PROGRESS IN THE DEVELOPMENT OF ISOTOPIC INDICATORS FOR LAND-TO-WATER NITROGEN TRANSFERS IN NEW ZEALAND

W Troy Baisden[1], P Mudge[2,3], L Schipper[2], N Wells[4], T Clough[4], A Ghani[3], L Wassenaar[5] and C Douence[1]

[1]*National Isotope Centre, GNS Science, Lower Hutt*
[2]*University of Waikato, Hamilton*
[3]*AgResearch, Hamilton*
[4]*Lincoln University, Lincoln*
[5]*Environment Canada, Saskatoon, Saskatchewan, Canada*

Introduction

New Zealand's intensive pastoral agricultural systems have a significant impact on water quality due to nitrogen loading in rivers. New Zealand's preference for capping 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 progress to date on the development soil N isotopes and O and N isotopes in streamwater NO_3 as quantitative indicators to support N budgets.

Our proposed indicators are intended to:

- Classify the vulnerability of farm units to ongoing losses of N
- Identify the proportion of river nitrate (NO_3) loads from differing farm types
- Quantify the proportion of NO_3 lost during transport

Our proposed on-farm indicator recognises that isotopes of N (^{14}N and ^{15}N) exist in nature, and that undesirable N loss pathways (including nitrification, denitrification and ammonia volatilization) discriminate against ^{15}N, causing measurable increases in the $^{15}N/^{14}N$ (commonly written as $\delta^{15}N$ and expressed in per mil, ‰) of total soil N that are roughly proportional to rates of N loss. As a proof-of-concept example of accumulated enrichment in ^{15}N associated with the duration and intensity of pastoral agriculture, we summarize the response of long-term treatments at the Winchmore experimental farm over ~50 years.

To report on progress in the development of N and O isotopes as indicators of the sources and fate of NO_3, this work describes the results of one year of monthly measurements at ~18 monitoring locations in the 1260 km^2 Upper Manawatu River catchment. The use of N and O isotope ratios in nitrate in New Zealand has considerable potential to elucidate the sources and fate of nitrate with greater precision than in most other nations due to the lack of nitrate in atmospheric deposition and the lack of nitrates used as fertilizer (Kendall et al., 2007). The catchment was chosen for study because it is among the most pastoral catchments in New Zealand, with little non-pastoral agriculture and limited forest area outside of the Tararua mountain range on the west side of the catchment. The patterns observed over one year are used to outline continuing work to push the use of N and O isotopes in NO_3 towards practical applications in New Zealand.

Methods

To assess the changes in soil $\delta^{15}N$ under long-term pastoral agriculture, samples from treatments imposed at Winchmore were selected from archives maintained by AgResearch. Isotopic analysis of N was carried out on a Europa 20/20 Isotope Ratio Mass Spectrometer via combustion in an elemental analyser at the University of Waikato's Stable Isotope Unit. Measurement accuracy and precision is 0.3‰ or better.

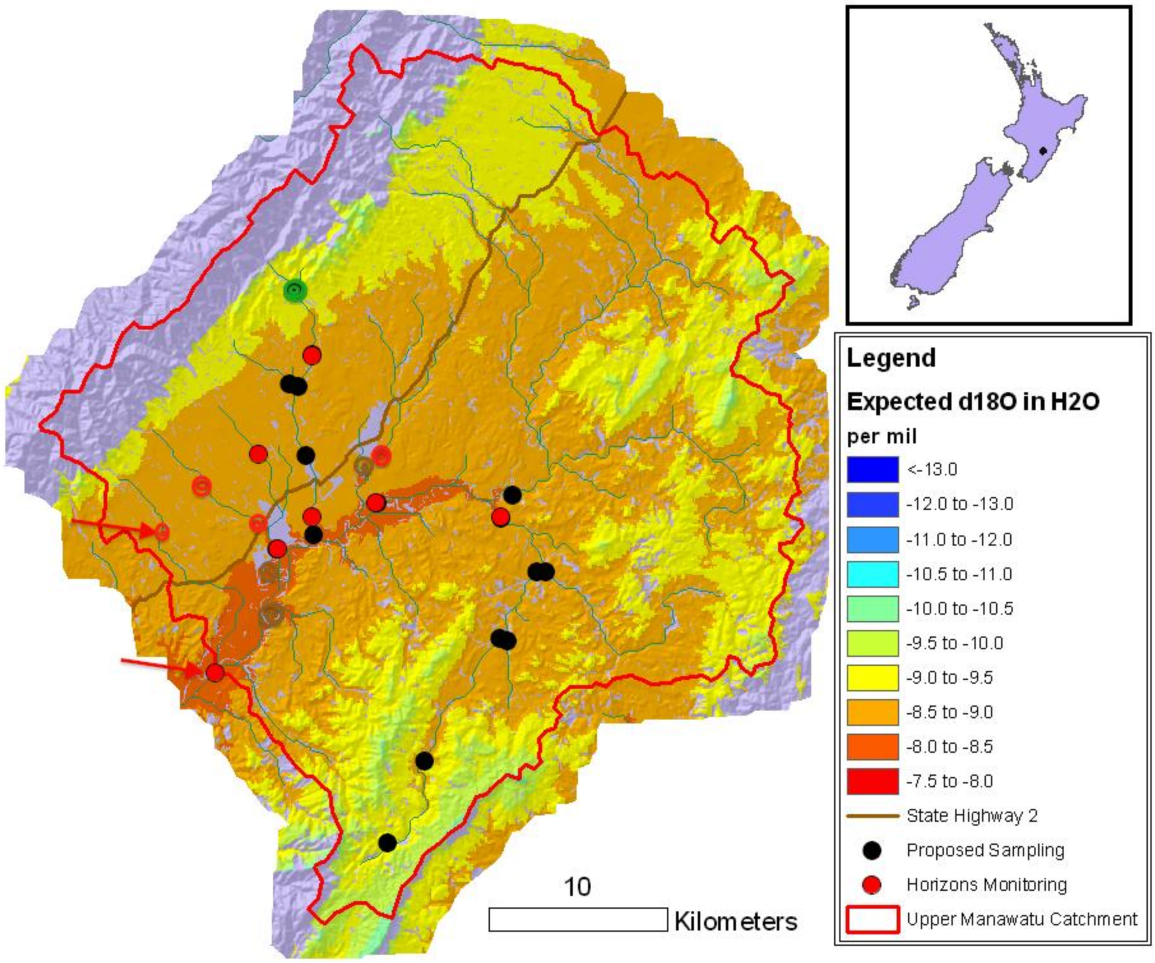

Figure 1. Upper Manawatu River Catchment, defined by the Manawatu@Hopelands station. Stations shown in red, green and brown were sampled in this study. Green shows the baseline site representing native bush. Red sites are standard Horizons monitoring sites reflecting pastoral land use. Brown shows point-source inputs, and includes the point source as well as upstream and downstream samples where possible. Forested land is shown in grey.

Samples for measurement of N and O isotopes in NO_3 were collected by Horizons Regional Council staff and stabilized at pH 11 for shipping to the National Isotope Centre. Samples were from Horizons monitoring stations in the Upper Manawatu River catchment shown in Figure 1, and were kept frozen and subsequently analysed. We measured N and O isotope ratios in nitrate plus nitrite using chemical denitrification method, and refer to the results as nitrate for brevity due to low nitrite concentrations. Our analyses used cadmium and azide to reduce NO_3 to NO_2 and then N_2O for analysis on an Isoprime Mass Spectrometer using a method modified from McIlvin et al (2005). Analytical reproducibility within this dataset is 0.5 – 1‰ for both $\delta^{15}N$ and $\delta^{18}O$.

Results and Discussion

The development of an indicator based on soil $\delta^{15}N$ values relies on the expectation that the ability of pasture soil to continue to store, rather than release, added N is related to the duration and intensity of past agricultural land use. Work to date from a range of long-term experiments demonstrates that soil $\delta^{15}N$ increases with both the duration and intensity of agricultural use, implying that this indicator provides the needed means to classify sites in the 'developing', 'developed' and 'highly developed' categories presently used in Overseer™. As an example of proof-of-concept data from long-term treatments at Winchmore, Table 1 demonstrates that soil $\delta^{15}N$ increases as expected across fertilisation and irrigation treatments that define different levels of the intensity of N cycling.

Table 1. Analyses of long-term experiments at Winchmore suggest that measures of agricultural intensity are related to rates of change in $\delta^{15}N$. These estimates are based on fitting trends to repeated measurements from 1958-2009 for fertilizer trials and 1959-2002 for irrigation trials. Production data from Metherell (2003) and Rickard and McBride (1986, 1987).

Treatment	Dry matter production (Mg ha^{-1} y^{-1})	Clover production (Mg ha^{-1} y^{-1})	Final $\delta^{15}N$ (‰)	$\delta^{15}N$ Change since 1960 (‰)
Fertilizer Treatments				
Nil P	4.7	0.45	3.1	-0.3
Resid	9.3	1.51	4.3	0.7
High P	12.0	2.58	4.6	1.1
Irrigation Treatments				
Dryland	7.1	2.03	3.9	0.5
10%	10.2	2.21	4.2	1.0
20%	12.2	2.80	4.7	1.5

Development of indicators for the percent of NO_3 from known sources and percent of NO_3 lost to denitrification during transport (attenuation) are more complex and rely on critical assumptions we have been testing. Our assumptions about the isotope systematics describing the sources of N and O isotopes in soil-derived NO_3 appear to be well supported within the precision of measurements. An assumption found to be problematic is that the N and O isotope shift associated with denitrification observed in the field can be estimated using laboratory 'batch' experiments that measure the isotope fractionation associated with denitrification biochemistry. Mathematical modeling demonstrates that diffusion of NO_3 into the anoxic sediments required for denitrification suppresses the isotope fractionation observed in flowing oxygenated typical of streams, drains and rivers. The model explains field data and implies that an isotope indicator for the percent attenuation due to denitrification will need to be calibrated in the field, and will be environment specific.

In our primary study catchment, the Upper Manawatu, 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 (green triangle), and the mainstem of the Manawatu River exiting the catchment at Hopelands on the upper end (black square). 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. An important explanation for variation off the 1:1 line may be differences in the $\delta^{18}O$ of soil water (see Figure 1 for estimated composition of rain water) where nitrification occurs, since water contributes 2 of the 3 oxygen atoms in the NO_3 molecule. If so, this variation can be understood by studying the isotope hydrology of the catchment.

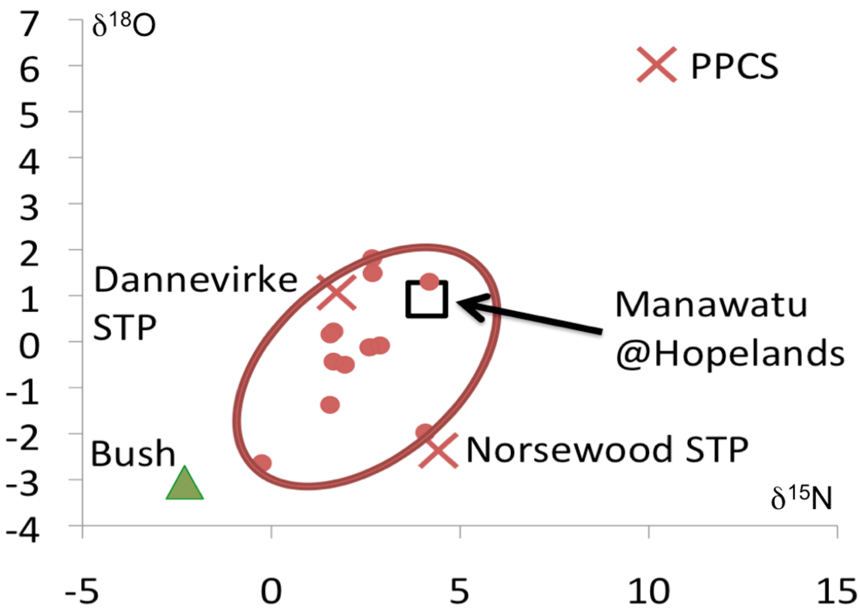

Figure 2. Annual averages of monthly data for each of the river stations and point sources. The site draining native bush is shown in green. Sites dominated by pastoral agriculture are shown as red dots, while effluent point sources are shown as red crosses. The Manwatu@Hopelands is shown as the black square. The ellipse defines the approximate area of the streamwater samples from pastoral agriculture.

Overall, our work to date has pointed to the need for intensive calibration studies in smaller catchments, including individual springs and drains. To undertake this, we are developing a new stream of work in the Wairarapa, focusing on the Mangatarere catchment, and also including efforts to understand interactions between groundwater and surface water. Future work is intended to benefit from improvements to the chemical denitrification method, enabling measurement of $\delta^{15}N$ and $\delta^{18}O$ with a reproducibility of 0.3‰ (s.d.).

Conclusions

Proof-of-concept data from long-term treatments at Winchmore suggests that soil $\delta^{15}N$ has strong potential as an indicator of the duration and intensity of pastoral land use. This result supports the theoretical basis we have proposed for indicator development – increasing soil $\delta^{15}N$ reflects accumulated signal from ongoing losses of excess N via the fractionating processes of ammonia volatilisation, nitrification and denitrification, and therefore is related to vulnerability to the ongoing loss of N via these pathways. With additional support from other sites, the use of soil $\delta^{15}N$ has potential to be used in N budgeting models such as Overseer™ within 1-3 years.

One year of monthly measurements of $\delta^{15}N$ and $\delta^{18}O$ in NO_3 at ~18 monitoring locations in the 1260 square km upper Manawatu River catchment suggests that the basic premises proposed for the development of isotopic indicators reflecting the sources and fate of streamwater nitrate are supported. These premises include expectations that the $\delta^{15}N$ of NO_3 sources is strongly related to the $\delta^{15}N$ of soil N, and that the $\delta^{18}O$ of NO_3 sources is related to $\delta^{18}O$ of soil water where NO_3 is formed. We further expected that variation in the $\delta^{15}N$ and $\delta^{18}O$ of NO_3 will both vary along a 1:1 line both in time and across the catchment reflecting the level of denitrification processes. Our data is consistent with these expectations, but work-to-date suggests further careful examination of the isotope systematics of nitrate formation and denitrification processes will be required for before a quantitative indicator reflecting the sources and fate of NO_3 can be widely applied. The need to develop a practical empirical tool to improve understanding of the sources and fate of NO_3 in New Zealand freshwater appears to be sufficient to justify ongoing work to develop understanding of the $\delta^{15}N$ and $\delta^{18}O$ of NO_3, leading to practical uses of these isotopic measurements as indicators over the next 3-10 years.

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