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# **Accounting of nitrogen attenuation in agricultural catchments**

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

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**in**

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This thesis is dedicated to my late grandmother,  
my parents, my wife Emilie and my son Adam.

Thank you for your encouragement, inspiration and unconditional love!



# Abstract

The transport and fate of the nitrate that leaches from the root zone of farms, via groundwaters, to receiving surface waters is poorly understood, particularly for New Zealand's agricultural catchments. Monitoring nitrate concentrations in rivers clearly demonstrates that not all of the nitrate leached across the catchment enters the river. As nitrate moves from land to receiving waters there is potential for subsurface denitrification and hence the attenuation of the nitrate flux to receiving surface waters. A good understanding of the influence of catchment characteristics on the spatial variations of nitrate attenuation is essential for targeted and effective water quality outcomes across agricultural landscapes.

This thesis analysed large datasets of geographical information (land use, soils and geology) and water quality records at 20 sites in two large agricultural catchments, the Tararua and Rangitikei, which are located in the lower parts of the North Island New Zealand. The results demonstrated that the influence of land use on river soluble inorganic nitrogen (SIN) concentrations in the Tararua catchment was outweighed by other catchment characteristics such as soil type and hydrological indices.

A simple approach, that is not data-intensive, was developed and applied to quantify the capacity of a catchment to attenuate nitrogen. The nitrogen attenuation factor ( $AF_N$ ) is a key component of this approach.  $AF_N$  is defined as the average annual land use nitrogen leaching losses minus the average annual river SIN river loads, divided by the average annual land use nitrogen leaching losses.  $AF_N$  was determined for 5 and 15 sub-catchments in the Rangitikei and Tararua catchments, respectively, and was found to be highly spatially variable with values ranging from 0.14 to 0.94.

To assess the uncertainty associated with  $AF_N$ , the uncertainty in the average annual river SIN loads was evaluated. Five load calculation methods (global mean GM, rating curve RC, ratio estimator RE, flow-stratified FS, and flow-weighted FW) and four sampling frequencies (2 days, weekly, fortnightly, and monthly) were investigated to calculate average annual river loads at one of the long-term, representative water quality monitoring sites in the study catchment. The FS method using a monthly sampling frequency resulted in the lowest bias (0.9%) for average annual river SIN loads and therefore was used in the quantification of  $AF_N$  across the study catchments.

A robust uncertainty analysis of  $AF_N$  showed two distinct groups of sub-catchments; sub-catchments with higher ( $>0.7$ ) and less uncertain nitrogen attenuation factors, and sub-catchments with lower ( $<0.4$ ) and more uncertain nitrogen attenuation factors. This supports the use and applicability of  $AF_N$  as a sub-catchment descriptor of the capacity of a sub-catchment to attenuate nitrogen.  $AF_N$  was positively related to poorly drained soils and mudstones, and negatively related to well-drained soils and gravels in the study catchments.

A novel but simple hydrogeologic-based model was developed to evaluate the potential to use soil and rock indices to predict average annual river SIN loads from different land uses in a catchment. Four different versions of the model (uniform nitrogen attenuation, variable nitrogen attenuation based on soil indices only; variable nitrogen attenuation based on rock indices only; and variable nitrogen attenuation based on both soil and rock indices) were developed. Accounting for the spatial distribution of the nitrogen attenuation capacities of both soils and rocks resulted in markedly better predictions of river SIN loads in the Tararua and Rangitikei sub-catchments.

The novel findings of this thesis clearly suggest that effective and targeted measures to improve water quality at a catchment scale should account not only for land use but also for other

catchment characteristics, such as the subsurface nitrogen attenuation capacity. This new knowledge will be instrumental in the future development of the models and planning tools required to reduce the detrimental impacts of agriculture, by aligning spatially intensive land use practices with high nitrogen attenuation pathways in sensitive agricultural catchments.





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I was struggling with English at primary school. One time, I saw a senior student writing three sentences in English. At that time, I believed it would be a great achievement if I manage to do like him one day. Today, I have managed to write my PhD thesis (slightly longer than three sentences) in English. The course of this PhD, with the highs and lows, has been an exciting journey. Throughout this significant journey, I have been privileged to receive such a considerable help from many people. I feel indebted to them and I want to express my sincere gratitude for their help and support along the way.

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# List of Publications

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## List of Abbreviations

$AF_N$	Nitrogen Attenuation Factor
BFI	Base flow Index
CRM	Coefficient of Mass Residual
DEM	Digital Elevation Model
DO	Dissolved oxygen
DOC	Dissolved Organic Carbon
DRP	Dissolved Reactive Phosphorus
EF	Model Efficiency
FS	Flow-Stratified
FSL	Fundamental Soil Layer
FW	Flow-Weighted
GIS	Geographic Information System
GM	Global Mean
ha	Hectare
HRC	Horizons Regional Council
IoA	Index of Agreement
kg	Kilogram
km	Kilometre
km <sup>2</sup>	Square kilometre
LRIS	Land Resource Information Systems
m <sup>3</sup>	Cubic metre
mg L <sup>-1</sup>	Milligram per litre
mm	Millimetre
MTC	Manawatu at Teachers College
N	Nitrogen
NH <sub>4</sub> <sup>+</sup> -N	Ammoniacal-nitrogen
NO <sub>2</sub> <sup>-</sup> -N	Nitrite-nitrogen
NO <sub>3</sub> <sup>-</sup> -N	Nitrate-nitrogen
NPS	Non-point source
NPS-FM	National Policy Statement for Freshwater Management

NZ	New Zealand
ORP	Oxidation-Reduction Potential
PLSR	Partial Least Squares Regression
PS	Point Source
QMAP	Quarter-million MAP (the 1:250 000 Geological Map of New Zealand)
RC	Rating Curve
RE	Ratio Estimator
RMSE	Root Mean Square Error
RMSECV	Cross-Validated Root Mean Squared Error
SIN	Soluble Inorganic Nitrogen
t	Tonne
TN	Total Nitrogen
TON	Total Oxidized Nitrogen
TP	Total Phosphorus
TSS	Total Suspended Solids
VIP	Variable Influence on Projection
WFPS	Water-Filled Pore Space
yr	Year