MEASURING ACTUAL DENITRIFICATION TO UNDERSTAND NITROGEN LOADS THROUGH AQUIFERS

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Aims

Denitrification is a natural process by which dissolved nitrate is eventually reduced to nitrogen gas (N_2). However, the extent of denitrification occurring within New Zealand's groundwater systems is largely unknown. Much emphasis has been placed on identifying where optimal redox conditions are present to allow for the facilitation of denitrification[4].

Unfortunately, assessment of the redox status of the groundwater only suggests whether denitrification may be possible in an aquifer, not whether it has actually occurred[1]. For example, a comparison of groundwater age versus redox status suggests that many reduced (anoxic) zones are, in effect, stagnant or very slow moving[2], and hence any potential for denitrification may have little effect on reducing nitrogen loads to receiving waters because the water does not flow through these zones.

Measurement of 'excess N_2', the product of the denitrification reaction, is the most promising method for directly measuring denitrification that has occurred in an aquifer[5,6]. All groundwaters contain dissolved gases derived from the atmosphere during recharge, including N_2. In addition to the dissolved atmospheric N_2, groundwaters can also contain excess N_2 that has accumulated from denitrification reactions. Measurement of a third gas, neon (Ne), can give the recharge temperature and excess air component by comparing the ratio of Ar and Ne dissolved in the groundwater. This enables differentiating the excess N_2 produced via denitrification reactions from atmospherically derived dissolved N_2 (Figure 1).
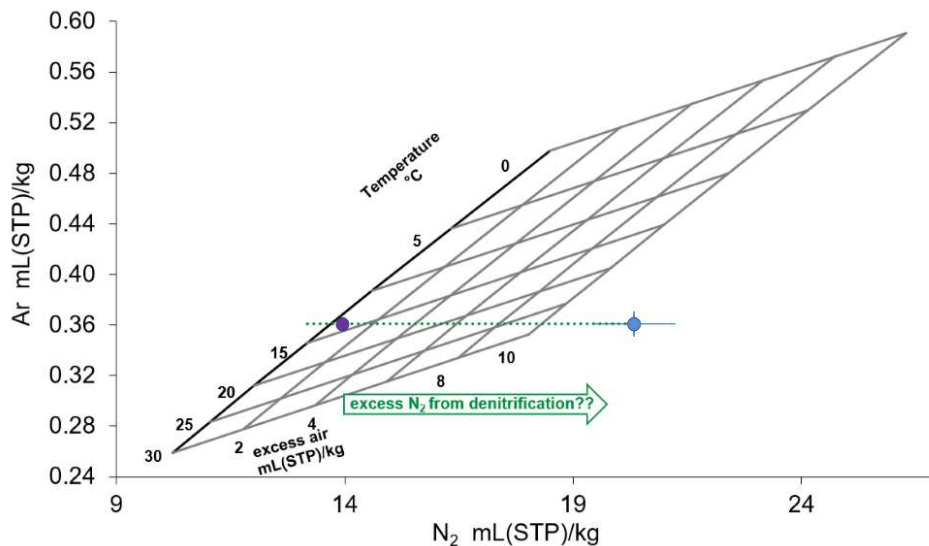

Figure 1: Example of initial contribution of N_2 (purple) calculated using the Ar Ne relationship and the total measured N_2 (blue) in a groundwater sample. The difference between the two N_2 concentrations is the contribution of N_2 from denitrification.

The aim of this study was to validates a method for identification of denitrification in an aquifer and quantification of the extent of any denitrification that actually has taken place.

Method

To validate the use of applying the Ne technique for measuring denitrification in groundwater systems, groundwater samples for Ne were collected from 27 piezometers in the Waikato, Canterbury and Horizons Region following the method described in Martindale et al. (2018)[3]. Many of the piezometers were sampled in pairs, where one piezometer was closely located next to the other but went to different depths. Other proxies for measuring denitrification, or for measuring that there is potential for denitrification to occur, were sampled in conjunction with the Ne samples. In the Canterbury Region these proxies included dissolved oxygen, $\delta^{15}N$ and chemistry. In the Horizons and Waikato Region in addition to $\delta^{15}N$ and chemistry, samples were collected for DNA analysis for the abundance of the *nirS*, *nirK* and *nosZ* genes. Additionally, Child's tests were carried out at the Waikato Region sampling sites. Age tracers, including tritium, CFC and SF_6 samples were also collected from some of the piezometers.

Results

Of the 27 sites sampled, 19 had N_2 in excess above the range of uncertainty. (eg. Figure 2). Of the 19 sites identified as having accumulated the product of active denitrification, 12 were highly anoxic. This is not unexpected. However, 5 of the sites had dissolved oxygen between 2.5 mg L^{-1} and 5.79 mg L^{-1}, indicating that complex flow pathways between the oxic and anoxic zones in the aquifer or in the well exist. Age tracers from the paired piezometers confirm this with groundwater ages differing between piezometers with depths varying by less than a metre.

The other proxies for identifying denitrification including $\delta^{15}N$ isotopic ratios, DNA analysis, chemistry and Child's test support the findings of the simultaneous measurement of Ne, Ar and N_2.
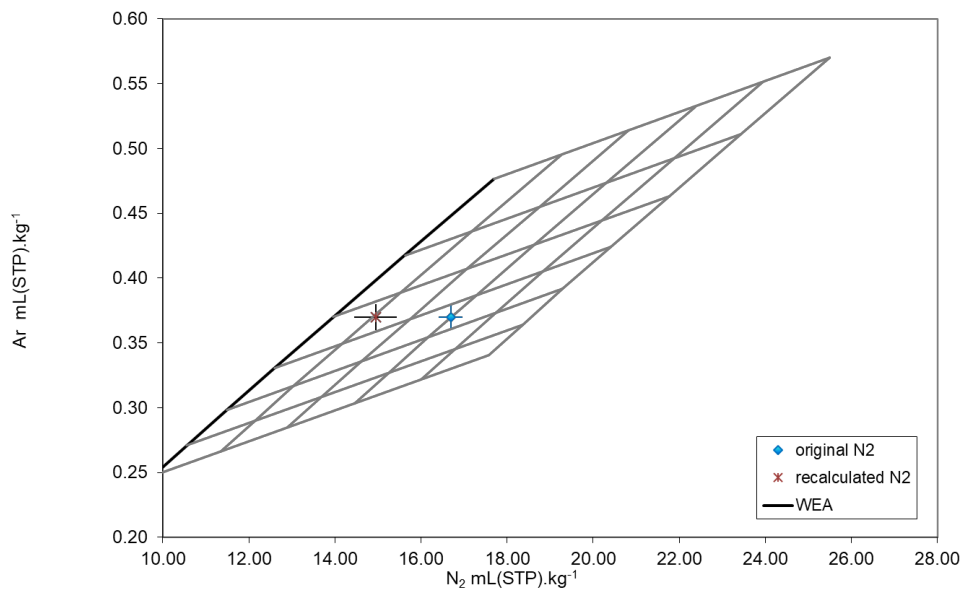

Figure 2: Initial contribution of N_2 (red), from 72_4970 in the Waikato Region, calculated using the Ar Ne relationship and the total measured N_2 (blue) in a groundwater sample.

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