AN ASSESSMENT OF THE DENITRIFICATION POTENTIAL IN SHALLOW GROUNDWATERS OF THE MANAWATU RIVER CATCHMENT

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Abstract

Denitrification in shallow groundwaters is an important nitrate attenuation process, occurrence of which depends on the characteristics of the contributing surface and subsurface environment. Little is known about the occurrence and factors contributing to the spatial variability of denitrification potential in shallow groundwater systems in the Manawatu River catchment. The objectives of the study, therefore, are (1) to determine the spatial variability of the denitrification potential in shallow groundwater, (2) to identify the factors affecting this denitrification potential, and (3) to quantify denitrification rates at selected sites in the catchment.

We conducted a groundwater survey during February-March 2014 sampling a total of 56 wells and piezometers well spread across the Tararua Groundwater Management Zone (TGWMZ), located in the eastern portion of the Manawatu River catchment. A preliminary analysis of sampled groundwater hydrochemical parameters reveals spatial variability in the potential of groundwater to denitrify. Anoxic groundwaters with potential to denitrify were found in the middle and northern parts of the TGWMZ, in contrast to the oxic groundwaters mostly found in the southern part. Factors affecting the denitrification potential of groundwater are being assessed using statistical analysis of collected groundwater hydrochemical data. This analysis shows a negative correlation between nitrate-nitrogen and silica, indicating that relatively older groundwater may have higher denitrification potential. Further analysis is being carried out to determine the role of other possible factors such as geology and overlying soil types on the denitrification potential of shallow groundwater in the study area.

We have established four detailed study sites in the catchment wherein three piezometers are installed to different depths and selected groundwater parameters are monitored monthly to obtain indications of temporal variability of denitrification characteristics. Moreover, push-pull tests are being conducted at these sites to quantify denitrification rate in shallow groundwater. Preliminary analysis of two push-pull tests conducted at one of the study sites during May and July 2014 support the occurrence of denitrification in shallow groundwater, with denitrification rates measured at approximately 0.5 mg N L^{-1} h^{-1}.

1. Introduction

Denitrification has been identified as an important nitrate attenuation process in groundwater systems (Rivett et al., 2008; Starr & Gillham, 1993). This occurs mainly as microbial-mediated processes which may reduce nitrate (NO_3^-) ‘a contaminant’ to dinitrogen (N_2) ‘a harmless gas'. Indeed, denitrification has been found to significantly reduce nitrate concentrations in groundwater (Anderson et al., 2014; Jahangir et al., 2013). The attenuation capabilities of groundwater systems depend on the characteristics of the contributing surface and subsurface environment. Areas with inputs of high labile organic matter from the surface environment to the groundwater system tend to have significant denitrification (Rivett et al., 2008). As such relatively higher denitrification is observed in riparian zones, wherein organic matter could accumulate from surface vegetation and roots in the subsurface with shallow groundwater conditions (Hill et al., 2000). The hydrogeological properties of the aquifer materials also contribute to the extent of denitrification by influencing the direction, flow rate, and residence time (and thus, reaction time) of nitrate-contaminated groundwater in the subsurface environment (Haag and Kaupenjohann, 2001; Hiscock et al., 1991). Given the diverse properties of the contributing surface and subsurface environment, the potential of groundwater to denitrify is expected to vary at different locations. By assessing these contributing factors, several studies have identified the variability of denitrification capabilities in the southern part of New Zealand (Rissmann, 2011) and in Denmark (Voutchkova, 2011).

The variability of groundwater denitrification characteristics has implications on the management and mitigation of the impacts of nitrate on surface water quality. Subsequently, it is important to investigate these characteristics to inform targeted measures to mitigate the impacts of agricultural activities on groundwater and surface water quality. However, there is currently little known about the occurrence, spatial variability, and factors contributing to denitrification potential in shallow groundwater systems in the Manawatu River catchment. The objectives of the study, therefore, were: (1) to determine the spatial variability of the denitrification potential in shallow groundwater in the Manawatu River Catchment, (2) to identify the factors affecting this denitrification potential, and (3) to quantify denitrification in selected sites in the catchment.

2. Methodology

2.1 Determining the spatial variability and factors of denitrification potential in groundwater

A groundwater survey was conducted sampling 56 wells and piezometers distributed across the Tararua Groundwater Management Zone (TGWMZ), comprising approximately 3,200 km^2 of the eastern part of the Manawatu River Catchment (**Fig. 1**). These wells vary from 2.6 to 135 m below ground level (bgl), with shallow wells (<10 m bgl) comprising 55% of the wells sampled. Groundwater samples were collected and analysed for several parameters namely: bromide, chloride, nitrate, nitrite and sulphate (analysed by ion chromatography); boron, iron, calcium, manganese, magnesium, potassium, sodium and silica (by inductively coupled plasma atomic emission spectroscopy); dissolved organic carbon (DOC) (by high temperature combustion); ammonium-N (by flow injection analysis); and bicarbonate (based on alkalinity measurements and on site pH measurements). A water quality meter (YSI Professional Plus) with multiple water quality probes was used to measure the following parameters on the sampling sites: temperature, electrical conductivity, dissolved oxygen, and oxidation-reduction potential (ORP).

The potential of groundwater to denitrify was assessed based on the threshold values of selected parameters as identified in published literature (e.g. Thayalakumaran et al., 2008). **Table 1** provides the list, criteria, and relevance of these water quality parameters. This study mainly uses DO and ORP as indicators of redox status as most of samples fall within the suitable range for pH and temperature. If electron donors (DOC, Fe^{2+}) are present above the threshold values in areas of reducing conditions, then such areas are considered to have significant denitrification potential.

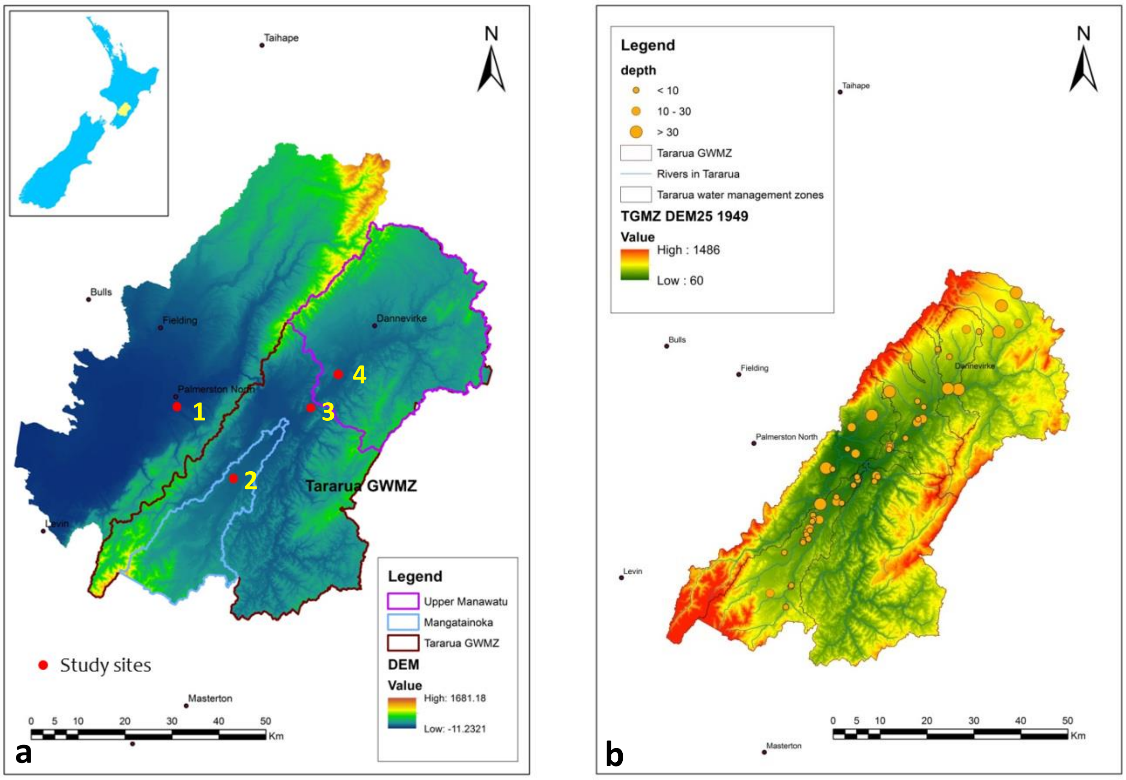

Figure 1 The Manawatu River catchment showing, (a) locations of detailed field study sites; and (b) locations of 56 wells sampled during groundwater survey in the Tararua Groundwater Management Zone (TGWMZ) in the eastern part of the catchment.

Table 1 Parameters assessed to determine denitrification potential in groundwater.

Parameter	Criteria	Relevance to denitrification	References
Dissolved oxygen (DO)	< 2 mg L^{-1}	Denitrification occurs in an anaerobic condition	Rivett et al., 2008; Rissmann, 2011; Thayalakumaran et al., 2008
pH	5.5 – 8.0	Indicator of acidity or alkalinity in water	Rust et al., 2000
Oxidation-reduction potential (ORP)	< 150 mV	Low redox potential indicates strong reducing tendency of groundwater	Jahangir et al., 2012
Temperature	2 – 50 °C	Temperature affects microbial activities, including denitrification	Brady and Weil, 2002
Dissolved organic carbon (DOC)	> 1 mg L^{-1}	Electron donor (heterotrophic denitrification)	Rivett et al., 2008
Ferrous iron (Fe^{2+})	> 1 mg L^{-1}	Electron donor (autotrophic denitrification)	Thayalakumaran et al., 2008

The collected groundwater quality parameters were subjected to a statistical analysis to determine factors affecting the denitrification potential in the study area. The quality of groundwater data was first assessed through determination of charge balance error (CBE) (Freeze & Cherry, 1979). All of the data had CBE of less than the acceptable ±10% (Güler et al., 2002), except for one sample; hence, all were used in the analysis. Afterwards, the normality of data for each parameter was assessed based on Fisher's measure of skewness (±1.95 is significant) and Shapiro-Wilk test for normality. When required, data were transformed until normal distribution is obtained. Most of the parameters had a log-normal distribution (e.g., electrical conductivity, pH, ammonium-N, nitrite-N, bicarbonate, bromide, chloride, calcium, ferrous iron, manganese, magnesium, potassium, silica, sodium, dissolved organic carbon, sulphate), while other parameters were power-transformed to achieve normal distribution (dissolved oxygen [exponent=1/2], nitrate-N [1/4]). The transformed data were used in the statistical analysis using IBM SPSS Statistics 22.

The groundwater survey provides only a snapshot of the denitrification characteristics of groundwater in the study area. In order to determine any changes in denitrification characteristics, we are conducting detailed temporal groundwater monitoring at four locations within the catchment (**Fig. 1**, **Table 2**). These sites were selected based on the results of the aforementioned groundwater survey to cover at least one location each in oxidised and reduced groundwater conditions. At each site, two to three piezometers were installed to sample shallow groundwater at different depths (**Table 2**). The shallow groundwater samples are being collected monthly and analysed for a range of water quality parameters. In addition to the field parameters mentioned above, other groundwater parameters measured include nitrate and ammonium (analysed by flow injection analysis), sulphate (by hydriodic acid reagent reduction), DOC (by potassium dichromate wet oxidation and titration), bicarbonate (based on alkalinity measurements and on site pH measurements), and the major cations namely, iron, manganese, calcium, magnesium, potassium, and sodium (by atomic absorption spectroscopy).

Table 2 Study sites for monitoring groundwater in the Manawatu River Catchment.

Site No.	Site Name/Location	Land Use	Depth of piezometers, m bgl	Rock type	Soil series and type
1	Palmerston North site, Palmerston North	Dairy	6.5 7.5	Alluvium	Manawatu fine sandy loam
2	Pahiatua site, Pahiatua	Dairy	4.4 5.4 6.4	Loess over gravel	Kopua stony silt loam
3	Woodville site, Woodville	Beef and sheep	5.0 6.0 7.5	Alluvium	Kairanga silt loam and clay loam
4	Dannevirke site, Dannevirke	Dairy	4.5 6.0 7.5	Alluvium	Kairanga silt loam and clay loam or Takapau silt loam*

Note: *Uncertainty on the soil type at the Dannevirke site. Soil type at this site was characterised as Kairanga silt loam and clay loam in the NZ Fundamental Soil Layers. However, the soil type was different from that at the Woodville site which was also characterised to have Kairanga silt loam and clay loam. Takapau silt loam is the soil type near the study site.

2.2 *Quantifying denitrification using the push-pull techniques*

The groundwater survey and monitoring provides indication of the potential of groundwater to denitrify, but it does not provide quantitative evidence of occurrence and extent of denitrification. Therefore, the push-pull test (Istok, 2013, 1997; Sanchez-Perez et al., 2003) was adopted for the direct quantification of denitrification at the selected field sites in the catchment. We have described in detail the push-pull test in Rivas et al. (2014a, 2014b). In brief, the push-pull test involves extraction of 100 L of groundwater into 20 L collapsible bags; preparation of test solution with the addition of sources of nitrate (KNO_3) and bromide (KBr) as a conservative tracer, and acetylene (C_2H_2); injection of the test solution; and collection of water samples at different times from time 0 (right after completion of solution injection) up to seven hours. Two sets of water samples were collected: three replicates of approximately 60 mL samples were filtered and collected in polyethylene bottles for the measurement of nitrate and bromide, and duplicate samples of 120 mL (May 2014) or 180 mL (July 2014) samples in vacuum pouches for the extraction of dissolved nitrous oxide gas. The collected samples for hydrochemical analysis were frozen until analysis. Nitrate and bromide were both determined by ion chromatography. The collected samples for nitrous oxide were kept chilled at 4 °C until the gas extraction, which was done within 24 hours. To extract dissolved nitrous oxide gas from the collected water samples, the phase equilibrium headspace extraction method (Addy et al., 2002; Lemon and Lemon, 1981) was adapted in which 50 mL (May 2014) or 60 mL (July 2014) of N_2 were added into each pouch, which were then placed on a shaker for 1.5 hours at 200 rpm under 20 °C. After shaking, 25 mL of gas samples were removed from each pouch and placed into 12 mL glass vials for analysis in a gas chromatograph. The use of larger sample, 180 mL in July 2014 (compared to 120 mL groundwater sample in May 2014), is presumed to increase the accuracy of measurements.

The difference between our push-pull tests from previous push-pull tests conducted in other similar studies is the use of both a conservative tracer (Bromide) and measuring an intermediate product of denitrification (N_2O) for determining the occurrence and rate of denitrification. Most of the studies use one method only to determine the denitrification rate: either using the nitrate and bromide concentrations (Istok, 2013; Tesoriero et al., 2000; Baker and Vervier, 2004; Trudell et al., 1986) or nitrous oxide concentrations (Sanchez-Perez et al., 2003; Well et al., 2003). In this study, denitrification rate was determined from the changes in the concentrations of nitrate with respect to bromide (see Rivas et al., 2014a). While denitrification rate can also be determined from nitrous oxide concentrations, the results from the measurements of nitrous oxide in this study are used only to provide a concrete supporting evidence of the occurrence of denitrification indicated by increasing N_2O concentrations during the test. The use of both methods to determine the denitrification rate and possible differences between the resulting rates will be a subject of a future study.

In this study, we assessed also the influence of the addition of acetylene in quantifying denitrification in push-pull tests. Several authors argued the possibility of enhanced denitrification with acetylene as the carbon source in denitrification assays particularly if carbon is limited (Tiedje et al., 1989; Yeomans and Beauchamp, 1982). The comparison of results from push-pull tests with or without added acetylene is expected to provide useful information on the effect of acetylene.

3. Results and Discussion

3.1 Spatial variability of denitrification potential in groundwater in the Tararua Groundwater Management Zone (TGWMZ)

Figure 2 shows the distribution of parameters related with redox conditions in the TGWMZ. It is clearly apparent that wells in the Mangatainoka sub-catchment (in the southern part of the TGWMZ) have higher dissolved oxygen content (> 2 mg L^{-1}). These areas correspond to wells with relatively higher nitrate concentrations (> 10 mg L^{-1}). This indicates the lower denitrification potential in the Mangatainoka sub-catchment, as supported by the low concentrations of electron donors (Fe^{2+} and DOC). Few locations in the northern part of the TGWMZ (Upper Manawatu) also have high nitrate concentrations along with DO concentrations of > 1 mg L^{-1}. The presence of electron donors at these locations may indicate the potential for denitrification to occur. However, the significant DO content in the groundwater may have hindered the denitrification process as microorganisms prefer O_2 to nitrate due to the higher energy generated in the O_2-reduction process (McMahon and Chapelle, 2008).

Using the criteria established in section 2.1 (**Table 1**), the areas with denitrification potential are shown in **Figure 3**. These areas are mainly located in the middle and northern parts of the TGWMZ. In contrast, low denitrification potential is indicated for the Mangatainoka sub-catchment.

To check whether this distribution of denitrification potential is reflected in the quality of surface water in the respective sub-catchments, an assessment was made comparing river nitrate-N loads in two sub-catchments (Upper Manawatu and Mangatainoka) where contrasting denitrification characteristics are observed (**Figure 3**). **Table 3** provides a comparison of the sub-catchments including the average N leaching rate (ton N km^{-2} yr^{-1}) and the average river N load (ton N km^{-2} yr^{-1}). Despite of differing land use characteristics, the average leaching rates in both sub-catchments were comparable. On the other hand, the estimated average river N loads (computed from soluble inorganic nitrogen concentration and flow rate at the specified sub-catchments outlet) were significantly different. Higher river N load was found in the Mangatainoka sub-catchment (1.228 ton N km^{-2} yr^{-1}**)** than in the Upper Manawatu (0.607 ton N km^{-2} yr^{-1}). This assessment does not consider travel time of water from farms to rivers and additional investigations are needed to determine whether denitrification is occurring in the soil, groundwater, riparian zones, and/or in the river itself. However, the results presented here provide some supporting evidence of the contrasting denitrification characteristics of the two sub-catchments based on the surface water quality parameters (**Table 3**).

3.2 Factors affecting the denitrification potential in groundwater

Factors affecting the potential of groundwater to denitrify may be deduced from the correlation among groundwater quality parameters (**Table 4**). A positive correlation between nitrate and DO (r =0.619, p <0.01) confirms the influence of DO on denitrification, given that denitrification is basically an anaerobic process. The negative correlation between nitrate and silica (SiO_2) (r =-0.495; p <0.01) indicates the higher potential of relatively older groundwater. Silica is used as a proxy for the relative age of groundwater as greater silica concentration could indicate longer residence time of the water in the ground (Burns et al., 2003; Morgenstern et al., 2015). On the other hand, whether low nitrate concentrations found in older groundwater especially in deeper wells were results of nitrate contamination being not yet able to reach the deeper groundwater needs further investigation. The negative correlation also between silica and DO (r =-0.625; p <0.01) reflects the reduction of DO with increasing residence time. The relatively younger groundwater in the Mangatainoka sub-catchment is reflected in a groundwater age study conducted in the Manawatu River Catchment (Morgenstern et al., 2014). Results of the study showed that river water sampled during baseflow conditions in the TGWMZ is young, ranging from 0 – 2 years of mean residence time. Further assessment is being done to understand the role of other possible factors, such as hydrogeological characteristics, on groundwater denitrification potential in the study area.

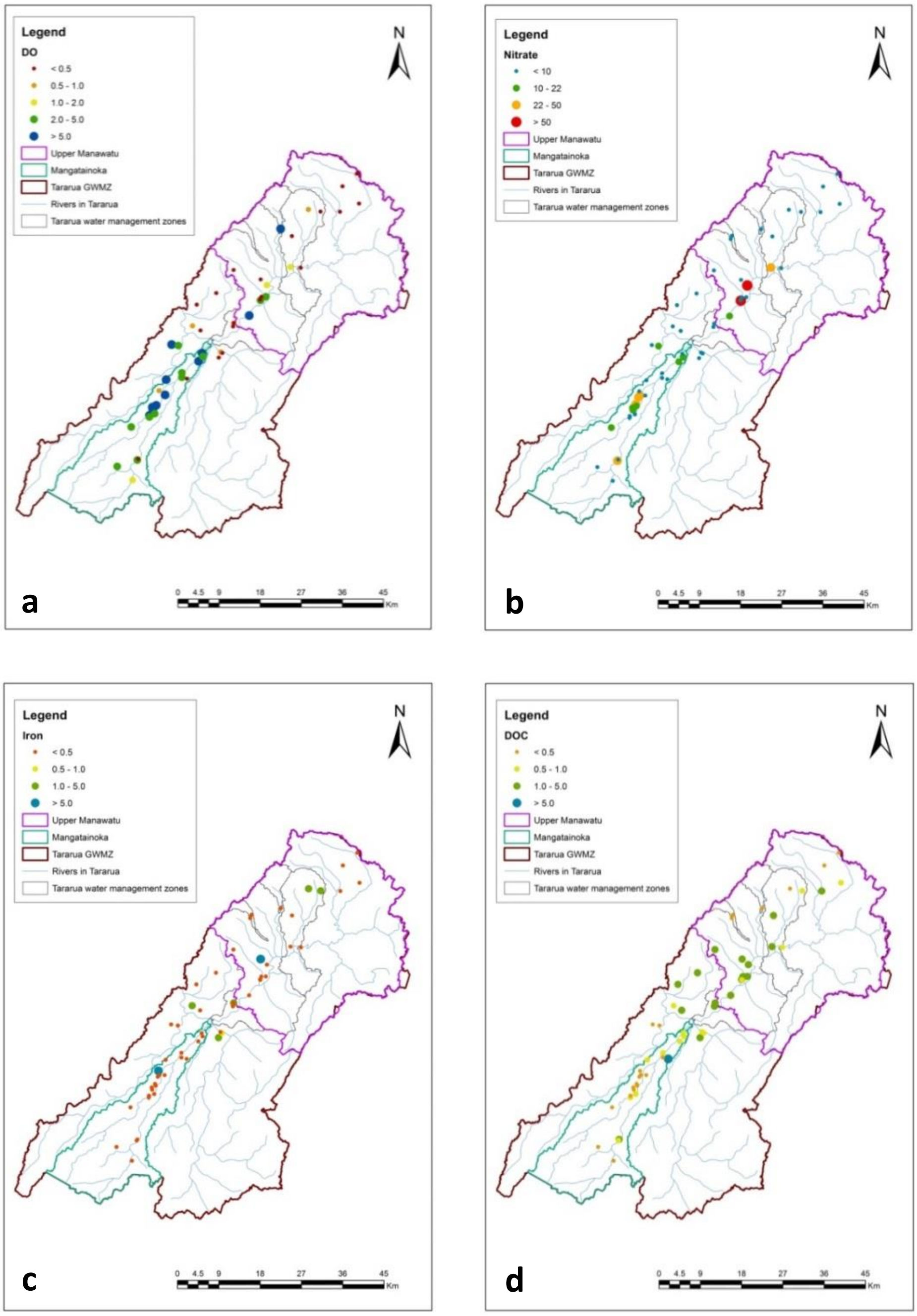

Figure 2 Distribution of (a) dissolved oxygen (mg L^{-1}), (b) nitrate (mg L^{-1}), (c) ferrous iron (mg L^{-1}), and (d) dissolved organic carbon (mg L^{-1}) in the Tararua Groundwater Management Zone.

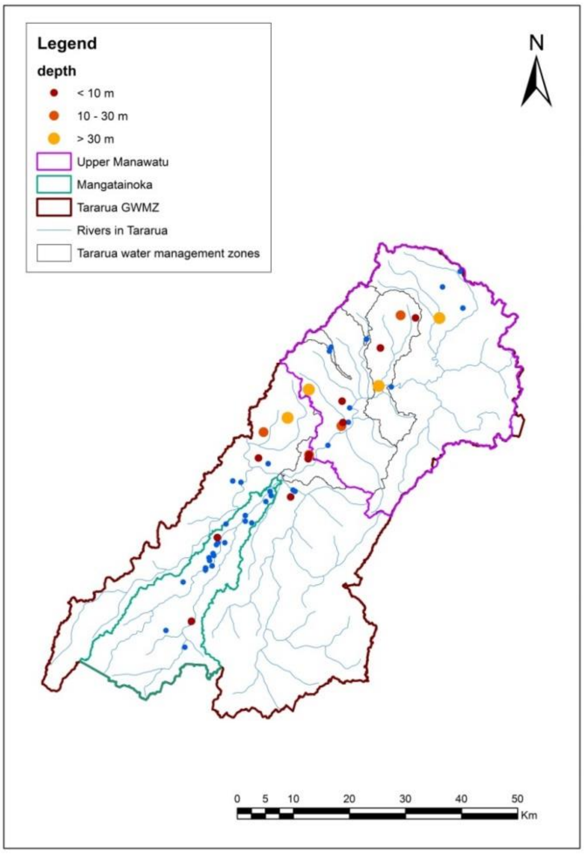

Figure 3 Locations of wells with denitrification potential in the Tararua Groundwater Management Zone. Wells in blue have low denitrification potential.

Table 3 Estimated average N leaching and river loading rates in the Upper Manawatu and Mangatainoka sub-catchments.

Sub-catchment	**Area, km^2**	**Ave. Nitrate-N at outlet[a], mg L^{-1}**	**Leaching rate[b], ton N km^{-2} yr^{-1}**	**River load[c], ton SIN km^{-2} yr^{-1}**
U. Manawatu	1262	0.794	1.729	0.607
Dairy	202			
Sheep/beef	889			
Mangatainoka	401	0.878	1.941	1.228
Dairy	140			
Sheep/beef	175			

Source: Elwan et al. (2015); A. Elwan (personal communication, 2015)

Notes:

[a] Sub-catchment outlets: Manawatu at Hopelands (Upper Manawatu), Mangatainoka at Pahiatua Bridge (Mangatainoka); nitrate-N is average of available monthly data from January 1990 to December 2014 from the Horizons Regional Council.

[b] See Elwan et al. (2015) for specific leaching rates for different land use types, such as dairy, sheep/beef, exotic cover and native cover.

[c] River load was computed from non-point sources only, i.e. excluding point sources (0.4 – 3% of total river load); SIN – soluble inorganic nitrogen.

Table 4 Pearson correlation coefficients (*r*) between selected groundwater quality parameters in the Tararua Groundwater Management Zone.

	DO	**SPC**	**pH**	**ORP**	**HCO_3^-**	**Fe^{2+}**	**Mn^{2+}**	**Silica**	**DOC**	**NO_3^-**	**NO_2^-**	**SO_4^{2-}**
SPC	-.626**											
pH	-.577**	.474**										
ORP	.791**	-.443**	-.749**									
HCO_3	-.766**	.743**	.856**	-.766**								
Fe^{2+}	-.681**	.244	.284	-.612**	.360*							
Mn^{2+}	-.747**	.222	.325*	-.610**	.425**	.730**						
Silica	-.625**	.467**	.433**	-.669**	.620**	.518**	.504**					
DOC	-.539**	.532**	.380**	-.298*	.539**	.168	.244	.216				
NO_3^-	.619**	-.177	-.575**	.757**	-.499**	-.640**	-.598**	-.495**	-.163			
NO_2^-	-.245	-.024	.512**	-.355*	.344*	.067	.265	.090	.078	-.146		
SO_4^{2-}	-.017	.220	-.176	.221	.072	-.047	.001	.015	.174	.392**	-.190	
NH_4^+	-.710**	.650**	.712**	-.644**	.726**	.329*	.336*	.534**	.494**	-.597**	.141	-.130

* Correlation is significant at the 0.05 level (2-tailed); ** Correlation is significant at the 0.01 level (2-tailed); Data used have been transformed to conform with normality requirement.

3.3 Variation of groundwater redox indicators at selected sites in the Manawatu River Catchment

Figure 4 reproduces the results from monthly groundwater monitoring at four sites in the Manawatu River Catchment (**Figure 1 & Table 1**). The depth to groundwater levels increased from October to January 2015, as expected during the summer period. The DO concentrations appear to decrease with time corresponding to drier conditions, indicating a direction toward more favourable condition for denitrification during summer period as found in other studies (e.g., Anderson et al., 2014). This seems to be reflected in the decreasing nitrate-N concentrations at the Dannevirke site. However, this is not observed at the Pahiatua site where the nitrate-N concentrations were measured to increase. The DO and nitrate-N concentrations at Pahiatua site were high, whereas very low DO and nitrate-N concentrations were observed at the Palmerston North, Woodville and Dannevirke sites (except for the shallowest piezometer). Low DO and nitrate-N concentrations at the middle and deeper piezometer at the Dannevirke site indicates the denitrification potential of the deeper profile.

Figure 4 clearly highlights the spatial variability of redox characteristics apparent among the monitored sites. Higher DO concentrations were found at the Pahiatua site, which was selected to represent areas of oxidised conditions as identified in the groundwater survey. On the other hand, low DO concentrations were found at the Woodville and Palmerston North sites and in the deeper piezometer of the Dannevirke site. These are also reflected in the ORP values with generally low redox potential at Palmerston North, Woodville and Dannevirke sites as compared to the Pahiatua site. The DO and nitrate-N concentrations monitored at these four sites (Figure 4), therefore, support the results of the groundwater survey with findings consistent to the redox properties and denitrification characteristics at these sites found in the survey.

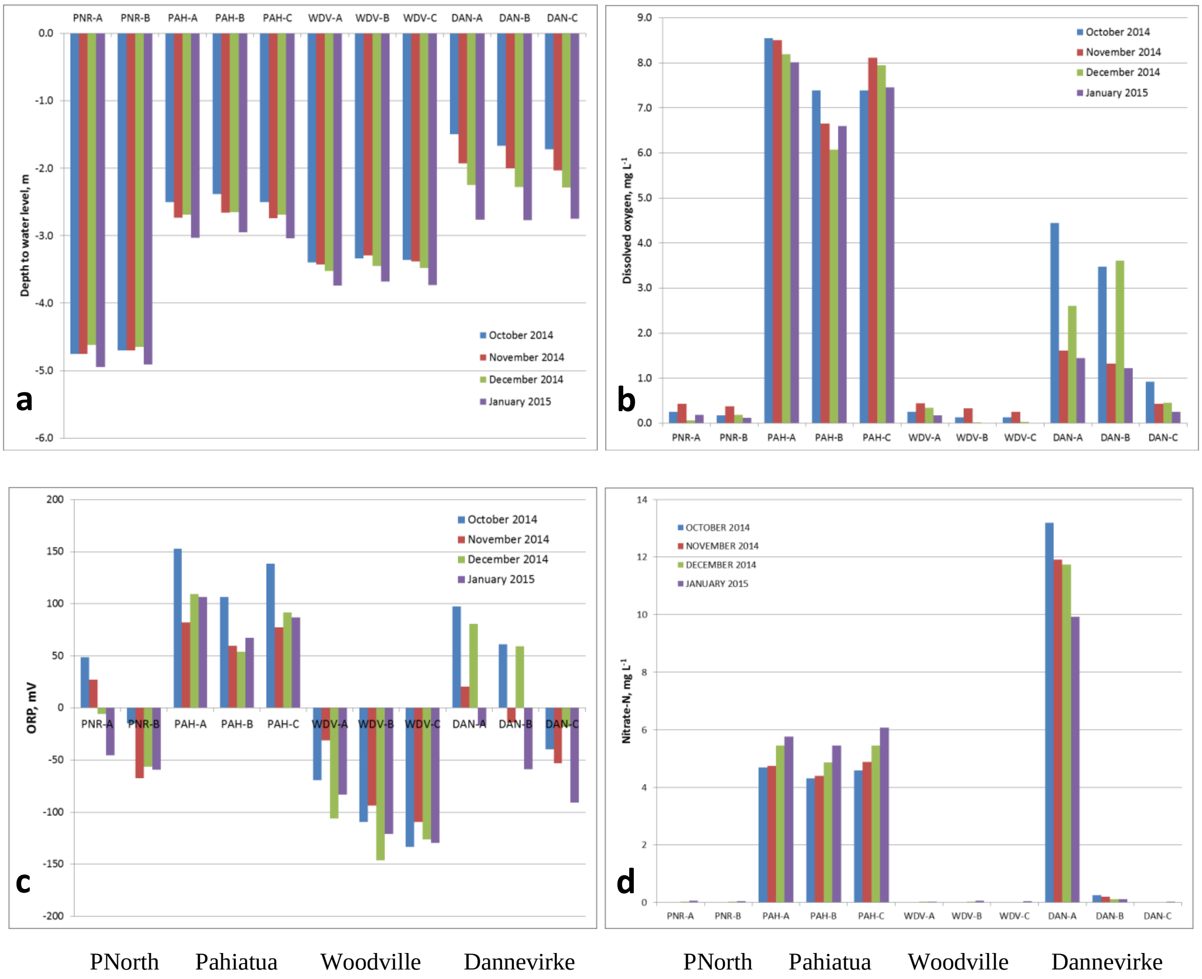

Figure 4 Temporal variations of selected shallow groundwater parameters from monthly monitoring at four sites in the Manawatu River Catchment; (a) depth to groundwater level; (b) dissolved oxygen (mg L^{-1}), (c) oxidation-reduction potential (ORP) (mV), and (d) nitrate-N (mg L^{-1}).

3.4 Quantitative indicators of denitrification in shallow groundwater

Figures 5, 6 and 7 present the results of two push-pull tests conducted at the Palmerston North site, one in May 2014 (**Figures 5 and 7**) and the other in July 2014 (**Figures 6 and 7**). Based on the dilution-corrected nitrate-N concentrations, the computed denitrification rates were 0.55 mg N L^{-1} h^{-1} and 0.44 mg N L^{-1} h^{-1} for the push-pull tests conducted in May and July 2014, respectively. These values, which are within the range of push-pull test results reported in the literature (0.01-1.12 mg N L^{-1} h^{-1}; Rivas et al., 2014a), reflect the consistency of the push-pull test to estimate the denitrification rate. The difference between the two rates could be due to the different times that the tests were conducted, indicating that the use of acetylene did not seem to affect the denitrification rate especially that significant amount of electron donor (DOC) was present during the test.

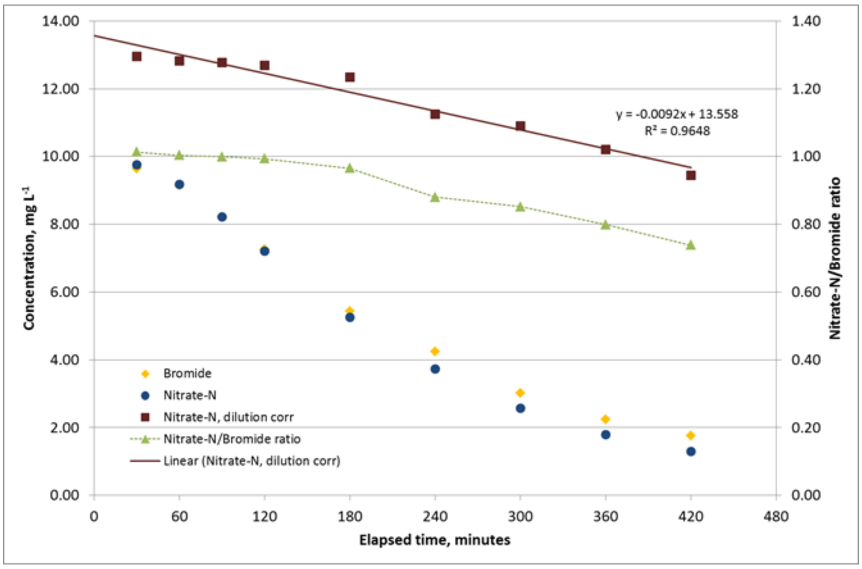

Figure 5 Trend in nitrate-N and bromide concentrations during the push-pull test conducted at the Palmerston North site in May 2014. No. of replicates per sampling time: 3. Background concentrations: Nitrate-N: <0.01 mg L^{-1} (level of detection) and bromide: 0.099 mg L^{-1}.

The increasing N_2O concentrations over the test duration strongly support the occurrence of denitrification (**Figure 7**). The measured N_2O-N concentrations of background (0.0001 mg N_2O-N L^{-1} in the July 2014 test) and time 0 samples (0.00045 and 0.0009 mg N_2O-N L^{-1} in May and July 2014, respectively) were very low. When acetylene was added in the test solution (as in the May 2014 test), N_2O concentrations appear to increase linearly during the test duration. This was expected as acetylene was used to inhibit the reduction of N_2O to N_2 gas (Yoshinari et al., 1977). For the July 2014 test in which no acetylene was added, N_2O concentration increased linearly until time 0.5 hr and then the increase slowed down and appears to be flat after 4 hours (**Figure 7**). This was not surprising as N_2O was expected to be converted to N_2 in the absence of inhibiting substance, such as acetylene. Although N_2 measurements are needed to confirm this, the conversion of N_2O to N_2 indicates the potential of complete denitrification in shallow groundwater as observed in other studies (e.g., Jahangir et al., 2012a). Such potential for complete denitrification underlines the significance of groundwater in the “long-term improvement” of water quality as dinitrogen gas (N_2), the end product of denitrification, is unlikely to be converted back to nitrate within the system (Starr and Gillham, 1993).

Further tests may be needed to assess the effect of acetylene in conditions with low electron donor concentrations. In this study, however, it is apparent that the use of acetylene in conditions where electron donors are present is helpful to support the results from hydrochemical data (nitrate-N and bromide).

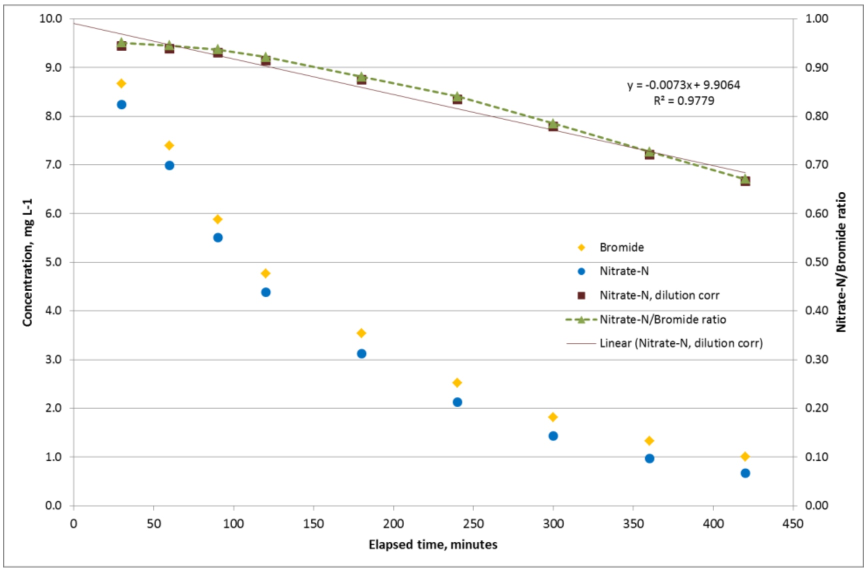

Figure 6 Trend in nitrate-N and bromide concentrations during the push-pull test conducted at the Palmerston North site in July 2014. No. of replicates per sampling time: 3. Background concentrations: Nitrate-N: <0.01 mg L^{-1} (level of detection) and bromide: 0.080 mg L^{-1}.

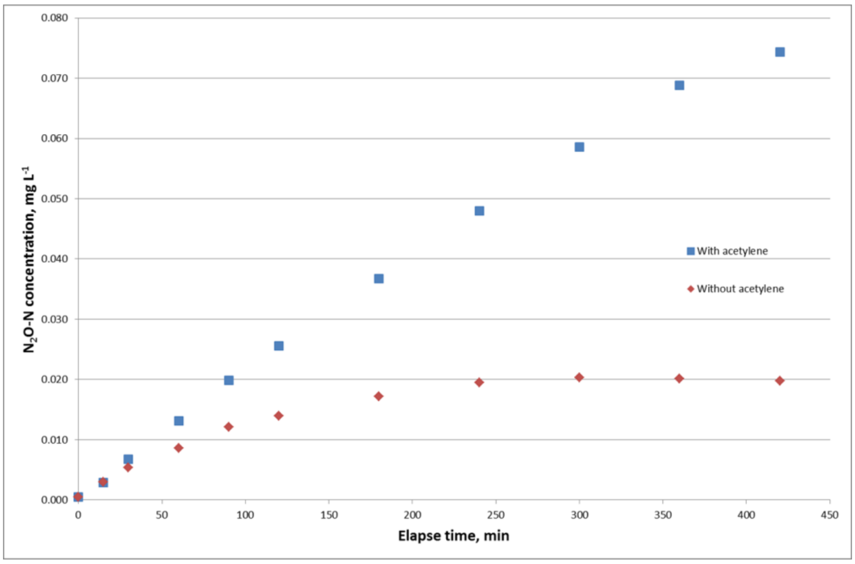

Figure 7 Changes in N_2O-N concentrations during the push-pull test conducted at the Palmerston North site in May (with acetylene) and July 2014 (without acetylene). No. of replicates per sampling time: 2. Background concentrations: 0.0001 mg N_2O-N L^{-1} (July 2014; no data collected in May 2014). Values are not corrected for dilution.

4. Concluding Remarks

While the results presented in this paper are preliminary, the variability of denitrification characteristics in groundwater in the Tararua Groundwater Management Zone was apparent. Low denitrification potential was found in the Mangatainoka sub-catchment, wherein high DO and nitrate concentrations were observed. High denitrification potential was found in groundwater in the middle and northern parts (Upper Manawatu) of the catchments with anoxic groundwater containing electron donors such DOC and ferrous iron. Correlations among selected hydrochemical properties revealed that residence time may have contributed to this denitrification potential with negative correlation being found between silica and DO, and between silica and nitrate, with silica used as a proxy for groundwater age. Further assessments are needed with regard to the presence or absence of electron donors in different areas, as well as on the role of other possible factors, such as geology and overlying soil types, on the denitrification potential of shallow groundwater in the study area.

The occurrence of denitrification in shallow groundwater at the Palmerston North site was quantified with the push-pull test. Two push-pull tests with or without acetylene added in the test solution provided comparable results indicating a denitrification rate of approximately 0.5 mg N L^{-1} h^{-1}. Push-pull tests with acetylene are helpful in investigations especially where groundwater already contains electron donor as nitrous oxide data provide strong support to the tracer (bromide) data. Although not used in this study, nitrous oxide data may also be used to compute the denitrification rate. If two rates are computed, further investigation is needed to reconcile denitrification rates based on nitrate and bromide data and based on nitrous oxide only. It should also be noted that the denitrification rates obtained in this study are specific to the method and concentrations of substrates used. Whether the rates differ with the use of different concentrations need further investigation.

The ongoing monthly groundwater monitoring at four selected sites in the catchment provides supporting evidence on the temporal and spatial variability of denitrification characteristics. Further results from the monthly monitoring and push-pull tests being conducted at these sites are expected to provide more information on the variability and factors affecting denitrification potential in the study catchment.

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