

ASSESSMENT OF NITROGEN FLOW PATHWAYS AND ITS POTENTIAL ATTENUATION IN SHALLOW GROUNDWATERS IN THE LOWER RANGITIKEI CATCHMENT

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Abstract

We assessed surface water and groundwater interactions, and nitrogen flow and its potential attenuation in shallow groundwater in the lower Rangitikei catchment. The study area covers about 850 km² between the townships of Bulls and Sanson in the east, Tangimoana in the south and Santoft in the north. A piezometric map, developed from measured depths to groundwater in about 100 wells in October 2014, suggests that groundwater flow, in particular the shallow groundwater (<30 m), is heavily influenced by the regional topography. Shallow groundwater flows mostly from elevated areas, such as Marton, in a south-westerly direction towards the Rangitikei River, whereas deeper groundwater (>30 m) showed relatively less topographic influence. Groundwater discharges to the river upstream and downstream of Bulls, while groundwater recharge or no interaction with the river is more likely to occur near the coast. The groundwater redox characterisation, based on sampling and analysis of 15 groundwater wells, suggests that in general the groundwater across the lower Rangitikei catchment is under anoxic/reduced conditions. The groundwater typically has low dissolved oxygen concentrations (<1 mg/L) and elevated levels of electron donors (particularly DOC and Fe²⁺) that are suitable for denitrification. We further measured NO₃⁻-N attenuation in shallow groundwater piezometers (3-6 m bgl) using the single-well push-pull tests. The push-pull tests showed NO₃⁻-N reduction at four of the five piezometers, with the rates of reduction varying from 0.04 mg N L⁻¹ hr⁻¹ to 1.57 mg N L⁻¹ hr⁻¹.

Keywords

Agriculture, Denitrification, Nitrate-nitrogen (NO₃⁻-N), Groundwater flow, Groundwater – surface water interactions, Redox reactions, and Push-pull test.

1. Introduction

Excess nutrients in surface water bodies can lead to a sudden growth in plants and algae, a process known as eutrophication. The impacts of eutrophication can include algal blooms, oxygen deficiency, loss of habitat, loss of ecosystem functioning and a loss of biodiversity (Rabalais, 2002). The Australian and New Zealand Environment Conservation Council has determined the trigger value for eutrophication of surface water to be just 0.44 mg/L NO₃⁻-N (Stenger et al., 2008). Intensive agricultural activities are generally associated with nitrogen leaching from soils which have the potential to percolate to groundwater (Harter et al., 2014). Fertiliser use, cow urine patches (Di & Cameron, 2002), irrigated agriculture and effluent spreading all have the potential to leach nitrate (NO₃⁻) over a large area and are therefore considered a diffuse source of contamination. In the New Zealand context, the increased use of fertilizers and intensification of agricultural activities have occurred in tandem with a

change in land use over the last two or three decades. Over the period 1990-2007, the area occupied by sheep and beef farming contracted 2.2 M ha as lowlands were converted to dairying, arable cropping and horticulture, while steeper hill country areas were planted into forestry (Quinn et al., 2009). Since 1990 there had been a major expansion in the dairy industry, with 515,000 hectares of sheep and beef farms converted to dairy farming and a 17% increase in the stocking rate (Quinn et al., 2009). The more intensive nature of dairy farming has meant a greater potential for NO_3^- -N leaching to groundwater and surface waters (Verloop et al., 2006).

Though fertiliser use in New Zealand has increased in recent decades, the biggest source of NO_3^- -N leaching is understood to be from cow urine patches (Di & Cameron, 2002). Only a small amount of nitrogen ingested by a grazing animal is actually removed from the pasture in animal products; a large proportion (between 60-90%) of the nitrogen ingested is returned to the soil in the form of urine and manure (Haynes & Williams, 1993; Jarvis et al., 1995). The nitrogen loading rate under a cow urine patch is equivalent to approximately $1000 \text{ kg N ha}^{-1}$ (Di & Cameron, 2002). Some of this nitrogen gets lost through volatilisation, but most of it gets nitrified, resulting in the accumulation of NO_3^- -N in the soil. Because of the high loading rate under the urine patch, and being well above the biological needs of the plant, there is a high potential for the NO_3^- -N to leach (Di & Cameron, 2002). The leaching potential is particularly high during the autumn-winter-spring period in New Zealand (May to September) when the soil is wet and excess water drains from the root zone (Di & Cameron, 2002).

Groundwater can contribute to the eutrophication of surface waters where they have some degree of connection and the groundwater is nutrient rich (Smith et al., 1999). However, leached NO_3^- -N may be reduced, or 'attenuated', through a process of denitrification if favourable conditions exist in the groundwater system (Korom, 1992). Under reducing conditions, the process of denitrification breaks down NO_3^- (5+ oxidation state) to N_2 (0 oxidation state) through intermediate compounds including NO_2^- , NO, and N_2O (van der Perk, 2012).

The rate of denitrification is most often related to the amount of dissolved organic carbon (DOC) in groundwater. DOC levels in most aquifers are relatively low, but sufficient for denitrification, at $<5 \text{ mg/L}$ (Rivett et al., 2007). If DOC is too low and becomes a limiting factor, other electron donors can take the place of DOC for electron transfer. In these cases, reduced inorganic species such as Mn^{2+} , Fe^{2+} and HS^- can serve as electron donors and denitrification is carried out by autotrophic microbes (Korom, 1992). Reduction of NO_3^- -N by Fe^{2+} can proceed either abiotically or biotically. In abiotic reduction, it is thought Fe^{2+} acts to promote denitrification where Fe^{2+} reduces NO_3^- to NO_2^- and is subsequently regenerated by the oxidation of organic carbon. NO_2^- can then be abiotically reduced in DOC-poor environments by the further oxidation of iron (Rivett et al., 2008).

In New Zealand there is now a growing body of literature on nitrate attenuation in the subsurface of agricultural catchments. Much of this work has taken place under the Groundwater Assimilative Capacity programme in partnership between ESR, Lincoln Ventures and AquaLinc Research (e.g. Stenger et al, 2012; Stenger et al., 2013). This work has also been complemented by the work the Massey University Fertilizer and Lime Research Centre (Massey FLRC) and Horizons Regional Council (HRC) has done in recent years on NO_3^- -N attenuation in shallow groundwater in the Horizons region (Rivas et al., 2014). As yet, no such studies have been carried out on the Lower Rangitikei catchment to estimate the denitrification capacity of the shallow groundwater.

The main objective of this study was to understand the groundwater flow pattern including its interactions with the river, and determine the extent to which NO_3^- -N could be potentially being attenuated in shallow groundwaters in the Lower Rangitikei catchment. Specifically, the objectives of this research were to:

- Conduct river and groundwater surveys to map groundwater flow direction and its interactions with the Rangitikei River;
- Survey groundwater quality to assess redox conditions of groundwater; and
- Measure ‘denitrification’ potential using groundwater monitoring and conducting single well ‘push-pull’ tests in shallow groundwaters in the Lower Rangitikei river catchment.

2. Study area description

The study area is located on the western coast of the North Island of New Zealand (Figure 1a). It covers the Lower Rangitikei River catchment, an area comprising the townships of Marton in the north, Sanson in the east, Tangimoana in the south and the Santoft area in the west.

The soils in the study area have developed in primarily two landscape types: soils of the sand country, and soils of the river flats and terraces (Cowie et al., 1967). The soils of the sand country occur on the dunes, sand plains and peaty swamps. The accumulation of wind-blown sand takes place not just in the Rangitikei district, but a wide area stretching from southern Wanganui down to Hokio in the Horowhenua along the Manawatu – Wanganui coastal belt. As the sand accumulates on the beaches it is simultaneously built into dunes by the wind as the shoreline progrades so that the youngest dunes and associated sand plains are nearest the coast. There have been four major dune building phases covering the last 25,000 years (Cowie et al., 1967). Soils of the river flats and terraces are derived from material brought down by the river and reworked sand from dunes during times of floods (Cowie et al., 1967). Soils of the terraces are formed from old sediments which are now sufficiently above the river level to be free from flooding and the accumulation of fresh alluvium. They have commonly received additions of windblown material known as loess, layers of which are thicker eastward from the coast (Cowie et al., 1967).

There are several primary geological units within the study area. The Torlesse greywacke basement rocks (260 – 150 Ma) underlie all other sediments but outcrop only far to the east forming the Ruahine and Tararua Ranges. The greywacke is primarily composed of hard quartzofeldspathic sandstone with interbedded mudstone. These rocks have experienced deformation from several episodes of folding and faulting creating large blocks of greywacke with a sheared mudstone matrix. These rocks typically lack porosity with a mineralised cement often filling the intergranular spaces (Begg et al., 2005).

Pliocene – Early Pleistocene deposits (3.6 – 0.7 Ma) mark the beginning of sedimentation within the southern Wanganui Basin, and approximately the first half of the Rangitikei Supergroup. The oldest formation described here marks the onset of regional subsidence and are therefore composed primarily of marine mudstone. Middle Pleistocene deposits (700 – 128 ka) represent the latest portion of the Rangitikei Supergroup and represents a major geological change where the northern region of the Wanganui Basin started to emerge from the sea (Begg et al., 2005).

The latest Quaternary deposits (<128 ka) represent all marine and terrestrial sediments deposited since the Last Interglacial Maximum (128 – 80 ka). It is these deposits that comprise the largest shallow groundwater resource in the study area. Last Glacial deposits and

Holocene deposits (Q2 to Q1, respectively) are dominated by alluvial gravel deposits, and marine sand and silts laid down during this period (Begg et al., 2005). An analysis of well logs within the study area do not demonstrate a widespread aquifer system, but rather a series of local aquifers that is best described as a large leaky system where it is locally confined, semi-confined and unconfined (Wilson, 2007).

Land use within the study area is primarily made up of sheep and beef farming at 42% of total land use, while dairy farming makes up another 24%. Exotic forestry makes up 15% though is most densely located in the coastal area. These figures were estimated in 2008 for a report into the land use and land use capability of the Manawatu-Wanganui region (Clark & Roygard, 2008). In the seven succeeding years, some changes could be expected, especially towards dairy intensification.

3. Methods and Materials

3.1 Groundwater Flow

In this study approximately 200 existing wells were identified to survey groundwater levels and map the groundwater flow direction. The wells were selected based on their spatial and depth distribution. The depth to groundwater was measured from just over half of the wells visited. Many of the wells were sealed, unable to be dipped, could not be located, or were pumping at the time of inspection. The measured groundwater depths were corrected to a common datum (Wellington datum) to be expressed as metres above sea level (masl). These measured groundwater levels were later visualised and analysed in ArcGIS 10.2.1, converting the data points into a raster file using the Inverse Distance Weighted function and then converted to a topographic map with the contour function. Contour intervals were set at 10 m.

3.2 Groundwater – Surface Water Interactions

Groundwater – surface water interactions were interpreted through a series of flow gauging measurements across the Lower Rangitikei River. The study covered approximately 25 km of the Lower Rangitikei River, from the Kakariki Bridge near Halcombe to a permanent river flow recording station near Tangimoana, 4 km from the coast. River discharge measurements were made using the Sontek River Surveyor M9, which was traversed across the channel at least 6 times with the data being transferred to a computer in real time as it was being collected.

Flow gauging was conducted twice at low flow conditions when no substantial rain had occurred recently (6 January 2015 and 20 January 2015). During the first survey (6 January 2015), flow gauging measurements were taken at four locations (Figure 2): the Kakariki Bridge, the Bulls Bridge, a quarry near the McDonnell Road and another quarry at the Campion Road. During the second survey (20 January 2015), flow gauging measurements were taken at the same locations with an addition location between the Kakariki Bridge and the Bulls Bridge (Figure 2). The most downstream flow measurements were taken from the permanent river flow monitoring station at Tangimoana. This river flow station is operated by Horizons Regional Council.

3.3 Groundwater Redox Conditions

A total of 15 groundwater wells area were selected and surveyed for groundwater quality analysis in December 2014. The depth of these wells ranged from 2 m to 116 m (bgl), though all but one was shallower and single screened. The wells were sampled according to the National Protocol for SOE Groundwater Sampling in NZ (Daughney, 2006), purging three times the volume of the well before sampling and stabilisation of suggested in-field water

quality parameters. Major ions and nutrients were analysed in a commercial laboratory, while standard water quality parameters including dissolved oxygen (DO), specific electrical conductivity, redox potential (ORP) and temperature were measured in the field using a multi parameter water quality YSI probe with flow cell. These parameters were used to assess and interpret the groundwater redox processes using the framework and concentrations thresholds developed by McMahon & Chapelle (2008) (Table 1).

Table 1: Threshold concentrations for identifying redox processes in aquifer systems (McMahon & Chapelle, 2008).

Redox Process	Water Quality Criteria (mg/L)					Comments
	O ₂	NO ₃ ⁻ -N	Mn ²⁺	Fe ²⁺	SO ₄ ²⁻	
Oxic						
O ₂ reduction	≥0.5	—	<0.05	<0.1	—	—
Suboxic						
—	<0.5	<0.5	<0.05	<0.1	—	Further definition of redox processes not possible
Anoxic						
NO ₃ ⁻ reduction	<0.5	≥0.5	<0.05	<0.1	—	—
Mn(IV) reduction	<0.5	<0.5	≥0.05	<0.1	—	—
Fe(III)/SO ₄ ²⁻ reduction	<0.5	<0.5	—	≥0.1	≥0.5	—
Methanogenesis	<0.5	<0.5	—	≥0.1	<0.5	—
Mixed						
—	—	—	—	—	—	Criteria for more than one redox process are met

3.4 Push-pull Tests

A set of three piezometers were installed on three sites within the study area. These areas were selected based on their naturally reduced groundwater and intensive land uses providing a likelihood of NO₃⁻-N being present in the shallow groundwater. Site 1 (Sanson) and 3 (Santoft) are dairy farms, while Site 2 (Bulls) is a cropping farm. At each site a 3 m (bgl) piezometer with a 0.5 m screen; a 6 m (bgl) piezometer with a 0.5 m screen; and a 6 m (bgl) piezometer with a 5.5 m screen were installed (Table 2).

Table 2: Details of shallow groundwater piezometers installed at three sites in the study area.

Piezometer	Depth m bgl	Screened depth m bgl
Sanson-A	3	2.5-3
Sanson-B	6	5.5-6
Sanson-C	6	0.5-6
Bulls-A	3	2.5-3
Bulls-B	6	5.5-6
Bulls-C	6	0.5-6
Santoft-A	3	2.5-3
Santoft-B	6	5.5-6
Santoft-C	6	0.5-6

These piezometers were made from a 30 mm diameter PVC pipe (28 mm inner diameter) and were used to monitor NO₃⁻-N, NH₄⁺-N and DO over March, April and May 2015. They were monitored to observe the background parameters of these sites and gain an understanding of the shallow groundwater chemistry and redox conditions. Further, two piezometers (A and B)

at each site were subjected to a push-pull test to measure rate of denitrification in the shallow groundwater (Istok, 2013). The push-pull test involved two primary steps. The ‘push’ phase of the test involved injecting a prepared solution of $10 \text{ mg L}^{-1} \text{ Br}^-$, $10 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$ and 50 mg L^{-1} acetylene into the piezometer. The solution was made up of groundwater taken from the piezometer the day before, and mixed with these chemicals in the morning of the test. This was followed by the ‘pull’ phase where the mix of solution and groundwater were sampled every 30 minutes for two hours, then every hour for the final four hours. The collected samples were analysed for Br^- , $\text{NO}_3^- \text{-N}$, and N_2O using ion chromatography at Massey University. These measurements were used to calculate the denitrification rate by considering how the $\text{NO}_3^- \text{-N}$ tracer declined over several hours relative to the decline in the Br^- tracer. The decline in Br^- concentrations represents the dilution effects. This assumes that both tracers naturally dilutes at same rate over time due to dispersion and advection influences (dilution) in the subsurface (Istok, 2013). Once these dilution effects are taken into account, the difference between the two tracers could be attributed to $\text{NO}_3^- \text{-N}$ reduction, i.e. denitrification. This was further assessed by measuring the N_2O produced during the push-pull tests.

4. Results and Discussion

4.1 Groundwater flow

Figure 1a reproduces the water table elevation for shallow groundwater (< 30 m), ranging from 1.58 m to 168.7 m above sea level (masl). The highest water table elevations are found in the northern part of the catchment in the Marton area.

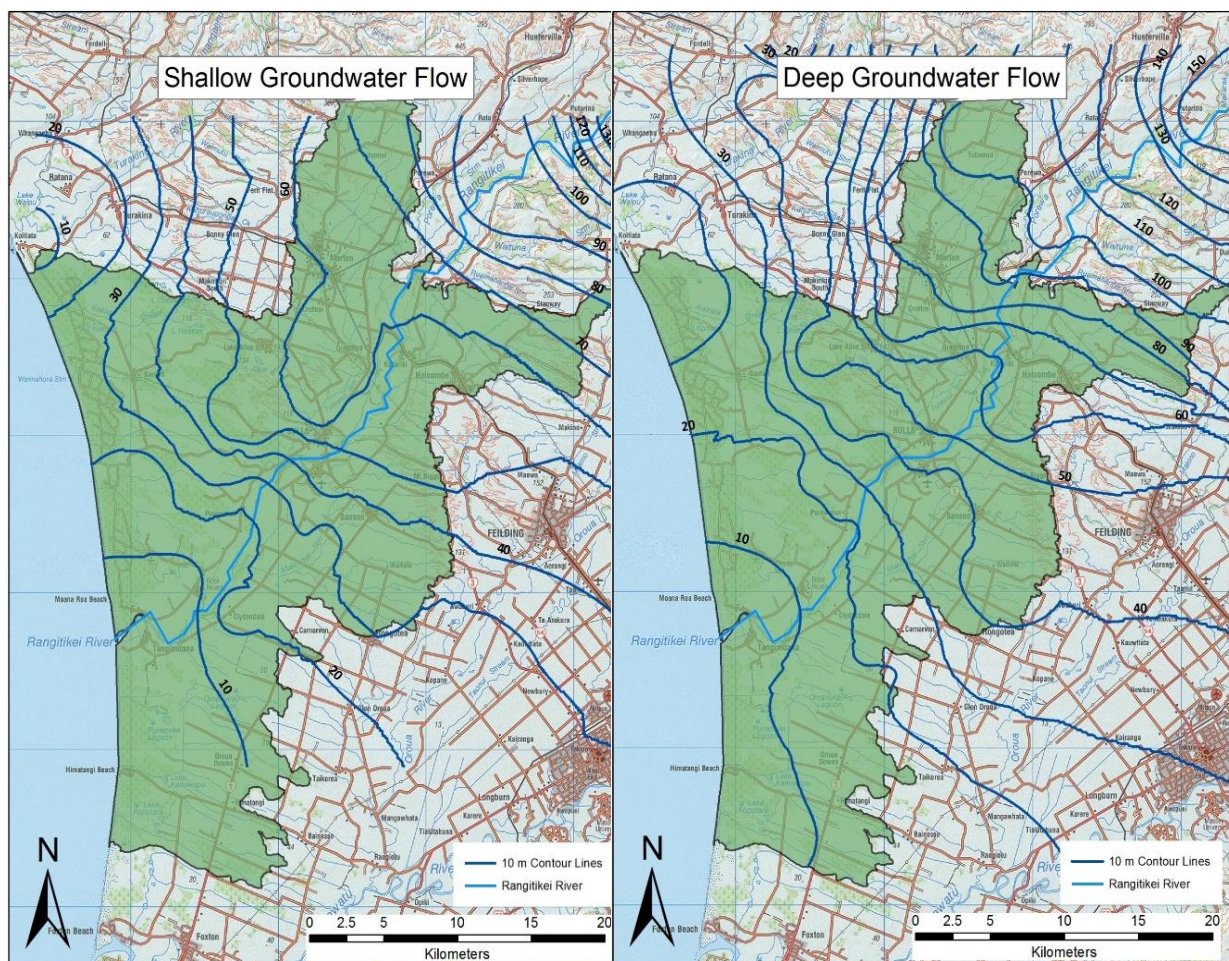


Figure 1a: Shallow groundwater flow from wells screened less than 30 m deep. Contours are masl.

Figure 1b: Deep groundwater flow from wells screened greater than 30 m deep. Contours are masl.

Groundwater flows from this topographical high down in a mostly southerly direction towards the Rangitikei River, suggesting some part of the groundwater flow interacts with the river water, most likely just upstream of Bulls. From Marton to Turakina, groundwater flows in a westerly direction, directly to the sea. From Marton to Bulls, the groundwater flows in a southerly direction, before gradually flowing to the south-west, reflecting the general topography of the area. As the topography flattens out, from Bulls and Sanson, the groundwater flow gradient also flattens out (indicated by the increasing gap between the groundwater contour lines) and groundwater flows towards the sea. Where the groundwater flows beneath the Rangitikei River, the contour lines appear to refract, possibly indicating interaction between the river water and groundwater.

For deep groundwater flow (Figure 1b), the water table elevation ranged from 1.32 m to 167.1 masl. The highest water table elevation was found further inland near Rewa, where groundwater is 160 masl. From here the trend shows a reasonably consistent south-west flow direction, where groundwater appears to discharge to the sea. Topographic influences are much gentler in the deep groundwater flow system, compared with the shallow groundwater flow. Groundwater flow gradients are also more consistent and evenly spaced in the deeper groundwater than the shallow, reflecting less influence from the surface topography.

4.2 Groundwater - surface water interactions

The flow gauging surveys reveal a dynamic relationship between the Rangitikei River and the alluvial aquifer beneath it (Figure 2). The surveys were taken two weeks apart, though they suggest a similar pattern of groundwater recharge and discharge along the river reaches. The reach between the Kakariki Bridge and the Bulls Bridge is gaining from groundwater, particularly just upstream of the Bulls Bridge. Downstream from this the Bulls Bridge is likely an area of groundwater recharge, as the measured river flow decreased on both survey dates. Further downstream the river appears to be gaining again slightly before losing towards the coast.

4.3 Groundwater redox conditions

Applying the framework developed by McMahon & Chapelle (2008), the dissolved concentration of five groundwater quality parameters (dissolved O₂, NO₃⁻-N, Mn²⁺, Fe²⁺, and SO₄²⁻) were used to interpret the redox condition of groundwater. Figure 3 and Table 3 displays the various redox processes that are active in the study area. Ten out of 15 the sites surveyed showed a purely anoxic condition, where the DO concentration is less than 0.5 mg/L. A further two sites were classed as anoxic, but could have more than one redox process occurring. Another three sites were assessed as mixed, having both oxic and anoxic redox categories, with a range of redox processes occurring.

Aerobic respiration

Using the threshold values provided in Table 1, aerobic respiration is expected to take place at three locations: 322071, 333005, and 323077 in the study area. According to the ecological succession of terminal electron acceptors (Rivett et al., 2008), dissolved oxygen is first depleted before other electron acceptors, due to its higher oxidation status. In this study, the wells 322071 and 333005 have high DO levels and also have relatively high NO₃⁻-N levels. As expected at these sites, the NO₃⁻-N has remained in favour of DO being reduced, thereby preserving the NO₃⁻-N in the shallow groundwater. However, at well 323077, DO was available in the groundwater, but there was very little NO₃⁻-N present.

Table 3: Redox assignment of 15 groundwater wells surveyed in December 2014 in the Lower Rangitikei catchment.

Redox Variables	DO	NO₃⁻-N	Mn²⁺	Fe²⁺	SO₄²⁻	Redox Category	Redox Process
Unit	mg/L	mg/L	mg/L	mg/L	mg/L		
Threshold Value	0.5	0.5	0.05	0.1	0.5		
312004	0.02	0.40	0.26	9.80	0.01	Anoxic	CH ₄
312020	0.00	0.02	0.19	0.39	109.01	Anoxic	Fe(III)/SO ₄
312001	0.00	0.01	1.33	9.90	<0.01	Anoxic	CH ₄
324067	0.02	0.02	0.33	20.37	118.55	Anoxic	Fe(III)/SO ₄
332025	0.01	0.04	0.70	8.87	2.41	Anoxic	Fe(III)/SO ₄
332009	0.07	0.01	0.63	0.32	<0.01	Anoxic	CH ₄
322045	0.00	1.17	1.03	0.01	43.10	Mixed (anoxic)	NO ₃ -Mn(IV)
322071	0.59	4.47	0.11	0.51	33.98	Mixed	O ₂ -Fe(III)/SO ₄
323097	0.00	<0.01	0.24	0.02	12.24	Anoxic	Mn(IV)
333005	0.93	1.90	0.02	0.86	127.69	Mixed	O ₂ -Fe(III)/SO ₄
313009	0.00	0.35	0.42	1.38	2.07	Anoxic	Fe(III)/SO ₄
343119	0.43	<0.01	0.25	4.20	10.32	Anoxic	Fe(III)/SO ₄
323091	0.39	1.78	0.46	1.29	58.34	Mixed (anoxic)	NO ₃ -Fe(III)/SO ₄
323077	0.76	<0.01	1.10	0.31	15.18	Mixed	O ₂ -Fe(III)/SO ₄
314065	0.44	<0.01	0.38	0.87	124.07	Anoxic	Fe(III)/SO ₄

Denitrification

Once DO has been depleted, NO₃⁻-N becomes the terminal electron acceptor (Rivett et al., 2008). This is expected to occur at well sites 322045 and 323091. These two sites have the only other relatively high NO₃⁻-N levels, compared with the other sites sampled in the study area. Nitrate at these two sites potentially may be being denitrified as the measured DO levels were lower than the suggested threshold of 0.5 mg/L (Table 3). These two sites, as well as 322071 and 333005, were the only sites with NO₃⁻-N levels above 1 ppm, with all other sites having less than half this level.

Manganese and Iron/Sulphate reduction

Once NO₃⁻-N has been exhausted, Mn⁴⁺ will become the primary electron acceptor the product of which is Mn²⁺. This is expected to occur at 323097 and 322045. Mn is commonly in the form of MnO₂. Iron/Sulphate reduction occurs at six locations: 312020; 324067; 332025; 313009; 343119; 314065. Fe³⁺ and SO₄²⁻ reduction do not actually occur simultaneously. Rather it is one limitation of the framework that it cannot distinguish between the two reduction processes.

Methanogenesis

Methanogenesis occur at three locations in the study area: 312004, 312001, and 332009. Methanogenesis is the reduction of CO₂ by methanogens, typically occurring when all other

electron acceptors have been consumed. It is the least efficient metabolic process for converting oxygen into energy and implies all other acceptors have been rejected.



Figure 2: Stream gauging locations and discharge (m^3/s) along the Rangitikei River. Results in black text refer to 6 January 2015; while results in red text refer to 20 January 2015.

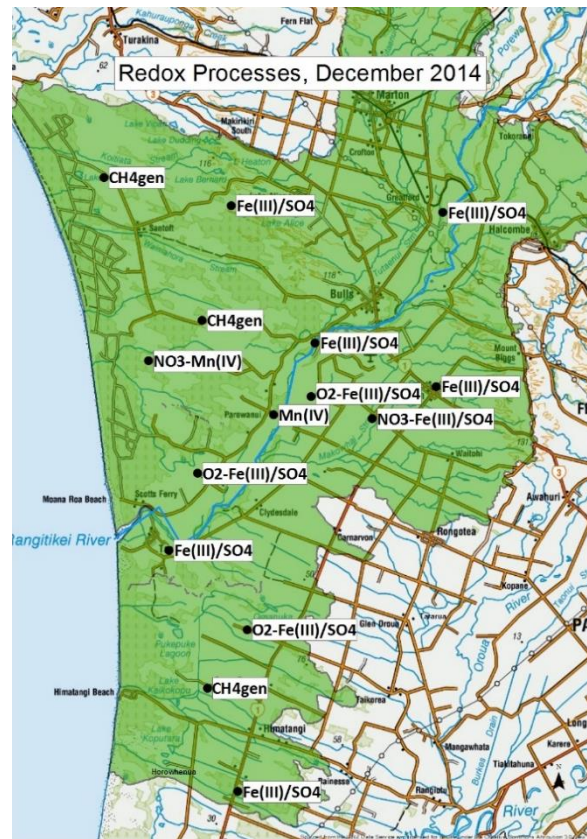


Figure 3: Redox processes occurring in the study area as at December 2014. Methanogenesis represented by CH_4gen .

4.4 Push-Pull Tests

Shallow groundwater chemistry and redox conditions

NO_3^- -N had mostly low concentrations at all the sites monitored, with the exception of Bulls-C and Santoft-C. These piezometers showed elevated NO_3^- -N concentrations in April, well above other readings, but also had elevated DO concentrations at the same time. In both these cases the groundwater level had risen since the previous sampling. NH_4^+ -N was generally around 1 mg/L or less at all the sites, though it was lowest at the Bulls and Santoft sites. DO was also generally low at <0.5 mg/L at all sites, with the exception of Bulls-C and Santoft-C, where DO reached around 2 mg/L, with associated elevated NO_3^- -N. The redox potential was generally between 0 and -150 mV over the monitoring period except in April where Bulls-C gave a result of 70.

Shallow Groundwater Denitrification

Figure 4 shows the dilution of both NO_3^- -N and Br^- over the course of the test, with NO_3^- -N usually showing a greater decline as the time progressed. The NO_3^- -N/ Br^- ratio is a more visual guide to the decline in NO_3^- -N relative to Br^- , with a decreasing trend showing a widening gap between the two tracers. The dilution-corrected NO_3^- -N concentration shows the reduction of NO_3^- -N after dilution effects have been taken into account. It is the slope of this line that gives the zero-order reaction rate for NO_3^- -N reduction. The red value in bold is the estimated rate of denitrification per hour.

Figure 5 shows how N₂O concentrations changed over time as the test progressed. The N₂O concentrations provide a supplementary indication of denitrification as NO₃⁻-N is denitrified.

The occurrence of denitrification was inconclusive at only one piezometer (Sanson-A), while all other test piezometers showed some level of denitrification. According to these results, the rate ranged from 0.04 mg N L⁻¹ hr⁻¹ to 1.57 mg N L⁻¹ hr⁻¹. Depth did not seem to be an indicator of the rate of denitrification, with the fastest and slowest rates (Bulls-A and Santoft-A respectively) occurring at the 3 m depth. Though at the Bulls site NO₃⁻-N was consistently observed at a higher concentration at 3 m, compared with 6 m, suggesting NO₃⁻-N is being reduced as it percolates down through the subsurface environment. The accumulation of N₂O has also provided a further indication of denitrification occurring and seems to accumulate in proportion to the rate of denitrification.

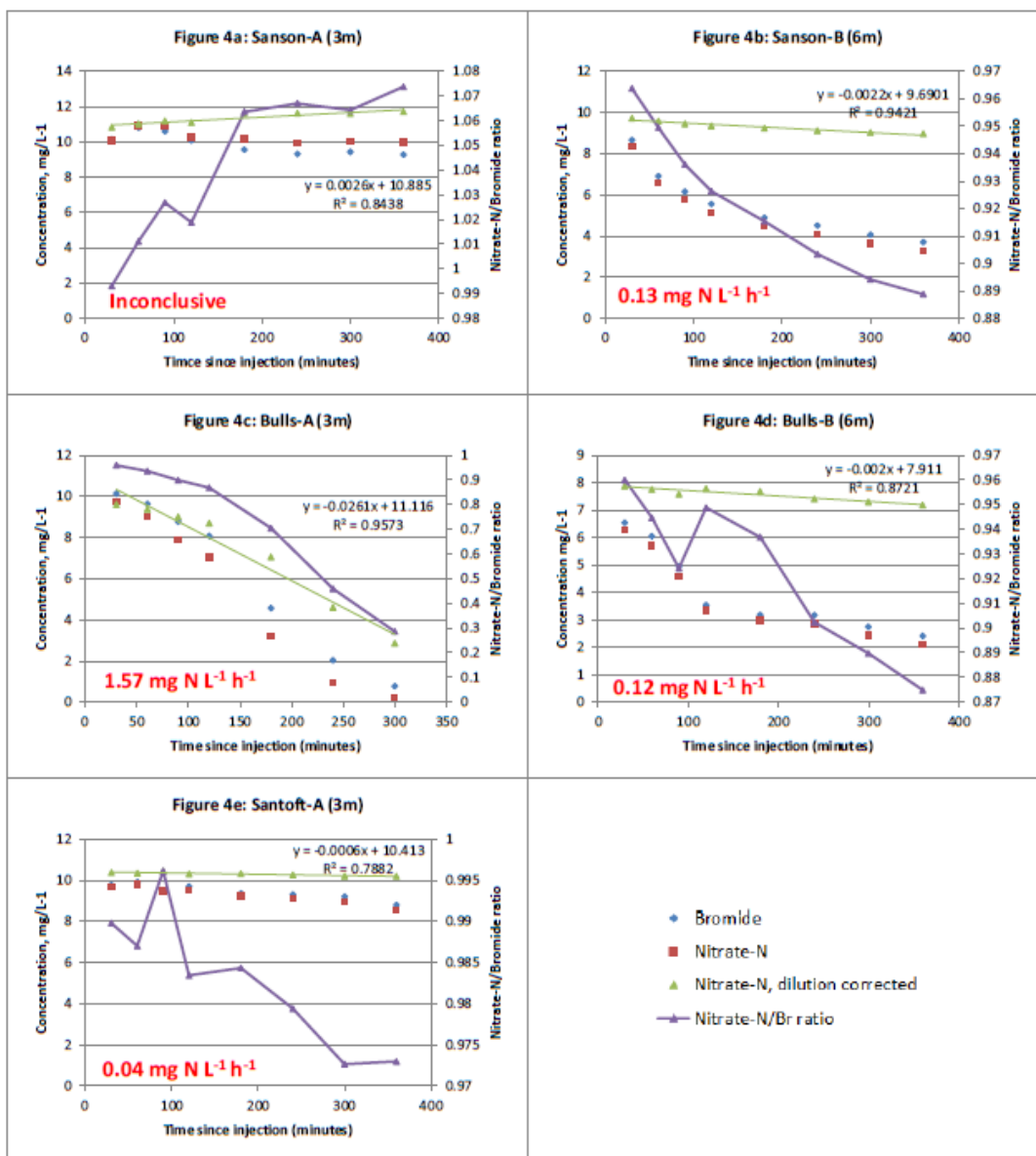


Figure 4: Results of push-pull tests showing Bromide and Nitrate-N concentrations, the dilution corrected Nitrate-N concentration and the Nitrate-N/Bromide ratio. The denitrification rate is shown in red.

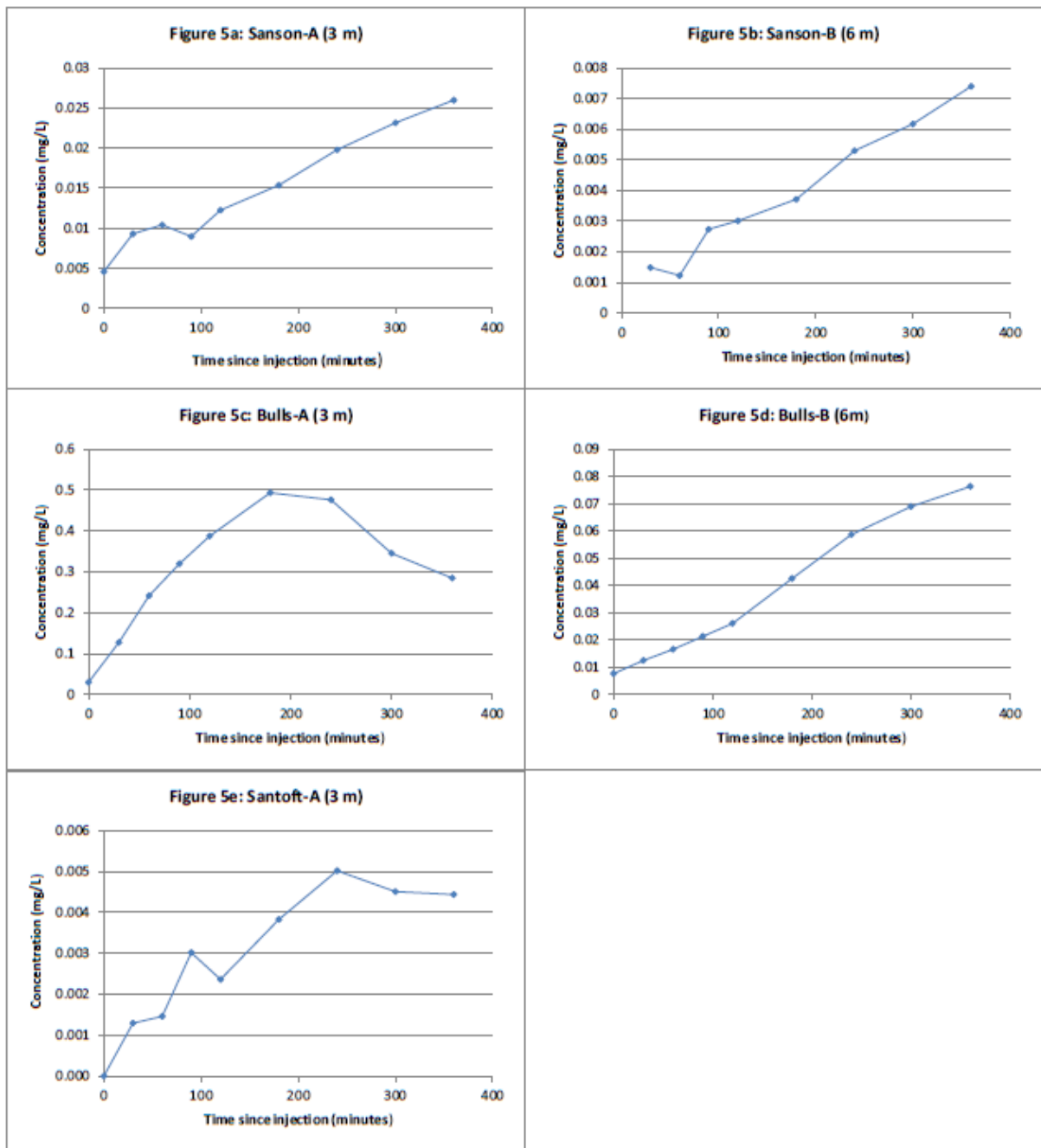


Figure 5: Concentration of N_2O-N during the push-pull test.

Conclusions and Recommendations

A sound understanding of the sources, transport, transformation and fate of nutrients leached from farms is a key component of managing and mitigating the likely impacts of these nutrients on water quality and ecosystem health in agricultural catchments.

Both the shallow and deep groundwater systems had similar flow patterns, though there is greater topographic influence occurring on the shallow groundwater. The piezometric maps demonstrate groundwater is generally flowing in the same direction as the Rangitikei River, essentially providing shallow groundwater opportunity for NO_3^- -N from upstream areas to enter the river and its tributaries. Gauging results suggest a dynamic relationship between the river and the underlying aquifer. Upstream of Bulls, groundwater likely discharges into the river, particularly just upstream of the bridge. Downstream of here, the river mostly provides for an area of groundwater recharge.

Using a range of common water quality measurements (DO, NO_3^- -N, Mn^{2+} , Fe^{2+} and SO_4^{2-}), the redox condition of groundwater was determined, revealing a mostly reduced groundwater environment. Not only is DO generally low in the area, providing no initial barrier or delay to NO_3^- -N reduction, but a range of suitable electron donors are available in the form of DOC and, potentially, Mn^{4+} and Fe^{3+} .

Having assessed the redox status of groundwater, actual shallow groundwater denitrification was tested using the single-well push-pull tests. Piezometers were installed at three locations (two dairy and one cropping farm) to observe how NO_3^- -N behaves in shallow groundwater relative to a conservative tracer, Br^- . The push-pull tests were conducted at each site, at two different depths, with a total of five tests performed. While one of the tests showed inconclusive results (Sanson-A), the other tests showed denitrification occurring, although at different rates. Under the test conditions, NO_3^- -N was reduced at a rate between $0.04 \text{ mg N L}^{-1} \text{ hr}^{-1}$ to $1.57 \text{ mg N L}^{-1} \text{ hr}^{-1}$. The intermediate product N_2O was also measured during the push-pull test. N_2O was found to increase at all sites, consistent with what is expected during denitrification, though interestingly N_2O also increased where results seemed inconclusive at Sanson-A.

Our results suggest that groundwater is likely connected with some reaches of the lower Rangitikei River. However, NO_3^- -N concentrations in the river and groundwater were generally low, especially at low flows. This suggests NO_3^- -N may be undergoing reduction within shallow groundwater before it has a chance to seep into the river. This is evident in the redox characterisation of reduced groundwater and observed NO_3^- -N reduction during the push-pull tests conducted. However, more spatial and temporal surveys and *in-situ* measurements of denitrification occurrence in the shallow groundwater of the study area are required.

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