NITRATES: KNOWN KNOWNS AND KNOWN UNKNOWNS

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ABSTRACT

In spite of changes to date, water quality is continuing to decline, amid increasing concerns around freshwater and drinking water quality. To address this, we need effective and equitable limit-setting processes that improve water quality, enhance/restore Te Mana o te Wai, and provide drinking-water safety. However, we do not currently have a good enough understanding the amount of nitrate stored in groundwater, and the time-lags involved in its transport, which is a pre-requisite for doing this.

A recent analysis of trends in nitrate-N concentrations across Canterbury indicates that the increasing concentrations that we are now observing, are not only being driven by recent dairying, but also by much earlier land use activities. However, the exact nature of the link between land use and water quality is not clear. Across Canterbury, the impacts of historic and current land use activities on water quality in different areas are quite marked, with wells in the Ashburton zone being close to the drinking water standards of 11.3 mg/l, whereas wells under much of Christchurch have less than 1 mg/l. Nitrates started to increase in all areas prior to the boom of dairying in the late 1990s, and it may be that the full effects of dairy have yet to be seen.

We can explain some of the reasons for the variability. There are "known knowns" such as historic local land use, depth to groundwater, and influence of river recharge on groundwater quality. However, there is a lot that remains to be explained: the "known unknowns", including time lags for nitrates to move through the groundwater system, and the ability of the system to remove nitrates (the attenuation capacity). In particular, whether the natural heterogeneity of our aquifer systems is resulting in variable transport rates, with some nitrate moving rapidly, and some being a slow-moving, "load to come", the impacts of which are not yet being seen. This paper explores existing data to show what we already understand about nitrate trends in Canterbury, and assesses what further work needs to be done to start to provide councils with the answers they are going to need to address freshwater and drinking water reforms.

If we want to achieve an improvement in drinking water and freshwater quality, we need to first understand what drives nitrate concentrations and what causes their variability. This should be of increasing concern to councils, given the likely requirements of current freshwater reforms and drinking water management reform.

KEYWORDS

Groundwater; nitrate; Canterbury

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

Any agricultural intensification has the unwanted side-effect of nutrient leaching from the land surface, and whilst there has been considerable focus on improving land use management recently, it is not possible to eliminate nitrate leaching. For example, heavy rain, especially when soils are close to field capacity, will generate recharge and result in nitrates leaching into groundwater. As a result, nitrate-N concentrations have been observed to be rising in many areas, and in several cases, groundwater samples show concentrations that exceed the 11.3 mg/l nitrate-N maximum admissible value (MAV). Recent research into links with colorectal cancer risks and low birthweight babies (Schullehner et al., 2018) raises concerns that much lower concentrations could be associated with health risks. This risk is the focus of ongoing research in New Zealand (Richards et al., 2021).

The use of nitrogenous fertiliser in New Zealand 20 has increased by a factor of ten since 1985 as a result of land use becoming more intensive (Ministry for the Environment 2007). An increase in the use of fertiliser 20 to 30 years ago still affects water quality on the Canterbury Plains, due to the long lag times in the groundwater (Hayman, 2016). It is quite possible that if the present groundwater quality is an indication of the increase in fertiliser use that occurred over 30 years ago, that the NO3-N concentrations in the next 30 years could show the effects of the conversion of dryland to dairy farms. If this is the case, then the groundwater quality is likely to decline further before the results from good management are observed.

Given the relatively slow movement of water through groundwater systems, it is possible that we are just now beginning to observe the consequences of these actions.

A 2018 survey of 306 wells across Canterbury showed that around 28% of all samples had nitrate-nitrogen concentrations at or above half the maximum acceptable value (MAV) (that is, above 5.6 mg/L compared to the MAV of 11.3 mg/L nitrate-nitrogen), whilst 48% had concentrations less than 3 mg/L (Canterbury Regional Council, 2019) (*Figure 1*). However, the poorer quality groundwater was not evenly distributed with either location or depth. In terms of the zones, the number of wells with average nitrate-nitrogen concentrations exceeding half MAV in the Ashburton and Selwyn-Waihora zones were 77% and 44%, respectively. As expected, the higher nitrate-nitrogen concentrations were predominantly at shallower depths.



Figure 4: Summary of nitrate concentrations sampled in the 2018 annual survey for each CWMS zone

Figure 1. Summary of nitrate concentrations samples in the 2018 annual survey for each CWMS zone

In order to improve the current situation, we need to understand the link between land use management and transport to a receiving water body or abstraction point. In spite of many years of sampling and investigation, we still do not understand the details of nitrate transport through groundwater systems, and, as a result, regional councils struggle to understand the time lag between changing land use, and water quality improvements. There is a critical knowledge gap in understanding the transport, storage/delay and attenuation of contaminants in NZ's alluvial aquifer systems.

Our aquifers are highly heterogeneous with high permeability open framework gravels (OFGs) surrounded by much lower permeability material (*Figure 2*). The current representation of groundwater systems as simple hydraulic units is inadequate for water quality considerations. However, the measurement, conceptualisation, and use of models that take into account these processes has been seen as too difficult to date.



Figure 2. Open framework gravels within a finer-grained matrix

2 DRIVERS OF NITRATE CONCENTRATIONS IN GROUNDWATER

2.1 HISTORIC LAND USE

Dairying has been held responsible for the increase in nitrate-nitrogen concentrations that we are now seeing in groundwater and groundwater-dependent surface waters (*The Economist*, 2017; Hutching, 2018). Dairy intensification occurred post-1980s in Canterbury, with the 'take off', in terms of substantial land use change, beginning in the early 1990s (Pangborn and Woodford, 2011). However, measured nitrate-nitrogen concentrations do not necessarily fit well with these observations, and earlier land management (cropping, point source discharges from meat works, or other sources) must also have played a role in the increase observed in nitrate-nitrogen concentrations.

Although we should understand historic land use, the details are somewhat limited. Locally, it is often possible to identify particular activities, such as meat works, that may be highly contaminating. On a broader scale, we can make generalised observations about land use across a region. For Canterbury, in the 1840s, forests were cleared for sheep farming. By the 1870s, there was a lot of conversion to wheat cropping. At the same time, races were being constructed, enabling stocking intensity to increase, and there was an increase in beef farming. The Rangitata Diversion Race was completed in 1944 and diverted water from the

Rangitata River to the Rakaia River and enabling irrigation of (ultimately) 100,000 ha of farmland in Mid-Canterbury. As a result, from 1945 onwards, there was increasing irrigation and stock intensification. From the 1990s onwards, there was a significant increase in dairying and irrigation with a doubling of irrigated area between the mid-1980s and 2000. The increase in dairy farming is reflected in the fact that there were 212K dairy cows in 1994 compared to 1,200k in 2012. In 2012, 89% of water abstracted was used for irrigation.

The increase in agricultural intensification is therefore well established, though the details, particularly on a local scale are often unknown but it is this detail that may be needed to help understand some of the variability.

2.2 DEPTH TO GROUNDWATER AND VERTICAL PROFILE OF NITRATES

It is often perceived that high nitrates occur at shallow depth, and that deeper wells will access "cleaner" groundwater. However, this is not consistently the case, and some areas show elevated nitrate-N at depth, for example, in the Darfield area, nitrate-N concentrations may exceed half MAV (5.2 mg/l), even at depths of over 200m. The different impacts in different areas is highlighted in Figure 3, showing nitrate concentrations in the Christchurch-West Melton zone compared with the Ashburton zone for three different decades. For the Christchurch-West Melton zone, increases in nitrate-N are observed predominantly at depth less than 50m. For the Ashburton area, there is a significant difference not only in nitrate-N concentrations at shallow depth, but, in fact, at all depths.



Figure 3. Average nitrate-N for individual bores, over each decade (left: Christchurch-West Melton, right: Ashburton).

This highlights the fact that nitrate concentrations can be elevated at great depths in some areas. If wells are deepened to attempt to obtain higher quality groundwater, it is essential to understand data such as these, to avoid disappointing outcomes.

2.3 INFLUENCE OF RIVER RECHARGE

It is evident from the available data, that river recharge can significantly affect groundwater quality, an advantage that is exploited by engineered near river recharge schemes, such as in the upper Hinds catchment. This scheme uses alpine water from the Rangitata Diversion Race to supplement flow and improve water quality in the Hinds River. The Christchurch-West Melton zone also benefits from recharge from the Waimakariri River on the northern boundary to the zone. From Halketts Corner, the river loses substantial flows to groundwater, recharging the groundwater that feeds into the city aquifer system. This recharge clearly influences nitrate-N concentrations under the city (Figure 4) and has done so for the past 60 years.



Figure 4. Effects of Waimakariri River recharge on nitrate-N concentrations under Christchurch, average concentrations from the 1980s.

2.4 EFFECTS OF LAND SURFACE RECHARGE

Whilst river recharge, with good quality alpine water, has a beneficial effect on groundwater quality, land surface recharge (LSR), because it transports nitrates from the land surface, can have the opposite effect. Whilst LSR causes leching of nitrate-N, the measured data start to highlight some of the complexities. We frequently observe an increase in nitrate-N in the autumn/winter, when the soil moisture deficit is overcome, and recharge starts, showing that nitrate-N can be transported rapidly through the system. This leads to a seasonal signal in nitrate concentrations in many areas. For example, Figure 5, shows nitrate-N concentrations of up to 70 mg/l as winter recharge starts, but declines to near zero in late summer.



Figure 5. Seasonal variability in nitrate concentrations for a site near Feilding

There is other evidence for the relatively rapid transport of nitrate-N. In Canterbury, there is a marked decrease in nitrate-N concentrations from the 1970s to the 1980s. This has been suggested (Rutter and Rutter, 2019) to be due to high recharge events in the late 1970s, which caused leaching of nitrates that had been held within the soil and unsaturated zone. Relatively low recharge in the early 1980s appeared to reduce the average nitrate concentrations in groundwater.

Further evidence for rapid transport can eb observed after significant recharge events. In South Canterbury, a late-May 2021 rainfall event resulted in 540 mm of rainfall at Mt Somers and 185 mm at Lowcliffe. There was extensive damage to land and structures, and the event initiated the 2021 winter recharge, resulting in groundwater levels recovering from record low groundwater levels in some areas. Following this event, extensive sampling was carried out over several weeks, with around 90% of samples showing an increase in nitrate concentrations. In most areas, the maximum increase occurred within two weeks, though in the lower Plains, on average, the increases were more gradual (Figure 6). The maximum increase was over 20 mg/l.



Figure 6. Response to end of May 2021 rainfall event in the Ashburton area, grouped by location in the Upper, Mid or Lower Plains.

This rapid response contrasts with other information suggesting very long lag times and trends increasing gradually over many years shown, for example in Figure 7, for an 83m deep well in the Ashburton area.



Figure 7. Nitrate concentrations in L36/1242, an 83m deep well in the Ashburton area

3 ANOMALOUS DATA

As described above, although we do have some understanding of influences on nitrate concentrations, the observations are not consistent: we are failing to conceptualise the complexities of nitrate transport. Anomalous sampling results include:

- Declining nitrate concentrations with length of pumping (Figure 8),
- Anomalous tracer test results with long tails,
- Delayed nitrate rebound after managed aquifer recharge (MAR) inputs cease (Figure 9),
- Nitrate concentrations responding to recharge events prior to a water level response (Figure 10).
- Inconsistent responses to recharge events in bores that are in proximity (Figure 11).



Figure 8. Illinois Drive well showing decline in nitrate-N concentrations with time of pumping



Figure 9. Nitrate-N rebound after cessation of artificial recharge



Figure 10. Balmoral nitrate sensor data showing nitrate-N concentrations responding in advance of water level response to recharge



Figure 11. Different responses to end of May 2021 rainfall event near Ashburton

These anomalies have never been systematically addressed and cannot be explained with our current level of knowledge. The contradiction between long term trends and short-term responses to recharge events highlights this lack of ability to conceptualise the systems and processes. All the anomalies bring into question what we are actually sampling when taking a pumped sample of groundwater. In the UK, anomalous sampling results (Foster, 1975) led to decades of research into nitrate transport, prediction of the nitrate "time bomb" and understanding as to how groundwater and surface-water will be affected by nitrate lags (Wang et al., 2012, Ascott et al., 2017).

Our thesis is that the observed anomalies are due to a lack of understanding of nitrate storage, attenuation and transport processes and pathways in NZ's alluvial aquifers.

4 DISCUSSION

NZ's alluvial aquifers function as dual-domain flow and transport systems (Figure 6). Water moves rapidly through high permeability (mobile) domains (known as open framework gravels – OFGs) (Dann et al., 2009), but a portion of the water (and nitrate) moves into low permeability ("immobile") pore space. Recent research has also established that there is movement between the different permeability zones, and that nitrate movement between mobile and less-mobile pore spaces may be a controlling process in terms of nitrate transport (Masciopinto and Passarella, 2018) (Figure 12). Overseas, slow transport through relatively immobile pathways, and diffusion between mobile and immobile pathways have been shown to delay nitrate transport through the vadose zone by decades (Ascott et al., 2016) and proved detrimental to MAR/ASR outcomes (Gale et al., 2002).

Slow transport of nitrates through this store can affect ground- and surface-water quality for decades and for a long time after introduction of measures reduce nitrate leaching.



Aquifer consisting of heterogeneous materials resulting in variable hydraulic conductivities Flow dominated by high perm pathways



'Mobile' Groundwater – groundwater that moves freely due to high hydraulic conductivity

'Immobile' Groundwater – groundwater that is unable to move or moves slowly due to low hydraulic conductivity

Figure 12. Theoretical conceptualisation of nitrate transport through dual domain gravel media

5 CONCLUSIONS

We are failing to conceptualise the processes of nitrate transport through many of our aquifer systems, as is shown by the anomalous results we observe. This also means that we do not fully understand what we are actually sampling when taking groundwater samples. This major gap in our comprehension of transport processes prevents us from being able to predict how land use change will affect water quality, and over what timescales it might occur. Considering the need to improve groundwater and surface water quality, both for ecosystem services and human health, this is a serious issue.

The issue will only be resolved through comprehensive sampling, development of new sampling approaches, and development of new approaches to modelling. If we can carry out such research, New Zealand will be in a far superior position to understand how to implement changes that will result in fundamental improvements in water quality.

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