FURTHER PROGRESS USING ISOTOPES TO TRACK THE SOURCES OF NITRATE IN SURFACE WATERS

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New Zealand's intensive pastoral agricultural systems have a significant impact on water quality due to nitrogen loading in rivers. Efforts to cap the total loads of N entering water places a strong focus on developing indicators to support N budgets at farm and catchment scales. We present an additional year of progress developing isotopic techniques to trace the sources of nitrate in New Zealand’s surface water.

Previously we reported over one year of measurements from the Upper Manawatu Catchment, where we have measured over a year of monthly $\delta^{15}N$ and $\delta^{18}O$ in NO_3 from over 15 Horizons monitoring stations. The annual averages span a range of $\delta^{15}N$ and $\delta^{18}O$ of 7‰, and spread approximately along a 1:1 ‘denitrification line’ with the unimpacted site at the Tararua Forest Park boundary on the lower end of the range, and the main stem of the Manawatu River exiting the catchment at Hopelands on the upper end. Monthly data throughout the year display movement almost entirely along the 1:1 denitrification line in some catchments, but display more complex patterns indicating multiple complex sources in other catchments, including the Manawatu at Hopelands. The data and related research suggested a need for substantially improved laboratory precision and detailed study at smaller scales. We have also focused on approaches to separate pastoral agricultural sources from other nitrate sources, such as sewage or animal processing effluent, nitrate fertilizer applied to crops. To undertake this, we are developing a new stream of work in the Wairarapa, focusing on the Mangatarere catchment.

Laboratory precision has been improved over threefold from approximately ~1‰ to ≤0.2‰ for both $\delta^{15}N$ and $\delta^{18}O$ in NO_3 for samples with concentrations in the range of 100 mg/m^3 NO_3-N and above. The procedural blanks are equivalent to ~2 mg/m^3 NO_3-N and are stable, leading to the ability to easily produce useful data for samples in the range of 10 mg/m^3 NO_3-N.

Another year of monitoring data in the Upper Manawatu catchment is yielding conclusions similar to those we presented last year, but more precise data enables additional exploration and new findings. The $\delta^{15}N$ and $\delta^{18}O$ in NO_3 in some streams follows a simple denitrification line while others show more complex behavior. In most cases, variations in the $\delta^{15}N$ and $\delta^{18}O$ in NO_3 appear to reflect nitrification that occurred in summer versus winter, based on the 1-2‰ differences in $\delta^{18}O$ in NO_3, compared to the local denitrification and mixing line. This is a result of seasonal variation in the $\delta^{18}O$ in H_2O from which 2 of the 3 oxygen atoms in nitrate originate. An example of a medium flow summer period in the Upper Manawatu catchment is shown in Figure 1. These differences imply that nitrification occurring in irrigated land may be differentiated from nitrification occurring in dryland agriculture.

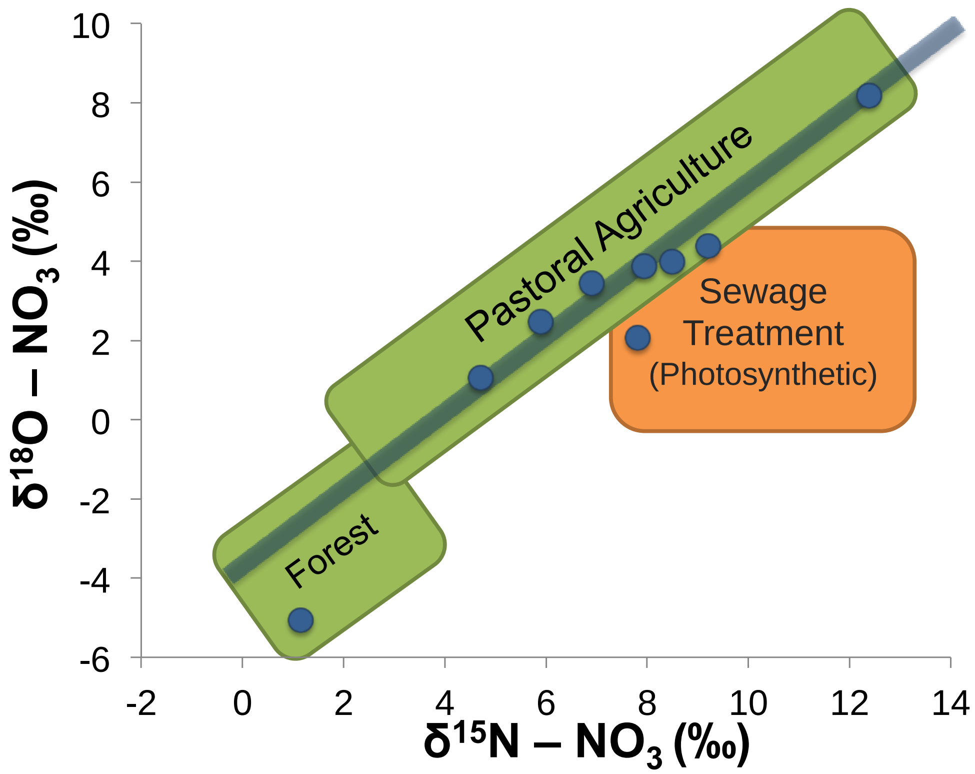

Figure 1. March 2011 $\delta^{15}N$ and $\delta^{18}O$ values in NO_3 for the Upper Manawatu catchment, at medium flow. The blue line shows a local "denitrification and mixing line". The forest site in this figure receives water from higher elevations, believed to lead to a lower $\delta^{18}O$ in NO_3.

Monitoring of 4 sewage treatment plant (STP) effluents suggests these sources have variable but often distinct signatures, enabling them to be differentiated from agricultural sources at downstream sites. Importantly, 1 of the 3 oxygen atoms in NO_3 is derived from O_2 and aquatic photosynthesis can therefore cause a lower $\delta^{18}O$ in NO_3 to be set. Stream stations showing relatively complex behavior may be related to groundwater/ surface water interactions. A major goal of our Mangatarere investigation is to track groundwater sources and delays in the hydrologic system at a smaller scale and where more previous work has been carried out. In this work, we are finding benefits in using H and O stable isotopes in H_2O to track the sources of water contributing to streamwater. Within this catchment, a bifurcation in $\delta^{15}N$ and $\delta^{18}O$ in NO_3 is observed in the upper catchment and this may be explained by seasonality and flowpaths. Accounting for these factors and local hydrogeology lead to expectations that the isotope tracer will yield significant insights into the contributions of piggery effluent and STP inputs to the Mangatarere catchment following this year's summer and winter monitoring campaigns.

Overall, current expectations for the application of the dual isotope tracer method for $\delta^{15}N$ and $\delta^{18}O$ in NO_3 can best be outlined using some example data plotted in Figure 2. The main agricultural NO_3 sources in the two areas appear to lie on a regional denitrification and mixing line, shown by the open black arrow. Seasonal variation of 1-2‰ can be explained by variation in the oxygen isotope composition of water from which the NO_3 is forming. This implies that summer- and winter-derived NO_3 may be differentiated through this technique, allowing management to target the primary. Movement up and down the denitrification and mixing line is associated with factors that enhance denitrification, including primarily more intensive agriculture but also factors such as temperature riparian characteristics. Sewage and wastewater treatment plant sources, particularly where photosynthetically-derived O_2, sets a lower $\delta^{18}O$ value in NO_3 derived from this source. Finally, we have encountered some examples where NO_3-bearing fertiliser or possibly industrial use and disposal of nitric acid have cause surface water signatures to deviate towards this source (shown in upper left corner of Figure 2).

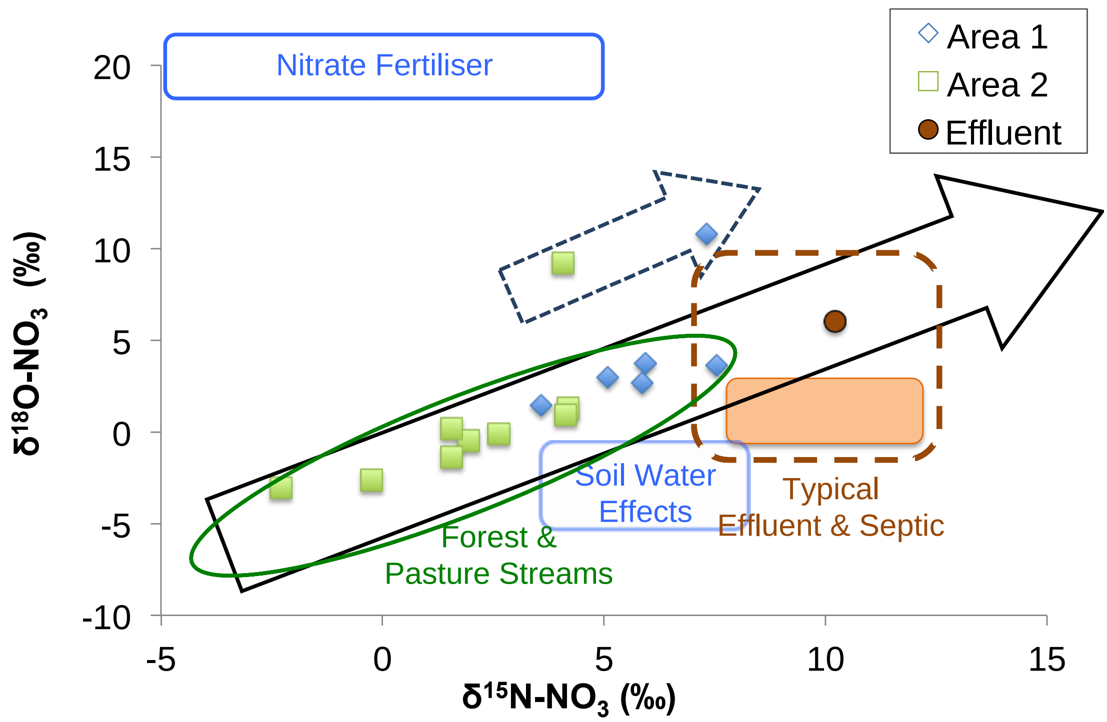

Figure 2. A constructed example showing how application of $\delta^{15}N$ and $\delta^{18}O$ in NO_3 can be applied in predominantly pastoral catchments throughout New Zealand.