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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 $\mu\text{g N g}^{-1}$ dry soil and 400 $\mu\text{g C g}^{-1}$ 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 $\text{mg N L}^{-1} \text{h}^{-1}$ 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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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 ₂ H 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
<i>Eh</i>	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 ₂ O	water
H ₂ SO 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 ₂ Cr ₂ O 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 ₂ O	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

