MULTI-PRONGED APPROACH TO ELUCIDATE NITRATE ATTENUATION IN SHALLOW GROUNDWATER

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Abstract

It is increasingly being recognised in New Zealand that denitrification occurring in the groundwater zone can result in a substantial reduction of the nitrate load leached from agricultural land before this load can reach water supply wells or discharge into groundwater-fed surface water bodies. This natural attenuation process provides an ecosystem service with regard to the protection of the quality of our freshwater resources that to date has not been adequately accounted for. This is largely due to the major challenges involved in trying to understand and quantify the denitrification occurring in a particular water management zone.

Based on the example of research conducted at the 'Waihora' site in the Lake Taupo catchment, we demonstrate a multi-pronged approach to elucidate the biogeochemical and hydrological controls on denitrification. The site is unique in New Zealand inasmuch as it has allowed investigating shallow groundwater underlying a pastoral hillslope in great detail using 11 multi-depth well clusters (comprising 26 wells in total).

As denitrification is only active under mildly reduced conditions, a systematic approach to characterise redox conditions based on measured concentrations of dissolved oxygen, nitrate, dissolved manganese, dissolved iron, and sulphate provided fundamental initial information on the denitrification potential of the groundwater system.

Determining stable isotope signatures of nitrate ($\delta^{15}N$, $\delta^{18}O$) and excess N_2 dissolved in the groundwater can help differentiate between denitrification potential and denitrification that has actually occurred in a given groundwater sample. As the interpretation of these data is strongly dependent on the understanding of the temporal and spatial variation of groundwater flows at the site, hydrological understanding proved critical.

Tritium, chlorofluorocarbons, and silica were determined on selected groundwater samples to gain insight into the distribution of groundwater mean residence times ('ages') at the field site and slug tests provided estimates of the hydraulic conductivity of the different deposits found in the shallow groundwater system.

Given that most biogeochemical and hydrological parameters analysed showed substantial spatial variation, hydrological modelling of the hillslope proved the only promising way to ascertain the overall effect denitrification may have on the groundwater nitrate discharges from this site.

Introduction

It is increasingly being recognised that not all nitrate lost from the root zone necessarily arrives at surface water bodies, for which the National Objectives Framework (NOF) defines water quality bands and bottom lines. In many instances there is some degree of attenuation occurring along the flow path, particularly denitrification occurring in anoxic groundwater zones. The extent to which denitrification affects the nitrate fluxes between source and impact sites depends on biogeochemical and hydrological controls (Fig. 1).

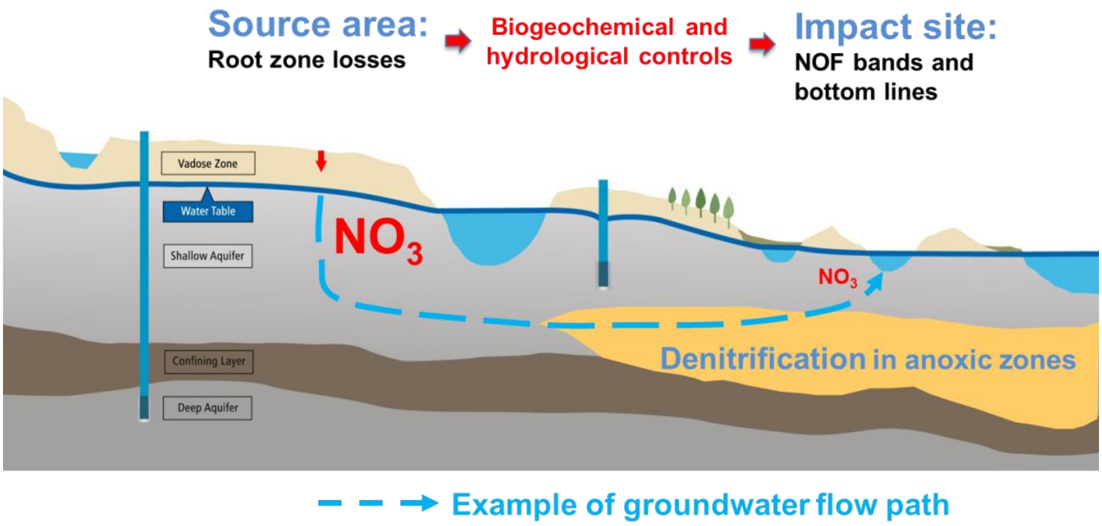

Fig. 1: Schematic of subsurface nitrate transfer from land to a surface water body.

Multi-pronged approach

To understand how these biogeochemical and hydrological controls apply to a particular site, it has proved useful to start with detailed groundwater monitoring, add field and lab experiments to address particular questions, and finally synthesise these findings supported by modelling (Fig. 2).

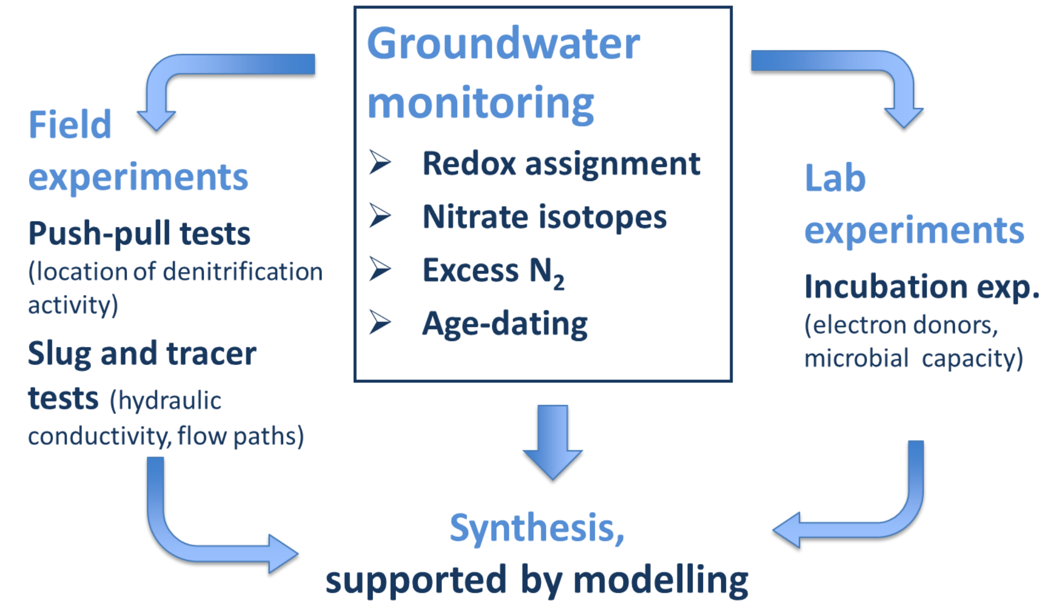

Fig. 2: Schematic of multi-pronged approach to elucidate nitrate attenuation.

Redox assignment

Identifying where in the ecological succession of redox processes (Fig. 3) a given groundwater system stands is a critical step in evaluating the nitrate attenuation potential of the system – the most crucial distinction is between oxic and anoxic (McMahon and Chapelle, 2008). All these redox processes are facilitated by microbes which gain energy by transferring electrons from donors (usually organic carbon) to acceptors. The preferred electron acceptor is oxygen, but once oxygen gets depleted nitrate can become the electron acceptor – in the process called denitrification. When nitrate gets depleted, oxidised forms of manganese and iron, and sulphate can get reduced and finally even methane generation can occur.

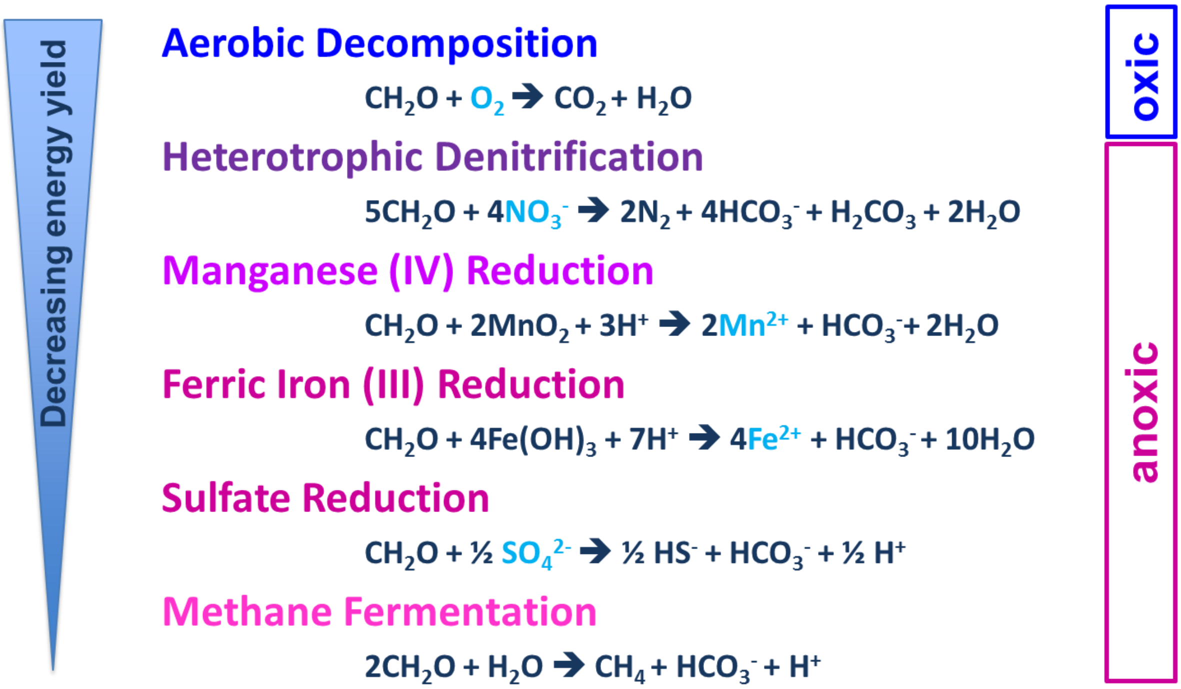

Fig. 3: Ecological succession of redox processes in groundwater.

By measuring dissolved oxygen, nitrate, reduced manganese and iron, and sulphate in groundwater (highlighted in light blue in Fig. 3), and using the classification scheme devised by McMahon and Chapelle (2008), one can work out which of these processes is the dominant one in a given groundwater sample. The default thresholds by McMahon and Chapelle (2008) are considered to be broadly applicable to the major aquifer systems in the US, but may not be the most suitable ones for particular sites. Accordingly, we have derived site-specific thresholds for our Waihora well field in the Lake Taupo catchment, as shown on the example of dissolved oxygen (DO) in Fig. 4. While McMahon and Chapelle (2008) use 0.5 mg L^{-1} DO for the onset of denitrification, our data suggest that substantial nitrate reduction begins already at a higher DO concentration. Accordingly, we have used a site-specific threshold of 1.5 mg L^{-1} DO in our redox assignment (Fig. 4).

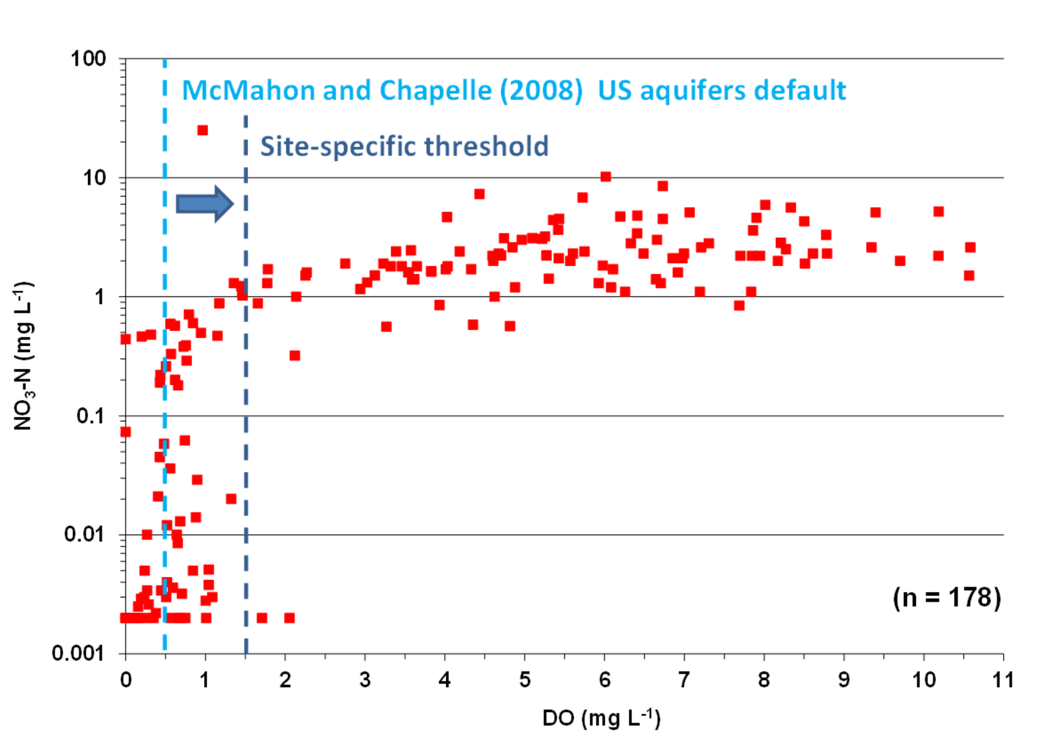

Fig. 4: Default and site-specific DO threshold for denitrification.

Applying this redox assignment to the multilevel well (MLW) clusters of the Waihora well field revealed that anoxic underlying oxic groundwater occurs at 7 of the 11 MLW clusters, indicating substantial denitrification potential at this site; independent of MLW position on the hill slope. Fig. 5 demonstrates that oxic conditions occur throughout the investigated groundwater zone in the upper part of the Downslope Transect, but vertical redox gradients with oxic groundwater overlying anoxic water in the lower part. Denitrification is identified as the dominant redox process in the upper part of the anoxic zone (D5 – D7), while more strongly reduced conditions are indicated in the deeper parts of well cluster D7.

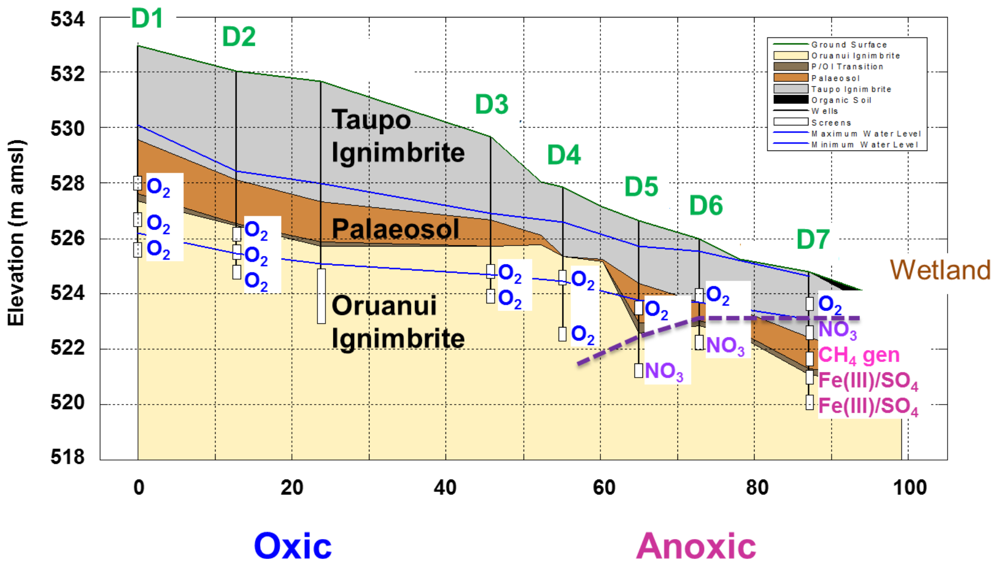

Fig. 5: Redox assignment for Downslope Transect at Waihora well field, Lake Taupo.

Nitrate isotopes
Measuring the nitrogen and oxygen isotopes of nitrate and analysing the $\delta^{18}O/\delta^{15}N$ signatures is one of the methods potentially suitable to obtain evidence for denitrification. While the method proved suitable for elucidating denitrification at a Gley soil site with seasonally saturated profile, challenges with this method arose at other sites. These included high temporal and spatial variability of isotopic signatures, measurement uncertainty at low nitrate concentrations, and frequent inability to determine isotopic signatures due to insufficient N mass in our groundwater samples (Clague et al., 2015a).

Excess N_2
Determining 'Excess dinitrogen (N_2)' is a second method for obtaining evidence of denitrification. The small number of measurements carried out at the Waihora well field confirmed the potential value of the method, with Excess N_2 generally increasing in a vertical profile where nitrate nitrogen was decreasing. However, the absolute concentrations of calculated excess N_2 did not correspond well with the decrease in nitrate concentrations, which may be due to the uncertainties involved in determining Excess N_2, the effect of lateral flow paths, and the temporal variation of nitrate inputs. Accordingly, understanding of the hydrological flow paths and water ages is required for the interpretation of Excess N_2 results.

Age-dating
Age-dating of water helps to understand the subsurface hydrology and helps to relate the nitrate nitrogen concentration of an oxic groundwater sample to the land use intensity prevailing when the water percolated from the soil zone (Morgenstern et al., 2010; Morgenstern and Daughney, 2012).

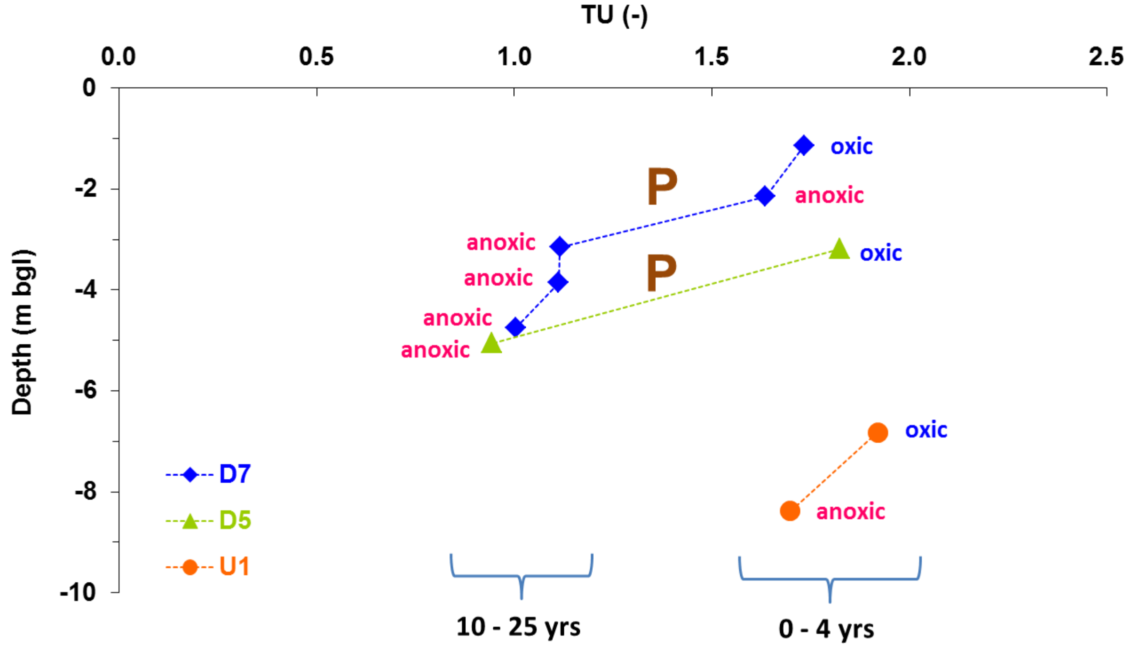

Fig. 6: Schematic showing measured tritium units (TU), calculated mean residence times (MRT in years) and redox status of three multilevel well clusters of the Waihora well field. P indicates the location of the Palaeosol in the D5 and D7 profiles; U1 is entirely located within Taupo Ignimbrite.

For example, the strong decrease in tritium concentrations in Fig. 6 in the depth range of the Palaeosols (P) suggest that they represent a zone of low vertical hydraulic conductivity.

Moreover, due to land use intensification, initial nitrate concentration were presumably lower in the samples with mean residence times (MRTs) between 10 and 25 years, as compared to those with 0 to 4 years. Finally, it helps to understand whether the redox status is related to the water age. In the example of three MLW clusters from the Waihora well field we see that oxic conditions were restricted to young water (MRT <4 yrs), while anoxic conditions occurred over the entire MRT range.

Field and laboratory experiments

As recently summarised by Clague et al. (2015b), it is difficult to determine where or when nitrate is reduced in groundwater systems if relying only on groundwater samples, since that nitrate may have been denitrified further up the flow path rather than close to the sampling point. For example, observational data of redox gradients in a shallow groundwater system, collected by Stenger et al. (2008), could only indicate that denitrification was likely to be occurring within the catchment. Isotopic analysis of nitrate in groundwater samples from the same catchment indicated that denitrification was occurring at selected locations, but could not elucidate where or when along the flow path the nitrate was reduced (Clague et al., 2015a). Similarly, while analysis of dissolved gases in groundwater samples (N_2O or Excess N_2) can provide evidence that denitrification has occurred, such analysis offers no information on the active zones or electron donors within the aquifer (Jahangir et al., 2013). In situ experiments like push-pull tests can provide information on the denitrification capacity of aquifer material but they do not provide evidence on the electron donors involved or possible limitations to the process, and such tests rely on specific hydrological conditions for success (e.g. low hydraulic conductivity) (Addy et al., 2002). In contrast, laboratory incubation experiments can assess both the denitrification capacity of aquifer materials (utilising native electron donors) and the denitrification potential of the microbial population when an electron donor is non-limiting (Yeomans et al., 1992; Clague et al., 2013, Clague et al., 2015b).

Conclusions

The combination of comprehensive groundwater monitoring, field and lab experiments allowed gaining in-depth understanding of the nitrate attenuation occurring in a groundwater system. However, it should be noted that the combination of groundwater redox assignment and age-dating alone already provides a very valuable starting point for initial assessments that are feasible outside of a dedicated research project.

Acknowledgments

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