Quantifying Actual Denitrification in Groundwater Systems

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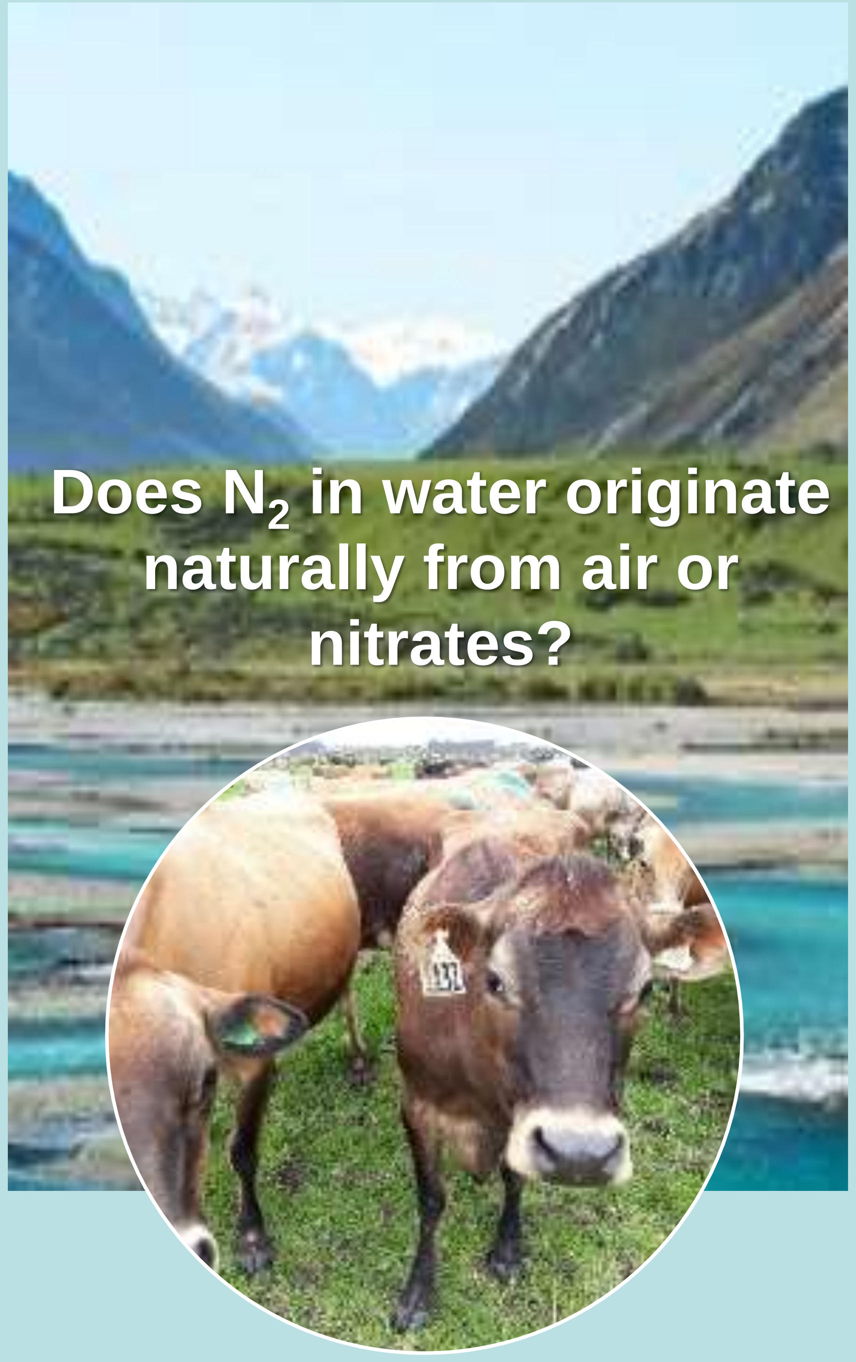
Introduction

Nitrate is a significant issue in New Zealand's groundwater systems and waterways. More than 40% of groundwaters are above natural concentrations. Nitrate promotes growth of algae in waterways and degrades aquatic habitat and affects the water's recreational value. Elevated nitrate levels are toxic to animals and humans.

Understanding the distribution and reduction rate of nitrates is critical for managing nitrogen loads in New Zealand's aquifers. GNS Science has developed the only in-situ method to measure the reduction of nitrates by co-analysis of argon, neon and excess nitrogen gas which occur from either natural atmospheric input or denitrification of nitrates.

$$NO_3 \rightarrow NO_2 \rightarrow NO_{(g)} \rightarrow N_2O_{(g)} \rightarrow N_{2\,(g)}$$

Denitrification is the best natural process for nitrate remediation. Nitrates are converted to nitrogen gas through a series of oxygen reduction processes.

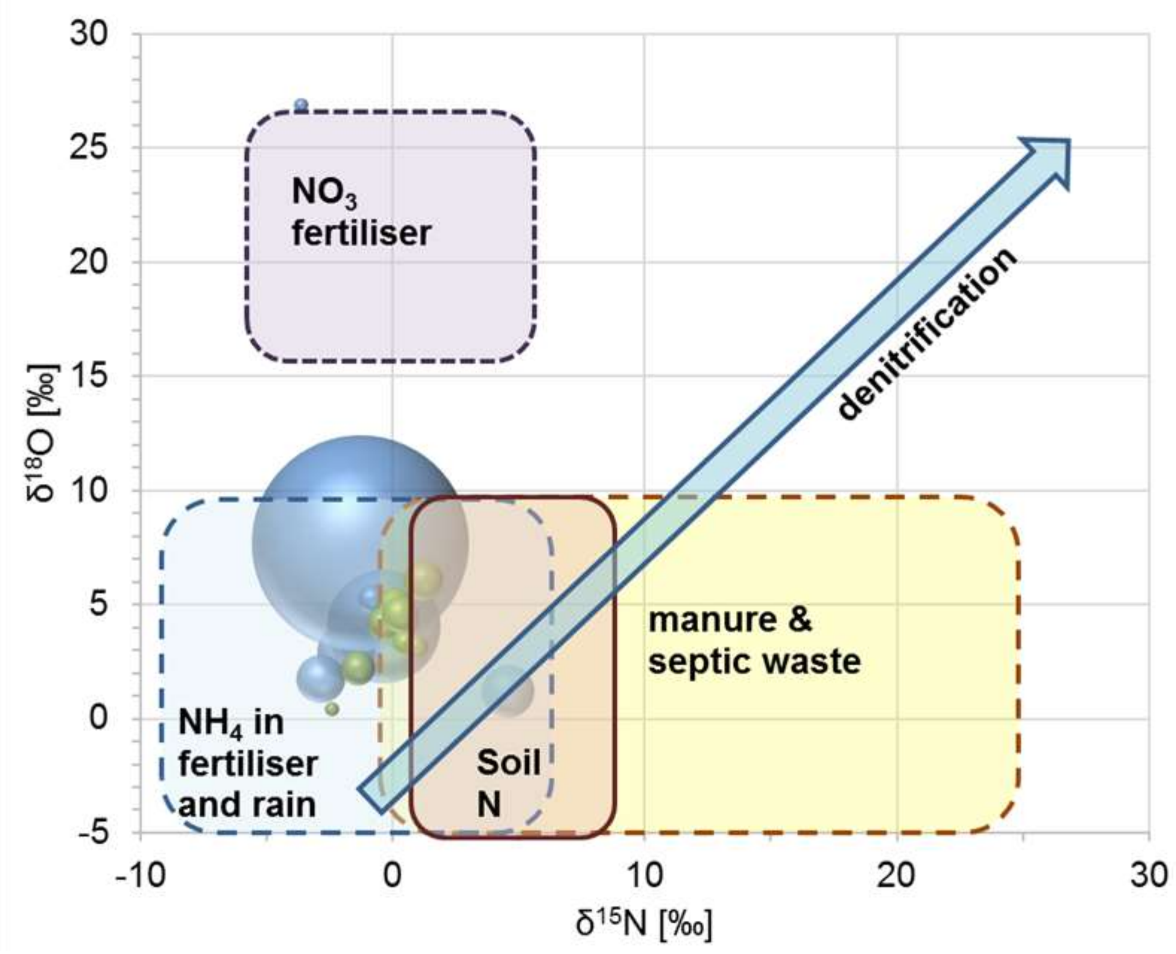


Method

Argon and neon are derived from the atmosphere, so their presence is used to quantify (or not) excess nitrogen gas which arises from reduction of nitrates during denitrification. Groundwater samples with dissolved gasses are collected in 1 litre flasks for analysis. The dissolved gases are extracted and measured, with the ratios of $Ar:N_2$ and $Ne:N_2$ indicating their origin. Either higher $Ar:N_2$ and $Ne:N_2$ for atmospheric input or lower $Ar:N_2$ and $Ne:N_2$ ratios for excess N_2 from denitrification.

Measurement of 'excess N_2' is the most promising method for directly measuring denitrification that has occurred in an aquifer. Current efforts to locate and characterise denitrification zones can also be confirmed by quantifying the extent of denitrification by measuring excess N_2 gas changes. Denitrification efficiency ability of sites can be determined for future land-use management.

Background

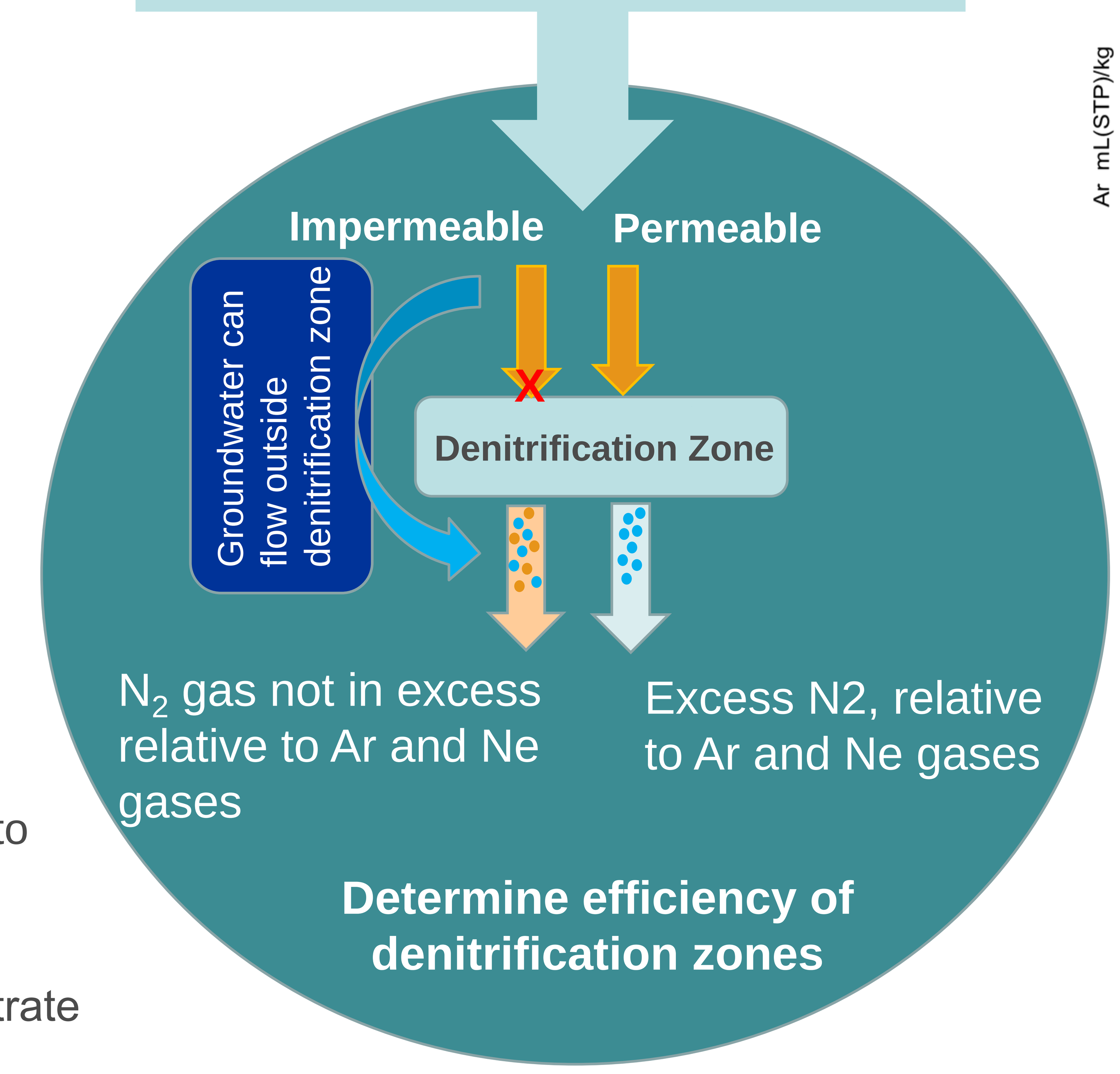


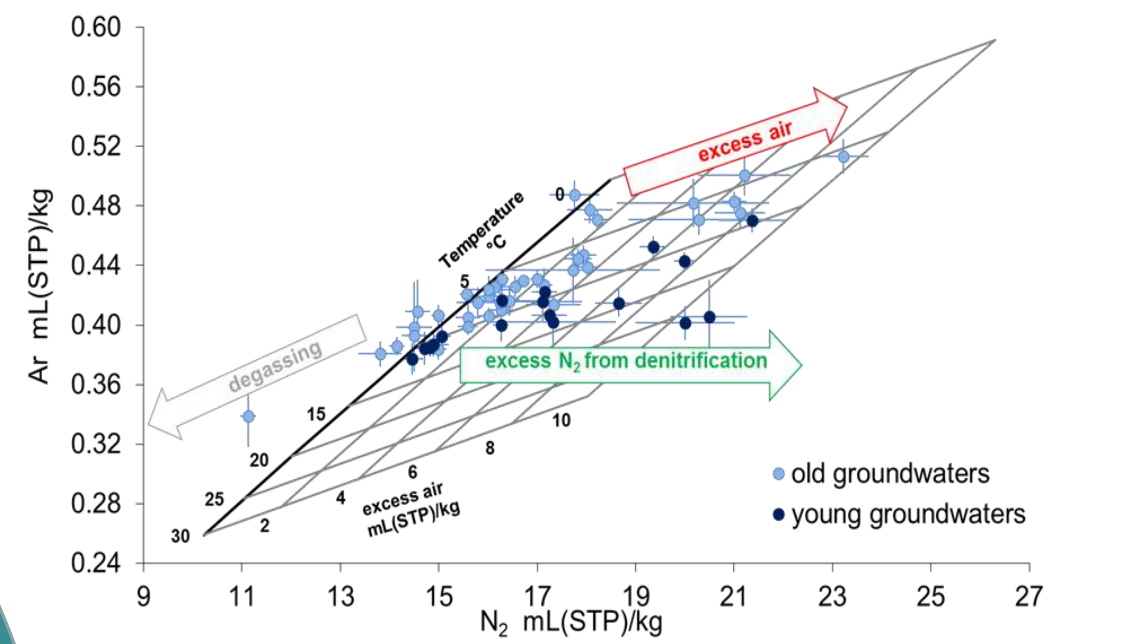
Previously we used redox mapping and isotopes to identify nitrate sources but the signal is lost with denitrification.

Denitrification hotspots can't be detected using nitrate isotopes.

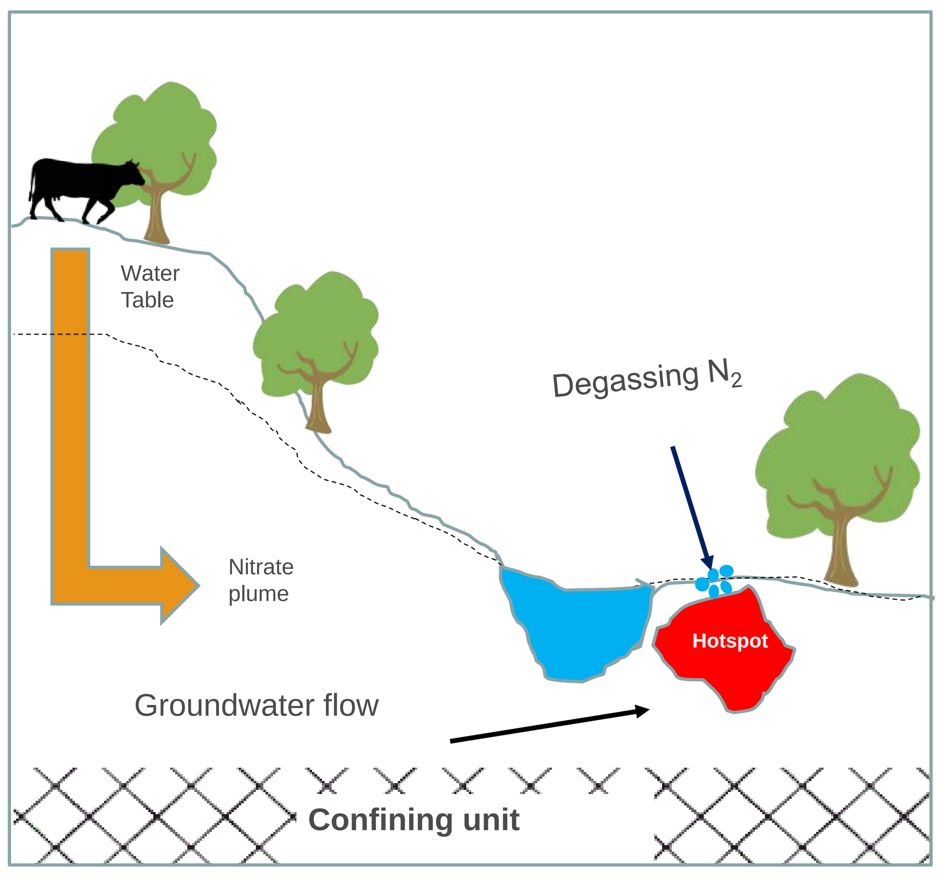
Quantifying excess N_2 gas allows for more accurate determination of denitrification.

Why measure denitrification?





Current results show the origin of N_2 gas in old groundwater is from air, while younger groundwaters is from nitrates.



Nitrates enter groundwater and are transported until they hit a denitrification zone (hotspot), where they transform to N_2 gas.

Purpose

We are now embarking on a new phase of methods development to improve sampling techniques and detection limits. We aim to map denitrification and identify zones for land use planning so are **seeking partners** who can provide samples to contribute to a series of field experiments to characterize denitrification zones.

Although the denitrification process is well known, **actual quantification** of groundwater systems will provide evidence to show effectiveness of various mitigation efforts or soil's natural denitrification ability.

Summary

- High nitrates negatively affect human health
- We quantify the end product (excess N_2) from the denitrification reaction using neon, argon and nitrogen gas analyses.
- Combined with water age tracers, the rate of denitrification can be found.
- From the data we can map denitrification zones and rates of denitrification.
- Improves land management services by identifying denitrification zones for land use planning to improve water quality

GNS Capability

Tracer	Advantages	Disadvantages
Nitrate Isotopes	Distinguishes nitrate contamination sources	Not useful for low level nitrates
Tritium	Dates groundwater and identifies flow pathways	Expensive, hard to define denitrification zones by itself
N_2, Ne, Ar Gas analysis	Identifies denitrification zones and N_2 reduction amount	Need to combine gas analysis with age tracers to obtain denitrification rates

Conclusion

Measurement of neon, argon and $N_{2(g)}$ identifies;
1. Excess $N_{2(g)}$ from denitrification of nitrates
2. In future, $N_{2(g)}$ can be determined using isotopes to analyse N origin (air or nitrates)
3. Combined tracer techniques are complimentary

References
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2. Stenger, R., Clague, J.C., Morgenstern, U., Clough, T.J. 2018. Vertical stratification of redox conditions, denitrification and recharge in shallow groundwater on a volcanic hillslope containing relict organic matter. Science of the Total Environment, 639:1205–1219.

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