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Assessment of biogeochemical transformation of nitrate in shallow
groundwater in the agricultural landscape.

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Abstract

In groundwaters, denitrification or subsurface denitrification (SD) has been identified as a key attenuation process. Where leached nitrate (NO_3^-) can be reduced to dinitrogen (N_2 — a harmless gas), offering an ecosystem service in terms of reducing water pollution. However, partial denitrification (PD) can release nitrous oxide (N_2O — a greenhouse gas), resulting in a pollution swap from liquid to gaseous pollution and adding to greenhouse gas emission. There is very limited information available about occurrence, characteristics and dynamics of subsurface denitrification in shallow groundwaters across New Zealand agricultural catchments.

We studied 6 pastoral farms (DF 1, 2, 3; SC 1, 2, 3; ARM 1, 2, 3; CAM 1, 3; SR 1, 2, 3; BUR 1, 2 and 3) located in various hydrogeological settings in the Manawatu and Rangitikei Rivers catchments, in the lower North Island of New Zealand. We collected 7 sets of monthly groundwater observations at 17 piezometers from March to September 2018 to characterize the groundwater monthly chemical variations. The collected groundwater samples were analyzed for groundwater redox status, including dissolved oxygen (DO), oxidation-reduction potential, pH, NO_3^- -N, iron (Fe^{2+}), manganese (Mn^{2+}) and sulphate (SO_4^{2-}). We also conducted a set of push-and-pull tests to gain insights into dynamics of subsurface denitrification occurring in the groundwater samples at the study sites. We quantified changes in concentration of NO_3^- -N, Br^- (tracer), dissolved N_2O -N and excess N_2 during the push-and-pull tests.

Our results suggested a spatially variable groundwater redox conditions and SD occurring across the study sites. The piezometers DF 2, 3; SC 1, 2; CAM 3; ARM 1, 2 and 3 showed anoxic redox status. Only the piezometers SC 3 and CAM 1 presented mixed redox condition. While the piezometers DF 1; SR 1, 2, 3; BUR 1, 2 and 3 indicated oxic conditions with some variability over the study.

Nitrate is being reduced in the anoxic piezometers DF 2, 3; SC 1, 3; ARM 1, 2, 3 and CAM 3, showing no NO_3^- -N accumulation ($< 0.5 \text{ mg L}^{-1}$). One of the piezometers with mixed redox condition (CAM 1) showed NO_3^- -N accumulation ($> 6 \text{ mg L}^{-1}$) while the piezometer SC 3 showed variability in NO_3^- -N accumulation ranging from 0.02 mg L^{-1} to 22.56 mg L^{-1} .

¹. The oxic piezometers SR 1, 2, 3; BUR 1, 2 and 3 showed NO₃⁻-N accumulation (> 3 mg L⁻¹) except for piezometer DF 1 that showed variability in NO₃⁻-N concentrations ranging from 0.01 mg L⁻¹ to 3.75 mg L⁻¹ over the study.

The concentrations of the electron donors Fe²⁺ and Mn²⁺ were found to be suitable for SD on anoxic piezometers DF 2, 3; SC 1, 2; CAM 3 and ARM 1, 2, 3 (> 1 mg L⁻¹ and > 0.05 mg L⁻¹ respectively). The piezometers with mixed redox status SC 3 and CAM 1 ranged just over the redox threshold for identifying redox processes (0.1 – 1.0 mg L⁻¹ and > 0.05 mg L⁻¹ respectively). In general, the piezometer with oxic redox status (DF 1, SR 1, 2, 3 and BUR 1, 2, 3) showed [Fe²⁺] and [Mn²⁺] below the threshold for identifying redox processes (< 0.1 mg L⁻¹ and < 0.05 mg L⁻¹ respectively) and not suitable to support SD.

The dominant terminal product of SD, whether was complete denitrification (N₂ — as end product) or partial SD (N₂O — as end product) spatially varied according to the redox status of the groundwater. Push-pull test results showed an increase in excess N₂ and N₂O-N concentrations at DF 3, ARM 3, CAM 3, BUR 3. The push-pull test conducted at SR 3 and SC 3 showed inconclusive results. Piezometers CAM 3 and ARM 3 showed the highest suitable conditions for SD followed by DF 3. Piezometer BUR 3 showed the highest partial SD rate. Therefore BUR 3 is considered in general, the less suitable piezometer for SD.

Our observations highlight the influence of different hydrogeological settings on spatial variability of partial (pollution swamp) or complete (ecosystem service) SD in shallow groundwaters. A better understanding and quantification of spatial and temporal variability of SD process will support information, design and formulation of targeted and effective management measures for sustainable agricultural production while protecting soil, water and air quality.

Key words: Groundwater, Groundwater quality, Nitrate, Partial and complete subsurface denitrification, Greenhouse gas, Excess N₂

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Chapter 1.

1.1 Introduction

Nitrate (NO_3^-) potential leaching to groundwater and runoff to surface water in agricultural landscapes are of increasing concerns for the degradation of receiving waters across agricultural landscapes (IPCC, 2001). The concerns are even more when the socio-economic context of agricultural land use requires to increase the inputs of nutrients (i.e. nitrogen) to maintain or increase agricultural production and quality. Scientists and politicians from all areas of study are currently facing a global challenge, as in the past 30 years the world's population has grown by 50% from 5.02 billion in 1987 to 7.53 billion people by 2017 (World Bank Group 2018). One of the biggest challenges facing today's society is to keep production rates, such as food and energy, while protecting freshwater ecosystems and their benefits for nature and human health.

Anthropogenic application of fertilizers in agricultural production systems has caused non-point sources for potential leaching and runoff of NO_3^- to receiving surface water and groundwater bodies in agricultural landscapes (Singh et al., 2014). Nitrate contamination and pollution in groundwater have become a significant environmental problem worldwide (Rivett et al, 2008) and in New Zealand (Bekesi and McConchie, 1999). Worldwide, livestock and fertilizer application are the major sources of NO_3^- in groundwater (Hu et al, 2000; Galloway et al., 2003). The same sources for leached NO_3^- has been observed in New Zealand (Singh et al., 2014; Clague et al., 2018; Bekesi and McConchie 1999).

Nitrate may be the most ubiquitous contaminant of groundwater worldwide (Tesoriero et al, 2000), posing a risk to the quality of public drinking water supplies and receiving freshwaters ecosystem health. Increased NO_3^- concentrations in freshwaters may cause eutrophication, algal bloom and fish poisoning (Puckett et al, 1999). At elevated levels, NO_3^- is considered toxic to aquatic species (e.g. fish) and also poses human health risks affecting the quality of drinking water sources (Horizons, 2013). Hence, a sound understanding of nitrogen (N) dynamics and transfer pathways are necessary to avoid and/or remediate the undesirable consequences of NO_3^- runoff/leaching to receiving freshwaters bodies.

To study the environmental implication of NO_3^- dynamics in the subsurface environment under the agricultural context it is necessary to understand the N cycle. Dinitrogen (N_2) has high stability and low reactivity, the main reservoir of N_2 is the atmosphere. N_2 transfer occurs within and from the atmosphere to the biosphere, geosphere and hydrosphere (Gruber et al., 2008). Atmospheric N fixation is the process where N is transferred from the atmosphere into the biosphere by micro-organisms. In the plant-soil-water system N is transformed into different species, including mineralization of organic N to inorganic N, nitrification of ammonium (NH_4^+) to NO_3^- , immobilization, assimilation and denitrification of NO_3^- in soil-plant-water system (Gruber et al., 2008; Rivas et al., 2018; Collins, 2015; Stein and Klotz, 2016; Kraft et al; 2011; Kuypers et al., 2018). Transformation processes of N in the plant-soil-water system is dependent on biotic and abiotic conditions such as temperature, humidity, the presence of specific micro-community, dissolved oxygen and pH. Although major transformation processes occur in the surface soil, there are evidence of significant denitrification activities in the subsurface environment as well (Luo et al., 1998). Much research has been done based on N dynamics in soil-water-plant systems, above ground and in the topsoil. Nevertheless, little is known about the fate of NO_3^- -N once reaches groundwater (Galloway et al., 2003).

The study of the production of nitrous oxide (N_2O) in the soil profile has increased considerably in recent decades as a consequence of increased N_2O concentrations in the atmosphere. Since the beginning of the industrial era, N_2O emissions have increased to around 15% (Baethgen and Martino, 2001). Currently, the focus of the studies is on the identification of sources, quantification of emissions from agricultural soil (root zone) and possible mitigation strategies (IPCC, 2001).

Agriculture is responsible for between 20 and 30% of the global production of N_2O (Di and Cameron, 2002). In the context of New Zealand's land use, the main source of N pollution in groundwaters is the use of fertilizers and animal excreta (Saggar et al., 2004b; Bekesi and McConchie, 1999). The use of fertilizers and the amount of N from animal excreta exceeds the soil attenuation capacity. The excess of NO_3^- that was not assimilated or emitted in gaseous form (NH_4^+ , nitric oxide (NO), N_2O , N_2), therefore, infiltrates to the unsaturated zone and saturated zone (Clough et al., 1996). The production of N_2O is a by-product of the nitrification and denitrification processes (Smith et al, 1988, de Klein and Eckard., 2008). In spite of this, N_2O production rates underneath the root zone are still

unknown. The research gaps related to NO_3^- attenuation processes vary from the uncertainty of the global contribution of N_2O from agricultural lands and the proportion of N_2O produced in the groundwater as sub-product of denitrification. Places and areas where NO_3^- can be attenuated (e.g. natural resilience of the system) had been poorly identified, and the limiting factors controlling the N transformation processes in the subsurface environment had been underestimated.

1.2 Objectives

The main aim of this study is to assess NO_3^- transport and transformation through the saturated zone (shallow groundwater) under agricultural conditions. Massey University's Fertilizer and Lime Research Centre (FLRC) and Horizons Regional Council has established a collaborative research program to better understand and characterise N flow pathways and its potential attenuation in groundwater across Manawatu and Rangitikei River catchments, located in the lower North Island. Nitrate contamination of surface and groundwaters is of concern in these predominantly agricultural land-use catchments (Horizons, 2013; Rivas, 2018).

The scientific research objectives of this study were:

- To assess the biogeochemical transformation of NO_3^- in shallow groundwater under different hydrogeological settings.
- To carry out laboratory and fields measurements to determine denitrification process and its reaction products (N_2O and N_2) in shallow groundwater; and
- To assess physical and biophysical factors affecting denitrification in shallow groundwater.

The research will add to a better understanding of NO_3^- transport and transformation processes in local shallow groundwaters. The outcomes of this research will contribute to knowledge to improve decision making for land use and water quality management in New Zealand's agricultural landscapes at a regional scale.

1.3 Thesis Outline

This thesis is composed of five chapters. **Chapter 1** gives a general introduction to the research context and outlines the scientific research objectives. **Chapter 2** presents a critical review of existing literature/studies on nitrogen dynamics, transport and transformation processes in soil-water systems. The biotic and abiotic factors influencing subsurface denitrification and the laboratory and in-field techniques to characterise the denitrification process with its end products (N_2O and/or N_2) are also reviewed in this chapter. **Chapter 3** describes in detail the geological settings and environmental conditions of the study area. This chapter also describes the procedure for push-pull test, the groundwater chemical analysis and explains the analytical procedures for laboratory analysis. The methodology and analytical procedures for in situ experiments (push-pull test) are also described. **Chapter 4** presents results of variation of groundwater redox status, chemical analysis and dissolved gas analysis from February to September 2018 and results of the push-pull test at each study site. The suitability of the geochemical environments for NO_3^- subsurface attenuation, through complete denitrification (N_2 as end product) and partial denitrification (N_2O as end product), is also described. **Chapter 5** summarizes the results obtained through in-situ and laboratory analysis, and a comparison between the sites under study.

Chapter 2. Literature review

The aim of this study is to assess NO_3^- attenuation through subsurface denitrification and redox status in the Manawatu and Rangitikei River catchments. Chapter 2 reviews and summarises the N cycle and its interactions; with main focus on the interaction of NO_3^- in the soil-water system; the denitrification process as the main pathway for NO_3^- attenuation in groundwater is also reviewed.

2.1 Anthropogenic N sources and environmental implications

The World Health Organisation (WHO) has set a NO_3^- -N limit of 11.3 mg L^{-1} in drinking water supply, which also applies to groundwater irrespective of its intended use (WHO, 2004). Countries such as the United States and Canada had established a maximum contaminant level for NO_3^- -N of 11.3 mg L^{-1} in drinking water (EPA, 2017). However, it has been determined that a lower concentration of NO_3^- -N (around $4.4 - 8.8 \text{ mg L}^{-1}$) may trigger eutrophication in oligotrophic surface water (Rivett et al, 2008). Higher concentrations of NO_3^- in water and long-term exposure have potential health effects that include blue baby syndrome (Haygarth and Jarvis, 2002). The toxicity of NO_3^- is caused by its rapid reduction to nitrite (NO_2^-) under the acidic conditions found in the stomach. As a result, haemoglobin in the presence of NO_2^- is converted into methaemoglobin, thereby inhibition of oxygen supply in the blood occurs resulting in anoxia and, in extreme cases, death (Haygarth and Jarvis, 2002). It is also known that NO_3^- in the human system forms nitrosamines; many studies had confirmed that some type of nitrosamines increase the risk of gastric cancer (Haygarth and Jarvis, 2002).

It is, therefore, important to gain a sound understanding of transport, transformation and fate of NO_3^- for managing risks associated with freshwater pollution to also protect groundwater. Hence protection of aquifers and groundwater quality enhance and protect the ecosystem health. Nitrate pollution in groundwater has been recognized around the world, including New Zealand. By 2014, the New Zealand government released the “National Policy Statement for Freshwater Management” (Freshwater NPS) under the Resource Management Act 1991 (Government of New Zealand, 2014). Freshwater NPS intends to minimise the negative impacts of agricultural practices for the protection of the

environment. By 2017, the government had already improved the policy and began requesting Regional Councils to increase their monitoring requirements for independent Freshwater Management Units (FMUs). Currently, Regional Councils must quantify nutrient levels (i.e. N and phosphorus) in freshwater ('freshwater resource accounts'), while also specifying goals for nutrient levels in the future; all information must publicly assessible. A better understanding of NO_3^- in the subsurface environment would allow spatially differentiated land management and legislation (Stenger et al., 2018).

2.2 Groundwater vulnerability

Groundwater aquifers are described as the area and volume of a geological formation that defines the saturated zone in the subsurface environment. Aquifers have the capacity to store water from short to long term (residence time) and the capacity to allow recharge and movement of groundwater through. The flow of water through saturated zones affect it biogeochemical properties, which depend on the water residence time, recharge rate and hydrogeochemical characteristics of parental rock material.

Groundwater vulnerability refers to the risk of a decline in groundwater quality. Groundwater quality deterioration depends on significant anthropogenic pressures (potentially contaminants) for aquifers and physical properties of the aquifer; as hydraulic properties (e.g. high hydraulic conductivity → higher vulnerability). Vrba and Zaporozec (1994) define groundwater vulnerability as "an intrinsic property of a groundwater system that depends on the sensitivity of that system to human and/or natural impacts." They classified the vulnerability of aquifers as an intrinsic and specific vulnerability.

- Intrinsic vulnerability represents the sensitivity or natural vulnerability of an aquifer. It is defined solely in terms of geologic, hydrologic and hydrogeological factors, which are the intrinsic properties of aquifers.
- Specific vulnerability is defined by the potential impact of specific uses and contaminants. This incorporates the risk of contamination placed on aquifers by human activities, e.g. agricultural management practices (i.e. irrigation system).

Physical and biochemical features of the subsurface environment can either enhance or limit the transport of pollutants in to aquifers (Abiy et al., 2015). While geologic,

hydrologic and hydrogeological factors control the movement of pollutants once in the aquifers. Aquifer vulnerability is the representation of all the factors combined.

Bekesi and McConchie (1999) acknowledge that agricultural management can be a significant pressure on aquifers with high vulnerability. They identified agricultural management as a key factor to prevent a decline in groundwater quality as a consequence of agricultural practices in the Manawatu Region, New Zealand. There is a need to provide the New Zealand authorities with a useful tool to support decision making in terms of optimizing land uses considering the vulnerability of groundwaters. The New Zealand government has taken the first steps into the matter by establishing groundwater contamination in agricultural landscapes as the main focus of groundwater research (Bekesi and McConchie, 2002). Aquifers of high vulnerability and under high agricultural pressures are the main targets considering that remediation of a polluted aquifer is an expensive and slow process (Rinaudo et al., 2005).

However, little is known about N transformation in the subsurface environment (Groffman et al., 2006, Kamewada, 2007) due to the variability of biogeochemical processes in space and time (Rivett et al., 2008).

2.3 Nitrogen and its transformations in the environment

Main reservoir of N_2 is the atmosphere being composed predominantly of argon (Ar), oxygen (O_2) and N_2 (approximately 0.9, 20.9 and 78.1 %, respectively). It circulates across different spheres of earth surface. The N cycle represents the flows between atmosphere, biosphere, geosphere and hydrosphere (Kuypers et al., 2018).

Nitrogen in air, soil and water goes through different transformation processes resulting in different forms of N and oxidation states (Table 1). Amongst all the transformations; the biogeochemical processes of nitrification and denitrification that occur in the soil-water system are the main responsible for changes in the oxidation states (Figure 1). The most stable forms of N are found in oxidation states 0 and +5 as N_2 and NO_3^- , respectively (Galloway et al., 2003). The energy needed to break the N_2 triple bond is $941 \text{ kJ}\cdot\text{mol}^{-1}$. While the decomposition of organic N is energetically favourable and requires a third of the energy compared to N_2 . The high stability of N_2 is given by the triple bond ($N\equiv N$), and

requires special conditions to break it. Only some prokaryotic organisms (cyanobacteria) are able to assimilate N_2 and use it as a source of energy through a fixation process (Kuypers et al., 2018). There are no known eukaryotic organisms capable of assimilating N_2 .

Table 1: Oxidation states for main forms of N.

Compound	Form	Oxidation state
Organic N	R-NH ₂	-3
Ammonium	NH ₄ ⁺	-3
Hydrazine	N ₂ H ₄	-2
Hydroxylamine	NH ₂ OH	-1
Dinitrogen	N ₂	0
Nitrous oxide	N ₂ O	+1
Nitric oxide	NO	+2
Nitrite	NO ₂ ⁻	+3
Nitrogen dioxide	NO ₂	+4
Nitrate	NO ₃ ⁻	+5

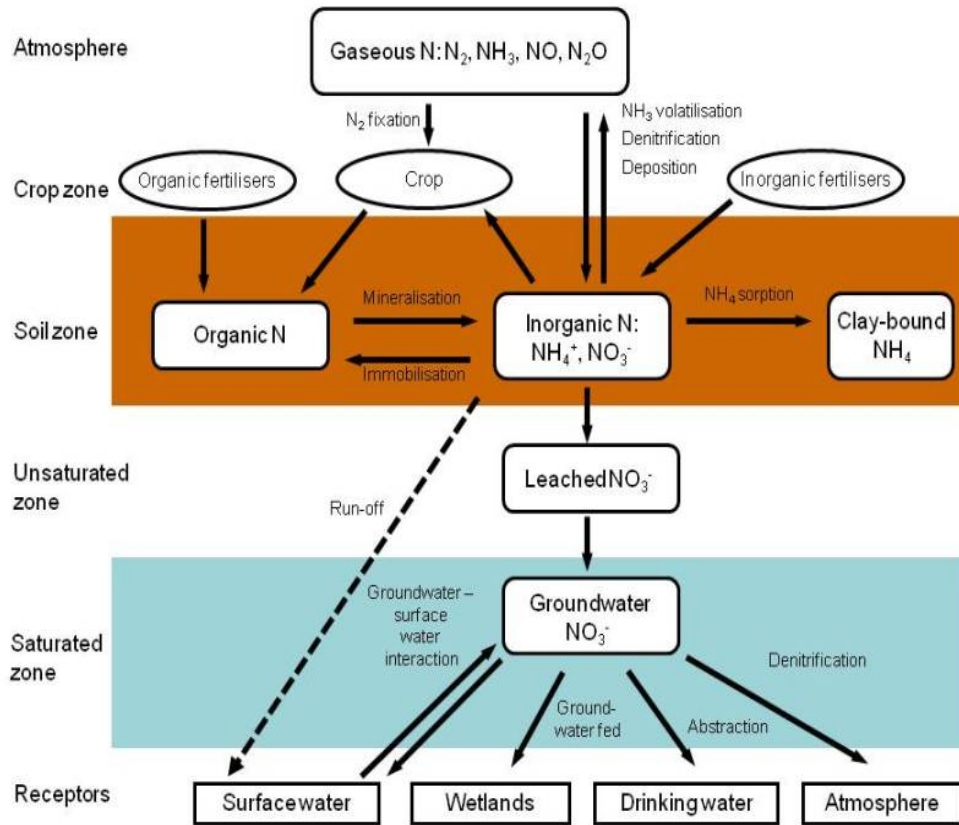


Figure 1: Scheme of transport and transformations of N in the soil-water system (Reproduced from Stuart et al, 2011).

In the soil-water system, N is found in either an organic or inorganic form. The organic fraction is more significant with 95% found as organic matter, proteins and nucleic acids, while only 2% is presented as inorganic form as NH_4^+ , NO_2^- and NO_3^- (Haygarth and Jarvis, 2002). Plants assimilate nitrogen only in forms of NO_3^- and NH_4^+ ; after the mineralization of organic N (Haygarth and Jarvis, 2002). Transformations of N depend on biotic components such as microbiological communities (Stein and Klotz, 2016), parent rock, land use (Boring et al., 1988), anthropogenic intervention (i.e. agricultural practices) and abiotic factors such as temperature, precipitation, soil characteristics and topography (Lu et al., 2011).

Microbiological communities play diverse roles contributing to the cycling of NO_3^- in soil-water systems mainly through the incorporation of N into the soil (Boring et al., 1988). The decomposition rate is limited in soils with high clay content as complex organic matter formation increases. Even though N concentration decreases considerably down through

the soil profile, Liao *et al.*, (2012) suggests that between 5 and 50% of the N applied to soils can leach into the saturated zone. Figure 2 represents the biochemical cycle of N expected to occur in the soil-water system. Figure 2 includes N fixation, mineralization and nitrification processes and NO_3^- attenuation processes (denitrification, chemo-denitrification, dissimilatory nitrate reduction to ammonium (DNRA) and anammox) in the soil-water system. The oxidation and reduction processes are shown as each N form with the respectable oxidation state (Figure 2) (Kuypers *et al.*, 2018). The N cycle in the biosphere will be briefly described below.

NITROGEN BIOCHEMICAL CYCLE

Marcela Gonzalez | October 11, 2019

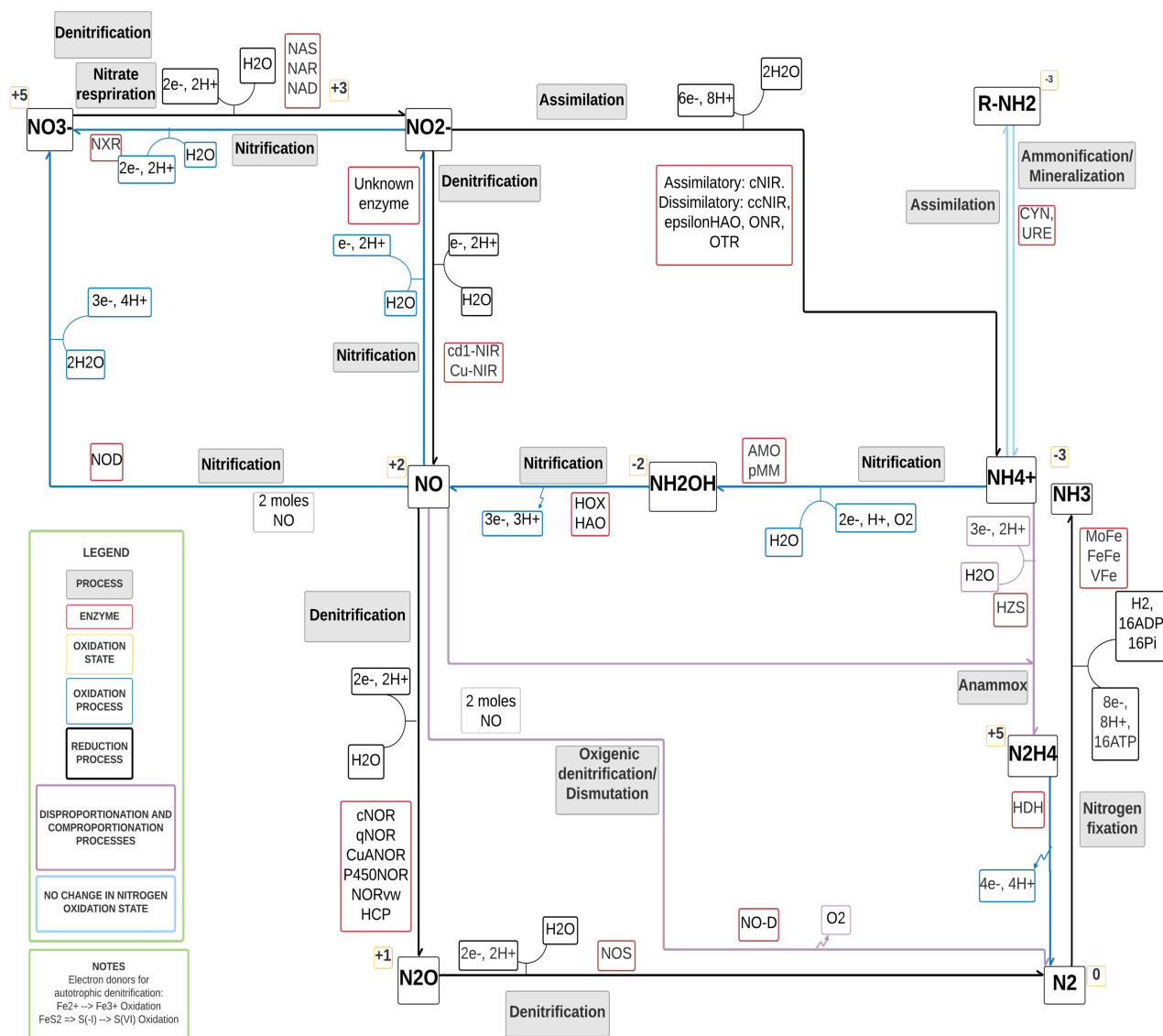
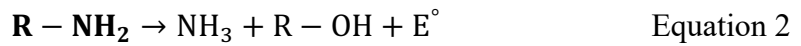


Figure 2: Nitrogen biogeochemical cycle (adapted from Kuypers *et al.*, 2018 and Zumft and Kroneck, 2003).

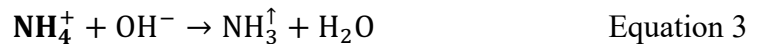
Atmospheric N fixation occurs through atmospheric depositions and biological fixation (Boring et al, 1988). N oxidation occurs mainly through **biological fixation** where N_2 is oxidized to ammonia (NH_3) in soils by nitrogen-fixing organisms that carry nitrogenase metalloenzyme. Bacteria and archaea that perform the N fixation process are found in soils and marine environments (Kuypers et al., 2018). Iron-iron (FeFe), vanadium-iron (VFe) and molybdenum-iron (MoFe) nitrogenases have different metal co-factor and are encoded by *anfDGGK*, *vnfDGGK* and *nifDK* respectively (Kuypers et al., 2018). The rate of biological fixation is greater than the non-biological fixation and depends on pH, organic matter content (OM), O_2 , soil moisture and soil bacteria (Gruber et al., 2008).

In **ammonification** the organic N is degraded into NH_3 ($pH > 7$) or NH_4^+ ($pH \leq 7$). Bacteria and archaea carrying the enzymes cyanase and urease (CYN and URE respectively) (Kuypers et al., 2018) decompose organic nitrogen (OM-N) into amine ($R-NH_2$) through deamination (Equation 1) and decarbonization (Equation 2) (Stein and Klotz, 2016) to finally obtain NH_3 / NH_4^+ .



NH_3 / NH_4^+ is used by microorganisms and plants as a source of energy, adsorbed by complexes of hummus and clays; and lost by volatilization.

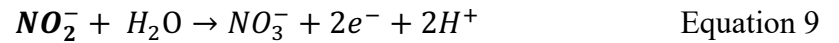
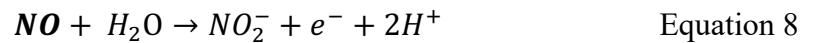
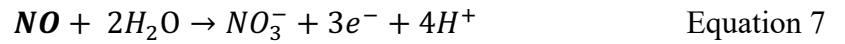
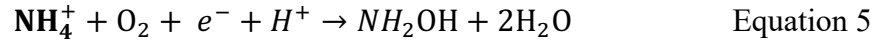
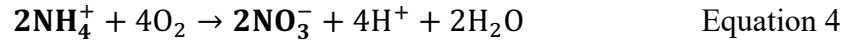
In soils, if the conditions for nitrification are not met; then the NH_4^+ faces two different fates. First, is volatilization (Equation 3) under favourable conditions that occur under moderate temperatures ($> 12^\circ C$), alkaline pH and low humidity.



The second option for NH_4^+ is clay fixation, due to the negative charge especially type 2 : 1 such as illite, vermiculite and montmorillonite. These types of clays have a high capacity of cation exchange that allows strong retention of NH_4^+ , penetrating the octahedron structure of the clays replacing cations such as potassium (K^+), calcium (Ca^{2+}), aluminium

(Al³⁺) and magnesium (Mg²⁺) (Scherer et al., 2014). However, the process is reversible and NH₄⁺ can be released over time.

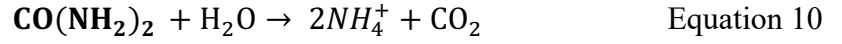
To continue with the N cycle; then NH₄⁺ could be oxidised through **nitrification** into NO₃⁻ (Equation 4) (Kraft et al., 2011 Stein and Klotz, 2016, Kuypers et al., 2018). During nitrification; NH₄⁺ oxidizers that carry the enzyme ammonia monooxygenase (AMO, pMMO) oxidise NH₄⁺ into hydroxylamine (NH₂OH) (Equation 5). The oxidation continues to NO by organisms that carry hydroxylamine oxidoreductase and hydroxylamine oxidase (HAO and HOX respectively) (Equation 6). The final step is the reduction to NO₃⁻ by organisms with the enzyme NO reductase (NOD) (Equation 7) (Kuypers et al., 2018). Or all the way to NO₃⁻ (Commamox) with NO₂⁻ as an intermediate in the process by microorganisms that carry the enzyme NO₂⁻ oxide reductase (NXR) (Equation 8 and 9) (Stein and Klotz, 2016, Kuypers et al., 2018).



Nitrogen biochemical processes depend on factors such as pH, humidity, temperature, agricultural practices and geochemical features. Another point to consider is the microbial density, which in general, is negatively correlated with increasing depth through the soil profile (Gruber and Galloway, 2008).

In the agricultural context; when fertilizers or any external source of N is applied and, as a result of chemical hydrolysis; **urea** (CO(NH₂)₂) is converted into NH₄⁺ (Equation 10 - 12) (Sigurdarson et al., 2018). If catalysed by urease enzyme the reaction rate is estimated

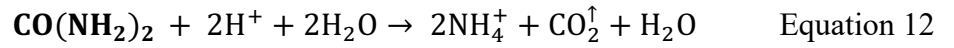
to be 10^{14} time higher (Zambelli et al., 2014). Following a general reaction of hydrolysis $\text{CO}(\text{NH}_2)_2$ is converted in NH_4^+ as follows:



The reaction depends on the pH of the soil solution, at a pH of greater than 6.3 the biochemical reaction follows as:



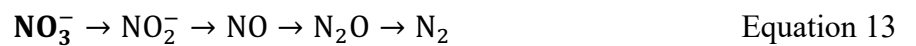
While at a pH below 6.2 the reaction follows as:



As final steps, a nitrification process takes place under oxic conditions, where NH_4^+ is finally oxidized into NO_3^- .

Agricultural practices (i.e. application fertilizers and effluents) have a strong influence on the C / N ratio. The C / N ratio can be used to estimate the capacity of the soil to transform the OM into mineral N assimilable by plants (Sigurdarson et al., 2018). A higher C / N ratio (> 30), the longer N retention time will be, decreasing the bioavailability of the element.

After the NO_3^- is produced and in the absence of O_2 (anoxic conditions), bacteria present in the soil solution and groundwater, use NO_3^- as an electron acceptor during cellular respiration. Facultative anaerobic bacteria (*Pseudomonas*, *Xanthomonas*, *Bacillus*, etc.) reduced NO_3^- to N_2 (a harmless gas) through the **denitrification** process (Equation 13). The process of denitrification is thus favoured in soils with low oxygen content, high moisture content and high OM content, and a C / N of at least 92% (Her and Huang, 1995).



It is widely accepted to say that NO_3^- **pollution** in agricultural landscapes is a consequence of the use of fertilizers in the form of urea ($\text{CO}(\text{NH}_2)_2$), NO_3^- or NH_4^+ , atmospheric depositions, and the use of sewage and manure (Rivett et al, 2008). In addition, under cattle

grazing, urine patches (“hot spot”) lead to N loading ranging from 200 up to 2000 kg N · ha⁻¹ (Selbie et al, 2015).

If the N source applied is in the NH₄⁺ form, the nitrification process would transform the NH₄⁺ into NO₃⁻ (Equation 3) through biological oxidation. If the source of N comes as (CO(NH₂)₂), and if environmental conditions allow it; the urea chemically hydrolyses producing NH₄⁺ and CO₂ (Equation 10) to continue with the nitrification process where NH₄⁺ is oxidised to obtain NO₃⁻ again (Sigurdarson et al., 2018). Consequently, NO₃⁻ reaches the aquifer mainly through leaching (Figure 2). Under high precipitation or irrigation rates, soils have greater **leaching** risks, especially soils with low clay content and high drainage capacity (i.e. sedimentary, volcanic and sandy soils) (Molloy, 1998). Even though N concentration decreases considerably down through the soil profile, Liao *et al.*, (2012) suggests that between 5 and 50% of the N applied to soils can leach into the saturated zone.

2.4 Nitrate attenuation processes in groundwater

Nitrogen reaches the saturated zone after **leaching** through the soil profile as NO₃⁻ (Puckett et al., 2004). The accumulation of NO₃⁻ in groundwater depends on hydrogeological settings, recharge and discharges rates and whether favourable conditions for attenuation processes are present in the aquifer (Elwan et al., 2015; Puckett, 2004; Jahangir et al., 2013). There are several known NO₃⁻ attenuation processes including DNRA, denitrification and chemo-denitrification processes (NO₃⁻ reduction to N₂) (Tesoriero et al., 2000, Tiedje et al., 1988). Denitrification is the most important one, as NO₃⁻ is converted into N₂, removing NO₃⁻ from the soil-water system (Kuypers et al., 2018).

Alongside the limited information about **denitrification** rate in New Zealand’s groundwater (Martindale et al., 2018), it is known that a high concentration of NO₃⁻ is being leached from dairy, beef and lamb farms (Waikato Regional Council, 2018). As one of many examples in the upper Manawatu River; Clothier et al., (2007) estimated that in some cases up to 50% of NO₃⁻ can be leached from farms into groundwater.

2.4.1 Subsurface denitrification

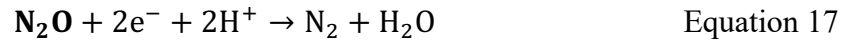
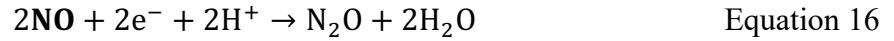
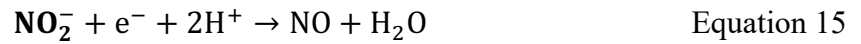
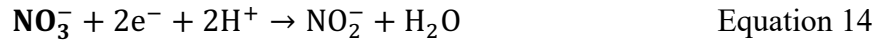
Leached NO_3^- can be potentially attenuated (reduced) by biogeochemical processes of subsurface denitrification in groundwater (Singleton et al., 2007). **Subsurface denitrification** process is an oxidation-reduction multi-step reaction, where the NO_3^- is reduced to N_2 . Micro-organisms reduce NO_3^- in reducing environments and in the presence of an electron donor that can be a C source or an inorganic source such as iron (Fe^{2+}) and/or manganese (Mn^{2+}) (Korom 1992; McAleer et al., 2016; Singh et al., 2014; Knowles, 1982; Stenger et al., 2013; Singh et al., 2014; Rivett et al., 2008). Facultative anaerobic bacteria such as bacterium *Gallionella ferruginea*, *Thiobacillus denitrificans* (Voguel et al., 1981) present in groundwater reduce NO_3^- into N_2 (Equation 13).

Even though NO_3^- can be chemically reduced to NO_2^- and N_2O , these are considered insignificant compared to **microbial reduction** (Rivett et al, 2008). Bacteria with a specific metabolic capacity are capable of reducing NO_3^- under favourable environmental conditions (Kuypers et al., 2018). Like O_2 , NO_3^- is an electron acceptor, in the oxidation-reduction processes (Korom, 1992). In subsurface macro or microsites with oxygen depletion where facultative anaerobes bacteria need an electron acceptor as an energy source for cell growth, the next electron acceptor (after O_2) favoured energetically is NO_3^- ($^\circ\text{G} -72.3 \text{ j mol}^{-1}$) (Rivett et al, 2008). The presence of electron donors completes the redox reaction. Electron donors susceptible to oxidation can be organic such as dissolved organic carbon (DOC) or inorganic such as Fe^{2+} ($^\circ\text{G} 4.6 \text{ j mol}^{-1}$) or Mn^{2+} ($^\circ\text{G} -50.3 \text{ j mol}^{-1}$) (Korom, 1992).

Nitrate reduction through subsurface denitrification could be a complete reduction (NO_3^- to N_2) or a partial reduction (NO_3^- to N_2O) depending on environmental conditions (Weymann et al., 2008). When complete subsurface denitrification is achieved, then the process serves as an ecosystem service (Weymann et al., 2008). Otherwise, partial subsurface denitrification releases N_2O , a greenhouse gas (Betlach and Tiedje, 1981; Thomas et al., 2011; Vilain et al., 2012).

Complete subsurface denitrification (NO_3^- reduction to N_2) occurs in 4 reactions (Equations 14 - 17) (Kraft et al., 2011; Stein and Klotz, 2016; Kuypers et al., 2018). The reduction of NO_3^- to NO_2^- is performed by the enzymes assimilatory NO_3^- reductase (NAS),

dissimilatory NO_3^- reductase (NXR) (Equation 14). Then NO_2^- is reduced to NO (Equation 15) by NO oxidase and NO_2^- reductase (Cu-NIR and cd_1 -NIR respectively). The reduction continues to N_2O by micro-organisms containing NO_2^- reductase (cNOR, qNOR) (Equation 16); NO reductase (Cu_aNOR , HCP and P_{450}NOR). Finally N_2O is reduced to N_2 by N_2O reductase (NOS) (Equation 17). If the conditions are partially met, or the micro-organisms do not possess NOS, then the reduction stops at N_2O (Equations 14 - 16); as partial subsurface denitrification.



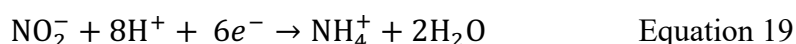
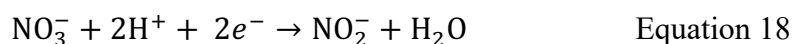
Excess N_2 is used to study the rate of N_2 produced by dissimilatory NO_3^- reduction (complete subsurface denitrification) in groundwater by micro-organisms (Weymann et al., 2008).

Partial subsurface denitrification is carried out by some microorganisms such as *Pseudomonas chlororaphis* (Kuypers et al., 2018) or when conditions for the reduction process are not met. The reduction of N_2O to N_2 is carried out by diverse bacteria such as proteobacteria that utilize N_2O reductase (NOS) and it is the main sink for N_2O (Kuypers et al., 2018). The status of subsurface denitrification (complete or partial) depends on the redox status, presence of denitrifying bacteria that carry NOS and the presence of suitable electron donors.

2.4.2 Dissimilatory nitrate reduction to ammonium - DNRA

In the soil-water system, NO_3^- is reduced to NH_4^+ through **dissimilatory nitrate reduction to ammonium (DNRA)** (Equation 18 and 19) under anaerobic conditions and low Eh (Rivas, 2018). Little is known about the extent of DNRA in groundwater and its importance

in the environment (Kuypers et al., 2018). Nevertheless, Tiedje et al (1988) defined that soil and water have the same type of denitrifying bacteria. The process is also favoured by the presence of electron donors such as organic carbon and Fe^{2+} (Kuypers et al., 2018). Especially when NO_3^- is limiting compared to organic carbon (Kraft et al., 2011).



Dissimilatory nitrate reduction to ammonium is considered a more efficient and significant process especially in oxic environments and when electron donors are relatively more abundant to NO_3^- (Tiedje, 1988). DNRA is, however, considered as a temporary attenuation process as NH_4^+ can be oxidized and again be converted into NO_3^- by bacteria under aerobic conditions. If an increased concentration of NO_2^- is found, it is acceptable to assume that DNRA is a leading process in the subsurface (Kraft et al., 2011).

2.4.3 Other processes of nitrate attenuation

2.4.3.1 Annamox

In the **annamox** process is carried out by micro-organisms that carry the enzyme hydrazine dehydrogenase (Kuypers et al., 2018). Annamox is also known as coupled nitrification – denitrification process or anaerobic ammonium oxidation (Stein and Klotz, 2016). In the process NH_4^+ is coupled with NO to produce N_2 (Figure 2) (Kraft et al., 2011, Kuypers et al., 2018; Stein and Klotz, 2016). Annamox is a major process in marine environments and in anaerobic environments (Stein and Klotz, 2016; Kraft et al., 2011).

2.4.3.2 Chemo-denitrification

Chemo-denitrification is an abiotic process where NO_2^- is chemically reduced to N_2O or N_2 (Korom, 1992; Rivas, 2018). Chemo-denitrification is likely to be seen in forest soils as the process is favourable under strong acidic conditions ($\text{pH} < 5$) (Rivas, 2018). Chemo-

denitrification is minor compared with biological denitrification, as consequence, the term denitrification refers to the process when is biologically mediated (Korom, 1992).

2.4.3.3 Nitrate removal via phreatophytes

Phreatophytes are trees with deep roots that allow nutrient uptake from aquifers or when the water table rises (Vidon and Hill, 2004).

Rivett (2008) suggested that NO_3^- can be removed through phreatophytes as the denitrification process can be enhanced by root exudates, enhancing conditions for denitrification. In New Zealand poplars, willows and cottonwood had been used as bioremediation (Franklin et al., 2016) enhancing the capacity of riparian zones to attenuate NO_3^- flows to groundwater.

2.5 Factors influencing subsurface denitrification

Subsurface denitrification in groundwater is strongly influenced by **hydro-geochemical** and geo-morphological settings. Subsurface denitrification increases by advection (Seitzinger et al., 2006), hence water residence time influence denitrification rate. Groundwater residence time ranges from days to years, depending on local hydrogeological settings. As there are many factors controlling the denitrification rate and the study of these factors have proven to be complicated; the determination of the denitrification rate is particularly sensitive to uncertainties. There are 4 main requirements for subsurface denitrification (favourable conditions) which are explained below.

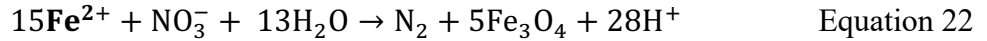
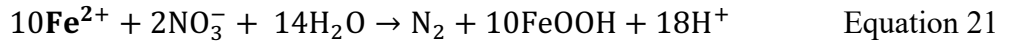
Subsurface denitrification occurs under anoxic conditions or very low O_2 availability, as oxygen has a higher reactivity ($^\circ\text{G} -78.5 \text{ kJ electron}^{-1}$) than NO_3^- as an electron acceptor in oxidation-reduction reactions. When DO levels in the aquifer are relatively low ($< 1 \text{ mg L}^{-1}$) and moderately stable; subsurface denitrification occurs continuously. By advection NO_3^- flows to macro or micro sites across the aquifer that are suitable for the denitrification process. The groundwater residence time and flow patterns can give an indication from where the NO_3^- was leached and introduced into groundwater (meters to kilometres) mainly by nitrification in overlaying soils and the distance travelled over time (years to decades) before the subsurface denitrification processes are completed.

When NO_3^- , the favourable energetically electron acceptor is available; an electron donor is needed for the oxidative-reduction process to start. If the electron donor in the process is an organic compound, then, heterotrophic denitrification (Equation 20) is the dominant process. The common bacterium responsible for this process are *Pseudomonas*, *Paracoccus*, *Thiobacillus*, *Bacillus* (Felgate *et al.*, 2012). For the last reduction reaction N_2O to N_2 , the presence of N_2O reductase enzyme NOS (Felgate *et al.*, 2012), which is inhibited in oxic environments.



In Equation 20, C symbolizes a source of organic carbon with an oxidation state of 0. In nature, carbon has 5 oxidation states (0, 1+, 2+, 3+, 4+), hence heterotrophic denitrification is limited (Korom, 1992) with organic carbon as the limiting factor of the reaction.

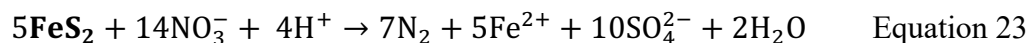
Nitrate attenuation process occurs through autotrophic denitrification when an inorganic compound is an electron donor such as Fe^{2+} , Mn^{2+} and HS^- . The stoichiometric equations for autotrophic iron-driven denitrification (Rivett et al, 2008) are given below.



The autotrophic denitrification reaction is pH dependent and positively correlated with the concentration of protons as end products of the reaction. *Gallionella ferruginea* (Nitrosomonas) is a common bacterium found in aquatic systems responsible for the NO_3^- reduction to NO_2^- (Korom, 1992). When the pH level is below 7, Goethite is formed and most likely to precipitate (Equation 21). If the pH is neutral or alkaline (> 7), ferric oxide (Fe_2O_3) is formed and precipitates (Equation 22), a process that serves as an iron sink within the aquifer (Rivett et al, 2008). As *Gallionella ferruginea* needs little presence of dissolved oxygen (DO) for growth, so in aquifers where Fe^{2+} and DO meet in an opposite gradient (oxic/anoxic) the reduction process is favourable (Weymann et al., 2010).

The process can also arise with sulphur (S) as an electron donor. The oxidation state of Sulphur can be +4 present as sulphate (SO_4^{2-}), -2 as H_2S , -1 in form of FeS_2 , 0 if its elemental state, +2 as thiosulphate or +4 in sulphate (SO_3^{2-}). However, in the subsurface

environment S is commonly found with the oxidation state -1 as pyrite (FeS₂) (Rivett et al, 2008), which is energetically favourable electron donor for subsurface denitrification (Equation 23). Pyrite is a highly prolific electron donor as S⁻¹ donates 7 electrons reducing to SO₄²⁻. In this process, 5 mol of pyrite are required to reduce 14 mol of NO₃⁻ producing 7 mol of N₂ by the bacteria Thiobacillus denitrifiers as follows (Korom, 1992).



Dissolved oxygen concentration gives an indication about the existing microbiology in the groundwater, e.g. denitrifying microbes are found under low or high DO environments, but under low DO denitrifiers are more active. DO is considered a limiting factor for microbial activity. Concentration and variability over time of DO in groundwater determine which microbial communities proliferate.

Overall, low DO, suitable bacteria and electron donors are the main 3 requirements for subsurface denitrification, avoiding NO₃⁻ accumulation. Nevertheless, other environmental factors can promote NO₃⁻ accumulation through direct or indirect processes (i.e. many processes are pH-dependent). If the denitrification kinetics is order zero, then the process is independent of NO₃⁻ concentration. It had been observed by many, that denitrification kinetics is order zero when NO₃⁻-N had accumulated (< 1 mg L⁻¹) (Korom, 1992, Rivett et al., 2008)

Other environmental and abiotic conditions have to be considered as they also contribute and limit NO₃⁻ reaction processes. Irrigation system, rainfall, temperature and water table affects directly NO₃⁻ concentration that leach into the subsurface environment. In the subsurface environment, heterotrophic denitrification is more effective when pH ranges from 5.5 and 8.

Reactions are also influenced by the ratio between carbon and N (Halling-Sorensen and Jorgensen, 1993). In aquifers where carbon is limiting; DNRA is likely to be the main process over denitrification (Hiscock et al., 1991; Seitzinger et al., 2006, Rivett et al., 2008, Korom, 1992). However, if at any stage a process is inhibited by hydro biogeochemical conditions within the subsurface environment the denitrification process is partial, releasing N₂O instead of N₂ (complete denitrification) .

2.5.1 Environmental implications for partial subsurface denitrification

The N cycle and its reactions involved in the soil-air-water matrices directly affect N distribution and its impact on the environment. The subsurface denitrification process is the main mechanism for NO_3^- attenuation in groundwater. The denitrification process is one of the critical steps in the N cycle, as it is the only process capable to remove N in the most stable form, like N_2 , from soil-water systems.

This reaction delivers positive environmental effects, i.e. reducing nutrient concentrations and avoiding eutrophication of receiving waters. However, when the reaction is not completed, N_2O a harmful greenhouse gas is released into the atmosphere (Galloway et al., 2003).

2.6 New Zealand studies on transport and transformation of N in the subsurface environment

In the New Zealand context; 44% of the land is covered by grassland and the national economy is based on dairy, and sheep and beef industries (10.08 million cattle) (STATS, 2018). Reay et al., (2012) stated that agricultural soils are the main source of N_2O emissions and NO_3^- leaching and they estimated the contribution of N_2O emissions from agricultural soils will increase reaching more than 5 Tg N_2O -N year^{-1} by 2030. The Ministry of the Environment through the “National Policy Statement for Freshwater Management” (NPSFM, 2017) recognises the role of subsurface environment for the NO_3^- attenuation process (NAP), which also is clearly identified in literature. Especially where the type of land use is predominantly dairy farming representing a greater risk of NO_3^- pollution of receiving waters. Several studies have been conducted in New Zealand surface soils (up to 1 m bgl) as a consequence of the harmful effects that comes with increasing NO_3^- concentrations in freshwater. However, there is still a lack of information about the transport and transformation of NO_3^- in groundwater. There is an increasing interest in the variability of subsurface denitrification and the influence of diverse hydrogeological settings. A deeper understanding of subsurface denitrification process can help inform policy design for better management of land and water resources.

Clague et al., (2018), for example, conducted push-pull tests and laboratory incubations from 2 sites in the Waikato Region. The sites have different land uses (high-intensity dairying and low-intensity pastoral agriculture) and present different geological settings. The push-pull test results showed no denitrification potential (DP) or denitrification capacity (DC), contrasting with laboratory incubations where DC was observed. In the same region, Stenger et al., (2018) conducted one of the only few studies investigating subsurface denitrification among a transect of shallow groundwater piezometers. The investigation included 10 multilevel well with 2 to 5 wells screened at different depths along 100 m downslope transect. In this study, 7 of the multilevel wells showed vertical redox gradients and variation in DP, and the study found DOC as a limiting factor in the wells. They also found that for quantification of the denitrification process in oxidized wells, a more accurate vertical biogeochemical patterns needed to be obtained.

Rivas et al., (2014) studied spatial variation of groundwater chemistry and redox conditions across Tararua areas of the Manawatu River Catchment, located in the lower part of North Island. The study was based on oxidation-reduction conditions, integrated with hydrogeochemical settings of a total of 56 groundwater wells sampled. They found that coarser soil texture and aquifer rock types influence groundwater, where well-drained soils and gravel rock type settings allow relatively faster groundwater recharge and movement resulting in an unfavourable oxidized groundwater environment. Under alluvial systems with fine soil texture and low permeability rock types the groundwater was generally assessed as reducing conditions with low levels of DO conducive for subsurface denitrification. However, their methodology does not allow one to measure directly subsurface denitrification and its dynamics, hence they did not assess denitrification status in the wells.

There is evidence to suggest conditions and processes leading to NO_3^- reduction in shallow groundwater in New Zealand. Still, there is limited information available about the potential occurrence, characteristics and dynamics of subsurface denitrification in New Zealand agricultural catchments. A better and deeper understanding of the nitrogen cycle in deep and shallow groundwater is essential due to the complexity within the 3 main matrices, especially when soil-water systems are the main producers of N_2O (Thomas et al., 2012). Also, a sound understanding of N transport and transformation in soil-water systems will help inform effective measures to reduce the effects of land uses and fertilizer

applications on the quality of receiving waters. In the proposed study, we aim to develop our understanding of the farm practices or environmental conditions, which will lead partial denitrification to complete denitrification producing N_2 as a final product.

2.7 Techniques to determine nitrate transformations in groundwaters

A range of different methodologies have been developed to quantify and gain a better understanding of NO_3^- attenuation process in groundwaters. These techniques include e.g. laboratory based, field-scale measurements, and catchment-scale N mass balance (Groffman et al., 2006). Specific techniques are used for different measures of denitrification at different scales (Istok et al., 2013). It is important to define if the objective is to determine the actual denitrification potential or denitrification capacity. Stenger et al., (2013) defined actual denitrification as the highest rate at which NO_3^- is reduced under anaerobic conditions without the addition of electron donors while Koops et al., (1996) defined that if an easily available carbon source is added the potential denitrification capacity is being evaluated. As little is known about subsurface denitrification and the lack of definitions applicable for subsurface denitrification; for the purpose of this research, we will apply definitions based on surface soil denitrification in the context of subsurface denitrification in groundwaters.

In-field techniques such as push-pull test are commonly used to measure denitrification processes in groundwaters (Istok, 2013).

2.7.1 Push-pull test

In 1986, Trudell et al., developed the ‘Push-Pull’ test to quantify discrete or localized subsurface denitrification rates in a shallow unconfined sand aquifer in an agricultural land in southern Ontario. Over the years this method has been further applied and tested; Istok *et al.*, (1997) for example, who perfected the technique to investigate a wider range of biochemical processes and reaction in groundwater systems. Push-pull tests are conducted to quantify in situ biogeochemical processes in shallow and deep groundwater. The capability of this test to quantify chemical and microbial reactions in situ allows to measure

and use of more accurate data for modelling processes and environmental decision making (Istok *et al.*, 1997).

A push-pull test involve two phases, during the first phase a test solution (TS) is injected or “pushed” into the well followed by extraction of the samples in the “pull” phase. The TS is composed by groundwater previously collected with the addition of the NO_3^- source and a nonreactive tracer (potassium bromide - KBr) to account for the dilution rate during the test.

There are two approaches to push-pull test experiments. On one hand, the denitrification potential (DP) can be estimated and on the other, the denitrification capacity (DC) can be quantified. To determine the DC, a source of NO_3^- and an electron donor source needs to be added to the TS, a C source in the form of glucose is the most common electron donor used for this purpose. To determine the DP, only one NO_3^- source must be injected to the TS since the objective is to determine the maximum subsurface denitrification rate that occurs under natural environmental conditions. Depending on the objectives of the research and hydrogeological settings of the test site, TS volumes ranging from 40 to 1000 L have been used (Istok, 2013). The collection of the sample can be made by continuous extraction pumping and sampling or periodic discrete sample over a certain period of time. Therefore, to successfully conduct a push-pull test, the location needs to be defined and with geochemical characteristics of the aquifer such as parental rock, soil type and recharge rate and temperature.

2.7.2 Other approaches

Nitrogen transport and transformation has been widely studied, involving denitrification, mineralization, leaching and travel time through the soil profile studied. Incubation methods are a common approach and are often coupled with isotopic techniques (N^{15}) (Luo *et al.*, 1998) which gives better accuracy from the measurements and higher sensitivity (precision) to the results (Tiedje *et al.*, 1989). Laboratory incubations of soils allow quantification of denitrification rate and denitrification capacity showing them to be an accurate and feasible technique (Groffman *et al.*, 2006).

Unfortunately, for subsurface denitrification studies laboratory incubation brings several issues to consider. When working with slurries of aquifer material or groundwater samples for laboratory incubation it is hard to obtain representative results due to the small size of the samples analysed and therefore high extrapolations are required (Bragan et al, 1997). Also, in-situ conditions are inevitable changed when the sample is isolated and transported to be studied under laboratory conditions, especially when most denitrifying bacteria while collecting the sample stayed attached to aquifers material (Korom, 1991; Korom, 1992, Smith and Duff, 1988). Groundwater samples are particularly sensitive for changes in pressure, aeration, temperature and light exposure. As a consequence, the subsurface denitrification rate calculated by laboratory incubations may not be accurate/representative (Groffman et al., 2006).

2.7.3 Implications for research

Subsurface denitrification studies have proven to be hard to accomplish and yet there is still much to understand about denitrification processes and their dynamics in groundwaters. The challenge is particularly complex, as changes in hydrogeological settings and land management can affect subsurface denitrification (Holden and Fierer, 2005). Subsurface denitrification is strongly correlated with the presence of electron donors such as dissolved organic carbon (DOC), Fe^{2+} and Mn^{2+} . Hence the study of all of these parameters and not just one while conducting subsurface denitrification studies are needed. To better interpret results and to gain a better understanding of subsurface denitrification process hydrogeological data needs to be considered. Hydraulic properties, such as mixing rates, flow rate and recharge rate are responsible for linking denitrifiers, NO_3^- and electron donor at the location where the reduction process occurs (Martindale et al., 2018). There are many uncertainties while conducting subsurface denitrification studies; it is fundamental to acknowledge them while reporting subsurface denitrification rates.

There is clear evidence of spatially variable conditions and processes leading to NO_3^- reduction in shallow groundwater in New Zealand. However, there is very limited information available about the potential occurrence, characteristics and dynamics of subsurface denitrification across New Zealand agricultural catchments (Martindale et al., 2018). Therefore, this study aims to develop our understanding of the farm practices or

environmental conditions, which lead to partial or complete denitrification, producing N_2 as a final product, across a range of hydrogeological settings in New Zealand agricultural landscape.

Chapter 3. Materials and methods

This chapter describes field and laboratory methods followed during the study period (February – September 2018). In order to determine hydrogeochemical properties, dissolved gases and excess dinitrogen in shallow groundwater samples collected from the Manawatu and Rangitikei River catchments. It outlines the climate conditions of the study area, land uses and soil types. Includes analytical procedures for chemical analysis and excess N₂ and validation of analytical methodologies.

3.1 Selection and description of study sites

A total of 6 sites were selected for this study. The study sites were selected, based on their different hydrogeological settings and NO₃⁻ reduction potential (Rivas et al., 2014, Collins et al, 2015). The study sites are located in the Manawatu and Rangitikei River catchments in the lower North Island of New Zealand (Figure 3), and have similar land uses (grazed pasture) and general management practices, such as fertilizer application and effluent irrigation, but different hydrogeological settings in terms of soil and rock geology types (Table 2, Chapter 1).

Due to meteorological conditions present in the Manawatu-Rangitikei river catchment and soil quality, the land can be used for a variety of purposes. The main developed industry is sheep and beef production. Manawatu-Whanganui has a total area of 1,286 million ha where 1,032 million ha are used for sheep and beef production counting the 80.2% of the region. While 0.205 million ha are used for dairy farming (15.9%). In relation to the total area of New Zealand, Manawatu-Whanganui is the third largest region with the largest area used for sheep and beef production, and the sixth largest in dairy production (Stats NZ, 2016). Data from 2002 to 2016 show a decreasing national trend in land used for sheep and beef production (from 10.6 to 8.5 million ha), but an increasing trend in land used for dairy farming (from 1.8 to 2.5 million ha).

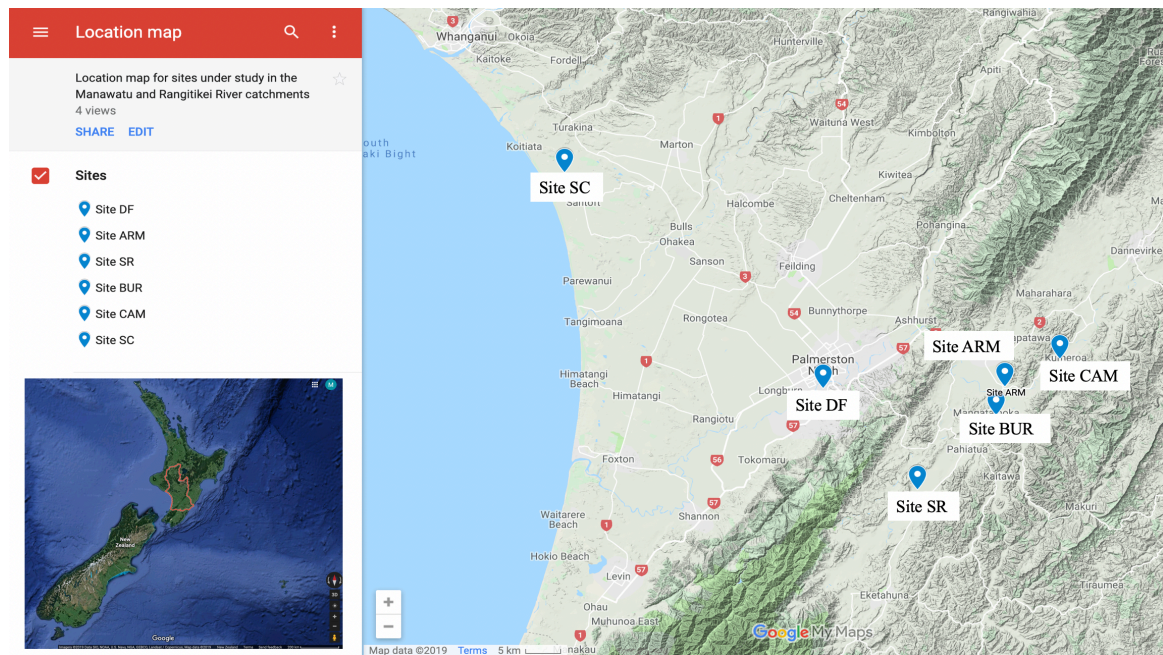


Figure 3: Location of shallow groundwater collection sites in the Manawatu and Rangitikei River catchments, New Zealand.

The 5 study sites are intended for dairy production and 1 for cattle and sheep (Table 2). The type of land use; and physical and chemical characteristics provide information to better understand subsurface denitrification capacity.

Table 2: Characteristics of the study sites for the collection of groundwater samples in the Manawatu and Rangitikei River catchment.

Study Site	Site Code	Land use	Soil type*	Rock type*
Palmerston North	DF	Dairy	Manawatu fine sandy loam	Alluvium
Santoft	SC	Dairy	Foxton brown sand-Pukepuke black sand, Himatangi sand	Sand flat
Woodville	ARM	Beef/Sheep	Kairanga silt loam and clay loam	Alluvium
Pahiatua	SR	Dairy	Kopua stony silt loam	Loess over gravel
Pahiatua	BUR	Dairy	Kopua stony silt loam	Loess over gravel
Dannevirke	CAM	Dairy	Takapau silt loam	Loess over gravel

*Collins et al., 2015, Rivas et al., 2014.

Each of the study site has 3 piezometers installed at different depths (Table 3) in order to give a better understanding of the influence of hydro, bio, geo and chemical properties on NO_3^- reduction on the profile of the subsurface environment. The suitability of the piezometer depths was determined to access and sample shallow groundwater reflecting effects of land use and nutrient leaching losses at each of the study sites. Analysis and quantification of groundwater samples involved the most important inorganic and organic components (described in 3.4 Push-pull test) associated with biogeochemical reactions during denitrification processes and push-pull test.

Table 3: Depth of piezometer (bgl, m) at sites for the collection of groundwater samples in the Manawatu and Rangitikei River catchments.

Site code	Piezometer 1*	Piezometer 2*	Piezometer 3*
DF	5.5	7.5	8.7
SC	3.4	5.2	6.4
ARM	5.0	6.0	7.5
SR	4.5	5.5	6.5
BUR	3.6	4.3	6.1
CAM	4.5	-	7.5

*Screen depth (m, bgl): 0.5 m at each piezometer.

Bgl = below ground level.

The study site DF is a dairy farm located in Palmerston North (Figure 3). The piezometers are installed under the fence between the dairy paddocks. The piezometers are approximately 1.5 m apart. The dairy farm SC is located northwest of Bulls in the Santoft area (Figure 3) in the Rangitikei Sand Country. The piezometers SC 1 and SC 2 are installed on a side 1.5 m apart and 1.5 m from a small drainage channel (Figure 4). The surface drainage channel exhibits greater flow during the wet months from July – September), though it remains relatively low flow during the warmer months (January – March). The piezometer SC 3 is located in a paddock separated by 800 m. This piezometer is surrounded by grassland. At site ARM in Woodville, the 3 piezometers are located next to the paddock fence approximately 1.5 m apart. Site CAM in Dannevirke has 3 piezometers installed of which CAM 1 presented a slow recharge flow, expressed through the slow pumping rate

that this site allowed CAM 2 presented extremely slow recharge flow consequently it was excluded from the study due to the extremely slow pumping rate. Only CAM 3 showed a relatively fast flow condition for groundwater sampling, allowing a pumping rate of approximately 1 L sec^{-1} . The 3 piezometers in the study site SR are installed in the middle of paddock within 1.5 m apart. At BUR site, the piezometer BUR 1 is located between a paddock and stream. While BUR 2 is located inside the paddock and close to the stream, and BUR 3 is located inside the paddock next to a gravel road. These 3 piezometers at BUR site are located approximately 1 km away from each other.

For this study, to reach groundwater at specified locations; PVC piezometers were used (28 mm inner diameter). The length of the piezometers ranging from 3 to 9 meters below ground level (m bgl) with 0.5 bottom screen. 5 mm holes, 1 cm apart and covered with 250 μm nylon mesh. The bottom of the piezometer is sealed with a nylon cap (Collins, 2015).



Figure 4: An example of groundwater being purged before groundwater sampling from the piezometer at the study site SC 1.

The Manawatu-Rangitikei area presents a temperate climate characterized by warm summer with an average temperature in the low 20 °C and winters are characterized by moderate rain, at about 980 mm a year, and temperature drops to 8 °C. Often mild winters are near the coast and plains, while in the hill country the tendency is frosty and clear with low winds (NIWA, 2015).

A record of meteorological data was obtained through meteorological stations closest to the sites (Table 4). The data was obtained from Climo's and Horizons data sets; which are of public access. The data was obtained from February 2018 to February 2019, including rainfall and temperatures.

The minimum temperatures of the stations range between 7.7 °C and 8.7 °C, with the lowest temperatures presented in June – August. The temperature records show that seasons can be easily identified during the year with lowest temperatures during winter (June, July and August) and higher temperatures during summer (December, January and February) (Figure 5). The same trend is observed with evapotranspiration rates (data not shown) where maximum evapotranspiration rates are found during days with higher temperatures and higher solar radiation rates in the summer season. Unlike temperature there is no clear trend observed for rainfall, the annual rainfall ranged between 1037.8 (site SC) and 1463.3 mm at site CAM. The site DF and SC presented 35 days with more than 10 mm of rainfall received per day, CAM 36 days; and SR, BUR and ARM 44 days where rainfall exceeded 10 mm.

Nevertheless, there is historical data of drought years like in 2013 and particularly rainy years such as 2015. Droughts can also affect seasonally for which irrigation systems are highly used especially from October to February.

Table 4: List of meteorological stations in close proximity to the study sites.

Site	Station
DF	Ngahere Park Climate Station*
SC	Raumai Climate Station*
SR	Mangatainoka at Pahiatua Dairy Factory*, **
BUR	Mangatainoka at Pahiatua Dairy Factory*, **
CAM	Akitio at Toi Flat**

*Daily values (public access) obtained through www.horizons.govt.nz/

**Daily values (public access) obtained through cliflo.niwa.co.nz/

The meteorological data hints to water balance and potential recharge rate of each of the study site. The water balance, groundwater recharge rate and residence time influence transport and fate of NO_3^- in an aquifer (Martindale et al., 2018).

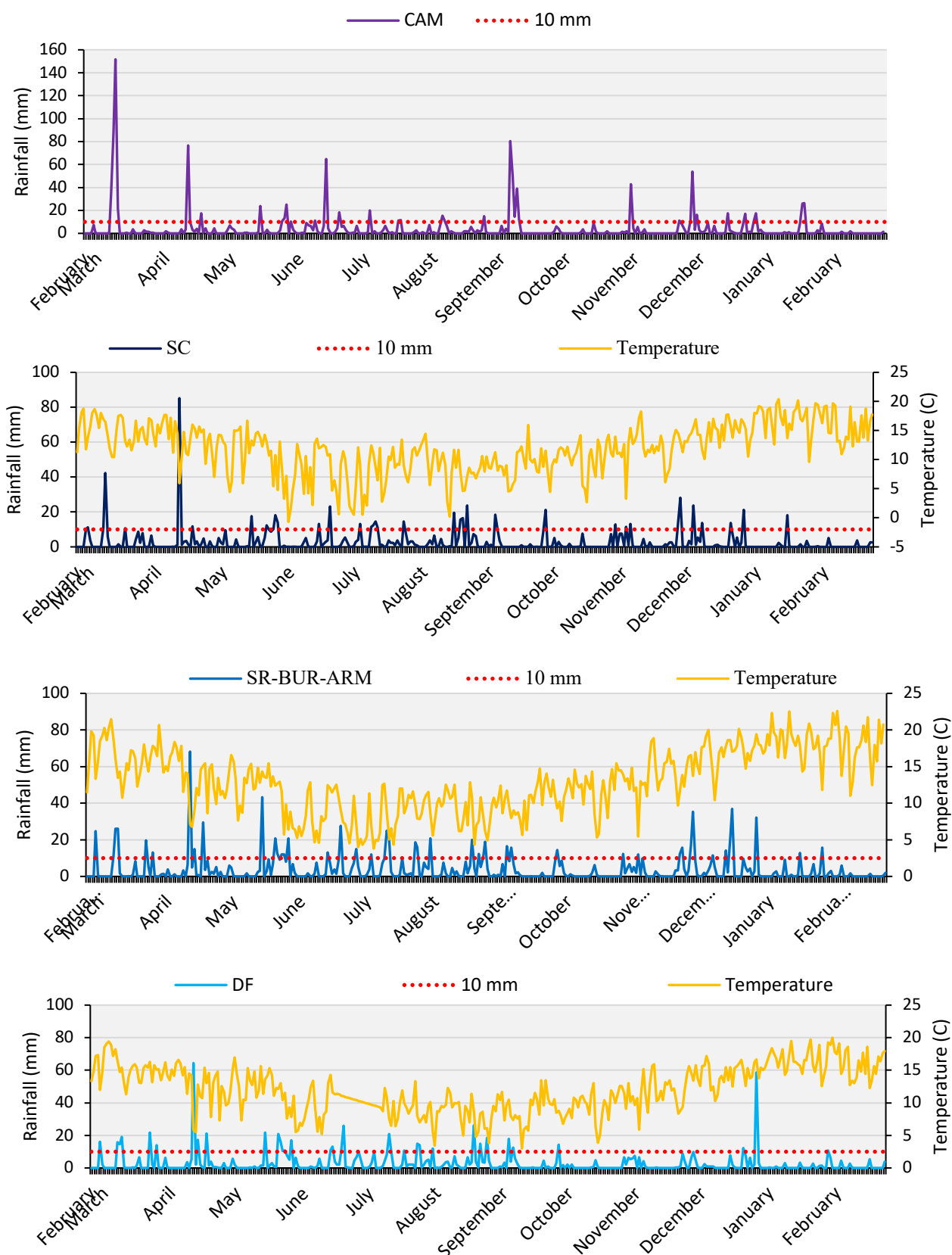


Figure 5: Variation of daily rainfall and mean temperature from February 2018 – February 2019 at the study sites DF, SR, BUR, ARM, SC and CAM (no temperature data available).

3.2 Monthly groundwater sampling

A monthly groundwater sampling was carried for over 8 months (from February to September 2018; except for July). The time frame was chosen to evaluate spatial and temporal variations in the hydro-geochemistry of shallow groundwaters at the study sites. The monthly groundwater samples were collected from the 3 piezometers in the six study sites, except for site CAM where only piezometer 1 and 3 were sampled. Before the collection of the groundwater samples, the water table (m, bgl) in each piezometer was measured with a water level meter. The recorded water table was used to determine the volume of water that needed to be purged before the collection of the sample. The “suspended groundwater” inside the piezometer needs to be purge as is not representative of the shallow groundwater environment. Hence, the collection of the groundwater sample (groundwater from the surrounding of the screen depth of the piezometer) should begin only and only if the “suspended groundwater” has been pumped out the piezometer.

Two different pumps were used for extracting the groundwater samples. A peristaltic pump was used for the collection of the groundwater samples for the analysis of redox condition and chemical analysis. A bladder pump was used for the collection of the groundwater samples for the analysis of dissolved gases $\text{N}_2\text{O-N}$ and excess N_2 . A bladder pump was required to avoid degassing of the groundwater sample due to the difference between the pressure inside of the aquifer and the outside of it (Weymann et al., 2008).

A YSI Professional Plus Handheld Multi-parameter Instrument (smarTroll multiparameter handheld, In-Situ) was connected to the pump. This instrument is used to measure in-situ water quality parameters such as pH, electrical conductivity (EC), DO, temperature (T°), and oxidation-reduction potential (ORP). The smarTroll was calibrated at the beginning and end of the sample collection period.

The stagnant water inside the piezometer does not have the same physical-chemical characteristics as the water inside the aquifer. Therefore, to ensure that the samples collected are chemically representative of the around the piezometer should purge 3 times the volume of stagnant water was purged as per the National Protocol for SOE Groundwater Sampling in NZ (Daughney, 2006). During the purging, values of EC, DO, T° , ORP of pumped groundwater were monitored through an enclosed flow cell on the SmarTroll

(Figure 5), and only after the stabilization of these parameters, the groundwater sample were collected for hydrochemistry and gaseous analysis.

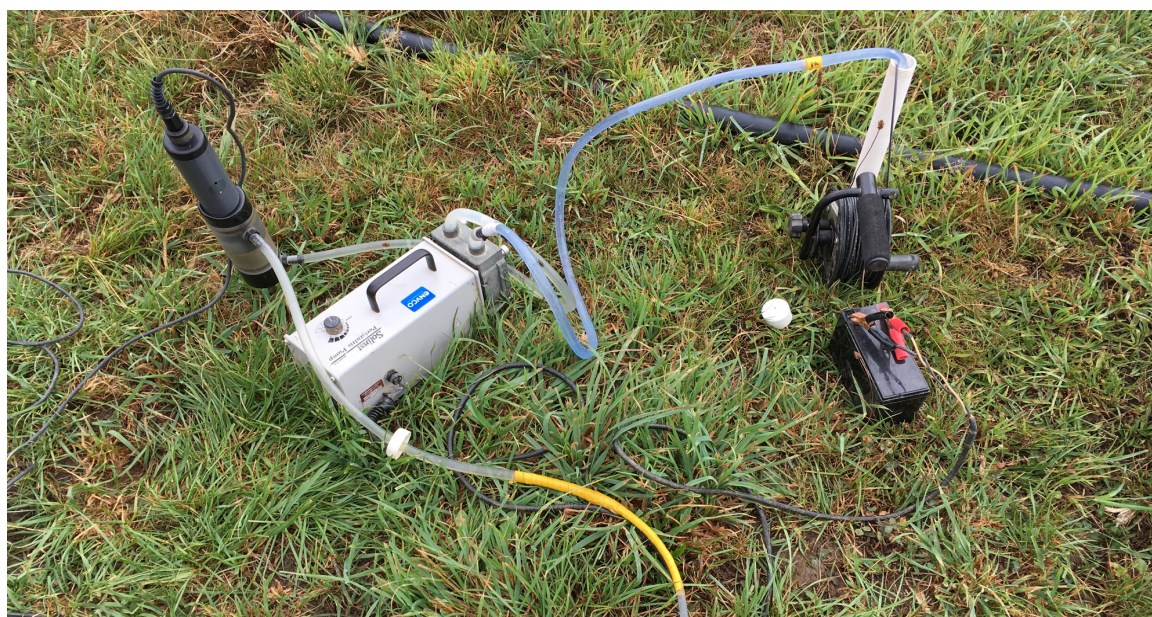


Figure 6: Scheme for groundwater purging including peristaltic pump, SmarTroll, and depth-meter.

The groundwater samples from each piezometer at every site were collected in **three replicates** for various hydrogeochemical analysis. For analytical analysis, the groundwater samples were collected following the instructions in the National Protocol for SOE Groundwater Sampling in NZ (Daughney, 2006). The samples were stored in different containers (Table 5) as per the guidelines. At each piezometer, unfiltered groundwater samples were collected in a plastic bottle (500 mL) for bicarbonate (HCO_3^-) analysis and amber coloured bottle (200 mL) for DOC analysis. For determination of cation, anion and metal ions the collected groundwater samples were filtered in-field through a $0.45 \mu\text{m}$ filter, stored in triplicates in pink top containers (50 mL) and acid preserved (concentrated nitric acid) for determination of metal ions. The sample bottles were filled directly with the sampling tube, and closed and stored in chilly bins with ice packs for further analysis. The DOC samples must be stored in dark due to UV sensibility of DOC.

Table 5: Guide for collection and chemical analysis of shallow groundwater samples.

Container	Quantity	Element for analysis	Filtered (0.45 μ m)	Preservation (HNO ₃ conc.)	Equipment
Plastic bottle (500 mL)	1	EC, HCO ₃ ⁻	No	No	Potentiometer and determination by H ₂ SO ₄ Titration
Amber glass bottle (250 mL)	1	DOC	No	No	TOC-L
Plastic containers (50 mL)	3	Cation (NH ₄ ⁺ -N)	Yes	No	Autoanalyzer
	3	Anions (NO ₃ ⁻ -N, Br ⁻ , Cl ⁻ , NO ₂ ⁻ -N, SO ₄ ²⁻)	Yes	No	Ion Chromatography (IC)
	3	Metal ions (Al ³⁺ , Mn ²⁺ , Fe ²⁺ , Ca ²⁺ , Na ⁺ , K ⁺ , Mg ²⁺)	Yes	Yes	Microwave Plasma Atomic Emission Spectroscopy (MP- AES)

For dissolved N₂O-N gas analysis (Table 6), the sampling tube was placed all the way to the bottom of a glass bottle (250 mL), and when the bottle was filled it was submerged in a bucket previously filled with the groundwater. The bottle was then continuously overflowed until the bottle received 3 times the total volume while rotating the sampling tube. The bottle was tapped to remove any air bubbles inside. After overflowing 3 times the glass bottle volume (250 mL), the sampling tube was carefully removed, and the bottles were sealed underwater with a rubber septum lids coated with silicone gel on aluminium crimps using a crimper.

For excess N₂ analysis (Table 6), the groundwater samples were collected in 12 mL glass exetainers by the same overflowing procedure as described above for the collection of the dissolved gas analysis (directly from the sampling tube using a bladder pump). After filling the exetainers to the brim a few drops of mercury chloride (5% Hg₂Cl₂) was added to eradicate microbial activity which stops the production of N₂ (reduction of NO₃⁻). The collected groundwater samples were kept in a chilly bin with ice until transported and stored in cold storage at 4 °C until further analysis. The collected groundwater samples were analysed within 2-4 weeks of the sampling.

Table 6: Guide for collection and analysis of dissolved gasses in shallow groundwater samples.

Container	Quantity	Element of analysis	Filtered	Preservation	Equipment
Glass bottles (250 mL)	3	Dissolved gasses (N ₂ O-N)	No	No	Gas Chromatography (GC)
Glass exetainers (12 mL)	3	Ar, N ₂ , Excess N ₂	No	Yes (5% Hg ₂ Cl ₂)	MIMS technique (NIWA Laboratory, Wellington)

Analysis of pH, EC, T°, DO, HCO₃⁻, DOC, NH₄⁺-N, NO₃⁻-N, bromide (Br⁻), chlorine (Cl⁻), NO₂⁻-N, sulphate (SO₄²⁻), Al³⁺, Mn²⁺, Fe²⁺, Ca²⁺, sodium (Na⁺), K⁺, Mg²⁺, N₂O-N, Ar and excess N₂ were measured in triplicates for in-situ parameters, monthly analysis and in-situ experiment.

3.3 Analytical procedures

3.3.1 Analytical procedures for chemical analysis

Presence of HCO₃⁻ in the collected groundwater samples was determined using titration technique by sulfuric acid (H₂SO₄). In this method, 2 drops of phenolphthalein were added

to 50 mL of groundwater sample. Phenolphthalein is used for the determination of alkalinity (CO_3^{2-} and OH^-), if no change in colour is observed then titration is not needed. Then, 2 drops of methyl orange indicator were added to the same flask and the groundwater sample was titrated with 0.02 N H_2SO_4 . Methyl orange indicator is used for the determination of total alkalinity; including the detection of $\text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^-$ with a pink colour as the endpoint. The results are expressed in mg L^{-1} of calcium carbonate (CaCO_3) and are obtained by applying Equation 24 and 25 as follows:

- Alkalinity

$$\text{Alkalinity} = \frac{P \cdot N \cdot 50000}{\text{mL of Sample}} \quad \text{Equation 24}$$

Where:

P = mL of H_2SO_4 used with Phenolphthalein as indicator

N = Normality of H_2SO_4 (Validated)

- Total Alkalinity

$$\text{Total Alkalinity} = \frac{T \cdot N \cdot 50000}{\text{mL of Sample}} \quad \text{Equation 25}$$

Where:

T = Total volume (mL of H_2SO_4) used after both titrations

N = Normality of H_2SO_4 (Validated)

Anions including Cl^- , Br^- , SO_4^{2-} , NO_3^- -N and NO_2^- -N were analysed using the Ion Chromatography (DionexTM AquionTM IC ThermoFisher Scientific). This instrument detection limit for each ion was as follows Cl^- 0.01 mg L^{-1} , Br^- 0.01 mg L^{-1} , NO_3^- -N 0.003 mg L^{-1} , SO_4^{2-} 0.01 mg L^{-1} , NO_2^- -N 0.01 mg L^{-1} . The quantification of NH_4^+ -N was carried out in an autoanalyzer (NO_x analyzer T200U, Teledyne) with a detection limit of 0.01 mg L^{-1} and a calibration curve NH_4^+ -N and NO_3^- -N with a range between 0 to 12 mg L^{-1} .

Cations including Ca^{2+} , Na^+ , K^+ , Mg^{2+} and metal ions such as Fe^{2+} , Mn^{2+} and Al^{3+} were analysed using the Microwave Plasma Atomic Emission Spectroscopy (MP-AES) instrument (4200 MP-AES (Agilent Technologies, Santa Clara, CA USA). This instrument detection limit for each ion was as follows Ca^{2+} 0.01 mg L⁻¹, Na^+ 0.01 mg L⁻¹, K^+ 0.01 mg L⁻¹, Mg^{2+} 0.01 mg L⁻¹, Fe^{2+} : 0.01 mg L⁻¹, Mn^{2+} : 0.01 mg L⁻¹, Al^{3+} 0.01 mg L⁻¹. The determination of ion metals was made directly with the groundwater sample (preserved in acid and filtered), while for Ca^{2+} , Na^+ , K^+ , Mg^{2+} ; the samples were prepared with 9 mL of groundwater sample and 1 mL caesium / strontium (Cs / Sr) 10,000 mg L⁻¹ in order to achieve a final concentration of 1,000 mg L⁻¹ Cs / Sr for cation stabilization. For measurement of DOC and dissolved inorganic carbon TOC analyzer (TOC-L, Shimadzu) was used. The instruments are located in Soil and Water Laboratory at Massey University.

3.3.2 Charge balance error

Analytical accuracy (validity and quality) of the analysis can be estimated by charge balance errors (CBE) (Table 8). In nature, aqueous solutions are electrically neutral, therefore total cation concentration is equal to the total anion concentration. CBE is a relative error and particularly sensitive to in water samples with a low concentration of anions and cations (e.g. groundwater). Accepted values for CBE are $\pm 15\%$, if it's positive then the sample might have a higher concentration of cations, but if negative, there is a higher concentration of anions. Undesirable results for CBE might be analytical errors during laboratory analysis or some major ion is not being considered. The concentration of every ion use for CBE calculations must be converted to milliequivalent per litre (meq L⁻¹) which represents the electrical charge in a defined volume. For that, the molecular weight (MW) was divided by the valance of the element (Table 7).

Table 7: Molecular weight and charge of element and molecules for charge balance error calculations.

Compound	MW (g mol ⁻¹)	Charge
NO₃⁻	61.01	-1
Br⁻	35.45	-1
SO₄²⁻	62.01	-2
Cl⁻	96.06	-1
HCO₃⁻	79.9	-1
Ca²⁺	40.08	+2
Mg²⁺	24.31	+2
Na⁺	22.99	+1
K⁺	39.1	+1

For trace elements, milliequivalents are not used as they do not form charged ions (e.g. silica), and they cannot necessarily be used for ions that have more than one valence state, such as iron (Fe²⁺ or Fe³⁺). Calculation of CBE for this study was based on results for major cations Ca²⁺, Mg²⁺, Na⁺ and K⁺ and the anions Cl⁻, Br⁻, NO₃⁻N, SO₄²⁻ and HCO₃⁻ (Table 7). Table 8 shows monthly CBE at each piezometer (April - September). The CBE for the majority of the piezometers were greater than 3%, and therefore not suitable for Piper Diagram analysis (Horizons, 2013). Sodium analysis have a high sensibility; in general, Na⁺ concentration showed a large discrepancy over the months, but within ranges excepted from these piezometers (Rivas, 2018). Sodium has a strong influence on the CBE, as in one of the major cations in the collected samples from the Manawatu and Rangitikei River catchments. The anions concentrations instead showed consistency over time and were used for analysis.

Table 8: Cation and anions values for calculation of charge balance error (%) (CBE) at each piezometer.

Site	Depth	Piezo	Sum cations						Sum anions						Charge balance error (%)					
			April	May	June	Aug	Sept	Avg	April	May	June	Aug	Sep	Avg	April	May	June	Aug	Sep	Avg
DF	5.5	1	3.36	3.42	2.81	-	3.00	3.15	1.48	1.59	1.70	1.64	1.77	1.64	38.83	36.59	24.55	-	25.87	31.46
	7.5	2	3.88	3.47	3.28	2.09	2.20	2.98	1.82	1.70	1.96	1.71	1.91	1.82	36.07	34.17	25.15	9.97	7.07	22.49
	8.7	3	3.92	3.60	3.33	2.22	2.92	3.20	1.86	1.81	1.87	1.68	1.87	1.82	35.62	33.08	27.97	13.91	21.75	26.47
SC	3.4	1	7.45	7.10	7.02	6.44	6.96	6.99	4.47	3.99	4.22	4.40	4.30	4.28	24.96	28.01	24.91	18.81	23.62	24.06
	5.2	2	7.74	6.78	6.22	5.98	6.58	6.66	5.19	5.29	4.72	3.49	4.27	4.59	19.71	12.37	13.69	26.32	21.28	18.67
	6.4	3	9.38	8.34	9.46	9.67	10.77	9.52	3.70	3.70	4.30	5.56	6.66	4.78	43.42	38.56	37.47	26.98	23.55	34.00
CAM	4.5	1	3.61	2.83	3.02	2.58	4.13	3.24	2.29	1.58	1.70	1.34	1.77	1.73	22.41	28.51	28.10	31.82	40.04	30.18
	7.5	3	4.23	3.01	3.79	3.06	2.24	3.27	2.33	2.06	2.16	2.18	2.23	2.19	28.84	18.75	27.45	16.82	0.23	18.42
ARM	5.0	1	3.95	3.25	3.81	2.80	4.74	3.71	1.85	1.86	1.88	1.84	2.03	1.89	36.16	27.27	33.94	20.65	40.01	31.61
	6.0	2	5.08	4.01	4.40	3.78	4.83	4.42	2.44	2.32	2.40	2.61	3.05	2.56	35.15	26.66	29.37	18.21	22.69	26.41
	7.5	3	6.42	4.53	5.38	4.68	1.55	4.51	3.19	2.90	3.06	3.07	2.87	3.02	33.70	21.86	27.52	20.79	- 29.90	14.79
SR	4.5	1	1.86	3.05	1.52	1.10	1.50	1.80	0.80	0.79	0.84	0.75	0.81	0.80	40.04	58.84	28.66	18.95	29.49	35.20
	5.5	2	1.90	2.75	1.50	1.09	1.56	1.76	0.82	0.71	0.84	0.67	0.85	0.78	39.83	59.01	28.28	23.59	29.70	36.08
	6.5	3	1.96	2.54	1.51	1.11	3.61	2.14	0.83	0.73	0.87	0.66	0.88	0.79	40.24	55.05	26.92	25.27	60.93	41.68
BUR	3.6	1	2.91	3.92	2.44	1.63	1.43	2.47	1.48	1.34	1.54	1.31	2.51	1.64	21.29	50.57	23.50	19.06	20.07	26.90
	4.3	2	2.29	3.86	2.68	2.01	2.38	2.64	1.49	1.27	1.66	1.37	1.59	1.47	32.54	49.09	22.60	10.82	- 27.37	17.54
	6.1	3	2.77	3.44	2.35	1.83	2.13	2.50	1.05	1.19	1.20	1.16	0.63	1.05	45.04	48.64	32.48	22.42	0.00	29.72

3.3.3 Analytical procedures for excess N₂

Excess N₂ represents the N₂ as a result of NO₃⁻ reduction in groundwater (Weymann et al., 2008; Clague et al., 2018). The measurement of N₂ in groundwater samples represents all dissolved N₂ in the groundwater. Dissolved N₂ in groundwater has 2 origins (atmosphere and subsurface denitrification) in 3 different portions (Weymann et al., 2008; Voguel et al., 1981; Martindale et al., 2018) corresponding to:

- N₂ in equilibrium with the atmosphere from recharge water (**N₂ EQ**)
- N₂ entrapped in air bubbles (excess air) within the aquifer material that enters the aquifer during recharge (**N₂ EA**)
- N₂ from subsurface NO₃⁻ reduction (**excess N₂**).

Even though excess N₂ represents NO₃⁻ attenuation processes (subsurface denitrification, anammox and NO dismutation) it is used to assess and quantify complete subsurface denitrification in the environment (Clague et al., 2018).

Groundwater excess N₂ analysed through membrane inlet mass spectrometry (MIMS) analysis (Martindale et al., 2018) measures the total concentration of dissolved N₂ and Ar concentration in the groundwater sample. As N₂ and Ar have a specific solubility depending on temperature, a ratio can be calculated between N₂ and Ar at different temperatures (Weymann et al., 2018b). The ratio of N₂ over Ar is used to infer the concentration of N₂ EQ, N₂ EA, excess N₂ or contamination during the collection of the groundwater samples (Weymann et al., 2008b; Martindale et al., 2018). Due to the noble gas properties of Ar such as high chemical stability makes Ar as one of the best element for this kind of technique. Neon (Ne) is another noble gas being used for this analysis.

Excess N₂ samples were analysed using the MIMS analysis by the National Institute of Water and Atmospheric Research (NIWA) laboratory in Wellington using a ratio between N₂ and Ar through MIMS technique.

N₂ in equilibrium with the atmosphere (**N₂ EQ**), the N₂ from the excess air (which are air bubbles entrapped in the soil profile and aquifer material during recharge periods) (**N₂ EA**)

and N₂ from subsurface denitrification (**excess N₂**) in groundwater samples were calculated using the equations as follows (Weymann et al., 2008):

- **Excess N₂ calculation:**

$$X_{\text{ExcessN}_2} = X_{\text{N}_2\text{T}} - X_{\text{N}_2\text{EA}} - X_{\text{N}_2\text{EQ}} \quad \text{Equation 26}$$

X: Molar concentration of the parameters.

N₂ T = Total dissolved N₂ in the groundwater sample.

N₂ EA = from excess air.

N₂ EQ = Dissolved N₂ in equilibrium with the atmospheric concentration.

- N₂ from **excess air (N₂ EA)**:

$$X_{\text{N}_2\text{EA}} = (X_{\text{Ar T}} - X_{\text{Ar EQ}}) * \left(\frac{X_{\text{N}_2\text{atm}}}{X_{\text{Ar atm}}} \right) \quad \text{Equation 27}$$

N₂ atm = atmospheric mole fraction of N₂

Ar atm = atmospheric mole fraction of Ar.

Ar T = total dissolved Ar in the groundwater sample.

Ar EQ = Dissolved Ar in equilibrium with the atmospheric concentration

- **Ar in equilibrium:**

$$Ar_{\text{EQ}} = Ar_{\text{atm}} * H_{RT}^{\text{N}_2} \quad \text{Equation 28}$$

- **N₂ in equilibrium (N₂ EQ):**

$$N_{2\text{EQ}} = N_{2\text{atm}} * H_{RT}^{\text{N}_2} \quad \text{Equation 29}$$

- **Uncertainty and temperature dependence:**

Henry's law defines: "at a constant temperature the amount of dissolved gas in any liquid is proportional to the partial pressure of the gas in equilibrium with the liquid".

$$H = Ca/p \quad \text{Equation 30}$$

Here, Ca is the concentration of a species in the aqueous phase and p is the partial pressure of that species in the gas phase under equilibrium conditions.

As the solubility of Ar and N₂ is affected by the temperature, different proportions of these gases are in the shallow groundwater and in the recharge water.

Gases Ar and N₂ have a specific Henry's solubility defined via concentration (H_{cp}) in water. Therefore, the specific value for Ar and N₂ of H_{cp} are calculated. With T corrected which represent the slope generated by solubility plots at a constant temperature, values for H_{cp} temperature-dependent were calculated with the constants (Fernandez-Pirini et al., 2003 cited in Sanders, 2015):

Table 9: Henry's law constant in water for N₂ and Ar in water.

Element	H_{cp} (mol (m ³ Pa) ⁻¹)	T corrected	Atmospheric molar fraction
Ar	1.40 10 ⁻⁵	1400	0.0093
N ₂	6.50 10 ⁻⁶	1200	0.7801

Despite the theory for excess N₂ calculation, there is still uncertainty when calculating the solubility of these gases as the recharge temperature of groundwater in the aquifer remains unknown (Weymann et al., 2008). Therefore, an estimate of the groundwater recharge temperature is required (Clague et al., 2018). However, the recharge water temperature can be calculated with the measurement of two noble gases (i.e. Ar and Ne) (Martindale et al., 2018).

In this study, the recharge water temperature was defined using the temperature of groundwater at the sampling time. The estimated recharge temperature ranged between the groundwater sample temperature and the mean air temperature for the study period (February to September 2018) (Clague et al., 2018) with slight uncertainty adjustments until positives values for excess N₂ max obtained.

A specific temperature was selected for each month (June, August and September) at each piezometer (Table 10). The temperature selected for the excess N₂ analysis at sites DF (1, 2, 3); ARM (1,2,3); CAM 3; SR (1,2,3) and BUR (1,2,3) were estimated lower than the temperature of the groundwater samples, except for August samples at the piezometers SC 1 and 3; and for September samples at the piezometers SC 1 and 3; and ARM 1.

Table 10: In-situ temperature (°C) of groundwater samples and estimates of groundwater recharge temperature used at each site for excess N₂ calculations.

Site	Piezo	September		August		June	
		Sample	Analysis	Sample	Analysis	Sample	Analysis
DF	1	15.2	14.0	13.6	13.5	15.2	14.0
	2	15.1	14.0	13.8	13.5	15.0	14.0
	3	14.4	14.0	13.5	13.5	15.5	14.0
SC	1	12.9	14.5	12.6	14.5	14.1	14.0
	2	13.5	14.5	12.8	14.5	15.4	14.0
ARM	1	13.8	14.0	14.0	14.0	15.0	14.0
	2	14.1	14.0	14.5	14.0	14.7	14.0
	3	14.2	14.0	14.2	14.0	15.0	14.0
CAM	3	14.3	13.5	14.6	13.5	14.7	13.5
SR	1	13.0	12.5	12.8	12.5	14.9	14.0
	2	13.2	12.5	12.9	12.5	14.4	14.0
	3	13.3	12.5	13.2	12.5	14.4	14.0
BUR	1	13.2	11.0	13.6	11.0	15.0	12.0
	2	12.6	11.0	13.2	11.0	14.9	12.0
	3	-	-	12.9	11.0	14.8	12.0

3.4 Push-pull test

In addition to the monthly groundwater monitoring, a set of 6 push-pull tests were conducted to gain insights into the dynamics of the denitrification process at the study sites. The push-pull tests (6 push-pull test in total) were carried out in the deepest piezometer at each site (DF 3, CAM 3, ARM 3, SR 3 and BUR 3), except for site SC where the push-pull test was conducted in piezometer SC 2.

The push-pull test involves two phases, during the first phase groundwater from the aquifer is extracted through a pumping system at a pumping rate of approximately 1 litre per minute. In the second phase, groundwater samples were collected at a discrete time step and stored for further analysis.

3.4.1 Collection of groundwater sample

Based on previous studies (Collins et al, 2017, Rivas et al., 2014), a 100 L of shallow groundwater was extracted for the push-pull tests. A peristaltic pump and a multi-parameter water quality probe (Smart troll) were used for the collection of the sample as described earlier (Section 3.2). The groundwater was pumped to 5 collapsible bags (20 L each) previously evacuated of any air, except for the CAM site only 3 bags (20 L each) were collected due to a slow groundwater discharge rate. The collapsible bags reduce contact between the groundwater (sample) and the atmosphere. After being filled, the bags were transported to a cold storage set at 12 °C (in order to keep the temperature as close to environmental conditions). The bags were stored for no more than two days until the second phase of the push-pull test was conducted.

3.4.2 Preparation and injection of test solution in the piezometer

The test solution was prepared in situ by adding 2.1651 g of potassium nitrate (KNO_3) and 0.4468 g of KBr to each of the 20 L bags to achieve a final concentration of 15 $\text{mg-NO}_3^- \text{N} \cdot \text{L}^{-1}$ and 15 $\text{mg-Br}^- \text{L}^{-1}$. The active compound (KNO_3) and the tracer were added in the field to avoid losses of NO_3^- and any premature chemical reactions outside the aquifer. After adding the reagent and tracer, the bags were shaken to ensure homogeneity. The test solution samples from each bag were collected to confirm the concentration of the reagent and the tracer. In these tests, no acetylene was added to the test solution to stop re reduction from N_2O to N_2 during the test. Instead, a set of groundwater samples were collected to analyse dissolved $\text{N}_2\text{O-N}$ and N_2 during the tests. Groundwater dissolved $\text{N}_2\text{O-N}$ and N_2 concentrations were analysed on a Shimadzu 2010-Plus gas chromatograph system (Shimadzu Corp, Kyoto, Japan), with an electron capture detector (ECD), flame-ionization detector (FID) and thermal conductivity detector (TCD) (McMillan et al., 2014).



Figure 7: An example of groundwater being injected for push-pull test at the ARM site.

The test solution (60 – 100 L) was injected using a peristaltic pump at a rate of approximately 1 litre per minute (Collins et al., 2016). The first phase (Figure 7) was followed by the second phase of the “pull”, in which the groundwater samples were extracted for analysis of the reactant and tracer.

3.4.3 Extraction of test solution from the piezometer

After the 100L of groundwater were “pushed”, a gap of 30 minutes was allowed for the test solution to infiltrate and mix from the base of the piezometer to the surroundings of it. The “pull” collection of groundwater samples was conducted at a discrete time step with the sample collected at 30, 60, 90, 120, 180, 240, 300 and 330 minutes.

3.4.4 Analytical procedures for dilution rate

The analytical procedures for chemical, dissolved gasses and excess N₂ of samples collected during the push-pull tests were similar as described above for the monthly groundwater sampling. The results obtained were interpreted by plotting the concentrations

of NO_3^- -N and Br^- over the time of analysis (330 min) in order to identify the denitrification trend. Dilution factor that occurs naturally after pushing the sample into the piezometer needs to be accounted for.

To include the effects of dilution on NO_3^- -N concentration that occurs naturally within the piezometer, the concentrations of NO_3^- -N were adjusted according to Equation 31 as follows:

$$C_{\text{sol}*} = \frac{C_{\text{sol}}}{[C/\text{Co}]_{\text{tr}}} \quad \text{Equation 31}$$

Where:

$C_{\text{sol}*}$ = adjusted dilution of NO_3^- – N in the sample extracted at time t.

$[C/\text{Co}]_{\text{tr}}$ = relative Br^- concentration in the sample extrated at time t.

The push-pull tests provide the information to gain insights into denitrification process, and to quantify the denitrification rate and its reaction order. According to Istok, (2013), reduction of NO_3^- -N is zero order, when the concentration NO_3^- -N decreases linearly over time. The reaction rate of a zero-order reaction is constant over time and independent from NO_3^- -N concentration. Therefore, subsurface denitrification rates at the study sites were calculated directly from dilution corrected NO_3^- -N concentrations measured during “pull” phase of the push-pull test.

3.5 Data analysis

All data collected in the monthly campaign and in situ experiments (push-pull tests) for shallow groundwater chemistry, including dissolved gases analysis, were analysed using Microsoft Excel. Results obtain for chemical analysis and dissolved gases analysis are presented with the standard error of the mean (SEM) from triplicates of samples. Linear regression was applied to the concentration of NO_3^- -N, excess N_2 and N_2O -N over time, to calculate NO_3^- attenuation rate, complete subsurface denitrification and partial subsurface denitrification rate respectively. Detailed results are shown in appendices 1, 2, 3 and 4.

Chapter 4. Results and discussion

This chapter presents results of the water quality parameter found over February – September 2018 in the Manawatu and Rangitikei River catchments. Water quality parameters were used to assess the redox condition of groundwater in the study area (17 piezometers). It presents monthly average results for groundwater chemistry (in-situ parameters, cations and anions) and for dissolved gas analysis. It also includes results for NO_3^- -N, NH_4^+ -N, NO_2^- -N, N_2O -N and excess N_2 measurements. Finally, presents the push-pull test results conducted at each site to quantify the potential for NO_3^- -N attenuation and reduction (complete and partial subsurface denitrification) through analytical analysis.

4.1 Variation in groundwater redox conditions

Cations and anions present in the aquifers have different oxidation states. These confer characteristic properties that affect the solubility during the interaction and formation of compounds. Reactions in which changes in the oxidation state can occur facilitate the solubilization of different elements. Reactions of this type are oxidation of sulphides, reduction of sulphates, oxidation-reduction of iron and manganese (electron donors in denitrification process), NO_3^- reduction and nitrification. Oxidation-reduction reactions in groundwater are catalysed by a large number of bacterial and archaeal enzymes.

Groundwater redox conditions were defined based on McMahon and Chapelle (2008) criteria (Table 11), using DO as the main indicator of groundwater redox status. Table 12 shows monthly redox status and processes across the study sites. When DO concentration is lower than 0.5 mg L^{-1} the sample is classified as anoxic. While greater than 0.5 mg L^{-1} , is classified as mixed or oxic and is depending on the other parameters. The criteria also include NO_3^- -N, Mn^{2+} , Fe^{2+} and SO_4^{2-} in assessing the groundwater redox conditions.

Table 11: The threshold concentration for identifying redox conditions in shallow groundwater samples (McMahon and Chapelle, 2008).

Threshold Concentrations for Identifying Redox Processes in Regional Aquifer Systems						
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

While collecting the samples; in situ measurements for groundwater redox potential (*Eh*) or oxidation-reduction potential (ORP) were monitored. ORP values (not recorded) indicate existing reducing conditions (150 – 300 mV) (EPA, 2017) within the piezometers at sites DF (1, 2, 3), SC (1, 2, 3), ARM (1, 2, 3) and CAM 3. Groundwater *Eh* is dependent on time and space (among other factors) due to groundwater movement, quantity and chemical composition of external inputs (e.g. effluents, surplus irrigation, fertilizer and nutrient inputs) (Christensen et al., 2000). The groundwater redox condition depends on O₂ availability and bacterial activity which influence the oxidation-reduction capacity in the subsurface environment. The degree of occurrence for the oxidation-reduction transformations is also affected by the groundwater recharge and flow rates in the environment (Ioka et al., 2017).

Table 12: Monthly redox status assignment for groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments.

			Redox Variables						
			DO	NO ₃ ⁻ -N	Mn ²⁺	Fe ²⁺	SO ₄ ²⁻		
			Threshold values	0.5	0.5	0.05	0.1	0.5	
Site	Piezo	Month	mg L ⁻¹					Redox Status	Redox Process
DF	1	February	1.43	0.01	0.01	0.02	5.15	Oxic	O ₂
	1	March	2.53	0.16	0.01	0.03	7.35	Oxic	O ₂
	1	April	4.54	0.19	0.01	0.09	3.66	Oxic	O ₂
	1	May	0.91	0.08	0.07	0.38	2.32	Mixed	O ₂ -Fe ³⁺ /SO ₄
	1	June	2.96	0.51	0.12	0.08	3.13	Mixed	O ₂ -Mn ⁴⁺
	1	August	1.90	3.75	0.18	3.35	0.27	Mixed	O ₂ -CH ₄ gen
	1	September	1.89	1.10	0.01	0.04	3.86	Oxic	O ₂
DF	2	February	0.93	0.01	0.19	3.74	2.29	Mixed	O ₂ -Fe ³⁺ /SO ₄
	2	March	0.06	0.02	0.18	3.67	2.23	Anoxic	Fe ³⁺ /SO ₄
	2	April	0.30	0.05	0.22	3.83	2.09	Anoxic	Fe ³⁺ /SO ₄
	2	May	0.10	0.10	0.18	3.78	1.93	Anoxic	Fe ³⁺ /SO ₄
	2	June	0.66	0.04	0.29	3.39	1.95	Mixed	O ₂ -Fe ³⁺ /SO ₄
	2	August	0.16	0.02	0.01	0.03	0.31	Sub-oxic	Sub-oxic
	2	September	0.21	0.02	0.08	0.02	1.81	Anoxic	Mn ⁴⁺
DF	3	February	0.21	0.02	0.21	3.75	2.25	Anoxic	Fe ³⁺ /SO ₄
	3	March	0.10	0.01	0.19	3.86	2.14	Anoxic	Fe ³⁺ /SO ₄
	3	April	0.18	0.02	0.24	4.09	1.95	Anoxic	Fe ³⁺ /SO ₄
	3	May	0.12	0.01	0.19	3.93	1.86	Anoxic	Fe ³⁺ /SO ₄
	3	June	2.96	0.03	0.29	3.41	1.91	Mixed	O ₂ -Fe ³⁺ /SO ₄
	3	August	1.90	0.04	0.16	3.15	0.31	Mixed	O ₂ -CH ₄ gen
	3	September	0.16	0.02	0.18	3.25	2.07	Anoxic	Fe ³⁺ /SO ₄
SC	1	February	0.12	0.01	0.84	6.58	3.36	Anoxic	Fe ³⁺ /SO ₄
	1	March	0.06	0.01	0.78	6.78	3.57	Anoxic	Fe ³⁺ /SO ₄
	1	April	0.08	0.16	1.04	7.72	3.51	Anoxic	Fe ³⁺ /SO ₄
	1	May	2.00	0.04	0.81	6.80	2.86	Mixed	O ₂ -Fe ³⁺ /SO ₄

	1	June	1.43	0.01	0.91	7.27	2.18	Mixed	O ₂ -Fe ³⁺ /SO ₄
	1	August	0.11	0.04	0.01	0.06	0.76	Sub-oxic	Sub-oxic
	1	September	0.57	0.07	0.85	7.35	1.02	Mixed	O ₂ -Fe ³⁺ /SO ₄
SC	2	February	0.08	0.02	0.21	4.89	13.74	Anoxic	Fe ³⁺ /SO ₄
	2	March	0.07	0.01	0.18	4.28	15.85	Anoxic	Fe ³⁺ /SO ₄
	2	April	0.11	0.22	0.27	4.16	17.40	Anoxic	Fe ³⁺ /SO ₄
	2	May	0.21	0.03	0.18	4.30	15.18	Anoxic	Fe ³⁺ /SO ₄
	2	June	1.81	0.02	0.31	3.91	15.50	Mixed	O ₂ -Fe ³⁺ /SO ₄
	2	August	0.11	0.03	0.01	0.04	0.53	Suboxic	Suboxic
	2	September	0.13	0.05	0.23	4.67	16.20	Anoxic	Fe ³⁺ /SO ₄
SC	3	February	0.30	0.02	1.00	0.86	9.70	Anoxic	Fe ³⁺ /SO ₄
	3	March	0.59	0.05	0.29	0.70	11.57	Mixed	O ₂ -Fe ³⁺ /SO ₄
	3	April	0.85	0.98	0.35	1.17	10.87	Mixed	O ₂ -Fe ³⁺ /SO ₄
	3	May	1.42	3.50	0.27	0.99	9.80	Mixed	O ₂ -Fe ³⁺ /SO ₄
	3	June	4.27	5.88	0.35	0.89	16.28	Mixed	O ₂ -Fe ³⁺ /SO ₄
	3	August	1.43	22.56	0.01	0.16	0.50	Mixed	O ₂ -CH ₄ gen
	3	September	0.09	15.92	0.13	0.15	24.19	Mixed*	NO ₃ -Fe ³⁺ /SO ₄
CAM	1	February	7.65	0.01	0.25	0.73	0.01	Mixed	O ₂ -CH ₄ gen
	1	March	3.65	5.42	0.31	0.07	9.35	Mixed	O ₂ -Mn ⁴⁺
	1	April	3.27	6.71	0.20	0.27	10.86	Mixed	O ₂ -Fe ³⁺ /SO ₄
	1	May	3.90	5.67	0.06	0.05	11.74	Mixed	O ₂ -Mn ⁴⁺
	1	June	7.19	5.94	0.14	0.03	13.14	Mixed	O ₂ -Mn ⁴⁺
	1	August	4.54	6.21	0.04	0.05	0.29	Oxic	O ₂
	1	September	4.07	6.69	0.03	0.04	12.63	Oxic	O ₂
CAM	3	February	0.16	0.06	0.92	0.29	3.01	Anoxic	Fe ³⁺ /SO ₄
	3	March	0.24	0.01	0.91	0.31	3.03	Anoxic	Fe ³⁺ /SO ₄
	3	April	0.20	0.01	1.38	0.59	3.01	Anoxic	Fe ³⁺ /SO ₄
	3	May	0.26	0.31	0.94	0.18	2.84	Anoxic	Fe ³⁺ /SO ₄
	3	June	0.64	0.11	1.02	0.20	3.08	Mixed	O ₂ -Fe ³⁺ /SO ₄
	3	August	0.15	0.12	0.89	0.18	0.37	Anoxic	CH ₄ gen
	3	September	1.21	0.08	0.91	0.16	3.11	Mixed	O ₂ -Fe ³⁺ /SO ₄
ARM	1	February	0.13	0.01	0.10	3.70	5.94	Anoxic	Fe ³⁺ /SO ₄
	1	March	0.08	0.01	0.09	3.59	5.52	Anoxic	Fe ³⁺ /SO ₄

	1	April	0.10	0.03	0.12	4.47	4.48	Anoxic	Fe ³⁺ /SO ₄
	1	May	0.16	0.01	0.11	4.01	3.07	Anoxic	Fe ³⁺ /SO ₄
	1	June	0.95	0.03	0.22	3.69	3.99	Mixed	O ₂ -Fe ³⁺ /SO ₄
	1	August	0.10	0.04	0.09	0.32	0.34	Anoxic	CH ₄ gen
	1	September	0.11	0.04	0.10	3.55	6.15	Anoxic	Fe ³⁺ /SO ₄
ARM	2	February	0.18	0.03	0.10	3.45	3.33	Anoxic	Fe ³⁺ /SO ₄
	2	March	0.06	0.01	0.08	3.56	3.19	Anoxic	Fe ³⁺ /SO ₄
	2	April	0.05	0.02	0.11	3.89	1.32	Anoxic	Fe ³⁺ /SO ₄
	2	May	0.14	0.03	0.08	3.81	1.30	Anoxic	Fe ³⁺ /SO ₄
	2	June	0.99	0.01	0.24	3.28	1.85	Mixed	O ₂ -Fe ³⁺ /SO ₄
	2	August	0.12	0.01	0.80	6.79	0.43	Anoxic	CH ₄ gen
	2	September	0.09	0.02	0.09	3.64	0.54	Anoxic	Fe ³⁺ /SO ₄
ARM	3	February	0.08	0.01	0.05	0.80	0.03	Anoxic	CH ₄ gen
	3	March	0.09	0.02	0.05	0.72	0.04	Anoxic	CH ₄ gen
	3	April	0.04	0.02	0.07	0.88	0.02	Anoxic	CH ₄ gen
	3	May	0.11	0.02	0.06	0.88	0.02	Anoxic	CH ₄ gen
	3	June	0.49	0.01	0.17	0.93	0.01	Anoxic	CH ₄ gen
	3	August	0.22	0.03	0.28	5.62	0.52	Anoxic	Fe ³⁺ /SO ₄
	3	September	0.09	0.04	0.05	0.76	0.06	Anoxic	CH ₄ gen
SR	1	February	7.24	3.73	0.01	0.01	4.53	Oxic	O ₂
	1	March	7.91	3.78	0.01	0.01	4.55	Oxic	O ₂
	1	April	8.30	3.29	0.01	0.04	5.17	Oxic	O ₂
	1	May	9.36	2.79	0.01	0.03	5.18	Oxic	O ₂
	1	June	7.98	3.22	0.09	0.06	5.34	Mixed	O ₂ -Mn ⁴⁺
	1	August	8.67	3.74	0.01	0.13	0.23	Mixed	O ₂ -CH ₄ gen
	1	September	8.75	3.78	0.03	0.06	4.84	Oxic	O ₂
SR	2	February	6.93	3.74	0.01	0.01	4.56	Oxic	O ₂
	2	March	6.77	3.82	0.01	0.01	4.56	Oxic	O ₂
	2	April	8.47	3.40	0.01	0.11	4.99	Mixed	O ₂ -Fe ³⁺ /SO ₄
	2	May	9.20	2.88	0.01	0.10	5.07	Mixed	O ₂ -Fe ³⁺ /SO ₄
	2	June	7.29	3.21	0.10	0.13	5.27	Mixed	O ₂ -Fe ³⁺ /SO ₄
	2	August	7.85	3.61	0.01	0.06	0.23	Oxic	O ₂
	2	September	8.69	3.71	0.01	0.04	4.96	Oxic	O ₂

SR	3	February	7.04	3.83	0.01	0.01	4.51	Oxic	O ₂
	3	March	7.09	3.87	0.01	0.02	4.52	Oxic	O ₂
	3	April	8.46	3.39	0.01	0.14	5.01	Mixed	O ₂ -Fe ³⁺ /SO ₄
	3	May	8.86	3.08	0.01	0.22	4.99	Mixed	O ₂ -Fe ³⁺ /SO ₄
	3	June	6.76	3.13	0.10	0.04	5.21	Mixed	O ₂ -Mn ⁴⁺
	3	August	8.56	3.59	0.01	0.06	0.22	Oxic	O ₂
	3	September	8.63	3.84	0.01	0.02	4.69	Oxic	O ₂
BUR	1	February	1.85	0.00	0.00	0.00	0.00	Oxic	O ₂
	1	April	4.29	5.86	0.01	0.04	6.79	Oxic	O ₂
	1	May	4.67	5.74	0.01	0.02	7.34	Oxic	O ₂
	1	June	6.15	7.28	0.11	0.06	6.97	Mixed	O ₂ -Mn ⁴⁺
	1	August	5.19	6.69	0.05	0.76	0.25	Mixed	O ₂ -CH ₄ gen
BUR	2	February	5.83	2.63	0.01	0.01	6.21	Oxic	O ₂
	2	March	5.85	2.40	0.01	0.01	6.00	Oxic	O ₂
	2	April	6.29	5.00	0.03	0.32	5.87	Mixed	O ₂ -Fe ³⁺ /SO ₄
	2	May	5.31	4.65	0.01	0.08	4.38	Oxic	O ₂
	2	June	7.29	7.89	0.11	0.39	7.51	Mixed	O ₂ -Fe ³⁺ /SO ₄
	2	August	4.78	6.47	0.09	3.59	0.27	Mixed	O ₂ -CH ₄ gen
	2	September	4.39	5.80	0.01	0.01	7.45	Oxic	O ₂
BUR	3	February	1.85	0.24	0.01	0.01	2.82	Oxic	O ₂
	3	March	3.58	0.74	0.01	0.01	3.30	Oxic	O ₂
	3	April	4.29	2.69	0.01	0.11	4.88	Mixed	O ₂ -Fe ³⁺ /SO ₄
	3	May	4.67	5.24	0.01	0.03	6.08	Oxic	O ₂
	3	June	6.15	5.27	0.10	0.03	5.68	Mixed	O ₂ -Mn ⁴⁺
	3	August	3.88	5.86	0.12	4.09	0.25	Mixed	O ₂ -CH ₄ gen
	3	September	3.43	5.06	0.01	0.04	5.25	Oxic	O ₂

The redox classification (Table 12) shows the monthly redox category, main analyte concentration and principal redox process for each piezometer at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

The piezometer DF 1 presented oxic status until April, then a mixed status until June and oxic again in September with varying redox processes (Table 12). The **overall** redox status

for piezometer **DF 1** is considered **oxic** (Table 13). The piezometers DF 2 and DF 3 presented anoxic redox status when DO concentrations were below the threshold ($< 0.5 \text{ mg L}^{-1}$). However, piezometers DF 2 (February and June); and at DF 3 (June and August) presented mixed conditions when DO was greater than 0.5 mg L^{-1} . The **overall** redox status for piezometers **DF 2** and **DF 3** are considered **anoxic** with $\text{Fe}^{3+}/\text{SO}_4$ as dominant redox process (Table 13).

Site SC showed variability on redox status over the time of the study (Table 12). At piezometer SC 1 anoxic conditions were found with low DO concentrations ($< 0.5 \text{ mg L}^{-1}$) during Autumn (February — March). At piezometer SC 1, mixed redox conditions were found when DO concentrations were greater than the threshold (as in May, June and September). The **overall** redox status for piezometers **SC 1** and **SC 2** are considered **anoxic** with $\text{Fe}^{3+}/\text{SO}_4$ as dominant redox process (Table 13). Overall the piezometer SC 2 presented anoxic conditions ($\text{DO} < 0.5 \text{ mg L}^{-1}$) except for June where DO level was greater than 0.5 mg L^{-1} . **Overall** piezometer **SC 3** showed **mixed** redox status (Table 13) except in June (anoxic status) when DO level was below 0.5 mg L^{-1} . The main redox process at SC 3 was $\text{O}_2\text{-Fe}^{3+}/\text{SO}_4$.

The piezometer CAM 1 showed mixed redox status from February to June, then oxic status in August and September with varying redox processes (Table 12). Dissolved oxygen concentrations were greater than 3 mg L^{-1} during the study. Piezometer CAM 3 showed anoxic redox status when DO levels were below the threshold ($< 0.5 \text{ mg L}^{-1}$) and mixed status in June when DO levels were greater than the threshold. At piezometer CAM 3, the predominant redox process observed was $\text{Fe}^{3+}/\text{SO}_4$. **Overall** piezometers **CAM 1** and **CAM 3** showed **mixed** and **anoxic** redox status respectively (Table 14).

Overall, the piezometers **ARM 1, 2 and 3** presented **anoxic** redox status over the period of February – September 2018 (Table 14). The piezometers ARM 1 and ARM 2 showed mixed redox status only in June when the DO levels were greater than 0.5 mg L^{-1} . The main redox process observed at piezometer ARM 1 and ARM 2 was $\text{Fe}^{3+}/\text{SO}_4$. In comparison with piezometer ARM 3 the main redox process was methanogenesis (CH_4gen) (Table 12).

Site SR showed DO concentrations greater than 6 mg L⁻¹ during the study (Table 12) and **overall oxic** redox status (Table 15). The piezometer **SR 1** presented oxic status until May, then a mixed status in June, August and September; with O₂ reduction as main redox processes. The piezometers **SR 2** and **SR 3** showed oxic redox status on February, March, August and September. While mixed status in April, May and June when Fe²⁺ concentrations were greater than the threshold (> 0.1 mg L⁻¹).

Site BUR showed variability on redox status over the time of the study (Table 12). The 3 piezometers presented concentrations of DO greater than 1 mg L⁻¹. Overall **BUR 1, 2 and 3** showed **oxic** redox status (Table 15). At piezometers **BUR 2** and **BUR 3** mixed redox status were found when Mn²⁺ or Fe²⁺ concentrations were over the threshold (0.05 and 0.1 mg L⁻¹ respectively).

Sites showing anoxic conditions appear to be favourable for subsurface denitrification, while piezometers varying between oxic and mixed appear to be less favourable for subsurface denitrification. Which is corroborated with NO₃⁻-N accumulation (> 5 mg L⁻¹) showed at the piezometer CAM 1, SR 1, 2, 3 and BUR 1, 2 and 3.

Table 13: Summary of redox status by month (February — September) at sites DF and SC.

	DF 1	DF 2	DF 3	SC 1	SC 2	SC 3
February	Oxic	Mixed	Anoxic	Anoxic	Anoxic	Anoxic
March	Oxic	Anoxic	Anoxic	Anoxic	Anoxic	Mixed
April	Oxic	Anoxic	Anoxic	Anoxic	Anoxic	Mixed
May	Mixed	Anoxic	Anoxic	Mixed	Anoxic	Mixed
June	Mixed	Mixed	Mixed	Mixed	Mixed	Mixed
August	Mixed	Suboxic	Mixed	Suboxic	Suboxic	Mixed
September	Oxic	Anoxic	Anoxic	Mixed	Anoxic	Mixed
Overall	Oxic	Anoxic	Anoxic	Anoxic	Anoxic	Mixed

Table 14: Summary of redox status by month (February — September) at sites CAM and ARM.

	CAM 1	CAM 3	ARM 1	ARM 2	ARM 3
February	Mixed	Anoxic	Anoxic	Anoxic	Anoxic
March	Mixed	Anoxic	Anoxic	Anoxic	Anoxic
April	Mixed	Anoxic	Anoxic	Anoxic	Anoxic
May	Mixed	Anoxic	Anoxic	Anoxic	Anoxic
June	Mixed	Mixed	Mixed	Mixed	Anoxic
August	Oxic	Anoxic	Anoxic	Anoxic	Anoxic
September	Oxic	Mixed	Anoxic	Anoxic	Anoxic
Overall	Mixed	Anoxic	Anoxic	Anoxic	Anoxic

Table 15: Summary of redox status by month (February — September) at sites SR and BUR.

	SR 1	SR 2	SR 3	BUR 1	BUR 2	BUR 3
February	Oxic	Oxic	Oxic	Oxic	Oxic	Oxic
March	Oxic	Oxic	Oxic	-	Oxic	Oxic
April	Oxic	Mixed	Mixed	Oxic	Mixed	Mixed
May	Oxic	Mixed	Mixed	Oxic	Oxic	Oxic
June	Mixed	Mixed	Mixed	Mixed	Mixed	Mixed
August	Mixed	Oxic	Oxic	Mixed	Mixed	Mixed
September	Oxic	Oxic	Oxic	-	Oxic	Oxic
Overall	Oxic	Oxic	Oxic	Oxic	Oxic	Oxic

The groundwater redox classification (Table 13 — 15) shows the redox category and principal redox process for each piezometer. Values represent the average of monthly values (7 months). Piezometers DF 2 and 3; SC 1 and 2; CAM 3; and ARM 1 and 2 complied with all conditions for anoxic redox status overall, with less than 0.5 mg L⁻¹ of DO and Fe³⁺/SO₄ as main redox process. The piezometer ARM 3 also showed an overall anoxic redox status; it differs from other piezometers as methanogenesis is the main redox process. The piezometers DF 1, SR 1, 2 and 3; and BUR 1, 2 and 3; presented oxic conditions with varying redox processes. Groundwater sample from piezometers SC 3; and CAM 1 presented a mixed redox status. This indicates that one or more of the conditions were not met for oxic or anoxic redox status.

Overall, the results suggested a spatially and slightly temporal (monthly) variable groundwater redox conditions between the piezometers and sites. Overall, the piezometers DF 2, 3; SC 1, 2; CAM 3; ARM 1, 2 and 3 showed anoxic redox status. Only piezometers SC 3 and CAM 1 presented overall mixed redox condition. While the piezometers DF 1; SR 1, 2, 3; BUR 1, 2 and 3 indicated overall oxic conditions.

4.2 Groundwater chemistry

Figures 8 – 16, in this section, presents variations in groundwater chemistry observed under different redox conditions across the study sites. Groundwater chemistry combined with redox status was used to assess the suitability of each piezometer for subsurface denitrification.

4.2.1 In situ measurements

In situ parameters including DO, EC and pH (Figure 8, 9 and 10 respectively) were measured. Each plot represents the average of 7 months of analysis. Monthly samples were collected over the study; therefore, the error bars on the bar plots represent the relative variability (SEM) of the parameters between months. A higher error bar indicates higher variability obtain during the period of study. Individual monthly results are shown in appendix 1.

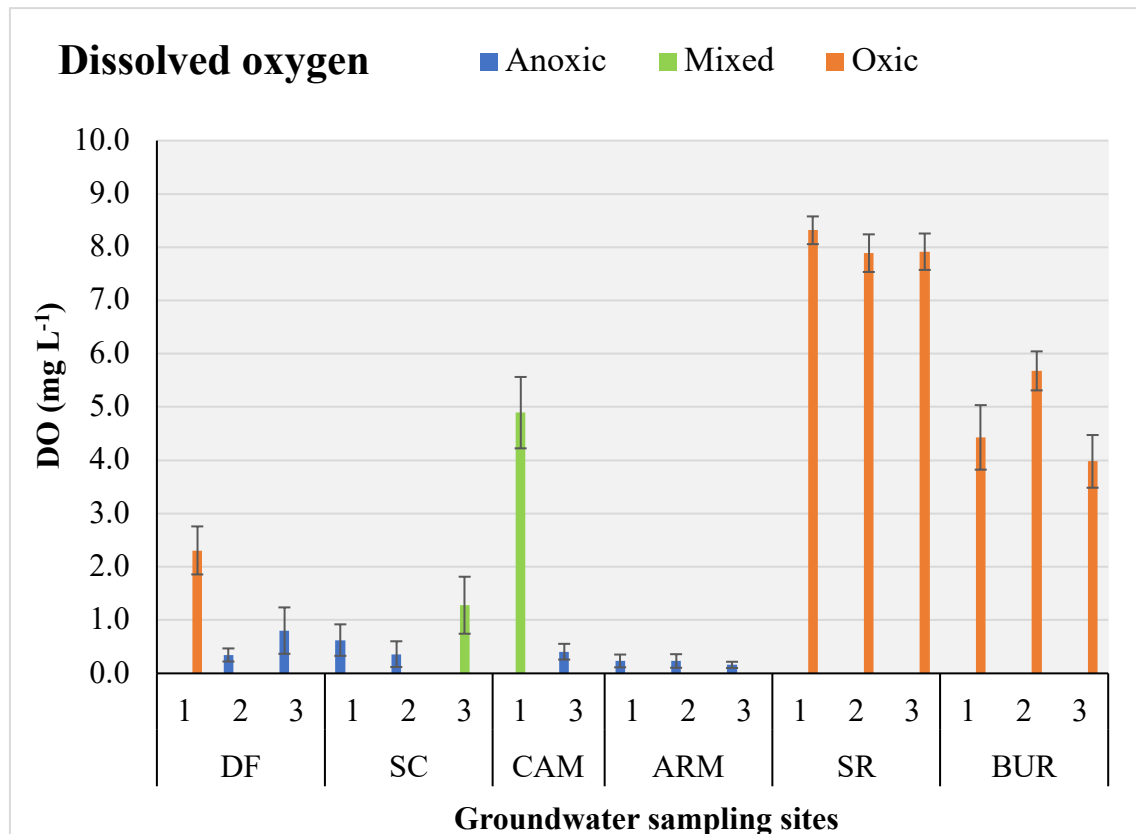


Figure 8: Dissolved oxygen content in groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments. Each bar represents average value from February to September 2018 ($n=7 \pm \text{SEM}$).

The piezometers DF 2, 3; SC 1, 2; CAM 3; and ARM 1, 2 and 3 presented reducing conditions with low average DO concentrations ranging from 0.16 to 0.8 mg L⁻¹. The piezometer SC 1 showed some variability over the study presenting DO values ranging from 0.06 up to 2 mg L⁻¹. The piezometers SC 3 and CAM 1 showed DO variability February — March ranging from 0.09 to 4.27 mg L⁻¹ and 3.27 to 7.65 mg L⁻¹ respectively. Variability in **DO** measurements is expected at piezometers with mixed redox status. The piezometers DF 1; SR 1, 2, 3; BUR 1, 2 and 3 showed relatively higher DO concentrations indicating oxidizing conditions (ranging from 2.31 to 8.32 mg L⁻¹). The results obtained are similar with ones obtain by Horizons regional council (2013) were sites closest to the coast present reducing conditions in contrast with the sites located inland (SR and BUR) that showed oxidizing conditions.

Piezometers that showed **oxic** and **mixed** conditions (DF 1, SC 3, CAM 1, SR 1, 2, 3; BUR 1, 2 and 3) showed **DO** concentrations less favourable for subsurface denitrification (> 2 mg L⁻¹) (Rivett et al., 2008; Rivas et al., 2014). In contrast, the piezometers with **anoxic**

conditions (DF 2, 3; SC 1, 2; CAM 3; ARM 1, 2 and 3) showed suitable DO concentrations for subsurface denitrification ($< 2 \text{ mg L}^{-1}$) (Rivett et al., 2008; Rivas et al., 2014). It is interesting to note the difference in DO values between piezometer 1 and 3 at CAM site. Even though the piezometers CAM 1 and CAM 3 are less than 4 meters apart and differ in its depth only by 3 m (Table 3), the average DO was recorded more than 10 times at piezometer CAM 1 (4.89 mg L^{-1}) as compared to CAM 3 (0.41 mg L^{-1}). This highlights the influence of hydrogeological settings on shallow groundwater chemistry.

There is evidence of an existing old drainage channel gravel at this site (Rivas, 2018). There are some indications suggesting that piezometer CAM 3 reach the drainage channel while being installed. During the groundwater sampling we observed relatively faster groundwater flow rates at piezometer CAM 3 indicating the sediments of relatively higher hydraulic conductivity and/or low porosity. While relatively much slow groundwater flow rates at piezometer CAM 1; suggests the sediments with low hydraulic conductivity and/or high porosity. A gravel channel has higher hydraulic conductivity, allowing faster recharge and percolation of groundwater while piezometer CAM 1 was placed within an area of low hydraulic conductivity, hence slow groundwater flow is the surrounding sediments.

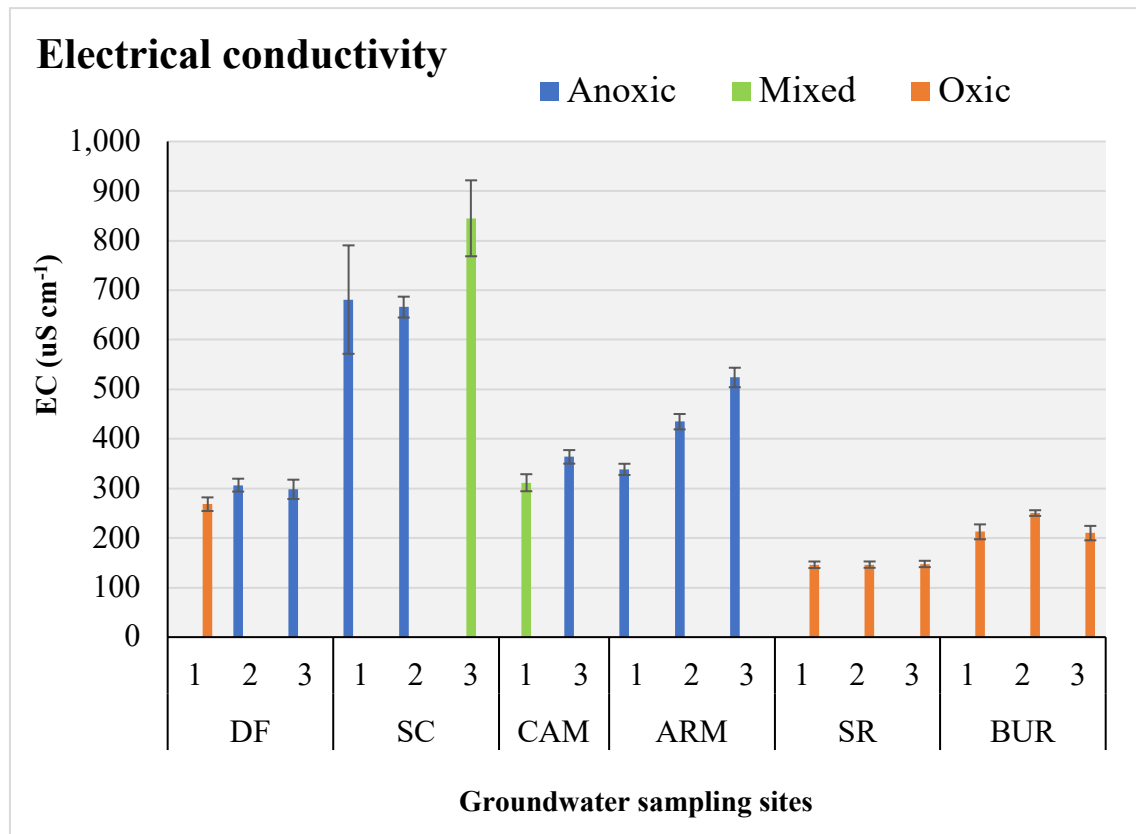


Figure 9: Electrical conductivity in groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments. Each bar represents average value from February to September 2018 ($n=7 \pm \text{SEM}$).

The monthly average groundwater temperature at each piezometer was stable ranging from 14 to 16 °C (data not shown) from February to September. In contrast, the average electrical conductivity (EC) showed a high variability ranging from 146.01 $\mu\text{S cm}^{-1}$ at SR 1, to 845.03 $\mu\text{S cm}^{-1}$ at piezometer SC 3 (Figure 9). A higher level of EC indicates a higher concentration of dissolved salts, and therefore more total suspended sediments (TSD). The results of EC are negatively correlated with DO results (Table 18). The piezometers SR 1, 2, 3; BUR 1, 2 and 3 presented the lowest EC values ranging from 146.01 to 250.31 $\mu\text{S cm}^{-1}$ (Figure 9). The piezometers at site SC have the highest values of EC; ranging from almost 600 $\mu\text{S cm}^{-1}$ to more than 1000 $\mu\text{S cm}^{-1}$. It suggests that groundwater from site SC has been in contact with parental rock and sediments for a longer period of time, allowing the dissolution of minerals (Rivas 2018, Horizons, 2013). The results obtained for EC are expected from shallow groundwater in the Manawatu and Rangitikei River catchments were in general groundwater shows levels below 800 $\mu\text{S cm}^{-1}$ (Horizons, 2013).

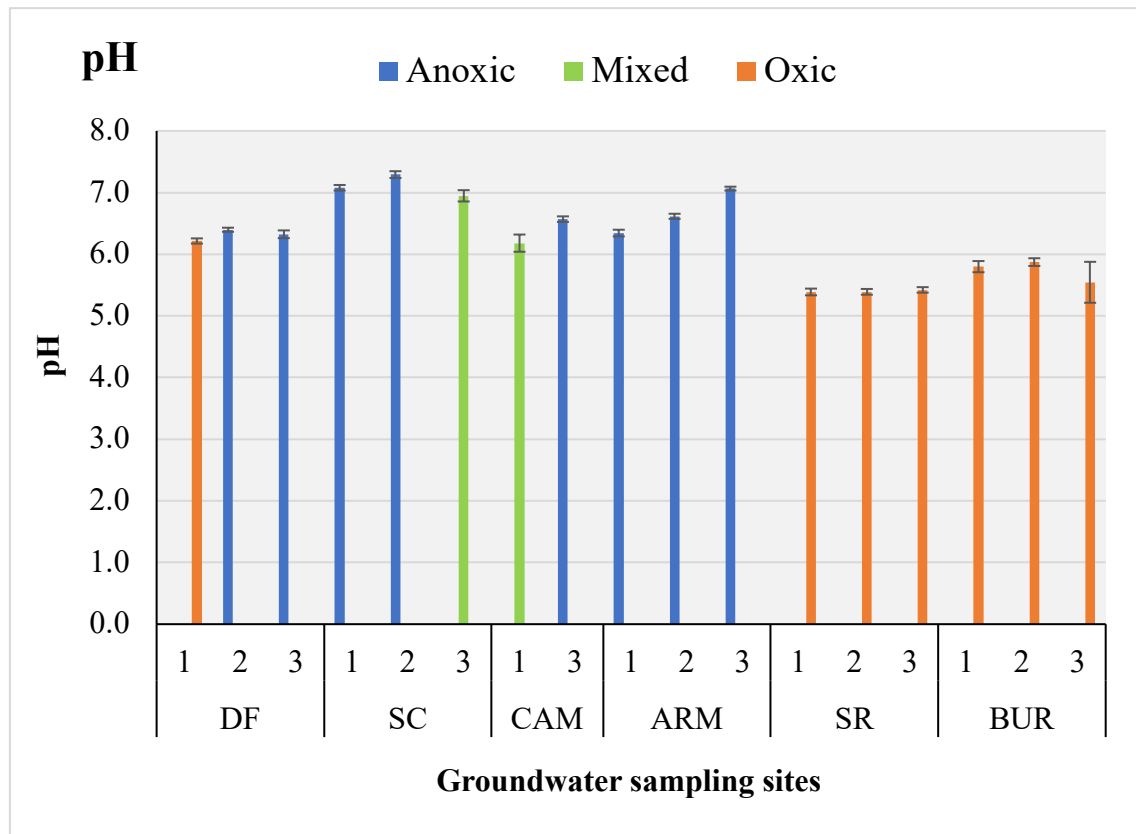


Figure 10: pH in groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments. Each bar represents average value from February to September 2018 ($n=7 \pm \text{SEM}$).

The reducing piezometers DF 2, 3; SC 1, 2, 3; CAM 3; and ARM 1, 2, 3; and the oxidising piezometer DF 1 presented in general neutral conditions (ranging between 6.18 and 7.29) with no important variations over the study period. While the oxidising piezometers at sites SR and BUR showed slightly acidic conditions with no important variations over the study period.

4.2.2 Cations measurements

The hydrogeological setting defines groundwater chemistry, therefore, to gain a better understanding and quantify subsurface denitrification process, groundwater chemistry must be studied. A monthly analysis and quantification of major and minor cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ and Fe^{2+} , Al^{3+} , Mn^{2+} and $\text{NH}_4^+\text{-N}$ respectively) and anions ($\text{NO}_3^-\text{-N}$, $\text{NO}_2^-\text{-N}$, Br^- , Cl^- , SO_4^{2-}) was conducted to create a baseline of shallow groundwater chemistry at each piezometer over the study period (February – September, 2018). Mean values observed at

each piezometer over the study period are analysed below. Mean and SEM values are given in Table 16 and 17 (monthly values are given in the Appendix 1).

4.2.2.1 Major cations

Calcium is a major cation in all piezometers. The monthly average concentration of Ca^{2+} between piezometers ranged between 8.78 and 123.32 mg L^{-1} (Table 16, Appendix 1).

In general, Ca^{2+} is the main cation in groundwater as high concentrations of it are found in parental material such as igneous (a constituent of silicates), sedimentary (mainly in the form of calcite and aragonite carbonate (CaCO_3), $\text{CaMg}(\text{CO}_3)_2$ (dolomite) or sulphate: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) or CaSO_4 (anhydrite). The concentration of Ca^{2+} has been observed to be below 90 mg L^{-1} in aquifers around the region (Rivas et al., 2014). In general higher concentrations closest to the coast (Horizons, 2013) as in the coastal sands of site SC.

Comparing between sites, higher concentrations of Ca^{2+} ($> 40 \text{ mg L}^{-1}$) are expected at site SC due to the geology of the underlying strata located on the Manawatu plains close to the coast (Horizons, 2013). Groundwater from piezometers SC 1, 2 and 3 is mainly controlled by carbonate reactions as it has relatively high Ca^{2+} (major cation) and HCO_3^- (Table 17) concentration suggesting the presence of calcium bicarbonate rich sediments as found in limestone and calcareous marine sediments (Horizons, 2013).

Sodium is a major cation in all piezometers, except for the piezometers SC 1, 2, and 3 where higher monthly average concentrations of Ca^{2+} over Na^+ (Table 15) was observed. The monthly average concentration of Na^+ between piezometers ranged between 23.6 and 50.68 mg L^{-1} (Table 15, Appendix 1) which is expected for the region (Horizons 2013).

4.2.2.2 Minor cations

The concentration of iron in groundwater is controlled by equilibrium and chemical processes as oxidation-reduction, precipitation and dissolution of hydroxides, carbonates and sulphides (Korom, 1992).

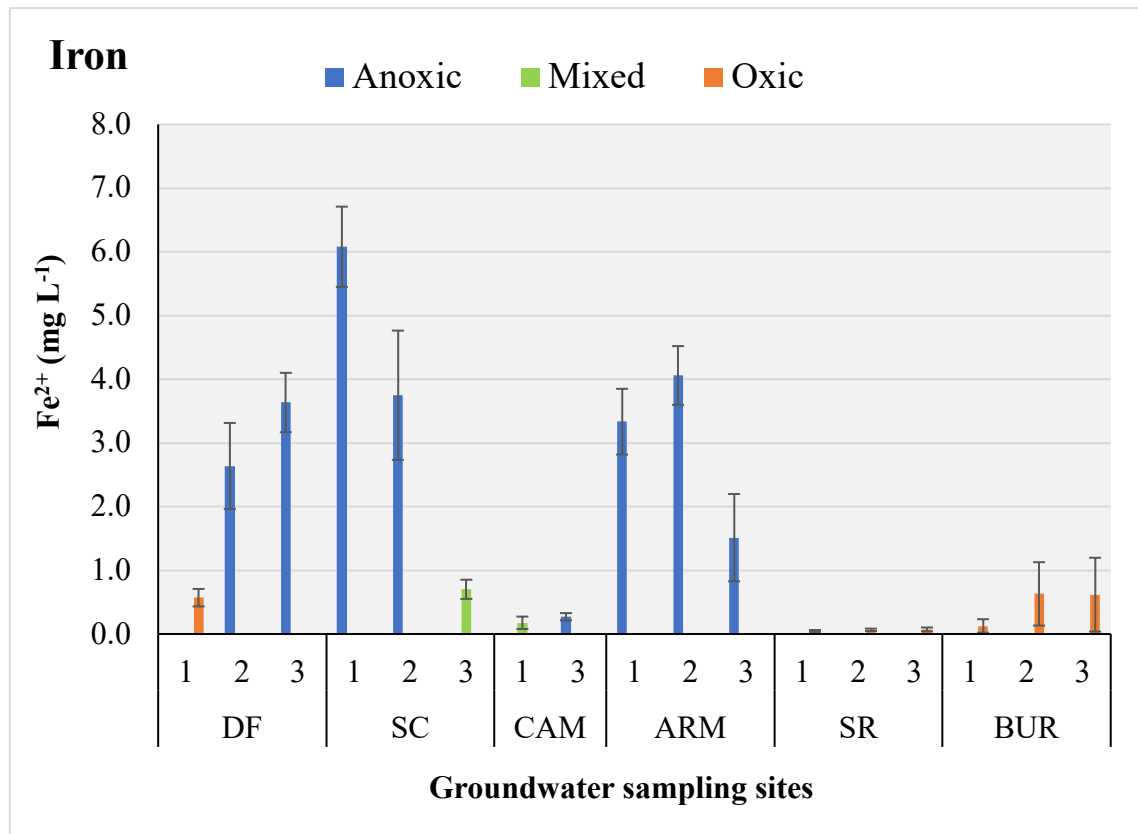


Figure 11: Iron concentration in groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments. Each bar represents average value from February to September 2018 ($n=8 \pm \text{SEM}$).

The reducing piezometers DF 2, 3; SC 1, 2 and ARM 1, 2 and 3 showed suitable Fe^{2+} concentrations for subsurface denitrification. Higher concentrations of Fe^{2+} ($> 1 \text{ mg L}^{-1}$) is an indication of suitable reducing conditions for subsurface denitrification (Rivett et al., 2008; Rivas et al., 2014). High concentration of Fe^{2+} ($> 1 \text{ mg L}^{-1}$) it is a characteristic feature in shallow groundwater with reducing redox conditions at the Manawatu and Rangitikei River catchments (Horizons, 2013; Rivas et al., 2014).

At site DF, the piezometers showed an increase in Fe^{2+} average concentration with depth (ranging from 0.57 to 3.63 mg L^{-1}), showing a stronger influence of the rock type found at site DF (alluvium). The piezometer SC 1 showed Fe^{2+} concentration almost 10 times higher than piezometer SC 2 (6.08 and 0.70 $\text{mg} \cdot \text{L}^{-1}$, respectively), these results can be attributed to soil properties. Soils at site SC has been built on Sand flat, with soil types Foxton brown sand and Pukepuke black sand (Table 2, Chapter 3). Puke-puke soils are characterized by a topsoil layer where iron can be oxidized (Malloy, 1998), increasing Fe^{2+} , especially in the shallowest piezometer (SC 1). The piezometers at site CAM showed values higher than the

threshold for Fe^{2+} ($> 0.1 \text{ mg L}^{-1}$) for anoxic redox classification (Table 12) but below the threshold to support subsurface denitrification ($< 1 \text{ mg L}^{-1}$) (Rivett et al., 2008; Rivas et al., 2014). No influence of groundwater depth was observed on Fe^{2+} between the piezometers at site CAM. In general piezometers under reducing conditions, except for CAM 3 showed the monthly average concentration of Fe^{2+} above the threshold ($> 1 \text{ mg L}^{-1}$) to support subsurface denitrification (Rivett et al., 2008; Rivas et al., 2017). The piezometers at site ARM showed relatively high values for Fe^{2+} ($> 1 \text{ mg L}^{-1}$), which is associated with poorly drained soils (Molloy, 1998) found at site ARM.

Only the oxidising piezometers at site SR showed the monthly average concentration of Fe^{2+} below the threshold ($< 0.1 \text{ mg L}^{-1}$) for the redox classification. The piezometers at site BUR presented Fe^{2+} monthly average concentrations (ranging from 0.1 to 0.6 mg L^{-1}) above the redox threshold yet, not high enough to support subsurface denitrification ($< 1 \text{ mg L}^{-1}$) (Rivett et al., 2008; Rivas et al., 2014). Low concentrations of Fe^{2+} it is a characteristic feature in shallow groundwater with oxidizing redox conditions at the Manawatu and Rangitikei River catchments (Horizons, 2013; Rivas et al., 2014).

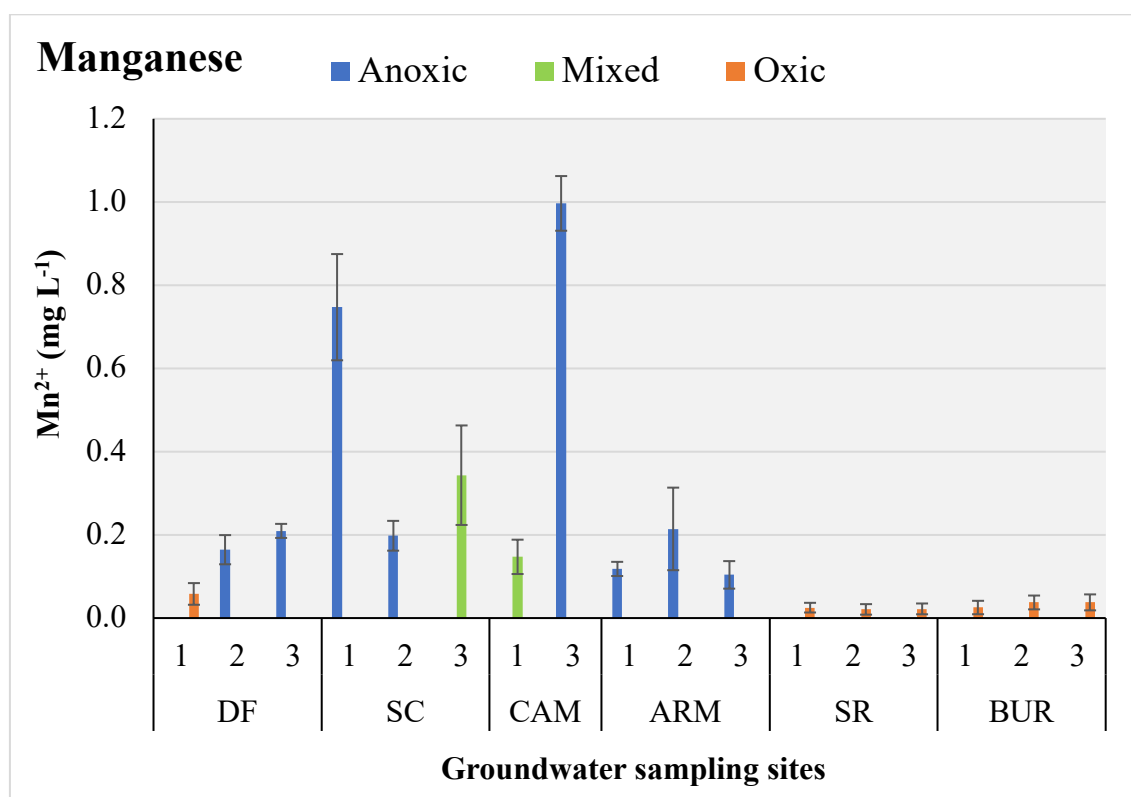


Figure 12: Manganese concentration in groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments. Each bar represents average value from February to September 2018 ($n=7 \pm \text{SEM}$).

In autotrophic subsurface denitrification, NO_3^- is an electron acceptor while Mn^{2+} serves as an electron donor (Korom, 1992; McMahon and Chapelle, 2008).

Groundwater samples with reducing and mixed conditions (DF 2, 3; SC 1, 2, 3; CAM 1 and 3; ARM 1, 2 and 3) showed monthly average concentrations of Mn^{2+} greater than the threshold ($> 0.05 \text{ mg L}^{-1}$). Contrasting, oxidising piezometers (DF 1; SR 1, 2, 3; BUR 1, 2 and 3) showed Mn^{2+} monthly average concentrations below the threshold ($> 0.05 \text{ mg L}^{-1}$). Shallow groundwaters with low oxidation capacity present low concentrations of Fe^{2+} and Mn^{2+} (Earl, S. and Krogh, E. 2004).

Concentrations of the electron donor Mn^{2+} was found to be suitable for SD at the anoxic piezometers DF 2, 3; SC 1, 2; CAM 3; ARM 1, 2 and 3 ($> 0.05 \text{ mg L}^{-1}$) and piezometers with mixed redox status SC 3; CAM 1 ($> 0.05 \text{ mg L}^{-1}$). In general, the piezometers with oxidizing redox conditions DF 1; SR 1, 2, 3; BUR 1, 2 and 3 showed unsuitable conditions for subsurface denitrification as Mn^{2+} concentrations at these piezometers were below the threshold ($< 0.05 \text{ mg L}^{-1}$) for identifying the redox classification (Figure 12).

Groundwater samples from piezometers SC 1 and CAM 3 showed Mn^{2+} monthly values (Appendix 1) above the maximum New Zealand drinking water standard (NZDWS MAV = 0.04 mg L^{-1}) (Horizons, 2013). Higher concentrations of Mn^{2+} (and Fe^{2+}) are expected in the Manawatu Plains coastal areas (Horizons 2013) as found at site SC but also at site ARM. A high concentration of Mn^{2+} and Fe^{2+} generally occurs simultaneously, as these elements are generally present in the same mineralogy types (Molloy, 1998) with high retention capacity for Mn^{2+} and Fe^{2+} . Values for Fe^{2+} and Mn^{2+} showed a strong negative correlation with DO concentrations in the study groundwater samples (Table 18).

4.2.2.3 Major anions

Groundwater samples showed concentrations of SO_4^{2-} ranging from 0.1 to 13.48 mg L^{-1} (Table 16). These concentrations are low compare with concentration found by Clague et al., (2018) in dairy farming catchments in the North Island in New Zealand. From No correlation was observed between SO_4^{2-} and DO concentration (Table 18) or SO_4^{2-} with any of the compounds to identify redox status (Table 18). Yet a strong positive correlation

was found between NO_3^- -N and SO_4^{2-} concentrations, suggesting subsurface denitrification.

Chlorine concentrations ranged between 10.07 and 48.4 mg L^{-1} (Table 16). The higher concentrations were observed closest to the coast at the piezometers at site SC (40.06 – 48.4 mg L^{-1}) (Table 17). While site SR and BUR showed the lowest Cl^- concentration as these sites are further inland, compare to the other sites (Table 16). This trend has been recognised by others (Rivas et al., 2014; Horizons, 2013). All samples were under drinking water guideline values for Cl^- (250 mg L^{-1}) (Ministry of Health, 2008).

Parental rocks generally present low concentrations of Cl^- (except for marine parental material). However, given the high solubility of its salts, Cl^- is quickly dissolved into the aqueous phase and can reach very high concentrations. The SO_4^{2-} comes from the washing inland formed in the marine environment, as found at site SC. Nevertheless, gypsum (sedimentary rock) solution ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite from igneous rock (CaSO_4) frequently represent a quantitatively more significant contribution of this ion to groundwater. This might explain high values of sulphate at piezometers SC 2 and (> 10 mg L^{-1}) compared to the other sites.

In general, groundwater samples showed HCO_3^- concentrations ranging from 24.15 to 298.46 mg L^{-1} (Table 16). In general anoxic piezometers showed the highest concentrations (> 120 mg L^{-1}) of HCO_3^- . While oxidizing piezometers showed the lowest concentrations, especially the piezometers SR 1, 2 and 3.

Table 16: Mean total cations concentration from February to September 2018 and major cations concentration from April – September 2018 in groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments.

Unit	mg · L ⁻¹	Fe ²⁺		Mn ²⁺		Ca ²⁺		Mg ²⁺		Na ⁺		K ⁺		NH ₄ ⁺ -N	
Site	Piezometer	Avg	SEM	Avg	SEM	Avg	SEM	Avg	SEM	Avg	SEM	Avg	SEM	Avg	SEM
DF	1	0.57	0.47	0.06	0.03	22.91	1.06	5.10	0.11	33.43	1.44	4.30	1.42	0.01	0.00
	2	2.64	0.68	0.16	0.04	23.58	3.35	5.27	0.40	29.93	4.24	2.49	0.38	0.06	0.02
	3	3.63	0.14	0.21	0.02	26.75	1.29	5.51	0.16	30.96	4.32	2.66	0.30	0.06	0.02
SC	1	6.08	1.01	0.75	0.13	86.12	2.38	9.25	0.11	40.53	2.21	7.41	3.31	0.14	0.05
	2	3.75	0.63	0.20	0.04	75.17	4.06	9.97	0.25	42.83	3.07	6.84	2.86	0.08	0.03
	3	0.70	0.15	0.34	0.12	123.32	7.19	14.00	0.71	45.09	5.80	10.60	3.60	0.12	0.00
CAM	1	0.18	0.10	0.15	0.04	17.68	0.72	9.14	0.36	34.72	4.40	3.48	1.53	0.01	0.00
	3	0.27	0.06	1.00	0.07	18.44	0.57	10.77	0.06	39.94	5.08	4.38	2.12	0.01	0.00
ARM	1	3.33	0.52	0.12	0.02	22.60	2.18	4.97	0.20	47.23	4.86	3.72	1.61	0.03	0.02
	2	4.06	0.46	0.21	0.10	32.82	1.70	5.92	0.20	50.68	4.13	3.53	1.50	0.04	0.02
	3	1.51	0.69	0.10	0.03	35.25	6.54	6.12	0.84	49.60	9.65	3.64	1.77	0.02	0.02
SR	1	0.05	0.02	0.03	0.01	8.78	0.20	2.79	0.06	24.77	6.56	0.84	0.22	0.01	0.01
	2	0.07	0.02	0.02	0.01	8.79	0.30	2.87	0.09	23.60	5.45	0.95	0.25	0.01	0.00
	3	0.07	0.03	0.02	0.01	10.67	1.82	4.04	1.11	27.29	5.92	1.05	0.28	0.01	0.01
BUR	1	0.13	0.11	0.03	0.02	14.97	1.46	3.96	0.18	36.95	8.73	4.23	0.51	0.00	0.00
	2	0.63	0.50	0.04	0.02	16.70	0.24	3.86	0.10	31.71	6.95	4.44	0.22	0.03	0.03
	3	0.62	0.58	0.04	0.02	15.62	0.48	3.10	0.07	31.03	5.44	1.88	0.34	0.00	0.00
Min		0.05		0.02		8.78		2.79		23.60		0.84		0.00	
Max		6.08		1.00		123.32		14.00		50.68		10.60		0.14	
Mean		1.66		0.20		32.95		6.27		36.49		3.91		0.04	
SD		1.87		0.27		31.73		3.21		8.51		2.51		0.04	
Coef. Var		1.12		1.33		0.96		0.51		0.23		0.64		1.14	

Table 17: Mean total anions concentration (NO_3^- -N, NO_2^- -N, Br^- , SO_4^{2-} and Cl^-) from February to September 2018 and for HCO_3^- from April – September 2018 in groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments.

Unit	$\text{mg} \cdot \text{L}^{-1}$	NO_3^- -N		NO_2^- -N		Br^-		SO_4^{2-}		Cl^-		HCO_3^-	
Site	Piezometer	Avg	SEM	Avg	SEM	Avg	SEM	Avg	SEM	Avg	SEM	Avg	SEM
DF	1	0.83	0.51	N.A	N.A	0.11	0.03	3.68	0.84	19.37	0.33	101.17	4.11
	2	0.04	0.01	N.A	N.A	0.09	0.00	1.80	0.26	21.53	0.35	123.15	3.88
	3	0.02	0.00	N.A	N.A	0.09	0.00	1.78	0.25	21.87	0.31	122.77	2.35
SC	1	0.05	0.02	N.A	N.A	0.20	0.00	2.46	0.45	48.41	0.79	295.10	6.41
	2	0.05	0.03	N.A	N.A	0.12	0.00	13.48	2.20	40.04	1.57	298.46	21.08
	3	6.99	3.34	0.11	-	0.22	0.01	11.84	2.72	64.33	12.91	233.43	12.78
CAM	1	5.23	0.89	0.03	-	0.10	0.02	8.29	2.15	23.15	3.89	55.24	9.52
	3	0.10	0.04	0.10	-	0.31	0.08	2.64	0.38	16.33	0.20	153.62	4.08
ARM	1	0.02	0.01	N.A	N.A	0.10	0.02	4.21	0.77	17.43	0.67	126.55	2.14
	2	0.02	0.00	0.01	-	0.10	0.00	1.71	0.44	25.74	0.35	180.25	10.97
	3	0.02	0.01	N.A	N.A	0.13	0.00	0.10	0.07	34.11	0.62	212.39	4.06
SR	1	3.48	0.15	N.A	N.A	0.10	0.01	4.26	0.68	10.11	0.49	25.75	1.26
	2	3.48	0.13	N.A	N.A	0.10	0.01	4.23	0.68	10.14	0.43	24.15	1.15
	3	3.53	0.13	N.A	N.A	0.11	0.01	4.17	0.66	10.29	0.41	25.36	1.57
BUR	1	4.33	1.16	N.A	N.A	0.09	0.03	3.77	1.33	9.30	2.59	71.53	20.46
	2	4.98	0.75	0.01	-	0.09	0.01	5.38	0.94	13.61	1.01	58.97	2.02
	3	3.59	0.89	0.01	-	0.08	0.01	4.04	0.78	12.37	0.91	41.84	2.06
	Min	0.02		0.01		0.08		0.10		9.30		24.15	
	Max	6.99		0.11		0.31		13.48		64.33		298.46	
	Mean	2.16		0.05		0.13		4.58		23.42		126.45	
	SD	2.38		0.05		0.06		3.54		15.30		90.75	
	Coef. Var	1.10		1.00		0.48		0.77		0.65		0.72	

4.2.3 Nitrogen measurements in different oxidations states.

In groundwater, N is presented in different oxidation (Table 1, Chapter 1). Nitrogen is found in solution as NH_4^+ , NO_2^- and NO_3^- and as a dissolved gas in the form of N_2O and N_2 .

4.2.3.1 Nitrogen in solution with groundwater

Nitrate-N and NO_2^- -N concentrations are used to assess groundwater quality as they are considered to be an environmental hazard (Horizons, 2103). Variations in groundwater chemistry can be indicatives of diffuse pollution (Horizons, 2103). Especially in the Manawatu and Rangitikei River catchments where intensive agricultural activities are a common practice.

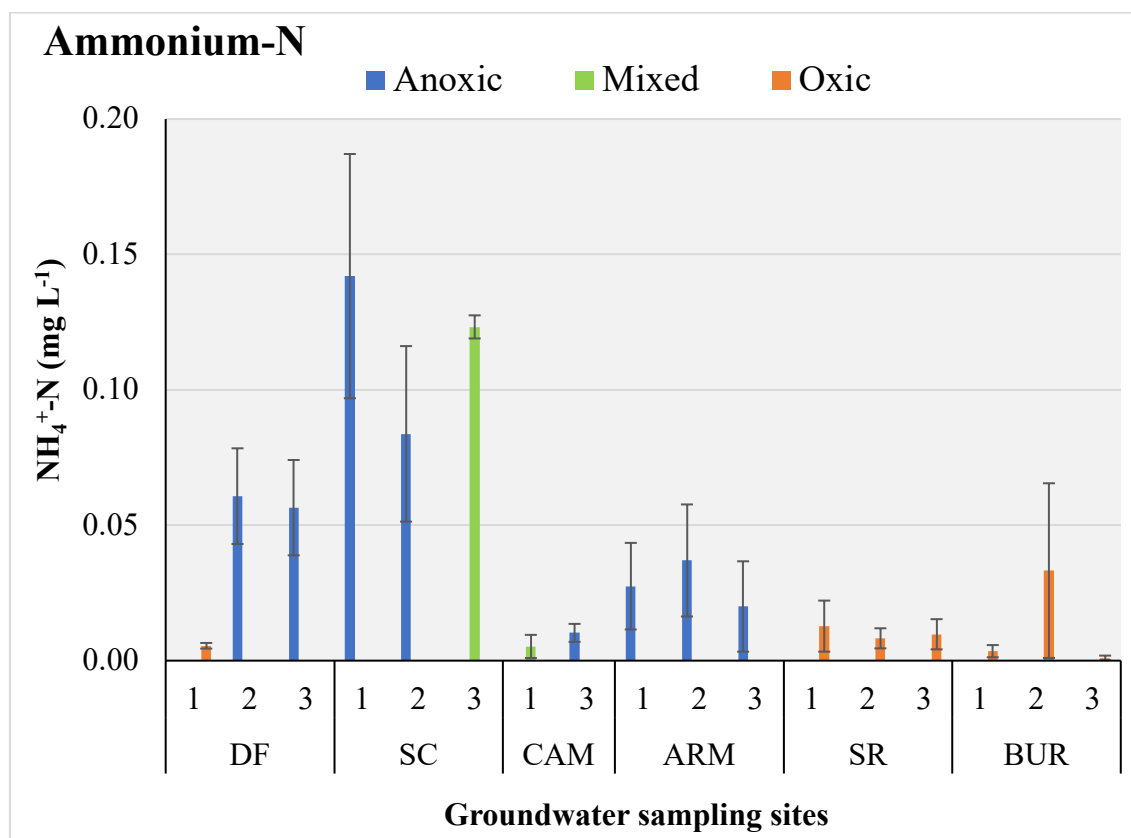


Figure 13: Ammoniacal-N ($\text{NH}_4^+\text{-N}$) concentration in groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments. Each bar represents average value from May to September 2018 ($n=5 \pm \text{SEM}$).

Ammoniacal-N concentrations ranged between below the detection limit ($< 0.01 \text{ mg L}^{-1}$) and 0.14 mg L^{-1} . Only piezometers SC 1 and 3 showed $\text{NH}_4^+\text{-N}$ monthly average concentrations above 0.1 mg L^{-1} . The monthly average $\text{NH}_4^+\text{-N}$ concentrations were low compared with results of groundwater quality in the Manawatu Region shown in the Groundwater Quality Monitoring Network Reports (2013) and with the survey conducted in the Tararua Range by Rivas et al, (2014). Low concentrations of $\text{NH}_4^+\text{-N}$ in the groundwater samples indicate that DNRA is not a predominant process for NO_3^- reduction. Ammonium-N showed a negative correlation with DO levels (Table 18). Hence, reducing piezometers presented higher concentrations of $\text{NH}_4^+\text{-N}$; as expected for groundwaters with low oxidising potential (Stenger et al., 2013; Horizons, 2013).

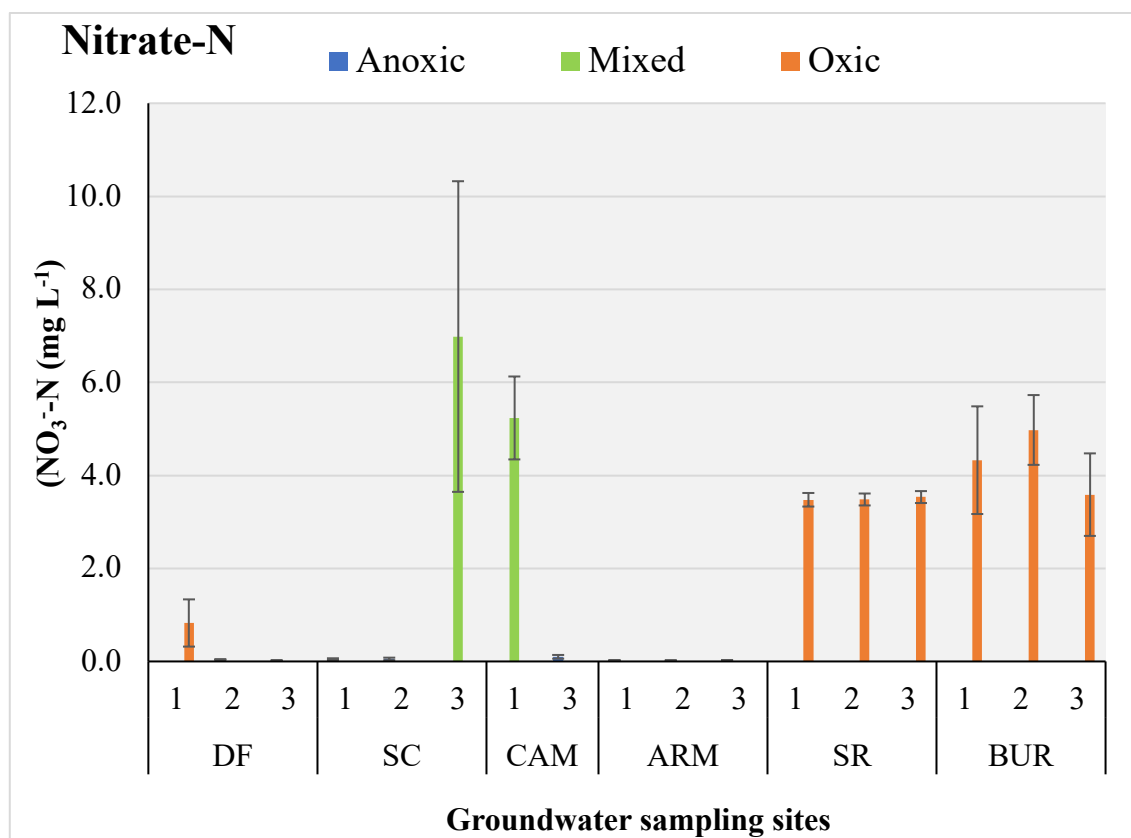


Figure 14: Nitrate-N (NO_3^- -N) concentration in groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments. Each bar represents average value from February to September 2018 ($n=7 \pm \text{SEM}$).

Heterotrophic subsurface denitrification occurs in environments with low DO concentration and in the presence of electron donor and denitrifying bacteria (Korom, 1992; Rivett et al., 2008; McMahon and Chapelle, 2008; Stenger et al., 2013; Kuypers et al., 2018; Horizons, 2013; Rivas et al., 2014; Rivas, 2018; Singh et al., 2014). The suitable conditions for subsurface denitrification were found at the reducing piezometers DF 2, 3; SC 1, 2; CAM 3; ARM 1, 2 and 3; as these showed NO_3^- -N monthly average concentrations below the redox classification threshold ($< 0.5 \text{ mg L}^{-1}$) (Table 12, Figure 14). Accumulation of NO_3^- is unlikely to be observed in groundwater with reducing conditions (Horizons, 2013). The piezometers with oxidising and mixed conditions (DF 1; SC 3; CAM 1; SR 1, 2, 3; BUR 1, 2 and 3) showed NO_3^- -N monthly average concentrations greater than 3 mg L^{-1} (Table 12, Figure 14), indicating NO_3^- accumulation and hence lower denitrification rates as compared to other sites with lower concentrations of NO_3^- -N. The piezometer DF

1 showed NO_3^- -N monthly average concentrations slightly higher than the redox threshold (0.5 mg L^{-1}).

Only the piezometer SC 3 showed very high variability in NO_3^- -N monthly values from February (0.02 mg L^{-1}) until August (22.56 mg L^{-1}) and decreased by September (15.92 mg L^{-1}). The recharge water carries the leached NO_3^- to groundwater. The chemical composition of recharge water is influenced by the soil temperature (Weymann et al., 2008) and agricultural management practices (Horizons, 2013). The piezometer SC 3 presented NO_3^- -N concentrations over the NZDWS MAV = 11.3 mg-N L^{-1} (Horizons, 2013; Ministry of Health, 2008) in August and September.

4.2.3.2 Dissolved gasses in groundwater: N_2O and excess N_2

The concentration of N_2 in groundwater represents 3 sources of N_2 ; from entrapped bubbles within the aquifer (excess air), N_2 from equilibrium with the atmosphere (recharge water) and N_2 as a result of microbial subsurface denitrification (Weymann et al., 2008).

Nitrogen-nitrous oxide - N_2O -N

Figure 15 presents N_2O -N monthly average concentration measured at each study piezometer during the study (February — September). In general, the piezometers under reducing conditions (DF 1, 2; SC 1, 2; ARM 1, 2 and 3) showed low or undetectable N_2O -N monthly average concentrations ($< 0.01 \text{ umol L}^{-1}$). Except for the piezometer CAM 3 that showed N_2O -N monthly average concentration of greater than 0.01 umol L^{-1}). The piezometers under mixed and oxidising conditions (SC 3; SR 1, 2, 3; BUR 1, 2 and 3) showed N_2O -N monthly average concentration ranging from 0.02 to 0.05 umol L^{-1} .

Nevertheless, in March 2018 significant peaks were measured at piezometers SR 1, 2 and 3 (Appendix 1). The N_2O -N peaks can be related to the variation of groundwater recharge rate and water table in the well, which influences groundwater chemistry (Horizons, 2013). As a consequence conditions for complete subsurface denitrification can be less favourable.

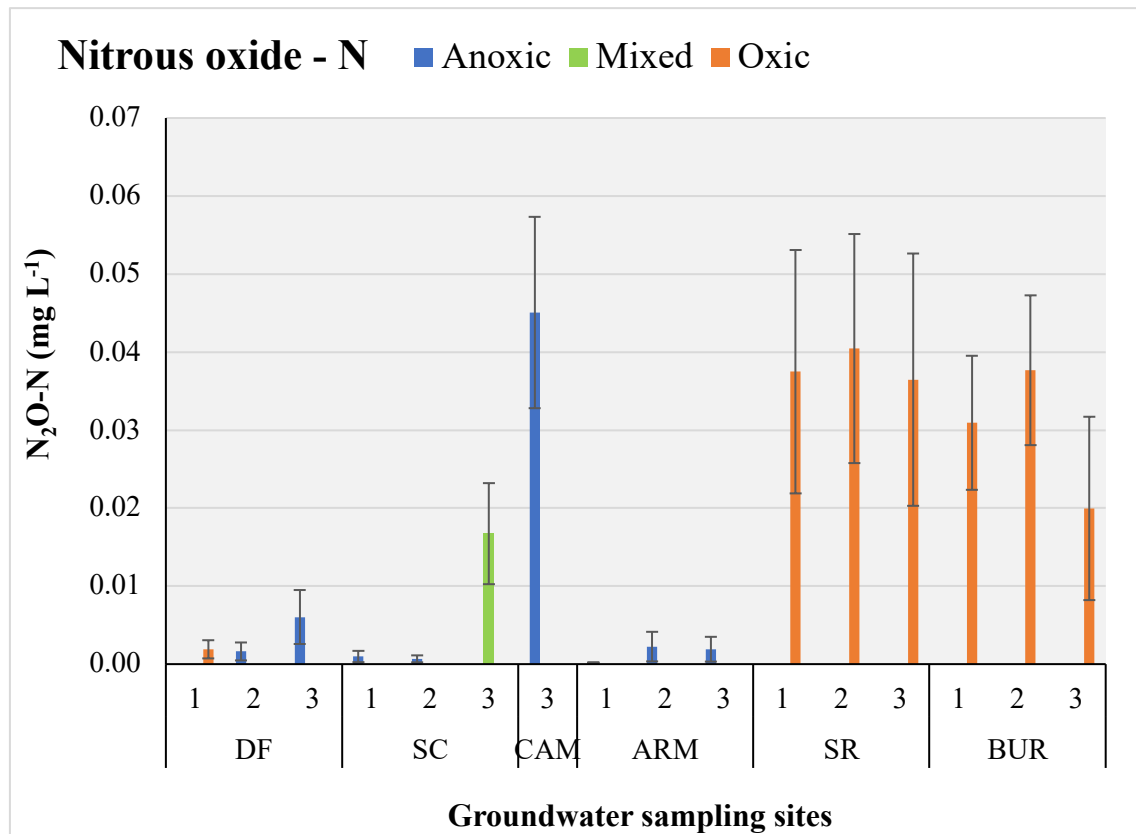


Figure 15: Nitrogen-nitrous oxide ($\text{N}_2\text{O-N}$) concentration in groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments. Each bar represents average value from February to September 2018 ($n=7 \pm \text{SEM}$).

Several authors have identified seasonality in the production of N_2O over time. For example, it has been observed in soils, the highest values of N_2O are observed in moments of high precipitation (Sagar et al., 2004b, Koops et al., 1997) and with the wettest years (Skiba et al., 1996). De Klein and Eckard (2008) indicate that high values of N_2O emission are produced as a result of denitrification under intensive livestock production. Environments with limited oxygen concentration enhance denitrification processes (Saggar et al., 2004b).

Jahangir et al. (2007) quantified monthly $\text{N}_2\text{O-N}$ concentrations in groundwater of Ireland over a 2 years period. The aquifers were under well-drained soils (representing 62% of Ireland soils); and moderate to poorly drained soils (representing 37% of Ireland soils) (Jahangir et al., 2007). In their study, the sites under reducing conditions also presented lower $\text{N}_2\text{O-N}$ concentration ($0.011 - 0.024 \text{ mg L}^{-1}$) compared with the oxidizing sites ($0.038 - 0.049 \text{ mg L}^{-1}$). Their results (concentration and range) were similar compared with

ours. To better understand NO_3^- transformation, a discussion of $\text{N}_2\text{O-N}$ results obtained in the monthly analysis are given next, combined with the forgoing excess N_2 results).

Excess N_2

Samples for excess N_2 were collected from all piezometers, except for the piezometer CAM 1 that showed low hydraulic conductivity (recharge rate is extremally slow) making it impossible to follow protocols of samples collection. For the piezometer SC 2 (results not shown) the recharge temperature needed (to obtain positive results) was over 28 °C. This temperature for analysis was considered not a logical value; we explain these results due to the degassing process while collecting the groundwater sample due to pressure differences between the surface and within the piezometer.

Figure 16 presents the average of **excess N_2** measured over 3 months (June, August and September 2018) at the study sites and $\text{N}_2\text{O-N}$ monthly average concentrations.

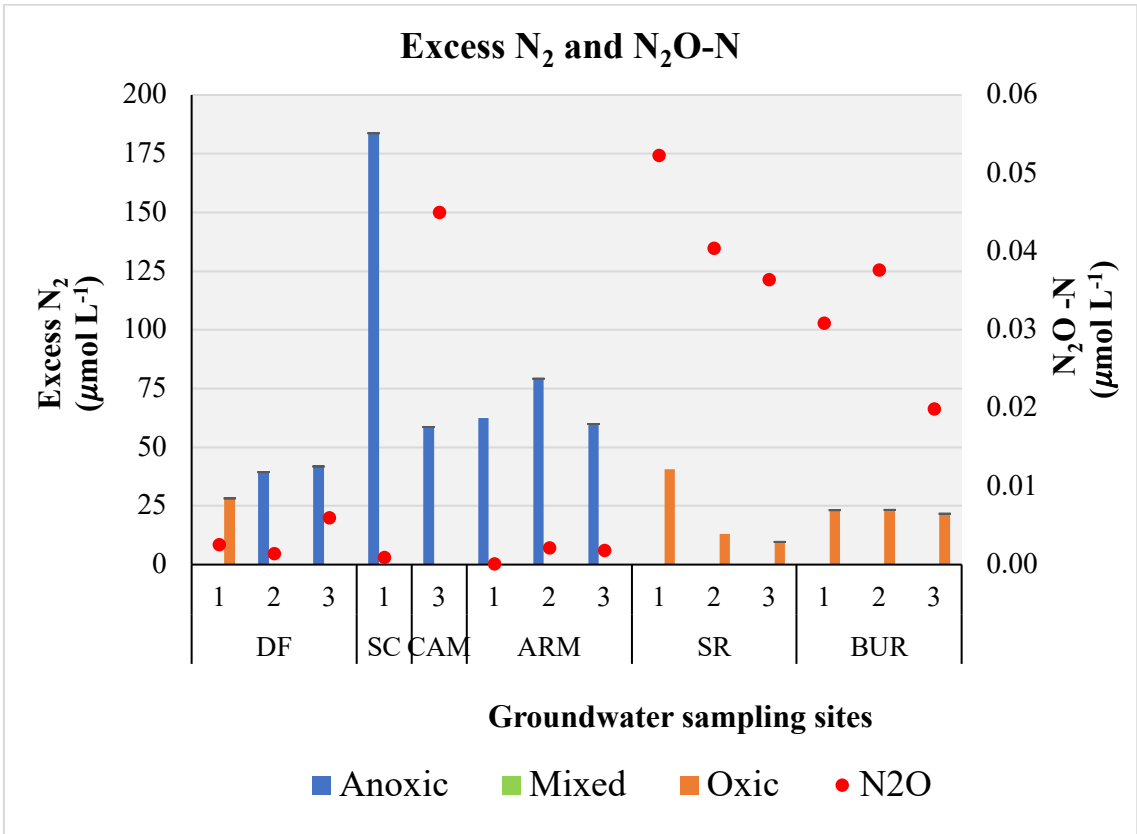


Figure 16: Excess N_2 and dissolved $\text{N}_2\text{O-N}$ concentration in groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments. Each bar represents average value of June, August and September 2018 ($n=3 \pm \text{SEM}$).

The piezometers under reducing conditions DF 2, 3; SC 1; CAM 3; ARM 1, 2, 3; showed the lowest NO_3^- -N monthly average concentration ($< 0.1 \text{ mg} \cdot \text{L}^{-1}$) (Table 11), very low N_2O -N concentration (Figure 16) (except for CAM 3), and relatively high **excess N_2** concentrations (Figure 16) ranging from 39.4 to $183.74 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$. **Excess N_2** results indicate that complete denitrification is the main process in shallow groundwaters at this study sites DF, ARM and SC. For the oxidizing piezometer DF 1; SR 1, 2, 3; BUR 1, 2 and 3 presented NO_3^- -N background concentration above the redox threshold ($> 0.5 \text{ mg L}^{-1}$) (Table 11), higher N_2O -N monthly average concentration ($> 0.02 \text{ mg L}^{-1}$), and relatively low excess N_2 concentrations (Figure 16) ranging from 9.65 to $40.58 \text{ } \mu\text{mol L}^{-1}$. Results of excess N_2 varied considerably within months, suggesting that complete subsurface denitrification showed spatial and temporal variability.

Complete subsurface denitrification process (excess N_2) and partial subsurface denitrification (N_2O production) are highly sensitive to DO concentrations (Saggar et al., 2004b). Changes in abiotic conditions such as temperature and recharge rates, modify oxygen diffusion. Higher values of N_2O -N were obtained during August monthly sampling (Appendix 2) this may be explained by intensive rain during the days of sampling. Many authors have found increasing rates of N_2O production in the soil profile during winter (Saggar et al., 2004b) while others have found the opposite trend with higher concentrations of N_2O being produced over summer (Christensen et al., 1990; Velthof et al., 1996a).

A mix of complete and partial subsurface denitrification can be identified at piezometer SC 3. Results obtained at piezometer SC 3 ranged from 18.96 to $159.43 \text{ } \mu\text{mol L}^{-1}$ of excess N_2 in September (Appendix 1) and over $0.03 \text{ } \mu\text{mol L}^{-1}$ of N_2O -N concentrations (Figure 16). It appears that complete denitrification is the main process at SC 1 (average excess N_2 : $183.23 \text{ } \mu\text{mol L}^{-1}$) as it has low N_2O -N concentration ($< 0.01 \text{ } \mu\text{mol L}^{-1}$). The piezometer SC 1 showed an anoxic redox category and low DO (limiting factor) ($< 1 \text{ mg L}^{-1}$) compared to the piezometer SC 3 (1.28 mg L^{-1}). Also, the piezometer SC 1 showed almost 10 times the concentration of Fe^{2+} (electron donor). Contrasting with piezometer SC 3, complete denitrification is favourable at piezometer SC 1 with comparably higher excess N_2 concentration up to $182 \text{ } \mu\text{mol L}^{-1}$.

The piezometer CAM 3 has interesting excess N_2 and $\text{N}_2\text{O-N}$ results ($58.61 \mu\text{mol}\cdot\text{L}^{-1}$ and $0.05 \mu\text{mol}\cdot\text{L}^{-1}$ respectively). The piezometers at CAM site are situated in Takapau silt loam soil. It is common to find Takapau soils on the intermediate stony terraces formed on the last period of loess deposition (loess over gravel rock type) under cold conditions (Molloy, 1998), defining how groundwater flows (moves) between the aquifer. At about 3 m from piezometer, CAM 3 is piezometer CAM 1; which has significantly higher concentrations of DO and $\text{NO}_3^- \text{-N}$ (Table 12 and; Figure 8 and 14 respectively). These features increase the possibility of microsites (due to high hydraulic conductivity) which explains that complete and partial denitrification is occurring at CAM 3 as excess N_2 and N_2O is being produced. Unfortunately, no excess N_2 or $\text{N}_2\text{O-N}$ measurements were taken from CAM 1 to corroborate this hypothesis.

The oxic piezometers SR 1, 2, 3 and BUR 1, 2, 3 (Figure 16) showed lower excess N_2 (low subsurface denitrification capacity); similar results have been found in Ireland under similar agricultural settings (Jahangir et al., 2012). However, piezometers BUR 1, 2, 3 have the highest values for $\text{N}_2\text{O-N}$ indicating that conditions are favourable for NO_3^- to be reduced to N_2O (partial denitrification). At piezometers SR 1, 2, 3 it appears to show some partial and complete denitrification. Concentrations of excess N_2 and $\text{N}_2\text{O-N}$ decreased while the groundwater depth increases despite the small variation in DO concentration (Figure 9).

The correlation analysis (Table 18) includes the results of chemical analysis and dissolved gas analysis, the main requirements for subsurface denitrification and its products ($\text{N}_2\text{O-N}$ and Excess N_2) are bold in red. The DO results show a strong positive correlation (> 0.5) between ORP, $\text{NO}_3^- \text{-N}$ and $\text{N}_2\text{O-N}$, and a negative correlation with Fe^{2+} , Mn^{2+} , $\text{NH}_4^+ \text{-N}$ and excess N_2 . A negative correlation between Fe^{2+} and $\text{N}_2\text{O-N}$ might suggest that iron was limiting subsurface denitrification at piezometers with low concentrations of the electron donor (as seen in the oxidizing piezometers). Similarly, $\text{NO}_3^- \text{-N}$ showed negative correlation with Fe^{2+} and Mn^{2+} (< -0.5); and -0.33 with depth. Excess N_2 in the groundwater samples showed a strong positive correlation (> 0.5) with Fe^{2+} , Mn^{2+} , $\text{NH}_4^+ \text{-N}$ and DOC, and a negative correlation with DO, $\text{NO}_3^- \text{-N}$ and $\text{N}_2\text{O-N}$ concentrations.

Our results indicate that groundwater from reduced piezometers DF 2, 3; SC 1, 2; CAM 3; ARM 1, 2 and 3 showed better suitability for subsurface denitrification. As reduced piezometers showed low concentrations of DO (Figure 8), $\text{NO}_3^- \text{-N}$ (Figure 14) and $\text{N}_2\text{O-N}$

(Figure 15) with an elevated concentration of Fe^{2+} (Figure 11), Mn^{2+} (Figure 12), $\text{NH}_4^+\text{-N}$ (Figure 13) and excess N_2 (Figure 16). In contrast with oxidizing piezometers and mixed condition piezometers where less suitable conditions were found. Groundwater under oxidizing conditions with $\text{NO}_3^-\text{-N}$ concentrations greater than 1 mg L^{-1} (SR 1, 2, 3; BUR 1, 2 and 3); showed sparse concentrations of electron donors (Fe^{2+} and Mn^{2+}) to support subsurface denitrification.

Table 18: Correlation analysis based on chemical and dissolved gas analysis of groundwater samples collected from six pastoral farms in Manawatu and Rangitikei River catchments.

	Depth	Temp																				
Temp	-0.08	*	DO																			
DO	-0.33	-0.41	*	EC																		
EC	-0.03	0.29	-0.67	*	pH																	
pH	0.11	0.42	-0.86	0.90	*	ORP																
ORP	-0.29	-0.48	0.92	-0.63	-0.85	*	DOC															
DOC	-0.24	0.40	-0.32	0.76	0.52	-0.25	*	Fe ²⁺														
Fe ²⁺	-0.05	0.24	-0.67	0.53	0.64	-0.77	0.34	*	Al ³⁺													
Al ³⁺	-0.27	0.01	0.54	-0.31	-0.37	0.39	-0.24	-0.35	*	Mn ²⁺												
Mn ²⁺	0.10	0.10	-0.50	0.49	0.53	-0.44	0.25	0.34	-0.14	*	Ca ²⁺											
Ca ²⁺	-0.10	0.25	-0.49	0.95	0.74	-0.45	0.87	0.45	-0.28	0.40	*	Mg ²⁺										
Mg ²⁺	0.06	0.40	-0.54	0.84	0.76	-0.52	0.60	0.24	-0.09	0.67	0.79	*	K ⁺									
K ⁺	-0.23	0.37	-0.54	0.90	0.75	-0.46	0.80	0.33	-0.34	0.46	0.91	0.83	*	NH ₄ ⁺ -N								
NH ₄ ⁺ -N	-0.12	0.28	-0.49	0.83	0.68	-0.53	0.85	0.68	-0.29	0.45	0.89	0.64	0.77	*	SO ₄ ²⁻							
SO ₄ ²⁻	-0.30	0.33	0.07	0.45	0.22	-0.01	0.57	-0.11	0.13	-0.06	0.54	0.54	0.55	0.34	*	Cl ⁻						
Cl ⁻	-0.01	0.32	-0.57	0.97	0.82	-0.54	0.57	0.47	-0.23	0.41	0.97	0.82	0.87	0.86	0.45	*	NO ₃ ⁻ -N					
NO ₃ ⁻ -N	-0.33	-0.07	0.65	-0.12	-0.47	0.70	0.22	-0.67	0.34	-0.33	0.06	0.03	0.11	-0.11	0.48	-0.01	*	NO ₂ ⁻ -N				
NO ₂ ⁻ -N	0.57	-0.11	-0.52	0.66	0.69	-0.24	0.43	-0.42	-0.10	0.78	0.59	0.90	0.71	0.50	0.43	0.58	0.11	*	N ₂ O-N			
N ₂ O-N	-0.16	-0.62	0.79	-0.53	-0.69	0.78	-0.32	-0.75	0.57	-0.02	-0.43	-0.27	-0.37	-0.46	0.02	-0.52	0.59	0.37	*	Excess N ₂		
Excess N ₂	-0.30	0.22	-0.54	0.89	0.73	-0.56	0.58	0.82	-0.08	0.65	0.95	0.68	0.74	0.85	-0.41	0.89	-0.56	0.25	-0.45	*		

4.4 Push-pull test

Under the agricultural context, the origin of NO_3^- in groundwater occurs mainly by diffuse contamination (Rivas, 2018). Nitrate is relatively stable but can be fixed by clays or microbially reduced to N_2 in environments with low DO concentration. Push-pull tests are used to quantify NO_3^- attenuation processes in groundwater (Istok, 2013). Nitrate concentration is often an indicator of pollution; with a clear stratification and predominance of higher concentrations in the upper part of unconfined aquifers.

4.4.1 Initial values for push-pull test.

A set of push-pull tests were developed at the deepest piezometer of each site during August-September 2018. Background Br^- concentration between sites ranged from 0.07 to 0.27 mg L^{-1} , while NO_3^- -N ranged from 0.04 to 5.25 mg L^{-1} (Table 19). A test solution of 60 or 100 L spiked with Br^- and NO_3^- was used to conduct the push-pull tests (Table 20). The test solutions showed NO_3^- -N and Br^- concentrations ranging from 9.63 to 17.06 mg L^{-1} and 10.18 to 17.93 mg L^{-1} (Table 17), respectively. The concentration of each test solution bag (20 L each) was supposed to be 15 mg L^{-1} of the tracer Br^- and for NO_3^- -N. The tracer Br^- and NO_3^- -N source were added on the field at each bag and handshaking (> 3 minutes), minutes prior to the push-pull test. Higher initial test solutions concentrations of Br^- and NO_3^- -N are possible when handshaking mixing and homogenisation are not achieved.

Table 19: Average background values for NO_3^- -N and DO at six pastoral farms in Manawatu and Rangitikei River catchments.

Site	Depth (m, bgl)	NO_3^- -N (mg L^{-1})	DO (mg L^{-1})	Br^- (mg L^{-1})
DF 3	8.7	0.02 ± 0.00	0.80 ± 0.44	0.09 ± 0.00
SC 2	5.2	0.05 ± 0.03	0.36 ± 0.24	0.12 ± 0.00
ARM 3	7.5	0.02 ± 0.01	0.41 ± 0.15	0.13 ± 0.00
CAM 3	7.5	0.10 ± 0.04	0.16 ± 0.06	0.31 ± 0.08
SR 3	6.5	3.53 ± 0.13	7.91 ± 0.34	0.11 ± 0.01
BUR 3	6.1	5.86 ± 0.02	3.98 ± 0.49	0.07 ± 0.00

Table 20: Average initial concentrations Br^- and NO_3^- -N measured in the push-pull test solutions.

Site	Volume (L)	NO_3^- -N (mg L^{-1})	Br^- (mg L^{-1})
DF 3	100	16.01 ± 1.88	17.93 ± 2.20
SC 2	100	13.71 ± 1.51	14.41 ± 1.56
ARM 3	100	9.63 ± 6.70	10.18 ± 7.15
CAM 3	60	13.72 ± 0.66	14.64 ± 0.66
SR 3	100	17.06 ± 1.27	14.10 ± 1.16
BUR 3	100	16.77 ± 7.43	13.13 ± 6.21

After the injection of the test solution back into the piezometer a natural dilution starts within the aquifer. The dilution occurs due to advection and dispersion influences (Istok, 2013). Therefore, a dilution factor is considered to determine subsurface denitrification rates. The denitrification rate is calculated based on how NO_3^- -N and Br^- concentrations declines as the push-pull test progress (5 hours/site) (Figures 16 — 21).

The measurements of NO_3^- -N and Br^- were adjusted subtracting the background values (Table 19) and the changes in Br^- (a conservative tracer) was used to quantify the natural dilution during the test (Istok, 2013). Nitrate dilution correction shows the concentration declined over the test after including the dilution effect. Subsurface denitrification is expected to have a zero-reaction order (Korom, 1992). In a zero-order reaction, the reaction rate is constant and independent of the concentration of NO_3^- -N.

No change in the ratio of NO_3^- -N over Br^- ratio suggests that no attenuation processes are happening, while a decrease in NO_3^- -N over Br^- ration suggests that NO_3^- -N is decreasing at a faster rate than compare to Br^- , hence NO_3^- is being reduced. With this analysis of the push-pull test, it is possible to quantify the amount of reactant that is being reduced. To complement this information, concentrations of denitrification reaction products expressed as excess N_2 and N_2O -N were also measured during the push-pull tests.

4.4.2 Analysis of push-pull test

Figures 17 — 22 present push-pull test results conducted at piezometers DF 3, SC 2, ARM 3, CAM 3, SR 3 and BUR 3. With an analysis of dilution rates, nitrate attenuation processes and dissolved gas analysis to assess subsurface denitrification status at each piezometer.

Piezometer DF 3

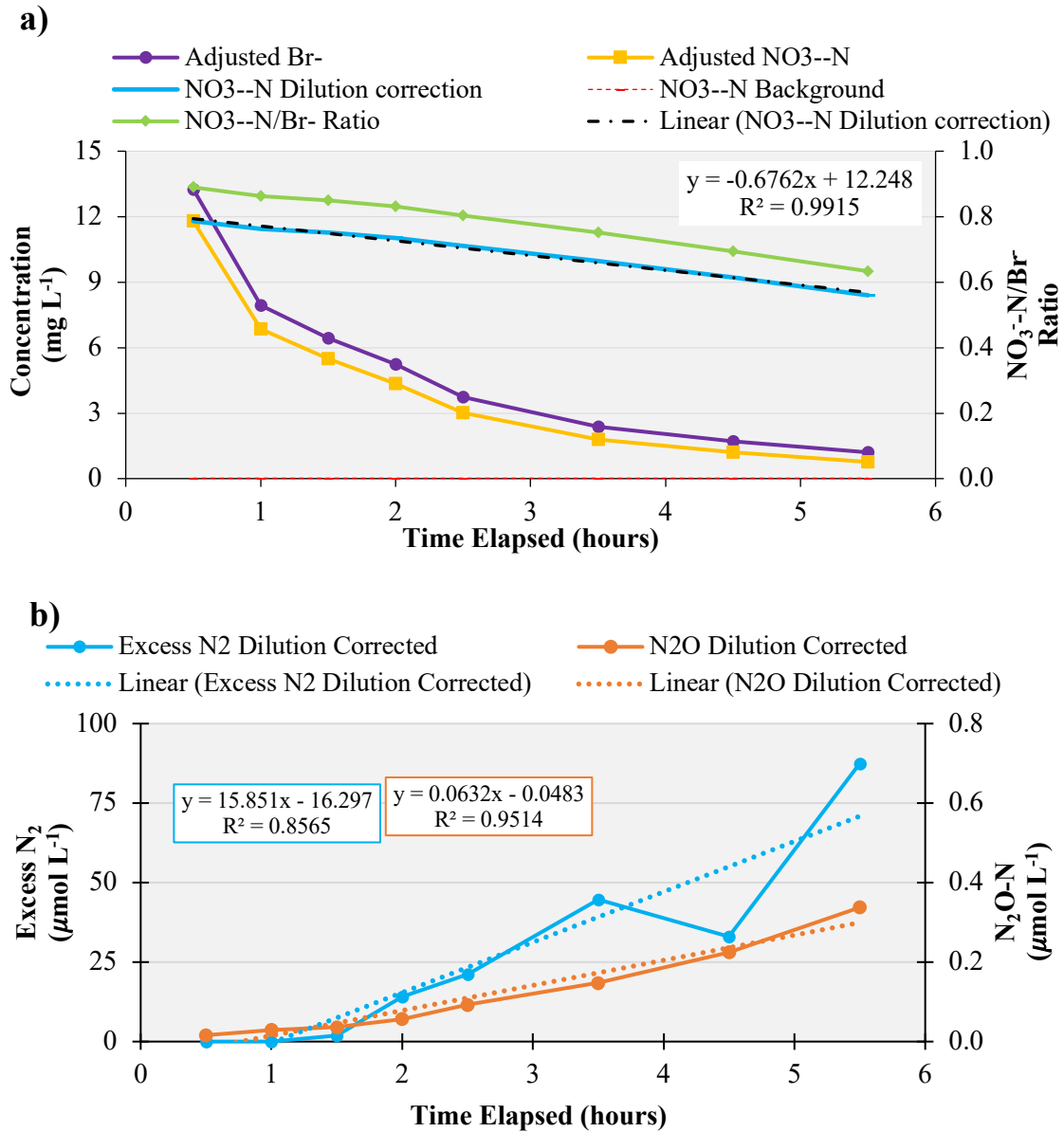


Figure 17: a) Adjusted NO₃⁻-N and Br⁻; NO₃⁻-N dilution correction, NO₃⁻-N background, NO₃⁻-N /Br⁻ ratio results of Push-pull test; b) Excess N₂ and N₂O-N results of Push-pull test conducted at piezometer DF 3, August 2018.

The push-pull conducted at site DF (Figure 17a) showed a higher NO₃⁻-N concentration reduction over Br⁻ dilution (Adjusted NO₃⁻-N and Br⁻ respectively) as the push-pull test

progressed. Which means that NO_3^- -N is decreasing at a faster rate than compared to Br^- . The **ratio** of NO_3^- -N over Br^- decreased from T0.5 (0.89) to T5.5 (0.63) (Figure 17a). After applying the dilution correction factor (Appendix 3), the piezometer DF 3 showed a **NO_3^- -N attenuation** (NO_3^- -N Dilution correction) of 3.4 mg L^{-1} over 5 hours (from 11.8 to 8.4 mg L^{-1}) (Figure 17a). Which **represents 28.8%** of NO_3^- -N attenuation by the end of the push-pull test (from T0.5) (Appendix 3).

Excess N_2 (dilution corrected) increased from $< 0.01 \text{ } \mu\text{mol L}^{-1}$ at T0.5 up to $87.5 \text{ } \mu\text{mol L}^{-1}$ by T5.5 during the push-pull test (Figure 18b). **N_2O -N** concentration (dilution corrected) also increased steadily from beginning to end ($0.02 \text{ } \mu\text{mol L}^{-1}$ at T0.5 to $0.34 \text{ } \mu\text{mol L}^{-1}$ by T5.5) (Figure 17b). However, the levels of N_2O -N were smaller relative to excess N_2 , resulting in an **average ratio** of 0.007 of N_2O -N over N_2O -N + excess N_2 during the push-pull test (T0.5 – T5.5) at site DF 3 (Appendix 4). At T5.5 the ratio of N_2O -N over N_2O -N + excess N_2 was 0.004 which greater than groundwater monthly ratios ($4.9 \cdot 10^{-4}$) (Appendix 4). The higher ratio of N_2O -N over N_2O -N + excess N_2 found at the end of the push-pull test suggests that NO_3^- reduction through subsurface denitrification was still continuing even after 5.5 hours. Presence of N_2O -N + excess N_2 suggests both partial and complete subsurface denitrification are responsible for NO_3^- attenuation at piezometer DF 3.

Subsurface denitrification status can be explained by groundwater chemistry and chemistry of the aquifer material. Understanding biogeochemical features of the soil profile and parental rock gives an insight into the subsurface denitrification process. In the unconfined aquifer at site DF, the upper boundary is the soil (in situ water table = 4 m, bgl) and the shallow aquifer parental material is river alluvium (Table 2). The Manawatu fine sandy loam soils found at site DF were built up from Alluvium deposition by infrequent flooding of the Manawatu River (Collins 2015). In general, the Manawatu fine sandy loam soils built up in the flats levees of the Manawatu River are well-drained (Cowie, J. D., and Rijkse, C. 1977), hence the low in situ water table measurements (data not shown).

Piezometer SC 2

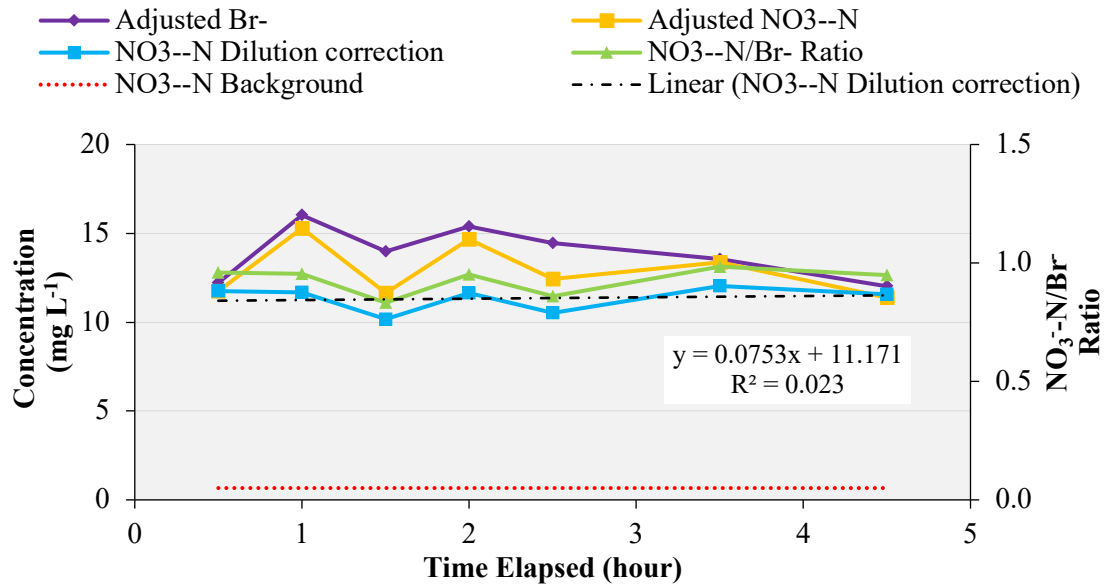


Figure 18: Adjusted NO_3^- -N and Br^- ; NO_3^- -N dilution correction, NO_3^- -N background, NO_3^- -N / Br^- ratio results of Push-pull test conducted at piezometer SC 2 on September 2018.

The push-pull conducted at piezometer SC 2 (Figure 18) very low NO_3^- -N and Br^- reduction (Adjusted NO_3^- -N and Br^- respectively) as the push-pull test progressed. The **ratio** of NO_3^- -N over Br^- showed no linearity ($r^2 = 0.023$) (Figure 18) and ranged between 0.83 to 0.98 (Appendix 2). After applying the dilution correction factor (Appendix 3), piezometer SC 2 showed **NO_3^- -N attenuation** (NO_3^- -N Dilution correction) of 0.16 mg L^{-1} over 5 hours (from 11.75 to 11.58 mg L^{-1}) (Figure 18). Which **represents 1.4%** of NO_3^- -N attenuation by the end of the push-pull test (from T0.5) (Appendix 3).

The low dilution rate was an unexpected result, as the rock type is Sand Flat and soil type Foxton brown sand-Pukepuke black sand and Himatangi sand (Table 2, Chapter 3). This rock and soil type are characterised for having good drainage and high recharge rate due to low porosity and high hydraulic conductivity of the aquifer material. Even though piezometer SC 2 showed no NO_3^- -N accumulation in the monthly analysis (Figure 14); little NO_3^- attenuation capacity in an aquifer must be considered while planning nutrient budgets. Especially when the natural nutrient status of those soils ranges from low to medium (Cowie, 1964), as found at site SC, and where leaching is highly probable. Soils from the Sand Country are characterised for low to very high exchangeable Ca^{2+} concentration and low K^+ (Cowie, 1964). Those features negatively correlate with values

observed in our groundwater samples; as site SC showed the highest concentration of Ca^{2+} and K^{+} compared to other sites (Table 16). Which might suggest a strong influence of fertiliser application on the topsoil on the groundwater chemistry over the influence of the soil type.

No logical results were observed on excess N_2 results at this site and only positives results were obtained when using a recharge temperature of 28 °C (data not shown). No $\text{N}_2\text{O-N}$ production was observed in any of the samples over the 5.5 hours of the test (data not shown). Based on the observed very low $\text{N}_2\text{O-N}$ concentrations combined with very slow $\text{NO}_3^{-}\text{-N}$ and Br^{-} dilution trend (Figure 18); the push-pull test at piezometer SC 2 was inconclusive.

For piezometer SC 2 another set of push-pull with a smaller volume of the test solution and a longer test is recommended to corroborate the $\text{NO}_3^{-}\text{-N}$ attenuation rate obtained. It would also be interesting to combine these results with another set of push-pull test in different seasons to compare the natural variation of subsurface denitrification capacity in different seasons (i.e. with raising water table).

Piezometer CAM 3

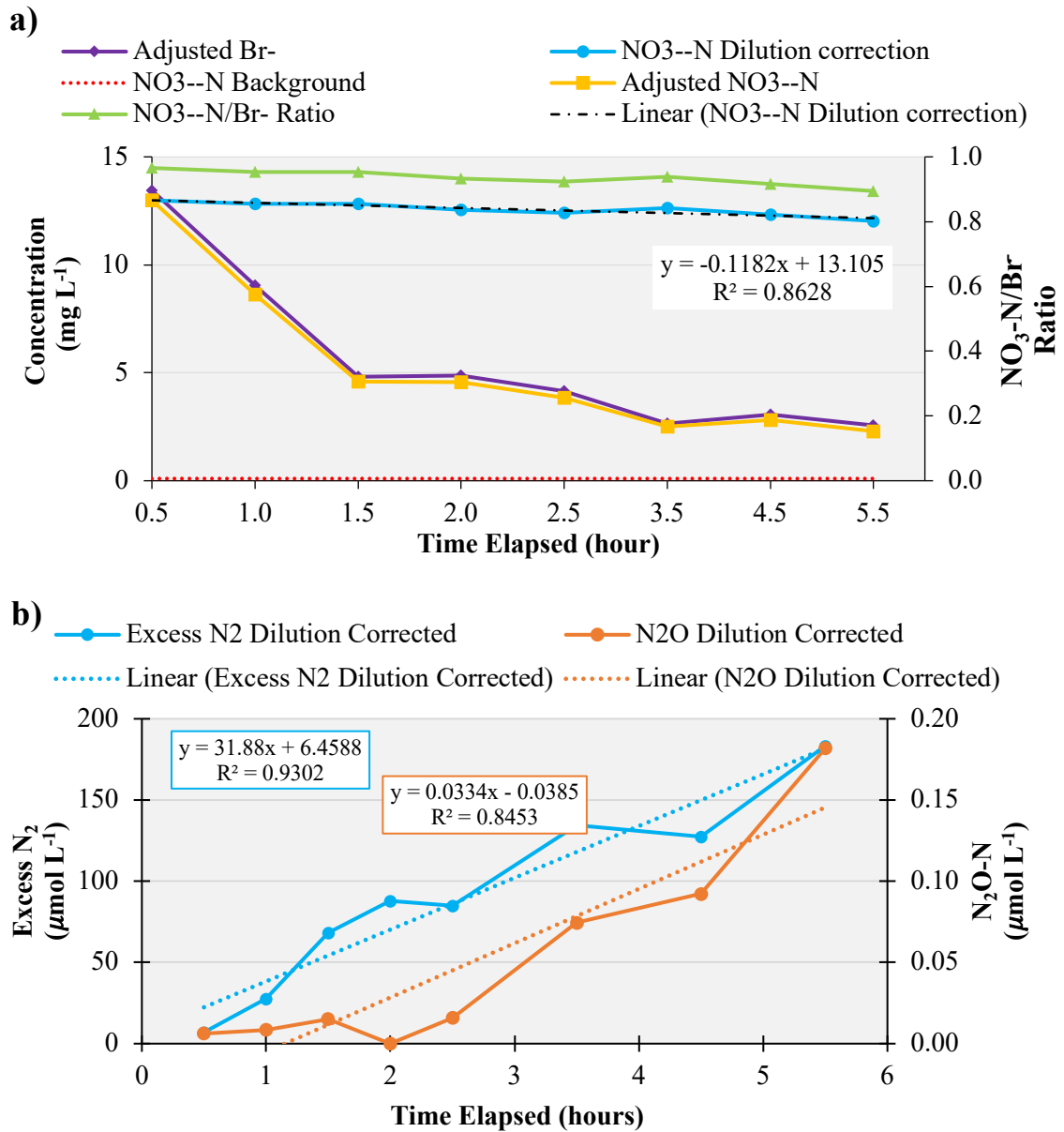


Figure 19: a) Adjusted NO₃⁻-N and Br⁻; NO₃⁻-N dilution correction, NO₃⁻-N background, NO₃⁻-N /Br⁻ ratio results of Push-pull test; b) Excess N₂ and N₂O-N results of Push-pull test conducted at piezometer CAM 3, August 2018.

The push-pull results conducted at piezometer CAM 3 (Figure 19a) showed a NO₃⁻-N reduction over Br⁻ dilution (Adjusted NO₃⁻-N and Br⁻ respectively) as the test progressed (Figure 20). The **ratio** of NO₃⁻-N over Br⁻ decreased slightly from T0.5 (0.97) to T5.5 (0.89). After applying the dilution correction factor (Appendix 3), piezometer CAM 3 showed a **NO₃⁻-N attenuation** (NO₃⁻-N Dilution correction) of 0.958 mg L⁻¹ over 5 hours (from 11.8

to 8.4 mg L^{-1}) (Figure 19a). Which **represents 7.4%** of $\text{NO}_3^- \text{N}$ attenuation by the end of the push-pull test (from T0.5) (Appendix 3).

After applying the dilution factor for dissolved gases (excess N_2 and $\text{N}_2\text{O-N}$), **excess N_2** showed concentrations (dilution corrected) ranging from 6.98 to $183.32 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$ between T0.5 to T5.5 (Figure 19b). The piezometer CAM 3 showed the most significant excess N_2 concentration by T5.5 compared with the other piezometers (Appendix 4). During the first transect (T0.5 - T2) $\text{N}_2\text{O-N}$ (dilution corrected) showed relatively stable concentration ($< 0.02 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$). After T2, $\text{N}_2\text{O-N}$ concentration increased steadily up to $0.18 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$ by T5.5 (Figure 19b). The piezometer CAM 3 presented the greatest increase in excess N_2 indicating favourable conditions for complete subsurface denitrification. Also the piezometer CAM 3 showed the lowest average ratio (0.0005) of $\text{N}_2\text{O-N}$ over $\text{N}_2\text{O-N} + \text{excess } \text{N}_2$ (Appendix 4). As a consequence, the piezometer CAM 3 showed the better suitable for subsurface denitrification compared to the others.

After 5.5 hours of test the ratio of $\text{N}_2\text{O-N}$ over $\text{N}_2\text{O-N} + \text{excess } \text{N}_2$ was 0.001 ; higher to the ratio found at piezometer CAM 3 during monthly samples (Appendix 4). An elevated ratio for $\text{N}_2\text{O-N}/(\text{N}_2\text{O-N} + \text{excess } \text{N}_2)$ at T5.5 suggested that NO_3^- was still being reduce even after the last sample was collected from the piezometer CAM 3.

Soils in the surroundings of Dannevirke and Pahiatua area of sampling for sites CAM, SR, BUR (Table 2) are developed on consecutive small basins of alluvium and tephra from the depositions of the Taupo Volcanic Zone (Molloy, 1982). Takapau series has therefore water-sorted tephra. After a development and consolidation period, the Takapau soils grade into Kopua soils where the annual rainfall increases to $\sim 1500 \text{ mm}$ as found at the sites BUR and SR (Molloy, 1988). The Takapau silt loam found at site CAM (Collins, 2015) site has good drainage. However, through in situ observation in the recharge rate at CAM 1 and CAM 3, it is possible to conclude there are different geological formations between 4.8 and 7.7 m (bgl) of the profile. The piezometer CAM 3 appeared to be installed in a high hydraulic conductivity layer, allowing groundwater flow in the surrounds of the piezometer CAM 3 (Rivas, 2018).

Piezometer ARM 3

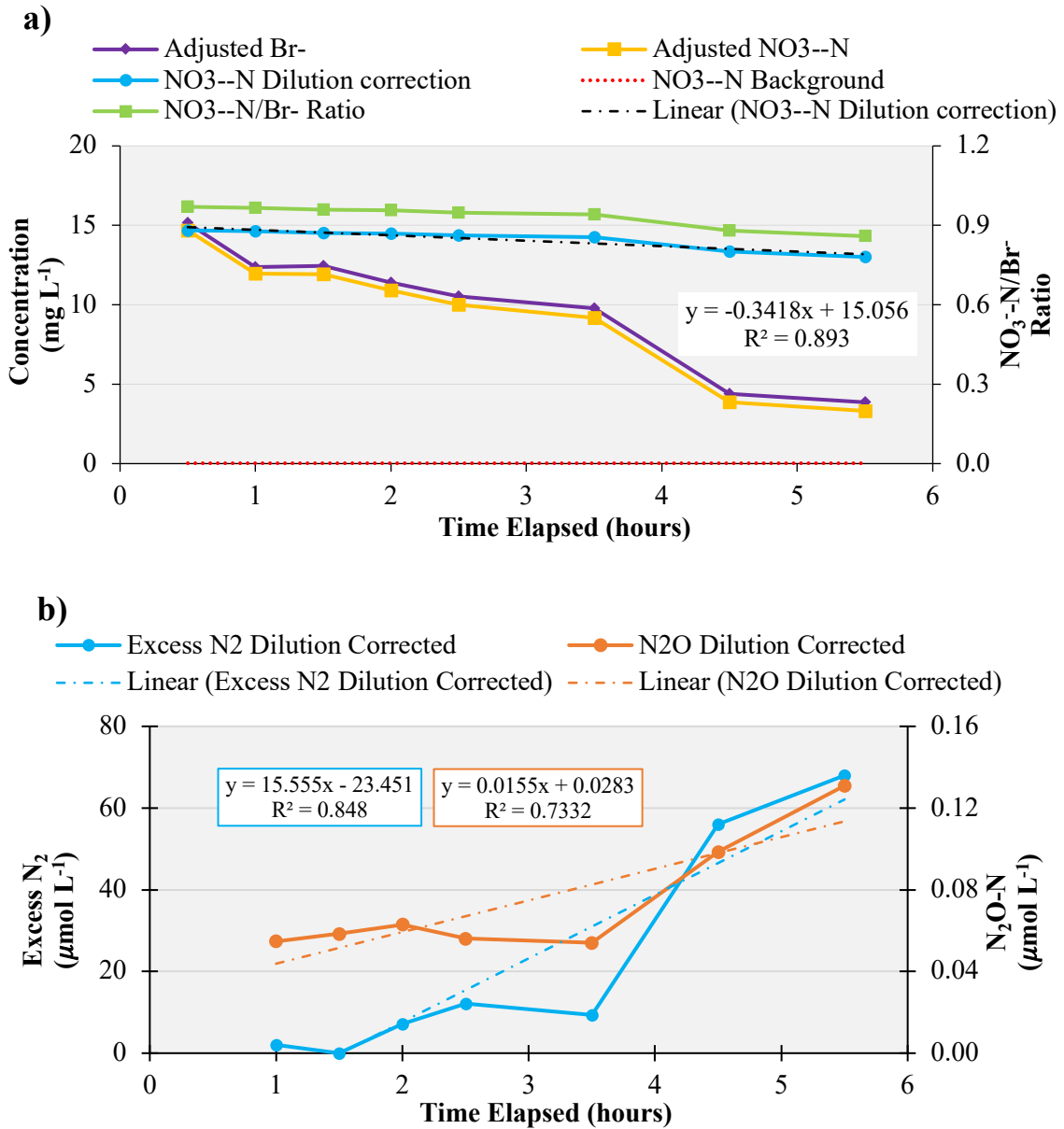


Figure 20: a) Adjusted NO_3^- -N and Br^- ; NO_3^- -N dilution correction, NO_3^- -N background, NO_3^- -N / Br^- ratio results of Push-pull test; b) Excess N_2 and N_2O -N results of Push-pull test conducted at piezometer ARM 3, August 2018.

The results for the push-pull test at site ARM (Figure 20a) showed a NO_3^- -N reduction over Br^- dilution (Adjusted NO_3^- -N and Br^- respectively) as the test progressed (Figure 19). The **ratio** NO_3^- -N / Br^- decreased from 0.97 at T0.5 to 0.86 at T5.5. After applying the dilution correction factor (Appendix 3), piezometer ARM 3 showed a **NO_3^- -N attenuation** (NO_3^- -N Dilution correction) of 1.68 mg L^{-1} over 5 hours (from 14.7 at T0.5 to 13.01 mg L^{-1} at

T5.5) (Figure 20a). Which represents **11.43%** of NO_3^- -N attenuation by the end of the push-pull test (from T0.5) (Appendix 2).

The **excess N_2** concentration (dilution corrected) increased from $< 0.01 \mu\text{mol} \cdot \text{L}^{-1}$ at T0.5 up to $67.99 \mu\text{mol} \cdot \text{L}^{-1}$ by T5.5 (Figure 20b). The **N_2O -N** concentration (dilution corrected) ranged from $0.01 \mu\text{mol} \cdot \text{L}^{-1}$ at T0.5 to $0.13 \mu\text{mol} \cdot \text{L}^{-1}$ by time T5.5 (Figure 20b). From time T0.5, excess N_2 and N_2O -N increased slightly until T3.5, where a sharp increase in the concentration excess N_2 and N_2O -N occurred within the last 2 hours of the push-pull test (Figure 19b).

Nevertheless, a slight increase in N_2O -N concentration is expected as N_2O is an intermediate step in the denitrification process (Figure 2). Resulting in an **average ratio** of 0.005 of N_2O -N over N_2O -N + excess N_2 during the push-pull test (T1 – T5.5) at piezometer ARM 3 (Appendix 4). At T5.5, the ratio between N_2O -N over N_2O -N + excess N_2 was 0.002 which greater than groundwater monthly ratios ($4 \cdot 10^{-6}$) (Appendix 4). A higher ratio of N_2O -N over N_2O -N + excess N_2 at the end of the push-pull test suggested that NO_3^- -N reduction through subsurface denitrification was still an ongoing process at piezometer ARM 3.

Even though piezometer ARM 3 showed the lowest excess N_2 concentration by T5.5 compared with the rest of the push-pull tests ($< 70 \mu\text{mol} \cdot \text{L}^{-1}$) (Appendix 4). Nevertheless, it has the second-lowest N_2O -N and excess N_2 ratio (Appendix 3) suggesting that complete subsurface denitrification is a major process for NO_3^- reduction. The piezometer ARM 3 showed a positive response for NO_3^- reduction when increasing NO_3^- -N inputs up to $\sim 10 \text{ mg} \cdot \text{L}^{-1}$.

Kairanga soils at site ARM (Table 2) are developed on river alluvium and are built on frequently flooded areas of the Manawatu River basins (Molloy, 1982). The small size particle of Kairanga silt loam and clay loam found at site ARM gives the poor soil drainage characteristic. Indeed, pugging was seen many times while collecting groundwater samples at the site. Poor soil drainage in explains the favourable conditions for anoxic redox status of groundwater samples at site ARM.

Piezometer SR 3

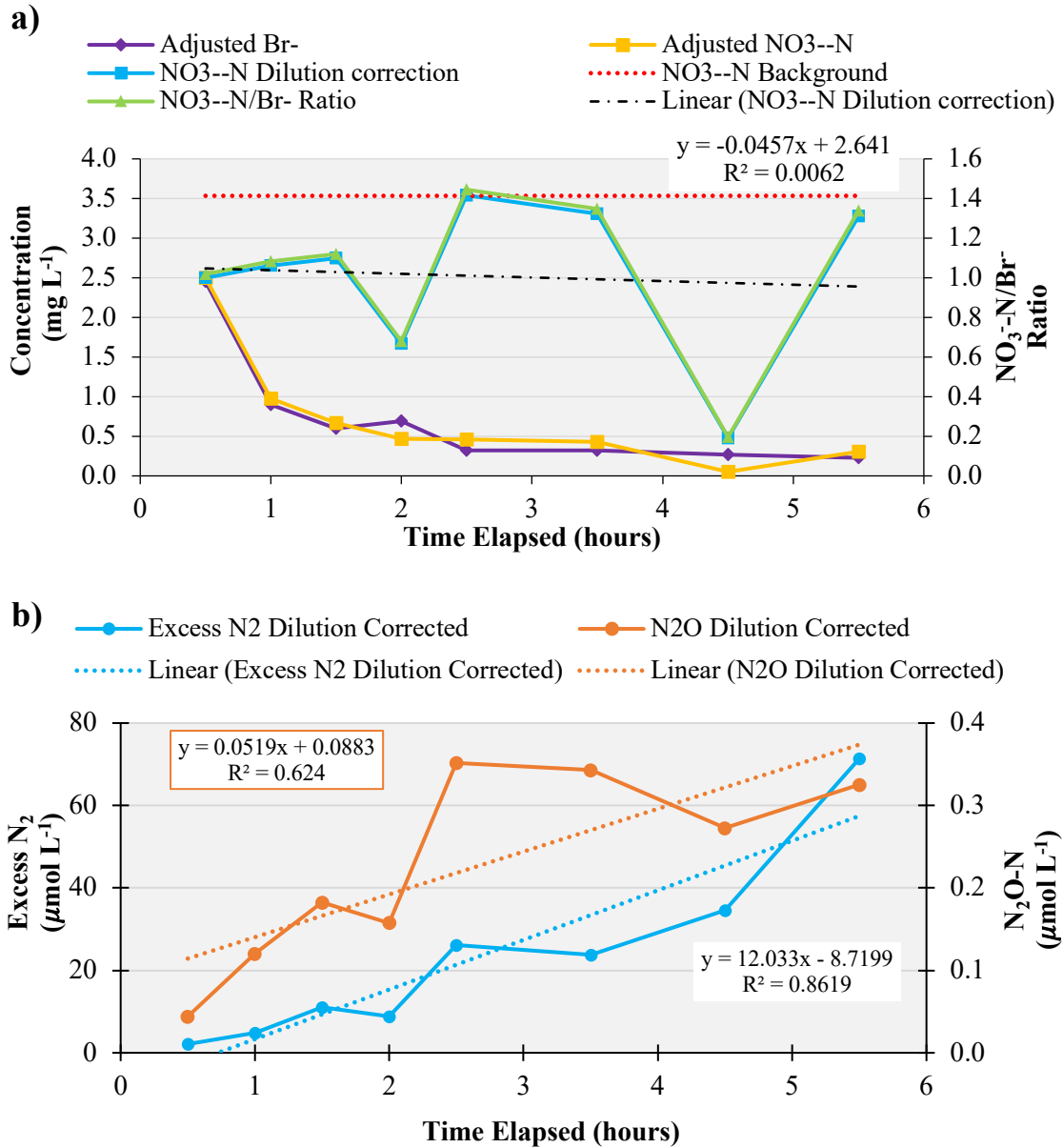


Figure 21: a) Adjusted NO₃⁻-N and Br⁻; NO₃⁻-N dilution correction, NO₃⁻-N background, NO₃⁻-N /Br⁻ ratio results of Push-pull test; b) Excess N₂ and N₂O-N results of Push-pull test conducted at piezometer SR 3, September 2018.

The push-pull conducted at piezometer SR 3 showed a very high dilution rate (Adjusted NO₃⁻-N and Br⁻ respectively) (Figure 21a). At T0.5, 82.6 % for Adjusted Br⁻ and 83.4 % for NO₃⁻-N was lost from the test solution (Appendix 3). The measured NO₃⁻-N concentration at T0.5 was less than double compared with the background values (Table 19). An analysis based on small concentration like the ones obtain at piezometer SR 3 must be treated carefully.

The **ratio** of NO_3^- -N over Br^- showed no linearity ($r^2 = 0.006$) (Figure 21a) and ranged between 0.2 to 1.44 (Appendix 2). After applying the dilution correction factor (Appendix 3), piezometer ARM 3 showed **NO_3^- -N attenuation** (NO_3^- -N Dilution correction) of 2.02 mg L^{-1} over 4 hours (from 2.50 to 0.48 mg L^{-1}) (Figure 21a). Which **represents 80.8 %** of NO_3^- -N attenuation by the end of the push-pull test (from T0.5) (Appendix 3). Due to dilution factors, **NO_3^- -N** attenuation results are considered invalid. No attenuation rate was calculated for piezometer SR 3 due to the high dilution rates and NO_3^- -N concentrations below the backgrounds levels (3.53 mg L^{-1}) (Appendix 3).

Result of excess N_2 and N_2O -N were assessed despite the extreme dilution observed while conducting the push-pull test at piezometer SR 3. The **excess N_2** concentration (dilution corrected) increased from $2.12 \mu\text{mol} \cdot \text{L}^{-1}$ at T0.5 up to $71.37 \mu\text{mol} \cdot \text{L}^{-1}$ by T5.5 (Figure 21b). The **N_2O -N** concentration (dilution corrected) ranged from $0.04 \mu\text{mol} \cdot \text{L}^{-1}$ at T0.5 to $0.33 \mu\text{mol} \cdot \text{L}^{-1}$ by time T5.5 (Figure 22b). The **average ratio** of N_2O -N over N_2O -N + excess N_2 was 0.015 during the push-pull test (T0.5 – T5.5) at piezometer SR 3 (Appendix 4). Piezometer SR 3 showed the highest average ratio, as a result, piezometer SR 3 was the less suitable for subsurface denitrification compared to the others. At T5.5 the ratio between N_2O -N and excess N_2 was 0.0045 which is greater than groundwater monthly ratios ($4.6 \cdot 10^{-5}$) (Appendix 2). A higher ratio of N_2O -N over N_2O -N + excess N_2 at the end of the push-pull test suggest that subsurface denitrification was still responsible for NO_3^- attenuation at piezometer SR 3. Yet, the presence of N_2O -N and excess N_2 and with the highest average ratio (0.015) (Appendix 4) suggests that at piezometer SR 3, NO_3^- is not being reduced completely and N_2O is being accumulated (partial subsurface denitrification) but not reduced to N_2 . Even though **excess N_2** and **N_2O -N** was observed while conducting the push-pull test (Appendix 4) the result should be treated carefully and another test is recommended at piezometer SR 3.

Piezometer BUR 3

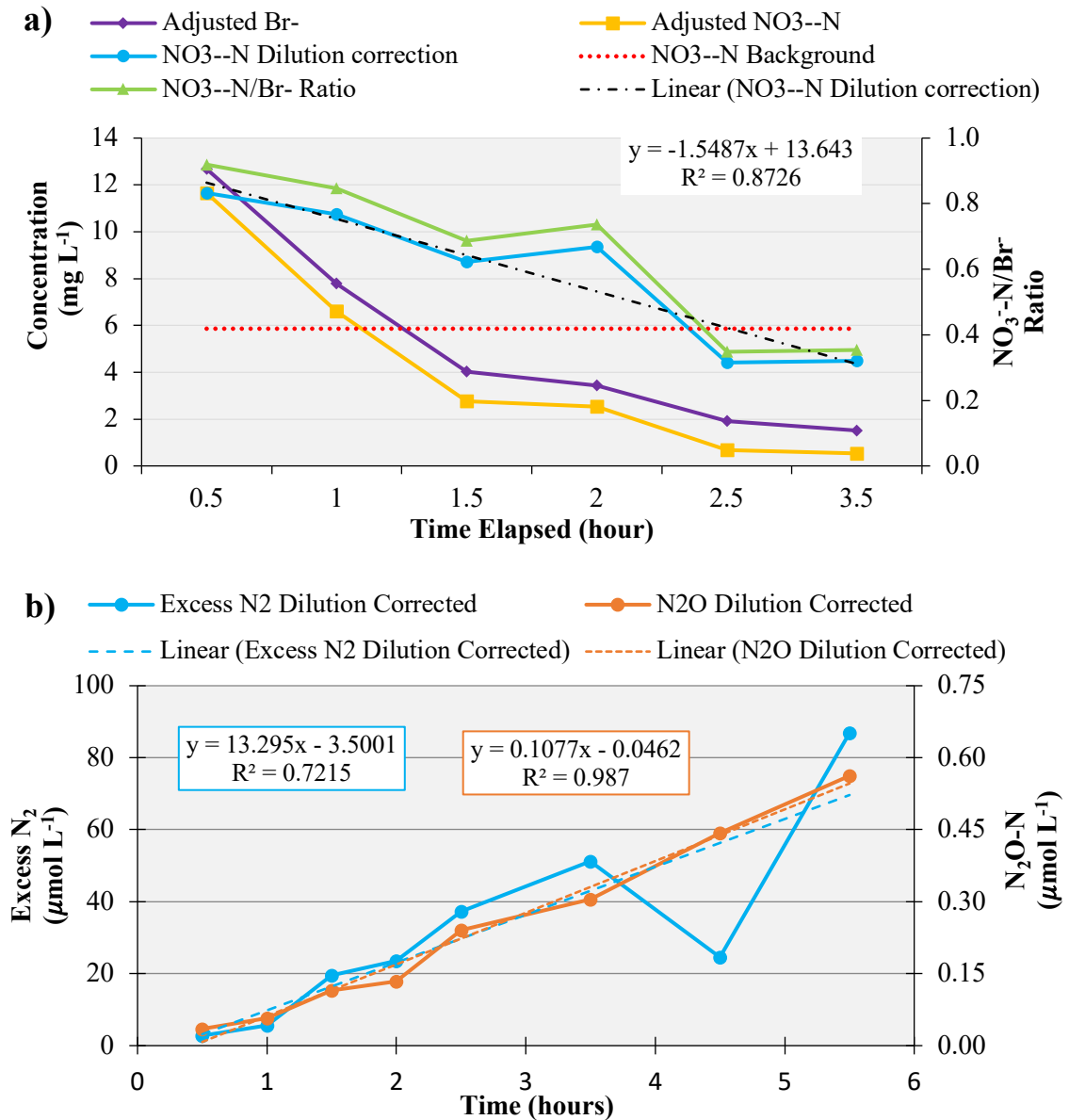


Figure 22: a) Adjusted NO₃⁻-N and Br⁻; NO₃⁻-N dilution correction, NO₃⁻-N background, NO₃⁻-N /Br⁻ ratio results of Push-pull test; b) Excess N₂ and N₂O-N results of Push-pull test conducted at piezometer BUR 3, September 2018.

The push-pull test at site BUR showed a high dilution rate (Adjusted NO₃⁻-N and Br⁻ respectively) (Figure 22a), but not as strong as compared with the dilution rate observed at piezometer SR 3. The groundwater samples collected at T1.5 had already lost 69.4 % of the tracer (Br⁻) and 83.6 % of NO₃⁻-N.

The **ratio** of NO₃⁻-N over Br⁻ decreased significantly from T0.5 (0.92) to T3.5 (0.35). After applying the dilution correction factor (Appendix 3), piezometer BUR 3 showed a **NO₃⁻-N**

attenuation (NO_3^- -N Dilution correction) of 7.17 mg L^{-1} over 3 hours (from 11.65 to 4.48 mg L^{-1}) (Figure 22a). Which **represents 61.6%** of NO_3^- -N attenuation by T3.5 (from T0.5) (Appendix 3).

The **excess N_2** concentration (dilution corrected) increased from $2.77 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$ at T0.5 up to $86.85 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$ by T5.5 (Figure 22b). The **N_2O -N** concentration (dilution corrected) ranged from $0.04 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$ at T0.5 to $0.56 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$ by time T5.5 (Figure 22b). The push-pull conducted at piezometer BUR 3 showed the highest concentration of excess N_2O -N (0.56 mg L^{-1}) produced by the end of the push-pull test (T5.5). The **average ratio** of N_2O -N over N_2O -N + excess N_2 was 0.009 during the push-pull test (T0.5 – T5.5) at piezometer BUR 3 (Appendix 4). At T5.5 the ratio of N_2O -N over N_2O -N + excess N_2 was 0.0064 which greater than groundwater monthly ratios ($1.4 \cdot 10^{-5}$) (Appendix 2). A higher ratio of N_2O -N over N_2O -N + excess N_2 at the end of the push-pull test suggest that subsurface denitrification was still an ongoing process at piezometer BUR 3. Yet, the presence of N_2O -N and excess N_2 with a higher ratio (compared with the others) suggests that at piezometer BUR 3, NO_3^- was not being reduced completely. Hence, N_2O is being produced (through partial subsurface denitrification) but not reduced to N_2 .

The stony soils found at site SR and BUR (Table 2) are characterised by good drainage (Cowie, 1964). We recommend another set of push-pull test at piezometer BUR 3 to corroborate our results. We suggest another test with bigger volume of test solution or/and a smaller window between groundwater sample collection (i.e. every 15 minutes within the first 2 hours).

4.4.3 Subsurface denitrification rates and assessment of piezometers.

Complete and partial subsurface denitrification rate indicates how fast excess N_2 and N_2O are being produced respectively, while conducting the push-pull tests. In other words, how shallow groundwater surrounding the piezometer respond to a strong and punctual pressure of NO_3^- inputs.

The reaction order indicates the behaviour of the speed with respect to the concentration of the reactant (reaction rate). When the reaction rate is constant and independent of the reactant concentration (e.g. $\text{NO}_3^- \text{-N}$) the reaction order is zero, therefore:

$$v^* = \frac{d[\text{NO}_3^- \text{-N}]}{dt} = \frac{d[\text{Excess N}_2]}{dt} = \frac{d[\text{N}_2\text{O-N}]}{dt} \quad \text{Equation 32}$$

*Reaction rate only showing the reactants and products under analysis.

$$v = k[\text{NO}_3^- \text{-N}]^0 \quad \Rightarrow \quad v = k \quad \text{Equation 33}$$

Then,

$$v = \frac{\partial[\text{NO}_3^- \text{-N}]}{\partial t} \quad \text{Equation 34}$$

Combining Equation 23 and 34;

$$-\frac{\partial[\text{NO}_3^- \text{-N}]}{\partial t} = k \quad \text{Equation 35}$$

$$-\partial[\text{NO}_3^- \text{-N}] = k \partial t \quad \text{Equation 36}$$

$$-\partial[\text{NO}_3^- \text{-N}_{\text{initial}} - \text{NO}_3^- \text{-N}_{\text{final}}] = k \partial t \quad \text{Equation 37}$$

In a zero-order reaction, the concentration of the reactant is inversely proportional to the elapsed time; and the concentration of the product (excess N_2 and $\text{N}_2\text{O-N}$) are directly proportional to the time elapsed. In a zero-order reaction, the reaction rate is represented by the slope of the line reactant $[\text{Ln NO}_3^- \text{-N}]$ over time (Appendix 3). As $\text{NO}_3^- \text{-N}$ is a reactant the slope is negative as concentration decreases over time. When a regression line is applied to the subsurface denitrification products $\text{N}_2\text{O-N}$ and excess N_2 , then the slope is positive.

The attenuation rate (Table 21) represents the speed at which $\text{NO}_3^- \text{-N}$ was attenuated while conducting the push-pull test. For the purpose of this analysis, the attenuation rate is represented by the sloped of $\text{NO}_3^- \text{-N}$ dilution correction (Figures 17 – 22). Complete subsurface denitrification rate (Table 21) represents the speed at which excess N_2 was produced while conducting the push-pull test. While the partial subsurface denitrification

rate (Table 21) shows the speed at which $\text{N}_2\text{O-N}$ was produced (that was not reduced to N_2) while conducting the push-pull test. **Complete and partial subsurface denitrification** rate was calculated through a linear regression analysis of each product (**excess N_2 and $\text{N}_2\text{O-N}$** respectively) over time (Appendix 4).

Table 21: Nitrate-N attenuation rate, complete and partial subsurface denitrification rate at the piezometers over push-pull test.

Piezo	NO_3^- -N attenuated [mg]	NO_3^- -N attenuation rate* [mg L^{-1} h^{-1}]	Complete subsurface denitrification rate** [$\mu\text{mol L}^{-1}$ h^{-1}]	Partial subsurface denitrification rate [$\mu\text{mol L}^{-1}$ h^{-1}]**
DF 3	3.40	0.68 ($r^2 = 0.99$)	15.85 ($r^2 = 0.86$) (0.44 mg L^{-1} h^{-1})	0.06 ($r^2 = 0.95$) (0.0017 mg L^{-1} h^{-1})
ARM 3	1.68	0.34 ($r^2 = 0.89$)	15.55 ($r^2 = 0.85$) (0.44 mg L^{-1} h^{-1})	0.02 ($r^2 = 0.73$) *** (0.0006 mg L^{-1} h^{-1})
CAM 3	0.96	0.12 ($r^2 = 0.86$)	31.88 ($r^2 = 0.93$) (0.89 mg L^{-1} h^{-1})	0.03 ($r^2 = 0.85$) (0.0008 mg L^{-1} h^{-1})
SR 3	2.02	-	12.03 ($r^2 = 0.86$) (0.34 mg L^{-1} h^{-1})	0.05 ($r^2 = 0.62$) *** (0.0014 mg L^{-1} h^{-1})
BUR 3	7.17	1.55 ($r^2 = 0.87$)	13.30 ($r^2 = 0.72$) (0.37 mg L^{-1} h^{-1})	0.11 ($r^2 = 0.99$) (0.0031 mg L^{-1} h^{-1})

* Slope of NO_3^- -N dilution correction (Figures 17 - 22)

**Regression analysis of [Product] over time on push-pull test (Appendix 4).

***Data adjusted to fit (Appendix 4).

The piezometer **DF 3** showed NO_3^- -N attenuation of 3.4 mg over the push-pull test, with a NO_3^- -N attenuation rate of 0.68 mg L^{-1} h^{-1} . The piezometer **ARM 3** showed NO_3^- -N attenuation of 1.68 mg over the push-pull test, with a NO_3^- -N attenuation rate of 0.34 mg L^{-1} h^{-1} . The piezometer **CAM 3** showed the slowest NO_3^- -N attenuation rate (0.12 mg L^{-1} h^{-1}), attenuating only 0.96 mg over the push-pull test. Yet, the piezometer CAM 3 showed the highest complete subsurface denitrification rate (31.88 $\mu\text{mol L}^{-1}$ h^{-1}). This is result can be associated with the high concentration of Mn^{2+} found at **CAM 3**, which would indicate that the Mn^{2+} is the main electron donors in the denitrification process at this piezometer. The piezometer **SR 3** did not fit a linear regression as an extreme dilution rate was observed

(Figure 21). The fastest NO_3^- -N attenuation rate was observed at piezometer **BUR 3** ($1.55 \text{ mg L}^{-1} \text{ h}^{-1}$) reducing 7.17 mg over the push-pull. However complete subsurface denitrification rate was only $13.3 \text{ } \mu\text{mol L}^{-1} \text{ h}^{-1}$ of excess N_2 and for partial complete subsurface denitrification rate was $0.11 \text{ } \mu\text{mol L}^{-1} \text{ h}^{-1}$ of $\text{N}_2\text{O-N}$, the highest compared with the other sites.

These results support the hypothesis that complete subsurface denitrification is promoted where shallow groundwater present anoxic conditions, showing a higher denitrification potential. In contrast, shallow groundwater under oxidizing conditions promote partial subsurface denitrification, where NO_3^- might be attenuated but not completely reduced, increasing the emissions of N_2O . In the agricultural context, farms with oxidizing conditions in shallow groundwater not only promote NO_3^- accumulation but can also promote partial subsurface denitrification, releasing N_2O .

Figure 23 shows the ratio of $\text{N}_2\text{O-N}$ over excess $\text{N}_2 + \text{N}_2\text{O-N}$ over the push-pull test. The ratio indicates the piezometers that showed better suitability for subsurface denitrification during the push-pull test (5.5 hours). It represents how the groundwater behaves after an incrementation of NO_3^- concentrations, in these cases it was through the injection of the test solution into the piezometers.

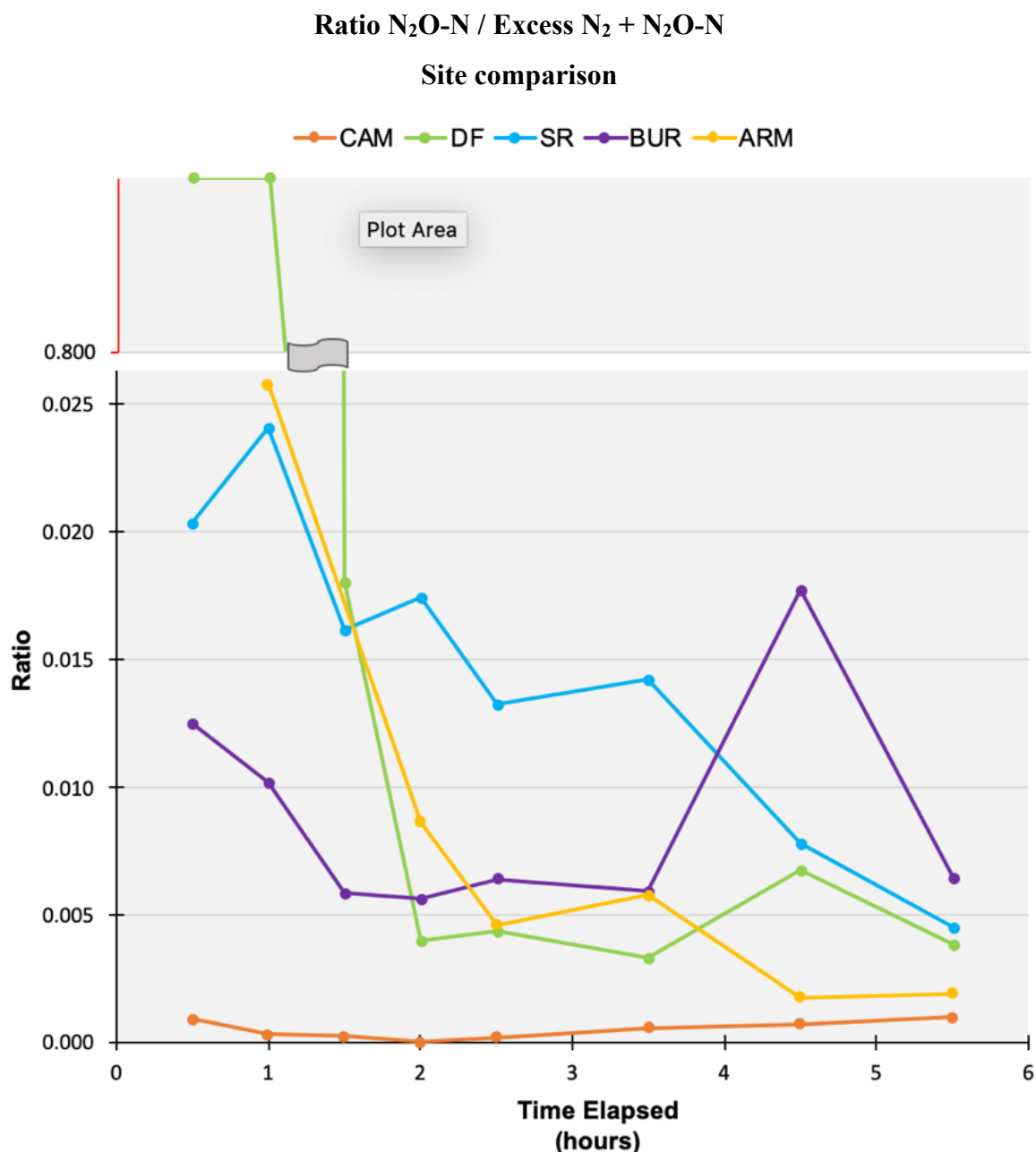


Figure 23: Ratio of N_2O-N / $N_2O-N + \text{Excess } N_2$ by piezometer over push-pull tests.

For the ratio of N_2O-N over excess $N_2 + N_2O-N$ is important to consider not only the average but also the trend over time. A negative trend indicates that the proportion of N_2O-N was decreasing respect to excess $N_2 + N_2O-N$ overtime, and so, N_2O was not being accumulated.

The reducing piezometer **DF 3**, **ARM 3** and **CAM 3** showed the best denitrification potential (DP) (i.e. best suitability for subsurface denitrification). These piezometer showed anoxic conditions (Table 13 and 14), with low DO monthly average concentration (< 1 mg

L⁻¹) (Figure 8), low NO₃⁻-N monthly average concentration (< 0.1 mg L⁻¹) (Figure 14); and enough concentration of electron donors (Fe²⁺ > 2 mg L⁻¹ and Mn²⁺ > 0.1 mg L⁻¹) (Figure 11 and 12 respectively). Which is supported by the lowest ratios of N₂O-N over excess N₂ + N₂O-N (Figure 23) obtained over the push-pull tests.

The oxidizing piezometers **SR 3** and **BUR 3** showed the worst DP (i.e. lowest suitability for subsurface denitrification). The piezometer SR 3 and BUR 3 showed oxic conditions (Table 15), NO₃⁻-N monthly average concentrations greater than 1 mg L⁻¹; and low concentration of the electron donors Fe²⁺ and Mn²⁺ (Figure 11 and 12 respectively). Which is supported by the highest ratios of N₂O-N over excess N₂ + N₂O-N (Figure 23) obtained over the push-pull tests.

The piezometer **CAM 3** showed a constant and low ratio of N₂O-N over excess N₂ + N₂O-N over the push-pull test (Figure 23). The piezometer CAM 3 showed the best suitability for subsurface denitrification as it presents anoxic redox condition (Table 13), a suitable concentration of the electron donors Mn²⁺ (Figures 12), the highest complete subsurface denitrification rate (Table 21) and the lowest ratio of N₂O-N over excess N₂ + N₂O-N (Figure 23). The piezometer **SR 3** showed an average ratio (0.015) of N₂O-N over excess N₂ + N₂O-N 30 times higher than piezometer CAM 3 (0.0005) (Appendix 3). These results show that after an incrementation on NO₃⁻ concentration in shallow groundwater, the piezometer **CAM 3** met the requirements for subsurface denitrification and showed the best DP compared to the other piezometers. While piezometer **SR 3** presented unsuitable conditions for subsurface denitrification and showed the worst DP compared to the other piezometers presenting a higher risk for NO₃⁻ accumulation.

5. Conclusions

Subsurface denitrification (SD) shows to be spatial and temporal variable considering the 4 main influence factors describe by Korom (1992). For simplicity, conclusions in this study are divided by type of analysis; as subsurface denitrification has proved to be a complex process influenced by many factors.

Based on the groundwater chemical analysis results conducted over 7 months (February-September 2018) in the Manawatu and Rangitikei River catchments the measured shallow groundwater. Subsurface denitrification showed to be a process dependent on the hydrogeological and geochemical features of the aquifer of each site:

- Complete SD (excess N_2) showed a strong positive correlation with reduced electron donors (Fe^{2+} and Mn^{2+}), pH and NH_4^+ -N in the groundwater samples.
- Complete SD (excess N_2) showed a strong negative correlation with DO levels in the groundwater.
- Nitrate-N showed a strong positive correlation with DO levels and N_2O -N (partial SD).
- Nitrate-N showed a strong negative correlation with reduced electron donors (Fe^{2+} , Mn^{2+}) and excess N_2 in the groundwater samples.
- Based on groundwaters monthly analysis results, the reducing piezometer DF 2, 3; SC 1, 2; CAM 3; ARM 1, 2 and 3 showed little NO_3^- -N accumulation compare with oxidizing piezometers DF 1; SR 1, 2, 3; BUR 1, 2 and 3.

The main conclusions based on monthly groundwater observations at 17 piezometers located at 6 agricultural lands in the Manawatu and Rangitikei River catchments are summarized in the following table.

Table 22: A summary of groundwater redox conditions, chemical and dissolved gas analysis in shallow groundwater at 6 agricultural lands in the Manawatu and Rangitikei River catchments.

Reducing conditions	DF 2, 3; SC 1, 2; CAM 3; ARM 1, 2, 3 > DF 1; CAM 1; SR 1, 2, 3; BUR 1, 2, 3
NO₃⁻ accumulation	DF 1, 2, 3; SC 1, 2; CAM 3; ARM 1, 2, 3 < CAM 1; SR 1, 2, 3; BUR 1, 2, 3

Based on the push-pull test results conducted at 6 piezometers at the Manawatu and Rangitikei River catchments it can be noted that a high NO₃⁻ attenuation potential does not imply an ecosystem service. Quantification of the end products of SD (Excess N₂ and N₂O) reveals if the attenuation process performs as an ecosystem service or as a pollution swamp. Table 23 summarise subsurface denitrification suitability between piezometer.

Table 23: Summary of suitability for subsurface denitrification in shallow groundwater at 6 agricultural lands in the Manawatu and Rangitikei River catchments.

NO₃⁻ Attenuation rate *	BUR 3 > DF 3 > ARM 3 > CAM 3
Complete subsurface denitrification rate*	CAM 3 > DF 3 > ARM 3 > BUR 3 > SR 3
Partial subsurface denitrification rate*	ARM 3 < CAM 3 < SR 3 < DF 3 < BUR 3
Suitability for subsurface denitrification**	CAM 3 > ARM 3 > DF 3 > BUR 3 > SR 3

* Based on push-pull test results (Table 21).

** Based on N₂O-N / N₂O-N + Excess N₂ average ratio (Appendix 4).

This research has proven that aquifers can have a high NO₃⁻ attenuation potential but can also be a source of N₂O contributing to greenhouse gas emissions. Hence, policies development for agricultural management in the Manawatu and Rangitikei River catchments should consider a sound understanding and measurement of the biogeochemical processes such as SD. Subsurface denitrification in the Manawatu and Rangitikei River catchments has proven to be spatial and temporal variable with unquestionable influence of hydrogeological and geochemical characteristics of the subsurface environment.

Overall, the piezometers **DF 2, 3; SC 1, 3; ARM 1, 2, 3 and CAM 3** met the main requirements (redox status and concentration of electron donors) for SD. As firstly they showed overall anoxic redox status (reducing conditions). Secondly, the concentration of electron donors (Fe^{2+} and Mn^{2+}) were found to be suitable for SD ($> 1 \text{ mg L}^{-1}$ and $> 0.05 \text{ mg L}^{-1}$ respectively). This conclusion is also supported as the reducing piezometers showed no NO_3^- -N accumulation ($< 0.5 \text{ mg L}^{-1}$), indicating that NO_3^- is being reduced.

The piezometers with mixed redox status (**SC 3 and CAM 1**) showed a concentration of electron donors ranging just over the redox threshold ($0.1 - 1.0 \text{ mg L}^{-1}$ and $> 0.05 \text{ mg L}^{-1}$ respectively). One of the piezometer with mixed redox condition (CAM 1) showed NO_3^- -N accumulation ($> 6 \text{ mg L}^{-1}$) while the other piezometer (SC 3) showed variability in NO_3^- -N accumulation ranging from 0.02 mg L^{-1} to 22.56 mg L^{-1} .

Overall, the piezometers **DF 1, SR 1, 2, 3 and BUR 1, 2, 3** did not meet the main requirements for SD. As firstly they showed overall oxic redox status (oxidizing conditions). Secondly, they showed a concentration of electron donors below the threshold to support SD and for identifying redox processes ($< 0.1 \text{ mg L}^{-1}$ and $< 0.05 \text{ mg L}^{-1}$ respectively). This conclusion is also supported as the oxidizing piezometers showed NO_3^- -N accumulation ($> 3 \text{ mg L}^{-1}$) except for piezometer DF 1 that showed variability in NO_3^- -N concentrations ranging from 0.01 mg L^{-1} to 3.75 mg L^{-1} over the study.

The dominant terminal product of SD, whether was complete SD (N_2 — as end product) or partial SD (N_2O — as end product) spatially varied according to the groundwater redox status and concentration of electron donors. Based on the monthly analysis and push-pull test results the piezometers **CAM 3** and **ARM 3** showed the highest suitable conditions for SD followed by the piezometer **DF 3**. The piezometer **BUR 3** showed the highest partial SD rate. Therefore BUR 3 is considered in general, the less suitable piezometer for SD. The push-pull test conducted at **SR 3** and **SC 3** showed inconclusive results.

The observations highlight the influence of different hydrogeological settings on spatial variability of **partial SD (pollution swamp)** or complete SD (**ecosystem service**) in shallow groundwaters. This information can be used to design and formulation of targeted and effective management measures for sustainable agricultural production while protecting soil, water and air quality. Agricultural land can be identified and classified in

areas under oxidizing, mixed and reducing shallow groundwater conditions for a targeted N management. Agricultural areas with oxidizing shallow groundwater should be more carefully managed with tighter N limits as they present a higher risk for NO_3^- accumulation and a potential source of the greenhouse gas, N_2O . For future agricultural and environmental management redox status can be used for decision making in the upcoming land use designation. Agricultural activities that present a high pressure in the environment (i.e. intensive agriculture) should be allocated in areas where the shallow groundwater can perform an ecosystem service through complete SD, limiting NO_3^- accumulation and with no undesirable end products (i.e. N_2O).

Bibliography

- Abiy A., Melesse A. M., Behabtu Y., and Abebe B. (2015). Groundwater Vulnerability Analysis of the Tana Sub-basin: An Application of DRASTIC Index Method. *Landscape Dynamics, Soils and Hydrological Processes in Varied Climates*, 435 - 461. DOI 10.1007/978-3-319-18787-7_21
- Baethgen, W., Martino, D., 2001. Greenhouse gas emissions in the agricultural and forestry sectors of Uruguay and opportunities in the carbon market. *Arch. Latinoam. Prod. Anim.* 9(2): 127 – 134.
- Bekesi, G. McConchie, J. 1999. Groundwater recharge modelling using the Monte Carlo technique, Manawatu region, New Zealand. *Journal of Hydrology* 224, 137-148. Elsevier. PII: S0022-1694(99)00128-6
- Bekesi G., and McConchie J. 2002. The use of aquifer-media characteristics to model vulnerability to contamination, Manawatu region, New Zealand. *Hydrogeology Journal* 10 (2), 322–331.
- Bragan, R., Starr, J., Parkin, T., 1997. Shallow groundwater denitrification rate measurement by acetylene block. *Journal of Environmental Quality* 26, 1531–1538.
- Boring L., Swank, W., Waide, J., Henderson, G. 1988. Sources, fates, and impacts of nitrogen inputs to terrestrial ecosystems: review and synthesis. *Biogeochemistry* 6: 119 – 159.
- Christensen, P. B., L. P. Nielsen, J. Sorensen, and N. P. Revsbech. 1990. Denitrification in nitrate-rich streams: diurnal and seasonal-variation related to benthic oxygen metabolism. *Limnology and Oceanography* 35:640-651.
- Christensen, T., Bierga, P., Banwartb, S., Jakobsenc, R., Hans-Jorgen, H. 2000. Characterisation of redox conditions in groundwater contaminant plumes. *Journal of Contaminant Hydrology*, Volume 45, Issue 3 - 4, pages 165 - 241.
- Clague, J. C. 2013. Denitrification in the shallow groundwater system of two agricultural catchments in the Waikato, New Zealand. Doctoral thesis, Lincoln University, Canterbury, New Zealand.
- Clague, J., Stenger, R., Morgenstern, U. 2018. The influence of unsaturated zone drainage status on denitrification and the redox succession in shallow groundwater. *Stoten*, <https://doi.org/10.1016/j.scitotenv.2018.12.383>
- CliFlo: NIWA's National Climate Database. (2017) Online <http://cliflo.niwa.co.nz/> (accessed on September 2018).

- Clough TJ, Sherlock RR, Cameron KC, Ledgard SF. Fate of urine nitrogen on mineral and peat soils in New Zealand. *Plant Soil* 178: 141 – 52.
- Cowie, J. D. 1964. Aokautere ash in the Manawatu district, New Zealand, *New Zealand Journal of Geology and Geophysics*, 7:1, 67-77, DOI: 10.1080/00288306.1964.10420157
- Cowie J. D. 1964. Loess in the Manawatu district, New Zealand, *New Zealand Journal of Geology and Geophysics*, 7:2, 389-396, DOI: 10.1080/00288306.1964.10420185
- Collins, S. (2015). Investigating the Transport and Fate of Nitrogen from Farms to River in the Lower Rangitikei Catchment. (Master of Science), Massey University, New Zealand.
- Collins, S., Singh, R., Palmer, A., Horne, D., Roygard, J., Matthews, A. 2016. Assessment of nitrogen flow pathways and its potential attenuation in shallow groundwater in the lower Rangitikei catchment. In: Integrated nutrient and water management for sustainable farming. Occasional Report N° 29. Fertilizer and Lime Research, Massey University, Palmerston North, New Zealand. 14 pages.
- Clothier, B., Mackay, A., Carran, A., Gray, R., Parfitt, R., Francis, G., Manning, M., Duerer, M., Green, S., 2007. Farm Strategies for Contaminant Management. Palmerston North, New Zealand.
- de Klein CAM, Eckard RJ. Targeted technologies for nitrous oxide abatement from animal agriculture. *Aust J Exp Agric*; 48: 14 - 20.
- Di, H.J., Cameron, K.C., 2002. Nitrate leaching in temperate agroecosystems: sources, factors and mitigating strategies. *Nutrient Cycling in Agroecosystems* 46, 237–256.
- Daughney, C., Jones, A., Baker, T., Hanson, C., Davidson, P., Zemansky, G., Reeve, R., Thompson, M., 2006. A National Protocol for State of the Environment Groundwater Sampling in New Zealand. Ministry for the Environment, Wellington, New Zealand.
- Elwan, A., Singh, R., Horne, D., Roygard, J., Clothier, B. 2015. Nitrogen attenuation factor: can it tell a story about the journey of nutrients in different subsurface environments. Conference paper. Conference: FLRC Workshop. Palmerston North, New Zealand.
- EPA, 2017. Operating procedure. Field measurement of Oxidation-Reduction Potential (ORP). Written by: Brian Stiggow. U.S. Environmental Agency. Region 4, Science and Ecosystem Support Division. Athens, Georgia.
- Felgate, H., Giannopoulos, G., Sullivan, M. J., Gate, A. J., Clarke, T. A., Baggs ,E, Rowley G, Richardson DJ. 2012. The impact of copper, nitrate and carbon status on the emission of nitrous oxide by two species of bacteria with biochemically distinct

- denitrification pathways. *Environ Microbiology* 14(7):1788-800. doi: 10.1111/j.1462-2920.2012.02789.x.
- Fernandez-Pirini et al., (2003) cited in Sanders, 2015: Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmospheric Chemistry and Physics*, 15, 43399 – 4981. DOI: 10.5194/acp-15-4399-2015
- Franklin H., McEntee D. and Bloomberg M., 2016. The potential for poplar and willow silvopastoral systems to mitigate nitrate leaching from intensive agriculture in New Zealand. Occasional Report No. 29. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 10 pages.
- Earl, S. and Krogh, E. 2004. Geochemistry of Gabriola's groundwater. *Shale*, No. 7, p 37 – 44.
- Galloway, J., Aber, J., Erisman, J., Seitzinger, S., Howarth, R., Cowling, E., Cosby, J. 2003. The Nitrogen Cascade. American Institute of Biological Sciences. *BioScience*, 53(4):341-356. DOI: [http://dx.doi.org/10.1641/0006-3568\(2003\)053\[0341:TNC\]2.0.CO;2](http://dx.doi.org/10.1641/0006-3568(2003)053[0341:TNC]2.0.CO;2)
- Government of New Zealand, 2014. National Policy Statement for Freshwater Management 2014.
- Groffman, P. M., Altabet, M. A., Böhlke, J. K., Butterbach-Bahl, K., David, M. B., Firestone M. K., Giblin, A. E., Kana, T. M., Nielsen, L. P., Voytek, M. A. 2006. Methods for measuring denitrification: diverse approaches to a difficult problem. *Ecological Applications*, 16(6), 2091 – 2122. Ecological Society of America.
- Gruber, N., and Galloway, J. 2008. An Earth-system perspective of the global nitrogen cycle. *Nature* Vol N°451. Doi: 10.1038/nature06592
- Halling-Sorensen, B., Jorgensen, S.E. 1993. Chapter 4. Process Chemistry and Biochemistry of Denitrification. In *Studies in Environmental Science*. Volume 54, 1993, Pages 119-151. doi.org/10.1016/S0166-1116(08)70526-0
- Haygarth, M., and Jarvis S., 2002. Agriculture, Hydrology and Water Quality. *Experimental Agriculture* 39(04):451 – 452. DOI: 10.1017/S0014479703281412
- Her JJ and Huang JS, 1995. Influences of carbon sources and C/N ratio on nitrate/nitrite denitrification and carbon breakthrough. *Technology* 54, 45 – 51.
- Hiscock, K.M., Lloyd, J.W., Lerner, D.N., 1991. Review of natural and artificial denitrification of groundwater. *Water Research* 25, 1099–1111. doi:10.1016/0043-1354(91)90203-3.
- Holden, P.A., Fierer, N., 2005. Microbial Processes in the Vadose Zone. *Vadose Zone Journal* 4, 1–21. doi:10.2136/vzj2005.0001

- Horizons 2013. Report on Horizons groundwater quality monitoring network. Report No. 2013/EXT/1318. ISBN 978-1-927250-23-5
- Horizons 2013. Review of Horizons coastal groundwater monitoring network. Report No. 2013/EXT/1317. ISBN 978-1-927250-22-8
- Hu, Q., Westerhoff, P., Vermaas, W., 2000. Removal of nitrate from groundwater by cyanobacteria: Quantitative assessment of factors influencing nitrate uptake. *Appl. Environ. Microbiol.* 66 (1):133. DOI: 10.1128/AEM.66.1.133-139.2000
- IPCC, 2001. Chapter 4: Atmospheric Chemistry and Greenhouse Gases, *TAR Climate change 2001: The Scientific Basis*.
- Ioka, S., and Suzuki, H, M. 2017. Redox potential of shallow groundwater by 1-month continuous in situ potentiometric measurements. *Appl Water Sci* (2017) 7: 3095. <https://doi.org/10.1007/s13201-016-0436-x>
- Istok, J.D., Humphrey, M., Schroth, M., Hyman, M., O'Reilly, K., 1997. Single-well, “push- pull” test for in situ determination of microbial activities. *Ground Water* 35, 619–631.
- Istok, J. D. 2013. Push and pull test for site characterization. Berlin, Germany: Springer-Verlag
- Jahangir, M., Johnston, P., Khalil, M., Hennessy, D., Humphreys, J., Fenton, O., Richards, K., 2012. Groundwater: A pathway for terrestrial C and N losses and indirect greenhouse gas emissions. *Agriculture, Ecosystem and Environment*. Volume 159; 40 – 48.
- Jahangir, M., Johnston, P., Barrett, M., Khalil, M., Groffman, P., Boeckx, P. 2013. Denitrification and indirect N₂O emissions in groundwater: Hydrologic and biogeochemical influences. *Journal of Contaminant Hydrology* 152, 70-81. Doi: 10.1016/j.jconhyd.2013.06.007
- Jahangir, M., Johnston, P., Barrett, M., Khalil, M., Groffman, P., Boeckx, P., Fenton, O., Murphy J., Richards, K. 2007. Denitrification and indirect N₂O emissions in groundwater: hydrologic and biogeochemical influences. *Journal of Contaminant Hydrology* Volume 152, September 2013, Pages 70– 81. DOI: 10.1016/j.jconhyd.2013.06.007
- Kamewada, K., 2007. Vertical distribution of denitrification activity in an Andisol upland field and its relationship with dissolved organic carbon: Effect of long-term organic matter application. *Soil Science and Plant Nutrition* 53, 401-412. DOI:10.1111/j.1747-0765.2007.00148.x

- Knowles, R., 1982. Denitrification. *Microbiological Reviews* 46, 43 – 70.
- Koops, J.G.; Oenema, O.; van Beusichem, M.L. 1996. Denitrification in the top and sub-soil of grassland on peat soils. *Plant Soil* 1996, 184, 1–10.
- Korom, S. F., 1991a. Denitrification in the unconsolidated deposits of the Heber Valley aquifer. PhD thesis, 176 pp., Utah, States University, Logan, Utah.
- Korom, S. 1992. Natural denitrification in the saturated zone: A review. *Water resources research*, Vol. 28, N°6, Pages 1657-1668.
- Kraft, B., Strous, M., Tegetmeyer, H., 2011. Microbial nitrate respiration – Genes enzymes and environmental distribution. *Journal of biotechnology* 155, 104 – 117. DOI: 10.1016/j.jbiotec.2010.12.025
- Kuypers, M., Marchant H., and Kartal B., 2018. The microbial nitrogen-cycling network. *Natures Reviews Microbiology* 16(5), 263 – 276.
- Liao, L., Green, C., Bekins, B. and Bohlke, J. 2012. Factors controlling nitrate fluxes in groundwater in agricultural areas. *Water Resources Research*, vol 48, W00L09. DOI:10.1029/2011WR011008
- Lu et al., 2011. Responses of the ecosystem nitrogen cycle to nitrogen addition: a meta-analysis. *The New Phytologist*, Vol. 189, No. 4, pp 1040 – 1050.
- Luo, J., Tillman, R.W., White, R.E., Ball, P.R., 1998. Variation in denitrification activity with soil depth under pasture. *Soil Biology and Biochemistry* 30, 897–903.
- Martindale, H., van der Raaij, R., Morgenstern, U., Hadfield, J. 2018. Measuring actual denitrification to understand nitrogen loads through aquifers. In: *Farm environmental planning – Science, policy and practice*. (Eds L. D. Currie and C. L. Christensen). <http://flrc.massey.ac.nz/publications.html>. Occasional Report No. 31. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 5 pages.
- Massey University, 2017. Information Sheet. N°1 Dairy Unit – Massey University. Available on line: <http://www.massey.ac.nz/massey/fms/Agricultural%20Services/No%201%20Dairy%20Farm/No%201%20Dairy%20Information%20Sheet.pdf>
- McAleer, E. B., Coxon, C. E., Richards, K. G., Jahangir, M. M. R., Grant, J., Mellander, P. E. 2016. Groundwater nitrate reduction versus dissolved gas production: A tale of two catchments. *Science of the total environment* 586: 372-389.
- McMahon, P. B. and Chapelle, F. H. 2008. Redox processes and water quality of selected principal aquifer systems. *Ground Water*, vol 46. N°2, pages 259-271. Doi: 10.1111/j.1745-6584.2007.00385.x

- McMillan, A., Phillips, R., Berben, P., Thilak, P., Jha, N., & Saggar, S. (2014). Automated N₂O/N₂ analysis- a new tool for studying denitrification dynamics and testing mitigation strategies. In L. D. Currie & C. L. Christensen (Eds.), *Nutrient Management for the Farm, Catchment and Community Occasional*
- Ministry of Health, 2008. *Drinking Water Standards for New Zealand 2005* (Revised, 2008). Wellington, New Zealand.
- Molloy, L. 1998. *Soils in the New Zealand Landscape: The living mantle*. Christchurch: New Zealand Society of Soil Science. ISBN : 9780908783373. 253 pages.
- NPSFM, 2017 Our fresh water Report 2017, publication date: April 2017. Publication reference number: ME 1305. Available in: <http://www.mfe.govt.nz/publications/environmental-reporting/our-fresh-water-2017>.
- Puckett, L.J. 1999. The effectiveness of riparian buffer zones in removing nitrate from ground water of the Atlantic Coastal Plain. *Proceedings, 6th Symposium on Wetland Biogeochemistry*, Fort Lauderdale, FL, 7/1999, 50.
- Puckett, L.J. and Cowdery, T.K. 2002. Transport and fate of nitrogen in a glacial outwash aquifer in relation to ground-water age, land use practices, and redox processes. *J. Environ. Qual.*, 31.
- Puckett, L. J. 2004. Hydrogeologic controls on the transport and fate of nitrate in groundwater beneath riparian buffer zones: results from thirteen studies across the United States. *Water Science and Technology*, Vol 49. N°3, pp. 47-53
- Reay, D. S., Davidson, E. A., Smith, K. A., Smith, P., Melillo, J. M., Dentener, F. and Crutzen, P. J. 2012. Global agriculture and nitrous oxide emissions. *Nature climate change*. Advance online publication www.nature.com/natureology. Doi: 10.1038/nclimate1458.
- Rinaudo J. D., Arnal C., Blanchin R., Elsass P., Meilhac A., and Loubier S. 2005. Assessing the cost of groundwater pollution: The case of diffuse agricultural pollution in the Upper Rhine valley aquifer. *Water Science & Technology* Vol 52 N° 9 pp 153–162.
- Rivas et al., 2018. *Characterisation of Denitrification in the Subsurface Environment of the Manawatu Catchment, New Zealand*. Doctoral thesis, School of agriculture and Environment, Massey University, Palmerston North, New Zealand.
- Rivas, A., Singh, R., Bishop, P., Horne, D., Roygard, J., Hedley, M. 2014. Measuring denitrification in the subsurface environment of Manawatu river catchment.

- Rivett, M., Buss, S., Morgan, P., Smith, J., Bemment, C. 2008. Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. *Water Research* 42 (2008) 4215 – 4232.
- Saggar, S., Bolan, N.S., Bhandral R., Hedley CB, Luo, J., 2004b. A review of emissions of methane, ammonia, and nitrous oxide from animal excreta deposition and farm effluent application in grazed pastures. *N Z J Agric Res* 2004b;47: 513 – 44.
- Saggar, S., Jha, N., Deslippe, J., Bolan, N.S., Luo, J., Giltrap, D.L., Kim, D., Zaman, M., Tillman, R.W., 2013. Denitrification and N₂O:N₂ production in temperate grasslands: Processes, measurements, modelling and mitigating negative impacts. *Science of the Total Environment* 465, 173–195. doi:10.1016/j.scitotenv.2012.11.050
- Seitzinger, S., Harrison, J., Bohlke, J., Bouwman, A., Lowrance, R., Peterson, B., Tobias, C., Drecht, G. 2006. Denitrification across landscapes and waterscapes: a synthesis. *Ecological Society of America. Ecological Applications*, 16(6), pp. 2064-2090.
- Selbie, D., Buckthought L., Shepherd M., 2015. The Challenge of the Urine Patch for Managing Nitrogen in Grazed Pasture Systems. *Advanced in Agronomy*, Volume 129. ISSN 0065-2113
- Sigurdarson, J., Svane, S., Karring, H. 2018. The molecular processes of urea hydrolysis in relation to ammonia emissions from agriculture. *Rev Environ Sci Biotechnology* (2018) 17:241–258 <https://doi.org/10.1007/s11157-018-9466-1>
- Singh, R., Rivas, A., Espanto, P., Elwan, A., Horne, D.J., Matthews, A., Clothier, B., 2014. Assessment of transport and transformation of nitrogen in the subsurface environment of Manawatu River catchment – work in progress, in: Currie, L., Christensen, C. (Eds.), *Nutrient Management for the Farm, Catchment and Community*. Fertiliser and Lime Research Centre, Massey University, Palmerston North, New Zealand, p. 11.
- Singleton, M. J., Esser, B. K., Moran, J. E., Hudson, G. B., McNab, W. W., Harter, T. 2007. Saturated zone denitrification: potential for natural attenuation of nitrate contamination in shallow groundwater under dairy operations. *Environmental Science and Technology*, 41, 759-765.
- Smith, R. L., Duff, J. H. 1988. Denitrification in a sand and gravel aquifer. *Appl. Environmental Microbiology*, 54(5), 1071-1078.
- Stats NZ, 2016. Main agricultural and horticultural land use by region. Available in: http://archive.stats.govt.nz/browse_for_stats/environment/environmental-reporting-series/environmental-indicators/Home/Land/land-use.aspx
- STATS NZ, 2018. New Zealand's Environmental Reporting Series: Environmental indicators Te taiao Aotearoa.

- Stein, LY and Klotz MG, 2016. The nitrogen cycle. *Current Biology* 26, R83 – R101.
- Stenger, R., Clague, J., Woodward, S., Moorhead, B., Wilson, S., Shokri, A., Wöhling, T., Canard, H. 2013. Denitrification – the key component of a groundwater system's assimilative capacity for nitrate.
- Stenger, r., Cague, J. C., Monrgestern, U., Clough, T. J. 2018. Vertical stratification of redox conditions, denitrification and recharge in shallow groundwater on a volcanic hillslope containing relict organic matter. *Science of the Total Environment* 639, 1205-1219, Elsevier.
- Stuart, M., Gooddy, D., Bloomfield, J. and Williams, A. 2011A review of the impact of climate change on the future nitrate concentrations in groundwater of the UK. *Science of the Total Environment*, 409 (15), 2859-2873.
- Scherer, H. W., Feils, E., Beuters, P. 2014. Ammonium fixation and release by clay minerals as influenced by potassium. *Plant Soil and Environment* 60(7):325-331
- Stenger, R., Barkle, G., Burgess, C., Wall, A., Clague, J., 2008. Low nitrate contamination of shallow groundwater in spite of intensive dairying: the effect of reducing conditions in the vadose zone – aquifer continuum. *Journal of Hydrology (New Zealand)* 47, 1–24.
- Tesoriero, A., Liebscher, H., Cox, S. 2000. Mechanism and rate of denitrification in an agricultural watershed: Electron and mass balance along groundwater flow paths. *Water Resources Research*, vol 36, N°6, 1545 – 1559.
- Tiedje, J., 1988. Ecology of denitrification and dissimilatory nitrate reduction to ammonium, in: Zehnder, A. (Ed.), *Biology of Anaerobic Microorganisms*. Wiley-Interscience Publication, New York, pp. 179–244.
- Tiedje, J.M., Simkins, S., Groffman, P.M., 1989. Perspectives on measurement of denitrification in the field including recommended protocols for acetylene based methods. *Plant and Soil* 115, 261–284. doi:10.1007/BF02202594
- Thomas, S., Dann, R., Close, M., 2012. Nitrous Oxide Dynamics in a Deep Soil-Alluvial Gravel Vadose Zone Following Nitrate Leaching. *Soil Science Society of America Journal* 76, 1333–1346. doi:10.2136/sssaj2011.0349
- Thomas, S. Watreland, H., Dann, R. Close, M. Francis, G. Cook F. 2011. Nitrous oxide dynamics in a deep soil-alluvial gravel vadose zone following nitrate leaching. *Soil and Water Management and Conservation. Soil Science Society of America Journal*.
- Trudell, M., Gillham, R., Cherry, J., 1986. An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer. *Journal of Hydrology* 83, 251–268.

- Vidon, P., Hill, A., 2004. Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology. *Biogeochemistry* 71: 259-283.
- Voguel, J. C., Talma, A. S., and Heaton, T. 1981. Gaseous nitrogen as evidence for denitrification in groundwater. *Journal of hydrology*, 50, 191-200.
- Vilain, G., Garnier, J., Tallec, G., Tournebize, J. 2012. Indirect N₂O emissions from shallow groundwater in an agricultural catchment (Seine Basin, France). *Biogeochemistry* 111:253-271. Doi: 10.1007/s10533-011-9642-7
- Vrba J., and Zaporozec A., 1994. Guidebook on mapping groundwater vulnerability. IAH. Vol. 16: 1-131. Verlag Heinz Heise. Hannover.
- Waikato Regional Council, 2018. Data and trends. Occurrence of nitrate in Waikato monitoring wells. Available in: <https://www.waikatoregion.govt.nz/environment/environmental-information/environmental-indicators/groundwater/gw1-report/gw1-data/>
- Weymann, D., Well, R., Flessa, H., von der Heide, C., Deurer, M., Konrad, C., Walther, W. 2008a. Groundwater N₂O emission factors of nitrate-contaminated aquifers as derived from denitrification progress and N₂O accumulation. *Biogeoscience*, 5, 1215-1226.
- Weymann, D., Well, R., Flessa, H., von der Heide, C., Deurer, M., Konrad, C., Walther, W. 2008b. Assessment of excess N₂ and groundwater N₂O emission factors of nitrate-contaminated aquifers in northern Germany. *Biogeosciences Discuss.*, 5, 1263 – 1292.
- Weymann, D., Geistlinger, H., Well, R., von der Heide, C., and Flessa, H. 2010. Kinetics of N₂O production and reduction in a nitrate-contaminated aquifer inferred from laboratory incubation experiments. *Biogeosciences*, 7, 1953–1972, doi:10.5194/bg-7-1953-2010.
- WHO, 2004. Drinking Water Directive 98/83/EC. Guidelines for Drinking Water Quality, third ed. WHO, Geneva.
- World Bank Group, 2018. Data World population. Available in: <https://data.worldbank.org/indicator/SP.POP.TOTL?end=2017&start=1987&view=chart>
- Zambelli, B., Baradi, A., Martin-Diaconescu, V., Mazzei, L., Musiani, F., Maroney, M. and Ciurli, S. 2014. Nickel binding properties of *Helicobacter pylori* UreF, an accessory protein in the nickel-based activation of urease. *Journal of Biological Inorganic Chemistry*, 19(3), 319-334. DOI: 10.1007/s00775-013-1068-3.

Zumft, W. and Kroneck, P. 2003. Respiratory transformation of nitrous oxide (N₂O) to dinitrogen by bacteria and archaea. *Advances in microbial physiology* Vol. 52.
DOI: 10.1016/S0065-2911(06)52003-X

APPENDIX 1

Groundwater chemistry

Table 1: Monthly average of dissolved oxygen (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Site	Depth (m, bgl)	Piezometer	DO (mg L ⁻¹)							Min	Max	Median	Avg	SEM
			Feb	March	April	May	June	Aug	Sep					
DF	5.5	1	1.43	2.53	4.54	0.91	2.96	1.90	1.89	0.91	4.54	1.90	2.31	0.45
	7.5	2	0.93	0.06	0.30	0.10	0.66	0.16	0.21	0.06	0.93	0.21	0.35	0.12
	8.7	3	0.21	0.10	0.18	0.12	2.96	1.90	0.16	0.10	2.96	0.18	0.80	0.44
SC	3.4	1	0.12	0.06	0.08	2.00	1.43	0.11	0.57	0.06	2.00	0.12	0.62	0.30
	5.2	2	0.08	0.07	0.11	0.21	1.81	0.11	0.13	0.07	1.81	0.11	0.36	0.24
	6.4	3	0.30	0.59	0.85	1.42	4.27	1.43	0.09	0.09	4.27	0.85	1.28	0.54
CAM	4.5	1	7.65	3.65	3.27	3.90	7.19	4.54	4.07	3.27	7.65	4.07	4.89	0.67
	7.5	3	0.16	0.24	0.20	0.26	0.64	0.15	1.21	0.15	1.21	0.24	0.41	0.15
ARM	5	1	0.13	0.08	0.10	0.16	0.95	0.10	0.11	0.08	0.95	0.11	0.23	0.12
	6	2	0.18	0.06	0.05	0.14	0.99	0.12	0.09	0.05	0.99	0.12	0.23	0.13
	7.5	3	0.08	0.09	0.04	0.11	0.49	0.22	0.09	0.04	0.49	0.09	0.16	0.06
SR	4.5	1	7.24	7.91	8.30	9.36	7.98	8.67	8.75	7.24	9.36	8.30	8.32	0.26
	5.5	2	6.93	6.77	8.47	9.20	7.29	7.85	8.69	6.77	9.20	7.85	7.89	0.35
	6.5	3	7.04	7.09	8.46	8.86	6.76	8.56	8.63	6.76	8.86	8.46	7.91	0.34
BUR	3.6	1	1.85	-	4.29	4.67	6.15	5.19	-	1.85	6.15	4.67	4.43	0.61
	4.3	2	5.83	5.85	6.29	5.31	7.29	4.78	4.39	4.39	7.29	5.83	5.68	0.37
	6.1	3	1.85	3.58	4.29	4.67	6.15	3.88	3.43	1.85	6.15	3.88	3.98	0.49

Table 2: Monthly average of electrical conductivity (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Site	Depth (m, bgl)	Piezometer	Electrical conductivity ($\mu\text{S cm}^{-1}$)										Avg	SEM
			Feb	March	April	May	June	Aug	Sep	Min	Max	Median		
DF	5.5	1	297.37	284.87	271.77	264.23	191.70	298.90	268.55	191.70	298.90	271.77	268.20	13.76
	7.5	2	327.10	323.40	340.37	291.90	238.57	325.33	300.00	238.57	340.37	323.40	306.67	12.99
	8.7	3	336.87	330.57	342.47	290.57	191.70	298.90	296.40	191.70	342.47	298.90	298.21	19.46
SC	3.4	1	718.23	713.33	749.57	780.87	58.30	764.27	982.57	58.30	982.57	749.57	681.02	109.41
	5.2	2	693.00	663.53	707.63	709.47	575.00	710.13	602.30	575.00	710.13	693.00	665.87	21.07
	6.4	3	744.77	795.77	841.20	963.17	791.67	1215.90	562.77	562.77	1215.90	795.77	845.03	76.61
CAM	4.5	1	263.93	366.80	340.63	363.97	260.67	284.23	300.67	260.67	366.80	300.67	311.56	17.16
	7.5	3	375.97	387.73	380.67	398.80	294.40	371.63	336.70	294.40	398.80	375.97	363.70	13.66
ARM	5	1	349.50	346.10	345.73	371.27	278.20	354.27	323.90	278.20	371.27	346.10	338.42	11.34
	6	2	463.03	450.33	445.50	466.13	347.80	448.60	421.40	347.80	466.13	448.60	434.69	15.49
	7.5	3	546.73	551.37	553.27	574.57	423.37	530.73	487.13	423.37	574.57	546.73	523.88	19.65
SR	4.5	1	156.63	171.87	146.20	147.50	114.57	147.10	138.20	114.57	171.87	147.10	146.01	6.61
	5.5	2	155.27	169.30	149.00	149.47	114.70	148.77	137.43	114.70	169.30	149.00	146.28	6.38
	6.5	3	156.83	171.70	149.93	151.87	116.43	147.40	139.43	116.43	171.70	149.93	147.66	6.41
BUR	3.6	1	151.90	-	216.03	254.73	200.67	239.00	-	151.90	254.73	216.03	212.47	15.01
	4.3	2	246.53	245.03	246.20	261.20	224.60	272.83	255.77	224.60	272.83	246.53	250.31	5.72
	6.1	3	151.90	170.63	216.03	254.73	200.67	250.77	224.33	151.90	254.73	216.03	209.87	14.57

Table 3: Monthly average of pH (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Site	Depth (m, bgl)	Piezometer	pH										Avg	SEM
			Feb	March	April	May	June	Aug	Sep	Min	Max	Median		
DF	5.5	1	6.27	6.20	6.24	6.15	6.30	6.01	6.34	6.01	6.34	6.24	6.21	0.04
	7.5	2	6.38	6.37	6.35	6.34	6.51	6.31	6.53	6.31	6.53	6.37	6.40	0.03
	8.7	3	6.34	6.36	6.40	6.30	6.30	6.01	6.56	6.01	6.56	6.34	6.32	0.06
SC	3.4	1	7.07	7.09	7.04	7.09	7.32	6.96	6.97	6.96	7.32	7.07	7.08	0.05
	5.2	2	7.24	7.26	7.25	7.31	7.60	7.14	7.23	7.14	7.60	7.25	7.29	0.06
	6.4	3	6.90	6.83	6.84	6.90	7.17	6.63	7.36	6.63	7.36	6.90	6.95	0.09
CAM	4.5	1	6.32	5.91	5.88	5.92	6.86	6.41	5.95	5.88	6.86	5.95	6.18	0.14
	7.5	3	6.56	6.43	6.52	6.52	6.77	6.49	6.69	6.43	6.77	6.52	6.57	0.05
ARM	5	1	6.42	6.25	6.21	6.27	6.45	6.22	6.58	6.21	6.58	6.27	6.34	0.05
	6	2	6.68	6.52	6.49	6.58	6.69	6.56	6.79	6.49	6.79	6.58	6.62	0.04
	7.5	3	7.13	6.96	6.99	7.06	7.09	7.02	7.20	6.96	7.20	7.06	7.06	0.03
SR	4.5	1	5.48	5.41	5.39	5.33	5.20	5.27	5.64	5.20	5.64	5.39	5.39	0.05
	5.5	2	5.47	5.39	5.39	5.33	5.24	5.30	5.61	5.24	5.61	5.39	5.39	0.05
	6.5	3	5.47	5.40	5.49	5.38	5.31	5.27	5.62	5.27	5.62	5.40	5.42	0.04
BUR	3.6	1	6.13	-	5.89	5.79	5.70	5.48	-	5.48	6.13	5.79	5.80	0.09
	4.3	2	6.07	6.07	5.87	5.82	5.65	5.70	5.93	5.65	6.07	5.87	5.87	0.06
	6.1	3	6.13	3.58	5.89	5.79	5.70	5.72	6.00	3.58	6.13	5.79	5.54	0.33

Table 4: Monthly average of iron (II) (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Site	Depth (m, bgl)	Piezometer	Fe ²⁺ (mg L ⁻¹)										Avg	SEM
			Feb	March	April	May	June	Aug	Sep	Min	Max	Median		
DF	5.5	1	0.02	0.03	0.09	0.38	0.08	3.35	0.04	0.02	3.35	0.08	0.57	0.47
	7.5	2	3.74	3.67	3.83	3.78	3.39	0.03	0.02	0.02	3.83	3.67	2.64	0.68
	8.7	3	3.75	3.86	4.09	3.93	3.41	3.15	3.25	3.15	4.09	3.75	3.63	0.14
SC	3.4	1	6.58	6.78	7.72	6.80	7.27	0.06	7.35	0.06	7.72	6.80	6.08	1.01
	5.2	2	4.89	4.28	4.16	4.30	3.91	0.04	4.67	0.04	4.89	4.28	3.75	0.63
	6.4	3	0.86	0.70	1.17	0.99	0.89	0.16	0.15	0.15	1.17	0.86	0.70	0.15
CAM	4.5	1	0.73	0.07	0.27	0.05	0.03	0.05	0.04	0.03	0.73	0.05	0.18	0.10
	7.5	3	0.29	0.31	0.59	0.18	0.20	0.18	0.16	0.16	0.59	0.20	0.27	0.06
ARM	5	1	3.70	3.59	4.47	4.01	3.69	0.32	3.55	0.32	4.47	3.69	3.33	0.52
	6	2	3.45	3.56	3.89	3.81	3.28	6.79	3.64	3.28	6.79	3.64	4.06	0.46
	7.5	3	0.80	0.72	0.88	0.88	0.93	5.62	0.76	0.72	5.62	0.88	1.51	0.69
SR	4.5	1	0.01	0.01	0.04	0.03	0.06	0.13	0.06	0.01	0.13	0.04	0.05	0.02
	5.5	2	0.01	0.01	0.11	0.10	0.13	0.06	0.04	0.01	0.13	0.06	0.07	0.02
	6.5	3	0.01	0.02	0.14	0.22	0.04	0.06	0.02	0.01	0.22	0.04	0.07	0.03
BUR	3.6	1	0.00	0.00	0.04	0.02	0.06	0.76	0.00	0.00	0.76	0.02	0.13	0.11
	4.3	2	0.01	0.01	0.32	0.08	0.39	3.59	0.01	0.01	3.59	0.08	0.63	0.50
	6.1	3	0.01	0.01	0.11	0.03	0.03	4.09	0.04	0.01	4.09	0.03	0.62	0.58

Table 5: Monthly average of manganese (II) (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Site	Depth (m, bgl)	Piezometer	Mn ²⁺ (mg L ⁻¹)							Min	Max	Median	Avg	SEM
			Feb	March	April	May	June	Aug	Sep					
DF	5.5	1	0.01	0.01	0.01	0.07	0.12	0.18	0.01	0.01	0.18	0.01	0.06	0.03
	7.5	2	0.19	0.18	0.22	0.18	0.29	0.01	0.08	0.01	0.29	0.18	0.16	0.04
	8.7	3	0.21	0.19	0.24	0.19	0.29	0.16	0.18	0.16	0.29	0.19	0.21	0.02
SC	3.4	1	0.84	0.78	1.04	0.81	0.91	0.01	0.85	0.01	1.04	0.84	0.75	0.13
	5.2	2	0.21	0.18	0.27	0.18	0.31	0.01	0.23	0.01	0.31	0.21	0.20	0.04
	6.4	3	1.00	0.29	0.35	0.27	0.35	0.01	0.13	0.01	1.00	0.29	0.34	0.12
CAM	4.5	1	0.25	0.31	0.20	0.06	0.14	0.04	0.03	0.03	0.31	0.14	0.15	0.04
	7.5	3	0.92	0.91	1.38	0.94	1.02	0.89	0.91	0.89	1.38	0.92	1.00	0.07
ARM	5	1	0.10	0.09	0.12	0.11	0.22	0.09	0.10	0.09	0.22	0.10	0.12	0.02
	6	2	0.10	0.08	0.11	0.08	0.24	0.80	0.09	0.08	0.80	0.10	0.21	0.10
	7.5	3	0.05	0.05	0.07	0.06	0.17	0.28	0.05	0.05	0.28	0.06	0.10	0.03
SR	4.5	1	0.01	0.01	0.01	0.01	0.09	0.01	0.03	0.01	0.09	0.01	0.03	0.01
	5.5	2	0.01	0.01	0.01	0.01	0.10	0.01	0.01	0.01	0.10	0.01	0.02	0.01
	6.5	3	0.01	0.01	0.01	0.01	0.10	0.01	0.01	0.01	0.10	0.01	0.02	0.01
BUR	3.6	1	0.00	0.00	0.01	0.01	0.11	0.05	0.00	0.00	0.11	0.01	0.03	0.02
	4.3	2	0.01	0.01	0.03	0.01	0.11	0.09	0.01	0.01	0.11	0.01	0.04	0.02
	6.1	3	0.01	0.01	0.01	0.01	0.10	0.12	0.01	0.01	0.12	0.01	0.04	0.02

Table 6: Monthly average of calcium (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (April – September 2018).

Site	Depth (m, bgl)	Piezometer	Ca ²⁺ (mg L ⁻¹)									
			April	May	June	Aug	Sep	Min	Max	Median	Avg	SEM
DF	5.5	1	23.08	25.30	19.56	24.90	21.68	19.56	25.30	23.08	22.91	1.06
	7.5	2	30.62	28.02	25.79	22.09	11.40	11.40	30.62	25.79	23.58	3.35
	8.7	3	31.28	27.73	25.34	23.95	25.44	23.95	31.28	25.44	26.75	1.29
SC	3.4	1	95.46	82.23	83.76	85.27	83.90	82.23	95.46	83.90	86.12	2.38
	5.2	2	90.79	67.61	70.66	74.42	72.39	67.61	90.79	72.39	75.17	4.06
	6.4	3	112.94	112.98	111.46	131.07	148.17	111.46	148.17	112.98	123.32	7.19
CAM	4.5	1	18.89	16.47	16.71	16.43	19.89	16.43	19.89	16.71	17.68	0.72
	7.5	3	18.77	16.61	19.55	18.81	-	16.61	19.55	18.79	18.44	0.57
ARM	5	1	21.09	20.76	19.97	19.91	31.27	19.91	31.27	20.76	22.60	2.18
	6	2	33.22	32.15	29.44	30.22	39.09	29.44	39.09	32.15	32.82	1.70
	7.5	3	45.55	42.37	39.76	39.07	9.50	9.50	45.55	39.76	35.25	6.54
SR	4.5	1	9.11	8.38	8.20	9.06	9.15	8.20	9.15	9.06	8.78	0.20
	5.5	2	9.70	8.46	8.05	8.50	9.23	8.05	9.70	8.50	8.79	0.30
	6.5	3	11.16	8.21	8.00	8.39	17.58	8.00	17.58	8.39	10.67	1.82
BUR	3.6	1	17.07	13.91	12.08	12.22	19.58	12.08	19.58	13.91	14.97	1.46
	4.3	2	15.89	16.45	17.11	17.11	16.94	15.89	17.11	16.94	16.70	0.24
	6.1	3	16.72	16.26	13.93	15.45	15.76	13.93	16.72	15.76	15.62	0.48

Table 7: Monthly average of magnesium (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (April – September 2018).

Site	Depth (m, bgl)	Piezometer	Mg ²⁺ (mg L ⁻¹)									
			April	May	June	Aug	Sep	Min	Max	Median	Avg	SEM
DF	5.5	1	5.14	5.17	4.67	5.34	5.19	4.67	5.34	5.17	5.10	0.11
	7.5	2	6.17	5.51	5.45	5.45	3.77	3.77	6.17	5.45	5.27	0.40
	8.7	3	6.14	5.46	5.42	5.24	5.27	5.24	6.14	5.42	5.51	0.16
SC	3.4	1	9.65	9.01	9.14	9.21	9.24	9.01	9.65	9.21	9.25	0.11
	5.2	2	10.95	9.81	9.59	9.90	9.62	9.59	10.95	9.81	9.97	0.25
	6.4	3	12.27	12.98	13.39	15.42	15.91	12.27	15.91	13.39	14.00	0.71
CAM	4.5	1	9.50	8.63	8.53	8.66	10.39	8.53	10.39	8.66	9.14	0.36
	7.5	3	10.95	10.61	10.77	10.74	-	10.61	10.95	10.76	10.77	0.06
ARM	5	1	4.85	4.57	4.78	4.94	5.72	4.57	5.72	4.85	4.97	0.20
	6	2	6.17	5.55	5.45	5.91	6.53	5.45	6.53	5.91	5.92	0.20
	7.5	3	7.48	6.72	6.79	6.78	2.81	2.81	7.48	6.78	6.12	0.84
SR	4.5	1	2.95	2.65	2.65	2.91	2.81	2.65	2.95	2.81	2.79	0.06
	5.5	2	3.08	2.67	2.67	2.90	3.02	2.67	3.08	2.90	2.87	0.09
	6.5	3	3.22	2.75	2.77	3.00	8.45	2.75	8.45	3.00	4.04	1.11
BUR	3.6	1	4.15	3.62	3.68	3.77	4.60	3.62	4.60	3.77	3.96	0.18
	4.3	2	3.52	3.74	3.92	4.08	4.05	3.52	4.08	3.92	3.86	0.10
	6.1	3	3.13	3.16	2.88	3.29	3.04	2.88	3.29	3.13	3.10	0.07

Table 8: Monthly average of sodium (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (March – September 2018).

Site	Depth (m, bgl)	Piezometer	Na ⁺ (mg L ⁻¹)						Min	Max	Median	Avg	SEM
			March	April	May	June	Aug	Sep					
DF	5.5	1	29.60	39.00	34.07	31.67	-	32.83	29.60	39.00	32.83	33.43	1.44
	7.5	2	28.97	40.40	36.37	33.93	10.70	29.20	10.70	40.40	31.57	29.93	4.24
	8.7	3	31.63	40.47	39.60	35.53	12.17	26.33	12.17	40.47	33.58	30.96	4.32
SC	3.4	1	42.53	40.37	39.77	45.70	30.50	44.30	30.50	45.70	41.45	40.53	2.21
	5.2	2	36.93	49.53	49.20	41.73	31.33	48.23	31.33	49.53	44.98	42.83	3.07
	6.4	3	46.80	59.10	23.07	61.20	37.17	43.23	23.07	61.20	45.02	45.09	5.80
CAM	4.5	1	34.37	42.10	24.30	33.03	23.10	51.43	23.10	51.43	33.70	34.72	4.40
	7.5	3	40.67	53.80	23.23	43.17	27.33	51.43	23.23	53.80	41.92	39.94	5.08
ARM	5	1	44.53	56.03	36.37	54.17	31.03	61.23	31.03	61.23	49.35	47.23	4.86
	6	2	50.50	65.83	39.10	55.87	39.93	52.83	39.10	65.83	51.67	50.68	4.13
	7.5	3		79.87	36.47	63.97	48.77	18.93	18.93	79.87	48.77	49.60	9.65
SR	4.5	1	20.50	26.07	55.47	19.83	8.67	18.10	8.67	55.47	20.17	24.77	6.56
	5.5	2	19.57	26.03	48.47	19.50	8.97	19.07	8.97	48.47	19.53	23.60	5.45
	6.5	3	19.80	25.17	43.67	19.67	9.53	45.93	9.53	45.93	22.48	27.29	5.92
BUR	3.6	1	-	36.23	65.37	32.55	13.63	-	13.63	65.37	34.39	36.95	8.73
	4.3	2	-	24.83	60.50	31.87	16.27	25.07	16.27	60.50	25.07	31.71	6.95
	6.1	3	22.93	37.00	54.13	31.37	16.77	24.00	16.77	54.13	27.68	31.03	5.44

Table 9: Monthly average of potassium (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (April – September 2018).

Site	Depth (m, bgl)	Piezometer	K ⁺ (mg L ⁻¹)									
			April	May	June	Aug	Sep	Min	Max	Median	Avg	SEM
DF	5.5	1	3.52	9.93	2.78	2.75	2.51	2.51	9.93	2.78	4.30	1.42
	7.5	2	3.57	1.42	2.79	2.76	1.91	1.42	3.57	2.76	2.49	0.38
	8.7	3	3.48	1.61	2.89	2.68	2.63	1.61	3.48	2.68	2.66	0.30
SC	3.4	1	5.15	20.60	3.88	3.91	3.53	3.53	20.60	3.91	7.41	3.31
	5.2	2	5.88	18.10	3.42	3.62	3.19	3.19	18.10	3.62	6.84	2.86
	6.4	3	6.50	24.71	5.14	9.42	7.21	5.14	24.71	7.21	10.60	3.60
CAM	4.5	1	2.31	9.58	1.97	1.81	1.74	1.74	9.58	1.97	3.48	1.53
	7.5	3	1.94	11.47	2.03	2.08		1.94	11.47	2.05	4.38	2.12
ARM	5	1	2.41	10.13	2.35	2.09	1.61	1.61	10.13	2.35	3.72	1.61
	6	2	2.18	9.51	2.17	1.86	1.91	1.86	9.51	2.17	3.53	1.50
	7.5	3	2.41	10.65	2.30	2.06	0.80	0.80	10.65	2.30	3.64	1.77
SR	4.5	1	1.31	0.00	1.00	1.04	0.82	0.00	1.31	1.00	0.84	0.22
	5.5	2	1.31	0.00	1.09	1.39	0.97	0.00	1.39	1.09	0.95	0.25
	6.5	3	1.52	0.00	1.12	1.00	1.58	0.00	1.58	1.12	1.05	0.28
BUR	3.6	1	5.69	3.17	4.68	4.61	2.97	2.97	5.69	4.61	4.23	0.51
	4.3	2	5.11	3.71	4.59	4.43	4.40	3.71	5.11	4.43	4.44	0.22
	6.1	3	2.56	0.59	2.18	2.19	1.91	0.59	2.56	2.18	1.88	0.34

Table 10: Monthly average of ammonium-N (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (May – September 2018).

Site	Depth (m, bgl)	Piezometer	NH ₄ ⁺ -N (mg L ⁻¹)					Min	Max	Median	Avg	SEM
			May	June	Aug	Sep						
DF	5.5	1	0.01	0.01	0.01	0.00		0.00	0.01	0.01	0.01	0.00
	7.5	2	0.01	0.08	0.08	0.08		0.01	0.08	0.08	0.06	0.02
	8.7	3	0.00	0.08	0.07	0.07		0.00	0.08	0.07	0.06	0.02
SC	3.4	1	0.01	0.19	0.20	0.17		0.01	0.20	0.18	0.14	0.05
	5.2	2	0.18	0.08	0.05	0.03		0.03	0.18	0.06	0.08	0.03
	6.4	3	0.12	0.11	0.13	0.13		0.11	0.13	0.12	0.12	0.00
CAM	4.5	1	0.02	0.00	0.00	0.00		0.00	0.02	0.00	0.01	0.00
	7.5	3	0.01	0.00	0.02	0.01		0.00	0.02	0.01	0.01	0.00
ARM	5	1	0.01	0.00	0.03	0.07		0.00	0.07	0.02	0.03	0.02
	6	2	0.00	0.00	0.06	0.09		0.00	0.09	0.03	0.04	0.02
	7.5	3	0.00	0.00	0.07	0.01		0.00	0.07	0.00	0.02	0.02
SR	4.5	1	0.00	0.00	0.00	0.04		0.00	0.04	0.00	0.01	0.01
	5.5	2	0.00	0.00	0.02	0.01		0.00	0.02	0.01	0.01	0.00
	6.5	3	0.00	0.00	0.01	0.03		0.00	0.03	0.01	0.01	0.01
BUR	3.6	1	0.00	0.00	0.00	0.01		0.00	0.01	0.00	0.00	0.00
	4.3	2	0.00	0.00	0.00	0.13		0.00	0.13	0.00	0.03	0.03
	6.1	3	0.00	0.00	0.00	-		0.00	0.00	0.00	0.00	0.00

Table 11: Monthly average of nitrate-N (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Site	Depth (m, bgl)	Piezometer	NO ₃ -N (mg L ⁻¹)							Min	Max	Median	Avg	SEM
			Feb	March	April	May	June	Aug	Sep					
DF	5.5	1	0.01	0.16	0.19	0.08	0.51	3.75	1.10	0.01	3.75	0.19	0.83	0.51
	7.5	2	0.01	0.02	0.05	0.10	0.04	0.02	0.02	0.01	0.10	0.02	0.04	0.01
	8.7	3	0.02	0.01	0.02	0.01	0.03	0.04	0.02	0.01	0.04	0.02	0.02	0.00
SC	3.4	1	0.01	0.01	0.16	0.04	0.01	0.04	0.07	0.01	0.16	0.04	0.05	0.02
	5.2	2	0.02	0.01	0.22	0.03	0.02	0.03	0.05	0.01	0.22	0.03	0.05	0.03
	6.4	3	0.02	0.05	0.98	3.50	5.88	22.56	15.92	0.02	22.56	3.50	6.99	3.34
CAM	4.5	1	0.00	5.42	6.71	5.67	5.94	6.21	6.69	0.00	6.71	5.94	5.23	0.89
	7.5	3	0.06	0.01	0.01	0.31	0.11	0.12	0.08	0.01	0.31	0.08	0.10	0.04
ARM	5	1	0.01	0.01	0.03	0.01	0.03	0.04	0.04	0.01	0.04	0.03	0.02	0.01
	6	2	0.03	0.01	0.02	0.03	0.01	0.01	0.02	0.01	0.03	0.02	0.02	0.00
	7.5	3	0.01	0.02	0.02	0.02	0.01	0.03	0.04	0.01	0.04	0.02	0.02	0.01
SR	4.5	1	3.73	3.78	3.29	2.79	3.22	3.74	3.78	2.79	3.78	3.73	3.48	0.15
	5.5	2	3.74	3.82	3.40	2.88	3.21	3.61	3.71	2.88	3.82	3.61	3.48	0.13
	6.5	3	3.83	3.87	3.39	3.08	3.13	3.59	3.84	3.08	3.87	3.59	3.53	0.13
BUR	3.6	1	0.01	0.01	5.86	5.74	7.28	6.69	4.71	0.00	7.28	5.74	4.33	1.16
	4.3	2	2.63	2.40	5.00	4.65	7.89	6.47	5.80	2.40	7.89	5.00	4.98	0.75
	6.1	3	0.24	0.74	2.69	5.24	5.27	5.86	5.06	0.24	5.86	5.06	3.59	0.89

Table 12: Monthly average of nitrite-N (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Site	Depth (m, bgl)	Piezometer	NO ₂ ⁻ -N (mg L ⁻¹)							Min	Max	Median	Avg	SEM
			Feb	March	April	May	June	Aug	Sep					
DF	5.5	1	N.A.	N.A.	N.A.	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
	7.5	2	N.A.	N.A.	N.A.	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
	8.7	3	N.A.	N.A.	N.A.	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
SC	3.4	1	N.A.	N.A.	N.A.	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
	5.2	2	N.A.	N.A.	N.A.	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
	6.4	3	N.A.	N.A.	N.A.	N.A	N.A	N.A	0.11	0.11	0.11	0.11	0.11	-
CAM	4.5	1	-	0.03	N.A.	N.A	N.A	N.A	N.A	0.03	0.03	0.03	0.03	-
	7.5	3	N.A.	N.A.	N.A.	0.11	0.10	N.A	N.A	0.10	0.11	0.10	0.10	-
ARM	5	1	N.A.	N.A.	N.A.	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
	6	2	0.01	N.A.	N.A.	N.A	N.A	N.A	N.A	0.01	0.01	0.01	0.01	-
	7.5	3	N.A.	N.A.	N.A.	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
SR	4.5	1	N.A.	N.A.	N.A.	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
	5.5	2	N.A.	N.A.	N.A.	N.A	N.A	0.00	N.A	N.A	N.A	N.A	N.A	N.A
	6.5	3	N.A.	N.A.	N.A.	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
BUR	3.6	1	-	-	N.A.	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
	4.3	2	0.01	N.A.	N.A.	N.A	N.A	N.A	N.A	0.01	0.01	0.01	0.01	-
	6.1	3	0.01	N.A.	N.A.	N.A	N.A	N.A	N.A	0.01	0.01	0.01	0.01	-

Table 13: Monthly average of bromide (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Site	Depth (m, bgl)	Piezometer	Br ⁻ (mg L ⁻¹)							Min	Max	Median	Avg	SEM
			Feb	March	April	May	June	Aug	Sep					
DF	5.5	1	0.08	0.08	0.08	0.08	0.08	0.29	0.07	0.07	0.29	0.08	0.11	0.03
	7.5	2	0.09	0.10	0.10	0.09	0.09	0.09	0.08	0.08	0.10	0.09	0.09	0.00
	8.7	3	0.10	0.10	0.10	0.09	0.09	0.09	0.09	0.09	0.10	0.09	0.09	0.00
SC	3.4	1	0.19	0.20	0.20	0.20	0.20	0.20	0.18	0.18	0.20	0.20	0.20	0.00
	5.2	2	0.11	0.13	0.14	0.12	0.11	0.11	0.13	0.11	0.14	0.12	0.12	0.00
	6.4	3	0.19	0.21	0.22	0.23	0.23	0.22	0.26	0.19	0.26	0.22	0.22	0.01
CAM	4.5	1	0.00	0.14	0.12	0.12	0.11	0.10	0.10	0.00	0.14	0.11	0.10	0.02
	7.5	3	0.13	0.13	0.14	0.67	0.48	0.33	0.27	0.13	0.67	0.27	0.31	0.08
ARM	5	1	0.07	0.07	0.08	0.08	0.08	0.08	0.22	0.07	0.22	0.08	0.10	0.02
	6	2	0.11	0.11	0.11	0.11	0.10	0.10	0.10	0.10	0.11	0.11	0.10	0.00
	7.5	3	0.14	0.14	0.14	0.13	0.13	0.12	0.11	0.11	0.14	0.13	0.13	0.00
SR	4.5	1	0.11	0.12	0.10	0.08	0.09	0.09	0.11	0.08	0.12	0.10	0.10	0.01
	5.5	2	0.12	0.12	0.10	0.09	0.09	0.08	0.10	0.08	0.12	0.10	0.10	0.01
	6.5	3	0.12	0.14	0.11	0.09	0.09	0.09	0.11	0.09	0.14	0.11	0.11	0.01
BUR	3.6	1	0.00	0.00	0.13	0.11	0.09	0.22	0.06	0.00	0.22	0.09	0.09	0.03
	4.3	2	0.09	0.11	0.14	0.08	0.10	0.08	0.07	0.07	0.14	0.09	0.09	0.01
	6.1	3	0.09	0.07	0.09	0.10	0.08	0.07	0.06	0.06	0.10	0.08	0.08	0.01

Table 14: Monthly average of sulphate (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Site	Depth (m, bgl)	Piezometer	SO ₄ ²⁻ (mg L ⁻¹)							Min	Max	Median	Avg	SEM
			Feb	March	April	May	June	Aug	Sep					
DF	5.5	1	5.15	7.35	3.66	2.32	3.13	0.27	3.86	0.27	7.35	3.66	3.68	0.84
	7.5	2	2.29	2.23	2.09	1.93	1.95	0.31	1.81	0.31	2.29	1.95	1.80	0.26
	8.7	3	2.25	2.14	1.95	1.86	1.91	0.31	2.07	0.31	2.25	1.95	1.78	0.25
SC	3.4	1	3.36	3.57	3.51	2.86	2.18	0.76	1.02	0.76	3.57	2.86	2.46	0.45
	5.2	2	13.74	15.85	17.40	15.18	15.50	0.53	16.20	0.53	17.40	15.50	13.48	2.20
	6.4	3	9.70	11.57	10.87	9.80	16.28	0.50	24.19	0.50	24.19	10.87	11.84	2.72
CAM	4.5	1	0.00	9.35	10.86	11.74	13.14	0.29	12.63	0.00	13.14	10.86	8.29	2.15
	7.5	3	3.01	3.03	3.01	2.84	3.08	0.37	3.11	0.37	3.11	3.01	2.64	0.38
ARM	5	1	5.94	5.52	4.48	3.07	3.99	0.34	6.15	0.34	6.15	4.48	4.21	0.77
	6	2	3.33	3.19	1.32	1.30	1.85	0.43	0.54	0.43	3.33	1.32	1.71	0.44
	7.5	3	0.03	0.04	0.02	0.02	0.01	0.52	0.06	0.01	0.52	0.03	0.10	0.07
SR	4.5	1	4.53	4.55	5.17	5.18	5.34	0.23	4.84	0.23	5.34	4.84	4.26	0.68
	5.5	2	4.56	4.56	4.99	5.07	5.27	0.23	4.96	0.23	5.27	4.96	4.23	0.68
	6.5	3	4.51	4.52	5.01	4.99	5.21	0.22	4.69	0.22	5.21	4.69	4.17	0.66
BUR	3.6	1	0.00	0.00	6.79	7.34	6.97	0.25	5.04	0.00	7.34	5.04	3.77	1.33
	4.3	2	6.21	6.00	5.87	4.38	7.51	0.27	7.45	0.27	7.51	6.00	5.38	0.94
	6.1	3	2.82	3.30	4.88	6.08	5.68	0.25	5.25	0.25	6.08	4.88	4.04	0.78

Table 16: Monthly average of chlorine (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Cl ⁻ (mg L ⁻¹)														
Site	Depth (m, bgl)	Piezometer	Feb	March	April	May	June	Aug	Sep	Min	Max	Median	Avg	SEM
DF	5.5	1	20.00	19.48	18.99	19.64	19.01	20.58	17.87	17.87	20.58	19.48	19.37	0.33
	7.5	2	21.87	22.29	21.78	20.77	22.14	22.08	19.78	19.78	22.29	21.87	21.53	0.35
	8.7	3	22.03	22.41	22.01	20.95	22.15	22.97	20.58	20.58	22.97	22.03	21.87	0.31
SC	3.4	1	46.75	48.40	47.29	45.76	50.52	51.68	48.50	45.76	51.68	48.40	48.41	0.79
	5.2	2	33.42	40.06	42.01	37.44	39.45	46.95	40.98	33.42	46.95	40.06	40.04	1.57
	6.4	3	43.65	40.76	36.67	38.24	66.97	109.08	114.95	36.67	114.95	43.65	64.33	12.91
CAM	4.5	1	0.00	27.85	28.40	26.12	28.34	25.76	25.61	0.00	28.40	26.12	23.15	3.89
	7.5	3	16.57	16.47	16.08	15.24	16.54	16.77	16.67	15.24	16.77	16.54	16.33	0.20
ARM	5	1	15.52	16.73	17.25	18.45	19.67	19.25	15.13	15.13	19.67	17.25	17.43	0.67
	6	2	25.65	25.01	26.44	24.71	26.48	27.04	24.86	24.71	27.04	25.65	25.74	0.35
	7.5	3	34.75	35.89	34.95	32.96	35.01	34.24	30.98	30.98	35.89	34.75	34.11	0.62
SR	4.5	1	11.61	11.59	9.36	8.01	9.41	10.21	10.57	8.01	11.61	10.21	10.11	0.49
	5.5	2	11.49	11.57	9.82	8.32	9.43	10.07	10.26	8.32	11.57	10.07	10.14	0.43
	6.5	3	11.60	11.54	9.97	8.52	9.65	10.16	10.57	8.52	11.60	10.16	10.29	0.41
BUR	3.6	1	0.00	0.00	17.60	13.15	13.74	11.47	9.14	0.00	17.60	11.47	9.30	2.59
	4.3	2	12.03	14.68	18.16	11.00	15.70	12.52	11.15	11.00	18.16	12.52	13.61	1.01
	6.1	3	10.03	10.72	14.78	15.90	11.86	13.58	9.73	9.73	15.90	11.86	12.37	0.91

Table 17: Monthly average of carbonate (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

			HCO ₃ ⁻ (mg L ⁻¹)									
Site	Depth (m, bgl)	Piezometer	April	May	June	Aug	Sep	Min	Max	Median	Avg	SEM
DF	5.5	1	91.84	104.00	109.00	91.00	110.00	91.00	110.00	104.00	101.17	4.11
	7.5	2	121.76	113.00	133.00	117.00	131.00	113.00	133.00	121.76	123.15	3.88
	8.7	3	124.86	122.00	126.00	114.00	127.00	114.00	127.00	124.86	122.77	2.35
SC	3.4	1	307.50	273.00	289.00	306.00	300.00	273.00	307.50	300.00	295.10	6.41
	5.2	2	333.29	352.00	304.00	238.00	265.00	238.00	352.00	304.00	298.46	21.08
	6.4	3	231.14	218.00	212.00	223.00	283.00	212.00	283.00	223.00	233.43	12.78
CAM	4.5	1	92.87	41.33	44.00	49.00	49.00	41.33	92.87	49.00	55.24	9.52
	7.5	3	165.10	141.00	149.00	158.00	155.00	141.00	165.10	155.00	153.62	4.08
ARM	5	1	121.76	125.00	123.00	130.00	133.00	121.76	133.00	125.00	126.55	2.14
	6	2	169.23	161.00	165.00	185.00	221.00	161.00	221.00	169.23	180.25	10.97
	7.5	3	224.95	204.00	215.00	215.00	203.00	203.00	224.95	215.00	212.39	4.06
SR	4.5	1	23.73	27.00	27.00	29.00	22.00	22.00	29.00	27.00	25.75	1.26
	5.5	2	24.76	20.00	27.00	24.00	25.00	20.00	27.00	24.76	24.15	1.15
	6.5	3	25.80	21.00	30.00	23.00	27.00	21.00	30.00	25.80	25.36	1.57
BUR	3.6	1	52.63	44.00	52.00	56.00	153.00	44.00	153.00	52.63	71.53	20.46
	4.3	2	59.85	54.00	55.00	61.00	65.00	54.00	65.00	59.85	58.97	2.02
	6.1	3	43.34	36.00	41.00	47.00	-	36.00	47.00	42.17	41.84	2.06

Table 18: Monthly average of nitrous oxide (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

N ₂ O-N (mg L ⁻¹)													
Site	Depth (m, bgl)	Piezometer	March	April	May	June	Aug	Sep	Min	Max	Median	Avg	SEM
DF	5.5	1	0.01	0.00	0.00	0.00	-	-	0.00	0.01	0.00	0.00	0.00
	7.5	2	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	8.7	3	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.01	0.00
SC	3.4	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5.2	2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	6.4	3	0.00	0.00	0.00	0.04	0.03	0.03	0.00	0.04	0.02	0.02	0.01
CAM	7.5	3	0.01	0.02	0.08	0.09	0.04	0.04	0.01	0.09	0.04	0.05	0.01
ARM	5	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	6	2	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	7.5	3	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
SR	4.5	1	0.12	0.02	0.01	0.04	0.09	0.03	0.01	0.12	0.04	0.05	0.02
	5.5	2	0.11	0.03	0.00	0.04	0.03	0.03	0.00	0.11	0.03	0.04	0.01
	6.5	3	0.12	0.03	0.00	0.04	0.00	0.03	0.00	0.12	0.03	0.04	0.02
BUR	3.6	1	-	0.03	0.03	0.06	0.00	0.03	0.00	0.06	0.03	0.03	0.01
	4.3	2	0.07	0.02	0.03	0.06	0.00	0.05	0.00	0.07	0.04	0.04	0.01
	6.1	3	0.00	0.00	0.00	0.07	0.00	0.05	0.00	0.07	0.00	0.02	0.01

Table 19: Monthly average of nitrous oxide (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Site	Depth (m, bgl)	Piezometer	Excess N ₂ (μmol L ⁻¹)							
			June	Aug	Sep	Min	Max	Median	Avg	SEM
DF	5.5	1	29.78	25.21	29.68	25.21	29.78	29.68	28.22	1.51
	7.5	2	33.55	37.96	46.67	33.55	46.67	37.96	39.40	3.85
	8.7	3	31.58	47.61	46.15	31.58	47.61	46.15	41.78	5.12
SC	3.4	1	188.05	183.23	179.94	179.94	188.05	183.23	183.74	2.35
	5.2	2	-	-	-	-	-	-	-	-
	6.4	3	18.96	82.53	159.43	18.96	159.43	82.53	86.97	40.61
CAM	4.5	1	-	-	-	-	-	-	-	-
	7.5	3	83.34	90.94	1.56	1.56	90.94	83.34	58.61	28.61
ARM	5	1	77.57	57.06	52.26	52.26	77.57	57.06	62.30	7.76
	6	2	102.48	73.67	61.32	61.32	102.48	73.67	79.16	12.19
	7.5	3	61.29	55.72	62.62	55.72	62.62	61.29	59.88	2.11
SR	4.5	1	15.99	5.50	100.27	5.50	100.27	15.99	40.58	30.00
	5.5	2	25.42	8.23	5.64	5.64	25.42	8.23	13.10	6.21
	6.5	3	12.58	12.14	4.24	4.24	12.58	12.14	9.65	2.71
BUR	3.6	1	39.26	7.15	-	7.15	39.26	23.20	23.20	13.11
	4.3	2	38.28	15.14	16.45	15.14	38.28	16.45	23.29	7.50
	6.1	3	49.16	13.70	2.09	2.09	49.16	13.70	21.65	14.16

APPENDIX 2

Excess N₂ Calculations for monthly analysis

Table 20: Parameters for calculations for N₂ dilution temperature dependent for excess N₂ calculations

	Hcp Mol (m³*Pa)⁻¹	Temperature corrected	Atmospheric molar fraction	Reference
Ar	1.40E-05	1400	0.0093	Fernandez-Prini et al (2003) cited in Sander 2015 ACP
N₂	6.50E-06	1200	0.7801	Fernandez-Prini et al (2003) cited in Sander 2015 ACP

Table 21: Parameters for Ar solubility range calculations.

	Representation for the equation of a line	Value
Standard Temperature (°C)		25
Standard Temperature (K)		298.15
1/Standard Temperature (K)	x	0.0034
Hcp		0.000014
Temperature corrected Ar	m	1400
ln (Hcp)	y	-11.18
y - mx	c	-15.87

Table 22: Solubility for Ar in the range of temperature (1 – 38 °C).

$m^*(1/\text{Temperature (K)})+c$				
Temperature (°C)	Temperature (K)	1/Temperature (K)	ln H(T)	H (T)
1	274.15	0.0036	-10.77	2.11E-05
2	275.15	0.0036	-10.78	2.07E-05
3	276.15	0.0036	-10.80	2.04E-05
4	277.15	0.0036	-10.82	2.00E-05
5	278.15	0.0036	-10.84	1.96E-05
6	279.15	0.0036	-10.86	1.93E-05
7	280.15	0.0036	-10.87	1.89E-05
8	281.15	0.0036	-10.89	1.86E-05
9	282.15	0.0035	-10.91	1.83E-05
10	283.15	0.0035	-10.93	1.80E-05
11	284.15	0.0035	-10.95	1.76E-05
12	285.15	0.0035	-10.96	1.73E-05
13	286.15	0.0035	-10.98	1.70E-05
14	287.15	0.0035	-11.00	1.68E-05
15	288.15	0.0035	-11.01	1.65E-05
16	289.15	0.0035	-11.03	1.62E-05
17	290.15	0.0034	-11.05	1.59E-05
18	291.15	0.0034	-11.06	1.57E-05
19	292.15	0.0034	-11.08	1.54E-05
20	293.15	0.0034	-11.10	1.52E-05
21	294.15	0.0034	-11.11	1.49E-05
22	295.15	0.0034	-11.13	1.47E-05
23	296.15	0.0034	-11.14	1.45E-05
24	297.15	0.0034	-11.16	1.42E-05
25	298.15	0.0034	-11.18	1.40E-05
26	299.15	0.0033	-11.19	1.38E-05
27	300.15	0.0033	-11.21	1.36E-05
28	301.15	0.0033	-11.22	1.34E-05
29	302.15	0.0033	-11.24	1.32E-05
30	303.15	0.0033	-11.25	1.30E-05
31	304.15	0.0033	-11.27	1.28E-05
32	305.15	0.0033	-11.28	1.26E-05
33	306.15	0.0033	-11.30	1.24E-05
34	307.15	0.0033	-11.31	1.22E-05
35	308.15	0.0032	-11.33	1.20E-05
36	309.15	0.0032	-11.34	1.18E-05
37	310.15	0.0032	-11.36	1.17E-05
38	311.15	0.0032	-11.37	1.15E-05

Table 23: Monthly average of excess (n=3) of groundwater samples at each piezometer in the Manawatu and Rangitikei River catchments (February – September 2018).

Site	Piezo	June		August		September	
		Excess N ₂		Excess N ₂		Excess N ₂	
		$\mu\text{mol L}^{-1}$	SD	$\mu\text{mol L}^{-1}$	SD	$\mu\text{mol L}^{-1}$	SD
DF	1	31.58	2.94	47.61	2.97	46.15	1.49
	2	33.55	0.63	37.96	4.04	46.67	1.43
	3	29.78	1.76	25.21	0.15	29.68	0.85
SC	1	18.96	11.90	82.53	1.22	159.43	4.33
	2	188.05	2.74	183.23	1.58	179.94	7.18
CAM	3	83.34	4.38	90.94	1.40	1.56	0.45
ARM	1	77.57	1.99	57.06	1.30	52.26	1.47
	2	102.48	9.27	73.67	0.69	61.32	0.44
	3	61.29	2.46	55.72	0.87	62.62	1.81
SR	1	15.99	6.08	5.50	1.58	100.27	2.13
	2	25.42	7.60	8.23	0.52	5.64	0.57
	3	12.58	1.43	12.14	2.54	4.24	0.19
BUR	1	49.16	5.69	13.70	0.41	2.09	0.64
	2	38.28	3.72	15.14	0.50	16.45	3.15
	3	39.26	0.92	7.15	0.67	-	-

Table 24: Dinitrogen and argon concentration, temperature of analysis and excess N₂ results in groundwater (g-w) samples at each piezometer in the Manawatu and Rangitikei River catchments (June, August, September 2018).

Site	Month	Depth (m, bgl)	Piezo	Total N ₂ ($\mu\text{mol L}^{-1}$)	Total Ar ($\mu\text{mol L}^{-1}$)	Ground- water Temp (°C)	Temp Analysis (°C)	Ar [H(T Analysis)] ($\mu\text{mol L}^{-1}$ atm ⁻¹)	N ₂ (H(T Analysis)) ($\mu\text{mol L}^{-1}$ atm ⁻¹)	Excess N ₂ ($\mu\text{mol L}^{-1}$)	Average Excess N ₂ ($\mu\text{mol L}^{-1}$)	Excess N ₂ STD
DF	June	5.5	1	688.30	16.76					33.82		
	June	5.5	1	676.52	16.64					29.03		
	June	5.5	1	660.50	16.42	15.50	13.50	1712.61	774.03	26.48	29.78	1.76
DF	June	7.5	2	673.94	16.52					33.88		
	June	7.5	2	682.42	16.68					32.67		
	June	7.5	2	671.34	16.48	15.01	13.50	1712.61	774.03	34.11	33.55	0.63
DF	June	8.7	3	681.97	16.75					27.83		
	June	8.7	3	678.64	16.63					31.89		
	June	8.7	3	672.63	16.48	15.19	13.50	1712.61	774.03	35.02	31.58	2.94
SC	June	3.4	1	784.66	15.81					184.18		
	June	3.4	1	790.75	15.81					190.18		
	June	3.4	1	786.86	15.75	15.39	14.00	1698.10	768.40	189.78	188.05	2.74
SC	June	5.2	2	893.68	12.46					383.69		
	June	5.2	2	847.56	11.86					374.52		
	June	5.2	2	848.98	11.74	15.99	32.70	1260.39	595.15	383.71		
SC	June	6.4	3	688.89	16.71					33.81		
	June	6.4	3	647.29	16.50					4.67		
	June	6.4	3	678.28	16.78	14.12	14.00	1698.10	768.40	18.40	18.96	11.90
CAM	June	7.5	3	734.87	16.61					82.03		
	June	7.5	3	737.34	16.60					84.65		
	June	7.5	3	758.86	16.83	14.67	14.50	1683.77	762.84	92.35	83.34	4.38

ARM	June	5	1	726.15	16.76					75.58		
	June	5	1	726.90	16.71					79.55		
	June	5	1	-	-	14.95	13.00	1727.29	779.71	-	77.57	1.99
ARM	June	6	2	799.96	17.38					111.74		
	June	6	2	-	-					-		
	June	6	2	712.45	16.24	14.99	13.00	1727.29	779.71	93.21	102.48	9.27
ARM	June	7.5	3	652.52	15.58					62.08		
	June	7.5	3	630.88	15.30					57.96		
	June	7.5	3	641.30	15.37	14.67	14.50	1683.77	762.84	63.84	61.29	2.46
SR	June	4.5	1	618.60	15.93					10.66		
	June	4.5	1	663.43	16.44					24.49		
	June	4.5	1	616.99	15.87	14.88	14.00	1698.10	768.40	12.81	15.99	6.08
SR	June	5.5	2	631.29	16.02					17.82		
	June	5.5	2	-	-					-		
	June	5.5	2	711.81	17.09	14.35	14.00	1698.10	768.40	33.02	25.42	7.60
SR	June	6.5	3	623.70	16.02					10.56		
	June	6.5	3	621.09	15.92					13.67		
	June	6.5	3	618.64	15.89	14.42	14.00	1698.10	768.40	13.53	12.58	1.43
BUR	June	3.6	1	655.03	16.41					41.48		
	June	3.6	1	640.03	16.22					38.48		
	June	3.6	1	633.35	16.12	14.80	11.00	1787.80	803.07	37.81	39.26	0.92
BUR	June	4.3	2	697.89	17.11					42.00		
	June	4.3	2	646.16	16.38					34.56		
	June	4.3	2	-	-	14.88	11.00	1787.80	803.07	-	38.28	3.72
BUR	June	6.1	3	713.56	17.12					57.15		
	June	6.1	3	639.87	16.12					44.26		
	June	6.1	3	654.56	16.33	15.02	11.00	1787.80	803.07	46.07	49.16	5.69
DF	August	5.5	1	699.13	17.06					25.49		

	August	5.5	1	698.67	17.06					25.30		
	August	5.5	1	702.94	17.13	13.50	13.60	1709.69	772.90	24.85	25.21	0.15
DF	August	7.5	2	679.63	16.60					33.97		
	August	7.5	2	676.62	16.51					36.42		
	August	7.5	2	675.85	16.38	13.80	13.60	1709.69	772.90	43.50	37.96	4.04
DF	August	8.7	3	671.64	16.20					50.69		
	August	8.7	3	669.77	16.20					48.54		
	August	8.7	3	667.53	16.24	13.60	13.60	1709.69	772.90	43.60	47.61	2.97
SC	August	3.4	1	785.30	15.81					181.13		
	August	3.4	1	781.12	15.70					183.64		
	August	3.4	1	780.83	15.67	12.80	14.50	1683.77	762.84	184.92	183.23	1.58
SC	August	5.2	2	876.92	12.27					392.45		
	August	5.2	2	875.27	12.15					398.09		
	August	5.2	2	875.08	12.22	12.90	30.00	1312.83	616.31	393.63		
SC	August	6.4	3	754.38	16.94					80.96		
	August	6.4	3	750.41	16.83					83.94		
	August	6.4	3	750.70	16.86	12.60	14.50	1683.77	762.84	82.68	82.53	1.22
CAM	August	7.5	3	747.16	16.69					88.98		
	August	7.5	3	745.34	16.62					91.62		
	August	7.5	3	743.70	16.58	14.60	14.50	1683.77	762.84	92.21	90.94	1.40
ARM	August	5	1	749.02	17.47					55.41		
	August	5	1	748.33	17.43					57.18		
	August	5	1	747.10	17.38	14.00	13.00	1727.29	779.71	58.58	57.06	1.30
ARM	August	6	2	708.88	16.52					72.87		
	August	6	2	709.16	16.51					73.58		
	August	6	2	707.96	16.48	14.20	13.00	1727.29	779.71	74.55	73.67	0.69
ARM	August	7.5	3	658.32	15.80					54.50		
	August	7.5	3	655.60	15.72					56.94		

	August	7.5	3	653.27	15.64	14.50	14.50	1683.77	762.84	59.20	55.72	0.87
SR	August	4.5	1	640.72	16.53					4.19		
	August	4.5	1	640.91	16.52					4.58		
	August	4.5	1	640.06	16.46	12.80	13.00	1727.29	779.71	7.72	5.50	1.58
	August	5.5	2	638.16	16.42					8.26		
SR	August	5.5	2	637.22	16.39					8.87		
	August	5.5	2	634.68	16.37	12.90	13.00	1727.29	779.71	7.58	8.23	0.52
	August	6.5	3	642.79	16.38					15.47		
SR	August	6.5	3	639.26	16.42					9.30		
	August	6.5	3	640.41	16.40	13.20	13.00	1727.29	779.71	11.65	12.14	2.54
	August	3.6	1	661.91	17.12					5.59		
BUR	August	3.6	1	659.67	17.05					7.47		
	August	3.6	1	659.92	17.04	12.90	11.00	1787.80	803.07	8.39	7.15	0.67
	August	4.3	2	678.42	17.24					14.86		
BUR	August	4.3	2	678.86	17.25					14.72		
	August	4.3	2	678.77	17.23	13.20	11.00	1787.80	803.07	15.83	15.14	0.50
	August	6.1	3	673.30	17.18					13.19		
BUR	August	6.1	3	672.18	17.15					14.19		
	August	6.1	3	675.63	17.21	13.60	11.00	1787.80	803.07	13.72	13.70	0.41
	Sept	5.5	1	690.16	16.89					27.72		
DF	Sept	5.5	1	688.70	16.83					30.05		
	Sept	5.5	1	687.50	16.79	14.38	13.50	1712.61	774.03	31.27	29.68	0.85
	Sept	7.5	2	686.69	16.51					47.13		
DF	Sept	7.5	2	686.00	16.49					48.16		
	Sept	7.5	2	684.31	16.51	15.12	13.50	1712.61	774.03	44.74	46.67	1.43
	Sept	8.7	3	692.05	16.65					44.43		
DF	Sept	8.7	3	690.54	16.60					45.95		
	Sept	8.7	3	690.58	16.56	15.22	13.50	1712.61	774.03	48.06	46.15	1.49

SC	Sept	3.4	1	780.99	15.92					169.79		
	Sept	3.4	1	791.36	15.84					185.01		
	Sept	3.4	1	792.50	15.86	13.53	14.50	1683.77	762.84	185.04	179.94	7.18
SC	Sept	5.2	2	865.27	12.49					370.95		
	Sept	5.2	2	866.78	12.38					379.35		
	Sept	5.2	2	865.97	12.35	14.44	29.30	1326.94	621.98	380.16		
SC	Sept	6.4	3	759.84	15.82					154.80		
	Sept	6.4	3	760.75	15.67					165.22		
	Sept	6.4	3	758.50	15.74	12.85	14.50	1683.77	762.84	158.28	159.43	4.33
CAM	Sept	7.5	3	631.87	16.38					0.65		
	Sept	7.5	3	633.10	16.39					1.25		
	Sept	7.5	3	632.83	16.38					1.56		
	Sept	7.5	3	632.08	16.35	14.31	13.50	1712.61	774.03	2.78	1.56	0.45
ARM	Sept	5	1	759.03	17.71					50.34		
	Sept	5	1	757.80	17.66					52.52		
	Sept	5	1	759.13	17.66	13.80	13.00	1727.29	779.71	53.93	52.26	1.47
ARM	Sept	6	2	697.54	16.34					60.98		
	Sept	6	2	698.64	16.36					61.05		
	Sept	6	2	696.01	16.30	14.08	14.50	1683.77	762.84	61.94	61.32	0.44
ARM	Sept	7.5	3	664.41	15.87					60.08		
	Sept	7.5	3	660.38	15.75					63.53		
	Sept	7.5	3	659.40	15.72	14.18	14.00	1698.10	768.40	64.24	62.62	1.81
SR	Sept	4.5	1	751.36	16.82					97.09		
	Sept	4.5	1	750.76	16.77					99.68		
	Sept	4.5	1	748.64	16.70					101.60		
	Sept	4.5	1	747.18	16.66	13.04	13.00	1727.29	779.71	102.70	100.27	2.13
SR	Sept	5.5	2	628.68	16.32					4.66		
	Sept	5.5	2	626.65	16.27					6.09		

	Sept	5.5	2	628.13	16.29					5.86		
	Sept	5.5	2	626.26	16.26	13.24	13.00	1727.29	779.71	5.95	5.64	0.57
SR	Sept	6.5	3	629.83	16.36					3.81		
	Sept	6.5	3	630.55	16.37					3.91		
	Sept	6.5	3	629.28	16.33					4.68		
	Sept	6.5	3	629.21	16.33	13.25	13.00	1727.29	779.71	4.55	4.24	0.19
	Sept	6.5	3	629.21	16.33	13.25	13.00	1727.29	779.71	4.55	4.24	0.19
BUR	Sept	3.6	1	-	-					-		
	Sept	3.6	1	-	-					-		
	Sept	3.6	1	-	-					-	-	-
BUR	Sept	4.3	2	665.81	16.93					20.89		
	Sept	4.3	2	658.72	16.93					13.94		
	Sept	4.3	2	657.94	16.91	12.60	11.00	1787.80	803.07	14.53	16.45	3.15
BUR	Sept	6.1	3	659.35	17.15					1.28		
	Sept	6.1	3	658.07	17.11					2.15		
	Sept	6.1	3	656.80	17.08	13.20	11.00	1787.80	803.07	2.84	2.09	0.64

*Values highlighted in red were not considered for the analysis.

APPENDIX 3

Push and pull test

Table 25: Test Solution concentrations of each bag at each push and pull.

	<i>Test solution (20 L)</i>	<i>Total Br (mg L⁻¹)</i>	<i>Total NO₃⁻-N (mg L⁻¹)</i>
<i>DF 3</i>	1	16.28	14.634
	2	20.67	18.434
	3	20.57	18.18
	4	16.03	14.388
	5	16.1	14.39
<i>ARM 3</i>	1	24.25	22.78
	2	5.29	5.06
	3	5.43	5.12
	4	8.76	8.6
	5	7.17	6.57
<i>SR 3</i>	1	12.12	14.81
	2	13.99	16.97
	3	14.87	17.91
	4	15.58	18.55
	5	13.94	17.05
<i>BUR 3</i>	1	3.36	4.24
	2	15.01	19.36
	3	14.58	19.20
	4	10.38	14.26
	5	22.30	26.79
<i>CAM 3</i>	1	15.17	14.21
	2	15.04	14.17
	3	13.71	12.78

Table 26: Adjusted NO_3^- -N, Br^- , NO_3^- -N dilution correction, NO_3^- -N background, NO_3^- -N/ Br^- ratio results of Push and pull test conducted at **site DF 3**, August 2018

	<i>Time (Hours)</i>	<i>NO_2^--N (mg L⁻¹)</i>	<i>Total Br^- (mg L⁻¹)</i>	<i>Total NO_3^--N (mg L⁻¹)</i>	<i>Br^- background (mg L⁻¹)</i>	<i>NO_3^--N Background (mg L⁻¹)</i>	<i>Adjusted Br^- (mg L⁻¹)</i>	<i>Adjusted NO_3^--N (mg L⁻¹)</i>	<i>NO_3^-- N/Br^- Ratio</i>	<i>Dilution factor</i>	<i>NO_3^--N Dilution correction (mg L⁻¹)</i>
DF 3	0.5	0.11	13.35	11.82	0.09	0.02	13.26	11.80	0.89	1.00	11.80
	1	0.18	8.03	6.87	0.09	0.02	7.94	6.85	0.86	1.67	11.45
	1.5	0.18	6.53	5.50	0.09	0.02	6.44	5.48	0.85	2.06	11.28
	2	0.19	5.32	4.37	0.09	0.02	5.23	4.35	0.83	2.54	11.03
	2.5	0.18	3.83	3.02	0.09	0.02	3.74	3.00	0.80	3.55	10.66
	3.5	0.17	2.47	1.81	0.09	0.02	2.38	1.79	0.75	5.58	9.97
	4.5	0.15	1.81	1.21	0.09	0.02	1.72	1.19	0.69	7.71	9.20
	5.5	0.13	1.29	0.78	0.09	0.02	1.20	0.76	0.63	11.03	8.40

Table 27: Adjusted NO_3^- -N, Br^- , NO_3^- -N dilution correction, NO_3^- -N background, NO_3^- -N/ Br^- ratio results of Push and pull test conducted at **site ARM 3**, August 2018.

	<i>Time (Hours)</i>	<i>NO_2^--N (mg L⁻¹)</i>	<i>Total Br^- (mg L⁻¹)</i>	<i>Total NO_3^--N (mg L⁻¹)</i>	<i>Br^- background (mg L⁻¹)</i>	<i>NO_3^--N Background (mg L⁻¹)</i>	<i>Adjusted Br^- (mg L⁻¹)</i>	<i>Adjusted NO_3^--N (mg L⁻¹)</i>	<i>NO_3^--N/Br^- Ratio</i>	<i>Dilution factor</i>	<i>NO_3^--N Dilution correction (mg L⁻¹)</i>
ARM 3	0.5	0.02	15.27	14.71	0.13	0.02	15.14	14.69	0.97	1.00	14.69
	1	0.04	12.51	11.99	0.13	0.02	12.38	11.97	0.97	1.22	14.64
	1.5	0.07	12.57	11.95	0.13	0.02	12.44	11.93	0.96	1.22	14.52
	2	0.09	11.52	10.92	0.13	0.02	11.39	10.90	0.96	1.33	14.49
	2.5	0.11	10.67	10.01	0.13	0.02	10.54	9.99	0.95	1.44	14.35
	3.5	0.14	9.89	9.21	0.13	0.02	9.76	9.19	0.94	1.55	14.25
	4.5	0.13	4.52	3.89	0.13	0.02	4.39	3.86	0.88	3.45	13.33
	5.5	0.14	3.99	3.34	0.13	0.02	3.86	3.32	0.86	3.92	13.01

Table 28: Adjusted NO₃⁻-N, Br⁻, NO₃⁻-N dilution correction, NO₃⁻-N background, NO₃⁻-N/Br⁻ ratio results of Push and pull test conducted at **site CAM 3**, August 2018.

	Time (Hours)	NO ₂ ⁻ -N (mg L ⁻¹)	Total Br ⁻ (mg L ⁻¹)	Total NO ₃ ⁻ -N (mg L ⁻¹)	Br ⁻ background (mg L ⁻¹)	NO ₃ ⁻ -N Background (mg L ⁻¹)	Adjusted Br ⁻ (mg L ⁻¹)	Adjusted NO ₃ ⁻ -N (mg L ⁻¹)	NO ₃ ⁻ -N/Br ⁻ Ratio	Dilution factor	NO ₃ ⁻ -N Dilution correction (mg L ⁻¹)
CAM 3	0.5	N.A	13.76	13.09	0.31	0.10	13.45	12.99	0.97	1.00	12.99
	1	0.005	9.36	8.74	0.31	0.10	9.05	8.64	0.95	1.49	12.83
	1.5	N.A	5.14	4.70	0.31	0.10	4.83	4.60	0.95	2.79	12.82
	2	N.A	5.19	4.66	0.31	0.10	4.88	4.56	0.93	2.75	12.55
	2.5	0.006	4.46	3.93	0.31	0.10	4.15	3.83	0.92	3.24	12.42
	3.5	N.A	2.97	2.60	0.31	0.10	2.66	2.50	0.94	5.05	12.63
	4.5	0.006	3.37	2.90	0.31	0.10	3.06	2.80	0.92	4.40	12.33
	5.5	N.A	2.87	2.40	0.31	0.10	2.57	2.30	0.89	5.24	12.03

Table 29: Adjusted NO₃⁻-N, Br⁻, NO₃⁻-N dilution correction, NO₃⁻-N background, NO₃⁻-N/Br⁻ ratio at **site SC 2**, push and pull test conducted on September 2018. Values highlighted in red were not considered for the analysis.

	Time (Hours)	NO ₂ ⁻ -N (mg L ⁻¹)	Total Br ⁻ (mg L ⁻¹)	Total NO ₃ ⁻ -N (mg L ⁻¹)	Br ⁻ background (mg L ⁻¹)	NO ₃ ⁻ -N Background (mg L ⁻¹)	Adjusted Br ⁻ (mg L ⁻¹)	Adjusted NO ₃ ⁻ -N (mg L ⁻¹)	NO ₃ ⁻ -N/Br ⁻ Ratio	Dilution factor	NO ₃ ⁻ -N Dilution correction (mg L ⁻¹)
SC 2	0.5	N.A	12.35	11.80	0.12	0.05	12.23	11.75	0.96	1.00	11.75
	1	N.A	16.14	15.34	0.12	0.05	16.02	15.29	0.95	0.76	11.66
	1.5	0.01	14.10	11.69	0.12	0.05	13.98	11.64	0.83	0.87	10.17
	2	0.01	15.53	14.72	0.12	0.05	15.41	14.67	0.95	0.79	11.64
	2.5	0.01	14.56	12.47	0.12	0.05	14.44	12.42	0.86	0.85	10.52
	3.5	0.03	13.68	13.40	0.12	0.05	13.56	13.35	0.98	0.90	12.04
	4.5	0.03	12.14	11.44	0.12	0.05	12.02	11.39	0.95	1.02	11.58
	5.5	0.03	10.17	10.78	0.12	0.05	10.05	10.73	1.07	1.22	13.06

Table 30: Adjusted NO₃⁻-N, Br⁻, NO₃⁻-N dilution correction, NO₃⁻-N background, NO₃⁻-N/Br⁻ ratio results of push and pull test conducted at **site SR 3**, September 2018

	Time (Hours)	NO ₂ ⁻ -N (mg L ⁻¹)	Total Br ⁻ (mg L ⁻¹)	Total NO ₃ ⁻ -N (mg L ⁻¹)	Br ⁻ background (mg L ⁻¹)	NO ₃ ⁻ -N Background (mg L ⁻¹)	Adjusted Br ⁻ (mg L ⁻¹)	Adjusted NO ₃ ⁻ -N (mg L ⁻¹)	NO ₃ ⁻ -N/Br ⁻ Ratio	Dilution factor	NO ₃ ⁻ -N Dilution correction (mg L ⁻¹)
SR 3	0.5	0.01	2.56	6.03	0.11	3.53	2.45	2.50	1.02	1.00	2.50
	1	0.01	1.00	4.51	0.11	3.53	0.90	0.97	1.08	2.73	2.66
	1.5	0.00	0.70	4.20	0.11	3.53	0.60	0.67	1.12	4.11	2.74
	2	N.A	0.80	4.00	0.11	3.53	0.69	0.47	0.68	3.54	1.66
	2.5	N.A	0.43	4.00	0.11	3.53	0.32	0.46	1.44	7.66	3.54
	3.5	0.01	0.43	3.97	0.11	3.53	0.32	0.43	1.35	7.64	3.31
	4.5	N.A	0.37	3.59	0.11	3.53	0.27	0.05	0.20	9.21	0.48
	5.5	N.A	0.33	3.84	0.11	3.53	0.23	0.31	1.34	10.75	3.28

Table 31: Adjusted NO₃⁻-N, Br⁻, NO₃⁻-N dilution correction, NO₃⁻-N background, NO₃⁻-N/Br⁻ ratio results of push and pull test conducted at **site BUR 3**, September 2018. Values highlighted in red were not considered for the analysis.

	Time (Hours)	NO ₂ ⁻ -N (mg L ⁻¹)	Total Br ⁻ (mg L ⁻¹)	Total NO ₃ ⁻ -N (mg L ⁻¹)	Br ⁻ background (mg L ⁻¹)	NO ₃ ⁻ -N Background (mg L ⁻¹)	Adjusted Br ⁻ (mg L ⁻¹)	Adjusted NO ₃ ⁻ -N (mg L ⁻¹)	NO ₃ ⁻ -N/Br ⁻ Ratio	Dilution factor	NO ₃ ⁻ -N Dilution correction (mg L ⁻¹)
BUR 3	0.5	N.A	12.75	17.51	0.07	5.86	12.68	11.65	0.92	1.00	11.65
	1	N.A	7.85	12.45	0.07	5.86	7.78	6.59	0.85	1.63	10.74
	1.5	N.A	4.08	8.61	0.07	5.86	4.01	2.75	0.69	3.16	8.70
	2	N.A	3.50	8.39	0.07	5.86	3.43	2.53	0.74	3.70	9.34
	2.5	N.A	1.99	6.53	0.07	5.86	1.92	0.67	0.35	6.61	4.41
	3.5	N.A	1.58	6.39	0.07	5.86	1.51	0.53	0.35	8.39	4.48
	4.5	N.A	1.12	5.56	0.07	5.86	1.05	-0.30	-0.28	12.13	-3.60
	5.5	N.A	0.88	5.48	0.07	5.86	0.81	-0.38	-0.47	15.64	-5.91

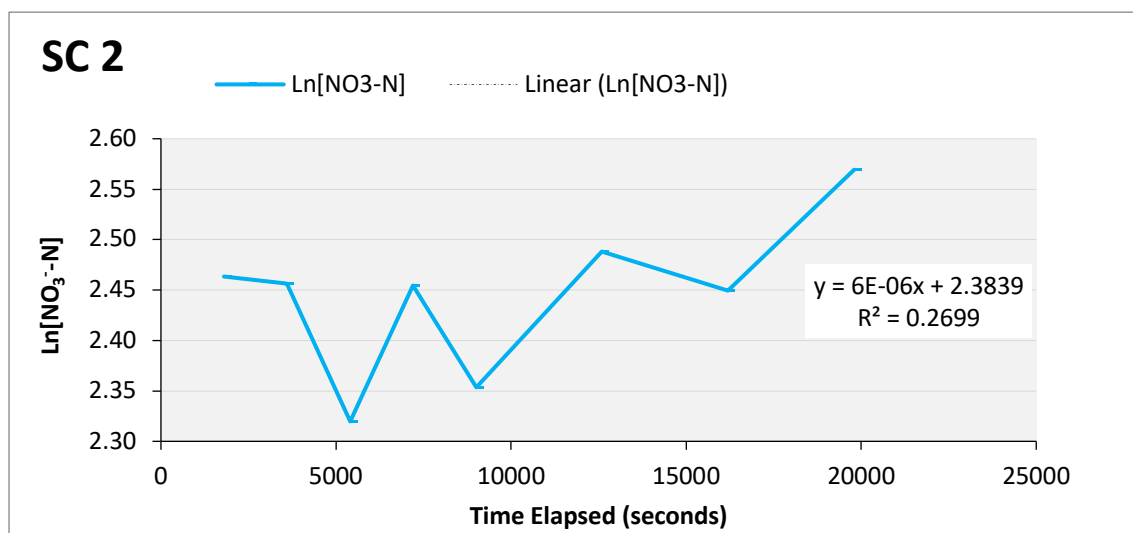
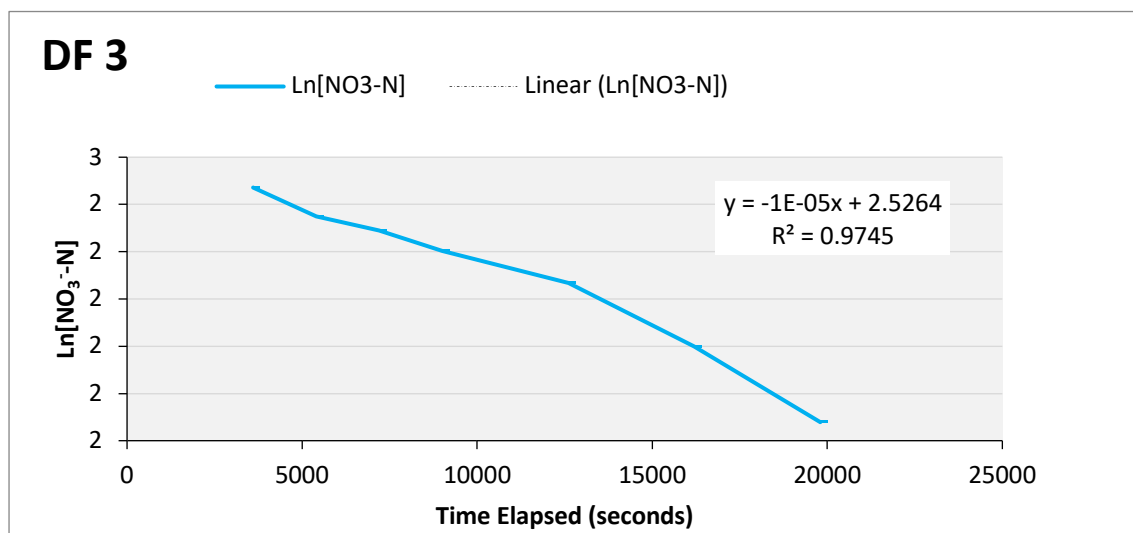
Table 32: Reaction order for NO_3^- -N reduction and denitrification rate of push-pull tests.

Piezometer	Time (Hours)	Time (s)	NO_3^- -N Dilution correction	$\text{Ln}[\text{NO}_3^-$ - N]	$1/[\text{NO}_3^-$ -N]	Denitrification rate (mg L^{-1})
DF 3	0.5	1800	11.80	2.47	0.08	0.68
	1	3600	11.45	2.44	0.09	
	1.5	5400	11.27	2.42	0.09	
	2	7200	11.03	2.40	0.09	
	2.5	9000	10.66	2.37	0.09	
	3.5	12600	9.97	2.30	0.10	
	4.5	16200	9.20	2.22	0.11	
	5.5	19800	8.40	2.13	0.12	
SC 2	0.5	1800	11.75	2.46	0.09	-0.26
	1	3600	11.66	2.46	0.09	
	1.5	5400	10.17	2.32	0.10	
	2	7200	11.64	2.45	0.09	
	2.5	9000	10.52	2.35	0.10	
	3.5	12600	12.04	2.49	0.08	
	4.5	16200	11.58	2.45	0.09	
	5.5	19800	13.06	2.57	0.08	
CAM 3	0.5	1800	13.02	2.56	0.08	0.19
	1	3600	12.87	2.55	0.08	
	1.5	5400	12.85	2.55	0.08	
	2	7200	12.59	2.53	0.08	
	2.5	9000	12.46	2.52	0.08	
	3.5	12600	12.66	2.54	0.08	
	4.5	16200	12.37	2.51	0.08	
	5.5	19800	12.07	2.49	0.08	
ARM 3	0.5	1800	14.69	2.69	0.07	0.34
	1	3600	14.64	2.68	0.07	
	1.5	5400	14.52	2.68	0.07	
	2	7200	14.49	2.67	0.07	
	2.5	9000	14.35	2.66	0.07	
	3.5	12600	14.25	2.66	0.07	
	4.5	16200	13.33	2.59	0.08	
	5.5	19800	13.01	2.57	0.08	
SR 3	0.5	1800	2.50	0.92		-0.16
	1	3600	2.66	0.98		
	1.5	5400	2.74	1.01		
	2	7200	1.66	0.51		
	2.5	9000	3.54	1.26		
	3.5	12600	3.31	1.20		
	4.5	16200	0.48	-0.74		
	5.5	19800	3.28	1.19		
BUR 3	0.5	1800	11.65	2.46	0.09	2.39
	1	3600	10.74	2.37	0.09	
	1.5	5400	8.70	2.16	0.11	
	2	7200	9.34	2.23	0.11	
	2.5	9000	4.41	1.48	0.23	

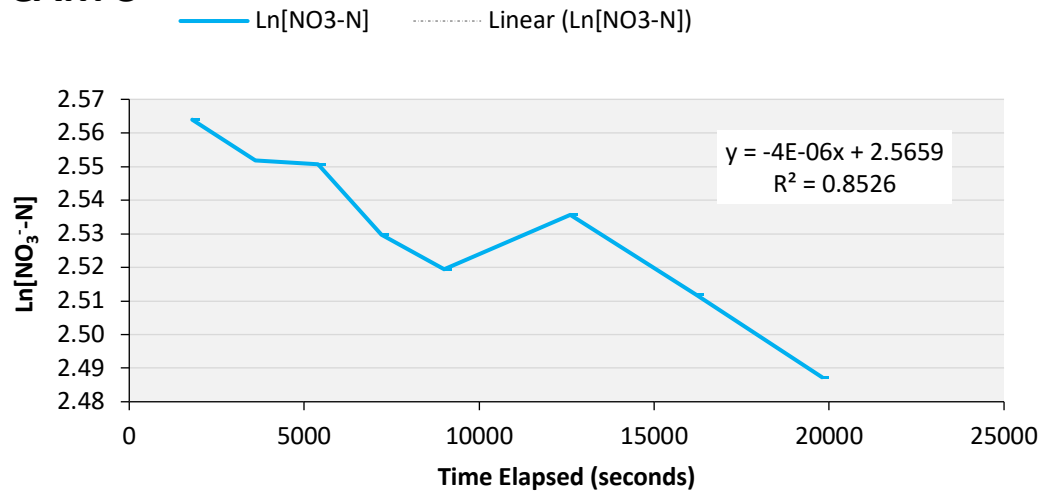
3.5	12600	4.48	1.50	0.22
4.5	16200	-3.60		
5.5	19800	-5.91		

*Values highlighted in red were not considered for the analysis.

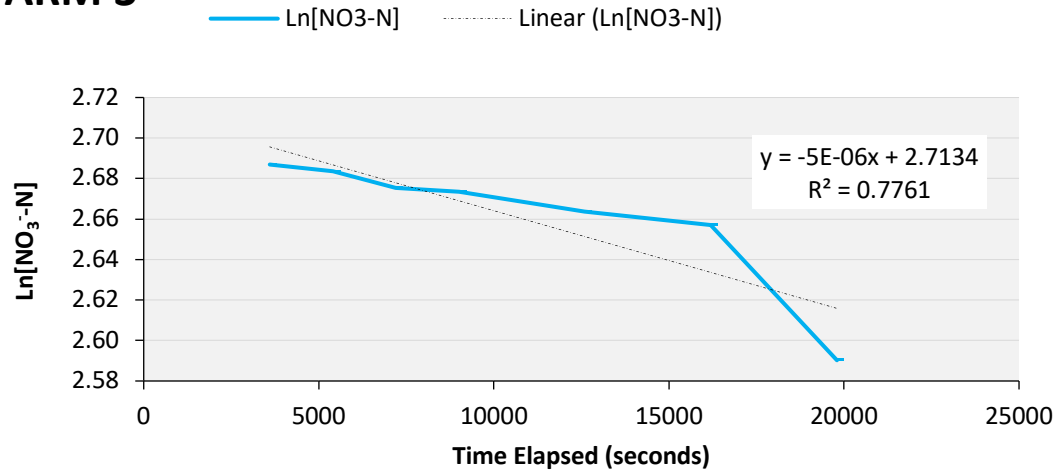
Plots (6 in total) of linear regression of NO_3^- -N concentration over time for calculation of denitrification rate at each piezometer during push-pull test.



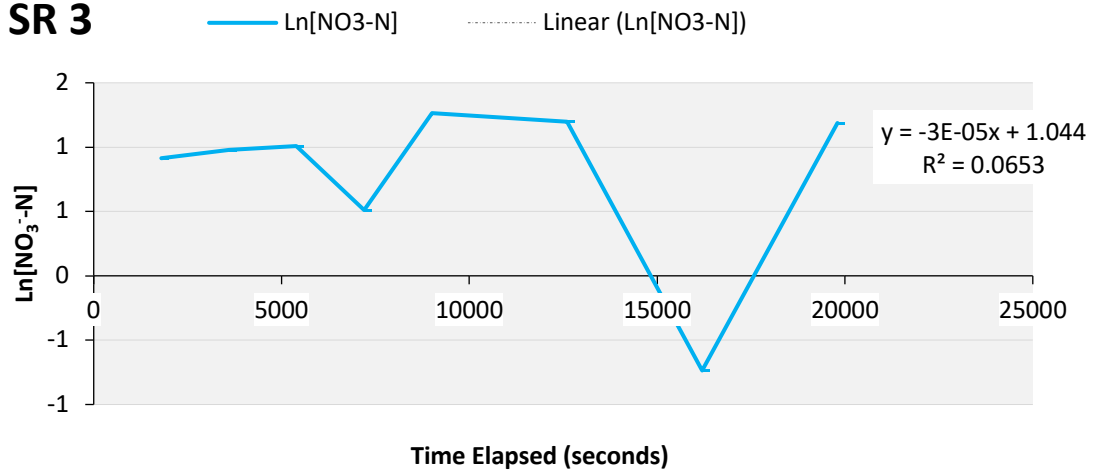
CAM 3

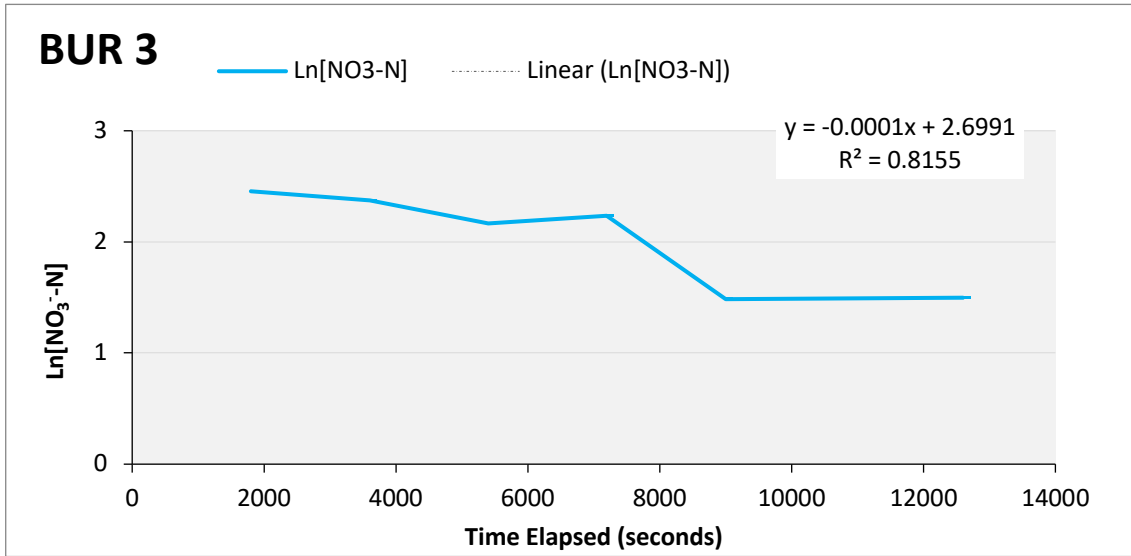


ARM 3



SR 3





Appendix 4

Dissolved gas analysis Push-pull tests

Table 33: Excess N₂ and N₂O-N results of Push and pull test conducted at each site, background (bkg) values, and ratios between N₂O-N and excess N₂ during wet season 2018

Bkg Values (Month)	Site	Time (hours)	Dilution factor	Bkg Excess N ₂ (μmol L ⁻¹)	Bkg N ₂ O-N (μmol L ⁻¹)	Excess N ₂ (μmol L ⁻¹)	N ₂ O-N (μmol L ⁻¹)	Excess N ₂ dilution corrected (μmol L ⁻¹)	N ₂ O-N dilution corrected (μmol L ⁻¹)	Ratio N ₂ O-N / N ₂ O-N +ExcessN ₂	Ratio ExcessN ₂ /N ₂ O-N +ExcessN ₂	Avg ratio N ₂ O-N / N ₂ O-N +ExcessN ₂
August	BUR 3	0.5	1.0	13.70	1.96E-04	16.47	0.035	2.77	0.035	0.0125	0.9875	
		1	1.6	13.70	1.96E-04	17.13	0.035	5.60	0.058	0.0102	0.9898	
		1.5	3.2	13.70	1.96E-04	19.85	0.036	19.45	0.115	0.0059	0.9941	
		2	3.7	13.70	1.96E-04	20.08	0.036	23.59	0.134	0.0057	0.9943	
		2.5	6.6	13.70	1.96E-04	19.34	0.036	37.24	0.241	0.0064	0.9936	
		3.5	8.4	13.70	1.96E-04	19.80	0.036	51.20	0.304	0.0059	0.9941	
		4.5	12.1	13.70	1.96E-04	15.72	0.037	24.51	0.443	0.0178	0.9822	
		5.5	15.6	13.70	1.96E-04	19.25	0.036	86.85	0.562	0.0064	0.9936	0.009
Monthly average	CAM 3	0.5	1.0	58.61	4.51E-02	65.59	0.006	6.98	0.006	0.0009	0.9991	
		1	1.5	58.61	4.51E-02	77.29	0.006	27.75	0.008	0.0003	0.9997	
		1.5	2.8	58.61	4.51E-02	83.09	0.005	68.19	0.015	0.0002	0.9998	
		2	2.8	58.61	4.51E-02	90.55	0.000	88.00	0.000	0.0000	1.0000	
		2.5	3.2	58.61	4.51E-02	84.84	0.005	85.04	0.016	0.0002	0.9998	
		3.5	5.1	58.61	4.51E-02	85.20	0.015	134.32	0.074	0.0006	0.9994	
		4.5	4.4	58.61	4.51E-02	87.61	0.021	127.54	0.092	0.0007	0.9993	
		5.5	5.2	58.61	4.51E-02	93.59	0.035	183.32	0.182	0.0010	0.9990	0.0005
June	DF 3	0.5	1.0	31.58	1.56E-02	27.03	0.032	0.00	0.016	1.0000	0.0000	
		1	1.7	31.58	1.56E-02	31.17	0.033	0.00	0.030	1.0000	0.0000	
		1.5	2.1	31.58	1.56E-02	32.54	0.033	1.97	0.036	0.0180	0.9820	
		2	2.5	31.58	1.56E-02	37.14	0.038	14.10	0.056	0.0040	0.9960	
		2.5	3.5	31.58	1.56E-02	37.57	0.042	21.26	0.093	0.0043	0.9957	
		3.5	5.6	31.58	1.56E-02	39.59	0.042	44.69	0.148	0.0033	0.9967	
		4.5	7.7	31.58	1.56E-02	35.86	0.045	32.97	0.225	0.0068	0.9932	
		5.5	11.0	31.58	1.56E-02	39.51	0.046	87.50	0.338	0.0038	0.9962	0.007

August	ARM 3	0.5	1.0	55.72	1.96E-04	53.04	0.013	-2.68	0.013	-0.0048	1.0048	-
		1	1.2	55.72	1.96E-04	57.41	0.045	2.07	0.055	0.0258	0.9742	
		1.5	1.2	55.72	1.96E-04	55.49	0.048	0.00	0.058	1.0000	0.0000	
		2	1.3	55.72	1.96E-04	61.16	0.048	7.23	0.063	0.0086	0.9914	
		2.5	1.4	55.72	1.96E-04	64.16	0.039	12.13	0.056	0.0046	0.9954	
		3.5	1.6	55.72	1.96E-04	61.73	0.035	9.32	0.054	0.0058	0.9942	
		4.5	3.5	55.72	1.96E-04	71.94	0.029	55.97	0.099	0.0018	0.9982	
		5.5	3.9	55.72	1.96E-04	73.05	0.034	67.99	0.131	0.0019	0.9981	0.005
Sept	SR 3	0.5	1.0	4.24	1.96E-04	6.36	0.044	2.12	0.044	0.0204	0.9796	
		1	2.7	4.24	1.96E-04	6.02	0.044	4.88	0.120	0.0241	0.9759	
		1.5	4.1	4.24	1.96E-04	6.94	0.045	11.10	0.182	0.0162	0.9838	
		2	3.5	4.24	1.96E-04	6.74	0.045	8.87	0.158	0.0175	0.9825	
		2.5	7.7	4.24	1.96E-04	7.66	0.046	26.17	0.352	0.0133	0.9867	
		3.5	7.6	4.24	1.96E-04	7.36	0.045	23.81	0.343	0.0142	0.9858	
		4.5	9.2	4.24	1.96E-04	8.00	0.030	34.62	0.273	0.0078	0.9922	
		5.5	10.8	4.24	1.96E-04	10.88	0.030	71.37	0.325	0.0045	0.9955	0.015

*Values highlighted in red were not considered for the analysis.

Table 34: Linear regression excess N₂ over push-pull for calculation of complete denitrification rate at **site DF 3**.

Complete Subsurface Denitrification Rate	
Regression Statistics	
Multiple R	0.92546643
R Square	0.85648811
Adjusted R Square	0.83256946
Standard Error	12.2464437
Observations	8

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	5370.37597	5370.37597	35.8083831	0.00097813
Residual	6	899.852298	149.975383		
Total	7	6270.22827			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-16.297131	8.191108	-1.9896125	0.09376638	-36.34005	3.74578836	-36.34005	3.74578836
X Variable 1	15.8507306	2.64884733	5.98401062	0.00097813	9.36923463	22.3322265	9.36923463	22.3322265

Table 35: Linear regression excess N₂ over push-pull for calculation of complete denitrification rate at **site ARM 3**.

Complete Subsurface Denitrification Rate

<i>Regression Statistics</i>	
Multiple R	0.92085743
R Square	0.84797841
Adjusted R Square	0.81757409
Standard Error	11.8599303
Observations	7

ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	3922.95927	3922.95927	27.8900651	0.003242
Residual	5	703.289731	140.657946		
Total	6	4626.249			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-23.451375	9.72084748	-2.4124825	0.06067778	-48.439609	1.53685937	-48.439609	1.53685937
X Variable 1	15.5545693	2.94532501	5.28110453	0.003242	7.98337028	23.1257682	7.98337028	23.1257682

Table 36: Linear regression excess N₂ over push-pull for calculation of complete denitrification rate at **site CAM 3**.

Complete Subsurface Denitrification Rate

Regression Statistics	
Multiple R	0.96448687
R Square	0.93023492
Adjusted R Square	0.9186074
Standard Error	16.4782847
Observations	8

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	21723.4992	21723.4992	80.002909	0.00010901
Residual	6	1629.2032	271.533867		
Total	7	23352.7024			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	6.45878632	11.0216005	0.58601165	0.5792286	-20.510099	33.4276712	-20.510099	33.4276712
X Variable 1	31.8795241	3.56417435	8.94443452	0.00010901	23.1583037	40.6007446	23.1583037	40.6007446

Table 37: Linear regression excess N₂ over push-pull for calculation of complete denitrification rate at **site SR 3**.

Complete Subsurface Denitrification Rate

<i>Regression Statistics</i>	
Multiple R	0.92836117
R Square	0.86185447
Adjusted R Square	0.83883021
Standard Error	9.09259533
Observations	8

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	3094.73935	3094.73935	37.4324584	0.00087047
Residual	6	496.051739	82.6752899		
Total	7	3590.79109			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-8.719858	6.08163744	-1.433801	0.2016193	-23.601089	6.16137274	-23.601089	6.16137274
X Variable 1	12.0325861	1.96668498	6.11820713	0.00087047	7.22028128	16.8448909	7.22028128	16.8448909

Table 38: Linear regression excess N₂ over push-pull for calculation of complete denitrification rate at **site BUR 3**.

Complete Subsurface Denitrification Rate

Regression Statistics	
Multiple R	0.84938842
R Square	0.72146069
Adjusted R Square	0.67503747
Standard Error	15.5925677
Observations	8

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	3778.44153	3778.44153	15.5409453	0.00760539
Residual	6	1458.769	243.128167		
Total	7	5237.21053			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-3.500058	10.4291833	-0.3356023	0.7485948	-29.01935	22.0192342	-29.01935	22.0192342
X Variable 1	13.2954577	3.37259798	3.94220056	0.00760539	5.04300769	21.5479076	5.04300769	21.5479076