Evaluation of the stable isotope signatures of nitrate to detect denitrification in a shallow groundwater system in New Zealand

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A B S T R A C T

Denitrification in the groundwater systems of agricultural catchments can provide a substantial 'ecosystem service' by attenuating leached nitrate (NO_3^-) before it reaches surface water bodies. Samples along a groundwater flow path with low dissolved oxygen and declining NO_3^- concentrations can indicate the occurrence of denitrification. Isotopic analysis of this NO_3^- can potentially identify and quantify denitrification activity. In this study, shallow groundwater samples (maximum 5 m below ground surface) were taken from three locations within a small agricultural catchment in the Waikato region of New Zealand. The $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- were analysed to try to determine where denitrification was occurring and at what rate. Results indicated that denitrification rates varied spatially, but interpretation was confounded by insufficiently understood flow paths and extremely low concentrations of NO_3^- in reduced groundwater. Seasonal denitrification was observed at a Gley soil site where the soil profile was periodically saturated to near the ground surface and $\delta^{15}N$-NO_3^- values reached +28.5‰ and $\delta^{18}O$-NO_3^- values up to +19.6‰. In contrast to expectations, NO_3^- in well-oxidised groundwater samples showed substantial variability in its $\delta^{15}N$ and $\delta^{18}O$ isotopic signature. This indicated that the NO_3^- originated from multiple sources, which restricted the quantification of denitrification.

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1. Introduction

Nitrate (NO_3^-) contamination of freshwater resources is a global issue due to its impact on potable water supplies and eutrophication of groundwater, streams and rivers (Vitousek et al., 1997). Water quality guidelines set the maximum acceptable value (MAV) for NO_3^- in drinking water at 11.3 mg NO_3^- −N L^{-1} (WHO, 2011). However, the trigger level at which ecological change occurs in lowland streams and rivers is much lower (0.44 mg N L^{-1}) (ANZECC, 2000). Recent statistics (1995–2008) for groundwater quality in New Zealand (NZ) show that almost 5% of the sites monitored exceeded the WHO drinking water standard, while 73% exceeded the ecosystem trigger level (Daughney and Randall, 2009). In NZ, year-round grazing of intensively managed pasture has resulted in many agricultural

catchments having ground and surface waters with elevated NO_3^- concentrations (MfE, 2007). Haynes and Williams (1993) and Moir et al. (2011) have estimated that 23–25% of a paddock grazed by dairy cows is covered in urine spots annually, and it is these high volume (2 L), high nitrogen (N) rate (ca. 600–1000 kg N ha^{-1}) events which are the main source of NO_3^- in groundwater in NZ. In contrast, the direct leaching of fertiliser-N is often negligible as application timing and rates are matched to meet plant demand (Ledgard et al., 1999).

In many catchment studies NO_3^- concentrations measured in streams are lower than would be expected based on estimated NO_3^- leaching losses from the root zone (Alexander et al., 2002; Woodward et al., 2013). However, these estimates do not take into account the flow paths (including their lag times) and potential N transformations which may occur below the root zone in the vadose and saturated zones before the groundwater discharges into surface water bodies. There exists a research gap pertaining to the understanding and quantification of denitrification in NZ groundwaters.

Many previous studies have inferred that denitrification is occurring, based on declining NO_3^- concentrations under reduced conditions (e.g. Gillham and Cherry, 1978; Postma et al., 1991).

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Groffman et al. (2006) highlight the difficulty of accurately measuring a process like denitrification. For example, a decline in groundwater NO_3^- concentrations can indicate denitrification is occurring or it may be due to dilution with NO_3^- free water. Analysis of the end product of complete denitrification, N_2, is also problematic since it cannot be directly determined in a groundwater sample, as groundwater already contains a significant amount of N_2 that is of atmospheric origin. Calculating the 'excess N_2', that can only be explained by denitrification requires supplementary analyses (e.g. noble gases like argon and neon) and assumptions about the groundwater recharge temperature to be made (Vogel et al., 1981). An alternative method used to identify and quantify denitrification is to measure changes in the stable isotopic composition ($\delta^{15}N$ and $\delta^{18}O$) and concentrations of the initial and residual NO_3^- pool over changing distance or time (Groffman et al., 2006).

Assuming no N transformations have occurred, the NO_3^- in groundwater samples from the oxidised zone of a groundwater system should have $\delta^{15}N$ and $\delta^{18}O$ values similar to the source (Kendall, 1998). If denitrification subsequently occurs downgradient then samples taken from the reducing zone of the groundwater system should contain NO_3^- enriched in ^{15}N and ^{18}O due to isotopic fractionation, and plot along a denitrification vector that typically has a slope of 2:1, starting at the isotopic signature of the NO_3^- in oxidised groundwater (Böttcher et al., 1990; Aravena and Roberston, 1998; Mengis et al., 1999; Baily et al., 2011). This is because microorganisms will preferentially use the lighter isotopes (^{14}N and ^{16}O), leaving the residual NO_3^- enriched in ^{15}N and ^{18}O. The resulting degree of enrichment in both isotopes will depend on the original NO_3^- source, what fraction of the original NO_3^- pool has been denitrified and other local conditions such as temperature, geological heterogeneity and the microorganisms involved (Mariotti et al., 1982). If the NO_3^- in the aquifer is from multiple sources and/or sampling flowpaths are not well defined, the $\delta^{15}N$ and $\delta^{18}O$ values will be difficult or impossible to interpret (Chen et al., 2009; Baily et al., 2011; Hosono et al., 2013). Similarly, if the isotope fractionation factors do not remain constant throughout the catchment, denitrification rate calculations will be problematic.

Previous work in the Toenepi catchment in NZ (Stenger et al., 2008) showed a discrepancy between estimated NO_3^- concentrations leaching from the root zone and the NO_3^- concentrations measured in the stream draining this catchment. The mean stream water transfer times (Morgenstern et al., 2010) demonstrated that this discrepancy could not be explained by long time lags in the groundwater system. Instead, analysis of hydrochemistry profiles in the shallow groundwater system (max. 5 m below ground surface) revealed the widespread occurrence of groundwater with both low dissolved oxygen (DO) and NO_3^- concentrations overlain by oxidised, NO_3^- -bearing water, indicating denitrification may have occurred. The purpose of this study was to use NO_3^- isotopic analysis to identify and confirm the extent and location of denitrification in the Toenepi catchment's shallow groundwater system.

2. Materials and methods

2.1. Study area – the Toenepi catchment

The Toenepi catchment is located in the Waikato region of the North Island of NZ (Fig. 1), and features gently rolling topography with an elevation of 30–130 m above mean sea level. The annual rainfall (mean ± standard deviation) during 2003–2012 was 1306 ± 95 mm year^{-1} and the mean air temperature was $14.1 \pm 0.4\,°C$. The predominant land use in the 15 km^2 catchment is intensive dairying and has been for over 50 years. The average stocking rate in 2003 for the 18 dairy farms in the catchment was 3.1 cows ha^{-1} and N fertiliser was widely applied, typically as urea (average rate 100 kg N ha^{-1} year^{-1}). Nitrogen input from atmospheric deposition is estimated at 2 kg N ha^{-1} year^{-1}. Three sites in the catchment were investigated: Topehaehae, Morrinsville and Kereone (Fig. 1), with 3–5 wells installed at each site. All wells in the catchment were constructed of 50 mm diameter PVC pipe, with 0.5 m long screens. Well screens were fabricated from 50 mm diameter PVC pipe, with 22 mm diameter holes arranged to give an open area of >30%. Stainless steel mesh (500 μm) was wrapped around the pipe to cover the holes and plastic welded on.

2.1.1. Topehaehae site
The Topehaehae site is comprised of a Typic Recent Gley Soil (NZ soil classification) (Hewitt, 1998) and was located on a river floodplain, derived of recent alluvial deposits. Gley soils account for only 9% of the catchment and are restricted to locations close to the Toenepi stream. The soil is characterised by a thin A horizon (0.1–0.15 m) which overlies a poorly drained sandy loam and silt loam materials (Wilson, 1980; Stevenson and Thornburrow, 2006).
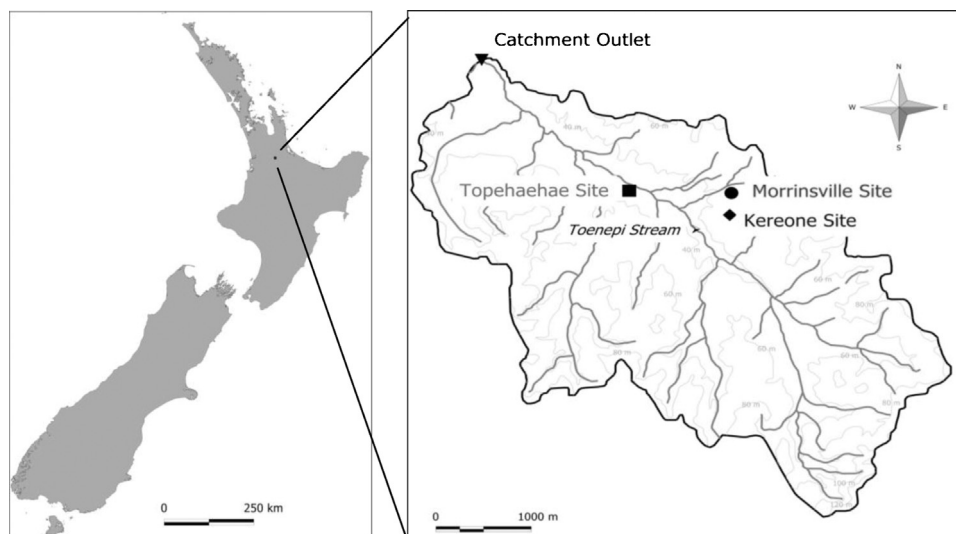

Fig. 1. Location of the Toenepi catchment in the North Island of New Zealand, and map showing the location of the study sites.