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Characterisation of Denitrification in the Subsurface Environment of the Manawatū Catchment, New Zealand

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ABSTRACT

A sound understanding of the quantity of nitrate lost from agricultural soils, as well as their transport and transformation in soil-water systems is essential for targeted and effective management and/or mitigation of their impacts on the quality of receiving waters. However, there is currently little known about the occurrence, variability, or factors affecting, nitrate attenuation by subsurface (below the root zone) denitrification in New Zealand, particularly in the Manawatū River catchment. This thesis developed and applied a combination of regional- and local-scale hydrogeochemical surveys and experiments, to gain an insight into the occurrence, variability, and hydrogeological features of subsurface denitrification in the Manawatū River catchment, particularly in the Tararua Groundwater Management Zone (GWMZ).

A regional survey and analysis of samples from 56 groundwater wells conducted in the Tararua GWMZ revealed mainly oxic groundwater with low denitrification potential in the southern part of the catchment (Mangatainoka sub-catchment), whereas mainly anoxic/reduced groundwaters with high potential to denitrify in the middle and northern parts (Upper Manawatū sub-catchments). Oxic groundwaters with enriched nitrate concentrations were generally correlated with coarse textured soil types and aquifer materials (e.g., well-drained soil, gravel rock type), allowing faster movement of percolating water and oxygen diffusion from surface to subsurface environments.

Local-scale laboratory incubations and in-field, push-pull test techniques were evaluated and optimised to measure and quantify denitrification in unsaturated (vadose) and saturated (shallow groundwater) parts of the subsurface environment. A novel incubation technique

using vacuum pouches was found to be more reliable than traditional Erlenmeyer flasks in determining denitrifying enzyme activity (DEA) in subsurface soils (>0.3 m depth) with low denitrification activity. A combination of 75 µg N g^{-1} dry soil and 400 µg C g^{-1} dry soil was also found to provide the optimum DEA in subsurface soils. In the evaluation of the push-pull test, denitrification rates estimated using the measurements of denitrification reactant (nitrate) were found to be significantly higher (6 to 60 times) as compared to the rates estimated using the measurements of denitrification product (nitrous oxide). The estimates of denitrification rates also differed depending on whether a zero-order or first-order kinetic model was assumed. However, either a zero-order or a first-order model appears to be valid to estimate the denitrification rate from push-pull test data.

The optimised laboratory incubation technique and in-field, push-pull test were applied at four sites with contrasting redox properties; Palmerston North, Pahiatua, Woodville, and Dannevirke. The incubation technique revealed that denitrification potential in terms of DEA is highest in the surface soil and generally decreased with soil depth. The push-pull test measured large denitrification rates of 0.04 to 1.07 mg N L^{-1} h^{-1} in the reduced groundwaters at depths of 4.5-7.5 m below ground level at two of the sites (Woodville and Palmerston North), whereas there were no clear indications of denitrification in the oxidised shallow groundwaters at the other two sites (Pahiatua and Dannevirke).

This new knowledge, information and techniques advance our scientific capability to assess and map subsurface denitrification potential for targeted and effective land use planning and water quality measures in the Manawatū catchment and other catchments across New Zealand's agricultural landscapes and worldwide.

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Rivas, A., Singh, R., Bishop, P., Horne, D., Roygard, J., Hedley, M.J., 2018. A novel acetylene inhibition incubation technique for accurate quantification of denitrifying enzyme activity in subsurface soils. *Soil Biology & Biochemistry* (submitted, under revision).

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Rivas, A., Singh, R., Horne, D., Roygard, J., Matthews, A., Hedley, M.J., 2018. Contrasting Denitrification Characteristics in the Vadose Zone and Shallow Groundwater Beneath Temperate Pasture Lands and their Implications for Nutrient Management in Agricultural Landscapes. *Journal of Environmental Quality* (in preparation).

Published Conference Proceedings (presented by A. Rivas)

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Rivas, A., Singh, R., Horne, D., Roygard, J., Matthews, A., & Hedley, M., 2014. Characterization of denitrification in the subsurface environment of the Manawatu River catchment, New Zealand. In *Proceedings of the 21st Century Watershed Technology Conference and Workshop*, American Society of Agricultural and Biological Engineers (ASABE), The University of Waikato, Hamilton, New Zealand. DOI: 10.13031/wtcw.2014-029.

Rivas, A., Singh, R., Bishop, P., Horne, D., Roygard, J., Hedley, M., 2014. Measuring denitrification in the subsurface environment of Manawatu River catchment. In: *Nutrient management for the farm, catchment and community*. (Eds L.D. Currie and C L. Christensen). http://flrc.massey.ac.nz/publications.html. Occasional Report No. 27. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 13 pages.

Published Conference Abstracts (presented by A. Rivas)

Rivas, A., Singh, R., Horne, D., Roygard, J., Matthews, A., Hedley, M., 2016. Variability in denitrification characteristics of the vadose and saturated zones in the Manawatu River catchment. In: *Integrated nutrient and water management for sustainable farming*. (Eds L. D. Currie and R. Singh). http://flrc.massey.ac.nz/publications.html. Occasional Report No. 29. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand.

Rivas, A., Singh, R., Horne, D., Roygard, J., Matthews, A., Hedley, M., 2015. Variability in Hydrogeochemical Conditions in Shallow Groundwater in the Manawatu River Catchment and Implications for Denitrification Potential. In: *NZ Hydrological Society Annual Conference: From Data to Knowledge*. NZ Hydrological Society, Hamilton, New Zealand, pp. 163–164.

Rivas, A., Singh, R., Horne, D., Roygard, J., Matthews, A., Hedley, M., 2014. Indications of denitrification potential and occurrence in groundwater in the Manawatu catchment. In: *NZ Hydrological Society Annual Conference: Integration: 'The Final Frontier'*. NZ Hydrological Society, Marlborough, New Zealand, pp. 225.

Rivas, A., Singh, R., Horne, D., Bishop, P., Hedley, M., Roygard, J., 2013. Evaluation of Acetylene Inhibition Method to Measure Denitrification in Unsaturated Zone. In: *Joint Conference of the NZ Hydrological Society and the Meteorological Society of NZ: Water & Weather: Solutions for Health, Wealth & Environment*. NZ Hydrological Society, Palmerston North, New Zealand, pp. 183-184.

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Published Conference Proceedings (full paper):

Collins, S. B., Singh, R., **Rivas, A.**, Palmer, A., Horne, D., Roygard, J., Matthews, A., 2016. Assessment of nitrogen flow pathways and its potential attenuation in shallow groundwaters in the Lower Rangitikei catchment. In: *Integrated nutrient and water management for sustainable farming*. (Eds L. D. Currie and R. Singh). http://flrc.massey.ac.nz/publications.html. Occasional Report No. 29. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 14 pages.

Singh, R., **Rivas, A.**, Espanto, P., Elwan, A., Horne, D., Roygard, J., Matthews, A., Clothier, B., 2014. Assessment of transport and transformation of nitrogen in the subsurface environment of Manawatu River Catchment – work in progress. In *Nutrient management for the farm, catchment and community*. L. D. Currie and C L. Christensen, eds. Occasional

Report No. 27. Palmerston North, New Zealand: Fertilizer and Lime Research Centre, Massey University.

Published Conference Abstracts:

Singh, R., Horne, D., Elwan, A., **Rivas, A.**, Roygard, J., Hedley, M. 2018. Influence of soil types and underlying geology on transport and transformation of nitrate in subsurface environment. *Soil science: beyond food and fuel. 21st World Congress of Soil Science*, 12-17 August 2018, Rio de Janeiro, Brazil. (submitted)

McGowan, P., Singh, R., **Rivas, A.**, Elwan, A., Palmer, A., Horne, D., Collins, S., Matthews, A., 2017. Redox characteristics of shallow groundwater in the Tararua Groundwater Management Zone. In: *New Zealand Hydrological Society Annual Conference: Filling the Knowledge Reservoir*. NZ Hydrological Society, Napier, New Zealand, pp. 139-140.

Singh, R., Horne, D., Elwan, A., **Rivas, A.**, Manderson, A., Roygard, J., and Hedley, M., 2017. Assessing and matching landuse with land suitability – the model development and landuse implications. In the proceedings of the international conference *'Innovative Solutions for Sustainable Nitrogen Management'*, June 26-30, Aarhus, Denmark. http://sustainablenconference.dnmark.org/?page_id=298

Collins, S., Singh, R., **Rivas, A.**, Palmer, A., Horne, D., Roygard, J. & Matthews, A., 2015. Transport and fate of nitrogen in the Lower Rangitikei Catchment. In: *NZ Hydrological Society Annual Conference: From Data to Knowledge*. NZ Hydrological Society, Hamilton, New Zealand.

Singh, R., **Rivas, A.**, Elwan, A., Heather, M., Horne, D.J., Burkitt, L., Morgenstern, U., Roygard, J., Matthews, A., Clothier, B., & Hedley, M. 2015. Research for catchment attenuation processes: advancing knowledge and tools to account for nitrogen transport and transformation in NZ agricultural catchments. In the proceedings of the international conference *'Catchment Science 2015'*, September 28-30th, 2015, Wexford, Ireland. http://www.teagasc.ie/agcatchments/cs2015/Presentations/Singh_R.pdf

Singh, R., **Rivas, A.**, Elwan, A., Horne, D.J., Burkitt, L., Roygard, J., Matthews, A., Clothier, B., & Hedley, M. 2015. Assessment of nitrogen attenuation in the subsurface environment of Manawatu River catchment, New Zealand. In the proceedings of the international conference *'Land Use and Water Quality 2015'*, September 21-24th, 2015, Vienna, Austria. http://web.natur.cuni.cz/luwq2015/download/oral/246_Singh%20et%20al._LuWQ2015_Manawatu%20Denitrification%20Case%20Study_Sept%202015.pdf

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LIST OF ABBREVIATIONS AND SYMBOLS

Ag	silver
AI	acetylene inhibition
Al	alluvium
amsl	above mean sea level
ANOVA	Analysis of Variance
APHA	American Public Health Association
BD	bulk density
bgl	below ground level
Br^-	bromide
C	carbon
Ca^{2+}	calcium
CBE	charge balance error
Cl^-	chloride
CO_2	carbon dioxide
C_2H_2	acetylene
DAN	Dannevirke
DEA	denitrifying enzyme activity
DEM	digital elevation model
DIC	dissolved inorganic carbon
DNRA	dissimilatory nitrate reduction to ammonium
DO	dissolved oxygen
DOC	dissolved organic carbon
Eh	redox potential
EU	European Union
FeS_2	pyrite
Fe^{2+}	ferrous iron
FSL	Fundamental Soil Layer
g	gram
GC	gas chromatograph
Gr	gravel
GWMZ	Groundwater Management Zone
h	hour
ha	hectare
HCO_3^-	bicarbonate
HWC	hot water-extractable carbon
H_2O	water
H_2SO_4	sulphuric acid
ICP-OES	Inductively coupled plasma optical emission spectrometry
K^+	potassium
KBr	potassium bromide
kg	kilogram
kJ	kilojoule
km	kilometre
km^2	square kilometre
KNO_3	potassium nitrate
$K_2Cr_2O_7$	potassium dichromate
L	litre

Lo	loess
LSD	Least Significant Difference
m	metre
M	million
MAV	maximum allowable value
mg	milligram
mg L^{-1}	milligram per litre
Mg^{2+}	magnesium
mL	millilitre
mm	millimetre
Mn^{2+}	manganese
mol	mole
MRT	Mean Residence Time
mV	millivolts
m^3	cubic metre
N	nitrogen
Na^+	sodium
NH_4^+	ammonium
NO	nitric oxide
NO_2^-	nitrite
NO_3^-	nitrate
NPSFM	National Policy Statement for Freshwater Management
N_2	nitrogen gas
N_2O	nitrous oxide
OC	organic carbon
ORP	oxidation-reduction potential
O_2	oxygen
P	phosphorus
PAH	Pahiatua
PCA	Principal Components Analysis
PE	polyethylene
PNR	Palmerston North
ppb	parts per billion
ppm	parts per million
PVC	polyvinyl chloride
rpm	revolution per minute
R^2	coefficient of determination
SO_4^{2-}	sulphate
SPC	specific conductance
UK	United Kingdom
WDV	Woodville
WFPS	water-filled pore space
yr	year
°C	degree Celcius
µg	microgram
µL	microlitre
µm	micrometre