# GROUNDWATER ASSIMILATIVE CAPACITY – AN UNTAPPED OPPORTUNITY FOR CATCHMENT-SCALE NITROGEN MANAGEMENT?

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**Abstract**
Not all nitrate leached out of the soil zone ultimately pollutes the groundwater system and groundwater-fed surface waters; some nitrate can be assimilated in the subsurface environment. How much nitrate can be assimilated without exceeding water quality limits depends on a combination of biogeochemical and hydrological factors.

Denitrification, i.e. the conversion of nitrate to gaseous forms of nitrogen ($N_2$, $N_2O$), is the key process determining the biogeochemical component of a catchment's assimilative capacity for nitrate. Denitrification is the only attenuation process that actually removes nitrogen from the subsurface rather than just storing or diluting it. Saturated zone denitrification is an environmentally benign process, as it predominantly returns inert $N_2$ to the atmosphere. Three requirements must be met for denitrification to occur: oxygen-depleted conditions, availability of suitable electron donors, and existence of a microbial community with the metabolic capacity for denitrification.

The second major attenuation process at the catchment scale is the dilution of nitrate-rich groundwater, typically recharged from agricultural land, with clean groundwater originating from low land use intensity areas (e.g. mountains, forests). This process is particularly relevant where different groundwater flowpaths converge in the lowland discharge zone of the large alluvial aquifers that occur in many eastern areas of New Zealand (e.g. Canterbury Plains).

Provided the groundwater flowpaths and the biogeochemical processes occurring along them were known, this knowledge could be used to optimise spatial land use intensity patterns in a catchment within agreed water quality limits. Rather than relying on root zone leaching estimates alone, the acceptable land use intensity for a given piece of land would take the subsurface system's assimilative capacity into account. Consequently, land uses with higher nitrate leaching losses would be possible where the assimilative capacity allows, while only lower losses would be acceptable on land with lower assimilative capacity.

It is anticipated that this approach would result in spatial land use intensity patterns that better protect environmental, economic, social, and cultural values than current practice and recently introduced approaches that are exclusively based on root zone leaching estimates. Statutory environmental standards and nutrient limits will in the future constrain development in some catchments. Comprehensive assimilative capacity assessments across catchments or sub-catchments would thus help to guide investment in land development and to allocate clean-up funding more effectively, and enable land to be directed towards its optimum use.

## Introduction

Establishment of defensible cause-effect relationships is essential to define the maximum land use intensity that is possible within given environmental constraints. Nutrient losses from agricultural land use are predominantly diffuse losses and as such not particularly amenable to quantification by measurements. Accordingly, nutrient balancing models like OVERSEER (http://www.overseer.org.nz) or 'look-up tables' based on empirical data and expert opinion (e.g. Lilburne et al., 2010) are typically used in NZ to estimate losses from farms. While surface runoff is the most significant loss mechanism for phosphorous (P) and microbes, nitrogen (N) is predominantly transported to surface water bodies on the subsurface pathway (Fig. 1).

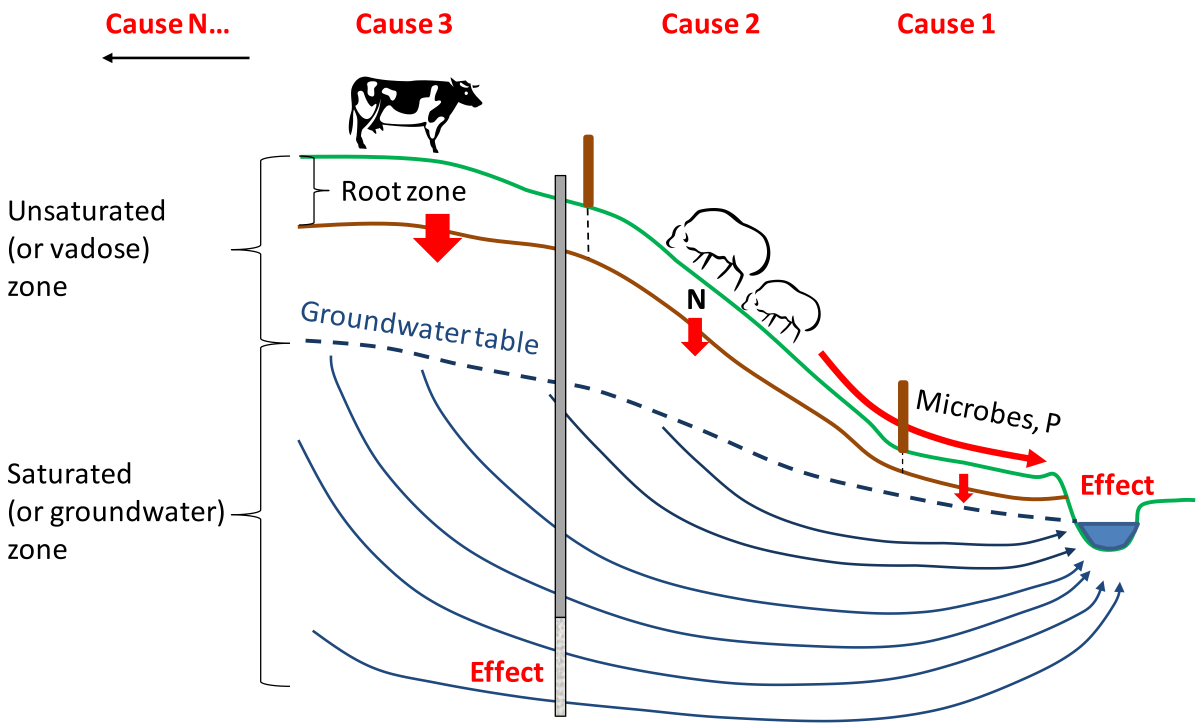


**Figure 1.** Schematic of nutrient loss pathways from land to surface water bodies, focusing on the subsurface pathway critical for nitrogen (predominantly in the form of nitrate).

Estimating the amount of nitrogen leached out of the root zone is in itself insufficient to defensibly evaluate the effect on a groundwater body or a groundwater-fed surface water body. The subsurface hydrology and biogeochemical processes possibly occurring along the flow path additionally need to be taken into account.

The hydrology determines which area of land affects which freshwater body, to which degree, and when. The nitrate discharge into a surface water body is determined by the cumulative effect of land surface recharge from all land uses that occur along the groundwater flow paths (Cause 1 – Cause N in Fig. 1). The groundwater catchment contributing to a particular surface water body may differ from the corresponding topographical catchment (e.g. Bidwell et al., 2008 and references therein; Rutherford et al., 2009). Very long groundwater lag times can mean that nitrogen lost from a farm arrives only several decades later in a freshwater body of interest (e.g. Morgenstern, 2008).

On the other hand, biogeochemical processes determine which portion of the nitrogen leached out of the root zone ultimately pollutes the groundwater system and groundwater-fed surface water bodies. Some nitrogen can be assimilated in the subsurface environment below the root zone (i.e. in the deeper part of the unsaturated zone and in the underlying groundwater zone, Fig. 1).

## Groundwater Assimilative Capacity (AC)[1]

While processes occurring in the deeper part of the unsaturated zone and particularly at the interface with the groundwater zone may be significant, for the sake of simplicity we include them in the term ‘Groundwater Assimilative Capacity'.

The assimilative capacity of a groundwater system for nitrate can be defined as the cumulative effect of all biogeochemical and hydrological processes that keep nitrate mass flux or concentration below a limit set for a given water body. Mass flux (or ‘load’) limits typically apply to lakes, while concentration limits are more appropriate for groundwater systems, streams and rivers. The term ‘attenuation capacity’ is often used synonymously to the term ‘assimilative capacity’.

### *Biogeochemical AC component: denitrification*

Denitrification is the key biogeochemical N attenuation process. It converts nitrate ($NO_3^-$) to gaseous forms of nitrogen; in groundwater systems predominantly to dinitrogen ($N_2$), which in contrast to nitrous oxide ($N_2O$), is environmentally benign. Complete denitrification of nitrate to dinitrogen effectively reduces the mass of a reactive form of nitrogen to an inert form, which makes up 78% of the earth’s atmosphere.

Apart from nitrate being present, there are three requirements for denitrification to occur. Firstly, there needs to be oxygen-depleted conditions. Concentrations of dissolved oxygen (DO) below 2 mg/L have often been found conducive to denitrification in groundwater systems (Korom, 1992). Secondly, suitable electron donors need to be available. Heterotrophic denitrification is fuelled by organic matter, which can either be mobile organic matter leached out of the root zone or particulate organic matter residing in the aquifer matrix. Reduced inorganic iron (Fe) and sulphur (S) compounds (e.g. pyrite) can fuel autotrophic denitrification. Finally, microbes with the metabolic capacity for denitrification are required. Nitrate and suitable microbes are generally considered ubiquitous under agricultural land use. Accordingly, the occurrence of denitrification at a particular location is largely determined by the local availability of electron donors and the existence of oxygen-depleted conditions.

### *Denitrification case study: Toenepi catchment*

Comprehensive data sets established by various research providers over several years make the Toenepi catchment a suitable case study to demonstrate the effect of groundwater denitrification on catchment-scale nitrogen fluxes. Dairy farming is the dominant land use in

[1] MSI currently funds a research programme on Groundwater Assimilative Capacity (C03X1001). As for the contaminants investigated, ESR leads the work streams on phosphorous and microbes, and LVL that on nitrogen.

this 15 $km^2$ lowland catchment near Morrinsville (Waikato), which was one of the 'Best Practise Dairying Catchments' (Wilcock et al., 2007). Approximately 90% of the catchment has well drained Allophanic and Granular soils. Poorly drained Gley soils occur in the lowest-lying areas adjacent to the stream. To investigate the reasons for the unexpectedly low nitrate concentrations in the groundwater in this catchment (Stenger et al., 2008), the groundwater redox chemistry has been studied at three multi-level well (MLW) sites (Stenger et al., 2009). One MLW site was established in each of the three soil zones (MLW1 Allophanic, MLW2 Granular, MLW3 Gley).

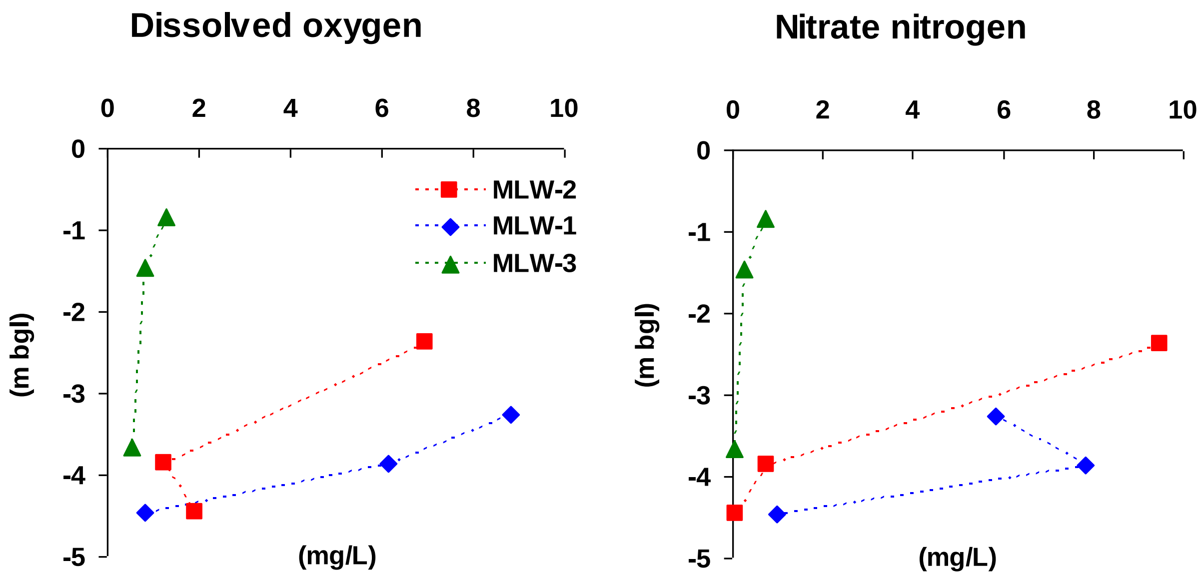


**Figure 2.** Mean concentrations of dissolved oxygen and nitrate-nitrogen measured in groundwater at three multilevel well sites (in mg/L; bgl = below ground level).

Predictably for a site where a poorly drained Gley soil forms the upper part of the groundwater system, concentrations of dissolved oxygen at MLW3 were below 2 mg/L throughout the entire sampled profile, even very close to the groundwater table (Fig. 2). Nitrate concentrations were correspondingly low throughout the profile.

In contrast, groundwater underlying well drained Allophanic (MLW1) and Granular soils (MLW2) showed distinct redox gradients within the profile. While groundwater was well oxidised and nitrate-bearing at shallow depths near the water table, it was oxygen and nitrate depleted at somewhat greater depth (Fig. 2).

Based on redox-sensitive parameters in the hydrochemical data sets (see Stenger et al. [2008] for detail) and supplementary $^{15}N/^{18}O$ nitrate isotope and excess $N_2$ data, we attribute most of the observed very low nitrate concentrations to denitrification occurring in the groundwater system.

To evaluate the effect of this process on catchment-scale nitrogen fluxes, we linked our findings to results of other research providers working in the catchment, as schematically shown in Fig. 3. Using the OVERSEER nutrient balancing model, researchers from AgResearch calculated mean leachate nitrate-nitrogen concentrations of 7 – 15 mg/L for the dairy farms and 3 – 4 mg/L for the drystock farms (Costall, pers. communication 2005). These values result in an area-weighted catchment average of approximately 7 mg/L. Based on NIWA monitoring data (Wilcock et al., 2006), the flow-weighted average of water leaving the catchment was estimated at approximately 3.5 mg/L, i.e. about half of the estimated leachate concentration.

Four processes could potentially explain this substantial discrepancy:

1) dilution of land surface recharge from the catchment with clean groundwater coming from outside the topographical catchment boundary;
2) recharge of groundwater with high nitrate concentrations to deep groundwater, which bypasses the stream monitoring site;
3) very long groundwater lag times;
4) denitrification occurring below the root zone.

Catchment water balances calculated for the eight calendar years (2003 – 2010) for which both NIWA's stream flow data as well as LVL's met station data was available, demonstrated a reasonably close match between mean annual streamflow (431 mm) and the mean climatic water balance (1284 mm precipitation – 833 mm actual evapotranspiration = 451 mm surplus). The climatic water balance being slightly greater than the measured streamflow, there is no reason to suspect that any significant amount of groundwater would have entered the catchment from outside the topographical catchment boundary. This data also indicates that recharge to deep groundwater bypassing the monitoring site may on average only amount to 20 mm per year. Recharge from areas with high nitrate concentrations bypassing the weir thus also cannot explain the low in-stream nitrate concentrations.

Stream water age dating undertaken in collaboration with GNS has revealed that baseflow can have mean residence times of 3 – 4 decades during summer, and > 100 years during drought conditions. However, mean transit times during high baseflow conditions in winter, when the vast majority of water leaves the catchment, are only 2 – 5 years (Morgenstern et al., 2010). This means that, in the absence of attenuation, NIWA's stream water chemistry data should reflect the recent land use intensity that was the basis for the calculation of the OVERSEER estimates.

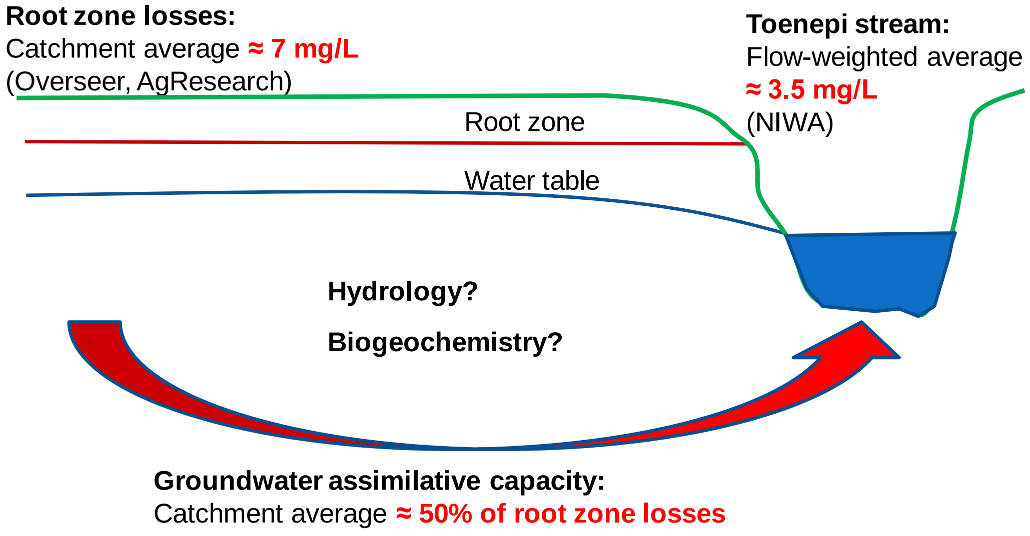


**Figure 3.** Schematic of catchment-scale nitrogen fluxes.

Given that none of these hydrological processes can explain the observed discrepancy between OVERSEER leachate estimates and in-stream concentrations, we infer that it is largely due to denitrification occurring in the groundwater system. This was first suspected after the initial groundwater monitoring project (Stenger et al., 2008) and has since then been shown to occur at the MLW sites, as briefly outlined above. The assimilative capacity for nitrate in this catchment would thus appear to equate to approximately 50% of the root zone losses.

***Hydrological AC component: mixing/dilution***
The AC of a catchment can have a substantial hydrological component, particularly if the land use intensity varies widely within the catchment. Land surface recharge from land uses with high leaching losses can get diluted by mixing with clean groundwater originating from conservation land or other low nitrate leaching land uses (e.g. plantation forests). While dispersion and diffusion occur everywhere along the groundwater flow lines, mixing of water is particularly intensive in discharge areas where flow lines converge (Fig. 4).

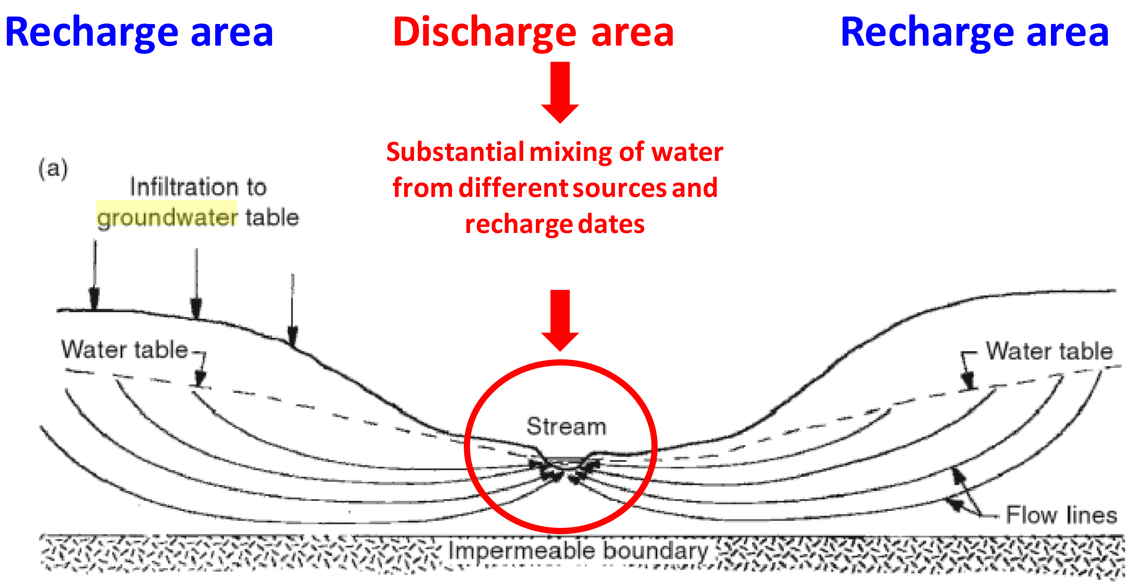


**Figure 4.** Schematic of groundwater flow lines, highlighting their convergence in discharge areas.

It is important to note that this process only results in a reduction of the nitrate concentration, whereas denitrification also results in a reduction of the nitrate mass in the system.

***Mixing/dilution case study: Canterbury Plains***
The mixing/dilution component of AC is particularly relevant for the big alluvial aquifers existing in eastern provinces of New Zealand in the lee-ward side of mountain ranges. Figure 5 shows a cross-section through the Canterbury Plains aquifer from the foothills of the Southern Alps in the west to the coast in the east. It was produced using the GIS-based AquiferSim model, which is a planning tool suitable to assess the effect of land use changes on freshwater quality (Bidwell and Good, 2007).

The cross-section demonstrates that recharge of nearly nitrate-free water from alpine rivers has a substantial beneficial effect on the aquifer underlying the agricultural land on the plains and on the springs occurring on the eastern fringe of the plains. While land surface recharge from the agricultural land has nitrate concentrations ranging approximately from 5 – 15 mg/L, groundwater discharge at the lowland springs has concentrations of only approximately 6 mg/L. This lower concentration is due to the dilution in the discharge area of the groundwater recharged under the plains with clean groundwater originating in the Southern Alps.

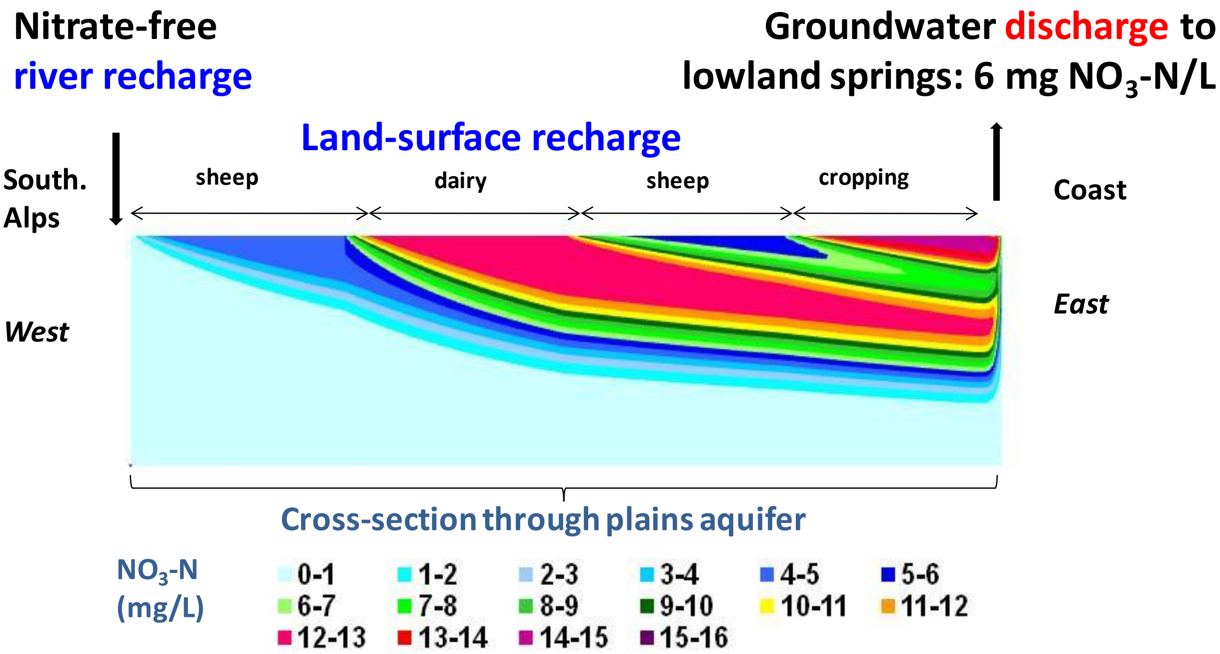


**Figure 5.** Cross-section through the Canterbury Plains aquifer demonstrating the dilution effect of river recharge originating from the Southern Alps (produced using the AquiferSim model developed by Vince Bidwell).

## Potential applications

### *Optimisation of clean-up fund investments*

Substantial investments are currently being made in NZ to restore and protect the quality of freshwater bodies. The Lake Taupo Protection Trust (LTPT), for example, is charged with reducing within 15 years, the manageable nitrogen leaching into the lake by 20%. This target is currently considered to amount to a reduction of the annual load leaving the root zone by 183 tonnes of N (http://www.laketaupoprotectiontrust.org.nz). To achieve this target, nitrogen discharge allowances (NDAs) are being purchased at a cost of several hundred dollars per kg of nitrogen permanently removed.

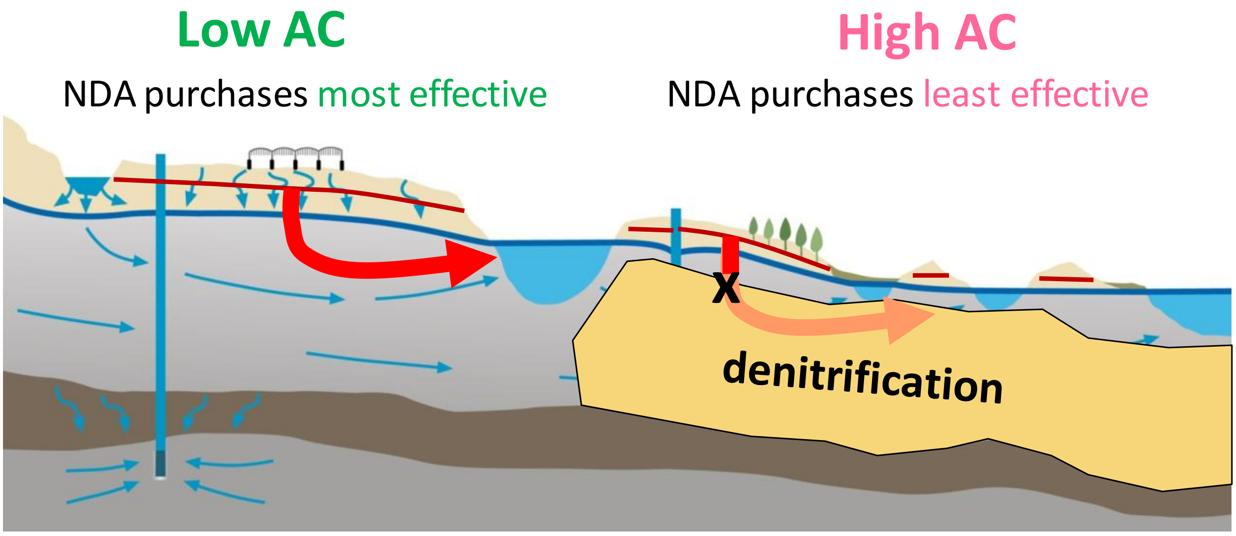


**Figure 6.** Schematic demonstrating the effect of AC on the effectiveness of NDA purchases.

How effective the purchase of NDAs is in reducing actual N input into the lake will depend on the extent of assimilative capacity existing along the subsurface flowpath from the bottom of the root zone to the discharge location into the lake. Where there is no assimilative capacity, NDA reductions will directly equate to reductions in the load entering the lake. However, NDA purchases in catchment areas with high assimilative capacity may only result in minor load reductions, as schematically shown in Fig. 6. The greatest load reduction into the lake per kg NDA purchased would be achievable if LTPT could specifically target NDAs from land known to have low assimilative capacity. However, while there is some corresponding research being undertaken by Waikato Regional Council and a couple of research organisations (e.g. Stenger, 2011), the spatial distribution of assimilative capacity within the catchment is currently not sufficiently understood to allow for this approach.

***Optimisation of land use planning***

Statutory environmental standards and nutrient limits will in the future constrain development in some catchments. Comprehensive assimilative capacity assessments across catchments or sub-catchments would thus help to guide investment in land development and enable land to be directed towards its optimum use. Land uses that are economically desirable, but resulting in higher leaching losses (e.g. dairying) would still be possible in areas with high AC, while land use intensity would have to be low in areas with low AC. Within given environmental constraints, matching land use intensity to AC would presumably result in better economic outcomes than current practice or approaches that are exclusively based on root zone leaching estimates.

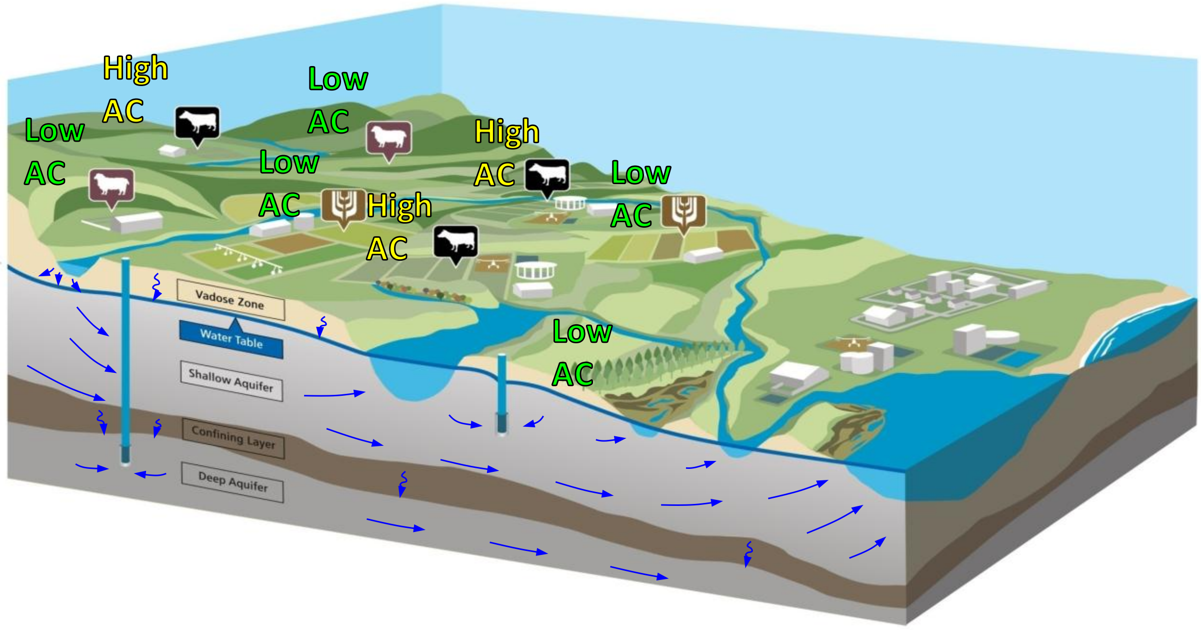


**Figure 7.** Schematic showing land use intensity pattern taking spatial distribution of groundwater assimilative capacity (AC) into account.

## Conclusions and outlook

If the groundwater biogeochemistry and hydrology of a catchment were sufficiently understood, and cost-effective procedures for catchment-scale assessment developed, management could be optimised by taking AC into account. As NZ is increasingly experiencing competition between different land uses, advanced methods for land use planning are being discussed (e.g. Mackay et al., 2011). To date, the focus has largely been on supportive capacities (like climate and soils), identifying for example that there is potential for dairy farming to move into the Lake Taupo catchment. Additionally including assimilative capacities in this concept may allow defining the 'carrying capacity' of a catchment that allows improved economic outcomes while maintaining the desired environmental quality. Understanding the spatial distribution of groundwater assimilative capacity and incorporating this knowledge in catchment-scale nitrogen management could be a first step towards defining the 'carrying capacity' of a catchment.

## Acknowledgments

We would like to thank the farmers in the Toenepi catchment for their co-operation, Bob Wilcock (NIWA) for the provision of stream data, Des Costall (AgResearch) for the OVERSEER estimates, and FRST/MSI for funding this research.

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