ASSESSMENT OF TRANSPORT AND TRANSFORMATION OF NITROGEN IN THE SUBSURFACE ENVIRONMENT OF MANAWATU RIVER CATCHMENT – WORK IN PROGRESS

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Abstract

A sound understanding of transport, transformation and fate of farm nutrients is a key component of managing and mitigating the likely impacts of these nutrients on freshwater quality and ecosystem health. While the cycling and leaching of nitrogen in the soil profile (root zone) is reasonably well understood, there is limited information available about its transport and transformation in the subsurface environment (below the root zone), particularly in the Manawatu River catchment. To address this, Massey University's Institute of Agriculture and Environment (IAE) and Horizons Regional Council has established a collaborative research study to monitor and model the transport and transformation of nitrate-nitrogen from farms to river via groundwater in the Manawatu River catchment.

A preliminary analysis of nitrogen attenuation factor (*NAF*), calculated using the estimates of nitrogen leaching from the root zone and nitrogen load in the river at eight sites in the Tararua Ground Water Management Zone (GWMZ), provides indications of spatially distributed nitrogen reduction in the subsurface environment in the Manawatu River catchment. Field measurements and laboratory experiments are being conducted to develop methods and procedures to assess and characterise the transport and transformation of nitrate-nitrogen in alluvial unsaturated and saturated (shallow groundwater) zones in the catchment. A test site has been established at Massey University's No. 1 Dairy Farm (located at 175.6017° E, 40.3842° S), near Massey Campus, Palmerston North. At this site, a total of 12 ceramic suction cups have been installed in replicates of three to monitor soil water at four depths (30, 60, 100 and 200 cm bgl) in the root zone (from 0 to 60 cm) and the unsaturated zone (from 0.6 to 4.5 m), and four PVC piezometers to monitor shallow groundwater at four depths (5.8, 6.3, 7.4 and 8.7 m bgl) in the saturated zone. The collected soil water and shallow groundwater samples are being analysed for; nitrate-nitrogen, ammonium, dissolved oxygen, and dissolved organic carbon. Preliminary measurements at this site indicate a significant reduction in nitrate-nitrogen concentrations, particularly in the saturated (shallow groundwater) zone.

The observational and experimental learnings from this test site at Massey Dairy No. 1 farm will be used to help assess and characterise the transport and transformation of nitrate-nitrogen in the subsurface environment at other selected sites in the catchment. The collected information will be used to develop a nitrogen flow model including transport and denitrification of nitrate-nitrogen in unsaturated and saturated zones in the Manawatu River catchment, with a focus on the Mangatainoka subcatchment. This research will bridge a gap in current knowledge between root zone and river based processes and help in the management of nitrogen loss from farms to rivers in the Horizons region.

1. Introduction

Nitrogen and phosphorus are two key nutrients for enhancing production in agricultural systems. While the benefits of these nutrients in agricultural production are obvious, these nutrients may leak from the soil and increase their concentrations in surface water and groundwater bodies. Elevated levels of nutrients in surface water bodies can lead to excessive biological growth and algal blooms in rivers and lakes (Carpenter et al., 1998; Di & Cameron, 2002; McArthur & Clark, 2007). This is giving rise to the growing concern about the impacts of elevated nitrogen and phosphorus concentrations on the qualities of surface and groundwater bodies across New Zealand. A sound understanding of transport, transformation, and fate of farm nutrients is a key component of managing and mitigating the likely impacts of these nutrients on freshwater quality and ecosystem health.

Nitrate is highly mobile in the soil-water system, and flows predominantly via subsurface drainage and groundwater to surface water bodies (Haag & Kaupenjohann, 2001). However, the contribution of the nitrate that is leached from the root zone to the nitrate flux in groundwater and the subsequent flux in surface water depends on the transport and transformation of nitrate in the subsurface environment. Naturally occurring processes such as denitrification under certain conditions may reduce, or attenuate, the nitrate flux as it flows from the root zone to the rivers and/or lakes (Knowles, 1982; Korom, 1992; Rivett et al., 2008). Denitrification – a microbial-mediated transformation of nitrate (NO_3^-) to harmless dinitrogen (N_2) gas – can significantly reduce the nitrate flux, particularly in the saturated zone below the water table (Rivett et al., 2008). This capacity is mainly governed by the physical, chemical and biological characteristics, and importantly by the nutrients and oxidisable carbon in nitrogen flow pathways (Rivett et al., 2008). Preliminarily investigations suggest that about 50% of the soluble inorganic nitrogen leached from the root zone is reduced before reaching the river in some parts of the Manawatu River catchment (Clothier et al., 2007).

The cycling and leaching of nitrogen in the soil profile (root zone) is reasonably well understood, but there is limited information available about its transport and transformation in the subsurface environment (below the root zone), particularly in the Manawatu River catchment. To address this, Massey University's Institute of Agriculture and Environment (IAE) and Horizons Regional Council have established a collaborative research study to monitor and model the transport and transformation of nitrate-nitrogen from farms to river via groundwater in the Manawatu River catchment. This project aims to fill a gap in our knowledge and understanding of the transport (time lag) and transformation (fate) of nitrate-nitrogen from farms to river in the Manawatu River catchment. The main research objectives of this project are to: (1) conduct a field survey and analysis of nitrate-nitrogen concentrations and indications of denitrification in shallow groundwater in the study area, (2) carry out laboratory and in-field measurements of denitrification in unsaturated and saturated zone sediments, (3) assess the denitrification potential or occurrence among the most common hydrogeologic settings (rainfall, topography, landuse, soil and rock types), and (4) develop catchment specific integrated modelling of water and nitrogen flow including denitrification in the subsurface environment.

2. Preliminary Results and Discussion

2.1 Indicative Nitrogen Attenuation in the Tararua Groundwater Management Zone

The nitrogen attenuation (reduction) capacity of a catchment can be indicated by analysis of the nitrogen load in the river as compared to the nitrogen leached from the root zone in the catchment (Clothier et al., 2007; Roygard & Clark, 2012). A nitrogen attenuation factor, noted as *NAF*, can be defined as follows;

$$NAF = (Q_d - Q_r) / Q_d \qquad \text{(Eq. 1)}$$

Where, Q_d is the nitrogen leaching from the root zone, and Q_r is the nitrogen load in the river. The nitrogen attenuation factor *NAF* quantifies the proportion of nitrogen reduced (attenuated), by different biogeochemical processes such as denitrification, uptake and assimilation, on its way from the root zone to the river/lake. According to this definition, a value of *NAF* equal to 0.70 implies that 70% of the nitrogen leached from the root zone is attenuated (transformed) before reaching the river.

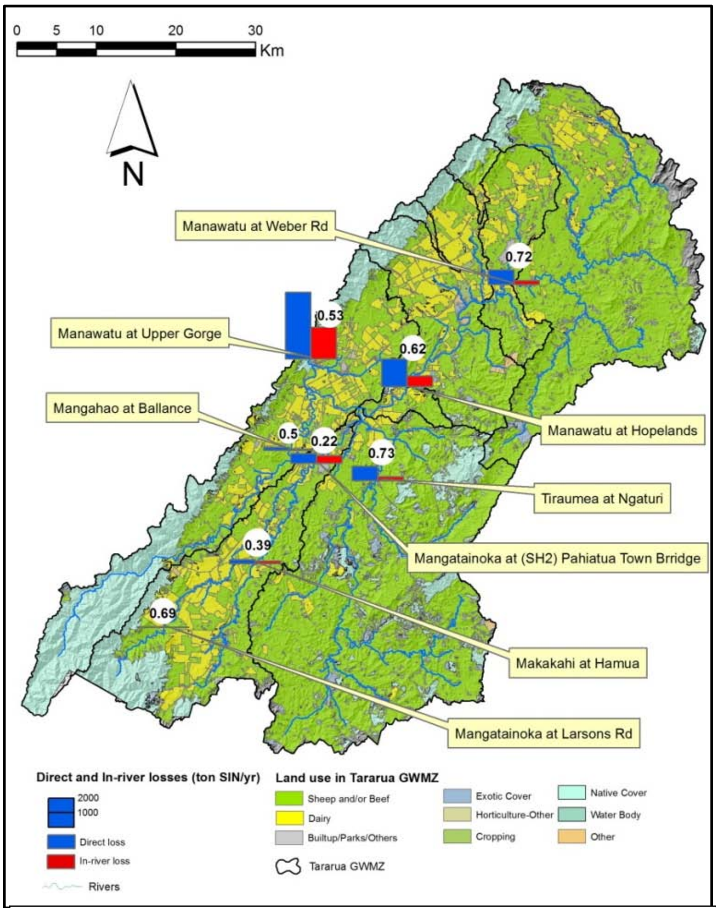

Figure 1: Preliminary estimates of nitrogen attenuation factors (*NAF*) for selected subcatchments in the Tararua Groundwater Management Zone, Manawatu River catchment.

We calculated the nitrogen attenuation factor, *NAF* based on the estimates of nitrogen leaching from the root zone and nitrogen load in the river at eight sites in the Tararua Ground Water Management Zone (GWMZ) of the Manawatu River catchment (Figure 1). The Tararua GWMZ was divided into eight subcatchments by delineating the catchment area upstream of each water quality monitoring site. The calculation of *NAF* for each subcatchment required the estimation of nitrogen leaching from the root zone, Q_d and the nitrogen load in the river, Q_r (Eq. 1) for the subcatchment.

The average annual river nitrogen load Q_r from non-point sources used in this analysis was obtained from Roygard & Clark (2012). They used the flow-stratified method to calculate Q_r using daily river flow and monthly soluble inorganic nitrogen concentrations during 2005 to 2011 at the eight selected sites in the Tararua GWMZ. The details of this method to calculate average annual nitrogen load can be found in Roygard & Clark (2012), Roygard & McArthur (2008), and Roygard et al. (2012).

The root zone nitrogen leaching was calculated by (1) assigning average annual nitrogen leaching rates (expressed as kg ha^{-1} yr^{-1}) for different land use categories; (2) multiplying these rates by the area of each land use in the subcatchment; and then (3) adding up the contribution of all land uses in the subcatchment to get the total average annual root zone nitrogen leaching Q_d for the subcatchment. The main land use areas (in ha) in the Tararua GWMZ were estimated as native cover (54,455 ha), exotic cover (9,822 ha), sheep & beef (203,014 ha), dairy (48,377 ha), cropping (491 ha), horticulture (88 ha), and built-up/others (3,082 ha) (Roygard & Clark, 2012). The average annual nitrogen leaching rates (kg ha^{-1} yr^{-1}) from these main land use types were also based on values given in Roygard & Clark (2012), i.e. 2.4 from native cover, 4.0 from exotic cover, 16.0 for sheep & beef, 26.8 for dairy, 50.5 for cropping, 40.0 for horticulture, and 3.0 from built-up/ other areas.

The calculated nitrogen attenuation factor (*NAF)* varies from 0.22 at Mangatainoka at (SH2) Pahiatua Town Bridge to 0.73 at Tiraumea at Ngaturi flow sites in the Tararua GWMZ (Figure 1). Considering the whole of Tararua GWMZ, the *NAF* is estimated at 0.53 for the Manawatu at the Upper George site. There is a degree of uncertainty in these estimates of nitrogen attenuation factors due to the imprecise nature of; the river load Q_r calculation method used (flow-stratified method) (Roygard & Clark, 2012), the average annual nitrogen leaching rates used for different land use types, and the area under different land use in the subcatchments. Given that the flow-stratified method is a composite load calculation method which increases the accuracy of estimates of nutrient load (Aulenbach & Hooper, 2006; Richards, 1998), the load in the rivers Q_r obtained from Roygard & Clark (2012) is not considered to be a major source of uncertainty. The average annual nitrogen leaching rates for different land use types are likely to contribute the most uncertainty to the estimates of *NAF*. If the average annual nitrogen leaching for horticulture is increased by 100% from 40 to 80 kg ha^{-1} yr^{-1}, the *NAF* values did not change much. This is because of the very small area of horticulture in each subcatchment. Similarly, if the average annual nitrogen leaching rates for areas that are built-up, or have cropping, exotic or native covers is varied by 100%, the *NAF* values do not change much. In contrast, when the average annual nitrogen leaching rate for sheep and/or beef is decreased from 16.0 to 10.0 kg ha^{-1} yr^{-1} (a 38% decrease), the *NAF* values change significantly and range from 0.06 at Mangatainoka at (SH2) Pahiatua Town Bridge to 0.60 at Mangatainoka at Larsons Road with a value of 0.36 for the Manawatu at Upper George site representing the whole of Tararua GWMZ. This was due to the larger area of sheep and/or beef which varied from 24% to 81% of the area of the subcatchments and represented about 64% of the total area of the Tararua GWMZ. The value used for the average annual nitrogen leaching rate for sheep and/or beef (16.01 kg ha^{-1} yr^{-1}) could be a major source of uncertainty. It is therefore recommended that the average nitrogen leaching rate from sheep and/or beef farms is identified using nutrient budgets, i.e. following the procedure outlined in Roygard & Clark (2012) for dairy farms.

Despite the potential uncertainties, the calculated *NAF* values indicate that there is significant nitrogen attenuation (reduction) in the Tararua GWMZ, and this appears to be spatially variable across the subcatchments. In future work, we will assess and quantify the influence of different subcatchment characteristics (e.g. soil type, rock type and baseflow index "*BFI*") on the derived nitrogen attenuation factors in the study area.

2.2 Soil water and shallow groundwater monitoring at Massey Dairy Farm No. 1

An experimental site has been established as a 'test site' at Massey University's No. 1 Dairy Farm (located at 175.6017° E, 40.3842° S) (Figure 2) to develop methods and procedures to assess and characterise transport and transformation of nitrate-nitrogen in the subsurface environment of the catchment. The current landuse at the test site is dairy farming and the soil type is the Manawatu fine sandy loam.

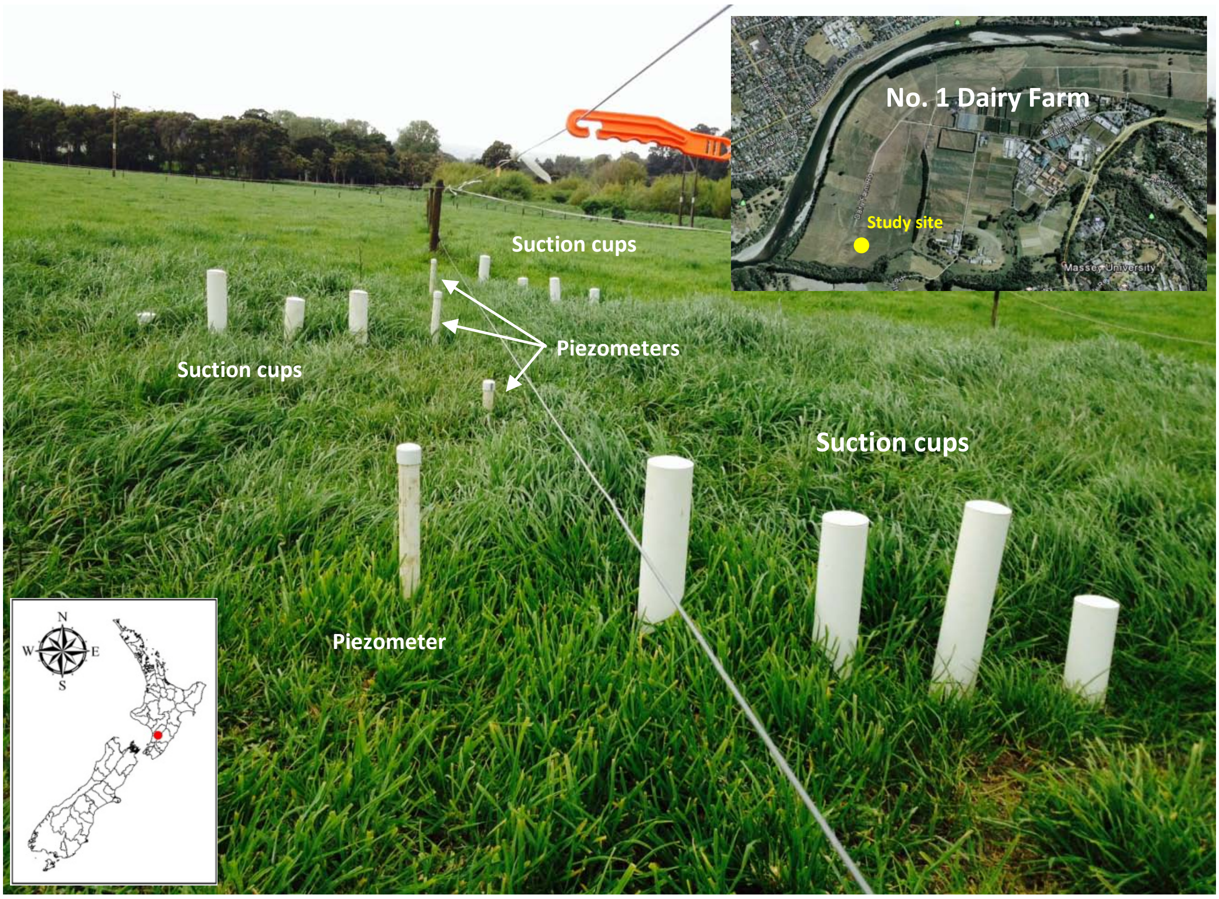

Figure 2: Experimental site established at Massey University's No. 1 Dairy Farm near Palmerston North.

Ceramic suction cups were installed in three replicates at multiple depths (30, 60, 100 and 200 cm below ground level) to monitor soil-water in the root zone (from 0 to 60 cm) and the unsaturated zone (from 0.6 to 4.5 m). Shallow groundwater is monitored in four PVC piezometers installed from 5.8 to 8.7 m below ground level (bgl). The collected soil-water and shallow groundwater samples are analysed for nitrate-nitrogen (nitrate-N), ammonium-nitrogen (ammonium-N), dissolved oxygen (DO), and dissolved organic carbon (DOC). On site measurements of shallow groundwater also include: depth to groundwater level (bgl), pH, electrical conductivity (EC), and oxidation-reduction potential (ORP). Soil-water and shallow groundwater sampling has been conducted fortnightly since August 2013 but this paper presents an analysis of the data collected only up to January 2014. During this period, water samples were collected 12 times.

The shallow groundwater level in the piezometers from August 2013 to January 2014 fluctuated between 3.8 and 5.0 m bgl indicating an upward movement of groundwater shown by slightly shallower groundwater levels in deeper piezometers. In general, nitrate-N concentrations were significantly higher in the unsaturated zone as compared to the saturated zone (shallow groundwater) where the concentrations were very low or negligible (< 0.5 mg L^{-1}) (Figure 3). Nitrate-N concentrations in the unsaturated zone (Figure 3a) were found to decrease from August to November, indicating decreasing input from the surface as the weather gets drier as opposed to higher leaching during wet conditions (Di & Cameron, 2002). This trend was not apparent in the shallow groundwater piezometers during the monitoring period in which nitrate-N levels were already very low (Figure 3b).

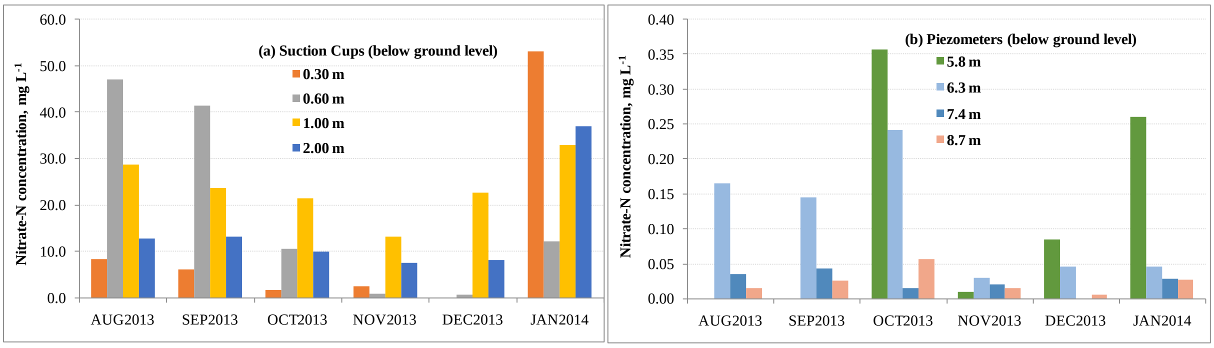

Figure 3: Temporal variability in average nitrate-N concentrations (mg L^{-1}) (a) in suction cups and (b) shallow groundwater piezometers at the experimental site on Massey No. 1 Dairy Farm from August 2013 to January 2014. Any gaps in the suction cups data are due to inability to collect a water sample.

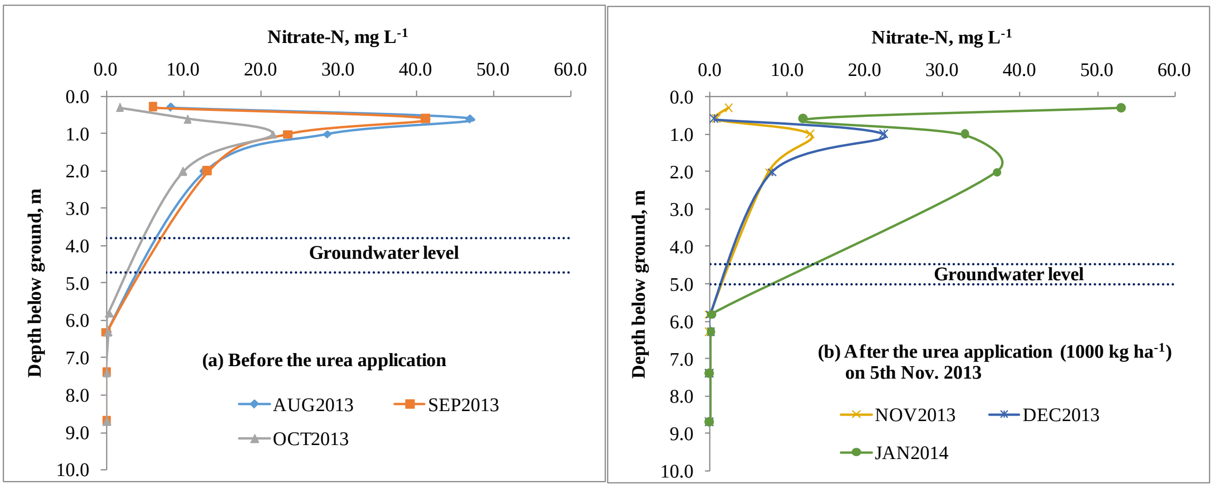

Figure 4: Spatial (vertical) variability in average nitrate-N concentrations (mg L^{-1}) (a) before and (b) after the urea application (1000 kg ha^{-1}) on 5th Nov, 2013 at the experimental site on Massey No. 1 Dairy Farm.

The increase in nitrate-N concentrations in the suction cups between November 2013 and January 2014 (Figures 3a and 4b) was due to the application of urea at the rate of 1000 kg ha^{-1} at the study site on 5th November 2013 along with bromide and fortnightly applications of irrigation thereafter as part of a tracer test. Before the urea application, nitrate-N concentrations were generally higher at 0.60 m depth (Figure 3a) and decreased to less than 0.5 mg L^{-1} in the shallowest groundwater piezometers (Figure 3b). This indicates nitrification occurring in the top 0.6 m of the soil profile. The effect of the urea application on inorganic N concentrations is clearly indicated in the ammonium-N concentrations, with very high ammonium-N in the topsoil layer (0.3 m) in November 2013 (Figure 5). However, ammonium-N was back to low concentrations in the following months at all depths, presumably due to nitrification as indicated in higher nitrate-N concentrations in the suction cups in December 2013 and January 2014 compared to November 2013 (Figure 3a).

Figures 3 and 4 clearly show a significant decrease in nitrate-N concentrations in piezometers (shallow groundwater) as compared to the suction cups (the unsaturated zone). This observed decrease in nitrate-N concentrations could possibly be due to (a) dilution, (b) denitrification, or (c) both dilution and denitrification. Microbial denitrification primarily occurs in low oxygen environments where a suitable electron donor (carbon source) and denitrifying microbes are present (Rivett et al., 2008; McMahon & Chapelle, 2008; Stenger et al 2013). Figure 6 shows nitrate-N and dissolved oxygen concentrations (mg L^{-1}) observed in shallow groundwater piezometers at the experimental site from August 2013 to January 2014. The dissolved oxygen levels were low in the shallow groundwater ranging from 0.23 to 4.65 with an average of 1.13 mg L^{-1}, indicating an environment conducive to denitrification. So long as an electron donor (e.g. organic carbon) is available, then on the basis of the thermodynamic sequence of electron-accepting processes, low dissolved oxygen levels (< 2 mg L^{-1}) or anaerobic environments are more suitable for denitrification (Rivett et al., 2008; McMahon & Chapelle, 2008; Stenger et al 2013). The pH values in the shallow groundwater piezometers (from 6.03 to 6.67) were also in the 'optimum' range for denitrification (5.5-8.0; Rust et al., 2000). The observed oxidation-reduction potential (ORP) values in the shallow groundwater piezometers were generally less than 150 mV, indicating the potential of the shallow groundwater to denitrify (Jahangir et al., 2012a).

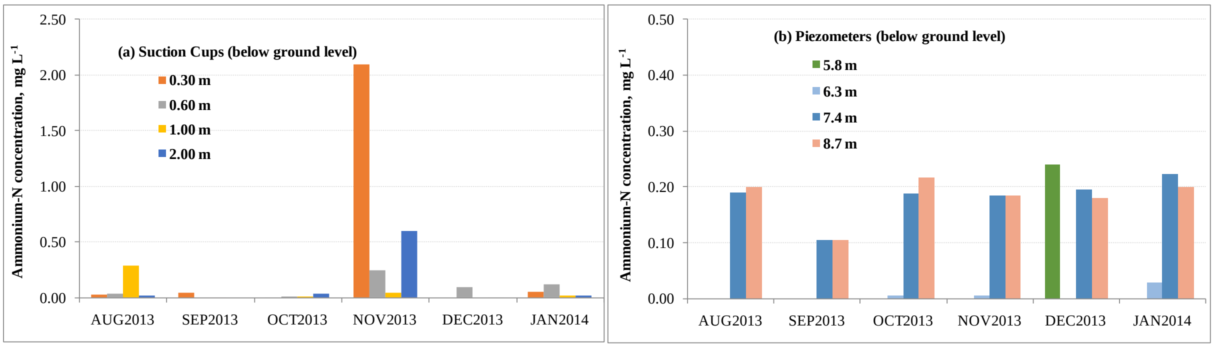

Figure 5: Temporal variability in average ammonium-N concentrations (mg L^{-1}) (a) in suction cups and (b) shallow groundwater piezometers at the experimental site on Massey No. 1 Dairy Farm from August 2013 to January 2014. Any gaps in the suction cups data are due to inability to collect a water sample.

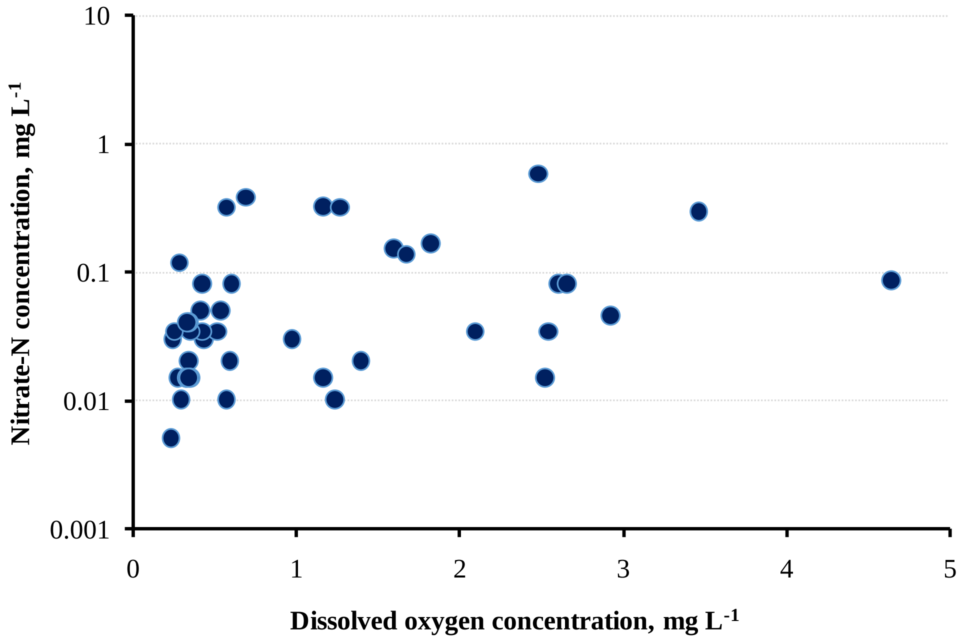

Figure 6: Dissolved oxygen and nitrate-N concentrations (mg L^{-1}) observed in shallow groundwater piezometers at the experimental site on Massey No. 1 Dairy Farm from August 2013 to January 2014.

The preliminary, limited hydrochemistry observations in soil water (suction cups) and shallow groundwater (piezometers) (Figures 3 to 6) indicate a significant reduction in nitrate-N concentrations especially in the shallow groundwater (saturated zone) at the experimental site on Massey Dairy No. 1 farm. While dilution could be an explanation for the very low nitrate-N concentrations in the shallow groundwater, denitrification may have also played a role. This is reflected in Figure 6 where very low nitrate-N concentration values are observed coupled with low dissolved oxygen levels (< 2 mg L^{-1}). This is in accordance with other studies that have reported < 2 mg L^{-1} dissolved oxygen as favourable for denitrification to occur (Rivett et al., 2008; McMahon & Chapelle, 2008; Stenger et al 2013).

The occurrence of denitrification in shallow groundwater on Massey No. 1 Dairy Farm was further demonstrated by Rivas et al. (2014) in a single well push-pull test (Addy et al., 2002) conducted in a piezometer located in a paddock adjacent to the experimental site. In this experiment, 40 L of prepared test solution containing 10 mg L^{-1} of Br^-, 10 mg L^{-1} of NO_3-N, and 50 ml L^{-1} of acetylene was injected into the shallow groundwater via a 28 mm diameter PVC piezometer installed at a depth of 6.5 m below ground level and perforated (5 mm diameter) at the bottom 50 cm. Following the injection, the test solution was retrieved over four hours and the collected samples were analysed for nitrate-N, ammonium-N, DOC, and bromide concentrations. The concentrations of both nitrate-N and bromide decreased over the experiment period (four hours). The concentration of bromide declined from 10 to 0.43 mg L^{-1} and the concentration of NO_3-N decreased from 10 to 0.28 mg L^{-1}. These were still higher than the background concentrations of 0.099 and 0.049 mg L^{-1} for bromide and NO_3-N, respectively. A higher reduction in NO_3-N concentration than the bromide concentration suggests that dilution could not fully account for the all of the nitrate-N reduction in the test solution (Rivas et al., 2014). This further reduction in nitrate-N could be attributed to denitrification. During the test, the NH_4^+-N concentrations were found very low or negligible (0-0.077 mg L^{-1}) indicating that dissimilatory nitrate reduction to ammonium (DNRA) was not responsible for the reduction in nitrate-N (Tesoriero et al., 2000). Moreover, the increasing N_2O concentration during the test (see Rivas et al., 2014) strongly indicates the occurrence of denitrification. Rivas et al. (2014) also indicate and present a measure of denitrification potential in the unsaturated zone based on incubation of subsoil samples taken from a nearby paddock on Massey No. 1 Dairy Farm. These preliminary results presented above indicate potential for, and occurrence of, denitrification in the subsurface environment (below the root zone) at the experimental site.

Concluding Remarks

Current nitrogen management efforts across New Zealand appear to be focused on identifying the intensive farms that leach the largest quantities of nitrogen from the root zone, and then developing management and mitigation practices to reduce the root zone nitrogen leaching so as to meet specified limits. This approach fails to consider the spatial differences in hydrogeologic settings that may or may not reduce, or attenuate, the nitrogen flux as it flows from the root zone to rivers or lakes. The contribution of nitrogen leached from the root zone to groundwater and subsequently to surface waters depends on the transport and transformation of nitrogen in the subsurface environment. While the cycling and transport of nitrogen in the root zone is reasonably well understood, little is known about its transport and transformation in the subsurface environment, particularly in the Manawatu River catchment.

The preliminary results from this on-going work provide indications of spatially distributed nitrogen reduction in the subsurface environment in the Manawatu River catchment. In particular, estimates of the nitrogen attenuation factor indicate the significant potential of the

Tararua GWMZ to reduce nitrate-nitrogen in the subsurface environment. This potential appears to vary among subcatchments. Further analysis is being carried out to confirm this and to determine the influence of different hydrogeological characteristics on nitrogen attenuation in the subcatchments. In determinations of the nitrogen attenuation factor it is important to accurately estimate the nitrate-nitrogen leaching from land under intensive agriculture, such as sheep/beef farms and dairy farms.

Preliminary field monitoring and experiments at a test site established on Massey University's No. 1 Dairy Farm indicate the potential and occurrence of denitrification in the subsurface environment in the catchment. At this site, denitrification appears to be occurring in the saturated zone (shallow groundwater) as reflected in very low nitrate-N concentration values coupled with dissolved oxygen levels generally < 2 mg L^{-1} in shallow piezometers from August 2013 to January 2014. This is further demonstrated by a single well push-pull test conducted in a piezometer located in a paddock adjacent to the experimental site.

Further monitoring, experiments and groundwater surveys are being planned and carried out in the Manawatu river catchment, with a focus on the Tararua Groundwater Management Zone. This will help identify factors affecting denitrification occurrence in different hydrogeologic settings (rainfall, topography, land use, soil and rock types), provide inputs for integrated water and nitrogen flow modelling including denitrification process in the subsurface environment, and fill an identified and important gap in the knowledge required for targeting management and mitigation of nitrogen leaching. The information generated in these research activities is expected to eventually help resource/nutrient managers to identify the most critical areas for targeting effort and investment, in the development of innovative solutions to the problem of unacceptably high nitrogen loads to rivers and lakes.

Acknowledgements

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