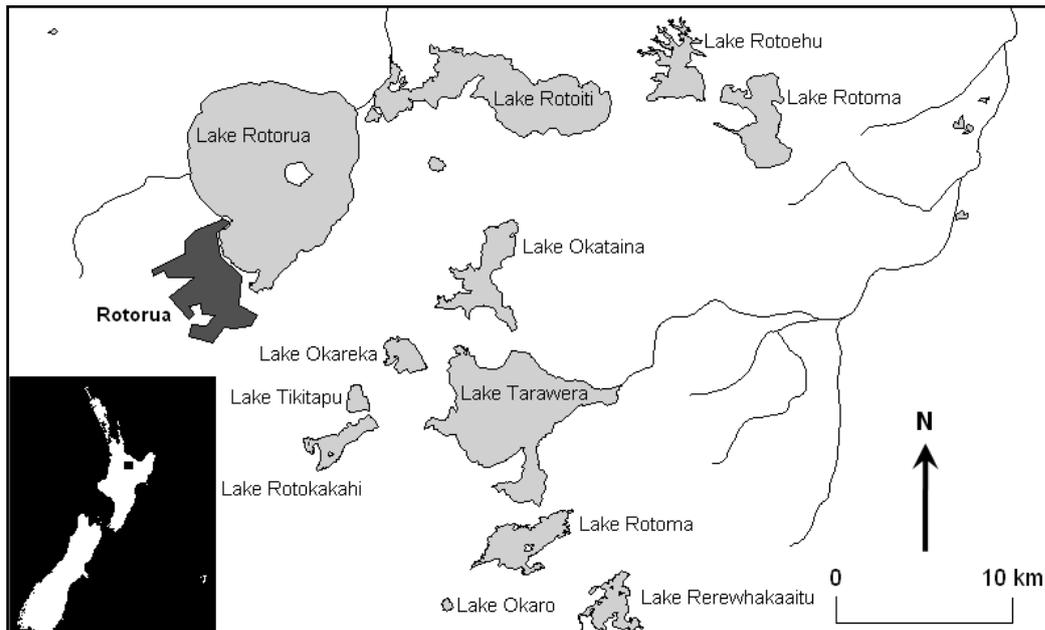


Figure 2 The twelve major Te Arawa lakes in the Bay of Plenty region of New Zealand

Deteriorating water quality

Water quality in several of the lakes has declined over the last 30 – 50 years due to excess nutrient inputs associated with development in the lakes' catchments (Hamilton 2003). The main sources of nutrients are farming activities, soil erosion, septic tanks and community sewerage schemes (PCE 2006), although natural geological sources of phosphorus are also significant in some catchments (GNS 2005). Treated sewage was historically discharged into the largest lake, Lake Rotorua, until 1991 (Burns et al. 1997); however, this direct discharge ceased following construction of the Rotorua City sewage treatment system. Since then, further works have been undertaken, or are currently underway, to improve sewage treatment and reduce reliance on septic tanks to minimise nutrient loads from these sources. By contrast, nutrient loads (particularly nitrogen) from farmland have increased in several catchments in response to an increased intensity of agricultural production. For example, nitrate concentrations in streams flowing into Lake Rotorua increased steadily between 1968 and 2002 as a result of greater export from pasture (NIWA 2003), which occupies 45% of the catchment. This source is now responsible for 75% of the nitrogen load and 46% of the phosphorus load to the lake each year (PCE 2006).

Table 1 provides a summary of the twelve major lakes. Water quality is assessed using a Trophic Level Index (TLI) (calculated from measurements of lake nutrients, chlorophyll *a* and clarity) and an Action Plan development process is triggered when water quality is below established targets (see Burns et al. 1999; 2005; 2009). Action plans are non-statutory documents drawn up in consultation with lake stakeholders to set nutrient reduction targets and establish catchment management actions for specific lakes, often closely linked to the TLI as a performance measure (Table 1). A major complication to lake restoration efforts is the issue of groundwater lags which delay the effects of nutrient loads arising from present-day land use. Water that enters the groundwater in some catchments today has been calculated to take up to 170 years to reach the lake (GNS 2005). This lag is further compounded in some lakes by the process of internal loading which results in nutrients that have accumulated in the lake bed being periodically released back into the water column during periods of de-oxygenation (Burger et al. 2008). In shallower, eutrophic lakes these sources can even dominate over external loads.

Table 1 Summary of the twelve major Te Arawa lakes. Data from Burns et al. (2009) and BOPRC et al. (2010)

| Lake | Lake area (ha) | Max depth (m) | Trophic state* | Long term trend in water quality over 16–20 years | Action status | Plan |
|---------------|----------------|---------------|----------------|---|--------------------------|-------------|
| Okataina | 1,173 | 78.5 | Oligotrophic | No change | Process not yet underway | Operational |
| Rotoma | 1,112 | 83.0 | Oligotrophic | Definite degradation | | |
| Tarawera | 4,115 | 87.5 | Oligotrophic | No change | Process underway | |
| Tikitapu | 144 | 27.5 | Oligotrophic | Possible degradation | Process underway | |
| Okareka | 334 | 33.5 | Mesotrophic | No change | Operational | |
| Rerewhakaaitu | 517 | 15.8 | Mesotrophic | No change | Process underway | |
| Rotokakahi | 433 | 32.0 | Mesotrophic | No data | Process not yet underway | |
| Rotoiti | 3,370 | 124.0 | Mesotrophic | No overall change but definite improvement since 2003 | Proposed | |
| Rotomahana | 902 | 125.0 | Mesotrophic | No change | Process not yet underway | |
| Rotoehu | 790 | 13.5 | Eutrophic | Degraded, no change | Operational | |
| Rotorua | 8,047 | 44.8 | Eutrophic | Degraded, no change | Proposed | |
| Okaro | 30 | 18.0 | Supertrophic | Definite improvement | Operational | |

*Trophic state refers to the primary productivity of a water body. It can range from oligotrophic (low) to supertrophic (very high). Perceived water quality typically declines with increasing trophic state.

Lake restoration: actions

Tables 2 and 3 summarise the lake restoration actions included in the Te Arawa Lake Action Plans, as well as additional actions that have been considered to remediate the impact of nutrient pollution on the lakes. Actions have been separated into two categories: those that are lake-based to reduce in-lake nutrients (Table 2) and those that are catchment-based to reduce external nutrient loads (Table 3).

Table 2 Lake based actions to reduce in-lake nutrient loads

| Lake restoration action | Status | Summary |
|--|--|---|
| Diversion of nutrient-rich inflows | Undertaken in Lake Rotoiti (Ohau Channel construction). | Reduces nutrient inputs to the lake. May adversely affect water bodies downstream. |
| Dredging | Under consideration for the Hamurana Stream which enters Lake Rotorua. Lakes Okareka, Rotorua, Rotoiti, Rotoehu and Tarawera have been identified as potentially suitable candidate lakes (A & E Consultants 2007). | Removes nutrients from the lake bed, reducing cycling through and from the sediments. A recognised method worldwide although it is expensive and a major logistical undertaking. Identifying a receptor site for dredged material is also difficult. |
| Sediment capping / phosphorus inactivation | Undertaken in lakes Okaro, Okareka and in Lake Rotorua inflows. Trialled in streams entering Lake Rerewhakaaitu | Certain materials such as natural clay minerals can render nutrients unavailable for plant growth and seal lake bed sediments. A modified zeolite product successfully reduced total phosphorus concentrations in Lake Okaro although improvements to water quality appear to occur more slowly (Özkundakci et al. 2010). |
| Hypolimnetic discharge | Previously considered for Lake Okareka. | Nutrient-rich water could be removed from the bottom layers while a lake is stratified and oxygen near the lake bed is depleted. |
| Bio-manipulation | Previously considered for all lakes. | Organisms such as the freshwater mussel (<i>Hyridella menziesii</i>) can assimilate nutrients or consume algae. The efficacy and the potential for adverse ecological impacts is uncertain (NIWA 2007). |
| Oxygenation/ destratification | Considered for Lake Rotoiti and under consideration for Lake Rotoehu (BOPRC et al. 2010). | Delivering oxygen directly to the bottom waters of a lake can prevent oxygen depletion and associated nutrient release from bottom sediments. Aeration can also be used to disrupt lake stratification and prevent the formation of oxygen-depleted bottom waters. |
| Weed harvesting | Undertaken in lakes Rotoehu and Rotoiti. | Nutrients can be removed from lakes by harvesting aquatic plants such as the invasive macrophyte hornwort (<i>Ceratophyllum demersum</i>). |

Table 3 Catchment based actions to reduce external nutrient loads from farmland

| Lake restoration Status action | Summary |
|---|---|
| Land use change | <p>The proposed Regional Policy Statement 2010 authorises district plans to require resource consent for land use change. The district Ten Year Plan is under review. Identified in the Action Plans for lakes Okareka and Rotoehu (BOPRC et al. 2010) and likely to be important for lakes Rotorua and Tarawera.</p> <p>Nutrient loss varies with land use and it is widely accepted that the redesign of catchment land use has a fundamental role in effecting change (Hamilton 2005; PCE 2006). Nutrient loss is generally lowest from native vegetation and plantation forest although this can vary depending on factors such as harvesting regime (Hamilton 2005). The potential for land use types to cause nitrate leaching typically follows the order: forestry < sheep/beef/deer farming < arable/mixed cropping < dairy farming < vegetable cropping (Menneer et al. 2004). The potential for phosphorus loss is often more variable, however high losses are likely to occur from land receiving direct fertiliser or manure applications (McDowell et al. 2005).</p> |
| Creation of riparian buffers | <p>Undertaken in some areas of all lake catchments (BOPRC et al. 2010).</p> <p>Riparian buffers are vegetated areas alongside waterbodies that can reduce the inputs of nutrients by trapping particulate forms of nutrients and increasing plant uptake of inorganic forms.</p> |
| Wetland construction | <p>A 2.3 ha wetland has been constructed alongside Lake Okaro (BOPRC 2006). Wetland construction has been earmarked for the catchment of Lake Rotoehu where floating wetlands are also being trialled (BOPRC et al. 2010).</p> <p>Wetlands can trap sediment and promote nutrient removal processes such as denitrification and uptake by plants.</p> |
| Adoption of Best Management Practices (BMPs) by farmers | <p>Applicable to all lakes, especially those with a high percentage of pastoral land.</p> <p>Suitable BMPs identified include: reduction of fertiliser use, removal of cattle from paddocks over winter, better effluent management and the use of nitrification inhibitors in feed and on soil (Ritchie 2008; AgResearch 2010).</p> |
| Installation of denitrification beds | <p>An 18 m³ bed of wood chips has been installed along a 10 m section of a Lake Rotoehu inflow. Monitoring over 13 months indicated that nitrate concentrations were reduced by approximately 50 % (Landcare Research 2008).</p> <p>Denitrification beds comprise containers or excavated areas filled with a carbon source such as woodchips. They promote the conversion of nitrate to di-nitrogen gas by microbes.</p> <p>Trials elsewhere in New Zealand have shown that denitrification beds can provide a low-cost solution for near complete removal of nitrate from dairy shed effluent (Schipper et al. 2010). Results will depend on local soil type and topography.</p> |

Lake restoration: policy

Implementing lake restoration actions requires the right mix of policies in place to facilitate change. An array of policy instruments are either in use or have been

proposed to reduce diffuse pollution from agricultural sources in the Te Arawa lakes (Figure 3).

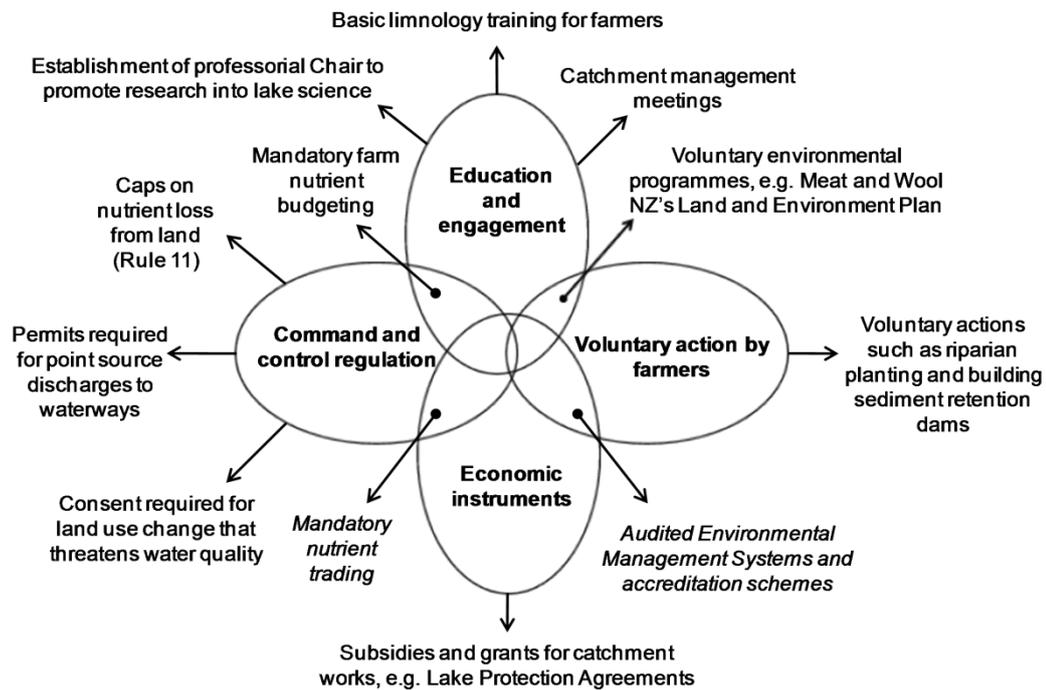


Figure 3 Policy instruments in use (bold) and proposed (italic) to reduce diffuse pollution from agricultural sources in the Te Arawa lakes

Discussion

The external cost of farming

Actions listed in Table 2 may be considered ‘end of pipe’ because they are designed to reduce nutrient loads once nutrients have already entered streams or lakes, rather than reducing nutrient loads at source. Experience from lake restoration programmes in the northern hemisphere has shown that physical, chemical or biological remediation techniques designed to reduce internal nutrients, but which do not simultaneously address external loads, are often of only limited success with benefits quickly eroded (Cooke et al. 2005). Improvements in water quality following specific remediation actions, particularly in large lakes, may be slow and restoration failures frequently occur (Søndergaard et al. 2007). Actions such as dredging also have the potential to cause adverse environmental impacts that require mitigation and may need to be repeated periodically. Despite these shortcomings, such actions, if feasible, are now essential, in combination with catchment-based actions, if water quality improvement targets are to be achieved in the short–medium term for the most degraded lakes. This is because sediments in lakes such as Lake Rotorua have

high internal stores of nutrients following decades of eutrophication (Burger et al. 2008) and therefore even complete cessation of all external nutrient loading would not achieve desired improvements in water quality.

While necessary, such actions have a high financial cost. For example, the Ohau Channel wall was completed in July 2008 and was designed to prevent water that is relatively high in nutrients from flowing from Lake Rotorua to Lake Rotoiti. The wall is estimated to have cost approximately NZ\$10 million, mostly funded by the regional council, with additional financial support coming from national government (BOPRC et al. 2010). While there are early indications that the wall has been successful in improving water quality in Lake Rotoiti (BOPRC et al. 2010), as previously noted, a large proportion of the nutrient loads entering Lake Rotorua originate from pasture, therefore the cost of mitigating the environmental impact of nutrients lost from farmland (i.e. the construction cost of the wall) is external to those groups responsible for the pollution. The same applies to the majority of the costs associated with the restoration of Lake Okaro where most of the nutrients that enter the lake also originate from agricultural sources, as pasture comprises approximately 90% of the catchment (BOPRC et al. 2010). The proposed cost of capping the sediments of Lake Okaro was NZ\$225 000 over three years, while the estimated cost of the construction of a wetland in the catchment was NZ\$520 000 (BOPRC 2006). Lake Okaro is the smallest of the Te Arawa lakes (see Table 1) and the combined cost of these two actions alone equates to approximately NZ\$25 000 per hectare of lake area. In 2008, a national level Government Funding Deed provided NZ\$72.1 million towards the cost of interventions designed to improve water quality in four lakes. This pledge was a 50% contribution towards the estimated cost, with the remainder to be made up by the regional and district councils. While some of this money is directed towards addressing nutrient loss from non-agricultural sources (e.g. by enhancing community wastewater systems), a significant proportion is directed towards reducing or remediating nutrient pollution from farming.

The national policy challenge

While the use of public money is now essential if water quality goals in these iconic and nationally renowned lakes are to be achieved, it is clear that in the longer term, allowing water bodies in predominantly agricultural catchments to become so degraded that their restoration requires costly, public-funded

engineering-based interventions is at odds with the Polluter Pays Principle (OECD 1972) and inconsistent with the New Zealand government's stated aim of achieving the "best value for society" from the country's water resources (MfE 2009, p. 4). It is therefore desirable to develop a policy framework that promotes the implementation of actions to reduce nutrient loads at source *before* water quality decline occurs. Owing to the 'multi-aspect' nature of the problem (i.e., water quality decline is dependent on when, where, how and in what form nutrients loss occurs in a catchment (OECD, 2007), the successful control of diffuse pollution requires a mix of different policy instruments. Below, we discuss four broad categories of policy instrument in use around the Te Arawa lakes (Figure 3) and consider further policies that could promote a reduction of diffuse nutrient pollution from pastoral land across New Zealand.

Education and engagement

Educating farmers and landowners about nutrient pollution and basic limnology has been instrumental for gaining support and prompting voluntary action (Burns et al. 2009). Workshops and meetings have provided a forum for lake managers to engage with stakeholders and gain community 'buy-in' for the various lake remediation actions. For example, the Lakes Water Quality Society, an active community organisation that seeks to protect and restore the region's lakes, regularly holds meetings including symposia attended by water quality experts from overseas. In a wider context, an active programme of research into lake science, primarily funded by the regional council, has been integral to informing lake management policy. Central to this has been the appointment in 2002 of the professorial Chair in Lakes Management and Restoration at the University of Waikato; an appointment funded by the regional council that has fostered an adaptive management approach to lake management whereby the findings of applied research are effectively communicated to regional managers and directly inform policy. Examples of this include monitoring to assess the efficacy of sediment capping products for reducing nutrient concentrations in the lake water column (Özkundakci et al. 2010) and the use of hydrological and ecological models to help lake managers to prioritise the control of different nutrient sources (Burger et al. 2008).

Throughout New Zealand, further education of the farming community about nutrient management issues could encourage change. Research in Australia

has shown that greater provision of training and education is at the top of a 'preference hierarchy' of policy instruments favoured by landowners (Cocklin et al. 2007). Numerous guidelines provide advice to farmers on issues such as effluent management (Dairy NZ 2011) although it remains a challenge to transfer this knowledge to farmers whose time for training events is limited. The wider establishment of farmer-led workshops supported by regional government, already being undertaken in some regions (e.g. Waikato), is one possible way to disseminate good practice. Such events need to be scheduled at times in the farming calendar when farmers are least busy although even well planned events will not reach those who are resistant to change. In addition to informing farmers, programmes that educate the public about the causes of water quality decline could prompt communities to collaboratively take action to address pollution sources. There is evidence of growing concern amongst the New Zealand public about the state of the nation's freshwaters (Land and Water Forum 2010). If the sight of livestock routinely standing in a stream were to have the same connotations as, for example, the sight of a smoke stack at a fossil fuel power station, then the rate of action could increase in response to an altered social 'license to operate' for the pastoral farming industry. Within the dairy industry, there is awareness of the importance of maintaining public support (NZFW 2011) and therefore a consolidated public outcry about farm environmental performance is likely to elicit a collective response from industry. Further analysis of the adverse economic impact of poor water quality on New Zealand's tourism brand could also provide further incentive.

Voluntary action

Voluntary action by farmers has a role in reducing nutrient losses, especially given that lake Action Plans are non-statutory documents that require co-operation from land users. Throughout New Zealand, the use of environmental farm plans provides a tool for farmers to strategically address the environmental impact of their activities, however, the use of such plans has so far been limited and fragmented (Manderson et al. 2007). At the industry level, there is a growing recognition by the agricultural sector of a need to demonstrate credible stewardship (Dairy NZ 2009), as demonstrated by the development of the Dairying and Clean Streams Accord in 2003. The Accord contains quantified performance targets that have been jointly agreed upon by dairy industry

representatives and the government to meet the goal of achieving “clean, healthy water” in dairying areas (Fonterra et al. 2003, p. 1). Doubt has been raised, however, regarding the success of the industry to meet its commitments (Deans and Hackwell 2008) and a review of progress towards meeting Accord targets found that the level of full compliance had dropped by 4% in 2008/2009 from the previous year, while the level of significant non-compliance had increased to an “unacceptable” level (Fonterra et al. 2010, p. 6). It is now widely acknowledged that voluntary action alone has only limited potential to contribute towards better water quality (Land and Water Forum 2010) and this is especially true for the most polluted lake catchments where the necessary remedial actions are often extensive and financially costly.

Regulation

Command and control regulation involves setting and regulating standards based on perceived environmental limits. It is often the best instrument to use when an absolute change in behaviour is required (Roberts 2004). In the Te Arawa lakes, a risk-based approach has been taken by imposing limits on nutrient loss from properties in the catchments of the worst affected lakes. ‘Rule 11’ of the regional Water and Land Plan (BOPRC 2008) prohibits loss of nutrients from pastoral land at rates greater than an individual farm benchmark level. A common difficulty, however, in applying regulation to control nutrient loss from farmland is that the diffuse nature of the pollution means that nutrient losses are hard to measure and attribute to specific individuals (Barnes et al. 2009). In this case, the solution is to use farm-scale modelling software (Overseer[®]) that allows nutrient losses from properties to be estimated and benchmarked (Burns et al. 2009). Around Lake Rotorua, catchment-based nutrient models have been coupled with models of lake processes to simulate possible future land use scenarios, thereby informing spatial planning for meeting water quality goals (NIWA 2011).

At the national scale, the recent NPS for Freshwater Management will now require regional councils to set freshwater quality limits (New Zealand Government 2011). This represents a major addition to national policy but defining and regulating the new limits poses a challenge to councils. In this respect, knowledge gained in Europe during work to achieve compliance with the Water Framework Directive (EC 2000) could provide guidance, for example, regarding identifying reference sites with high ecological integrity from which

limits can be based. Once established, planning controls are likely to be an important tool for councils to enforce limits and a risk-based approach to enforcement has efficiency advantages. An example of such an approach in practice is the EU Nitrates Directive which requires Member States to identify 'Nitrate Vulnerable Zones' where farmers are required to limit the application of nutrients (170 kg/ha of nitrogen) and adhere to certain practices (EC 1991). Although extensive work would be required to identify 'at risk' areas throughout New Zealand, this work is already underway in many areas on a regional basis and, as described above, numerous modelling tools have been developed to estimate nutrient loss for catchments (McDowell et al. 2005). Use of such models to calculate pollutant Total Maximum Daily Load (TMDL), a concept used in the U.S.A. (EPA 1991), could also support compliance with introduced standards. Definitions such as TMDLs could help catchment managers to focus on critical source areas of pollution and prompt debate about relative contributions of polluters to a defined TMDL.

Economic instruments

Finally, economic instruments are a form of policy with potentially the greatest scope for further adoption. So called 'market based instruments' (MBIs) are often regarded as more efficient than regulation, allowing environmental objectives to be achieved more cost effectively than with regulation alone (Lubbe-Wolff 2001). This will often be the case for diffuse pollution, as large polluters can often achieve greater nutrient reductions at a lower average cost than others. Subsidies for catchment works so far represent the main use of this instrument around the Te Arawa lakes with grants being made available to encourage landowners to undertake fencing and planting in retirement areas and riparian margins. Lake Protection Agreements have provided a mechanism to administer subsidies and bind landowners to collaboratively agreed reductions in nutrient loss from their land. A more radical MBI is nutrient trading which has been proposed for use in the Lake Rotorua catchment (MOTU 2008) and a form of which is already successfully operating at Lake Taupo in the Waikato region (WRC 2010). Nutrient trading involves assigning nutrient loss allowances to individual properties that are in proportion to a set nutrient-loss benchmark, to achieve an established nutrient reduction target. Modelling tools can then be used to estimate actual nutrient loss, and tradable permits required to be purchased to cover

excessive losses. Although there are precedents, nutrient trading is a novel tool and its implementation would require extensive communication with stakeholders, not to mention a progressive attitude from enforcement agencies and politicians. It is unlikely to be feasible to implement at the national scale due to the extensive amount of catchment information required (e.g. quantification of groundwater flows and nutrient reduction targets) and likely administrative work involved. Nevertheless, nutrient trading has been shown to be compatible with the existing legislative framework (Rive et al. 2008) and, given its successful adoption in Taupo and potential to result in almost immediate realisation of nutrient reduction targets, nutrient trading warrants serious consideration as a tool to control pollution in New Zealand's most sensitive and iconic catchments. Other MBIs that could also hold promise include environmental taxes (e.g. on fertilisers) and eco-labelling schemes. The latter instrument would involve consumers paying a premium for agricultural produce that has been certified as originating from farms that adhere to an audited Environment Management System (EMS), thereby providing an economic incentive for farmers to make positive changes. The success of such an initiative would be contingent on undertaking robust analysis to determine the requisite market-drivers to promote uptake; research in Australia has shown that dairy farmers who trialled the adoption of a simplified EMS were reluctant to continue their involvement without external facilitation or the threat of increased regulatory measures (Cary & Roberts 2011). Additionally, there may be greater potential for initiatives that are designed primarily to reduce national greenhouse gas emissions to also contribute towards reducing nutrient export by promoting positive land use change. Incentive for 'carbon farming' is set to increase when obligations for agricultural participants under the New Zealand Emissions Trading Scheme come into force in 2015 (Climate Change Response (Moderated Emissions Trading) Amendment Bill, 2009). Therefore, a target for land managers is to ensure that opportunities are sought to enhance water quality whilst concurrently reducing farmers' carbon liabilities. For example, afforestation resulting from an Afforestation Grant Scheme or the Permanent Forest Sink Initiative could be targeted at critical nutrient source areas in catchments to support combined water quality and climate change mitigation goals. Lastly, a more radical MBI proposal is to pay farmers for the provision of ecosystem services, as suggested by Baskaran (2009) who showed that New Zealanders may be willing to pay approximately NZ\$39 per year in additional

taxes if farmers were to reduce nitrogen loss to waterways by 30%. Such a policy potentially represents the ultimate step in recognising the importance of the non-economic services provided by farmland; however, its use would first require significant further research and would represent a major shift in policy.

Conclusion

The emphasis of New Zealand's pastoral industries on maintaining international competitiveness has created drivers for 'stand alone' efficiencies that have led many farmers to intensify their practices in good faith, seeking profitability through production increases. The disadvantage of this focus on production has been a decrease in the overall environmental sustainability of farming and, as a result, many agricultural catchments now fail to meet community expectations regarding water quality goals. Decades of high nutrient inputs from human sources to the Te Arawa lakes have meant that lake managers now have to resort to large-scale and expensive engineering-based remediation methods in some instances to reduce internal nutrient loads in the worst affected lakes. Such actions are only the first step towards improving water quality and they are being supported by a range of further actions implemented using a mix of policy instruments to reduce nutrient loads in the long term. Initial signs are that the comprehensive remediation programme is working for some of the lakes but communities need to be realistic about the time scales involved and difficult decisions remain to be made if water quality goals for the worst affected lakes are to be achieved. Until very recently, there has been an absence of policy at the national scale to discourage similar situations in catchments elsewhere and, where policies that could effect change do exist at higher levels, there has been reticence by some politicians to use these policies to achieve water quality goals (e.g. by using the Resource Management Act to impose land use controls). Recent issue of the first NPS for Freshwater Management has contributed towards addressing this policy gap. By requiring freshwater quality limits to be set and explicitly recognising the importance of protecting ecosystem services, the NPS represents an environmentally progressive step for water governance in New Zealand. The extent of regional implementation of the NPS has, however, yet to be seen, and without a comprehensive and integrative shift towards sustainable land use practices, it is likely that water quality decline will continue for the foreseeable

future, leaving more communities faced with making difficult decisions about remediating polluted lakes in their region.

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Appendix 2 – Photographs



Photograph 1
Automatic sampling apparatus



Photograph 2
Puarenga Stream sampling site,
October 2011



Photograph 3
Sampler intake hose at Ngongotaha
Stream sampling site during base
flow, March 2011



Photograph 4
Sampling site at Ngongotaha Stream,
during storm flow, March 2012.



Photograph 5
View southwards along
the shore of Lake Rotorua
to the mouth of the
Ngongotaha Stream



Photographs 6 and 7
BioFish instrument deployed in Lake Rotorua
outside (left) and within (right) the apparent path of
the Ngongotaha Stream inflow, December 2011