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Identifying control points of excessive nitrate load in a pastoral catchment to support lake management

A thesis

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Lake Ōkaro, as seen from its catchment area.

Abstract

Excessive leaching of nitrogen (N) from pasture grazing catchments continues to challenge sustainable freshwater and lake management. However, managing contaminant export from diffuse agricultural sources is difficult due to the lack of detailed knowledge of specific sources and delivery mechanisms controlling contaminant transport over various spatial and temporal scales. This study systematically investigated nitrate dynamic flow from a small pastoral catchment into a eutrophic lake located in the central plateau of New Zealand's North Island. This study aimed to determine where and when hot spots and hot moments can be characterised as control points for freshwater contaminant losses in the pastoral catchment. Multi-isotope analysis, high-frequency data collection, and modelling were utilised in identifying and describing potential nitrate sources and biogeochemical transformations involved that affect nitrate export from catchment to receiving waters. A distinct difference in the isotopic signature of nitrate taken during high flow compared to nitrate from low flow conditions highlights the importance of considering hydrological conditions when determining the source and dominant biogeochemical processes of N within the catchment. Nitrate in the stream was mainly derived from the mineralisation of soil organic N during low flow conditions; however, the contribution from urine and urea fertiliser sources was dominant during high flow conditions. Antecedent catchment wetness of ~95 mm was identified as a hydrological threshold influencing different sources and transport mechanisms of nutrients in the lake catchment. Above the threshold, rainfall events led to the mobilisation of nitrogen from the overland flow pathway. In contrast, events below the threshold led to pronounced organic N release from subsurface runoff. The catchment model Soil and Water

Assessment Tool (SWAT) was used to simulate hydrological processes, simulate nutrient load, and investigate whether incorporating insights from isotope data in parameterisation can improve the performance of the model. Findings indicated that using isotope data as soft calibration resulted in improved simulated model output and better represented nitrogen balance in the catchment. The annual average of water yield varied from 617 – 856 mm and nitrate loads varied from 0.2 to 5.9 kg ha^{-1}. A range of scenario simulations suggest that a 50% fertiliser reduction scenario effectively reduced nitrate load by 86.4% compared to the baseline scenario. These results indicate that better management of fertiliser application is essential to control the excessive nutrient load flowing from the catchment to Lake Ōkaro. The combined analysis in this study is useful for improving the understanding of complex water flow and contaminant dynamics in the pastoral catchment, and for indicating directions and challenges for future measurements and modelling of pastoral contaminants. The integrated approach presented in this study combines stable isotope hydrology and water quality monitoring programs thereby enabling consideration and management of the dominant controlling mechanisms of different contaminant losses from land to receiving water bodies, particularly for nitrate. Such an approach provides a framework that can aid in developing water quality mitigation strategies that better anticipate the impacts of significant rainfall events.

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Table of Contents

List of Tables

List of Figures

Chapter One

Introduction

1.1 Background and motivation

Lakes provide various ecosystem services in terms of biodiversity, fisheries, climate change mitigation, recreation and tourism, and hydroelectricity (Schallenberg et al., 2013). While comprising only a small proportion of surface water, lakes play a significant role in the hydrological cycle (Shi et al., 2017). However, the cumulative effects of global change and anthropogenic factors continue to put lakes worldwide under environmental pressure. Similarly, lakes in New Zealand have experienced declining water quality. For example, an estimated 46% of lakes larger than 1 ha in New Zealand are in poor or very poor ecological health (Ministry for the Environment & Stats NZ, 2022).

One of the foremost threats to the ecosystem services of lakes is the excessive diffuse contaminant loads from the catchment, which encompasses nitrogen (N), phosphorus (P), sediment, and faecal microorganisms. Nitrogen in the form of nitrate (NO_3^-) is often considered the most widespread concern of nutrients causing water quality problems in New Zealand. Nitrate (and dissolved reactive phosphorus) are perhaps the most significant concern among solutes in lakes, mainly because these elements are most immediately and readily available for plant and algal growth (Davies–Colley, 2013) and can have a toxic effect on aquatic species (Camargo et al., 2005; Levit, 2010). Elevated nitrate concentrations contribute to eutrophication and algae development in lakes, which is often followed by fish kills due to oxygen depletion (Kendall & Doctor, 2003). Lakes in the North Island Central Volcanic Plateau

(CVP), including Rotorua Te Arawa Lakes, can be limited by nitrogen (Abell et al., 2010; Hamilton, 2005) and experience frequent harmful algae blooms (Paul et al. 2008). Therefore, the control of excessive nitrate loads in New Zealand's fresh water is essential to sustain the lake ecosystems.

Pastoral agriculture land, the dominant land use in New Zealand is considered the primary source of diffuse contaminants (e.g., nitrate) entering the aquatic environment (Howard-Williams et al., 2010). The level of nitrate in New Zealand's water has increased significantly due to the intensified application of N fertiliser in agriculture (Joy et al., 2022; Monaghan et al., 2005). This finding is also consistent with a global review that confirms a growing and intensified livestock industry as a pivotal contributor to freshwater pollution (Mateo–Sagasta et al., 2017). Consequently, most lakes in catchments dominated by pastoral land use have poor water quality (Abell et al., 2010; Verburg et al., 2010). Nutrient enrichment from pastoral land use shows a distinct pattern with respect to lake water quality (Scholes & McIntosh, 2010). Figures show that disproportionate nitrogen loads (37%) come from pastoral land use which comprises only 6.8% of the total land area; this makes pastoral land the critical land-based sources of nitrogen in New Zealand (Elliott et al., 2005). As agriculture is one of the primary industries that significantly contribute to national wealth, mitigating contaminant export requires win-win solutions that retain agricultural production and profit while maintaining ecosystem function.

Limiting nutrient delivery from the catchment is fundamental for improving lake water quality. Hence, sustained reduction in external load has been identified as a critical step in lake restoration projects (Abell, 2018; Hamilton et al., 2016; Jeppesen et al., 1999). Norton and Kelly (2010) defined a catchment nutrient limit as a sufficient level of nutrient load that will both maintain the health of freshwater and consider social, cultural and economic effects. Nevertheless, setting nutrient load limits from diffuse sources such as agriculture is challenging due to the lack of knowledge of responsible mechanisms controlling contaminant transport over the spatial-temporal scale**.**

Identification of hot spots and hot moments (hereafter HSHM); a concept synthesised by McClain et al. (2003) and expanded with new terminology to be ‘ecosystem control points’ by Bernhardt et al. (2017), can provide better considerations for water quality management. However, it remains challenging to untangle the HSHM of contaminant production, mobilisation, removal, and delivery in a quantitative way. Bernhardt et al. (2017) recommend four types of mechanisms in applying the HSHM concept in an ecosystem that can be recognised as biogeochemical activities (permanent and activated control points) and hydrologic connectivity (export and transport control points). Hence, more specific data related to biogeochemical and hydrological mechanisms are required to assist in the identification of contaminant controls. Further challenges are how to incorporate HSHM phenomena into quantitative models as management tools and for decision-making (Groffman et al., 2009) and how to increase the value of the HSHM information in reducing the enrichment of nitrate in water bodies.

1.2 Study area

A small pastoral catchment, the Lake Ōkaro catchment, was selected as the focus of this study. The catchment flows into the eutrophic Lake Ōkaro, part of Te Arawa Lakes, located in the Bay of Plenty region in the North Island, New Zealand. Lake Ōkaro has been extensively studied (e.g., Forsyth et al., 1988; Özkundakci et al., 2010; Santoso et al., 2021) with its inflow catchment well-characterised (Hudson & Nagels, 2011; Özkundakci et al., 2011). The lake has targets for improving its trophic state (Environment Bay of Plenty, 2006) within a region where lakes can be at least partially N-limited (Abell et al., 2010).

1.3 Research aims

This study is one of the limited number of studies to determine HSHMs of high nitrate loss rates across dominated pastoral catchment in New Zealand by examining the connection between the biogeochemical processes and hydrological behaviour of contaminant export from land to freshwaters. In this study, a new simplified approach is used to estimate potential nitrate loss within the HSHM concept (McClain et al., 2003; Bernhardt et al., 2017) using the definition from Source-Mobilisation-Delivery (SMD) framework proposed by (Granger et al., 2010) and readily available data. The SMD concept provides three key aspects for nitrate transport from land-to-water: the application or presence of constituent sources in a catchment, the mobilisation of these constituents from their sources, and their delivery to receiving streams and water bodies. This framework of the water contaminant transfer continuum has been adopted widely for designing mitigation strategies and targeting monitoring for the estimation of mitigation impacts (e.g., Bende–Michl et al., 2013; Bloodworth et al., 2015; Reaney et al., 2019). Using a range of field assessments and a catchment model, this thesis addresses three specific research objectives relating to source, mobilisation, and delivery of excessive nitrate from pastoral-dominant catchment, namely:

1. to identify potential sources of nitrate and to assess the dominant biogeochemical processes contributing to nitrate export from the pastoral catchment.
2. to analyse the variations in mobilisation and delivery of nitrate as a response to hydrological conditions, and
3. to simulate hydrological and nutrient delivery processes using a catchment-based model as a base to improve understanding of control points for nitrate loss from the pastoral catchment.

1.4 Thesis overview

This thesis comprises six chapters, three of which main research chapters (Chapters 3 – 5) were developed as a series of stand-alone studies and specifically address each of the three research objectives studies described above. The way in which these chapters are combined is illustrated in Figure 1.1. Each of these chapters has been written independently in a format acceptable to peer-reviewed scientific journals, with its introduction, methods description, and relevant discussion of the results as they relate to previously published literature. Therefore, there may be some repetition in the methodological details and context provided in the introduction section.

Chapter 1 – is an introduction to the topic of identifying control points (i.e., hot spots and hot moments) for excessive nitrate under the source, mobilisation, and delivery framework in the pastoral catchment, as a basis for management strategies.

Chapter 2 – focuses on a literature review of the dynamics of land-to-water processes for excessive nitrate transport from a catchment and presents a potential approach in controlling the impacts of agricultural land use on lake enrichment. This chapter provides a theoretical base of concepts for the research that was conducted and identifies shortcomings in the current understanding of nitrogen loss processes from catchment to freshwater. The chapter identifies and highlights the knowledge gaps, which inform and advance research on the study topic.

Chapter 3 – is the first research article of this thesis. It explains the interpretation of isotopic signatures along with hydrochemical data to identify nitrate sources and determines dominant biogeochemical processes affecting nitrate dynamics in the Lake Ōkaro catchment. This approach used a detailed dataset from a two-year survey (2019 – 2020) of stream flow and water quality measurement across the catchment. The variations in nitrate concentration and isotopic composition were discussed in the context of hydrological conditions.

Chapter 4 – is the second research article. It presents the application of a similar isotope tracer approach to identify nutrient dynamics as a response to hydrological rain events. The chapter demonstrates the utilisation of extensive monitoring and event-based sampling to understand the role of hydrological behaviour in the mobilisation and delivery of nutrient loads from the pastoral catchment to Lake Ōkaro.

Chapter 5 – is the third research article. It presents the results of the SWAT+ model used in simulating the hydrological processes and nutrient balance in the lake Ōkaro catchment. Additionally, the chapter specifically addresses the potential of applying the SWAT+ model enhanced with insights from isotope data derived from two previous chapters (Chapters 3 and 4).

Chapter 6 – summarises the overall results and conclusions. It provides a synthesis of the key findings from the preceding research chapters, and discusses their main research limitations and identifies the main conclusions about understanding sources and transport mechanisms of excessive N. This chapter focuses on potential implications and recommendations for future research, based on findings from this study.

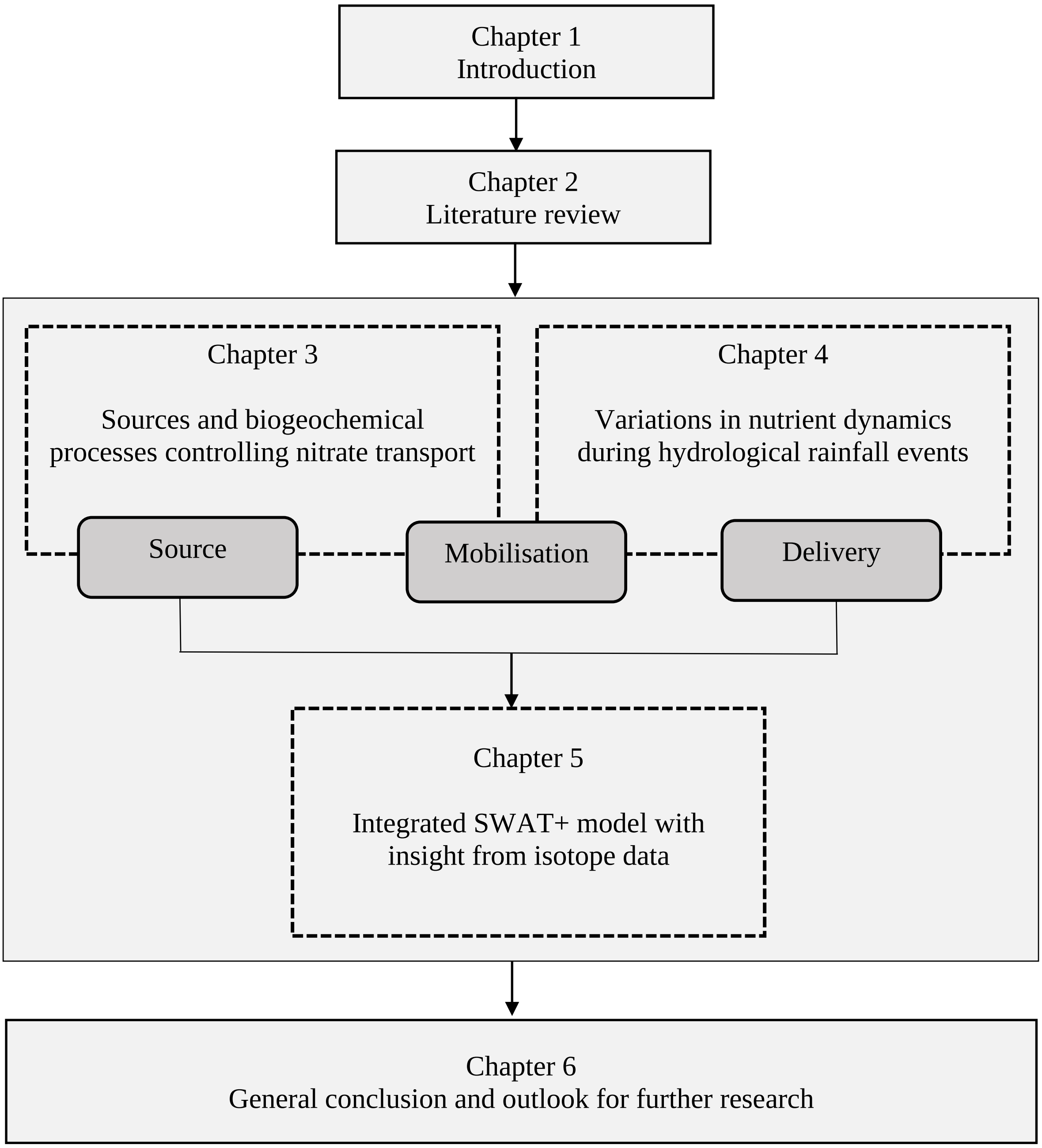

Figure 1.1 Schematic of the chapters presented in this thesis.

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Chapter Two

Literature Review

2.1 Land-to-water nutrient losses: a basis for mitigation options

Nutrient loads from pastoral farming to freshwater (especially lakes) are one of the biggest environmental management challenges for New Zealand (Dodd et al., 2016; Gluckman et al., 2017; McDowell et al., 2020). Therefore, understanding nutrient pathways from land to receiving waters is indispensable for improving catchment management strategies (Tesoriero et al., 2009; Veizaga et al., 2016), especially when observed nutrient loads (for example, N) in the surface water are not fully representative of the actual nutrient losses (Meissner et al., 1999). Identifying, classifying, and quantifying hot spots, areas that exhibit high activity relative to the other locations nearby, and hot moments, the short time that shows high reaction rates compared to more extended intervening periods (McClain et al., 2003) will improve the understanding of nutrient mobilisation, removal and delivery in freshwater ecosystems, and will aid in the design of management strategies (Zhu et al., 2012) in which intervention measures can create considerable benefits by reducing nutrient loads (Ferrier et al., 2005).

Since McClain et al. (2003) introduced the term hot spots and hot moments (HSHMs); several studies have attempted to recognise HSHMs for nitrogen with the hope of informing stakeholders of the need to manage the negative impacts of excessive N on freshwater ecosystems. For instance, a systematic review of nitrogen removal through hyporheic and riparian zones to reduce N transport to receiving waters was reported by Zhao et al. (2021). This review supports earlier literature

(Dwivedi et al., 2018; Vidon et al., 2010) that found a basic understanding of the biogeochemical and hydrological processes through riparian zones offers an opportunity to better inform management strategies that improve nutrient removal on the catchment scale. Wetlands also have also been identified as playing a critical role in nutrient processing and N retention (Cheng & Basu, 2017; Woodward et al., 2009) thus potentially reducing lake eutrophication. The hot moments of nutrient export are varied depending on many environmental factors, e.g., land use, soil, season, hydrology (Zhu et al., 2011), but are mostly related to the variability of precipitation (Silva et al., 2002; Zhao et al., 2021). Several studies have identified changes in rainfall patterns as hot moments in nutrient concentrations and export (Castellano et al., 2012; Jacobs et al., 2018; Liu et al., 2020).

To date, research has generally focused on the HSHM (i.e., ecosystem control points) concept to guide better contaminant management practices (e.g., Dwivedi et al., 2017; Rosenzweig et al., 2008; Vidon et al., 2010); however, this research is often on non-pastoral (e.g., forested system, urban, mixed agricultural) catchment. New research is necessary to understand the processes that regulate nitrate transport from intensively N fertilised catchments such as pastoral area to water bodies. In pastoral catchment, for instance, urine patches may be hot spots for N leaching and excessive N load (Chicota et al., 2010). Often, transport hot moments are associated with episodic hydrological events that occur in response to rainfall (Vidon et al., 2010). Under heavy rainfall on pastoral land, overland flow can transport substantial quantities of contaminant to stream and it is unlikely that vegetated buffer strips will particularly effective at attenuating such high-energy flow conditions (Collins & Rutherford, 2004). Therefore, insights describing when and how contaminants are mobilised by water in a pastoral landscape are essential for effective decision-making in catchment management, particularly for catchments with high input into already nutrient-enriched lakes, such as Lake Ōkaro. Nevertheless, understanding the evolving role of hot spots (e.g., riparian zones, wetlands) and hot moments (e.g., short duration of rainfall) in contaminants removal and delivery also challenging because catchments are known to be vulnerable to land use and climate alteration (Ranalli & Macalady, 2010).

2.2 Sources, mobilisation, and delivery of nitrogen in the pastoral system

Land-to-water nitrogen losses at the catchment scale is a function of the availability of nutrients, transport pathways to get them from their source to waterways, and intervening removal processes along the transport pathways (McDowell et al., 2011). Understanding how contaminant sources are mobilised and their delivered to receiving water is essential providing an underpinning knowledge of nutrient transfer processes. This understanding is necessary to support sustainable agricultural management while maintaining land sustainability in the context of adaptive management, climate, and land use changes (Howard–Williams et al., 2010). However, specific potential sources and catchment processes that control excessive nitrogen losses from pastoral systems relatively understudied.

In agricultural areas (e.g., pastoral farming), sources of N are commonly multiple and could include chemical fertiliser, atmospheric deposition, precipitation, microbial fixation, animal excreta and soil nitrogen (Xue et al., 2013; Nestler et al., 2011). Under New Zealand pastoral systems, inorganic fertiliser (Carran & Clough, 1996) and animal urine patches (Ledgard, 2001) are the most significant inputs of N that have a direct impact on excessive N in the environment. Despite the understanding that excessive rates of N inputs and cycling will lead to high direct impacts on the environment, defining the point where excess starts (Carran & Clough, 1996) and determining the fate of N (Galloway et al., 2008) remain a major problem. Thus, to assist decision-making for controlling excessive N, accurate and precise identification of the primary sources and biogeochemical processes that affect the transport of contaminants in streams is essential before effective mitigation methods can be implemented.

Transformations and cycling of nutrients, such as N, in streams are essential factors in the magnitude of overall nutrient export from catchments (Mulholland et al., 2009; Rode et al., 2016). The important drivers of the nitrate concentration are not only related to sources but are also affected by biogeochemical processes, such as nitrification, denitrification, and assimilation (e.g., Matiatos et al., 2021; Zhang et al., 2018). Nitrogen can be transported by water in several different forms, including dissolved inorganic N (nitrate, nitrite, and ammonium), dissolved organic N and particulate-associated N (e.g., particulate organic N and adsorbed ammonium) (McKergow, 2007). In soil, nitrate, the most common contaminant in New Zealand's freshwater ecosystem, is predominantly derived from the mineralisation process that converts organic N to ammonium, and ammonia that, in turn, is denitrified into nitrate by very specific populations of nitrifying bacteria through nitrification.

Nitrification refers to the sequential oxidation of relatively immobile ammonium into highly mobile nitrate via nitrite by nitrifying bacteria during aerobic respiration (Granger & Wankel, 2016). There is a two-step process of nitrification, carried out by distinct types of microorganisms. Ammonia is first oxidised to nitrite by ammonia–oxidising archaea and/or bacteria, then to nitrate by nitrite–oxidising bacteria (Huang et al., 2021; van Kessel et al., 2015). The rapid conversion of unavailable N during nitrification to the nitrate form leads to losses via leaching from subsurface (soil and groundwater), thus creating a great potential for eutrophication of receiving water. In an agricultural system, losses of N associated with and following nitrification are considerable and limit the effectiveness of fertiliser application (Subbarao et al., 2006). Denitrification is the process of microbial reduction of nitrate to nitrogen gas under anaerobic conditions (Song et al., 2022). Denitrification is often regarded as the most significant biogeochemical process for nitrate removal (Duncan et al., 2013; Morse et al., 2015; Wexler et al., 2014), however, there are several mechanisms such as biomass assimilation, dissimilatory nitrate reduction to ammonium, anaerobic ammonium oxidation, and nitrate reduction coupled to iron oxidation recognised as possible nitrate removal pathways (Burgin & Hamilton, 2007).

It is well known that mobilisation processes (i.e., nitrate leaching through soil profile) from an unsaturated zone to a saturated zone before it is transferred to surface water are essential in the export of nitrate from the catchment. Hence, soil characteristics are significant in the transport and transformation of leached nitrate–N from land to rivers or lakes (Rivas et al., 2017; Smethurst et al., 2014). Nitrate loss from the root zone in soils due to leaching is not only one of the most critical problems in farm systems but is also the main cause of excessive nitrate concentrations in freshwater ecosystems. Therefore, understanding how nitrate is mobilised/leached from the soil is crucial to comprehending the pathways of nitrate loss to streams (Cirmo & McDonnell, 1997), and has become a significant focus of protecting freshwater from excess nitrate (Xu et al., 2013).

Generally, the amount and the spatial pattern of nitrate leached varies across a field due to the differences in the level of soil nitrate and drainage conditions. Several factors controlling nitrate leaching include augmented N cycling and application of fertiliser (Carran & Clough, 1996), pre-fertiliser conditions and soil hydrologic properties (Causse et al., 2015), mineralisation and timing of crop uptake (Dupas et al., 2017), as well as mean annual rainfall and stocking density (Dymond et al., 2013). Higher nitrate loss could likely occur from pastoral systems because the upper input of N soil and well-drained drainage that led this system is prone to leaching (Burkitt et al., 2014).

Removal of N occurs in catchments between the root zone and monitoring stations where loads are monitored. More than 55% of N inputs to a landscape may "disappear" before reaching the outlet (Alexander et al., 2007; Howart et al., 1996). Many studies have found high levels of nitrate removal from an ecosystem (e.g., Howarth et al., 2012); however, it is commonly unclear whether this retained in temporary sinks (e.g., soils or plant uptake) or turned to gaseous forms of N (Sutton et al., 2011). In-stream processing and nitrate losses has been also observed with the catchment (Hester et al., 2016; Ranalli & Macalady., 2010), and these need to be taken into account when measuring nitrate load from the catchment.

In New Zealand, the N budgets as an indicator of environmental pressure has been estimated at various scales, ranging from farm-scale (Selbie et al., 2013), catchment (Heggie et al., 2009), and across regions (Parfitt et al., 2012). Most of these studies highlight nitrate losses as dominant forms in freshwater and pastoral farming as the central roles in N budget estimation. There remains a lack of clarity, or even precise discussion, about where and when nitrate removal rate is limited by HSHM processes and by the interaction between catchment topography and biogeochemistry in the pastoral system. Accordingly, the nitrate removal process and pathways in pastoral catchments are important to downstream water quality.

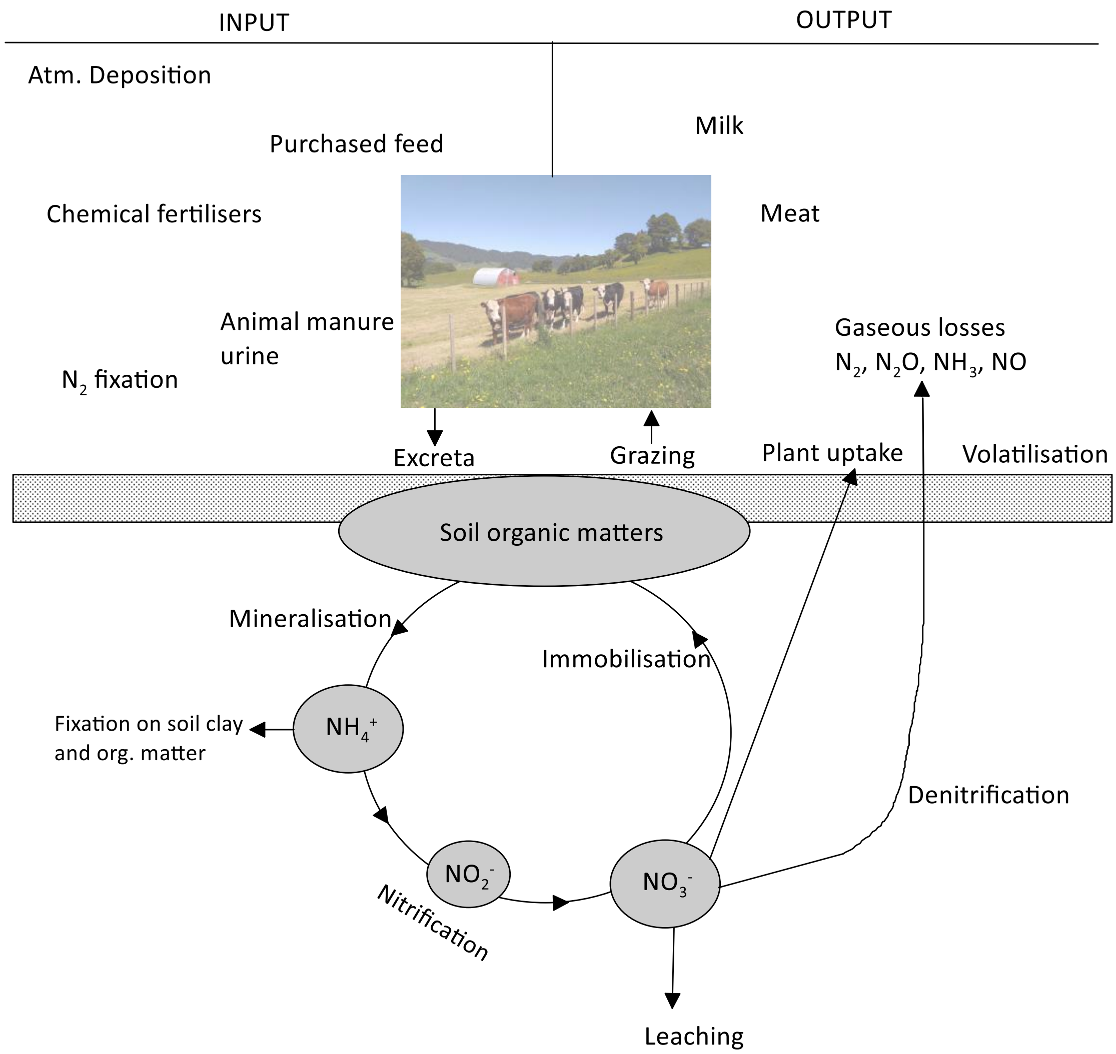

Figure 2.1 The nitrogen balance in pastoral system (modified from Cameron, 1992; Ledgard et al., 2001).

2.3 Hydrological control on contaminant transport

The successful control of diffuse contamination from pasture must target not only the sources and mobilisation of contaminant in soil but also the potential hydrological controls on their movement (McDowell et al., 2002). Water is the driving force controlling contaminant export from land to receiving water bodies because it provides the energy for contaminant movement (McKergow et al., 2007). In fact, appreciating how water moves along hydrologic pathways is indispensable to understanding the mechanisms that control biogeochemical HSHM phenomena. Water enhances biogeochemical fluxes in two ways. It transports elements across space, and it provides conditions that enhance biogeochemical cycling rates (McClain et al., 2003). While climate and soil characteristics determine the generation of nitrate export (i.e., their availability), hydrological processes (precipitation, infiltration, runoff, and erosion) drive their mobilisation and delivery to water bodies. Hence, water movement and hydrological processes can significantly affect the transport of water quality contaminants.

As previously mentioned, N exports are dominated by nitrate that does not adsorb onto soil particles. Consequently, the delivery of nitrate to streams is strongly determined by dominate hydrologic flow pathways (Outram et al., 2014) that drive distinctive patterns of nitrate dynamics in different types of catchments. Delivery of nitrate to fresh waters is influenced by the extent to which flow paths intersect suitable redox conditions for biotic reactions, including denitrification (Tesoriero et al., 2009). Nitrate flux removed via denitrification per unit length of the channel is appreciably reduced during months of high discharge and nitrate flux and increases during months of low discharge and flux (Alexander et al., 2008). The percentage of the stream nitrate load that is delivered to the catchment outlet is strongly affected by the cumulative removal of nitrate in headwater and higher order streams during transport in the river networks (Alexander et al., 2007; Peterson et al., 2001).

Understanding the relationship between nitrogen concentration and runoff flow rate has provided a better grasp of how catchment hydrology and land use interactively regulate nitrogen inputs to stream water and downstream water bodies. Shift in temperature, vegetation structure, fertiliser rate and nitrification – denitrification processes accumulated across all contributing flow paths (Duncan et al., 2017) causes the variability of nitrate concentration – discharge and patterns to become more complicated (Lloyd et al., 2016). The seasonal variation in hydrological conditions has been found to be the predominant controlling factor of in-stream N transformations. For instance, Wong et al. (2018) showed that enriched nitrate concentration from agricultural activities is significant during wet period.

Typically, the pathways by which diffuse contaminants enter water bodies can be broadly considered to be overland flow (i.e., quick flow; part of storm flow which moves quickly to a stream via surface runoff), interflow (lateral flow in unsaturated zone), and base flow (water derived from seepage of groundwater; without the influence of storm flow); however, in nature, these pathways may not be as distinctly separated (Mellander et al., 2012) and appropriate methods are still evolving to associate areas and flow paths with contaminants being delivered (Rissman et al., 2019). The importance of these pathways varies based on meteorological conditions, soil type, topography, land management, and agricultural practices. The classification proposed by Haygarth et al. (1999) used rainfall as the main hydrological driver of diffuse contaminants to describe the nature of pollutant delivery to water bodies. The reason is that often, one pathway may carry more than one hydrological response. Moreover, stormflow periods are likely to add new water sources during storm events, and they may mobilise new and distinctly different sources of contaminants (e.g., nitrate) compared to baseflow (Buda & DeWalle, 2009). However, many catchments are characterised by a rapid hydrological response to rainfall input yet show only limited fluctuations in many streamwater solute concentrations (Hrachowitz et al., 2016). Therefore, rainfall–runoff mechanisms must be understood in order to regulate contaminant loads from land to receiving water.

One of the fundamental challenges in catchment hydrology is to understand the flow paths of water movement within catchments and the interplay of biogeochemical and hydrologic processes within a catchment ecosystem. It is essential to understand the hydrologic source compartments and drainage pathways that control runoff patterns and processes in catchment ecosystems (Raymond et al., 2012). Aqueous chemistry evolves and changes in response to biogeochemical processes and hydrologic routing as water moves down a stream drainage gradient. An additional challenge on the hydrological response of a catchment is assessing the impacts due to climate change. Increases in more frequent and intense rainfall events due to climate change have projected to increase nutrient contaminant loads from the land (e.g., Andersen et al., 2006; Longfield & Macklin, 1999), in fact, the latest report of Environment of Aotearoa (Ministry for the Environment & Stats NZ, 2019) revealed climate change to be further pressure on freshwater due to increased nutrient contamination from pastoral farming.

2.4 Stable isotopes for improved management of nitrate contaminations

Terrestrial and in-stream biogeochemical processes are complex; hence, identification and quantification of nutrient export to receiving water are not accessible if only using concentration data (Barnes & Raymond, 2010). Isotope data is useful to explain the path and occurrence of water containing isotopic elements at more integrative scales (McGuire & McDonnell, 2007). Due to their unique characteristics (Fry, 2006; Kendall & Caldwell, 1998), environmental isotopes (i.e., hydrogen, carbon, nitrogen, and oxygen) can serve as tracers of water and nutrients cycling in the environment.

2.4.1 Water isotopes

Identifying hydrological pathways by which water moves on its way to the stream not only can provide essential information of flow generation itself but also regarding delivered soluble nutrient (i.e., nitrate) from their sources. Isotope tracers of water ($\delta^2H–H_2O$ and $\delta^{18}O–H_2O$) have the advantage to provide preliminary indication in origins, flow paths and biogeochemical transformations of water contaminants (Abbott et al., 2016; Jung et al., 2019). Stable isotopes of water and hydrograph separation techniques have long been used in hydrologic studies to differentiate relatively "old" (uniform) water and the more variable "new" water or the processes that formed them since they have unique isotopic compositions (e.g., Richey et al., 1998; Sklash & Farvolden 1979). For instance, the precipitation (new water) that triggers the runoff is often isotopically different from the water already in the catchment (old water) (Generaux & Hooper, 1998; Pionke & DeWalle, 1992). Isotopic hydrograph separation provides meaningful relationship between streamflow components (pre-event and event water), which can be used to infer the flow path and residence time (Kim et al., 2017; Wels et al., 1991) and to understand the extent of nitrate export from the catchment (Andersson & Lepistö, 1998; Kennedy et al., 2012). However, Genereux and Hooper (1998) indicated that the isotopic data do not necessarily separate the sources of water (e.g., groundwater, precipitation). Studies have shown that a high degree of uncertainty exists in the identification of flow paths because waters within a single flow path can be derived from several different sources (Liu et al., 2004; Ogunkoya & Jenkins 1991). Using isotope tracers combined with hydrochemical observations (Buttle & Peters, 1997; Klaus & McDonnell, 2013) and hydrological models (Smith et al., 2022; Stadnyk & Holmes, 2020; Windhorst et al., 2014) opens opportunities to enhance the understanding of hydrological processes and nutrient dynamics by reducing limitations associated with isotopic hydrograph separation.

2.4.2 Nitrate isotopes

Isotope tracers of nitrate have been recognised as the most promising tool to investigate the transport and sinks of nitrate. The isotopic composition of N in nitrate (expressed as $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ in ‰) acts as fingerprints that can distinguish the different sources and related processes of nitrate such as atmospheric N_2, soil, chemical fertilisers, and nitrification (Xue et al., 2009). Values of isotope nitrate are vary greatly between N fertilisers (typically close to or <0 ‰) and animal waste (generally > 10‰) (Kendall, 1998) and between isotopic composition of nitrate from precipitation and nitrate produced by nitrification (Kendall et al., 2007). Therefore, stable analysis of nitrate in water is the prevailing tool used to identify nitrate sources and to estimate their contribution to nitrate enrichment of freshwater (Voss et al., 2006; Wassenaar, 1995).

The identification of nitrate sources using isotopes in agricultural setting are well presented in the reviews by Xue et al., 2009. These nitrate isotope ($\delta^{15}N$ alone or combined with $\delta^{18}O$) approaches have assisted in tracing the sources of nitrate that drive reduction in water quality. One of the most important discoveries includes the detection and quantification of denitrification as a natural nitrate removal process (Granger & Wankel, 2016) and useful indicator of potential N losses in soil systems (Stevenson et al., 2010). Furthermore, the use of nitrate isotope tracers has also been key to improved management of excessive nitrate (Nestler et al., 2011) that may result in a better understanding of an ecosystem. It can be said that stable nitrate isotope tracing and analysis is a reliable way to quantitatively identify catchments–derived nutrient export.

However, several limitations in applying nitrate isotope tracer also need to be acknowledged. The main limitation in their application historically has been in being able to constrain the highly variable end member concentrations (Mengis et al., 2001; Zhang et al., 2018). Identifying nitrate sources is potentially biased by complex fractionations of multiple N-cycling processes (Kellman, 2005). Thus, the magnitude of the isotope effects associated with individual transformations in the N cycle need to be assessed (Denk et al., 2017). Xue et al. (2009) provides a comprehensive review of how complex processes of N cycle, from nitrification to ammonium volatilisation, can lead to biased interpretations of nitrate sources. Moreover, there is a lack of understanding of what controls natural variability within observed isotopic signatures (Finlay & Kendall 2007; Kendall et al., 2007; Martínez del Rio et al., 2009). A study conducted by Wells et al. (2019) revealed that hydrologic and biologic processes have significant implications for nitrate source apportionment. However, significant uncertainties remain in understanding how N from various sources moves through landscapes to streams and the extent to which N cycling processes alter these sources during transport (Schlesinger et al., 2006). These uncertainties indicate a need to relate the sources of nitrate in the entire N cycle, nitrate transport in the water phase, and natural variability of nitrate in the application of isotope as nitrate flow tracers.

2.4.3 Integration of isotope tracers with other approaches

Amidst the successful studies using a dual isotope of nitrate and water isotope as the environmental tracer, further focus has also been given to solving the limitations of this approach to characterise sources, mobilisation and transport of contaminants, particularly in relation to improved management strategies for pollutant reduction. Geochemical data has long been recognised as supplementary isotopic data to determine the mechanism of nitrate removal (Böhlke & Denver, 1995). Combining isotope tracers with other biogeochemical transformation processes at multiple scales is potentially useful for generating contaminant transport data across a catchment (Abbott et al., 2016). The geochemical transformations, which may possibly occur during transport of the nitrate or co-migrating tracers also need to be well understood, since these transformations may affect both the concentration and isotopic signature of the tracers (Nestler et al., 2011). Monitoring nitrate concentrations and other water quality parameters such as dissolved inorganic carbon (DIC) and electrical conductivity (EC) allows for identification of nitrate excess, particularly in an area where remedial actions are needed to reduce nitrate loads in a lake (Biddau et al., 2019; Ogrinc et al., 2019; Torres-Martínez et al, 2020).

Kendall and Doctor (2003) emphasised that integration of multiple tracers (including solute concentrations and solute isotopes) with the hydrology and biogeochemical model approach is essential to determine flow paths of water and contaminants (e.g., nitrate). This view is supported by Burns et al. (2009) and Nestler et al. (2011) maintain that knowledge of the hydrological and biogeochemical processes that affect mobilisation and delivery in a study area is necessary to understanding the main water flow and contaminant transport paths. Thus, incorporating isotope tracers into conventional methods — biogeochemical tracers, water quality assessment, and hydrogeological characterisation — is now recognised as a more successful to quantitatively determine management strategies for controlling nutrient enrichment in water (Ogrinc et al., 2019) and resolve the old water paradox (the old water paradox describes the rapid mobilisation of previously stored water via subsurface flowpaths during a storm event; Bishop et al. 2004). The integration of hydrochemical data and isotopic techniques has been shown to provide a holistic understanding of sources and fate of nitrate and other contaminants in varying land use on a global scale (e.g., Saccon et al., 2013), nevertheless, similar information remains rare for catchments dominated by pastoral land use.

2.5 Hydrological catchment model

2.5.1 General overview

The complexity of hydrological and nutrient processes on a catchment scale can be simplified using a modelling approach. The modelling method is a valuable tool for estimating water quality dynamics and estimating the consequences of possible management actions. The output of catchment models is potentially useful in identifying HSHMs and supporting lake restoration efforts (Parshotam & Robertson, 2018).

There are different types of catchment models, which can be categorised based on model input and parameters, process representation, spatial representation, and time representation (Devia et al., 2015; Parshotam & Robertson, 2018; Pechlivanidis et al., 2011). Following the implementation of models, reviews and comparative evaluations of the hydrological catchment models are continually conducted. Ejigu (2021) reviewed catchment models and their applicability for quality assessment, and found that when selecting suitable models, it is important to consider the availability of data, intended objectives, model assumptions and uncertainties. A previous review by Yang and Wang (2010) highlighted that selected model should be able to: (1) generate reliable simulated results of water quality and quantity; be applied on a catchment or larger scale; take into account both point source and diffuse contaminants; calculate the complex nutrient biochemical processes in different types of soil; model for different land use; and predict climate change impacts.

Modelling approaches of contaminant mitigation have been used worldwide to estimate water and nutrient transport over various spatial and temporal scales; for example, to simulate nitrogen mass balance and nitrate transformations in unsaturated zones (Andrews et al., 1997; Nolan et al., 2010), and in saturated zones (Hansen et al., 2009; Harbaugh et al., 2000). Application of models also can be site–specific but can also be implemented on a broader level, such as in England where a simple yet conceptual model, the nitrate time bomb (NTB), was utilised to simulate nitrate transport and estimate the peak of nitrate loadings at catchments on a national scale (Wang et al., 2012; Wang et al., 2017). The numerical models HYDRUS can be used to simulate solute transport in soil and groundwater (Šimůnek et al., 2008), and simulate removal of nitrate from constructed wetlands (Langergraber and Šimůnek, 2012). The Soil and Water Assessment Tool (SWAT) has also been widely used to calculate contaminant fate and transport from land to streams at a catchment scale in places such as France (Conan et al., 2003), Iran (Akhavan et al., 2010), and Germany (Pohlert et al., 2005). In New Zealand, a few catchment-scale models have been used to support management decision-making, such as WAM (Watershed Assessment Model, Collins, 2001), ROTAN (Rotorua and Taupo Nitrate model, Rucinski et al., 2006), SPARROW (Spatially Referenced Regression on Watershed Attributes, Alexander et al. 2002), CLUES (Catchment Land Use for Environmental Sustainability, Semadeni–Davies et al. 2016). The description of models available in New Zealand is presented by Cichota and Snow (2009) and Fenton (2009)

2.5.2 SWAT+ model description

The Soil and Water Assessment Tool (SWAT) is a catchment scale model developed by the USDA Agricultural Research Service (USDA – ARS). It is physically based and continuous time model that uses readily available inputs (Neitsch et al., 2011). The SWAT model launched its original version (SWAT94.2) in early 1990s and has undergone some significant updates with the latest version of model is SWAT 2012. Gassman et al. (2007) discussed the development history of SWAT model including a wide range of SWAT applications, model limitations, and future research needs. The SWAT model has been used everywhere in the world for various applications and is known to be robust in simulations of water quality in agricultural catchment. In the last decade, 3591 peer-reviewed journal articles reported in https://www.card.iastate.edu/swat_articles/.

The SWAT model is public domain software and available online for free through https://swat.tamu.edu/, however the code for the most popular GIS-coupled SWAT (ArcSWAT) is not open source since it is licenced to ArcGIS software. Whereas another version of the SWAT model is SWAT+ that is an open-source GIS interface for the SWAT model using QGIS. The SWAT+ model developed to be more flexible in term of spatial representation and is expected to improve simulations of processes within catchment (Bieger et al., 2017).

The current interface of SWAT+ model performs similar functions to SWAT (Dile et al., 2016), where the hydrologic cycle simulated in the SWAT model is based on the water balance equation as follows:

$$SW_t = SW_0 + \sum_{i=1}^{t}\left(R_{day} - Q_{surf} - E_a - W_{seep} - Q_{gw}\right) \qquad \text{(Eq. 2.1)}$$

where SW_t is the final water content of the soil (mm H_2O), $SW_0$is the water content in the early stage of the soil (mm H_2O), *t* is time (days), $R_{day}$is the daily precipitation (mm H_2O), $Q_{surf}$is the surface runoff on day i (mm H_2O), $E_a$is the daily evapotranspiration (ET), $W_{seep}$is the daily percolation, and $Q_{gw}$is the daily return flow.

2.5.3 Previous estimates of water quality in the Lake Ōkaro catchment

Several models using a variety of approaches and degrees of complexity have been applied in the Lake Ōkaro catchment. Four years after the construction of the wetland, Hudson and Nagels (2011) evaluated that the wetland able to retain significant proportion of nitrate load (77 – 78%) from the catchment using the LOADEST model (Runkel et al., 2004). LOADEST calculated the loads based on regression model. LOADEST can produce biased load estimates when the selected model is a poor representation of the relationship between load and the explanatory variables. Problems with load bias may be identified through careful analyses of model residuals. LOADEST has therefore been modified since its initial release to include several features that facilitate residual analysis and bias identification. It should also be noted that the wetland is one of a series of restoration tools that have been applied in the Lake Ōkaro catchment (Environment Bay of Plenty, 2006). Determining the overall performance of the wetland requires consideration of the contributions of the other catchment attenuation activities.

Mallet (2015) simulated water quality and investigated the efficacy of management practices in the Lake Ōkaro catchment using the INtegrated CAtchment (INCA) model. INCA is a semi-distributed physically based model that uses a mass-balance approach to simulate flow and nutrient pathways (Whitehead et al., 1998; Wade et al., 2002). Based on the study, the model efficiently simulated the variability of flows and nutrients. However, it also identified that a key limitation in the model is the lack of in-channel nutrient dynamics for N.

Wilcon (2022) performed water balance and nutrient loads for the Greater Tarawera Lakes and their catchments, including the Lake Ōkaro catchment. The study applied Overseer®, a farm-based model that estimates nutrient transfers and losses (Wheeler et al., 2006). Findings from the study were that the variation in nutrient loads is dependent on climate and land use. Although the study considered uncertainty in the calculation of streamflow and nutrient loads, raised concerns with Overseer® implementation in an understanding of nitrogen losses should be acknowledged (Ministry for the Environment and Ministry for Primary Industries, 2021).

The above studies have documented a need for a tool for developing a better understanding of land-to-water nutrient dynamics at the pastoral catchment scale for improved lake and catchment management. Environmental tracers such as stable isotopes have received a great deal of attention due to their ability to assist identification of sources and transport of nutrients (i.e., nitrate) in hydrologic systems, however, this approach is also hampered by a limited understanding of hydrological and biogeochemical processes controlling isotopic compositions. There is thus an opportunity to implementation of effective methods by integrating isotopic signatures with hydrochemical data from high-frequency monitoring and catchment model for improving the understanding of complex water flow and nutrient dynamics in pastoral catchments.

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Chapter Three

Sources and dominant mechanisms of land-to-water diffuse pastoral contaminants: insight from hydrochemical and isotope data

3.1 Introduction

Lakes provide various ecosystem services in terms of biodiversity, fisheries, climate change mitigation, recreation and tourism, and hydroelectricity (Schallenberg et al., 2013). While comprising only a small proportion of surface water, lakes play a significant role in the hydrological cycle (Shi et al., 2017). However, the continuous flows of nutrients to lakes globally have resulted in declining water quality (i.e., eutrophication) that restricts their ecological function and provision of ecosystem services (Abell et al., 2011; Beklioğlu et al., 2017; Bhateria & Jain, 2016; Suárez et al., 2019).

Controlling the input of nutrients at the catchment scale is generally considered a critical step for the effective water quality management of nutrient-enriched lakes. Reducing external nutrient loads by mitigating hot spots and during hot moments (McClain et al., 2003; Zhu et al., 2012) continues to be a priority in lake restoration projects (Abell, 2018; Jeppesen et al., 1999). There is an ongoing discussion regarding the specific origins of nutrient loading from the catchment and nutrient transport pathways linking the lake to its catchment (Arora et al., 2022; Bernhardt et al., 2017; Johnes et al., 1999).

Nutrient enrichment in freshwater ecosystems, including lakes, is often dominated by diffused nitrate sources (McDowell et al., 2020), which are more significant in areas with intensive agricultural activities. Of particular concern is pastoral agricultural land, the dominant primary production land use in New Zealand, because it is considered a major driver of diffuse contaminants in the aquatic environment (Howard–Williams et al., 2010). Most lakes in catchments dominated by pastoral land use have poor water quality (Abell et al., 2010; Verburg et al., 2010); lakes contain disproportionate nitrogen loads from pastoral land use (37% of the load) but comprise only 6.8% of the total land area in New Zealand (Elliott et al., 2005). However, managing contaminant export from diffuse sources, such as agricultural operations, is challenging due to the lack of detailed knowledge of specific sources and delivery mechanisms controlling contaminant transport over various spatial and temporal scales.

Hydrology and climate are important factors contributing to nitrate export on various temporal scales (e.g., Perakis, 2002; Rusjan & Vidmar, 2017; Welsh et al., 2019). Especially in streams highly impacted by non–point sources in agriculture catchments, excessive nitrate transport at times of high flow is mainly dominated by these discharges (Burns et al., 2018). Monaghan et al. (2016) also found that wet conditions create critical flow pathways for increased nitrate loss from farm production systems. In their study, nitrate exported from land to receiving water decreased during low flow conditions due to a change in the nitrate source and dominant processes of nitrate production.

Understanding the water sources that reflect the change in water quality of stream water is of critical importance in agricultural areas where nutrient management on farms is a key component of nitrate source control. Identifying the hydrologic pathways and source components of stream water (i.e., precipitation, groundwater, surface water) associated with delivered soluble nutrients from the catchment can be achieved by quantifying water isotope ratios of $\delta^{2}H–H_2O$ and $\delta^{18}O–H_2O$ (i.e., Hu et al., 2019; Ohte et al., 2010). Yi et al. (2008) demonstrated the utilisation of isotopic composition in determining the proportional contributions of input water to lakes in western Canada. Based on a study in a lowland catchment during drought conditions, Kleine et al. (2021) reported that the stable isotopes of water greatly assisted in estimating various water contributions to nutrient fluxes. Others have investigated the isotopic signatures in different water sources of streamflow and critical processes (e.g., evaporation) in river systems (Trinh et al., 2016) and lake water balance (Shi et al., 2017).

Isotopic compositions of nitrate ($\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$) have been frequently used to identify the source and characterise the dominant processes of nitrate transformation in stream water (Nestler et al., 2011; Xu et al., 2016; Xue et al., 2009). Dual isotope nitrate can be used to distinguish various potential sources such as atmospheric precipitation ($\delta^{15}N$: –13 to +13‰, $\delta^{18}O$: +25 to +75 ‰), nitrate fertiliser ($\delta^{15}N$: –5 to +5‰, $\delta^{18}O$: +17 to +25‰), manure and sewage $\delta^{15}N$: >+9 to +25‰, $\delta^{18}O$: –10 to +15‰; soil nitrogen ($\delta^{15}N$: –1.4 to +8‰, $\delta^{18}O$: –5.7 to +14.7‰), ammonium fertiliser ($\delta^{15}N$: –5 to +5‰, $\delta^{18}O$: –5 to +15‰, and urine - urea sources ($\delta^{15}N$: –5 to +1.6‰) (Heaton, 1986; Kendall, 1998; Rock et al., 2011; Wells et al., 2015; Xu et al., 2016; Xue et al., 2009). Nitrate isotopic signatures also can be used as indicators of different N transformation processes, i.e., nitrification, denitrification, and ammonia volatilisation (Kendall, 1998; Mariotti et al., 1981). The preferential use of heavier isotopes (^{15}N and ^{18}O) over lighter isotopes (^{14}N and ^{16}O) at every stage of the biogeochemical processes is termed isotope fractionation (Fry, 2006) and leads to different isotopic signatures. During denitrification and ammonia volatilisation, the residual nitrate is enriched in the heavier isotope; in contrast, the nitrification process induces the production of an isotopically lighter nitrate (Kendall, 1998). Information on the stable nitrate isotopic composition in freshwater systems has aided in understanding the nitrogen dynamics in agricultural catchments (e.g., Dong et al., 2022; Harris et al., 2022; Liu et al., 2021; Torres–Martínez et al., 2021). However, due to the large ranges of isotopic values for each potential source, limitations exist in complex environments where multiple nitrogen sources coexist (Nestler et al., 2011; Xue et al., 2009). The coupling of isotope data with the Bayesian mixing models, which incorporate uncertainty by design, can clarify the relative proportional importance of different sources and processes of nitrate (Cao et al., 2022; Divers et al., 2014; Gibrilla et al., 2020).

Very few studies have been carried out to characterise nutrient export by linking variations in flow conditions to changes in isotopic composition. Such research would be helpful, as it would better inform catchment-lake management. This study combined multi-isotope data with hydrochemical data to investigate the source and fate of nitrate in a pastoral catchment of a eutrophic lake in the North Island, New Zealand. This two-year study explored a method for improved nitrate source investigation in a pumice soil area that has a permeable surface layer with potential nitrate sources from diffuse applications of chemical fertiliser, soil organic nitrogen, manure and sewage, and urine–urea sources. The specific objectives of the study were (1) to identify the primary sources of nitrate in the study catchment using a multi-isotope tracer, (2) to estimate the relative proportion of nitrate loss using a Bayesian mixing model, and (3) to elucidate the dominant processes contributing to land-to-water nitrate transport.

Because nitrogen management will be an ongoing focus to improve freshwater quality in New Zealand and elsewhere, this current study expected will aid the development of appropriate mitigation options for more widely controlling diffuse contamination from livestock and agricultural activities.

3.2 Methods

3.2.1 Catchment characteristics and study site

The study site, the Lake Ōkaro catchment, is located in the Bay of Plenty region in the North Island, New Zealand. The catchment drains into Lake Ōkaro. The area is part of the Ōkataina caldera complex (Figure 3.1). About 72% of the Lake Ōkaro catchment (3.98 km^2) is pasture grazing land (dairy, deer, beef, and sheep), the remainder being riparian zones, production forestry, and artificial wetland. The catchment has a minimum and a maximum altitude of 411 and 561 meters above mean sea level, respectively, with an average slope of 23%. Dominant soil types of the catchment, as given in the New Zealand Soil Classification are Orthic Pumice and Tephric Recent Soils (Hewitt, 2010). The geology of the Lake Ōkaro catchment mainly consists of alluvium lying on a low permeability geological layer (i.e., Rotomahana mud), so it is assumed that no significant groundwater inflows occur into the catchment (Gillon et al., 2009). In 2007, a constructed wetland was designed to reduce nutrient loads into the lake (Environment Bay of Plenty, 2006; Hudson & Nagel, 2011). Two main streams drain the catchment and enter the lake through the wetland from the northwest part of the lake. A bypass channel drains the flow once water height reaches the weir's crest at the Northern stream and enters directly into the lake. The Lake Ōkaro catchment has contributed significant nutrient inputs to Lake Ōkaro, resulting in frequent algae blooms in spring and summer (Paul et al., 2008). The result is that Lake

Ōkaro is the most eutrophic lake of the Rotorua Te Arawa Lakes (Özkundakci, 2011; Wood et al., 2009).

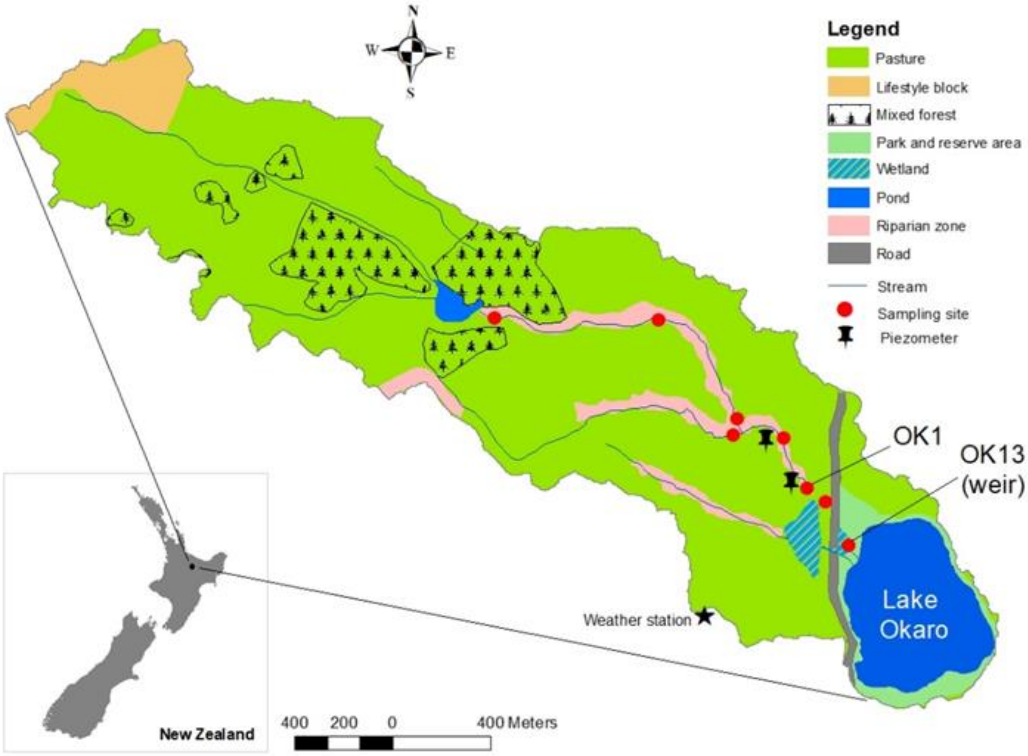

Figure 3.1 Map of the Lake Ōkaro catchment in the North Island's central plateau, New Zealand. Land use classification is based on the interpretation of satellite imaginery 2016.

3.2.2 Monitoring, sample collection and analysis

Water sampling campaigns were conducted over two years (February 2019 to December 2020). Samples were predominantly collected at a wetland inlet (OK1; Figure 3.1) and opportunistic sampling at a wetland outlet (OK13), shallow groundwater (P, piezometer), and the lake. To provide representative samples of nutrient dynamics under different hydrological flow conditions, samples were collected as a combination of discrete (monthly interval) and sampling during rainfall events. Event-based samples were collected using a Manning VST portable vacuum sampler during the study period. In addition, a one-off longitudinal sampling campaign spanning upstream to downstream in the northern stream (at c. 100 to 700 m intervals) was conducted in July 2019, a period of high flow conditions. The sampling sites are shown in Figure 1.

Prior to sampling, new collection containers were rinsed using *in situ* water. The autosampler sample bottles and hoses were acid–washed in 10% nitric acid and rinsed with analytical-grade deionised water before use. Upon retrieval, water samples were filtered through a 0.45 µm cellulose-acetate membrane filter for analysis of dissolved inorganic nitrogen (DIN) and nitrate isotopes. Unfiltered samples were taken for analysis of total nitrogen (TN). Water samples were kept on ice, transported to the laboratory quickly after sampling, and stored at 4°C until further analysis. Samples were analysed for nitrite–N (NO_2^-–N), nitrate–N (NO_3^-–N), Total Kjeldahl Nitrogen (TKN), and ammoniacal nitrogen (NH_4^+–N). These analyses were carried out in Hill laboratories, Hamilton, New Zealand, using a Flow Injection Analysis Calorimetry method (APHA 4500), including the use of automated cadmium reduction to distinguish nitrate from nitrite (Baird et al., 2017). Total nitrogen was then calculated as the sum of TKN, nitrite–N, and nitrate–N, while organic N was determined as TKN minus ammonium. Samples for dissolved inorganic carbon (DIC) concentration and carbon isotope analysis were treated as described in Kusakabe (2001) with mercuric chloride was used as preservative.

At OK1, the monitoring system of the Lake Ōkaro catchment was established in July 2019. Continuous data logging (15 minutes intervals) of electrical conductivity (EC), water level, and water temperature was carried out using a digital Mayfly data logger station developed by Stroud Water Research Center (Hicks et al., 2015;

Hund et al., 2016). Dissolved oxygen (DO) and pH were measured using a Yosemitech Y4000 sonde. For other sites, each sampling campaign used a pre-calibrated multi-meter (YSI ProSolo) to measure temperature, EC, and DO on-site. In addition, a Solinst level logger was used to measure the water level in shallow groundwater sites, covering low and high flow variations during the study period. To achieve accurate water chemistry readings of the multi-parameter sonde, maintenance, and calibration procedures, including regular cleaning of the sensors, were carefully followed. Reference materials were used to calibrate every run of each instrument and to provide a record of analytical performance, calculated as:

$$\frac{(measured\ value - known\ value)}{known\ value} * 100 \qquad \text{(Eq. 3.1)}$$

Data of rainfall and soil moisture were accessed from the Bay of Plenty Regional Council (BoPRC) environmental data portal (https://envdata.boprc.govt.nz/Data). Air temperature data were obtained through the NIWA climate database (cliflo.niwa.co.nz), extracted from the Virtual Climate Station Network (VCSN) based on the spatial interpolation of actual data observations at climate stations located around New Zealand. Technical errors in water level measurement occurred at the major stream (OK1) during a significant part of the study, so streamflow was estimated using water level observations at the wetland outlet (OK13). Water level readings were converted using the rating curve developed from historical data at the Lake Ōkaro catchment (Hudson & Nagels, 2011) provided by BoPRC.

3.2.3 Isotopic analyses

Water samples were analysed for stable isotopes of water: oxygen ($\delta^{18}O$–H_2O) and hydrogen (δ^2H–H_2O). The isotopic compositions of water samples in 2 mL glass vials were measured with a Los Gatos Research (LGR) TIWA laser spectrometer. The isotope ratios are reported in per mil (‰) relative to VSMOW–SLAP for two internal working standards (AURORA2: δ^2H = +1.63‰, $\delta^{18}O$ = –0.8‰ and ANT01: δ^2H = +1.63‰, $\delta^{18}O$ = –0.8‰) that had been previously calibrated using VSMOW2 ($\delta^{18}O$ = 0‰ and δ^2H = 0‰) and GRESP (δ^2H = –257.8 ‰, $\delta^{18}O$ = –33.39 ‰) international reference standards. To minimise memory effects, isotopic values were determined by averaging isotopic values from the last four out of seven injections. A detailed description of the analysis technique is given by Wassenaar et al. (2008). The analytical uncertainty for results based on an IAEA Water Stable Isotope Intercomparison (Wassenaar et al., 2021) test was ~0.2‰ and ~0.09‰ for δ^2H, and $\delta^{18}O$, respectively.

Stable isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O$) were analysed at the National Isotope Centre (GNS Science) using the cadmium-azide method as described in Wells et al. (2015). All results are reported with respect to AIR for $\delta^{15}N$ and VSMOW for $\delta^{18}O$, normalized to the international standards; USGS 34 (-1.8‰ for $\delta^{15}N$ and -27.9‰ for $\delta^{18}O$), IAEA-NO3 (4.7‰ for $\delta^{15}N$ and 25.6‰ for $\delta^{18}O$) and to internal standard; KNO3b (10.7‰ for $\delta^{15}N$ and 11.7‰ for $\delta^{18}O$). The analytical precision for these measurements is 0.3‰ for $\delta^{15}N$ and $\delta^{18}O$.

The $\delta^{13}C$ of was analysed in GNS Science, Wellington, New Zealand. The data were normalised for the isotopic fractionation measured in the Accelerator Mass Spectrometer (AMS). Conventional Radiocarbon Age and $\Delta^{14}C$ are reported as defined by Stuiver and Polach (Radiocarbon 19:355–363, 1977). $\Delta^{14}C$ is reported only if the collection date was supplied and is decay corrected to that date.

3.2.4 Data analyses and statistical methodology

Time series streamflow data were analysed using 'fasstr' package in R to summarise the trend of historical streamflow data (2008 to 2020). Streamflow data were categorised into different flow types, high flow (≥ 75th percentile) and low flow (≤ 25th percentile), which were used in the further analysis for nitrate isotope analysis, 0.039 $m^3\ s^{-1}$ and 0.023 $m^3\ s^{-1}$.

During nitrification, oxygen exchange may occur between oxygen atoms from the soil water and atoms from atmospheric oxygen (Amberger & Schmidt 1987; Buchwald et al., 2012). Therefore, the expected $\delta^{18}O$ of nitrate derived from microbial nitrification can be estimated using known or measured $\delta^{18}O$ for H_2O and O_2, considering the variations of oxygen atoms sources or isotopic fractionations during the two–step process of nitrification (Boshers et al., 2019; Casciotti et al., 2002; Kool et al., 2007; Sigman et al., 2005). While several factors can confound this relationship (Xue et al., 2009; Snider et al., 2010) and even when $\delta^{18}O$ of oxygen is assumed constant (23.5‰), this approach is a good approximation for the $\delta^{18}O$ of nitrate derived from microbial nitrification (Matiatos et al., 2021).

Dual nitrate isotopes were used to determine the extent of denitrification by plotting the $\delta^{15}N–NO_3^-$ versus the natural log of nitrate concentration based on Rayleigh fractionation (Kendall & McDonnell, 1998):

$$\delta_t = \delta_0 + \varepsilon \ln\left(\frac{C_t}{C_0}\right) \qquad \text{(Eq. 3.2)}$$

The Rayleigh equation uses the slope of linear regression between the relative change in corresponding isotopic values and the nitrate concentration (C) at time t relative to the initial substrate (0), to estimate the enrichment factor of denitrification (ε). The evidence for denitrification also was identified using the probability of falsely a trend (p–value) derived from linear regressions of $\delta^{18}O–NO_3^-$ and $\delta^{15}N–NO_3^-$. Positive $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ (Granger & Wankel, 2016) and negative $\delta^{15}N:\ln[NO_3^-]$ (Kendall & McDonnell, 1998) slope as primary evidence of denitrification assuming fractionation associated with first–order kinetics. The assumed existence of denitrification was validated by testing the isotopic fingerprint of denitrification for significant deviation in the ratio of $\delta^{18}O–NO_3^-$ and $\delta^{15}N–NO_3$ from the predicted 2:1 (Nestler et al., 2011) to 1:1 (Granger et al., 2008) denitrification fractionation pattern.

Water quality and isotopic composition samples were provided for statistical analysis. The normality of the data was evaluated using the Shapiro-Wilk test and the homogeneity of variances using the Levene test. One-way analysis of variance (ANOVA) type III was performed to test the difference in the measured variables between the high and low flow. All statistics were conducted in R statistical software package (R Development Core Team, 2006) and the statistically significant level for all tests was defined as $p < 0.05$. The variability of nutrient concentrations was visualised using boxplots.

3.2.5 Estimation of nitrate source contributions from the Bayesian mixing model

The proportional contribution of nitrate sources was estimated using Bayesian stable isotope mixing models as described in Parnell et al. (2013). To estimate the relative contribution of potential nitrate sources to streamwater, the Bayesian mixing model provided in the R package SIAR (stable isotope analysis in R) was used, following the Bayesian model framework (Chen et al., 2009; Xue et al., 2013). Due to the unavailability of site–specific isotopic values from different NO_3–N sources in our study area, the end member sources were defined from the mean values and standard deviation of nitrate isotopic signatures of literature–based estimates (Parnel et al., 2013, Xue et al., 2009; Table 3.1). The literature's $\delta^{15}N$–NO_3^- and $\delta^{18}O$–NO_3^- values of different nitrate sources are global averages, which are basically applicable (Gibrilla et al., 2020) in the absence of local nitrate source values for case studies (Cao et al., 2020). The model used in SIAR can be expressed as follows:

$$X_{ij} = \sum_{k=1}^{k} P_k \left(s_{jk} + c_{jk}\right) + \varepsilon_{ij}$$

$$s_{jk} \sim N\left(\mu_{jk}, \omega_{jk}^2\right),$$

$$c_{jk} \sim N\left(\lambda_{jk}, \tau_{jk}^2\right),$$

$$\varepsilon_{ij} \sim N\left(0, \sigma_j^2\right) \qquad \text{(Eq. 3.3)}$$

where X_{ij} represents the isotope value j of the mixture i, in which $i = 1,2,3, \dots i$ and $j = 1,2,3, \dots j$; P_k is the proportion of source k, which obtained from the SIAR model; s_{jk} is the source value of k on isotope j $(k = 1,2,3, \dots k)$ and is normally distributed with mean and standard deviation μ_{jk} and ω_{jk}, respectively; c_{jk} is the fractionation factor for isotope j of source k and is normally distributed with mean λ_{jk} and standard deviation τ_{jk}; and ε_{ij} is the residual error representing the other unaccounted deviation between individual mixtures and is normally distributed with mean 0 and standard deviation σ_j.

Table 3.1 Nitrate source endmember statistics used for Bayesian source mixing model. Values for standard deviation are given in parentheses.

Source	$\delta^{15}N$ (‰)	$\delta^{18}O$ (‰)	References
Ammonium, urine–urea (AFU)	1.24 (1.44)	3.44 (2.47)	[1], [2]
Soil nitrogen (SN)	3.26 (1.99)	2.51 (2.04)	[1]
Manure & sewage (MNS)	19.3 (3.24)	7 (2.7)	[1]

[1] Burbery (2018), Ding et al. (2014), Xu et al. (2016), Xue et al. (2009), Zhang et al. (2018)
[2] Wells et al. (2015), Minet et al. (2012), Rock et al. (2011)

3.3 Results

3.3.1 Temporal variations in hydroclimatic variables

The study period covers a drought period from February 2019 to December 2020 relative to the 13-year record available for Ōkaro. Total precipitation for the period of analysis was 1196 mm and 986 mm in 2019 and 2020, respectively, which is lower than the long-term average from 2008 – 2020 (Figure 3.2). Major rainfall events generally occur in winter (June to August) and autumn (March to May), but in 2019 – 2020, more intense spring (September to November) rainfall was observed.

The discharge pattern from the study area at OK13 varied over the hydrological year (Figure 3.3). An average of 31.7% of total flow was delivered in the spring, 28.1 % during winter, with autumn flow contributing the least to overall flow (17.5%). The high flow was characterised by higher soil moisture ($p < 0.05$, $R^2 = 0.6$, Figure 4.2). The shallow groundwater levels were correlated with the flow at OK13 ($R^2 = 0.80$, $p < 0.05$, Figure A.1).

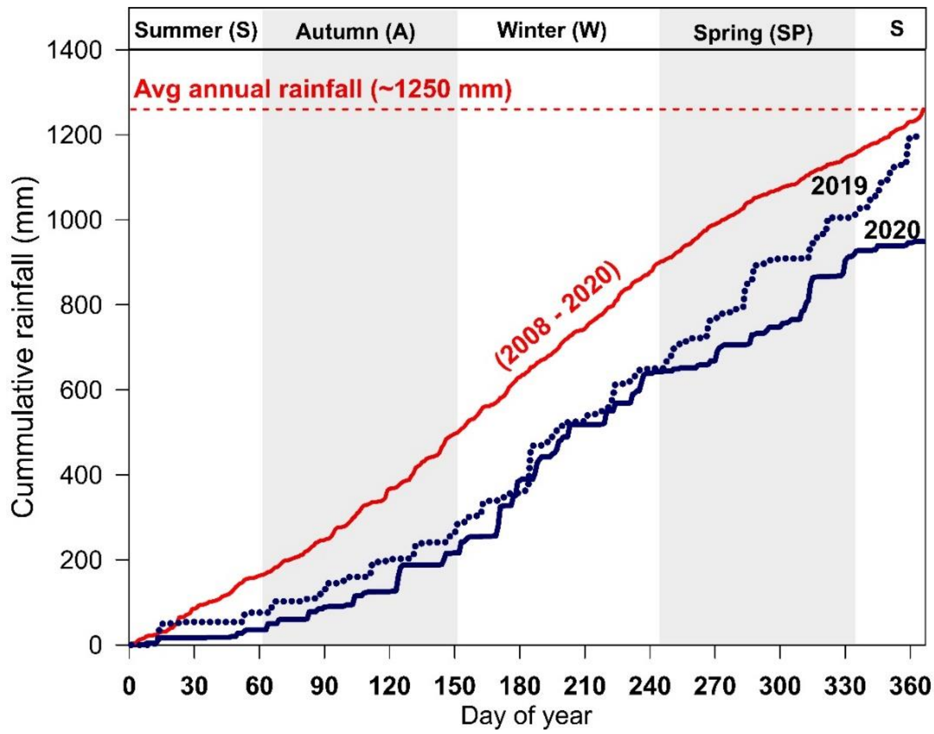

Figure 3.2 Annual cumulative rainfall during the study period (2019 – 2020) compared to the long-term annual average at Lake Ōkaro catchment.

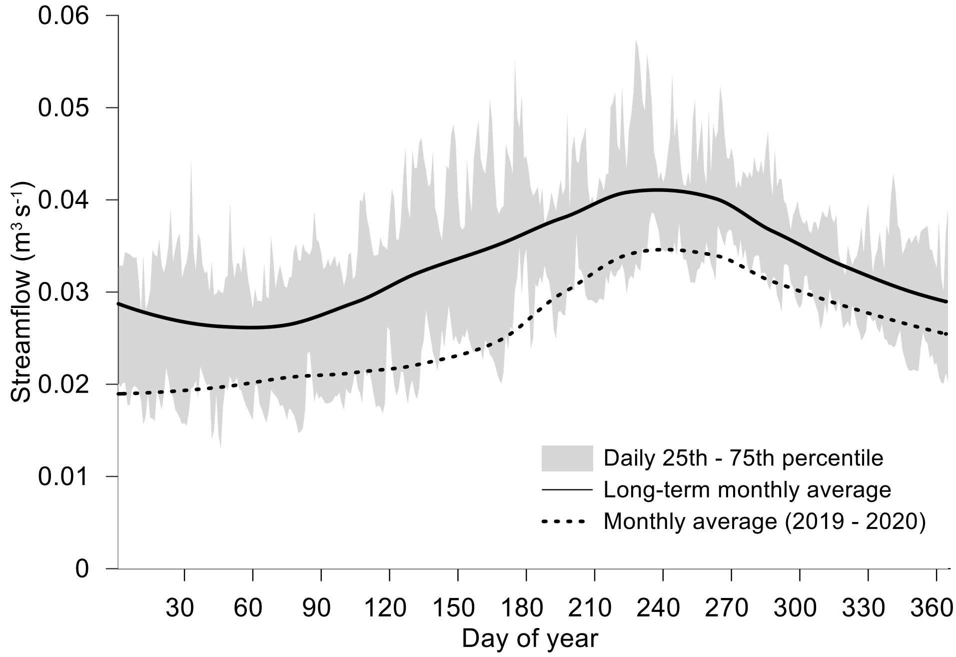

Figure 3.3 The monthly streamflow at OK13 for the study period (2019 – 2020) relative to the long–term monthly streamflow (2008 – 2020) for low flow (25th percentile) and high flows (75th percentile).

3.3.2 Variations in water chemistry

An evident spatio-temporal variation in physicochemical and isotopic compositions was observed across the Lake Ōkaro catchment (Table 3.2). The surface water EC values at OK1 and OK13 ranged between 59 – 116.41µs cm^{-1} with mean values of 84.36 and 100.04 µs cm^{-1} during high flow and low flow conditions, respectively. The EC in shallow groundwater ranged from 184.85 – 694.50 µs cm^{-1}. Values of DO ranging from 2.83 to 9.98 mg L^{-1} and 0.39 to 0.84 mg L^{-1} for surface water and shallow groundwater, respectively. Stream water temperature averaged 12.8 ± 2.70, and water temperature in shallow groundwater averaged 13.26 ± 2.70. The pH values only available for surface water ranged from 5.41 and 7.62 (with a mean value of 6.05).

Table 3. 2 The mean, standard deviation, and sample size (in brackets) for selected properties of sampled water in wetland inlet, wetland outlet, and shallow groundwater.

Site	P (shallow groundwater)	OK1 (wetland inlet)	OK13 (wetland outlet)
Low Flow			
DO (mg L^{-1})	0.62±0.17 (6)	9.04±0.71 (15)	5.13 ± 1.26 (8)
SpCond/EC (µs cm^{-1})	486.52±220.85 (4)	103.0±5.26 (15)	110.35±7.55 (8)
Nitrate–N	< 0.05 (4)	0.31±0.10 (15)	0.03 ±0.02 (6)
Ammonium–N	1.82±1.70 (4)	0.04±0.03 (12)	0.09±0.07 (3)
Total nitrogen	4.87±2.70 (4)	0.54±0.13 (13	0.26±0.06 (3)
High flow			
DO (mg L^{-1})	0.90±0.8 (5)	8.31±0.86 (17)	6.81 ± 1.48 (5)
SpCond/EC (µs cm^{-1})	444.21±200.87(5)	92.70±7.80 (17)	132.52±45.82 (5)
Nitrate–N	< 0.05 (4)	0.76±0.41 (17)	0.20 ±0.07 (4)
Ammonium–N	0.93±0.70 (2)	0.05±0.03 (8)	0.07 (1)
Total nitrogen	4.91±3.23 (2)	1.82±2.65 (8)	0.57±0.14 (2)

At site OK1, the northern stream NO_3^-–N concentrations were significantly higher (p < 0.05) in high flow than in low flow (Figure 3.4). Nitrate was the predominant N form of TN, accounting for 23.30% to 70.50% (ranged between 0.18 – 1.54 mg L^{-1}), with the highest NO_3^- concentrations in the stream coinciding with the peak flows of the first winter events (see Chapter 4 Figure 4.9). High organic N values (7.3 – 9.2 mg L^{-1}) were found during specific high flow conditions. Ammonium concentration was consistently low, with the highest concentration measured being 0.15 mg L^{-1}, and the mean concentration of ammonium was 0.04 mg L^{-1}. There was a strong positive linear relationship between nitrate–N and flow ($p < 0.05$, $R^2 = 0.78$).

At site OK13, organic N was the dominant N form of TN during low flow, whereas nitrate–N dominated during high flow. Seasonal variations were also noted where a higher nitrate concentration occurred during winter (Figure A.2). Lower concentrations of nitrate were also observed in shallow groundwater. Most samples collected in the piezometer had nitrate concentrations below the detection limit (<0.05 mg L^{-1}) and therefore, they could not proceed for further analysis of nitrate isotopes.

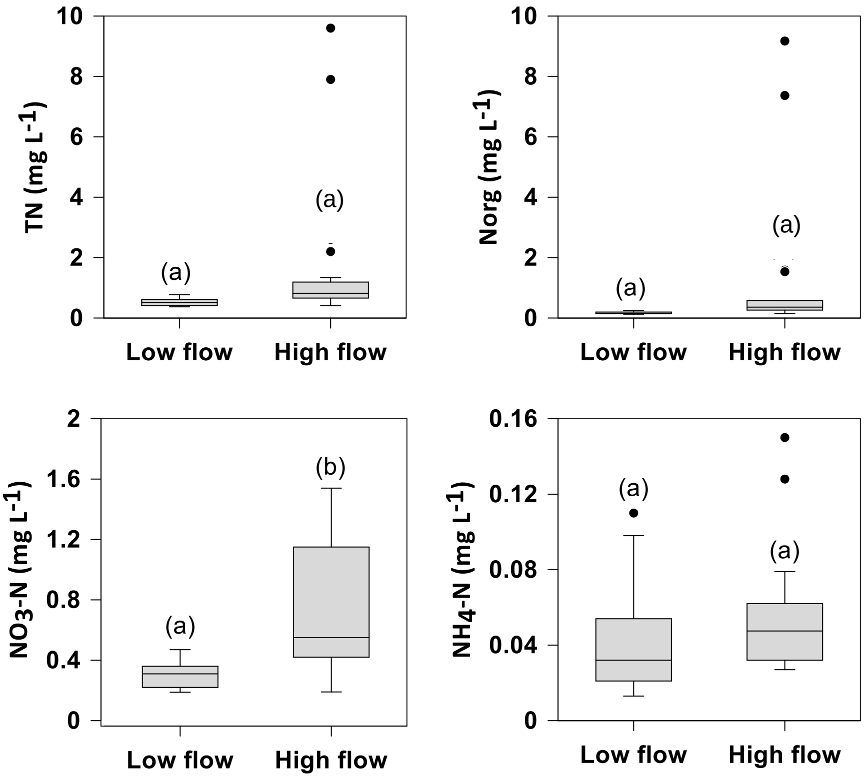

Figure 3.4 Distribution concentration of nutrients between low flow and high flow at the main stream site (OK1) over the study period. Different letters between the pairs within each plot indicate significant differences ($p < 0.05$). Note the different scales for each plot. The outliers shown in this figure were omitted from the statistical analysis to meet the data assumptions.

3.3.3 Isotopic compositions of water sources

Water isotopic composition in stream water varied from –41.3 to –33.8 ‰ for δ^2H (mean = –38.52 ‰ ± 3.38 SD) and –5.79 to –7.04 ‰ for δ^{18}O (–6.38 ± 0.60). The isotopic composition of precipitation during the study spanned from –83.5 to –10.8 ‰ (–36.9 ± 15.84) and –11.51 to –2.94 ‰ (mean = –6.20 ± 1.98) for δ^2H and δ^{18}O, respectively. Local Meteoric Water Line (LMWL) was plotted above the line parallel to the Global Meteoric Water Line (GMWL), suggesting that stream water in the Lake Ōkaro catchment was affected by evaporative fractionation (Figure 3.5). The slope of the evaporation line (slope = 5.0) was lower than LMWL (slope = 7.72). The isotopic difference between precipitation and stream water and overlapping water isotopic compositions between stream water and shallow groundwater indicate mixing sources of stream water. The isotopic composition of water within the wetland and the stream flow plotted along one local evaporation line (LEL), which varied only over the two-year study period, indicate a common water source dominated by rapid winter recharge via shallow groundwater.

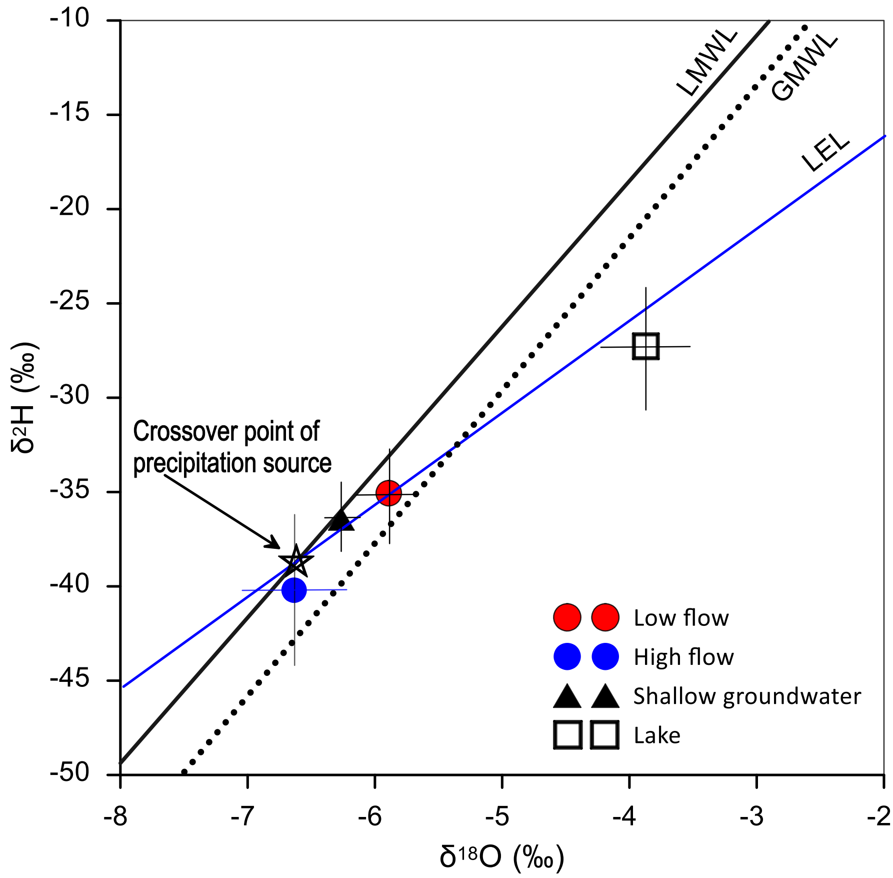

Figure 3.5 The isotopic plot of $\delta^{18}O$–H_2O and $\delta^{2}H$–H_2O values showing the distribution of water samples for Lake Ōkaro and the Ōkaro catchment. The mean and standard deviation of the delta values of samples are also shown. Global Meteoric Water Line (GMWL), Local Meteoric Water Line (LMWL) is a regression line of measured isotopic composition from local precipitation, and the Local Evaporation Line (LEL) is a regression constructed from all stream water samples.

Stream water $\delta^{13}C$ was comparable between OK1 (–14.20 ± 1.60‰) and OK13 (–13.83 ± 1.56‰). The measured DIC averaged between 62.25 mgC/kgH_2O in OK1 and 8.7 mgC/kgH_2O in OK13. The results of $\Delta^{14}C$ analysis for samples collected at OK1 and OK13 showed values ranging between 8.1 and 35.4 ‰ (SD=9.40). However, based on ^{14}C and $\delta^{13}C$ values, the study area's sampled waters are of relatively recent origin.

3.3.4 Spatiotemporal variations of nitrate isotopic compositions

To qualitatively determine the potential source of NO_3^- and differences in NO_3^- biogeochemistry in the Lake Ōkaro catchment, a dual isotope biplot of $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ was used (Figure 3.6). The $\delta^{15}N–NO_3$ values in OK1 ranged between 2.45 ‰ and 8.22 ‰, and the $\delta^{18}O–NO_3$ values ranged from –6.07 ‰ to 2.86 ‰. During high flow conditions, $\delta^{15}N–NO_3$ values ranged from 3.14 to 8.67 ‰ (6.86 ± 1.40), while $\delta^{18}O–NO_3$ values ranged from –6.07 to 3.32‰ (1.06 ± 2.44). The isotopic compositions of nitrate were generally more enriched during low flow conditions, ranging from 3.19 to 7.38‰ (6.13 ± 1.29), and –3.31 to 1.68‰ (0.20 ± 1.49), for $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$, respectively. The slope of the regression line between $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ for all samples was 1.12, or enrichment of ^{15}N relative to ^{18}O of 2.2, indicating a potential denitrification process in collected stream water samples. Enrichment of ^{15}N was accompanied by a consistent increase in $\delta^{18}O–NO_3^-$ with a significant regression between $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ (R^2 = 0.70, p <0.05) and calculated isotope enrichment from low flow (0.93) to high flow (1.62). At OK13, the isotopic compositions of nitrate appear to be plotted close to a regression line for denitrification with $\delta^{15}N$: $\delta^{18}O$ ratio 2:1.

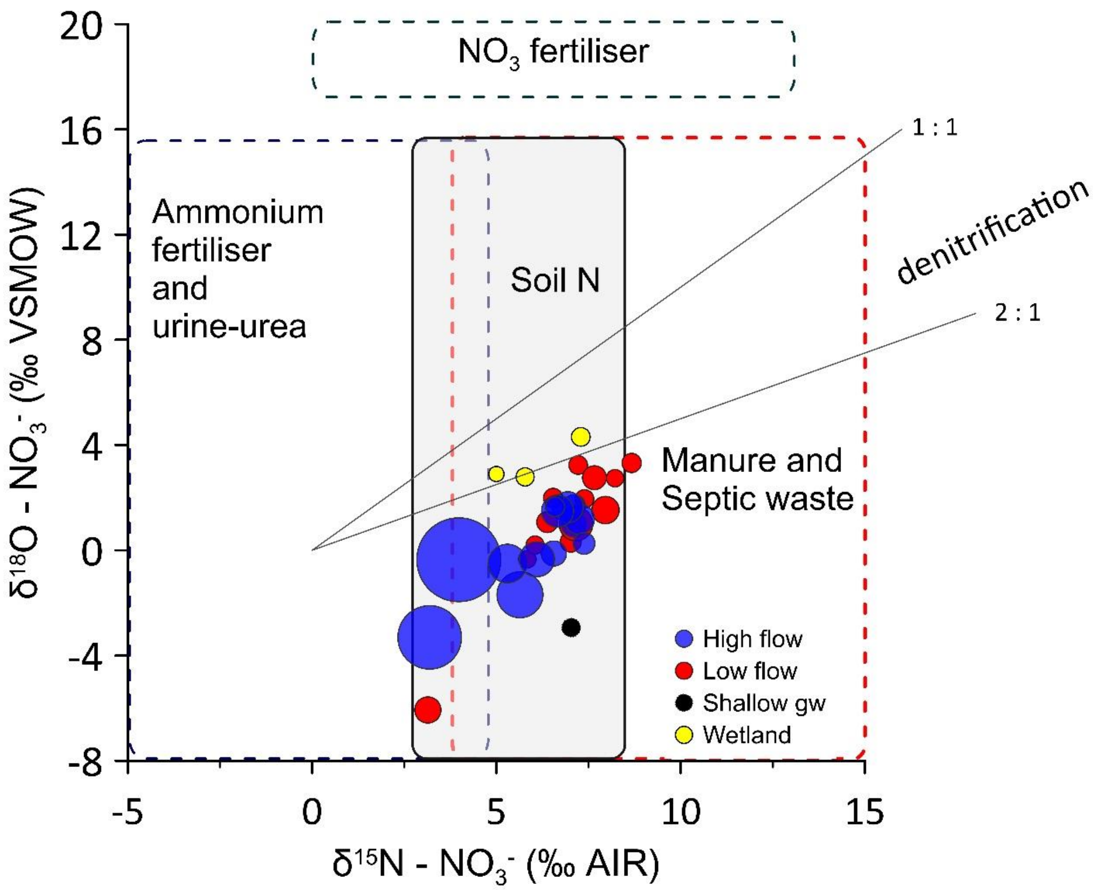

Figure 3.6 $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ in the Lake Ōkaro catchment. Boxes that delineate commonly expected isotopic compositions for nitrate (Xue et al., 2009; Nestler et al., 2011; Xu et al., 2016). Denitrification would result in a movement along a 1:1 or 1:2 enrichment line (solid line, Granger et al., 2008). Bubble size indicates the proportion of nitrate–N concentrations from all water samples (0.15 – 1.54 mg L^{-1}).

Based on samples taken during high flow conditions (July 2019), the northern stream showed apparent longitudinal patterns in nitrate concentration and isotopic compositions (Figure 3.7). Nitrate concentration increased from upstream to downstream along the catchment before decreasing at the wetland outlet. The isotopic composition of nitrate decreased between upstream and downstream. Soil N contributions remained dominantly stable over the study period, regardless of spatial and temporal variations.

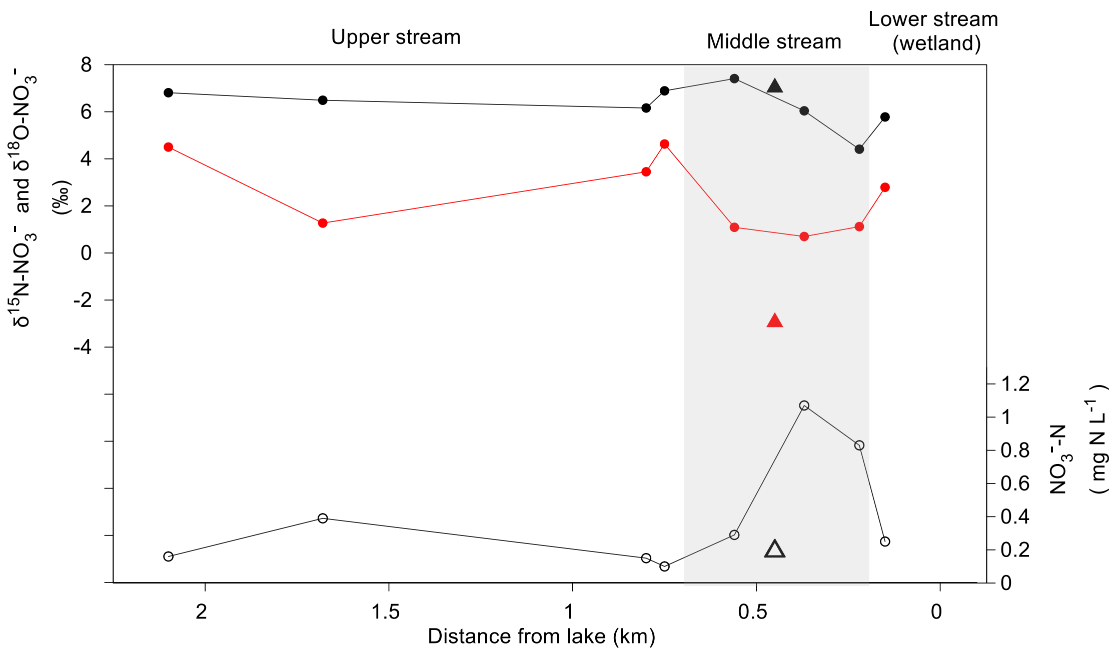

Figure 3.7 Longitudinal variation of nitrate concentrations and nitrate dual isotopes in stream water (circle) and shallow groundwater (triangle). Black closed circles correspond to $\delta^{15}N–NO_3^-$ while red closed circles are for $\delta^{18}O–NO_3^-$.

For the mixing model analysis in the study area, nitrate was assumed to be sourced from the three potential nitrate sources: artificial fertiliser and urine urea (AFU), soil nitrification (SN), and manure-sewage (MNS). The results were reported as mean proportional estimate and 95% credible intervals (CI). Quantitative estimation of N source contributions using the SIAR mixing model showed that soil N (SN) contributed the most, 49% (±19% CI) and 56% (±15%), during high flow and low flow, respectively (Figure 3.8). During high flow, 37% (±17%) of stream water nitrate export is sourced from AFU, whereas during low flow, AFU's contribution was much lower (19% ±13%). Nitrate contributions from MNS were higher during low flow (mean value of 25%±3%) than during high flow (mean value of 14% ±5%).

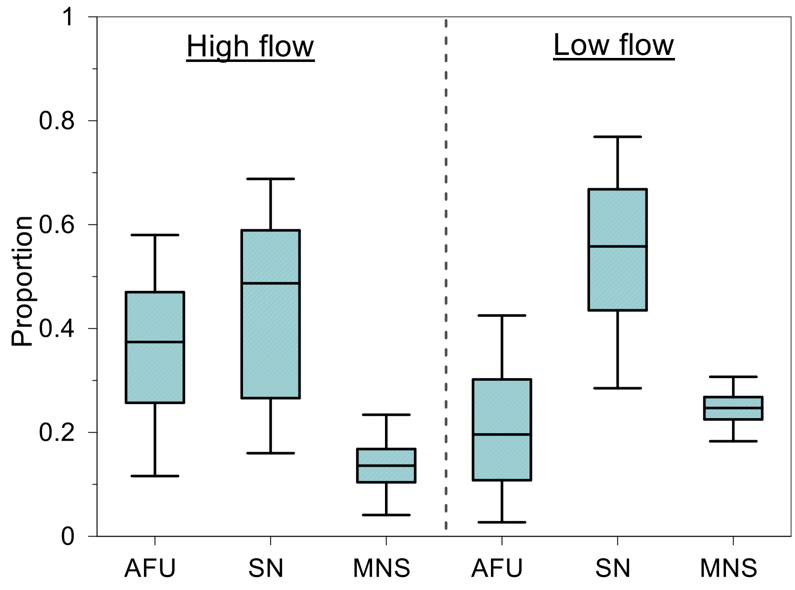

Figure 3.8 Contribution of different nitrate sources in different hydrological conditions. The 5%, 25%, 75% and 95% percentiles are shown for the probability distribution calculated for each potential source.

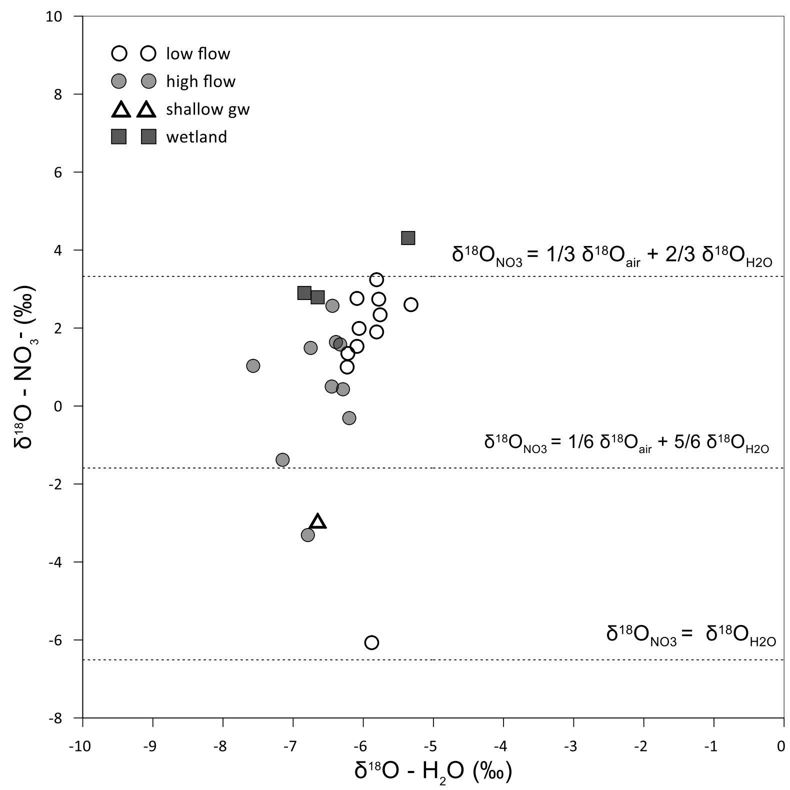

Figure 3.9 Relationship between $\delta^{18}O$ of NO_3^- and $\delta^{18}O$ of H_2O based on different theoretical nitrification. Three lines represent the theoretical line for expected $\delta^{18}O$–NO_3^- produced by the nitrification process in different conditions. A constant $\delta^{18}O$ (23.5‰) of air and $\delta^{18}O$ of water (average values measured in the study area) to estimates $\delta^{18}O$ of nitrate produced from nitrification.

3.4 Discussion

3.4.1 Isotopic evidence in variations of nitrate sources in the stream

3.4.1.1 Water isotopes

Variations in the stable isotope composition in a catchment water balance are caused by natural variations of local precipitation (Bowen et al., 2011) and processes involved, such as mixing with pre–existing waters, sub–surface flow and evaporation (Gonfiantini et al., 1998; Sprenger et al., 2016) that can be intensified by anthropogenic activities (Yang et al., 2020). By plotting $\delta^{18}O–H_2O$ and $\delta^2H–H_2O$ for the Lake Ōkaro catchment, the results suggest that climatic conditions (i.e., precipitation and evaporation) also influence the changes in source water, and these conditions must be considered to understand the transport pathways of nitrate within a catchment.

Stream water samples in the Lake Ōkaro catchment are dominated by recent precipitation, as indicated by a substantial change in isotopic compositions due to precipitation. This influence was especially pronounced during high flow following rainfall events which indicated that the stream became isotopically depleted and tended to be isotopically similar to recent precipitation. This finding is analogous to that of Birkel et al. (2012), who found that stream isotope values during higher streamflows fluctuated in the same direction as water isotope in precipitation. Likewise, von Freyberg et al. (2018) studied temporal changes of water isotopes in streamwater and precipitation and revealed that high flow typically contains higher young water proportions corresponding to precipitation sources. Coincidentally, isotopic composition in the stream was most depleted (i.e., $\delta^{18}O$ value of –7.9‰ and δ^2H of –44.1‰) when the EC in the stream water was lowest (59 µs cm^{-1}). EC was widely applied as an environmental tracer to understand hydrological processes and distinguish water sources (e.g., Cano–Paoli et al., 2019; Mosquera et al., 2018; Zuecco et al., 2019). Together, these results indicate a higher runoff contribution to stream flow during high flow associated with rainfall events, supporting the assumption that the study catchment is a closed catchment system (Gillon et al., 2006), and precipitation is the dominant input of water to the catchment, which is directly linked to the changes in the inflow to the lake.

The observed slope of the evaporation line highlights that evaporation strongly influences stream hydrology in the study area. Because isotopic fractionation during evaporation exhibits isotopic enrichment in $\delta^{18}O$ and $\delta^{2}H$ of the water along an evaporation line with a lower slope relative to the source water, the comparison of LMWL and LEL in this study suggests strong evaporative enrichment of stream water (Gonfiantini, 1986). The slope in this study (7.72) was higher than the stream water slope reported by Yang et al. 2020 (6.07) in the Lake Tarawera catchment, approximately 12 km from the study area with a lower catchment elevation (320 a.s.l). This finding supports evidence of an altitude effect on the water isotopes, where the isotopic precipitation compositions have become more enriched with decreasing elevation (e.g., Kerr et al., 2013; Viswanathan et al., 2016). In the context of a broader spatial scale, stream water has a higher slope (5.00) than Lake Ōkaro (4.02), reflecting a lower potential for evaporation and the residence time of stream water than the theoretical mean residence time estimated for Lake Ōkaro (~ 5 months, Bruesewitz et al., 2011 to ~ 1.5 years, Özkundacki et al., 2011). Knowledge of residence time would help to estimate N sources and transport (Miller et al., 2016) and understand nitrate attenuation capacity (Einsiedl et al., 2009; Frei et al., 2020), which could aid in determining mitigation actions in controlling nitrate load from the catchment.

3.4.1.2 Nitrate isotopes

Results of the N and O isotopic analysis of nitrate for water samples across the study area provide insight into the sources of stream nitrate in the Lake Ōkaro catchment. As expected, $\delta^{15}N$ and $\delta^{18}O$ values of nitrate for all samples fell within the regions of soil N, chemical fertilisers, and manure and sewage. Most of the values of surface water and groundwater samples fell into the range of soil N (see Figure 3.6), indicating that the mineralisation of soil organic and nitrification of the chemical fertiliser process is evident in the Lake Ōkaro catchment. Chemical fertilisers were identified as one of the potential anthropogenic sources rather than farming effluent in the Lake Ōkaro catchment due to the isotopic source signatures of samples falling into mixed soil nitrogen (SN) and fertiliser zones. In general, isotopic compositions observed in this study are within the range reported for nitrate in agricultural catchments (e.g., Chang et al., 2002), likely due to the long-term applications of synthetic fertilisers.However, most of the data fell outside the expected ^{15}N-enriched in the manure-sewage domain ($\delta^{15}N$ value of ~ 5 – 25‰, Xue et al., 2009), reflecting that most of the water samples contained a mixture of sources. Mixed nitrate sources identified in this study also corroborates recent study of Rogers et al. (2023), who demonstrated that New Zealand's freshwater nitrate isotopes dominated by signature of soil N retention, and urine-urea fertiliser, resulted from mixing of sources and biogeochemical processes. The contribution of nitrate to stream water from atmospheric deposition (AD) in the Lake Ōkaro catchment appears to be limited, since the isotopic composition in this study was relatively depleted and none of the samples fell into the isotopic range typically observed for nitrate originating from AD reported in Xue et al. 2009 ($\delta^{18}O$ values from 25 to 75 ‰). This finding is consistent with other studies in New Zealand that found contributions from atmospheric nitrate are considered to be negligible compared to other sources (Stevenson et al., 2010; Stewart & Aitchison–Earl, 2020; Wells et al., 2016).

Although agricultural activities dominate the Lake Ōkaro catchment, none of the water samples was within the nitrate fertiliser range. It also can be noted that fertilisers applied in the pastoral area in New Zealand are mainly urea and ammonium sulphate (Stat NZ, 2019; Penny MacCorwick, personal communication) and show typical $\delta^{15}N–NO_3^-$ ranging from –3 to +3‰ (Stewart et al., 2011). Thus, the isotopic composition of nitrate derived from fertiliser sources was mostly within the expected range for nitrate coming from ammonium in chemical fertilisers (Rock et al., 2011).

The correlation of nitrate isotopic composition with nitrate concentration varied during high and low flow periods, indicating that the interplay between source availability, mobilisation and delivery in the Lake Ōkaro catchment changed throughout the year under different hydrological conditions. High flow samples showed higher nitrate concentration with more depleted isotopic compositions of nitrate, implying that $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ decreased with increasing runoff. Other studies also documented a similar trend of depleted $\delta^{15}N$ with increasing flow generation (Kaushal et al., 2011; Yue et al., 2014). The shift towards lighter $\delta^{15}N–NO_3^-$ associated with relatively higher nitrate concentrations indicates oxidation of N–species with isotopically lighter isotopic compositions to nitrate (i.e., nitrification of ammonium fertilisers and urine sources), which were reported in other studies (e.g., Lin et al., 2019). Low isotopic composition of nitrate coincides with elevated nitrate concentration; this supports the argument that high flow conditions are important hot moments (see McClain et al., 2003) for excessive nitrate loads in the Lake Ōkaro catchment (e.g., Cui et al., 2019; Sigler et al., 2020).

According to the SIAR results, soil organic nitrogen (SN) and chemical fertiliser were the main sources of nitrate in the Lake Ōkaro catchment. The difference in the proportion of nitrate sources between high flow and low flow is that during high flow, there was a shift of nitrate sources in stream water from dominated by soil nitrification sources to urine and urea-derived sources (AFU). During high flow, mostly represented in rain event samples, the proportion of urea–ammonium fertilisers sources increased compared to low flow, where base flow proportion is more dominant. Therefore, SN mineralisation and overland flow are the main factors leading to changes in isotopic composition in the Lake Ōkaro catchment.

It should be noted that relevant nitrate sources used in this study, particularly MNS and AFU, had relatively wide ranges of isotopic compositions based on global literature values (e.g., Xue et al., 2009, Nestler et al., 2011), which caused a high degree of uncertainty in the proportional contributions of nitrate sources. This uncertainty would be reduced by taking additional site-specific water samples (Cao et al., 2022; Niu et al., 2021) and incorporating isotope fractionation in the SIAR model (Zhao et al., 2020).

The longitudinal variation in the isotopic composition of nitrate from upper to lower reach in the main stream during high flow suggests that changes in land use along the length of the stream could be responsible for the isotopic compositions of nitrate due to varying sources and biogeochemical processes involved (Burns et al., 2009, Barnes & Raymond, 2010). The upper stream of the study area is characterised by forest–dominated land use and shows lower nitrate concentration and $\delta^{15}N–NO_3^-$ of ~5‰ within the range of soil N-dominated sources (Xue et al., 2009). The middle stream located after the tributaries that flow through the pastoral area exhibited higher nitrate concentration and relatively depleted isotopic compositions of nitrate, suggesting more inputs from agricultural activities. Thus, stable isotope nitrate has proven its usefulness to differentiate isotopic land-use signatures and different nitrogen processing mechanisms across the land use gradient (Wong et al., 2018).

3.4.2 Nitrate transformation process in the pastoral catchment

3.4.2.1 Nitrification

In freshwater ecosystems, nitrate produced by nitrification has a wide range of $\delta^{18}O$ and $\delta^{15}N$ signatures from –10 to +15‰ (Kendall et al., 2007; Nestler et al., 2011; Xu et al., 2016 and references therein). Most values of $\delta^{18}O$ in the stream water during our study fell within the expected range for a nitrification source (Figure 3.9), suggesting that the pathway of N flow in the Lake Ōkaro catchment was dominated by nitrification. However, some samples of high flow collected during rainfall events in the early winter season exhibited lower $\delta^{18}O–NO_3^-$ values compared to the theoretical line. High flow conditions generally lead to an increased nitrate concentration, and a simultaneous decrease in $\delta^{18}O–NO_3^-$, which might form from an increased nitrification rate. A possible reason is that high flow conditions could alter the isotopic fractionation by using more O atoms derived from H_2O and thus to low $\delta^{18}O–NO_3^-$ in water (Kool et al., 2011; Sigman et al., 2009). In contrast, low flow conditions during summer may have led to the increase of $\delta^{18}O–NO_3^-$ value due to the evaporation of soil water and the respiration of O_2 in the atmosphere (Kendall et al., 2007).

Collectively, the $\delta^{15}N$ and $\delta^{18}O$ of nitrate indicate that the source of nitrate in Lake Ōkaro catchment is most likely nitrification of fertiliser rather than manure, especially during high flow. The depleted $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ ~ (–4‰) and ~ 2‰, respectively and consistently low concentrations of NH_4^+ during the study period suggests rapid nitrification of ammonium fertiliser as explained in Rock et al. (2011). The present finding corroborates the ideas of Yang et al. (2020). Their study suggested that an aerobic environment with higher DO concentrations and lower ammonium concentrations confirm the occurrence of nitrification. As the catchment progressively became wetter following rainfall events, nitrified nitrate in soil was more likely to be transported from the source areas to receiving waterways, reducing the residence time in the catchment.

The characterisation of mixing processes may be complicated by distinctive isotopic signatures such as denitrification (Lu et al., 2015) and the fact that the isotopic composition of the end member rarely stays constant over time. Plotting $\delta^{15}N$ against NO_3^- concentration should yield a straight line if mixing two end members with distinct nitrate concentrations and isotopic delta values occurs (Kendall et al., 2007). A significant and linear positive regression of $\delta^{15}N$ and nitrate concentration and the straight line in the Keeling plot $\delta^{15}N$ vs $1/[NO_3^-]$ (Figure 3.10a) in this study suggest mixing between two or more N mixing processes such as a dilution – flushing effect due to precipitation, the addition of chemical fertiliser, and denitrification (Kendall, 1998), especially during the high flow.

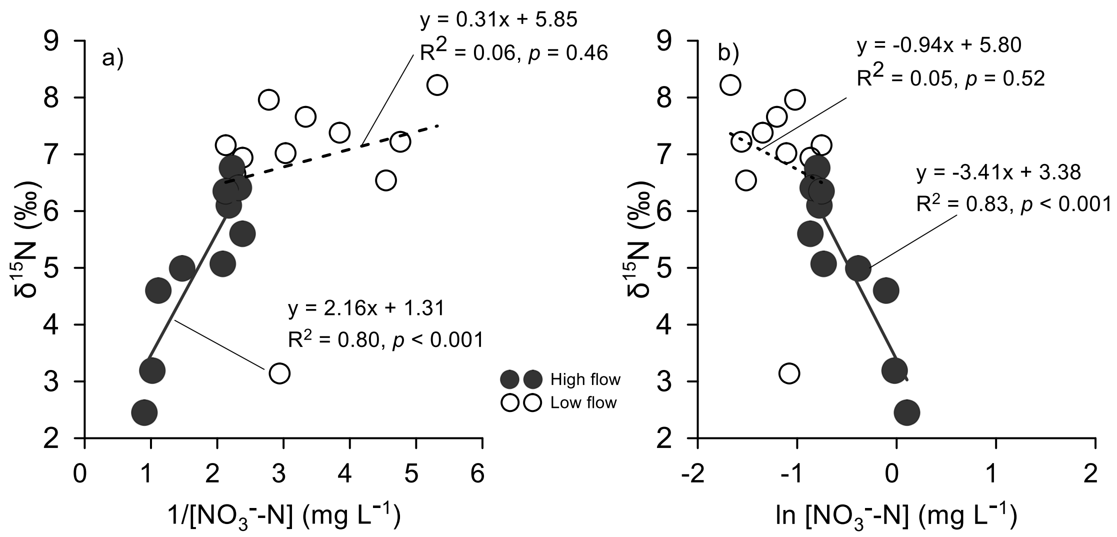

Figure 3.10 Relationship between $\delta^{15}N–NO_3^–$ and $1/[NO_3^–]$ for different hydrological conditions. The y–intercept of the Keeling plots indicates the dominant initial source.

3.4.2.2 Denitrification

During denitrification, the substrate's $\delta^{15}N–NO_3^–$ and $\delta^{18}O–NO_3^–$ values increase with decreasing $NO_3^–$ concentrations (Nikolenko et al., 2018). Except for the wetland, the isotopic signal and hydrochemistry suggest that there is weak evidence for denitrification in the Lake Ōkaro catchment. Relatively consistent high DO in the stream water also potentially ruled out the possibility of denitrification since denitrification usually occurs when DO < 2 mg $L^{–1}$ (Rivett et al., 2008; Wong et al., 2018). However, this does not imply that denitrification is not occurring (Hernández–del Amo et al., 2018; Xuan et al., 2022). Increasing $\delta^{15}N$ values with decreasing nitrate concentration and a significant relationship between $\delta^{15}N–NO_3^–$ and $\delta^{18}O–NO_3^–$ with a positive slope of ~1 may indicate denitrification (Granger & Wankel, 2016). Additional insight into potential denitrification can be gleaned from the positive relationship between nitrate and DO (R^2 = 0.5, p <0.05) and confirms the influence of DO on denitrification under anaerobic conditions. One plausible explanation for the lack of a pronounced denitrification signal is that the process likely occurred prior to nitrate entering the streams (Wong et al., 2018) and that it was nearly complete (Böhlke et al., 2006), or its concurrent nitrate production by nitrification during removal (Granger & Wankel, 2016; Husic et al., 2020). The original source isotopic signature masked by various N transformations in the soil–plant–animal system before being leached to stream is typical in New Zealand's agricultural catchments (Collins et al., 2003).

Interestingly, a significant negative regression of $\delta^{15}N$: ln [NO_3^-] (Figure 3.10b) was observed during high flow conditions, indicating a denitrification signal as depicted in Kendall et al. (2007). This result signifies that denitrification might occur in stream water; however, different hydrological conditions may also determine the degree of denitrification. Wells et al. (2016) conducted a study on pasture-dominated production found that high flow conditions following rainfall attributed to high N attenuation.

Although nitrate isotopic compositions cannot confirm it due to limited data in shallow groundwater samples, this groundwater likely contains detectable yet minor of nitrate concentrations. Shallow groundwater had a consistently low nitrate concentration (< 1 mg L^{-1}) with low DO levels, suggesting that anaerobic conditions were favourable for denitrification. Based on the consistently high ratio of NH_4^+:NO_3^- found in groundwater sites (Figure A.3), the current findings also support that denitrification potentially occurred in our study area, in line with findings described in previous studies (e.g., Yang et al., 2020).

Biplot dual nitrate isotope analysis suggests denitrification contributions in wetlands, where isotopic values increase linearly and align along the denitrification line with a ratio of 2:1 (see Figure 3.6). Denitrification is also revealed by the decrease of NO_3^- concentrations accompanied by higher DIC in the wetland through oxidation of organic matter (Otero et al., 2009). Therefore, the low concentrations of nitrate detected in wetlands can be attributed to denitrification as a dominant process in the wetland, thus providing evidence of the effectiveness of wetlands for retaining and attenuating external nitrate load to Lake Ōkaro (Hudson & Nagel, 2011; Mallet, 2015).

Ammonia volatilisation is the escape of nitrogen from the surfaces of soils or water bodies to the atmosphere as ammonia gas and is favoured at pH >9.3 (Kendall, 1998; Zhang et al., 2022). Values of pH in the stream water during the study period were < 9.3. Thus, ammonia volatilisation effects on N concentrations and isotopic compositions can be ignored in the Lake Ōkaro catchment, which is consistent with findings of other studies in the pastoral catchments with high urine–treated and fertilised soils, where the effect of NH_3 volatilisation tends to be inhibited by N recycled through the soil organic N pool (Wells et al., 2015).

3.4.3 Limitations of the study

Results of this study show that ambient N stable isotope help to reveal N transformation in the pastoral system and adds to the emerging stable isotope literature (i.e., Wells et al., 2016; Rayner et al., 2020). However, several limitations to this study need to be acknowledged. Overlapping of isotopic values made it difficult to differentiate between all potential sources used in this study and is generally considered a disadvantage of using nitrate isotopes in a system where multiple sources and transformation processes coexist (Wong et al., 2018; Xue et al., 2009). The isotope data alone cannot differentiate whether this new nitrate is sourced via allochthonous or autochthonous (Husic et al., 2020; Sánchez–Carrillo & Álvarez–Cobelas, 2019). The differences observed between high flow and low flow could result from changes in various factors such as air temperature (Burns et al., 2009), soil properties (Groffman et al., 2009) and microbial activities (Wexler et al. 2012). However, for this study, no data was gathered that would enable the differentiation of these factors. This would be an avenue for future research. Other geochemical or anthropogenically introduced tracers and stable isotopes could help to further constrain agricultural end member assessment. Further research on combining isotope-based approaches and process-based models at the catchment scale could provide a tool to alleviate this uncertainty and elucidate processes not revealed by data alone (Bai et al., 2012; Husic et al., 2020; Jensen et al., 2018).

3.4.4 Implication for the lake – catchment management

The current findings from the studied area have implications for providing additional insight from multi–isotopes for reducing nutrient loading to enriched lakes through catchment-based actions. Information from isotopic compositions combined with hydrochemical data of the catchment indicated that stream N dynamics were regulated by contributing sources, nitrification, and denitrification processes, as well as hydrological conditions.

The results highlight that control of excessive N requires particular attention to soil N management in addition to having adequate N input strategies on a catchment scale. Integrated management practices, such as modifying the N content in the diet of grazing animals (Giltrap et al., 2021), using fertilisers efficiently in terms of type, amount, timing (Monaghan et al., 2021), improving the timing of grazing associated with N–leaching (Rayner et al., 2020) and promoting denitrification through organic carbon enriched soil (Tomasek et al., 2019) and constructed wetlands (Tanner et al., 2005) could facilitate reduction of excess N in pasture grazing systems.

This study shows variation in the nature and timing of nitrate losses reaching freshwater, yet it enables simplified conclusions to be derived via understanding that varying nitrate losses are derived from common sources. This is not surprising as both the catchment's hydrological conditions and agricultural management (Birchall & Paterson, 2011) undergo temporal changes. Identifying high flow events as hot moments of nitrate export during the drought years study can have significant implications for freshwater quality, as more dry days have been predicted to occur in the future (Ministry for the Environment, 2018). The significance of such events on nutrient loading becomes more apparent when considered in the context of the increased climate uncertainty observed over recent decades in New Zealand (Manning et al., 2015; Ministry for the Environment, 2018), which could also affect catchment responses to rain events (Arnell, 2011; Sun et al., 2017). Thus, there is a need to understand the dynamic nature of contaminant loading in the context of changing hydrological patterns to improve water quality in inflows and receiving lakes.

The results also highlight more general inferences for future sampling approaches. A sampling of events to represent high flow condition is more important for understanding fluctuations or dynamics in nutrient export relative to discrete monthly samples (Lessels & Bishop, 2015), which are important for providing a baseline but are unlikely to verify load peaks and estimate rapid mobilisation (Bende–Michl et al., 2013; Outram et al., 2014; Schwientek et al., 2013; Wang et al., 2020). In addition, measuring isotopic compositions of samples collected that are still relatively limited could add value to the monitoring programs for lake ecosystem management (Kendall et al., 2010).

3.5 Conclusion

The present study investigated the spatiotemporal variability of nitrate sources and transformation over a drought-year period in the Lake Ōkaro catchment. The study area with intensive pastoral activities is a typical rain-fed agricultural catchment in New Zealand. Using an integrated multi-isotope approach combined with hydrochemical elements, the potential sources and dominant N transformation processes subject to hydrological conditions were identified. The water source was relatively recent, with residence time in the catchment being lower than in the lake. The results indicate that the influence of precipitation was prominent during high flow, while the stream was predominantly shallow groundwater-fed during low flow. Soil N (SN) was identified as the predominant source in our study area. The strong urine-urea nitrate (AFU) signature was overridden by the influence of soil nitrogen flushed from agricultural activities during high–flow conditions. Isotopic compositions of nitrate identified in the study area demonstrated typical sources of nitrate in New Zealand's agricultural area, resulted from mixing of multiple sources (soil N, urine-urea fertilisers) and transitioning of biogeochemical processes.

The fingerprint based on N and O isotopes of nitrate can also provide insight into a degree of biogeochemical processing not observed with elemental data streams alone. Although this study showed excessive nitrate transport generally controlled by nitrification, denitrification signals were also found in the pastoral system but highly determined by hydrological conditions. The hydrochemical and isotopic investigations of surface water in the Lake Ōkaro catchment have aided in improving the knowledge about the water source and pathways of nitrate and its variability across different hydrological conditions. Such understanding is important for sustainable catchment–

lake management in a temperate region. The conjunctive application of isotopic, hydrochemical and numerical analysis has led to a much clearer understanding of streamflow-generating processes at the Lake Ōkaro catchment. Moreover, there is now an opportunity to extend the application of isotope analysis in water quality monitoring to aid mitigation strategies of excessive nutrient control.

3.6 References

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Chapter Four

Effect of rainfall events on nutrient inputs from a pastoral catchment to a eutrophic New Zealand Lake

4.1 Introduction

Eutrophication of freshwater is a global problem (Steffen et al., 2015) and is one of the most widespread problems affecting lake water quality in New Zealand (Abell et al., 2010; Paul et al., 2008). For many of New Zealand's rivers and lakes, excessive nitrogen inflow in its various forms is the main issue (Ministry for the Environment and Ministry for Primary Industry, 2021). Deteriorating lake water quality is linked to nutrient loading from agricultural catchments (Abell et al., 2013; Verburg et al., 2010), yet for many lakes, reliable information on the quality and quantity of water, which could contain and export excessive nutrient levels, from their catchment areas remains lacking.

Water quality studies in a catchment level is more challenging because a high volume of surface runoff (and high concentrations of leached nutrients) is observed under specific meteorological conditions (i.e., rain events). Several studies have identified that contaminant transport to the aquatic environment during rain events can be elevated as discharge increases (Arnell et al., 2011; Kozak et al., 2019; Tomer et al., 2010); hence, stormflows are often identified as hot moments (sensu McClain et al., 2003; Sigler et al, 2020; Wey et al., 2022). However, questions have been raised about what rainfall characteristics that lead to significant nitrate export. Therefore, understanding the processes governing the generation of runoff from rainfall is essential for nutrient limitation in catchments (e.g., Kirsch, 2020; Monaghan et al., 2016). Numerous studies have examined the hydrologic response of catchments to specific rainfall events (e.g., Detty & McGuire, 2010; Pavlin et al., 2021; Saffarpour et al., 2016) or have reported the influence of rainfall characteristics on the quantity and quality of runoff (Lintern et al., 2018; Macrae et al., 2010; Sapač et al., 2020). These studies highlight the need to consider a hydrological threshold, defined as those at or above which significant hydrological impacts (i.e., rain event and antecedent moisture), in controlling catchment runoff generation when describing the catchment response to rainfall events. Knowledge gaps, however, exist regarding the relationships between hydrological responses, the range of rainfall events, and when and why nutrient loads vary; especially in pastoral catchments that feed into lakes (Abell et al., 2013; Levine et al., 2021; Menneer et al., 2004). The significance of such events on nutrient loading becomes more apparent when considered in the context of the increased rainfall uncertainty observed over recent decades in New Zealand (Manning et al., 2015; Ministry for the Environment, 2018), which could affect catchment responses to rain events (Arnell, 2011; Sun et al., 2017). Thus, to improve water quality in inflows and receiving lakes, there is a need to understand the dynamic nature of contaminant loading in the context of changing hydrological patterns.

Rainfall-runoff patterns at the event scale can be examined with high-frequency measurements of water quality to capture better the temporal variability of hydrochemical responses (Heathwaite & Bieroza, 2021; Ross et al., 2019), to explain the event–specific changes in nutrient concentration (Mihiranga et al., 2021; Shafiei & McLoughlin, 2017; Tomer et al., 2010), and to estimate loads more accurately (Blaen et al., 2017; Elwan et al., 2018; Miller et al., 2016). Outram et al. (2014) demonstrated that using high temporal resolution data helps identify sources and quantify variability in responses of catchment nutrient delivery pathways to rain events. Their findings have implications for designing mitigation strategies. Such a monitoring strategy may thus be an essential component in developing mitigation strategies to control the excessive nutrient transport from pastoral catchments that are important sources of nutrient enrichment in freshwater (Larned et al., 2020; Verburg et al., 2010).

Environmental tracer studies are common approaches used to identify differences in potential sources and transport pathways of nutrients between stormflow and baseflow (Buda & DeWalle, 2009; Janke et al., 2014; Zhu et al., 2011). For example, Buda & DeWalle (2009) showed that new nitrate sources added to a stream during rain events were distinctly different from those at baseflow. The use of stable isotope tracers allows for exploring the pathways and transformations of nitrate and other contaminants during transport from soil to receiving water. The isotopic ratios of N and O in NO_3^- (expressed as $\delta^{15}N$–NO_3^- and $\delta^{18}O$–NO_3^- in ‰ notation) provide a signature that can potentially distinguish different sources of nitrate such as atmospheric N_2, soil, chemical fertilisers, and nitrification (Xue et al., 2009). Previous studies have focused on combining NO_3^-–N isotope methods with hydrology to better understand NO_3^- transport (e.g., Yang & Toor, 2017; Yue et al., 2019). However, these nutrient transport pathways within a catchment may not be easily separated (Mellander et al., 2012). Stable isotopes of water (δ^2H and $\delta^{18}O$) and hydrograph separation techniques have long been used in hydrologic studies to differentiate relatively "old" (uniform) water and the more variable "new" water (Jefferson et al., 2015; Klaus & McDonnell, 2013; Richey et al., 1998; Sklash & Farvolden, 1979). These methods provide insights into catchment flow paths that influence nutrient transport (e.g., Tetzlaff et al., 2018; Kendall & Doctor, 2003). By coupling isotope tracers and using high-resolution time series data (Yue et al., 2020) at an event-based scale, the mechanisms of excess nutrient transport within a catchment can be more clearly understood.

The current study was motivated by contaminant loading and associated impacts on the trophic status of Lake Ōkaro as a representative case for detailed investigations of the hydrology governing N losses to freshwater from New Zealand pastoral agriculture. Lake Ōkaro has been extensively studied (e.g., Forsyth et al., 1988; Özkundakci et al., 2010; Santoso et al., 2021) with its inflow catchment well–characterized (Hudson & Nagels, 2011; Özkundakci et al., 2011). The lake has targets for improving its trophic state (Environment Bay of Plenty, 2006) within a region where lakes can be at least partially N limited (Abell et al., 2010). This study presents an analysis of extensive monitoring efforts and event-based sampling combined with stable isotope tracers of nitrate and water in an agricultural catchment aimed at elucidating: (1) the hydrological threshold behaviour as a response to rainfall at the catchment scale, (2) the relative importance of stormflow on the delivery of N loads, (3) the usability of stable isotope data to estimate the contribution of sources and transport mechanisms of water and nutrients during rain events, and (4) how nutrient export has responded to the hydrological drivers. This work progresses our understanding of the role of runoff in agricultural catchments generally and, further, provides more specific information on one of the most nutrient-enriched of the Rotorua Te Arawa Lakes.

4.2 Methods

4.2.1 Study site

The site of this study was the Lake Ōkaro catchment, which drains into Lake Ōkaro, located in the North Island's central plateau at 38°17'60" S and 176°23'59.98" E (Figure 1). About 72% of its catchment (3.98 km^2) is pastoral area (dairy, deer, beef, and sheep), the remainder being riparian zones, production forestry, and artificial wetlands. The catchment has a minimum and a maximum altitude of 411 and 561 meters above mean sea level, respectively, with an average slope of 23%. Dominant soil types of the catchment within the New Zealand Soil Classification are Orthic Pumice and Tephric Recent Soils (Hewitt, 2010). Two streams enter the lake from the northwest part of the catchment. The Lake Ōkaro catchment has contributed significant nutrient inputs to Lake Ōkaro, resulting in frequent algae blooms in spring and summer (Paul et al., 2008). The result is that Lake Ōkaro is the most eutrophic of the Rotorua Te Arawa Lakes and displays a rapid advance in eutrophication (Özkundakci, 2011; Wood et al., 2009). In 2007, an artificial wetland was designed and constructed to reduce nutrient loads into the lake (Environment Bay of Plenty, 2006; Hudson & Nagel, 2011).

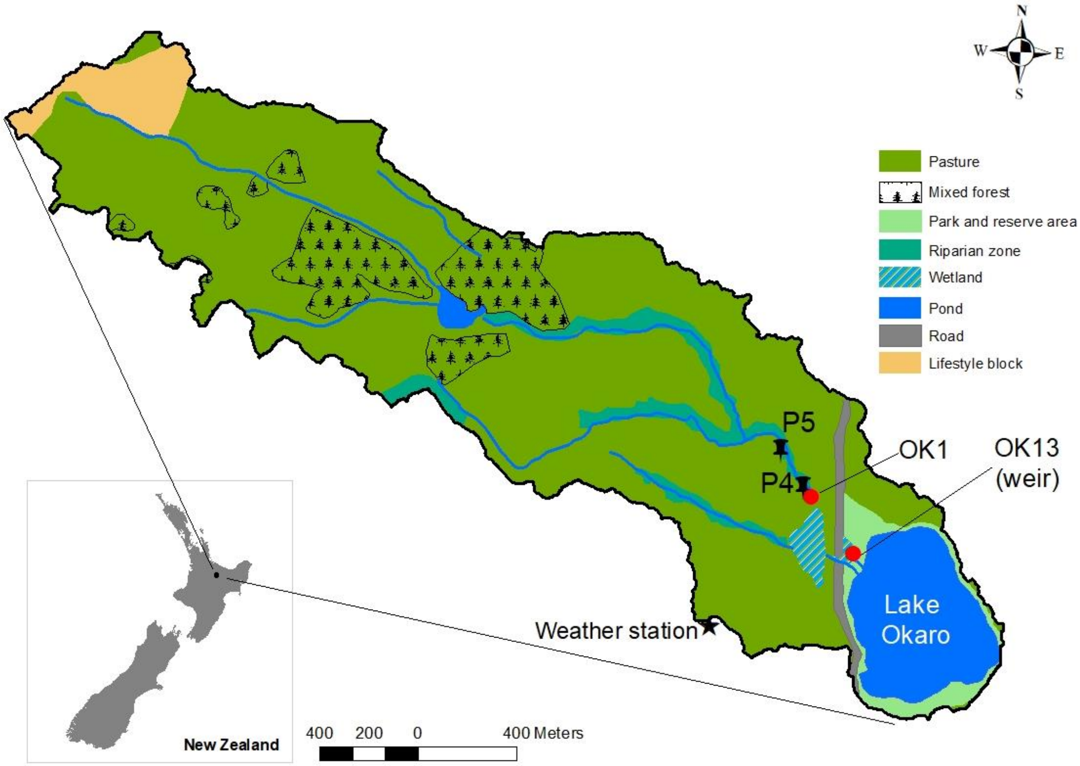

Figure 4.1 Location of the studied catchment in in the North Island's central plateau, New Zealand.

4.2.2 Hydroclimatic conditions and catchment monitoring

Hydrological and physico-chemical monitoring occurred between July 2019 and December 2020. Data of rainfall and soil moisture was downloaded from the Bay of Plenty Regional Council (BoPRC) environmental data portal (https://envdata.boprc.govt.nz/Data). Air temperature data was obtained through the NIWA climate database (cliflo.niwa.co.nz), extracted from the Virtual Climate Station Network (VCSN) based on the spatial interpolation of actual data observations at climate stations located around New Zealand.

Continuous data logging (15 minutes intervals) of conductivity, water level, and the water temperature was carried out using a digital Mayfly data logger station developed by Stroud Water Research Center (Hicks et al., 2015; Hund et al., 2016). Turbidity, dissolved oxygen (DO), and pH were measured using a Yosemitech Y4000 Sonde. During three winter event-based samplings, an ISE nitrate probe (YSI ProDSS multiparameter, Figure B.3) was deployed to provide consecutive observations of nitrate concentration with a logging frequency of 15 minutes. Technical errors in water level measurement occurred at the major stream (OK1) during a significant part of the study, so streamflow was estimated using water level observations at the wetland outlet (OK13). Water level readings were converted using the rating curve developed from historical data of the Lake Ōkaro catchment (Hudson & Nagels, 2011) provided by BOPRC.

To analyse event behaviour, it was necessary to specify the start and end of each rainfall-runoff event. In this study, rainfall events were defined as more than six mm of rainfall separated by at least six hours without rain (e.q., Hopkins et al., 2020; Pavlin et al., 2021; Rose et al., 2018). Rainfall (amount, intensity, length) and flow (i.e., peak, elapsed time to peak) characteristics were defined for each event. In addition, the role of antecedent soil moisture conditions on runoff was assessed by computing the antecedent moisture index (ASI, Haga et al., 2005), with soil moisture being represented as the amount of the soil water stored in the top of 250 mm of the profile. The hydrological analysis focused on comparing hydrograph characteristics, quick–flow runoff, and runoff coefficients (ratio of runoff to rainfall on an event basis). The quick runoff component of the storm hydrograph was computed using the 'baseflowseparation' function in the R statistical package 'EcoHydRology' (Fuka et al., 2018); this function implements a one-parameter recursive digital filter to separate the streamflow into baseflow and quick flow (see Lyne & Hollick, 1979; Nathan & McMahon, 1990;).

4.2.3 Water sampling and analysis

In this study, samplings were undertaken on a day without rainfall (for baseflow) and during a rain event (stormflow). Baseflow water samples were collected from stream water (OK1) and from two temporary in-stream piezometers in shallow groundwater (P4 and P5; see Figure 4.1). Site P4 was located on a riparian zone adjacent to OK1, whereas P5 was installed on a sloped area ~15 m from the main stream. Event-based samples were collected with an autosampler (Manning model VST, Manning Environmental Inc., USA) installed at the OK1 site. The autosampler was set up with intervals of 1 to 1.5 h to cover the hydrograph's rising and falling limb. Water from the autosampler was collected during seven rain events: 4 July (R1), 17 December (R2) 2019, 3 (R3), 5 July (R4), 8 August (R5), 18 August (R6), and 24 November (R7) 2020.

Additional discrete samples were collected once in pre– and post–rain event periods. Prior to sampling, new collection containers were rinsed using *in situ* water. The autosampler sample bottles and hoses were acid-washed in 10% nitric acid and rinsed with analytical grade deionized water before use. Upon retrieval, baseflow and stormflow water samples were filtered through a 0.45 µm cellulose–acetate membrane filter to analyze dissolved inorganic nitrogen (DIN) and isotopes. Unfiltered samples were also taken for total nitrogen (TN) and total suspended sediment (TSS). Water samples were kept on ice, transported to the laboratory quickly after sampling, and stored at 4°C until further analysis could be conducted. Samples were analysed for nitrite–N (NO_2^-–N), nitrate–N (NO_3^-–N), Total Kjeldahl Nitrogen (TKN), and ammoniacal nitrogen (NH_4^+) based on an automated cadmium reduction method

(APHA 4500). Total nitrogen was then calculated as the sum of TKN, NO_2^-–N, and NO_3^-–N, while N_{org} was determined as TKN minus NH_4^+.

Flow–weighted mean concentrations (FWMC, Equation 4.1) in mg L^{-1} were used to quantify the weighted concentration proportional to corresponding flow for both baseflow and stormflow (Jani et al., 2020; Zhu et al., 2011)

$$FWMC = \frac{\sum_1^n (C_i \ x \ Q_i)}{\sum_1^n Q_i} \qquad \text{(Eq. 4.1)}$$

where *c* is the concentration and *Q* is discharge in the *i*th sample. Further, the event–based load was determined by multiplying FWMC with the corresponding discharge during the stormflow period (Mihiranga et al., 2021; Ruzycki et al., 2014).

4.2.4 Isotopic analysis

Water samples were analysed for stable isotopes of water: oxygen ($\delta^{18}O$–H_2O) and hydrogen (δ^2H–H_2O). The isotopic compositions of water samples in 2 mL glass vials were measured with a Los Gatos Research (LGR) TIWA laser spectrometer. The isotope ratios are reported in per mil (‰) relative to VSMOW–SLAP for two internal working standards (AURORA2: δ^2H = +1.63‰, $\delta^{18}O$ = –0.8‰ and ANT01: δ^2H = +1.63‰, $\delta^{18}O$ = –0.8‰) that had been previously calibrated using VSMOW2 ($\delta^{18}O$ = 0‰ and δ^2H = 0‰) and GRESP (δ^2H = –257.8 ‰, $\delta^{18}O$ = –33.39 ‰) international reference standards. To minimise memory effects, isotopic values were determined by averaging isotopic values from the last four out of seven injections. A detailed description of the analysis technique is given by Wassenaar et al. (2008). The analytical uncertainty for results based on an IAEA Water Stable Isotope Intercomparison (Wassenaar et al., 2021) test was ~0.2‰ and ~0.09‰ for δ^2H, and $\delta^{18}O$, respectively.

An orthogonal regression analysis was used to develop the Local Meteoric Water Lines (LMWLs, IAEA, 1992) that were then compared to the Global Meteoric Water Lines (GMWLs, Craig, 1961) in a conventional δ^2H versus $\delta^{18}O$ diagram. Isotopic hydrograph separation (IHS) was used to quantify each pre-event and event water contribution (Sklash & Farvolden, 1979). The two-component model of hydrograph separation follows the equation:

$$Q_e = Q_s((\delta^{18}\, O_s - \delta^{18}\, O_{pe})/(\delta^{18}\, O_e - \delta^{18}\, O_{pe})) \qquad \text{(Eq. 4.2)}$$

where *c* describes the stable isotope composition of stormflow (stream water), baseflow (pre-event water), and rainfall (event water); these are indicated by subscripts *s*, *pe*, and *e*, respectively.

Stable isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O$) were analysed at the National Isotope Centre (GNS Science) using the cadmium-azide method described in Wells et al. (2015). All results are reported with respect to AIR for $\delta^{15}N$ and VSMOW for $\delta^{18}O$, normalized to the international standards; USGS 34 (-1.8‰ for $\delta^{15}N$ and -27.9‰ for $\delta^{18}O$), IAEA-NO3 (4.7‰ for $\delta^{15}N$ and 25.6‰ for $\delta^{18}O$) and to internal standard; KNO3b (10.7‰ for $\delta^{15}N$ and 11.7‰ for $\delta^{18}O$). The analytical precision for these measurements is 0.3‰ for $\delta^{15}N$ and $\delta^{18}O$.

4.2.5 Characterising nutrient export regime using c–Q relationship.

The relationship between concentration (c) and discharge (Q) was analyzed to describe nutrient transport dynamics in the catchment. All concentration and discharge data were log-transformed prior to regression analysis to assess the patterns of dilution, concentration increase, or chemostasis for nitrate. The export regime of nutrients was characterized and visualized using a combination of relatively simple metrics between the slope (β) of the log(c)–log(Q) relationship and coefficient of covariance (CV) for c and Q (Musolff et al., 2015; Thompson et al., 2011). The export regime is considered chemostatic for CV_C/CV_Q near zero and as chemodynamic for high CV_C/CV_Q (Musolff et al., 2015). The ratio of the coefficient of covariance (CV_c/CV_Q) for individual rainfall events (R1 – R7) was calculated as follows:

$$CV_c/CV_Q = (\mu_Q/\mu_c)\ x\ (\sigma_Q/\sigma_c) \qquad \text{(Eq. 4.3)}$$

where, μ represents the mean, and σ represents the standard deviation.

4.2.6 Statistical analyses

Correlation between rainfall characteristics (P_{amount}, P_{int}), soil moisture (ASI), a sum of P and ASI (denoted as catchment wetness), and flow generation parameters (quick flow and runoff coefficient) were examined using regression analysis. Piecewise linear regression was implemented using the 'segmented' package in R (Muggeo, 2017) to determine the presence of hydrological threshold behaviour. Beforehand, the assumption of heteroscedasticity and requirements on independency in the regression analysis were tested. The variability of nutrient concentrations among rain events and baseflow was visualised using boxplots. All statistical analyses were performed in R statistical software package, except if stated otherwise, and the statistically significant level for all tests was defined as $p < 0.05$.

4.3 Results

4.3.1 Hydrologic characteristics across rainfall events

The 1.5-year monitoring period from July 2019 to December 2020 in the Ōkaro catchment captured various hydrological conditions, including low and high flow periods (Figure 4.2). The observed daily average flow at the main stream (OK1) during the investigated period was 0.02 $m^3 s^{-1}$, while the historical average (2008 – 2010) was 0.03 $m^3 s^{-1}$ (Hudson & Nagels, 2011).

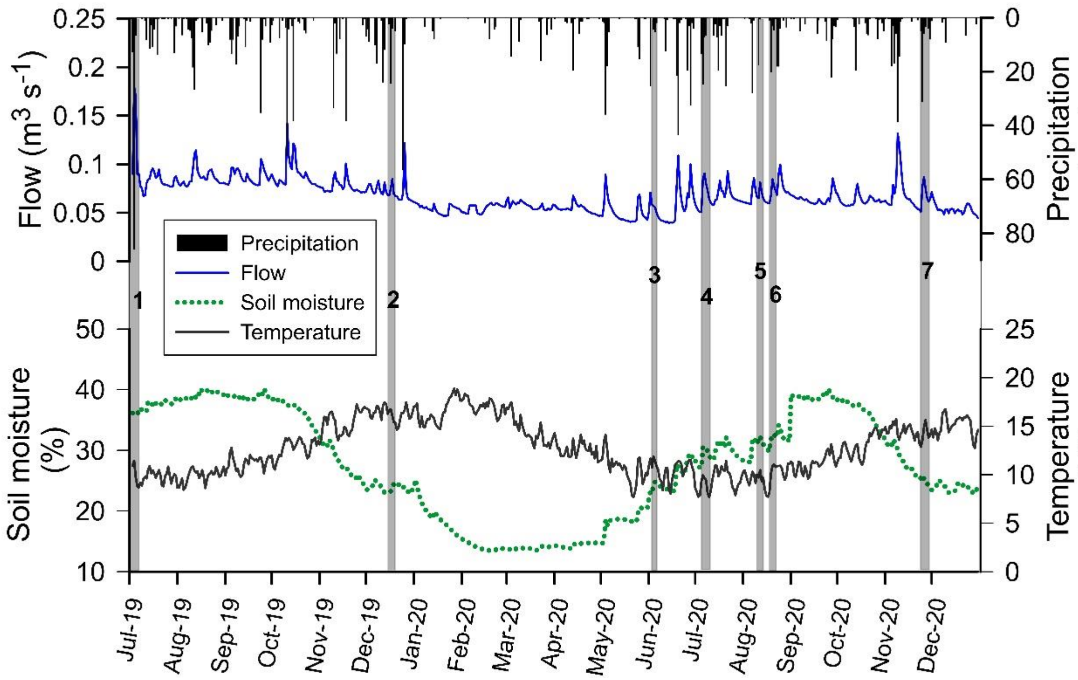

Figure 4.2 Daily rainfall, flow, soil moisture, and air temperature in the Ōkaro catchment between July 2019 and December 2020. The shaded areas indicate the event-based sampling examined in this chapter. The numbers in the figure identify the rain events referred to in Table 4.1.

Annual rainfall of 1196 mm and 986 mm were recorded in the Lake Ōkaro catchment for 2019 and 2020, respectively, lower than the average from 2007 – 2020 (see Figure 3.2). Hence, the study period is considered a drought with dry summers relative to the typical hydrology of this region. Interestingly, in the Lake Ōkaro catchment, the rainfall pattern is not always seasonal. Major rainfall events generally occur in winter (June to August) and autumn (March to May), but in 2019 – 2020, more intense spring rainfall was observed.

A total of 79 rainfall-runoff events were identified between July 2019 and December 2020. These events provide information on threshold hydrological responses to various rainfall events. Although rainfall amount (P) exhibited a statistically significant relationship with the resulting quick flow component ($R^2 = 0.62$, $p < 0.05$; Figure 3a), the data dispersion was high, so threshold hydrological response based on only rainfall amount could not be determined in the Ōkaro catchment. However, when antecedent moisture conditions (ASI) were considered (Figure 3.3b), rain event responses were distinguishable above a threshold of P+ASI (also denoted as catchment wetness). A piecewise regression analysis identified two regression lines on either side of a hydrological catchment wetness threshold of ~ 95 mm (standard error ± 2.30 mm). Above this threshold, a significant relationship in runoff behaviour was found ($R^2 = 0.73$, $p < 0.05$). Below the threshold, the observed hydrological response was more variable ($R^2 = 0.12$, $p < 0.05$). Other correlations between rainfall components were also considered; however, P showed a non–significant correlation with the runoff coefficient ($R^2 = 0.005$, $p > 0.05$) indicating that the same amount of rainfall could produce contrasting runoff coefficient responses. When P+ASI was compared with the runoff coefficient, the result was significant but with a low coefficient of determination value ($R^2 = 0.01$, $p < 0.05$) (Figure B.1).

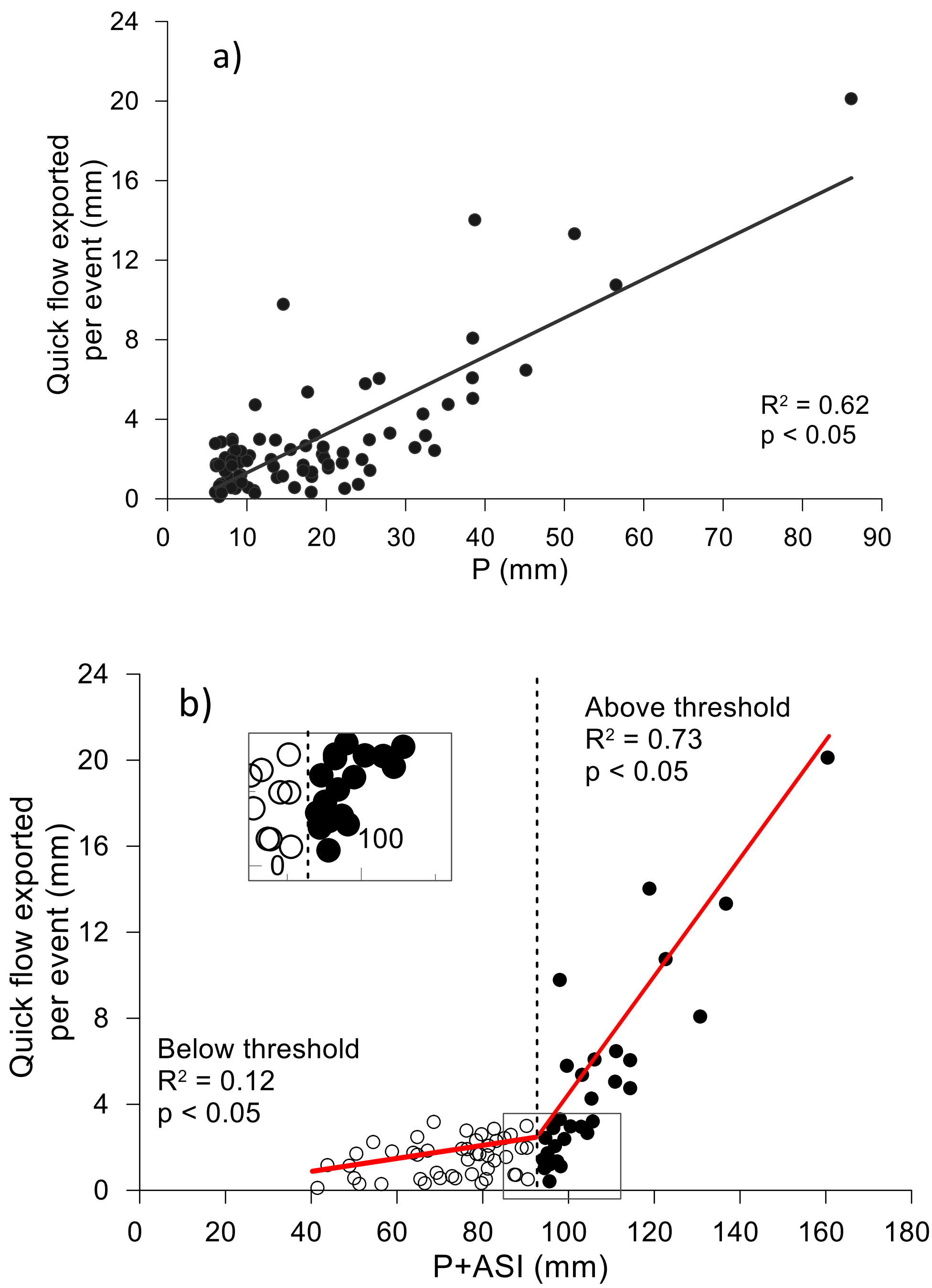

Figure 4.3 (a) Relationship between event–related quick flow and rainfall amount (P); (b) Quick flow for all identified events and the sum of rainfall amount and antecedent soil moisture index (P+ASI). Events occurring above the threshold (shaded circle) and lower threshold (open circle) are differentiated by red lines based on the best-fit lines for the piecewise linear model.

Among seven rainfall events sampled during the study period, three events (R1, R4, and R5) were identified above the wetness catchment threshold, while the other four events (R2, R3, R6, and R7) were below the threshold (Table 1).

Table 4.1 Characteristics of rain events. The runoff coefficient (RC, dimensionless) is defined as the ratio between the quick flow of a particular event and the amount of rainfall received.

Rain event (R)	Date	AMC (%)	P_{length} (h)	P_{amount} (mm)	P_{mean} (mm/h)	P+ ASI	Peak flow ($m^3 s^{-1}$)	Quick flow (mm)	RC
				Above threshold events					
R1	4–Jul–19	29.71	30.00	86.13	2.87	160.42	0.310	20.12	0.24
R4	5–Jul–20	27.06	18.60	38.41	2.06	106.07	0.192	6.08	0.16
R5	11–Aug–20*	32	9.55	18.17	1.90	98.17	0.178	1.72	0.10
				Below threshold events					
R2	17–Dec–19	26.30	27.50	24.50	0.89	90.26	0.085	2.26	0.10
R3	3–Jun–20	23.16	13.00	6.14	0.47	64.74	0.057	1.46	0.17
R6	18–Aug–20*	29.95	22.75	20.24	0.88	95.11	0.174	1.12	0.10
R7	24–Nov–20*	22.14	23.43	31.17	1.33	86.53	0.095	1.656	0.06

*) A complete set of samples was collected across the stormflow hydrograph

4.3.2 Comparison of water quality during stormflow and baseflow

Higher nutrient concentrations were observed in stormflow compared to baseflow (Figure 4.4). The concentration of total nitrogen (TN) in seven rainfall events ranged from 0.4 to 9.6 mg L^{-1}. Except for R4 and R5, nitrate–N was the predominant TN compound in stormflow (46.40 – 60.33%) and baseflow (50.20 – 70.50%). Nitrate–N concentrations displayed variations between events (0.21 – 1.54 mg L^{-1}) and under baseflow conditions (0.18 – 0.47 mg L^{-1}). Spikes of organic N (N_{org}) concentration were found at the end of the winter event (R6) and late spring event (R7), falling between 0.18 – 9.17 mg L^{-1} and 0.15 – 2.52 mg L^{-1}, respectively. Although there was a variation of ammonium concentrations between rain events and baseflow, the concentration of ammonium was consistently low over the study period, with the highest concentration measured being 0.15 mg L^{-1}. The mean concentration of ammonium was 0.04 mg L^{-1}.

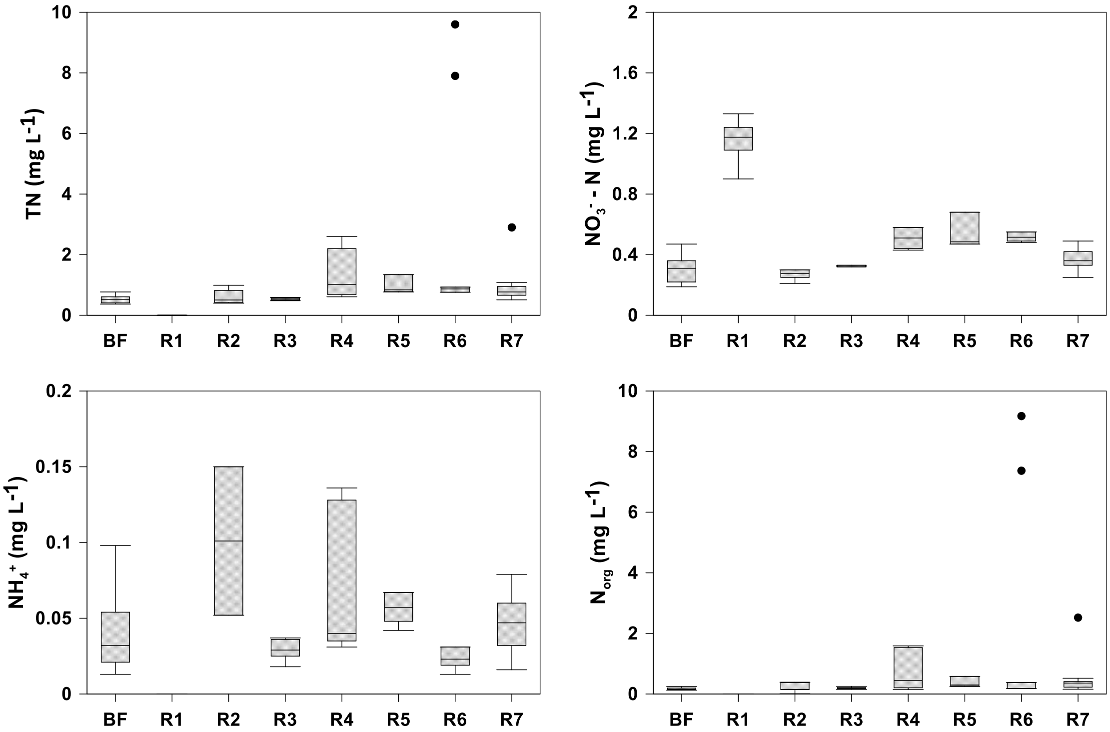

Figure 4.4 Boxplots showing the median (line inside box), 25th and 75th percentiles (box), and 5th/95th percentiles (whiskers) of water quality at OK1 over seven rainfall events sampled between July 2019 and December 2020. BF = baseflow and R=rain event conditions. Only nitrate–N (NO_3^-) data is available for the R1 event.

Nitrate load varied between rain events and was significantly related to the P+ASI values (R^2 = 0.88 and p < 0.05). High nitrate load ranging from 6.85 kg d^{-1} to 15.09 kg d^{-1} for R1, R4, R5, and R6 coincide with large winter rainfall events occurring when soils are at or near saturation. Lower loads ranging from 1.58 kg d^{-1} to 4.78 kg d^{-1} for R2, R3, and R7 occurred for other rain events.

4.3.3 Isotopic compositions of the Ōkaro stream in response to rainfall events

Figure 4.5 shows the temporal variation of water isotope values in rainfall and streamflow sampled during the study period at the Ōkaro catchment. The $\delta^{18}O$ values are similar because of the high correlation between δ^2H and $\delta^{18}O$ (Figure 4.6), so, for simplicity, this work presents δ^2H values for plots and discussion unless noted otherwise. Rainfall δ^2H values spanned –83.5 to –10.8‰, with the amount–weighted mean being –36.9 ‰ and d–excess ranging from 7.32 – 22.04‰ with an average of 12.48‰. A seasonal pattern of water isotopic composition in rainfall is evident from this data series. The lowest δ^2H values were observed in winter, and the highest in summer.

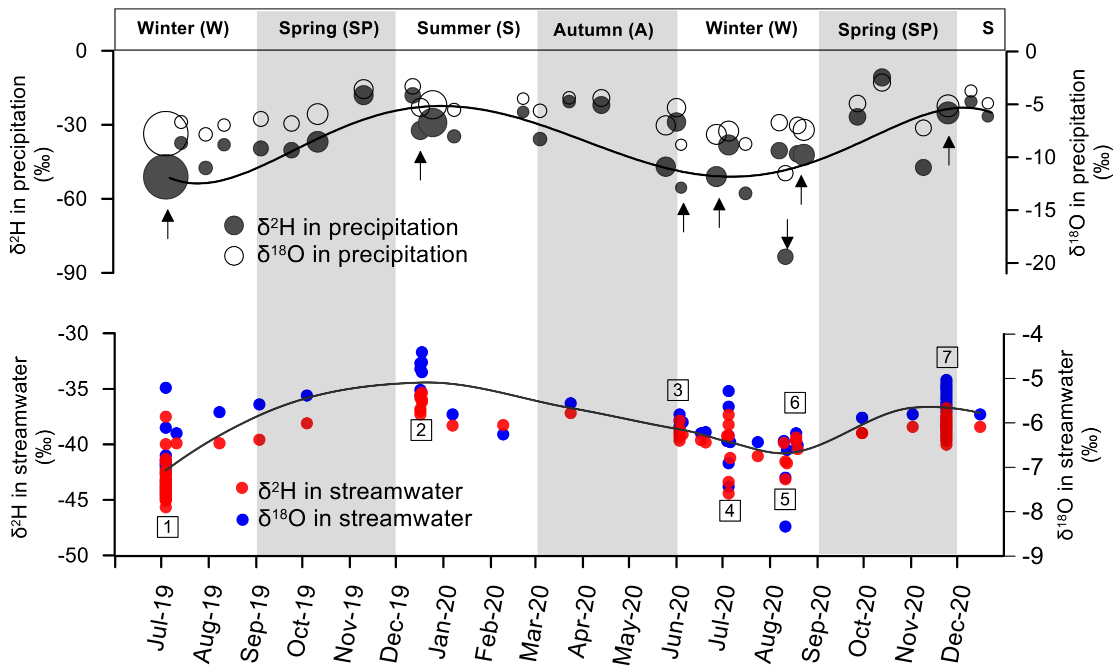

Figure 4.5 Temporal variations of water isotopes in rainfall and stream water. The number and the arrows indicated rain events discussed in this chapter. The bubble size at the bottom plot indicates the magnitude of rainfall amount with the absolute shown in Table 1. Locally estimated scatterplot smoothing (LOESS) for δ^2H data was applied to help visualise the temporal variation of water isotopes.

In contrast to wide variation in rainfall values, stream water δ^2H and $\delta^{18}O$ values were relatively stable over the monitoring period. Isotopes in stream water varied from –41.3 to –33.8‰ for δ^2H and –5.79 to –7.04 ‰ for $\delta^{18}O$. However, various rainfall events produced distinct isotopic responses in the corresponding streamflow hydrograph (Figure 4.5). The magnitude of rainfall and the corresponding isotopic responses in streamflow δ^2H varied considerably throughout the study period. For instance, event R1 generated the largest streamflow increase following 98.28 mm of rain but showed minimum isotopic variations (–44.9 to –41.0‰). Across event 3 (R3), with only 6.4 mm of rain, δ^2H values were in a narrow range between –38.8 and –37.3‰. Event 5 (R5, 17.65 mm rainfall) was characterised by a large change in δ^2H that varied between –50.7 to –40.0 ‰. Except for R5, the isotopic response of the pre-event streamflow δ^2H value to rainfall was always toward a more positive δ^2H. Consequently, the variation of isotopic composition of rainfall and stream water reflected the relative contributions of event water to stormflow (Table B.1).

The isotopic data points of rainfall tend to be scattered along the LMWL, indicating there are relatively large variations in δ^2H and $\delta^{18}O$ in rainwater (Figure 4.6). Figure 4.6 also demonstrates that stream water samples are scattered with respect to stable isotope ratios suggesting there are multiple water sources for the stream. The local stream water line (evaporation line) for the Ōkaro stream has a significant correlation (R^2 = 0.94), and its slope (5.07) is lower than that of the LMWL (7.72), indicating that water recharging the stream is subject to further evaporation after rainfall. This finding is consistent with the presence of detainments and small ponds in the catchment. The δ^2H values of shallow groundwater (piezometer) samples ranged from –41.3 to –33.8‰, showing there was a uniform and less varied isotopic signature in groundwater compared to the isotopic composition of stream water.

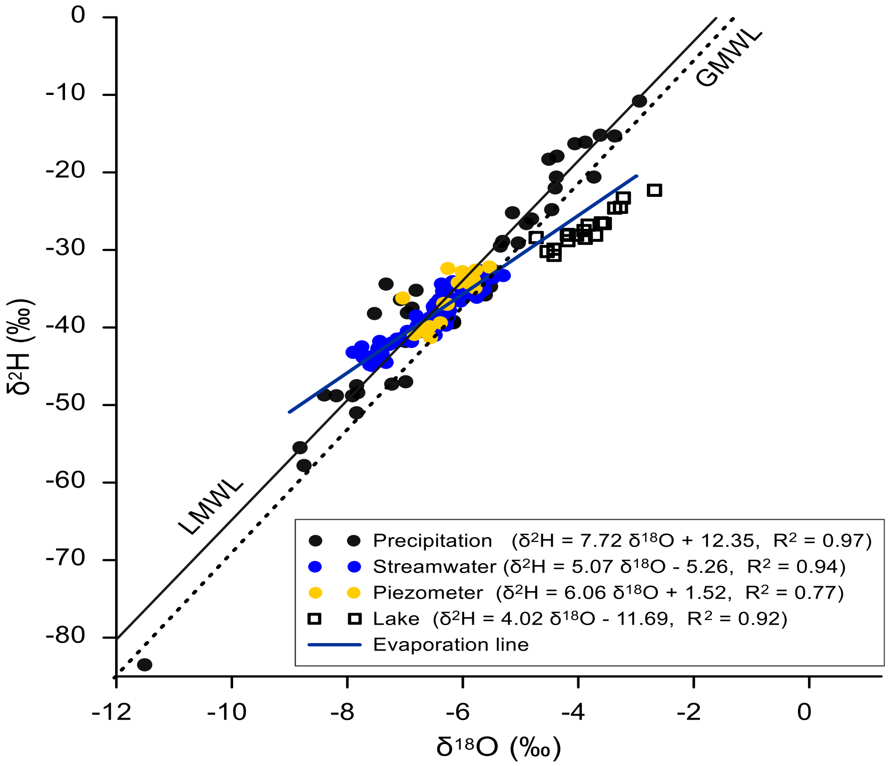

Figure 4.6 The stable isotope distribution of water for Lake Ōkaro and the Ōkaro catchment. Regression equations and symbols are color–coded by association with the source of water samples. GMWL, global meteoric water line, and LMWL, local meteoric water line.

Overall, the isotopic compositions of nitrate in stream water from event samples spanned between 3.1 – 8.67‰ for $\delta^{15}N$ and –6.07 – 3.86‰ for $\delta^{18}O$. Different primary sources of nitrate–N across rainfall events are highlighted in Figure 4.7. More enriched nitrate–N isotope values were typically observed during events below the threshold, and typical of soil N. In contrast, most nitrate isotope compositions above the threshold events were relatively depleted (≤ 4‰), indicating 'urine–urea' sources.

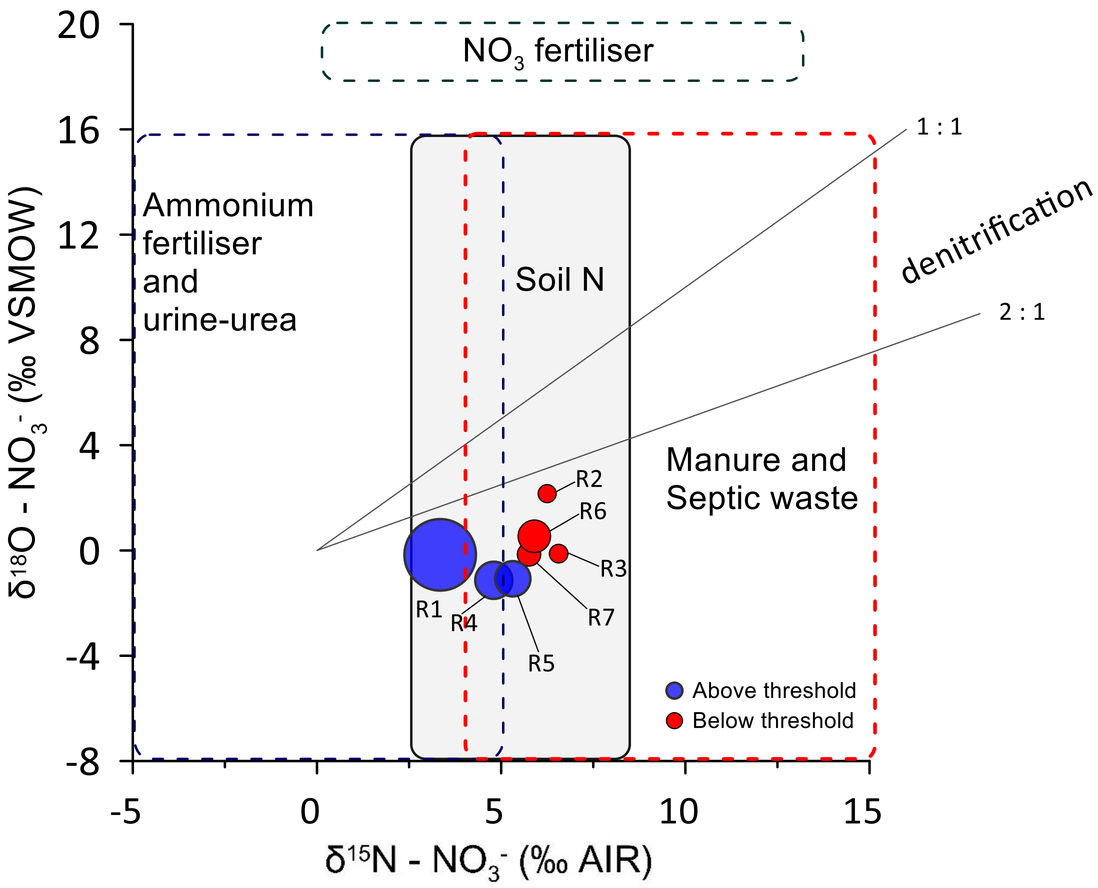

Figure 4.7 Nitrate isotopic composition of stream water during rain events with the background of potential nitrate sources (adapted from Xue et al., 2009; Nestler et al., 2011; Xu et al., 2016). Bubble size indicates the proportion of flow-weighted mean concentrations of nitrate–N for each rain event ranged from 1.58 – 15.09 mg L^{-1}.

4.3.4 Contrasting patterns in N transport revealed by c–Q relationship and high-frequency data

The patterns associated with nitrate–N concentration–discharge (c–Q) relationships differed between rain events, reflecting differences in the sourcing or internal processing of nitrate–N export to the stream (Figure 4.8). Chemodynamic export patterns are variable combinations of discharge generating zones with different solute source strengths, travel times, and reactivity along the flow paths within a catchment (Ebeling et al. 2021). These patterns with enhanced nitrate–N concentrations were observed during the above threshold events R1, R4, and R5. Dilution patterns were exhibited at the end of the winter season (R6), a less intense rain event (R3), and an event below the hydrological threshold (R7). The baseflow condition also demonstrated a dilution pattern, but the low β value signifies a slight variation of concentration change relative to discharge. Meanwhile, R2 showed a weak c–Q relationship close to the chemostatic line.

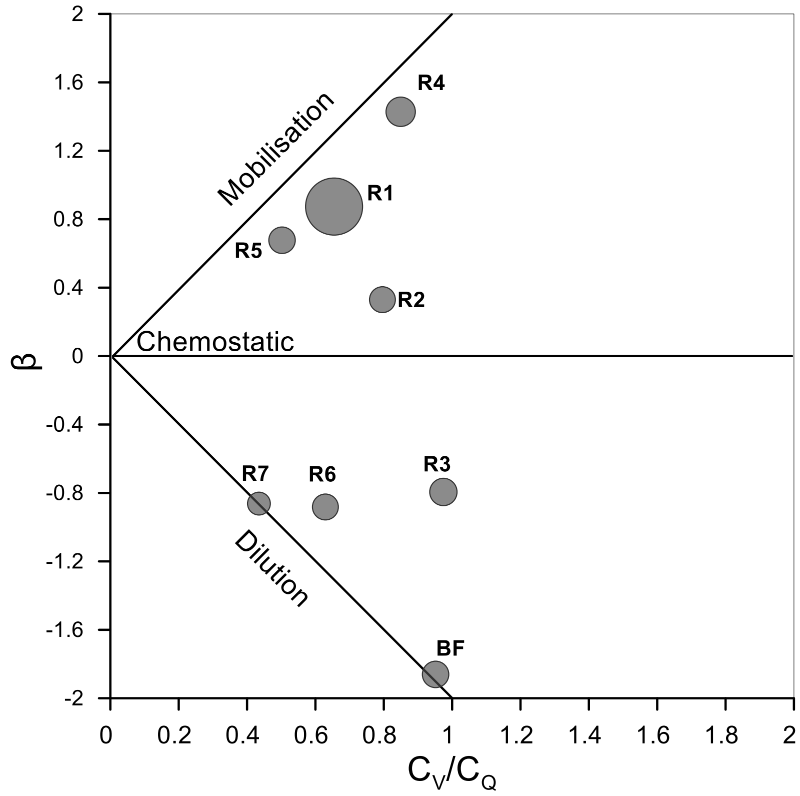

Figure 4.8 The plot shows slope β vs. coefficient of variance ($CV_c\ /CV_Q$) for nitrate–N for each of the seven samplings during rainfall events (labels 'R') and baseflow (BF) following the classification scheme provided in Musolff et al. (2015). The circle size indicates the magnitude of flow–weighted mean concentrations of nitrate–N for individual rain events and bulk baseflow.

Nitrate transport during three of the four winter season events registered clockwise hysteretic loops with differing slope values (Figure B.2). These three events

(R1, R4, and R5) are rain events above the catchment wetness threshold. The clockwise hysteresis pattern occurred when greater nitrate–N concentrations were observed on the hydrograph's falling limb compared to the hydrograph's rising limb. Events beginning the winter season (R1 and R4) have wider loops due to distinctive variability in nitrate–N concentrations.

Interestingly, there were differences in runoff mechanisms contributing to the N transport in the Ōkaro catchment subject to rainfall events, as illustrated in hydrographs and chemographs (Figure 4.8). Two contrasting events provide a representative example: R4 (above the threshold) and R7 (below the threshold) had relatively similar rainfall amounts, yet R7 had a longer duration and lower intensity (Table 4.1).

The hydrographs of R4 and R7 events showed different responses during the rising limbs of the hydrograph but relatively similar patterns on recession limbs after the end of rainfall. The peak flow of R7 was delayed compared to R4 (Table 4.1 and Figure 8). Isotopic two–component hydrograph separation (IHS) analysis indicates increased event water contributions to streamflow with higher event size and wet antecedent hydrological conditions. The R4 hydrograph showed that surface runoff (event water) contributions began about 03:00 AM on 6 July 2020, about 14 hours after the rain started. Whereas the contribution of event flow in stream water was limited during the rising limb of the hydrograph in R7, higher event water contribution occurred during the recession limb of the hydrograph. The IHS results also showed about 38% and 17% of the total stream flow was associated with the event water at R4 and R7, respectively (Table B.1).

The concentration of N species changed noticeably and R4 and R7 showed contrasting patterns. In R4, the peak concentrations of TN (2.6 mg L^{-1}) and nitrate–N (0.93 mg L^{-1}) occurred during the rising limb of the hydrograph. During R7, the highest concentration of TN (2.9 mg L^{-1}) was reached during the recession period, with the peak of N_{org} (2.5 mg L^{-1}) following the peaks in storm flow. Compared with R4, nitrate–N concentrations in R7 exhibited less variation, ranging between 0.3 and 0.49 mg L^{-1}. The nitrate–N concentration accounted for 46% of TN in R4 and 38% in R7.

An apparent pattern occurred during events above the hydrological threshold, where isotopic compositions of nitrate decreased as flow increased (Figure 4.9a). Moreover, it was observed that the highest proportion of nitrate load (~ 89%) derived from urine–urea sources in R4 coincided with the peak flow. During R7, the relative contribution of soil N mineralisation to nitrate load was dominant (~ 92%) and constant during the event ($\delta^{15}N$ values of nitrate–N around 6 to 7‰; Figure 4.9b).

Electrical conductivity responded rapidly to rainfall intensity during the events, and the responses varied with hydrological conditions (ranging between 59 and 104.7 µS cm^{-1}). The event above the threshold level had a quick recession of EC, which suggests that the stormflow contained a large proportion of ‘new’ water and that the EC recovered to its pre-event level after the rainfall peak. In contrast, the event below the threshold level showed a major increase of stream water EC at the beginning of the event as a response to rainfall, with values ranging between 84.8 and 104.7 µS cm^{-1}.

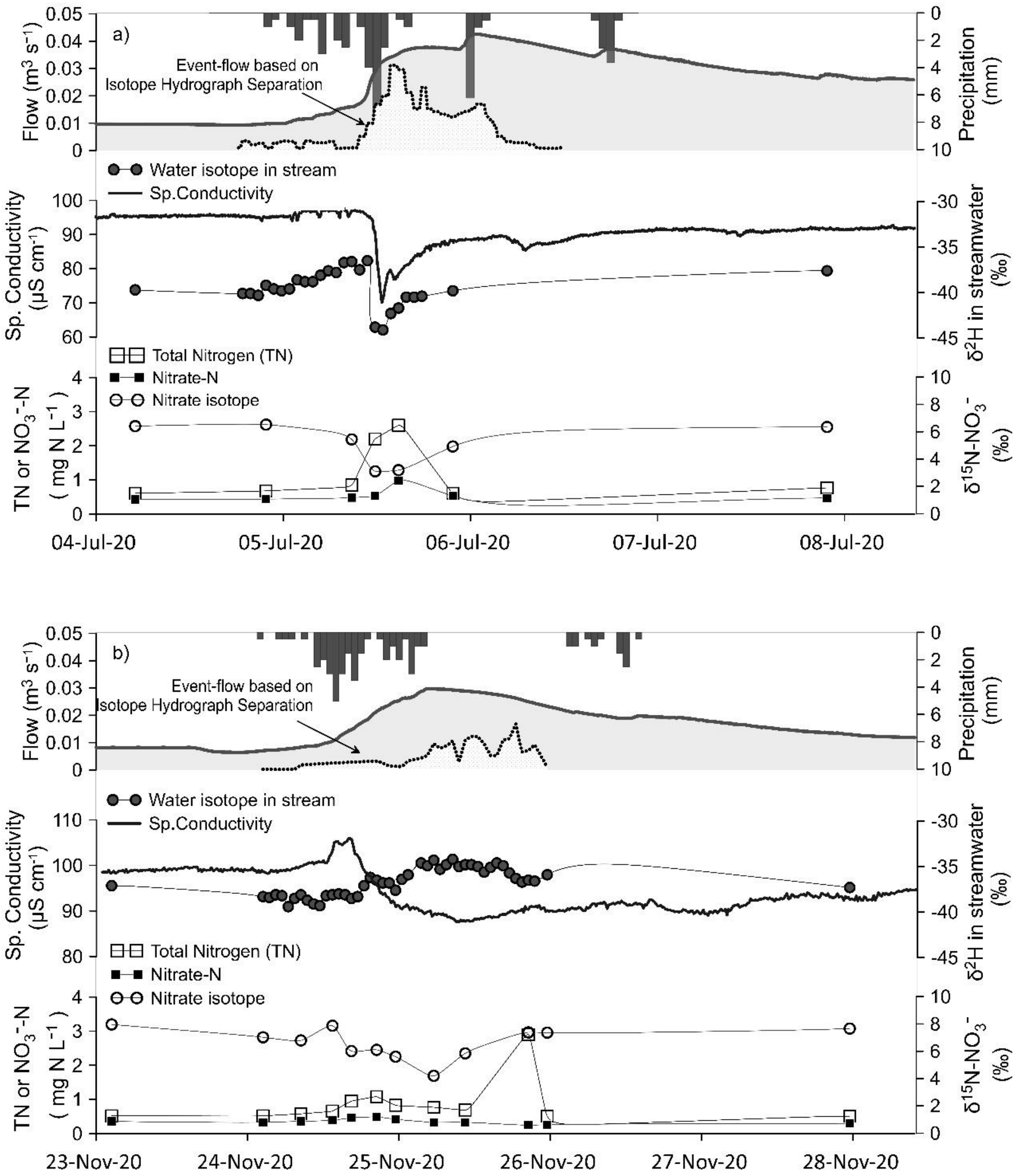

Figure 4.9 Temporal dynamics of water quality, flow, and isotopic composition in selected rainfall-runoff events. (a) is an event above the threshold (R4, 5 July 2020), and (b) is an event below the threshold (R5, 24 November 2020).

4.4 Discussion

Estimating the sources of nitrogen loading from agricultural catchments to surface water bodies is crucial for creating management strategies that combat the effects of eutrophication. In this study, I sought to identify the threshold behaviour of N loading as a response to rainfall in a pastoral catchment by using analysis of stable isotope ratios in water combined with in-stream high-frequency physicochemical data. The results show that antecedent catchment wetness above a threshold of ~95 mm led to nitrogen mobilisation from overland flow, dominated by nitrate–N and characterized by dual-isotope nitrate–N isotope values consistent with a urine–urea nitrogen source ($\delta^{15}N \leq 4‰$). In contrast, events below the threshold led to pronounced organic N release from subsurface runoff. These findings indicated that nitrogen runoff mitigation strategies in agricultural catchments could be targeted toward hydrological thresholds to different flow path contributing to total runoff.

4.4.1 Variation of nutrient dynamics under the hydrological threshold

Quick flow displayed a consistent threshold response to a combination of rainfall amount and antecedent soil moisture indices (P+ASI), observable using water and nitrate isotopes, concentrations of N species, and ancillary data such as EC. In the Lake Ōkaro catchment, catchment wetness (P + ASI) of ~95 mm represents a threshold for a hydrologic response, which increases with an increase in antecedent hydrologic conditions in the catchment. A weaker hydrologic response below this threshold is typical (Detty & Mcguire, 2010) and is demonstrated by a less significant relationship between P+ASI and quick flow in this study. This result demonstrates the importance of linking a catchment wetness 'threshold' to runoff generation mechanisms.

The findings regarding strong correlation between nitrate load and catchment wetness conditions suggests that rainfall events and antecedent soil moisture conditions are major drivers of nitrate transport in the Lake Ōkaro catchment. The N concentration patterns during rainfall provide further insights into the processes driving N transport; the increased nitrate concentration during rainfall events was associated with increased catchment wetness from early winter to the end of spring when high rainfall and high flow conditions coincided. Higher nitrate losses during early winter with more intense rainfall can be explained by heavy rainfall that can penetrate the subsoil via macropores and saturate the deep soil over impermeable soil layers thus generating immediate subsurface lateral flow during and after rainfall (Tarboton, 2003; Zhang et al., 2011). Therefore, high nitrate leaching was likely triggered by a hydrological event indicating this period as a hot moment, which can be described as a short time that shows high reaction rates compared to more extended intervening of excess N in the pastoral Lake Ōkaro system.

The finding that rainfall characteristics (i.e., depth or amount) and antecedent soil moisture conditions influenced runoff generation and hydrochemical export is consistent with other studies on agricultural catchments (Blaen et al., 2017; Cain et al., 2022; Knapp et al., 2020; Pavlin et al., 2021). However, nutrient export is not expected to act in concert with stormflow, and the transport of these materials may vary across and between events (e.g., Soulsby et al., 2003). Other authors have identified a complex array of processes that contribute to nutrient mobilisation and delivery during rainfall events, including different associated sources, dominant transmission pathways, rainfall–related characteristics (Mihiranga et al., 2021), and non–linear relationships between nutrient sources and hydrologic pathways (Macrae et al., 2010). These factors may be partially relevant in the Lake Ōkaro catchment consider that the sources and dominant mechanisms of nitrate export response may vary with catchment wetness at temporal timescale because of different factors.

The study has enhanced the understanding of catchment wetness conditions; a combination of rainfall and antecedent soil moisture factors can determine the differences in nutrient transport between events. The disparate responses to rainfall drove variation in–stream water quality, notably represented by nitrate, and exhibited seasonal patterns consistent with pastoral farming activities and hydrological mixing across the year. Generally, catchment wet conditions and high rainfall resulted in more sensitive and rapid catchment responses to rainfall-runoff events. The different transport mechanisms described in this study reflect distinct effects of rainfall in terms of sources and flow paths of nitrate in the Ōkaro catchment: (i) a first-flush effect contributed contaminants from the surroundings, thereby increasing the N concentration at the beginning of hydrograph; and (ii) dilution effect, diluting contaminants and decreasing concentrations at the end of the hydrograph.

The stormflow hydrograph of R4, the event that exceeded the P+ASI threshold, implies surface runoff by showing a rapid runoff without a significant delayed hydrochemical response. Nutrient concentrations increased and peaked simultaneously with the peak flow, indicate that the flushing of N-rich near-surface sources (i.e., ruminant urine-N) activated during periods of high saturation in the catchment. Further, the nitrate dynamics during this event can be interpreted as being controlled by mobilisation processes (see Figure 4.8).

The first-flush effect during R4 event expected to occur when soil nitrate concentrations are high prior to a rainfall event. Due to accumulated nitrate during low soil moisture and after N fertilisation, nitrate becomes mobilised and leached by water to the stream

(Di & Cameron, 2002; Sigler et al., 2020). Thus, the accumulation of nitrate corresponding to fertiliser and urine/dung from livestock in soil profile has been identified as a major concern in pastoral systems (Buckthought et al., 2015; Clark et al., 2010; Monaghan et al., 2016; Wells et al., 2015).

The R7 event was below the threshold and displayed differently in runoff generation and nutrient dynamics. The nitrate concentrations slightly increased during the rising limb of the hydrograph and reflected the dilution trend on nitrate delivery. The dilution pattern in response to rainfall events is likely to result from a change in the source of N over time, and a higher contribution of event water only occurred after the event (Darwiche–Criado et al., 2015; Schwientek et al., 2013).

The different responses of exported N during contrasting events in this study are consistent with other studies in agricultural catchments (e.g., Bauwe et al., 2015; Jiang et al., 2010). These results also align with grassland agricultural studies (Huebsch et al., 2014), suggesting that wet conditions are crucial to determining whether mobilisation or dilution processes predominate in rainfall events. However, the results in this study, which observed that more nitrate was mobilised during light rainfall, differ from published studies in catchments dominated by natural vegetation (Yue et al., 2019) and fertilised agricultural fields (Welsh et al., 2019).

Overall, these findings suggest that event–scale load estimates are essential in controlling nutrient delivery within the catchment. The event–scale analysis describes nitrate transport processes with detail not available in monthly or annual data. This allows for a better understanding of total loads entering receiving environments. Detailed analysis of event nitrate–N export showed that this pastoral catchment displays temporal variation in nitrate–N load, depending on rainfall characteristics. The differences in c–Q behaviour between stormflow and baseflow and among rain events suggest that catchment systems respond dynamically but predictably, shifting between nitrate–N export patterns in response to hydrologic forcing. This interpretation is broadly consistent with previous studies that have demonstrated that rainfall periods have a critical role in understanding freshwater quality and quantity drivers and their potential impact on ecosystems (Blaen et al., 2017; Heathwaite & Bieroza, 2021; Inserillo et al., 2017).

4.4.2 Identifying nitrate sources and flow paths using stable isotopes

Temporal variations of water isotope compositions between different components (Figure 4.5) satisfied the assumptions (Sklash & Farvolden, 1979; Turner et al., 1992) of isotope hydrograph separation (IHS), thus allowing its application in the Ōkaro catchment. Two–component isotope hydrograph separation quantifies stream water source components. It allows differentiation of the relative contributions of rainfall (event) from water that has been stored in the catchment (pre-event) to the stormflow hydrograph.

Identifying the water source contributing to nutrient transport during rain events through stable isotopes was beneficial in this study. The isotopic data collected over the study period provides complementary information about the temporal variability of water sources and runoff generation mechanisms (Klaus & McDonnell, 2013; Ocampo et al., 2006; Weiler et al., 2003) and therefore provides a tool to elucidate the contribution of soil water to streamflow under different catchment wetness conditions. Moreover, the variation of isotopic composition in stream water and rainfall over the study period highlights the temporal dynamics of rainfall water across hydrological events, reflects water supply relationship and suggests different sources present in stream water (Figure 4.5 and 4.6). Wallace et al. (2021) similarly found that isotopic analysis is valuable in quantifying water sources and that the contribution of pre-event/event water during a storm is a function of temporal variation in flow pathways between the channel and the potential sources.

Stream water isotope responses varied noticeably over the study, with event water contributions ranging between 14 – 45% of total flow during the event (Table B.1). The IHS results presented in this study (Figure 4.9 and Table B.1) suggest that the stormflow hydrograph was dominated by pre-event water. Given this, I assume the subsurface flow (i.e., baseflow) is essential in the Ōkaro catchment; however, the saturation excess is also expected to generate a quick flow of event water when the catchment wetness exceeds the threshold of ~ 95 mm. Above this threshold, rain events produced a higher proportion of event water released through overland flow, whereas below threshold events produced limited runoff and were characterised by the shallow subsurface flow. This difference was related to the combined effect antecedent conditions and rainfall amount, described by the catchment wetness threshold. This result also accords with earlier observations (Saffarpour et al., 2016), which showed that stormflow runoff is a combination of subsurface flow and saturation excess overland flow.

The dual isotopes plot of nitrate stable isotope signatures ($^{18}O–NO_3^-$ and $^{15}N–NO_3^-$) supports the finding that variations in rainfall event character contribute to the mobilisation of different sources of nitrate in stream water. The isotopically depleted $\delta^{15}N–NO_3^-$ values during rainfall above the threshold identified in this study were consistent with a range previously reported for urine and urea fertiliser (Loo et al., 2017; Wells et al., 2015). On a seasonal timescale, we observed a hot moment of nitrate excess transport released from urine/urea fertiliser concurrent with the early winter period, likely due to autumn urine deposition (Buckthought et al., 2015). Differences in nitrate signatures across rainfall indicate that rainfall amount drives nitrate release from urine and urea fertiliser sources. These release events appear to be preferentially mobilised above the threshold (~0 ‰) over background nitrate representative of mineralising soil organic matter (~6 ‰). Furthermore, the different sources of nitrate and flow path distributions in the Lake Ōkaro catchment could be critical factors in determining the nitrate load in stream water during rainfall–runoff events. Ultimately, specific nitrate mobilisation processes linked to urine or urea isotope signatures appear to amplify the role of event water so that nitrate mobilisation can dominate loads during events. They could potentially be more significant during wetter periods than in the drier 2019 and 2020; therefore, more events would cross the observed threshold toward nitrate mobilisation.

4.4.3 Implication for nutrient mitigation strategies

The results for the Lake Ōkaro catchment show that identifying the catchment wetness threshold can determine the response of the storm hydrograph and nitrate export to rainfall events under various hydrological conditions and understanding the response can assist in developing mitigation strategies on a catchment scale.

This study resolved two main types of N dynamics using a combination of stable isotope tracers and hysteresis patterns from the c–Q relationship. Understanding the nature of nutrient export, especially during high flow, has implications for managing agricultural landscapes effectively. The peaks of N load were observed and linked to sources only by intensive sampling, implying that high–resolution monitoring is essential for a reasonable estimation of nutrient load, assessing rainfall effects on water quality, and identifying sources to be mitigated. These results have demonstrated the need for representative, high-frequency hydrometric, and chemical data collection to understand how shifting storm behaviour can alter solute transport in these sensitive ecosystems.

The results of the present study also suggest that the antecedent soil moisture state is one of the dominant controls on event runoff generation on the catchment scale examined in this paper. These findings must be considered in the context that our high–temporal resolution of sampling was carried out during comparatively dry years. From a management perspective, monitoring soil moisture continuously provides a valuable predictive understanding of flow processes and runoff generation on the catchment scale (Blume et al., 2007) and reducing nutrient losses under specific hydrological conditions (Drewry et al., 2019). Further, recognising that antecedent soil moisture exerts a critical control on nutrient export may allow improved interpretation of results collected during relatively dry or wet periods to provide representative estimates of long–term average nutrient yields.

These study results have implications for planning water management measures to reduce nitrate loads in agricultural catchments. Measures such as controlled flow could be designed to handle significant flow events (above threshold) associated with high nitrate–N concentrations. The active management of land should preferably be conducted in the winter after heavy rainfall and when soil moisture conditions are wet (above threshold). Moreover, implementing N–based Best Management Practices (BMPs) can limit options regarding acceptable risks associated with rainfall characteristics and soil moisture stage, especially when the N composition changes with discharge and different patterns exist under variable flow conditions. Best management practices aimed at controlling non–point source pollution from agricultural catchments should be selective and effective in controlling overland flow, nutrient leaching, and subsurface lateral flow. This strategy may be essential in areas where heavy rain intersects with highly permeable or relatively impermeable soils. Identifying appropriate and effective mitigation measures is crucial to enhancing N use efficiency and minimizing N losses to receiving water (EUROPE, 2020). For instance, adopting improved timing of grazing associated with N–leaching (Rayner et al., 2020) and modification of N content in animal feed (Giltrap et al., 2021) are potential strategies for reducing N excess in pasture grazing systems and reducing the nitrate load observed in this study.

4.5 Conclusions

The study catchment provided a unique feature in that the sources and transport mechanisms of nutrients in the stream could be identified based on the threshold of hydrological response. Likewise, the stable isotopes and hydrochemical data provide supporting evidence to suggest a temporal variation in how and when N excess is exported in response to rainfall events. This study demonstrates that increased nutrient export is generally observed under wetter antecedent hydrologic conditions due to increased hydrologic response (i.e., quick flow volume and runoff coefficient) and increased nutrient concentrations, likely due to increased connectivity with the surface. However, this study demonstrates the complex catchment hydrologic and nutrient export responses to rain events and antecedent conditions. The study's findings emphasise the need for an improved understanding of the role of rainfall characteristics on temporal patterns of hydrochemical export in a pastoral setting.

This study contributes to ongoing efforts to manage nutrient inputs, control contamination in the eutrophic lake, and show the benefits of including isotopic sampling in the monitoring program. It highlights the benefits of increasing high–resolution event samplings to monthly monitoring, which can elucidate the complex relationship between rain events and catchment response and characterise N loads in regions where intense rainfall occurs on porous soils. Moreover, future studies into event–based transport and transformation of N species could further contribute to an understanding of hydrological variations and nitrogen cycling in this eutrophic lake catchment.

This study has implications for planning water quality management measures that reduce N losses from pastoral catchments. Suppose management practices can be implemented to reduce N excess associated with urine and urea N deposited on pasture. In that case, reductions in mobilisation and delivery could be reasonably expected to follow. It is possible that improved timing of grazing and optimised nitrogen intake through the animal feed can maintain production yet reduce N excess deposited as urine and therefore reduce N–leaching and loads in the catchment.

4.6 References

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Chapter Five

Simulating water balance and nutrient losses in a pastoral catchment using the SWAT+ model: added value of isotope data

5.1 Introduction

Increased eutrophication pressure on freshwater bodies (i.e., lake, river) has been long a global concern, with agricultural activities a leading source of impacts (Albert et al., 2021; Zhang et al., 2021). One of agriculture's most common sources of excessive nutrient loading is released from fertilised soils and livestock operations (Food and Agriculture Organization, 2018; Song et al., 2022). Thus, freshwater in countries with a significant share of area for pasture agriculture, such as New Zealand, are particularly vulnerable to the impacts of eutrophication. Elevated nitrogen (N) loads in rivers and lakes due to intensified agricultural practices has led to deteriorating water quality in New Zealand (Abell et al., 2013; Howard–Williams et al., 2010; Verburg et al., 2010). An estimated 46% of lakes larger than 1 ha in New Zealand are in poor or very poor ecological health, and agriculture land use is directly responsible for the nitrogen (N) leached into freshwaters (Ministry for the Environment & Stats NZ, 2022).

Improved pastoral management practices have been implemented to minimise the impact of excessive nutrient transport and enrichment in freshwater ecosystem (e.g., Hamilton et al., 2016; McKergow et al., 2016). However, there is still limited understanding of the quantitative effectiveness of these practices (Monaghan et al., 2021). Catchment model approaches can overcome this limitation by identifying of hot spots and hot moments (McClain et al., 2003) of excessive nutrients and guiding decisions to improve management strategies (Behera et al., 2006; Schilling et al., 2009; Teshager et al., 2017). A modelling approach is useful for comprehensively integrating the available data and knowledge of fundamental processes. Such an approach can also describe a system better than can be accomplished by using subjective human judgments (Cichota & Snow, 2009).

The Soil and Water Assessment Tool (SWAT), a process–based semi–distributed catchment model, has become one of the most widely used hydrologic models, applied to catchments worldwide and employed in thousands of peer–reviewed studies in the last decades (Akoko et al., 2021; Tan et al., 2019). SWAT can simulate hydrological characteristics and nutrient loadings pertaining to different land use scenarios at a catchment scale (Schilling et al., 2008; Rajib et al., 2016; Zhang et al., 2013), climate change (Fan & Shibata, 2015; Woznicki et al., 2011) and changes in agricultural management practices (Epelde et al., 2015). The versatility of SWAT makes it a widely used hydrology–related tool to assist decision making in catchment management strategies, and it has been extensively used for long–term simulation of streamflow and nutrient loading in agricultural catchments and for soil and water conservation (e.g., Gharibdousti et al., 2019; Himanshu et al., 2019). Nevertheless, examples from pastoral catchments in New Zealand is limited (Hoang, 2019; Me et al., 2018).

Despite the wide–ranging use of the SWAT model, the uncertainty associated with model parameters often limits the usability of the process–based models such as SWAT (Barnhart et al., 2018). In few studies, soft data calibration (qualitative knowledge from the experimentalist that cannot be used directly as exact value for model parameters) has been considered in order to verify the catchment model and can improve a model's performance (Parajka et al., 2007; Randall Etheridge et al., 2014). According to Arnold et al. (2015), soft data is information on a basic understanding of individual processes within the catchment, e.g., surface runoff and baseflow ratio, nutrient removed in yield, biogeochemical transformation in nitrogen balance (i.e., denitrification, nitrification, mineralisation).

Stable isotopes have been demonstrated to be helpful in identifying hydrological process information such as water sources, evaporation, and mixing processes (Yang et al., 2020). The hydrologic pathways and source components of stream water (i.e., precipitation, groundwater, surface water) associated with delivered soluble nutrients from the catchment can be identified by quantifying the water isotope ratios of $\delta^{2}H$–H_2O and $\delta^{18}O$–H_2O (i.e., Ohte et al., 2010; Hu et al., 2019). Similarly, nitrate isotopic signatures ($\delta^{15}N$–NO_3^- and $\delta^{18}O$–NO_3^-) have been extensively used to identify the source of the nitrates, and determine biogeochemical transformations in the nitrogen balance (Nestler et al., 2011; Xu et al., 2016; Xue et al., 2009).

This study examined the performance of SWAT in simulating hydrology and nutrient transport in a small agricultural catchment in North Island, New Zealand. The study evaluated the simulation of hydrology and nitrate–N dynamics and provided deeper insights into the model's performance by using isotope data. More specifically, the objectives of this study were to (1) calibrate and validate the SWAT+ model to simulate hydrological processes for an agricultural catchment, (2) investigate whether incorporating insight from isotope data into the SWAT model can improve the model's performance, and (3) test its applicability in predicting nitrate loading and simulating nutrient delivery processes. How the change in land use and fertiliser application affected nutrient loads were also examined.

5.2 Methods

5.2.1 Study site

The study site, the Lake Ōkaro catchment, is located in the Bay of Plenty region in the North Island, New Zealand, and drains into Lake Ōkaro. The catchment has an area of 3.98 km^2 and is predominantly pasture grazing land (dairy, deer, beef, and sheep). The climate in the study area is moderate, and the annual average precipitation is 1252 mm. The catchment has a minimum and a maximum altitude of 411 and 561 meters above mean sea level, respectively, with an average slope of 23%. Dominant soil types of the catchment, are Orthic Pumice and Tephric Recent Soils, based upon the New Zealand Soil Classification (Hewitt, 2010). The geology of the Lake Ōkaro catchment mainly consists of alluvium over a low permeability layer, so can be assumed that no significant groundwater inflows occur into the catchment (Gillon et al., 2009). In 2007, a wetland was constructed to reduce nutrient loads entering the lake (Environment Bay of Plenty, 2006; Hudson & Nagel, 2011). The Lake Ōkaro catchment has contributed significant nutrient inputs to Lake Ōkaro resulting in frequent algae blooms in spring and summer (Paul et al., 2008). Lake Ōkaro is the most eutrophic of the Rotorua Te Arawa Lakes (Özkundakci, 2011; Wood et al., 2009).

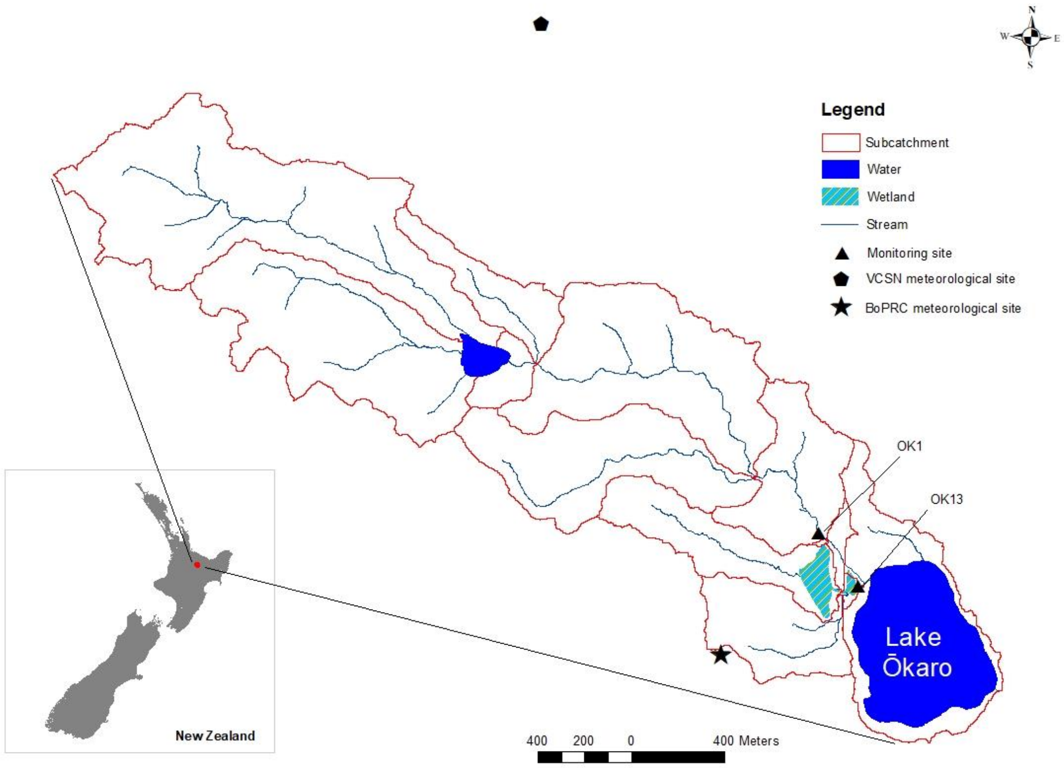

Figure 5.1 Location map of the Lake Ōkaro catchment

5.2.2 SWAT+ model description

SWAT+ (Arnold et al., 2018) is a reconstructed version of the SWAT model developed to be more flexible when configuring the model (Bieger et al., 2017). The primary contribution of SWAT+ is that spatial objects are constructed as independent modules (hydrologic response units [HRUs], aquifers, channels, ponds, reservoirs, point sources, and inlets) to ease model maintenance and development. In addition to modularisation, there are also other major improvements to the performance of the model, such as the creation of landscape unit units (LSUs). LSUs delineated based on channel threshold within the subbasin allow the separation of upland process from wetlands (Chawanda et al., 2020). More information about this model can be obtained from the literature (Neitsch et al., 2011; Bieger et al., 2017; Yen et al., 2019).

In the simulation processes, some of the critical parameters considered for the analysis of variation in the hydrological parameters are water yield, runoff, evapotranspiration and groundwater recharge. The SWAT+ model estimates catchment water yield (W_{yld}) based on the Equation 5.1 as follows.

$$W_{yld} = Q_{surf} + Q_{gw} + Q_{lat} - T_{loss} \quad \text{(Eq. 5.1)}$$

where, Q_{surf} is the surface runoff (mm), Q_{gw} is the groundwater contribution to the streamflow (mm), Q_{lat} is the lateral flow contribution to the stream (mm) and T_{loss} is the transmission loss. The model simulates surface runoff volumes and peak runoff rate for each HRU using daily rainfall or sub–daily rainfall amounts. Surface runoff is calculated using a modification of the Soil Conservation Service (USDA, 1972) curve number method, which is an empirical function of the soil's permeability, land use and antecedent soil water conditions.

The SWAT model simulates the nitrogen cycles in the soil profile and in the shallow aquifer (Neitsch et al., 2011). In soil and water, nitrogen is extremely reactive and exists in several dynamic forms. It may be added to the soil through fertiliser, manure or residue application, bacteriological fixing, and rain. It can be removed from the soil through plant uptake, soil erosion, leaching, volatilisation and denitrification. Denitrification is a function of water content, temperature, and the presence of carbon and nitrate. The SWAT+ model has five different pools of nitrogen in the soil. Two pools are inorganic forms of nitrogen (ammonium and nitrate), while the other three are organic forms of nitrogen (fresh organic N, stable organic N, and active organic N). Nutrient transformations in the stream used in the SWAT model are adapted from water quality algorithms used in the QUAL2E model (Brown & Barnwell, 1987) that contains the major interactive factors such as nutrient cycles, algae production, and benthic oxygen demand. Neitsch et al. (2011) comprehensively described the N component in the SWAT model.

5.3.2 Model input and configuration

5.2.3.1 Digital elevation model (DEM), land use, and soil data

The QGIS interface for SWAT+ version 2.2.3 and the SWAT+ Editor 2.1.2 was used to compile the SWAT+ input files. The first step in using this model is to divide a catchment into sub–catchments based on topography through the watershed delineation process. In this study, the SWAT+ model divided the Lake Ōkaro catchment into 12 subbasins (Figure 5.1). SWAT subsequently determined HRUs by overlapping slope, soil and land use maps in quantum GIS and integrating them into the modelling. Three slope classes (i.e., 0 – 15%, 15 – 30%, and >30%) were defined for the discretisation of a digital elevation model (DEM). DEM data (elevation range 144 – 559 m; 2 m x 2 m raster resolution) was obtained from the Bay of Plenty Regional Council (BoPRC), the regional environmental management agency. The land use data of 2007 were provided by BoPRC and combined with a visual interpretation from Google Earth. There were eight land use classes in this catchment (Figure. 2c): water (WETW), wetland (WETN), riparian zones (RNGB), pasture (PAST), forest (FRST), park and reserve area (MIGS), lifestyle block (URLD), and road (UTRN). For simplicity in the model simulation, pasture grazing land for different purposes (i.e., dairy, beef, dairy support, sheep) was classified as single land use, which is pastoral agriculture (PAST). A soil map with two classes and a database table of soil characteristics for different soil layers (e.g., soil hydrologic soil, bulk density) was obtained from S–map developed by Manaaki Whenua Landcare Research, available at (Manaaki Whenua Landcare Research, 2020) and combined with laboratory analyses results of soil sampled in the study area. This process resulted in 842 HRUs for the model setup in the Lake Ōkaro catchment.

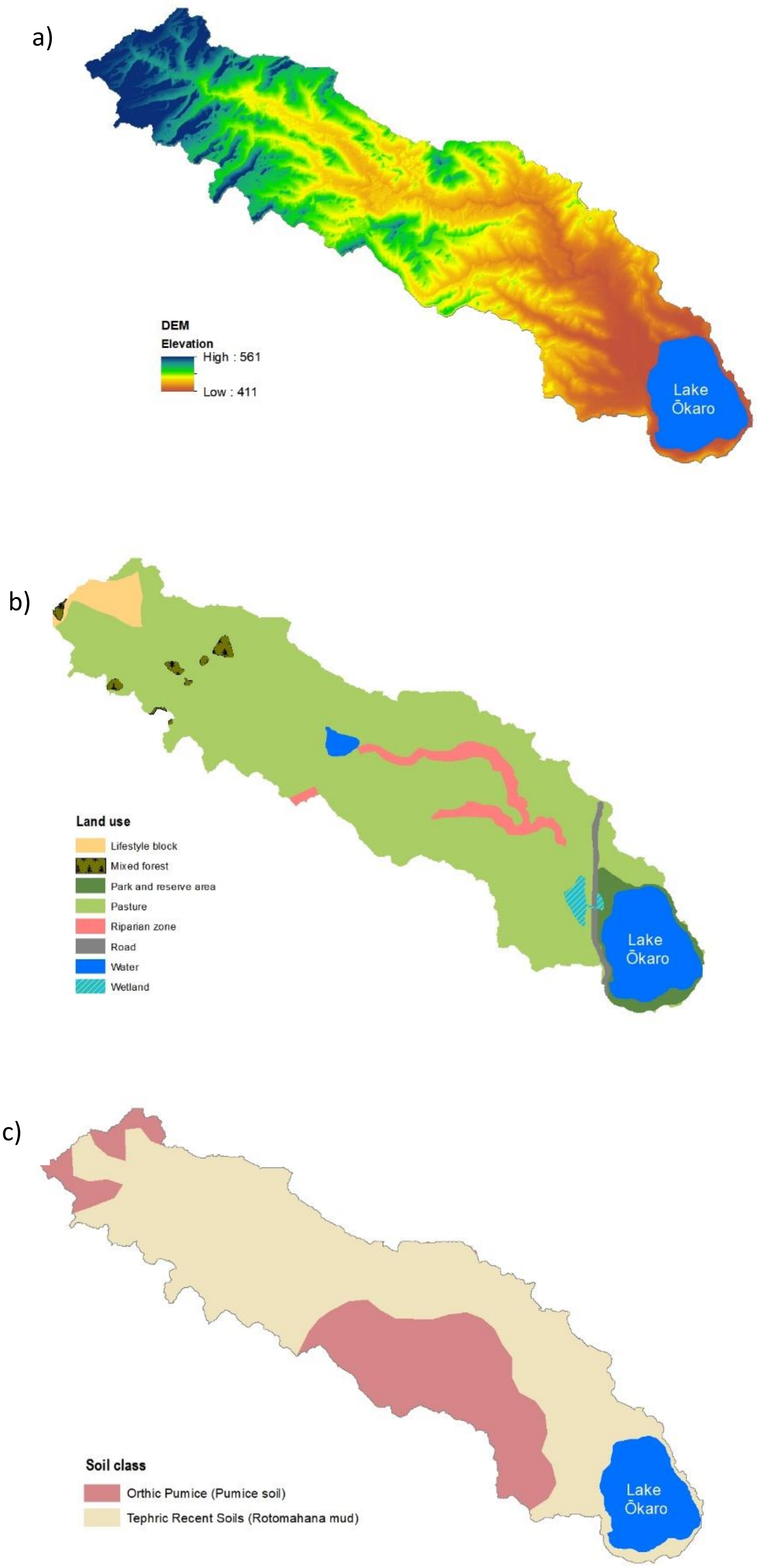

Figure 5.2 The topography for the Lake Ōkaro catchment using a digital elevation map (DEM) map (a), land use 2007 map (b) and soil map (c) used as model setup and baseline (scenario 1).

5.2.3.2 Hydrometeorological and management practices input data

The simulation in the SWAT+ model requires meteorological data including daily maximum and minimum air temperature (°C), solar radiation (MJ m^{-2}), relative humidity (as a fraction), wind speed (m s^{-1}); these were extracted from the Virtual Climate Station Network (VCSN) of the NIWA climate database at the nearest site to the Lake Ōkaro catchment (VCS31041), available at https://cliflo.niwa.co.nz/ (Figure 3). The precipitation data, available from June 2007, was obtained from the BoPRC environment data portal, https://envdata.boprc.govt.nz/Data. Annual mean precipitation is 1252 mm with major rainfall events generally occurring in winter (June to August) and autumn (March to May). As a comparison, annual mean precipitation at VSC31041 over the period 2008 – 2020 is 1462 mm. Average values are temperature 12.2 °C (maximum is 16.9 °C and minimum is 7.4 °C), relative humidity 83%, wind speed 3.9 m s^{-1}, and solar radiation 14.5 MJ m^{-2}.

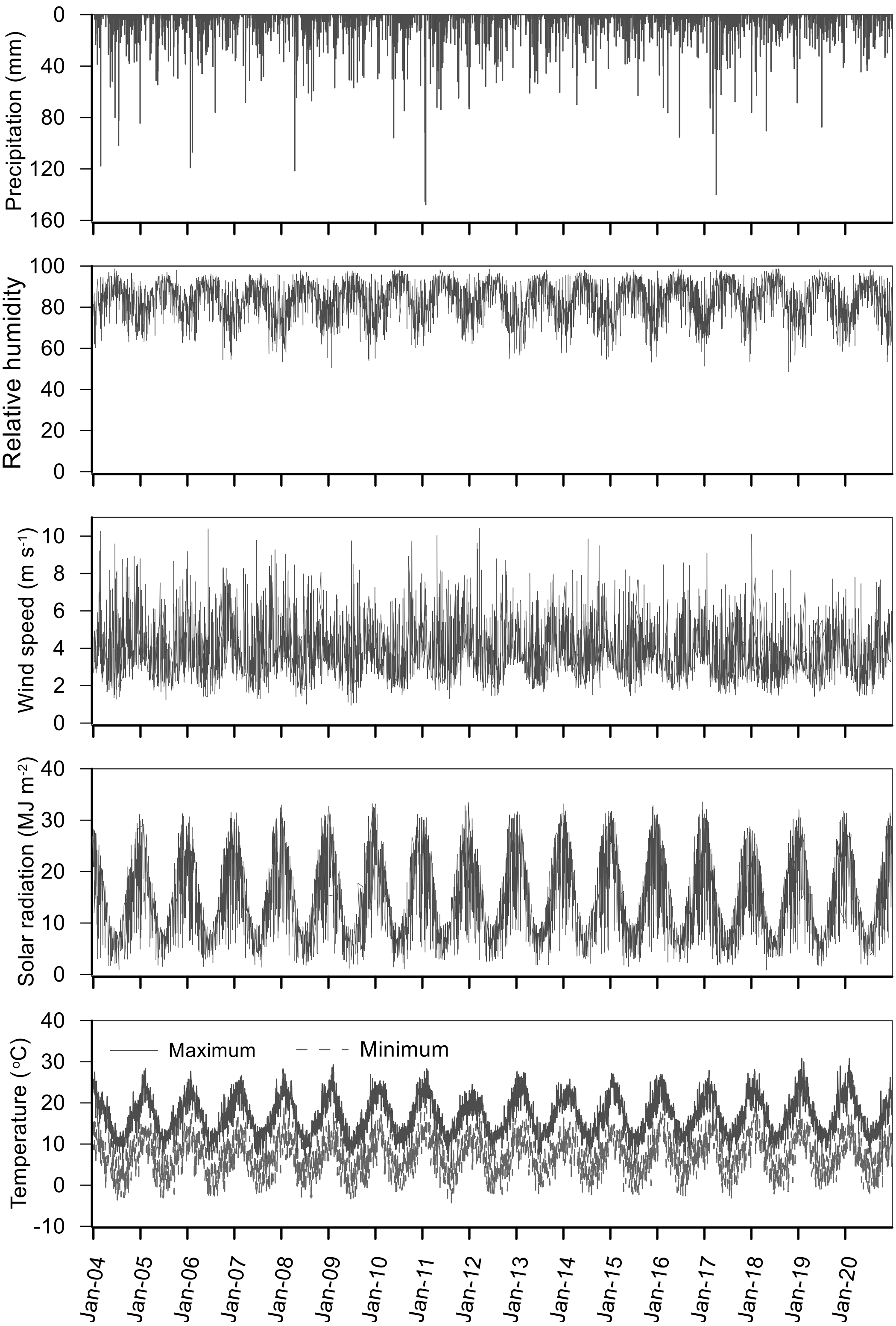

Figure 5.3 Daily meteorological data used in this study as input to the SWAT+ model. 2004 – 2007 was used as warm–up period, 2008 – 2009 was calibration period and 2010 – 2012 was validation period. Precipitation data available since June 2007 at BoPRC meteorological site, VCSN from NIWA used to substitute the lack of observed data.

The observed flow data and water quality were provided by BoPRC. Flow was obtained from stage height measurements at OK1 and OK13 sites at 15–minute intervals and subsequently aggregated to daily then to monthly values for calibration and validation. Observed monthly monitoring data water were converted to loads based on total flow volume on the corresponding day. The observed monthly loads were then used to calibrate parameters by comparing them with the simulations of nutrient loads from SWAT+ model on that sampling day. Timing and rate of fertiliser application in the study area was provided by Penny MacCormick (personal communication) and described in Table 3 as follows.

Table 5.1 Applied fertiliser in the SWAT model

Fertiliser	Amount	Time
Urea	25 kg ha^{-1}	March
Urea	28 kg ha^{-1}	May
Urea	15 kg ha^{-1}	September
Urea	40 kg ha^{-1}	November
Sulphur super	235 kg ha^{-1}	May

5.2.3.3 Coupling SWAT+ model with isotope data

In this study, information from stable isotope analyses (see Chapters 3 and 4 for details) was utilised as soft data to set constraints during calibration (Arnold et al., 2015; Jensen et al., 2018) and to improve the process representation of nitrate dynamics within the catchment.

The relative contribution of precipitation and shallow groundwater to streamflow in the Lake Ōkaro catchment was estimated using isotopes of water. Stream water was assumed to be a mixture of precipitation and baseflow recharge. Water isotope variations in stream water can be viewed conceptually as combining two components: a relatively stable baseflow end member and a seasonally variable stormflow end member. To estimate the contribution of the two distinct water sources, (precipitation and shallow groundwater), a linear mixing model can be applied. This method, proposed by Nakamura et al. (2017) and Belachew et al. (2016), is based on a mass balance method, as defined in Equation 5.2.

$$\delta_{sw} = \left(\delta_{gw} V_{gw}\right) + \left(\delta_p V_p\right) \qquad \text{(Eq. 5.2)}$$

where δ describes the stable isotope composition and V is streamflow; stream water, groundwater, and precipitation are indicated with subscripts *sw, gw* and *p*, respectively.

The isotopic signatures of water for the Lake Ōkaro catchment highlights that precipitation and evaporation strongly influence stream hydrology in the study area (see Chapter 3). Water isotopic composition in stream water varied from –44.90 to –32.60 ‰ for δ^2H (mean = –38.52 ‰ ± 3.38 SD) and –5.79 to –7.04 ‰ for δ^{18}O (–6.38 ± 0.60). The isotopic composition of precipitation during the study spanned –83.5 to –10.8 ‰ (–36.9 ± 15.8) and –11.51 to –2.94 ‰ (mean = –6.20 ± 1.98) for δ^2H and δ^{18}O, respectively. The isotopic compositions of baseflow source ranged from –41.3 to – 39.4 ‰ for δ^2H (mean = –40.24 ‰ ± 0.71 SD) and –6.84 to –6.37 ‰ for δ^{18}O (–6.57 ± 0.16). Isotopically distinguishable streamflow components allowed a separation of baseflow and surface flow, 70% and 30%, respectively.

To provide a reliable evaluation of nitrogen balance, the isotope signature of δ^{15}N–NO_3^- and δ^{18}O–NO_3^- was used to elucidate nitrate sources and the processes that lead to N losses within the catchment. Results of the N and O isotopic analysis of nitrate for water across the study area samples provide insight into the sources of stream nitrate in the Lake Ōkaro catchment (see Chapter 3). The isotopic signature of nitrate indicates that mineralisation of soil organic and nitrification of the chemical fertiliser process is evident in the study area and thus is used as the main input of nitrogen balance in the SWAT+ model. The contribution of nitrate to stream water from atmospheric deposition appears to be limited and is considered negligible compared to other nitrate sources. Based on the relationship between $\delta^{15}N$ and $\delta^{18}O$ of nitrate and nitrate concentrations, in–stream processing was evident (Figure 3.6 in Chapter 3); therefore, the SWAT+ model was simulated by activating in-stream water quality code (WQ_CHA.bsn) to 1.

In terms of nitrogen removal, isotopic signatures indicate that denitrification is the dominant N removal process within the catchment. Dual nitrate isotopes were used to determine the extent of denitrification, based on Rayleigh fractionation (Equation. 5.3). The Rayleigh equation (Kendall & McDonnell, 1998) uses the slope of linear regression between the relative change in corresponding isotopic values and nitrate concentration (C) at the time t relative to the initial substrate (0), to estimate the enrichment factor of denitrification (ε). Furthermore, the proportion of N attenuation was estimated using Equation 5.4 (Wells et al., 2016):

$$\delta_t = \delta_0 + \varepsilon \, ln \, ln \left(\frac{C_t}{C_0}\right) \qquad \text{(Eq. 5.3)}$$

$$Attenuation = 1 - e^{\left(\frac{\delta_t - \delta_0}{\varepsilon}\right)} \qquad \text{(Eq. 5.4)}$$

The average calculated attenuation value of 46% was used as a constraint in parameterisation of the SWAT+ model. In the Lake Ōkaro catchment, and consistent with findings of another study in the pastoral catchment (Wells et al., 2015) that ammonia volatilisation effects on N balance to be inhibited by N recycled through soil organic N pool. Thus, ammonia volatilisation is not considered to be an important process in this study.

5.2.4 Model calibration and evaluation

The calibration process was conducted using the SWAT+ Toolbox (integrated into an QGIS interface)—a free tool that assists users with uncertainty and calibration analysis—and the model check developed by Celray James (https://swat.tamu.edu/software/plus/). Calibration of the automated SWAT includes uncertain model parameters, model simulations and extraction of output results (Bekele & Nicklow 2007; Eckhardt & Arnold 2001). In this study, the selected SWAT+ parameters for streamflow and nitrogen loads simulations (Table 5.2) were each tested and calibrated until they achieved the required modelling performance. The flow–related parameters are much less sensitive to the only nitrogen–process–related parameters (Arnold et al., 2013). Therefore, the model variables for nitrogen were calibrated after the flow–related parameters had been updated with the calibrated values.

Table 5.2 Catchment processes evaluated during parameterisation in the SWAT+ model using insight from isotope data.

Process	Data	Source and analysis	Implementation in SWAT+ for the Lake Ōkaro catchment
Water balance			
Ratio of surface runoff to total streamflow	water isotope	linear mixing model [a)]	constraint the water balance output
Ratio of baseflow to total streamflow	water isotope	linear mixing model [a)]	constraint the water balance output
Nitrogen balance			
Mineralisation of soil organic	nitrate isotope	biplot dual isotope nitrate	constraint the nitrogen balance output
Chemical fertiliser	nitrate isotope	biplot dual isotope nitrate	constraint the nitrogen balance output
N atmosphere	nitrate isotope	biplot dual isotope nitrate	ATMODEP in WEATHER–STA.CLI set to 'null'
Denitrification	nitrate isotope	Rayleigh equation	constraint the nitrogen balance output, manual calibration for denitrification–related parameters
Ammonia volatilisation	nitrate isotope	[b)]	constraint the nitrogen balance output
In–stream processing	nitrate isotope	Bayesian mixing model	WQ_CHA.bsn set to "1"

a) Belachew et al. (2016) and Nakamura et al. (2017)

b) Wells et al., 2016

Table 5.3 Optimised parameters values for SWAT+ model input.

SWAT+ variable	Unit	Definition	Default range	Optimal value
		Flow		
k	mm/h	saturated hydraulic conductivity	0 – 2000	559.53
awc	mm_H_2O/mm	available water capacity of the soil layer (mm H2O/mm soil)	0.01 – 1	0.165
chn		channel lte Manning's N	–0.01 – 0.3	0.186
cn2		SCS curve number	35 – 95	42.44
esco		soil evaporation	0 – 1	0.08
ovn		Manning's "n" value for overland flow	0.010 – 30	0.534
canmx	mm/H_2O	maximum canopy storage	0 – 100	8.504
epco		plant uptake conventation factor	0 – 1	0.011
bd	mg/m^3	moist bulk density	0 – 2.5	1.363
surlag	days	surface runoff lag coeffcient	0.05 – 24	7.513
evrch		reach evaporation adjustment factor	0.5 – 1	0.502
alpha	days	baseflow alpha factor	0 – 1	0.002
bf_max	mm	baseflow rate when entire area is contributing to baseflow	0.1 – 2	0.732
flo_min	m	minimum aquifer storage to allow return flow	0 – 50	57.9
revap_co		groundwater revap coefficient	0.02 – 0.2	0.104
revap_min	mm	threshold depth of water in the shallow aquifer for "revap" or percolation to the deep aquifer to occur	0 – 2000	0.02
gw_lte		groundwater lateral	0 – 10000	9257.962
gwflo_lte	mm	initial shallow aquifer flow	0 – 10	3.844

	Nitrogen		
denit_exp	denitrification exponential rate coefficent	0 – 3	1.4
denit_frac	denitrification threshold water content	0 – 1	0.46
orgn_min	rate factor for humus mineralisation of active organic nutrients	0.001 – 0.003	0.0003
n_uptake	nitrogen uptake distribution parameter	0 – 100	20
n_perc	nitrate percolation coefficient	0 – 1	0.5
rsd_decomp	residual decomposition coefficient	0.02 – 0.1	0.05
nitrate	nitrate in soil surface	7	
nh3_pref	algal preference factor for ammonia	0 – 1	0.5
alg_resp	algal respiration rate at 20 ºC (day^{-1})	0.05 – 0.5	0.3
alg_grow	maximum specific algal growth rate at 20 ºC (day^{-1})	1.1 – 3	2
nh3n_no2n	biological oxygen rate of NH_3 to NO_2 in reach at 20 ºC (day^{-1})	0.1 – 1	0.55
no2n_no3n	biological oxygen rate of NO_2 to NO_3 in reach 20 ºC (day^{-1})	0.2 – 2	1.1
ptln_stl	organic N settling rate in reach (day^{-1})	0.001 – 0.1	0.05
ptln_nh3n	hydrolysis rate of organic N to ammonia in reach at 20 ºC	0.2 – 0.4	0.21

The SWAT+ model was calibrated for two years (2008 – 2009) and further validated from 2010 to 2011 using monthly streamflow using data from two sites, OK1 (wetland inlet) and OK13 (wetland outlet). Four years (2004 – 2007) were used as a warm–up period to stabilize the model. Due to the limitations of the observed data, only data from OK13 was used for the calibration and validation of nitrate. Modelled daily loads were compared with concentrations measured during monthly grab sampling, with monthly instantaneous measurements assumed equal to concentrations on a corresponding day.

The SWAT+ Toolbox was also utilised to test the sensitivities of parameters related to streamflow. A Sobol method with 1000 iterations was used to examine observed data at the monitoring points until the most suitable parameters were fitted and fixed. Sobol's method (Sobol, 2001) is a variance–based global sensitivity analysis (GSA) method in which the total output variance within an ensemble is decomposed into the variance caused by each parameter. This method was chosen because of its ability to incorporate parameter interactions and the relative straightforwardness of its indices (Zhang et al., 2013). In this study, sensitivity analysis was applied to prioritise the most sensitive inputs parameters to the SWAT+ model that was further calibrated using insight obtained from isotope data. SWAT+ Toolbox still has limited options for sensitivity analysis of parameters involved in the nitrogen cycle. Therefore, the calibration for nitrogen balance was performed without a prior sensitivity analysis.

Furthermore, the step two calibration procedure was performed by using insights from isotope data. At this stage, the results obtained from the isotope investigation were first compared and then incorporated into the SWAT+ model constraints during calibration. Isotope analyses provided additional information on baseflow contribution to the results generated by the SWAT+ model. The estimated percentage of streamflow component from runoff and baseflow compared with simulated baseflow and runoff proportion in the model. If the model parameter did not satisfactorily agree with the isotope result, the parameters in the SWAT+ model were adjusted. This process was repeated until the simulated water balance in the model fitted within values obtained from isotopes. A similar process was conducted to simulate nitrogen balance with a focus on denitrification–related parameters: denitrification exponential rate coefficient (DENIT_EXPCDN) and denitrification threshold water content (DENIT_FRAC) that were calibrated manually to produce realistic N removal by denitrification based on the value from isotope analysis.

The model's performance was assessed using the goodness–of–fit objective function, which includes Nash–Sutcliffe Efficiency (NSE), percent of model bias (PBIAS) and coefficient of determination (R^2). The NSE is a normalised statistic that indicates how well the observed and predicted data fit the 1:1 line (Nash & Sutcliffe, 1970). The PBIAS indicates the average tendency of the simulated data to be larger or smaller than the observed data. Positive PBIAS values denote a model bias towards underestimation, whereas negative values denote model overestimation (Gupta et al., 1999). The R^2 value describes the variance in measured data explained by the model, with R^2 ranging from 0 to 1. Model performance was evaluated by using standard criteria recommended by Moriasi et al. (2007) for NSE and PBIAS (Table 1). According to Santhi et al. (2001), the model performance is considered satisfactory if the threshold value for $R^2 > 0.5$. The three statistical evaluation metrics are calculated as follows:

$$NSE = 1 - \frac{\sum_{i=1}^{N}(Q_{m,i} - Q_{s,i})^2}{\sum_{i=1}^{N}(Q_{m,i} - Q_{s,i})^2} \qquad \text{(Eq. 5.5)}$$

$$PBIAS = 100 * \frac{\sum_{i=1}^{N}(Q_m - Q_s)_i}{\sum_{i=1}^{N} Q_{m,i}} \qquad \text{(Eq. 5.6)}$$

$$R^2 = \frac{\sum_{i=1}^{N}[\,(Q_{m,i} - Q_m)\,(Q_{s,i} - Q_s)]^2}{\sum_{i=1}^{N}(Q_{m,i} - Q_m)^2 \ \sum_{i=1}^{N}(Q_{s,i} - Q_s)^2} \qquad \text{(Eq. 5.7)}$$

where, Q is a variable such as streamflow and nitrate loads, m and s stand for measured and simulated values, i is the ith measured for simulated data. The model performance statistics for step one calibration (without soft data from isotopic composition) and step two calibration (with soft data from isotopic composition) were compared.

Table 5.4 General performance ratings for monthly time step.

Model performance rating	NSE	PBIAS	
		Streamflow	N
Very good	0.75 < NSE ≤ 1.00	PBIAS <±10	PBIAS < ±25
Good	0.65 < NSE ≤ 0.75	±10 ≤PBIAS < ±15	±25 ≤PBIAS < ±40
Satisfactory	0.50 < NSE ≤ 0.65	±15 ≤PBIAS < ±25	±40 ≤PBIAS < ±70
Unsatisfactory	NSE ≤ 0.50	PBIAS > ±25	PBIAS > ±70

Following the calibration and validation of the SWAT+ model, 13–year simulations of nitrate export were carried out over the period 2008 to 2020. The period 2008 to 2020 was arbitrarily chosen to illustrate the catchment scale pattern of a recent period.

5.2.5 Scenario simulations

To evaluate the hydrological and nutrient loading response to changes in land use and chemical fertiliser application, five scenarios were considered in this study. Different land use scenarios and fertiliser application were applied for assessing the efficiency of management strategies for nitrate load reduction in the Lake Ōkaro catchment. This study involves simulating different scenarios in managing nutrient loss from agriculture–use areas of the catchment to freshwater. The scenarios include changes in land use and chemical fertiliser application. The five scenarios are described in the following and shown in Figure 5.4.

- Scenario 1, baseline simulation using land use 2007, the year of the wetland was constructed. Scenario 1 has land use proportions of PAST (83.1%), FRST (1%), and RNGB (4.6%) (Figure 5.2).
- Scenario 2, hypothetical scenario of land use 2007 without wetland. This scenario determines the effectiveness of the wetland (Figure 5.4a).
- Scenario 3, simulation using land use 2016, in general, represents existing land use. In 2016, Lake Ōkaro restoration was undertaken including 26 hectares planted in production forestry and increasing riparian zones. PAST decreased to 70.9%, FRST increased to 10.4%, and riparian zone increased to 5.4% from baseline scenario (Figure 5.4b).
- Scenario 4, a variation of scenario 3 with fertiliser reduction by 50%. The scenario is implemented in SWAT by changing the amount of fertiliser applied in the pastoral area at any given time and in the specified area (Figure 5.4c). The fertiliser schedule is depicted in Table 5.1.

- Scenario 5, hypothetical scenario of a complete conversion to native forest intended as the best nutrient load scenario. Supposes that all PRST will be converted to FRST, and the rest of the land uses remain unchanged.

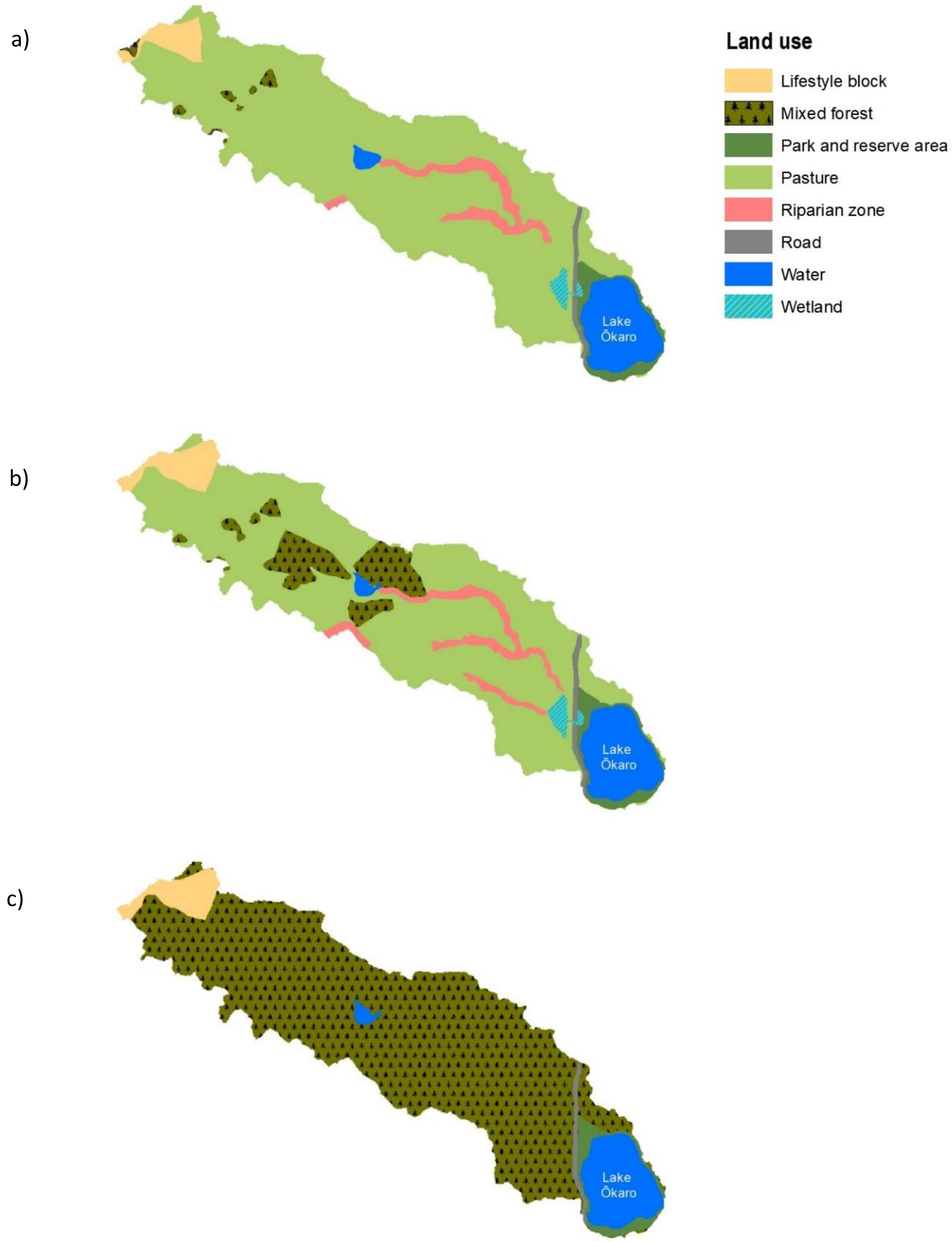

Figure 5.3 Land use proportions for scenario 2 (a), 3 (b), and 5 (c).

5.3 Results

5.3.1 SWAT+ calibration

This study determined optimum calibrated parameters with acceptable model performance (Table 1). In the Lake Ōkaro catchment, streamflow is shown to be more sensitive to saturated hydraulic conductivity (K), available water capacity of the soil layer (AWC), average slope steepness in HRU (SLOPE), channel Manning's CN (CHN), and soil evaporation compensation factor (ESCO). These selected parameters were calibrated manually at the catchment level in the step two calibration constrained by soft information from results of isotope analyses.

The streamflow in the study area shows a seasonal variation triggered by precipitation input especially during winter. The SWAT+ model was able to reproduce the observed streamflow covering both the high– and low–flows periods, although, daily mean values during dry periods were often underestimated (Figure 6). This visual interpretation of the hydrograph is supported by the statistics of model performance (Table 4). The goodness–of–fit objective function results of the SWAT+ model for the Lake Ōkaro catchment were considered to be a satisfactory to very good prediction for streamflow during calibration and validation.

For the calibration period, NSE was good for both OK1 (0.68) and OK13 (0.65). PBIAS was very good for OK1 (10.84) and OK13 (14.53) with positive values indicating that the simulated streamflow is consistently lower than observed values. Values of R^2 were very good for OK1 (0.86) and OK13 (0.85). For the validation period, the combinations gave acceptable model performance from satisfactory to very good for both OK1 and OK13.

For nitrate load prediction, nitrogen-related parameters that potentially are the most sensitive in determining nitrate losses were selected to calibrate the model (see Table 5.2). Due to limited data, calibration and validation process for nitrate load simulation was only conducted in OK13. The results indicate that the SWAT model performed well in predicting nitrate load according to the criteria recommended by Moriasi et al. (2007). The SWAT+ model provided good values for R^2 (0.76), NSE (0.70), and PBIAS (33.48) for calibration, whereas for validation, R^2 (0.65) and PBIAS (17.36) were good results, but NSE (0.46) was unsatisfactory.

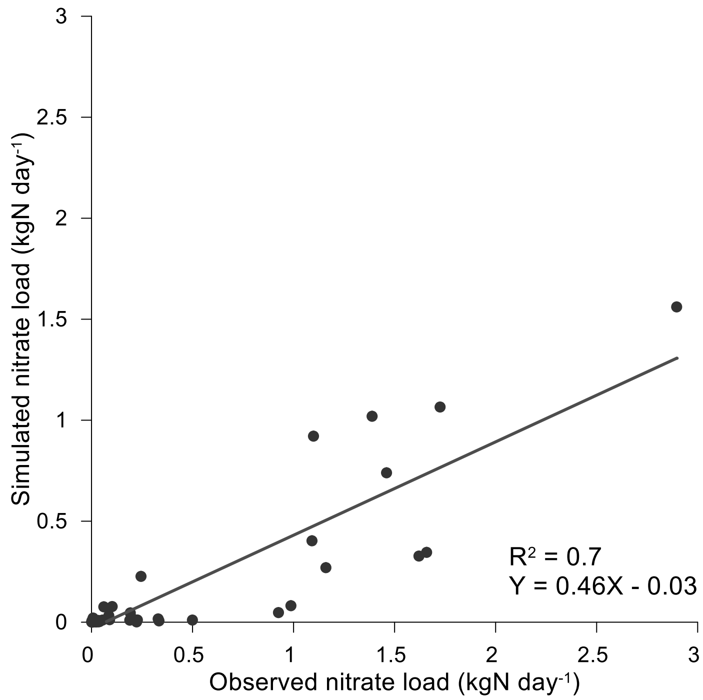

Figure 5.4 Observed and simulated nitrate loads during the calibration and validation period at OK13.

5.3.2 Comparison of SWAT+ model performance with and without adding insight from isotope data

Adding insight from isotope data generally improved the model's performance (Table 5.5), better captured the peak flows (insert in Figure 5.6), and better represent the nitrogen relevant processes in the catchment. During calibration, NSE improved from 0.68 to 0.82 at OK1 and 0.65 to 0.82 at OK13 for SWAT+ model and SWAT+_Iso, respectively. R^2 improved from 0.86 to 0.90 at OK1, and 0.85 to 0.86 at OK13 when SWAT+ was compared with SWAT+_Iso. PBIAS at OK1 increased from 10.84 for SWAT+ to 14.53 for SWAT+_Iso; however, both values were classified as satisfactory. PBIAS at OK13 improved from 14.53 for SWAT+ to 10.40 for SWAT+_Iso. During validation, SWAT+ model performance improved for NSE, R^2 and PBIAS.

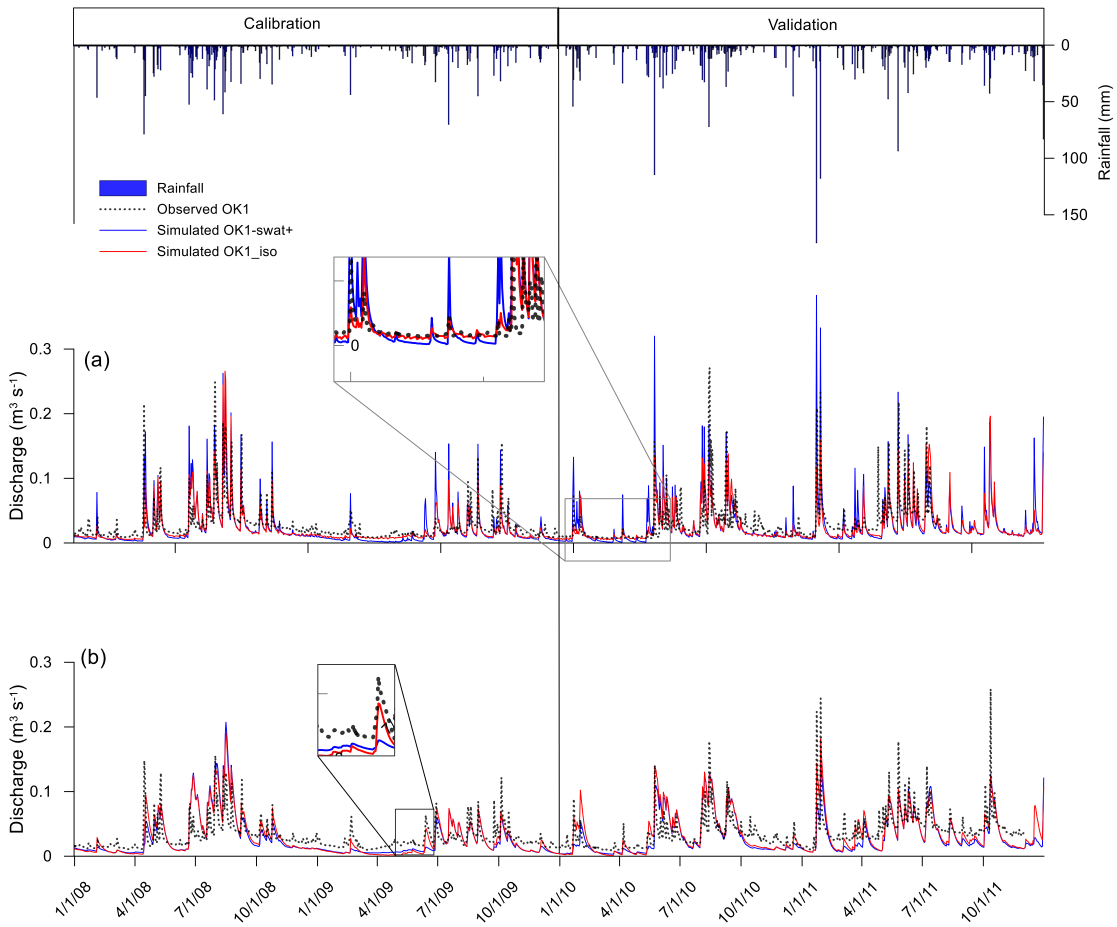

Figure 5.5 Comparing daily streamflow during calibration (2008 – 2009) and validation (2010 – 2011) at OK1 (a) and OK13 (b). The image in insert shows that SWAT+ model with insight from isotopes was able to produce a better daily flow estimation during high flow and low flow.

Based on the nitrate isotope analysis, denitrification–related parameters of denitrification exponential rate coefficient (DENIT_EXP) and denitrification threshold water content (DENIT_FRAC) were changed to adjust the denitrification proportion. As a result of these changes, the model's performance increased and resulted in improving nutrient balance estimation in the Lake Ōkaro catchment (Table 5.5). Therefore, including isotope investigations into the modelling improved the model simulation and thus better represented the processes occurring in the catchment.

Table 5.5 Summary statistics of model performance for SWAT+ in the Lake Ōkaro catchment with (SWAT+_Iso) and without (SWAT+) insight from isotope data. An increase in model performance of the SWAT+_Iso compared to default SWAT+ model was indicated by an increase in the R^2 and NSE values and a decrease in the PBIAS value based on Moriasi et al. (2007) and Santhi et al. (2001).

Output	Model performance	OK1				OK13			
		Calibration		Validation		Calibration		Validation	
		SWAT+	SWAT+_Iso	SWAT+	SWAT+_Iso	SWAT+	SWAT+_Iso	SWAT+	SWAT+_Iso
Flow	R^2	0.86	0.90	0.75	0.84	0.85	0.86	0.72	0.80
	NSE	0.68	0.82	0.58	0.67	0.65	0.82	0.65	0.72
	PBIAS	10.84	13.18	16.06	13.12	14.53	10.40	10.24	11.38
Nitrate	R^2	–	–	–	–	0.76	0.80	0.65	0.71
	NSE	–	–	–	–	0.70	0.75	0.46	0.61
	PBIAS	–	–	–	–	33.48	29.53	17.36	10.25

5.3.3 Water and nitrogen balance

The calibrated SWAT+ using isotope data was applied to simulate the water and nitrogen balance for period 2008 – 2020. Figure 7 shows the long-term mean monthly and annual water balance for the Lake Ōkaro catchment as simulated by SWAT+ model for baseline scenario (1). An estimated 30% (386 mm) of annual precipitation (1252 mm) was lost through evapotranspiration, while about 68% (855 mm) was discharged into the stream as water yield, with greater water yield in the northern side of the catchment and upper catchment (Figure 5.7). Surface runoff (225 mm) and baseflow (629 mm) were the main pathways of water loss. Percolation to shallow groundwater (9 mm) and recharge to deep aquifer (1 mm) was minimal.

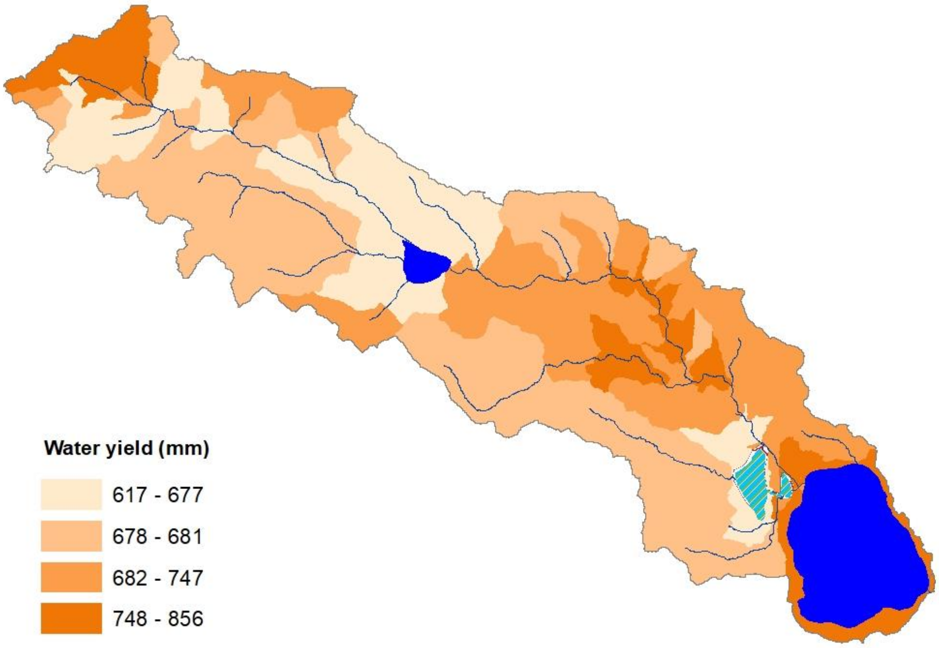

Figure 5.6 Spatial distribution of annual average water yield across the Lake Ōkaro catchment for baseline scenario.

The SWAT+ model simulated the seasonal variability of water balance (Figure 5.7a). The mean monthly evapotranspiration decreased from April (24 mm) to August (8 mm). The baseflow and surface runoff contributions to streamflow also increased during the wet period following precipitation period. The share contributed by individual components of water balance changes each year depending on precipitation input. The lowest precipitation was recorded in 2009 (733 mm) and the highest precipitation was in 2017 (1807 mm). In 2009, the evapotranspiration was 311 mm (42% of precipitation) and surface runoff 91 mm (22% of water yield). In 2017, evapotranspiration from soil and plants was 364 mm (20%); surface runoff was 490 mm (34%).

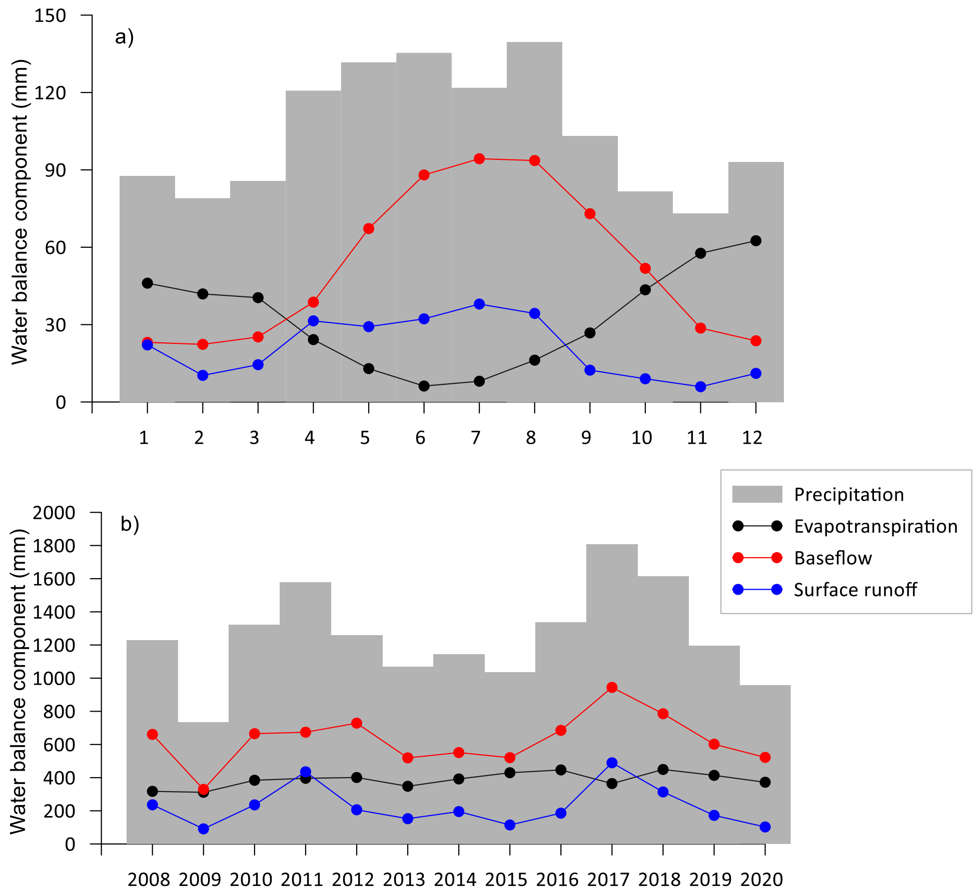

Figure 5.7 Long–term monthly average and annual water balance for the Lake Ōkaro catchment under baseline scenario

For the annual average nitrogen balance, the inputs were higher than output. Mineral N (230 kg ha^{-1} yr^{-1}) and fertiliser (152 kg ha^{-1} yr^{-1}) were considered as the main N input, while plant uptake (203 kg ha^{-1} yr^{-1}) was the main output. Other nitrogen pools in the Lake Ōkaro catchment are active stable N (–55 kg ha^{-1} yr^{-1}), active nitrogen N (164 kg ha^{-1} yr^{-1}) and nitrate in surface, lateral and groundwater flow (12 kg ha^{-1} yr^{-1}). Annual average of nitrate load under the calibrated baseline scenario indicated variation in spatial distribution across the catchment. Higher nitrate loads, dominated by surface nitrate loss, were identified in middle area of catchment with high slope conditions, the northern part of the catchment and near the catchment outlet (Figure 5.8).

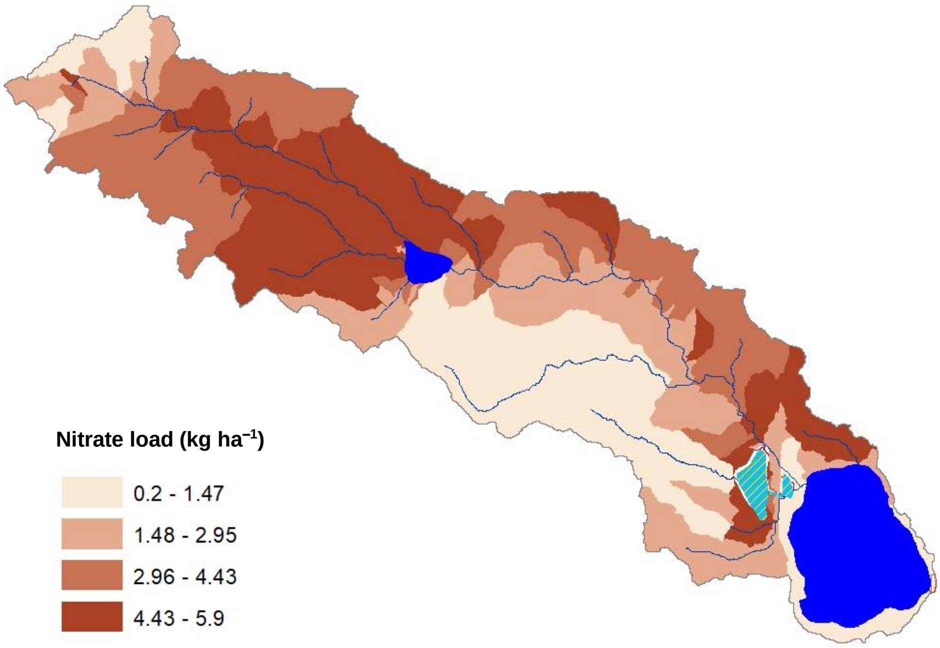

Figure 5.8 Spatial distribution of annual average nitrate load across the Lake Ōkaro catchment for baseline scenario.

5.3.4 Impact of land use change and fertiliser scenarios on nitrogen loads

The SWAT+ model outputs for total nitrogen, nitrate and organic N loadings were simulated to provide insights regarding the impact of different scenarios on nitrogen losses in the catchment. Table 5.6 presents the overall change and percentage of each nitrogen component as annual average for simulation period 2008 – 2020. The loads of total nitrogen (TN), nitrate, and organic N for baseline scenario (scenario 1) were 4513 kg N yr^{-1}, 2641 kg N yr^{-1}, and 841 kg N yr^{-1}, respectively. The increase in nitrogen load under scenario 2 was estimated to reach 1026 kg N yr^{-1} (22.7%) compared to baseline scenario 1. Nitrogen load under scenario 4 showed a reduction of 3113 kg N yr^{-1} (68.6%) compared to scenario 1 and 1831 kg N yr^{-1} (56.6%) relative to scenario

3. The largest effect on loads was found for scenario 5, where nitrate load declined by 914 kg N yr^{-1} (79.7%). Organic N load increased under scenarios 2 and 3, and decreased under scenarios 4 and 5; however, the change was minimal for all scenarios. For example, organic N increased by 43 kg N yr^{-1} (5.1%) in scenario 2. In contrast, under scenario 4, organic N decreased by 3.3 kg N yr^{-1} (0.45) under scenario 4.

Table 5.6 Changes in annual average (2008 – 2020) and percentage of change (in parentheses) total N, nitrate and organic N in kg N yr^{-1} under different scenarios in the Lake Ōkaro catchment.

	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Nitrogen (kg N yr^{-1})	4513	5540	3232	1401	914
	0 (0)	1026 (22.7)	–1281 (–28.4)	–3131 (–68.6)	–3599 (–79.7)
Nitrate (kg N yr^{-1})	2641	3447	1658	357	134
	0 (0)	805 (30.5)	–983 (–37.2)	–2283 (–86.4)	2511 (–95.0)
Organic N (kg N yr^{-1})	841	884	910	837	827
	0 (0)	43 (5.1)	69 (8.2)	–3.3 (–0.4)	–13 (–1.6)

According to Table 5.6, the annual average of nitrate loads also changed under different scenarios. The absence of the wetland led to an 805 kgN yr^{-1} (30.5%) increase in nitrate load. In contrast, a 10.4% increase in the forested area decreased the nitrate load of 983 (37.2%). Nitrate loads also decreased by 86.4% under fertiliser reduction (scenario 4) and 95% under afforestation (scenario 5). Model simulations showed that nutrient loads transported from the Lake Ōkaro catchment vary yearly for each scenario (Figure 5.9). Nitrate loads under baseline scenario (Scenario 1) ranged from 933 kg N yr^{-1} to 6006 kg N yr^{-1} for the simulation period of 2008 – 2020, 1243 kg N yr^{-1} to 8004 kg N yr^{-1} for scenario 2, 432 kg N yr^{-1} to 3281 kg N yr^{-1} for scenario 3, 89 kg N yr^{-1} to 706 kg N yr^{-1} for scenario 4, and 27 kg N yr^{-1} to 329 kg N yr^{-1} for scenario 5. Furthermore, Figure 10 indicates that, relative to scenario 1, the nitrate load showed an increase under scenario 2, and decrease under scenarios 3, 4, and 5 with the exception of scenario 3 in 2018 when it showed an increase.

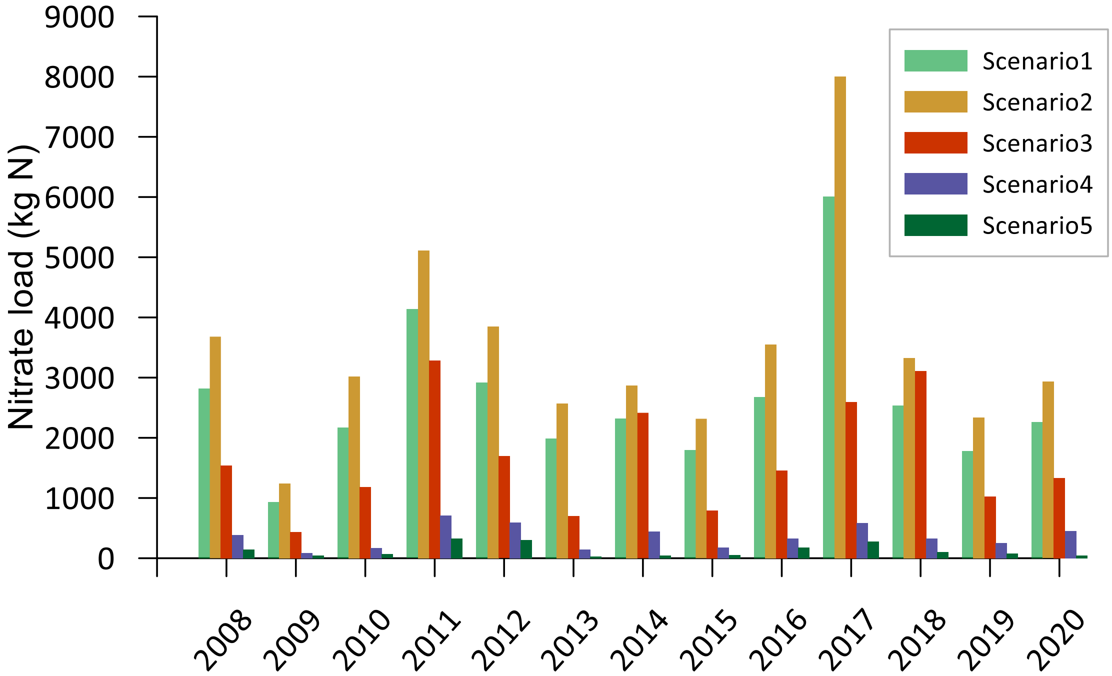

Figure 5.9 Simulated nitrate load during the simulation period (2008 – 2020) under different scenarios.

5.4 Discussion

5.4.1 SWAT+ application in the pastoral system

This study utilised the process-based SWAT+ model in simulating hydrological and nutrient processes in a small agricultural catchment. SWAT parameters associated with baseflow (K and CHN), soil moisture (AWC) and evaporation (ESCO) were identified as being highly sensitive to calibration in the Lake Ōkaro catchment. A high value of K potentially increases the baseflow contribution in water balance, which is expected as the study area is characterised by pumice soil with high infiltration capacity (Selby et al., 1971; Sparling et al., 2001). Another sensitive parameter supports this, CHN, together they indicate that the Lake Ōkaro catchment stores the large amount of water as baseflow before it is released across the catchment following hydrological events. These results are similar to those of a previous study in a highly agricultural catchment (Ligaray et al., 2017); this study identified hydraulic conductivity (K) and tributary channel (CHN) as sensitive parameters in modelling the fate and transport of nutrients. Overall, considering that the model is a simplification of complex dynamics and processes in the catchment, the reported sensitive parameters are the best representation of uncertainties (i.e., best estimates for this model, variables, and data used) and model assumptions governed by model equations that describe water flow and hydrological process (Pulighe et al., 2019).

Because SWAT is process-based model, adding insights from isotope data allows for a more realistic representation of the model output. While the default calibrated SWAT+ model was generally able to reproduce satisfactory streamflow and nitrate loads, using insight from isotope data would improve the model performance and better represent the processes occurring in the Lake Ōkaro catchment (Table 5.4). The improved SWAT model performance in this study can be attributed to that fact that the SWAT model can be made conceptually consistent with regional hydrological conditions (Zhang et al., 2020) by calibrating surface runoff and baseflow separately (Arnold et al., 2015). This finding supports previous research that integrating numerical models with contributions from different water sources based on the water isotopes significantly improved the SWAT mode performance (Jafari et al., 2021).

Moreover, our results support previous assertions that incorporating soft information can improve SWAT performance in predicting total nitrogen loading (Yen et al., 2014). Previous studies have highlighted the shortcoming of the SWAT+ model in simulating water quality (Brighenti et al., 2019; Panagopoulos et al., 2011). While the calibrated SWAT+ generated adequate model results, adding a soft calibration approach using isotope data provides more representative nitrogen balance components because the model has accounted sources, and dominant biogeochemical processes both of which are important in nutrient balance (see Chapter 3). For example, without insights from the isotope data, the calibrated SWAT+ model estimates relatively low mineralisation inputs and nitrate removal by denitrification. However, after using isotope information in parameterising the model, SWAT+ model produced more reliable output data based on the model's performance statistics. It is therefore reasonable to conclude that by incorporating isotope data as a constraint (Jensen et al., 2018) into SWAT+, the model can be used with higher confidence in simulation scenarios for the study catchment.

Despite underestimating the simulated nitrate load, the model's performance was within satisfactory to good results based on model evaluation criteria outlined by Moriasi et al. (2007). The SWAT+ model in our study can be considered to reasonably simulate nitrate load given that the estimation was developed from monthly samples. These results indicate the potential of using the SWAT+ model in simulating and interpreting the nitrogen balance in the Lake Ōkaro catchment.

Simulating nutrient loads using a hydrological model can give insights about the pressure that a catchment is subjected to and can aid in the creation of management strategies to control excessive load entering freshwater systems. One of the advantages of using SWAT is that it provides the spatial distribution of water yields and nutrient loads. The modelling results highlight that some areas (i.e., sub-catchments) may contribute more nitrate load than other areas. With careful assessment, this information could be used to identify where pasture management needs to be better targeted in the Lake Ōkaro catchment to reduce nitrate load and improve lake water quality.

5.4.2 Comparison of nitrogen loss estimations between different scenarios

Based on the calibrated and validated SWAT+ model, the impacts of land use changes and fertiliser application on nitrogen loads, with larger focus given on nitrate load, were simulated. The model simulations indicate that the implementation of good agricultural practices could lead to a significant decrease in nitrate loss. At the catchment outlet, annual average nitrate load increased in the absence of the constructed wetland (scenario 2). A reduction in nitrate load was simulated if the forest area was increased in the catchment (scenario 3), was almost completely afforested (scenario 5), and fertiliser application was reduced (scenario 4). These findings seem to be consistent with research conducted in other agricultural studies using a hydrological model. For instance, Liang et al. (2017) highlighted that land use was the dominant factor affecting nitrate load, with agricultural land contributing higher nitrate exports than forested land. That a strategic reduction in fertiliser use from agricultural sources reduces nitrate loss has been proven elsewhere, such as for a highland agricultural catchment in South Korea (Jang et al., 2017), an Italian catchment (Malagó et al., 2019), and a Danish catchment (Thodsen et al., 2015).

Wetlands play an important role in the attenuation of nitrate (e.g., Yousaf et al. 2021). The model simulations suggest that the constructed wetland in the Lake Ōkaro catchment attenuated total N in the order of 1026 kg yr^{-1}, or 22.7% when compared to the baseline scenario. Following the entire establishment of the plants, the annual percentage removal of total N by the wetland has previously been estimated to be 45% (165–210 kg yr^{-1}) (Tanner et al., 2007). The simulated removal of total N is somewhat lower, so it remains unclear whether the wetland performs less effectively than previously estimated or whether methodological differences in estimating nitrogen loading between the studies explains the discrepancy. Notwithstanding these differences, the modelling results support other studies that constructed wetlands retain a high quantity of N that may initiate eutrophication in the receiving water (Wang et al., 2010; Wu et al., 2008). Targeted monitoring of N loading into and out of the wetland would be useful to test the long-term performance of the wetland, further validate the catchment model, and inform a management plan to extend the N retention in the constructed wetland.

Increasing forested areas in the Lake Ōkaro catchment would decrease nitrate loads. The hypothetical scenario of a complete conversion to native forest suggests an approximately 80% reduction in total nitrogen load could be achieved in the catchment. Interestingly, Özkundakci et al. (2011) used a lake ecosystem modelling approach to simulate water quality in Lake Ōkaro and found that a 75–90% reduction in external loading (nitrogen and phosphorus) would be needed to shift the lake from a highly eutrophic to a mesotrophic state. A complete shift from the current land use to predominantly native forest in the catchment is unlikely, but the results for scenario 5 highlight the need for additional and substantial management strategies to reduce N (and phosphorus) load to the lake. For example, the model simulations indicate that a reduction of nitrate load by as much as 69% could be achieved with a 50% reduction in fertiliser use. Therefore, to maximise reductions of excessive nutrient loading, catchment interventions should focus on careful fertiliser management as a mitigation method in areas with intensive fertiliser applications.

Land use changes and intensive fertiliser application could affect the excessive load and deterioration of lake water quality (Gao et al., 2015; Liu et al., 2019; Costa et al., 2021). The modelling approach taken in this study could thus be helpful in assessing the effects of catchment management (i.e., managing fertiliser input) on achieving lake water quality targets. Coupling the SWAT catchment model with existing lake models (e.g., Özkundakci et al. 2011) would be a next logical step in developing the models further to support the ongoing management of the Lake Ōkaro catchment and the lake itself. Further research is needed to better understand the effects of catchment management strategies on livestock production and farm productivity (Cichota & Snow, 2009; Serebrennikov et al., 2020). Incorporating simulations of phosphorus load into the model simulation is crucial, as N load reduction alone will not affect the trophic state of the Lake Ōkaro, since it is both N and phosphorus-limited (Abell et al., 2010).

Overall, this study revealed a significant capacity of the SWAT model simulation to describe how relative differences of land use in measures change on a catchment scale. The SWAT model is widely used to assess the performance of different operational management strategies (i.e., add riparian planting, grass waterways) in terms of controlling excessive nutrient loads (Haas et al., 2017; Shrestha et al., 2016; Ricci et al., 2022; Plunge et al., 2022). Therefore, the use of SWAT+ offers an alternative option for the effective and efficient management of excessive nutrient loads (Ministry for the Environment, 2021).

Annual average of TN loss for scenario 1 (4513 kg yr^{-1}) and scenario 5 (914 kg yr^{-1}) was slightly higher than a pervious study in the same catchment by Wilcon

(2022), who estimated a TN load of 3900 kg yr^{-1} and 839 kg yr^{-1} to the Lake Ōkaro using a scenario similar to the baseline scenario used in this study, and an assumed conversion to native forest, respectively, using the Overseer® model. A direct comparison of these results is, however, somewhat difficult due to differences in model complexity and assumptions of the nutrient budgeting model Overseer® compared with a physical-based model used in this study.

5.4.3 Limitations

Even though the SWAT+ application in the Lake Ōkaro catchment met the criteria for satisfactory model performance, calibration and validation hydrographs showed that SWAT+ tended to underestimate predicted streamflow at low periods and generated higher differences than peak flow periods. This indicates that the model efficiency differs between wet and dry conditions in the study area. The simplification of model parameters between wet and dry periods used in this study potentially produced differences in simulation efficiency between the wet years and dry years, especially for the Lake Ōkaro catchment that has notable annual differences in precipitation input and water yield. Separating wet and dry periods during calibration of the SWAT model improves SWAT performance (Gao et al., 2018; Yuan et al., 2021), and indirectly contributes to enhanced nutrient simulation efficiency (Mehdi et al., 2018; Zhang et al., 2015). Moreover, long-term data from the Lake Ōkaro catchment was limited, which restricted the model's calibration and validation. It should be noted that the model was calibrated for a short period (2008 – 2009) when all the components were available. The year 2009 is considered a dry year and thus there would be different sensitive parameters compared to a wet year.

Difficulties in predicting peak flows and low flows have been found in similar SWAT model applications (Shrestha et al., 2016, Wu & Johnston, 2008; Tan et al., 2020). Even though this was an acceptable result because the SWAT model was not calibrated for single-event high streamflow conditions (Saha et al., 2014), it does affect the extreme value of the surface runoff and nutrient loadings (Tessema et al., 2014). The implications of peak flows in water and nutrient balance using high resolution rain event data as model input could be explored in future studies of the Lake Ōkaro catchment.

5.5 Conclusions

In this study, a physical-based model SWAT was applied to the Lake Ōkaro catchment for the period 2008 – 2020. This work provided several new insights through characterising the impact of land use on nitrate load and water yield by using the SWAT model, and stable isotopes as soft information, in the calibration process. The use of both water and nitrate isotopes as soft information in parameterisation SWAT+ model resulted in improved model performance. This study offers promising evidence that SWAT+ applications that incorporate isotope data can aid management strategies in the Lake Ōkaro catchment.

The model adequately reproduced nitrate loads, despite the scarcity of input calibration data, which is crucial for modelling nutrient dynamics. The application of the model showed that the Lake Ōkaro catchment exported on average 4513 kg N yr^{-1} (as TN), 1023 kg N yr^{-1} (as nitrate), 841 kg N yr^{-1} (as organic N). This study demonstrated a considerable decrease in nitrate load following the reduction of fertiliser inputs, indicating that managing fertiliser in the catchment is essential to controlling excessive nutrient load to Lake Ōkaro. The constructed wetland has a considerable influence on the retention of nitrates, and management of the wetland ensures that this system can continue to take advantage of natural nutrient removal processes, such as sedimentation, denitrification, and plant uptake.

5.6 References

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Chapter Six

Synthesis

6.1 General summary

This thesis aimed to address knowledge gaps in understanding land-to-water mechanisms of excessive nitrate at a catchment scale. The following section summarises the previous three chapter's conclusions and links them back to the objectives of this research project. By integrating multi-isotopes tracers, hydrochemical data and a SWAT+ model, this thesis has elucidated the sources, mobilisation, and delivery controls on nitrate export in the Lake Ōkaro catchment (Table 6.1). Where applicable, the findings of this study have been placed in an applied context to assist lake water quality improvement management strategies in terms of a monitoring program and utilisation of catchment-scale model. In Chapter 1, three main ideas for research were identified which can summarised as follows:

6.1.1 Sources and biogeochemical processes of nitrate in a pastoral catchment

The findings of this study are important for identifying typical sources of available nitrate and when nitrate is delivered to streams. A key finding presented in Chapter 3 was that the potential sources and N transformations in the Lake Ōkaro catchment indeed changed throughout the year subject to hydrological conditions and seasonal changes. Analysis of hydrochemistry and isotopic signatures in the study area shows that nitrate becomes available from a mixture of sources and processes originating from external inputs (i.e., chemical fertiliser, excreta, and grazing) and internal inputs (soil N) cycled through the soil system. Associated hydrological conditions determine the variation in sources and pathways of nitrate. High concentrations of nitrate during high flow were characterised by external inputs of urine and urea, delivered via high-energy pathways associated with precipitation. In contrast, during low flow, nitrate sources are dominated by soil N through subsurface pathways. Soil nitrification is an important pathway of nitrogen transformation in the Lake Ōkaro catchment, so it is suggested that management strategies should consider effective ways to improve nitrogen retention in the long term and to reduce the susceptibility of nitrogen to leaching.

6.1.2 Hydrologic mobilisation and delivery of nutrient dynamics

Based on the findings outlined in Chapter 3, a more detailed investigation of how and when excessive nitrate is exported in response to rainfall events was undertaken, the results of which are described in Chapter 4. The integration of high-frequency measurements and isotopic compositions of water and nitrate provides the context to explore the temporal dynamics and drivers of nutrients, especially during hot moments such as rainfall events. Notably, the findings detailed in Chapter 4 highlight that the catchment wetness threshold of ~95 mm (sum of precipitation and soil moisture factors) is important for understanding the mechanisms of nitrate transport in the Lake Ōkaro catchment. Nutrient dynamics exhibited some variations in their response to changing catchment wetness conditions. Strengthening the previous results, mobilisation mechanisms related to the isotope signature of the urine–urea nitrogen sources dominated nutrient dynamics during high flow conditions and likely more significant when the rainfall events are above the threshold. Meanwhile, nitrate delivered to the stream during rainfall events below the threshold is controlled by the release of mineralised organic N and reflects the dilution effect in response to rainfall.

The elevated nitrate concentration demonstrates there is a need for more efficient N use throughout the study area. These changing conditions provide information regarding control of nutrient loads from the catchment.

6.1.3 Using catchment modelling to support management of catchment nutrient loads

In Chapter 5, use of the SWAT+ model to simulate the hydrological processes and nitrogen balance in the Lake Ōkaro catchment is described. Additional understanding of nitrate export mechanisms from the isotopic signatures explained in Chapter 3 and 4 also incorporated in model parameterisation. It was found that insight from isotope data improved the SWAT+ model performance and better represented the relevant nitrogen processes within the catchment. The impact of changes in land use and fertiliser application on nutrient loads to the lake was also described. It was observed that changes in the pastoral area and fertiliser application impacted the nutrient loads. Based on the SWAT+ model simulations using one hypothetical land use scenario of afforested catchment as inputs, nutrient loads were decreased by 80%. The simulations also indicated that reduced fertiliser application resulted in lower nitrogen loads. In theory, optimisation of fertiliser management in terms of timing and application rate is an important variable in controlling excessive nutrient loads. However, this suggestion will be difficult to implement given the widely held belief that fertiliser addition translates directly into improved pasture-based production. At the catchment scale, SWAT+ model identified hotspots for prioritising the reduction in nutrient loads. The relative changes in nutrient loads complemented by spatial distribution (hotspots) under different scenarios may assist decision–making in controlling excessive N load while optimising the productivity of pastoral systems.

A novel aspect of this research was used integration of multi-isotope tracers, high-frequency monitoring, and application of a catchment-based model to identify dominant sources, key processes, and mechanisms controlling the excessive nutrient loads from a pastoral catchment. Based on the conclusions that the use of isotope data has improved overall model performance and arguably a more robust conceptualisation of processes within SWAT+, it can be argued that the usefulness of a catchment model has improved and can therefore be used with higher confidence in a decision-making process. There are now opportunities to employ this approach in future catchment modelling studies that are aimed at informing catchment management actions elsewhere.

Table 6.1 Potential control points developed in this study and proposed management practices in controling excessive nitrate.

Identified control points	Management implications	References refer to suggested management actions
High flow conditions leading to nitrate export from urine and urea fertiliser sources. (Chapter 3)	Enhance nitrogen retention capacity of the soil.	Wilcock et al. (2013)
Wetland as hot spot for denitrification in the catchment. (Chapter 3)	Maximise the denitrification potential in wetland (i.e., managing organic carbon supply).	Hansen et al. (2016); Martínez-Espinosa et al. (2021)
Hot moments of nitrate export coinciding with peaks in flow during rainfall above ~ 95 mm hydrological threshold. (Chapter 4)	The need for high-frequency monitoring of freshwater quality using reliable yet low-cost sensors to avoid missing "hot moments" during rain events.	Blaen et al. (2017) ; Frazar et al. (2019) ; Suchy et al. (2018)
In-stream channel hot spot for N transformation. (Chapter 3 and 4)	The importance to include in-stream process in nitrogen simulations.	Jensen et al. (2016); Yuan and Chiang (2015).
Spatial distribution of nitrate loads at the catchment scale. (Chapter 5)	Nutrient catchment-based model to predict future changes in freshwater pressures.	Heathwaite (2010); Ministry for the Environment and Ministry for Primary Industries (2021).

6.2 Direction for future work

Insight from this study and limitations of the work highlighted in each main chapter, lead to the following recommendations for future research.

To achieve the research objective of Chapter 3, this study used isotopic signatures of potential nitrate sources from global literature values. Although selected literature pertains to agricultural-based catchment and the results presented here are justified by other parameters, site-specific nitrate isotopic compositions could reduce the uncertainty of quantitative assessments of nitrate sources. Future studies need to measure nitrate isotopic compositions over a large geographic area to provide a better spatial-temporal interpretation of isotopic signatures in a catchment area.

This thesis has used a water and nitrate isotopes approach to identifying control points of nitrate loads on a catchment scale. This approach identified the potential to identify hot spots and hot moments that can aid in prioritising management strategies for reducing nitrate export; however, the possible sources and biogeochemical processes in groundwater are not well captured. Therefore, the efficacy of stable isotope use can be enhanced by expanding the sampling of groundwater and soil water and using other environmental tracers (e.g., bromide, chloride, tritium). These improvements will allow for a better understanding of the interactions between water components and the effect on excessive nutrient loads.

Chapter 4 describes the deployment of high-frequency monitoring to capture nutrient dynamics during rainfall events. The increased rate of monitoring provided insights into the important processes controlling hot moments of nitrate load that would be impossible to achieve using discrete sampling collection. Given that precipitation is expected to shift with more extreme events due to climate change, there is a need to include more spatially distributed high-frequency water quality measurements in a lake-catchment management monitoring program.

The application of the catchment-based model detailed in Chapter 5 has demonstrated that modelling approach can estimate nutrient loads for different land use scenarios and management practices (e.g., fertiliser application). Simulations could be re-run using different climate datasets such as for climate change scenarios and sub-daily resolution using high-frequency data.

6.3 References

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Appendices

Appendix A – Supplementary materials for Chapter 3

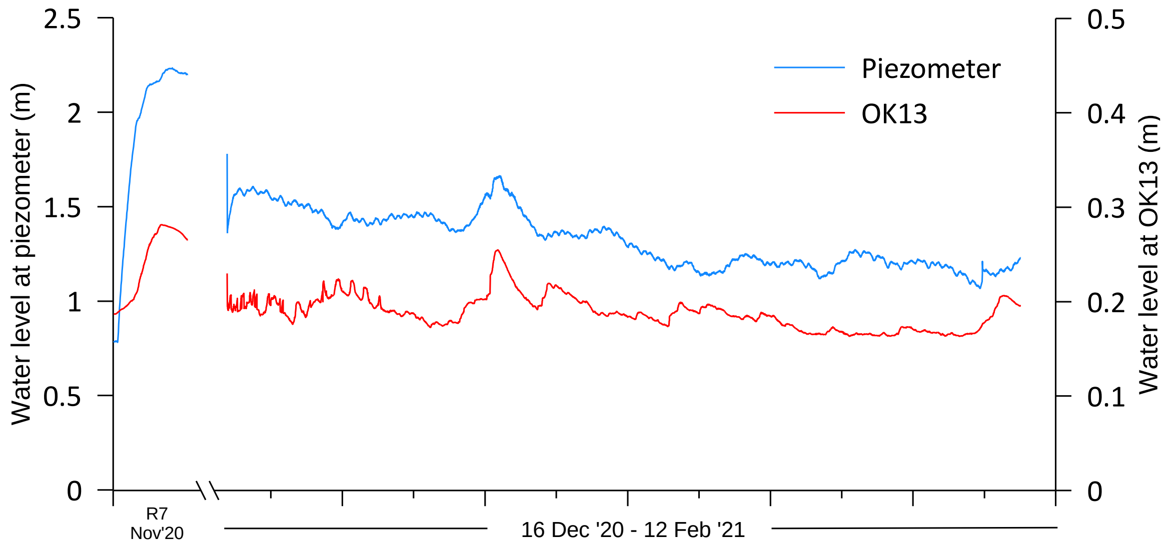

Figure A.1 Water level comparison at OK13 and piezometer during R7 (24 November 2020) and from 16 December 2020 to 12 February 2021. Note that axis labels are different to show variations during the measurement period.

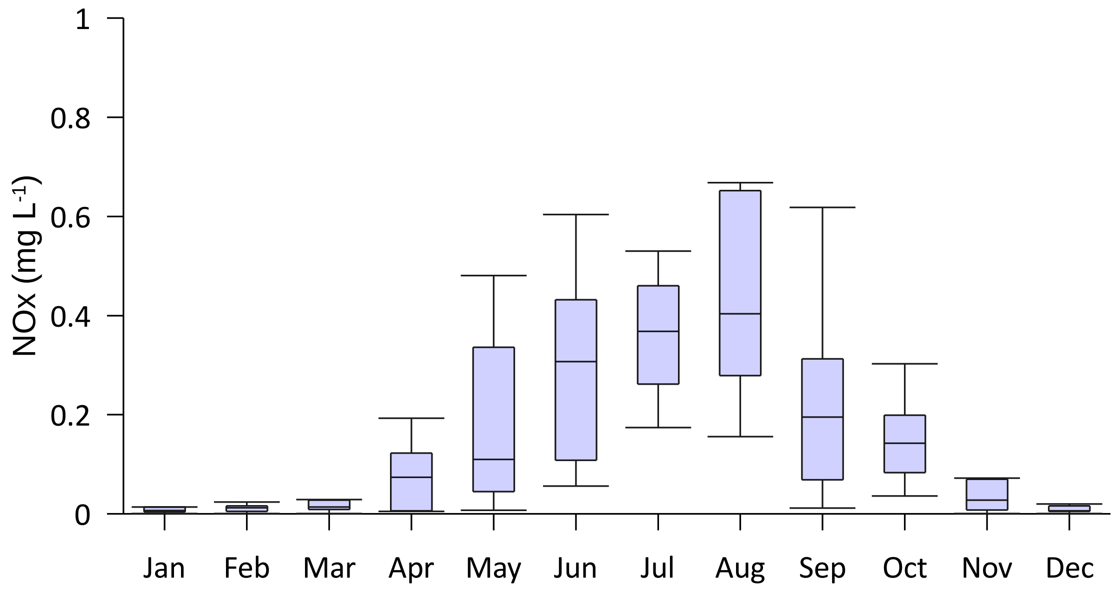

Figure A.2 Seasonal variations of nitrate concentrations (reported in NOx) at OK13, derived from 2007 to 2020 data (Source, BoPRC)

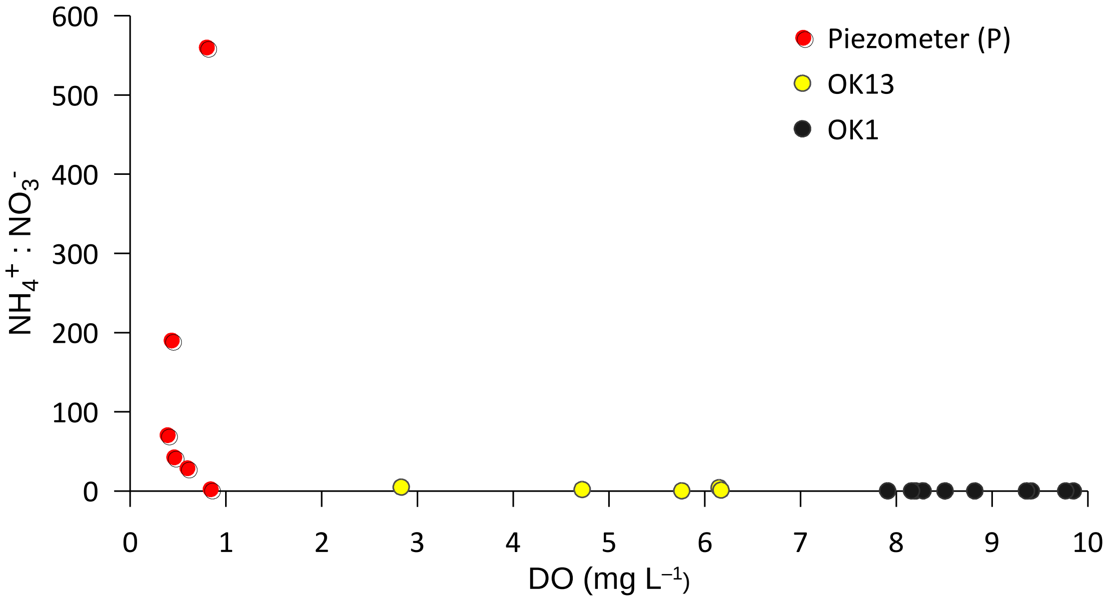

Figure A.3 Ratio of NH_4^+:NO_3^- vs. DO concentration shows that shallow groundwater was dominated by denitrification, while OK1 and OK13 was dominated by nitrification.

Appendix B – Supplementary materials for Chapter 4

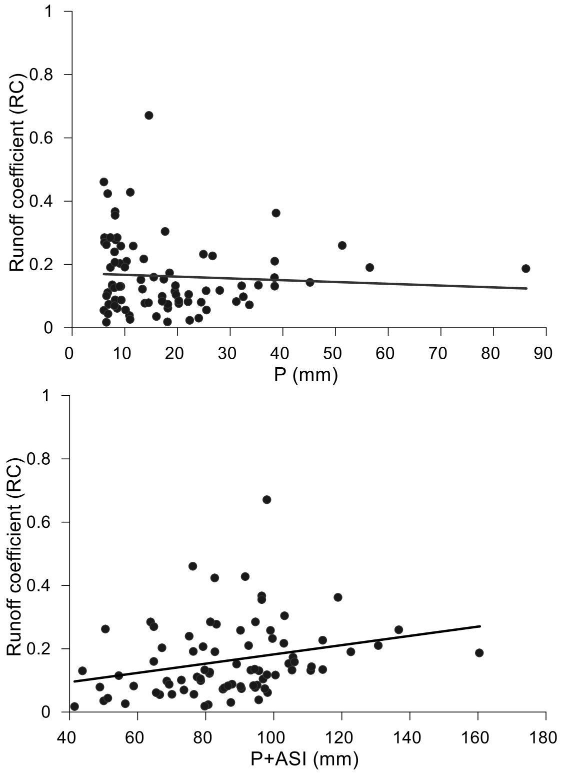

Figure B. 1 Relationship between P and P+ASI with runoff coefficient (RC)

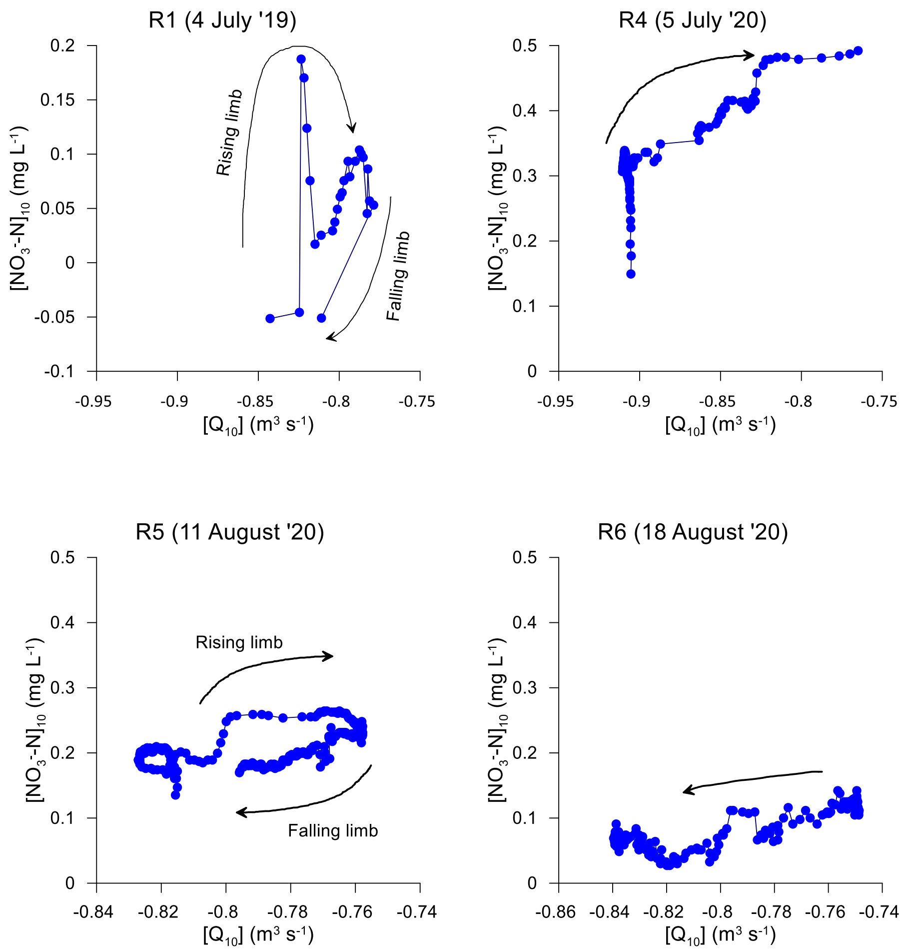

Figure B.2 Examples of nutrient concentration and hysteresis behaviour during winter events. The arrows show the direction of hysteresis. Nitrate–N concentration data for the R1 plot were derived from laboratory analysis, whereas R4 – R6 was based on ISE nitrate probe measurement. Note that the axes scales vary between events.

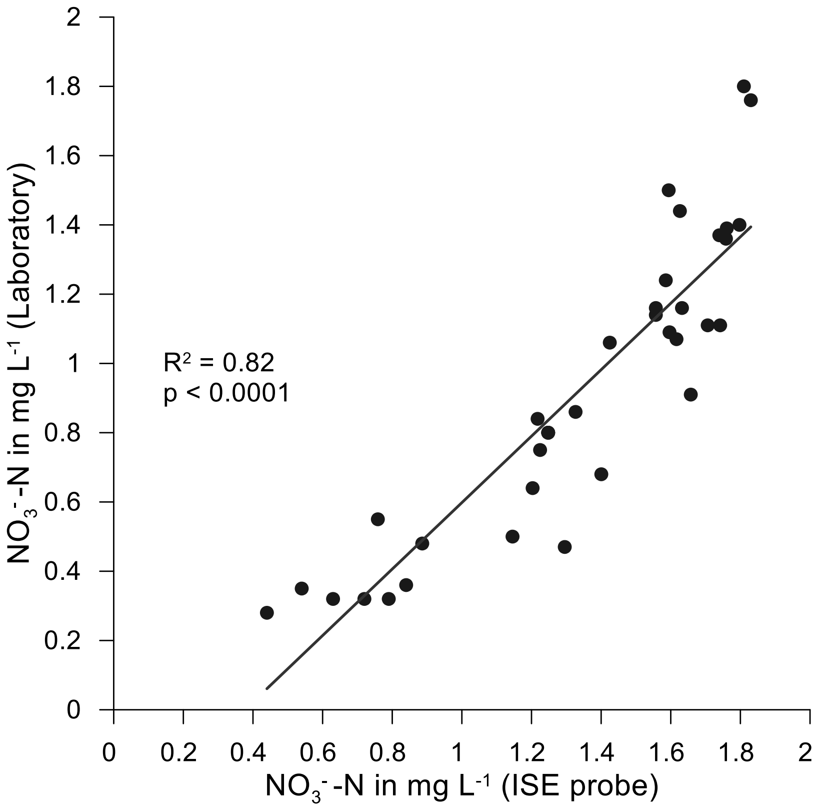

Figure B.3 Comparison of nitrate ISE probe measurement in the field and analysis results in laboratory.

Table B.1 Pre-event and event water contribution based on isotope hydrograph separation (IHS) analysis.

Rain event (R)	Date	P+ ASI (mm)	Pre-event (%)	Event (%)
		Above threshold		
1	4–Jul–19	160.42	66	34
4	5–Jul–20	106.07	62	38
5	11–Aug–20	98.17	86	14
		Below threshold		
2	17–Dec–20	90.26	55	45
3	3–Jun–20	64.74	91	9
6	18–Aug–20	95.11	69	31
7	24–Nov–20	86.53	83	17

Appendix C – List of published conference abstract arising from materials in this thesis

Yulianti, M., Baisden, W.T, Murray, R.H., and Eyberg, C.E. 2020. How a small pastoral cacthment respond to variation of storm events. *In: the joint 2020 conference of the New Zealand Hydrological Society, the New Zealand Rivers Group and the New Zealand Fresh Water Sciences Society: Weathering the storm*. Invercargill, New Zealand. 1 – 4 December 2020.

Yulianti, M., Baisden, W.T, Murray, R.H., and Eyberg, C.E. 2021. Identifying mechanisms of nitrogen excess across a threshold during rain events in a pastoral lake catchment. *In: 35th Congress of the International Society of Limnology: Biodiversity and ecosystems services for healthy rivers, lakes and humans.* Republic of Korea. 22 – 27 August 2021.

Baisden, W.T., **Yulianti, M.**, Murray, R.H., Clinton Rissmann, C., Eyberg, C.E., and Clough, T.J. 2021. Quantifying the potential to reduce excess nitrogen flows within pasture–based agricultural systems in Aotearoa New Zealand: designing isotope tools. *In: AGU Fall meeting.* New Orleans, United States. 13 – 17 December 2021.

Yulianti, M., Deniz Özkundakci, D., Baisden, T.W., and Ridwansyah, I. 2022. Identifying control points of nitrogen excess from pastoral catchment using stable isotopes enabled with the SWAT model. *In: the 2022 International SWAT conference.* https://swatconference.tamu.edu/#/book–of–abstracts/2022–prague. Prague, Czech Republic. 11 – 15 July 2022.

Yulianti, M., Deniz Özkundakci, D., Baisden, T.W., and Murray, R.H. 2022. Nutrient export from agricultural catchments to eutrophic lake in New Zealand: insight from isotopes to inform catchment management. *In: 36th Congress of the International Society of Limnology:the next 100 years – sensing and safeguarding inland waters.* Berlin, German. 7 – 10 August 2022.

Yulianti, M., Deniz Özkundakci, Ridwansyah. I, D., Baisden, T.W., and Murray, R.H. 2022. Identifying control points of freshwater contaminants in agricultural catchment: insight from isotopes and SWAT catchment model. *In: the NZMSS and NZFSS joint conference.* Auckland, New Zealand. 21 – 24 November 2022.

Appendix D – Co-authorship forms

THE UNIVERSITY OF WAIKATO
Te Whare Wānanga o Waikato

Co-Authorship Form

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Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Sources and dominant mechanisms of land-to-water diffuse pastoral contaminants: insight from hydrochemical and isotope data

Nature of contribution by PhD candidate	Conceptualisation, data collection and analysis, interpretation, writing original manuscript preparation
Extent of contribution by PhD candidate (%)	90

CO-AUTHORS

Name	Nature of Contribution
Deniz Özkundakci	Supporting data interpretation, manuscript editing
Rachel H. Murray	Collaboration on data collection and analysis, manuscript editing

Certification by Co-Authors

The undersigned hereby certify that:

- the above statement correctly reflects the nature and extent of the PhD candidate's contribution to this work, and the nature of the contribution of each of the co-authors; and

Name	Signature	Date
Deniz Özkundakci	D. Özkundakci	22/02/2023
Rachel H. Murray	Rachel Murray	22/02/2023

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Co-Authorship Form

This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. **Please include one copy of this form for each co-authored work.** Completed forms should be included in your appendices for all the copies of your thesis submitted for examination and library deposit (including digital deposit).

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Simulating water balance and nutrient losses in a pastoral catchment using the SWAT+ model: added value of isotope data

Nature of contribution by PhD candidate	Conceptualisation, data collection and analysis, interpretation, writing original manuscript preparation
Extent of contribution by PhD candidate (%)	90

CO-AUTHORS

Name	Nature of Contribution
Deniz Özkundakci	Supporting data interpretation, manuscript editing
Iwan Ridwansyah	Collaboration on data analysis and interpretation, manuscript editing

Certification by Co-Authors

The undersigned hereby certify that:
- the above statement correctly reflects the nature and extent of the PhD candidate's contribution to this work, and the nature of the contribution of each of the co-authors; and

Name	Signature	Date
Deniz Özkundakci	[signature]	22/02/2023
Iwan Ridwansyah	[signature]	February 22, 2023