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**Assessment of the transport and transformation of nitrogen in the
unsaturated and saturated zones under two dairy farms in the
Manawatu River catchment**

A thesis presented in partial fulfilment of the requirements for the
degree of

Master
in
Environmental Management

at the Institute of Agriculture and Environment,
Massey University, Palmerston North, Manawatu, New Zealand

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2015

Abstract

The importance of dairy farming in New Zealand is reflected in the country's export and gross domestic product earnings. While the economic and food production benefits are evident, there is an increasing concern about the effects of excess nutrient runoff on water quality and ecosystem health. Studies on the transport and transformation of nutrients, specifically nitrogen, are limited or mainly focused on the management and reduction of nutrient losses from the root zone. This is also the case in the Manawatu River catchment of New Zealand. The goal of this study was to assess the transport and transformation of nitrogen in the unsaturated (below the root zone) and saturated zones using field measurements, a tracer test, and identification of redox conditions in the shallow groundwater.

Two sites were chosen in the Manawatu River catchment: Site 1 (Massey Dairy Farm No. 1, Palmerston North) and Site 2 (Te Matai Road, Whakarongo). Soil-water and groundwater were extracted using 12 porous cups (0.3, 0.6, 1.0, 2.0 m bgl) and four piezometers (5.8, 6.3, 7.4, 8.7 m bgl) installed at Site 1, and six piezometers (12, 18, 33, 51, 66, 87 m bgl) installed at Site 2. The extracted water samples were analysed for nitrate-nitrogen ($\text{NO}_3\text{-N}$) and other water quality parameters. The average $\text{NO}_3\text{-N}$ concentrations in the unsaturated zone (0.3 – 2.0 m bgl) decreased with depth.

At Site 1, a tracer test was conducted in November, 2013, using an application of urea (467 kg N/ha) and bromide (206 kg Br/ha). After fertiliser application, $\text{NO}_3\text{-N}$ concentrations increased in the root zone. The bromide reached only until the 2-m depth porous cup in January, 2014, after a total irrigation depth of 478 mm. The early appearance of bromide in the 0.3 m depth root zone suggested preferential flow, a pathway that speeds up transport of potential contaminants in the groundwater.

The observed data of $\text{NO}_3\text{-N}$, dissolved oxygen (DO), iron, manganese, and sulphate were utilised to assess the redox condition in groundwater at both sites. The decreasing $\text{NO}_3\text{-N}$ concentrations with increasing depth indicated dilution and/or the occurrence of denitrification in the groundwater. The groundwater redox conditions were mixed oxic-anoxic in the 5.8 – 51 m bgl and mainly anoxic below 51 m groundwater depth.



Acknowledgements

Above all, I thank the Lord God Almighty for making this thesis a success. Indeed, I can do all things through Christ who strengthens me (Philippians 4:13, NIV).

I want to sincerely thank my thesis supervisor, Dr Ranvir Singh, for helping me to finish this thesis. I acknowledge all his support, encouragement, ideas, and continued thesis supervision even if I am miles away and the submission has been extended several times. You are a big part of this thesis and it was made possible because of your unwavering support.

Also, my sincere appreciation goes to the people who have helped me a lot in my thesis work. To the Institute of Agriculture and Environment (IAE) staff: Dr John Holland, Dr Mike Hedley, Dr Dave Horne, Dr James Hanly, Mr. Ian Furkert, Mr. David Feek, Mrs. Glenys Wallace, Mr. Mark Osborne, and Ms. Sharon Wright, thanks for all the administration support, for helping me establish my experimental plot, for teaching me how to use the laboratory equipment, and for helping me in analysing my samples.

To the Massey Dairy Farm No.1 and AgResearch Grassland staff: Ms. Jolanda Amoore, Ms. Fiona Brown, Mr. Tom Phillips, and Mr. Chris Hunt, thanks for giving me access to Massey Dairy Farm No. 1 even beyond working hours and for all the information you have provided. To the Horizons Regional Council: Dr Jon Roygard and Mr. Paul Peters, thanks for giving me access to the monitoring wells at Te Matai Road and also for helping me out during my field work there.

Special mention goes to my friend Aldrin Rivas. Thanks for the ‘tutorials’ and assistance every time I conducted my fieldwork. I realise that everything would have been harder without your help and mentoring. I wish you success in your PhD, Aldrin; I know you will be able to make it in God’s perfect time. To my flatmates who journeyed with me: Jules, Alain, Melissa, Bryan, Afele, Edlynn, and Ray Anne, thank you for all the good memories, and I look forward to seeing you again in the future!

To the New Zealand Government through the NZAid ASEAN Scholarship Awards, thank you for the very rare opportunity to study and learn in your beautiful country. To the International Student Support Office at Massey University, Palmerston North, headed by Mrs. Sylvia Hooker, thank you very much for the love and support you gave me while I was studying at Massey and far away from my family.

To the Director and Management of the Bureau of Soils and Water Management, Philippines, thank you very much for allowing me to study in New Zealand and take time off from my work to gain more knowledge and training.

Finally, I would like to dedicate this achievement to my wife, Ritchelle, and three beautiful children, Faith, Czarina, and Shekinah. Thank you for the moral support and encouragement while I was doing this thesis. This is for you.

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Chapter 1. INTRODUCTION

Agriculture, one of the primary industries of New Zealand, contributes to 70% of export revenues and 12% of gross domestic product earnings (Ministry for Primary Industries (MPI), 2013). In 2007, the agriculture industry, including dairy, beef, and sheep farming, generated about \$16.1 billion in export earnings (Ministry for the Environment (MfE), 2007). These figures indicate the importance of agriculture industry to New Zealand leading the country as the world's largest dairy and sheep meat exporter (MPI, 2013). Although the production numbers of sheep and beef have continued to decline from 2007, the dairy industry has increased production by 18.75% from 2007 to 2012 (Statistics New Zealand, 2013). The New Zealand government aims to continue being the top exporter of dairy products by maximising export opportunities, improving sector productivity and increasing sustainable resource use (MPI, 2014b). One of the strategies to achieve this is to provide funding programmes in areas like sustainable farming, irrigation acceleration, and Primary Growth Partnerships (PGPs). These funding programmes will invest in farmer-, grower-, and forester-led projects, maximise potential for irrigated agriculture, and boost productivity and profitability through research and development (MPI, 2014a). The dairy industry aims to increase production by expanding brands, meeting supply demands to existing customer countries, and providing equal opportunities to emerging markets (Fonterra, 2014). While the benefits of farming are evident in terms of food production and economy, there is an increasing concern regarding its effects on land, freshwater quality and ecosystem health. In particular, dairy farming poses risks of effluent and nutrient runoff to water bodies (Betteridge, Costall, Lou, Ganesh, & Sun, 2013). This is one of the industries in agriculture that causes pressure on New Zealand's land-use and state of water quality, which can result in potential contamination or pollution of the environment.

Land-use conversion and intensification are seen as options to increase primary production. Land-use intensification involves increasing farm inputs to increase farm product outputs (Houlbrooke, Paton, Littlejohn, & Morton, 2011). Increases in fertiliser application, animal effluent, and land-use conversions have been evident in the past 20

years (MfE, 2013a). All these practices have helped to increase dairy production (MfE, 2007). However, these can also bring pollution to the aquatic environment through losses of nutrients, such as nitrogen and phosphorus (McDowell, Van der Weerden, & Campbell, 2011), and faecal bacteria contamination of the ground and surface water through leaching and runoff of farm effluents (Wilcock et al., 2011). As an example, in 2012, a total of 458 beaches (210 freshwater and 248 coastal) in New Zealand were graded to indicate suitability for recreational purposes. Of these 458 sites, 21% and 3% for freshwater and coastal recreational sites, respectively, have been graded as ‘very poor’ based on the levels of *Escherichia coli* (*E. coli*) in fresh water and *enterococci* in coastal waters (MfE, 2013c). For groundwater monitoring sites, out of 914 sites monitored for the period 1995 to 2008, 5% have nitrate (NO₃) levels exceeding health-related maximum acceptable value (MAV) of 50 mg/L as nitrate (NO₃) or 11.3 mg/L as nitrate-nitrogen (NO₃-N) (Ministry of Health, 2008). Regional trends in nitrate levels also indicate that almost 20% of 914 groundwater monitoring sites have significant increases (MfE, 2013b). Excess nutrient loadings to the aquatic environment can be harmful to humans and animals. Abundance of nutrients in surface waters can trigger periphyton growth and algal blooms, affecting levels of dissolved oxygen. Along with these are the decline in drinking water quality and eutrophication of water bodies affecting aquatic life.

The harmful effects of excess nutrients on water quality highlight the need to identify and understand the dynamics of their transport pathways and transformation in order to minimise their impacts on the receiving environments and improve current farm management practices. In particular, nitrate-nitrogen has become a subject of interest for many nutrient transport studies from farms to water bodies. Many studies have focused more on the root zone processes such as nitrogen input (Parfitt et al., 2012), plant uptake (Moir, Edwards, & Berry, 2013) and surplus to runoff and leaching (Christensen, Hedley, Hanly, & Horne, 2012; Shepherd & Phillips, 2010). The amount of leached nitrate-nitrogen below the root zone, however, may not be the same amount that will reach the groundwater and/or surface water. It can be attenuated or reduced because of biogeochemical processes such as denitrification in the subsurface environment (below the root zone), riparian zones, and seepage wetlands (Schipper, Barkle, & Vojvodic-Vukovic, 2005; Thomas et al., 2012). These are just some of the

factors that may affect the attenuation of nitrogen from the root zone to ground or surface water. Studies on the nitrogen transport and transformation processes happening below the root zone, however, are limited and less well understood, particularly in the New Zealand environment (Barkle, Clough, & Stenger, 2007; Rivas et al., 2014). Preliminary studies suggest a significant reduction in nitrogen on its way from farms to the river in the Manawatu River catchment (Clothier et al., 2007), but there is a lack of study in the Manawatu River catchment area on the transport and transformation of nitrogen in the subsurface environment of the catchment. Most studies conducted in the Manawatu River catchment area are limited to surface soils (Jha, Sagggar, Tillman, & Giltrap, 2011; Luo, Tillman, White, & Ball, 1998). Although it is difficult to characterise and measure the transport and transformation of nitrogen in the subsurface environment, this study attempts to assess transport and transformation processes of nitrogen below the root zone in the unsaturated and saturated (shallow groundwater) zones using field measurements and redox conditions in the shallow groundwater at two sites in the Manawatu River catchment.

1.1 Objectives

The main aim of this study is to assess the transport and transformations of nitrogen as it enters and leaves the root zone, and travels down the unsaturated and saturated zones at selected sites in the Manawatu River catchment. The specific objectives are to:

- a. Characterise transport and transformation of nitrogen in unsaturated and saturated zones using field measurements and a tracer test; and
- b. Assess the variability of redox conditions in the shallow groundwater through monitoring of relevant groundwater quality parameters such as temperature, dissolved oxygen (DO), pH, oxidation reduction potential (ORP), and other hydrochemical measures.

Two sites were selected for the study: 'Site 1' is located at the Massey Dairy Farm No. 1 (Palmerston North) and 'Site 2' is located at Te Matai Road (Palmerston North) where a groundwater monitoring site is observed and managed by the Horizons Regional Council (HRC). At Site 1, a small field plot was isolated and installed with ceramic porous cups and piezometers to measure nitrogen leaching, shallow groundwater

quality, and conduct a tracer test to assess transport and transformation of nitrate-nitrogen in the unsaturated and saturated zones. At Site 2, only redox conditions in the shallow and deep saturated zone were studied by observing the existing piezometers managed by the HRC.

1.2 Thesis Outline

This thesis is comprised of five chapters. Chapter 1 gives a general background and sets out the aim and objectives of the study. Chapter 2 is the review of relevant literature which explains concepts and processes of transport and transformation of nitrogen in the subsurface environment, including shallow groundwater. It enumerates the sources of nitrogen and explains in detail the processes happening within the nitrogen cycle in the soil-water system. It also discusses the transmission pathways of nitrogen from the soil to the aquatic environment, including the denitrification in the subsurface environment. In the latter section of the chapter, existing methodologies and techniques employed to determine transport and transformation of nitrogen in the subsurface environment are reviewed and presented. These include laboratory and field measurements, and use of analytical or numerical models. This study, however, did not test any model due to the lack of time to collect input data and validate the results.

Chapter 3 outlines the materials and methods used in the study. This chapter is divided into four sections. In the first section, the field experimental sites are described in terms of geographic location, climate, land-use, and their physical environment. The criteria for selection of the study sites is also presented. In the second section, the experimental design, data collection and sampling are described and includes the instrumentations and sampling procedures used. It is then followed by the section describing the laboratory analysis and field measurements, particularly methods to analyse soil, and soil-water and groundwater samples.

Chapter 4 presents the results and discussion of the study. It is organised into two main sections. The first section focuses on the transport and transformation of nitrate-nitrogen in the unsaturated and saturated zone, and the second section focuses on the assessment of redox conditions in the shallow groundwater.

Chapter 5 summarises the main findings and recommendations that could be drawn from the results and discussion of the study. It presents an overall conclusion by combining the obtained results and underscores key recommendations to help improve future studies on the same subject area.

Chapter 2. LITERATURE REVIEW

This chapter provides an overview of the concepts and processes explaining the transport and transformation of nitrogen in the subsurface environment, including shallow groundwater. It also touches on the sources of nitrogen and its cycle in the soil-water system. It covers discussion of the transmission pathways of nitrogen from the soil to the aquatic environment and the harmful effects to the receiving environment. In the latter section of the chapter, existing methodologies and techniques employed to determine transport and transformation of nitrogen in the subsurface environment are reviewed and presented including field measurements, laboratory analysis, and use of analytical or numerical models. Several New Zealand studies on the transport and transformation of nitrogen are also reviewed and discussed in the final section of this chapter.

2.1 Nitrogen cycle

Nitrogen (N), together with carbon (C) and oxygen (O), is one of the most complex and crucial elements essential for life (Keeney & Hatfield, 2008). The transfer and transformation of N between the atmosphere, biosphere, geosphere, and hydrosphere is described by the N cycle (Bothe, Ferguson, & Newton, 2007). In this cycle, nitrogen is transformed into different forms in different environments through different processes and undergoes the same cycle with the involvement or interference of human activities (Meng et al., 2011). The major processes in the N cycle are nitrogen fixation, mineralisation, ammonification, nitrification, immobilisation, assimilation, and denitrification.

2.1.1 Organic and inorganic sources of nitrogen

Nitrogen in the soil originates from indigenous organic and inorganic forms. Organic N is a natural composition of soil as a fraction of the soil organic matter. Approximately 98% of N in soil is in an organic form and only about 2% is inorganic (Fertiliser and Lime Research Centre (FLRC)), 2013). A typical New Zealand pastoral soil contains 5.4 up to 12 tonnes of N/ha in the top 15 cm of the soil (FLRC, 2009, 2013). It can come from crop residues, animal manure and urine, and products of non-biological or

biological N fixation. Inorganic sources of N in soils are usually derived from applied fertilisers with N content, ranging between 10 and 82% (Gardiner & Miller, 2008). Inorganic forms of N are also the by-products of the mineralisation of organic N forms. Inorganic forms of N include ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-), which are all readily available for plant uptake in the soil-water system.

2.1.2 Nitrogen transformation processes

In the nitrogen cycle, several processes happen in different environments, which transform N from one form to another. These processes mostly occur in the subsurface environment and are facilitated by soil microorganisms (e.g., bacteria, fungi) under favourable environment conditions. Figure 2-1 illustrates the N cycle, and the succeeding subsections explain the major processes involved in the N cycle.

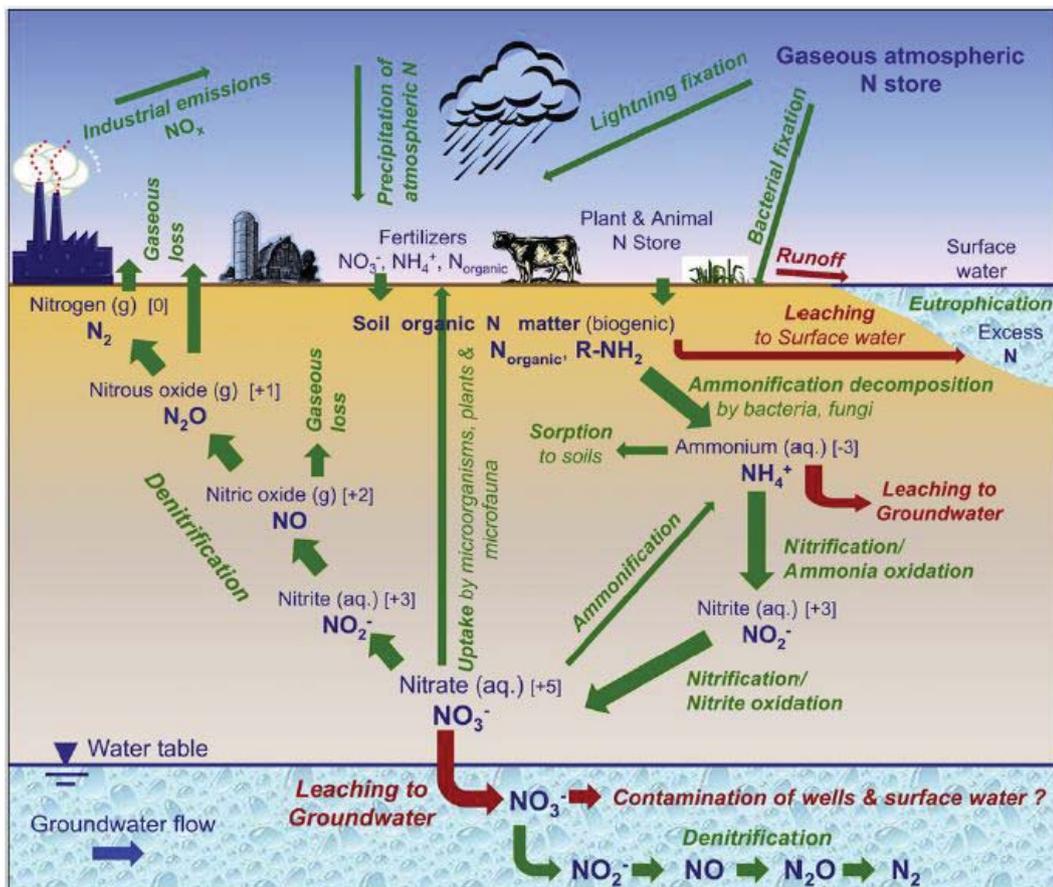


Figure 2-1. The nitrogen cycle (adapted from Rivett, Buss, Morgan, Smith, & Bemment (2008)).

2.1.2.1 Nitrogen fixation

In its elemental form, dinitrogen (N₂) gas, N is abundant accounting for 78% of the earth's atmosphere (Follett, 2008). Nitrogen in the atmosphere in the form of N₂ is converted into ammonia (NH₃) through the process of biological and non-biological N fixation. The non-biological N fixation process occurs during lightning storms and heat emission from fossil fuels which combine N₂ and O₂ to produce nitrogen oxides (e.g., nitrous, nitric). These nitrogen oxides are deposited from the atmosphere into the soil through dry and wet deposition. Estimates of atmospheric N depositions from non-industrial to industrial areas are less than 5 and 20 kg N/ha/yr, respectively (FLRC, 2009). Furthermore, the dry and wet deposition estimates for ammonia are 5.2 and 2.8 kg N/ha/yr, respectively, for ambient air with annual average pollutant concentrations of 1 µg/m³ (Stevenson, Hally, & Noonan, 2000). Estimates of atmospheric N depositions in New Zealand could be more or less 5 kg N/ha/yr since New Zealand's land area is predominantly agricultural.

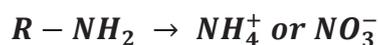
Biological N fixation, as compared to non-biological N fixation, is larger in terms of quantity and is the more dominant N fixation process. It involves symbiotic and non-symbiotic organisms which fix N₂ gas into bioavailable N forms (Follett, 2008). Examples of these organisms are Rhizobia, Azotobacter, Clostridium, and blue-green algae. In a symbiotic relationship, one organism containing chlorophyll converts it to carbohydrates using light energy and the other organism uses the carbohydrates as an energy source to enzymatically fix atmospheric N₂ to NH₃. In New Zealand, annual biological fixation rates of N from low to high fertility status lowland pastures are estimated to be between 10 and 200 kg N/ha/yr, respectively (FLRC, 2009).

2.1.2.2 Mineralisation

Mineralisation is a soil biogeochemical process involving the transformation of organic compounds into inorganic compounds (Coyne & Thompson, 2006). When completely mineralised, organic N compounds are decomposed into basic inorganic N compounds, such as NH₄⁺, NO₃⁻, and NO₂⁻ which are readily available for plant uptake in the root zone (Cameron, Zaman, & Di, 1999). There are several factors affecting the mineralisation rates of the soil. Among these are available pool of organic compounds, soil temperature (Moberg, Johnson, & Sullivan, 2013), soil moisture content (Gutiñas,

Leirós, Trasar-Cepeda, & Gil-Sotres, 2012), and microbial biomass (Hopkins, Waite, & O'Donnell, 2011). Depending on the combination of these factors, mineralisation rates vary from one location to another and cannot be generalised to be directly affected by a single factor (Zaman & Chang, 2004). Equation 2-1 describes the mineralisation process, with 'R' representing an amine functional group or other organic compound which is transformed into the inorganic N compounds.

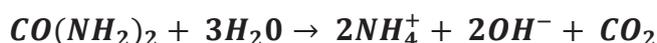
Equation 2-1



2.1.2.3 Ammonification

Ammonification is a chemical process of transforming amino groups (NH₂) associated with organic N to its inorganic forms, such as NH₃ or NH₄⁺ (Strock, 2008). This term is used interchangeably with mineralisation (Coyne & Thompson, 2006) because the chemical reactions start with organic compounds and partly end up with the same by-products. However, ammonification is a more particular process while mineralisation is a general one. It can be understood that ammonification is one of the sub-processes of mineralisation. In the case of urea fertilisers, the ammonification reaction is also known as 'urea hydrolysis' where NH₄⁺ ions are produced (FLRC, 2009). Equation 2-2 illustrates the ammonification reaction of urea.

Equation 2-2



2.1.2.4 Volatilisation

Volatilisation is a gaseous loss of N as NH₃ (Marshall & Debell, 1980), commonly happening when N fertilisers are applied. This process, together with denitrification, is a mechanism which brings N back into the atmosphere. Several conditions lead to an increased volatilisation rate. These conditions are soil pH above 7, rapid accumulation of NH₃ and NH₄⁺ following fertiliser application or soil amendments applied together with liming treatments, increased soil temperature, and soil moisture (FLRC 2009; Marshall & Debell, 1980; Tian, Cai, Cao, & Li, 2001). In dairy farms, sources of volatilised N, aside from applied fertilisers, are animal wastes, such as urine and faeces.

Volatilisation from these sources occur during slurry storage and application, and grazing with an estimate of 17-46 kg NH₃-N/cow/yr (Bussink & Oenema, 1998). Equation 2-3 depicts the chemical reaction of the volatilisation process.

Equation 2-3



2.1.2.5 Nitrification

Nitrification is the biological process of converting NH₄⁺ to NO₃⁻. The conversion of NH₄⁺ to NO₃⁻ is a result of a two-part oxidation reaction. The first part is the conversion of NH₄⁺ to NO₂⁻ where the NH₄⁺ ion is oxidised to NO₂⁻ and the second part is the oxidation of NO₂⁻ into NO₃⁻ (Subbarao et al., 2013). This process is biological because it is brought about by two specific nitrifying bacteria: *Nitrosomonas*, in charge of the first part, and *Nitrobacter*, in charge of the latter part (McLaren & Cameron, 1990). Like biological N fixation, mineralisation, and ammonification, nitrification also takes place in the upper-root zone of the soil profile. Nitrification rates vary as factors such as temperature, the initial amount of NH₄⁺, and biomass or population of bacteria affect the process. Equation 2-4 shows the chemical reaction of the nitrification process.

Equation 2-4



2.1.2.6 Plant uptake

Part of the N cycle is the plant uptake of bioavailable forms of nitrogen (NH₄⁺ and NO₃⁻), which takes place in the root zone. Normally, only 2-3% of the total soil N (inorganic plus organic N) is available in the soil-solution for plant uptake (FLRC, 2009). This fraction of N in the soil-solution is easily depleted by plant uptake and leaching. Once assimilated by plants, nitrogen is stored in its parts (roots, stems and leaves) and later used up, depending on the plant's growth stage (Gislum & Griffith, 2004). Other factors that affect the plant N uptake are seasonal climate variability and quantity of available N stored in the soil. Several studies have related the amount of N recovered by plants from applied fertilisers through herbage nitrogen yields. For example, pasture crops, such as ryegrass and clover, increase the herbage nitrogen yield with increasing application rate

of nitrogen fertilisers (Ball, Molloy, & Ross, 1978; Labuschagne, Hardy, & Agenbag, 2009). The indicative annual recovery rates of nitrogen through herbage range between 38% and 46% of applied nitrogen fertiliser for ryegrass-clover pasture (Ball et al., 1978). A portion of stored N in plants is restored back to the soil by the incorporation of crop residues which again undergo the mineralisation process.

2.1.2.7 Immobilisation

Immobilisation is a process in which inorganic N compounds in the soil, usually in the form of NO_3^- , become unavailable or limited for plant uptake because they are assimilated by the microbial population (McLaren & Cameron, 1990; White, 2006). This process is affected by the ratio of carbon to nitrogen (C:N ratio) of the soil and the organic matter added to it. Normally, the C:N ratio of the soil is lower than the organic matter incorporated to it. A typical New Zealand soil has a C:N ratio of 10-14:1 (FLRC, 2013). To be able to mineralise C in the organic matter, there has to be a decomposition activity of a wide range of soil microbes. When the N level in the soil exceeds the required quantity needed by the microbial population, then there is a surplus of N, a condition called *net mineralisation*. On the other hand, when the quantity of N required by soil microbes is higher than the amount available, a condition called *net immobilisation* occurs (McLaren & Cameron, 1990). Organic residues that have a C:N ratio less than 20:1 may result in net-mineralisation of N, while a C:N ratio exceeding 40:1 may temporarily net-immobilise N (FLRC, 2013).

2.1.2.8 Denitrification

After the conversion of NH_4^+ to NO_3^- through the process of nitrification, a reduction or anaerobic condition process transforms NO_3^- back into its simplest molecular gas form, N_2 . Along this transformation process are the by-products nitrogen dioxide (NO_2^-), nitric oxide (NO), and nitrous oxide (N_2O). This process is called denitrification. Denitrification is an important process in the N cycle because it is one of the mechanisms by which N_2 is returned to the atmosphere (Hutchinson, 1995). The denitrification process mostly occurs in the subsurface and aquatic environment. The denitrification process in soils is categorised into chemical and biological denitrification where the former happens in acidic soils (pH <5.0) also containing NO_2^- and the latter is influenced by microorganisms under partially to totally anaerobic conditions (Drury,

Myrold, Beauchamp, & Reynolds, 2008). Denitrification in the aquatic environment is affected by redox conditions and the thermodynamic sequence of electron-accepting processes (McMahon & Chapelle, 2008; Rivett et al., 2008). Shallow groundwater with low dissolved oxygen (DO) levels is favourable for denitrification. The threshold level of DO for denitrification to occur is reported to be at 2 mg/L (Rivett et al., 2008). However, the denitrification process can still occur even in oxic water at microbial hotspots (Jahangir et al., 2012) and anoxic microsites (Mengis et al., 1999).

The denitrification process has positive and negative effects in the environment depending on its by-product. On the positive side, denitrification is a mechanism that reduces the amount of NO_3^- that can potentially leach in the soil and reach the ground or surface water (Jahangir et al., 2012). On the negative side, it can also potentially increase the emission of N_2O , a greenhouse gas which contributes to climate change and global warming (Brown et al., 2012). Equation 2-5 illustrates the reduced forms of N in a denitrification process.

Equation 2-5



2.1.3 Human influences

Human activities, such as the application of fertilisers, animal production, and changing the existing land use, have affected the natural N cycle in the soil-water-atmosphere-plant environment. These are all triggered by the food demand of the increasing population and the desire to boost economic growth. Available soil-N supplies are often inadequate for optimum crop production, and the nutrients supply in the soil must be maintained at levels that will provide the best growing conditions for plants. For these reasons, the application of fertilisers has increased over the past years. The increase in total fertiliser application in New Zealand for the period 1986 to 2002 has been 113% (1.9 million tonnes to 4.3 million tonnes) (Statistics New Zealand, 2006). On top of this are also the increased deposition of animal excreta (i.e. urine and manure) and the application of dairy effluent on the soils. Although the land-use for agricultural purposes in New Zealand has decreased by 27% (21.3 million hectares to 15.6 million hectares) from 1986 to 2002, the land area allocated for dairy farming has increased by

47% (1.4 million hectares to 2.0 million hectares) during the same period (Statistics New Zealand, 2006). The increased applications of nutrients in the soil have also increased the quantity of N involved in the N cycle.

2.1.4 Environmental impacts

Because of the excessive application of fertilisers and farm dairy effluents, the risks of polluting the aquatic environment have also increased. In some places, farm N losses brought about by N leaching in the groundwater have increased the levels of nitrate-nitrogen above 11.3 mg/L MAV for drinking water (Ministry of Health, 2008). Surface waters being affected are increasing due to nutrient enrichment or eutrophication as a result of nutrient runoff and point source discharges of wastewater. Along with this is also the decline of aquatic biodiversity due to algal bloom and low levels of dissolved oxygen. Looking at the disadvantageous effect of the denitrification process, levels of nitrous oxide (N₂O), a greenhouse gas, have increased in the atmosphere, resulting in global warming and climate change. This is a unique case for New Zealand where the inventory of greenhouse gas emissions to the atmosphere is dominated by methane (CH₄) and N₂O coming from the agriculture sector, contributing to 87% (CH₄) and 96% (N₂O) of the total emissions in the atmosphere (Bhandral, 2005). These are the harmful impacts to the environment mainly as a consequence of anthropogenic influences in the N cycle.

2.2 Transmission pathways of nitrogen from soil to the aquatic environment

In the N cycle, not all N are cycled back to the atmosphere, stored in the soil, or even assimilated by plants. Nitrogen that is present in the soil zone is affected by the hydrologic cycle and the chemical and physical properties of soil which can lead to leaching and runoff of N from the soil profile (Follett, 2008). These losses can end up in the groundwater or surface water. The transport of N from the soil to the aquatic environment is primarily driven by the amount of water from rainfall or irrigation that infiltrates in or runs off the soil profile. Nitrate-nitrogen, in particular, is more prone to runoff and leaching because of its high mobility in the soil-water system. Infiltration, which is the process of water entry into the soil surface (Schwab, Fangmeier, Elliot, & Frevert, 1993), directly affects the N transport from the soil to the aquatic environment

(Andres & Sims, 2013). Upon infiltration, water movement is partitioned into lateral flow or seepage and vertical flow or deep percolation, which ends up in the surface or groundwater environment.

2.2.1 Runoff

Runoff happens when the rainfall intensity or irrigation application rate exceeds the infiltration rate of the soil. Other factors which affect runoff rate are soil cover, slope, soil organic matter, and initial soil moisture content. Dissolved N (ammoniacal-nitrogen) attached to soil particles finds its way to surface water because of runoff (MfE, 2014). This process not only results in nutrient loss, but also significantly pollutes natural waterways and streams (Alva et al., 2006). Aside from the N content of runoff water, the direct deposition of animal excreta, point domestic, and industrial wastewater discharges also contribute to the increased nutrient load in surface waters.

2.2.2 Leaching

Further water movement down the soil profile is termed as deep percolation. Deep percolation can be categorised into matrix or piston flow and bypass or preferential flow. Matrix or piston flow is a slow or even movement of water through the soil following a convective-dispersion theory (Cornell University, 2013) while bypass or preferential flow is the rapid movement of water along the macropore walls of the soil (Sigunga, Janssen, & Oenema, 2008). Leaching happens below the root zone when nitrogen is no longer extracted by plants for uptake. Since NO_3^- is a negatively charged ion, it is repelled by the cation exchange sites in the soil and moves freely in the soil-solution. Studies have linked the relationship between leaching and the percolation of water in the soil matrix. It was found that leaching caused by bypass flow can lead to movement of nitrate-nitrogen beyond the reach of the plants (Sigunga et al., 2008), it favours contaminant transport in the groundwater (Allaire, Roulier, & Cessna, 2009), and it contributes to non-point source pollution of the groundwater (Alva et al., 2006).

2.3 Transport and fate of nitrogen in subsurface environment

Before N reaches the groundwater system and/or surface water body, it may undergo transformation processes such as those mentioned in the previous subsections (Section 2.1.2). Various N transformation processes are present in the upper-root zone but as the

depth of the unsaturated zone increases, the transformation processes become limited to denitrification only. This is because NO_3^- is the only dominant N form that can be further subjected to denitrification in the deeper profile of the unsaturated zone. Finally, when NO_3^- reaches the groundwater or the saturated zone, it can still undergo a further denitrification process under reduction-oxidation (redox) conditions. In the groundwater, the degradation of a compound depends on the variety of available electron donors and acceptors. Reduction reaction happens when a compound gains an electron. In contrast, oxidation reaction happens when a compound loses electrons. Based on the electron configuration of N in its outer shell, it can be oxidised up to a maximum state of +5 and reduced up to a maximum state of -3 (Illinois State Water Survey, 2013). Redox conditions are facilitated by microorganisms whose energy is derived from transferring electrons from donors, usually organic C, to electron acceptors such as dissolved oxygen (DO), NO_3^- , manganese (Mn(IV)), iron (Fe(III)), sulfate (SO_4^{2-}), and carbon dioxide (CO_2) (Jurgens, McMahon, Chapelle, & Eberts, 2009; McMahon & Chapelle, 2008). This process is termed the thermodynamic sequence of electron-accepting process (McMahon & Chapelle, 2008; Rivett et al., 2008). Under anoxic groundwater conditions ($\text{DO} < 2 \text{ mg/L}$), NO_3^- is the next favourable electron acceptor, followed by the other previously mentioned. Because of this, nitrate is attenuated or reduced through denitrification in the subsurface environment.

2.4 Techniques to determine transport and transformation of nitrogen in the subsurface environment

This section reviews various techniques employed in assessing and characterising the transport and transformation of nitrogen in the unsaturated and saturated zones. The techniques reviewed and presented are categorised into laboratory or field measurements, and modelling methods. This study, however, did not test any model due to the lack of time to collect input data and validate the results.

2.4.1 Laboratory or field measurements

2.4.1.1 Mineralisation

The mineralisation rate determines the actual or potential amount of mineralisable N the soil can produce in a specific length of time given a particular soil moisture and

temperature conditions (Curtin & Campbell, 2008). This can be done using the incubation technique. Soil samples are collected from the field and incubated for a certain length of time in the laboratory. Recent studies suggest conducting on-site soil incubation to simulate the actual soil and temperature variations in the field (Duran, Morse, & Groffman, 2012). This is also practical whenever incubation rooms or equipment are not available. After incubation, inorganic N are extracted by leaching the samples with N-free solution (Curtin & Campbell, 2008) or by using 2 M potassium chloride (KCl) solution (Blakemore, Searle, & Daly, 1987). The mineralisation rate can be calculated by plotting the inorganic N concentrations of the incubated samples with the sample incubation period and obtaining its correlation equation. Mineralisation rates can either be in zero- or first-order kinetics.

2.4.1.2 Leaching

Many studies on quantifying N leaching from the soil profile or root zone use vadose zone samplers such as soil cores, lysimeters, porous cups, or a combination of these devices (Close, Bright, Stanton, & Flintoft, 2004; Patterson, Franzmann, Rayner, & Davis, 2000). These instruments are installed at different depths in the soil profile where soils or soil-solution samples are extracted for the laboratory analysis of inorganic N content. Among these instruments, the most expensive in terms of materials and installation costs is the lysimeter. The installation of lysimeters often involves the use of machines, such as trailers and cranes, to create large diameter holes for the casing of lysimeters (Close, Dann, Flintoft, Havelaar, & Peterson, 2012). Normally, the installation of lysimeters are limited to the upper 1 m of the soil profile (Close et al., 2004), but recent techniques have been developed to install lysimeters to over 1 m in depth. A study done by Close et al. (2012) used a novel method for sampling unconsolidated deep vadose zones where lysimeters were installed up to 8.3 m deep. Several cylindrical steel sections, 1.15 m-diameter by 1.5 m-high, were used and bolted together to provide temporary casing for the auger hole. As soon as these sections were installed, sensors and data loggers could be attached to measure real time data on soil temperature, soil moisture, and the concentration of various gases at the subsurface level. These sophisticated accessories make the lysimeter advantageous over the use of porous cups. In contrast with lysimeters, the use of porous cups combined with soil coring is cheaper because of the low cost of installation, maintenance, and ease of

operation. These could be some of the reasons that explain the preference of many researchers to use porous cups over the use of lysimeters as a method of investigating leaching without compromising the quality of data. Along with porous cups, soil moisture and other sensors can be installed separately. Another advantage of using porous cups is the minimal disturbance of the soil during installation. Porous cups have smaller diameters (< 2.80 cm) and are not labour intensive upon installation. Porous cups can also be installed at greater depths, unlike the lysimeter, which is usually confined in the upper 1 m of the soil profile. Installation of ceramic porous cups can be done vertically, horizontally, or inclined at an angle using a spike, auger, or air rotary drill (Close et al., 2004; Patterson et al., 2000). The depth and method of installation of porous cups dictate the installation cost and among the three methods mentioned, vertical installation using the spike method was found to be the cheapest (Close et al., 2004).

In the saturated zone, the use of piezometers (for shallow groundwater) or groundwater bores (for deep groundwater) are commonly employed. Piezometers and groundwater bores are used to collect water samples for the analysis of multiple hydrochemical parameters and groundwater level monitoring. These can be installed using several drilling methods, such as auger, mud rotary, air rotary, cable tool, and dual-wall reverse circulation (Smith, 1990). In this study, piezometers were installed using a post rammer (see Section 3.2.6). Depending on the depth of installation and soil geologic formation, each of these has its advantages over the other. Piezometers and groundwater bores are typically made of polyvinyl chloride (PVC) or steel. Similarly, depending on the purpose of accessing the groundwater, the selected pipe material has its advantages over the other.

2.4.1.3 Denitrification

Incubation methods are also used to quantify denitrification rates of the soil. Soil core samples are collected at different depths of the soil profile and treated with nitrogen-15 (^{15}N) prior to incubation. The method commonly used is the acetylene (C_2H_2) inhibition technique where C_2H_2 is used to block the conversion of N_2O to N_2 in the incubated samples (Drury et al., 2008; Klute & Page, 1986). After incubation, evolved gas

samples are extracted and analysed for N₂O using gas chromatography. The amount of produced N₂O corresponds to the denitrification rate of the soil.

In the groundwater, the denitrification rate experiment can also be done using a single well push-pull method (Jahangir et al., 2013) where water of considerable volume is extracted or 'pulled' from a well or piezometer and treated with dosing solution containing NO₃⁻ and a tracer such as Br. After the treatment, water is pumped back or 'pushed' into the well. Water is extracted again at discrete time intervals from the well and analysed for NO₃⁻ and Br concentrations, and evolved N₂O or N₂ gas. The reduction rate of NO₃⁻ concentration (excluding dilution) or production rate of NO₂ or N₂ gases corresponds to the denitrification rate in the aquifer or groundwater.

2.4.1.4 Travel time

One way of characterising the transport of anions from the soil surface down to the groundwater is by determining its travel time. This can be done through tracer tests. Depending on the physical characteristics of the soil, travel time may vary from days up to months or years. Commonly used elements in the tracer technique are bromide (Br), chlorine (Cl), and ¹⁵N (Close, 2010; Richards, Coxon, & Ryan, 2005). Bromide has been used as a tracer to study solute and water transport because it is not easily adsorbed in the soil particles and its background concentrations in the aquatic environment is very low (Richards et al., 2005). The amount of water that enters the soil primarily affects the solute transport because it is the driving force of the transport process. Other factors include soil texture and the presence of preferential flow paths (Flury, Fluhler, Jury, & Leuenberger, 1994). The travel time of Br in the unsaturated and saturated zone can be estimated by creating a breakthrough curve of the occurrences of peak Br concentrations from the start of the Br application. The soil depth divided by the time corresponding to the occurrence of the peak concentration at that depth is the travel time of Br (depth/time). In the experiment of Richards et al., (2005), the background Br concentration of 0.02 mg/L in the ceramic porous cups at 0.5 m depth increased to 0.22 mg/L after eight days from the application date on January 16, 1996. The corresponding travel time, therefore was estimated at 0.5 m divided by 8 days, resulting in 0.0625 m/d. The maximum observed concentration at the monitoring depth of 1.5 m occurred 65 days after the application. In the groundwater (22.96 m bgl), the maximum Br

concentration of 15 mg/L was observed after 77 days from the application date giving a travel time of 0.29 m/d.

2.4.2 Modelling

A number of models have been developed to simulate transport and the transformation of N in the subsurface environment. These models can be categorised as being analytical-, numerical-, empirical-, and process-based. Analytical models use parameters which are solved by straight-forward equations. These equations are the analytical solutions to the problem. So for a given analytical equation, a solution can be derived once the required parameters are supplied. Numerical models however, are more complex equations interlinked to one another. They use iterations to arrive at the best estimate solution. These equations cannot be easily solved. More often, numerical models use computer programmes to perform complex calculations. Empirical models are based on the results of experiments rather than ideas or theories. These models use computer programming languages. Process-based models differ from empirical models such that the former are based on a theoretical understanding of a certain process and explicitly state assumptions for easier interpretation (Cuddington et al., 2013).

Depending on the focus of a study, different models have been used to study the transport and transformation of N in the subsurface environment. Some models only estimate the N cycling processes in the unsaturated zone and do not include the saturated zone. This discrepancy is a disadvantage over other models, especially for models which estimate the whole N cycling process from soil surface to the groundwater. Examples of these models are reviewed and discussed below, stating their advantages/disadvantages and applicability to simulate transport and transformation of N in unsaturated and saturated zones.

2.4.2.1 Analytical models

NEMIS is a field scale analytical model to predict the actual denitrification rate in the unsaturated zone. It was formulated by Hénault and Germon (2000), based on experiments and data on potential denitrification rates from undisturbed soil core samples, soil moisture content, soil temperature, NO_3^- content, and respiration rate. The model is described in Equation 2-6.

Equation 2-6

$$D_A = D_P F_N F_W F_T$$

Where:

D_A – actual denitrification rate (kg N/ha/day)

D_P – potential denitrification rate (kg N/ha/day)

F_N – soil nitrate content (dimensionless)

F_W – soil water-filled pore space (dimensionless)

F_T – soil temperature (dimensionless)

This model determines the actual denitrification rates of soil from the results of potential denitrification rate measurements as influenced by varying levels of NO_3^- content, soil water content and soil temperature. In the laboratory experiment conducted, soil core samples were treated and incubated with C_2H_2 (Drury et al., 2008). After incubation, gas samples were extracted to measure the amount of N_2O produced. The amount of N_2O gas produced is the result of the denitrification process. The incubation temperature used was 20°C and the amount of deionised water applied was 500 mL, resulting in 59-80 % water-filled pore space. Increasing concentrations of NO_3^- as potassium nitrate (KNO_3) were used from 0-0.008-0.015-0.03-0.06-0.1 M solution. The dimensionless soil nitrate, water, and temperature factors in the NEMIS model were parameterised based on the laboratory experiments done. This means that the numerical values for the dimensionless factors will change depending on the variations to be made in the experiment. The results of these treatments gave the equation to estimate the actual denitrification rate. According to Hénault and Germon (2000), the main limitation of this model is its high sensitivity to the water-filled pore space (WFPS) which affects the potential denitrification rate.

Another example of an analytical model is the RISK-N. The RISK-N model is a physically-based, analytical nitrate transport model developed to simulate N cycling in the soil profile, and transport and transformation of NO_3^- in the unsaturated and saturated zone. This model was developed by Gusman and Mariño (1999) from the University of California, Davis. One of the advantages of this model over other available N cycling models is the fewer required input parameters to simulate the complete system including both the unsaturated and saturated zones. Another advantage

of the RISK-N model is its capability to predict long term NO_3^- levels in groundwater up to 100 years. This gives a picture of NO_3^- concentration levels in the groundwater over a long period of time if rainfall conditions and fertiliser application rates, among others, remain constant. In contrast, RISK-N can also be run over a short time period to consider change in weather patterns, land-use, and fertiliser application rates. RISK-N input parameters can also be easily adjusted to local settings, making it versatile in terms of adaptability. In terms of computer hardware and operating system requirements, RISK-N can still run on the latest computer software and hardware available. The executable file of the RISK-N model is a Microsoft Quick-Win application written in FORTRAN 77 and 90. Although the model was developed in the late 1990s and there have been wide advances in computer architecture and programming technology today, the RISK-N model is not obsolete and can still run on the latest platforms. The processes simulated by RISK-N include mineralisation, nitrification, denitrification, plant uptake, and leaching. The RISK-N model simulates the processes by subdividing the unsaturated zone into three subzones, namely the upper-root zone, lower-root zone, and intermediate-vadose zone. These soil zones make up the model schematic for agricultural setting Figure 2-2. Another subzone, the sub-drain field zone, can also be added in the unsaturated zone. The sub-drain field zone is optional and only used to account for N additions from septic system drain fields. The processes simulated in the upper-root zone are mineralisation, nitrification, denitrification, and plant uptake. Only two processes are simulated in the lower-root zone: the denitrification and plant uptake processes. For the intermediate-vadose zone and saturated zone, only the denitrification process is simulated.

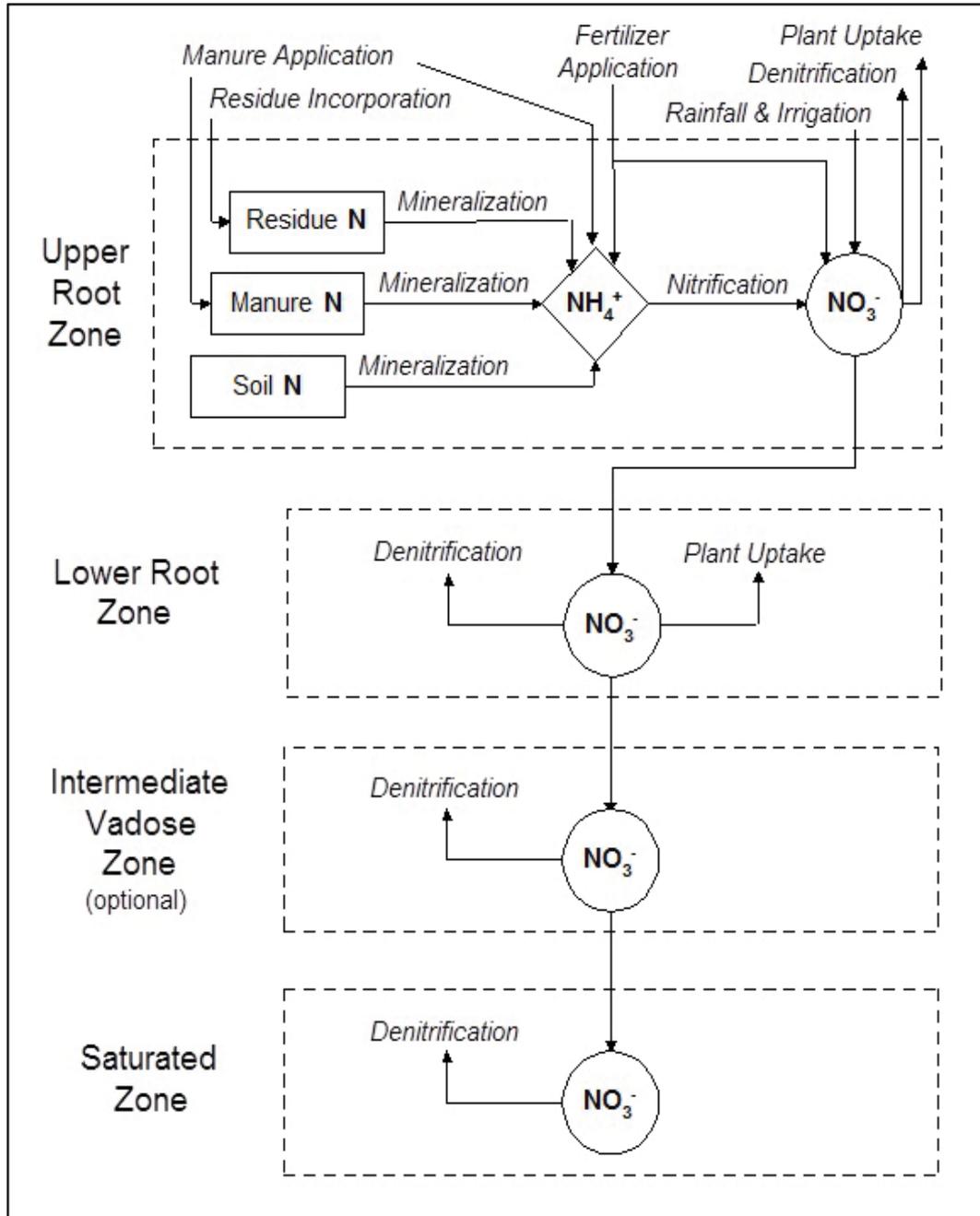


Figure 2-2. RISK-N model schematic for agricultural area (adapted from Gusman and Mariño (1999)).

2.4.2.2 Numerical models

DRAINMOD-N is one of the modified versions of the original DRAINMOD hydrology model. DRAINMOD-N is a field scale model which includes predicting the transport and transformation of N from agricultural lands particularly in artificially drained soils (Brevé, Skaggs, Parsons, & Gilliam, 1998). Nitrate is the main N pool considered in this model as it is easily leached down the soil profile. Other processes accounted in this model are atmospheric N deposition from rainfall, mineralisation of organic and inorganic forms of nitrogen, denitrification, plant uptake, surface runoff, and subsurface drainage losses. This model is advantageous in soils with artificial drainage systems and shallow groundwater tables.

2.4.2.3 Empirical models

OVERSEER is a nutrient budget model that is developed to provide estimates of nutrients N, P, K, and S in a farm system (FRLC, 2009). It is an empirically-based nutrient budget tool rather than a detailed process-based model (Wheeler, Cichota, Snow, & Shepherd, 2011). It also calculates the nutrient flows in a farming system and helps identify potential environmental risks caused by the nutrient loss in leaching, runoff and greenhouse gas emissions (OVERSEER, 2013a). The model was conceptualised and developed in the early 1990s and was started by the Computerised Fertiliser Advisory Service (CFAS). Prior to CFAS, fertiliser recommendations were based on the ‘rules of thumb’, published experimental results, and local knowledge (OVERSEER, 2013b). The model evolved over time, starting from nutrient budgets linked to fertiliser advice to its current version, which is a decision support tool that uses nutrient budget information. One of the limitations identified in this model is that all the processes simulated are confined to the unsaturated zone. The OVERSEER model does not take into account processes, such as denitrification, happening in the saturated zone.

2.4.2.4 Process-based models

DNDC stands for DeNitrification DeComposition. This is a process-based model developed in the United States of America (USA) to estimate emissions of greenhouse gases from agricultural soils (Li, Frohling, & Frohling, 1992). It models processes such as soil C dynamics, crop growth, soil temperature and moisture regimes, N leaching,

and emissions of trace gases like N₂O, NO, N₂, NH₃, methane (CH₄), and CO₂ (University of New Hampshire, 2014). The DNDC model can also be run at regional to national scales and has been used in many studies in several countries like China, Germany, Canada, the United Kingdom (UK), and India (Giltrap, Ausseil, Thakur, & Sutherland, 2013; Landcare Research, 2013). NZ-DNDC is a modified version of the DNDC model which caters specifically for New Zealand grazed pastoral systems (Saggar et al., 2004). There are particular limitations to the original version of the DNDC which have been addressed to be able to apply the model to New Zealand pastoral soils and climatic conditions (Landcare Research, 2013). The modifications include the following:

- i. Pasture growth – multiplicative day length factor to account for seasonal variations in pasture growth and N uptake rates;
- ii. Soil infiltration and drainage – drainage followed infiltration to achieve much better correspondence with measured soil moisture;
- iii. Air-soil temperature relationship – surface temperature is greater than the air temperature by 1.3; and
- iv. WFPS denitrification threshold – the trigger point used for the production of N₂O was the field capacity instead of the original threshold of 35% WFPS.

The modified NZ-DNDC model was tested in a study to determine seasonality of N₂O fluxes in both grazed and ungrazed pasture (Saggar et al., 2004). The results of model simulation were compared to the actual measurements of N₂O fluxes. On the daily average of N₂O fluxes, the NZ-DNDC model performed well but overestimated spring emissions and underestimated summer emissions. This over and underestimation were brought about by the changes in soil temperature and moisture. Annual emissions of N₂O from dairy and sheep farms were also modelled by NZ-DNDC and compared to actual measurements of emissions and the IPCC methodology, the current methodology used by New Zealand to estimate N₂O emissions. The simulated results of the NZ-DNDC model were close to the measured emissions, while the IPCC method was far off. This led to further studies to fine tune the model and develop emission factors accounting for variability of soil temperature, soil moisture, and the effect of fertiliser application rates (Giltrap et al., 2013). Two of the limitations of this model is the lack of

capability to simulate N transformation and transport processes in the saturated zone, such as denitrification, and the advective-dispersive effect in the groundwater.

2.5 New Zealand studies on transport and transformation of nitrogen in the subsurface environment

Several studies on the transport and transformation of N in the subsurface environment have been conducted in New Zealand addressing N cycling processes, such as leaching, mineralisation, denitrification, and travel time using field experiments and simulation modelling methods. Most of these studies were conducted in a pastoral land-use area since 37% of New Zealand's total land area is pastoral (MfE, 2007). The results and findings of the main and relevant studies are reviewed and discussed below.

2.5.1 Mineralisation and nitrification

The study of Zaman, Di, and Cameron (1999) involved the relationships of gross mineralisation and nitrification rates to microbial biomass and enzyme activities in soils treated with dairy effluent and ammonium fertiliser. The study was conducted in Lincoln, Canterbury in 1996 on a 12 – 1 m² plot. Results showed that the gross mineralisation rate in soils treated with dairy effluent were significantly higher compared to soils treated with ammonium (NH₄Cl) fertiliser. The mineralisation rate in the soils treated with dairy effluent and ammonium (NH₄Cl) fertiliser were 4.3 – 6.1 µg N/g soil/day and 2.6 – 3.4 µg N/g soil/day, respectively. This can be explained by the presence of readily mineralisable organic substrates in the dairy effluent enhanced by microbial and enzyme activities. In contrast, nitrification rates were higher in soils treated with ammonium (NH₄Cl) fertiliser than in soils treated with dairy effluent. Nitrification rates were 1.7 – 1.2 µg N/g soil/day and 0.97 – 1.5 µg N/g soil/day for soils treated with ammonium (NH₄Cl) fertiliser and dairy effluent, respectively. This can be explained by the presence of ammonium available for nitrification. In this experiment, significant mineralisation and nitrification activities were observed in the first 16 days, after which rates were not significantly variable.

2.5.2 Nitrate leaching

Close et al. (2004) studied N leaching at a site near Te Pirita in Central Canterbury in 1998. In this study, several installation methods of ceramic porous cups were evaluated.

Twenty two ceramic porous cups were installed at depths of 1.3, 2.5, and 5.0 m. Results of the study suggested that installation cost is proportional to the desired installation depth. This means that the deeper the ceramic porous cups are installed, the higher the installation cost will be. The authors also found that the variability of solute concentrations became less as the sampling depth increased (% coefficient of variation of measured NO_3^- concentration decreased from 177% at the shallow depth (1.3 m) to 83% at the deeper depth (2.5 m)). This suggests that fewer numbers of ceramic porous cups can be used when investigating solute concentrations at greater depths. The average nitrate-nitrogen leaching loss estimated from all the ceramic porous cups ranged between 38 and 58 kg N/ha/yr.

In another leaching study by Hoogendoorn et al. (2011) in the Lake Taupo catchment area, ceramic porous cups were used and installed at 600 mm depth to examine the variability of leaching from three different species of grazers. The study was conducted from May, 2004, to January, 2007. Forty samplers were installed per 0.4 – 0.5 ha paddock. Average estimates of leached nitrate-nitrogen from intensively grazed pastures were 37, 26, and 25kg N/ha/yr for cattle-, sheep- and deer-grazed areas, respectively. Leaching of NH_4^+ was estimated at 3 kg N/ha/yr, for all three species of grazers. These estimates were not significantly different as reported.

The OVERSEER model is used in New Zealand studies as a nutrient management tool to investigate the leaching of nutrients and greenhouse gas emissions, assess farm productivity outputs, and to create nutrient budgets from one to several farm management blocks. An example of a study which used the OVERSEER model is from Horne, Dijkstra, Palmer, and Carey (2012). The study investigated nitrate leaching and the nutrient supply advantage of organic farms over conventional farms. This study suggested that nitrate leaching in organic farms is 56-60% less than the quantity lost in conventional farms, but the benefits are outweighed when yield is taken into account. OVERSEER has also been used to study the link between N conversion efficiency and N leaching (Wheeler, Power, & Shepherd, 2011). Ideally, N leaching should decrease as N conversion efficiency increases, but this study using OVERSEER indicated that there was no relationship between the N leaching and N conversion efficiency. Aspects to

look at are where the bias in this kind of study came from and what additional analyses should be undertaken.

2.5.3 Denitrification and Br tracer

Denitrification attenuates NO_3^- contamination of the groundwater. On the other side of the denitrification process, it also emits greenhouse gases as a by-product. Denitrification studies are often coupled with tracer experiments to characterise the behaviour of NO_3^- as it travels down the soil profile. Tracer experiment results are correlated to concentrations of leached Br and leached NO_3^- to the production of N_2O . This is what has been done in the study by Thomas et al. (2012). The study was conducted in Lincoln, Canterbury, from November, 2004, to November, 2007. The travel time of NO_3^- along the 7 m soil profile was investigated using Br as a tracer. After two applications of 200 kg Br/ha and 400 kg N/ha, the concentrations of leached NO_3^- and Br were monitored at different depths using ceramic porous cups. Sixty days after the first application, concentrations of NO_3^- in the ceramic porous cups at 0.6 m depth increased to a maximum of 106 mg/L, while at the 1, 3, 5, and 7 m depths, NO_3^- concentrations increased to a maximum of 81, 93, 90, and 69 mg/L, respectively, 74 days after the first application. The overall NO_3^- to Br ratio was 1.8 for the first application. Following this ratio, Br concentrations in all the sampling depths (0.6 to 7 m) were 58, 44, 51, 49, and 38 mg/L. The travel time of Br for all depths was 0.01, 0.01, 0.04, 0.07, and 0.09 m/d. For the second application, a lower ratio was achieved (1.4) because of the low drainage volume.

Evolved gas in the soil profile was measured using a gas sampler installed at 0.2, 1, 2, 3, 5, and 7 m depths. The N_2O concentration at the 0.2 m depth remained at 0.8 mg $\text{N}_2\text{O}/\text{m}^3$, which is close to ambient air N_2O concentrations. For the succeeding depths, N_2O concentrations increased as the concentrations of NO_3^- increased. The same pattern of increasing N_2O concentrations with increasing NO_3^- concentrations was observed in the second fertiliser application. The study concluded that there was a strong relationship between N_2O gas concentrations to NO_3^- concentrations at each depth. The decline of NO_3^- to Br ratio within the top 1 m over time and the lower ratios below 1 m indicate attenuation of NO_3^- because of denitrification and hence the source of N_2O in the lower depths.

Denitrification in the shallow groundwater of two contrasting agricultural catchments in the Waikato Region, New Zealand, was also investigated using isotopic analysis of NO_3 in terms of the degree of variation of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ enriched groundwater (Clague, 2013). Using push-pull tests *in situ*, denitrification in the shallow groundwater was not clearly exhibited, even with the addition of a carbon substrate. However, laboratory incubations of aquifer material taken from the vicinity of the well screens demonstrated denitrification potential. With the addition of a carbon substrate (glucose), the total N gas increased. This indicated that denitrification in the groundwater may be limited by carbon availability. Although the denitrification rates were very low in the groundwater, they could still have a significant effect on the attenuation of nitrate in the groundwater provided the reaction time is long enough. This study is one of the few New Zealand studies that focused on the transport and transformation of nitrogen in the subsurface environment. In particular, little information is available on the transport and transformation of nitrogen in the subsurface environment in the Manawatu River catchment area.

Chapter 3. MATERIALS AND METHODS

This chapter describes the materials and methods used in this study to achieve the objectives enumerated in the first chapter. The research undertaken in this study involved a combination of field experiments and laboratory analyses. The field and laboratory instruments and methods were employed based on their practicality given the limited resources and time available for the study.

3.1 Field experimental sites and instrumentation

A total of two field sites were chosen for this study. These sites were selected according to the following criteria:

- a. Sites are located within the Manawatu River catchment;
- b. Current land-use is pastoral dairy farming, which is assessed as a major contributor to nitrogen loadings in the catchment;
- c. Sites were already installed or there was the possibility of installing piezometers to sample shallow groundwater quality; and
- d. None or few similar studies have been conducted at these sites.

The floodplains of the Manawatu River catchment are one of the most fertile areas in the south-western North Island of New Zealand and cover an area of around 1000 km² (Figure 3-1). The flatter areas of the catchment have intensive cropping and dairy farming while the hill country areas are dominated by sheep and beef farming. Following the above mentioned criteria, a total of two experimental sites were established in two separate locations in the floodplains of the Manawatu River catchment, with both sites located near Palmerston North, Manawatu (Figure 3-1).

The first site, Site 1, was located at the Massey Dairy Farm No. 1, situated on the true left side of the Manawatu River (Figure 3-2). The second site, Site 2, was located on a private farm along Te Matai Road, Whakarongo, situated on the true right side of the Manawatu River (Figure 3-2). Each respective site has been operating as a dairy farm since 1929 (Site 1) and 1996 (Site 2).

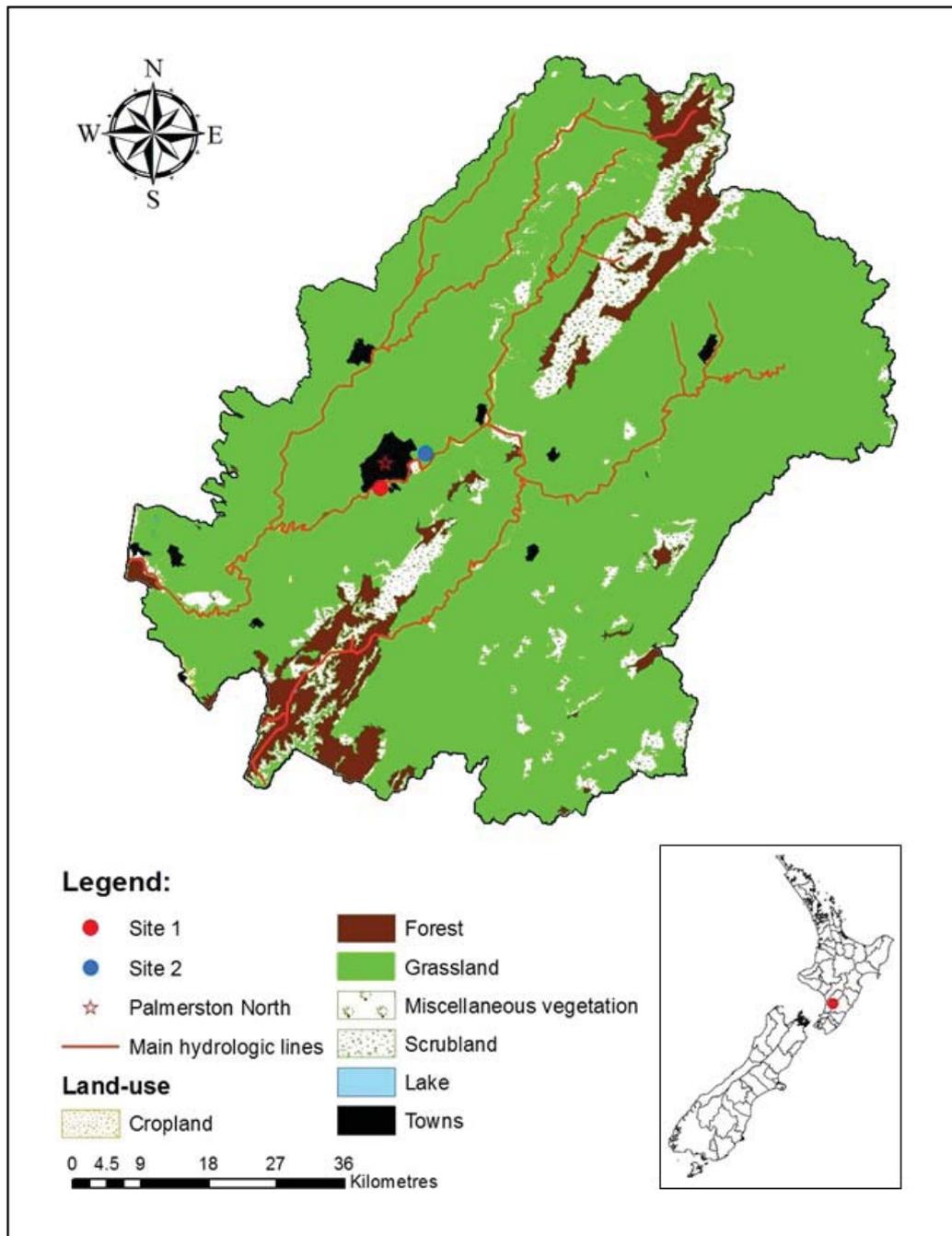


Figure 3-1. Location of the study sites in the Manawatu River catchment.

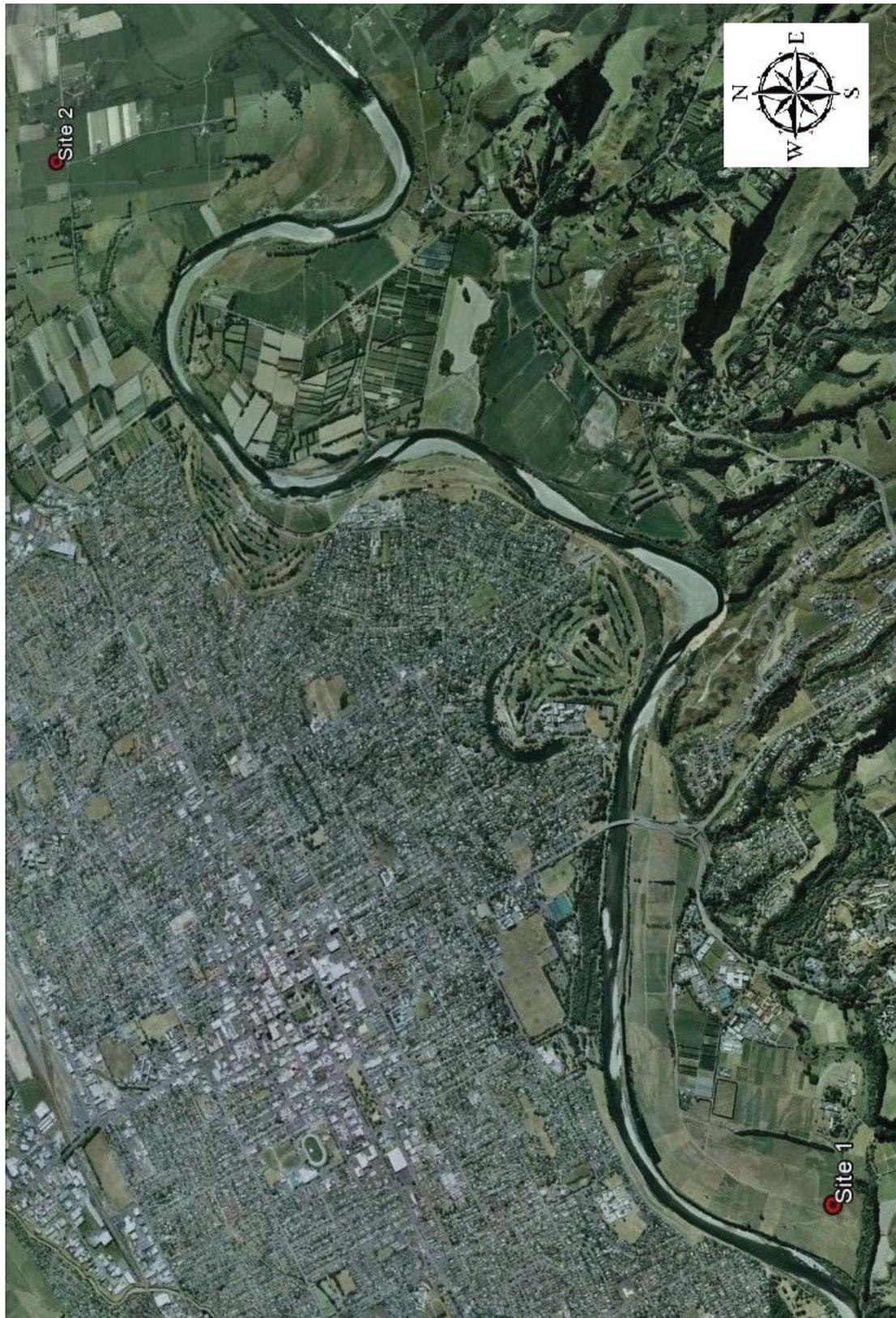


Figure 3-2. Location of the study sites in the Manawatu River catchment.

The plains of the Manawatu catchment where both experimental sites were located receive an annual average rainfall of 960 mm and do not experience severe droughts, unlike the eastern parts of the lower North Island (Zarour, 2008). The seasonal variation of temperature and rainfall in Palmerston North is presented in Table 3-1.

Table 3-1:

Historical variation of temperature and rainfall in Palmerston North, New Zealand.

Seasons	Months	Lowest	Highest	Rainfall, mm
		Ave. Temp., °C		
Winter	Jun-Aug	-2.0	17.0	252
Spring	Sep-Nov	0.7	21.7	227
Summer	Dec-Feb	5.3	27.7	225
Autumn	Mar-May	2.0	24.0	172

Source: Metservice (2014).

3.1.1 Massey Dairy Farm No. 1 (Site 1)

Massey Dairy Farm No.1 is composed of 65 paddocks. It covers 142.7 ha, 119.7 ha of which is effectively farmed for dairy production (Massey University, 2015). The root zone (upper 60 cm of the soil) is associated with a loamy silt and fine sand (Figure 3-3 and Figure 3-4) while at 60 cm to 200 cm the unsaturated zone is a combination of fine sand and gravel which was observed during the installation of porous cups. The majority of the soils on the farm are free-draining recent alluvial soils and classified as Manawatu silt to sandy loam and Rangitikei silt loam to sandy loam (Figure 3-5). In the February 2004 floods, 90% of the farm was inundated, depositing significant amount of silt after recession of the flood (NZCPA, 2005, as cited in Killick, 2013). Figure 3-5 presents a map of Massey Dairy Farm No. 1 showing the distribution of paddocks, soil map, and location of the first research site, Site 1.

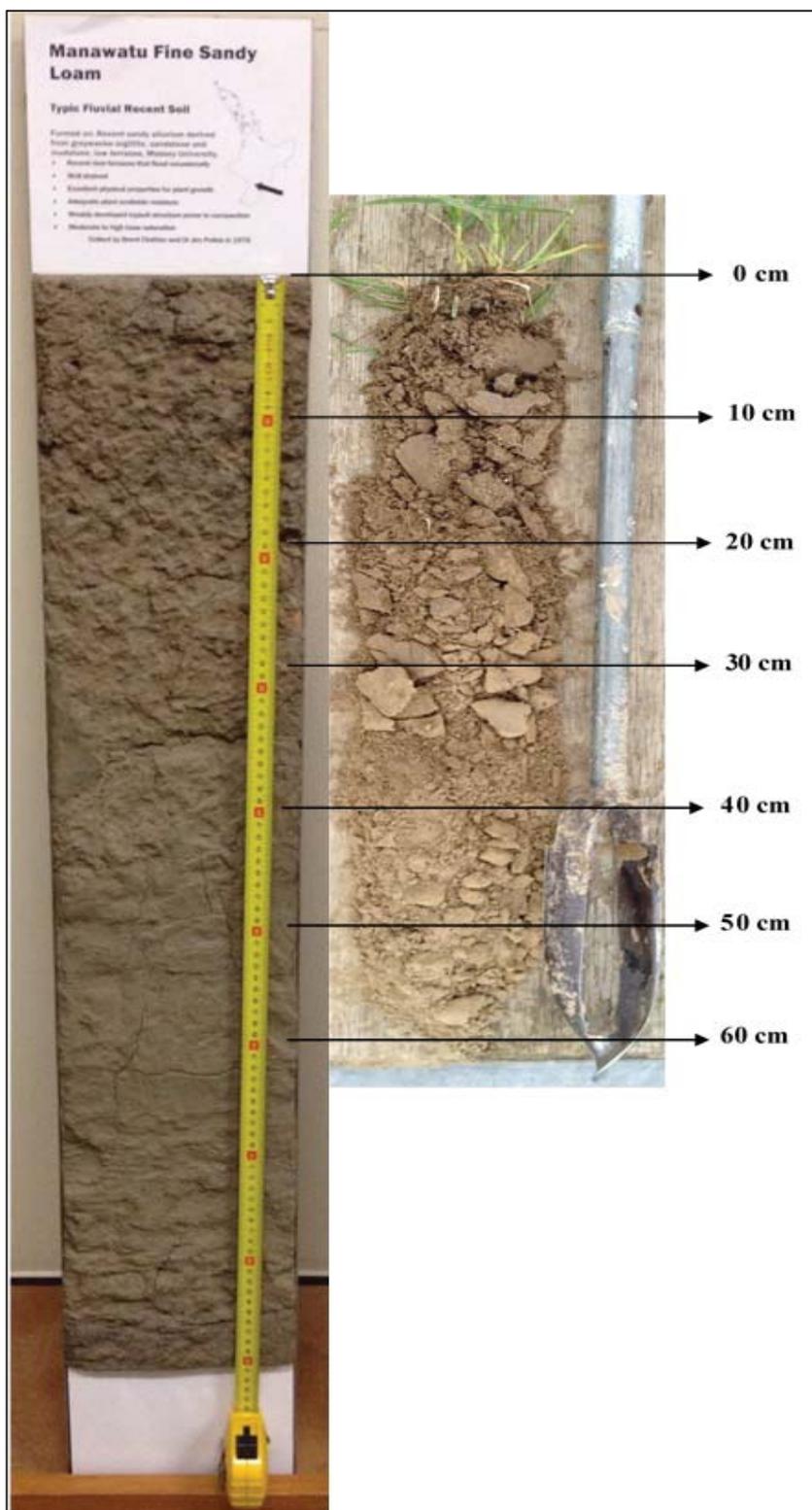


Figure 3-3. Comparison of soil profile at top 60 cm between soil monolith (left) and augered samples (right) collected at paddock 20 at Massey Dairy Farm No. 1.

cm		hzn	description
0			
10		Apg	Loamy silt (some fine sand), pale greyish brown, very pale for an A horizon, red-brown mottles, firm nutty structure.
25		AB	Loamy silt (much fine sand), medium brown with paler brown inclusions, nutty structure.
54		Bw	Loamy silt (much fine sand), dull yellowish brown, weak nutty structure.
75+		2C	Sand, dull yellowish brown, loose, unstructured.

Figure 3-4. Soil profile at paddock 23 at Massey Dairy Farm No. 1 Site 1 (adapted from Killick (2013)).

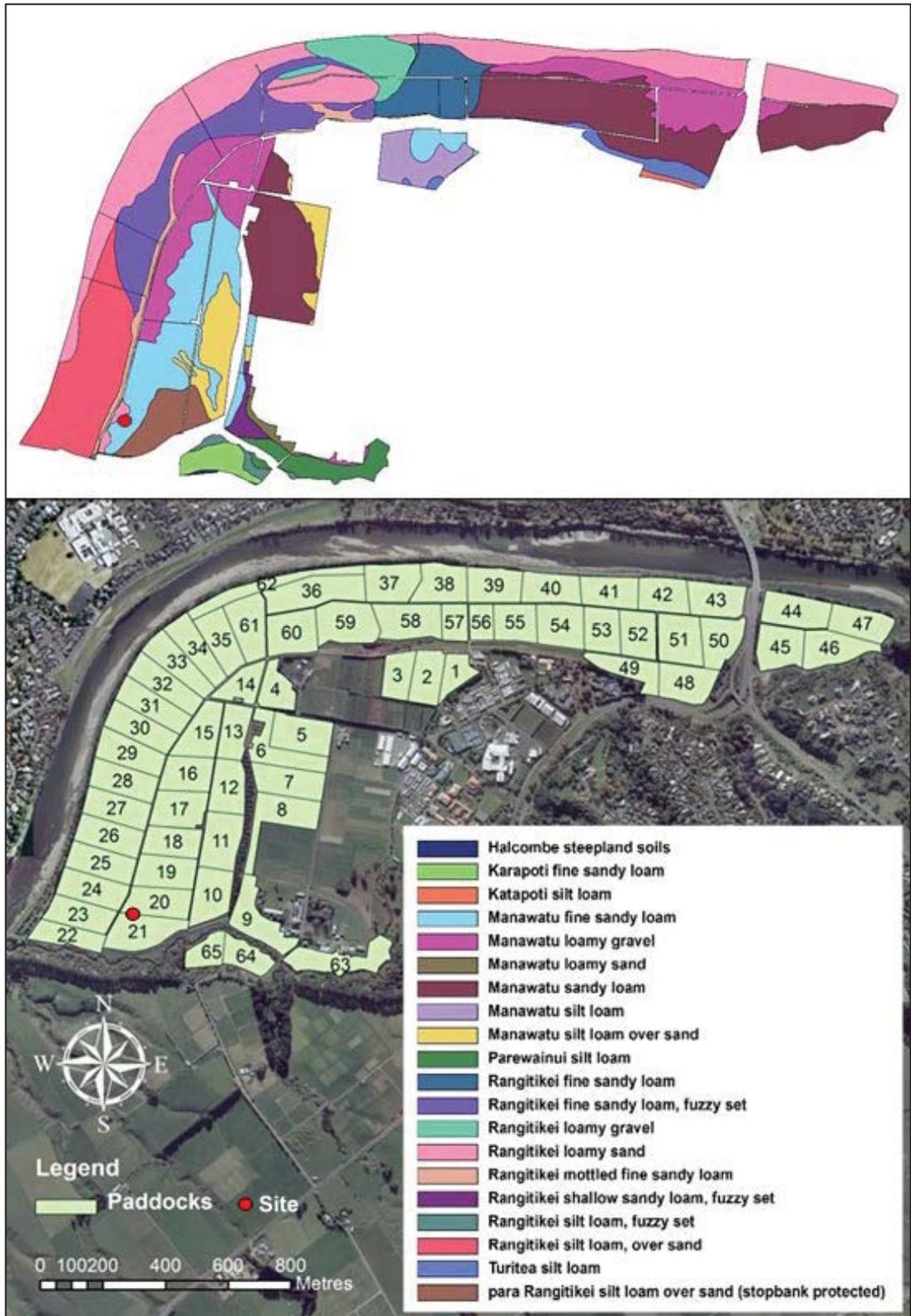


Figure 3-5. Soil map of Massey Dairy Farm No.1 (top) and distribution of paddocks and location of the study site Site 1 (bottom).

The research Site 1 is a composite block of paddocks 20 and 21 with coordinates of 175.6027, -40.384. The altitude is about 35m above mean sea level. The experimental plot was a composite of two paddocks chosen to minimise disturbance from farm activities such as grazing cows and operation of farm machineries. The plot has an area of 100 m² enclosing installed porous cups and piezometers (Figure 3-6).

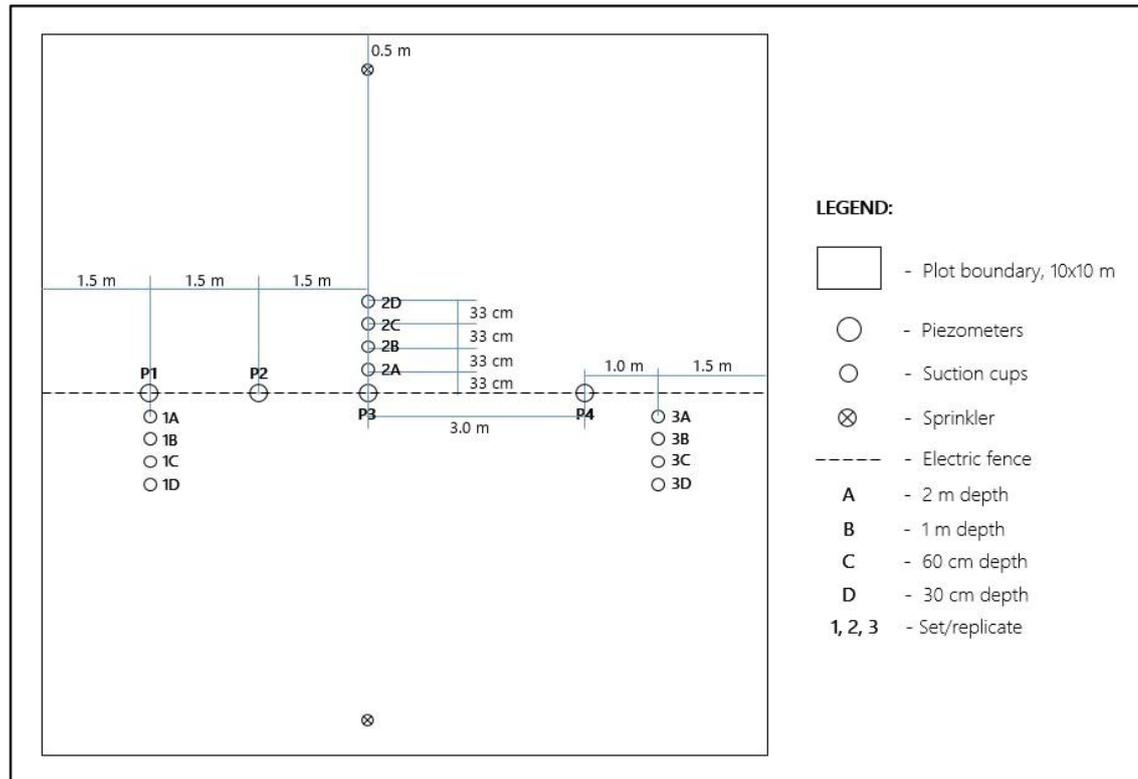


Figure 3-6. Experimental plot layout at the Massey Dairy Farm No. 1 Site 1.

A total of 12 ceramic porous cups were installed to extract soil-solution samples from the unsaturated zone. Three sets or replicates of ceramic porous cups were installed at four depths at 30, 60, 100, and 200 cm below the soil surface. Each set consisted of four porous cups installed in a perpendicular line, starting at a depth of 30 to 200 cm below the soil surface towards the fence line. The porous cups were equally spaced apart at about 33 cm, while the replicates were spaced parallel to each other at least 3 m apart. For sampling shallow groundwater, four piezometers were installed parallel to the fence line at depths of 5.8, 6.3, 7.4, and 8.7 m below the soil surface. The installation profiles of ceramic porous cups and piezometers are presented in Appendix A. This experimental plot at Site 1 was completely established by Aldrin Rivas (PhD student, Massey, IAE) with the help of David Feek (Senior Technician, Massey, IAE).

3.1.2 Te Matai Site (Site 2)

The second study site, Site 2, is located upstream of Site 1 on a private farm along Te Matai Road, Whakarongo, with coordinates of 175.670, -40.341 (Figure 3-2). At this site in 1996, the Horizons Regional Council (HRC) installed six multilevel piezometers (Figure 3-7 and Figure 3-8). This groundwater monitoring setup is part of an extensive groundwater level monitoring network in the region. Groundwater level data at depths of 12, 18, 33, 51, 66, and 87 m below the soil surface is automatically measured and transmitted to HRC via telemetry every 15 minutes. The purpose of this setup is to collect frequent groundwater level data for State of the Environment assessment and groundwater model purposes (Zarour, 2008). Since the installation of these piezometers, only groundwater level data is being collected. For this study, this site served as a groundwater quality monitoring site. I sampled and measured nitrate, ammonium, dissolved oxygen, pH, conductivity, ORP, and temperature for all six multilevel piezometers at this site from September to December, 2013.

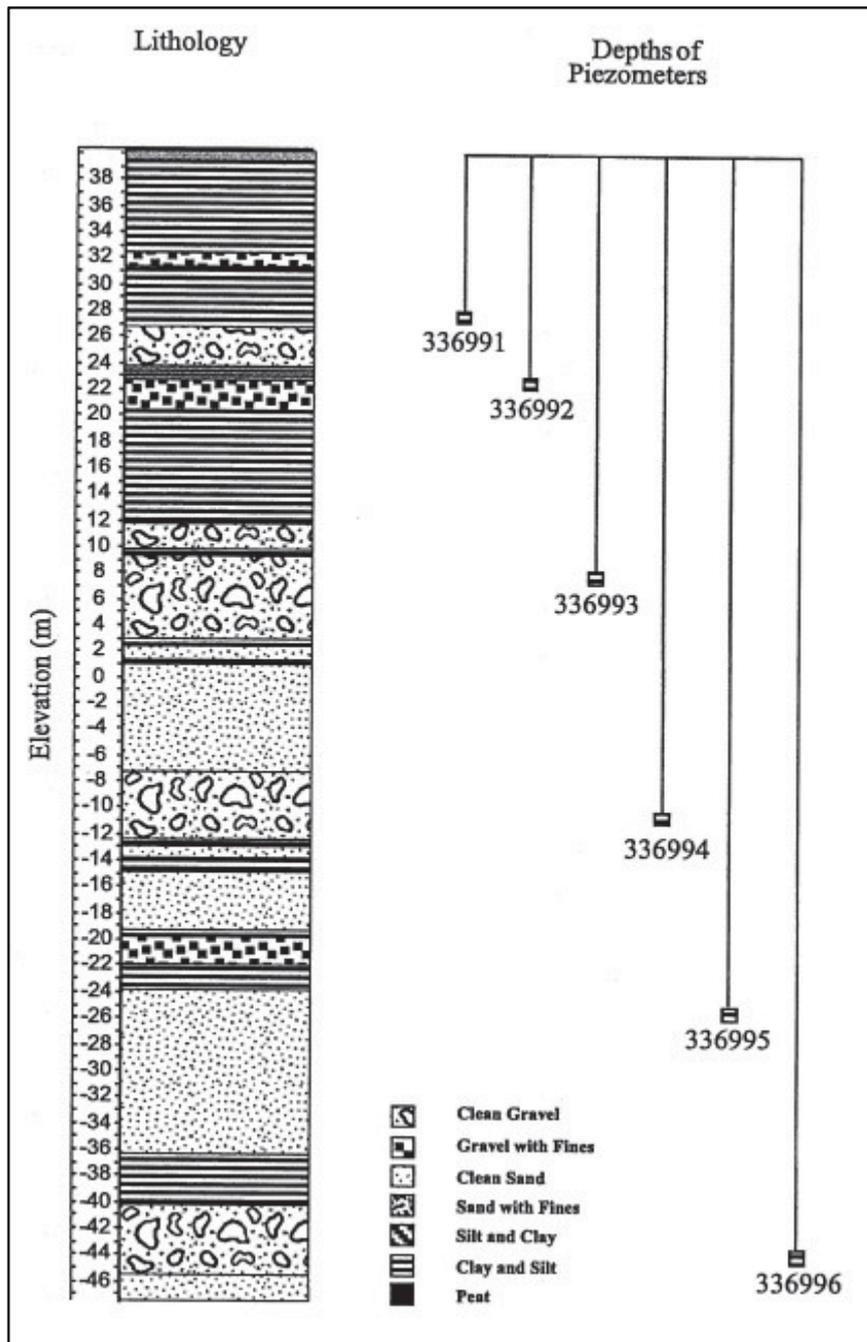


Figure 3-7. Multilevel piezometer profile at the Te Matai Road Site 2 (adapted from Zarour, (2008)).

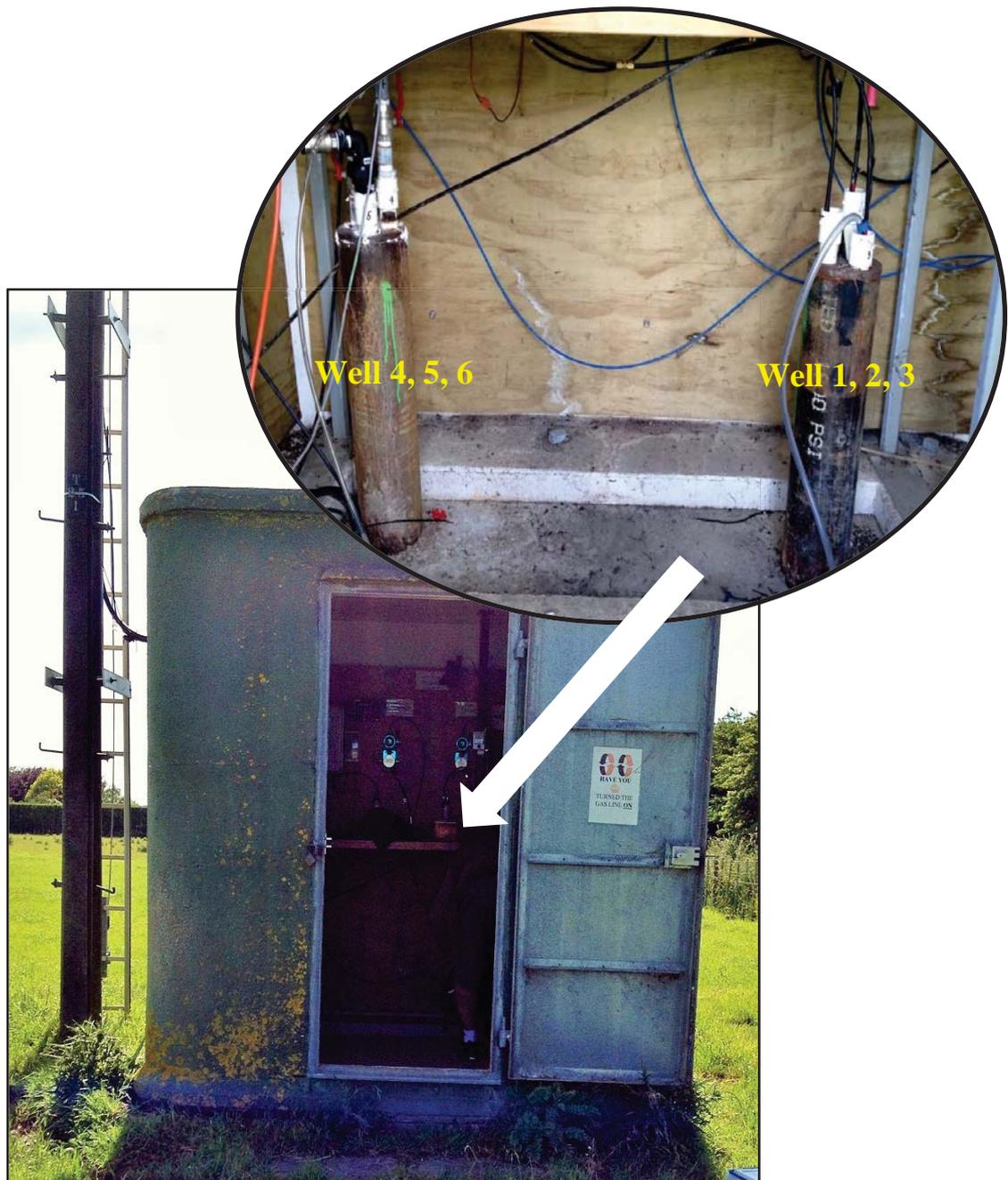


Figure 3-8. Multilevel piezometers at Te Matai Road Site 2.

3.2 Experimental design, data collection and sampling

3.2.1 Climate data

Climate data such as rainfall, solar radiation, air temperature, humidity, and soil temperature were collected from the meteorological station nearest to the study sites. At Site 1, the nearest meteorological station is located within a 1 km radius, (coordinates 175.609, -40.380) and managed by AgResearch Grassland Ltd in Palmerston North. Daily climate data from January, 2013, to January, 2014, were requested and obtained from AgResearch by email and sent on a monthly basis. The collected climate data was utilised to compute the potential evapotranspiration.

3.2.2 Soil samples

Intact soil core samples and disturbed soil samples were collected for the analysis of physical and chemical properties of the soil at Site 1 in July, 2013. The soil samples were specifically taken inside paddocks 20 and 21 but outside the experimental plot. The intact soil core samples were obtained using a slotted 10 cm long by 5 cm outside diameter PVC pipe (Figure 3-9). The PVC core sampler is encased by a metal pipe which is driven into the ground using a 9 kg waratah post driver (Figure 3-10).

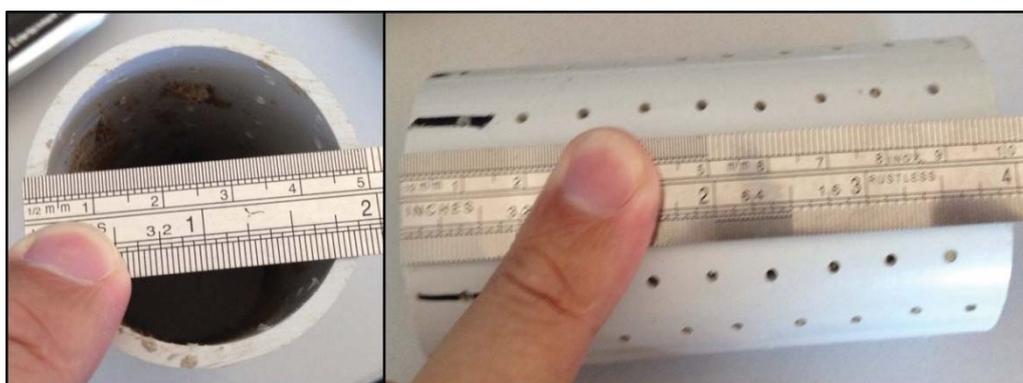


Figure 3-9. PVC soil core sampler.



Figure 3-10. Soil core sampling using waratah posing driver.

Using this post driver, a constant force was applied when released at a certain head, ensuring minimal compaction. The slots around the PVC wall also provided air spaces to minimise soil compaction as it is driven into the ground. A bigger soil auger was then drilled into the previously sampled core in preparation for the next soil core sample. A total of nine core samples were collected at depths of 0 – 15, 15 – 30, and 30 – 45 cm, replicated three times per depth. At 45 – 60 cm depth, the PVC core sampler could not be used because of gravelly soil. The intact soil core samples were collected only once for the analysis of soil physical properties, such as bulk density and particle density.

The disturbed soil samples were collected using the 8-cm diameter soil auger. For soil organic matter content analysis, a total of 12 composite soil samples were collected at

depths of 0 – 15, 15 – 30, 30 – 45, and 45 – 60 cm, replicated three times each. The disturbed soil samples were also collected several times on a monthly basis for soil moisture content analysis. At least eight soil samples were collected each month at depths of 0 – 30 and 30 – 60 cm, replicated four times per depth. The intact and disturbed soil samples were collected outside the experimental plot to avoid creating holes which can be a medium for preferential flows. The spots for soil samples were chosen randomly.

3.2.3 Urea and bromide fertiliser application

In November 2013, a dose of urea ($\text{CO}(\text{NH}_2)_2$) and potassium bromide (KBr) was applied at the rate of 1000 kg/ha (466.7 kg N/ha) and 307.14 kg/ha (206.23 kg Br/ha), respectively, by means of a synthetic urine (Figure 3-11). These application rates were comparable to the application rates used in other tracer tests conducted by Thomas et al., (2012) at 400 kg N/ha and 200 kg Br/ha; Richards et al. (2005) at 349.5 kg Br/ha; and Dann et al. (2013) at 980 kg N/ha and 400 kg Br/ha. Both fertilisers were dissolved in 140 L of water and applied manually into the experimental plot using graduated buckets (Figure 3-11). A 1m x 1m box was constructed and used as guide in applying the synthetic urine to ensure a uniform application rate. The synthetic urine had a theoretical concentration of 22,490 mg/L of inorganic N and 10,254 mg/L Br.

The purpose of this experiment was to characterise the transport and transformation of $\text{NO}_3\text{-N}$ until it reached the saturated zone using a bromide tracer. Bromide is an ideal tracer because it is not absorbed by plants in large quantities, it is not adsorbed in the negatively charged soil minerals, and its natural background concentration is small (Flury & Papritz, 1993).



Figure 3-11. Synthetic urine application at Site 1.

3.2.4 Irrigation

Irrigation was applied five times from December, 2013 to January, 2014 at Site 1 in relation to the bromide tracer test. Also during this period, rainfall was scarce and less frequent. To hasten the transport of bromide to a deeper profile of the soil, irrigation was needed. Two sprinklers installed at 9 metres apart were used for irrigation (Figure 3-12). Several buckets were placed inside the plot every irrigation event to measure the amount of water applied after each irrigation. On average, 95.74 mm per irrigation event was applied. The source of irrigation water was from the farm's water supply.



Figure 3-12. Installed sprinkler irrigation at the experimental plot at Massey Dairy Farm No. 1 Site 1.

3.2.5 Soil-solution samples

Soil-solution samples at different depths were extracted using ceramic porous cups. Porous cups are commonly used devices for extracting soil-solution samples to analyse the concentration of ions, such as nitrate and ammonium in the vadose zone (Nielsen & Johnson, 1990). For this study, a round-bottom-straight-wall porous ceramic cup, polyvinyl chloride (PVC) pipe, nylon tubing, and polycarbonate stopcocks were used to fabricate the porous cups (Figure 3-13). The ceramic cup (part number 0652X10-B01M3) has the following specifications: outside diameter of 2.223 cm, length of 8.890 cm, high flow air entry value at 1 Bar, effective pore size of 2.5 micron, hydraulic conductivity of 0.0000086 cm/sec, and approximate porosity of 45% by volume (Soil Moisture Equipment Corporation, 2013). The porous cups were preconditioned after fabrication and before installation by soaking and repeated washing with deionised water. This was done to ensure that the ceramic cups were free of unwanted contaminants left from the production process (Curley, O'Flynn, & McDonnell, 2010). A total of 12 ceramic porous cups were installed vertically on July 3 – 4, 2013, at soil depths of 30, 60, 100, and 200 cm using a percussion corer (Figure 3-14).

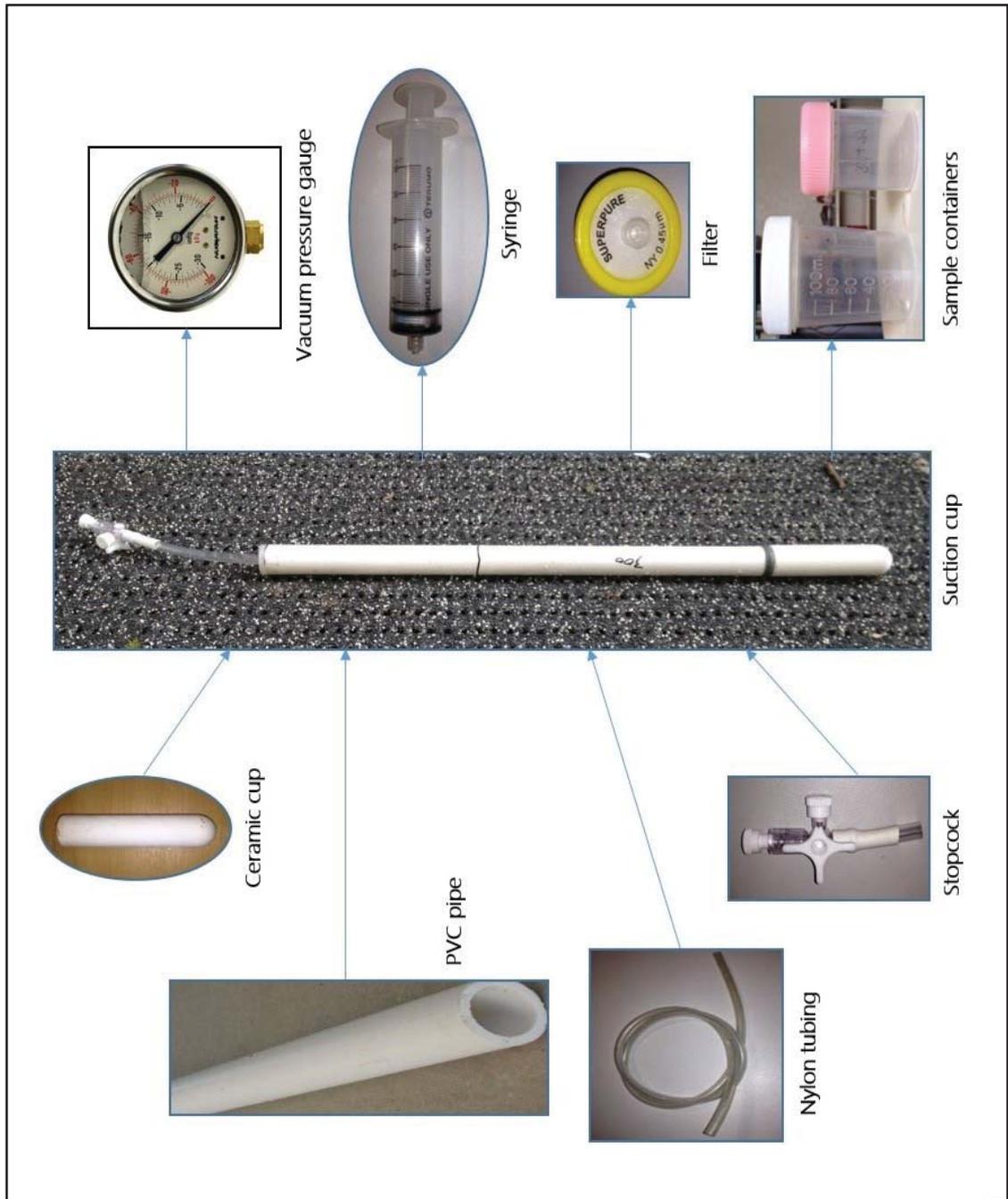


Figure 3-13. Materials used in ceramic porous cup assembly (left group) and sampling soil-solution (right group).



Figure 3-14. Percussion corer used to create a hole for installing vertical porous cups.

A metal rod with a diameter of 3.1 cm was driven vertically to make a hole just wide enough for the PVC pipe of the ceramic porous cup to fit in. Other methods of installation can be horizontal and inclined at an angle (Close et al., 2004; Dann et al., 2013), but the vertical method was chosen because of ease of installation and the availability of the instrument for the installation. By using the percussion corer, soils were minimally disturbed since the rod (only slightly bigger than the PVC pipe diameter of the porous cup) was pushed and no soils were removed. After making a hole for the PVC pipe to fit in, the space around the PVC wall was backfilled with appropriate materials illustrated in Appendix A. An access tube was installed for porous cups installed at 1 and 2 m deep for easy maintenance purposes in case these porous cups malfunctioned. This method was adapted from the study of Close et al. (2004). After installation, porous cups were checked for possible pressure loss using a vacuum gauge. All installed porous cups were functioning very well and no pressure losses were observed after testing. After successful installation and testing of the ceramic porous

cups, the first few extracted samples were discarded. Samples were obtained by applying a vacuum pressure of 70 kPa for at least 24 hours prior to extraction. Based on several studies, vacuum pressure can be applied in a range of 60 – 90 kPa (Close et al., 2004; Curley et al., 2010; Morrison & Lowery, 1990; Patterson et al., 2000), depending on the soil type and moisture content prior to extraction. After vacuum pressure was applied, soil-solution samples were taken out of the porous cups using a Luer lock tip syringe attached to the polycarbonate stopcock (Figure 3-15).



Figure 3-15. Sampling soil-solution in porous cup.

The collected soil-solution samples were filtered using a 0.45 micron filter prior to analysis. The soil-solution samples were stored frozen if not analysed on the same day. For each ceramic porous cup, two samples were collected and sampling was done on a fortnightly interval, starting August, 2013, until January 30, 2014. The collected soil-solution samples were analysed for nitrate-nitrogen, ammonium-nitrogen, bromide, and dissolved organic carbon in the laboratory at the Institute of Agriculture and Environment (IAE), Massey University, Palmerston North. The YSI Model 55 Handheld Dissolved Oxygen System (YSI, 2013a) was used in the field to measure dissolved oxygen and temperature of the soil-solution samples. It was difficult but efforts were made to reduce the effects of exposure to atmosphere on DO and temperature measurements in the soil solution samples.

3.2.6 Groundwater level and quality parameters

Groundwater quality parameters were measured on site using YSI Professional Plus Handheld Multi-parameter Instrument, model 6050000 (YSI, 2013b). This meter measured dissolved oxygen, temperature, specific conductance, pH, and oxidation-reduction potential. The collected groundwater samples were also analysed for nitrate- and ammonium-nitrogen. These parameters were measured to determine indications of redox conditions in the groundwater. Along with these parameters, the depth to water table was also measured using a water level meter.

3.2.6.1 Shallow groundwater samples at Massey Dairy Farm No. 1 Site 1

Shallow piezometers are commonly employed to collect groundwater samples for the purpose of analysing nitrate concentrations at different depths of the shallow aquifer (Nielsen & Johnson, 1990). In this study, a total of four piezometers were installed at Site 1 on August 13, 2013. These piezometers were installed using a post rammer (Figure 3-16) at depths of 5.8, 6.3, 7.4, and 8.7 m below the soil surface. PVC pipes with a diameter of 2.80 cm were used for the piezometers. In this procedure, a cased metal rod (casing and rod diameter – 8.0 and 2.8 cm, respectively) was rammed into the soil at the desired depth to make a bore for the PVC pipe. The metal rod was slowly pulled out while leaving the casing intact to prevent earth materials from collapsing. The PVC pipe was then inserted into the hole and the metal casing carefully removed. The walls were backfilled with a mix of bentonite, fine sand, and parent material to ensure good contact between soil and PVC to avoid preferential flow along the PVC walls. The bottom 0.5 m of the PVC pipe was circumferentially perforated at a diameter and interval of 5.0 mm (Appendix A). The 0.5 m perforation was wrapped with a fine nylon mesh to filter fine sand. This part of the piezometer served as the screen where groundwater enters when extracted.

Unlike the ceramic porous cups, only a few piezometers were installed. This is because complete mixing of anions is assumed in the shallow groundwater and that due to this mixing a few piezometers were enough for a representative sample. The sampling regime and frequency is discussed in Section 3.3.6.

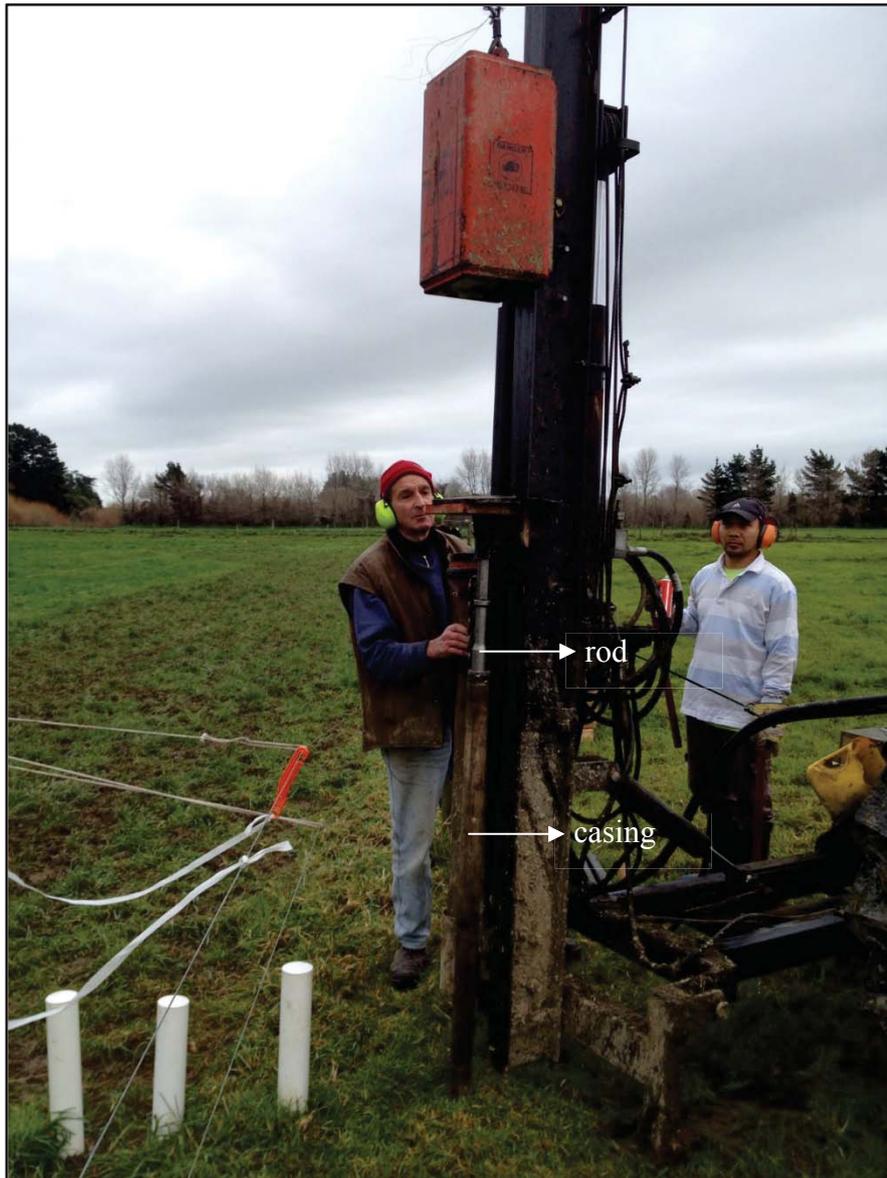


Figure 3-16. Post rammer used to install piezometers at Massey Dairy Farm No. 1 Site 1.

3.2.6.2 Groundwater samples at the Te Matai Rd Site 2

At Site 2, there were already six multilevel piezometers installed at depths of 12, 18, 33, 51, 66, and 87 m below the soil surface as shown in Figure 3-7. Generally, the top 26 m of the profile is made up of clay and silt with thin layers of gravel spaced in between (Figure 3-7). Below 26 m of the profile, the majority is made up of sand, alternately overlain with thin layers of silt and clay and thick layers of gravel. The groundwater level has been monitored at this site since 1996. The sampling regime and frequency of the groundwater are discussed in Section 3.3.6.

3.3 Laboratory Analysis and Field Measurements

The collected soil samples, soil-solution samples, and groundwater samples were analysed in the laboratory for various soil physical and chemical properties, soil moisture, and for nitrate-nitrogen, ammonium, dissolved organic carbon, and bromide. This was done to characterise the initial conditions of the research area prior to the study and their temporal change in the unsaturated and saturated zones.

3.3.1 Soil physical properties

3.3.1.1 Bulk density

The soil bulk density from 0 to 60 cm depth at Site 1 was determined by the core method (Blake & Hartge, 1986a) using the PVC core sampler described in Section 3.2.2. The collected soil samples were oven-dried at 105°C for at least 16 hours. After oven-drying, the weight of the samples was recorded. The soil (dry) bulk density was then calculated as the ratio of oven-dried sample weight and volume of the core sampler. Equation 3-1 gives the formula for soil bulk density.

Equation 3-1

$$\rho_b = m_d/V_{cs}$$

Where: ρ_b – Dry bulk density, g/cm^3
 m_d – Oven-dried weight of the sample, g
 V_{cs} – Volume of core sampler used, cm^3

3.3.1.2 Particle density

The particle density from 0 to 60 cm at Site 1 was determined using pycnometer method (Blake & Hartge, 1986b). A pycnometer is an apparatus used to specifically determine the mass and volume occupied by the soil. In the bulk density value, the mass is the combined weight of soil and air, while the volume is the total volume occupied by the soil sample prior to oven-drying. With the use of a pycnometer, the corresponding soil weight and the volume it occupies can be determined.

3.3.1.3 Other physical soil properties

Killick (2013) undertook analysis of other soil physical properties, such as porosity, electrical conductivity, and texture, at Site 1. Although the sampling points were not at the same site of this study, the results can be adopted and do not vary significantly. The soil physical properties results are presented in Appendix B.

3.3.2 Soil chemical properties

3.3.2.1 Organic matter

The soil organic matter content at Site 1 was determined by the loss on ignition method using a muffle furnace (Goldin, 1987). Soil samples were obtained at 15 cm depth interval up to 60 cm having three replicates per depth. From these fresh soil samples, 10 g of soil was placed in a beaker and into the muffle furnace. The temperature of the furnace was set to 375°C and the samples were heated four hours. After four hours, the furnace was cooled down for an hour while leaving the soil samples inside. Soil samples were immediately weighed after one hour. Soil moisture content of these samples was determined using duplicate samples, which were oven-dried at 105°C for at least 16 hours. The difference in weight of the samples before and after ignition in the muffle furnace represented the organic matter content, also taking into account its initial moisture content as a moisture factor (Blakemore et al., 1987). Equation 3-2 gives the formula for computing the soil organic matter content using the loss-on-ignition method.

Equation 3-2

$$\% OM = (w_i * m_f - w_f) / (w_i * m_f) * 100$$

Where: OM – Organic matter, %

w_i – Pre-ignition weight of the soil sample, g

m_f – Moisture content factor, soil sample fresh weight/soil sample oven dried weight

w_f – Post-ignition weight of the soil sample, g

3.3.2.2 Mineralisation, extractable nitrate, and ammonium

On-site aerobic incubation was employed to determine the mineralisation rates of the soil. This was chosen to simulate mineralisation under field conditions. The method used was a modified buried bag method (Duran et al., 2012). Fresh soil samples at 0-30 cm depth were collected, homogenised, and placed in polyethylene bags. These bags were buried in a covered PVC cylinder 30 cm deep and incubated for two weeks. The set-up maintained a constant soil-moisture while the temperature varied under field conditions. The use of polyethylene bags prevented nutrient leaching from the samples. Soil samples were collected from these bags at days 0, 5, 8, and 13. The amount of nitrate and ammonium present in the soil was determined by employing the KCl extraction method (Maynard, Kalra, & Crumbaugh, 2008). From collected field moist incubated soil samples, 3g samples were weighed and dissolved with 30 mL 2M KCl in polypropylene tubes. Four replicates were used. The tubes were then placed in a rotary shaker for one hour and centrifuged at 4900 rpm for four minutes. After centrifuging, the soil-KCl solution was filtered by Whatman no. 42 filter paper and filtrates were analysed for nitrate and ammonium using the autoanalyser method. For incubated samples, the mineralisation rate was determined by taking into account the difference in nitrate and ammonium concentrations before (day 0) and after the incubation (day 13) (Neill et al., 1997).

3.3.3 Soil moisture

Soil moisture content was determined using the gravimetric method (Gardner, 1986). For volumetric soil moisture content, the PVC core sampler in Section 3.2.2 was used to get soil samples. Fresh soil samples were weighed and then placed in the oven at 105°C for at least 16 hours. After oven-drying, samples were reweighed immediately to account for the weight change. The percent difference in the weight multiplied by the bulk density is the volumetric soil moisture content. Equation 3-3 presents the computation of soil moisture content by volume.

Equation 3-3

$$SMC \left(\% \frac{v}{v} \right) = \frac{(m_w - m_d)}{m_w} * 100 * \rho_b$$

Where: $SMC \left(\% \frac{v}{v} \right)$ – Volumetric soil moisture content, %
 m_w – Fresh weight of soil sample, g
 m_d – Oven-dried weight soil sample, g
 ρ_b – Dry bulk density, g/cc

3.3.4 Water NO_3 -N and NH_4 -N

The colorimetric autoanalyser method was used to determine the nitrate-nitrogen and ammonium content of soil-water and groundwater samples (Blakemore et al., 1987). The concentration of samples was determined based on the range of nitrate and ammonium standards measured by the autonalyser. The concentrations of standards used in this method were 0.25, 0.50, 1.0, 2.0, 4.0, 8.0, and 12.0 ppm. The determination of nitrate and ammonium is based on the production of visible dye, which is colourimetrically measured (red azo dye for nitrate and indo-phenol Prussian blue dye for ammonium). Two replicates per sample (approx. 8 mL per sample) were used in this method, and the average reading of both samples was used.

3.3.5 Bromide

The bromide content of water samples was analysed by the Lachat IC5000 system machine using the ion chromatography Quick Chem Method 10-510-00-1-A(1). This method is similar to Landcare Research's Method 312 when analysing inorganic anions using ion chromatography (Landcare Research, 2014). A water sample is pumped through a 0.8 μ m disc filter into an injection valve which is connected to a stream of carbonate-bicarbonate eluent. Anions are then separated in the analytical column and pass through a suppressor bathed in flowing acid regenerant solution. Anions are converted to their highly conductive form in the suppressor and the carbonate-bicarbonate eluent converted to weakly conductive carbonic acid. The separated anions in their acid forms are measured by conductivity. They are identified based on their retention time compared to standards and quantitated based on the peak area. The concentrations of standards used for bromide were 0.05, 0.1, 0.5, 1.0, and 2.5 ppm. The volume of sample used was 5 mL and replicated twice. This analysis was done only when the bromide tracer experiment started on November 5, 2013. Prior to application of KBr, the background concentrations of soil-solution and groundwater samples were analysed. For the synthetic urine, analysed bromide content was 10,550 mg/L which

was close to the theoretical concentration of 10,254.29 mg/L. Figure 3-17 illustrates the ion chromatograph set-up of the Lachat IC5000 system for bromide analysis.

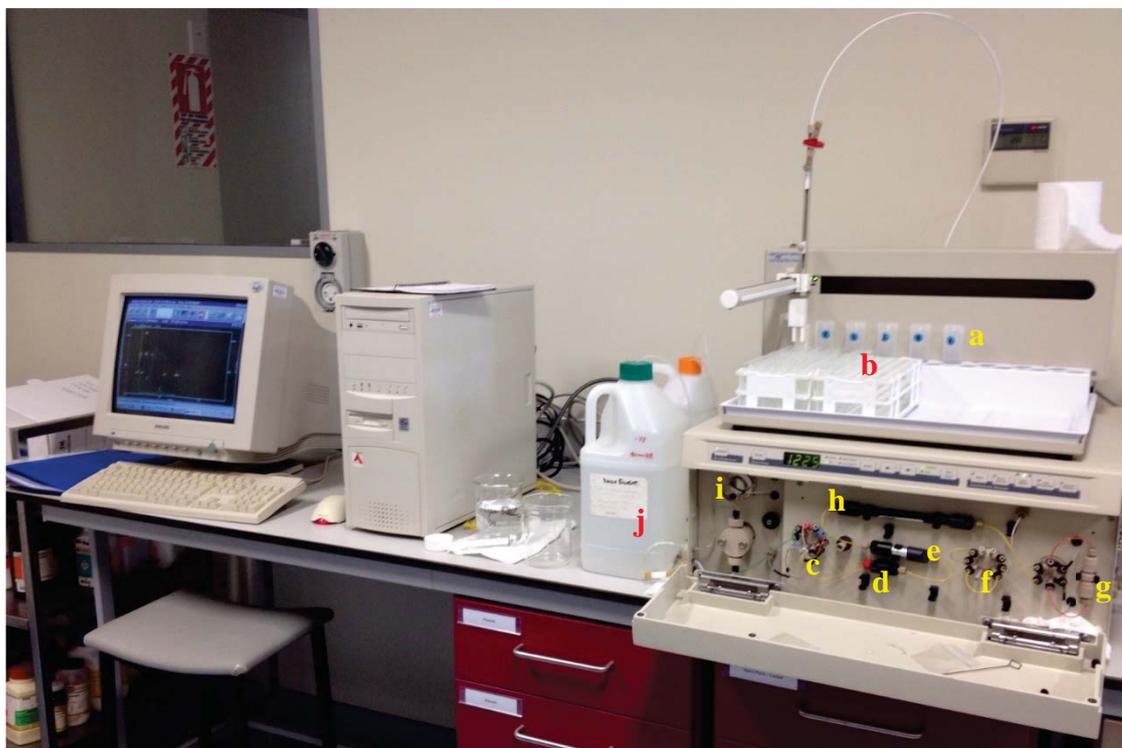


Figure 3-17. Lachat IC5000: a) standards, b) samples, c) dual loop injection valve, d) cations guard column, e) anions guard column, f) column switching valve, g) microsuppressor, h) anions analytical column, i) gradient generator and j) carbonate-bicarbonate eluent reservoir.

3.3.6 Groundwater level and quality parameters

The protocol for groundwater sampling in New Zealand (Daughney et al., 2006) was used in this study. Groundwater samples were extracted using a nylon hose connected to a peristaltic pump. Water samples enter a flow cell to avoid exposure of samples to the atmosphere and go through the water quality meter where parameters are measured (Figure 3-18). Prior to groundwater quality sampling, the groundwater level was recorded using a water level meter and then the volume of water to be purged was computed. The standing water was then pumped out of the piezometer at a pumping rate between 0.5 to 2.0 litres per minute. Groundwater quality parameters were monitored while purging using the YSI Professional Plus Handheld Multi-parameter Instrument, model 6050000 (YSI, 2013b). Prior to taking water samples, at least three volumes were

purged or until the difference between the last two measurements were within the following limits enumerated in Table 3-2.

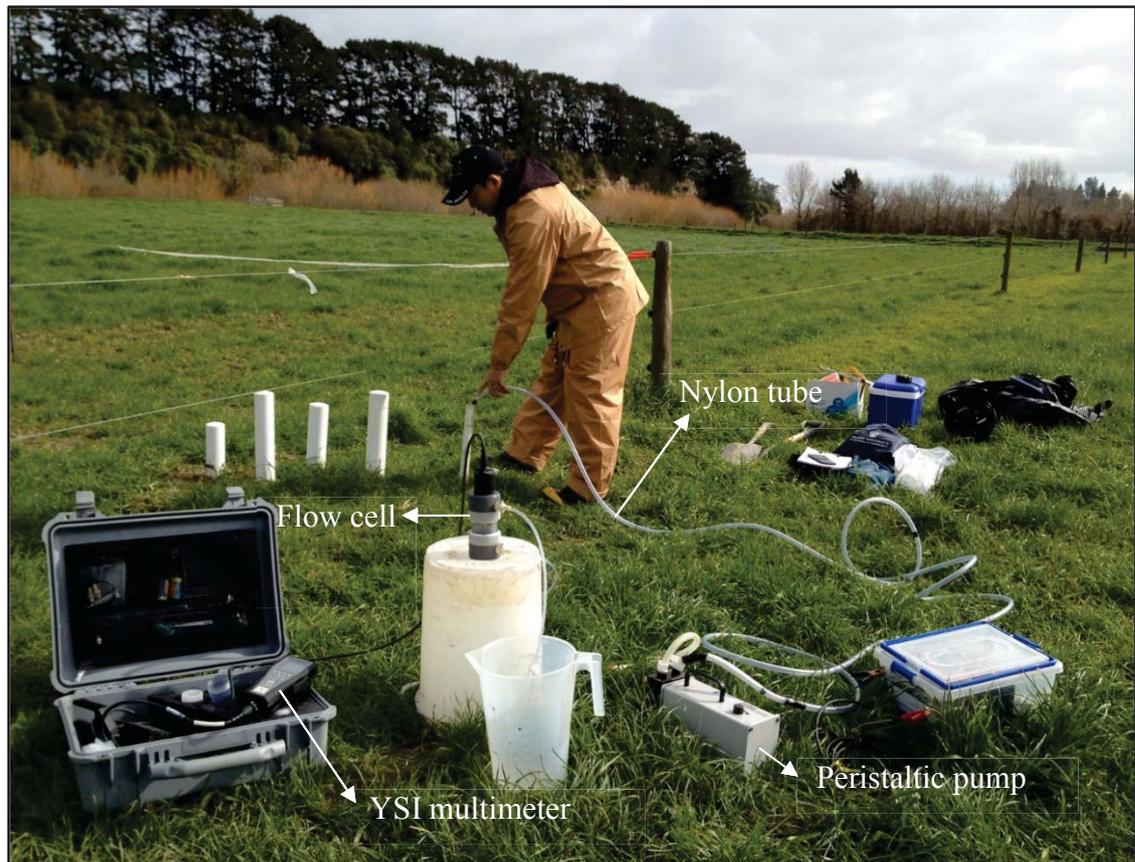


Figure 3-18. Extraction of shallow groundwater samples at Massey Dairy Farm No. 1 Site 1. Connections are as follows: Nylon tube from piezometer to peristaltic pump to flow cell to YSI multimeter.

Table 3-2

Required water quality criteria prior to groundwater sampling.

Parameters	Criteria
Temperature	± 0.2 °C
Conductivity	$\pm 3\%$ ($\pm 5\%$ if <100 $\mu\text{S}/\text{cm}$ at 25 °C)
pH	± 0.1 pH unit
Dissolved oxygen	± 0.3 mg/L

Source: Daughney et al.(2006).

Once the criteria was met, samples were collected and filtered with a 0.45 μm pore size filter and preserved at 4°C for later analysis or stored frozen at $< 0^\circ\text{C}$ for future analysis. Further details on sampling procedures can be found in the protocol used in

this study. For each piezometer, two samples were taken (80-100 mL). The sampling interval was every two weeks, starting on August 22, 2013, and continuing until January 30, 2014. For the soil-solution in the ceramic porous cups, a separate handheld YSI dissolved oxygen meter (YSI, 2013a) was used. Soil-solution samples were measured for dissolved oxygen and temperature. The probe of the handheld YSI meter was dipped into the samples and stabilised for 30 seconds before taking a reading.

3.3.7 Dissolved organic carbon

The dissolved organic carbon (DOC) content of soil-solution and groundwater samples was analysed using the digestion and titration method (Ghani, Dexter, Carran, & Theobald, 2007; Ghani, Dexter, & Perrott, 2003). Eight mL of groundwater or soil-solution samples was used and digested with 2.0 mL of 0.0667M $K_2Cr_2O_7$ and 16 mL of a $H_2SO_4-H_3PO_4$ mixture for 30 minutes. After digestion, six to eight drops of phenylanthranillic indicator were added to the digested samples and titrated with ferrous ammonium sulphate (FAS, $Fe(NH_4)_2(SO_4)_2$). The titration was stopped once an immediate change in colour of the sample was observed (dark purple to dark green). The volume of FAS titrated corresponding to the change of colour was recorded. The same procedure was done using deionised water as a sample to compute for background concentrations. The titration volume of samples was converted to the concentration of DOC using Equation 3-4. Only one replicate per sample was used to conserve the sample for other analyses. Figure 3-19 briefly illustrates this process.

Equation 3-4

$$DOC = (V_B - V_S) * N * f * 2000 / v$$

Where: DOC – Concentration of dissolved organic carbon, ppm

V_B – Volume of FAS titrated for blank samples (deionised water), mL

V_S – Volume of FAS titrated for non-blank samples (groundwater or soil-solution), mL

v – Volume of sample used, mL

N – Normality of FAS

f – Recovery factor

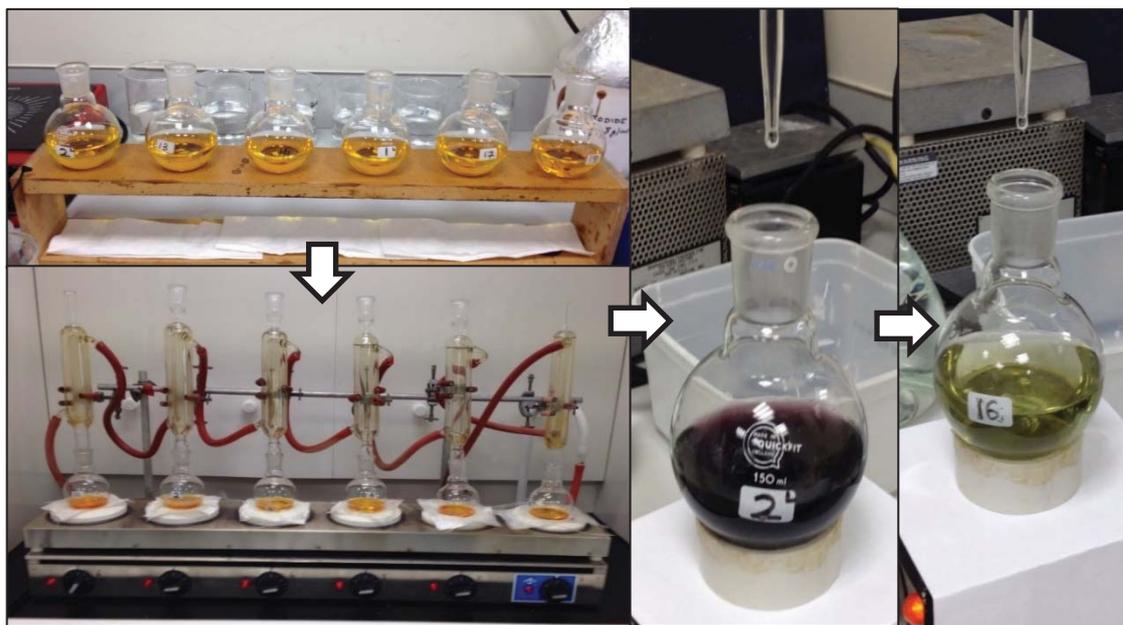


Figure 3-19. Preparation and analysis of DOC using digestion and titration method.

3.3.8 Groundwater redox conditions

The redox conditions of shallow groundwater at Site 1 and deep groundwater at Site 2 were assessed using the parameters nitrate-nitrogen, dissolved oxygen, iron, manganese, and sulphate. The nitrate-nitrogen and dissolved oxygen concentrations at Sites 1 and 2 were measured every two weeks for the entire duration of the study. However, the remaining three other parameters (iron, manganese, and sulphate) were not measured. Data on the concentrations of iron, manganese, and sulphate were obtained from historical observations in 647 wells distributed in the Manawatu catchment from 1958 to 2007. These data can be found in the report of Daughney et al. (2009).

An excel spreadsheet created by McMahon and Chapelle (2008) was used to assess the redox conditions at Site 1 and Site 2. The redox conditions were categorised into oxic, suboxic, and anoxic based on the different threshold values set for DO, $\text{NO}_3\text{-N}$, Mn, Fe, and SO_4^{2-} . The average monthly concentrations of $\text{NO}_3\text{-N}$ and DO for the months of August, 2013 to January, 2014 were used based on the groundwater quality measurements in this study (section 3.3.6). For Mn, Fe, and SO_4^{2-} , average monthly concentrations for the months of August to January were used based on historical observations in 647 wells distributed in the Manawatu catchment from 1958 to 2007 (Daughney et al., 2009). These values, when entered in the excel sheet, were processed

and assigned a redox category of either oxic, suboxic, anoxic, or mixed oxic-anoxic condition based on a set of threshold values (Table 4-3).

Chapter 4. RESULTS AND DISCUSSION

This chapter presents the results obtained from the field experiments and monitoring, and laboratory analyses. Also presented here are discussion and interpretation of the results addressing the objectives of the study. This chapter is basically divided into three main sections; the first section focused on the transport and transformation of nitrate-nitrogen in the unsaturated and saturated zones. Before this section is presented and discussed, the physical characteristics and climatic conditions observed at the experimental site during the study period are noted. The second section focuses on the tracer test, and the last section on the assessment of redox conditions in the groundwater at Site 1 and Site 2.

4.1 Physical characteristics and climate conditions

This section discusses the physical characteristics and climatic factors of the experimental site at Massey Dairy Farm No. 1. These conditions have a direct effect on the transport and transformation of nitrogen both in the unsaturated and saturated zones.

4.1.1 Soil physical characteristics

The soil type at Massey Dairy Farm No. 1 Site 1 is classified as Manawatu fine sandy loam. The majority of the soils on the farm are free-draining recent alluvial soils and are rich in organic matter content (Massey University, 2015). The Manawatu River flood in February 2004 caused a deposition of sediment in the entire farm which was estimated at 12-13 cm depth (NZCPA, 2005 as cited in Killick, 2013). Many studies have already been conducted on Massey Dairy Farm No. 1 and characterised the physical properties of the soil. A recent study by Killick (2013) described the upper 60 cm of the soil (taken in paddocks 22-24 which was adjacent to Site 1) as loamy silt with fine sand, pale greyish to dull yellowish brown, having a weak nutty structure while the lower 60 cm is sand, dull yellowish brown, loose, and unstructured (Figure 3-4). The same characteristics were observed during the installation of the ceramic porous cups and piezometers at Site 1 except for the presence of gravel materials in the 60 to 200 cm depth of the soil. Because of this, soil samples were taken only until 60 cm depth for the analysis of bulk density, particle density, and porosity.

The average bulk density ranged from 1.25 to 1.38 g/cm³, the particle density from 2.20 to 2.49 g/cm³, and the porosity from and 0.40 to 0.43. Table 4-1 summarises these values. The bulk and particle density, and porosity increased with soil depth. These values were close to the measured values in the study of Killick (2013).

Table 4-1

Soil physical characteristics at Massey Dairy Farm No. 1 Site 1.

Physical characteristics	Depth, cm			
	0-15	15-30	30-45	45-60
Bulk density, g/cm ³	1.25	1.34	1.38	-
Particle density, g/cm ³	2.20	2.24	2.40	2.49
Porosity	0.43	0.40	0.42	-

4.1.2 Climate data

Weather parameters, such as rainfall, solar radiation, soil moisture, humidity, and air and soil temperature, were monitored at Site 1 from January, 2013 to January, 2014. These data were collected from the meteorological station managed by AgResearch Grassland Ltd in Palmerston North. The meteorological station is about 1 km away from Site 1. For the purpose of monitoring nitrate-nitrogen leaching and transformation, only rainfall and soil temperature data were utilised. The other parameters were used in the computation of evapotranspiration.

4.1.2.1 Rainfall

The total annual rainfall recorded in 2013 was 772.4 mm from January to December. The maximum monthly rainfall in the year was recorded in April (128.2 mm) while the minimum was recorded in January (29 mm) (Figure 4-1). The historical average annual rainfall data in Palmerston North is 876 mm (Metservice, 2014), having the highest monthly rainfall in December (94 mm) and the minimum in March (42 mm). Comparing both rainfall data (Figure 4-1), the total annual rainfall in 2013 measured at Site 1 was 12% lower than the historical average annual rainfall from New Zealand Metservice. However, the highest monthly rainfall in 2013 was 36% higher than the historical data. This variation can be explained by the 50% year-to-year coefficient of variation of rainfall for any particular month at any location in New Zealand (FLRC, 2009). Although there is a variation in the amount and temporal distribution of rainfall between the historical and measured data, the Palmerston North area is still expected to

experience a high amount of rainfall at the onset of winter (June) to early spring (September) (Figure 4-2).

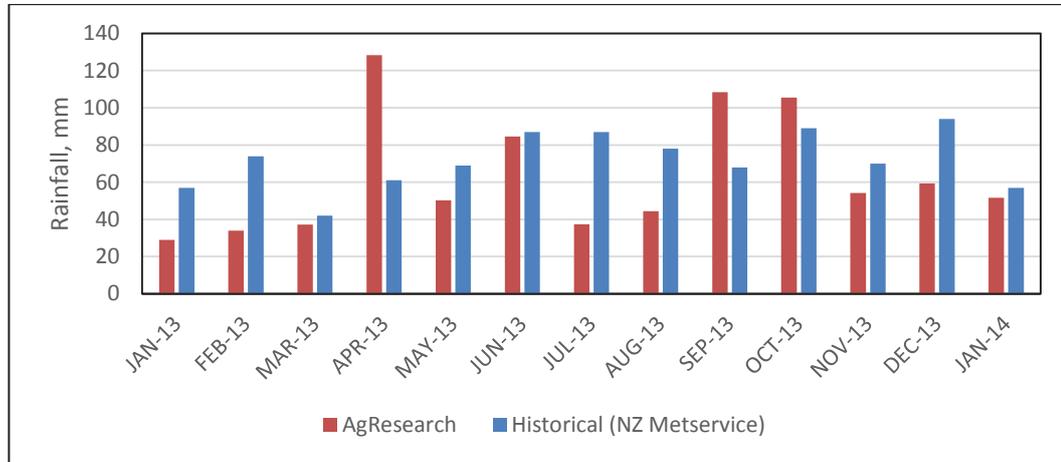


Figure 4-1. Monthly rainfall distribution at AgResearch met station (Site 1) and NZ Metservice (Palmerston North) from January, 2013 to January, 2014.

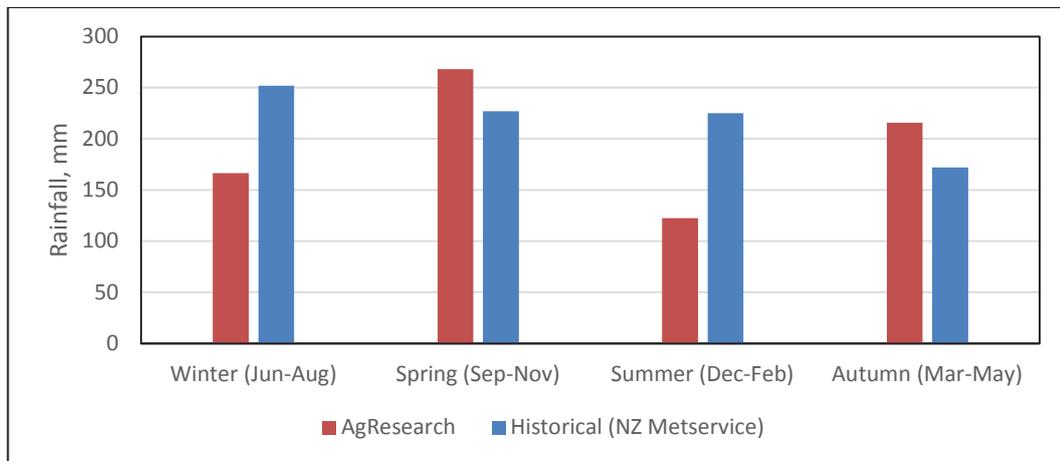


Figure 4-2. Comparison of 2013 seasonal rainfall distribution at AgResearch met station (Site 1) and NZ Metservice (Palmerston North).

The amount of excess rainfall (i.e. rainfall less evapotranspiration) is very important in the transport of nitrate-nitrogen as it drives the flow and leaching from the soil profile. This will be evident in the latter discussion of nitrate-nitrogen leaching in the unsaturated zone.

4.1.2.2 Air and soil temperature

The daily mean, minimum, and maximum air and soil temperature were directly measured at the AgResearch meteorological station. These data were used to calculate the monthly mean, minimum, and maximum air and soil temperatures at Site 1. The maximum monthly ambient air temperature ranged from 17 to 30°C while the minimum monthly ambient air temperature ranged from -3 to 6°C (Figure 4-3). This did not vary significantly from the historical data for monthly maximum and minimum temperatures (17 to 29°C and -2 to 6°C, respectively) in Palmerston North.

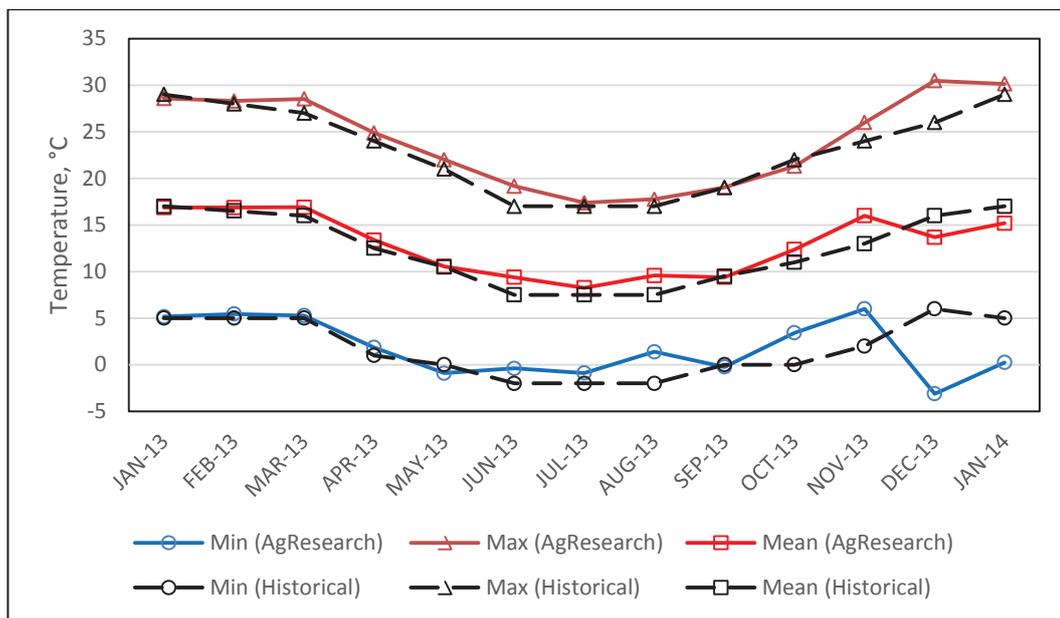


Figure 4-3. Monthly minimum, mean, and maximum ambient air temperature at AgResearch met station (Site 1) and NZ MetService (Palmerston North) from January, 2013 to January, 2014.

Soil temperature was measured at 10, 20, 50, and 100 cm depths. For the monthly maximum soil temperatures, the standard deviations at multiple depths ranged from 0.3 to 1.5°C. During the winter to early spring season (June to October 2013), the standard deviations at various depths ranged only from 0.3 to 0.6°C. During this period, the maximum soil temperatures at 10, 20, 50, and 100 cm depths were almost the same (Figure 4-4).

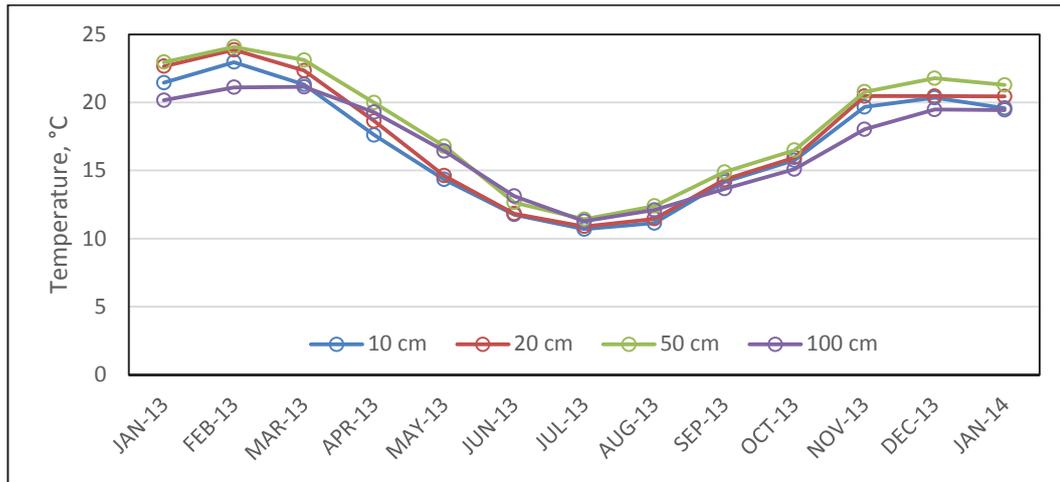


Figure 4-4. Monthly maximum soil temperature at AgResearch met station (Site 1) at multiple depths (10, 20, 50, and 100 cm) from January, 2013 to January, 2014.

The monthly minimum soil temperatures at multiple depths were a lot more variable compared to the maximum soil temperatures (Figure 4-5). The standard deviations at multiple depths ranged from 1.2 to 4.1°C. The soil temperatures increased with soil depth.

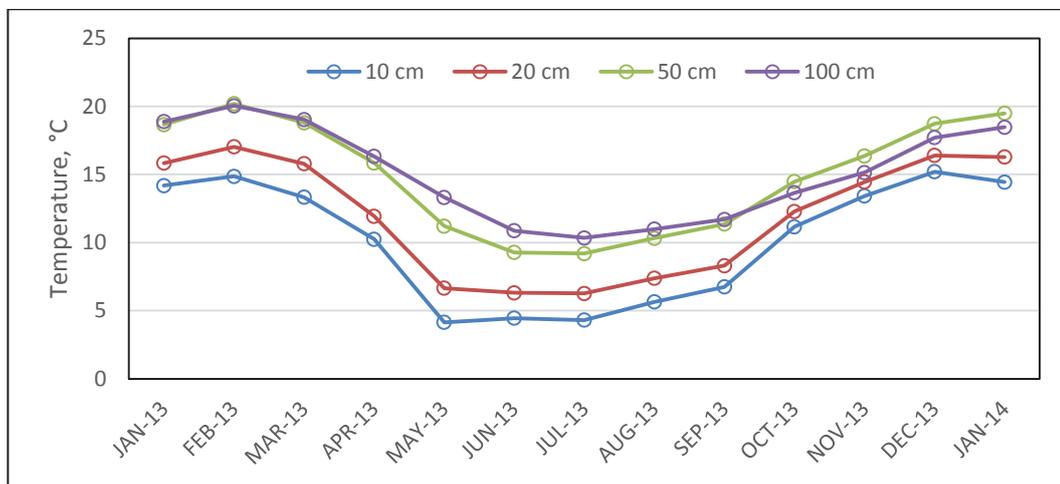


Figure 4-5. Monthly minimum soil temperature at AgResearch met station (Site 1) at multiple depths (10, 20, 50, and 100 cm) from January, 2013 to January, 2014.

The monthly mean soil temperatures were generally lowest at the 10 cm depth and increased with depth (Figure 4-6). The mean soil temperature at 10 cm depth is the same as the behaviour of mean ambient air temperature (Figure 4-3). Both temperatures were in the range between 7.5 and 19°C.

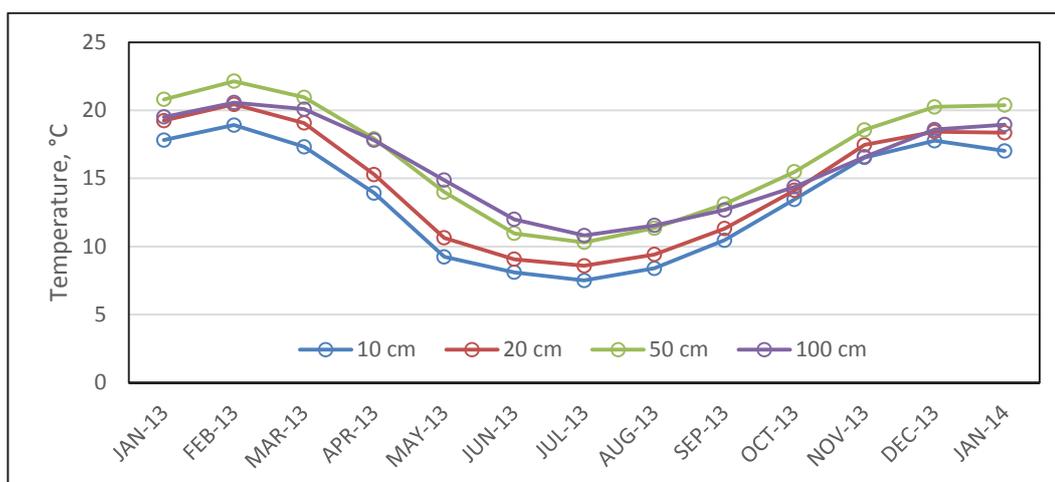


Figure 4-6. Monthly mean soil temperature at AgResearch met station (Site 1) at multiple depths (10, 20, 50, and 100 cm) from January 2013, to January, 2014.

4.2 Transport and transformation of nitrate-nitrogen in the unsaturated and saturated zones

This section discusses the transport and transformation of nitrate-nitrogen from the root zone down to the groundwater. It includes the factors which affect the transport and transformation such as initial soil nitrogen concentrations, irrigation, and the addition of inorganic fertilisers. It also includes a discussion of the tracer test conducted to characterise how nitrate-nitrogen behaved in comparison to bromide as a conservative tracer. This section only applies to Massey Dairy Farm No. 1 Site 1.

4.2.1 Bromide tracer test

A dose of bromide (as KBr) and urea ($\text{CO}(\text{NH}_2)_2$) was applied to the experimental plot in November 2013 in the form of a synthetic urine at the rate of 307 kg/ha (206 kg Br/ha) and 1000 kg/ha (467 kg N/ha), respectively. After the application of the bromide and urea, the experimental plot was irrigated prior to extraction of soil-solution and shallow groundwater samples. This was done to hasten the leaching of bromide and urea in the soil profile. During the monitoring period from November, 2013, to January, 2014, the measured rainfall at Site 1 ranged from 51 to 60 mm/month, which was less than the historical average monthly rainfall from 57 to 94 mm (Figure 4-1). Excess rainfall would have been negative since the monthly potential evapotranspiration during this period at Site 1 ranged from 104 to 122 mm. Irrigation was done five times (once in

the middle of December, 2013, and four times in January, 2014) at an average application rate of 96 mm/day. Accounting for the applied irrigation, the total amount of water applied from November, 2013, to January, 2014 was 479 mm (Figure 4-7).

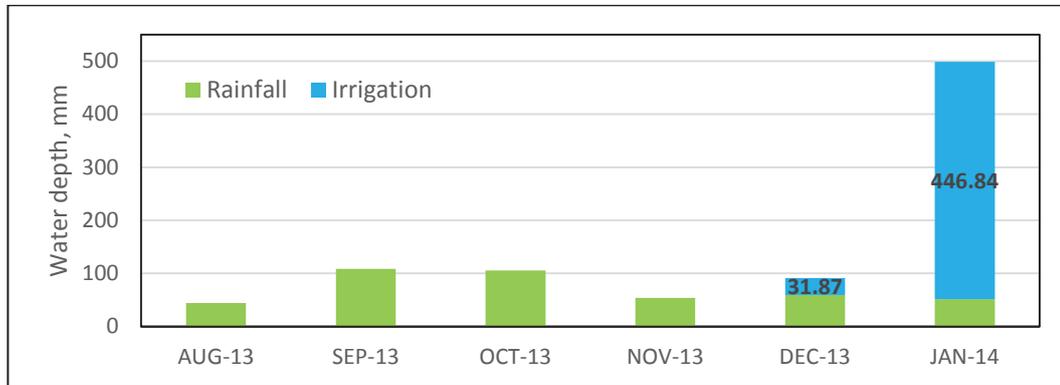


Figure 4-7. Cumulative rainfall and irrigation recorded at the experimental plot Site 1 from August, 2013, to January, 2014.

4.2.1.1 Br^- and NO_3-N concentrations in the unsaturated and saturated (shallow groundwater) zones

Prior to the application of synthetic urine, the background concentration of bromide prior to the application of fertilisers in the ceramic porous cups and piezometers was measured from 0.1 mg/L to nil. Two days after the application of synthetic urine, the average bromide concentration increased to 38 mg/L at 0.3 m soil depth (Figure 4-8). The maximum average bromide concentration recorded was 60 mg/L, at 0.3 m depth, three days after the synthetic urine application. There was a slight increase in bromide concentration at 2 m depth on November 7, just two days after the application of bromide. This increase could be attributed to cross-contamination of samples during laboratory analysis or sample collection. There was no significant amount of rainfall that could have driven the bromide all the way down to 2 m (Figure 4-9) after two days of the synthetic urine application. Therefore, the bromide concentration reading at the 2 m depth in the first sampling after the synthetic urine application could be disregarded. In other ceramic porous cups, there were no recorded significant increases in bromide concentrations in the first two samplings after the synthetic urine application.

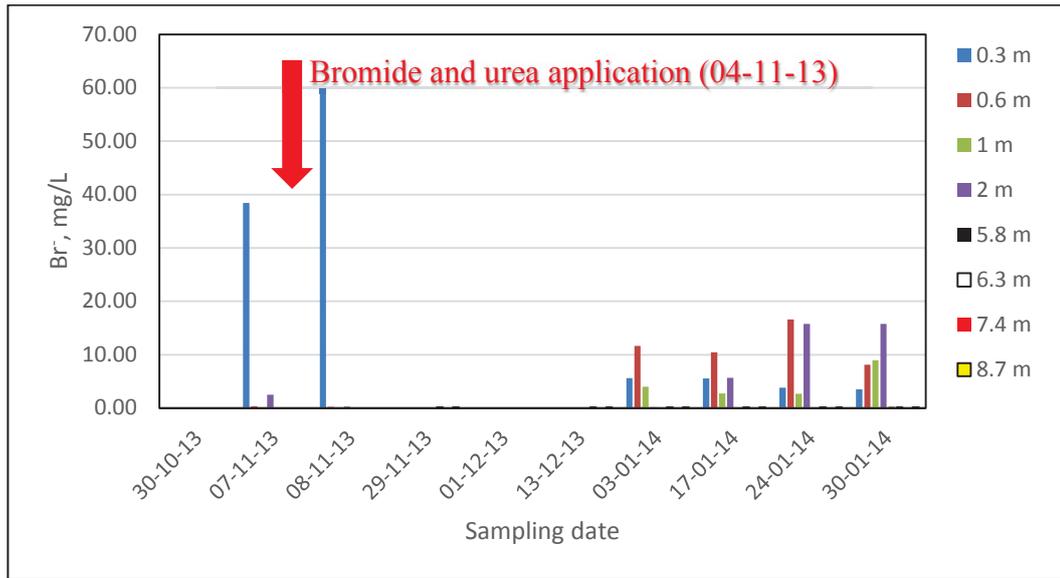


Figure 4-8. Bromide concentrations in the unsaturated and saturated zone post-application of synthetic urea and bromide at the experimental plot on Massey Dairy Farm No. 1 Site 1.

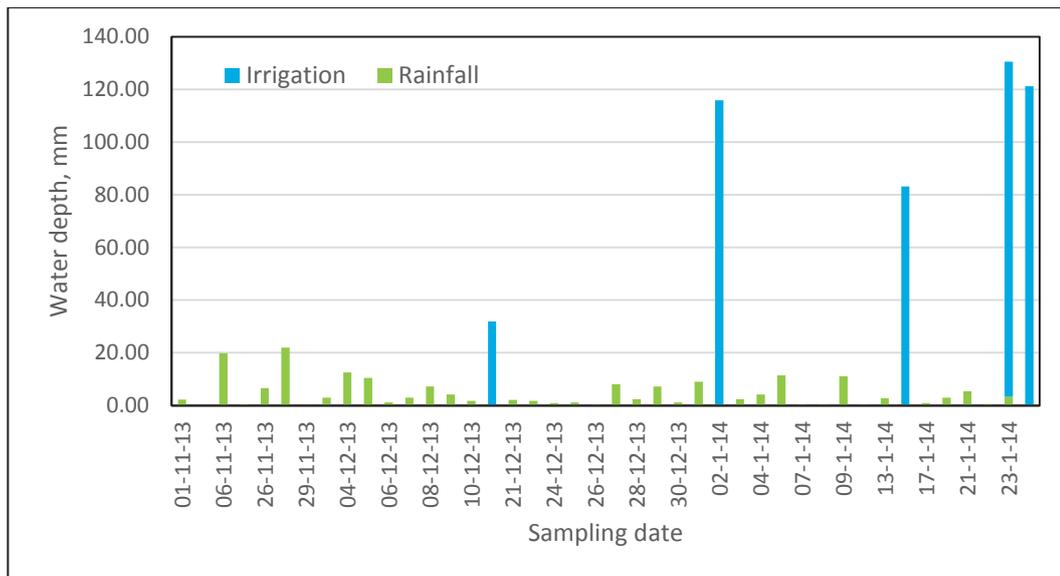


Figure 4-9. Rainfall and irrigation depth applied at the experimental plot on Massey Dairy Farm No. 1 Site 1.

In the three succeeding samplings (November 29 to December 13), there were no water samples collected at 0.3 and 0.6 m depths. At 1 m down to 8.7 m, there were water samples collected but the average concentrations of bromide were still low (Figure 4-8). During this period, the measured rainfall ranged from 0.20 to 12.60 mm per day. The long-term average potential evapotranspiration during this period is about 3.5 mm/day.

Rainfall should be greater than this potential evapotranspiration rate and the soil storage capacity for excess water to leach further down the soil profile. During this period, the soil moisture in the top 60 cm of the soil profile was less than the field capacity (Figure 4-10). After applying a substantial amount of irrigation over 30 days (500 mm combined irrigation and rainfall) in January, 2014 (Figure 4-8), the bromide concentrations decreased at 0.3 and 0.6 m depths, but increased at 1 and 2 m depths. This was corroborated by the increasing trend in the average nitrate-nitrogen concentrations at the same depths (1 and 2 m) as illustrated in Figure 4-11.

The average nitrate-nitrogen concentration at the 0.3 m depth peaked at 102 mg/L on January 03, 2014. This was 59 days or almost two months after the application of the urea. This time lag can be interpreted as the combined time it took for the hydrolysis of synthetic urea and nitrification process to convert ammonium to nitrate. There is a two-part process that needs to take place before nitrate appears and becomes available. From the hydrolysis of urea, the initial by-product would be ammonium. In Figure 4-17, the average ammonium-nitrogen concentrations prior to the application of urea in November, 2013, were below 0.5 mg/L at 0.3 m depth. After the application of urea, the average ammonium-nitrogen concentrations at 0.3 m depth reached 2.1 mg/L; this value was several times over the background concentrations and could be attributed to the initial hydrolysis of the synthetic urea applied. The process that comes next with ammonification of urea is the nitrification. It is a biological process brought about by nitrifying bacteria (e.g., *nitrosomonas*, *nitrobacter*) (McLaren & Cameron, 1990) wherein the ammonium ion is oxidised into nitrite and then to nitrate (Subbarao et al., 2013). Hence, a peak average nitrate-nitrogen concentration at 0.3 m depth was observed on January 3, 2014.

From January 3, 2014, onwards, the trend in the average nitrate-nitrogen concentration at 0.30 m depth was decreasing due to the effect of heavy irrigation, resulting in leaching of nitrate-nitrogen to deeper soil depths (Figure 4-11). At 0.6 m depth, the nitrate-nitrogen concentration was increasing, reaching 30 mg/L on January 24, 2014. This was due to the nitrate-nitrogen flux from 0.3 m depth driven by the heavy irrigation.

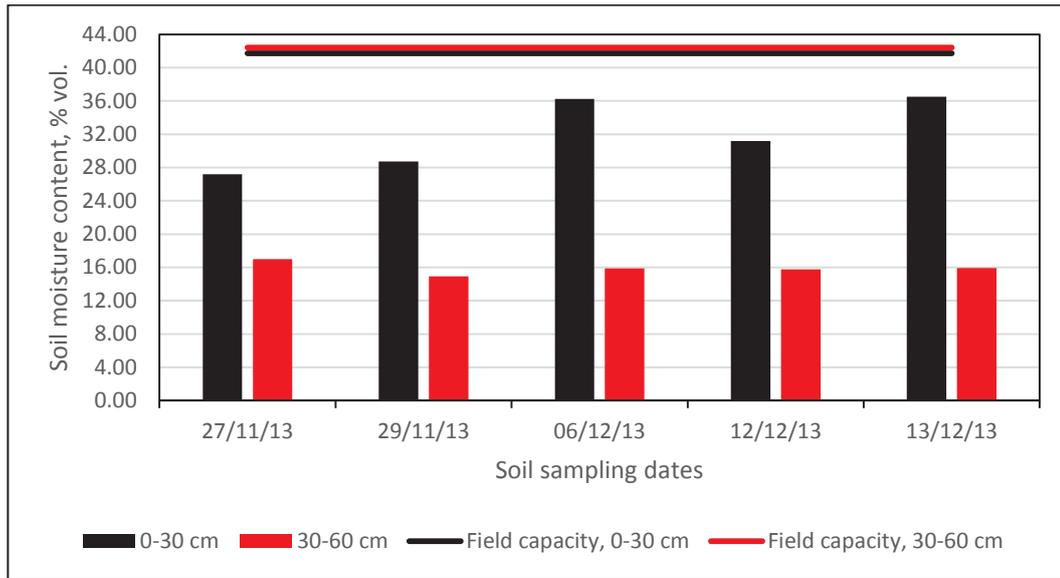


Figure 4-10. Soil moisture content (% vol.) at 0-30 and 30-60 cm soil depth at the experimental plot on Massey Dairy Farm No. 1 Site 1.

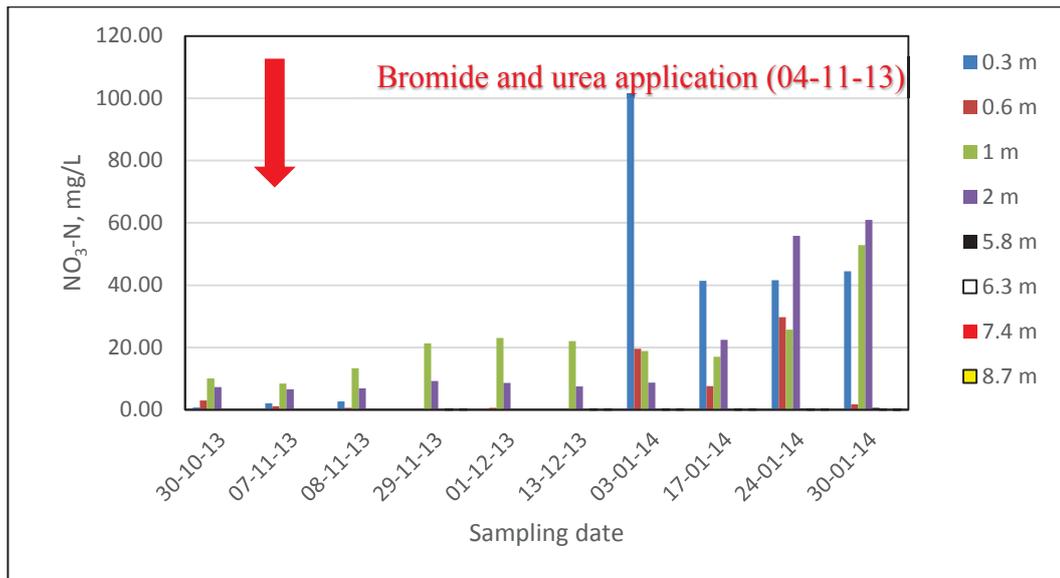


Figure 4-11. Nitrate-nitrogen concentrations in the unsaturated and saturated zones post-application of synthetic urea and bromide at the experimental plot on Massey Dairy Farm No. 1 Site 1.

However, the nitrate-nitrogen concentration at 0.60 m depth dropped to 2 mg/L (30 January, 2014) within a week’s time. This was also because of the effect of heavy irrigation of 248 mm during this week from 24-30 January, 2014 (Figure 4-9). At 1 and 2 m depths, the nitrate-nitrogen concentrations continued to increase indicating continued nitrate-nitrogen flux from the 0.6 m depth. Again, this trend was the same as

that observed in the bromide concentrations at 0.6, 1, and 2 m depths of the soil profile (Figure 4-8).

In the saturated zone (shallow groundwater), there was no appearance or high concentration of nitrate-nitrogen and bromide observed until January 30, 2014 (Figure 4-8 and Figure 4-11). This was because of the large gap (almost 4 m) between the deepest ceramic porous cup at 2 m depth and the shallowest piezometer at 5.8 m depth. The concentrations of nitrate-nitrogen (Figure 4-12) and bromide in shallow groundwater samples were still below 0.5 mg/L and at a background level of < 0.1 mg/L, respectively.

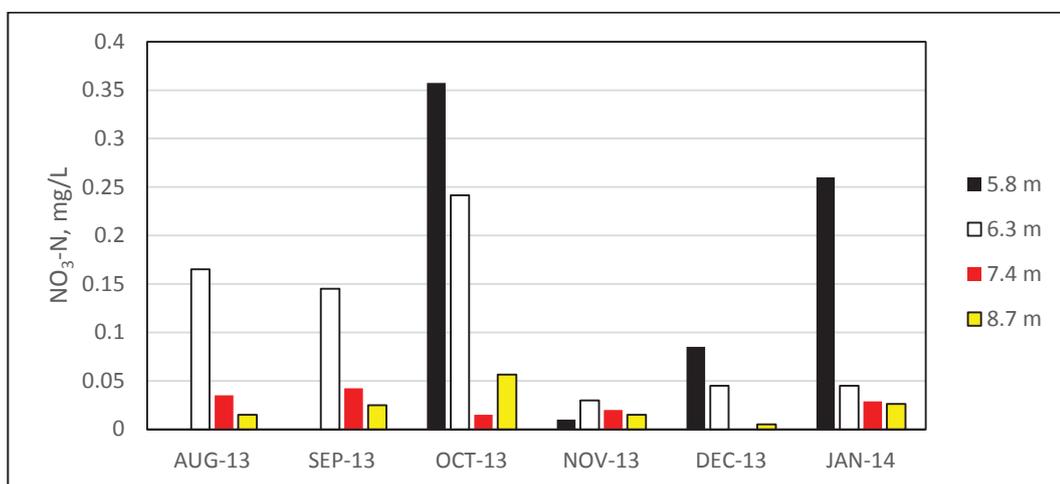


Figure 4-12. Nitrate-nitrogen concentrations in groundwater samples from different depths of the saturated zone (shallow groundwater) at the experimental plot Site 1 from August, 2013, to January, 2014.

4.2.1.2 Bromide travel time from the unsaturated zone to the shallow groundwater

The transport of bromide from 0 to 2 m soil depth bgl was driven by the total applied water depth of 644 mm (combined rainfall and irrigation) from November 4, 2013 to January 30, 2014 (Figure 4-7). During the same period, the total potential evapotranspiration (PET) was computed to be 337 mm. It was assumed that the actual ET was equal to the PET. The net amount of water that percolated the soil profile (i.e. rainfall + irrigation – PET) was estimated to be 307 mm. With this net amount of water, the rate at which bromide travelled was 0.65 cm/mm (depth of soil/net amount of water applied). This means that for every mm of net amount of water applied, the bromide would advance a depth of 0.65 cm below the soil profile. Using this approximated travel

rate of 0.65 cm/mm, the net amount of water that will drive the bromide to the shallow groundwater (4.60 m bgl measured average water level at the Massey Dairy Farm No.1) can be estimated at 707 mm. The excess rainfall generally occurs in the autumn, winter, and spring seasons when the rainfall received is generally higher than the PET (Table 4-2). The water deficit is experienced during the summer season from December to January when PET is higher than the rainfall received. This was the case in 2013 when a net rainfall deficit was experienced in summer (Table 4-2).

Table 4-2

Seasonal measured rainfall and computed PET at the Massey Dairy Farm No. 1 Site 1 for the year 2013.

Season	Rainfall, mm	PET, mm	Excess Rainfall, mm
Winter (JJA)	166.4	90.1	76.3
Spring (SON)	268.0	235.6	32.4
Summer (DJF)	122.4	385.9	-263.5
Autumn (MAM)	215.6	185.7	29.9
Total	772.4	897.3	-124.9

The result of the tracer test suggests that, normally, nitrogen takes a longer time to be leached in the shallow groundwater if rainfall is the only source of infiltrating water in the soil profile. The transport of nitrogen to the shallow groundwater can be hastened by heavy irrigation application and the presence of preferential pathways.

4.2.1.3 Limitations of the tracer test conducted

There were some limitations in the tracer test conducted. The bromide tracer itself is sufficient for the test. However, the nitrogen fertiliser and the timing of application did not help to fully meet the objective of the test. First, the nitrogen fertiliser applied should be potassium nitrate (KNO_3) or any fertiliser whose nitrogen component is in nitrate form (e.g., NH_4NO_3 , NaNO_3). Urea was chosen because it was the only fertiliser available to use at the time of the experiment. The limitation of urea is that it has to first undergo ammonification and nitrification before the nitrate-nitrogen form appears as a process by-product. If all the urea were volatilised or taken-up by the plant, it would also be possible to have no appearance of high nitrate-nitrogen concentration down the soil profile. On the contrary, the appearance of high nitrate-nitrogen concentrations down the soil profile could be interpreted as derived from the hydrolysis of urea (Figure

4-11). Second, the tracer test should have been done earlier to provide ample time for monitoring the shallow groundwater. In this study, bromide and nitrate-nitrogen appeared in high concentrations only up to the 2 m depth ceramic porous cups. They did not appear in the shallow groundwater because there was almost a 3 m gap between the deepest ceramic porous cup and the shallow groundwater level. It is expected that the bromide and nitrate-nitrogen would appear in the shallow groundwater after 3 years only if effective rainfall could be relied upon or less than 3 years if supplemented with irrigation. Therefore, a continued monitoring of this site is recommended to further investigate the transport and transformation of Br and NO₃-N in the shallow groundwater.

4.2.2 Transport and transformation of nitrate-nitrogen in unsaturated zone

Nitrate-nitrogen and ammonium-nitrogen were monitored in the unsaturated zone at Site 1 using ceramic porous cups. The ceramic porous cups were installed vertically in July 2013 at depths of 30, 60, 100, and 200 cm below ground level (bgl). A total of 12 ceramic porous cups (three replicates each) were installed at Site 1. In August 2013, monitoring started on a fortnight basis by extracting soil-solution from the ceramic porous cups. After the extraction, samples were analysed for nitrate and ammonium content (Sections 3.2.5 and 3.3.4).

Prior to fortnightly sampling of soil-solution and groundwater, concentrations of soil nitrogen and organic matter were measured to determine their background concentrations in the soil profile. The background concentrations of soil-N and organic matter indicate the pool of nitrogen mass that is absorbed in the soil and available for plant uptake and leaching.

4.2.2.1 Initial soil-N and organic matter content

The initial soil-N concentrations analysis indicate a high amount of ammonium- and nitrate-nitrogen mass in the soil particularly in the upper 15 cm of the profile (Figure 4-13). High organic matter content (5.83%) in the upper 15 cm of the soil was also measured, but this decreased as the soil depth increased (Figure 4-14). Ammonium was relatively higher than nitrate at all soil depths. Nitrate mass was only high in the upper 15 cm (14.31 µg N/ g soil) while in the succeeding depths, nitrate mass was less than

6.5 $\mu\text{g N/g soil}$. The higher ammonium-nitrogen mass at all soil depths could be due to the combined earlier deposition of urine and faeces from grazing cows and mineralisation process of organic matter. Animal excreta, particularly urine, is a major source of leached nitrogen in New Zealand farms (Cameron, Di, Moir, & Roberts, 2007; Wachendorf, Taube, & Wachendorf, 2005). Nitrate mass decreased as depth increased because nitrate is more mobile than ammonium, thus easily leached.

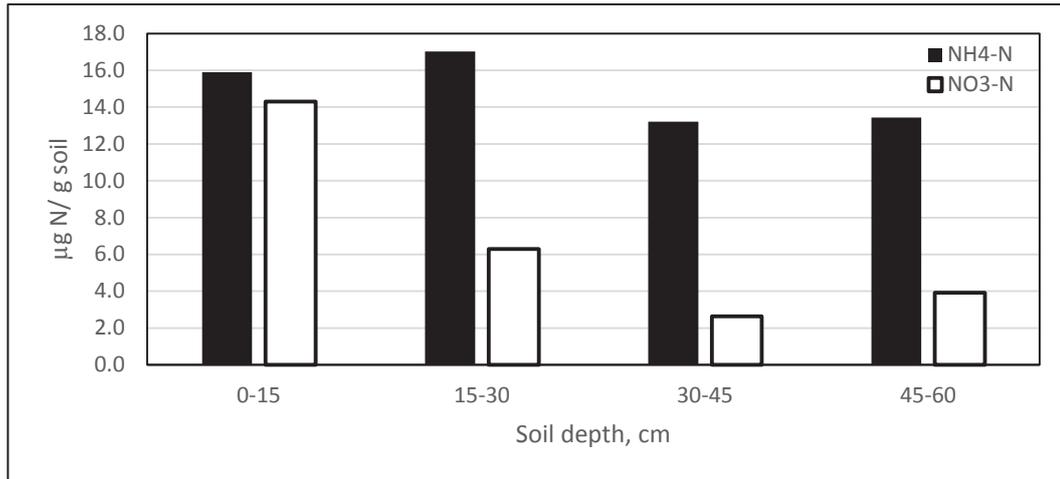


Figure 4-13. Soil-N concentrations at Massey Dairy Farm No. 1 Site 1 measured on July 17, 2013.

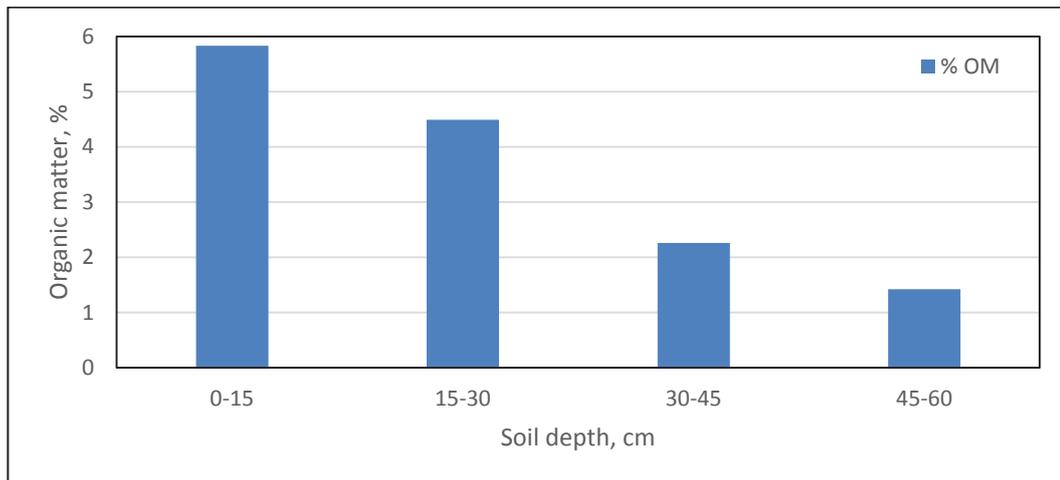


Figure 4-14. Soil organic matter content (%) at Massey Dairy Farm No. 1 Site 1 measured on July 17, 2013.

4.2.2.2 Mineralisation in top (0-30 cm) soil profile

A 14 day on-site soil incubation from September 19 to October 2, 2013, was done to determine the soil mineralisation rate under field conditions. The incubation was carried out using a modified buried bag method (Duran et al., 2012). The set-up maintained constant soil moisture while the temperature varied under field conditions. Soil samples collected at 0-30 cm depth were incubated and at days 0, 5, 8, and 13, the samples were taken and analysed for extractable nitrate-nitrogen and ammonium-nitrogen using the KCl extraction method (Maynard et al., 2008).

During this period of incubation, soil temperature was increasing at 20 cm soil depth (Figure 4-15). As the temperature increased, the ammonium- and nitrate-nitrogen mass also increased, but the ammonium-nitrogen mass was higher than the nitrate-nitrogen mass. This could be due to the high initial ammonium-nitrogen mass of the soil at day 0 and further ammonification process happening as the temperature increased (Zaman & Chang, 2004). In addition, prior to the incubation, the initial soil ammonium- and nitrate-nitrogen contents were already high, ranging from about 14 to 16 $\mu\text{g N/g}$ soil at 0-15 cm and 6-17 $\mu\text{g N/g}$ soil at 15-30 cm soil depth (Figure 4-13). The organic matter content was also high at 5.83 % at 0-15 cm soil depth (Figure 4-14). On day 5, an increase in nitrate-nitrogen took place (Figure 4-15) indicating the occurrence of the nitrification process. A further increase in the soil nitrate-nitrogen mass was observed towards the end of the incubation period. While the ammonium-nitrogen mass was still high, it can be expected that extended incubation would have decreased the ammonium-nitrogen and eventually increased the nitrate-nitrogen mass of the soil (Zaman & Chang, 2004). Based on the slope of the regression line (Figure 4-15), the zero-order mineralisation rate in the upper 30 cm depth soil is $0.49 \mu\text{g NO}_3\text{-N g}^{-1} \text{ soil d}^{-1}$. This mineralisation rate is comparable to other mineralisation rates (up to $0.6 \mu\text{g NO}_3\text{-N g}^{-1} \text{ soil d}^{-1}$) obtained using the same incubation method (Duran et al., 2012).

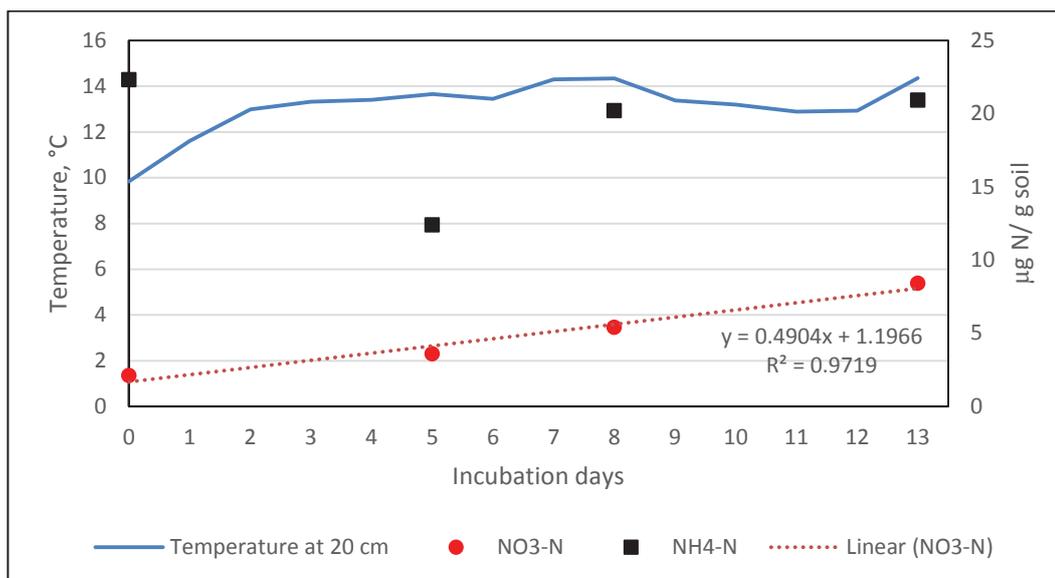


Figure 4-15. Soil mineralisation rate in 0 to 30 cm soil depth at Massey Dairy Farm No. 1 Site 1 measured from September 19 to October 2, 2013.

4.2.2.3 Nitrate-nitrogen in unsaturated zone

Soil-solution was extracted from the 12 installed ceramic porous cups from August, 2013, to January, 2014. Of all the ceramic porous cups, nitrate-nitrogen concentrations at 0.6 m depth were highest, particularly in the months of August and September. This could indicate mineralisation of organic matter leading to nitrification at the top 0.6 m of the soil profile or less plant uptake of nitrate-nitrogen by plants due to cooler temperatures. The monthly mean soil temperature at 50 cm was also increasing from July to February (Figure 4-6) which is favourable for mineralisation.

Nitrate-nitrogen concentrations at 0.3 m depth were lower as compared to the 0.3 - 0.6 m depth. This could be due to relatively higher uptake of nitrate by plant roots in the 0-0.3 m soil profile. As shown in Figure 4-14, organic matter was high in the upper 0.3 m of the soil profile, suggesting higher plant root density.

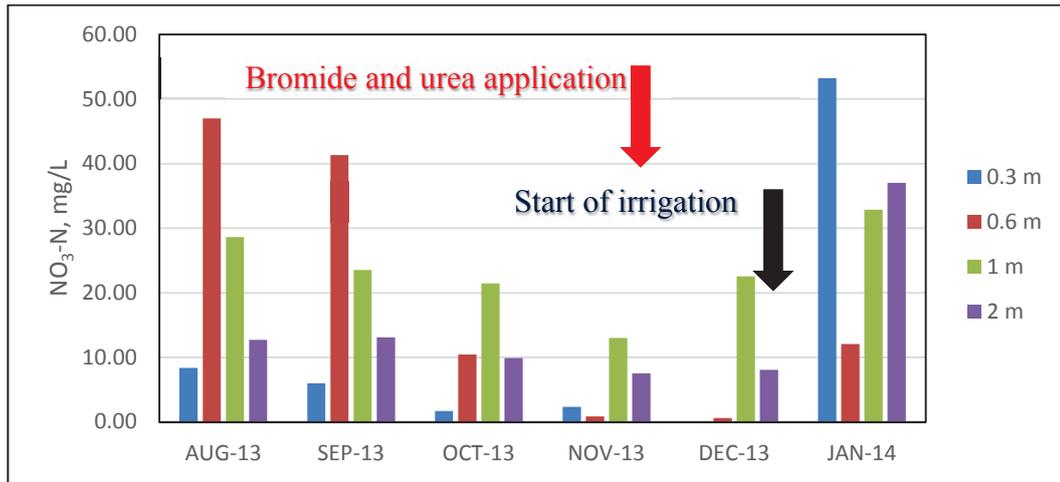


Figure 4-16. Average nitrate-nitrogen concentrations in soil-solution collected from different depths of the unsaturated zone at the experimental plot Site 1 from August, 2013, to January, 2014.

In general, average nitrate-nitrogen concentrations in the unsaturated zone (0-200 cm bgl) decreased from August to November, 2013, particularly in 0 - 0.6 m soil profile (Figure 4-16). This could be due to the decreasing urine and dung deposition at the surface since the experimental plot was fenced in mid-September, 2013, to prevent plot access from grazing cows. This was evident in December, 2013, when average nitrate-nitrogen concentrations at 0.3 m and 0.6 m were measured lowest, despite recorded rainfall being highest in September (108.4 mm) and almost the same amount in October (105.4 mm) (Figure 4-1).

Nitrate-nitrogen concentrations measured at 1 m depth were second highest after 0.6 m depth. The concentrations ranged from 13.04 to 28.63 mg/L. This could indicate that nitrate-nitrogen tends to 'stay longer' at 1 m depth due to weak attenuation or weak nitrate reduction process. However, the nitrate-nitrogen concentrations at the 2 m depth porous cups were lower compared to the nitrate-nitrogen concentrations at the 1 m depth porous cups. This could be due to cycling of nitrogen deposits and its subsequent transport and/or attenuation 'denitrification' of nitrate-nitrogen in the profile.

After the application of urea at the rate of 1000 kg/ha on November 4, 2013, there was an increase in nitrate-nitrogen concentrations in the ceramic porous cups from November, 2013, to January, 2014. This application could be the only possible reason for the increase in nitrate-nitrogen concentrations since there were no other fertiliser

applications done prior to that date. On top of the excess rainfall, the leaching of nitrate-nitrogen was hastened by irrigation applications at an average rate of 95 mm per irrigation event starting December, 2013. The total amount of irrigation water applied from December, 2013, to January, 2014, was about 479 mm (Figure 4-7). Nitrate-nitrogen levels were high in January, 2014, particularly at the top soil (0.3 m), even higher than the measured concentrations in August to September at the top 0.6 m of the soil profile. The increasing trend of nitrate-nitrogen concentrations after the application of urea fertiliser could be attributed to the hydrolysis of urea which is evident in the ammonium-nitrogen levels in the top soil. This is discussed in the next subsection.

4.2.2.4 Ammonium-nitrogen in unsaturated zone

The average ammonium-nitrogen concentrations from August, 2013 to January, 2014 were generally low (less than 0.50 mg/L) except for the month of November 2013 when a dose of urea was applied (Figure 4-17). In November 2013, average levels of ammonium-nitrogen were high particularly at the surface of the soil (0.3 m). A month after the application of urea, ammonium-nitrogen levels went to background concentrations in all installation depths of the ceramic porous cups. This suggests a nitrification process occurred wherein ammonium ions are oxidised to form nitrate, resulting in high concentrations of nitrate-nitrogen. The average nitrate-nitrogen concentrations at multiple depths increased a month after urea application (Figure 4-16).

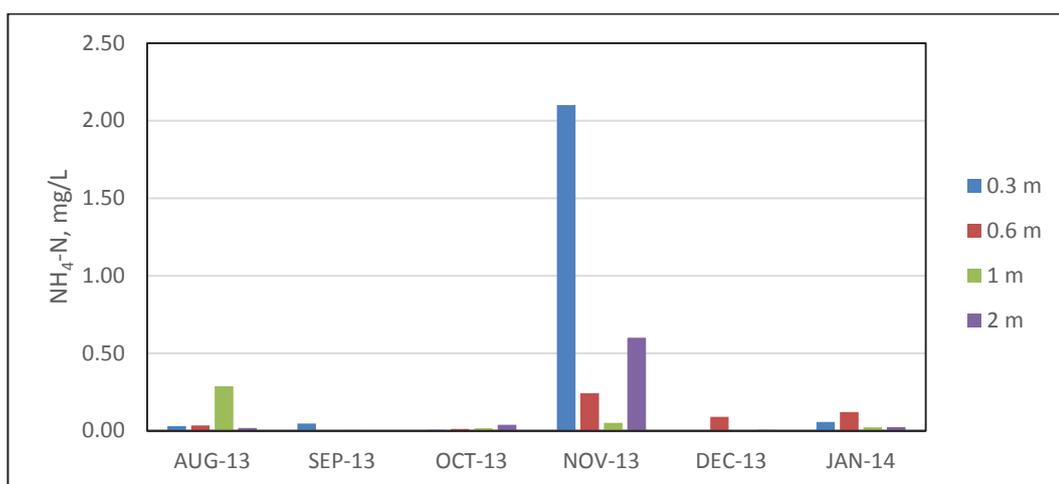


Figure 4-17. Average ammonium-nitrogen concentrations in soil-solution collected from different depths of the unsaturated zone at the experimental plot Site 1 from August, 2013, to January, 2014.

4.2.2.5 Dissolved oxygen in unsaturated zone

The dissolved oxygen (DO) levels in the soil-solution at multiple depths were measured using the handheld YSI dissolved oxygen meter (YSI, 2013a). It was difficult but efforts were made to reduce the effects of exposure to atmosphere on DO measurements in the soil solution samples. The probe of the hand-held YSI meter was dipped into the samples and stabilised for 30 seconds before taking a reading. The average DO concentrations at 0.3, 0.6, 1.0, and 2.0 m depths were generally above 5 mg/L, except for the months of October and November where DO levels dropped below 5 mg/L (Figure 4-18). The amount of rainfall received could have affected the average DO levels particularly at the soil surface, since the infiltrating water is exposed to the oxygen-rich atmosphere. In September, October, and January when high DO levels were recorded, the cumulative monthly rainfall and irrigation was above 100 mm as compared to November and December when rainfall was less than 100 mm (Figure 4-7). Although December and January were the dry months, the applied irrigation during these months contributed to the increased DO levels.

The DO levels showed a tendency to decrease as the depth increased (Figure 4-18). Soil microorganisms use oxygen (in the form of DO) as substrate to support active microbial metabolism. This is facilitated by the transfer of electrons from donors (usually organic C) to acceptors (e.g., DO, nitrate, etc.) (Jurgens et al., 2009; McMahon & Chapelle, 2008). As the levels of dissolved oxygen decrease, the next most energetically favourable substrate is nitrate (McMahon & Chapelle, 2008). Rivet, Buss, Morgan, Smith, and Bemment (2008) cited threshold values of dissolved oxygen below which denitrification activity has been observed. These values range from 0.2 to 4 mg/L. The DO concentrations were correlated with nitrate-nitrogen concentrations in the unsaturated zone (Figure 4-19). Although there were low nitrate-nitrogen concentrations corresponding with low DO levels, there appears to be no clear relationship between nitrate-nitrogen and DO levels that indicate the occurrence of denitrification in the unsaturated zone. However, this analysis of relationship between measured nitrate-nitrogen and DO levels in the soil solution may have limitations to infer occurrence or absence of denitrification in the unsaturated zone. One reason is that microsites where nitrate reduction is likely to occur may have lower intrinsic permeability and hence diffusivity to oxygen. These microsites may also be 'wetter' and this may further affect

the diffusivity of oxygen. Also, suction cups may draw water preferentially from the intrinsically more permeable and better aerated region of the soil as compared to the lower intrinsic permeability microsites where nitrate reduction is likely to occur.

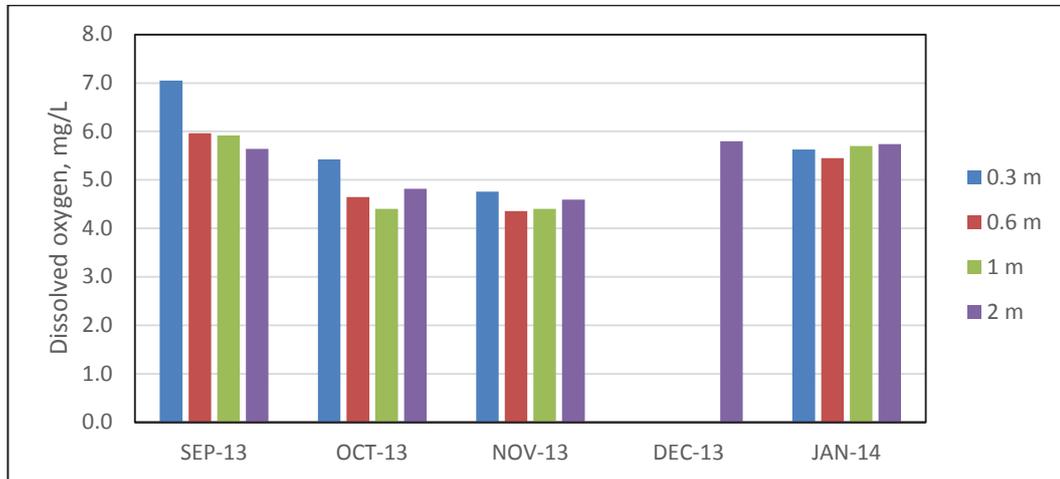


Figure 4-18. Average dissolved oxygen concentrations in soil-solution at different depths of the unsaturated zone at the experimental plot Site 1 from September, 2013, to January, 2014.

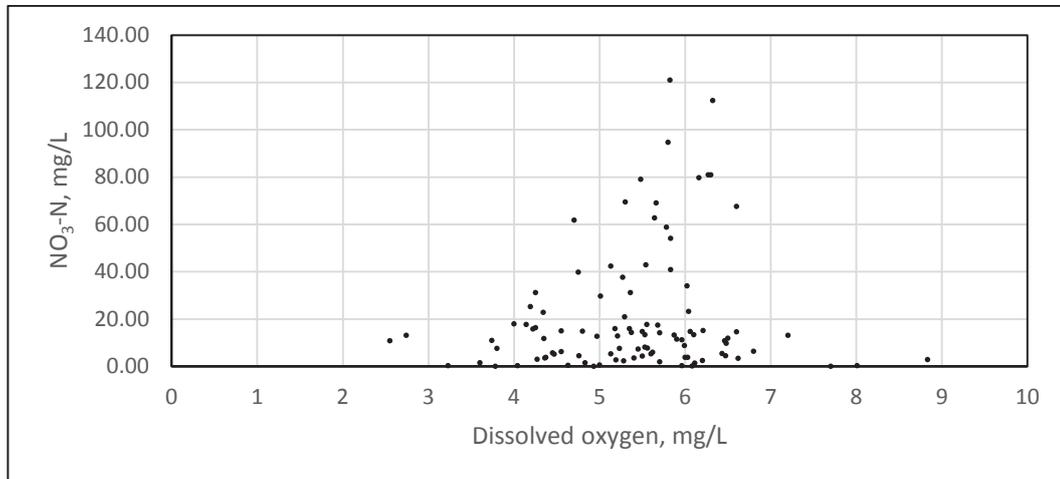


Figure 4-19. Relationship between dissolved oxygen and nitrate-nitrogen concentrations from soil-solution samples in the unsaturated zone at the experimental plot Site 1 from September, 2013, to January, 2014.

4.2.2.6 Dissolved organic carbon in unsaturated zone

The collected soil-solution samples were analysed for dissolved organic carbon (DOC) content using the digestion and titration method. The average value of DOC in the unsaturated zone was 19 mg/L, which is higher compared to 4.5 mg/L obtained from the

study by Chibnall (2013). The high DOC values could be due to the earlier deposition of urine and faeces from grazing cows and decomposition of residual plant biomass at Site 1 prior to the conduct of this study.

The DOC values were correlated with the concentrations of nitrate-nitrogen. The concentrations of nitrate-nitrogen seem to be influenced by the levels of DOC: as DOC increased, the nitrate-nitrogen decreased (Figure 4-20). The high values of DOC indicate a large pool of electron donor to nitrate ions in the unsaturated environment. Although organic fertilisers were not applied in the experimental plot, other possible carbon sources could have contributed to the high DOC concentrations. These could be from hydrologic transport processes, such as soil-solution infiltration (Kolka, Weishampel, & Fröberg, 2008). Carbon sources seem to not be a limiting factor for potential denitrification in unsaturated zones at the Site 1, rather denitrification could be limited by the recharge and diffusivity of oxygen with the drainage water.

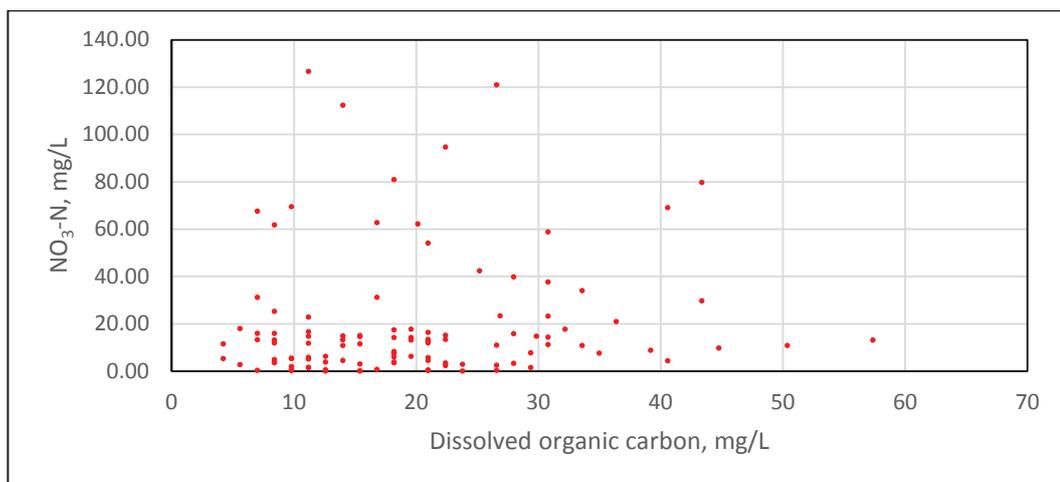


Figure 4-20. Relationship between dissolved organic carbon and nitrate-nitrogen concentrations from soil-solution samples in the unsaturated zone at the experimental plot Site 1 from August, 2013, to January, 2014.

4.2.3 Shallow groundwater monitoring

Four PVC piezometers were installed at multiple depths below ground level (5.8, 6.3, 7.4, and 8.7 m bgl) to monitor nitrate-nitrogen content in the shallow groundwater at Site 1. Other parameters measured and analysed along with the nitrate-nitrogen were: ammonium-nitrogen, dissolved oxygen, dissolved organic carbon, temperature, pH, specific conductance, and oxidation-reduction potential.

4.2.3.1 Nitrate-nitrogen in the shallow groundwater

The average nitrate-nitrogen concentrations in shallow groundwater at Site 1 were very low (<0.4 mg/L) compared to the concentrations measured in the unsaturated zone (Figure 4-12). Of the four piezometers, the shallowest one (5.8 m bgl) exhibited the highest nitrate-nitrogen concentration, followed by the second shallowest (6.3 m bgl). There seems to be no significant difference in the concentrations of nitrate-nitrogen in all four piezometers. The big difference in nitrate-nitrogen concentrations between the unsaturated and saturated zones (Figure 4-16 and Figure 4-12) indicates a high denitrification potential with depth in the shallow groundwater. This is supported by the trend of other measured parameters which is discussed in the succeeding subsections.

4.2.3.2 Ammonium-nitrogen in shallow groundwater

The ammonium-nitrogen concentrations in shallow groundwater at all depths were generally low (< 0.25 mg/L) and did not vary significantly with time and depth (Figure 4-21). The ammonium-nitrogen concentrations seem to be low compared to the nitrate-nitrogen concentrations, but slightly higher when considering background levels in groundwaters. This behaviour is expected since ammonium is less mobile than nitrate, but ammonium is also susceptible leaching from soil surface or ammonification of organic matter within the aquifer itself.

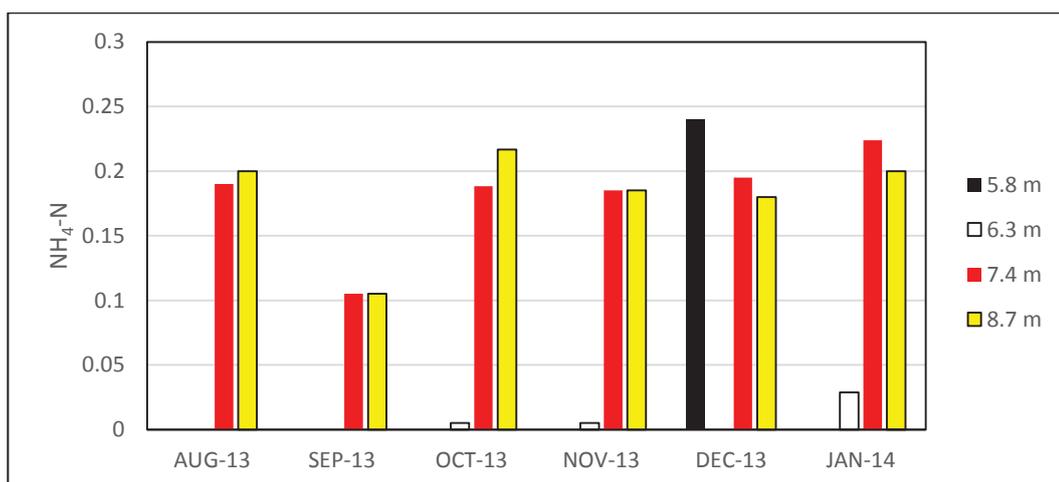


Figure 4-21. Ammonium-nitrogen concentrations in groundwater samples from different depths of the saturated zone (shallow groundwater) at the experimental plot Site 1 from August, 2013, to January, 2014.

4.2.3.3 Dissolved oxygen in shallow groundwater

The average DO levels in the shallow groundwater were less than 5 mg/L as compared to average DO concentrations measured in the unsaturated zone exceeding 5 mg/L. In the saturated zone, the higher DO levels were recorded in December and January at 5.8 m depth (Figure 4-22), suggesting a mixed oxic-anoxic groundwater conditions. Nitrate-nitrogen concentrations corresponding to DO concentrations were very low (< 0.6 mg/L), which indicates high denitrification potential in the shallow groundwater (Figure 4-23). Anaerobic environments are favourable for denitrification as nitrate is the next preferred electron acceptor after oxygen based on the ecological succession of terminal electron-accepting processes (McMahon & Chapelle, 2008). In an anoxic environment, when DO levels become very low, nitrate levels consequently become very low as well. This can be attributed to the denitrification process where nitrate is reduced to nitrous oxide and eventually to nitrogen gas. Varying threshold levels of dissolved oxygen for denitrification to happen were reported by Rivett et al. (2008). As mentioned in the previous sections, these values range from 0.2 to 4 mg/L of dissolved oxygen. The measured DO concentrations in the saturated zone (Figure 4-22) are well within this range, and the occurrence of denitrification is very likely to happen. This is consistent with slightly elevated levels of ammonium-nitrogen concentrations observed in the shallow groundwater, indicating occurrence of reduced groundwater conditions (Figure 4-21).

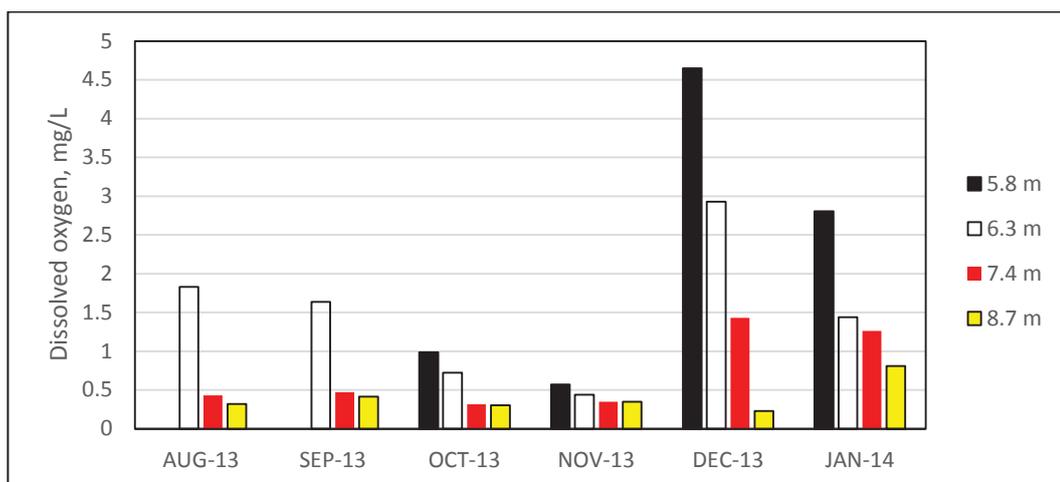


Figure 4-22. Average dissolved oxygen concentrations in groundwater samples from different depths of the saturated zone (shallow groundwater) at the experimental plot Site 1 from August, 2013, to January, 2014.

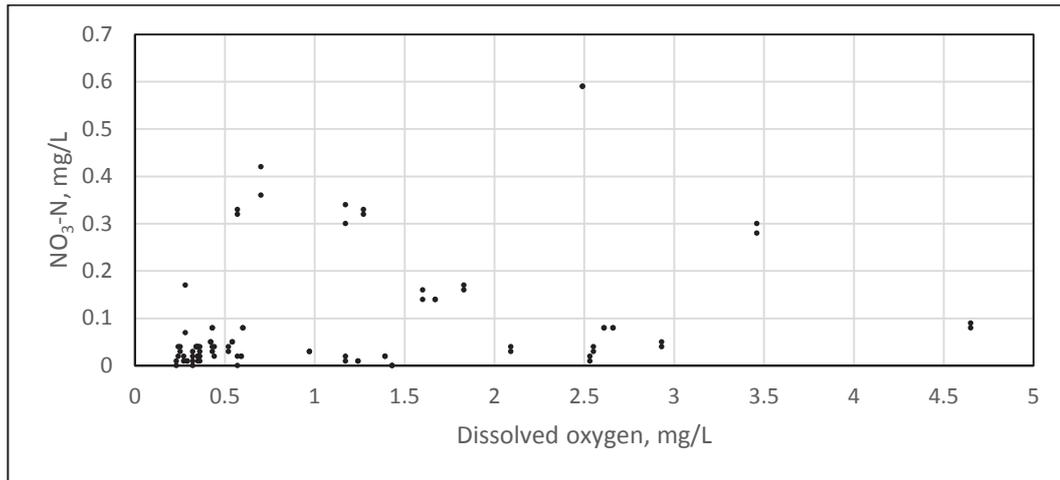


Figure 4-23. Relationship between dissolved oxygen and nitrate-nitrogen concentrations in shallow groundwater samples at the experimental plot Site 1 from August, 2013, to January, 2014.

4.2.3.4 Temperature of shallow groundwater

The average temperature of shallow groundwater samples ranged from 14 – 17 °C during the study period (Figure 4-24). The average temperature in the shallowest piezometer was slightly higher than the rest, especially in the warm months (October to January), probably because of the influence of the ambient air temperature. From August to December, the trend in temperature was increasing for all piezometers as in the case of mean air temperature (Figure 4-6). However, there was no significant difference observed in the monthly average temperature at various depths of the shallow groundwater (Figure 4-24).

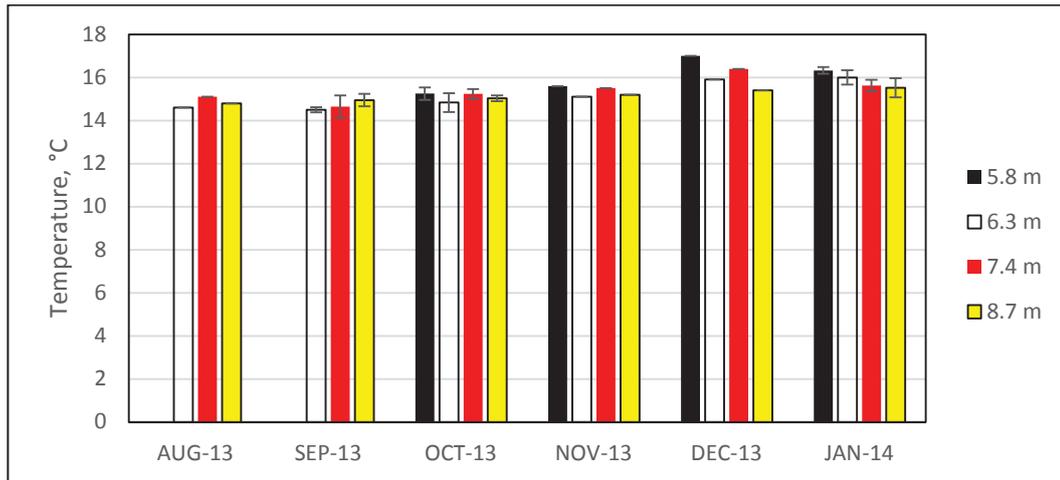


Figure 4-24. Average temperature in groundwater samples from different depths of the saturated zone (shallow groundwater) at the experimental plot Site 1 from August, 2013, to January, 2014. Error bars are based on standard deviation.

4.2.3.5 pH of shallow groundwater

The average pH values of shallow groundwater samples at various depths were almost the same and have no significant difference with time (Figure 4-25). The deeper piezometers have slightly higher pH values than the shallower piezometers. According to Rust, Aelion, and Flora (2000), the pH preferred by heterotrophic denitrifiers ranges between 5.5 and 8.0. Heterotrophic soil microorganisms cannot fix elemental or atmospheric carbon and, therefore, use organic carbon as an alternative. Outside this pH range, the denitrification process could be hindered (Rust et al., 2000). The measured average pH in shallow groundwater samples at Site 1 was well within the suggested pH range for denitrification to occur.

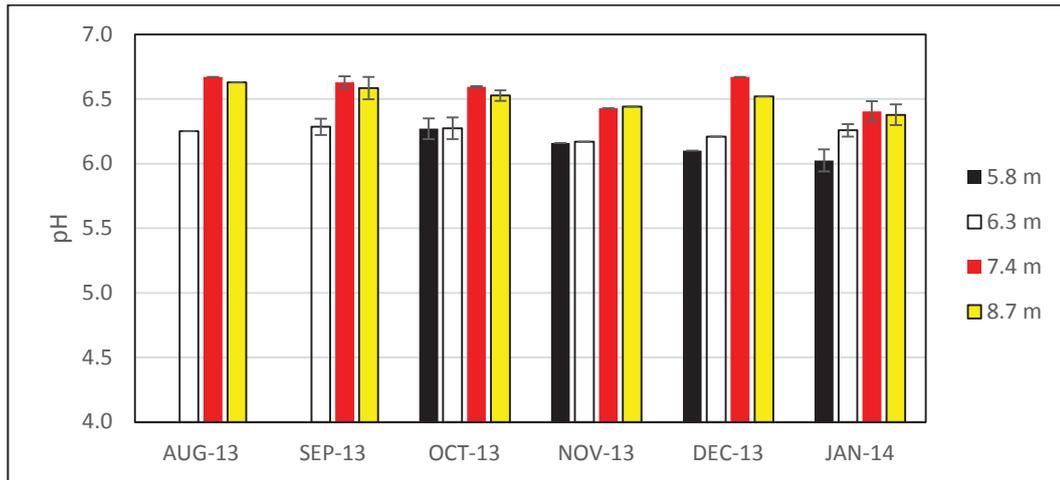


Figure 4-25. Average pH in groundwater samples from different depths of the saturated zone (shallow groundwater) at the experimental plot Site 1 from August, 2013, to January, 2014. Error bars are based on standard deviation.

4.2.3.6 Specific conductance of shallow groundwater

The average specific conductance (also termed as electrical conductivity, EC) measured at multiple depths of the shallow groundwater at Site 1 behaved similar to the pH. The deeper piezometers (7.4 and 8.7 m bgl) have slightly higher conductivity values than the shallower ones (5.8 and 6.3 m bgl) (Figure 4-26). The measured values of EC were almost the same with time at various depths. Few groundwater monitoring sites within the Manawatu-Wanganui region have been reported to have EC values exceeding the ANZECC 2000 guidelines for irrigation water, which is 60 mS/m for sensitive crops in poorly drained soils and 1280 mS/m for more tolerant crops in well-drained soils (Daughney et al., 2009). In the case of the shallow groundwater at Site 1, the measured values of EC ranged from 25 – 30 mS/m and did not exceed the ANZECC 2000 guidelines. The groundwater monitoring sites in the Manawatu-Wanganui region which exceeded the ANZECC 2000 guidelines may be influenced by upward-moving groundwater from a basement fault (Daughney et al., 2009). This indicates that the groundwater at Site 1, particularly the deeper ones (7.4 and 8.7 m bgl), could also be influenced by the upward movement or perhaps the horizontal movement of groundwater from nearby areas.

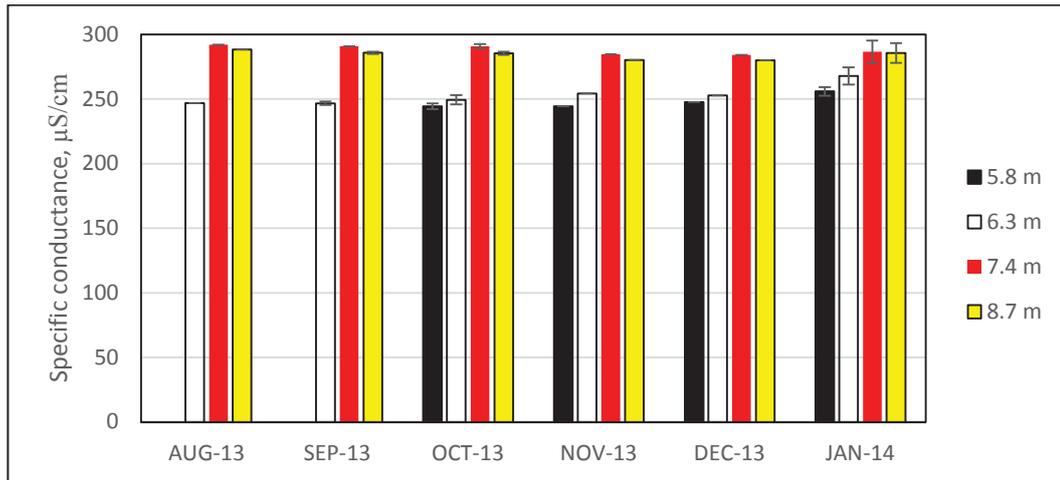


Figure 4-26. Average specific conductance in groundwater samples from different depths of the saturated zone (shallow groundwater) at the experimental plot 'Site1' from August, 2013, to January, 2014. Error bars are based on standard deviation.

4.2.3.7 Oxidation-reduction potential in shallow groundwater

The oxidation-reduction potential (*ORP*) values measured in the shallow groundwater were less than 150 mV (Figure 4-27). The shallower piezometers (5.8 and 6.3 m bgl) had positive *ORP* values, indicating an oxidising environment, while the deeper piezometers (7.4 and 8.7 m bgl) had negative *ORP* values indicating a reducing environment. The shallower piezometers (5.8 and 6.3 m bgl) had positive *ORP* values as they are the immediate recipients of oxygen-rich rainfall recharge water. Recently recharged aquifers usually have high *ORP* values (Daughney et al., 2009). A reducing groundwater environment has the potential to attenuate nitrate and is favourable for the denitrification process. Although threshold levels of *ORP* values for denitrification to occur vary from one groundwater to another, Rivett et al. (2008) reported a threshold level of +231 mV for the denitrification to take place in the groundwater. The measured *ORP* values in shallow groundwater at Site 1 were below the threshold level and supported by other measurements such as pH and DO levels which indicate a suitable environment for the denitrification process in the shallow groundwater.

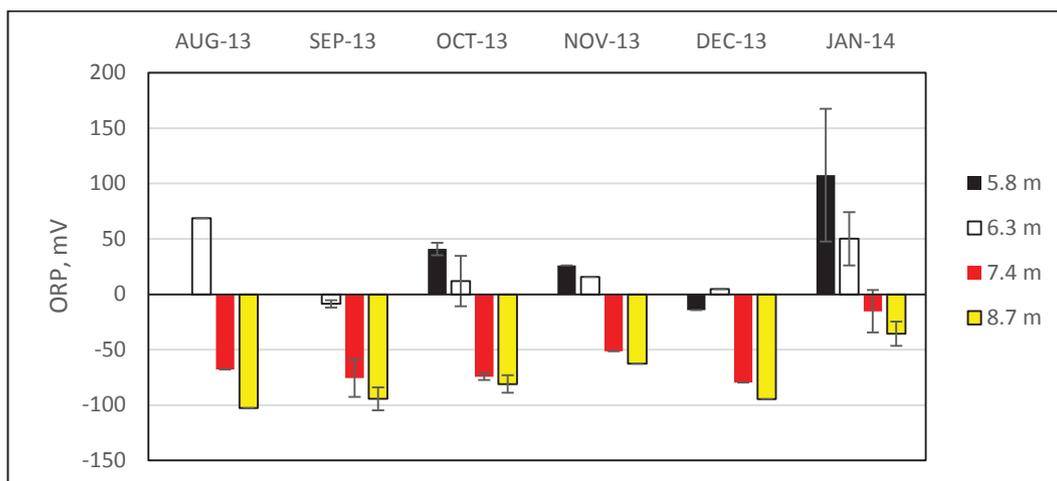


Figure 4-27. Average oxidation-reduction potential in groundwater samples from different depths of the saturated zone (shallow groundwater) at the experimental plot Site 1 from August, 2013, to January, 2014. Error bars are based on standard deviation.

4.3 Assessment of reduction-oxidation (redox) conditions in the shallow and deep groundwaters

This section presents and discusses the data used from a large data base of water quality parameters to assess the redox conditions in the shallow and deep groundwaters sampled at both sites, Site 1 and Site 2.

4.3.1 Groundwater quality monitoring in Site 1 and Site 2

Nitrate-nitrogen, dissolved oxygen, iron, manganese, and sulphate were the parameters used to determine groundwater redox conditions at the Massey Dairy Farm No. 1 ‘Site 1’ and the Te Matai Road ‘Site 2’. These two sites are within the Manawatu River catchment (Figure 3-1). Four piezometers at Site 1 and six piezometers at Site 2 were sampled on a fortnightly basis from August, 2013 to January, 2014. The collected samples were analysed for nitrate-nitrogen and dissolved oxygen content. To assess the redox conditions of the groundwater at these sites, three additional parameters were required: iron, manganese, and sulphate. These parameters, however, were not monitored or measured in both sites. The data on the concentrations of dissolved iron (Fe^{2+}), manganese (Mn^{2+}), and sulphate (SO_4^{2-}) were obtained from historical observations in 647 wells distributed in the Manawatu catchment (Figure 4-28) over the period from 1958 to 2007. These data can be found in the report of Daughney et al. (2009). Since the measurement of nitrate-nitrogen and dissolved oxygen in Sites 1 and 2

were done in the months of August, 2013, to January 2014, the historical monthly average concentrations of dissolved iron, manganese, and sulphate of 647 wells in the Manawatu River catchment during these same months were also selected and utilised.

The historical average concentrations of dissolved iron, manganese, and sulphate in 647 groundwater monitoring wells in the Manawatu River Catchment for the months of August to January, 1958-2007, are shown in Figure 4-29 to Figure 4-35. The majority of the wells were deep (> 18 m), up to a maximum depth of 377 m. Based on the temporal distribution of iron (Fe^{2+}), manganese (Mn^{2+}), and sulphate (SO_4^{2-}), it appears that sulphate had the highest concentration in all months followed by iron and manganese (Figure 4-35). The trend in monthly average sulphate concentrations decreased from wet to drier months. This could indicate deposition and leaching of sulphur through rainfall which influenced the elevated sulphate levels in the groundwater. Areas near the west coast also receive more sulphur from rainfall than those areas in the east coast (Figure 4-36). This could have contributed to the elevated levels of sulphate in the Manawatu River catchment since it is geographically located near the west coast of the lower North Island. The intermittent eruptions of Mt. Ruapehu could also have added elemental S in ashfall (FLRC, 2009). Some groundwater monitoring reports conducted in the Manawatu River catchment, on the other hand, attributed the elevated levels of sulphate from the leaching of applied inorganic fertilisers (Zarour, 2008). Inorganic sulphate is leached along with nitrate since it is not strongly adsorbed by most New Zealand soils. In areas of intensive landuse sulphate leaching from inorganic fertilisers could be large and dominate sulphate levels in shallow groundwaters.

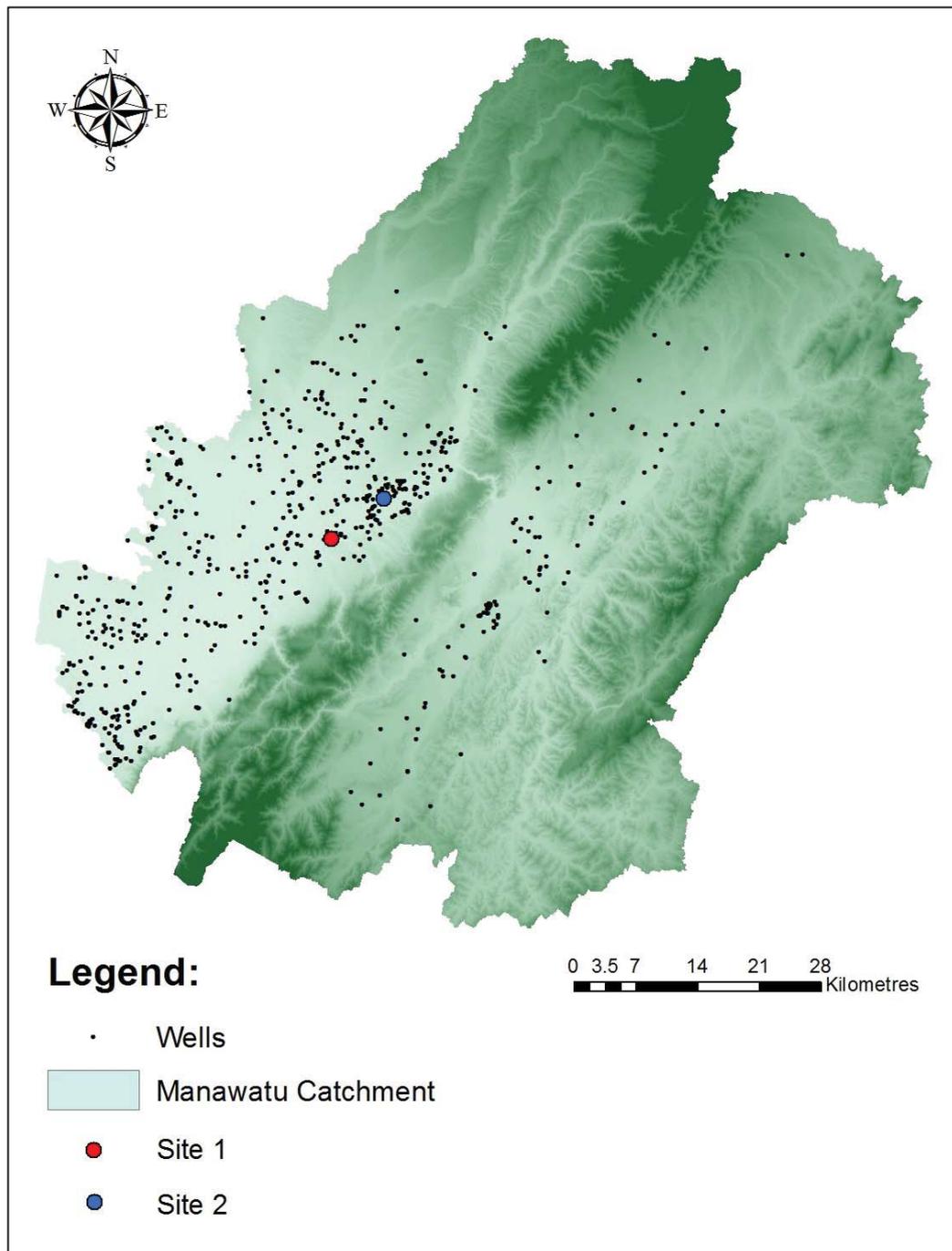


Figure 4-28. Well distribution in the Manawatu River catchment.

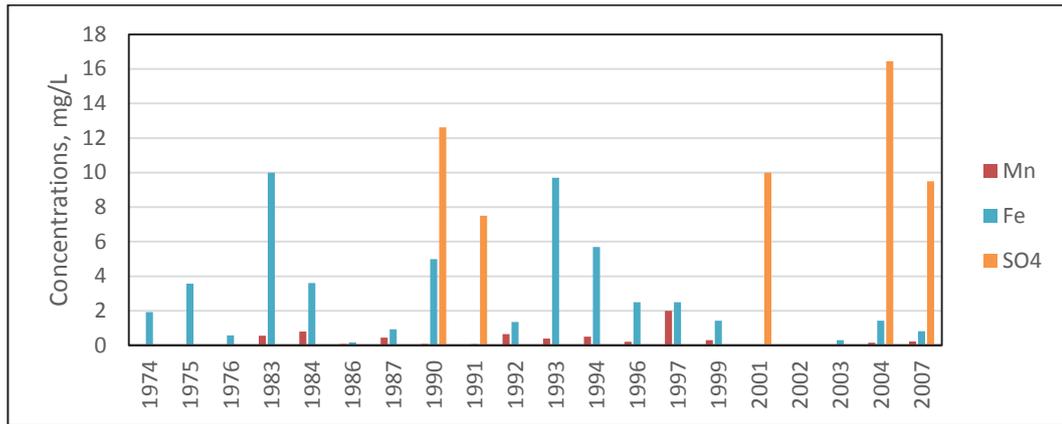


Figure 4-29. Historical average concentrations of dissolved Mn^{2+} , Fe^{2+} , and SO_4^{2-} in 647 groundwater monitoring wells in Manawatu River Catchment for the month of January, 1974-2007.

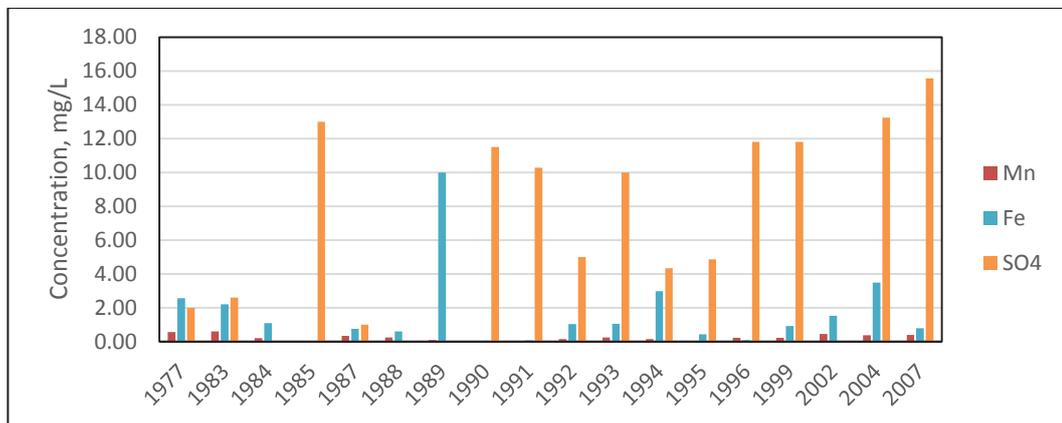


Figure 4-30. Historical average concentrations of dissolved Mn^{2+} , Fe^{2+} , and SO_4^{2-} in 647 groundwater monitoring wells in Manawatu River Catchment for the month of August, 1977-2007.

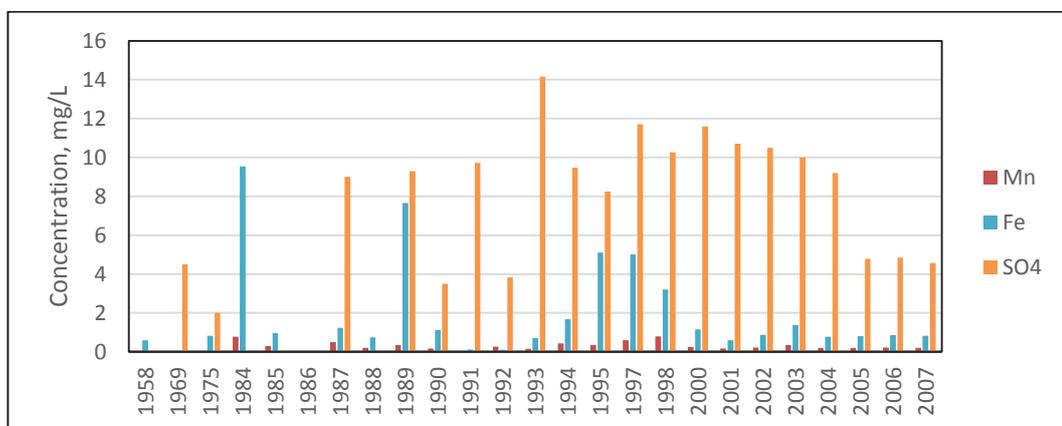


Figure 4-31. Historical average concentrations of dissolved Mn^{2+} , Fe^{2+} , and SO_4^{2-} in 647 groundwater monitoring wells in Manawatu River Catchment for the month of September, 1958-2007.

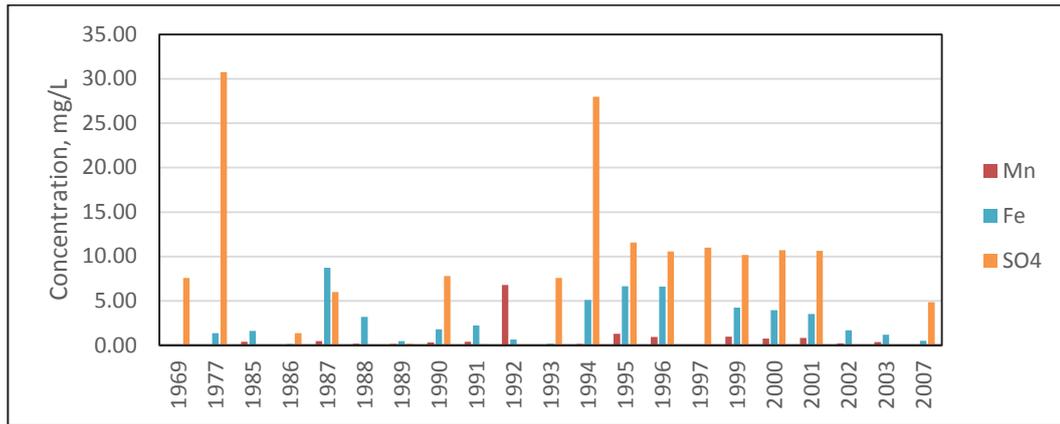


Figure 4-32. Historical average concentrations of dissolved Mn²⁺, Fe²⁺, and SO₄²⁻ in 647 groundwater monitoring wells in Manawatu River Catchment for the month of October, 1969-2007.

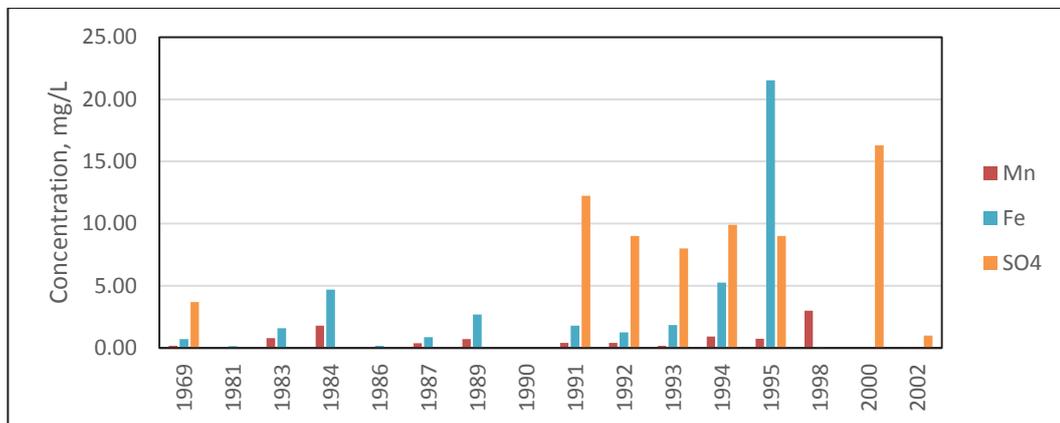


Figure 4-33. Historical average concentrations of dissolved Mn²⁺, Fe²⁺, and SO₄²⁻ in 647 groundwater monitoring wells in Manawatu River Catchment for the month of November, 1969-2007.

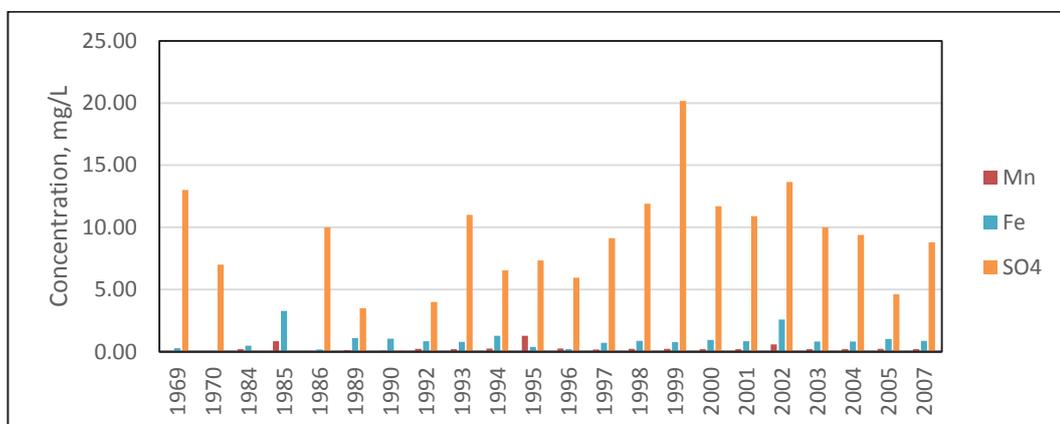


Figure 4-34. Historical average concentrations of dissolved Mn²⁺, Fe²⁺, and SO₄²⁻ in 647 groundwater monitoring wells in Manawatu River Catchment for the month of December, 1969-2007.

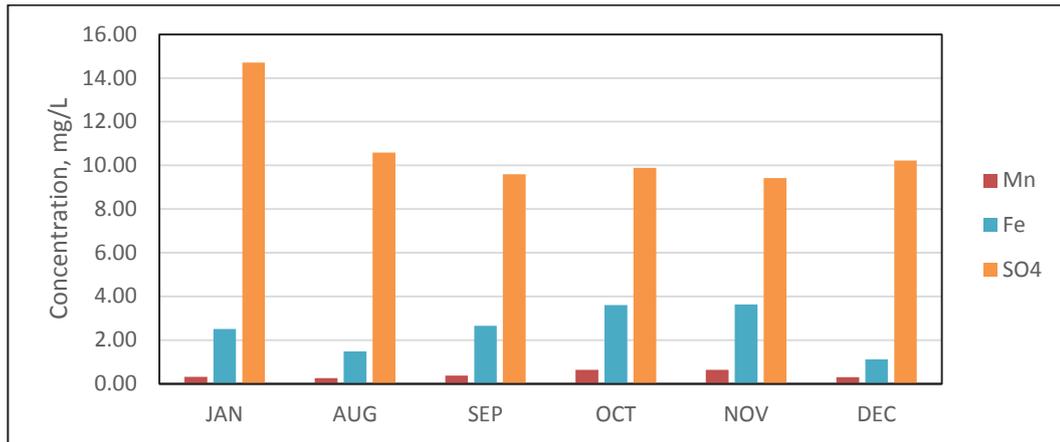


Figure 4-35. Historical average concentrations of dissolved Mn^{2+} , Fe^{2+} , and SO_4^{2-} in 647 groundwater monitoring wells in Manawatu River Catchment for the months of August to January, 1958-2007.

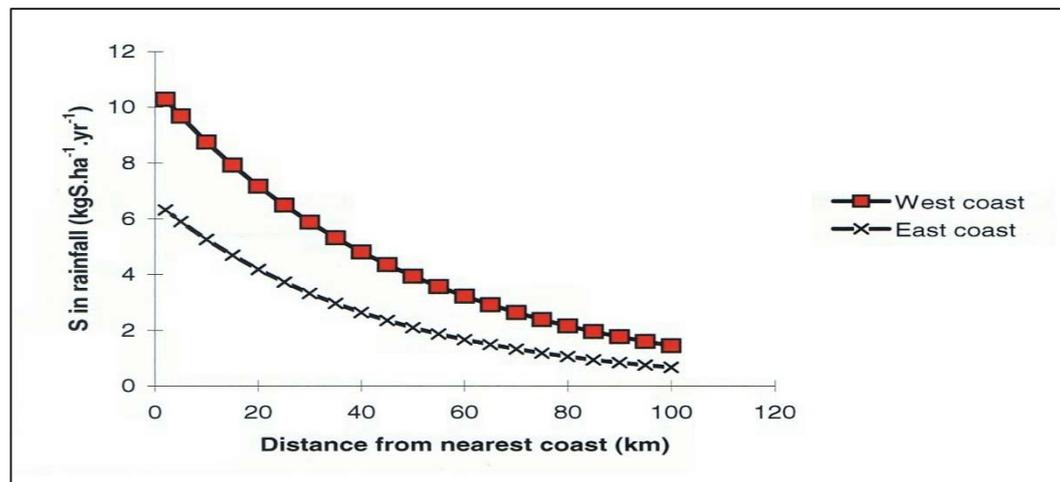


Figure 4-36. The influence of distance from coast on amounts of sulphur in rainfall in New Zealand (adapted from FLRC, 2009).

4.3.2 Assessment of redox conditions

An excel workbook created by Jurgens et al. (2009) was used to assess the redox processes in the groundwaters measured at both sites Site 1 and Site 2. The excel programme is based on the redox framework devised by McMahon and Chapelle (2008) and extended by Chapelle, Bradley, Thomas, and McMahon (2009). From the water-quality data, the redox state of the groundwater sample can be defined by the redox reaction or process occurring in the sample. There are basically four redox categories used in the excel workbook, which are oxic, suboxic, anoxic, and mixed. Each of these redox categories has threshold values for nitrate-nitrogen, DO, manganese, iron, and

sulphate. Depending on the concentrations of these parameters, a redox process can be assigned. If carbon sources are not a limiting factor, the predominant electron acceptor in the groundwater would follow the ecological succession from DO, to nitrate, to manganese, to iron and then to sulphate (Jurgens et al., 2009).

An oxic groundwater environment has levels of dissolved oxygen of at least or greater than 0.5 mg/L where oxygen as DO is principal electron acceptor. The suboxic groundwater environment has the DO and nitrate-nitrogen levels of less than 0.5 mg/L. The anoxic groundwater environment, on the other hand, has several redox processes, depending on the levels of nitrate-nitrogen, manganese, iron, and sulphate but commonly having DO levels of below 0.5 mg/L. The mixed redox category is a combination of the oxic and anoxic environment. Table 4-3 summarises the redox categories and processes, and the threshold values of the electron acceptors.

Table 4-3

Criteria and threshold concentrations for identifying redox processes in groundwater.

Redox category	Redox process	Threshold values, mg/L				
		DO	NO ₃ -N	Mn	Fe	SO ₄ ²⁻
Oxic	O ₂	≥0.5	—	<0.05	<0.1	—
Suboxic	Suboxic	<0.5	<0.5	<0.05	<0.1	—
Anoxic	NO ₃	<0.5	≥0.5	<0.05	<0.1	—
Anoxic	Mn(IV)	<0.5	<0.5	≥0.05	<0.1	—
Anoxic	Fe(III)	<0.5	<0.5	—	≥0.1	≥0.5
Anoxic	Fe(III)/SO ₄	<0.5	<0.5	—	≥0.1	≥0.5
Anoxic	SO ₄	<0.5	<0.5	—	≥0.1	≥0.5
Anoxic	CH ₄ gen	<0.5	<0.5	—	≥0.1	<0.5

At Site 1, the shallower piezometers (5.8 and 6.3 m bgl) have a mixed oxic-anoxic (O₂-Fe(III)/SO₄) redox condition, while the deeper piezometers (7.4 and 8.7 m bgl) generally have an anoxic (Fe(III)/SO₄) redox condition (Table 4-4). The same results were obtained at Site 2. The shallower wells (12 and 18 m bgl) have a mixed oxic-anoxic (O₂-Fe(III)/SO₄) groundwater environment, and the deeper wells tend to have a more anoxic (Fe(III)/SO₄) groundwater environment (Table 4-5). This trend could be due to the fluctuating DO concentrations brought about by rainfall recharge events or atmospheric pumping of oxygen under high pressure systems. The groundwater in the shallow aquifers often has high DO levels since it is recently recharged while deep

aquifers have old groundwater and have very low DO concentrations (Daughney et al., 2009). At Site 2, the intermediate wells (33 and 51 m bgl) had interchanging mixed oxic-anoxic (O₂-Fe(III)/SO₄) and anoxic (Fe(III)/SO₄) redox conditions. This is because the levels of nitrate-nitrogen were only high in the shallow well but were very low (<0.5 mg/L) in all the rest of the wells (Figure 4-37), and the concentrations of DO in the intermediate wells were the next highest after the shallower wells (Figure 4-38).

Table 4-4

Groundwater redox category and process at Massey Dairy Farm No. 1 Site 1.

Depth, m	AUG-13	SEP-13	OCT-13	NOV-13	DEC-13	JAN-14
5.8	—	—	M	M	M	M
6.3	M	M	M	A	M	M
7.4	A	A	A	A	M	M
8.7	A	A	A	A	A	M

Note: **M** – Mixed (oxic-anoxic) O₂-Fe(III)/SO₄, **A** – Anoxic, Fe(III)/SO₄

Table 4-5

Groundwater redox category and process at the Te Matai Rd Site 2.

Depth, m	SEP-13	OCT-13	NOV-13	DEC-13
12	M	M	M	M
18	M	M	M	M
33	M	A	A	M
51	A	M	M	M
66	A	A	A	A
87	A	A	A	A

Note: **M** – Mixed (oxic-anoxic) O₂-Fe(III)/SO₄, **A** – Anoxic, Fe(III)/SO₄

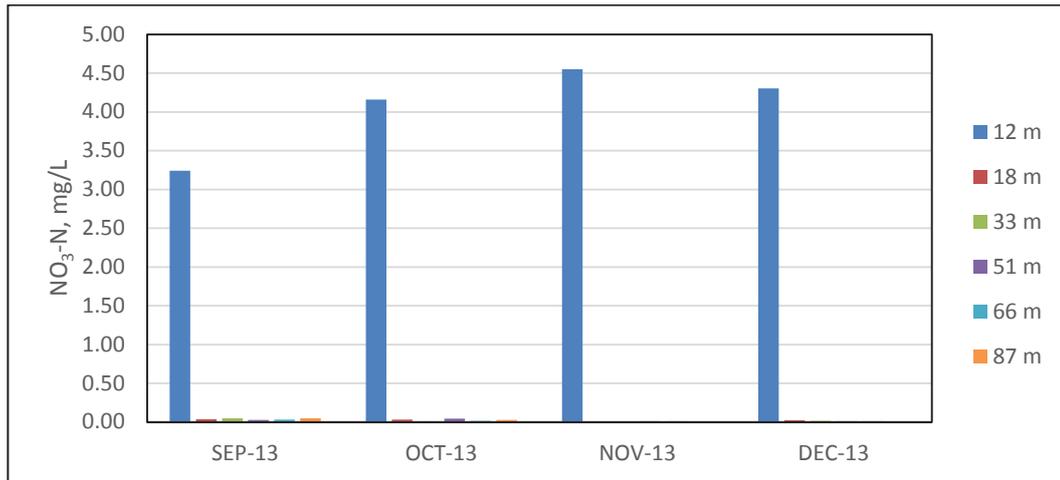


Figure 4-37. Average nitrate-nitrogen concentrations in groundwater samples from different depths at the Te Matai Road Site 2.

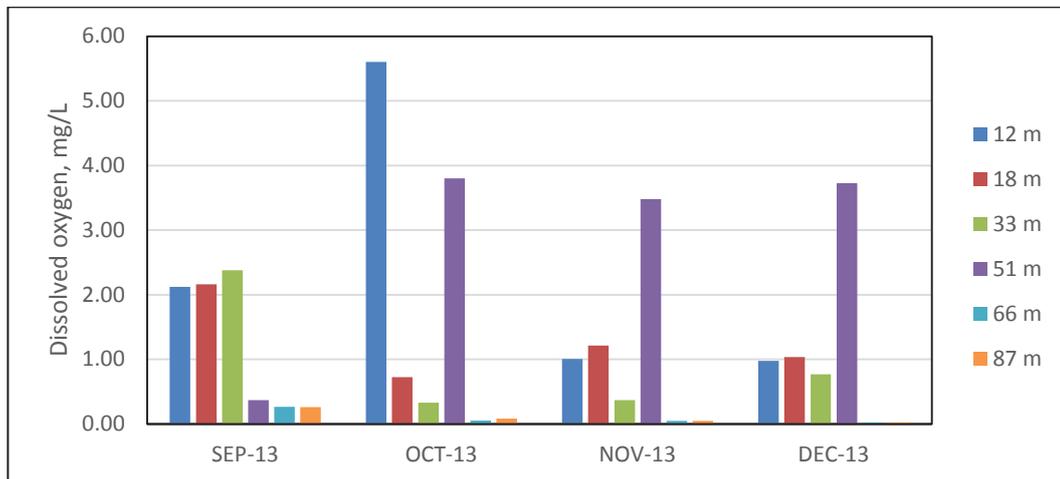


Figure 4-38. Average dissolved oxygen concentrations in the groundwater samples from different depths at the Te Matai Road Site 2.

Based on the results, there was no anoxic redox category that was influenced or dominated by nitrate-nitrogen (i.e. Anoxic, NO_3). This is because the concentrations of nitrate-nitrogen were very low (<0.5 mg/L) even in the shallow groundwater (Figure 4-12 and Figure 4-37), while the levels of DO fluctuated with the depth (Figure 4-22 and Figure 4-38). The threshold levels of DO for denitrification to occur is about 0.2 to 0.3 mg/L (Seitzinger et al., 2006) and 2 mg/L in some aquifers (McMahon, Böhlke, & Christenson, 2004; Rivett et al., 2008). The anoxic (Fe(III)/ SO_4) condition is dominant in the groundwaters at both Site 1 and Site 2, primarily because of the elevated sulphate content, followed by iron. These results support other observations and findings in this

study that there is a high denitrification potential at Site 1 and Site 2. It could also be inferred from the results of the redox categorisation and redox processes identification using collected and historical water-quality data that the groundwater at Sites 1 and 2 has a favourable environment for denitrification.

Chapter 5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Main findings

The overall goal of this thesis was to assess the transport and transformation of nitrogen as it leaves the root zone and ends up in the saturated zone by using field measurements, a tracer test, and redox categorisation. An experimental plot was set-up at Massey Dairy Farm No. 1 Site 1 where 12 ceramic porous cups and four piezometers were installed to extract soil-water and groundwater samples. Based on the field measurements of nitrate-nitrogen concentrations using ceramic porous cups and piezometers at Massey Dairy Farm No.1 Site 1, the average nitrate-nitrogen concentrations in the unsaturated zone from 0.3 to 2.0 m depth bgl reached up to a maximum concentration of 47 mg/L in August, 2013. It continued to decrease due to the limited source of N input and continuous plant N uptake in the experimental plot at the site. After the application of urea and bromide in November, 2013, the average concentrations of nitrate-nitrogen began to increase until January, 2014. The highest average concentration of nitrate-nitrogen after urea application was 53.22 mg/L at 30 cm depth. The average dissolved oxygen (DO) concentrations were measured as high as 7.0 mg/L in the unsaturated zone. There were no denitrification measurements conducted in the unsaturated zone, but it can be inferred from the measured DO concentrations that there is a limited or low denitrification activity since levels of nitrate-nitrogen and DO do not clearly correspond with each other. In the saturated zone (5.8 to 8.7 m bgl), the average nitrate-nitrogen and DO concentrations reached a maximum of 0.36 mg/L (October, 2013) and 4.65 mg/L (December, 2013), respectively. The measured concentrations of DO and nitrate-nitrogen exhibited a decreasing trend with increase in piezometer depth, which suggested denitrification potential increasing with the depth at Site 1.

A dose of urea ($\text{CO}(\text{NH}_2)_2$) and potassium bromide (KBr) was applied at the rate of 1000 kg/ha (466.7 kg N/ha) and 307.14 kg/ha (206.23 kg Br/ha), respectively, by means of a synthetic urine for the tracer test. The conducted bromide tracer test showed that in a typical situation, preferential flow paths exist and cannot be avoided. This was evident in the appearance of bromide at the 30 cm depth ceramic porous cup two days after

application of potassium bromide. Bromide reached the 2-m depth porous cup after applying a total cumulative irrigation depth of 478 mm after two months. However, no appearance of bromide was observed in the shallow groundwater, indicating it has not yet reached the saturated zone. Using only the total excess rainfall amounts in winter, spring, and autumn for 2013 (total of 139 mm/yr) and approximated travel rate of 0.65 cm/mm, the bromide travel time is estimated to be about 2.2 years to reach the 2 m depth porous cups and 5.1 years to reach the 4.6 m shallow groundwater level at Massey Dairy Farm No. 1 Site 1.

Groundwater quality monitoring was conducted at the two sites, Site 1 and Site 2, using installed piezometers and groundwater bores. At Site 2, the groundwater bores sampled were managed by the HRC. The groundwater quality data on nitrate-nitrogen, dissolved oxygen, manganese, iron, and sulphate which were obtained from 647 wells in the Manawatu River catchment area, including the four piezometers at Site 1 and six piezometers at Site 2, indicated mixed oxic-anoxic (O₂-Fe(III)/SO₄) conditions in groundwater depths of 5.8 to 51 m due to fluctuating levels of DO and nitrate-nitrogen. For deeper groundwater at Site 2 (> 51 m depth), anoxic (Fe(III)/SO₄) conditions existed dominated by high concentrations of dissolved iron (1.12 – 3.63 mg/L) and sulphate (9.43 – 14.71 mg/L). Based on the groundwater quality data, redox categorisation, and process identification, it can be inferred that the groundwater at the study sites has a favourable environment for denitrification.

5.2 Recommendations

The use of ceramic porous cups and piezometers were satisfactory and economical in estimating point concentrations of solute at a certain depth in the unsaturated and saturated zones. If financial sources do not limit installation of many porous cups and piezometers in a study area, it is recommended to install as many numbers of ceramic porous cups and piezometers as possible to increase the coverage of the sampling area.

For the tracer test, it is recommended to conduct the tracer test for a longer period, depending on the desired monitoring depth. In this study, the tracer test was only conducted for three months. After three months, the bromide was only observed at the 2-m depth of the soil profile but did not appear in the groundwater. It is recommended,

therefore, that the monitoring of bromide at Site 1 be continued to further check its transport and transformation, along with nitrate, in the subsurface.

The major findings of this study were that denitrification appears to be playing a vital role in the attenuation of nitrate-nitrogen in the saturated zone. This observation was supported by actual field measurements and redox categorisation. This study, on the other hand, did not conduct field measurements of the denitrification process. It is therefore recommended that future researches on the transport and transformation of nitrogen should focus on the field measurements of the denitrification process in the groundwater and even in the intermediate-vadose zone. This is one step in determining the capability of a particular catchment to 'eliminate' nitrogen as a potential contaminant in the groundwater. It will give an idea how much leached nitrogen below the root zone can be attenuated prior to its entrance in the groundwater. I would also recommend inclusion of a model to validate and complement the field measurements.

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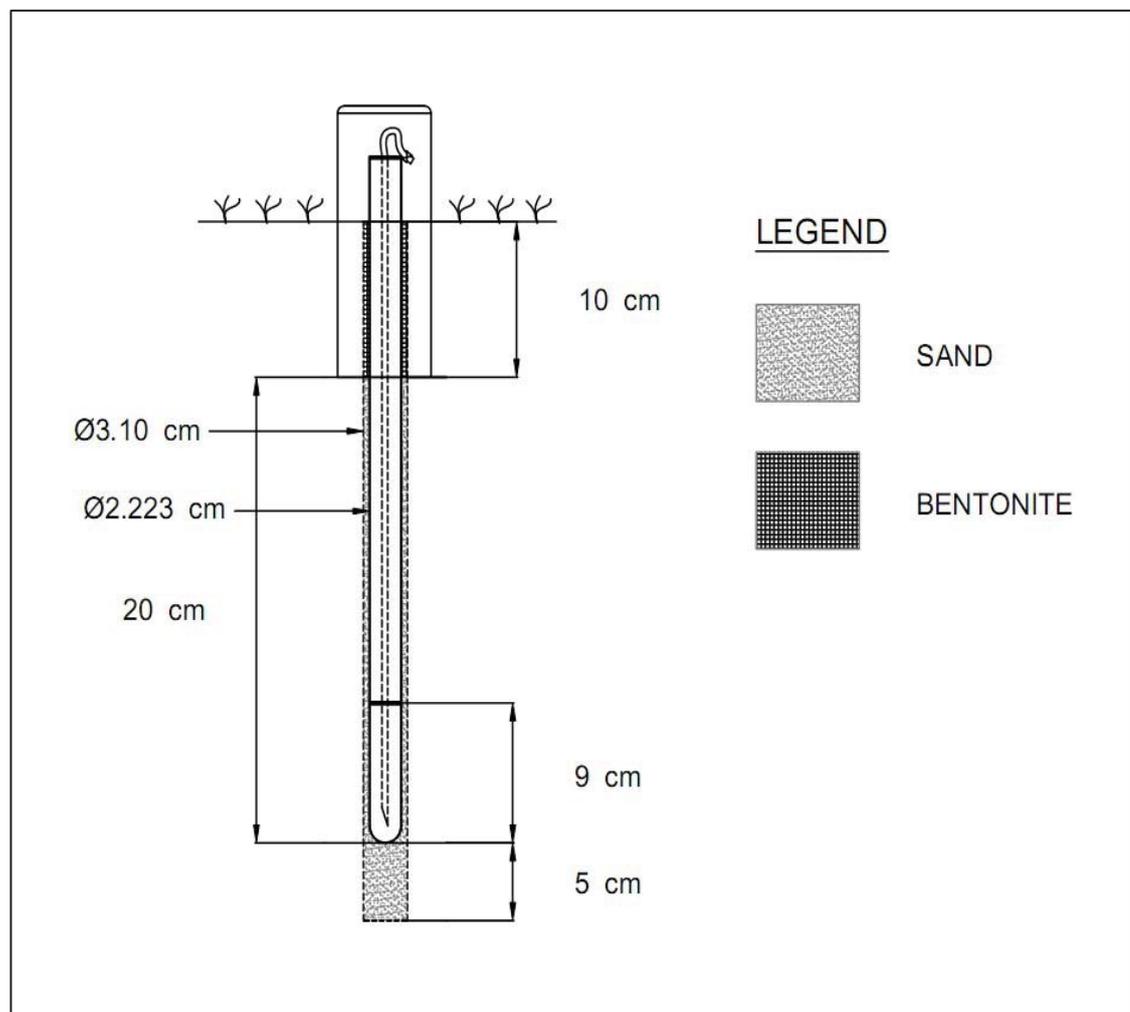
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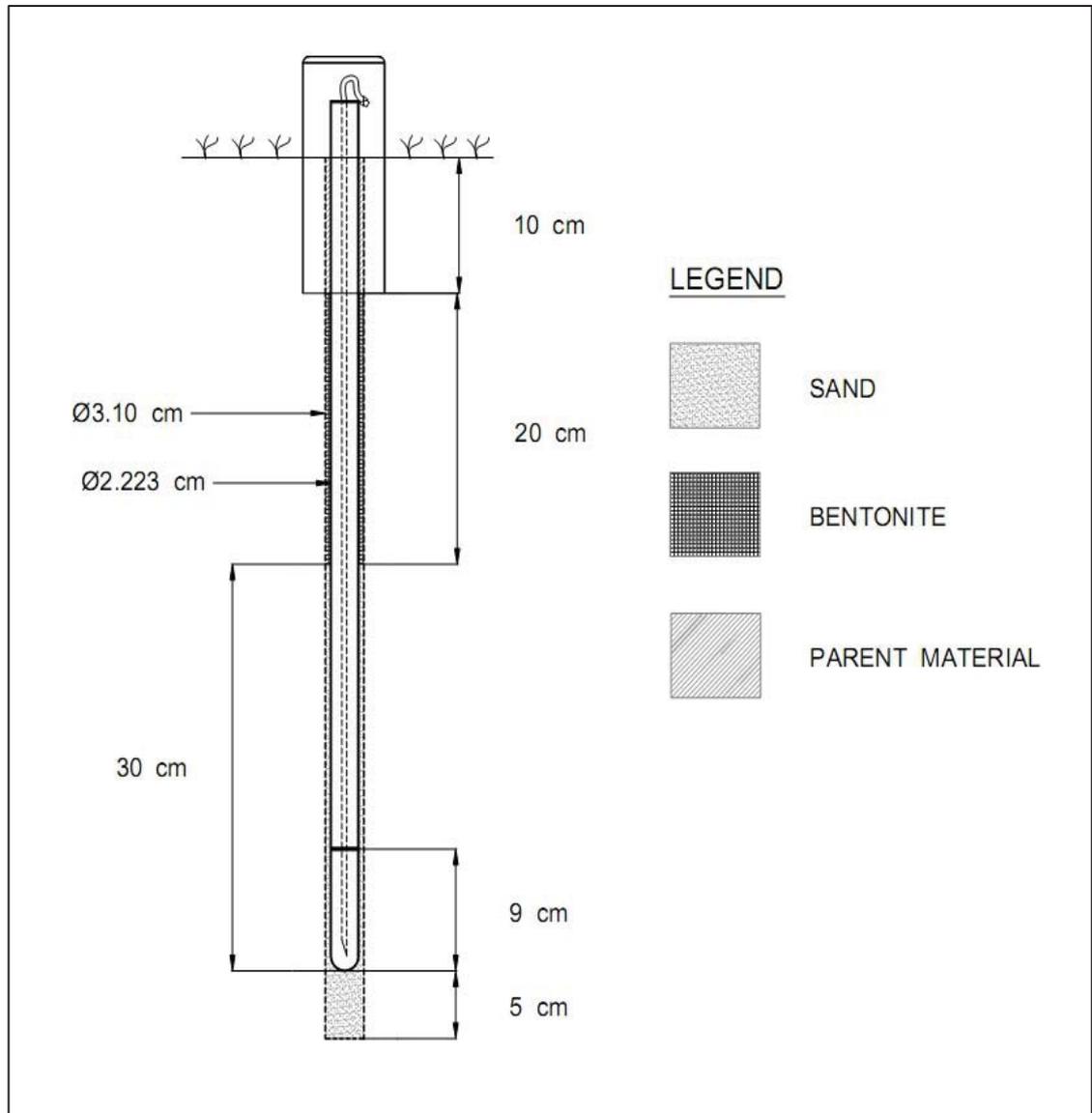
Appendices

Appendix A: Installation profiles of ceramic porous cups and piezometers at Massey Dairy Farm No. 1 Site 1.

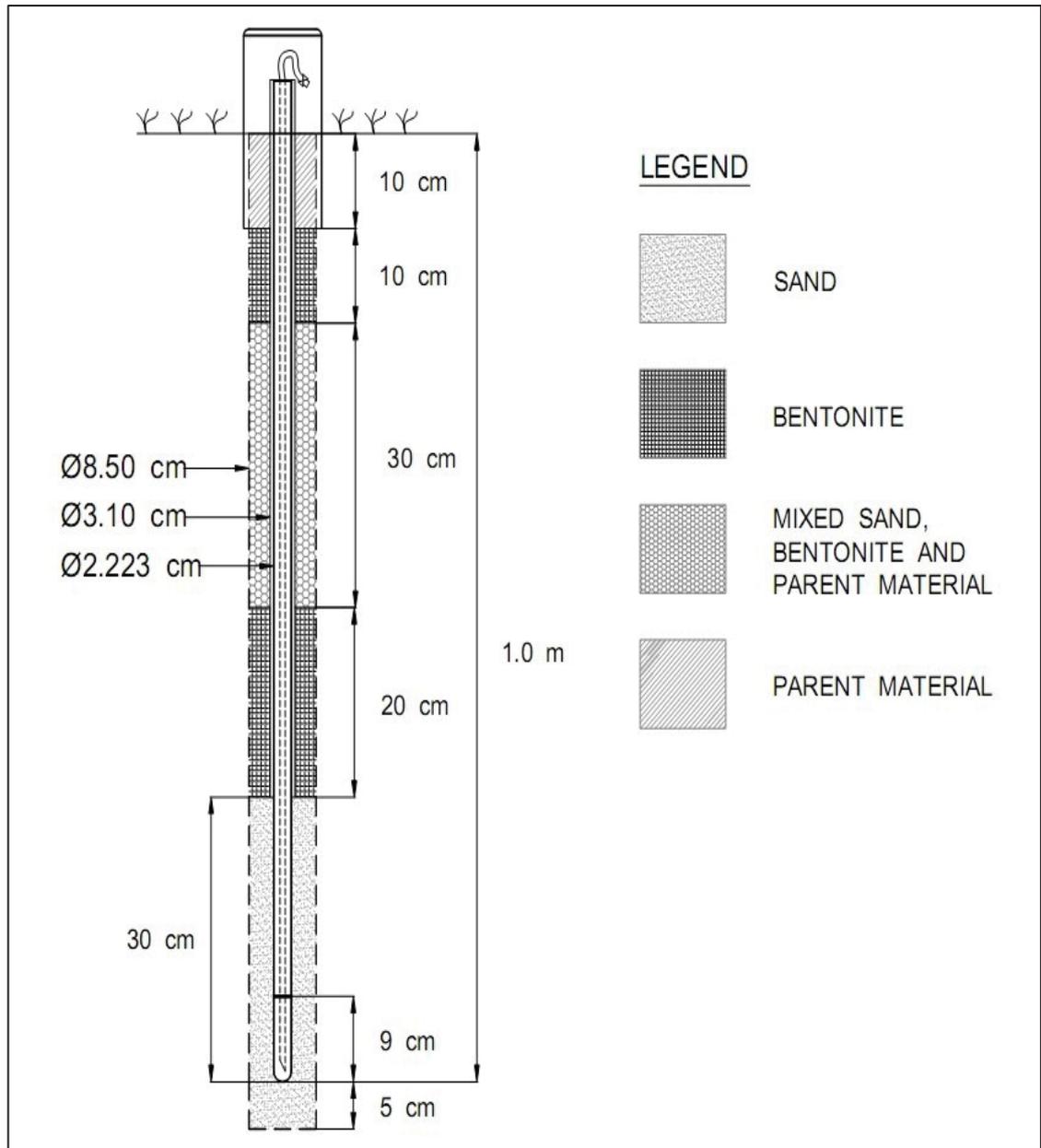
30 cm CERAMIC POROUS CUPS



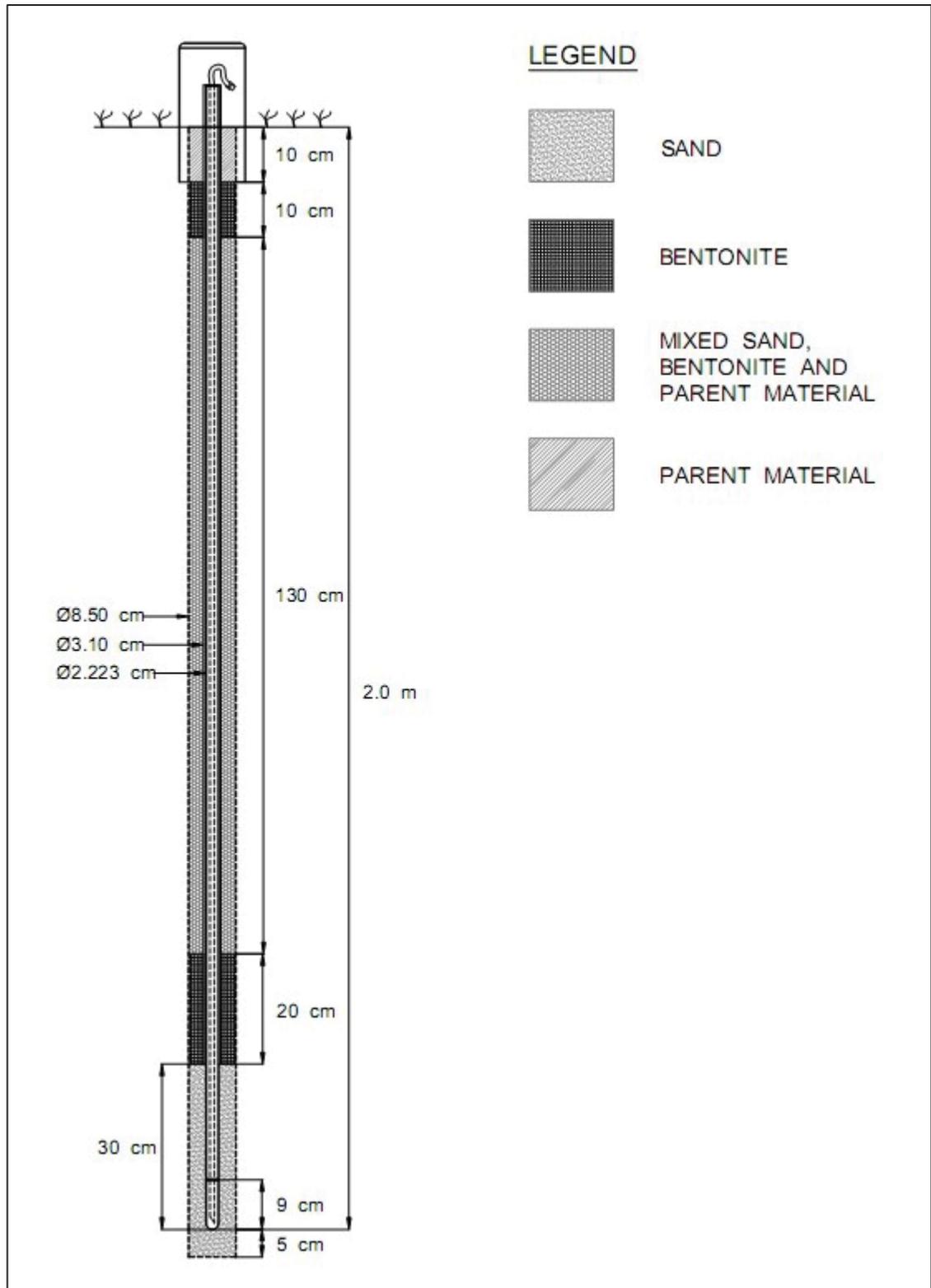
60 cm CERAMIC POROUS CUPS



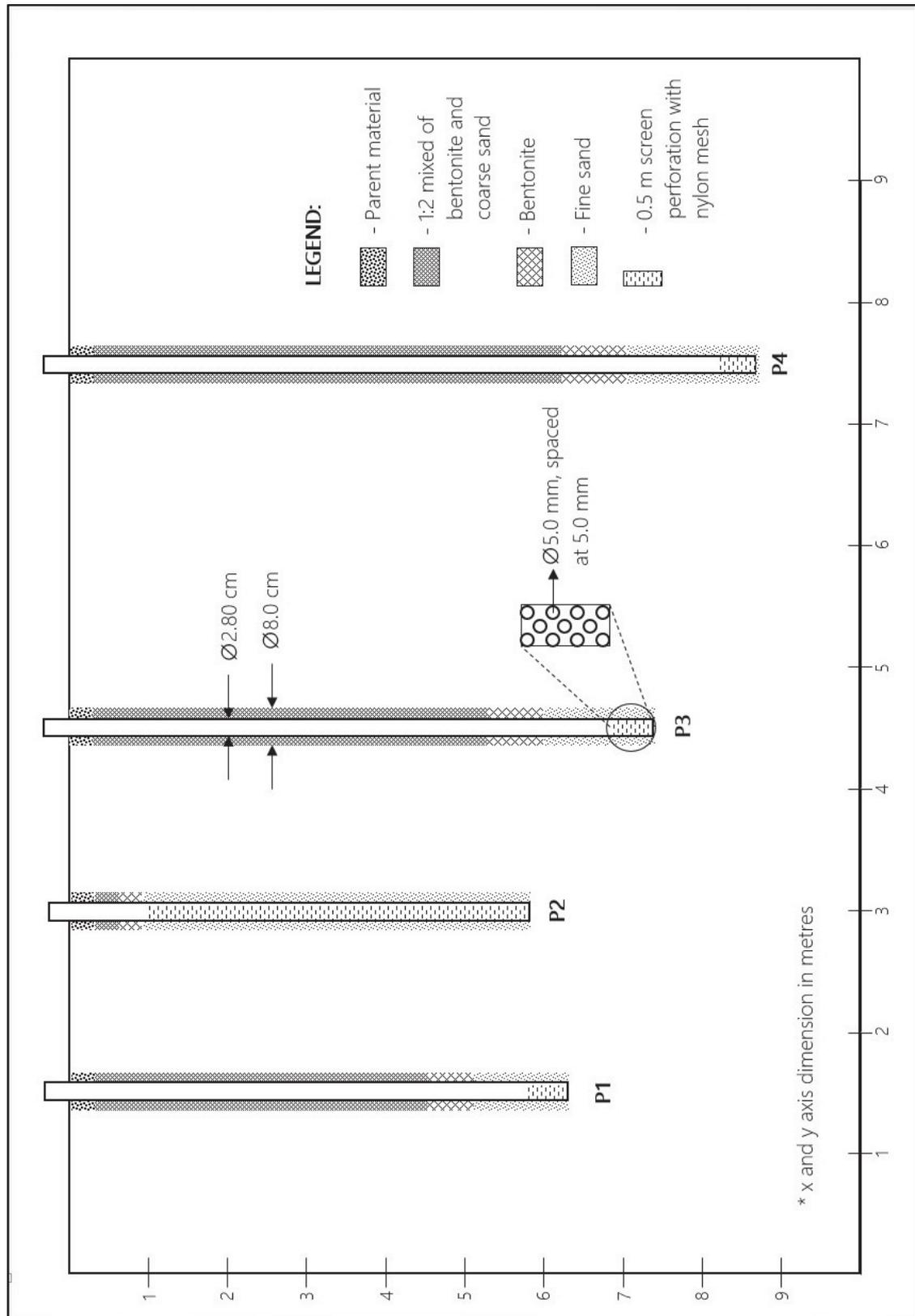
100 cm CERAMIC POROUS CUPS



200 cm CERAMIC POROUS CUPS



PIEZOMETERS



Appendix B: Soil physical and chemical characteristics at Massey Dairy Farm No. 1 conducted by Killick, 2013.

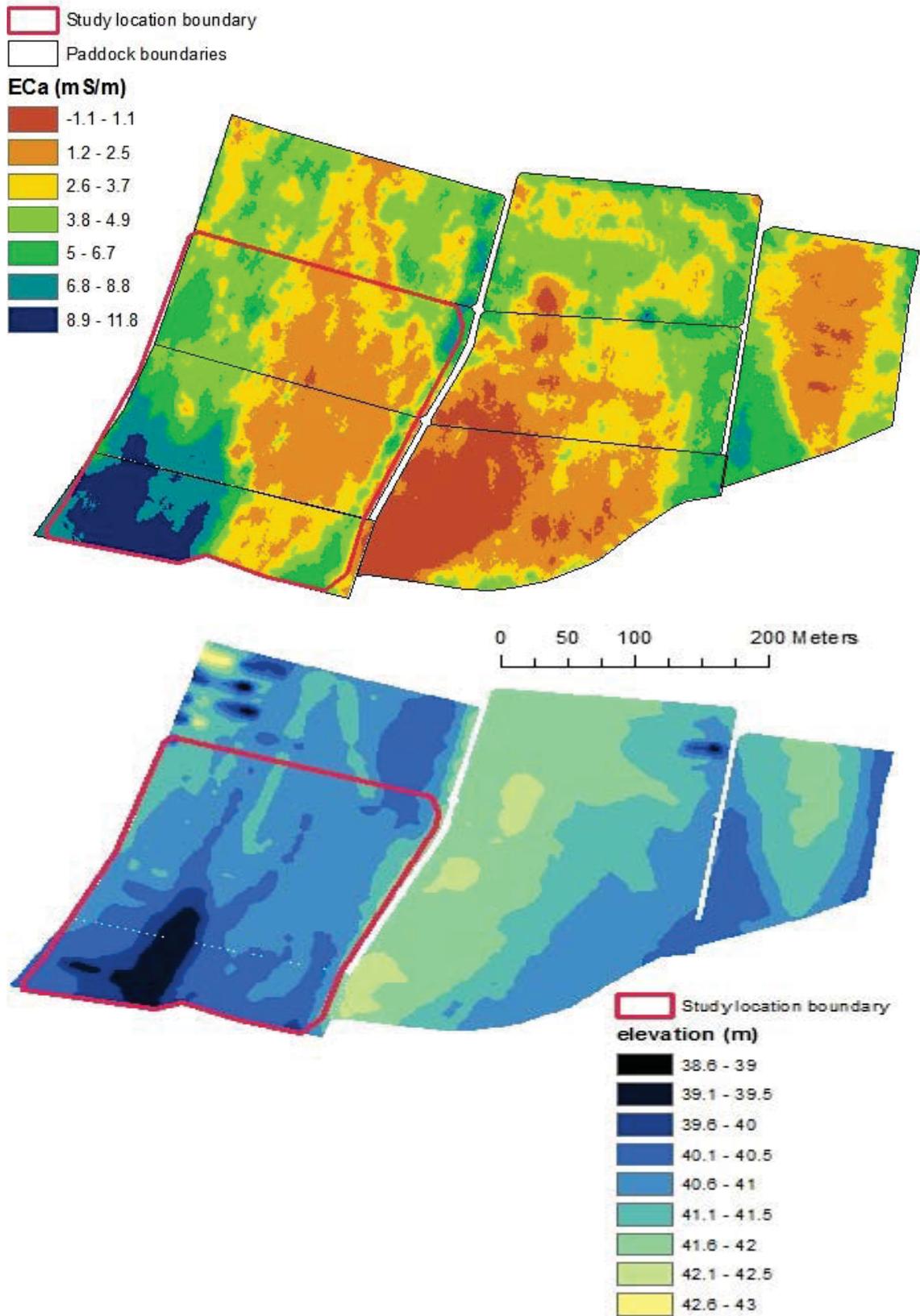
Soil sample sites at Massey Dairy Farm No. 1



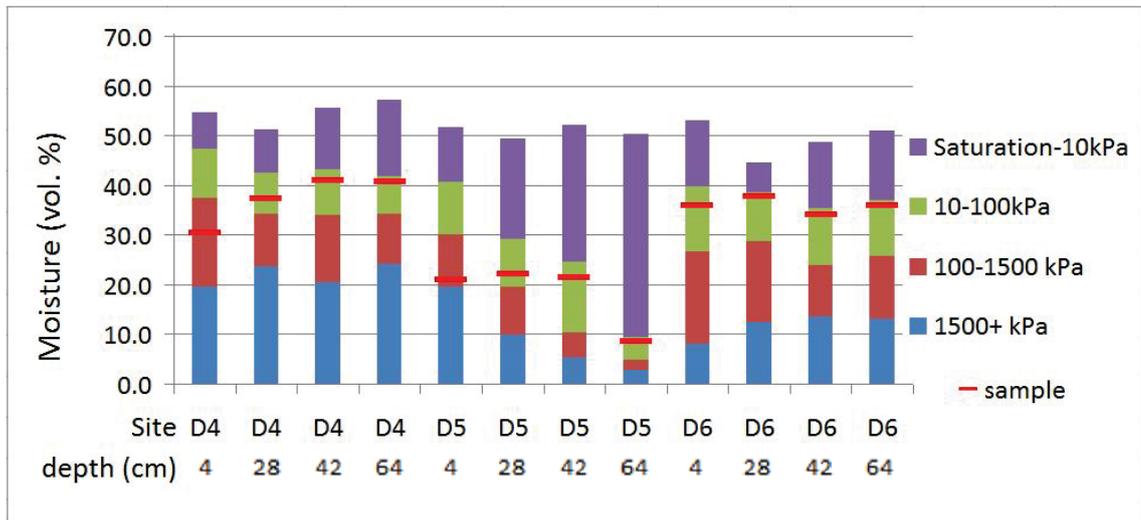
Soil texture properties

	D4	D5	D6
% Sand	7.6	31.0	25.8
% Silt	83.5	65.3	68.1
% Clay	8.9	3.7	6.1
Fineness	2.8	1.9	2.3

Topography and EC



Soil volumetric moisture at different matric potential at Massey Dairy Farm No. 1



Soil profiles

cm		hzn	description
0			
14		Ap	Silt (some fine sand), mixed appearance: pale brown, pale reddish brown and darker brown (melanised) peds, overall pale for an A horizon, firm nutty structure.
34		ABg	Silt (some fine sand), dull greyish brown (humified), faint reddish mottles, firm nutty structure.
70		Bg	Silt, dull greyish brown, reddish brown mottles, crumbly, nutty structure.
105		Bg2	Silt (no sand felt), small amount clay, dull greyish brown, reddish brown mottles but less gleyed than Bg, wet, soft, smooth.
130		Bg3	As for Bg.
140+		2C	Sand, loose, dark olive; many red brown mottles at upper boundary.

Figure A9.04. Soil profile at sample site D4, No.1 Dairy.
Profile is a generalisation from 3 holes dug with spade on 27.12.11.

