NITRATES IN GROUNDWATER AND IMPACTS OF CLIMATE CHANGE

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ABSTRACT

Nitrate-N[1] concentrations in groundwater (and groundwater-fed streams and rivers) are not constant over time, and even locations when concentrations are increasing or decreasing do not show a linear trend. The transport of nitrates from the land surface to a stream or other receiving water body is complex and not well understood. Changes in rainfall intensity or long-term patterns have the potential to impact nitrate leaching from the land and subsurface. High winter recharge has been found to be associated with elevated nitrate concentrations, and recent investigations in Canterbury have highlighted just how important rainfall is in terms of driving nitrate leaching. On a broad scale, the high winter recharge in the later 1970s is thought to be responsible for high nitrate-N concentrations in the 1970s in some Canterbury regions that still haven't been exceeded (Rutter and Rutter, 2018).

The potential impacts of climate change on nitrate-N concentrations are broader than just the likely increase in leaching, as warmer or drier soils also affect the soil microbiology that influences the nitrogen cycle within the subsurface. Existing approaches to reduce nitrate-N leaching have focused on fertiliser or livestock management. However, these have resulted in sometimes only modest reductions in nitrate-N losses (Bowles et al., 2018). There is increasing evidence that climate change will influence agricultural management and plant–soil–microorganism interactions and subsequently the nitrogen cycle processes, limiting the benefits of common practices to reduce nitrate-N losses.

To understand the nature of climate change impacts on groundwater nitrate-N concentrations, three areas need to be addressed:

1. Source: What are the likely changes to agricultural practices and how may these affect nitrate-N leaching from the soil zone?
2. Pathway: What are the likely changes to groundwater recharge mechanisms and groundwater levels?
3. Receptor: What are the likely changes to nitrate-N concentrations in groundwater and the consequential impact on groundwater receptors?

This paper primarily focuses on the pathway, and the impacts that climate change may have on that. However, it is important to also consider the source and receptor components.

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[1] Nitrate concentrations are referred to as nitrate-N (the nitrogen part of the nitrate compound). Drinking water standards have nitrate concentrations of 50 m/g as acceptable; this is 11.3 mg/l nitrate-N. The National Policy Statement for Freshwater aims for a "bottom line" of 2.3 mg/l nitrate-N.

The available data show that the transport of nitrate-N through aquifer systems is complex and not well understood. The rapid response to rainfall, even at considerable depth, shows that contaminants can be transported very rapidly. With more extreme rainfall events under climate change, there could be more opportunity for greater losses of nitrate-N from the root zone and into the groundwater system.

Although their transport mechanisms are somewhat different, microbes can get transported with the rapidly recharging water and have very obvious and immediate health risks. This is supported by recent sampling post-July 2022 that has shown increased exceedance of microbes in groundwater.

This paper will present data from recent sampling and monitoring to assess the impacts of long term rainfall and extreme events on nitrate-N concentrations. The potential implications in terms of our understanding of nitrate sampling results and trends will be discussed, and further research needs will be identified that will add to our understanding of nutrient transport.

KEYWORDS

Nitrate; groundwater; climate change

PRESENTER PROFILE

Dr Helen Rutter is a Principal Hydrogeologist with Aqualinc Research Ltd, having over 25 years' experience working in hydrogeology in the UK, Botswana, and New Zealand. She has in-depth understanding of physical hydrogeology, including resource assessment, recharge processes, groundwater flooding, catchment characterisation, geology and geochemistry. She has carried out extensive research into the hydrogeological impacts of the Canterbury Earthquake Sequence, including a Marsden-funded research project. She has an increasing interest in water quality and transport of nitrates through groundwater. She is also involved in developing methods to delineate source protection zones for drinking water supplies.

1. INTRODUCTION

Globally, humans add approximately three times more reactive nitrogen to terrestrial ecosystems than natural sources (Bowles *et al.*, 2018). However, nitrogen added to pasture and crops is not all taken up by plants and much is lost with wide-ranging impacts across different scales. The trade-off between agricultural production and adverse effects is complex, dynamic and spans interacting biophysical, technical, social and economic elements. For example, reducing stocking density to minimise nitrate losses has a potential economic consequence, but consequences of excess nitrogen in surface waterways or drinking water have wide-ranging potential impacts on biodiversity, recreation and health.

The losses from intensive agriculture occurs for many reasons, including spatial and temporal mismatches between fertiliser application and crop nitrogen demand, surplus fertiliser application, high stock numbers (and the ubiquitous urine patches that come with this), low water-holding capacities for water in some soils (particularly stony soils) and challenges predicting and managing soil nitrogen mineralisation. Even when everything else is optimised, factors that limit crop growth can leave substantial surpluses of unused nitrogen in soils which is then potentially available for leaching.

In order to understand groundwater nitrate-N concentrations, three areas need to be addressed:

1. Source: What are the likely changes to agricultural practices and how may these affect nitrate leaching from the soil zone?
2. Pathway: What are the likely changes to groundwater recharge mechanisms and groundwater levels?
3. Receptor: What are the likely changes to nitrate concentrations in groundwater and the consequent impact on groundwater receptors?

There are uncertainties when evaluating all of these, which makes understanding nitrate-N concentrations in groundwater a complex issue. The climate change implications for nitrate-N leaching to groundwater are even less well understood. The few studies which consider the whole nitrogen cycle show likely changes in nitrate-N range from small increases to a possible doubling of aquifer concentrations by 2100 (Stuart *et al.,* 2011). We do know that climate change will affect the hydrological cycle with changes to recharge, groundwater levels and resources, and flow processes, and that this is likely to result in a change in transport processes, both through the unsaturated and saturated zones.

This paper focuses primarily on the nitrate-N pathway, and the impacts that climate change may have on that, though it is important to also consider the source and receptor. It firstly describes the source, pathway and receptor components of nitrate transport, and then considers the potential effects of climate change.

1.1 SOURCE

The main inputs of nitrate-N to groundwater are from agricultural sources. Whilst “dirty dairying” is typically seen as the driver, other forms of agriculture are likely to contribute even higher concentrations in infiltrating water. Land use change is often seen as the solution to reduce the source loading, but changes in temperature, precipitation quantity and distribution, and atmospheric carbon dioxide concentrations can also affect the loading through changes in soil processes and agricultural productivity. This wider picture is not usually considered but adds to the complexity of understanding climate change on nitrate leaching totals.

To understand the significance of climate change to the production of nitrate-N, it is useful to have an understanding of the nitrogen cycle.

The initial step of the nitrogen cycle takes atmospheric nitrogen (N_2) and converts it into usable ammonia (NH_3). Nitrogen fixation can occur either by atmospheric fixation (by lightening), or industrial fixation through manufacturing ammonia and nitrogen-rich fertilisers. The process of nitrogen fixation is completed by symbiotic bacteria, known as Diazotrophs. Nitrite-N is formed by the oxidation of ammonia with the help of Nitrosomonas bacteria species. Later, the produced nitrite is converted into nitrate by Nitrobacter species. Plants then take in the nitrogen compounds from the soil through their roots, the most useful being nitrate.

There is also nitrogen deposited as organic matter when a plant or animal dies or urine or faecal matter is returned to the ground. This is released back into the soil as organic nitrogen. Decomposers, namely bacteria or fungi present in the soil, convert the organic matter back into ammonium which may then is converted back to nitrate.

Denitrification is the process in which the nitrogen compounds make their way back into the atmosphere by being converted from nitrate (NO_3) into gaseous nitrogen (N_2). This process occurs in the absence of oxygen. Denitrification is carried out by the bacterial species Clostridium and Pseudomonas, which process nitrate to gain oxygen and produce free nitrogen gas as a by-product.

Clearly, the nitrogen cycle processes all involve soil bacteria, and one emerging concept is that prolonged drought periods can affect the viability of the soil biota. Rupp *et al.* (2021) observed that after drought conditions, reoccurrence of seepage was associated with exceptionally high nitrogen concentrations and leaching losses, which exceeded the drinking water limits by many times and posed a significant risk to water quality. They had observed in several studies (e.g. Werisch *et al.*, 2021) that excess nitrogen was immobilised in the soil organic nitrogen pool where it was later mobilised again depending on mineralisation conditions. Rewetting after droughts caused reactivation and rapid growth of microbes, and mineralisation and mobilisation of accumulated nitrogen, resulting in enhanced nitrate leaching.

Bowles *et al.*, (2018) observed that existing approaches to reduce the nitrate source, which have focused on fertiliser or livestock management, have provided only modest reductions in nitrogen losses. They considered that there is increasing evidence that the interaction of climate with agricultural management and plant–soil–microorganism interactions affect nitrogen cycle processes, limiting the benefits of common practices to reduce nitrogen losses.

1.2 PATHWAY

Precipitation and soils moisture are also the primary drivers of losses through leaching. Hence, changing climate is likely to have an impact on nitrate loss from soils.

Physical transport of nitrate through the soils and groundwater are poorly understood, especially in highly heterogeneous media (such as the Canterbury Plains alluvial gravels, which constitute up to around 500m of gravel, sand and silt). This type of sediment has been deposited by braided rivers and glacial outwash, and flow and transport through them is dominated by open framework gravels (OFG) that are believed to account for up to 98% of the flow (Dann *et al.,* 2008). There is much slower flow and transport through the vast majority of the aquifer thickness which has a finer-grained matrix. Dann *et al.* (2008) suggested that flow velocities would be in the order of 100 m/d through the OFGs.

The consequence of this is that solutes can be transported rapidly through the OFGs, but a solute breakthrough curve would show a very long tail, as the slower-moving parts of the system continue to contribute at the measurement point.

A recent study by Environment Canterbury (ECan, 2023) provides evidence for rapid transport of nitrate-N, suggesting that the impacts of land use intensification might be observed quite rapidly. However, due to the variable flow and transport pathways, the reverse (that is, improvement in water quality) could take a long time to occur.

1.3 RECEPTOR

Even without climate change, changes in the nitrate source and the complex transport pathways will result in variable nitrate-N concentrations at a receptor (such as groundwater, surface water and groundwater-fed wetlands).

Groundwater flow paths vary greatly in terms of travel time from the point of recharge to a receiving water body (see Figure 1), and this can complicate the interpretation of observations.

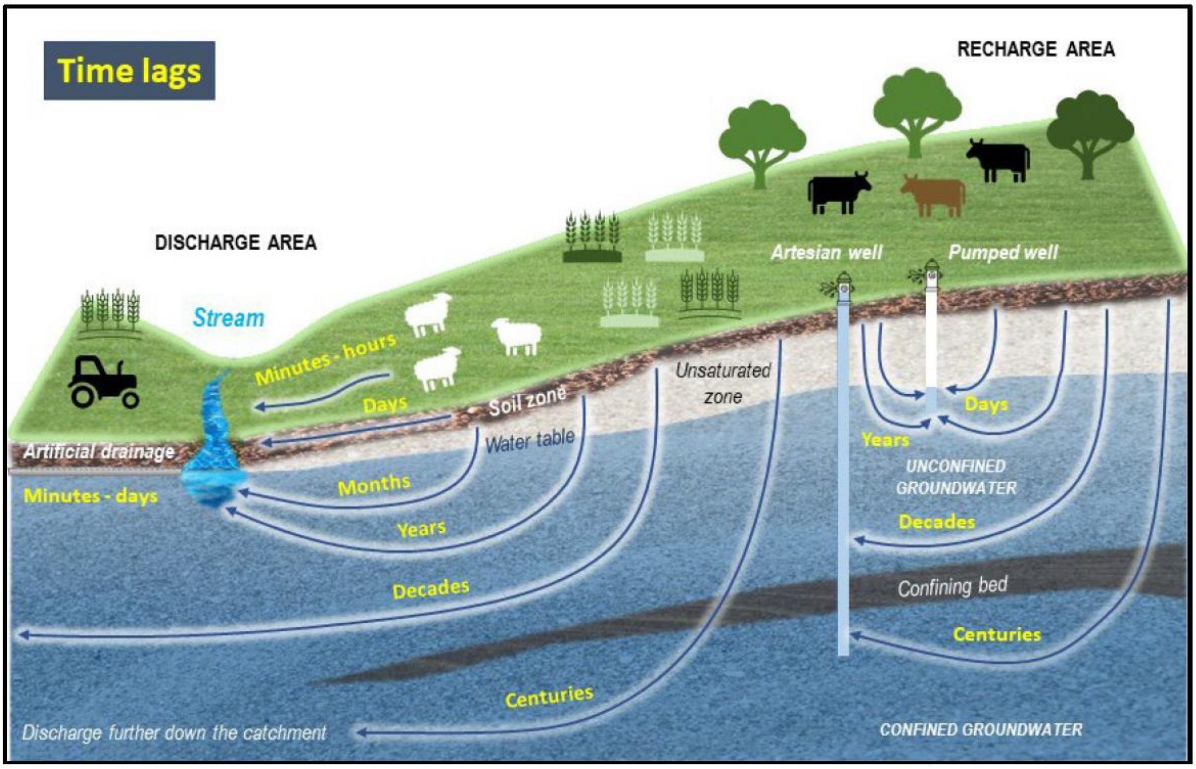

Figure 1. Groundwater flow paths and travel times (reproduced from ECan, 2023).

2. POTENTIAL CLIMATE CHANGE IMPACTS ON NITRATE TRANSPORT

Groundwater recharge is not only controlled by the spatial and temporal variability of climate but also on land surface properties, the depth and hydraulic properties of the soils, and vegetation. Climate change may have both positive and negative impacts (Jyrkama and Sykes, 2007). For example, increased precipitation leads to increased groundwater recharge (and subsequent raised groundwater levels); decreased precipitation leads to decreased recharge and falling water levels. Eckhardt and Ulbrich (2003) also predicted pronounced changes in the annual cycle of streamflow and groundwater recharge influenced by changes in the pattern of snowmelt. Stewart *et al.* (2011) suggested that the result of climate change, in general, is an enhanced contrast between winter and summer patterns. There may be also changes in the amount of runoff relative to recharge due to loss of permeable soils during periods of ground saturation.

Soil moisture depends on a balance between precipitation and evapotranspiration, and the winter period when soils are at field capacity is when most recharge is likely to occur. A change in agricultural land use (including irrigation) may also change soil moisture and associated recharge.

In many areas, the distribution of precipitation, temperature and other climate factors under climate change have changed (or will change). This has influenced rainfall amounts and intensity and temperatures, and therefore recharge and nitrate-N fluxes. In addition, both temperature and precipitation affect various ecosystem and soil processes that influence nitrate leaching, such as:

- Temperature influences both nitrogen mineralisation and plant growth; and
- Precipitation stimulates both soil water fluxes and nitrogen input by biological fixation, which is linked to evapotranspiration.

Changes in the pattern and intensity of precipitation will probably exacerbate nitrate losses and concentrate them in fewer, larger pulses - or what have been called ‘hot moments’ for nitrogen loss. Wagner-Riddle *et al.* (2020) suggested that hot moments caused by rewetting may increase post-event rates up to 4,500-fold and 1,000-fold compared to pre-event rates, respectively, and may last from a few days to a month. Greater frequency of large precipitation events may accelerate nitrate leaching, and based on data available for New Zealand, there is some evidence that this does occur.

For the east coast of New Zealand, a predicted warmer climate will intensify the hydrological cycle and is expected to increase precipitation extremes with more intense but less frequent rainfall. For Canterbury for example, predictions suggest an overall decrease in recharge and a subsequent lowering of groundwater levels, plus due to increased winter rainfall, likely enhanced seasonal variations in groundwater levels. The shifts in precipitation patterns may be at least as prevalent as changes in precipitation amounts. For instance, reduced summer rainfall, together with higher air temperatures, could establish droughts faster and with greater intensity. Shifts in precipitation patterns and rainfall will alter soil moisture dynamics and plant productivity, with potentially important but largely unknown feedbacks to plant–soil nitrogen cycling and losses.

It is likely that with the increase in temperature and decrease in summer precipitation that irrigation will need to increase. The increase in soil moisture caused by irrigation may mean that extreme rainfall events result in more immediate infiltration.

Soils that are vulnerable to cracking may also have particular issues (such as cyclic swelling, sealing, shrinkage, and cracking) during and after rain and following dry periods. This could greatly affect the movement of water in the soil as the cracks develop deeper and rapidly transmit water to lower depths within the profile.

Increased extreme rainfall events may also change the amount of flow and transport through preferential flow paths, such as alluvial open framework gravels. Sugita and Nakane (2007) examined the effects of rainfall patterns on transport of nitrate in dual-porosity media simulated by sand with artificial macropores. They showed that the proportion of solute moving by preferential flow increased with the amount of artificial rainfall. For the Pacific region they estimated that the chance of nitrate leaching could increase by perhaps 25% due to higher frequencies of heavier rainfall events resulting from climate change. Therefore, an increase in high-intensity winter rainfall, as predicted by climate change models, could lead to increased winter preferential flow. This may lead to (at least) a seasonal increase in nitrate-N concentrations in groundwater. However, assessing the nitrogen balance overall, the impacts of increased rainfall and increased dilution on nitrate-N concentrations also needs to be evaluated.

3. OBSERVATIONS OF CLIMATE-DRIVEN CHANGES IN NITRATE-N CONCENTRATIONS

It is quite usual to see seasonal fluctuations in nitrate concentrations in groundwater, with autumn/winter recharge resulting in clear increases, and decreases in the summer. Recent investigations in Canterbury have highlighted just how important rainfall is towards driving nitrate leaching. At a broad scale, high winter recharge in the later 1970s is thought to be responsible for the nitrate-N peak in the 1970s in some Canterbury regions. Figure 2 shows the average decadal nitrate-N concentrations for the Selwyn-Waihora zone in Canterbury, with wells grouped into different depth intervals (Rutter and Rutter, 2018). The peak in shallow wells in the 1970s has not been exceeded, even in the 2010-2020 decade.

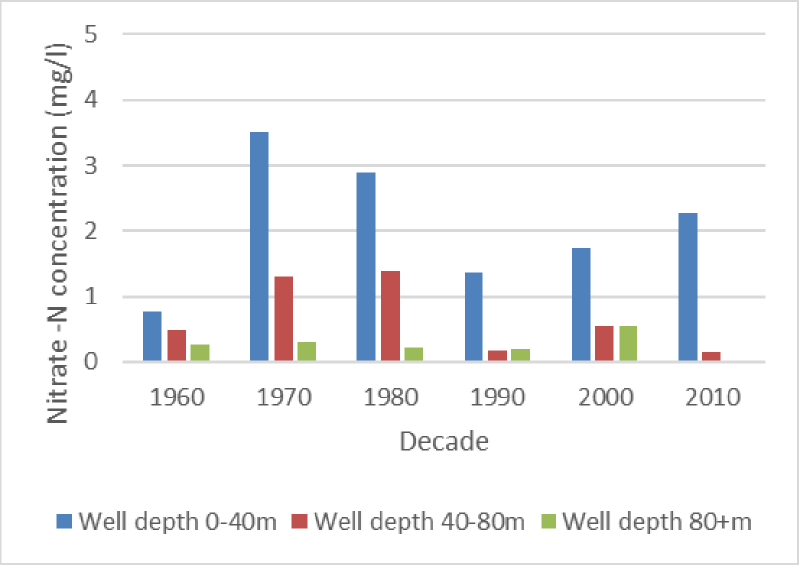

Figure 2: Average nitrate-N concentrations in wells from the Selwyn-Waihora groundwater allocation zone, grouped by well depth and decade.

From the above discussions, it is obvious that climate drivers complicate interpreting the effects of land use change and may obscure or confuse this. For example, the effects of the cessation of on-site wastewater disposal from septic tanks close to Christchurch was assessed in a local bore. Septic tanks had been used for a prolonged period of time until the late 1990s when infrastructure was put in place to pipe wastewater to Christchurch. This was thought to be partly the reason for relatively high nitrate concentrations in groundwater (see Figure 3).

In order to assess the possible improvements from piping wastewater as opposed to disposing to land, nitrate-N concentrations were compared with cumulative departure from the mean rainfall[2]. This can be used to show longer term variability in rainfall patterns. Periods where the curve slopes downwards indicate dry periods (below average rainfall), and similarly upward slopes indicate wet periods (above average rainfall). The cumulative departure from the mean rainfall (based on monthly data) was calculated from 1992 through

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[2] Cumulative departure from the mean rainfall is a concept that measures how much the actual rainfall differs from the normal or average rainfall over a period of time. It is calculated by calculating the mean, then subtracting this from each data point and adding up the differences over time to show longer term variability in rainfall patterns

to 2022, this being the period for which we had data. Figure 3 shows this together with nitrate-N concentrations in groundwater. Through the period from approximately 2000 to 2006, nitrate concentrations were relatively high, between around 8 and 12 mg/l nitrate-N during a period of below average rainfall. From 2006, nitrate-N concentrations respond to increasing rainfall with several large peaks due to winter recharge. There is then quite a marked decline in concentrations from 2013 to 2021 which was initially assumed to be due to the cessation of septic tank disposal. However, when compared with the cumulative departure from mean rainfall, it appears that, the downward trend in nitrate-N was also due to a period of low rainfall and the major rainfall events in 2017 (both April and July onwards), July 2021 and July 2022 all contributed to a reversal in the downward trend. Therefore, although there appears to be an improvement due to changing practices, the assessment of the effects of these changes is very much complicated by climate. This illustrates that the effects of climate (particularly extreme or sustained rainfall) can confuse the interpretation of the effects of land use change.

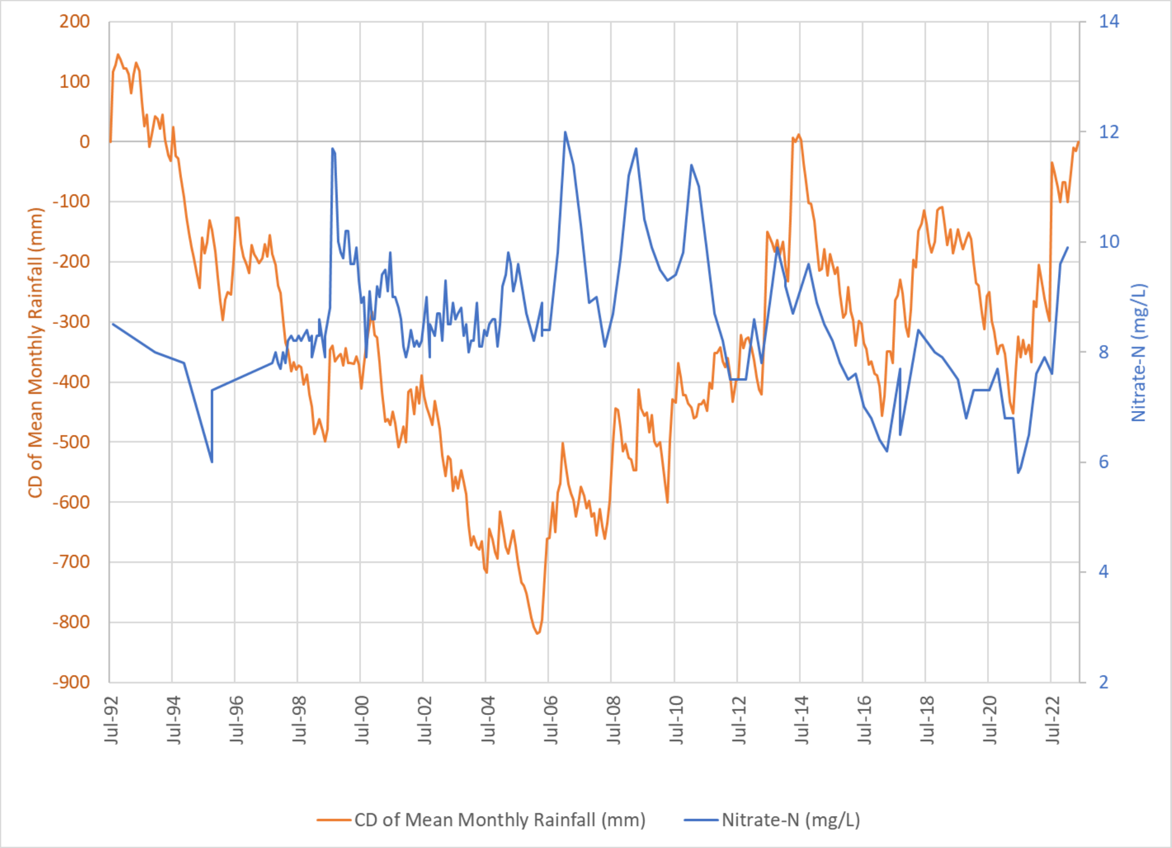

Figure 3. Nitrate concentration and cumulative departure from mean rainfall.

Continuous monitoring is now becoming more common, and what we see is providing a much greater insight into how higher resolution pulses of nitrate enter the groundwater system. Figure 4 shows nitrate data from 2020 to 2022 in a 24 m deep well near Balmoral, Canterbury. Again, cumulative departure from the mean rainfall i(based on daily data) s used to compare nitrate-N concentrations with the trends in rainfall over longer time periods. In 2021, nitrate-N concentrations rise from a baseline level of less than 1 mg/l nitrate-N to well above the 11.3 mg/l drinking water limit, but then decline again following each recharge event. This change of two orders of magnitude may be ’hot moments’ as described by Wagner-Riddle *et al.* (2020), driven by both soil biological processes following prolonged dry periods and physical recharge. Further evidence for the role of soil biology being involved is potentially provided by the fact that the first nitrate peak in 2021 (end of May/start of June) followed a rainfall event of much greater magnitude (110 mm over three days), than the later June rainfall event (38 mm over two days) but the later event resulted in a higher peak in nitrate concentration.

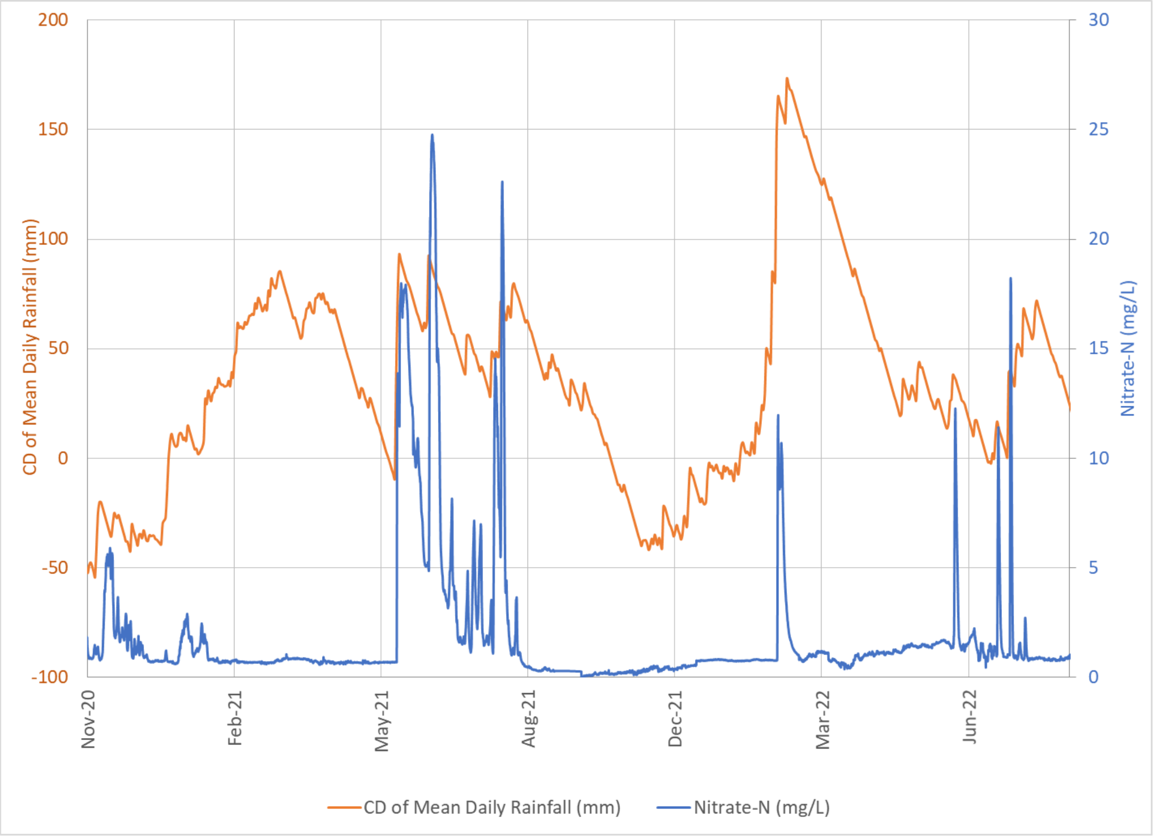

Figure 4. Water level and nitrate-N data from 2020 for a site near Balmoral Forest

This data demonstrates that, at least in some cases, the first winter recharge pulse is not responsible for leaching all of the accumulated nitrogen through the profile, but that a substantial store can remain and be leached by subsequent pulses of recharge.

It is also interesting to observe the response in February 2022, when a relatively wet period was followed by 134 mm of rain over 5 days. Although this was during summer, the prolonged rainfall was sufficient to cause a major recharge event, with a response seen in groundwater levels.. However, the concentrations observed were relatively low, possibly due to the wet summer allowing the soil microbiology to flourish, mineralise nitrogen and allow efficient uptake by plants. It may also reflect the major leaching during the previous winter, with relatively little nitrogen stored within the soil profile.

4. CONCLUSIONS

The effects of climate change on nitrate concentrations in groundwater (and subsequently in drinking water, surface waters and/or coastal waters) are hugely complex, not only due to uncertainties around the impacts of climate change but also the unknowns and uncertainties around how climate change will affect soil microbiological processes and recharge. The information available suggests that not only extreme or prolonged rainfall/recharge events will impact on the amount of nitrogen leached from soils, but that prolonged dry periods may also affect the availability of mineralised nitrate for leaching. Added to this are the complexities and lack of understanding around actual transport processes within heterogeneous media (such as the dual porosity/permeability Canterbury alluvial gravels).

The examples used illustrate the temporal variability of nitrate concentrations in groundwater and raise many issues when assessing nitrate concentration data. Observations should be considered in light of recent climate events as well as whether there have been prolonged dry periods that may have affected the soil microbiology. As research is carried out in this area, we should be able to move towards a much better understanding as to what land use change is required, and how climate change will impact on, our attempts to improve groundwater quality.

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