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Hydrochemical dynamics of stream following rainfall events at agricultural catchments in New Zealand

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Abstract: One of the prerequisites for efficiently managing lake water quality is reliable data regarding the quantity and quality of inflows water, mainly the export of nutrients from the catchment area during rainfall events. We investigated the dynamic characteristics of hydrochemicals concerning rainfall events in agricultural stream waters flowing into eutrophic lakes situated on the North Island's central plateau of New Zealand. We utilized isotopic composition of water (δ^2H-H_2O and $\delta^{18}O$-H_2O) and nitrate ($\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-) along with high-frequency hydrochemical data for source identification of water and nitrate during a drought period (2020). Our findings indicate that it is essential to initially grasp the fundamental mechanisms associated with rainfall events to formulate effective strategies for minimizing nutrient losses. The methodology outlined in this research integrates stable isotope hydrology with water quality monitoring initiatives, facilitating the understanding and managing the primary governing mechanisms behind diverse contaminant losses from land to adjacent water bodies, explicitly focusing on nitrates. This approach establishes a framework that can assist in devising measures for water quality improvement capable of anticipating the repercussions of substantial rainfall events more effectively.

Keywords: water isotopes, nitrate isotopes, agricultural catchment, event-based sampling, high-frequency data

1. Introduction

Although lakes constitute a minor fraction of surface water, they offer diverse ecosystem benefits such as supporting biodiversity, leisure and tourism, fisheries, hydroelectricity and climate change mitigation (Schallenberg *et al*., 2013). Nevertheless, the combined impacts of global change and human-induced factors persist in exerting environmental stress on lakes globally. A parallel trend is observed in New Zealand, with lakes facing deteriorating water quality. Specifically, around 46% of lakes in New Zealand with an area larger than 1 hectare are assessed to be in poor ecological condition, exemplifying the extent of the issue (Ministry for the Environment & Stats NZ, 2022).

The primary cause of diffuse contaminants, particularly nitrates, entering New Zealand's aquatic environment is pastoral agriculture, which stands as the predominant land use in the country (Howard-Williams *et al*., 2010). The rise in nitrate levels in New Zealand's water is notably linked to the increased application of nitrogen fertilizer in agriculture (Joy *et al*., 2022; Larned *et al*., 2020). This trend aligns with a global assessment highlighting the amplified livestock farming industry as a critical contributor to freshwater contamination (Mateo–Sagasta *et al*., 2017). Hence, lakes situated in catchment

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areas primarily characterized by pastoral land use often exhibit inferior water quality, a pattern observed in various studies, including those by Abell *et al*. (2010) and Verburg *et al*. (2010). Statistical data reveal a disproportionate contribution to nitrogen loads from livestock farming land, equivalent to 6.8% of the total land area but accounting for 37% of nitrogen loads. This underscores pastoral land as the primary source of land-based nitrogen in New Zealand (Elliott *et al*., 2005). Given the significance of agriculture to the national economy, addressing contaminant export necessitates finding mutually beneficial solutions that preserve agricultural production and profitability while upholding ecosystem function.

Studying water quality at the catchment level is increasingly complex due to the substantial surface runoff, accompanied by elevated levels of leached nutrients, discerned during specific meteorological conditions, such as rain events. Various studies, including those by Kozak *et al*. (2019), Arnell *et al*. (2011), and Tomer *et al*. (2010), have indicated that contaminant transport to the aquatic environment is heightened during rain events with increased discharge, leading to the identification of stormflows as hot moments (Wey *et al*., 2022; Sigler *et al*., 2020; McClain *et al*., 2003). Despite this recognition, questions persist regarding which rainfall characteristics contribute significantly to nitrate export. Therefore, it is crucial to comprehend the mechanisms controlling the generation of runoff from rainfall, particularly when considering nutrient management in catchments, as highlighted in studies by Kirsch (2020) and Monaghan *et al*. (2016).

Numerous investigations have focused on the hydrologic response of catchments to particular rainfall occurrence, such as those by Pavlin *et al*. (2021), Saffarpour *et al*. (2016), and Detty & McGuire (2010), or have reported on the impact of rainfall characteristics on runoff quantity and quality, as seen in studies by Sapač *et al*. (2020), Lintern *et al.* (2018), and Macrae *et al*. (2010). However, there are existing knowledge gaps regarding the relationships between hydrological responses, various rainfall events, and the reasons for variations in nutrient loads, particularly in pastoral catchments that contribute to lake inflows (Levine *et al*., 2021; Abell *et al*., 2013; Menneer *et al.,* 2004). Consequently, to enhance water quality in both inflows and receiving lakes, it is imperative to comprehend the dynamic nature of contaminant loading within the context of changing hydrological patterns.

Identifying and quantifying nutrient export to receiving waters is challenging due to the complex nature of terrestrial and in-stream biogeochemical processes. Relying solely on concentration data, as Barnes & Raymond (2010) emphasized, is insufficient. Using isotope data proves valuable in elucidating the pathways and occurrences of hydrogen and oxygen isotopes in water on a more comprehensive scale (McGuire & McDonnell, 2007). Environmental isotopes, including hydrogen, carbon, nitrogen, and oxygen, possess distinctive characteristics (Fry, 2006; Kendall & Caldwell, 1998) that make them effective tracers for understanding the cycling of water and nutrients in the environment.

Gaining insights into the hydrological pathways through which water reaches the stream is crucial for understanding flow generation and transporting soluble nutrients, particularly nitrate, from their sources. Nitrogen, primarily nitrate (NO_3^-), is a widespread concern for water quality in New Zealand (Singh *et al*., 2019; Davies-Coley, 2013). The use of isotope tracers for water ($\delta^2H–H_2O$ and $\delta^{18}O–H_2O$) offers a valuable initial indication of the origins, flow paths, and biogeochemical transformations of water contaminants, as discussed by Jung *et al*. (2019) and Abbott *et al*. (2016). In hydrologic studies, stable isotopes of water, along with hydrograph separation techniques, have been extensively employed to distinguish "old" (uniform) water from the more variable "new" water or the processes that gave rise to them, owing to their unique isotopic compositions. This approach has been utilized for an extended period, as demonstrated in studies by Li et al. (2020), Richey et al. (1998), and Sklash & Farvolden (1979). For instance, precipitation (representing new water) that initiates runoff often exhibits isotopic differences from the water already present in the catchment (representing old water), as observed in studies by Tan *et al.* (2021), Boutt *et al.* (2019), and Pionke & DeWalle (1992).

Isotopic tracers of nitrate are widely acknowledged as a highly promising tool for investigating the transport and destinations of nitrate. The isotopic composition of N in nitrate, expressed as $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ in per mil (‰), serves as distinctive markers enabling the differentiation of various sources and associated processes of nitrate, including atmospheric N_2, soil, chemical fertilizers, and nitrification (Xue *et al.*, 2009). Isotope nitrate values exhibit significant variations between nitrogen fertilizers (typically close to or <0 ‰) and animal waste (generally > 10‰) (Nestler *et al.*, 2011; Xue *et al.*, 2009; Kendall, 1998) as well as between the isotopic composition of nitrate from precipitation and nitrate generated through nitrification (Kendall *et al.*, 2007). Consequently, the stable analysis of nitrate in water is the predominant tool employed to discern nitrate sources and estimate their contributions to the enrichment of freshwater with nitrate (Voss *et al.*, 2006; Wassenaar, 1995).

The motivation for this study stems from concerns about contaminant loading and its effects on the trophic status of a lake, chosen as a representative case for in-depth examinations of the hydrological processes influencing nutrient losses to freshwater originating from pastoral agriculture. This research advances our comprehension of the role of runoff in agricultural catchments. It furnishes detailed insights into nutrient-enriched lakes in the Central Plateau of the North Island, New Zealand.

2. Materials and Methods

2.1 Study areas

This research was conducted in the Bay of Plenty region situated on the North Island of New Zealand, as illustrated in Figure 1. The study focused on two sites within the Te Arawa Lakes Catchment, specifically Ōkaro and Ngongotaha. The Lake Ōkaro catchment, which feeds into the eutrophic Lake Ōkaro, has been extensively examined in previous studies (e.g., Santoso *et al.*, 2021; Özkundakci *et al.*, 2010; Forsyth *et al.*, 1988), and its inflow catchment has been well-characterized (Hudson & Nagels, 2011; Özkundakci *et al.*, 2011). Lake Ōkaro has established targets for enhancing its trophic state as per Environment Bay of Plenty (2006), particularly in a region where lakes may be partially nitrogen-limited (Abell *et al.*, 2010). The Lake Ōkaro catchment has been a significant source of nutrient inputs to Lake Ōkaro, leading to frequent algae blooms in spring and summer (Paul *et al.*, 2008). Consequently, Lake Ōkaro stands as the most eutrophic among the Rotorua Te Arawa Lakes, rapidly progressing in eutrophication (Özkundakci, 2011; Wood *et al.*, 2009). The other site investigated in this study was the Ngongotaha stream catchment. These one of nine major stream tributaries flows into Lake Rotorua, a sizable eutrophic and polymictic lake located in the Bay of Plenty Region of New Zealand. The water condition in Lake Rotorua has deteriorated since at least the 1960s, primarily attributed to an excess of nutrient input, leading to eutrophication, undesirable algal blooms, and a prioritized need for remediation (Abell *et al.*, 2013). Both catchments are predominantly characterized by pastoral agriculture, with areas comprising approximately 72% and 51% relative to the catchments for the Lake Ōkaro catchment (3.98 km^2) and Ngongotaha stream catchment (60 km^2), respectively.

2.2 Water sampling and analysis

This study was focused on understanding hydrochemical dynamics during rainfall events; thus, event-based samplings were conducted at two sites coinciding with winter events in July 2020. Water samples were collected utilizing a Manning VST portable vacuum sampler (Manning Environmental Inc, USA). The autosamplers were configured to operate at 1-h intervals, ensuring the rising and falling limb hydrograph coverage. To capture baseflow conditions, further discrete samples were obtained once in pre– and post–rain event periods. Precipitation samples were collected over a year (2019 – 2020) using free-evaporation bucket containers to develop a Local Meteoric Water Line (LMWL) for each site.

Before collecting samples, freshly acquired containers were washed with water from the sampling location. The sample containers and hoses of the autosampler underwent an acid-washing procedure using 10% nitric acid, followed by rinsing with high-quality deionized water prior to deployment. Following retrieval, water samples were subjected to filtration using a 0.45 µm cellulose-acetate membrane to assess dissolved inorganic nitrogen (DIN) and isotopes. Unfiltered samples were also obtained to assess total nitrogen (TN). The transported water samples were kept at a low temperature on ice during transportation to the laboratory, where they were promptly stored at four °C until subsequent analysis. The analysis encompassed the determination of nitrite–N (NO2—N) and nitrate–N (NO_3^-–N) as total oxidized nitrogen using a flow injection analyzer based on an automated cadmium reduction method (APHA 4500, modified 23rd ed. 2017). Nitrite–N was analyzed based on automated azo dye colorimetry. Thus, nitrate–N was calculated from total oxidized nitrogen minus nitrite–N. Total Kjeldahl Nitrogen (TKN) was analyzed based on the colorimetric method. Total nitrogen concentration was determined by adding the values for TKN, NO_2^-–N, and NO_3^-–N.

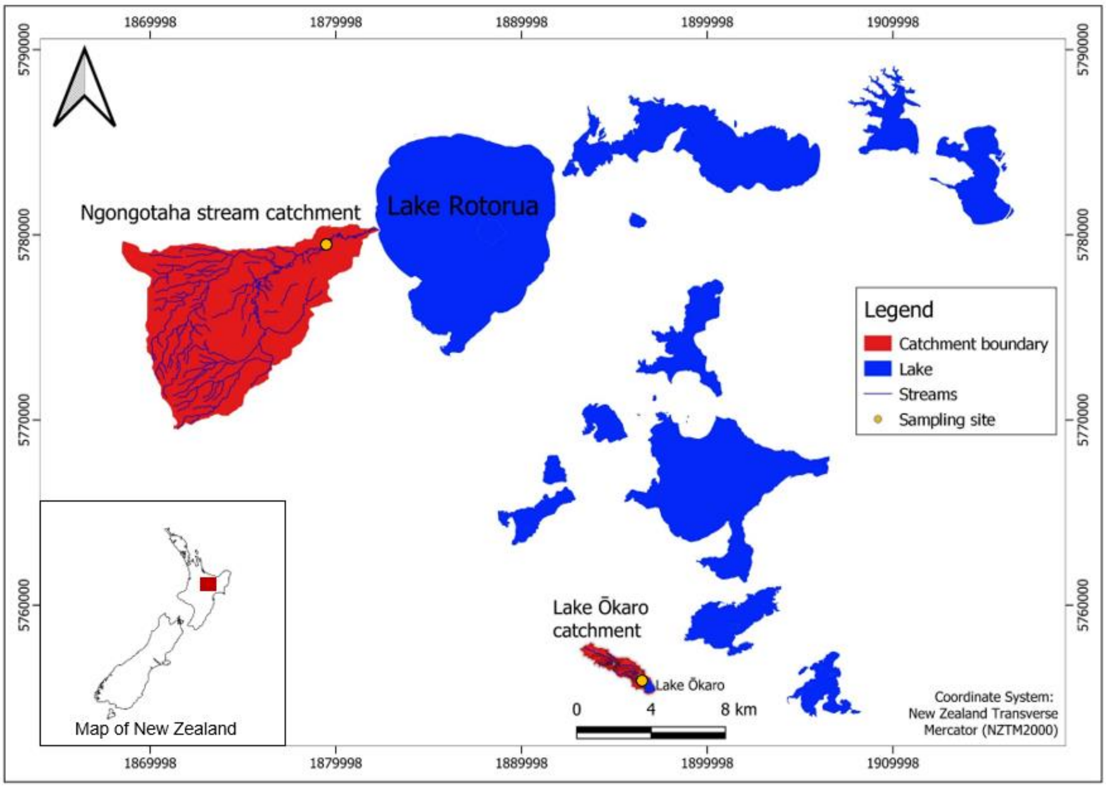

Figure 1. Map of study areas situated in a complex of Te Arawa Lakes, Rotorua, Bay of Plenty Region

2.3 Isotope analysis

Water samples underwent analysis for stable water isotopes, specifically oxygen ($\delta^{18}O$–H_2O) and hydrogen (δ^2H–H_2O). The isotopic compositions of the water samples, contained in 2 mL glass vials, were measured using a Los Gatos Research (LGR) TIWA laser spectrometer. The reported isotope ratios are presented in per mil (‰) relative to VSMOW–SLAP, referencing 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‰), which were previously calibrated with VSMOW2 ($\delta^{18}O$ = 0‰ and δ^2H = 0‰) and GRESP (δ^2H = –257.8‰, $\delta^{18}O$ = –33.39‰) international reference standards. Following the method described by Wassenaar *et al.* (2008), isotopic values were determined by averaging the last four out of seven injections to minimize memory effects. The analytical uncertainty, selected through an IAEA Water Stable Isotope Intercomparison test

(Wassenaar *et al.*, 2021), was approximately 0.2‰ and 0.09‰ for δ^{2}H and δ^{18}O, respectively. Additionally, an orthogonal regression analysis was employed to establish Local Meteoric Water Lines (LMWLs, IAEA, 1992), which were then compared to the Global Meteoric Water Lines (GMWLs, Craig, 1961) in a conventional δ^{2}H versus δ^{18}O diagram.

Nitrate stable isotopic composition (δ^{15}N and δ^{18}O) was examined at the National Isotope Centre (GNS Science) using the cadmium-azide method outlined in Wells *et al.* (2015). All results are reported to AIR for δ^{15}N and VSMOW for δ^{18}O, normalized against the international standards; USGS 34 (-1.8‰ for δ15N and -27.9‰ for δ18O), IAEA-NO3 (4.7‰ for δ15N and 25.6‰ for δ18O) and internal standard; KNO3b (10.7‰ for δ^{15}N and 11.7‰ for δ^{18}O). The analytical precision of these measurements is reported as 0.3‰ for both δ^{15}N and δ^{18}O.

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2.4 Additional data

Information regarding rainfall, soil moisture, and flow was obtained from the environmental data portal of the Bay of Plenty Regional Council (BoPRC) (https://envdata.boprc.govt.nz/Data). The recording of continuous data (15-minute intervals) of electrical conductivity (EC) and water level was conducted using a digital Mayfly data logger station developed by Stroud Water Research Center (Hicks et al., 2015; Hund et al., 2016). Water level measurements were transformed utilizing the rating curve established from each study area supplied by BoPRC.

3. Results and discussion

3.1 Hydroclimatic characteristics

The Lake Ōkaro catchment recorded an annual rainfall of 1250 mm, while the Ngongotaha stream catchment experienced a higher average of 1519 mm. The year 2020 was characterized as a drought year with an arid summer, deviating from the typical hydrological pattern of the Rotorua area. Notably, the rainfall distribution did not strictly adhere to seasonal patterns. Although substantial precipitation events usually occur in winter (June to August) and autumn (March to May), 2020 exhibited an interesting deviation with more intense spring rainfall.

By comparing the two sites, it was found that there was a difference in discharge patterns during the year 2020. The hydrograph at Lake Ōkaro catchment has more peaks and is flashier in response to rainfall. The hydrological characteristics of two catchments can differ markedly because of factors both natural and anthropogenic, including their size, topography, land use, and soil properties (Lei *et al.*, 2021; Stephens *et al.*, 2021; Omer *et al.*, 2020). Understanding these differences is crucial for efficiently managing water resources, preserving the environment, and promoting sustainable development in each catchment. Additionally, assessing the impact of anthropogenic changes on the catchment's hydrology can provide insights into potential areas for mitigation and sustainable water resource management.

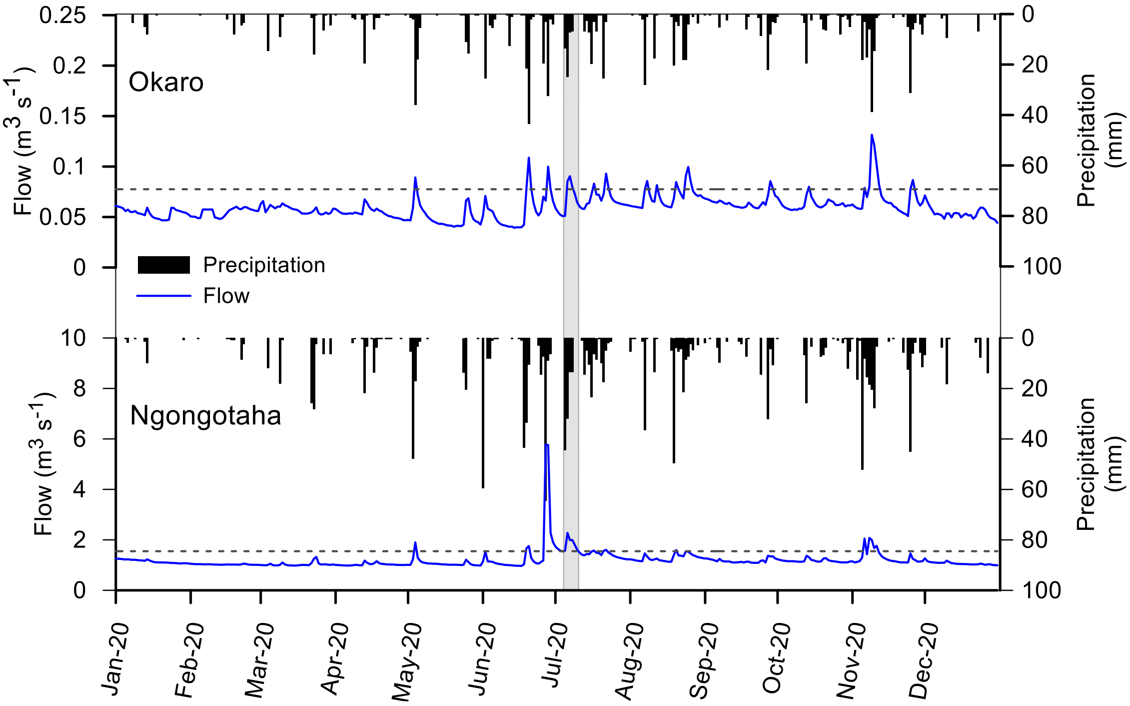

Figure 2. Daily rainfall and flow in the Lake Ōkaro and the Ngongotaha stream catchments during 2020. The shaded area indicates the event-based sampling examined in this study. The dashed line indicates the 95th flow percentile of flow.

3.2 Isotopic compositions related to rainfall events

Figure 3 shows the biplot of the isotopic composition of precipitation sampled during 2020 and stream water during July 2020 rainfall at the study areas. Rainfall δ^2H values spanned –67.9 to –4.8‰ and δ^{18}O spanned -9.81 to -1.91‰ for the Lake Ōkaro catchment. Meanwhile, for the Ngongotaha stream catchment, isotope values spanned –47.5 to –7.5‰ and –7.5 to –4.98‰ for δ^2H and δ^{18}O, respectively. This dataset reveals a seasonal fluctuation in rainfall's water isotope values. Winter exhibited the lowest δ^2H values, while the highest values were observed in summer. The LMWL trend, with a more downward slope and intercept of relative to GMWL, indicates additional evaporation following rainfall. However, it is important to acknowledge that the study period of the rainfall observation period is insufficient for constructing an LMWL, making it potentially unrepresentative of long-term precipitation patterns.

Figure 3 also illustrates that stream water samples were dispersed around LMWL, suggesting a relatively significant influence of δ^2H and δ^{18}O from rainwater. This influence was particularly evident during elevated runoff after rainfall events, indicating that the stream exhibited isotopic depletion and reflected the characteristics of recent precipitation. This observation aligns with the finding of Birkel *et al.* (2012), indicating that stream isotope values during increased streamflows exhibited fluctuations in the same direction as water isotope in precipitation. Similarly, von Freyberg *et al.* (2018) investigated temporal variations in water isotopes in stream water and rain, revealing that high-flow periods characteristically have elevated fractions of recently derived water from precipitation origins (new water).

In general, the isotopic compositions of nitrate within stream water from samples during the event ranged from 3.19 – 6.52‰ to δ^{15}N and –3.31 – 025‰ for δ^{18}O in the Lake Ōkaro catchment. In the Ngongotaha stream catchment, the corresponding ranges were from 2.38 – 5.09‰ for δ^{15}N and –5.98 – 3.63‰ for δ^{18}O. Typically, more depleted isotopic values of nitrate–N were noted during events than baseflow isotope values (Figure 4). Baseflow values were characterized by lower concentration and δ^{15}N–NO_3^- within the range associated with soil nitrogen-dominated sources (Xue *et al.*, 2009). Potential sources shifted from soil nitrogen to urine-urea sources during rainfall, as indicated by relatively depleted (≤ 4‰) nitrate isotopic composition.

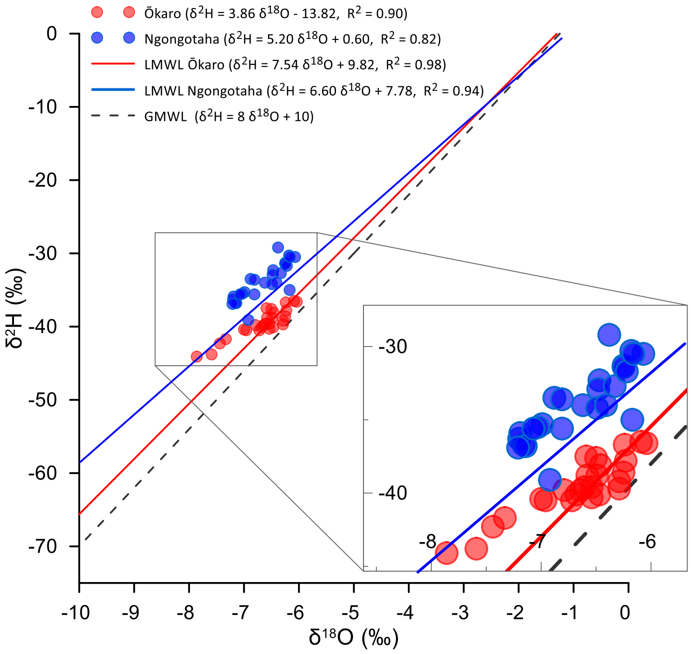

Figure 3. The distribution of stable isotopes in stream water for Lake Ōkaro and the Ngongotaha stream catchments is depicted. Regression equations and symbols are color–coded based on their association with the source of water samples. GMWL represents the global meteoric water line, and LMWL represents the local meteoric water line.

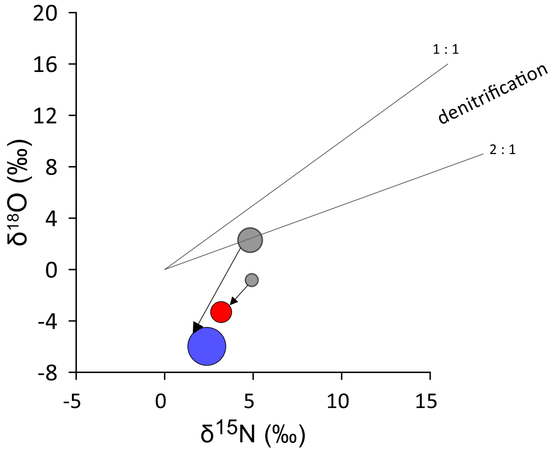

Figure 4. The plot of δ18O versus δ2H illustrates changes in nitrate isotopes from base flow (represented by a grey circle) to peak flow (represented by a colored circle) during rainfall events in July 2020. The red circles denote the Lake Ōkaro catchment, and the blue circles represent the Ngongotaha stream catchment. The movement along a 1:1 or 2:1 enrichment line suggests denitrification (solid line, Granger et al., 2008), referring to the stoichiometry of the reaction of nitrate that is reduced to nitrogen gas, indicating the molar ratios of nitrogen compounds involved in the denitrification process. The bubble size shows the proportion of nitrate–N concentrations in water samples ranging from 0.5 – 1.8 mg L-1.

3.3 Variation in hydrochemistry during events

The investigation into the variation in nitrogen concentration during the observed rainfall event yielded insightful findings. The hydrograph and chemograph overlay illustrated a lag time between rainfall initiation and corresponding peaks in nitrogen-related concentration, shedding light on the intricate dynamics of nitrogen mobilization within the watersheds (Figures 5a and 5b). Events in Ōkaro and Ngongotaha displayed slightly distinct responses during the ascending portions of the hydrograph; however, they exhibited comparatively similar trends during recession limbs following the end of rainfall. The peak flow in Ngongotaha was lagged of Ōkaro. Analysis of water isotope analysis indicates that augmented rainfall contributes to streamflow, particularly in instances of increased precipitation and wet antecedent hydrological conditions.

A discernible alteration in the concentration of N species coincided with the flow rising during rainfall events, emphasizing the complexity of nitrogen transformations during hydrological events. The data exhibited a nuanced temporal pattern in both sites, showcasing fluctuations in nitrogen concentrations and predominant TN compound throughout the event. Total nitrogen (TN) concentration ranged from 0.61 to 2.6 mg L^{-1} and 1.14 to 3.4 mg L^{-1} for the Lake Ōkaro and the Ngongotaha stream catchment, respectively. Overall, nitrate–N constituted the major portion of total nitrogen in stormflow in the Ōkaro site (50.44%) and in the Ngongotaha site (62.78%), and peaks in nitrate concentration were observed at specific intervals, especially during the rising limb of the hydrographs.

The time-series analysis of isotopic compositions of nitrate revealed dynamic shifts in response to changing precipitation patterns. Notably, a discernible increase in nitrate–N levels as flow increased coincided with the depleted values of nitrate isotopes, suggesting the potential nitrate sources for wash-off from surfaces. An apparent pattern was identified: the peak fraction of anticipated nitrate load originating from urine-urea sources coincided with the commencement of rainfall. Similar observations of depleted $\delta^{15}N$ with increased flow generation have been documented in other studies (Yue *et al.*, 2014; Kaushal *et al.*, 2011). The shift towards lighter $\delta^{15}N–NO_3^-$, coupled with relatively higher nitrate concentrations, suggests the oxidation of N–species with isotopically more lightweight compositions to nitrate (such as the nitrification of ammonium fertilizers and urine sources), as reported in other studies (e.g., Lin *et al.*, 2019).

Electrical conductivity (EC) exhibited swift reactions to the intensity of rainfall events, and the responses differed based on catchment conditions. In the Lake Ōkaro catchment, there was a rapid decline in EC during the event, indicating that the stormflow predominantly consisted of 'new' water (from rainfall), and EC returned to its pre-event level after reaching the peak of rainfall. In contrast, the event in the Ngongotaha stream catchment displayed an initial rise in stream water EC in response to the onset of rainfall.

A substantial variation in hydrochemistry between Ōkaro and Ngongotaha highlights the close connection between precipitation and stream hydrochemistry. Overall, these findings emphasize the necessity for thoroughly comprehending nitrogen's spatial and temporal patterns during rainfall events. This understanding is crucial for effective water quality management and well-informed land-use planning.

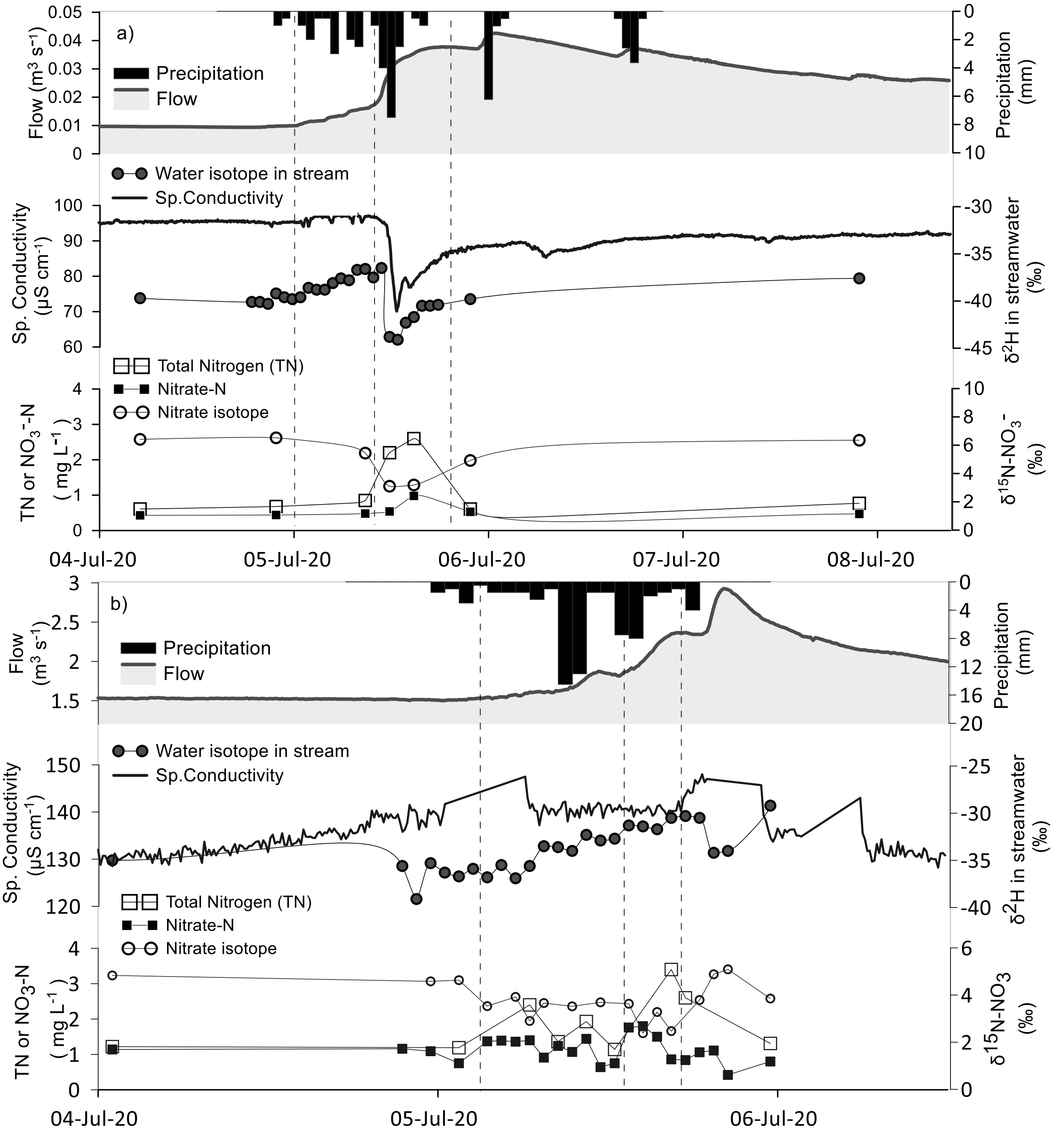

Figure 5. Temporal dynamics of hydrochemistry in July 2020 for Lake Ōkaro catchment (a) and Ngongotaha stream catchment (b). The dotted line highlights the dynamics of nitrate concentration, which increases when there is an increase in flow and decreases when the flow reaches its peak.

3.4 Implications for lake management

Understanding the processes of nutrient delivery in agricultural (i.e., pastoral) catchments is crucial for predicting and addressing excessive nitrogen (N) in surface waters (Galloway *et al.*, 2008). This study illustrates that heightened nutrient export is typically observed in wetter antecedent hydrologic conditions, primarily due to an amplified response to rainfall and elevated nutrient concentrations. This is likely a result of enhanced connectivity with the surface. The study underscores the importance of a more nuanced understanding of the influence of rainfall characteristics on the temporal dynamics of hydrochemical export in a pastoral environment. A broader implication is the recognition that rainfall and pre-rainfall conditions significantly determine nutrient export patterns.

The elucidation of the association between nitrogen concentration and runoff flow rate has advanced our comprehension of the joint influence of catchment hydrology and land use on nitrogen inputs into streamwater and downstream aquatic systems. Diverse factors, encompassing temperature shifts, alterations in vegetation structure, rate of fertilizer application, and the processes of nitrification–denitrification, have aggregated throughout all contributing flow paths (Duncan *et al.*, 2017), contribute to the complexity of nitrate concentration discharge variations (Lloyd *et al.*, 2016). The dominant controlling factor for in-stream nitrogen transformations is the seasonal variability in hydrological conditions. For example, Wong *et al.* (2018) demonstrated that nitrate concentration arising from agricultural activities exhibits significant elevation during increased precipitation.

Identifying nitrogen load peaks and their linkage to sources through intensive sampling implies the essential nature of high-resolution monitoring for a robust estimation of nutrient loads, particularly in assessing the impact of rainfall on water quality. These findings emphasize the benefits of transitioning from monthly monitoring to increased high-resolution event samplings, shedding light on the intricate relationship between rain events, catchment response, and the characterization of nitrogen loads in regions with intense rainfall on porous soils.

In cases where nitrate contamination is a concern, isotopic analysis can aid in identifying nitrate sources, providing crucial information for implementing targeted management practices to mitigate nutrient loading. This research adds to initiatives to regulate nutrient inputs and contamination control in the eutrophic lake. It emphasizes the benefits of integrating isotopic sampling into monitoring initiatives. Subsequent research endeavors focusing on the event-driven transport and transformation of nitrogen species can advance our comprehension of hydrological fluctuations and nitrogen cycling within the catchment of these eutrophic lakes. The broader significance of this study pertains to informing water quality management strategies designed to mitigate nitrogen losses from pastoral catchments. Implementing management practices to address excess nitrogen associated with urine and urea nitrogen deposition on pastures can substantially enhance water quality.

4. Conclusion

The findings from the study, which investigated nutrient dynamics in two agricultural catchments contributing to nutrient enrichment in lakes, underscore the critical role of understanding the complexities of nutrient transport during rain events. Hydrograph analysis, stable isotope tracers, and high-frequency hydrochemical data contribute to a more holistic view of nutrient transport processes. This knowledge is essential for formulating effective and timely mitigation strategies, ultimately aiding the sustainable management of agricultural landscapes and preserving water quality in associated water bodies.

Data availability statement

The data included and used in this study is not confidential and available upon request.

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Conflict of interests

The authors declare no conflicts of interest.

Author contribution

MY and **RM** contributed to data collection and analysis. **MY** wrote the manuscript and **RM** provided critical feedback and revision.

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