# MEASURING ACTUAL DENITRIFICATION TO UNDERSTAND NITROGEN LOADS THROUGH AQUIFERS

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Aims

Measurement of denitrification is vital for managing nitrogen loads through New Zealand's aquifers. Nitrate is the most pervasive groundwater contaminant with approximately 40% of long-term groundwater monitoring sites showing above-natural concentrations (Daughney and Wall, 2007; Moreau et al, 2016). Denitrification is a natural process whereby dissolved nitrate is metabolised by microorganisms, eventually reducing the nitrate to dissolved nitrogen gas (Equation 1).

$$NO_3 \rightarrow NO_2 \rightarrow NO_{(g)} \rightarrow N_2O_{(g)} \rightarrow N_{2(g)} \qquad \text{Equation 1}$$
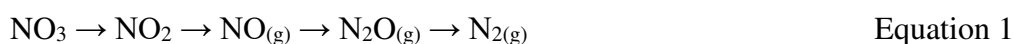
Denitrification can therefore remove nitrate from groundwater by conversion to gaseous forms, potentially leading to a significant nitrate reduction in the aquifer and lessening of nitrogen loads into receiving waters such as groundwater-fed streams, springs and lakes. Knowledge of the location and capacity of this process for nitrate remediation is useful for land use management planning.

All groundwaters contain dissolved gases derived from the atmosphere at the time of recharge, including N_2. Comparing the ratio of the two gases argon (Ar) and nitrogen (N_2) dissolved in the groundwater to the known ratio of gases in atmospheric air allows for the calculation of recharge conditions. When denitrification occurs, the concentration of dissolved N_2 increases, distorting the relationship between Ar and N_2, and therefore the calculated recharge conditions (Figure 1).
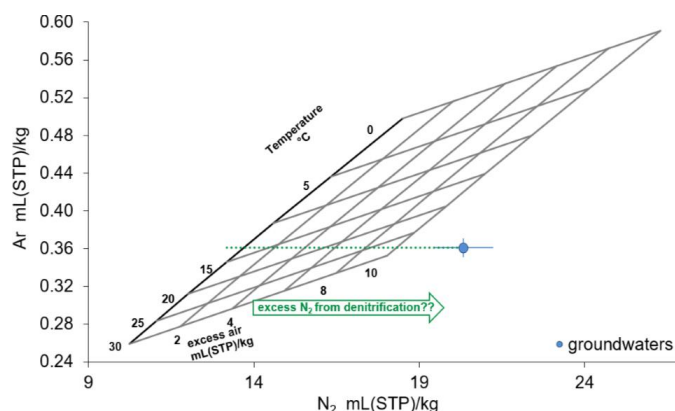

Figure 1: Graphical relationship of the concentrations of N_2 and Ar in a groundwater sample where denitrification has occurred and the recharge temperature of the water (blue symbol). The bold line on the left of the grid defines gas concentrations in equilibrium with the atmosphere. The dotted green line represents the possible initial concentrations of N_2 before denitrification occurred.

Measurement of a third dissolved atmospheric non-reactive gas, e.g. neon (Ne), can be used to determine the ratio of dissolved atmospheric gases, which in turn will allow for the determination of any excess N_2 from denitrification (Figure 2).
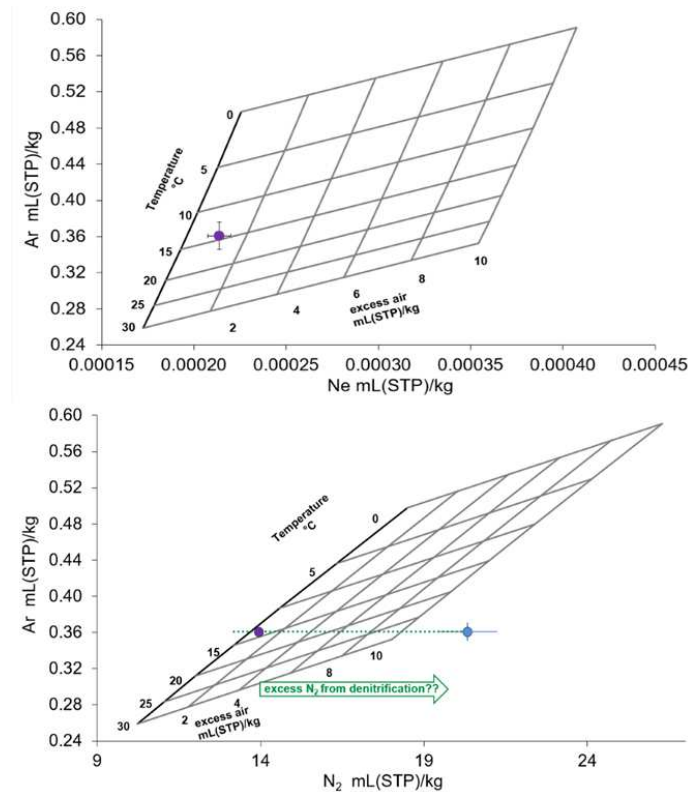

Figure 2: Graphical relationship of the atmospheric concentrations of Ne and Ar in a groundwater sample and the recharge temperature of the water (top graph). The Ar-Ne relationship can then be used to calculate the initial contribution of N_2 (purple) from the total measured N_2 (blue) in a groundwater sample (bottom graph).

Ne is an inert, soluble, gas which is present in air and has been used in international studies to understand recharge conditions (Wilson and McNeill, 1997). The aim of establishing a sampling and analysis technique for Ne is two-fold: (i) enable the quantification of excess nitrogen in the groundwater and thus, denitrification, and (ii) improve groundwater dating via gas tracers by providing the correct recharge temperature and excess air to obtain more robust age tracer concentrations.

Method
Ne samples are collected in 1 L glass sample flasks, following standard groundwater sampling protocols for collecting dissolved gas samples. Only 900 mL of sample water is collected in the flask which allows most of the Ne in the water to degas from the water into an air space (Figure 3a), referred to as the head space method. This head space is then transferred via pressure differential into an open, evacuated 200 mL syringe. The gas is then compressed in the syringe, before it is fed through our gas chromatography setup (Figure 3b) and finally through the detectors. The Ne sample is measured on a pulse discharge detector (PDD) and a thermal conductivity detector (TCD) at the same time. The PDD provides the sensitivity required to measure Ne, while the TCD allows for the simultaneous measurement of Ar and N_2 gas.

Figure 3: (a) Full Ne flask during sampling (left). (b) syringe and chromatography inlet system (right).

Ne samples have been collected from "paleo" groundwaters in Taranaki and Marlborough. Dissolved Ne has been previously measured in these waters by Selzer et al. (2015). In addition to the Ne samples, CFC samples were collected at all sites. N_2 and Ar are also measured simultaneously when CFCs are analysed and are calibrated to a known standard.

Results

The samples collected from the paleo groundwaters were measured and compared to the previously measured Ar and Ne concentrations. The results from our measurement system correlate closely to the 2013 results (Figures 4-6), validating our Ne measurement method.
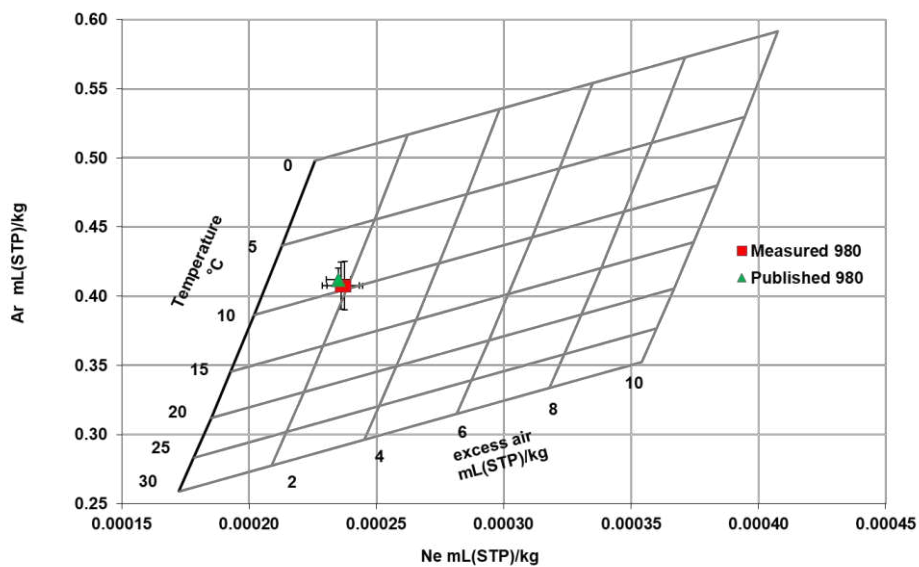

Figure 4: Comparison of measured (red) and published (green) concentrations of Ar and Ne from a Marlborough well, p28w/0980, containing "paleo" water.
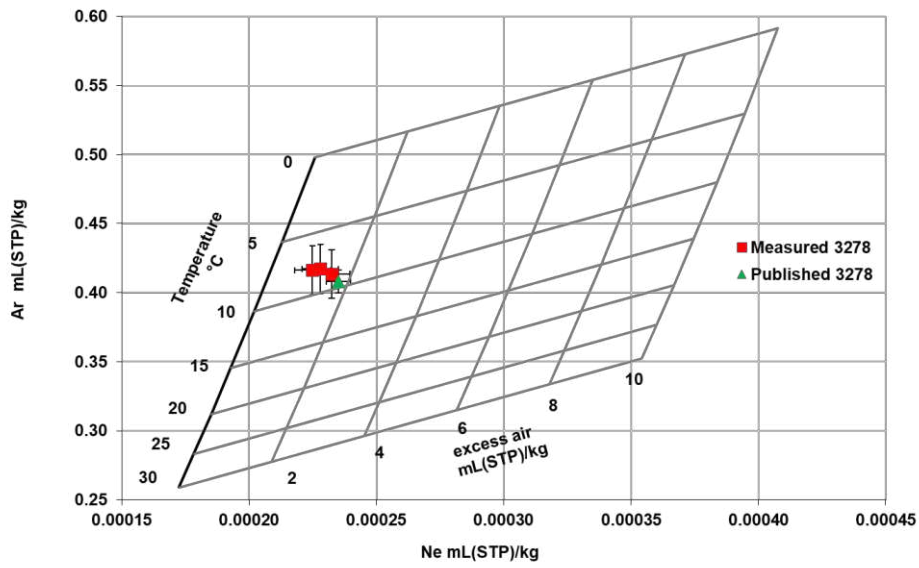
Figure 5: Comparison of measured (red) and published (green) concentrations of Ar and Ne from a Marlborough well, p28/3278, containing "paleo" water.
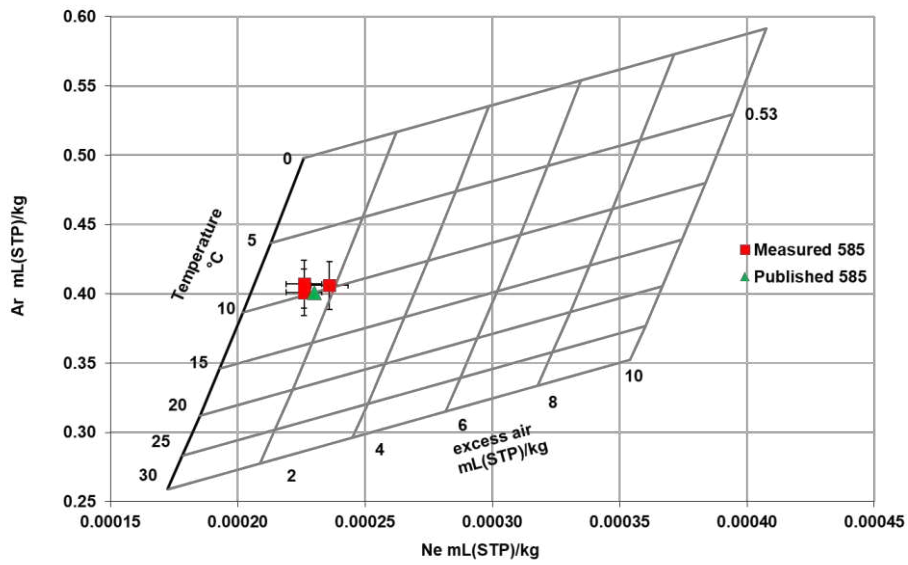

Figure 6: Comparison of measured (red) and published (green) concentrations of Ar and Ne from a Taranaki well, GND585, containing "paleo" water.

References

Daughney CJ, Wall M. 2007. Groundwater quality in New Zealand : state and trends 1995-2006. Lower Hutt (NZ): GNS Science. *GNS Science consultancy report; 2007/23*

Moreau M, Riedi MA, Aurisch K. 2016. Update of national groundwater quality indicators : state and trends 2005-2014. Lower Hutt (NZ): GNS Science. *GNS Science consultancy report; 2015/107.*

Seltzer AM, Stute M, Morgenstern U, Stewart MK, Schaefer JM. 2015. Mean annual temperature in New Zealand during the last glacial maximum derived from dissolved noble gases in groundwater. *Earth and planetary science letters*. 431:206-216. doi:http://dx.doi.org/10.1016/j.epsl.2015.09.032.

Wilson, G., McNeill, G., 1997. Noble gas recharge temperatures and the excess air component. *Applied Geochemistry,* 12(6): 747-762.