

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

**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

Patrick Benson B. Espanto

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.

Table of Contents

Abstract	ii
Acknowledgements	iv
Table of Contents	vi
List of Figures	xi
List of Tables	xvii
Chapter 1. INTRODUCTION	1
1.1 Objectives	3
1.2 Thesis Outline	4
Chapter 2. LITERATURE REVIEW	7
2.1 Nitrogen cycle	7
2.1.1 Organic and inorganic sources of nitrogen	7
2.1.2 Nitrogen transformation processes	8
2.1.2.1 Nitrogen fixation	9
2.1.2.2 Mineralisation	9
2.1.2.3 Ammonification	10
2.1.2.4 Volatilisation	10
2.1.2.5 Nitrification	11
2.1.2.6 Plant uptake	11
2.1.2.7 Immobilisation	12
2.1.2.8 Denitrification	12
2.1.3 Human influences	13
2.1.4 Environmental impacts	14

2.2	Transmission pathways of nitrogen from soil to the aquatic environment	14
2.2.1	<i>Runoff</i>	15
2.2.2	<i>Leaching</i>	15
2.3	Transport and fate of nitrogen in subsurface environment	15
2.4	Techniques to determine transport and transformation of nitrogen in the subsurface environment	16
2.4.1	<i>Laboratory or field measurements</i>	16
2.4.1.1	<i>Mineralisation</i>	16
2.4.1.2	<i>Leaching</i>	17
2.4.1.3	<i>Denitrification</i>	18
2.4.1.4	<i>Travel time</i>	19
2.4.2	<i>Modelling</i>	20
2.4.2.1	<i>Analytical models</i>	20
2.4.2.2	<i>Numerical models</i>	24
2.4.2.3	<i>Empirical models</i>	24
2.4.2.4	<i>Process-based models</i>	24
2.5	New Zealand studies on transport and transformation of nitrogen in the subsurface environment	26
2.5.1	<i>Mineralisation and nitrification</i>	26
2.5.2	<i>Nitrate leaching</i>	26
2.5.3	<i>Denitrification and Br tracer</i>	28
Chapter 3.	MATERIALS AND METHODS	31
3.1	Field experimental sites and instrumentation	31
3.1.1	<i>Massey Dairy Farm No. 1 (Site 1)</i>	34
3.1.2	<i>Te Matai Site (Site 2)</i>	39

3.2 Experimental design, data collection and sampling	42
3.2.1 Climate data	42
3.2.2 Soil samples	42
3.2.3 Urea and bromide fertiliser application	44
3.2.4 Irrigation	45
3.2.5 Soil-solution samples	46
3.2.6 Groundwater level and quality parameters	50
3.2.6.1 Shallow groundwater samples at Massey Dairy Farm No. 1 Site 1	50
3.2.6.2 Groundwater samples at the Te Matai Rd Site 2	51
3.3 Laboratory Analysis and Field Measurements	52
3.3.1 Soil physical properties	52
3.3.1.1 Bulk density	52
3.3.1.2 Particle density	52
3.3.1.3 Other physical soil properties	53
3.3.2 Soil chemical properties	53
3.3.2.1 Organic matter	53
3.3.2.2 Mineralisation, extractable nitrate, and ammonium	54
3.3.3 Soil moisture	54
3.3.4 Water $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$	55
3.3.5 Bromide	55
3.3.6 Groundwater level and quality parameters	56
3.3.7 Dissolved organic carbon	58
3.3.8 Groundwater redox conditions	59

Chapter 4. RESULTS AND DISCUSSION	61
4.1 Physical characteristics and climate conditions	61
4.1.1 Soil physical characteristics	61
4.1.2 Climate data	62
4.1.2.1 Rainfall	62
4.1.2.2 Air and soil temperature	64
4.2 Transport and transformation of nitrate-nitrogen in the unsaturated and saturated zones	66
4.2.1 Bromide tracer test	66
4.2.1.1 Br⁻ and NO₃-N concentrations in the unsaturated and saturated (shallow groundwater) zones	67
4.2.1.2 Bromide travel time from the unsaturated zone to the shallow groundwater	71
4.2.1.3 Limitations of the tracer test conducted	72
4.2.2 Transport and transformation of nitrate-nitrogen in unsaturated zone	73
4.2.2.1 Initial soil-N and organic matter content	73
4.2.2.2 Mineralisation in top (0-30 cm) soil profile	75
4.2.2.3 Nitrate-nitrogen in unsaturated zone	76
4.2.2.4 Ammonium-nitrogen in unsaturated zone	78
4.2.2.5 Dissolved oxygen in unsaturated zone	79
4.2.2.6 Dissolved organic carbon in unsaturated zone	80
4.2.3 Shallow groundwater monitoring	81
4.2.3.1 Nitrate-nitrogen in the shallow groundwater	82
4.2.3.2 Ammonium-nitrogen in shallow groundwater	82
4.2.3.3 Dissolved oxygen in shallow groundwater	83
4.2.3.4 Temperature of shallow groundwater	84

4.2.3.5	<i>pH of shallow groundwater</i>	85
4.2.3.6	<i>Specific conductance of shallow groundwater</i>	86
4.2.3.7	<i>Oxidation-reduction potential in shallow groundwater</i>	87
4.3	Assessment of reduction-oxidation (redox) conditions in the shallow and deep groundwaters	88
4.3.1	<i>Groundwater quality monitoring in Site 1 and Site 2</i>	88
4.3.2	<i>Assessment of redox conditions</i>	93
Chapter 5.	CONCLUSIONS AND RECOMMENDATIONS	99
5.1	Main findings	99
5.2	Recommendations	100
References	102
Appendices	111
Appendix A: Installation profiles of ceramic porous cups and piezometers at Massey Dairy Farm No. 1 Site 1.	111
Appendix B: Soil physical and chemical characteristics at Massey Dairy Farm No. 1 conducted by Killick, 2013.	116

List of Figures

Figure 2-1. The nitrogen cycle (adapted from Rivett, Buss, Morgan, Smith, & Bemment (2008)).	8
Figure 2-2. RISK-N model schematic for agricultural area (adapted from Gusman and Mariño (1999)).	23
<i>Figure 3-1.</i> Location of the study sites in the Manawatu River catchment.	32
<i>Figure 3-2.</i> Location of the study sites in the Manawatu River catchment.	33
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.	35
Figure 3-4. Soil profile at paddock 23 at Massey Dairy Farm No. 1 Site 1 (adapted from Killick (2013)).	36
<i>Figure 3-5.</i> Soil map of Massey Dairy Farm No.1 (top) and distribution of paddocks and location of the study site Site 1 (bottom).	37
<i>Figure 3-6.</i> Experimental plot layout at the Massey Dairy Farm No. 1 Site 1.	38
<i>Figure 3-7.</i> Multilevel piezometer profile at the Te Matai Road Site 2 (adapted from Zarour, (2008)).	40
Figure 3-8. Multilevel piezometers at Te Matai Road Site 2.	41
Figure 3-9. PVC soil core sampler.	42
Figure 3-10. Soil core sampling using waratah posing driver.	43
Figure 3-11. Synthetic urine application at Site 1.	45
Figure 3-12. Installed sprinkler irrigation at the experimental plot at Massey Dairy Farm No. 1 Site 1.	46
Figure 3-13. Materials used in ceramic porous cup assembly (left group) and sampling soil-solution (right group).	47
Figure 3-14. Percussion corer used to create a hole for installing vertical porous cups.	48
Figure 3-15. Sampling soil-solution in porous cup.	49
Figure 3-16. Post rammer used to install piezometers at Massey Dairy Farm No.1 Site 1.	51

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.	56
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.....	57
Figure 3-19. Preparation and analysis of DOC using digestion and titration method. ...	59
Figure 4-1. Monthly rainfall distribution at AgResearch met station (Site 1) and NZ Metservice (Palmerston North) from January, 2013 to January, 2014.	63
Figure 4-2. Comparison of 2013 seasonal rainfall distribution at AgResearch met station (Site 1) and NZ Metservice (Palmerston North).	63
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.	64
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.....	65
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.....	65
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.....	66
Figure 4-7. Cumulative rainfall and irrigation recorded at the experimental plot Site 1 from August, 2013, to January, 2014.....	67
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.....	68
Figure 4-9. Rainfall and irrigation depth applied at the experimental plot on Massey Dairy Farm No. 1 Site 1.....	68
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.....	70

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.....	70
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.....	71
Figure 4-13. Soil-N concentrations at Massey Dairy Farm No. 1 Site 1 measured on July 17, 2013.	74
Figure 4-14. Soil organic matter content (%) at Massey Dairy Farm No. 1 Site1 measured on July 17, 2013.....	74
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.	76
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.....	77
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.....	78
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.	80
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.	80
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.....	81
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.....	82
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.....	83

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. 84

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. 85

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. 86

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. 87

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. 88

Figure 4-28. Well distribution in the Manawatu River catchment. 90

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. 91

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. 91

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. 91

Figure 4-32. 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 October, 1969-2007. 92

Figure 4-33. 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 November, 1969-2007.	92
Figure 4-34. 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 December, 1969-2007.	92
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.	93
Figure 4-36. The influence of distance from coast on amounts of sulphur in rainfall in New Zealand (adapted from FLRC, 2009).	93
Figure 4-37. Average nitrate-nitrogen concentrations in groundwater samples from different depths at the Te Matai Road Site 2.	96
Figure 4-38. Average dissolved oxygen concentrations in the groundwater samples from different depths at the Te Matai Road Site 2.	96

List of Tables

Table 3-1. Historical variation of temperature and rainfall in Palmerston North, New Zealand.....	34
Table 3-2. Required water quality criteria prior to groundwater sampling.....	57
Table 4-1. Soil physical characteristics at Massey Dairy Farm No. 1 Site 1.....	62
Table 4-2. Seasonal measured rainfall and computed PET at the Massey Dairy Farm No. 1 Site 1 for the year 2013.....	72
Table 4-3. Criteria and threshold concentrations for identifying redox processes in groundwater.....	94
Table 4-4. Groundwater redox category and process at Massey Dairy Farm No.1 Site 1.....	95
Table 4-5. Groundwater redox category and process at the Te Matai Rd Site 2.....	95