Groundwater redox-stratification and water table dynamics determining nitrate discharge into a lowland stream

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Seasonally varying nitrate concentrations and a positive correlation between stream flow rate and nitrate concentration have been reported for Toenepi Stream in New Zealand (Wilcock et al., 2006). Such patterns have been reported internationally for many streams and rivers in oceanic to humid continental climate zones. A range of possible reasons have been put forward (e.g. Wriedt et al., 2007, and references therein), but our research suggests that a previously unreported mechanism is responsible for the pattern observed in the Toenepi Stream catchment. Based on a combination of groundwater and stream monitoring and modelling of stream flow generation, we conclude that the observed pattern is due to seasonally varying proportions of discharge from an upper, oxidised and nitrate-bearing groundwater zone and a deeper, reduced and virtually nitrate-free groundwater zone. This finding underlines that subsurface flow paths and transformation processes, which affect timing and degree of stream pollution, need to be taken into account when nitrate concentrations in streams are to be related to diffuse losses from agricultural land use.

Figure 1 Map of Toenepi catchment, showing stream network and locations of catchment outlet weir (COW), headwater weir (HWW), multilevel well sites (MLW-1 to MLW-3), and meteorological station.

The Toenepi Stream catchment (15 km^2) comprises low rolling downlands and alluvial plains, and is located in a long-established dairying region in the North Island of New Zealand (Fig. 1). Well-drained Allophanic and Granular soils dominate the catchment; poorly drained Gley soils are found in the lowest-lying areas. Groundwater chemistry and water table dynamics were monitored at three multilevel well (MLW) sites that represent the major soil types. Stream flow time series were available from the catchment outlet weir (Wilcock et al., 2006). Meteorological data recorded in the catchment were used to predict stream flow using an extension of the eigenmodel approach described in Bidwell et al. (2008). Silica concentrations were used as a simple age indicator for groundwater and stream water, as they reflect the contact time the water has had with silica-bearing minerals in the subsurface.

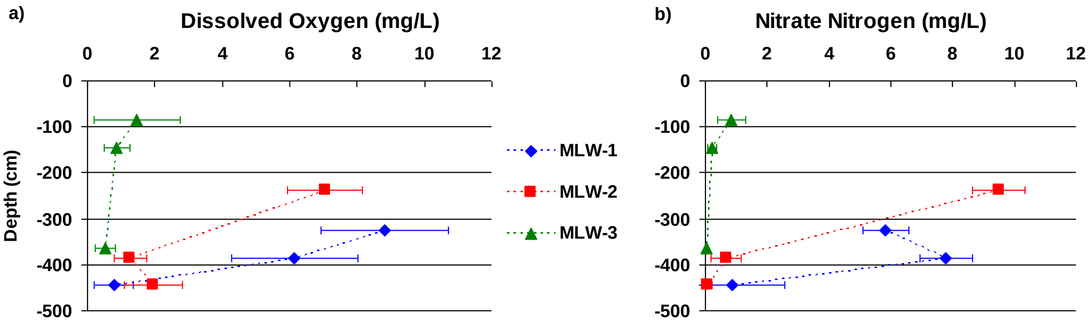

Figure 2 Depth profiles of a) dissolved oxygen, and b) nitrate nitrogen in groundwater at three multilevel well (MLW) sites (Means ± standard deviations shown).

As expected for a poorly drained alluvial Gley site, groundwater at MLW-3 was very low in dissolved oxygen and nitrate throughout the profile (Figure 2). By contrast, the uppermost groundwater underlying the Allophanic and Granular soils had dissolved oxygen concentrations nearly in equilibrium with the atmosphere and nitrate (approx. 6 – 10 mg/L NO_3-N) in the range expected for dairying land use. However, strong redox gradients at both sites meant that deeper groundwater was oxygen-depleted and nearly devoid of nitrate. Circumstantial evidence (hydrochemistry, $\delta^{15}N$ and $\delta^{18}O$ of nitrate) suggested that the very low nitrate concentrations result from heterotrophic denitrification occurring in the groundwater.

Figure 3 depicts, using the example of MLW-2, that the upper, oxidised groundwater zone can be up to 2.5 m thick after fresh recharge in winter, but as a result of continued lateral groundwater discharge into the stream can shrink to only 1.0 m in autumn. Nitrate and silica concentrations support the hypothesis that this uppermost, young and oxidised groundwater zone accounts for most of the discharge into the stream at the high stream flow rates observed during winter/spring. In contrast, discharge from the deeper, older and reduced groundwater zone becomes relatively more important when the thickness of the upper groundwater zone, as well as the stream flow rate, approach their minimum in summer/autumn. This explanation is in agreement with the finding that the mean transit time of baseflow in Toenepi Stream shows a very strong seasonal variation (Morgenstern et al., 2010).

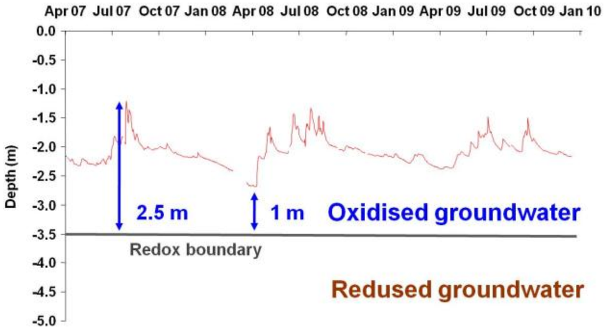

Figure 3 Water table dynamics recorded at MLW-2. The arrows highlight the temporally varying thickness of the oxidised groundwater zone above the redox boundary.

Eigenmodel simulations suggested that near-surface flow accounted on average for 11% of the annual stream flow, fast (shallow) groundwater for 84%, and slow (deep) groundwater for 5%. However, while slow groundwater contributed only a minor portion of the total flow, it dominated stream water chemistry for more than half of the year (Figure 4). The effect of this deeper groundwater on the stream ecology is thus much longer-lasting than its small flow volume contribution would suggest.

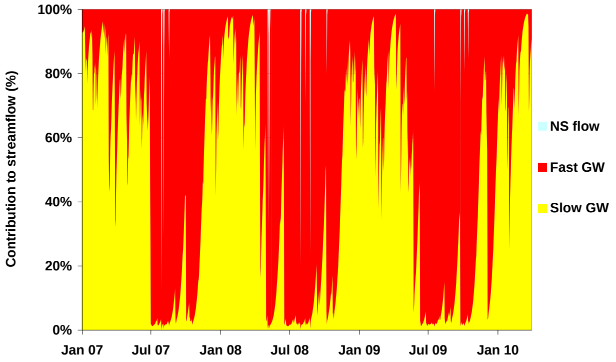

Figure 4 Relative contributions of near-surface water (NS), fast groundwater (Fast GW), and slow groundwater (Slow GW) to streamflow.

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