

DENITRIFICATION

– THE KEY COMPONENT OF A GROUNDWATER SYSTEM'S ASSIMILATIVE CAPACITY FOR NITRATE

**Roland Stenger¹, Juliet Clague¹, Simon Woodward¹, Brian Moorhead¹, Scott Wilson²,
Ali Shokri¹, Thomas Wöhling¹, Hugh Canard²**

Lincoln Agritech Ltd.

¹*Private Bag 3062, Hamilton 3240, New Zealand*

²*PO Box 133, Lincoln, Christchurch 7640, New Zealand*

Email: roland.stenger@lincolnagritech.co.nz

Abstract

For environmental as well as economic reasons, minimising nitrate losses from the root zone should be given highest priority in agricultural nitrogen management. However, even the best management practices available for a given land use may result in root zone losses that are incompatible with water quality limits, especially in sensitive catchments (e.g. Lake Taupo). It has become evident in recent years that denitrification can significantly reduce the mass of nitrate in some groundwater systems before the contaminated groundwater reaches a water supply well or a surface water body. Taking this natural assimilative capacity into account when making decisions on land use type and intensity can therefore provide a second line of defence with regard to contamination of freshwater resources.

Denitrification converts nitrate (NO_3^-) to gaseous forms of N. In contrast to unsaturated zone denitrification, where incomplete denitrification can result in substantial emissions of the greenhouse gas nitrous oxide (N_2O), complete denitrification to inert dinitrogen (N_2) prevails under the usually more stable redox conditions of reduced groundwater zones.

For denitrification to occur, four requirements must be met. Apart from nitrate being present, there need to be oxygen-depleted conditions, a suitable electron donor, and microbes with the metabolic capacity for denitrification. Nitrate and suitable microbes are considered ubiquitous under agricultural land use. Accordingly, the occurrence of denitrification at a particular location is largely determined by the existence of oxygen-depleted conditions (< 2 mg/L dissolved oxygen) and the availability of electron donors. Heterotrophic denitrification is fuelled by organic matter, while reduced inorganic iron and sulphur compounds (e.g. pyrite) can fuel autotrophic denitrification.

Through a combination of hydrochemical analyses, isotopic analyses, excess N_2 determinations and lab incubations it has been ascertained that denitrification occurs in the groundwater systems of the Toenepi Stream and Lake Taupo catchments. Particulate organic matter residing in the groundwater zone has been identified as the main electron donor, but additional contributions from reduced inorganic substrates (e.g. pyrite) cannot be excluded.

While measurements allow denitrification to be detected locally, quantifying its effect on nitrate fluxes through a sub-catchment or catchment requires modelling based on a sound understanding of the biogeochemical and hydrological conditions.

Introduction

Considerable effort, ranging from ‘Best Management Practices’ to ‘Precision Agriculture’, has gone in recent years into improving agricultural nutrient management. While there remains substantial potential for further increases in nutrient use efficiency, some nitrate leaching losses from agricultural land, where hundreds of kilograms of nitrogen per hectare are cycled annually, are inevitable. Particularly in sensitive catchments (e.g. Lake Taupo), even these inevitable losses may be incompatible with water quality limits.

To date it has widely been assumed in New Zealand that nitrate losses from the root zone will inevitably result in the contamination of groundwater and groundwater-fed surface water bodies, as nitrate was thought to be a conservative contaminant below the root zone. Accordingly, environmental legislation has focused on restricting root zone losses by allocating ‘nitrate discharge allowances’. The nutrient budgeting model OVERSEER is increasingly being used to check compliance with these allowances.

However, denitrification occurring below the root zone can significantly reduce the mass flux of nitrate through some groundwater systems before the groundwater reaches a water supply well or discharges into a surface water body. While northern hemisphere publications on groundwater denitrification began appearing in the late 1970s (e.g. Gillham and Cherry, 1978), apart from a few early publications touching upon the topic (McLarin et al., 1999; Kensington et al., 2004), corresponding New Zealand publications have started emerging only in recent years (e.g. Barkle et al., 2007; Stenger et al., 2008; Burbery et al., 2013; Clague et al., 2013).

Denitrification is the key component of a groundwater system’s assimilative capacity for nitrate, as it removes nitrate rather than just diluting or temporarily storing it. Matching the land use intensity to the groundwater system’s assimilative capacity may therefore provide a second line of defence with regard to contamination of freshwater resources. Land uses that are economically desirable, but have relatively high unavoidable leaching losses may still be possible in those areas where high assimilative capacity reduces the nitrate load sufficiently. Conversely, land use intensity may have to be decreased in areas with low assimilative capacity (Stenger et al., 2012).

Denitrification process

In the following section, we provide an overview of denitrification occurring in groundwater systems. For more detailed information, the reader is referred to published reviews (e.g. Korom et al., 1992; Rivett et al., 2008).



Figure 1. Schematic of the denitrification reaction sequence.

Denitrification is a multi-stage process that converts nitrate (NO_3^-) via nitrite (NO_2^-) into gaseous forms of nitrogen (NO , N_2O , N_2). Complete denitrification results in dinitrogen (N_2), an inert gas that makes up 78% of the earth’s atmosphere. For denitrification to occur, four requirements must be met. Apart from nitrate being present, there need to be oxygen-depleted conditions, a suitable electron donor, and microbes with the metabolic capacity for

denitrification. Nitrate and suitable microbes are considered ubiquitous under agricultural land use. The spatial distribution of denitrification is thus largely determined by the local existence of suitable electron donors and oxygen-depleted conditions (which are often interrelated). Dissolved oxygen (DO) concentrations below 2 mg/L have often been found to be conducive to denitrification. The term 'reduced groundwater' is subsequently used to describe groundwater with DO concentrations below 2 mg/L.

There are two main denitrification pathways. Heterotrophic denitrification requires organic matter (OM) as the electron donor for the microbes. This can either be:

1. Mobile, dissolved organic matter (DOM), or
2. Resident, particulate organic matter (POM).

Heterotrophic denitrification can be formulated as:

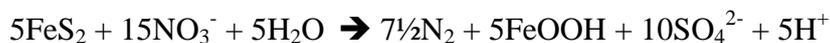


Resident OM in the groundwater zone is often found in alluvial and volcanic situations and where peat or lignite measures occur.

Autotrophic denitrification, on the other hand, requires reduced inorganic substrates as electron donor. The most common ones are:

1. Sulphides (e.g. pyrite [FeS_2]), and
2. (Other) Fe(II)-containing minerals.

Autotrophic denitrification (using pyrite oxidation as an example) can be formulated as:



Reduced inorganic substrates are particularly common in association with lignite and in marine sediments.

A considerable body of research on soil zone denitrification has been build up in New Zealand, largely driven by the need to quantify and manage the emissions of the greenhouse gas nitrous oxide (N_2O) from agricultural soils. N_2O is an obligatory intermediate in the denitrification process (Fig. 1) and substantial N_2O emissions from the soil can occur under conditions that favour incomplete denitrification.

It is important to note that for two reasons groundwater zone denitrification results only in minor N_2O emissions relative to soil zone denitrification. Firstly, the more stable redox conditions in reduced groundwater zones strongly favour complete denitrification to N_2 , while the spatially and temporally much more dynamic redox conditions in the soil zone provide more opportunities for incomplete denitrification to occur. Secondly, the very limited gas exchange between the groundwater system and the atmosphere additionally restricts emission of any produced N_2O . Accordingly, N_2O emissions resulting from groundwater denitrification are accounted for in the Intergovernmental Panel on Climate Change (IPCC) system as indirect emissions that occur where groundwater discharges into surface waters. Reflecting the knowledge gain achieved, the corresponding IPCC emission factor has substantially been revised downwards since its inception (e.g. Weymann et al., 2008).

Field studies

As exemplarily shown in the following sections, we have used a combination of field- and lab-based approaches to identify and quantify denitrification occurring in the groundwater zone at two New Zealand field study sites:

1. A lowland catchment dominated by intensive dairy farming (Toenepi, near Morrinsville)
2. An upland site with low-intensity sheep & beef farming (Waihora, near Lake Taupo).

For background information on these field sites, please refer to Stenger et al. (2008) and Clague et al. (2013), respectively.

All groundwater data presented in the following originate from sampling multi-level well clusters, where two to five individual well screens of only 50 cm length are installed at depths up to approximately 9 m below the ground surface. This approach allows sampling of discrete depths and establishment of vertical groundwater profiles. This information cannot be gained by sampling of existing water supply wells, as the typically much longer well screens of the latter only allow taking of a single mixed sample. Moreover, to ensure security of supply, water supply wells are usually screened well below the groundwater table and therefore tend to draw groundwater recharged decades or centuries ago. In contrast, the multi-level well clusters cover the uppermost groundwater zone, which is most responsive to changing land use.

Hydrochemical analyses were carried out by Hill Laboratories (Hamilton), isotopic analyses predominantly by the University of California in Davis (and to a small extent by GNS), and dissolved N₂ concentrations were determined by GNS (Lower Hutt).

Hydrochemistry data approach

Hydrochemistry data, particularly the concentrations of redox-sensitive parameters like dissolved iron (Fe^{2+}), dissolved manganese (Mn^{2+}) and dissolved oxygen (DO), can be used to assess the denitrification capacity in a groundwater system.

A very wide range of DO concentrations, ranging from nearly fully oxidised (≈ 10 mg/L DO) to entirely oxygen-depleted (≈ 0 mg/L DO) was observed at both field sites, as shown in Figure 2 for the Waihora site. The large percentage of samples below the 2 mg/L DO threshold demonstrates that conditions suitable for denitrification are prevalent. However, this does not imply that the very low $\text{NO}_3\text{-N}$ concentrations in these samples are entirely due to denitrification. Low nitrate concentrations in older groundwater (independent of redox status) can simply reflect that this water was recharged at a time when there was very little nitrate in the system.

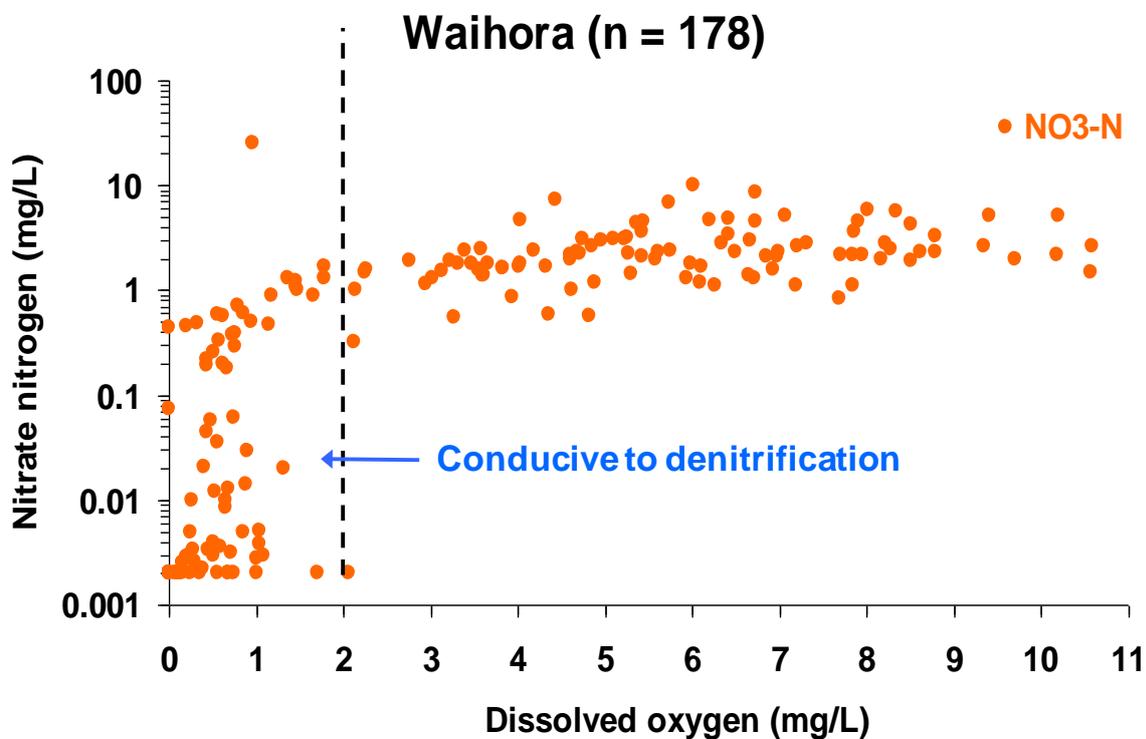


Figure 2. Nitrate nitrogen concentrations from the Waihora site graphed against dissolved oxygen concentrations. Note the log scale on the y-axis. N = 178, Aug 2007 – Nov 2011.

Based on the data from New Zealand's National Groundwater Monitoring Programme, Morgenstern and Daughney (2012) have suggested that a threshold concentration of 0.25 mg/L $\text{NO}_3\text{-N}$ can be used to differentiate between natural baseline and the commencement of agricultural land use and 2.50 mg/L $\text{NO}_3\text{-N}$ to mark the onset of high-intensity land use. Age dating of groundwater can help to differentiate between the possible reasons for observed low nitrate concentrations, while the determination of excess N_2 can provide direct evidence for denitrification (see below).

$\delta^{15}\text{N}/\delta^{18}\text{O}$ dual isotope approach

The dual isotope approach can be used for two main purposes: to identify the source of nitrate and to detect denitrification (Kendall, 1998), as shown in Figure 3 using data from our Toenepi site.

The signatures of nitrate in oxidised groundwater suggest that the nitrate is predominantly derived from mineralisation of soil N and/or manure. As denitrification is known to result in isotopic enrichment of oxygen and nitrogen at a ratio close to 1:2, residual nitrate that has undergone denitrification was expected to plot along the denitrification vector shown in Figure 3. Many reduced groundwater samples indeed plot in the vicinity of this denitrification vector, but substantial variability is evident in the isotopic signatures.

This high variability, particularly strong in the reduced groundwater samples characterised by very low nitrate concentrations (c.f. Figure 2), and the fact that analytical uncertainty limited analysis to samples with NO_3^- concentrations above 0.03 mg/L $\text{NO}_3\text{-N}$ limited the usefulness of this approach. As also found by other researchers (e.g. Hosono et al., 2013), interpretation of the isotopic signatures was most conclusive where good knowledge on the groundwater flow exists and sample pairs can be taken along well-defined flow paths.

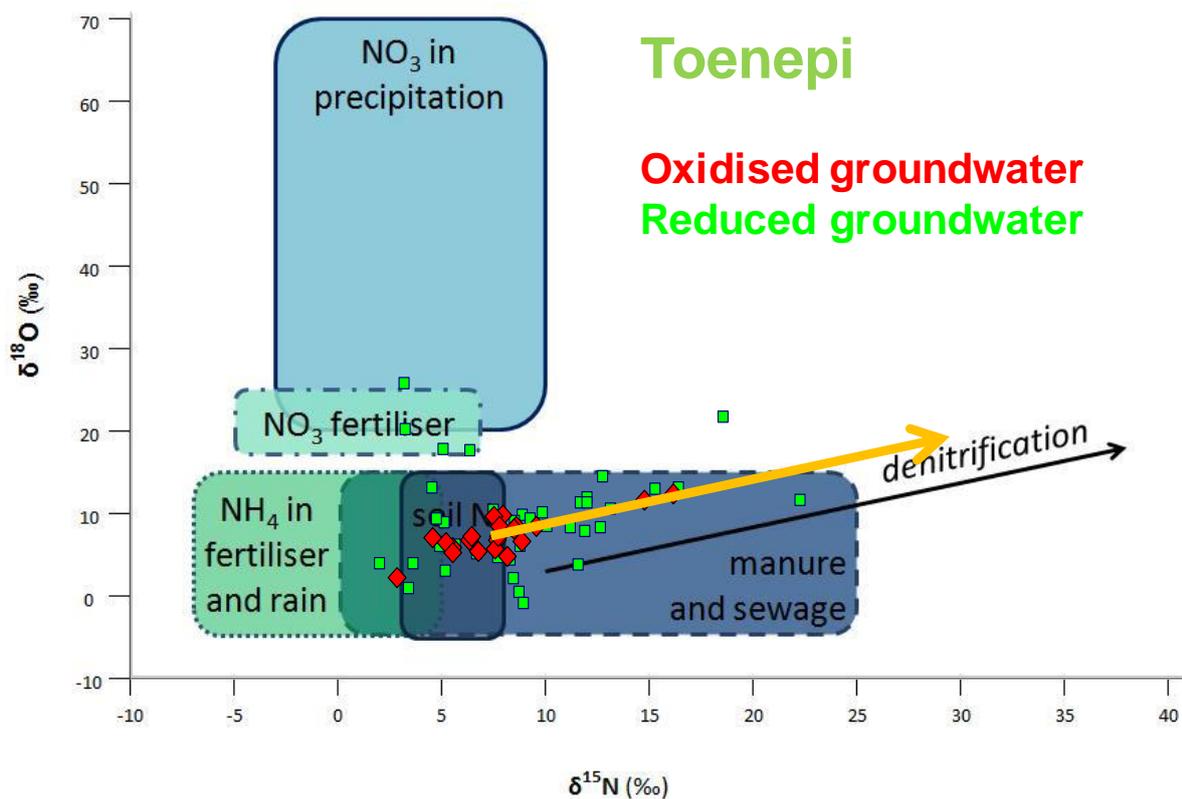


Figure 3. $\delta^{15}\text{N}/\delta^{18}\text{O}$ isotope signatures of nitrate in Toenepi groundwater samples. Oxidised groundwater shown in red, reduced groundwater in green.

Excess N₂ approach

Dinitrogen (N₂) gas dissolved in groundwater can principally originate from two sources, either from the atmosphere (78% N₂) or from denitrification occurring in the groundwater system (Vogel et al., 1981). The ratio in a groundwater sample of the N₂ concentration to the concentration of an inert noble gas (usually Argon), can help to differentiate between these sources. The N₂ that can only be explained by denitrification is called excess N₂. As it quantifies the reaction product, this approach is the only one that can provide direct evidence for denitrification.

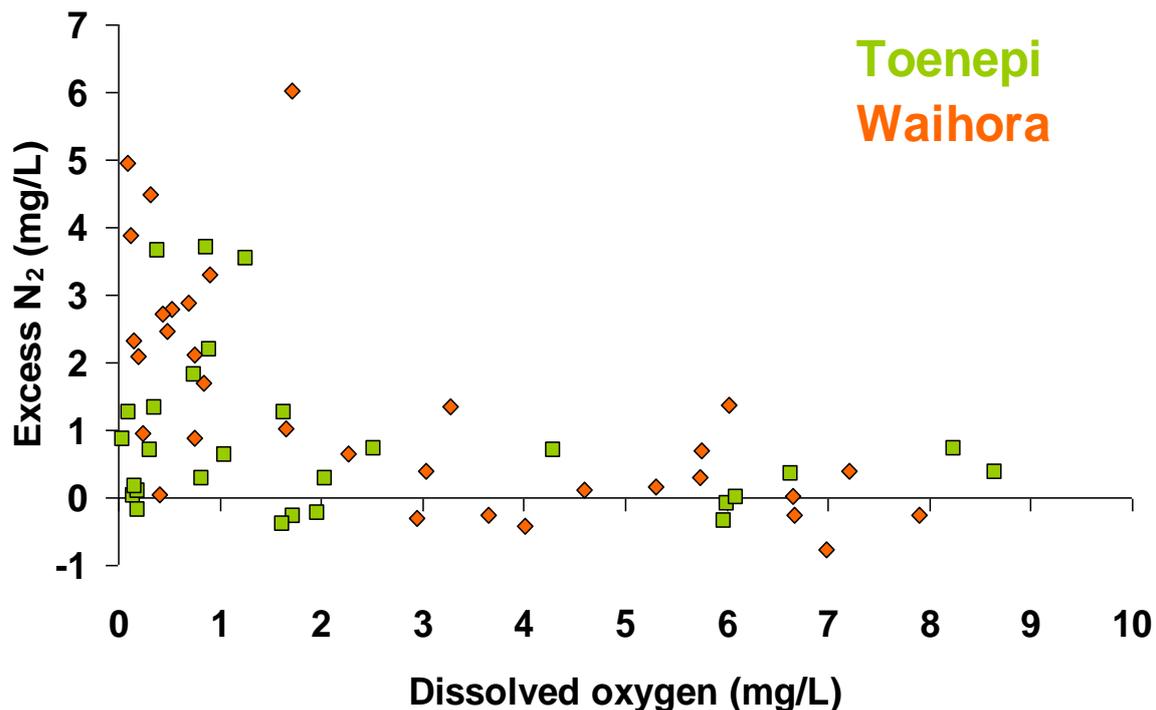


Figure 4. Excess N₂ (mg/L N₂) determined on Toenepi and Waihora groundwater samples graphed against concentrations of dissolved oxygen (mg/L DO).

The excess N₂ calculations should theoretically result in near-zero excess N₂ concentrations in oxidised groundwater, but values between approximately -1 and +1.5 mg/L excess N₂ have been calculated, as shown in Figure 4. This range reflects the measurement and calculation uncertainty of the approach. Concurrently measuring the concentration of a second noble gas (usually Neon) would help to reduce this uncertainty, but this lab service is not yet available in New Zealand.

Notwithstanding this uncertainty range, it is evident that the majority of reduced groundwater samples from Toenepi and Waihora contain excess N₂ resulting from denitrification in the groundwater system. Two significant advantages of this approach are that a meaningful interpretation of an analytical value is possible even if there is only a single sample and in the absence of flow path knowledge.

Laboratory incubations

Incubation experiments conducted under controlled laboratory conditions and using ^{15}N -labelled nitrate allowed determination of the denitrification capacity (DNC) and denitrification potential (DNP) of samples taken from different profiles and geological strata.

While DNC experiments aim to ascertain the degree of denitrification that is possible when only the ambient electron donors are available, electron donors (usually organic carbon) are added in DNP experiments to ascertain the maximum denitrification possible when electron donors are non-limiting.

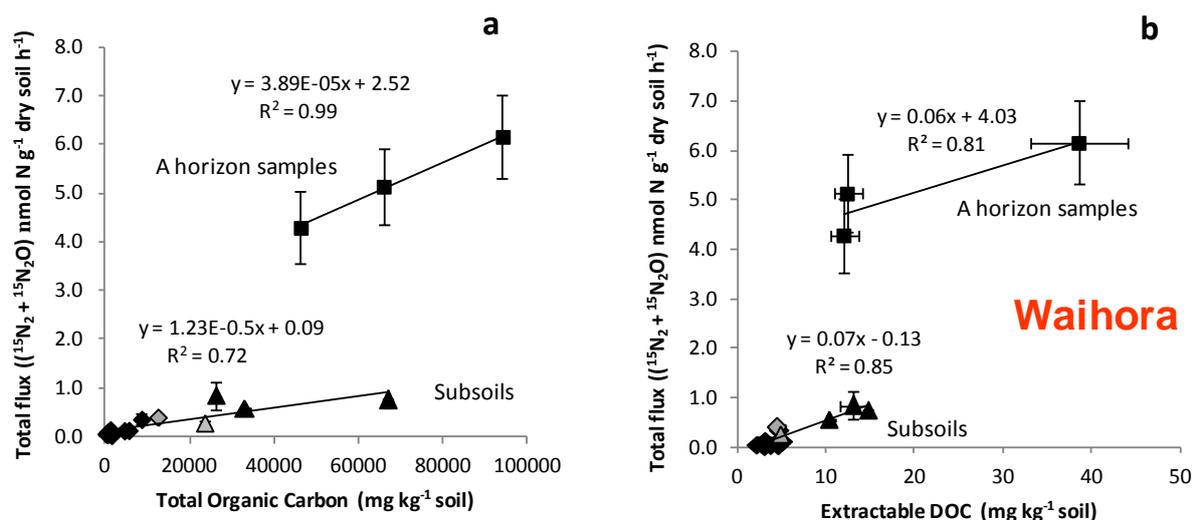


Figure 5. Total N gas flux (nmol/g dry soil/h) measured on Waihora profile samples in a DNC experiment, graphed against concentrations of a) total organic carbon, and b) extractable dissolved organic carbon (both in mg/kg soil); from Clague et al., 2013.

Total N gas production of the incubated Waihora site materials (from 0 – 4.4 m below ground surface) was by far the highest in A horizon samples, but substantial fluxes were also observed in palaeosol samples containing relict soil organic matter (approximately 2 – 4 m depth).

Total N gas production was strongly correlated with the carbon content of the samples (Fig. 5). Gas production of the A horizon samples was more closely correlated with the total carbon concentration (Fig. 5a), while all other samples showed a stronger relationship with the concentration of extractable dissolved organic carbon (Fig. 5b). The observation that the regression equations shown in Fig. 5 account for 72 to 99% of the variation in N gas fluxes support the hypothesis that organic carbon was the dominant electron donor.

The substantial difference in the amount of N gas produced per unit of carbon between the A horizon samples and all other samples reflects differences in organic matter quality and microbial activity. Extrapolation of these denitrification rates to field conditions suggests that the DNC of profiles containing relict soil organic matter in the groundwater zone exceeds the estimated N leaching from the root zone (Clague et al., 2013).

Modelling

The approaches described above help to identify denitrification capacity and/or actual denitrification within a catchment. However, catchment-scale quantification of denitrification requires modelling, as the effect of local denitrification on catchment-scale N fluxes is largely determined by subsurface hydrology. Zones with high denitrification capacity may be of little relevance, if the groundwater flux through these zones is small. Conversely, zones with relatively low denitrification capacity may still have a significant effect on overall fluxes if a high portion of the nitrate-bearing water flows through them.

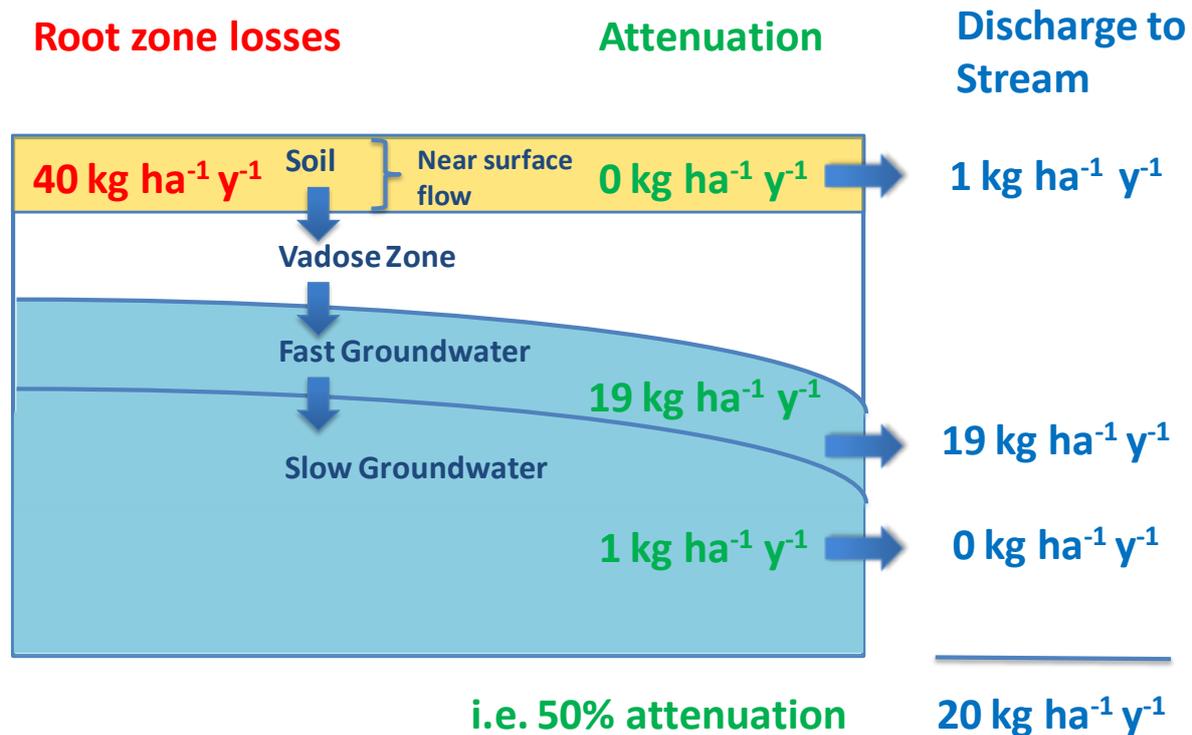


Figure 6. Schematic showing the major nitrate fluxes (including attenuation) through the Toenepi catchment as described by the StreamGEM model (Woodward et al., this issue).

Based on a conceptual understanding of the water and nitrate fluxes through the Toenepi catchment that was informed by monitoring data and experimental work, the lumped catchment model ‘StreamGEM’ was developed (Woodward et al., this issue). Apart from rain and evapotranspiration data, it relies only on the availability of stream flow and stream nitrate concentration time series data. Such time series exist for a few research catchments and a larger number of catchments monitored by Regional Councils. This data is used in an inverse modelling approach to fit a range of model parameters. The calibrated model can subsequently be used to estimate the contributions made by near-surface fluxes, fast groundwater, and slow groundwater to stream flow generation and nitrate fluxes.

Applying this approach in the Toenepi catchment, the average nitrate nitrogen yield in the Toenepi catchment (equivalent to root zone losses) was estimated to be 40 kg/ha/year NO₃-N (Fig. 6), in broad agreement with OVERSEER estimates and monitoring data from shallow groundwater. Only 1 kg/ha/year NO₃-N was estimated to be transferred from the land to the stream via the near-surface flow path. Fast (shallow) groundwater contributed the majority of

nitrate nitrogen to the stream (19 kg/ha/year NO₃-N), while slow (deeper) groundwater contributed almost no nitrate nitrogen. Total discharge into the stream amounted to 20 kg/ha/year NO₃-N.

As well as transferring the largest portion of the nitrate nitrogen to the stream, the fast groundwater reservoir also accounted for the greatest attenuation (19 kg/ha/year NO₃-N), equating to 50% attenuation in the groundwater system. It is noteworthy that the slow groundwater reservoir, which based on field research has the greatest denitrification capacity, is relatively insignificant for the attenuation occurring in the catchment, as it makes only a small contribution to stream flow (Woodward et al., this issue).

Conclusions

Our research has demonstrated that denitrification can substantially reduce the nitrate load in some New Zealand groundwater systems. Interpretation of hydrochemical data allows a first screening of the likely denitrification capacity of groundwater systems. The dual nitrate isotope method proved most conclusive where at least two samples could be taken along a well-defined flow path. While there is relatively high uncertainty at the low concentrations (still) observed in many New Zealand groundwater systems, the determination of excess N₂ appears most promising for gaining quantitative evidence for denitrification. Supplementary laboratory incubations help to understand processes and relationships that are difficult to explore under heterogeneous and dynamic field conditions. Modelling facilitates the essential integration of biogeochemical and hydrological knowledge and enables catchment-scale assessments to be made that are impossible to achieve solely based on measurements.

Acknowledgements

We would like to thank the farmers in the Toenepi catchment, Landcorp Farming, and Armer Farms Ltd (Waihora Farm) for their collaboration. This work was funded under the New Zealand Foundation for Research, Science and Technology “Groundwater Quality” (LVLX0302) and “Groundwater Assimilative Capacity” (C03X1001) contracts.

References

- Barkle, G., Clough, T., and Stenger, R. (2007) Denitrification capacity in the vadose zone at three sites in the Lake Taupo catchment, New Zealand. *Australian Journal of Soil Research*, 45:91-99.
- Burbery, L.F., M.J. Flintoft, M.E. Close (2013) Application of the re-circulating tracer well test method to determine nitrate reaction rates in shallow unconfined aquifers. *J. Cont. Hydrol.* 145:1-9.
- Clague, J.C., Stenger, R., Clough, T. (2013) The impact of relict organic materials on the denitrification capacity in the unsaturated-saturated zone continuum of three volcanic profiles. *Journal of Environmental Quality*. 42:145-154. Doi:10.2134/jeq/2012.0239.
- Hosono, T., Tokunaga, T., Kagabu, M., Nakata, H., Orishikida, T., Lin, I.-T., Shimada, J (2013) The use of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ tracers with an understanding of groundwater flow dynamics for evaluating the origins and attenuation mechanisms of nitrate pollution. *Water Research*, doi:10.1016/j.watres.2013.02.020.

- Kendall, C. (1998) Tracing Nitrogen Sources and Cycling in Catchments. In: *Isotope Tracers in Catchment Hydrology* (1998), C. Kendall and J. J. McDonnell (Eds.). Elsevier Science B.V., Amsterdam. pp. 519-576.
- Kensington, C.G.; Richards, K.; Murray, D.L.; Peake, B.M. (2004) Distribution of nitrogen species in groundwater in the Taieri Plain aquifer, New Zealand. *Journal of Hydrology (NZ)* 43: 39-57.
- Korom, S.F. (1992) Natural Denitrification in the Saturated Zone: A Review. *Water Resources Research* 28: 1657-1668.
- McLarin W., Bekesi G., Brown L., McConchie J. (1999) Nitrate contamination of the unconfined aquifer, Manakau, Horowhenua, New Zealand. *Journal of Hydrology (NZ)* 38 (2): 211-235.
- Morgenstern, U.; Daughney, C.J. (2012) Groundwater age for identification of baseline groundwater quality and impacts of land-use intensification: The National Groundwater Monitoring Programme of New Zealand. *J. of Hydr.*, 456/457: 79-93.
- Rivett, M.R., S.R. Buss, P. Morgan, J.W.N. Smith and C.D. Bemment (2008) Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. *Water Res.* 42: 4215-4232.
- Stenger, R., Barkle, G., Burgess, C., Wall, A., Clague, J. (2008) Low nitrate contamination of shallow groundwater in spite of intensive dairying: the effect of reducing conditions in the vadose zone - aquifer continuum. *Journal of Hydrology (NZ)* 47(1), 1-24.
- Stenger, R., Bidwell, V., Wall, A., Clague, J., Moorhead, B. (2009) Nitrogen contamination of surface waters: What are the important flowpaths in the Toenepi dairying catchment? Progress Report No. 3653/3, September 2009, Lincoln Ventures Ltd, Hamilton, New Zealand, 55 pp.
- Stenger R, Clague JC, Woodward SJR, Moorhead B, Burberry L, Canard H (2012). GROUNDWATER ASSIMILATIVE CAPACITY – AN UNTAPPED OPPORTUNITY FOR CATCHMENT-SCALE NITROGEN MANAGEMENT? In: *Advanced Nutrient Management: Gains from the Past – Goals for the Future*. (Eds L.D. Currie and C L. Christensen). <http://flrc.massey.ac.nz/publications.html>. Occasional Report No. 25. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 10 pages.
- Vogel, J.C., A.S. Talma, T.H.E. Heaton (1981) Gaseous nitrogen as evidence for denitrification in groundwater. *Journal of Hydrology*, 50:191-200.
- Gillham, R.W.; Cherry, J.A. 1978: Field evidence of denitrification in shallow groundwater flow systems. *Water Pollut. Res. Can.* 13: 53-71.
- Weymann, D., R. Well, H. Flessa, C. von der Heide, M. Deurer, K. Meyer, C. Konrad, and W. Walther (2008) Groundwater N₂O emission factors of nitrate-contaminated aquifers as derived from denitrification progress and N₂O accumulation. *Biogeosciences*, 5, 1215–1226, 2008.
- Woodward, S, Stenger, R, Bidwell, V (2013). USING STREAM FLOW AND CHEMISTRY DATA TO ESTIMATE CATCHMENT SCALE GROUNDWATER AND NITRATE FLUXES. In: *Accurate and efficient use of nutrients on farms*. (Eds L.D. Currie and C L. Christensen). <http://flrc.massey.ac.nz/publications.html>. Occasional Report No. 26. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 12 pages.