

Groundwater nitrate attenuation in a volcanic environment (Lake Taupo, New Zealand)

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Abstract Pastoral farming is considered responsible for early signs of deterioration of the water quality of Lake Taupo. The potential for nitrate attenuation to occur below the bottom of the root zone was considered negligible when 'Nitrogen Discharge Allowances' were set for all farms in the catchment. However, we found reduced and virtually nitrate-free groundwater at 5 – 7 of our 12 well sites in spite of the high porosity of the young volcanic subsurface materials and their perceived lack of an electron donor. Reduced groundwater was regularly observed where residual organic debris from the vegetation destroyed by the Taupo eruption 186 AD occurred below the water table. It would thus appear that this old organic matter is still a sufficient electron donor for heterotrophic denitrification.

Keywords denitrification; nitrous oxide, dinitrogen, redox conditions; palaeosol; interaction of biogeochemical and hydrological factors.

INTRODUCTION

Land use change over the last 50 years from tussock, shrub-land and indigenous forests to plantation forests and particularly to pastoral farming is considered responsible for early signs of deterioration of the still near-pristine water quality of Lake Taupo (622 km²). The estimated amount of nitrate leaving the root zone of pastoral land has been used to define a 'Nitrogen Discharge Allowance' for each farm in the catchment. The potential for nitrate attenuation to occur below the root zone was considered negligible, due to the high porosity of the volcanic deposits and their perceived lack of an electron donor.

To test this assumption we investigated the chemistry of shallow groundwater underlying a gentle hillslope leading from the upper catchment boundary to a wetland.

MATERIAL AND METHODS

The subsurface materials at the research site on a sheep and beef farm encompass a young volcanic soil developed on the underlying unwelded Taupo Ignimbrite (1.8 ka BP) followed by an older soil (Palaeosol), and Oruanui Ignimbrite material below (26.5 ka BP). The water table resides predominantly within the Oruanui Ignimbrite in upslope locations, but reaches into the Taupo Ignimbrite in downslope locations (cf. Fig. 3).

Ten multi-level well clusters consisting of 2 to 5 wells each and two single wells were established. The depth of these 27 wells ranged from approx. 1.5 to 9 m below the ground surface and their well screen was a maximum of 5 m below the water table. To characterize the spatial and temporal variation, field (DO, EC, pH) and laboratory analyses (N and C species, dissolved Fe and Mn, sulphate) were undertaken up to 7 times (May 07 – Nov 08). In November 2008, samples from selected wells have additionally been analysed for the dissolved gases N₂O, Ar, N₂, and CH₄.

RESULTS AND DISCUSSION

The measured concentrations of dissolved oxygen (DO) demonstrate that the aeration status of the sampled groundwaters varied from fully oxidised to completely oxygen depleted (Fig. 1). The vast majority of very low nitrate concentrations occurred in poorly aerated groundwaters, which suggests that denitrification had occurred in these waters. Of all samples with a DO below 2 mg L⁻¹, a concentration often considered the upper limit for denitrification (cf. Korom, 1992), 77% had nitrate nitrogen concentrations below 0.44 mg L⁻¹ (AUS/NZ trigger value for eutrophication of surface waters). The wide range of DO and NO₃-N concentrations evident in this data set is partly due to spatial and partly due to temporal variation.

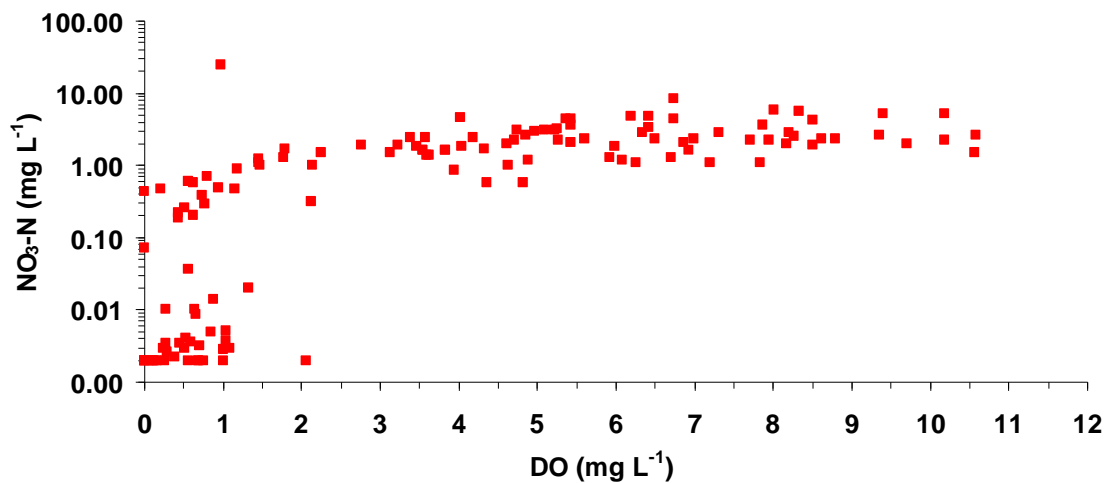


Fig. 1 Relationship between groundwater nitrate concentrations (NO₃-N) and concentrations of dissolved oxygen (DO), (n = 132; May 07 - Sep 08).

On the example of results from November 2008, Fig. 2 demonstrates that the groundwater chemistry varied between multi-level well sites and at most sites also between different sampling depths.

DO concentrations at most sites decreased with depth. However, at 5 sites they remained above 2 mg L⁻¹ throughout the investigated depth range, suggesting that there was very little potential for denitrification (WR18, WR17, WR21, WR23, Spydia). In contrast, at 7 sites DO was already below that concentration in the shallowest well (WR25, WR27) or dropped below it with increasing depth (WR20, WR19, WR24, WR26, WR22).

NO₃-N concentrations showed the same trends as DO concentrations at poorly aerated sites, but were independent of DO at the better aerated sites. Nitrous oxide (N₂O), indicating incomplete reduction of nitrate, was highest in waters which still contained more than 4 mg L⁻¹ DO (WR25-1 excepted). In contrast, excess N₂, resulting from complete reduction of nitrate, occurred in more strongly reduced waters (particularly WR20-3 and WR20-4, WR25-1 and WR25-2, WR26-2).

Enhanced concentrations of dissolved iron indicate that redox conditions in several waters had passed the nitrate reduction stage and were reduced enough for ferric iron reduction to occur (particularly WR20-3 to WR20-5, WR26-1 and WR26-2).

Sulphate reduction (data not shown) and methane fermentation is indicated for some even more strongly reduced waters (WR26, WR25, WR20-3).

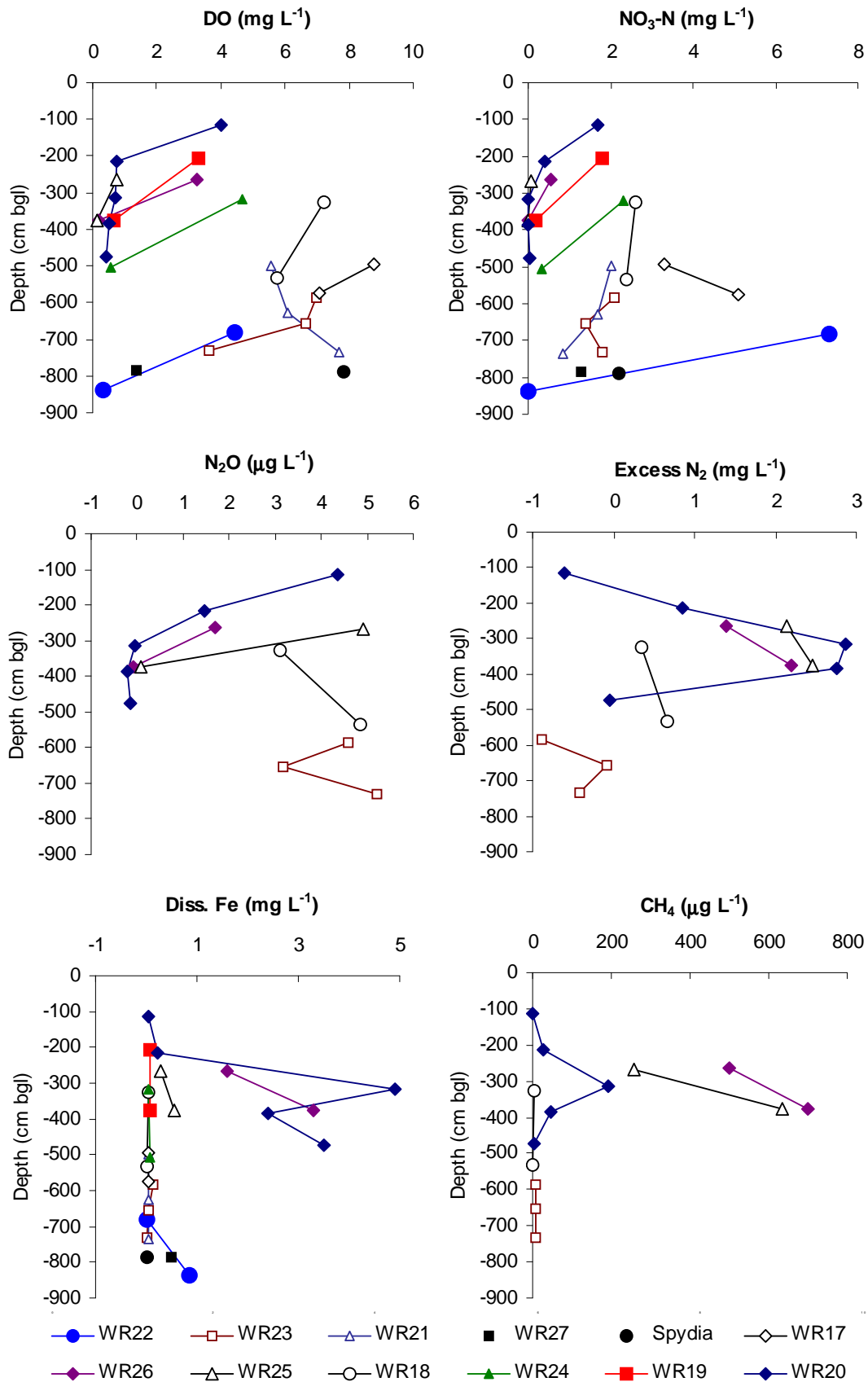


Fig. 2 Selected parameters analysed on samples from up to 12 well sites sampled in November 2008 (bgl = below ground level).

The measured concentrations of dissolved organic carbon (DOC; data not shown) did not show a clear relationship with the redox status of the groundwater, suggesting that DOC recharging from the soil zone is not the electron donor driving denitrification. Logging of subsurface materials during well installation in combination with the groundwater analyses suggests that organic debris remaining from the vegetation destroyed by the Taupo eruption 186 AD acts as a relict, solid-phase electron donor. Reduced groundwater was consistently found at all well sites where organic debris at the bottom of the Taupo Ignimbrite had been documented during well installation and where this debris was located below the water table. Reduced groundwater was only found in a few instances where this debris had not been documented.

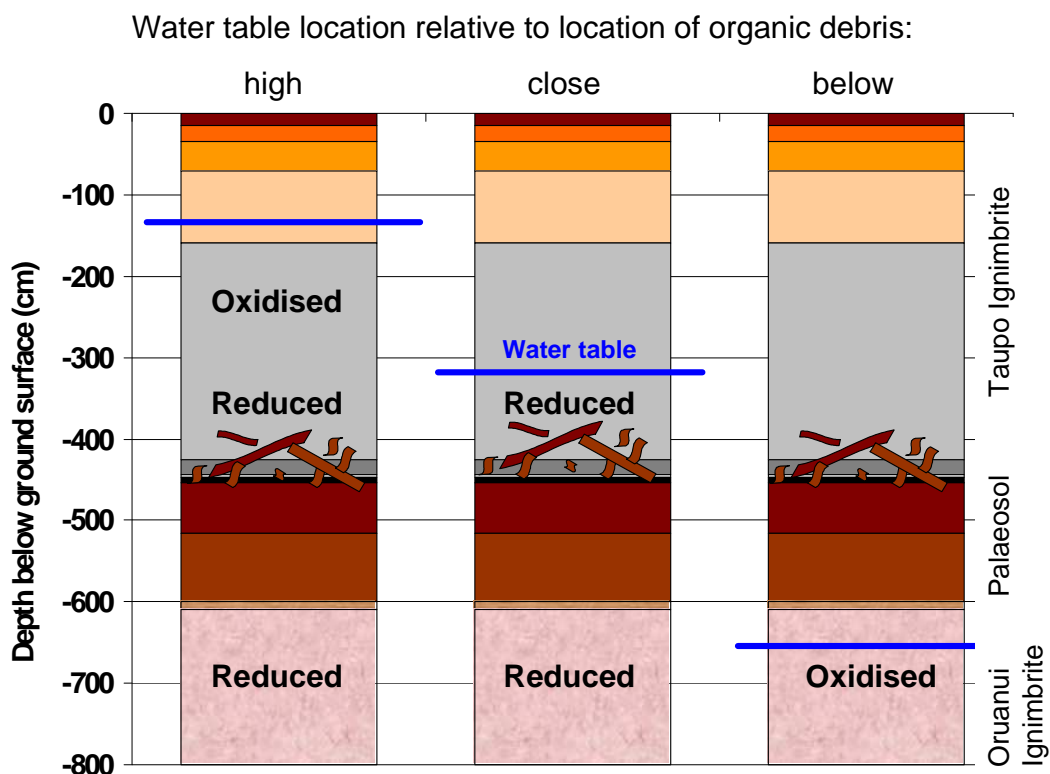


Fig. 3 Groundwater redox status as determined by the interaction of the water table location with the location of organic debris from the Taupo eruption 186 AD.

Fig. 3 describes schematically how the interaction of biogeochemical and hydrological factors determines the redox status of the groundwater at the research site. A thin layer of oxidized groundwater is overlying reduced groundwater where (spatially) or when (temporally) the water table is well above the organic debris. Only reduced groundwater is found if the water table is just above the debris. However, groundwater is likely to be oxidised at sites where the water table lies consistently below the organic debris. This is due to the high porosity of the volcanic materials that under unsaturated conditions should allow for sufficient gas exchange with the atmosphere to prevent reducing conditions.

REFERENCES

Korom, S.F. (1992) Natural Denitrification in the Saturated Zone: A Review. *Wat. Resour. Res.* **28**(6), 1657-1668.