

Assessing flow and nutrient contributions from rheocrene springs and groundwater seepage in two urban waterways

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Few studies have quantified the contribution of nutrients into waterways from instream spring vents (rheocrene springs) and streambed seepage. Nutrients can be toxic to biota and cause eutrophication, and levels within urban streams of Christchurch exceed guideline levels. To investigate the contribution of nutrients from springs and groundwater seepage to two urban waterways in Christchurch, we used a combination of (1) streamflow gauging and water quality sampling of surface water, and (2) discrete sampling of streambed seepage and spring vents, using seepage meters and mini-piezometers, over two time periods to determine seasonal variations. The streams showed three distinct patterns of inflow: (1) an upstream reach with many spring vents that had high inflow in September and low inflow in March (with many vents drying up), (2) a middle section with few discrete springs and low inflow rates, due to low groundwater pressures downstream of the spring vents, and (3) a downstream section with few spring vents, but high streambed seepage due to high groundwater pressures. Nitrogen concentrations were similar between spring vents, general streambed seepage and shallow groundwater bores in the area, with concentrations higher at upstream locations, which received the shallowest groundwater input to the stream. Seasonal variations were recorded, with higher concentrations in September compared to March. Dissolved reactive phosphorus inflows were more variable, with localised areas of higher concentrations. This was likely due to the release of organic matter built up in the streambed as groundwater inflows occur through areas of low streambed redox potential. The contribution of nutrients from springs and seepage recorded in this study gives a better understanding on where to focus management to improve nutrient concentrations in these spring-fed waterways. These investigation techniques could be applied easily and quickly elsewhere, to help quantify the input of any groundwater contaminant to surface water.

Measuring actual denitrification to understand nitrogen attenuation

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Many New Zealand rivers and lakes have nitrate loadings which predominantly come through groundwater discharge rather than surface water runoff or point source contamination [3]. Denitrification, a natural process by which dissolved nitrate in groundwater is eventually reduced to nitrogen gas (N₂), has potential to attenuate nitrate loads to rivers and lakes. However, the extent of denitrification occurring within New Zealand's groundwater systems is largely unknown.

Measurement of 'excess N₂', the product of the denitrification reaction, is the most promising method for directly measuring denitrification that has occurred in an aquifer [4,5]. Thus the aim of this study was to validate a method for identification of denitrification in an aquifer and quantification of the extent of any denitrification that actually has taken place.

Neon samples were collected from 27 piezometers in the Waikato, Canterbury and Horizons Region following the method described in Martindale et al. (2018) [2]. Other proxies for measuring denitrification, or for measuring that there is potential for denitrification to occur, were sampled in conjunction with the Ne samples. These proxies included dissolved oxygen, $\delta^{15}\text{N}$, hydrochemistry, Child's tests and DNA analysis for the abundance of denitrifying genes (nirS, nirK and nosZ) [1]. Age tracers, including tritium, CFC and SF₆ samples were also collected from some of the piezometers.

Of the 27 sites sampled, 19 had N₂ in excess above the range of uncertainty. Twelve of these 19 sites were highly anoxic, as expected. However, 5 of the sites had dissolved oxygen between 2.5 mg L⁻¹ and 5.8 mg L⁻¹, indicating that complex flow pathways between the oxic and anoxic zones in the aquifer or in the well exist. Age tracers from the paired piezometers confirm this with groundwater ages differing between piezometers with depths varying by less than a metre.

[1] Bakken, L. and P. Dörsch (2007). Chapter 25 - Nitrous Oxide Emission and Global Changes: Modeling Approaches. *Biology of the Nitrogen Cycle*. S. J. F. ermann Bothe, William E. Newton, Elsevier: 381-395.

[2] Martindale, H.; van der Raaij, R.W.; Daughney, C.J.; Morgenstern, U. 2017 Measurement of neon in groundwaters for quantification of denitrification in aquifers. Lower Hutt, N.Z.: GNS Science. GNS Science