Accounting of nitrogen attenuation in agricultural catchments

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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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Elwan, A., Singh, R., Patterson, M., Roygard, J., Horne, D., Clothier, B., Jones, G., 2018. Influence of sampling frequency and load calculation methods on quantification of annual river nutrient and suspended solids loads. Environ. Monit. Assess. 190. doi:10.1007/s10661-017-6444-y (Chapter 4)

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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^2	Square kilometre
LRIS	Land Resource Information Systems
m^3	Cubic metre
mg L^{-1}	Milligram per litre
mm	Millimetre
MTC	Manawatu at Teachers College
N	Nitrogen
NH_4^+-N	Ammoniacal-nitrogen
NO_2^--N	Nitrite-nitrogen
NO_3^--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

Chapter 1: Introduction

1.1 Background

Growing population and economic prosperity is putting increasing pressure on agriculture to meet growing demands for food production (Foley et al., 2011). One of the main negative impacts of agriculture intensification is the leaching of farm nutrients, mainly nitrogen, to ground and surface waters across farming landscapes (Di and Cameron, 2002; Harding et al., 1999; Hooda et al., 2000; Wilcock et al., 2006). Elevated nitrogen concentrations in surface waters can cause severe environmental impacts such as eutrophication, nuisance periphyton growth and loss of aquatic biodiversity (Carpenter et al., 1998; Di and Cameron, 2002; Ledgard et al., 1999; Monaghan and Smith, 2004). New Zealand also has some of the highest levels of threatened fish species in the world (OECD, 2017). Furthermore, drinking water with high levels of nitrate is a health issue as it can cause diseases such as methaemoglobinaemia (blue baby syndrome), especially in infants (Ward et al., 2005). The high levels of nitrate in drinking water in certain areas in Canterbury led to the Canterbury District Health Board recommending pregnant women and mothers of bottle-fed babies to use other water sources to avoid the risk of methaemoglobinaemia (OECD, 2017).

The responses to deteriorating water quality, worldwide, are in the forms of policy initiatives and management actions to mitigate the negative impacts of intensive agricultural practices on water quality. Examples include, the European Union Nitrate Directive (European Commission, 1991), the Total Maximum Daily Load (TMDL) program under the Clean Water Act (CWA) in the USA (USEPA, 1999), and the National Policy Statement for Freshwater Management (NPS-FM) in New Zealand (Ministry for the Environment, 2014).

New Zealand has one of highest rates of agricultural intensification over recent decades (OECD/Food and Agriculture Organization of the United Nations, 2015). Much of this intensification has been due to the shift from sheep and/or beef systems to intensive dairy farming. From 1994 to 2017, the number of sheep has decreased by approximately 45% (from 49.46 million in 1994 to 27.37 million in 2017) and the number of dairy cattle increased by around 69% (from 3.84 million in 1994 to 6.47 million in 2017) (Stats NZ, 2017). This intensification resulted in an increase in the quantity of nitrogen leached from agricultural soils. For example, approximately 29% more N was leached in 2012 than 1990 (i.e. an increase of around 1.5 million kilograms per year) (Ministry for the Environment and Statistics NZ, 2015). According to Dymond et al. (2013), livestock urine accounted for around 78% of the nitrogen leached from agricultural soils in New Zealand in 2012. Over the same period (1990-2012), total nitrogen levels in rivers increased by 12% (Ministry for the Environment and Statistics NZ, 2015). According to the Ministry for the Environment and Stats NZ (2017), nitrate-nitrogen in rivers increased at 61% of the 175 monitoring sites in pastoral farming catchments.

To address threats to water quality in New Zealand, the Ministry for the Environment has developed the National Policy Statement for Freshwater Management (NPS-FM) (Ministry for the Environment, 2014). The NPS-FM requires the regional environmental management authorities (i.e. Regional Councils) across New Zealand to complete, each five years, a set of ‘freshwater accounts’ for individual Freshwater Management Units (FMUs). For this purpose, they aim to build a freshwater-quality accounting system for relevant contaminants loads (measured, modelled or estimated) in ground and surface waters. However, effective management of water quality requires a sound understanding of the controls (i.e. catchment characteristics and related processes) on transport and transformations of nitrate between the root zone on farms and the receiving rivers.

On its journey from farms to rivers, water soluble nitrate can be attenuated through a number of processes. These processes include dissimilatory nitrate reduction to ammonium (DNRA)

(Korom, 1992; Robertson et al., 1996; Tiedje et al., 1983); assimilation of nitrate into microbial biomass (Hu et al., 2000); nitrate uptake through phreatophytes (Franklin et al., 2016; Masclaux-Daubresse et al., 2010); and denitrification (Burgin and Hamilton, 2007; Hiscock et al., 1991; Martin et al., 1999; Rivett et al., 2008; Saggar et al., 2013). Denitrification is the process by which nitrate is transformed through a series of microbial reduction reactions to gaseous nitrogen forms (Knowles, 1982; Korom, 1992; Rivett et al., 2007), and it was found to be the main process of nitrate attenuation in the subsurface environment (Rivett et al., 2007). Four conditions are required for denitrification to occur: 1) an anoxic/anaerobic or low dissolved oxygen (DO) environment; 2) the availability of electron donors such as Mn^{2+} and Fe^{2+}; 3) availability of bacteria with metabolic capacity; and 4) the presence of nitrate as the electron acceptor (Korom, 1992). Therefore, denitrification varies spatially (McAleer et al., 2017; Song et al., 2012) and vertically in the subsurface environment (Hill et al., 2004). Many studies have shown that denitrification is influenced by catchment characteristics (e.g. soil and rock properties) that affect the leaching rate, flow rate, flow pathway length and residence time of nitrate-enriched water in the subsurface pathways between farms to surface water bodies (Fenton et al., 2009; Jahangir et al., 2012b; McAleer et al., 2017; McMahon and Chapelle, 2008; Vidon and Hill, 2004; Wu et al., 2018). Therefore, a sound understanding of these characteristics and their influence on the fate of nitrate as it moves from farms to rivers in agricultural landscape is essential for effective management of water quality at a catchment scale (Roygard et al., 2012).

1.2 Rationale of the study

Effective and spatially targeted water quality management requires a sound understanding of the capacity of different land units to attenuate nitrate, through denitrification, on its way from farms to receiving waters. There are few studies of denitrification in the subsurface, especially in the saturated zone (Murray et al., 2004; Vilain et al., 2012). Traditionally, field and laboratory measurements are conducted to quantify denitrification in soils and groundwaters. These field studies showed that denitrification rates are variable between catchments and/or within the same catchment (Clague et al., 2015, 2013; Collins et al., 2017; Jahangir et al., 2012b, 2012c; McAleer et al., 2017; Rivas et al., 2017). Field studies are essential to the understanding of denitrification at field scale. However, field studies to quantify denitrification spatially across agricultural landscape are laborious, time-consuming and expensive to conduct. Also, it is difficult to extrapolate the results of such studies to the assessment of subsurface denitrification at the catchment scale (Barclay et al., 2015). Furthermore, denitrification has been well researched at the field scale and consequently is well understood whereas there is a general lack of understanding of the extent and impacts of this process at larger scales (Capel et al., 2008). Therefore, catchment-scale assessments of subsurface denitrification as nitrate attenuation potential is required to inform effective and targeted management of water quality at the catchment scale (Clague et al., 2013).

To better manage water quality at a catchment scale, many studies have evaluated the influence of catchment characteristics (e.g. land-use types, land-use patterns, morphology, hydrology, soil type, soil texture, soil drainage, and geology) on river water quality (e.g. nitrate and total oxidised nitrogen) (Davies and Neal, 2007; Jarvie et al., 2002; Meynendonckx et al., 2006; Onderka et al., 2012; Schilling and Lutz, 2004; Thornton and Dise, 1998; Zhou et al., 2017). Most of the aforementioned studies used multivariate statistics to assess the relationship between catchment characteristics and river water quality. However, multiple linear regression does not account for the co-linearity between the independent variables (Yeniay and Goktas, 2002). Another limitation of the multiple regression technique is the number of observations compared to the number of predictors. Carrascal et al., (2009) illustrated that lower number of observations compared to the number of predictors results in a II-type error (i.e. the error of failing to reject a null hypothesis). Therefore, methods such as partial least squares regression (PLSR) should be used when there are: 1) co-linearity between the predictors; and 2) the number of observations is lower than the number of predictors (Carrascal et al., 2009; Cramer, 1993; Yeniay and Goktas, 2002). The limited studies that have used robust statistical analysis that account for co-linearity (e.g. PLSR; Onderka et al., 2012; Zhou et al., 2017) did not account for subsurface characteristics that influence the fate and transport of nitrogen from farms to rivers. For example, Onderka et al. (2012) did not evaluate the influence of soils on river dissolved inorganic nitrogen fluxes in the Alzette catchment, Luxembourg. Also, Zhou et al. (2017) did not evaluate the influence of either geology, or soils, on nitrate concentrations in the Hujiashan watershed, China. Similarly, in New Zealand, the only study to our knowledge is by Julian et al. (2017), who evaluated the relationship between catchment characteristics and oxidised nitrogen concentration, did not account for the influence of geology. In summary, none of the abovementioned studies has evaluated the relationship between catchment subsurface characteristics (such as soils and rocks) and river nitrate concentration, stratified by flows, using robust statistical techniques that account for multi-collinearity. Hence, there is a need to fill this gap to improve our limited understanding of the influence of catchment characteristics on the concentrations of soluble inorganic nitrogen in rivers.

Estimations of the annual soluble inorganic nitrogen river load are essential for water quality management at a catchment scale. Hence, annual load estimation is at the core of management plans such as the Total Maximum Daily Load (TMDL) program in the United States and the National Policy Statement for Freshwater Management (NPS-FM) in New Zealand. However, there are few studies that have quantified the uncertainty in annual soluble inorganic nitrogen loads in medium-size catchments in temperate climates. In New Zealand, there is no study that quantified the uncertainty in annual river loads as a function of sampling frequency and load estimation method, despite the essential importance of river load estimation in the NPS-FM (Roygard et al., 2012).

Effective management of water quality at a catchment scale requires methods for assessing nutrient flows and attenuation that account for the influence of the source (land use), the receptor (rivers and stream) and the transport factor (soils and rocks) (Burt and Pinay, 2005; Meynendonckx et al., 2006; Roygard et al., 2012). In recent decades, researchers and water managers have increasingly devoted significant efforts to the development and applications of catchment-scale water and nitrogen flow models (Almasri and Kaluarachchi, 2007; Baalousha, 2013; Hadfield, 2007; Krause et al., 2008; Peña-Haro et al., 2010). A number of studies simulated the nitrate attenuation in the subsurface for a single catchment only using different models such as SWAT-MODFLOW-MT3DMS by Conan et al., (2003); DAISY and MIKE SHE by Styczen and Storm (1993); mRISK-N, MODFLOW and RT3D by Wriedt and Rode (2006). Only a limited number of studies simulated the spatial distribution of attenuation in the subsurface. Those studies that did investigate the spatial variability in denitrification (e.g. Hansen et al., 2014, 2009) used data-intensive models: however, the required data is not available for all catchments. For example, only a limited number of parameters, such as river flow and river water chemistry, are frequently monitored, across most of the catchments, by water regulatory authorities such as Regional Councils in New Zealand (Woodward et al., 2013). Also, very limited research has been done to establish the relationship between the spatial distribution of nitrogen attenuation and catchment characteristics. Therefore, there is a need for research to fill these gaps. Little is known about the effects of a catchment's characteristics on nitrogen flow pathways and potential attenuation, particularly in New Zealand agricultural landscapes (Collins et al., 2017; Rivas et al., 2017; Stenger et al., 2014, 2008).

Hence, there is a need for simple hydrogeologic models that can make use of readily available data to relate land-based nitrogen losses (source) to river loads (receptor) taking into account different catchment characteristics (transport factor).

1.3 Research objectives

The overarching research objective of this thesis is to investigate the influence of catchment characteristics (the transport factor ‘soils and rocks’) on the fate of soluble inorganic nitrogen, on its subsurface journey from source (different land-use types) to receptor (rivers).

The specific research objectives of this thesis are:

- To evaluate the influence of different catchment characteristics on river soluble inorganic nitrogen concentrations at different river flows;
- To quantify the spatial distribution of nitrogen attenuation capacity across agricultural catchments;
- To quantify the uncertainty associated with the assessment of nitrogen attenuation capacity through quantification of uncertainty in annual river soluble inorganic nitrogen concentrations as a function of sampling frequency and load estimation methods;
- To evaluate the relationship between catchment characteristics and the spatial distribution of nitrogen attenuation factor; and
- To build a simple hydrogeologic-based model, which accounts for the effects of different hydrogeological settings on spatial variations in nitrogen attenuation capacity and predict land-based soluble inorganic nitrogen (SIN) loads to surface waters in agricultural catchments.

1.4 Study areas

Two large agricultural catchments, the Tararua and Rangitikei catchments, were selected as the focus of this study. The catchments were selected as they are representative of large tracts of agricultural landscape across New Zealand. In addition, the catchments were selected due to their deteriorated water quality. Roygard & Clark (2012) found that the measured diffuse (non-point sources) soluble inorganic nitrogen (SIN; measure of nitrate-nitrogen, nitrite-nitrogen and ammoniacal-nitrogen) load at the outlet of the Tararua and Rangitikei catchments were approximately 46.9% and 54.3% respectively higher than the target loads. In light of the above, the two catchments were selected in this study.

The Tararua catchment is located in the upstream part of the Manawatu catchment, to the east of the Manawatu Gorge, in the lower North Island, New Zealand. It covers an area of around 3192 km^2. The elevation ranges from 60 m to 1497 m with an average of 316 m above mean sea level. The catchment has a temperate climate with a mean annual rainfall that varies from 945 mm yr^{-1} to 6265 mm yr^{-1}, with an average of 1520 mm yr^{-1} (based on 30 years "1978-2007" of rainfall data) (Tait and Sturman, 2008). The dominant land uses are sheep/beef farming (64%), native cover (17%) and dairy farming (15%) (Clark and Roygard, 2008).

The Rangitikei catchment is located in the lower part of the North Island, New Zealand. It covers an area of around 3887 km^2. The elevation ranges from 7 m to 1727 m with an average of 684 m above mean sea level. The catchment has a temperate climate with a mean annual rainfall that varies from 811 mm yr^{-1} to 2866 mm yr^{-1}, with an average of 1282 mm yr^{-1} (based on 30 years "1978-2007" of rainfall data) (Tait and Sturman, 2008). The dominant land uses are sheep/beef/dairy (50%) and NOF "i.e. Blocks not otherwise used for farming, such as indigenous forest" (42%) (AsureQuality, 2015).

1.5 Thesis structure

The thesis is divided into six chapters. The research chapters were formatted as manuscripts for submissions to peer-reviewed journals. Therefore, there will be some repetition in the 'Introduction' sections and the descriptions of the study area in some chapters. A journal article, based on Chapter 4, has been published in the *Journal of Environmental Monitoring and Assessment* (Elwan et al., 2018). Two manuscripts, based on Chapters 3 and 5, have been submitted to the *Journal of Environmental Management*. A brief description of each chapter is provided below:

Chapter 1 (current chapter) presents an introduction to the entire thesis. It provides the general background, rationale of this research, and the general and specific objectives of this thesis. Also, it presents the outline of this thesis.

Chapter 2 provides a literature review about the attenuation of nitrate in the subsurface environment and the influence of catchment characteristics (e.g. soils and rocks) on variable subsurface nitrate attenuation across agricultural catchments. It also reviews a few studies available that have classified soils and rocks according to their attenuation capacities. The chapter identifies and highlights the knowledge gaps to inform and advance research on the study topic.

Chapter 3 studies the influence of catchment characteristics on river soluble inorganic nitrogen concentrations at different flow conditions in the study catchment. In particular, it investigates the magnitude and direction of the influence of various catchment characteristics such as land use (e.g. dairy, sheep and beef), hydrogeology (e.g. base flow index BFI, soil texture, soil drainage status, and subsurface rock types) and morphology (e.g. drainage density) on river soluble inorganic nitrogen concentrations, using datasets stratified by flows, at 15 sites in the Tararua catchment.

Chapter 4 quantifies the uncertainty in the estimates of the annual river load of 6 water quality parameters (nitrate-nitrogen 'NO_3^--N', soluble inorganic nitrogen 'SIN', total nitrogen 'TN', dissolved reactive phosphorus 'DRP', total phosphorus 'TP', and total suspended solids 'TSS') as a function of four sampling frequencies (2 days, weekly, fortnightly, and monthly), and five load calculation methods (global mean GM, ratio estimator RE, flow-stratified FS, and flow-weighted FW, and rating cure RC). This uses a detailed dataset of one year of river flow and water quality measurements for the Manawatu River at the 'Teachers College' site from May 2010 to April 2011.

Chapter 5 quantifies the spatial distribution of nitrogen attenuation capacity across 15 and 5 sites in the Tararua and Rangitikei catchments, respectively. Also, it evaluates the relationship between the spatially variable nitrogen attenuation capacities and catchment characteristics across the Tararua catchment. Furthermore, it analyses the spatial effects of soils and the underlying geology characteristics on the modelling of the variation of nitrogen attenuation capacity and prediction of river SIN loads across Tararua and Rangitikei sub-catchments. This chapter evaluates a series of simple hydrogeologic-based models to predict average annual river SIN loads based on either uniform or spatially variable nitrogen attenuation capacity of the subsurface environment.

Chapter 6 summarizes the main findings of the thesis and discusses the implications for water quality management and applications of different scenarios to spatially align land use intensity with attenuation capacity. Also, it provides recommendation for the research required to gain the greater insight required for more certain, effective and targeted water quality management at a catchment scale.

Chapter 2: Literature review

2.1 Introduction

This chapter provides a review of the nitrate attenuation processes in the subsurface. It also reviews the influence of hydrogeological characteristics on nitrate attenuation in the subsurface environment. Finally, the chapter identifies and highlights knowledge gaps to inform and advance research on the study topic.

2.2 Land use and water quality

Intensive agricultural practices, the associated increase by over 800% in nitrogen (N) global fertiliser application over the last 50 years (Foley et al., 2011), and livestock ruminants that are considered inefficient users of dietary nitrogen as they excrete larger part (70-95%), of the consumed nitrogen, mainly as urine (Oenema et al., 2005; Selbie et al., 2015), caused detrimental impacts on freshwater resources (Foley et al., 2005; Pimentel et al., 2004; Thornton and Herrero, 2010; Tilman et al., 2002). One of the main negative impacts of agriculture intensification is leaching of farm nutrients, mainly nitrogen, to ground and surface waters across agricultural landscapes (Di and Cameron, 2002; Harding et al., 1999; Hooda et al., 2000; Wilcock et al., 2006). In surface waters, elevated levels of nitrogen concentrations can cause negative environmental impacts such as eutrophication, nuisance periphyton growth and loss of aquatic biodiversity (Carpenter et al., 1998; Di and Cameron, 2002; Ledgard et al., 1999; Monaghan and Smith, 2004). On its journey from farms to rivers, the fate and transport of water soluble nitrate is influenced by different catchment characteristics. Therefore, to better manage water quality at a catchment scale, many studies have evaluated the influence of catchment characteristics (e.g. land-use types, land-use patterns, morphology, hydrology, soil type, soil texture, soil drainage, and geology) on river water quality (e.g. nitrate and total oxidised nitrogen) (e.g. Davies and Neal, 2007; Jarvie et al., 2002; Julian et al., 2017; Meynendonckx et al., 2006; Onderka et al., 2012; Thornton and Dise, 1998; Zhou et al., 2017). While all aforementioned studies accounted for the influence of land use on river water quality not all of them investigated the influence of subsurface catchment characteristics (soils and rocks) on river water quality. For example, Onderka et al. (2012) did not evaluate the influence of soils on river dissolved inorganic nitrogen fluxes in the Alzette catchment, Luxembourg. Also, Zhou et al. (2017) did not evaluate the influence of either geology, or soils, on nitrate concentrations in the Hujiashan watershed, China. Similarly, in New Zealand, the only study to my knowledge is by Julian et al. (2017), who evaluated the relationship between catchment characteristics and river oxidised nitrogen concentration, did not account for the influence of geology.

Also, to my knowledge, none of these studies evaluated the relationship between catchment characteristics and river water quality (e.g. nitrate) using a river dataset stratified by flows. Stratification of water quality data by flows (the highest and lowest 25% of flows) can give additional insights on how older water (low flows; deeper flow paths), versus younger water (high flows; near-surface flow paths), are influenced by catchment characteristics (Woodward et al., 2016).

2.3 Transport and fate of nitrate in the subsurface of agricultural catchments

2.3.1 Transport mechanisms

Nitrate is water-soluble and therefore moves with water from land to waterways (Follett, 2008; Follett and Delgado, 2002; Haag and Kaupenjohann, 2001). Given its solubility in water, the main transport mechanisms for nitrate are leaching and surface runoff from soil profile (Follett, 2008). The loss of dissolved nitrogen in surface runoff is a function of rainfall intensity, landscape and soil characteristics that influence infiltration rate (Follett and Delgado, 2002). Infiltration rate is controlled by initial soil water content, organic matter and soil permeability. Well-drained soils (such as sandy textured soils) are characterised by high infiltration rate and consequently low surface runoff potential. In contrast, soils with higher percentage of clay (poorly drained soils) are characterised by low infiltration rate and therefore have higher surface runoff potential (Follett, 2008). Also, landscape characteristics such as slope and vegetation cover influence surface runoff with larger surface runoff associated with steeper slopes and less surface runoff with vegetation cover that enhance infiltration (Follett, 2008).

Based on the soil-water partitioning coefficient for nitrate (Logan, 1993), leaching and groundwater discharge ‘baseflow’ is considered the main transport process for nitrate to surface water, whereas nitrate transport through surface runoff is of less importance (Haag and Kaupenjohann, 2001; Kröger et al., 2007; McDowell et al., 2013; Stenger et al., 2012; Tesoriero et al., 2009). This has been supported by a number of studies. For example, in agricultural catchment in the Georgia Coastal Plains, USA, Jackson et al. (1973) found that subsurface flow represented 80% of the total stream flow and nitrate-nitrogen was mainly transported through groundwater discharge. Also, Ritter (1986) found that the majority of nitrogen load (>50%) was carried through baseflow in six agricultural catchments in the Coastal Plain area, Delaware, USA. Ritter (1986) also found that higher nitrogen loads were in catchments with well-drained soils. This has been confirmed by the findings of Mellander et al. (2012) who investigated the influence of soil drainage on the transport of total oxidised nitrogen (TON = nitrate-nitrogen +nitrite-nitrogen) in four agricultural catchments (two with well-drained soils and the other two with poorly to moderately drained soils) in Ireland. They found that subsurface transfer pathways contributed 92-98% of total stream flow and 95-97% of TON loads in the two catchments with well-drained soils. On the other hand, they found that, in the catchments with poorly to moderately drained soils, subsurface transfer pathways contributed 45-79% of total stream flow and 50-80% of TON loads. Conan et al. (2003) reported that nitrate was mainly carried through baseflow that represented the major component of stream flow in the Coët-Dan watershed, the Brittany region, France. Schilling and Zhang (2004) estimated that around two-thirds (17.3 kg ha^{-1} yr^{-1}) of mean annual nitrate-nitrogen export (26.1 kg ha^{-1} yr^{-1}) was contributed through baseflow in the Raccoon River catchment, west-central Iowa, USA. Rozemeijer and Broers (2007) found that groundwater was the main source of nitrate-nitrogen in the surface water in the Noord-Brabant agricultural province, the Netherlands. Zhu et al. (2011) found that majority of nitrate-nitrogen and total nitrogen (75% and 65%, respectively) were transported through baseflow which in turn accounted for 64% of total flow in a sub-catchment located in the Mahantango Creek catchment, Pennsylvania, USA.

In New Zealand, Mckergow et al. (2007) investigated the contribution of different flow pathways in transporting total nitrogen, using seven generic scenarios (including dairy, intensive sheep/beef and hill country sheep/beef farms). These seven generic scenarios were loosely based on monitored research catchments for different landscapes and farming types (e.g. Bog Burn, Toenepi and Whatawhata). They found that total nitrogen load are mostly transported through subsurface flow pathways. Yet, they found that in the ‘intensive sheep/beef along with heavy subsoil' scenario, surface runoff contributed around 25-50% of the total nitrogen load. Also, in New Zealand, Woodward et al. (2013) found that shallow (fast) groundwater accounted for 80% of the annual stream flow and around 91% of nitrate-nitrogen load discharging to the stream in the Toenepi catchment in the Waikato region.

Transport of nitrate is also influenced by the preferential flow pathways in soils. The large continuous pores (macropores such as cracks in clay soils) result in rapid movement of water and nitrate in what is known as short-circuiting or preferential flow (Bouma, 1991; Dekker and Bouma, 1984; Haag and Kaupenjohann, 2001). This preferential flow is not conducive to subsurface denitrification (Dekker and Bouma, 1984; Tindall et al., 1995) and therefore results in higher concentrations of nitrate in groundwater (Bronswijk et al., 1995).

Artificial drainage is another way through which nitrate can be transported to the surface water without being attenuated in the subsurface (Fennessy and Cronk, 1997; Haag and Kaupenjohann, 2001; Rozemeijer et al., 2010; Vought et al., 1994). In the Hupsel brook catchment, The Netherlands, Rozemeijer et al. (2010) found that artificial drainage had a significant influence on surface water quality as it accounted for 80% of the discharge and around 90% of nitrate load.

2.3.2 Attenuation processes of nitrate

Nitrate attenuation processes include nitrate uptake through phreatophytes; assimilation of nitrate into microbial biomass; assimilatory nitrate reduction; denitrification and dissimilatory nitrate reduction to ammonium as discussed below.

2.3.2.1 Nitrate removal through plant uptake

Most plants acquire the nitrogen needed for growth and production within the root zone. On the other hand, fewer plants have deeper roots that reach the water table (phreatophytes) (Rivett et al., 2008). Examples of the phreatophytes include poplars and willows that have high biomass production and consequently higher potential for nitrogen uptake (Franklin et al., 2016; Rockwood et al., 2004; Roygard et al., 2001). Poplar trees convert soluble inorganic nitrogen, after taking it up through the roots, into protein and nitrogen gas (Licht and Schnoor, 1993). Also, phreatophytes can enhance subsurface denitrification through plant root exudates (Rivett et al., 2008). Therefore, there is a growing use of phreatophytes to remediate soil and/or groundwater nitrate contamination (McKeon, 2003). Plant uptake could contribute significantly to nitrate removal in riparian areas. A number of studies found plant uptake was significant in nitrate removal in riparian areas (Groffman et al., 1992; Licht and Schnoor, 1993; Schoonover et al., 2003). Conversely, other studies found plant uptake to be less significant in nitrate removal in riparian areas (Cey et al., 1999; Hill, 1996; Hinkle et al., 2001).

In New Zealand, Franklin et al. (2016) highlighted the potential of using poplar and willows to intercept leached nitrogen at deeper depths in the Canterbury Plains in the South Island. They highlighted that the high evapotranspiration and growth rates of these deep rooting species (poplar and willows) are likely to enhance nitrogen uptake and hence reduce the impact of intensive farming on water quality.

2.3.2.2 Assimilation of nitrate into microbial biomass

Microbes in the soil can convert either ammonium (NH_4^+) or nitrate (NO_3^-) to meet their nitrogen requirement for their growth (Follett, 2008; Rivett et al., 2008). Although ammonium is the first preference for microbes (Hill, 1996), removal of nitrate could take place through microbes uptake (Jackson et al., 1989; Rivett et al., 2008; Stark and Hart, 1997). However, this process is reversible, or temporary, as mineral nitrogen is released back to groundwater after the death of microbes (Rivett et al., 2008).

2.3.2.3 Assimilatory nitrate reduction

In assimilatory nitrate reduction, nitrate is reduced into ammonium, by several types of microorganisms (Megonigal et al., 2004). Through this process nitrate is assimilated into organic nitrogen compounds (e.g. amino acids) (Megonigal et al., 2004). Assimilatory nitrate reduction is inhibited by low concentrations of ammonium or organic carbon (Rice and Tiedje, 1989). Thus, assimilatory nitrate reduction is considered negligible because of the inhibition by ammonium (Megonigal et al., 2004).

2.3.2.4 Denitrification

Denitrification is the process by which nitrate is transformed through a series of microbially mediated reduction reactions to gaseous nitrogen forms (nitric oxide NO, nitrous oxide N_2O) and dinitrogen gas N_2 as the end product (Knowles, 1982; Korom, 1992; Rivett et al., 2008; Starr and Gillham, 1993), as shown by Equation 2.1 (Knowles, 1982).

$$\mathrm{NO_3^-} \longrightarrow \mathrm{NO_2^-} \longrightarrow \mathrm{NO} \longrightarrow \mathrm{N_2O} \longrightarrow \mathrm{N_2} \qquad (2.1)$$

Denitrification is considered to be the main nitrate attenuation process in the subsurface (Appelo and Postma, 2005; Knowles, 1982; Korom, 1992; Rivett et al., 2008). The organisms capable of denitrification (chemotrophs) get their energy from oxidation of organic and inorganic species. The organism can be heterotrophic (organotrophic), if the electron donor is organic; and autotrophic (lithotrophic) if the electron donor is inorganic (Korom, 1992; Rivett et al., 2008). Therefore, there are two types of denitrification, discussed below, based on the source of electron donor. Regardless of the electron donor type, the denitrification reaction can be expressed by Equation 2.2, that highlights the role of electron donor in the reduction of nitrate (electron acceptor) (Tesoriero et al., 2000).

$$2NO_3^- + 12H^+ + 10e^- \longrightarrow N_2 + 6H_2O \qquad (2.2)$$

Denitrification can be either heterotrophic or autotrophic as a function of the electron donor, as reviewed and described below.

a. Heterotrophic denitrification

In heterotrophic denitrification, the electron donors, needed to provide energy to heterotrophic (organotrophic) microorganisms, come from organic source (mainly from microbial oxidation of organic carbon) (Korom, 1992). Therefore, the major limiting factor in heterotrophic denitrification is the amount of organic carbon (Devito et al., 2000; Rivett et al., 2008). The rate of heterotrophic denitrification is a function of the concentration of dissolved organic carbon (DOC) rather than solid fraction of organic carbon in the geological layers (Rivett et al., 2008). In general, DOC levels in most aquifers are low (<5 mg/L DOC) (Rivett et al., 2007) and may not be enough for denitrification to occur as DOC needs to be oxidised initially by dissolved oxygen (Fig. 2.1) (Rivett et al., 2008). Thus, in “fully oxygenated groundwater” (e.g.

recently infiltrated recharge water), the low levels of DOC might not develop anaerobic conditions required for denitrification to occur (Rivett et al., 2008).

The general heterotrophic denitrification reaction can be described by the following chemical equation (Appelo and Postma, 2005).

$$5CH_2O + 4NO_3^- \longrightarrow 2N_2 + 4HCO_3^- + H_2CO_3 + 2H_2O \qquad (2.3)$$

According to Appelo and Postma (2005), a decrease in NO_3^- concentrations accompanied by an increase in HCO_3^- concentrations can be used as indication of oxidation of organic matter and occurrence of heterotrophic denitrification.

b. Autotrophic denitrification

In autotrophic denitrification, the electron donors, needed to provide energy to the lithotrophic microorganisms, are inorganic such as reduced manganese (Mn^{2+}), ferrous iron (Fe^{2+}) and sulphides (Korom, 1992). The autotrophic denitrification through reduced sulphur (in groundwater aquifer this is mainly iron sulphide, pyrite, FeS_2) can be described by Equation 2.4 (Appelo and Postma, 2005).

$$5FeS_2 + 14NO_3^- + 4H^+ \longrightarrow 7N_2 + 5Fe^{2+} + 10SO_4^{2-} + 2H_2O \qquad (2.4)$$

As shown by the previous equation, the autotrophic denitrification through pyrite involves the oxidation of both ferrous iron and sulphur (Appelo and Postma, 2005). Thus, higher concentrations of ferrous iron and sulphate can be used as indication of autotrophic denitrification by pyrite (Appelo and Postma, 2005; Thayalakumaran et al., 2008).

Examples of autotrophic denitrification facilitated by reduced iron (Fe^{2+}) can be expressed by the following equations (2.5 and 2.6) (Appelo and Postma, 2005; Ottley et al., 1997).

$$10Fe^{2+} + 2NO_3^- + 14H_2O \longrightarrow 10FeOOH + N_2 + 18H^+ \quad (2.5)$$

$$15Fe^{2+} + NO_3^- + 13H_2O \longrightarrow 5Fe_3O_4 + N_2 + 28H^+ \quad (2.6)$$

The previous equations illustrate that groundwater with high concentrations of reduced iron will contain little or no nitrate. This negative relationship between ferrous iron and nitrate has been found in a number of studies (Korom, 1992; Thayalakumaran et al., 2008). Ferrous iron, that may be used in autotrophic denitrification, are present in clay minerals, detrital silicates (such as pyroxenes and biotite) and magnetite (Appelo and Postma, 2005).

According to Appelo and Postma (2005), the energy yield through the oxidation of sulphide is higher than that of ferrous iron oxidation. Thus, if there are higher levels of pyrite in the geological layers, ferrous iron is generally not oxidised (Appelo and Postma, 2005). Also, heterotrophic denitrification is thermodynamically favoured over autotrophic denitrification and thus heterotrophic should occur before autotrophic denitrification. Yet, the reaction kinetics influence the order of denitrification type (Appelo and Postma, 2005).

Regardless of the type (heterotrophic or autotrophic), for denitrification to occur, four conditions are required: an anoxic/anaerobic or low dissolved oxygen (DO) environment; the availability of electron donors such as dissolved organic carbon (DOC), Mn^{2+} and Fe^{2+}; the availability of bacteria with metabolic capacity (autotrophic and organotrophic); and the presence of nitrate as an electron acceptor (Korom, 1992).

As the reduction of dissolved oxygen is thermodynamically favoured over denitrification (Fig. 2.1) because of the higher energy yield, the onset of denitrification is generally at lower thresholds of dissolved oxygen concentrations (i.e. anaerobic conditions) (McMahon and

Chapelle, 2008; Rivett et al., 2008). The range of dissolved oxygen concentrations suggested for denitrification occurrence is variable across studies. However, in general most studies found that the required threshold for denitrification to occur is <1 mg L^{-1} or <2 mg L^{-1} (Böhlke et al., 2002; Buss et al., 2005; Jahangir et al., 2012b; Rissmann, 2011; Starr and Gillham, 1993; Thayalakumaran et al., 2008). Yet, the optimal threshold is considered to be 0.2 mg L^{-1} (Hiscock et al., 1991; Seitzinger et al., 2006; Trudell et al., 1986).

Denitrification is also a function of pH (Buss et al., 2005). The optimal range of pH for heterotrophic denitrification is considered to be 5.5 to 8 (Rust et al., 2000) or 7 – 8 (Hiscock et al., 1991; Knowles, 1982). Strongly acidic environment with pH values less than 5 are considered to inhibit denitrification (Bremner and Shaw, 1958; Buss et al., 2005). On the other hand, higher levels of pH are also suggested to inhibit denitrification with pH of 8.3 as the acceptable upper threshold (Rust et al., 2000).

Denitrification is also influenced by temperature (Buss et al., 2005; Rivett et al., 2008) with an optimum range of 25 to 35 °C (Rivett et al., 2008). However, it can occur over a wide range, from 2 to 50 °C, and has an exponential increase with the increase in temperature (Buss et al., 2005).

Figure 2.1. Fate of oxidation of organic matter in the saturated zone with the sequence of different electron acceptors (Rivett et al. (2008) after Korom (1992)).

In New Zealand, a number of studies have been conducted to investigate denitrification in soils (mostly surface soils) and groundwater. These studies have been conducted across New Zealand in the Waikato (e.g. Barkle et al., 2007; Clague et al., 2013; Stenger et al., 2008); Manawatu (e.g. Luo et al., 1998; Rivas et al., 2014; Ruz-Jerez et al., 1994; Singh et al., 2014).; and Canterbury (e.g. Peterson et al., 2013; Thomas et al., 2012) regions. Also, a number of studies have been conducted to investigate groundwater denitrification in the Waikato (e.g. Burbery et al., 2013; Clague et al., 2015, 2013, Stenger et al., 2018, 2008; Zaman et al., 2008); Manawatu (e.g. Collins et al., 2017; Rivas et al., 2017, 2014); and Southland (e.g. Burbery et al., 2013) regions.

2.3.2.5 *Dissimilatory nitrate reduction to ammonium (DNRA)*

As its name implies, DNRA is the process through which nitrate is reduced to ammonium (similar to assimilatory nitrate reduction) as shown by Equation 2.7 (Korom, 1992; Robertson et al., 1996).

$$2H^{+} + NO_3^- + 2CH_2O \longrightarrow NH_4^+ + 2CO_2 + H_2O \qquad (2.7)$$

The required conditions for DNRA to occur are similar to those of denitrification, such as low oxygen levels (anaerobic environment) (Tiedje, 1988); low redox potential (Eh); and available nitrate and carbon (Thayalakumaran et al., 2008). Although denitrification is the preferred process when electron acceptors (nitrate) are abundant (carbon is limiting), DNRA is the preferred process when electron donors (carbon) are abundant (nitrate is limiting) (Korom, 1992; Thayalakumaran et al., 2008; Tiedje, 1988). According to Yin et al. (1998), significant DNRA occurred at carbon/nitrate (C/NO_3^-) ratio larger than 12 in paddy soils in China. Although a number of studies showed the occurrence of DNRA in soils and river bed sediments (Groffman et al., 2006; Lansdown et al., 2012; Rütting et al., 2011; Silver et al., 2001; Yin et al., 1998), DNRA is barely found to be the main process of nitrate reduction in groundwater aquifers. In general, DNRA is less favoured than denitrification due to the lower energy yield associated with DNRA (-1796 kJ mol^{-1} glucose with DNRA compared to -2669 kJ mol^{-1} glucose with denitrification) (Rütting et al., 2011). In four agricultural catchments, Ireland, Jahangir et al. (2012b) highlighted the occurrence of DNRA in bed rock aquifer as reflected by the negative relationship between nitrate-nitrogen and ammonium in the groundwater (low nitrate-nitrogen concentration compared to higher ammonium concentration). Smith et al. (1991) showed that DNRA is a less significant process of nitrate reduction compared to denitrification in sand and gravel aquifer, Cape Cod, Massachusetts, USA.

The ammonium resulting from DNRA can be oxidised, in aerobic conditions, to nitrate or taken up by plants (Rütting et al., 2011).

2.4 Influence of hydrogeological characteristics on nitrate attenuation in subsurface environment

As described above (Section 2.3.1.1) that given nitrate solubility in water, nitrate is transported through water into and out of any hydrogeological system. In subsurface flow, in addition to the conditions required for denitrification to occur (anaerobic environment, electron donors and denitrifying bacteria), residence time can be considered as the main important factor in improving water quality through denitrification (Fennessy and Cronk, 1997). Residence time can be defined as the time through which a unit of water remains in the subsurface environment (Fennessy and Cronk, 1997). The longer the residence time, the higher the potential for geochemical reactions to work on improving water quality through denitrification (Fennessy and Cronk, 1997).

2.4.1 Influence of soil characteristics on nitrate attenuation

2.4.1.1 Soil texture

Among the factors that influence residence time is the soil texture and therefore soil texture was found by a number of studies to influence denitrification (Gaines and Gaines, 1994; Gilliam et al., 1978; Gurdak and Qi, 2006). The coarser the soil texture, the faster the movement of water and hence less potential for denitrification. On the other hand, the finer the texture of the soil, the slower the water movement and thus higher potential for denitrification (Gaines and Gaines, 1994; Gilliam et al., 1978; Gurdak and Qi, 2006). According to Haag and

Kaupenjohann (2001), soils that are unstratified with coarse texture generally lack anaerobic conditions which are required for denitrification to occur, as mentioned above. Using four California soils in laboratory columns, Gilliam et al. (1978) found that soils with heavy texture resulted in nitrate attenuation. They highlighted that spatial distribution of denitrification is highly likely to be a function of spatial distribution of water flow which in turn is influenced by soil texture. Using four soil samples in a laboratory experiment in the United States, Gaines and Gaines (1994) found that soil texture influences the rate of nitrate-nitrogen leaching and hence the potential for denitrification. They found that soil with coarse texture, such as sand, have faster nitrate-nitrogen leaching rate and consequently lower potential for denitrification. Conversely, they found that soils with fine texture, such as sandy clay loam and clay loams, have slower nitrate-nitrogen leaching rate and consequently higher potential for denitrification. To understand the influence of soil texture on nitrate fate and transport under unsaturated conditions, Tindall et al. (1995) conducted experiments on two different agricultural soils: structured clay from Missouri, USA, and unstructured sand from Florida, USA. They were expecting to find higher potential for denitrification in clay soil than in sand soil due to the longer residence time (slower leaching) of nitrate in the clay soil compared to sand soil; however, the opposite was true. They found that clay had lower potential for denitrification compared to the unstructured sand. They attributed this to the existence of macropores and the preferential flow through these pores in the structured clay and consequently denitrification was inhibited.

The findings of the influence of soil texture on subsurface denitrification from the aforementioned laboratory experiments (Gaines and Gaines, 1994; Gilliam et al., 1978) have been supported by field studies (Fenton et al., 2009; Goss et al., 1998; Jahangir et al., 2012a). Based on groundwater quality survey of 1292 wells in Ontario, Canada, Goss et al. (1998) evaluated the influence of soil texture on the vulnerability of groundwater to nitrate contamination. They found that wells located in soils with coarse texture (permeable sands and gravels) had the highest nitrate contamination. Conversely, wells located in soils with fine texture (clay) had the lowest nitrate contamination. Similarly, Jahangir et al. (2012b) found that soils with coarse texture (e.g. coarse sandy textured soils) were associated with higher leaching rate of nitrate compared to higher nitrate attenuation capacity associated with fine-textured soils (clay), in four agricultural catchments in Ireland. Also, in county Wexford, Ireland, Fenton et al. (2009) found that fine-textured soils (clay and silt) that are characterised by lower permeability resulted in lower nitrogen leaching and therefore higher potential for nitrate-nitrogen attenuation through denitrification. Conversely, they found that coarse-textured soils (glaciofluvial sand and gravel) characterised by higher permeability were associated with higher nitrogen leaching and therefore less potential for denitrification. In New Zealand, Thomas et al. (2012) found that major denitrification occurred in the soil with fine texture in a field trial at Lincoln, Canterbury. Also, in New Zealand, Rivas et al. (2017) found soil texture to be among the main factors that influenced the potential for denitrification in the Tararua groundwater management zone in Eastern parts of Manawatu catchment in lower North Island. They found that soils with coarse texture (such as sand, sand and stony gravel, and stony loam) are associated with higher dissolved oxygen levels in groundwater. They concluded that soils with coarse texture create oxidised conditions that are unsuitable for subsurface denitrification to occur.

2.4.1.2 Soil drainage

Soil drainage was found by a number of studies to influence the potential for denitrification (Griffith et al., 1997; Howard and Falck, 1986). Griffith et al. (1997) found that poorly-drained clay loam soil in western Oregon, USA, are characterized by anaerobic and reducing conditions conducive for potential denitrification to occur. Meynendonckx et al. (2006) in the Upper-

Scheldt catchment, Belgium, found a positive correlation between the proportion of well-drained soils and nitrate concentrations in the rivers. They attributed it to the higher infiltration capacity of well-drained soils, causing higher soil water percolation and consequently higher nitrogen leaching from the soil profile and therefore less potential for denitrification to occur.

Soil drainage was found to influence the denitrification not only in the unsaturated zone but also in the groundwater. For example, the higher infiltration capacity of well-drained soils influences the denitrification characteristics of groundwater through fast transport of greater unattenuated fluxes of nitrate-nitrogen to groundwater and increases the levels of dissolved oxygen in groundwater. Howard and Falck (1986) found in Ontario, Canada, that low nitrate concentrations in the groundwater are generally associated with regions of imperfectly drained soils. Spalding and Exner (1993) found the highest levels of nitrate concentrations in groundwater under well-drained soils in Minnesota, Washington, Arizona, California, and Nebraska, USA. They attributed that to the fast vertical transport of nitrate through well-drained soils. Based on 1230 wells from the United States Geological Survey National Water Quality Assessment Program (NAWQA), Nolan (2001) found that well-drained soils were associated with groundwater nitrate contamination. On the other hand, Nolan (2001) found that poorly drained soils, which are characterised by being saturated, had reducing conditions favourable for denitrification, and therefore groundwater below poorly drained soils had less potential for nitrate contamination. Jahangir et al. (2012b) found that poorly drained soils (clay loam and dense gravels intermixed with dense clay) were associated with the lowest levels of dissolved oxygen and nitrate-nitrogen concentrations, in Southeast Ireland. Conversely, they found that well drained soils (sandy clay loam over gravels and sandy textured soils with interbedded clay band) were associated with the highest levels of dissolved oxygen and nitrate-nitrogen concentrations. Clague et al., (2015) found that well drained soils (silt loam soils) were associated with the highest levels of dissolved oxygen and nitrate-nitrogen concentrations in shallow groundwater at two sites in the Toenepi catchment in the North Island, New Zealand. Rivas et al. (2017) found poorly drained soils to be associated with lower levels of dissolved oxygen and nitrate-nitrogen concentrations in groundwater in the Tararua groundwater management zone, New Zealand. They also found soil drainage class to be among the most influential factors on the potential for denitrification.

2.4.1.3 Soil carbon content

Another soil characteristic that is considered to be a key factor influencing denitrification is the soil carbon content. Being an electron donor that is used by denitrifying bacteria for nitrate reduction, soil carbon in different forms (mainly dissolved organic carbon DOC) was found by many studies to be a limiting factor for denitrification (Haag and Kaupenjohann, 2001; McCarty and Bremner, 1992; Parkin and Meisinger, 1989; Starr and Gillham, 1993; Yeomans et al., 1992).

Parkin and Meisinger (1989) investigated the denitrification capacity of low-organic-matter, well-drained silt loam soil in the Atlantic Coastal Plain, USA. They found no significant denitrification activity below 180 cm. Their results showed that organic carbon levels below the root zone were too low to maintain anaerobic conditions required for denitrification to occur. McCarty and Bremner (1992) found that the denitrification of four Iowa soils, USA, was limited by the lack of organic carbon required for microorganisms for nitrate reduction. Spalding and Exner (1993) found that soils with high organic carbon attenuated nitrate through denitrification in the Piedmont Plateau and Coastal Plain in the south eastern USA. Brettar et al. (2002) found a positive relationship between denitrification and soil organic carbon (labile carbon) in the floodplain soils, Rhinau, France. Cannavo et al. (2004) found that denitrification activity of 160 cm of soil (fluvic hypercalcaric cambisol) decreased downwards as the DOC decreased downwards, in Avignon, France. They found that in the top 90 cm, the denitrification rate was limited by carbon availability. Kamewada (2007) investigated the relationship between DOC concentrations and denitrification enzyme activity in a soil (classified as high humic Andisol) in Utsunomiya, Japan. The results showed, from the surface to 1m depth, a positive correlation between DOC and denitrification enzyme activity. Thomas et al. (2012) found that denitrification was limited, below 1m of the Pahau silt loam, by the lack of soil total carbon, in a field trial at Lincoln, Canterbury, New Zealand. Jahangir et al. (2012a) investigated the relationship between denitrification and soil carbon in 3 randomly selected locations in Wexford, Ireland. The studied soil was moderately well-drained and had textures ranging from loam to clay loam 'gley soil'. They found a significant positive relationship between potential denitrification rate and soil organic carbon. Clague et al. (2013) found a positive correlation between DOC concentrations and total ^{15}N gas fluxes due to the relict organic matter in paleosols 'old soils buried by volcanic deposits' in Waihora, Tutaeuaua catchment, New Zealand. They concluded that heterotrophic denitrification was the dominant nitrate reduction process below the A horizon. They found little or no denitrification where paleosol was absent.

2.4.1.4 Soil water content

Soil water content (or water filled pore space WFPS) is a key factor in controlling denitrification as it influences the oxygen availability (Tindall et al., 1995). Due to the lower diffusion rate of oxygen in water, the increase in WFPS decreases oxygen supply to denitrifying bacteria and hence create conditions favourable for denitrification (Tindall et al., 1995). Tindall et al. (1995) found that clay soil from Missouri, USA, had little to no denitrification capacity under unsaturated conditions. In New Zealand, Thomas et al. (2012) found that the highest WFPS in the soils resulted in conditions conducive for denitrification, in a field trial at Lincoln, Canterbury. Rafique et al. (2011) found that poorly drained gley soils (in south Ireland) that had high WFPS (frequently water logged) resulted in denitrification being complete. They found that gley soils resulted in the lowest N_2O emissions (higher N_2). Jahangir et al., (2012c) found that soils with the highest WFPS had the highest total denitrification potential in four agricultural catchments, Ireland.

2.4.2 Influence of subsurface geology on nitrate attenuation

Similar to the influence of soils on denitrification, subsurface geological material (rocks) also influence nitrate attenuation by influencing groundwater flow (and hence residence time) and groundwater chemistry (and hence the availability of electron donors for denitrification) (Haag and Kaupenjohann, 2001).

Among the factors that influence residence time is the rock permeability and therefore permeability was found by a number of studies to influence denitrification (Tesoriero and Voss, 1997) . The higher the permeability, the faster the movement of water and hence less potential for denitrification. On the other hand, the lower the permeability of rocks, the slower the water movement and thus higher potential for denitrification (Haag and Kaupenjohann, 2001). In analysis of data from 3696 wells in the Puget Sound Basin, Washington, USA, Tesoriero and Voss (1997) found the groundwater in coarse glacial deposits had the highest vulnerability to elevated nitrate concentrations (less potential for denitrification). They attributed that to the shorter flow paths (i.e. less residence time) of groundwater in the coarse glacial deposits. On the other hand, they found that alluvial and fine glacier deposits had longer flow paths (i.e. longer residence time) and hence higher potential for denitrification. Nolan (2001) reported that the Devonian aquifer in northern Iowa, USA, had high nitrate concentrations in karst areas. Karst (eroded limestone) is characterised by extreme permeability due to the presence of fractures and sinkholes that act as conduits for faster transport of water and nitrate (less residence time) and therefore less potential for denitrification in karst aquifers (Haag and Kaupenjohann, 2001; Nolan, 2001). Also, Fenton et al. (2011) reported that low attenuation potential of Irish bed rock aquifers was due to “their fractures and karstified nature”. According to Buss et al. (2005), the Permo-Triassic sandstone aquifers, in UK, have the potential for denitrification, despite the deficiency in electron donors, if permeability is too low and hence groundwater flow is sufficiently slow to allow longer residence time and contact between water and the aquifer.

Jahangir et al. (2012c) investigated the influence of aquifer permeability on nitrate-nitrogen at four agricultural catchments in Ireland (two high permeability aquifers with saturated hydraulic conductivity K_s ranging from 0.05 to 0.3 m d^{-1}; and two low permeability aquifers with saturated hydraulic conductivity K_s ranging from 0.001 to 0.02 m d^{-1}). They found the highest nitrate-nitrogen concentrations in high permeability aquifers and the lowest concentrations in low permeability aquifers. These findings highlight that permeability (and hence groundwater residence time) is inversely related to nitrate-nitrogen attenuation (Jahangir et al., 2012b).

McAleer et al. (2017) investigated the factors influencing groundwater denitrification in two catchments with different lithologies (slate and sandstone) in Ireland. They found that high permeability in the slate catchment resulted in faster groundwater flow that suppressed denitrification. This was the same for weathered zones in the sandstone catchment. However, they found that lower permeability (lower saturated hydraulic conductivity) at depth in the sandstone catchment resulted in longer residence time that promoted denitrification (lower nitrate concentrations). This has been reflected by the significant negative correlation between saturated hydraulic conductivity and both nitrate and dissolved oxygen.

Orr et al. (2016) investigated the influence of the hydrogeologic settings on the fate of nitrate in two bedrock aquifers with contrasting permeability (higher permeability limestone aquifer with transmissivity up to 750 m^2 d^{-1} in the Nuenna Catchment, County Kilkenny, Ireland; and lower permeability greywacke sandstone shale aquifer with most transmissivity values < 50 m^2

d^{-1} in Glen Burn Catchment, County Down, Northern Ireland). They found that denitrification was the dominant process in the low permeability aquifer.

In the Tararua groundwater management zone, Rivas et al. (2017) found that permeable rocks (e.g. gravel) with faster groundwater movement were characterised by higher levels of dissolved oxygen concentrations. This creates oxic conditions unsuitable for nitrate-nitrogen attenuation through denitrification.

Regardless of the permeability of rocks, electron donors (in different forms) are a key limiting of denitrification in rocks. According to McMahon and Chapelle (2008) geological factors (e.g. sediment source and depositional environment) control the availability of electron donors and acceptors. They reported that oxic conditions can exist for thousands of years with long flow paths (kilometres) in the alluvial and fluvial aquifers in the western United States as they lack electron donors required for denitrification to occur. On the other hand, they found that abundance of electron donors (pyrite and buried wood) promote denitrification along short flow paths in the glacial deposits in the northern United States. Min et al. (2003) found that availability of electron donors (organic carbon) from a 20 m thick silt layer promoted denitrification and resulted in decreased nitrate concentrations in the alluvial aquifer, Yongdang, Korea. Also, Kim et al., (2009) found the silt (with abundant organic matter such as plant debris) promoted nitrate attenuation through denitrification in alluvial aquifer in Osong, central Korea. Buss et al., (2005) reported that chalk in the UK is characterised by very low electron donors (e.g. organic carbon, Fe^{2+}, Mn^{4+}) and therefore has less potential for denitrification.

Böhlke and Denver (1995) investigated the influence of geology on denitrification in two agricultural catchments (the Chesterville Branch and Morgan Creek), Maryland, USA. They found that in the Morgan Creek catchment, nitrate in the groundwater was attenuated through denitrification before its discharge to the stream. They highlighted that this was due to groundwater flow through "buried calcareous glauconitic marine sediments" rich in electron donors that promoted denitrification. In contrast, most of the groundwater flow in the Chesterville Branch catchment was not through buried calcareous glauconitic marine sediments. Therefore, there was less potential for denitrification in the Chesterville Branch catchment and therefore groundwater with high nitrate concentrations discharged to the stream. Haag and Kaupenjohann (2001) highlighted the importance of electron donors (organic carbon) in classifying the hydrogeological settings in central Europe. They categorised the hydrological settings into three categories: 1) consolidated aquifers with thin soil cover and high permeability (conditions unsuitable for denitrification); 2) unconsolidated aquifers with limited organic carbon (low potential for denitrification); and 3) unconsolidated aquifers with abundance of organic carbon (high potential for denitrification). According to Haag and Kaupenjohann (2001), permeability and biogeochemical characteristics control whether aquifers can act as conduits (e.g. karst aquifers) or nitrate sinks (e.g. low permeability and high denitrification potential).

2.4.3 Soils and rocks classification according to nitrate attenuation potential

To my knowledge, limited studies have classified rocks and/or soils according to their potential denitrification (attenuation) capacity. For example, the sediments in the Patuxent River Basin, Maryland, USA, were classified by Krantz and Powars (2000) into three classes (high, medium and low nitrogen attenuation potential) according to their potential for denitrification. They suggested that sediments that have high potential for denitrification are those sediments with high proportions of reduced compounds such as organic carbon, iron sulfide minerals (e.g. pyrite FeS_2), and/or glauconite (clay mineral with reduced iron) that can react chemically to remove nitrate through denitrification. They provided examples of sediments with high potential for denitrification which included sandy silts, muddy sands, silt and silty sand. These sediments had high proportions of organic matter, pyrite and glauconite. On the other hand, Krantz and Powars (2000) suggested that unreactive sediments (i.e. sediments with lower proportions of organic matter, pyrite and glauconite) had lower potential for denitrification. Examples of these sediments include fluvial coarse sands and gravels that are composed mainly of unreactive quartz, chert and feldspar and are characterised by high permeability. Krantz and Powars (2000) assigned intermediate potential for denitrification for geological units with variable composition, and hence a variable ability to attenuate nitrate. Examples of sediments with intermediate potential for denitrification include sand and silty sand with variable amounts of glauconite and pyrite.

Following the classification of Krantz and Powars (2000), Rissmann (2011) classified the rocks in the Southland groundwater management zone (South Island, New Zealand), into high, intermediate and low nitrogen attenuation potential according to their potential for denitrification. Close et al. (2016) assigned scores (1 to 5) to soils and rocks, in the Waikato and Canterbury regions in New Zealand, according to their redox potential. They assigned low scores to rocks and soils that are highly likely to be inert (unreactive) and therefore will be associated with oxidizing conditions; and high scores to soils and rocks that are more reactive and hence are characterised by reducing conditions. In the classification of Close et al. (2016), rocks with high scores (i.e. reducing conditions) include mudstone, lignite and peat; and rocks with low scores (i.e. oxidising conditions) include dacite and gravel. Also, in the classification of Close et al. (2016), New Zealand soil order with high scores (i.e. reducing conditions) include gley and organic; and New Zealand soil order with low scores (i.e. oxidising conditions) include Allophanic, Brown, Pallic and Pumice.

2.5 Modelling nitrate transport and fate on catchment scale

2.5.1 Nitrate models on catchment scale

Different hydrological models have been used to model nitrate transport and fate on catchment scale. These models differ in terms of complexity and process descriptions from semi-distributed conceptual models to fully distributed physically-based catchment models. In the semi-distributed conceptual models, the process descriptions are semi-empirical and the transport of water and nitrate occurs through routing between a number of storages (Hansen, 2014). In these models, the groundwater component is limited. The spatial distribution of catchment characteristics is accounted for through dividing the catchment into sub-catchments that have unique combinations of catchment characteristics. Examples of these models include INCA (Whitehead et al., 1998) and SWAT (Arnold et al., 1993; Arnold et al., 1998).

On the other hand, the distributed physically-based catchment models are characterised by complex physically-based process descriptions such as the three-dimensional simulation of groundwater flow (Hansen, 2014). In these models, the catchment is divided into grid and the spatial distribution of catchment characteristics is represented by assigning different values to the grid cells. Examples of these models include MODFLOW (McDonald and Harbaugh, 1988) and MIKE SHE (Abbott et al., 1986; Refsgaard and Storm, 1995).

In many nitrate modelling studies, physically-based models have been coupled with root zone and solute transport models to simulate the fate and transport of nitrate in the unsaturated and saturated zones (Conan et al., 2003; Styczen and Storm, 1993).

Below is a discussion of different models/model combinations that have been used by a number of studies to simulate the fate and transport of nitrate on a catchment scale.

2.5.1.1 SWAT-MODFLOW-MT3DMS

a. **SWAT**

Soil and Water Assessment Tool (SWAT) is a model that can simulate flow, nutrients (P and N) and erosion. SWAT is a catchment-scale model that operates on daily time step. It subdivides the catchment into sub-basins and generates the stream network based on digital elevation model. In addition, it discretizes a sub-basin to virtual areas, with unique combinations of soil and land use, called Hydrologic Response Units (HRUs). The land phase, in SWAT, is subdivided vertically into four different storage volumes; surface, root zone, shallow aquifer and deep aquifer. SWAT divides precipitation into surface flow, evapotranspiration, lateral flow, percolation, return flow and deep aquifer recharge, and water balance is achieved in these four control volumes. Daily water balances are computed, in SWAT, from meteorological, soil, and land use data (Arnold et al., 1993; Arnold et al., 1998).

Regarding nutrients, the model considers both the natural (wet deposition of nitrate, nitrogen fixation and organic matter mineralisation) and artificial (non-point sources such as fertiliser application and point sources such as waste water treatment plants) sources. Concerning nitrate, the basic transformation processes simulated include mineralization, denitrification, volatilization, and plant uptake. (Arnold et al., 1998; Grizzetti et al., 2003; Neitsch et al., 2005). For SWAT, the required input data are digital elevation model, soil map, land use map, slope map, rainfall, temperature, relative humidity, solar radiation, wind speed, point source discharge, stream flow, surface water quality, water abstraction, fertilizer applications (rates and time), livestock densities and grazing periods and crop rotations.

b. MODFLOW

MODFLOW is a three dimensional model that simulates groundwater flow by solving three dimensional flow equation using block centred finite difference method (Harbaugh, 2005). The model can simulate steady and non-steady groundwater flow in heterogeneous aquifers. The aquifer layers can be simulated as confined, unconfined or a combination of both. The ability to deactivate specific regions with the model domain allows the modeller to simulate complex irregular system easily (Harbaugh, 2005; Kim et al., 2008; McDonald & Harbaugh, 1988; Winston, 2009). MODFLOW can simulate several interactive surface-subsurface processes such as river-aquifer interaction and evapotranspiration (Sophocleous et al., 1997). The required data for MODFLOW are digital elevation model, observation and pumping wells, measured groundwater abstraction, groundwater levels, groundwater-bearing lithological units and their thickness, hydraulic conductivity, river network, riverbed conductance, stream flow, stream stage and recharge.

MODFLOW is limited in calculating distributed groundwater recharge which is an essential input to MODFLOW. On other hand, SWAT is limited with groundwater flow because of its lumped nature. As a result, using the two models (SWAT and MODFLOW) enables better estimation of the hydrological components (Kim et al., 2008).

c. MT3DMS

The Modular Three-Dimensional Multi-Species Transport (MT3DMS) model (Zheng and Wang, 1999) is a solute transport model which can simulate changes in dissolved constituents in groundwater considering advection, dispersion, dual-domain mass transfer and chemical reactions.

The output head and cell-by-cell flow data computed by MODFLOW is used by MT3DMS to establish groundwater flow field (Zheng and Wang, 1999). MT3DMS uses the concentration of nitrate percolation generated by SWAT, for every sub-basin and every time step, as a monthly recharge concentration terms throughout the simulation period (Conan et al., 2003). The concentration and availability of dissolved oxygen, organic matter, divalent manganese, and/or pyrite are used to determine the denitrification process. This is because nitrate is removed naturally only by denitrification as it neither precipitates nor is adsorbed and does not form insoluble materials (Chapelle, 1993; Conan et al., 2003) in MT3DMS.

2.5.1.2 DAISY-MIKE SHE

a. **DAISY**

DAISY is a one-dimensional soil-plant-atmosphere model (Abrahamsen and Hansen, 2000; Hansen et al., 1991) that simulates crop growth (crop production and yield), water and nitrogen dynamics in the root zone in agro-ecosystems based on information on weather and agricultural management practices. The flow and leaching of solutes is modelled by DAISY through three possible pathways: matrix flow, macro pore flow and drain flow (Hansen et al., 2009). The simulation of water movement in the soil is based on a numerical solution of Richards equation (Abrahamsen and Hansen, 2000). The transport and transformation processes of nitrogen simulated by DAISY include mineralisation-immobilisation, nitrification and denitrification, nitrogen uptake by plants and nitrogen leaching from the root zone (Hansen et al., 1990). Denitrification is simulated through defining a potential denitrification rate (i.e. ‘rate under complete anaerobic conditions’). In DAISY, denitrification is influenced by: soil water content, soil temperature and CO_2 evolution rate.

The required input is global radiation, precipitation, air temperature, relative humidity, wind speed, potential evapotranspiration, humus and inorganic nitrogen content in soils, tillage operations, crop rotations, irrigation and fertilization.

b. MIKE SHE

MIKE SHE is a physically-based distributed hydrological model that can simulate the flow of water and solutes on a catchment scale (Abbott et al., 1986; Refsgaard and Storm, 1995). MIKE SHE can perform the numerical solutions of two-dimensional overland flow (Saint-Venant equation), one-dimensional unsaturated flow (Richards equation), three-dimensional saturated flow (Darcy equation). MIKE SHE can be coupled with MIKE 11 to model the exchange of water and solutes between groundwater and surface water. MIKE 11 is a one-dimensional river model designed to simulate flow, water quality and sediment transport. The MIKE 11 hydrodynamic (HD) module solves the vertically integrated Saint-Venant equations (DHI, 2017a, 2017b, 2017c).

DAISY can be coupled with MIKE SHE sequentially without any feedback from the river and groundwater to the root zone. This means that DAISY first simulates the water and nitrogen budget for the root zone of different field blocks in the catchment. Then, the outputs of the field blocks (percolation of water and total nitrogen leaching below the root zone) are aggregated as daily net values and used as input to MIKE SHE model (Hansen et al., 2009).

The required inputs, for MIKE SHE, include model extent, topography, precipitation, reference evapotranspiration, air temperature, solar radiation, sub-catchment delineation, river morphology (geometry and cross sections to calculate river flow and water level), land use, soil and subsurface geology (DHI, 2017a).

2.5.1.3 mRISK-N-MODFLOW- RT3D

This approach is similar to SWAT-MODFLOW-MT3DMS. However, in this approach, mRISK-N and RT3D are used instead of SWAT and MT3DMS, respectively.

a. **mRISK-N**

RISK-N is a physically-based, analytical model that simulate nitrogen cycling in the soils in addition to nitrate transport and fate in the soils and groundwater. To simulate nitrogen processes in the RISK-N model, the unsaturated soil zone is separated into upper-root, lower-root, sub-drainfield and intermediate vadose zones. In unsaturated soil zones, transport is simulated based on complete mixing of nitrogen concentrations through averaging the nitrogen convective-dispersive partial differential equations. In RISK-N, the denitrification can be estimated based on a constant denitrification coefficient at 15°C with reduction functions that account for water content and temperature; or denitrification rate can be supplied by the user (Gusman and Mariño, 1999a, 1999b). The mRISK-N model was developed through combining RISK-N model with the SIMPEL (soil water balance model) (Wriedt, 2004). The mRISK-N can be used to simulate the groundwater recharge and nitrogen leaching which can then be used as input for groundwater models (e.g. MODFLOW) (Wriedt, 2004).

The input data include climate data (precipitation, potential evapotranspiration, air temperature and radiation), land use, management records with information on crop types and fertilizer additions, soil map and soil physical properties.

b. RT3D

RT3D (Reactive Transport in 3-Dimensions) is a finite difference three-dimensional model that simulates the three-dimensional, multi-species reactive transport in groundwater (Clement, 1997). RT3D is based on MT3D (Zheng, 1990). Similar to MT3D, RT3D requires MODFLOW (McDonald and Harbaugh, 1988) in computing and spatial and temporal distribution of groundwater head. Wriedt (2004) developed a reaction module for RT3D to simulate the nitrate transformations in groundwater. This module includes the oxidation of organic matter by oxygen, nitrate and sulphate in addition to pyrite oxidation by oxygen and nitrate. The module also accounted for secondary reactions such as nitrification (Wriedt and Rode, 2006).

RT3D requires a number of parameters, that indicate the influence of groundwater aquifer characteristics on solute transport, such as porosity, transverse dispersivity, longitudinal dispersivity and first-order denitrification rate constant.

2.5.1.4 MODEST

MODEST (Model of Diffuse Emissions via Subsurface Trails) is a GIS embedded grid-based conceptual hydrogeologic model that can simulate groundwater flow in addition to fate and transport of nitrate at the regional scale (Dannowski et al., 2002; Merz et al., 2009, 1999). A conceptual hydrogeological data model is a prerequisite for simulating groundwater flow, nitrate fate and transport. Modelling of steady-state groundwater flow is based on the Darcy (piston flow) approach to get the spatial distribution of residence time. Denitrification rate is quantified based on a first order decay process. Denitrification rate in the grid model is described by a time-dependent function in which half-life of nitrate degradation is used. The spatial distribution of a groundwater flow based attenuation potential for nitrate is calculated using the residence time and half-life of denitrification in each grid cell (Merz et al., 2009).

The required datasets include effective porosity; digital elevation model; thickness of unsaturated and saturated zones; potentiometric surface; extent and hydraulic conductivity of the aquifers; extent and thickness of aquitards; hydraulic connections between aquifers; spatial distribution of redox potential and ferrous/ferric iron concentration; and first order rate constant.

2.5.2 Spatial variations of subsurface nitrate attenuation

A number of studies have simulated nitrate attenuation in the subsurface. For example, Conan et al. (2003) used SWAT-MODFLOW-MT3DMS to simulate the nitrate attenuation in the Coët-Dan watershed (12 km^2) in Brittany, France. They found that 65% of the nitrate that leached from the root zone was attenuated in the subsurface. Styczen and Storm (1993) used DAISY and MIKE SHE to simulate nitrate attenuation in the Karup River catchment (425 km^2) in Denmark. They found that around 50% of the leached nitrate was attenuated at the redoxcline. Wriedt and Rode (2006) used mRISK-N, MODFLOW and RT3D to simulate nitrate attenuation in the Schaugraben catchment (20 km^2) in Germany. They found that 80% of the leached nitrate was attenuated in the subsurface. Hansen et al. (2009) used DAISY and MIKE SHE/MIKE 11 to simulate the spatial distribution of denitrification across 14 sub-catchments in the Odense Fjord catchment (1046 km^2) in Denmark. They found that denitrification varied from 47% to 94% across the 14 sub-catchments without accounting for the wetland and river processes (denitrification varied from 53% to 94% when wetland and river processes were accounted for). Overall, they found that 57% of the leached nitrate was attenuated in the subsurface between the root zone and the catchment outlet. Merz et al. (2009) used a 2D steady-state GIS model (MODEST) to simulate the spatial distribution of nitrate attenuation in the State Brandenburg in Germany. They found that the attenuation varied spatially from < 50 to >75% in Brandenburg, Germany. Hansen et al. (2014) used stochastic geological models and MIKE SHE to simulate the nitrate attenuation potential in the Norsminde fjord catchment (101 km^2) in Denmark. They found that the nitrate attenuation potential varied spatially from 0% to 100% across the Norsminde fjord catchment, Denmark. In New Zealand, Woodward et al. (2013) used a lumped catchment scale model (StreamGEM) to simulate the nitrate attenuation in a small Toenepi stream catchment (15.1 km^2), in the Waikato region of New Zealand. They found that around 45% of the leached nitrate was attenuated in the subsurface.

2.6 Research needs

It is evident from the above reviewed studies that hydrogeological characteristics influence transport and fate on nitrate in the subsurface environment. However, our understanding and knowledge is yet limited regarding the spatial distribution of nitrogen attenuation in the subsurface environment, particularly in the New Zealand landscape. Very limited research has been conducted to investigate the relationships between catchment characteristics and spatial variation in the nitrogen attenuation capacity across New Zealand's agricultural catchments. A sound understanding of the influence of catchment characteristics on the spatial variability of attenuation capacity is required for effective management of water quality at a catchment scale. Hence, there is a need for further studies that relate the land-use nitrogen losses (source) to the river loads (receptor) taking into account influence of different catchment characteristics (transport factor) on spatial variability of transport and transformation (attenuation) of nitrogen in its flow paths from lands to receiving waters.

Also, the limited number of studies quantified the spatial variability of nitrogen attenuation using models that are data-intensive. This means that the required data, for these models, is not available for all catchments. This is due to the limited information (mainly flow and water quality parameters) monitored by water regulatory authorities. Therefore, there is a need for a simple modelling approach that makes use of limited available data to quantify and account for spatial variability of nitrogen attenuation capacity for effective and spatially targeted management of water quality on a catchment scale.

Chapter 3: Influence of catchment characteristics on soluble inorganic nitrogen concentrations in streams and rivers in agricultural landscape

3.1 Abstract

A good understanding of catchment characteristics and their influence on spatial and temporal variations of nutrient concentrations in rivers is essential for targeted and effective water quality management across agricultural landscapes. We investigated the magnitude and direction of various catchment characteristics that highly influence soluble inorganic nitrogen (SIN = ammoniacal-nitrogen + nitrite-nitrogen + nitrate-nitrogen) concentrations in streams and rivers in the Tararua catchment, New Zealand. Partial least squares regression (PLSR) was used to evaluate the relationship of the catchment's land use (e.g. dairy, sheep and beef), hydrogeological (e.g. base flow index "BFI", soil texture, soil drainage, and subsurface rock types) and morphological (e.g. drainage density) characteristics with the SIN concentrations. This relationship was evaluated at different flows (all flows, highest 25% flows and lowest 25% flows) at 15 sites for 8 years (2009-2016) in the study area.

We found that the river SIN concentrations are mainly influenced by the BFI, well-drained soils and poorly drained soils at all flows, the highest 25% of flows and the lowest 25% flows, respectively. None of the morphological indices showed any influence on the river SIN concentrations at all flows and highest 25% flows. Yet, at the lowest 25% flows, two morphological indices, the mean slope and drainage density, were found to influence the river SIN concentrations. Further, land use as dairy, and sheep/beef pastoral farming, are found to be amongst the major influential variables on the river SIN concentrations at the highest and lowest 25% flows, respectively. However, the influence of land use on the river SIN concentrations are generally outweighed by the other catchment characteristics such as drainage classes and hydrological indices (e.g. BFI).

We suggest that accounting for land use, in combination with other catchment characteristics, instead of only considering land use, is important for targeted and effective water quality management at a catchment scale.

Keywords: Water quality, Nutrients, Land use, Surface water, Partial least squares regression, Attenuation

3.2 Introduction

Growing population, urbanisation, and economic growth are putting pressure on agriculture to expand and intensify for increased food production worldwide. One of the main adverse impacts of this agriculture intensification has been identified as the runoff and leaching of farm nutrients, mainly nitrogen and phosphorus, to receiving water bodies across agricultural landscapes (Di and Cameron, 2002; Harding et al., 1999; Hooda et al., 2000; Wilcock et al., 2006). Elevated levels of nitrogen and phosphorus concentrations in freshwaters can lead to undesirable environmental impacts such as eutrophication and algal blooms. Eutrophication can cause severe water quality impacts such as depletion of dissolved oxygen levels, increased pH levels, and loss of aquatic biodiversity (Carpenter et al., 1998; Gillingham and Thorrold, 2000). The concerns regarding occurrence and impacts of eutrophication on surface water quality are leading to new policy and management actions worldwide to protect water resources. For example, the European Union Nitrate Directive aims to protect water resources against the pollution caused by nitrate due to agricultural practices (European Commission, 1991). In the United States, the Total Maximum Daily Load (TMDL) program under the Clean Water Act (CWA) is another example of managing and protecting fresh water quality (USEPA, 1999). In New Zealand, the Ministry for the Environment has issued the National Policy Statement for Freshwater Management (NPS-FM) for management of freshwater quality impacts (Ministry for the Environment, 2014). To achieve the goals of these policy recommendations and management actions, water management authorities will require a good understanding of the impact of catchment characteristics on the spatial and temporal variations in nutrient concentrations in streams and rivers across agricultural landscapes.

A number of studies have investigated the relationship between catchment characteristics and nutrients (mainly nitrate) concentrations and loads in streams and rivers of agricultural catchments worldwide. For example, Thornton and Dise (1998) used multiple regression to evaluate the relationship between catchment characteristics (land use, atmospheric deposition, soil type and geology) and the flow-weighted mean nitrate concentration in the streams of central Lake District, Cumbria, UK. They found a positive correlation between thick porous soil, the proportion of agriculture, and the flow-weighted mean nitrate concentration in the 55 streams of central Lake District, Cumbria, UK. Jarvie et al. (2002) used stepwise multiple linear regression to analyse the relationship between catchment characteristics (land use, morphology, hydrology and geology) and the total oxidised nitrogen (TON; sum of nitrate and nitrite) in the Humber catchment, UK. Their results suggested that the TON concentration in the Humber catchment, UK, is negatively correlated with elevation, rainfall, upland vegetation and slope of the catchment. On the contrary, a positive correlation was found between lowland arable, calcareous geology and the TON concentration in the Humber catchment, UK. Jarvie et al. (2002) stressed that hydrology is a major controlling factor of the river water quality in this catchment. Meynendonckx et al. (2006) used a non-parametric Spearman rank correlation analysis and a partial regression analysis to define the relationship between catchment characteristics (hydrology, morphology, land use, soil texture and soil drainage) and the river nitrate concentration in the Upper- Scheldt and the Nete catchments, the River Scheldt Basin, Flanders, Belgium. Their results showed that soil properties (e.g. soil drainage and soil texture) are significantly correlated with the nitrate concentration than morphological characteristics, land use, point source and precipitation in the Upper-Scheldt and the Nete catchments. They found a negative correlation between the proportion of forest and the nitrate concentration in the Upper-Scheldt catchment. They suggested that using land use only to interpret nutrient concentrations in surface water bodies can lead to erroneous assumptions. Davies and Neal (2007) used linear regression to define the relationship between catchment characteristics (land use and hydrology) and mean nitrate-nitrogen concentration across many catchments in the UK. They found a strong positive correlation between the percentage of arable area and the mean nitrate-nitrogen concentration. In addition, they found a positive, but less significant, correlation between the base flow index (BFI), proportion of urban area and mean nitrate-nitrogen concentration. On the contrary, a strong negative relationship was found between the mean nitrate-nitrogen concentration and both the proportion of upland and the effective rainfall (ER). Onderka et al. (2012) used partial least squares regression (PLSR) to investigate how catchment characteristics (hydrology, land use, geology and physiography) influence dissolved inorganic nitrogen (DIN) fluxes in the Alzette catchment (1092 km^2), in the Grand Duchy of Luxembourg. They found that geology (schist and sand) had a significant influence on DIN fluxes, with higher the schist and sand proportions, higher the DIN fluxes in the Alzette catchment, Luxembourg. Zhou et al. (2017) also used PLSR to investigate the influence of catchment characteristics (hydrology, physiography, land-use types and land-use patterns) on (annual, dry and wet) nitrate concentrations in the Hujiashan watershed (~23 km^2), China. They found that the proportions of agricultural, forest, and residential land areas have the highest influence on nitrate concentrations, with positive, negative and positive regression coefficients, respectively.

In New Zealand, Julian et al. (2017) used stepwise regression to evaluate the relationship between catchment characteristics (morphometric, soil, hydro-climatological, land use and land disturbance variables) and the oxidised nitrogen (in forms of nitrite and nitrate) concentration for 77 diverse catchments. They found that land use intensity, as measured by the stock unit density of cattle, was the main predictor of the river oxidised nitrogen concentrations.

Most of the abovementioned studies have used multivariate statistics to assess the relationship between catchment characteristics and river water quality. However, multiple linear regression does not account for the interdependence (or co-linearity) between independent variables (predictors) (Yeniay and Goktas, 2002). Another limitation of the multiple regression technique is the number of predictors is limited by the number of observations. Carrascal et al., (2009) illustrated that lower number of observations compared to the number of predictors results in a II-type error (i.e. false negative, or the error of failing to reject a null hypothesis). Therefore, methods such as partial least squares regression (PLSR) should be used when there are: 1) co-linearity between the independent variables; and 2) the number of independent variables is larger than the number of observations (Carrascal et al., 2009; Cramer, 1993; Yeniay and Goktas, 2002). The PLSR is a technique that combines features from both multiple linear regression and principal component analysis (PCA) (Abdi, 2010). Similar to PCA, PLSR is a dimension reduction technique as it reduces the independent variables to fewer variables. The difference between PCA and PLSR is that PLSR performs regression between the independent and the dependent variables. Thus, the robustness of PLSR is based on its ability to analyse collinear, noisy and even incomplete variables (both independent and dependent) (Abdi, 2010; Wold et al., 2001). The very limited studies that have used robust statistical analysis that account for co-linearity (e.g. PLSR; Onderka et al., 2012; Zhou et al., 2017) did not account for subsurface characteristics that influence that fate and transport of nitrogen from farms to rivers. For example, Onderka et al. (2012) did not evaluate the influence of soils on river dissolved inorganic nitrogen fluxes in the Alzette catchment, Luxembourg. Also, Zhou et al. (2017) did not evaluate the influence of either geology, or soils, on nitrate concentrations in the Hujiashan watershed, China. Similarly, in New Zealand, the only study to our knowledge is by Julian et al. (2017), who evaluated the relationship between catchment characteristics and oxidised nitrogen concentration, did not account for the influence of geology.

Upon leaching from the root zone, the water soluble nitrate is attenuated, mainly through denitrification (among other processes), in the subsurface on its way from different land uses to rivers and streams (Rivett et al., 2007). A number of studies showed that denitrification is influenced by catchment characteristics such as soil and rock properties, that influence the leaching and flow rate, flow pathway length, residence time, and consequently the time for biogeochemical reactions that attenuate water soluble nitrate in the subsurface on its journey from farms to rivers (Fenton et al., 2009; Jahangir et al., 2012b; McAleer et al., 2017; McMahon and Chapelle, 2008; Vidon and Hill, 2004; Wu et al., 2018). Therefore, upon investigation of the relationship between catchment characteristics and nitrate concentrations in the streams and rivers, it is important to account for subsurface catchment characteristics (such as soil and rock properties) that influence denitrification.

Also, to our knowledge, none of the studies evaluated the relationship between catchment characteristics and SIN using a river dataset stratified by flows. Stratification of water quality data by flows (the highest and lowest 25% of flows) can give additional insights on how older water (low flows; deeper flow paths), versus younger water (high flows; near-surface flow paths), are influenced by catchment characteristics (Woodward et al., 2016).

In summary, to our knowledge, none of the studies have used a combination of: 1) catchment characteristics that included subsurface characteristics (both soils and rocks); 2) statistical analysis that is robust in dealing with co-linear data (e.g. PLSR); and 3) a water quality dataset stratified by flow conditions (low and high flows) to investigate the influence of catchment characteristics on river soluble inorganic nitrogen (SIN) concentrations in agricultural catchments. This is particularly the case for pastoral agricultural catchments across temperate regions such as lower parts of North Island in New Zealand. The main objective of this study, therefore, was to assess the influence of different catchment characteristics including subsurface characteristics (such as rocks and sub-rocks) on river SIN concentrations at different flow categories (all flows, highest 25% flows and the lowest 25% flows) in a temperate pastoral agricultural catchment. To our knowledge, this is the first study to analyse a unique set of catchment characteristics including subsurface characteristics (soils and rocks) to evaluate the magnitude and direction of their relationships with river SIN concentrations at different flows conditions in a pastoral temperate agricultural catchment. This provides policy makers and water regulatory authorities with the necessary information for formulation and implementation of targeted and effective water quality management solutions in pastoral agricultural catchments across New Zealand and similar conditions elsewhere.

3.3 Materials and Methods

3.3.1 Study area

The Tararua catchment is located in the upstream part of the Manawatu catchment, to the east of the Manawatu Gorge, in lower North Island, New Zealand (Fig. 3.1). It covers an area of around 3192 km^2. The elevation ranges from 60 m to 1497 m with an average of 316 m above mean sea level. The catchment has a temperate climate with a rainfall that varies from 945 mm yr^{-1} to 6265 mm yr^{-1}, with an average of 1520 mm yr^{-1}, based on 30 years "1978-2007" of rainfall data (Tait and Sturman, 2008). The dominant land-use types are sheep/beef farming (64%), native cover (17%) and dairy farming (15%) (Clark and Roygard, 2008).

The Tararua catchment is surrounded, in the west, by the Tararua and Ruahine ranges and the active Wellington-Mohaka Fault; and in the east by Waewaepa and Puketoi ranges (Rawlinson and Begg, 2014). The broad depression between these ranges is called the Pahiatua basin (Lee and Begg, 2002). The tectonic uplift of the Tararua and Ruahine axial ranges, around 1-1.5 Ma ago, was linked to the start of movement on the Wellington Fault. During this tectonic uplift, the Manawatu Gorge was formed by a river cutting through the axial ranges (Rawlinson and Begg, 2014; Zarour, 2008). The Triassic to late Early Cretaceous basement in the catchment is intensely faulted creating a series of highs (ridges) and lows (troughs). These ridges and depressions are filled with Tertiary (late Early Cretaceous to latest Pliocene) sediments (Rawlinson and Begg, 2014). The Tertiary sediments are mainly marine mudstone and sandstone with variable thickness (from < 1 m to around 2.2 km). The thick Tertiary sediments are overlaid by thin Quaternary (Holocene to early Pleistocene) sediments with thickness that has a maximum of around 228 m (Rawlinson and Begg, 2014). The major soil textures in the Tararua catchment, are silt loam (52%) and sandy loam (16%) (Newsome et al., 2008).

According to Zarour (2008), the groundwater table is controlled by the topography in the catchment. Rawlinson and Begg (2014) illustrated that the groundwater flow is a replica of the catchment topography. The groundwater is recharged mainly by infiltration of rainfall over the ranges that surround the catchment in the east and the west (Bekesi, 2001). The rainfall infiltration recharge was estimated to be 814 x 10^6 m^3 yr^{-1} (i.e. around 255 mm yr^{-1}) (Callander and Thomas, 2013). There is a strong connection between the surface water and the groundwater in the catchment (Zarour, 2008). This is reflected by the large fraction of the baseflow in the total stream flow. Analysis of 8 years of stream flow data (2009 to 2016) showed that the average stream flow at the outlet of the Tararua catchment via the Manawatu Gorge was 7.2 x 10^6 m^3 day^{-1} and the average baseflow was estimated to be 4.6 x 10^6 m^3 day^{-1} (i.e. base flow index "BFI" = 0.64).

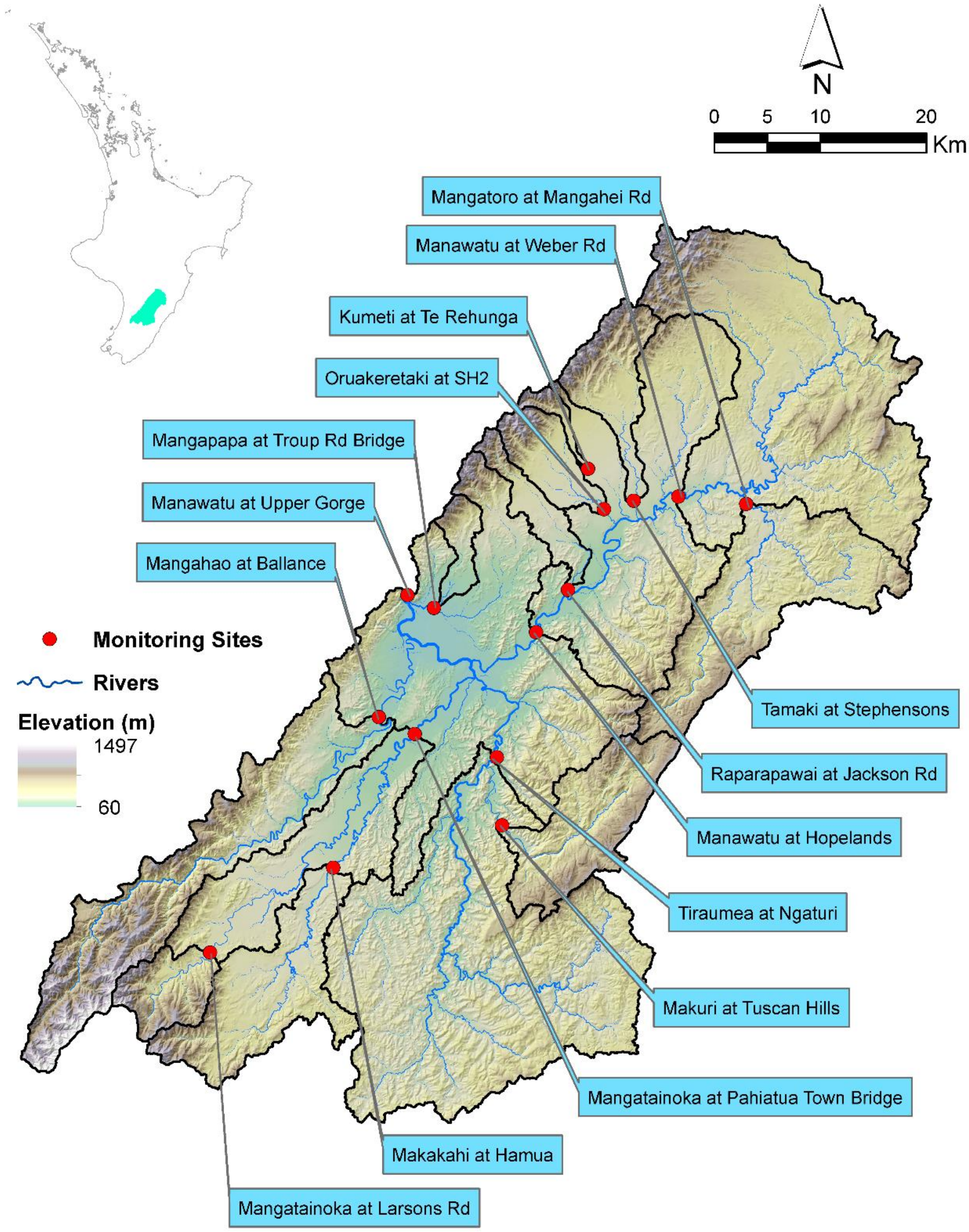


Figure 3.1. Location and extent of the Tararua catchment and its 15 river monitoring sites.

3.3.2 Available data and its processing

Figure 3.2 presents a flow chart of geographical, climatic, hydrological and river water quality data collection, processing and analysis to investigate the influence of catchment characteristics on SIN concentrations measured at all flows, highest 25% flows and lowest 25% flows at 15 river monitoring sites across in the Tararua catchment (Fig. 3.1). Table 3.1 summarises the independent and dependent variables used in this analysis along with their abbreviations and units. Horizons Regional Council (HRC) monitors continuous river flow, every 15 minutes based on stage-discharge relationship, at several sites in the Manawatu-Wanganui region. They provided the mean daily river flow measurements (m^3 s^{-1}) for the 15 monitoring sites in the Tararua catchment (Fig. 3.1) for 8 years (from 2009 to 2016).

In addition to the river flow measurements, HRC also monitors a number of water quality parameters across their monitoring network on a monthly basis. We obtained the monthly water quality measurements, nitrate-nitrogen, nitrite-nitrogen, ammoniacal nitrogen and total oxidized nitrogen (TON = nitrate-nitrogen+ nitrite-nitrogen) concentrations, measured over 8 years from 2009 to 2016. The soluble inorganic nitrogen "SIN" concentration was calculated as the sum of nitrate-nitrogen, nitrite-nitrogen and ammoniacal-nitrogen concentrations measured. As ammoniacal-nitrogen represent the smallest fraction of SIN, we used TON plus ammoniacal nitrogen, or TON only if ammoniacal nitrogen is missing, as a substitute for SIN whenever any nitrate-nitrogen or nitrite-nitrogen measurements were missing.

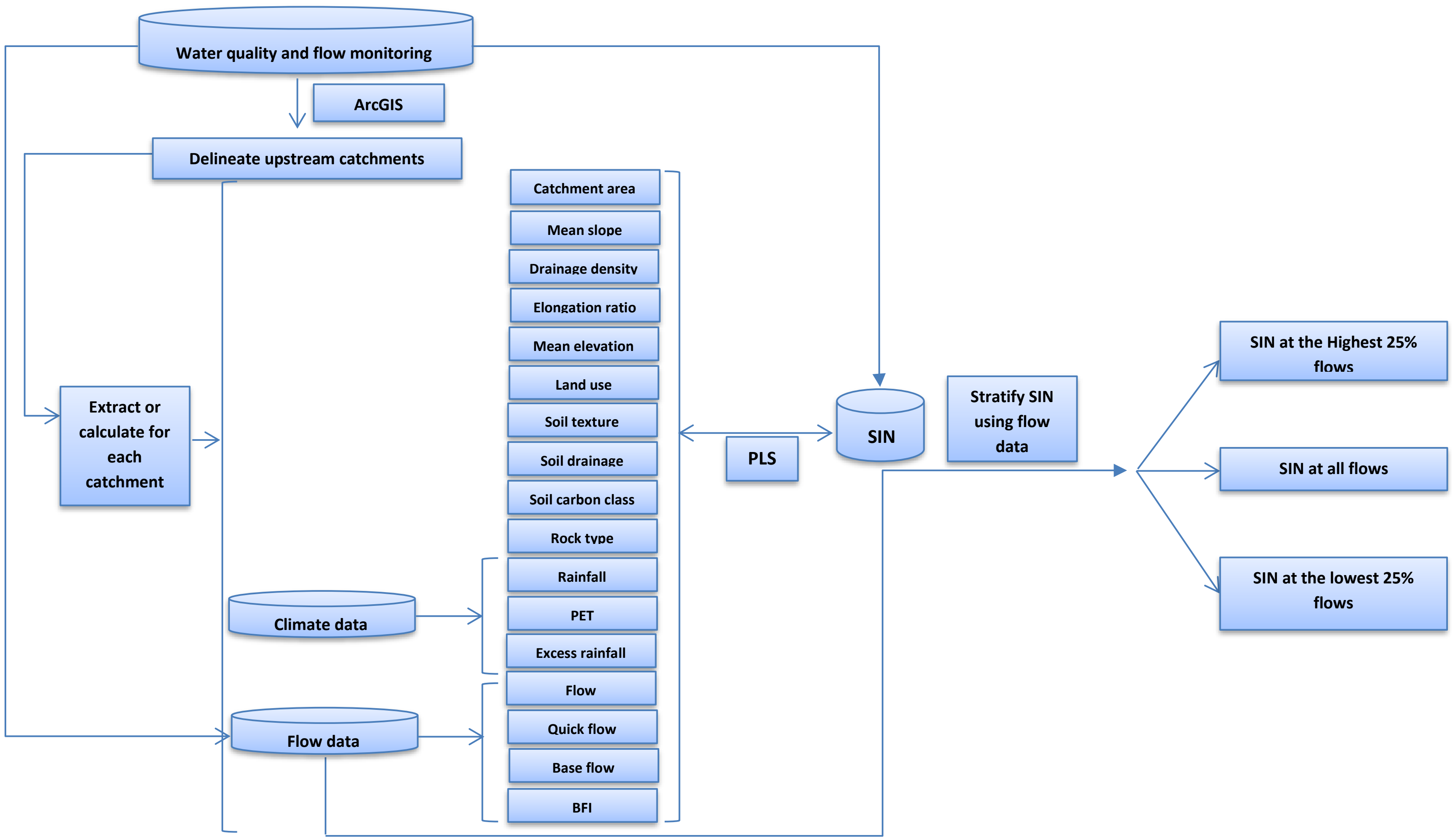


Figure 3.2. A flowchart for geographical, climatic, hydrological and river water quality data collection, processing and analysis used to investigate the influence of catchment characteristics on soluble inorganic nitrogen (SIN) at all flows, highest 25% flows and lowest 25% flows sin the Tararua catchment, New Zealand.

The river flow records were stratified into 20 equal flow quantile bins, with each bin representing 5% of the flow. Our analysis considered mean SIN concentrations for all flows, plus mean SIN concentrations for the highest 25% flows and mean SIN concentrations for the lowest 25% flows (Fig. 3.3; Appendix A). This was repeated to investigate the influence of different catchment characteristics on river SIN concentrations at different flows in the Tararua catchment.

The selected 15 river monitoring sites in the Tararua catchment (Fig. 3.1) were used to delineate the catchment area upstream of the site. The shapefiles resulting from this delineation were used to extract all sub-catchments characteristics (apart from the hydrological indices) for each site. To estimate the base flow index (BFI), base flow was separated from daily stream flow records at each site (Appendix A) using recursive digital filter (Lyne and Hollick, 1979; Nathan and McMahon, 1990) as per Equation 3.1.

$$q_{f(i)} = \alpha q_{f(i-1)} + (q_{t(i)} - q_{t(i-1)}) \frac{1+\alpha}{2} \tag{3.1}$$

where:

$q_{f(i)}$	= filtered quick flow at the *ith* sampling instant;
$q_{t(i)}$	= stream flow at the *ith* sampling instant;
α	= coefficient (recommended value 0.925); and
$q_{b(i)}$	= filtered baseflow ($q_{t(i)} - q_{f(i)}$) at the *ith* sampling instant.

In addition to the average daily flow and BFI, we included the average daily quick flow (flow – base flow) and base flow in the analysis (Tables 3.1 and 3.2). The daily climatic data, on a 0.05° latitude/longitude grid (i.e. around 4 km) (Wratt et al., 2006), was obtained from the National Institute of Water and Atmospheric Research (NIWA) for 8 years (from 2009 till 2016). This data was used to extract the climatic variables (average daily rainfall and evapotranspiration) for each sub-catchment. The average daily excess rainfall, for each sub-catchment, was estimated (Table 3.2) by subtracting evapotranspiration from rainfall (Gomez and Jones, 2010).

The morphological characteristics included the sub-catchments area (km^2), mean elevation (m), mean slope (%), drainage density ($km\ km^{-2}$), and elongation ratio (-). A digital elevation model (DEM) with a resolution of 25x25 m, obtained from the Land Resource Information Systems (LRIS) portal (Barringer et al., 2002), was used to calculate the mean elevation (m) and mean slope (%) for each sub-catchment (Table 3.3). The drainage density ($km\ km^{-2}$) for each sub-catchment was calculated by dividing total stream length (km) by the sub-catchment area (km^2). The elongation ratio (-) for each sub-catchment was calculated as defined by Schumm (1956) as the ratio of a diameter of a circle that has an area equals to the catchment to the maximum catchment length (Table 3.3).

Table 3.4 summarizes the estimates of the areal percentage of main land use, soils and subsurface rocks characteristics (23 independent variables) in the 15 study sub-catchments. Our analysis was limited to the catchment characteristics that were estimated equal to, or larger than 5% of, the total area of the Tararua catchment. A land-use layer, obtained from the HRC (Clark and Roygard, 2008), was used to extract areal percentage of main land-use types including native cover, sheep and/or beef and dairy in each sub-catchment (Table 3.4). This land-use layer has been compiled using three datasets. These datasets are: Land Cover Database

2 (LCDB2) with 15 m spatial resolution which was created using satellite imagery over summer 2001/2002; Agribase^{TM} dataset; and Horizons Regional Council's land parcel/consents database (Maree Patterson, personal communication, 2018; Clark and Roygard, 2008) . The 1:50 000 Fundamental Soil Layer "FSL" (Newsome et al., 2008) was used to extract the areal percentage of main soil texture in each sub-catchment. According to the FSL, there are 18 soil texture types in the Tararua catchment. In addition to soil texture, the FSL was used to extract the areal percentage of different soil carbon classes in each sub-catchment. According to the FSL, there are 5 soil carbon classes ranging from 1 as a very high carbon content (20-40 % Total Carbon 'TC' g C/100 g soil) to 5 being very low carbon content (0.1-1.9 % TC). However, there are only 4 soil carbon classes (from carbon class 2 to carbon class 5) found in the study sub-catchments. Finally, the FSL was also used to extract the areal percentages of soil drainage classes in the study sub-catchments. According to the FSL, there are 5 soil drainage classes ranging from 1, as very poorly drained soils, to 5 being well drained soils. In the study sub-catchment, there are only 4 soil drainage classes (from drainage class 2 to drainage class 5). For rock types, the 1:250 000 Geological Map of New Zealand, called QMAP "for Quarter-million MAP" (Heron, 2014) was used to extract the areal percentage of main rocks and subrocks in the study sub-catchments.

Table 3.1. Description of dependent (soluble inorganic nitrogen) and independent variables (catchment characteristics) used in the analysis.

Category	**Variable**	**Abbreviation**	**Unit**
Water quality	Soluble Inorganic Nitrogen (all flows)	SIN_All	mg L^{-1}
	Soluble Inorganic Nitrogen (Highest 25% flows)	SIN_H25	mg L^{-1}
	Soluble Inorganic Nitrogen (Lowest 25% flows)	SIN_L25	mg L^{-1}
Hydrological indices	Flow	h_F	m^3 day^{-1}
	Quick Flow	h_QuFl	m^3 day^{-1}
	Base Flow	h_BF	m^3 day^{-1}
	Base Flow Index	h_BFI	
	Rainfall	h_Ra	mm day^{-1}
	Potential Evapotranspiration	h_PET	mm day^{-1}
	Excess Rainfall	h_ER	mm day^{-1}
Morphological indices	Area	m_A	km^2
	Mean Elevation	m_MeEl	m
	Mean Slope	m_MeSl	%
	Elongation Ratio	m_ElRa	

Category	Variable	Abbreviation	Unit
	Drainage Density	m_DrDe	km/km^2
Land use	Dairy	l_Da	areal percentage
	Native Cover	l_NaCo	areal percentage
	Sheep and/or Beef	l_ShBe	areal percentage
Soil texture	Sandy Loam	s_SaLo	areal percentage
	Silt Loam	s_SiLo	areal percentage
	Stony Loam	s_StLo	areal percentage
	Stony Silt Loam	s_SSiLo	areal percentage
Soil carbon classes	Carbon Class 2	c_C2	areal percentage
	Carbon Class 3	c_C3	areal percentage
	Carbon Class 4	c_C4	areal percentage
Soil drainage classes	Drainge Class 2	d_D2	areal percentage

Category	Variable	Abbreviation	Unit
	Drainge Class 3	d_D3	areal percentage
	Drainge Class 4	d_D4	areal percentage
	Drainge Class 5	d_D5	areal percentage
Main rocks	Coquina	Mr_Co	areal percentage
	Gravel	Mr_GRAv	areal percentage
	Greywacke	Mr_GREy	areal percentage
	Mudstone	Mr_Mu	areal percentage
	Sandstone	Mr_Sa	areal percentage
Sub rocks	Limestone	Sr_Li	areal percentage
	Sand Loess Silt	Sr_SaLoSi	areal percentage
	Sandstone Conglomerate Coquina Tephra	Sr_Scct	areal percentage
	Sandstone Mudstone Basalt Chert Limestone	Sr_Smbcl	areal percentage

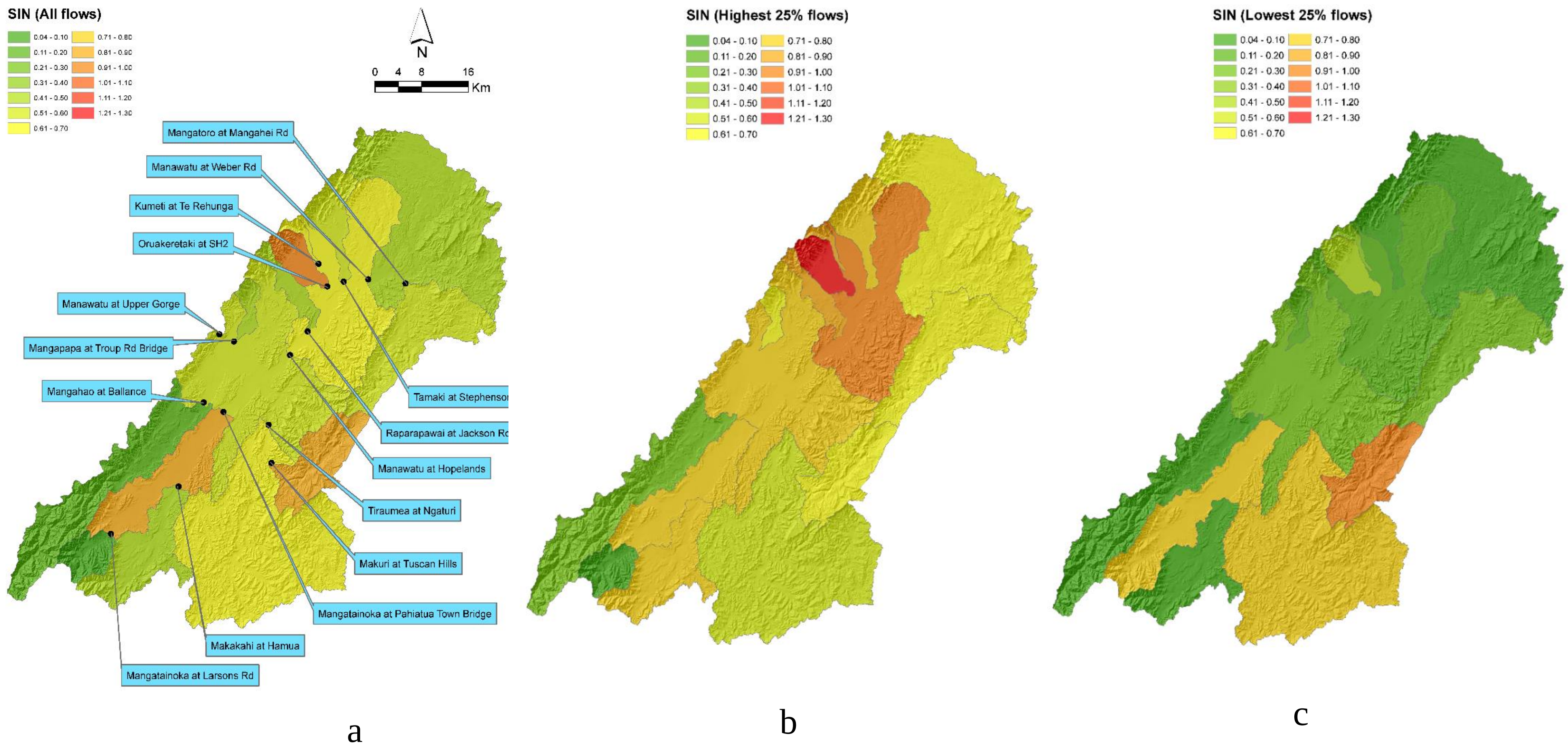


Figure 3.3. Spatial variations of the mean soluble inorganic nitrogen (SIN) concentration (mg L^{-1}) at all flows (a); highest 25% flows (b); and the lowest 25% flows (c), for the 15 monitoring sites in the Tararua catchment measured for 8 years (from Jan., 2009 to Dec., 2016).

Table 3.2. A summary of hydrologic indices estimated at all flows, highest 25% of flows, and lowest 25% flows for the 15 study sub-catchments in the Tararua catchment (Fig. 3.1). Abbreviations for the variables and units are listed in Table 3.1.

Site	All flows							Highest 25%							Lowest 25%						
	h_F	h_QuFl	h_BF	h_BFI	h_Ra	h_PET	h_ER	h_F	h_QuFl	h_BF	h_BFI	h_Ra	h_PET	h_ER	h_F	h_QuFl	h_BF	h_BFI	h_Ra	h_PET	h_ER
Kumeti_at_ Te_Rehunga	458.6	119.9	338.7	0.7	4.4	2.4	3.6	1041.4	326.8	714.2	0.7	6.2	1.8	5.4	101.2	14.6	86.6	0.9	2.9	3.1	2.2
Makakahi_ at_Hamua	5816.9	2603.8	3213.2	0.6	4.8	2.4	4.0	15773.7	6557.3	9213.9	0.6	8.2	1.7	7.3	564.0	147.4	416.2	0.7	2.8	3.4	2.1
Makuri_at_ Tuscan_Hills	4875.3	1262.6	3612.8	0.7	4.1	2.4	3.4	9657.9	3261.1	6396.8	0.7	7.1	1.7	6.3	2298.8	124.0	2173.6	0.9	2.4	3.1	1.9
Manawatu_at_ Hopelands	25021.4	8795.0	16226.4	0.6	3.7	2.5	3.0	63956.4	24068.3	39897.7	0.6	5.5	1.6	4.8	4455.3	663.5	3789.7	0.9	2.3	3.5	1.7
Manawatu_at_ Upper_Gorge	83016.3	30180.9	52835.4	0.6	4.1	2.4	3.3	197778.3	65529.9	132174.3	0.7	5.7	1.8	4.8	16453.8	2837.0	13606.3	0.8	2.6	3.4	1.9
Manawatu_at_ Weber_Road	13146.2	5162.4	7983.7	0.6	3.6	2.5	2.9	35966.1	15416.1	20550.0	0.6	5.4	1.5	4.8	2134.0	248.3	1885.0	0.9	2.2	3.5	1.6
Mangahao_at_ Ballance	13738.9	6432.6	7306.3	0.5	6.6	2.2	5.8	36205.2	15774.1	20431.1	0.6	10.8	1.9	9.9	2572.1	431.6	2138.4	0.8	3.6	2.9	3.0
Mangapapa_at_ Troup_Rd	675.3	312.1	363.2	0.5	3.7	2.5	3.0	1846.4	807.9	1038.5	0.6	6.5	1.8	5.7	63.9	19.6	44.2	0.7	1.7	3.6	1.2
Mangatainoka_at_ Larsons_Road	4864.8	2539.6	2325.9	0.5	9.4	2.2	8.7	13306.1	5522.3	7778.3	0.6	18.9	1.7	17.9	676.4	133.2	542.6	0.8	3.8	2.9	3.3
Mangatainoka_at_ Pahiatua_Town_Bridge	17051.3	7104.3	9947.0	0.6	5.1	2.4	4.3	43568.9	16081.8	27484.0	0.6	7.6	1.8	6.6	2443.4	534.4	1906.4	0.8	3.2	3.3	2.5
Mangatoro_at_ Mangahei_Road	3987.5	1481.4	2506.1	0.6	3.3	2.5	2.7	10484.0	4612.9	5871.1	0.6	5.3	1.5	4.7	903.0	72.9	829.8	0.9	2.3	3.3	1.7
Oruakeretaki_at_ SH2_Napier	2089.8	673.1	1416.7	0.7	4.9	2.4	4.1	4790.6	1528.2	3262.4	0.7	7.8	1.7	7.0	434.4	73.8	360.2	0.8	2.5	3.4	1.8
Raparapawai_at_ Jackson_Rd	1046.0	393.9	652.1	0.6	4.0	2.4	3.3	2604.7	872.1	1732.6	0.7	6.5	1.6	5.7	145.2	41.2	103.8	0.7	2.0	3.5	1.4
Tamaki_at_ Stephensons	3380.5	1199.9	2180.6	0.6	4.8	2.4	3.9	8224.6	2895.9	5326.7	0.6	7.1	1.8	6.3	639.5	123.7	515.5	0.8	2.8	3.4	2.0
Tiraumea_at_ Ngaturi	15004.0	6048.6	8955.5	0.6	3.6	2.5	2.9	39813.5	16903.3	22910.2	0.6	5.0	1.6	4.3	3096.5	219.2	2875.8	0.9	2.1	3.4	1.5

Table 3.3. A summary of morphologic characteristics for the 15 study sub-catchments in the Tararua catchment (Fig. 3.1). Abbreviations for the variables and units are listed in Table 3.1.

Site	**m_A**	**m_MeEl**	**m_MeSl**	**m_ElRa**	**m_DrDe**
Kumeti_at_Te_Rehunga	11.77	549.25	40.55	0.32	1.70
Makakahi_at_Hamua	163.19	328.67	19.53	0.36	1.73
Makuri_at_Tuscan_Hills	135.39	451.43	28.77	0.45	1.57
Manawatu_at_Hopelands	1261.88	343.41	19.65	0.39	1.68
Manawatu_at_Upper_Gorge	3191.83	316.31	22.82	0.50	1.64
Manawatu_at_Weber_Road	714.57	362.37	19.67	0.42	1.65
Mangahao_at_Ballance	278.69	470.26	38.77	0.26	1.53
Mangapapa_at_Troup_Rd	26.58	280.56	19.97	0.41	1.74
Mangatainoka_at_Larsons_Road	57.35	521.56	39.85	0.45	1.62
Mangatainoka_at_Pahiatua_Town_Bridge	401.28	308.44	19.10	0.34	1.70
Mangatoro_at_Mangahei_Road	220.41	362.23	22.87	0.43	1.63
Oruakeretaki_at_SH2_Napier	53.36	385.66	22.55	0.47	1.96
Raparapawai_at_Jackson_Rd	42.31	312.29	17.87	0.32	1.81
Tamaki_at_Stephensons	77.35	466.72	29.46	0.38	1.55
Tiraumea_at_Ngaturi	744.65	288.97	25.77	0.43	1.53

Table 3.4. A descriptive summary of the areal percentage of landuse, soils and subsurface rocks characteristics for 15 study sub-catchments in the Tararua catchment (Fig. 3.1). Abbreviations for the variables are listed in Table 3.1.

Site	c_C2	c_C3	c_C4	d_D2	d_D3	d_D4	d_D5	l_Da	l_NaCo	l_ShBe	Mr_Co	Mr_GRAv	Mr_GREy	Mr_Mu	Mr_Sa	s_SaLo	s_SiLo	s_SSiLo	s_StLo	Sr_Li	Sr_Scct	Sr_SaLoSi	Sr_Smbcl
Kumeti_at_ Te_Rehunga	6	55	39	6	0	30	64	22	65	11	0	35	10	0	55	0	68	0	9	0	0	31	10
Makakahi_at_ Hamua	10	48	43	3	6	17	74	37	17	43	0	31	28	28	0	4	47	10	17	0	28	13	16
Makuri_at_ Tuscan_Hills	2	88	11	4	5	17	75	0	17	81	55	5	7	22	0	50	40	4	0	2	22	5	0
Manawatu_at_ Hopelands	8	52	40	3	21	12	63	16	10	70	7	40	6	11	35	23	51	4	3	6	6	8	2
Manawatu_at_ Upper_Gorge	6	53	41	6	21	19	54	15	17	64	8	31	14	28	16	16	52	5	7	5	22	12	10
Manawatu_at_ Weber_Road	4	60	36	1	23	13	63	8	7	82	8	32	3	10	43	26	50	4	1	7	1	1	0
Mangahao_at_ Ballance	6	59	35	0	16	40	44	9	66	23	4	19	68	8	0	0	29	17	48	4	8	7	68
Mangapapa_at_ Troup_Rd	17	6	76	24	9	0	68	16	27	52	0	32	28	0	40	9	74	0	0	0	0	29	28
Mangatainoka_at_ Larsons_Road	1	75	23	0	1	71	28	1	65	33	0	12	77	10	0	0	17	26	45	2	6	0	77
Mangatainoka_at_ Pahiatua_Town_Bridge	6	48	47	7	3	21	69	35	20	43	3	39	26	27	0	2	48	10	16	3	26	21	21
Mangatoro_at_ Mangahei_Road	0	74	26	0	33	23	43	0	4	91	21	7	11	14	45	41	36	2	2	3	4	5	0
Oruakeretaki_at_ SH2_Napier	23	33	44	17	1	6	76	43	33	23	0	59	15	0	26	1	70	0	5	0	0	41	15
Raparapawai_at_ Jackson_Rd	32	18	50	12	27	5	56	35	23	40	0	51	20	15	14	25	62	0	1	0	15	34	20
Tamaki_at_ Stephensons	14	51	35	1	7	12	80	22	36	39	0	41	4	0	55	0	71	12	1	0	0	0	4
Tiraumea_at_ Ngaturi	1	71	28	5	34	26	35	2	11	81	11	11	1	67	5	22	61	1	0	1	48	10	0

3.3.3 Statistical analysis

We used a PLSR analysis to investigate the magnitude and direction of the relationship between estimates of different catchment characteristics (Table 3.2, 3.3 and 3.4) and the mean soluble inorganic nitrogen (SIN) concentrations, at different flows (all flows; highest 25% flows; and lowest 25% flows) (Fig. 3.3), in the study sub-catchments. Prior to the use of PLSR, a Pearson correlation was used to investigate the co-dependence between the independent variables (catchment characteristics), including hydrologic indices calculated at all flows, highest 25% flows and lowest 25% flows.

The PLSR regression coefficients are commonly used to show the direction of the relationship between the independent variables and the dependent variable (e.g. Onderka et al., 2012; Yan et al., 2013). A number of studies have also used the variable influence on projection or variable importance on projection (VIP) as another index used to show the most influential independent variables (e.g. Nash and Chaloud 2011; Onderka et al. 2012; Shi et al. 2014; Zhou et al. 2017). As per Equation 3.2, the average VIP equals 1 when the sum of squares for all VIP values equals the number of independent variables. Consequently, if all predictors have equal contribution to the PLSR model, they will have VIP value of 1. Therefore, as a rule of thumb, variables that have VIP > 1 are considered the most influential variables (Chong and Jun, 2005; Galindo-Prieto et al., 2014).

$$\mathrm{VIP_j} = \sqrt{p\sum_{a=1}^{A}\left[SS_a\left({w_{aj}}/{\|w_a\|^2}\right)\right] / \sum_{a=1}^{A} SS_a} \tag{3.2}$$

where:

VIP_j = variable influence on projection for the *jth* variable;

p = total number of independent variables (predictors);

SS_a = sum of the squares for *ath component*;

A = total number of components;

w_a = weight of the *ath* component; and

w_{aj} = weight of *jth* variable for the *ath* component.

Therefore, in this study we used PLSR regression coefficients and VIP values to infer the magnitude and direction of the relationship between the independent variables that highly influence the soluble inorganic nitrogen (SIN) concentrations in the rivers of the Tararua catchment. To prevent the different scales of the independent variables from unduly influencing their importance in the PLSR analysis, they were standardized to create a matrix of z-scores (Hammond and McCullagh, 1978; Snedecor and Cochran, 1980). Apart from using ArcGIS 10.4.1® for extracting the spatial data (morphometric indices and areal percentage of land use, main rocks, sub rocks, and soil texture, drainage and carbon classes), the entire analysis was completed in R software (Appendix C) version 3.4.2 (R Core Team, 2017).

3.4 Results

Figure 3.4 reproduces the Pearson correlation matrix between the independent variables at all flows for the 15 study sub-catchments. It clearly indicates that there are high co-dependencies (either in a negative or positive direction) between several catchment characteristics such as the strong positive correlation between rainfall and all of greywacke, moderately well drained soils (D4), and native cover. This suggests the use of PLSR is required as it accounts for the co-linearity between the predictors (Carrascal et al., 2009; Cramer, 1993; Yeniay and Goktas, 2002).

Table 3.5 presents a summary for the PLSR analysis conducted at all flows, highest 25% flows and lowest 25% flows in the study sub-catchments. For SIN at all flows, the cross-validated root mean squared error (RMSECV) reached its minimum value (0.17) with four components (Table 3.5). An additional increase in the number of components (component 5) led to an increase in the prediction error (RMSECV), suggesting the use of four components in the PLSR analysis. The first and second components explained around 51% and 35%, respectively, of the total variance in the SIN concentration at all flows across the study sub-catchments. Thus, the first two components cumulatively explained around 86% of the total variance in the SIN concentrations at all flows. The first four components cumulatively explained around 93% of the total variance in the SIN concentrations at all flows (Table 3.5).

Figures 3.5, 3.7 and 3.8 reproduce the VIP values and regression coefficients for the independent variables, grouped into 8 categories (land use, hydrology, morphology, soil texture, soil carbon, soil drainage, and main rock, sub rock), at all flows, highest 25% flows and lowest 25% flows. The values were ordered in descending order, according to VIP values, within each group. To highlight the influential predictors, with VIP > 1, they were ranked

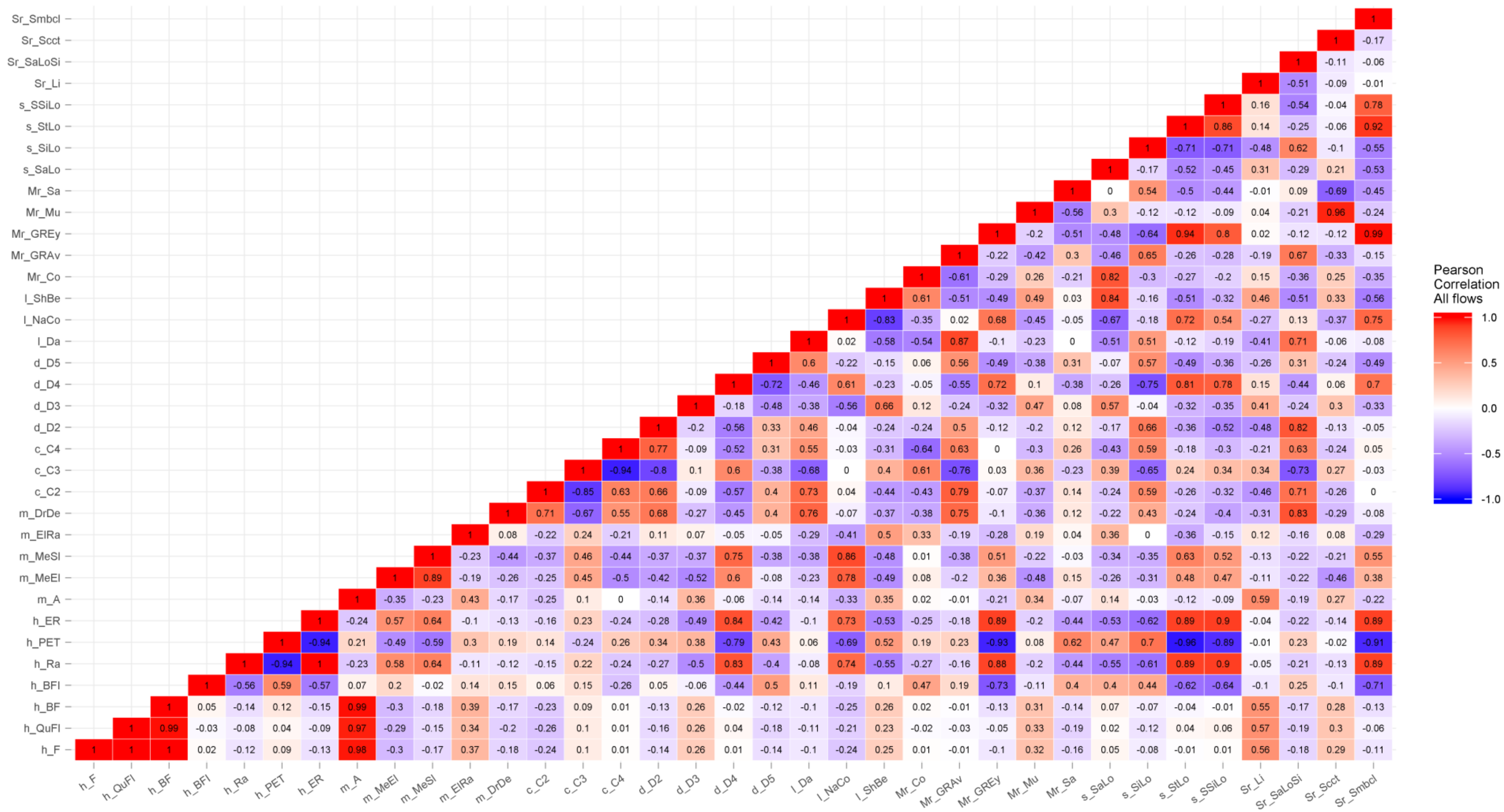


Figure 3.4. Pearson correlation between the independent variables (catchment characteristics) at all flows for the 15 study sub-catchments in the Tararua catchment. The magnitude and direction of the co-dependence are indicated by the different colours and their intensity.

Table 3.5. Summary of the partial least squares regression (PLSR) analysis for the 15 sub-catchments of Tararua catchment at all flows, highest 25% flows and lowest 25% flows. RMSECV is the cross-validated root mean squared error.

Flows category	Dependent	Component	% of explained variability	Cumulative explained variability	RMSECV
All flows	SIN	1	51.5	51.5	0.228
		2	34.8	86.3	0.184
		3	3.0	89.3	0.186
		4	3.3	92.6	0.175
		5	2.7	95.3	0.200
Highest 25% flows	SIN	1	72.4	72.4	0.221
		2	13.2	85.6	0.184
		3	8.3	93.9	0.168
		4	1.6	95.5	0.174
		5	1.1	96.6	0.187
Lowest 25% flows	SIN	1	35.5	35.5	0.336
		2	40.0	75.5	0.306
		3	6.5	82.0	0.283
		4	4.6	86.6	0.269
		5	5.4	92.0	0.270

consecutively to show their relative importance on SIN concentrations at all flows, highest 25% flows and lowest 25% flows.

At all flows, the predictors with the highest VIP values (Fig. 3.5) were: base flow index “BFI” (VIP = 1.96, positive regression coefficient), soil drainage class 5 “D5” (VIP = 1.56, positive regression coefficient), soil drainage class 2 “D2” (VIP = 1.38, positive regression coefficient), soil drainage class 3 “D3” (VIP = 1.36, negative regression coefficient), potential evapotranspiration “PET” (VIP = 1.33, positive regression coefficient), and excess rainfall “ER” (VIP = 1.18, negative regression coefficient).

For SIN at the highest 25% flows, the RMSECV reached its minimum value (0.168) with three components (Table 3.5). An additional increase in the number of components (component 4 and component 5) led to an increase in the prediction error (RMSECV), suggesting the use of three components in the PLSR analysis. The first and second components explained around 72% and 13%, respectively, of the total variance in the SIN concentrations at the highest 25% flows. Thus, the first two components cumulatively explained around 86% of the total variance in the SIN concentrations at the highest 25% flows. The addition of the third component increased the cumulative percentage of explained variance to around 94 % of the total variance in the SIN concentrations at the highest 25% flows.

At the highest 25% flows, the predictors with the highest VIP values (Fig. 3.7) were: soil drainage class 5 “D5” (VIP = 1.49, positive regression coefficient), land use as dairy “Da” (VIP = 1.44, positive regression coefficient), soil texture as silt loam “SiLo” (VIP = 1.431, positive regression coefficient), drainage density “DrDe” (VIP = 1.43, positive regression coefficient), main rock as gravel “GRAv” (VIP = 1.429, positive regression coefficient), and BFI (VIP = 1.422, positive regression coefficient).

For SIN at the lowest 25% flows, the RMSECV reached its minimum value (0.269) with four components (Table 3.5). An additional increase in the number of components (component 5) led to an increase in the prediction error (RMSECV), suggesting the use of four components in the PLSR analysis. The first two components cumulatively explained around 76% of the total variance in the SIN concentrations at the lowest 25% flows. The addition of the third and fourth components increased the cumulative percentage of explained variance to around 87% of the total variance in the SIN concentrations at the lowest 25% flows (Table 3.5).

At the lowest 25% flows, the predictors with the highest VIP values (Fig. 3.8) were: soil drainage class 2 "D2" (VIP = 1.79, positive regression coefficient), soil drainage class 3 "D3" (VIP = 1.55, negative regression coefficient), sub-rock as sand loam silt "SaLoSi" (VIP = 1.47, positive regression coefficient), main rock as coquina "Co" (VIP = 1.34, positive regression coefficient), BFI (VIP = 1.27, positive regression coefficient), and sub-rock as limestone "Li" (VIP = 1.23, negative regression coefficient).

Figures 3.5, 3.7 and 3.8 show that although all independent variables are, to a certain degree, related to the SIN concentrations (at all flows, highest 25% flows and lowest 25% flows), only those with VIP > 1 are considered the most influential variables (Nash and Chaloud, 2011). Therefore, the further discussion of the results obtained is mainly focused on the most influential independent variables (with VIP > 1) to investigate the relationships between different catchment characteristics and river SIN concentrations in the study sub-catchments.

3.5 Discussion

3.5.1 SIN at all flows

At all flows (Fig. 3.5), our results showed that the soil characteristics (mainly all soil drainage classes and to a lesser extent specific soil carbon classes and specific soil textures), specific hydrological parameters (base flow index 'h_BFI', potential evapotranspiration 'h_PET', excess rainfall 'ER', and rainfall 'h_Ra') and certain main rocks types (sandstone 'Mr_Sa' and coquina 'Mr_Co') have the highest influence (VIP > 1) on the river SIN concentrations in the study sub-catchments. Interestingly, none of the land-use types was found to be major influential factor (VIP <1) on the river SIN concentrations at all flows (Fig. 3.5). Our results match the results of Meynendonckx et al. (2006) who also found soil characteristics (drainage class) to supersede the land-use effects on the river nitrate concentrations variability in the Nete catchment, Belgium. Also, Norton and Fisher (2000) found out that soil characteristics completely outweigh the land-use effects on the stream nitrate concentration in the Choptank and Chester basins, the Delmarva Peninsula, USA.

At all flows, the first most influential independent variable on the river SIN concentrations was found to be the base flow index "BFI" with a positive regression coefficient (Fig. 3.5). Our results correspond with the findings of other studies that have also showed a positive relationship between BFI and nitrate concentrations in rivers. For example, Jordan et al. (1997) found a positive relationship between BFI and river nitrate-nitrogen concentrations in the Coastal Plain, Chesapeake Bay, USA. Also, Vanni et al. (2001) found a positive relationship between BFI and river nitrate-nitrogen concentrations in the Upper Four Mile Creek watershed, USA. This implies that the higher the BFI, the higher the river SIN concentrations in the study sub-catchments. The base flow index represents how geology influences water flow pathways

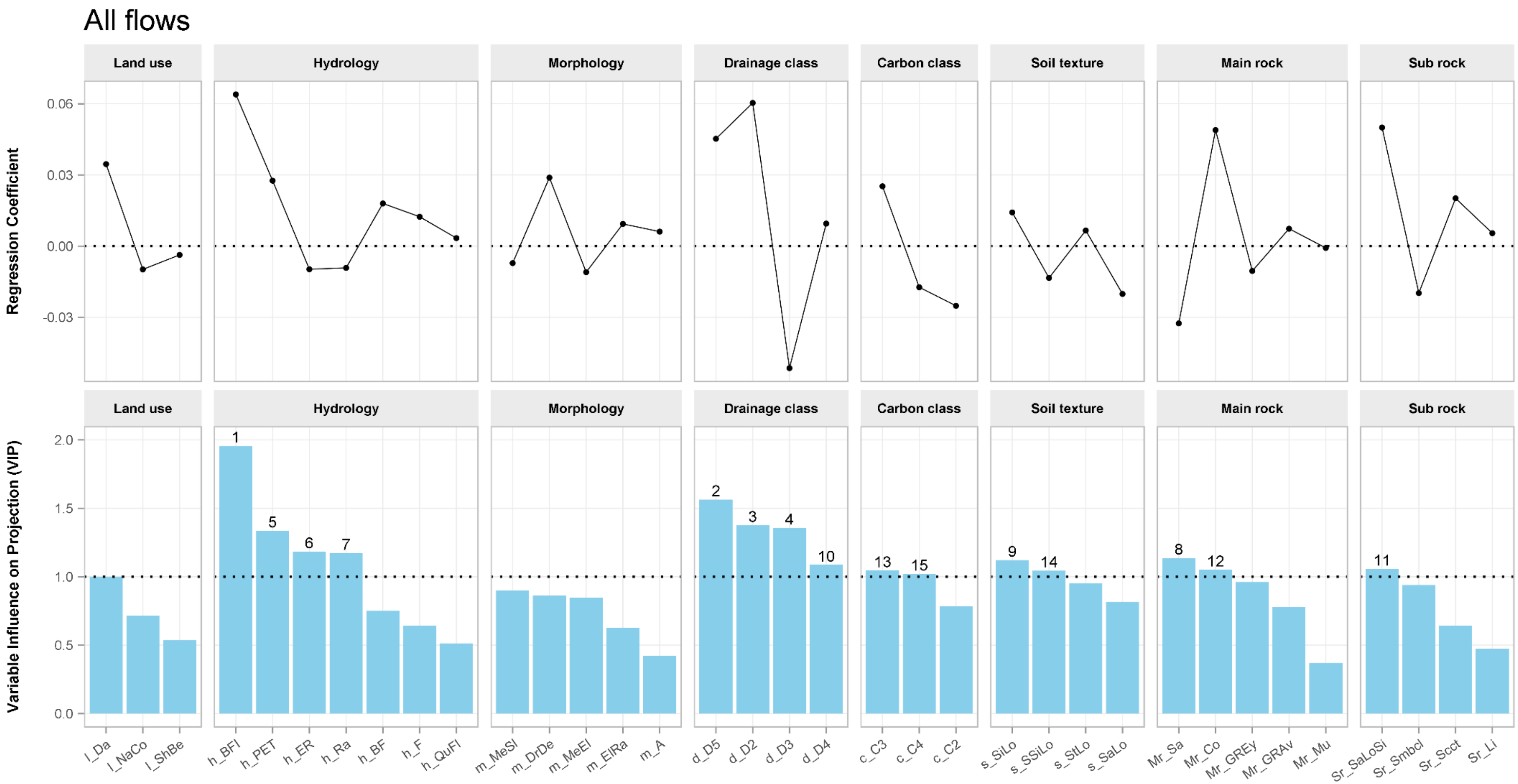


Figure 3.5. Partial least squares regression (PLSR)'s variable influence on projection (VIP) and regression coefficients for different catchment characteristics and river soluble inorganic concentrations (SIN) measured at all flows across the 15 sub-catchments in the Tararua catchment. Independent variables are arranged in descending order within each category (hydrology, landuse, main rock, sub rock, soil, morphology, drainage and carbon) based on their VIP values. Influential independent variables (VIP > 1) are ranked consecutively to illustrate their importance. The dashed lines in the regression coefficients differentiate between positive and negative directions whereas dashed line in the VIP (VIP =1) is to highlight the important independent variables located above the line.

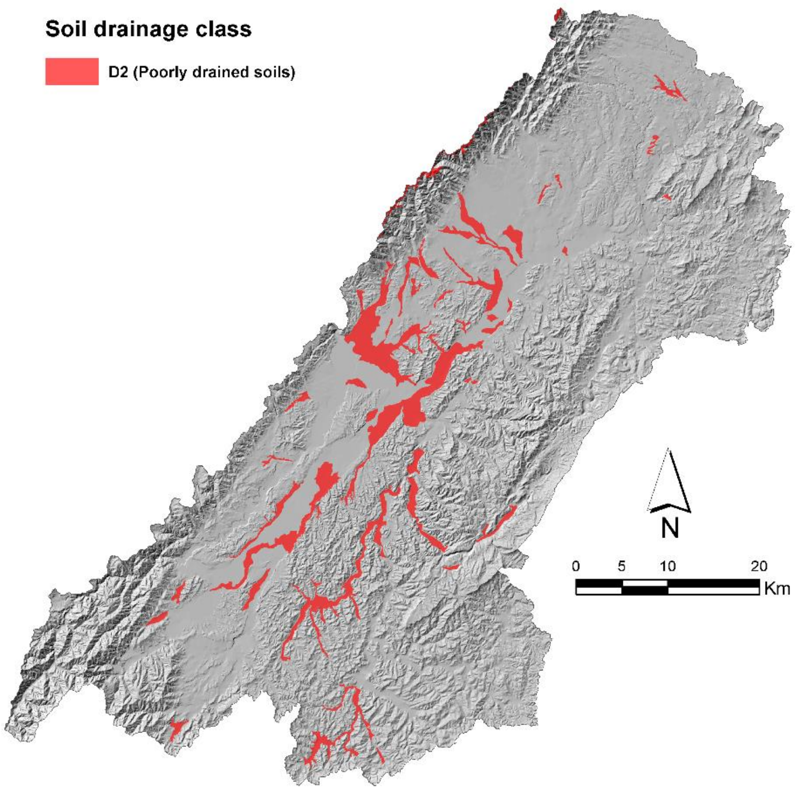
and therefore can be considered as a catchment descriptor (Smakhtin, 2001). A higher value of BFI suggests a permeable catchment while a lower BFI value suggests a relatively impermeable catchment (Lacey and Grayson, 1998; Tallaksen and Van Lanen, 2004). Thus, higher BFI values, and their indication of permeable catchments, suggests faster water flow and less residence time in the subsurface. This faster water flow could indicate less water residence time for potential denitrification in the subsurface environment and consequently higher SIN concentrations in the rivers.

At all flows, the second, third and fourth influential independent variables were found to be the soil drainage classes D5 (well drained soils), D2 (poorly drained soils), and D3 (imperfectly drained soils), respectively (Fig. 3.5). The soil drainage class D4 (moderately drained soils) was ranked as the 10th most influential independent variable (VIP >1). The soil drainage class was the only category (among the 8 categories of catchment characteristics: land use, hydrology, morphology, soil drainage class, soil carbon class, soil texture, main rocks and sub rocks) that had all of its levels (D2, D3, D4 and D5) as the most influential variables (VIP >1) on the river SIN concentrations at all flows. Soil drainage class 5 (D5 = well drained soils) was ranked as the second most influential variable with a positive regression coefficient on the river SIN concentrations at all flows. Soil drainage class 4 (D4 = moderately well drained soils) was found to have a positive regression coefficient (similar to D5 but to a lesser extent) with the river SIN concentrations (Fig. 3.5). This suggests that the study sub-catchments with higher proportions of well and moderately well drained soils are expected to have higher river SIN concentrations at all flows. This could be attributed to the higher infiltration capacity of well-drained soils causing higher soil water percolation and consequently higher nitrogen leaching from the soil profile. This also could lead to faster and oxic groundwater flow, and therefore less potential for denitrification in the subsurface environment (Mueller et al., 1997). Our results correspond with the study of Meynendonckx et al. (2006) in the Upper-Scheldt catchment, Belgium, where they also found a positive correlation between the proportion of well drained soils and nitrate concentrations in the rivers.

Soil drainage class 3 (D3 = imperfectly drained soils) was ranked as the fourth most influential variable with a positive regression coefficient on the river SIN concentrations at all flows (Fig. 3.5). This implies that the higher the proportions of imperfectly drained soils, the lower the river SIN concentrations in the study sub-catchments. Howard and Falck (1986) also found in Ontario, Canada, that low nitrate concentrations in the groundwater are generally associated with regions of imperfectly drained soils.

In contrast to soil drainage class 3 (D3 = imperfectly drained soils), the soil drainage class 2 (D2 = poorly drained soils) was ranked as the third most influential variable, but with a positive regression coefficient on the river SIN concentrations at all flows (Fig. 3.5). This implies that higher the proportions of poorly drained soils, higher the river SIN concentrations in the study sub-catchments. This is contrary to an expected negative relationship between poorly drained soils and SIN concentrations, as poorly drained soils would generally be characterized by anaerobic and reducing conditions conducive for potential denitrification to occur (Griffith et al., 1997). Yet, this positive relationship between the poorly drained soils (D2) and the river SIN concentrations in the study sub-catchments could be explained by the existence of artificial drainage in areas with poorly drained soils. In the Tararua catchment, poorly drained soils (D2) (Fig. 3.6a) was found to show a strong match with the estimated extent of artificially drained land with high confidence (high fuzzy probability; >0.6) (Fig. 3.6b) (Manderson, 2018). This artificial drainage will highly likely result in soil water bypassing poorly drained soils that are conducive to potential denitrification, and hence higher SIN concentrations in the drainage water would discharge to rivers and streams without denitrification.

(a)



(b)

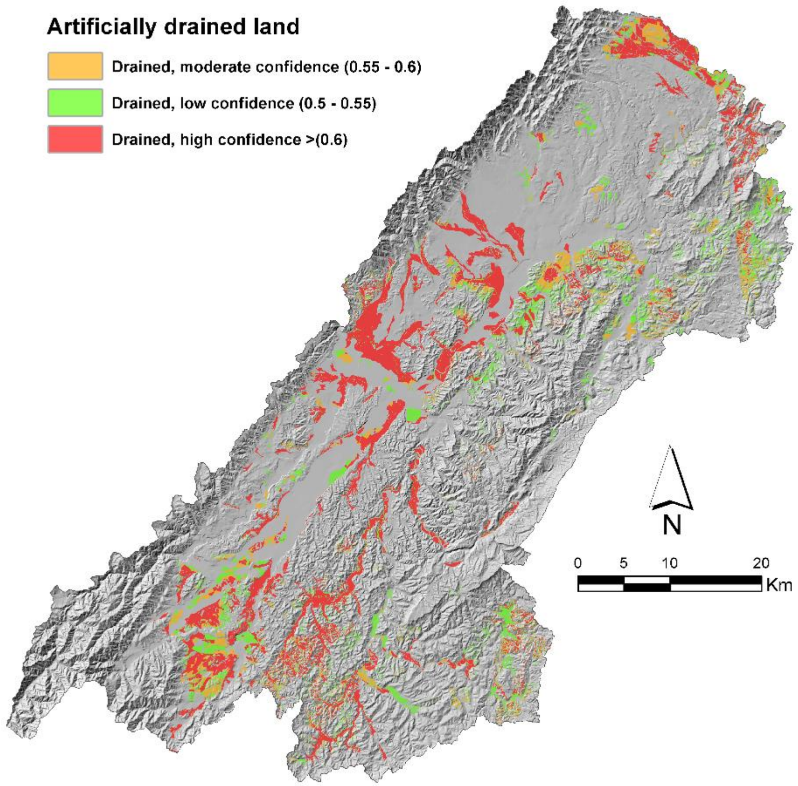


Figure 3.6. (a) Poorly drained soils (D2) from the Fundamental Soil Layer (FSL; Newsome et al., 2008) in the Tararua catchment; and (b) The estimated extent of artificially drained land in the Tararua catchment (fuzzy probability expressed as confidence classes) (Manderson, 2018)

The fifth, sixth and seventh most influential independent variables on the river SIN concentrations at all flows were found to be the potential evapotranspiration (PET), excess rainfall (ER) and rainfall (Ra), respectively (Fig. 3.5). The PET has a positive regression coefficient, whereas excess rainfall (ER) and rainfall (Ra) have negative regression coefficients. This reflects the effects of the sub-catchment's hydrology on the river SIN concentrations, where the sub-catchments with higher PET and lower excess rainfall (rainfall minus PET) could lead to less soil drainage and higher concentration of the SIN levels in the streams and rivers. On the other hand, the sub-catchments with higher rainfall (Ra) and excess rainfall (ER) could lead to high soil drainage and dilute the SIN levels in the streams and rivers (Lake et al., 2003). Davies and Neal (2007) also found a negative relationship between excess rainfall and mean river nitrate-nitrogen concentrations across many catchments in UK. Jarvie et al. (2002) also found a negative correlation between rainfall and river total oxidized nitrogen (sum of nitrate and nitrite) concentration in the Humber region, UK. Similarly, Meynendonckx et al. (2006) also found a negative relationship between rainfall and river nitrate concentration in the Upper Scheldt catchment, Flanders, Belgium.

Soil carbon classes 3 and 4 (C3 = 4 - 9.9% total carbon "g C/100 g soil over 0-0.2 m soil profile"; C4 = 2 - 3.9% total carbon) had positive and negative regression coefficients, respectively with the river SIN concentrations at all flows in the study sub-catchments (Fig. 3.5). Several studies showed that soil denitrification is a function of soil carbon content (e.g. Weier et al. 1993) with higher denitrification rates occurring in soils with higher carbon content (Adelman and Tabidian, 1996; Webster and Goulding, 1989). However, our study analysis showed an opposite relationship with soils with higher carbon content (C3) having a positive regression coefficient whereas soils with lower carbon content (C4) have a negative regression coefficient. In our study, the highest soil carbon class 2 (C2 = 10-19.9% total carbon) showed a negative regression coefficient with the river SIN concentrations at all flows (Fig. 3.5; VIP

<1) and lowest 25% flows (Fig. 3.8). This is consistent with the higher potential for denitrification in soils with higher carbon content. On the other hand, soil carbon class 2 had a positive regression coefficient with the river SIN concentrations at highest 25% flows (Fig. 3.7). The reason for this observed discrepancy with previous studies (e.g. soils with lower carbon content C4 have negative regression coefficients) is unclear, but the soil carbon classes have relatively low VIP values (though higher than 1) indicating their relatively weak influence on the river SIN concentrations in the study sub-catchments. It could be due to an unaccounted factor that could be associated with soil carbon class and river SIN concentrations, such as soil water content, or soil moisture availability for soil denitrification.

In addition to BFI and soil drainage classes, soil texture and subsurface rock types are also suggested to be influential on the river SIN concentrations at all flows (Fig. 3.5). Soil textures as silt loam "SiLo" and sand silt loam "sSiLo" had positive and negative regression coefficients, respectively with the river SIN concentrations (Fig. 3.5). The main rock type as sandstone (Mr_Sa) was ranked as the 8^{th} most influential independent variable on the river SIN concentrations at all flows with a negative regression coefficient. This could be attributed to lower saturated hydraulic conductivity generally associated with sandstone leading to longer residence time that promote the occurrence of subsurface denitrification, given the suitable conditions (low oxygen and existence of electron donors). McAleer et al. (2017) showed that denitrification could be as high as 94% in sandstone in two agricultural catchments in Ireland. The other main rock type as coquina (Mr_Co) was found to be an influential variable on the river SIN concentrations at all flows with a positive regression coefficient (Fig. 3.5). This could be attributed to higher permeability in coquina promoting faster flow which means less residence time and consequently less time for subsurface denitrification. The same also could be used as interpretation for the positive regression coefficient associated with the sand-loam-silt sub rock (SaLoSi), which is the only sub-rock found to influence on the river SIN at all flows (Fig. 3.5). However, the influences of soil texture and rock types are suggested to be less, in general, compared to the influence of base flow index and soil drainage classes on the river SIN at all flows (Fig. 3.5).

3.5.2 SIN at the highest 25% flows

While none of the land-use types are suggested as an important influential variable (VIP >1) on the river SIN concentrations at all flows (Fig. 3.5), dairy farming was found to be the only influential land-use type (VIP >1) with a positive regression coefficient on the river SIN concentrations at the highest 25% flows (Fig. 3.7). Highest 25% flows can be used as an indication of younger, shallower and faster moving groundwater (Woodward et al., 2016). The positive Pearson correlation between dairy and all of drainage class 5 (well drained soils), gravel suggests that water leached from dairy farms will move faster through well-drained soils and gravel and reach the stream and river through shorter, shallower flow paths at the highest 25% flows. This is also reflected by the positive Pearson correlation between dairy and base flow index (BFI) at the highest 25% flows. This shows that subsurface catchment characteristics (well-drained soils and gravel) below dairy farming are highly likely the influential factors on on river SIN concentration at the highest 25% flows.

Similar to all flows, the hydrological variables (BFI, rainfall, and excess rainfall) were also suggested among the most influential variables on the river SIN concentrations at the highest 25% flows (Fig. 3.7). However, potential evapotranspiration (PET) was shown not to be influential (i.e. VIP <1) at the highest 25% flows (Fig. 3.7) as compared to all flows (i.e. VIP >1) (Fig. 3.5). This could be due to relatively lower potential evapotranspiration (compared to rainfall and excess rainfall) at higher 25% flows compared to the potential evapotranspiration at all flows (Table 3.2).

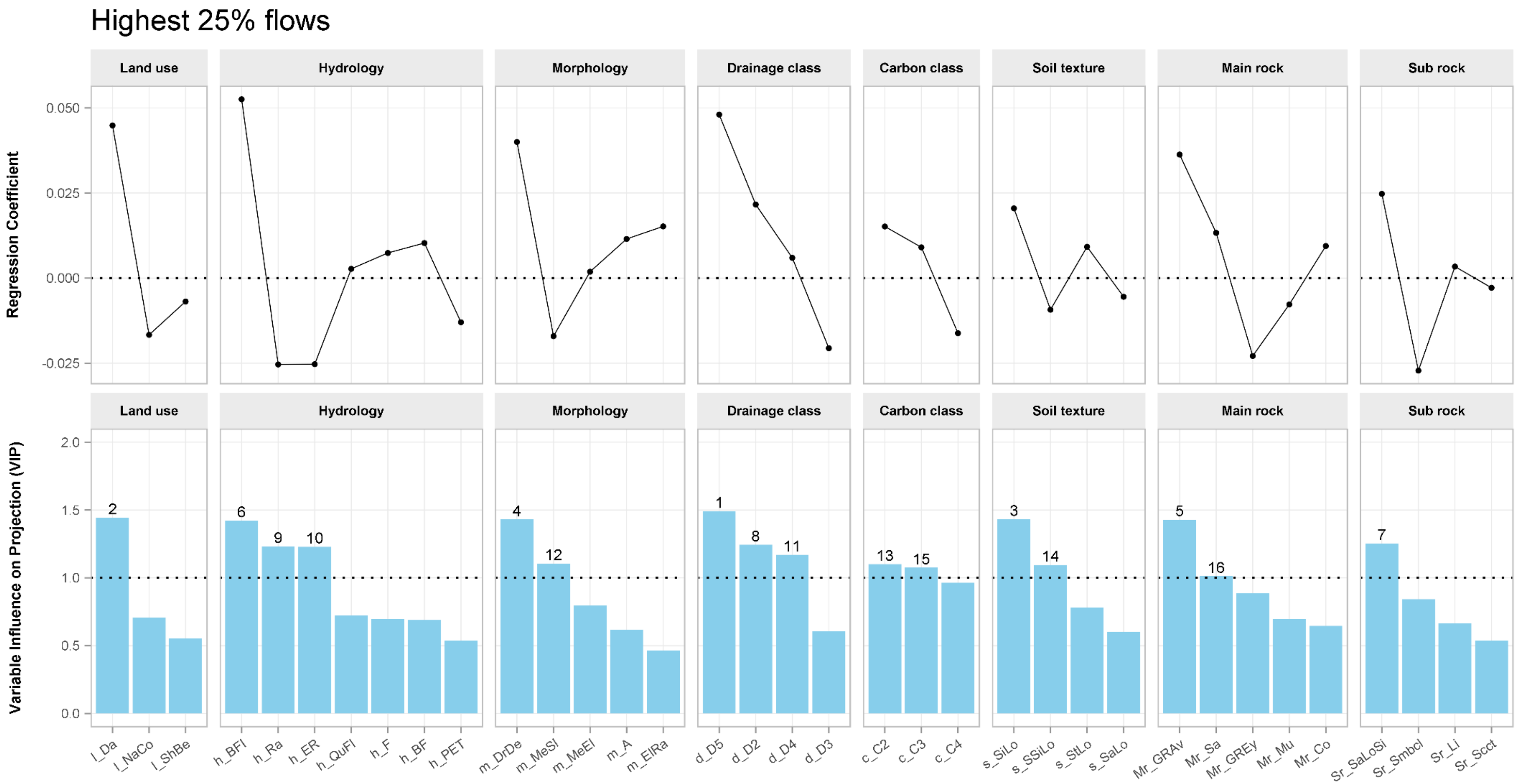


Figure 3.7. Partial least squares regression (PLSR)'s variable influence on projection (VIP) and regression coefficients for different catchment characteristics and river soluble inorganic concentrations (SIN) measured at highest 25% flows across the 15 sub-catchments in the Tararua catchment. Independent variables are arranged in descending order within each category (hydrology, landuse, main rock, sub rock, soil, morphology, drainage and carbon) based on their VIP values. Influential independent variables (VIP > 1) are ranked consecutively to illustrate their importance. The dashed lines in the regression coefficients differentiate between positive and negative directions whereas dashed line in the VIP (VIP =1) is to highlight the important independent variables located above the line.

Soil drainage classes (D5, D2 and D4) were also found to be among the most influential independent variables on the river SIN concentrations at the highest 25% flows. Soil drainage class 5 was ranked as the first most influential variable with a positive regression coefficient on the river SIN concentrations at the highest 25% flows (Fig. 3.7).

None of the morphological parameters were influential on the river SIN concentrations at all flows (Fig. 3.5). However, at the highest 25% flows, two morphological characteristics as drainage density "DrDe" and mean slope "MeSlPe" were influential on the river SIN concentrations (Fig. 3.7). The drainage density "DrDe" and mean slope "MeSlPe" showed a positive and negative regression coefficients, respectively with the river SIN concentrations at the highest 25% flows. Higher drainage densities suggest that catchments are highly dissected and consequently runoff lengths are shorter and water movement is faster and thus denitrification is hampered (Franklin et al., 2002; Young et al., 1996). Combining this with the highest 25% of flows (that indicate shorter, faster pathways), could explain the influential positive relationship between drainage densities and SIN at the highest 25% flows. Conversely, the negative relationship between slope and SIN concentration at the highest 25% flows could be due to dominance of native cover and consequently river water with lower SIN concentrations at catchments with higher slopes (e.g. Mangatainoka_at_Larson_Road and Mangahao_at_Ballance) (Table 3.2, 3.3 and 3.4). Jarvie et al. (2002) also found a negative relationship between catchment slope and total oxidized nitrogen in the Humber catchment, UK.

Similar to all flows (Fig. 3.5), soil textures as silt loam and sand silt loam and sub rock as sand loam silt were among the influential variables on the river SIN concentrations at the highest 25% flows (Fig. 3.7).

Interestingly, main rock types as gravels (Mr_GRAv) was among the most influential variables with a positive regression coefficient on the river SIN concentrations at the highest 25% flows (Fig. 3.7). This could be attributed to the faster water recharge and movement in gravels, leading to oxic groundwater with less residence time, and consequently less potential for denitrification in the subsurface environment (Fenton et al., 2009; Rivas et al., 2017).

3.5.3 SIN at the lowest 25% flows

Figure 3.8 suggests soil drainage classes (D2, D3 and D5), BFI, main rocks (as coquina and sandstone), sub rocks (as sand loam silt and limestone), and land use (as sheep and beef farming) are among the most influential variables on the river SIN concentrations at the lowest 25% flows. Sheep and/or beef was the only land-use type found to be influential (VIP >1) with a positive regression coefficient on the river SIN concentrations at the lowest 25% of flows (Fig. 3.4). This is highly likely due to the subsurface catchment characteristics below sheep and/or beef. For example, Tiraumea_at_Ngaturi that has higher mean river SIN concentrations at the lowest 25% flows than that at all flows (Fig. 3.3), is characterised by higher proportions of sheep and/or beef (Table 3.4), and relatively higher proportions of mudstone. Therefore, there is a positive Pearson correlation between sheep and/or beef and mudstone. The lowest 25% flows can be used as an indication of older, deeper slow moving groundwater (Woodward et al., 2016). Therefore, in sub-catchments with higher proportions of sheep and/or beef along with mudstone (such as Tiraumea_at_Ngaturi), water takes longer and deeper flow paths to reach the river. This suggests that the influence of sheep and/or beef on SIN at the lowest 25% in Tiraumea_at_Ngaturi sub-catchment is highly likely due to the subsurface catchment characteristics (mudstone). This could have been highly likely the case with dairy on the same subsurface catchment characteristics.

Similar to all flows, none of the morphological variables were found to influence the river SIN concentration at the lowest 25% flows (Fig. 3.8). Also, soil texture had no major influence on the river SIN concentrations at the lowest 25% flows.

On the other hand, most of the soil drainage classes (D2, D3 and D5) were found to be among the most influential variables on the river SIN concentrations at the lowest 25% flows. Soil drainage class 2 (D2 = poorly drained soils) was ranked as the first most influential variable on the river SIN concentrations with a positive regression coefficient at the lowest 25% flows. This could be due to the high Pearson correlation between the drainage class 2 and sand loam silt (Sr_SaLoSi) which in turn has a positive regression coefficient with SIN concentrations at the lowest 25% flows.

Also, similar to all flows (Fig. 3.5), main rocks as coquina and sandstone were among the most influential variables on the river SIN concentrations at the lowest 25% flows (Fig. 3.8). Coquina showed a positive regression coefficient, while sandstone showed a negative regression coefficient with the river SIN concentrations the lowest 25% flows. Interestingly, gravel as main rock was not an influential variable on the river SIN concentrations at the lowest 25% flows (Fig. 3.8). This suggests that relatively slower movement subsurface material such as sandstone is perhaps a major contributor of the river flow and SIN concentrations at the lowest 25% flows in the study sub-catchments. Sub rocks as sand loam silt (Sr_SaLoSi) and limestone (Sr_Li) were among the most influential variables (VIP >1) on the river SIN concentrations at the lowest 25% flows (Fig. 3.8). Sub-rock sand loam silt (Sr_SaLoSi) showed a positive regression, while sub-rock limestone (Sr_Li) showed a negative regression

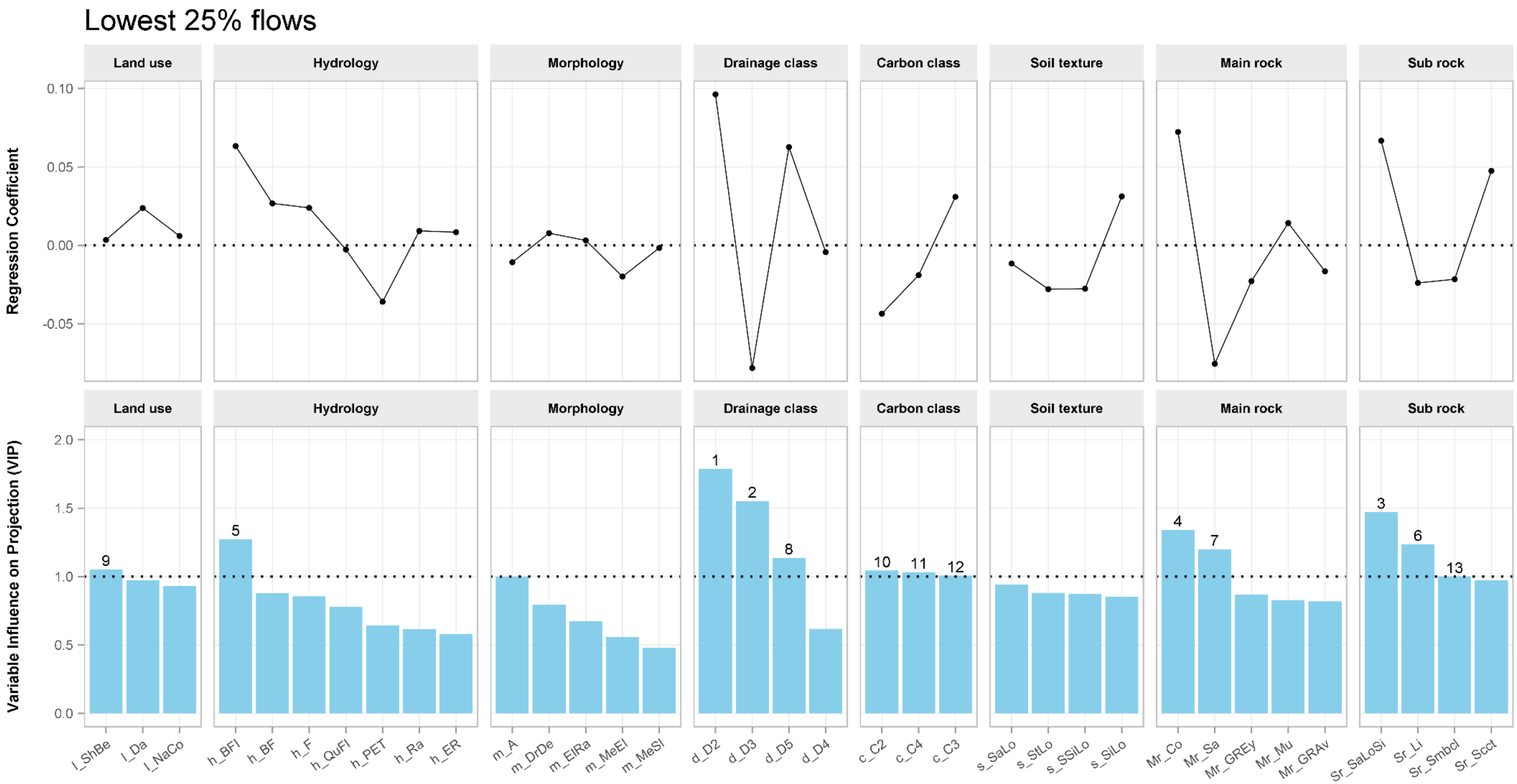


Figure 3.8. Partial least squares regression (PLSR)'s variable influence on projection (VIP) and regression coefficients for different catchment characteristics and river soluble inorganic nitrogen concentrations (SIN) measured at lowest 25% flows across the 15 sub-catchments in the Tararua catchment. Independent variables are arranged in descending order within each category (hydrology, landuse, main rock, sub rock, soil, morphology, drainage and carbon) based on their VIP values. Influential independent variables (VIP > 1) are ranked consecutively to illustrate their importance. The dashed lines in the regression coefficients differentiate between positive and negative directions whereas dashed line in the VIP (VIP =1) is to highlight the important independent variables located above the line.

coefficient with the river SIN concentrations at the lowest 25% flows. The marine origin of limestone (Rawlinson and Begg, 2014) might suggest it contains variable quantities of glauconite and pyrite (Krantz and Powars, 2000) which are conducive for denitrification. This could be a possible explanation for the negative regression coefficient between limestone and river SIN at the lowest 25% flows.

3.5.4 Implications for water quality management

Our analysis highlights that land use is not the first main influential independent variable on the river SIN concentrations at any of the flows (all flows, highest 25% flows and lowest 25% flows). This suggests that effective management of non-point (diffuse) nitrogen sources to the river SIN concentrations cannot be based on focusing only on the intensive land-use types in the study sub-catchments. Clearly, there are other catchment characteristics that have a major influence on the transport and fate of SIN flows from different land-use types to rivers. This means that policy makers should account not only for land-use types (source factor) but also relevant catchment characteristics such as soil drainage classes, hydrology and subsurface rock material (transport factors) for targeted and effective management of water quality at catchment scale.

Our results suggest that different land-use types influence the river SIN concentrations as function of the river flow in the study catchments. Dairy farming is found to be the only land-use type influencing the river SIN concentration at the highest 25% of flows, whereas sheep/beef is suggested as the only land-use type influencing the river SIN concentrations at the lowest 25% flows. This suggests that policy makers should account for these temporal variations for better management of water quality at the catchment scale.

Our results also suggest that, regardless of the flow, well-drained soils and base flow index are among the most influential parameters on the river SIN concentrations in the study sub-catchments. This indicates that the sub-catchments with higher BFI and/or well-drained soils are likely to have higher SIN concentrations in streams and rivers. The catchments with relatively higher permeable subsurface rocks, such as gravels and coquina, are also likely to have higher SIN concentrations in streams and rivers. The catchments with well-drained soils and relatively higher permeable subsurface rocks (e.g. gravels and coquina) allow relatively higher soil water percolation, nitrogen leaching and faster groundwater flow leading to oxic groundwater and less residence times, and consequently less potential for denitrification in the subsurface environment. In these catchments, it is highly likely that dissolved nitrogen losses from intensive farms will reach rivers and lakes through faster groundwater flow (i.e. baseflow). However, further field surface and groundwater surveys are warranted to locate critical source areas and pathways for nitrogen flows in sensitive agricultural catchments.

3.6 Conclusions and recommendations

Effective water quality management at the catchment scale requires identification and consideration of the catchment characteristics that highly influence nutrient concentrations (SIN) in the receiving water bodies. We have investigated the magnitude and direction (either in a negative or a positive direction) of the catchment characteristics that highly influence soluble inorganic nitrogen (SIN) at all flows, highest 25% flows and lowest 25% flows, in 15 nested catchments in the Tararua catchment located in lower parts of the North Island, New Zealand. A partial least squares regression analysis was used due to its robustness in dealing with highly co-dependent data and the limited number of observations available.

Our analysis found that land use is not the only influential variable on the river SIN concentrations at any of the flows (all flows, highest 25% flows and lowest 25% flows) in the study catchment. The only land-use types to influence the river SIN concentrations at the highest and lowest 25% flows are dairy and sheep/beef, respectively. However, the influence of land use on the river SIN concentrations are generally outweighed by the other catchment characteristics. Other catchment characteristics that have the most influence (highest VIP) on the river SIN concentrations are the base flow index (BFI) at all flows; well drained soils at the highest 25% flows; and poorly drained soils at lowest 25% flows. The positive relationship between the river SIN concentrations and both BFI and well drained soils suggests that the catchments with higher BFI values and proportions of well drained soils are likely to have higher SIN concentrations in their streams and rivers. A larger proportion of well-drained soils and relatively higher permeable subsurface rocks such as gravels and coquina leads to higher soil water percolation, nitrogen leaching and faster groundwater flow with less potential for nitrogen attenuation in the subsurface environment.

Our findings show that accounting for land use in combination with other catchment characteristics, instead of only considering land use, is important for targeted and effective water quality management at the catchment scale. Our analysis has provided insights into the magnitude and direction of the relationship between different catchment characteristics and the river SIN concentrations in the study sub-catchments. Yet, there are a number of limitations to this analysis. These limitations include the low sample size of 15 catchment observations only. Although PLSR is robust in dealing with data with smaller sample size compared to the number of independent variables, increasing the sample size and including other catchments would be expected to give better insights. Therefore, it is recommended to carry further studies to investigate the complex relationship between catchment characteristics and SIN concentrations in receiving waters, using a larger number of sites for better insights in nitrogen flow pathways in temperate agricultural catchments. These studies should use higher resolution GIS layers for different catchment variables in addition to detailed field studies as a ground truth. Also, more field studies are recommended to investigate the relationship between saturated hydraulic conductivity for rocks and potential for denitrification in the subsurface environment. Furthermore, additional field measurements to investigate the redox status in different soils and rock types and extrapolating them to catchment scale are recommended. Further studies will provide more robust information for policy makers and water managers for spatially targeted and effective management of critical source areas and pathways for nitrogen flows at a catchment scale.

3.7 Acknowledgments

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Chapter 4: Influence of sampling frequency and load calculation methods on quantification of annual river nutrient and suspended solids loads

4.1 Abstract

Better management of water quality in streams, rivers and lakes requires precise and accurate estimates of different contaminant loads. We assessed four sampling frequencies (2 days, weekly, fortnightly, and monthly) and five load calculation methods (global mean GM, rating curve RC, ratio estimator RE, flow-stratified FS, and flow-weighted FW) to quantify loads of nitrate-nitrogen (NO_3^--N), soluble inorganic nitrogen (SIN), total nitrogen (TN), dissolved reactive phosphorus (DRP), total phosphorus (TP), and total suspended solids (TSS), in the Manawatu River, New Zealand. The estimated annual river loads were compared to the reference 'true' loads, calculated using daily measurements of flow and water quality from May 2010 to April 2011, to quantify bias (i.e. accuracy) and root mean square error (RMSE measuring accuracy and precision).

The GM method resulted into relatively higher RMSE values and a consistent negative bias (i.e. underestimation) in estimates of annual river loads across all sampling frequencies. The RC method resulted in the lowest RMSE for TN, TP and TSS at monthly sampling frequency. Yet, RC highly overestimated the loads for parameters that showed dilution effect such as NO_3^--N and SIN. The FW and RE methods gave similar results and there was no essential improvement in using RE over FW. In general, FW and RE performed better than FS in terms of bias, but FS performed slightly better than FW and RE in terms of RMSE for most of the water quality parameters (DRP, TP, TN and TSS) using a monthly sampling frequency.

We found no significant decrease in RMSE values for estimates of NO_3^--N, SIN, TN and DRP loads when the sampling frequency was increased from monthly to fortnightly. The bias and RMSE values in estimates of TP and TSS loads (estimated by FW, RE and FS), however, showed a significant decrease in the case of weekly or 2 day sampling. This suggests potential

for a higher sampling frequency during flow peaks for more precise and accurate estimates of annual river loads for TP and TSS, in the study river and other similar conditions.

Key words: Uncertainty, Load estimation methods, Nutrients, Suspended solids, Water Quality, Water resources management

4.2 Introduction

Increasing demand for food production is leading to the expansion and intensification of agricultural land use, which if not managed properly may have detrimental impacts on freshwater resources worldwide (Pimentel et al., 2004). One of these adverse impacts is potential runoff and/or leaching of farm nutrients (such as nitrogen (N) and phosphorus (P)) and their effects on freshwater quality and eutrophication (Mason, 2002; Vitousek et al., 1997) which is becoming a widespread problem in both freshwater (lakes, rivers) and marine (seas, oceans) ecosystems (National Research Council 1992). Therefore, precise and accurate estimates of river nutrient and suspended solids loads are important to (1) assess the state of water quality (Quilbé et al., 2006); (2) calculate the proportion of point sources (PS) and non-point sources (NPS) in the annual river loads (Roygard et al. 2012); (3) estimate the difference between measured and target river loads (Roygard et al. 2012); (4) highlight critical areas that require effective management strategies to reduce loads to the rivers; (5) calibrate catchment scale models (Gassman et al. 2007; Ullrich and Volk 2010); and (6) evaluate long-term trends in river loads (Littlewood et al. 1998; Schilling and Zhang 2004). In New Zealand, the National Policy Statement for Freshwater Management (NPS-FM) requires Regional Councils to establish a freshwater quality accounting system and set ‘bottom line’ limits for water quality in defined catchments (Ministry for the Environment, 2014). This requires a cost effective freshwater quality monitoring system that involves gathering updated information about measured, modelled or estimated loads of relevant water contaminants in stream, rivers, lakes and groundwater aquifers. Similarly, cost effective and efficient water quality monitoring is essential to help restore and/or enhance water quality and inform water quality management in rivers and streams worldwide (e.g. Total Maximum Daily Load (TMDL) program in the United States, (USEPA, 1999) and the European Union Water Directive Framework (European Community, 2000)).

The load of a specific water contaminant is defined as the rate (weight per unit time, e.g. tonnes per year t yr^{-1}) it flows across the river or the outlet of the catchment (Norton and Kelly, 2010). Its estimation requires information about its two components; the flow (Q) and the contaminant concentration (C). These vary across time and space in streams and rivers in a catchment (Quilbé et al. 2006; Richards 1998). In general, the flow can be measured with high frequency. However, the concentration of a specific water contaminant is usually measured less frequently because of the high cost associated with sampling and analysis. Therefore, a number of load calculation methods have been developed to make use of infrequent water quality measurements and frequent flow measurements to quantify contaminant loads in streams and rivers. These methods, according to Quilbé et al. (2006), can be categorized into average, ratio estimator, regression (or rating curve), stratification and planning level load estimation methods. The choice of a suitable load calculation method depends on several factors (Quilbé et al. 2006) such as (1) the frequency and distribution of water quality sampling (Aulenbach and Hooper, 2006); (2) catchment area (Phillips et al. 1999); (3) variability of contaminant as a function of flow and season (Richards and Holloway 1987); (4) the sampling scheme of the flood flows (the flows that transport the major proportion of the annual load within a short time); and (5) human activities such as land use and fertilization in a catchment.

A number of studies have estimated the uncertainty in river load estimates as a function of sampling frequency and load calculation method (e.g. Birgand et al. 2011, 2010; Cassidy and Jordan 2011; Guo et al. 2002; Jiang et al. 2014; Moatar and Meybeck, 2005; Zamyadi et al. 2007). Many of these studies have evaluated the uncertainty in annual load estimates of only one contaminant. These include Birgand et al. (2010) and Guo et al. (2002) who evaluated the uncertainty in NO_3^--N loads in 50 catchments in Brittany, France and in the Upper Sangamon River in central Illinois, US, respectively. Also Cassidy and Jordan (2011) and Johnes (2007) evaluated the uncertainty in TP loads in 3 agricultural catchments, Ireland and 17 mixed land use catchments, UK, respectively. In addition, many of these studies focused on small scale catchments (less than 10 km^2; e.g., Cassidy and Jordan 2011; Zamyadi et al. 2007). In New Zealand, a number of studies have quantified annual river loads for different water contaminants using a number of load calculation methods (e.g. Ledein et al., 2007; Stephens, 2015; Woodward, 2015). However, none of these studies have evaluated the uncertainty in annual river loads as a function of sampling frequency and load calculation method. Thus, there is a need to assess further the effects of sampling frequency and load calculation methods on quantification of annual river nutrient and suspended sediments loads in rivers that drain catchments of few thousands of square kilometres (especially in New Zealand). In addition, there is lack of such studies in temperate environments (such as New Zealand) where river flow dynamics are more quick (relatively flashy hydrograph), and contaminant concentrations (e.g. nitrate) are relatively low. Hence, this study offers new and original contribution that is widely applicable to any catchment with similar characteristics (e.g. catchment size, land use and flow regime).

The objective of this paper is to estimate the uncertainty in the annual river contaminant loads as a function of sampling frequency and load calculation methods in the Manawatu River catchment (~3911 km^2), New Zealand. It used the daily measurements (from May, 2010 to

April, 2011) of river flow and six water quality parameters in the Manawatu River at Teachers College monitoring site in Palmerston North in Lower North Island of New Zealand.

4.3 Materials and methods

4.3.1 Study area

The Manawatu at Teachers College monitoring site (MTC) is located in Palmerston North to monitor the flow and water quality of the Manawatu River downstream of the confluence of the Manawatu river (coming out of the Manawatu Gorge) with its tributary Pohangina river on the western side of the Tararua and Ruahine ranges (Figure 4.1). The MTC monitoring site drains an area of around 3911 km^2 on both sides of the Tararua and Ruahine ranges. The topography of the catchment upstream of the MTC site varies from around 29 m to 1549 m with an average of 335 m above mean sea level. The main soil types upstream of the MTC site are silt loam (51.74%) and sandy loam (17.56%). The main land use types are sheep and/or beef farming (61.98%), native cover (20.24%), and dairy farming (13.63%) in the catchment.

The MTC is a historical river monitoring site in New Zealand where the Manawatu-Wanganui (Horizons) Regional Council has been monitoring river flow continuously since 1925, and monthly water quality sampling since 1999. To our knowledge, the MTC site is the only site in New Zealand where high-resolution (daily) monitoring of water quality parameters has been undertaken from May, 2010 to July, 2011.

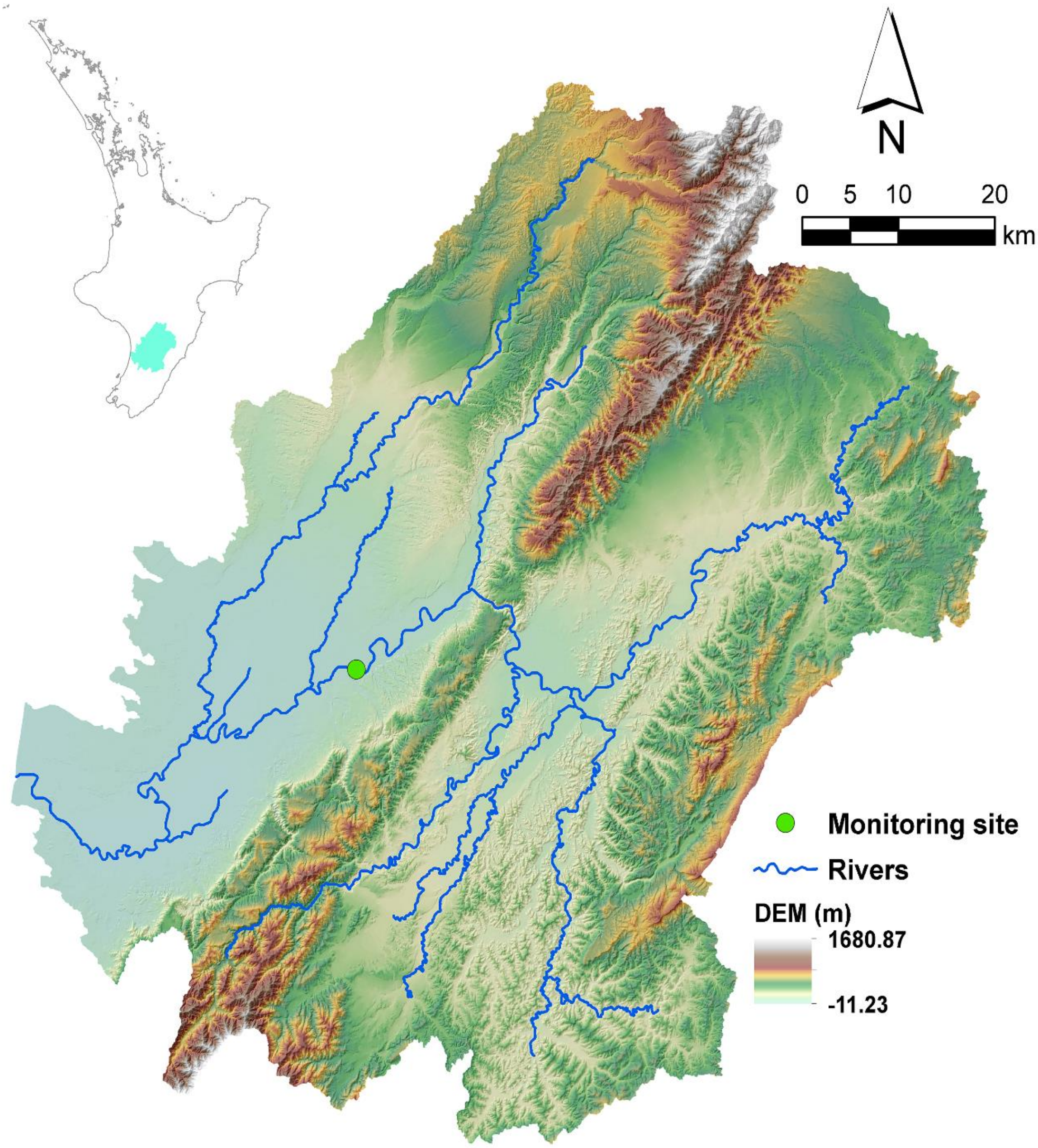

Figure 4.1. Location of the Manawatu at Teachers College (MTC) monitoring site in the Manawatu River Catchment in Lower North Island of New Zealand.

4.3.2 Available data and its analysis

Horizons Regional Council (HRC) is monitoring the flow using stage-discharge relationship every 15 minutes, and several water quality parameters (at a monthly sampling frequency) at many sites including the Manawatu at Teachers College monitoring site (MTC) in the Manawatu River Catchment. However, from May, 2010 to July, 2011, HRC conducted daily measurements of several water quality parameters including NH_4^+-N, NO_3^--N, NO_2^--N, TN, DRP, TP and TSS at the MTC site. We used one year (from 1-May-2010 to 30-April-2011) of daily measurements of these water quality parameters in this study. Figure 4.2 shows a flowchart of the methodology followed in this study. All the analysis were completed in R software (Appendix C) version 3.1.3 (R Core Team, 2017).

4.3.2.1 Data processing

The collected water-quality data series were first checked for missing or below detection limit values. In this dataset (observation year 2010/2011), there were several measurements recorded below detection limit. Any value recorded as below detection limit was converted to a value by dividing the detection limit for the water quality parameter by the square root of two (Sanford et al., 1993). There were also 31 missing values for NH_4^+-N, NO_3^--N, NO_2^--N and TSS and 30 missing values for TN, DRP and TP. The majority of these missing values were between December 2010 and January 2011 when flow in the river was predominantly low flow 'baseflow'. To fill in these missing values, we tested three methods (M1 = Last observation carried forward; M2 = Linear interpolation; and M3 = Cubic spline interpolation) using the R package 'zoo' version 1.7-12 (Zeileis et al., 2015). In order to compare which method performs the best, we used 5 months (from July to November, 2010) without any missing data. Using these 5 months, we created artificially 15 random missing values to give the same proportion of missing values as in the entire dataset. Then, we used the three methods (M1, M2 and M3) to fill in the missing data. After hundreds of simulations, we found out that the sum of squared errors of M2 and M3 were close to each other but both performed better than M1. However, in general, M2 performed better than M3 for the water quality parameters tested (NH_4^+-N, NO_2^--N, NO_3^--N, TN, DRP, TP and TSS). Therefore, we used M2 to fill in missing water quality data points to complete one year (from 1-May-2010 to 30-April-2011) of daily measurements of water quality parameters for the study site. After filling in the missing data, we calculated the daily values of soluble inorganic nitrogen (SIN) as the sum of NH_4^+-N, NO_2^--N and NO_3^--N for each day.

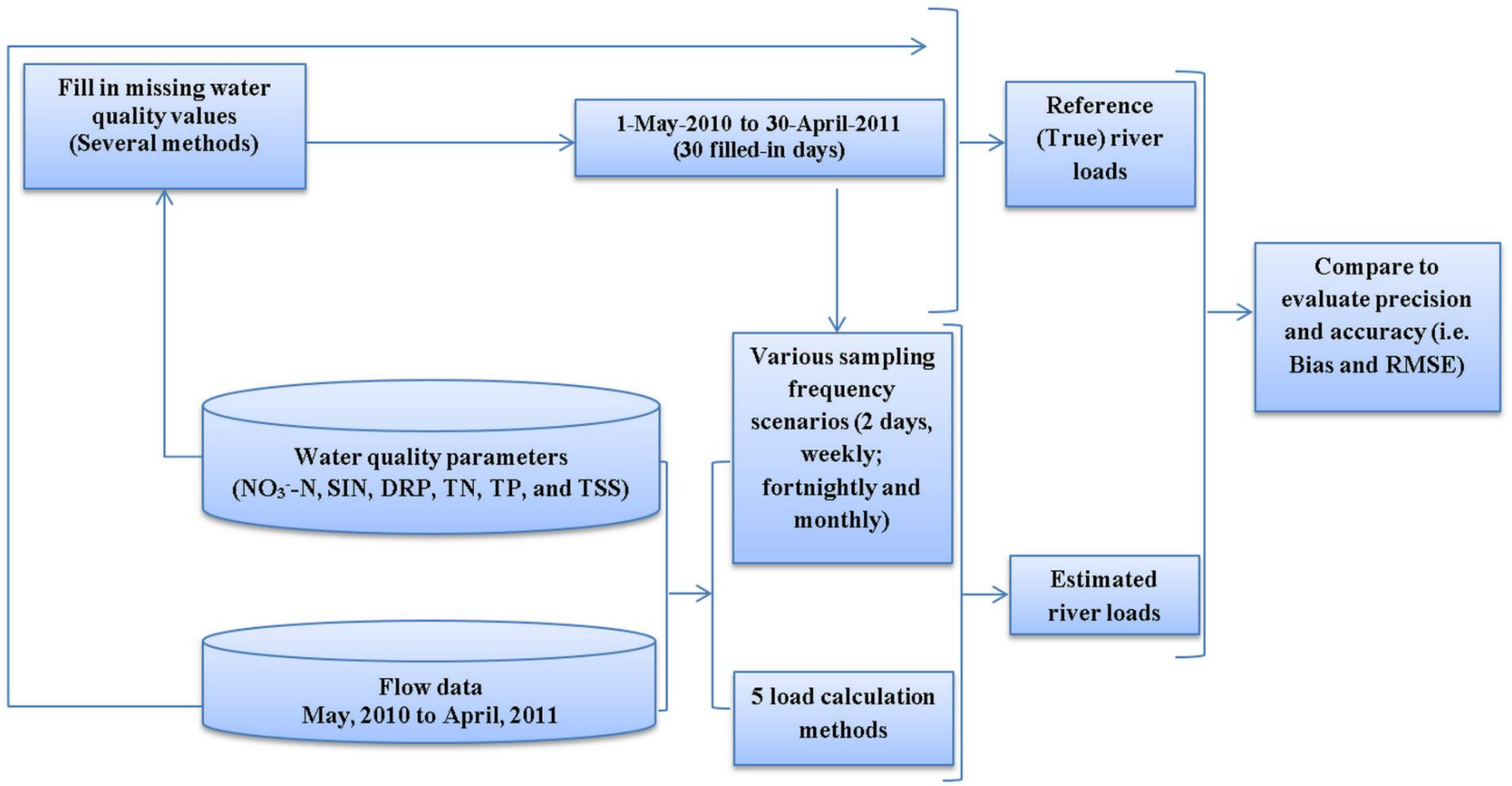

Figure 4.2. A flowchart for river flow and water quality data analysis used to estimate uncertainty in annual river loads in the Manawatu River catchment, New Zealand.

4.3.2.2 Calculation of reference 'true' river load

The daily concentrations (mg L^{-1}) of selected water quality parameters (NO_3^--N, SIN, TN, DRP, TP and TSS) and mean daily river flow (m^3 s^{-1}) were used to calculate their reference 'true' annual river loads (t yr^{-1}) using Equation (4.1):

$$L_t = m \sum_{i=1}^{n} C_i Q_i \tag{4.1}$$

where:

L_t = Reference 'true' annual river load (M/T);

m = Conversion factor to convert the calculated values into a specific unit;

C_i = Contaminant concentration (M/L^3) measured at the *i*th day; and

Q_i = Mean daily river flow (L^3/T) at the *i*th day.

4.3.2.3 Load calculation methods

We tested five different calculation methods to quantify annual river loads for the water quality parameters in this study. Load estimation methods were chosen based on commonly used methods that cover the spectrum of different categories of load estimation methods. Thus, we selected average (GM and FW), regression (Rating Curve RC), ratio estimator (RE) and stratification (FS) methods to estimate the annual river loads. For each of the methods selected, four water quality sampling frequencies (2 days, weekly, fortnightly and monthly) were used resulting in a total of 2, 7, 14 and 30 scenarios simulated, respectively. To illustrate the number of scenarios, for example in the weekly sampling frequency, if water quality sample is collected on one of the days of week, every week, for the whole year, this means there are seven possible scenarios representing sampling on each different day of the week. The same applies for other sampling frequencies, providing 2 scenarios for 2 day sampling, 14 scenarios for fortnightly sampling, and 30 scenarios for the monthly sampling.

a. Rating Curve (RC) method

Regression (or rating curve) method defines an empirical relationship between flow Q and measured nutrient concentration C using a power function $C = \mathrm{a}Q^b$ (Huang et al., 2012; Quilbé et al., 2006). This equation could be used, after being fitted to the available data by least square regression, to estimate the concentration and the load for days without measurements as expressed by Equations (4.2 and 4.3) (Huang et al., 2012; Quilbé et al., 2006).

$$\log_{10}(C) = a + b.\log_{10}(Q) \tag{4.2}$$

$$L = m\sum_{i=1}^{n} C_i\, Q_i = m\sum_{i=1}^{n} aQ_i^{b+1} \tag{4.3}$$

where:

L = Annual river load (M/T);

m = Conversion factor to convert the calculated values into a specific unit;

C_i = Contaminant concentration (M/L^3) measured at the *i*th sampling day;

Q_i = Mean daily flow (L^3/T) measured at the *i*th day; and

n = Number of samples.

b. Global Mean (GM) method

The Global Mean (GM) method (Huang et al., 2012) calculates annual river load as a product of the total annual flow and average contaminant concentration for the period of the record, as expressed by Equation 4.4 (Shih et al., 1994) below:

$$L = mQ_t\left(\sum_{i=1}^{n}\frac{C_i}{n}\right) \tag{4.4}$$

where:

L = Annual river load (M/T);

m = Conversion factor to convert the calculated values into a specific unit;

C_i = Contaminant concentration (M/L^3) measured at the *i*th sampling day;

Q_t = Total annual flow (L^3/T); and

n = Number of samples.

c. Flow weighted (FW) method

The Flow Weighted (FW) method (Huang et al., 2012) involves multiplying the flow-weighted mean concentration by the total annual flow, as expressed by Equation 4.5 (Littlewood, 1992) below:

$$L = mQ_t \left(\frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \right) \tag{4.5}$$

where:

L = Annual river load (M/T);

m = Conversion factor to convert the calculated values into a specific unit;

C_i = Contaminant concentration (M/L^3) measured at the *i*th day;

Q_i = Mean daily flow (L^3/T) measured at the *i*th day**;** and

Q_t = Total annual flow (L^3/T).

d. Ratio Estimator (RE) method

The Ratio Estimator (RE) calculates the load as a product of the average annual concentration (mean daily load divided by mean daily flow), the total annual flow, and an adjustment factor (Aulenbach and Hooper, 2006). This adjustment factor accounts for covariance between load and flow values at time of sampling divided by flow variance (Cohn, 1995). It is derived from the ratio estimator developed by Beale (1962) and can be expressed mathematically as shown by Equation (4.6) (Cohn, 1995) below:

$$L = mQ_t \left(\frac{\bar{L}}{\bar{Q}} \right) \left(\frac{1 + \frac{1}{N} \frac{S_{LQ}}{\bar{L}_{\bar{Q}}}}{1 + \frac{1}{N} \frac{S_{Q^2}}{\bar{Q}^2}} \right) \tag{4.6}$$

where $\bar{L} = \sum_{i=1}^{n} \frac{C_i Q_i}{n}$, $\bar{Q} = \sum_{i=1}^{n} \frac{Q_i}{n}$

$$S_{LQ} = \frac{1}{n-1} \sum_{i=1}^{n} (Q_i - \bar{Q})(C_i Q_i - \bar{L}) \quad , \quad S_{Q^2} = \frac{1}{n-1} \sum_{i=1}^{n} (Q_i - \bar{Q})^2$$

and where:

L = Annual river load (M/T);

m = Conversion factor to convert the calculated values into a specific unit;

C_i = Contaminant concentration (M/L^3) measured at the *i*th day;

Q_i = Mean daily flow (L^3/T) measured at the *i*th day;

Q_t = Total annual flow (L^3/T);

$\bar{L}$ = Mean of daily loads (M/T) for days in which concentration was measured;

n = Number of samples;

$\bar{Q}$ = Mean of daily flows (L^3/T) for days in which concentration was measured;

S_{LQ} = Covariance between flow and contaminant flux;

S_{Q^2} = Variance of flow based on the days in which concentration was measured; and

N = Expected population size (365 for a year; 366 on leap years).

e. Flow-Stratified (FS) method

The Flow-Stratified (FS) method illustrates an application of stratification to the averaging methods (Roygard et al. 2012). According to Roygard and Clark (2012), this method stratifies the flow into equal flow categories (flow decile bins) based on the flow exceedance percentile. Then, the measured contaminant concentration is assigned to the flow decile bin that contains the flow value at the time of sampling. For each flow decile bin the load is calculated by multiplying the average flow by the average contaminant concentration for the bin. The load of each decile bin is then multiplied by a factor (number of days per year/number of flow quantile bins). Finally, the loads for all quantile bins are added to calculate the total annual river load. We used the flow data and quantile function in R to define the flow quantile bins. The default number of flow quantiles are 10 so each flow quantile bin will account for 10% of the flow. This was to enable the estimation of loads at flood flows (the highest 20% of flows). In this analysis, however, the quantile bin width (hence, number of quantile bins) is based on the sampling frequency and the number of water quality measurements within each quantile. For example, using 10 flow quantile bins with monthly sampling frequency (i.e. 12 measurements per year) is not applicable. This is because there are not enough water quality measurements to cover the whole 10 flow quantile bins. Therefore, lower sampling frequency results in larger width of the flow quantile bins (fewer quantiles). Thus, the number of quantile bins decreased as the sampling frequency decreased from 2 days to monthly sampling frequencies. We used 10, 10, 5, and 3 flow quantile bins for 2 days, weekly, fortnightly and monthly sampling frequencies, respectively. The reason we used 5 and 3 flow quantile bins for fortnightly and monthly sampling frequencies, respectively, is that there were no enough water quality measurements to use higher number of quantiles.

This method can be expressed by Equation (4.7) below:

$$L = m \sum_{i=1}^{n^\circ} (Q_{avg} * C_{avg})_i * \left(\frac{N}{n^\circ}\right) \tag{4.7}$$

where:

L = Annual river load (M/T);

m = Conversion factor to convert the calculated values into a specific unit;

C_{avg} = Average contaminant concentration (M/L^3) of the *i*th flow quantile bin;

Q_{avg} = Average flow (L^3/T) of the *i*th flow quantile bin, i is the flow quantile bin;

N = Expected population size (365 for a year; 366 on leap years); and

n° = Number of flow quantile bins.

4.3.2.4 Comparison of the different calculation methods to the reference (true) load

The quantified annual river loads for the six water-quality parameters (NO_3^--N, SIN, TN, DRP, TP and TSS) were compared to the reference (true) river loads using bias and root mean square error (RMSE). The bias, calculated as the difference between quantified load and reference (true) load, measures the accuracy of the annual river loads whereas the RMSE is a measure of both bias (accuracy) and standard deviation (precision) as shown by Equations 4.8 and 4.9 below. An estimator is considered to perform the best when it is both accurate (low bias values) and precise (low standard deviation values). Generally, an estimator with low RMSE values is considered to perform the best (Guo et al. 2002; Zamyadi et al. 2007).

$$Bias = \sqrt{\left(L_{avg} - L_t\right)^2} \tag{4.8}$$

$$RMSE = \sqrt{\sum_{i=1}^{N} \frac{(L_i - L_t)^2}{N}} \tag{4.9}$$

where:

L_t = Reference 'true' annual river load (M/T);

L_i = Annual estimated river load (M/T);

L_{avg} = Average annual estimated river load (M/T); and

N = Number of individual estimated loads for each sampling frequency.

4.4 Results and Discussion

4.4.1 Variation in river flow and water quality concentrations

Two distinct relationships are observed between flow peaks and concentrations of different water quality parameters in the MTC site during the observation year 2010/2011 (Figure 4.3). Firstly, the NO_3^--N and SIN concentrations decreased as the flow increased, showing a concentration trough in the chemograph during the flow peaks (Figure 4.3). This reflects a dilution effect of increased surface runoff on NO_3^--N and SIN concentrations during the high flow conditions in the river. Secondly, TP, TN and TSS showed a concentration peak in the chemograph during the flow peaks (Figure 4.3). However, there was no distinct pattern in behaviour of DRP concentrations in relationship to flow peaks. Similar relationships between flow and contaminants have been observed in different areas. For example, in three tributaries to Lake Erie, Ohio, US, both TSS and TP showed concentration effect (i.e., increase in concentration) whereas NO_3^--N showed dilution effect (i.e., decrease in concentration) along with the flow peaks (Richards and Holloway 1987). In addition, in Lestolet catchment, France, NO_3^--N concentrations showed dilution effect along with flow peaks (Birgand et al., 2010). Also, in a mixed land use catchment in North Carolina, US, NO_3^--N showed dilution effect whereas TP and TSS showed concentration peaks along with flow peaks during winter (Birgand et al., 2011). These dilution and concentration effects were found to have an effect on the uncertainty in annual load estimates (e.g. Birgand et al. 2011, 2010) as will be explained later.

We found that the concentration of the contaminants varies differently in relation to river flow (Figure 4.4). TSS concentrations are lower and less variable at low and medium flows (flow decile bins 5 to 10; flows < 40th exceedance percentile), while higher and more variable at high flows (decile bins 1 to 4; flows > 40th exceedance percentile). This might be due to erosion resulting from heavy rainfall and subsequent transport of suspended sediments to river flow through surface runoff during high flows (Baker, 1982). In addition, particle re-suspension and bank erosion during high flows might be other factors leading to elevated and variable values of TSS at high flows (Figure 4.4). The pattern in TP is observed to be similar to TSS (Figure 4.4), mainly because the major portion of TP is particulate phosphorus that is adsorbed onto sediments (Baker, 1982). Surface runoff during high flows mainly transports sediments (e.g. TSS) and sediment-bound chemicals (e.g. phosphorus) as a result of soil erosion (Baker, 1982). In contrast, DRP, which represents a minor portion of the TP, showed lower values and less variability only in the lowest 20% of flows (9 and 10 decile bins) (Figure 4.4). In the rest of the flow decile bins, there was no clear pattern between the river flow and DRP concentrations. Relatively higher concentrations of DRP observed during low flows could be due to contributions from point sources discharges of secondary treated wastewater in the river system.

The concentrations of NO_3^--N and SIN increased with an increase in the river flow. Interestingly, the NO_3^--N concentration values at the highest 20% of the flows (flow decile bins 1 and 2) were observed to be less variable and lower in values than NO_3^--N concentrations in flow decile bins 3 (flows < 20th exceedance percentile) to 6 (flows > 60th exceedance percentile) (Figure 4.4). These high values of NO_3^--N, at flows below the 20th exceedance percentile might represent the contribution of elevated NO_3^--N in baseflow that mainly contributes to the river flow after the surface runoff during the high flows. The dissolved nutrients (e.g. NO_3^--N and SIN) mainly leach from the soil profile and flow with subsurface drainage and/or groundwater contribution ‘baseflow’ to the river flow (Baker, 1982). The lower values of NO_3^--N at flows > 20th exceedance percentile (compared to the values within flows < 20th exceedance percentile and > 60th exceedance percentile) might be due to the dilution effect during high flow events. SIN showed a similar pattern to NO_3^--N (Figure 4.4), mainly because the major part of SIN is NO_3^--N. TN also showed a clear increase in values as flow increased. However, TN values at the highest 20% of the flows were observed to be more variable. This might be due the concentration effect observed in TN (Figure 4.3) during runoff events (i.e. increase in TN concentration during runoff events). On the other hand, the slight variability observed in TN values at low flows might be due to the inputs from point sources.

Figure 4.5 shows relatively higher seasonal (monthly) variations in dissolved nutrients (NO_3^--N, SIN and DRP) and TN concentrations, with higher values in winter (from June to August) and spring (from September to November) and lower values in summer (from December to February) and autumn (from March to May). The SIN concentrations showed a similar pattern to NO_3^--N concentrations, mainly because the majority of SIN is NO_3^--N in the study area. A possible explanation is that these increased levels of NO_3^--N and SIN from September to October, 2010, are associated with relatively higher contributions of groundwater 'baseflow' to the river flow. For instance, when flow decreased from September, 2010 (mean flow = 417.42 m^3 sec^{-1}) to October, 2010 (mean flow = 141.74 m^3 sec^{-1}), NO_3^--N increased from 0.695 mg L^- (mean concentration in September, 2010) to 0.751 mg L^- (mean concentration in October, 2010). We separated the baseflow from total river flow for the observation year 2010/2011 and found that the baseflow index (baseflow over total river flow) increased from September to October, 2010. A similar pattern of an increase in levels of nitrate-nitrogen associated with increased levels of baseflow was found by Bobbi (1999) in Pipers River catchment, Tasmania, Australia for the observation year 1998. On the other hand, TP and TSS, which are characterised by the concentration effect (Figure 4.3), showed relatively less monthly variations except for their highest values in September, 2010 (Figure 4.5). This is because they are mainly transported to river flow through high runoff events that happened mainly in September 2010 in the study river.

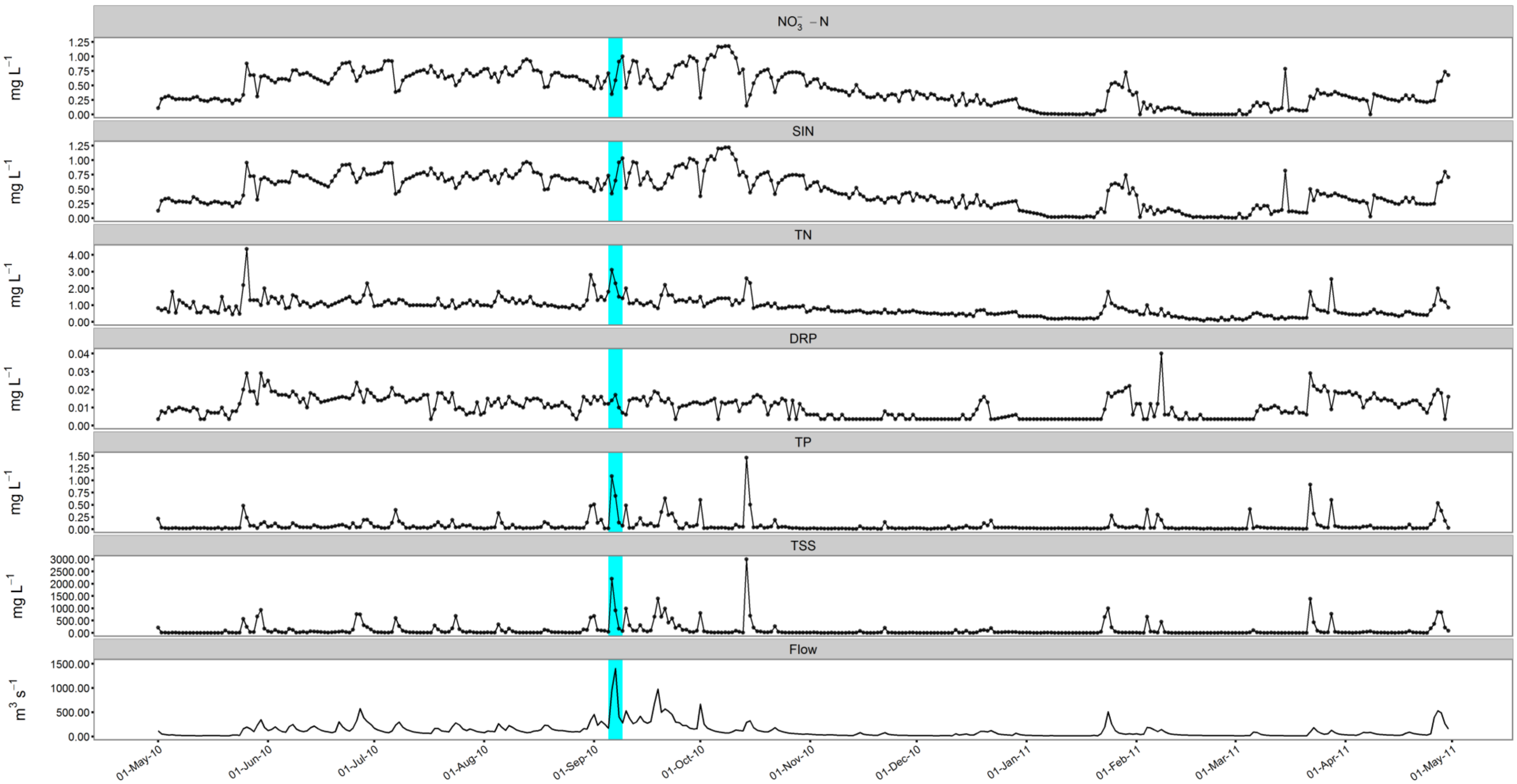

Figure 4.3. Hydrograph and chemographs of NO_3^--N, SIN, TN, DRP, TP, and TSS measured in the Manawatu River at Teachers College (MTC) site for the observation year 2010/2011. Each marker represents one measurement. The highlighted area shows an example of the peaks (concentration effect) and troughs (dilution effect) for different water quality parameters in relationship to a flow peak.

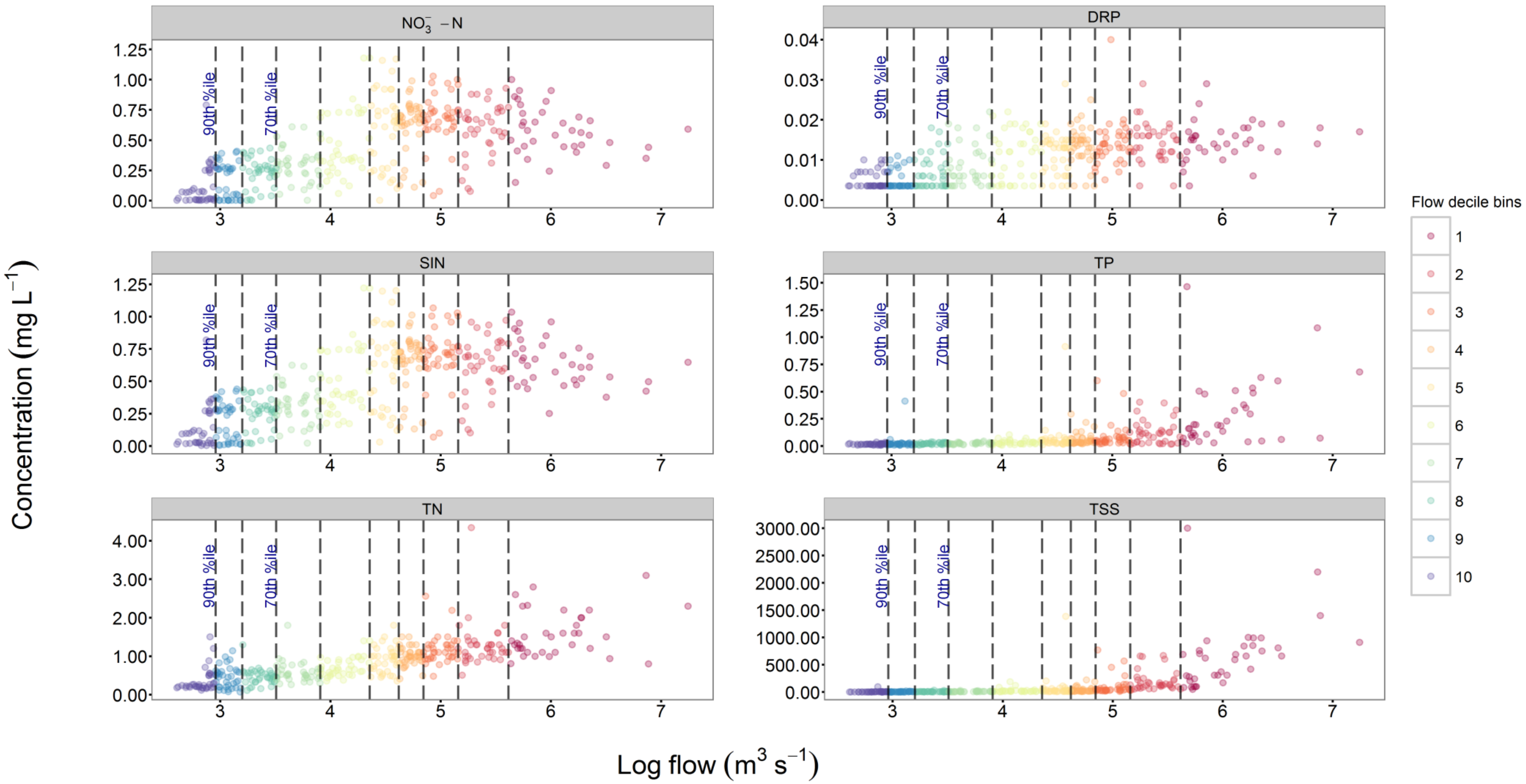

Figure 4.4. Concentration (mg L^{-1}) of water quality parameters (NO_3^--N, SIN, TN, DRP, TP, TSS) and river flow (m^3 s^{-1}) measured in the Manawatu River at Teachers College (MTC) site for the observation year 2010/2011. The colour of the data is according to the 10 flow decile bin with the 1st flow decile bin (right) as the highest 10% of flow and the 10th decile bin (left) as the lowest 10% of flow. The vertical dashed lines (flow exceedance percentiles "%ile") are the breaks between the 10 flow decile bins with 90th %ile and 70th %ile as the values that have been exceeded 90% and 70% of the time, respectively. We used log flow so that the values spread across the figure and would not be skewed to the left part of the figure.

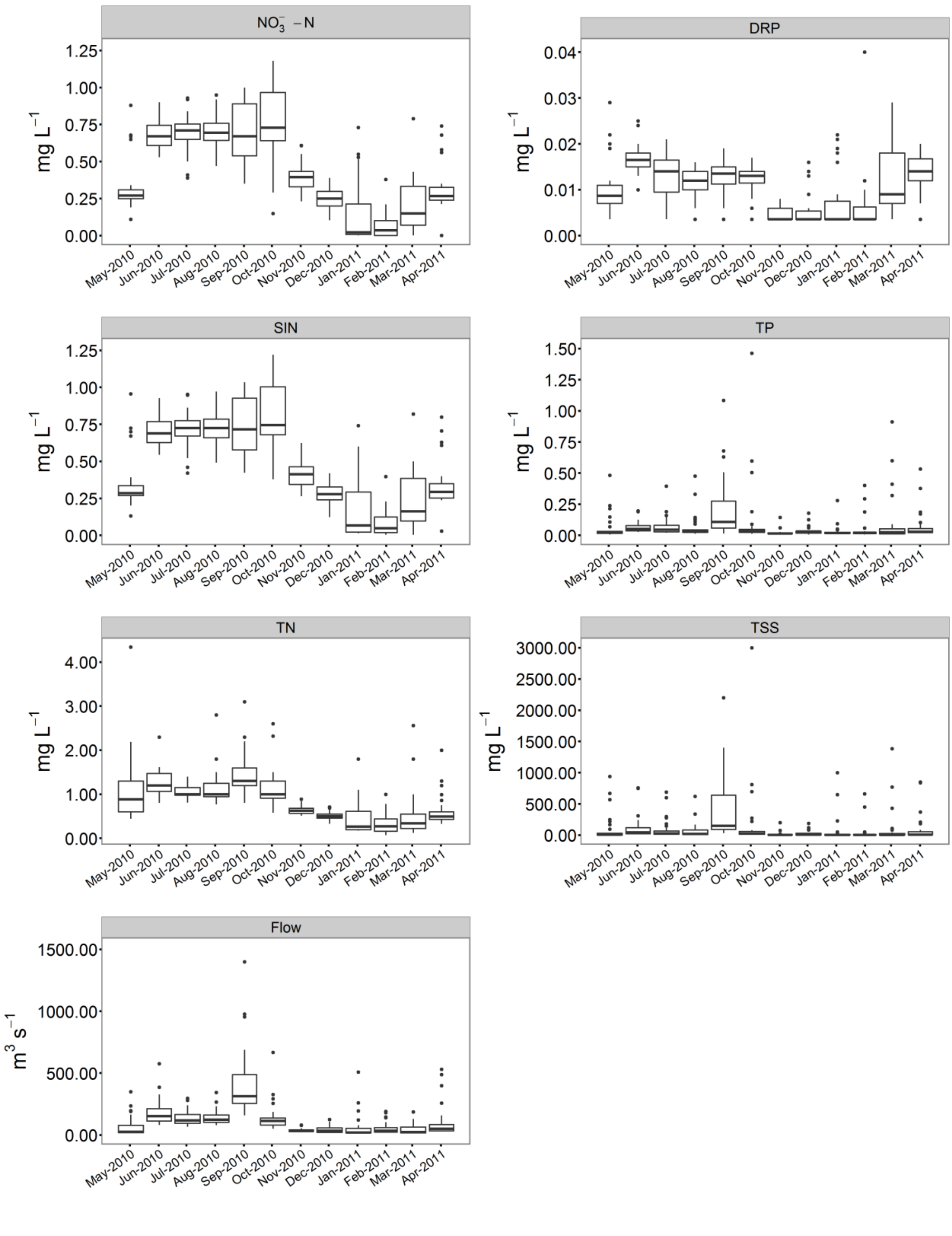

Figure 4.5. Temporal (monthly) variation in concentration (mg L^{-1}) of water quality parameters (NO_3^--N, SIN, TN, DRP, TP, TSS) measured in the Manawatu River at Teachers College (MTC) site for the observation year 2010/2011.

4.4.2 Reference (true) load and its variations

The reference (true) annual loads for NO_3^--N, SIN, TN, DRP, TP and TSS were quantified to be 2112.36, 2263.76, 4769.81, 51.20, 687.01 and 1340816.11 (t yr^{-1}) respectively in the MTC site for the observation year 2010/2011. Seasonal (monthly) variations in the river flow are clearly reflected in the seasonal variations of the reference (true) loads for NO_3^--N, SIN, DRP and TN, with higher river flows and loads recorded in winter (June to August) and spring (mainly September and October) months (Figure 4.6). The months of September and June have the highest monthly river flows and highest loads for NO_3^--N, SIN, DRP and TN (Figure 4.6). On the other hand, the highest loads for TP and TSS were observed in September and October months. This might be due to high runoff events that happened mainly in September and October and transported TP and TSS to the river flow. It is interesting that just eight percent of the time (i.e. September; the first month in the spring for the study area) accounted for about one third (~33%) of the total annual river flow and total annual loads for NO_3^--N, SIN, DRP and TN, and about half (~50%) of the total annual loads for TP and TSS (Figure 4.6).

Water quality parameters in the Manawatu River at Teachers College (MTC) site showed similar relationship between river flow and daily loads (Figure 4.7). In general, all parameters showed less variation in daily loads at lower flows and increase in variation at higher flows, particularly TP and TSS. Particles, such as TP and TSS (that showed concentration effect during runoff events) (Figure 4.3), showed the highest variance in daily loads at the highest 10% of flows (1st flow decile bin), whereas almost no variation in their daily loads for flows < 10th exceedance percentile (2nd to 10th flow decile bins) (Figure 4.7). On the other hand, for dissolved nutrients such as NO_3^--N and SIN, the variation in daily loads started to increase as flow increased from the 5th flow decile bin (flows > 50th exceedance percentile). Guo et al.

(2002) observed a similar pattern between NO_3^--N and flows in the Upper Sangamon River in central Illinois, US.

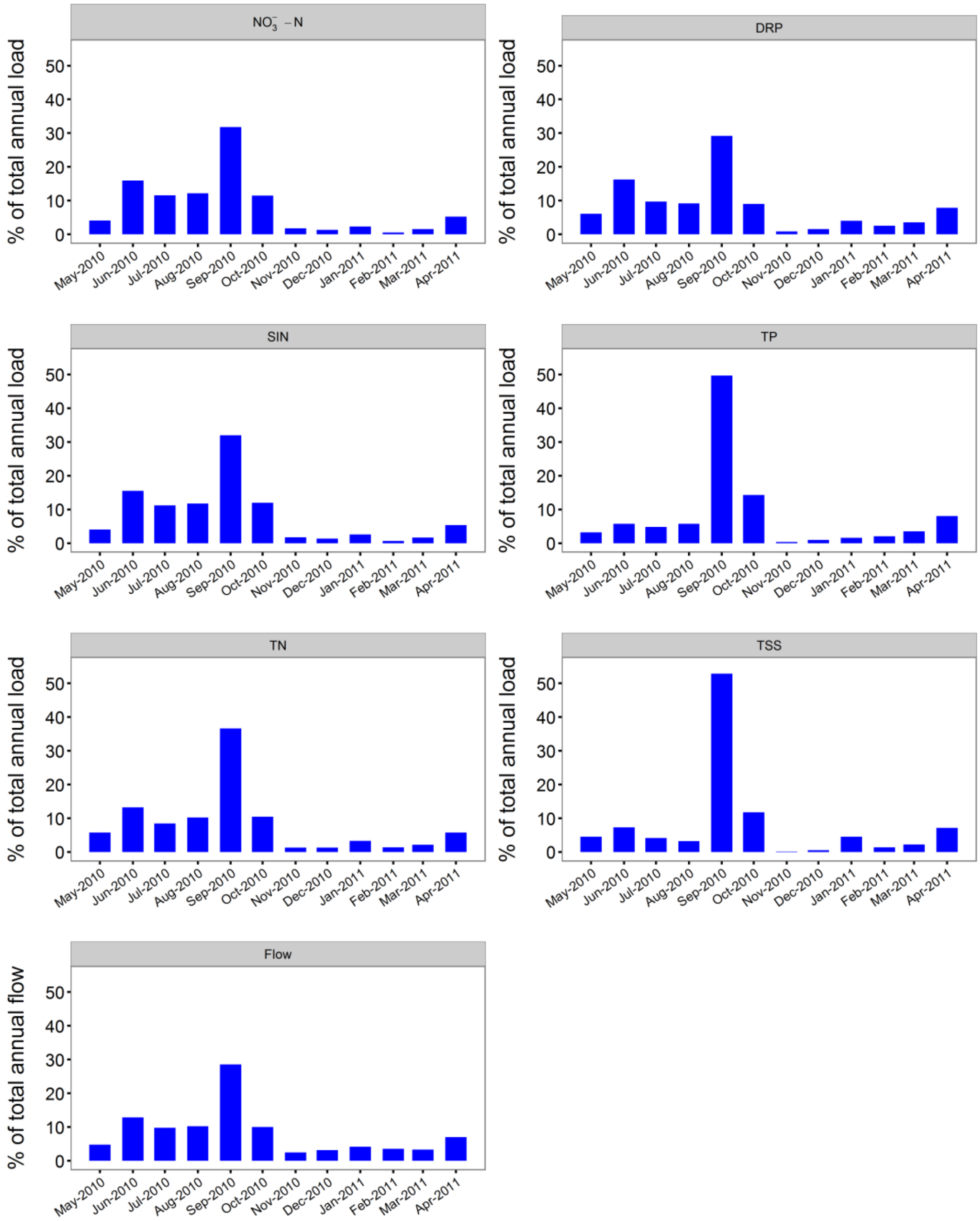

Figure 4.6. Temporal variations of the monthly contributions (in percent) to the total annual river flow and total reference 'true' annual loads (calculated using daily measurements of water quality parameters 'NO_3^--N, SIN, TN, DRP, TP and TSS' and river flow) in the Manawatu River at Teachers College (MTC) site for the observation year 2010/2011.

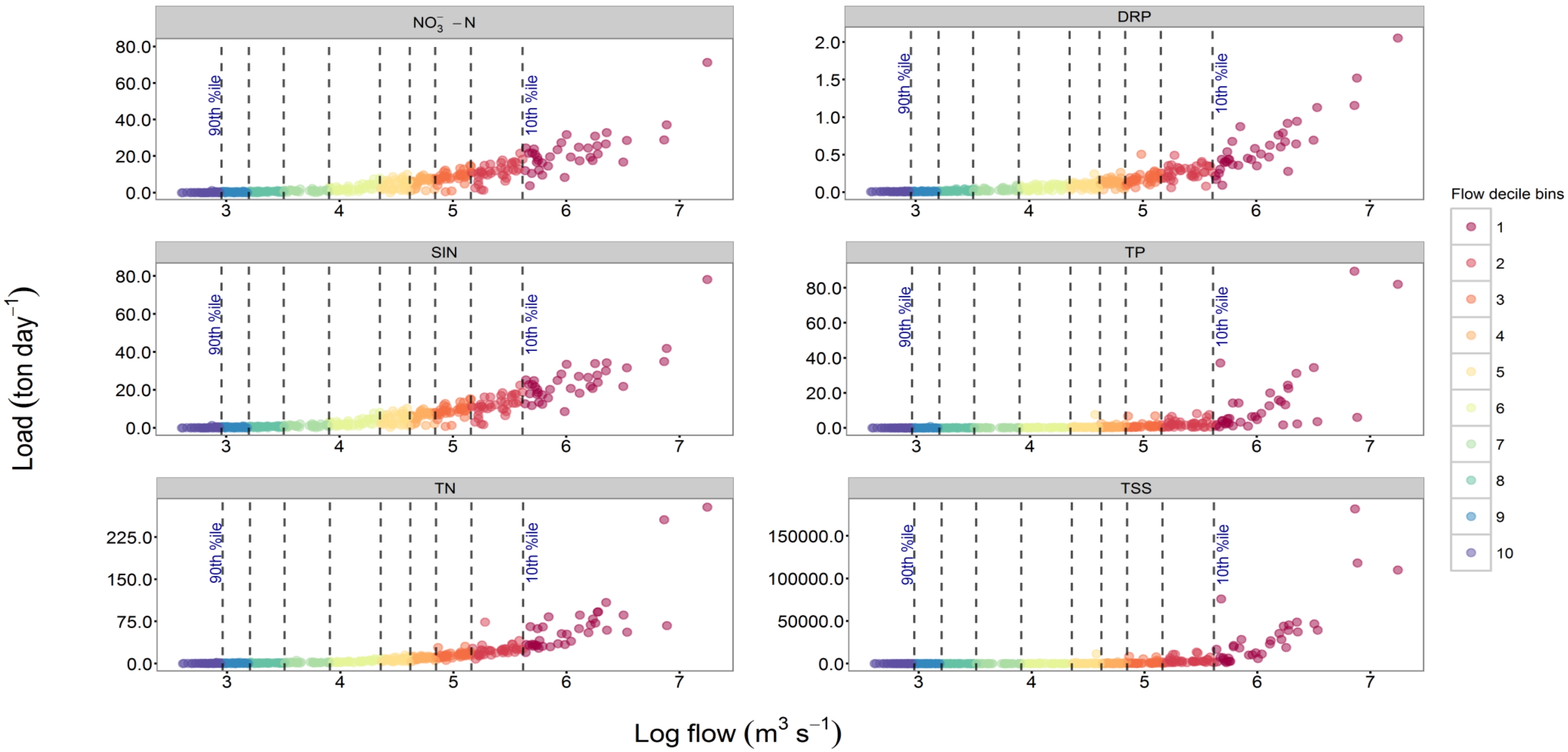

Figure 4.7. Relationship between daily average river flow (m^3 s^{-1}) and daily river loads (t day^{-1}) of water quality parameters (NO_3^--N, SIN, TN, DRP, TP and TSS) measured in the Manawatu River at Teachers College (MTC) site for the observation year 2010/2011. The colour of the data is according to the 10 flow decile bin with the 1st decile bin (right) as the highest 10% of flow and the 10th decile bin (left) as the lowest 10% of flow. The vertical dashed lines (flow exceedance percentiles "%ile") are the breaks between the 10 flow decile bins with 10th %ile (right) and 90th %ile (left) as the values that have been exceeded 10% and 90% of the time, respectively.

4.4.3 Uncertainty in annual river loads

A total of 20 combinations comprising five different load calculation methods (GM, RC, FW, RE and FS) and four sampling frequencies (2 days, weekly, fortnightly and monthly) were used to quantify annual loads of different contaminants in the river (Figure 4.8). There is a general trend of an increase in the variability of quantified annual loads with a decrease in the sampling frequency from 2 days to monthly (Figure 4.8). This could be attributed to the increase in the number of scenarios along with the decrease in sampling frequency from 2 days to monthly (Zamyadi et al. 2007). This highlights the effects of choice of a fixed sampling day to quantify annual river loads for a given sampling frequency. For example, depending on the day used fixed for monthly sampling, the NO_3^--N annual load could vary from 1588.08 t yr^{-1} to 2694.46 t yr^{-1} using the FS method.

The quantified annual river loads, for NO_3^--N, SIN, DRP, TN, TP and TSS, using five calculation methods and four sampling frequencies, were compared to the reference "true" annual river loads by calculating the bias (Equation 4.8) and root mean square error (RMSE) (Equation 4.9) as performance measures (Table 4.1).

4.4.3.1 Effects of different load calculation methods

Our results showed that GM was, in general, the least accurate and least precise method. The bias and RMSE values of GM were the highest for all water quality parameters at different sampling frequencies (Table 4.1), except for NO_3^--N and SIN loads estimated by RC at all sampling frequencies, TP loads estimated by RE and FW at fortnightly and monthly sampling frequencies and TSS loads estimated by RE and FW at monthly sampling frequency. This corresponds with the results of Moatar and Meybeck (2005) as they also found the GM method to give better results (lower RMSE values) for TP "using monthly sampling frequency" than the other methods they used, including FW.

The GM method, however, underestimated the annual river loads for all water quality parameters regardless of the sampling frequency (Figure 4.8 and Table 4.1). The negative bias values ranged from about -22% for DRP, NO_3^--N and SIN to -32% for TN; -58% for TP; and -69% for TSS (Table 4.1). These negative bias values were almost the same across different sampling frequencies indicating GM's consistent underestimation of annual river loads regardless of sampling frequency. This might be explained by the fact that the GM method fails to consider variations in river flow measurements in estimating annual river loads (Birgand et al., 2010; Huang et al., 2012). In addition, this might be due to the lower contaminant concentration at low to medium flows that leads to an overall low mean annual concentration, using infrequent sampling, resulting into an underestimation of the annual river loads.

The RC method overestimated the annual load estimates of all water quality parameters (except TP and TSS) regardless of the sampling frequency. This could be attributed to the way RC estimates the loads. As discussed earlier, RC depends on the relationship between flow and contaminant concentrations to estimate annual loads. For NO_3^--N and SIN, there is a dilution effect at high flows (Figures 4.3 and 4.4) that is not accounted for by the RC method. Thus, the NO_3^--N and SIN loads estimated by RC were extremely higher than the reference "true" loads. For NO_3^--N loads estimated by RC method, the bias ranges from about 54% to about 115% of the reference load, and RMSE ranges from about 54% to about 192% of the reference load. For SIN loads estimated by RC method, the bias ranges from about 31% to about 59% of the reference load, and RMSE ranges from about 31% to about 96% of the reference load. Other studies found similar extremely high NO_3^--N load estimates by RC. For example, Snelder et al., (2017) found out that using the rating curve method to estimate NO_3^--N loads in 77 catchments in New Zealand resulted in highly overestimated NO_3^--N loads.

On the other hand, RC results in the lowest RMSE for TN, TP and TSS load estimates at monthly sampling frequency compared to other methods. This could be explained by the concentration effect that is exhibited by the three parameters (TN, TP and TSS) at high flows.

The RE method was developed to enhance the total suspended solids loads estimated by the FW method (Richards and Holloway 1987). Nevertheless, our results showed that RE and FW gave similar bias and RMSE for all water quality parameters (NO_3^--N, SIN, DRP, TN, TP, and TSS) throughout all sampling frequencies (Table 4.1). This corresponds with the results described by Birgand et al. (2010) who also found that there was no significant improvement in annual river load for NO_3^--N estimated by RE over those estimated by FW.

The FW, RE and FS resulted in lower bias and RMSE for all water quality parameters regardless of sampling frequencies (Table 4.1). The FW and RE have the lowest bias values for all water quality parameters at each sampling frequency except for SIN loads estimated by FS at monthly sampling frequency; however, this difference was not significant (Table 4.1). In addition, FW and RE have the lowest RMSE for all water quality parameters at 2 days sampling frequency except for DRP loads estimated by FS (Table 4.1). Although FW and RE performed better at the highest sampling frequency (i.e. 2 days) in terms of bias and RMSE values, the FS performed slightly better than FW and RE (in terms of RMSE) for most of the water quality parameters (DRP, TP, TN and TSS) at monthly sampling frequency. The FS resulted in the lowest RMSE values for most of the water quality parameters using weekly sampling frequency, for TN and DRP using fortnightly sampling frequency, and for DRP using monthly sampling frequency.

The better performance of FS, in terms of RMSE compared to FW and RE, could be attributed to the composite approach (Richards 1998; Roygard et al. 2012). The FS employs a composite load calculation technique through stratifying and averaging river flow and contaminant concentrations into different flow decile bins (Roygard et al. 2012) rather than only averaging the contaminant concentration for the whole year (as done by GM) or just considering the flow at time of sampling and multiplying the flow weighted concentration with the total annual flow (as done by FW). Richards and Holloway (1987) found that the use of flow stratified sampling along with RE resulted in the most precise load estimates. Roygard et al. (2012) illustrated that FS reduces the bias resulting from lower sampling frequencies, i.e. monthly, that do not capture all flows. The better performance of FS over FW and RE upon decreasing the sampling frequency suggests that FS could perform better than other methods using long records of water quality datasets. However, this hypothesis needs to be tested using longer records of higher resolution measurements of river flow and water quality datasets that we do not have for the study area.

4.4.3.2 Effects of different sampling frequencies

Sampling frequency could also affect the annual river load estimates for all water quality parameter analysed (Table 4.1). In general, our results showed that the bias values increased with the decrease of sampling frequency from 2 days to weekly and then to fortnightly (except for loads estimated by GM and RC). However, interestingly, the bias values slightly decreased with the decrease of sampling frequency from fortnightly to monthly for NO_3^--N, SIN and DRP (except for loads estimated by GM, and DRP loads estimated by FS and RC methods). On the other hand, the bias values of TN, TP and TSS loads estimated by GM, FW, RE and FS, and DRP loads estimated by FS, continued to increase from fortnightly to monthly (the exception to this pattern was TSS load estimated by GM as there was no change from fortnightly to monthly). This pattern in bias values (increase from 2 days to fortnightly and then decrease from fortnightly to monthly) is similar to results of other studies. For example, this pattern has been reported by Guo et al. (2002) for NO_3^--N loads in in the Upper Sangamon River in central Illinois, US, and by Zamyadi et al. (2007) for ammonium, sediment, nitrates and total nitrogen loads in the Turmel Brook watershed, Québec, Canada. The difference in the bias values obtained could be partly explained by the increase in number of scenarios simulated for fortnightly (14 scenarios) to monthly (30 scenarios) sampling frequencies (Zamyadi et al., 2007).

The RMSE values also showed a general pattern of increase with the decrease of sampling frequency from 2 days to monthly (Table 4.1). The exception to this pattern was the NO_3^--N and SIN loads estimated by FS, and TN loads estimated by FW, RE and FS; and NO_3^--N, SIN and TN loads estimated by RC (where RMSE values decreased upon the decrease of sampling frequency from fortnightly to monthly). In general, we found that the higher the sampling frequency (i.e. 2 days), the more reliable the estimated annual contaminant loads (Guo et al., 2002; Zamyadi et al., 2007).

However, there was no substantial increase in the RMSE values with the decrease of sampling frequency from fortnightly (26 samples per year) to monthly (12 samples per year). Moreover, the decrease in sampling frequency from fortnightly to monthly resulted in a slight decrease of the RMSE values of NO_3^--N and SIN loads estimated by FS; and TN loads estimated by FW, RE and FS; and NO_3^--N, SIN and TN loads estimated by RC (Table 4.1). This suggests that if water quality sampling were taken fortnightly instead of monthly, there would be no substantial gains in accuracy and precision of river load estimates of all water quality parameters (NO_3^--N, SIN, DRP, TN, TP, and TSS) at the study site. However, there would be considerable gains in accuracy and precision for river load estimates of NO_3^--N and SIN if weekly sampling frequency was adopted instead of the current monthly sampling. To illustrate this, the RMSE (accuracy and precision) values for NO_3^--N loads decreased from 13.33% for FW and 13.73% for FS at monthly sampling frequency to 4.20% for FW and 3.39% for FS at weekly sampling frequency (Table 4.1). Nevertheless, these considerable gains in accuracy and precision would come at about a three-fold increase in the monitoring cost if the weekly sampling frequency was to be adopted instead of the monthly sampling frequency. This increase in sampling frequency, however, did not necessary lead to an increase in accuracy and precision equally in all water quality parameters. For example, for TN, the RMSE values decreased slightly (compared to SIN) from 19.66% for FW and 15.14% for FS at monthly sampling frequency to 17.38% for FW and 14.25% for FS at weekly sampling frequency (Table 4.1).

We found that increasing the sampling frequency, and the monitoring budget accordingly, result in different RMSE values as a function of the water quality parameter. For dissolved nutrients (NO_3^--N and SIN) that showed dilution effect during runoff events (Figures 4.3 and 4.4), adopting weekly sampling frequency (using FW, RE or FS) resulted in RMSE lower than 5% of the reference (true) annual river load (Table 4.1). On the other hand, for parameters such as TN, TP and TSS that showed concentration effect during runoff events (Figures 4.3 and 4.4), adopting weekly sampling frequency (using FW, RE or FS) resulted in relatively higher RMSE values ranging from about 14 to 51% of the reference (true) annual river load. This implies that increasing the sampling frequency (e.g. from monthly to weekly), and consequently the monitoring budget, to achieve higher level of accuracy and precision for dissolved nutrients (e.g. NO_3^--N, SIN and DRP) would not be sufficient for accurate and precise estimates of parameters such as TP and TSS. Our results corresponds with the suggestion by Richards and Holloway (1987) that designing a sampling program to achieve high level of accuracy and precision for TSS, "a volatile parameter", would be sufficient for accurate and precise estimates of dissolved nutrients (e.g. NO_3^--N, SIN and DRP).

In light of the concentration and dilution effects, infrequent sampling has less chance to reflect the flow peaks. These peak flow events disproportionally account for most of the annual river load, particularly for TN, TP and TSS parameters. According to Birgand et al. (2011), water quality parameters (such as NO_3^--N and SIN) that have dilution effect during peak flow events, generally show a positive bias (i.e. overestimation) in quantification of their annual river loads. On the other hand, water quality parameters (such as TN, TP and TSS) that have concentration effect during peak flow events, show a negative bias (i.e. underestimation) in quantification of their annual river loads. This pattern is also clear in our results as NO_3^--N and SIN loads showed a relatively lower and positive bias, while TN, TP and TSS loads showed a relatively higher negative bias, particularly at fortnightly and monthly sampling frequency (Table 4.1). The use of a higher sampling frequency, particularly 2 day sampling, resulted in a significant decrease in bias and RMSE values for TN, TP and TSS loads (Table 4.1).

If ±20% deviation (i.e. RMSE) from the reference (true) load is considered acceptable for water regulatory authorities, the results (Table 4.1) can be used to suggest the minimum sampling frequencies for different contaminants. This means, in case of NO_3^--N, SIN, TN and DRP, monthly sampling frequency, using FW, RE and FS, is considered enough to yield load estimates within the acceptable level of deviation from reference “true” loads. For TN, however, it is important to consider that FW and RE result in deviation larger than ±20% in case of fortnightly sampling. Therefore, FS (even if it is less accurate than FW and RE in case of fortnightly and monthly sampling) should be used along with monthly sampling to estimate TN loads as FS will result in more precise load estimates than FW and RE.

Conversely, for TP and TSS, this analysis shows that the minimum sampling required to yield results with the acceptable level of error is higher than weekly sampling but not as frequent as 2 days sampling (using FW, RE and FS methods). This clearly suggests that the monthly sampling program for TP and TSS currently used by most, if not all, regional councils in New Zealand will yield highly imprecise and inaccurate TP and TSS load estimates. Worldwide, other studies equally suggested that monthly sampling is insufficient in case of TSS and will result in large errors. For example, Coynel et al. (2004) recommended that the Garonne and Nivelle rivers in France to be sampled for suspended particulate matter (SPM) at least every 3 days and 7 hrs, respectively, to get load estimates within acceptable deviation (±20%) of the reference loads. Also, Moatar et al. (2013) found that monthly sampling for SPM will result in load estimates with uncertainties close to ±100%.

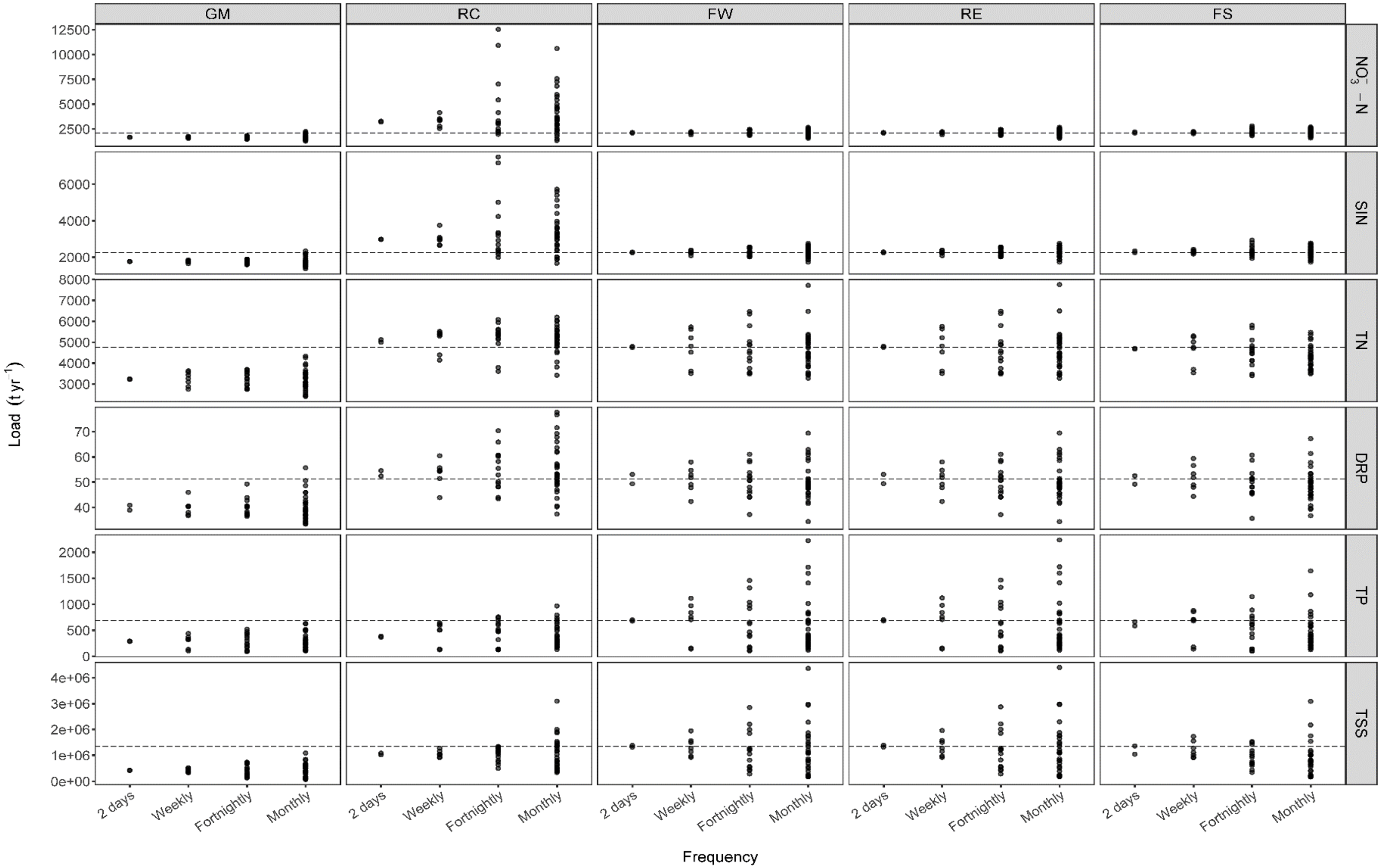

Figure 4.8. Variation in estimated annual river loads for six water quality parameters (NO_3^--N, SIN, TN, DRP, TP and TSS), using combinations of four sampling frequencies (2 days, weekly, fortnightly and monthly) and five load calculation methods (GM, RC, FW, RE and FS), in the Manawatu River at Teachers College (MTC) site for the observation year 2010/2011. The dashed lines plots the reference 'true' loads calculated based on daily measurements of water quality concentrations and river flow at the study site.

Table 4.1. Bias and RMSE (as % of the reference 'true' load) of different load estimation methods and sampling frequencies used in quantification of annual river loads of NO_3^--N, SIN, TN, DRP, TP and TSS in the Manawatu River at Teachers College (MTC) site for the observation year 2010/2011 (1-May-2010 to 30-April-2011)

Parameter	Method	2 days		Weekly		Fortnightly		Monthly	
		Bias %	RMSE %	Bias %	RMSE %	Bias %	RMSE %	Bias %	RMSE %
	GM	-21.54	21.54	-21.54	21.73	-21.52	22.14	-21.46	24.02
	RC	53.65	53.69	56.54	61.02	115.49	191.92	91.89	133.18
NO_3^--N	FW	-0.02	1.44	-0.06	4.20	1.67	9.90	1.32	13.33
	RE	-0.03	1.45	-0.06	4.22	1.69	9.95	1.35	13.37
	FS	1.22	3.23	1.59	3.39	4.99	13.91	1.71	13.73
	GM	-21.93	21.93	-21.93	22.09	-21.91	22.39	-21.93	24.14
	RC	31.45	31.45	32.97	36.18	59.44	96.13	47.73	68.15
SIN	FW	-0.01	0.93	-0.02	4.02	1.42	8.57	1.08	11.26
	RE	-0.01	0.94	-0.01	4.03	1.45	8.61	1.11	11.30
	FS	1.32	2.28	1.56	3.84	4.15	12.75	0.92	11.96
	GM	-32.24	32.24	-32.22	32.87	-32.21	32.96	-32.59	34.19
	RC	6.07	6.21	6.38	12.62	8.95	16.78	7.46	14.87
TN	FW	-0.01	0.60	-1.12	17.38	-2.57	20.27	-3.88	19.66
	RE	0.18	0.63	-0.97	17.49	-2.45	20.35	-3.76	19.76
	FS	-1.76	1.77	-3.41	14.25	-5.19	15.25	-10.28	15.14
	GM	-22.22	22.30	-22.21	22.93	-22.21	23.19	-22.10	24.34
	RC	4.47	4.93	4.54	10.20	7.01	16.88	8.08	21.48
DRP	FW	-0.06	3.61	-0.60	9.21	-1.99	12.42	-1.54	13.85
	RE	0.02	3.63	-0.53	9.23	-1.95	12.45	-1.49	13.87
	FS	-0.80	3.39	0.99	9.41	-3.54	12.11	-4.95	13.41
	GM	-58.22	58.22	-58.15	60.47	-58.17	61.76	-58.62	62.58
	RC	-45.39	45.41	-35.30	46.21	-35.43	48.46	-41.83	51.67
TP	FW	-0.03	1.65	-2.90	51.30	-8.61	63.62	-11.41	75.06
	RE	0.56	1.80	-2.42	51.64	-8.26	63.93	-11.14	75.43
	FS	-9.59	11.02	-14.05	43.59	-24.82	51.49	-31.24	56.28
	GM	-68.82	68.82	-68.80	69.01	-68.84	70.60	-68.84	71.48
	RC	-22.02	22.19	-21.71	23.45	-23.09	30.29	-20.58	49.73
TSS	FW	0.04	2.68	-1.34	25.22	-11.14	56.78	-12.13	73.06
	RE	0.73	2.74	-0.72	25.55	-10.74	57.03	-11.78	73.45
	FS	-10.99	16.09	-9.57	24.13	-31.92	42.20	-37.66	60.27

4.5 Conclusions

For better management of water quality at a catchment scale, load estimation of different contaminants in the rivers is inevitable. Accurate and precise estimates of these loads requires accounting for the uncertainty resulting from sampling frequency and load estimation methods.

Our results indicate that methods that does not consider flow at the time of sampling (such as GM) will yield imprecise and inaccurate load estimates. On the other hand, methods that rely on the relationship between flow and concentration (such as RC) will result in highly overestimated loads for parameters that show dilution effect at high flows (such as NO_3^--N and SIN). Thus, based on our findings, for catchments with similar flow regime and relationship between flow and water quality parameters, it is not recommended to use RC for parameters that exhibit dilution effect at high flows. The flow weighted (FW) and ratio estimator (RE) methods gave similar results for all water quality parameters across different sampling frequencies. The RE was developed to enhance the suspended solids load quantified by FW. However, we found no essential improvements in river loads estimated by RE over FW for suspended sediments and other water quality in this study. The FW, RE and FS resulted in lower bias and RMSE values at highest sampling frequency, i.e. 2 day sampling.

Sampling frequency resulted in significant effect on bias and RMSE values for annual river load estimates for all water quality parameter analysed. In general, bias and RMSE values decreased with an increase in the sampling frequency from monthly to weekly or 2 days, using FS, RE and FW, for most of the water quality parameters analysed. However, river water quality is generally monitored at a relatively lower frequency because of the cost associated with sampling and analysis. In New Zealand, most Regional Councils monitors river water quality parameters on a monthly basis. Thus, if accuracy and precision of 80% (i.e. RMSE =

20%) of the estimated loads is considered acceptable for the regulatory authorities, this means monthly sampling frequency for NO_3^--N, SIN, TN and DRP is sufficient to estimate accurate and precise loads within the acceptable threshold using FW, RE and FS methods. Conversely, monthly sampling is not sufficient to get accurate and precise load estimates within the acceptable threshold for TP and TSS regardless of the load estimation method. This is because monthly sampling does not capture flow peaks. Our results showed that sampling TSS and TP more than once per week but not as frequent as each 2 days will result in load estimates within the acceptable threshold. We recommend further studies to be conducted to investigate how flow-based sampling (sampling that capture flow peaks) either by grab samples or auto sampler can improve the accuracy and precision of TP and TSS load estimates without having to sample every 2 days.

4.6 Acknowledgments

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Chapter 5: Spatial modelling of nitrogen attenuation capacity and land-based nitrogen loads to rivers

5.1 Abstract

The qualities of New Zealand's surface and ground waters are being degraded by the leaching of nitrogen from intensive agricultural activities. However, on its journey from farms to rivers and lakes, nitrate can be attenuated through a number of processes including denitrification in groundwater. The extent of this denitrification depends on the hydrogeochemical settings of the subsurface environment. The nitrogen attenuation factor, AF_N, is defined and quantified as a descriptor of the capacity of a catchment to attenuate nitrogen. AF_N is identified by comparing the estimates of average annual leaching losses of nitrogen from the root zone for different land uses with the measured average annual loads of soluble inorganic nitrogen (SIN) in the river. AF_N was determined at 15 and 5 sites in the Tararua and Rangitikei River catchments, respectively, in the lower part of the North Island, New Zealand. AF_N is highly variable (0.14 to 0.94) in different sub-catchments within the study catchments. A partial least squares regression (PLSR) analysis revealed that the AF_N is positively related to the presence of poorly drained soils and mudstones. It also showed a negative relationship with the presence of well-drained soils and gravels.

The aforementioned catchment's soils and rocks types were assessed and classified into high, moderate and low nitrogen attenuation capacities, depending on their texture, drainage rate and carbon content. Four models (uniform nitrogen attenuation, and variable nitrogen attenuation for soils only; rocks only; and for both soils and rocks) were developed and evaluated by comparing the predicted with measured average annual loads of SIN in the Manawatu and Rangitikei rivers. Modelling the spatial effects of both soils and rocks on subsurface nitrogen attenuation resulted in the best predictions of land-based SIN loads to the rivers.

This new knowledge will be instrumental in the future development of the models and planning tools required to help reduce the negative impacts of intensive agricultural practices on water quality by assessing and spatially aligning intensive land use practices with high nitrogen-attenuation pathways in sensitive agricultural catchments.

Keywords: Agriculture; Diffuse Pollution; Nutrient; Water Quality; Tararua and Rangitikei Catchments; Denitrification

5.2 Introduction

Intensive agricultural activities, driven by increasing demands for food production and farm profitability, have an adverse impact on freshwater resources in agricultural landscapes (Foley et al., 2005; Tilman et al., 2002). Leaching and runoff from these intensive agricultural activities increase the levels of nutrients (nitrogen and phosphorus) in receiving groundwaters and surface waters (Di and Cameron, 2002; Hamill and McBride, 2003; Harding et al., 1999; Hooda et al., 2000; Tilman, 1999; Wilcock et al., 2006). To address this issue, the New Zealand Ministry for the Environment has gazetted the National Policy Statement for Freshwater Management (NPS-FM) (Ministry for the Environment, 2014). The NPS-FM requires the Regional Councils across New Zealand to complete, each five years, a set of 'freshwater accounts' for individual Freshwater Management Units (FMUs). For this purpose, they will build a freshwater-quality accounting system for relevant contaminants loads (measured, modelled or estimated) in groundwater and surface waters. Similar worldwide regulations to protect freshwater resources include, but not limited to, the European Union Water Directive Framework (European Community, 2000) and the Total Maximum Daily Load (TMDL) program under the Clean Water Act (CWA) in the United States (USEPA, 1999).

In the light of the NPS-FM guidelines, Regional Councils in New Zealand monitor river flow and a range of water quality parameters (e.g. ammoniacal-nitrogen, nitrate-nitrogen, and nitrite-nitrogen) in the rivers to estimate annual river loads. In addition, they use nutrient budgeting tools (e.g. OVERSEER®; Wheeler et al., 2003) to quantify nutrient leaching from the root zone, on a farm scale. Similar farm-scale nutrient models are used, worldwide, to quantify nutrient flows and leaching from root zone on a farm scale (Cichota and Snow, 2009). These models, however, are limited in their capacity in assessing nutrient flows mainly within the farm boundary and prediction of nutrients losses from the root zone (Wheeler and Shepherd, 2013). More generally, water-quality management in agricultural catchments appears to focus on identifying and reducing nutrient losses from the root zone of intensive farming activities (Almasri and Kaluarachchi, 2004; Clothier et al., 2007; Dinnes et al., 2002; Libutti and Monteleone, 2017; Manderson, 2008; Stenger et al., 2014).

During its journey from farms to rivers through the subsurface environment, nitrate can be attenuated by a number of processes. These processes include dissimilatory nitrate reduction to ammonium (Korom, 1992; Robertson et al., 1996; Tiedje et al., 1983); assimilation of nitrate into microbial biomass (Hu et al., 2000); nitrate uptake through phreatophytes (Franklin et al., 2016; Masclaux-Daubresse et al., 2010); and denitrification (Burgin and Hamilton, 2007; Hiscock et al., 1991; Martin et al., 1999; Rivett et al., 2008; Saggar et al., 2013). Among these processes, denitrification was found to be the main process of nitrate attenuation in the subsurface (Rivett et al., 2007). Denitrification is the process by which nitrate is transformed through a series of microbially mediated reduction reactions to gaseous nitrogen forms (Knowles, 1982; Korom, 1992; Rivett et al., 2007). For denitrification to occur, four conditions are required: an anoxic/anaerobic or low dissolved oxygen (DO) environment; the availability of electron donors such as Mn^{2+} and Fe^{2+}; the availability of bacteria with metabolic capacity; and the presence of nitrate as an electron acceptor (Korom, 1992). Therefore, denitrification varies both spatially (McAleer et al., 2017; Song et al., 2012) and vertically in the subsurface (Hill et al., 2004). Many studies have shown that denitrification is influenced by catchment characteristics that affect; leaching rate, flow rate, flow pathway length and the residence time of water enriched in nitrate on its subsurface pathway from farms to surface water bodies (Fenton et al., 2009; Jahangir et al., 2012b; McAleer et al., 2017; McMahon and Chapelle, 2008; Vidon and Hill, 2004; Wu et al., 2018).

For better understanding of the spatial and temporal dynamics of farm-nutrient flows and their transformations along flow pathways from farms to receiving groundwater and surface waters, researchers and water managers are increasingly devoting significant efforts to the development and application of catchment-scale water and nitrogen flow models (Almasri and Kaluarachchi, 2007; Baalousha, 2013; Hadfield, 2007; Krause et al., 2008; Peña-Haro et al., 2010). A number of studies have simulated nitrate attenuation in the subsurface. For example, Conan et al., (2003) used SWAT-MODFLOW-MT3DMS to simulate the nitrate attenuation in the Coët-Dan watershed (12 km^2) in Brittany, France. They found that 65% of the nitrate that leaches from the root zone is attenuated in the subsurface. Styczen and Storm (1993) used DAISY and MIKE SHE to simulate nitrate attenuation in the Karup River catchment (425 km^2) in Denmark. They found that around 50% of the leached nitrate is attenuated at the redoxcline. Wriedt and Rode (2006) used mRISK-N, MODFLOW and RT3D to simulate nitrate attenuation in the Schaugraben catchment (20 km^2) in Germany. They found that 80% of the leached nitrate is attenuated in the subsurface. Hansen et al. (2009) used DAISY and MIKE SHE/MIKE 11 to simulate the spatial distribution of denitrification across 14 sub-catchments in the Odense Fjord catchment (1046 km^2) in Denmark. They found that denitrification varies from 47% to 94% across the 14 sub-catchments without accounting for the wetland and river processes. Denitrification varied from 53% to 94% when wetland and river processes were accounted for. Overall, they found that 57% of the leached nitrate was attenuated in the subsurface between the root zone and the catchment outlet. Merz et al. (2009) used a 2D steady-state GIS model (MODEST) to simulate the spatial distribution of nitrate attenuation in the State Brandenburg in Germany. They found that the attenuation varied spatially from < 50 to >75%. Hansen et al. (2014) used stochastic geological models and MIKE SHE to simulate the nitrate attenuation potential in the Norsminde fjord catchment (101 km^2) in Denmark. They found that the spatial distribution of the nitrate attenuation potential varies from 0% to 100%. In New Zealand, Woodward et al. (2013) used a lumped catchment scale model (StreamGEM) to simulate the nitrate attenuation in a small Toenepi stream catchment (15.1 km^2), in the Waikato region of New Zealand. They found that 44.9% of the leached nitrate is attenuated in the subsurface.

To our knowledge, there are few studies that have simulated the spatial distribution of nitrate attenuation in the subsurface. Studies like those of Hansen et al., (2009, 2014) that have attempted to do so have used models that are data-intensive but this required data is not always available for all catchments. Studies that used models that require less information (e.g. Woodward et al., 2013), have not simulated the spatial variability of attenuation. Also, according to our knowledge, very limited research has been conducted to quantify the relationships between catchment characteristics and spatial variation in the nitrogen attenuation capacity (Collins et al., 2017; Elwan et al., 2015a; Rivas et al., 2017; Stenger et al., 2014, 2008). This is particularly the case for many of New Zealand's agricultural catchments where an understanding of these relationships is required to help predict land-based nitrogen loads to surface waters. Hence, there is a need for simple hydrogeologic models that can make use of readily available data to relate land-based nitrogen losses to river loads taking into account different catchment characteristics.

The main objectives of this study were to; assess and quantify the spatial distribution of nitrogen attenuation capacity; evaluate the relationship between the spatially variable nitrogen attenuation capacities and catchment characteristics; and build a simple hydrogeologic-based model, which accounts for the effects of different hydrogeological settings on spatial variations in nitrogen attenuation capacity, to predict land-based soluble inorganic nitrogen (SIN) loads to surface waters in agricultural catchments.

5.3 Materials and Methods

5.3.1 Study areas

5.3.1.1 Tararua catchment

The Tararua catchment is located in the upstream part of the Manawatu catchment, to the east of the Manawatu Gorge, in the lower North Island, New Zealand. It covers an area of around 3192 km^2. The elevation ranges from 60 m to 1497 m with an average of 316 m above mean sea level. The catchment has a temperate climate with a mean annual rainfall that varies from 945 mm yr^{-1} to 6265 mm yr^{-1}, with an average of 1520 mm yr^{-1} (based on 30 years “1978-2007” of rainfall data) (Tait and Sturman, 2008). The dominant land uses are; sheep/beef farming (64%), native cover (17%) and dairy farming (15%) (Fig. 5.25.1) (Clark and Roygard, 2008).

The Tararua catchment is surrounded, in the west, by the Tararua and Ruahine ranges and the active Wellington-Mohaka Fault; and in the east by Waewaepa and Puketoi ranges (Rawlinson and Begg, 2014). The broad depression between these ranges is called the Pahiatua basin (Lee and Begg, 2002). The tectonic uplift of the Tararua and Ruahine axial ranges around 1-1.5 Ma ago is linked to the start of movement on the Wellington Fault. During this tectonic uplift, the

Manawatu Gorge was formed by a river cutting through the axial ranges (Rawlinson and Begg, 2014; Zarour, 2008). The basement (Triassic to late Early Cretaceous) in the catchment is intensely faulted creating a series of highs (ridges) and lows (troughs). These ridges and depressions are filled with Tertiary (late Early Cretaceous to latest Pliocene) sediments (Rawlinson and Begg, 2014). The Tertiary sediments are mainly marine mudstone and sandstone of variable thickness (from < 1 m to around 2.2 km). The Tertiary sediments are overlaid by thin Quaternary (Holocene to early Pleistocene) sediments with a maximum thickness of around 228 m (Rawlinson and Begg, 2014). The major soil textures in the Tararua catchment are silt loam (52%) and sandy loam (16%) (Fig. 5.1) (Newsome et al., 2008).

According to Zarour (2008), the groundwater table is controlled by the topography in the catchment. Rawlinson and Begg (2014) illustrated that the groundwater flow is a replica of the catchment topography. The groundwater is recharged mainly by infiltration of rainfall over the ranges that surround the catchment in the east and the west (Bekesi, 2001). The rainfall infiltration recharge was estimated to be 814 x 10^6 m^3 yr^{-1} (i.e. around 255 mm yr^{-1}) (Callander and Thomas, 2013). There is a strong connection between the surface water and the groundwater in the catchment (Zarour, 2008). This is reflected by the large fraction of baseflow in the total stream flow. Analysis of 8 years (2009 to 2016) of stream flow data (Elwan, unpublished) showed that the average stream flow at the outlet of the Tararua catchment (i.e. the Manawatu Gorge) was 7.2 x 10^6 m^3 day^{-1} and the average baseflow was estimated to be 4.6 x 10^6 m^3 day^{-1} (i.e. base flow index BFI = 0.64).

5.3.1.2 Rangitikei catchment

The Rangitikei catchment is located in the lower part of the North Island, New Zealand. It covers an area of around 3887 km^2. The elevation ranges from 7 m to 1727 m with an average of 684 m above mean sea level. The catchment has a temperate climate with a mean annual rainfall that varies from 811 mm yr^{-1} to 2866 mm yr^{-1}, with an average of 1282 mm yr^{-1} (based on 30 years "1978-2007" of rainfall data) (Tait and Sturman, 2008). The dominant land uses are sheep/beef/dairy (50%) and NOF "i.e. Blocks not otherwise used for farming, such as indigenous forest" (42%) (Fig. 5.2) (AsureQuality, 2015).

The Rangitikei catchment is located in the Pliocene-Pleistocene Wanganui Basin (Bekele and Rawlinson, 2014). According to Begg et al. (2005), two regional tectonic processes affect the groundwater in the catchment. The first is the tectonic uplift that raised the Wanganui Basin from the sea. This uplift might have been caused by the subduction of the Pacific plate below the Australian plate and its associated deeper crustal processes. The second is the Rangitikei-Leedstown-Galpin Fault. This active fault cuts through the Rangitikei catchment to the west of the Rangitikei River. In the catchment, basement rocks (Jurassic to Early Cretaceous age) are mainly hard quartzo-feldspathic sandstone and interbedded mudstone that are heavily faulted and folded (Bekele and Rawlinson, 2014). In these rocks, water storage capacity is a result of jointing and shearing that creates specific locations with higher secondary permeability (Bekele and Rawlinson, 2014). Pliocene – early Pleistocene sediments (Late Tertiary to Early Quaternary) overlie the basement. These sediments consist mainly of siltstone, mudstone, sandstone and pumiceous sand. The older part of these sediments is mostly mudstone with the sandstone fraction increasing as the sediments get younger. The thickness of these sediments varies from 1.5 km to 4 km. Pleistocene – Holocene sediments (Early–Late Quaternary) were deposited during the uplift of the region from the sea (Begg et al., 2005). The sandstones and shell bed layers of these sediments are known to contain water resources (Townsend et al., 2008). Holocene deposits (Late Quaternary) cover the southern part of the catchment (Bekele and Rawlinson, 2014). These deposits consist mainly of alluvial gravel and sand. The major soil textures in the Rangitikei catchment are; silt loam (36%), sandy loam (30%) and loam/loamy sand (13%) (Fig. 5.2) (Newsome et al., 2008).

According to Zarour (2008), the groundwater table in the Rangitikei catchment is a reflection of the topography. The groundwater is recharged mainly by infiltration of rainfall and occasionally by losses from the river (Zarour, 2008). Similar to the Tararua catchment, there is a strong connection between the surface water and the groundwater in the Rangitikei catchment (Zarour, 2008). This is reflected by the large fraction of baseflow in the total stream flow. Analysis of 8 years (2009 to 2016) of stream flow data (Elwan, unpublished) showed that the average stream flow at the outlet of the Rangitikei catchment (i.e. Rangitikei at McKelvies) was 6.2 x 10^6 m^3 day^{-1} and the average baseflow was estimated to be 4.3 x 10^6 m^3 day^{-1} (i.e. base flow index BFI = 0.69).

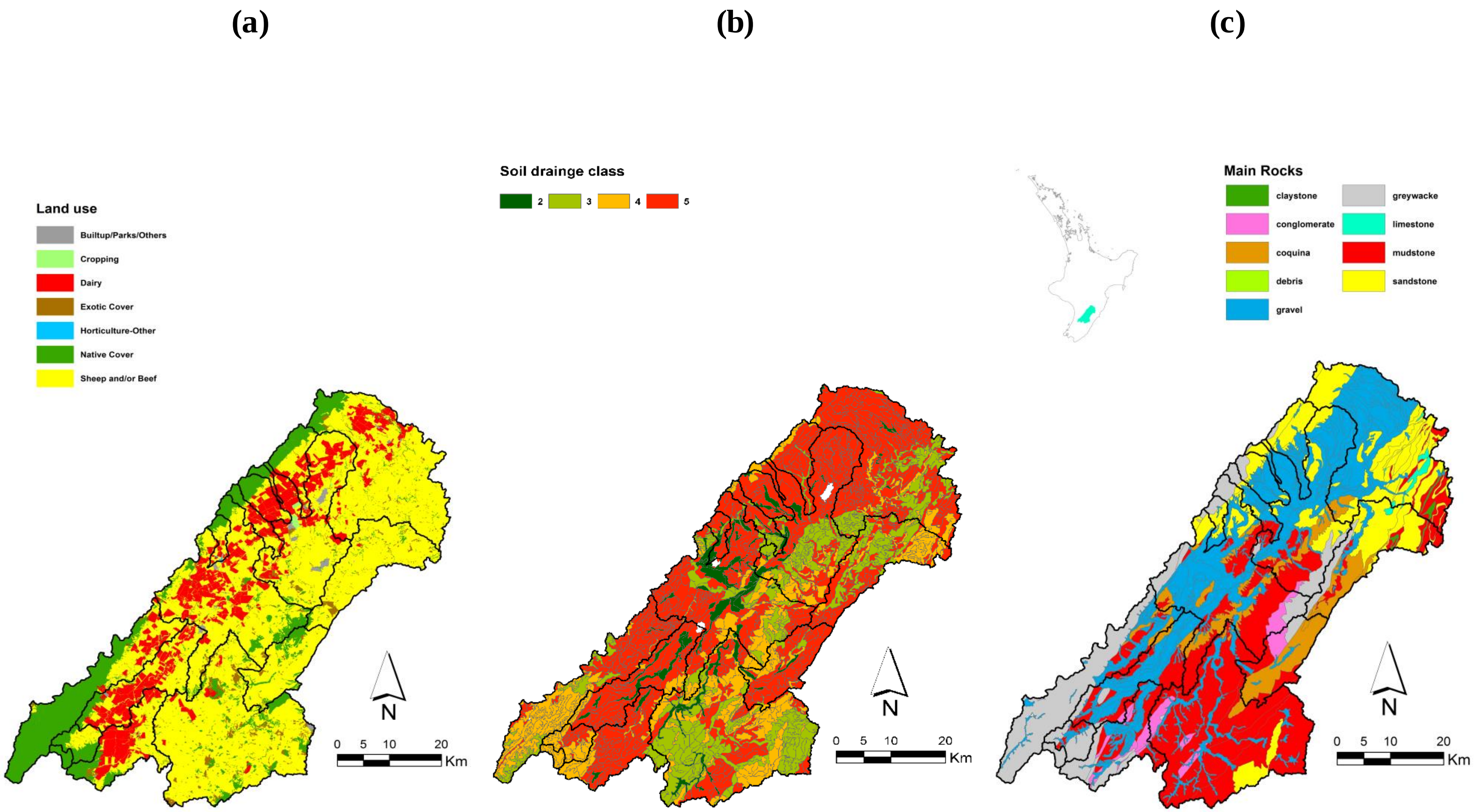

Figure 5.1. From left to right: (a) land use, (b) soil drainage classes, and (c) main rocks for the Tararua catchment. The bold black polygons represent the boundaries of the sub-catchments upstream of the monitoring sites. For the names of subcatchments see Fig. 5.3a.

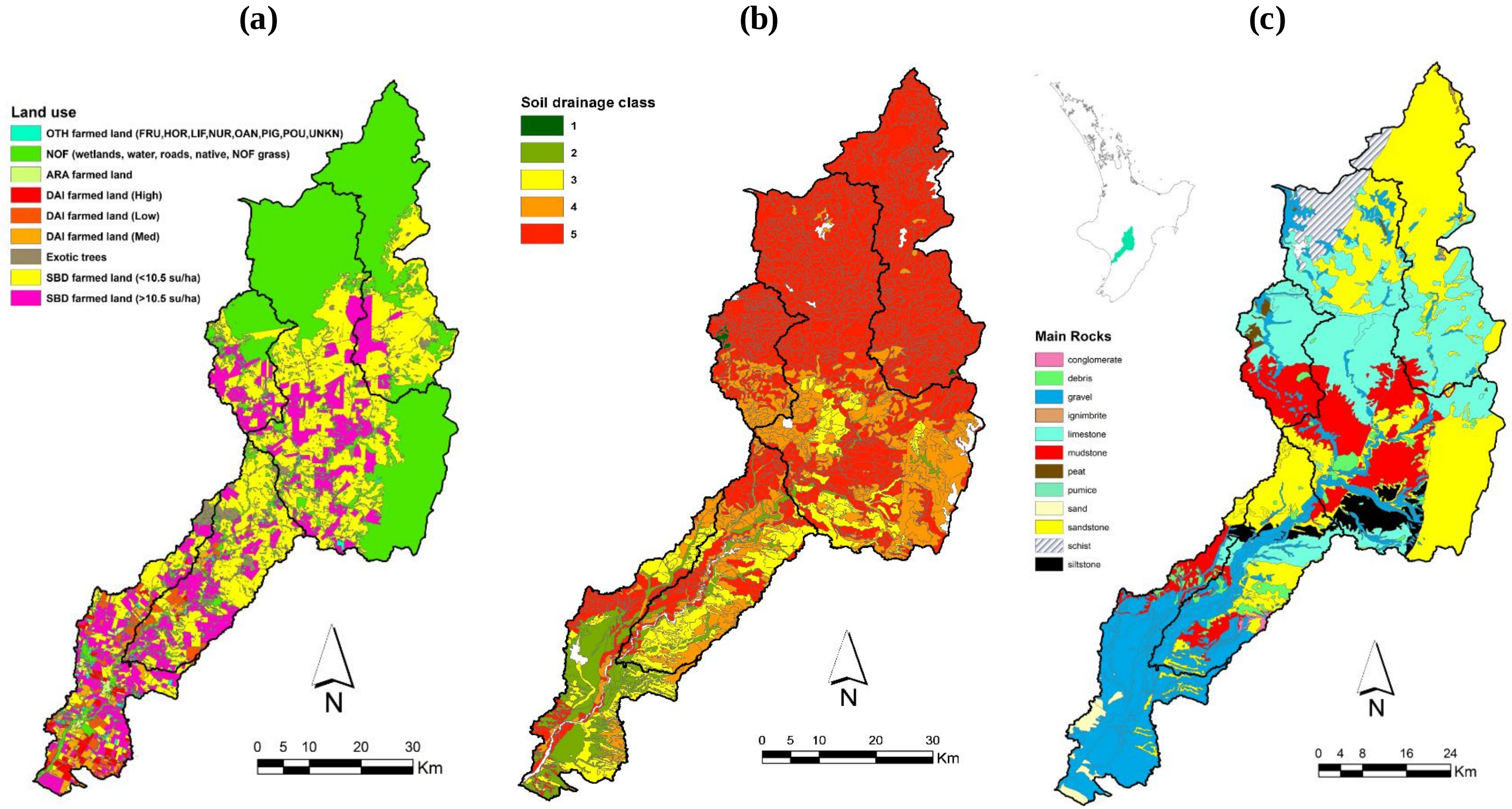

Figure 5.2. From left to right: (a) landuse, (b) soil drainage classes and (c) the main rock types of the Rangitikei catchment. The bold black polygons represent the boundaries of the catchments upstream of the monitoring sites. In the landuse layer, ARA = Arable farm; NOF = Blocks not otherwise used for farming; DAI = Dairy farm; OTH farm + <10 ha = Other farm type (minor) + pastoral farms <10 ha; and SBD = Sheep/beef/deer farm. For the names of subcatchments, see Fig. 5.3b.

5.3.2 Collection of geographical and water quality information

This study required geographical information including land uses, soil types, underlying geology, along with measurements of river flows and water quality in the study areas. Horizons Regional Council (HRC) monitors water quality and river flow at 15 and 5 monitoring sites in the Tararua and Rangitikei catchments, respectively (Fig. 5.3). The HRC monitors river flow as a function of the river stage each 15 minutes, while water quality parameters are measured on a monthly basis. This study analysed eight years (from January 2009 to December 2016) of data for mean daily flow (m^3 day^{-1}) and monthly water quality measurements for; ammoniacal-nitrogen (NH_4^+-N), nitrite-nitrogen (NO_2^--N), nitrate-nitrogen (NO_3^--N), and total oxidized nitrogen (TON = NO_2^--N + NO_3^--N) in mg L^{-1} (Appendix B). Water quality measurements below detection limits were converted into numerical values by dividing the detection limit of the water quality parameter by the square root of two (Sanford et al., 1993). The soluble inorganic nitrogen (SIN) concentration was calculated as the sum of NH_4^+-N, NO_2^--N and NO_3^--N. In some cases, when there were no measurements for NO_2^--N and/or NO_3^--N, the SIN was calculated as the sum of TON plus NH_4^+-N. In other cases, when NH_4^+-N and either NO_2^--N or NO_3^--N were not measured, SIN was equalized to TON values. This approach reflects the fact that NH_4^+-N represents the smallest fraction of SIN.

The required geographical information (Figs 5.1&5.2) was collected from existing databases, e.g. the 1:50 000 fundamental soil layer (FSL; Newsome et al., 2008), and 1:250 000 Geological Map of New Zealand (called QMAP "for Quarter-million MAP" (Heron, 2014). HRC provided a detailed land use map for the Tararua catchment (Clark and Roygard, 2008) and Landcare research provided a similar map for the Rangitikei catchment (AsureQuality, 2015).

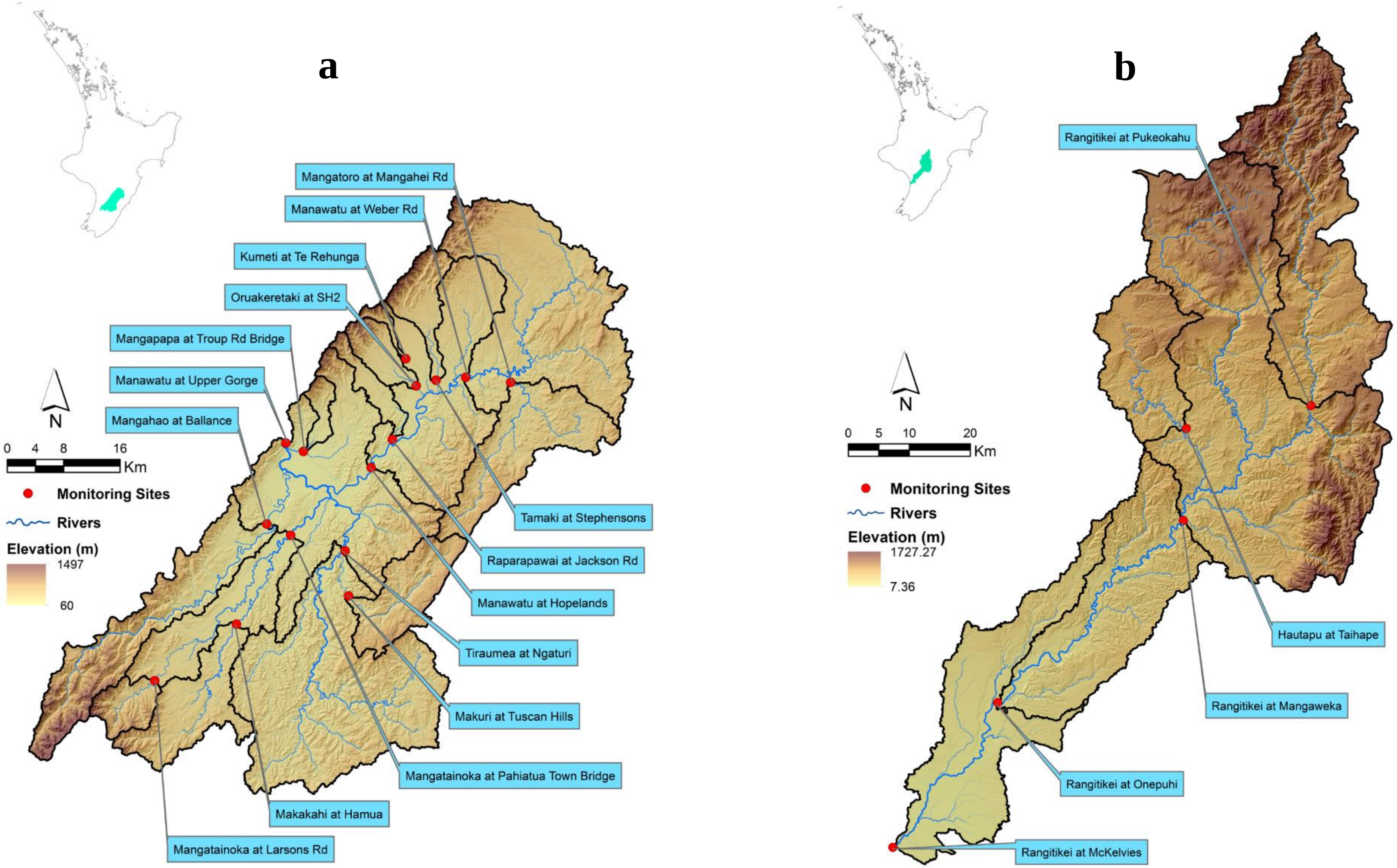

Fig. 5.3. Location of monitoring sites in: a) the Tararua catchment; and b) the Rangitikei catchment.

5.3.3 Definition and quantification of nitrogen attenuation factor

We defined and quantified the nitrogen attenuation capacity as a nitrogen attenuation factor (AF_N), by comparing the losses of nitrogen from the root zone (i.e. the nitrogen leached from the root zone in different land uses in the catchment) and the measured loads of SIN in the river, expressed in Equation (5.1) as follows:

$$AF_N = (N_{Root\ zone} - N_{River\ load})/N_{Root\ zone} \tag{5.1}$$

where:

$N_{Root\ zone}$ = Nitrogen leaching from the root zone (t yr^{-1}); and

$N_{River\ load}$ = Soluble inorganic nitrogen (SIN) load in the river (t yr^{-1}). This is the non-point (diffuse) source load.

According to this definition, the AF_N varies from 0 (no attenuation) to 1 (full attenuation) to quantify nitrogen attenuation capacity in a study catchment. For example, a value of AF_N = 0.65 can be interpreted as 65% of the nitrogen leached from the root zone is attenuated (reduced) in its flow pathways from farms to river. In other words, it means that only 35% of leached nitrogen from root zone reaches the river. This definition and interpretation of AF_N requires that quantification of nitrogen leaching from root zone and SIN measured in the river are achieved on an average annual basis over sufficiently long-term period to remove any effects of change in nitrogen storage in the system under study.

In this study, the average annual estimates of nitrogen leaching from the root zone, $N_{Root\ zone}$ (t yr^{-1}) (Equation 5.1), were calculated based on farm nutrient budget modelling in the study areas. In New Zealand, OVERSEER® is the most commonly used model to assess potential

N-leaching losses from farms (Wheeler et al., 2003). This model simulates nutrient flows and budgets at whole-farm and sub-farm management block levels, accounting for inputs describing soil types, climate conditions, topography, livestock or crop production, and a range of farm management practices. For Tararua catchment, Taylor et al., (2014) applied OVERSEER® to estimate average annual N-leaching losses (kg N ha^{-1} yr^{-1}) for a number of dairy farms. Also, other studies (Clothier et al., 2007; Roygard and Clark, 2012) estimated the N-leaching losses (kg N ha^{-1} yr^{-1}) associated with different land use types in the Tararua catchment. For Rangitikei catchment, Manderson et al. (2016) applied spatially–informed OVERSEER® modelling to estimate average annual N leaching losses (kg N ha^{-1} yr^{-1}) from the majority of agricultural land uses, and used reference N-loss values (kg N ha^{-1} yr^{-1}) from literature for the remaining non-agricultural areas (forestry, natural areas and urban). These estimates of average annual N-leaching losses (kg N ha^{-1} yr^{-1}) for different land use types in Tararua catchment (Clothier et al., 2007; Roygard and Clark, 2012; Taylor et al., 2014) and Rangitikei catchment (Manderson et al., 2016) were multiplied by the area of each land use and summed across all land use types to quantify $N_{Root\,zone}$ (t yr^{-1}) in Tararua and Rangitikei catchments.

The continuous improvements in OVERSEER® are highly likely to result in differences in the estimates of N leaching losses (kg N ha^{-1} yr^{-1}) between different OVERSEER® versions. These changes in the estimates of N leaching losses are highly likely to change the estimates of the root zone load, $N_{Root\,zone}$ (t yr^{-1}), especially if there were significant changes in N leaching losses for dominant land-use types. On the other hand, minor changes in the estimates of N leaching losses, between different OVERSEER® versions, for minor land-use types on a catchment scale, may result in slight changes in the estimates of the root zone load. In case of significant differences in the estimates of N leaching losses between different OVERSEER®

versions, field measurements will be essential to compare with modelled N-leaching by OVERSEER®.

The flow-stratified (FS) load estimation method was used to quantify average annual river SIN loads, combining available river mean daily flows (m^3 day^{-1}) and monthly observations of (SIN) concentrations (mg L^{-1}) over 8 years (2009 to 2016) at selected 15 and 5 river monitoring sites in Tararua and Rangitikei catchments, respectively (Fig. 5.3). The calculated river SIN loads included contributions from both the non-point (diffuse), and point (rural wastewater discharges) sources in the study catchments. The point source (PS) loads were also estimated using the FS method. The PS loads were estimated using available monthly observations of SIN concentrations (mg L^{-1}) over 8 years (2009 to 2016) at 9 and 8 PS sites in the Tararua and Rangitikei catchments, respectively. Due to limitations in data, average flow measurements at each PS site (McArthur and Clark, 2007) were used as average flow measurements across all flow decile bins. The average annual SIN loads from point sources were subtracted from the river SIN loads, giving the river SIN loads from non-point (diffuse) sources termed as $N_{river\ load}$ (t yr^{-1}) (Equation 5.1).

5.3.3.1 Uncertainty in the nitrogen attenuation factor

Quantification of AF_N (Equation 5.1) as described above could be subject to some degree of uncertainty as it was based on estimates of the root zone load, $N_{Root\ zone}$ (t yr^{-1}), and river SIN loads , $N_{river\ load}$ (t yr^{-1}), from non-point (diffuse) sources. The uncertainty of $N_{Root\ zone}$ stems from land use area A (ha); and modelled average nitrogen leaching from root zone N (kg N ha^{-1} yr^{-1}) for different land use types. In absence of data regarding change in land use, we assume there was no changes in the land use over the 8 years (2009-2016) used in the analysis in this study. Based on this assumption, the uncertainty in the root zone load, $N_{Root\ zone}$, stems only from the average nitrogen leaching from root zone N (kg N ha^{-1} yr^{-1}). Similarly, the uncertainly of $N_{river\ load}$ stems from accuracy in river flow (m^3 day^{-1}) and water quality measurements (mg L^{-1}), e.g. sampling frequency, timing and number of samples collected and analysed. In this study, we have assumed the uncertainty in the river load to be due to the sampling frequency and load estimation method. Elwan et al. (2018) evaluated uncertainty of annual river contaminant loads estimates in Manawatu at Teachers College monitoring site, New Zealand, from May 2010 to April 2011. They found out that the flow stratified (FS) load estimation method performed better than the other methods of global mean, flow-weighted, ratio estimator and rating curve. The FS method resulted into lowest bias for river SIN load at a monthly water quality sampling frequency, when compared with the reference 'true' river SIN load quantified based on daily water quality sampling. The bias and root mean square error (RMSE) of the FS method for annual river SIN load at monthly sampling frequency were estimated at 0.9% and 12% of the reference (true) river SIN load, respectively (Elwan et al., 2018). Ledgard and Waller (2001) was the only study to estimate the uncertainty associated with OVERSEER® estimate. They found the imprecision (95% confidence interval) to be ±20%.

We used parametric bootstrapping (Efron and Tibshirani, 1993) to estimate the uncertainty in AF_N estimates due to the uncertainties in root zone and river loads. We quantified the 95% confidence interval as the 0.025 and 0.975 quantiles of the bootstrap distribution.

We estimated and used the standard errors of root zone load, $N_{Root\ zone}$, and river SIN loads $N_{river\ load}$ to be 23% and 2%, respectively, in the parametric bootstrap to assess uncertainty in AF_N for selected sites in both Tararua and Rangitikei catchments. The standard error in root zone N leaching $N_{Root\ zone}$ was based on the estimate by Ledgard and Waller (2001), and in river SIN loads $N_{river\ load}$ was based on the estimate by Elwan et al., (2018).

5.3.4 Relationship between nitrogen attenuation factor and catchment characteristics

We further assessed the influence of different catchment characteristics on spatial variability of AF_N across different sub-catchments in the Tararua catchment (Fig. 5.3a). The location of water quality monitoring sites was used to delineate surface water sub-catchments upstream of 15 sites in Tararua catchment (Fig. 5.3a), using DEM with a resolution of 25x25m obtained from Land Resource Information Systems (LRIS) portal (Barringer et al., 2002). The resulting sub-catchment shapefiles were used to extract relevant catchment characteristics such as soil texture, soil drainage class, soil carbon content, and main- and sub-rocks. These catchment characteristics were extracted from the Fundamental Soil Layer (FSL; Newsome et al., 2008) and the Geological Map of New Zealand (QMAP; Heron, 2014), and were quantified using their relative area (in percentage) in different sub-catchments. The direction and magnitude of the relationship between the quantified AF_N and the extracted catchment characteristics for each sub-catchment in Tararua area (Fig. 5.3a) were evaluated using a Partial Least Squares Regression (PLSR). The PLSR technique combines features from two methods; multiple linear regression and principal component analysis. Thus, the robustness of PLSR is based on its ability to analyse collinear, noisy and even incomplete variables (both independent and dependent) (Abdi, 2010; Wold et al., 2001).

5.3.5 Prediction of land-based river nitrogen loads

Elwan et al. (2015b) developed a simple hydrogeologic model that makes use of spatial effects of nitrogen attenuation capacities for different rock types to predict soluble inorganic nitrogen (SIN) loads to streams and rivers. Yet, other catchment characteristics such as soil texture, soil drainage and carbon content have been identified as factors influencing redox conditions and nitrogen attenuation in the subsurface environment (Beyer et al., 2016; Clague et al., 2013; Close et al., 2016; Haag and Kaupenjohann, 2001; Hiscock et al., 1991; Højberg et al., 2017; Orr et al., 2016; Rivas et al., 2017). On the surface, in-stream nitrogen uptake and transformations could influence levels of SIN concentrations, and hence the measured river SIN loads (Heathwaite, 1993). Singh et al. (2017b) further updated the model, developed by Elwan et al. (2015b), to account not only for the spatial effects of nitrogen attenuation capacities associated with different rock types, but also for the nitrogen attenuation capacities of soil types and in-stream uptake of nitrogen, described in Equation (5.2) as follows:

$$River\ SIN\ load = m\left[\sum_{i=1}^{n} A_i * N_i * \left(1 - AF_{N\,RT}\right)\left(1 - AF_{N\,ST}\right)\right] - N_{up} \qquad (5.2)$$

where:

$\boldsymbol{m}$ = Conversion factor;

$\boldsymbol{n}$ = Number of landuse types in the catchment;

$\boldsymbol{A_i}$ = Area of land use type (ha);

$\boldsymbol{N_i}$ = Root-zone nitrogen loss rate for different land use type (kg-N ha^{-1} yr^{-1});

$\boldsymbol{AF_{N_{RT}}}$ = Nitrogen attenuation capacity (factor) for different rock types (-);

$\boldsymbol{AF_{N_{ST}}}$ = Nitrogen attenuation capacity (factor) for different soil types (-); and

$\boldsymbol{N_{up}}$ = In-stream nitrogen uptake (t yr^{-1}).

5.3.5.1 In-stream uptake

Several in-stream processes (e.g. uptake, decomposition, nitrification and denitrification) can transform and attenuate nitrogen in streams and rivers (Heathwaite, 1993). Biological growth in stream and rivers (e.g. periphyton) could transform significant part of soluble inorganic nitrogen (SIN) to organic N. However, neither direct measurements nor locally calibrated models to estimate in-stream nitrogen uptake by periphyton growth were available for the study catchments. Therefore, we used the simple model developed by (Singh et al., 2017b) to quantify the in-stream uptake (t yr^{-1}) in streams and rivers (larger than stream order 1) in the study catchments (Appendix B).

5.3.5.2 Classification of soils and rocks nitrogen attenuation capacity

There were no direct measurements available of the potential for nitrogen attenuation of different combinations of soils and underlying geology in the study catchments. To our knowledge, few studies have classified rocks and/or soils according to their potential denitrification (attenuation) capacity. For example, Krantz and Powars (2000) classified sediments in the Patuxent River Basin, Maryland, in the United States, into three classes (high, medium and low) according to their potential for denitrification. They suggested that sediments that have high potential for denitrification are those sediments that contain high proportions of reduced compounds such as organic carbon, iron sulfide minerals (e.g. pyrite "FeS_2"), and/or glauconite (clay mineral with reduced iron) that can react chemically to remove nitrate through denitrification. They provided examples of sediments with high potential for denitrification which included sandy silts, muddy sands, silt and silty sand that contain high proportions of organic matter, pyrite and glauconite. On the other hand, Krantz and Powars (2000) suggested that unreactive sediments (i.e. sediments with lower proportions of organic matter, pyrite and glauconite) have lower potential for denitrification. Examples of these sediments include fluvial coarse sands and gravels that are composed mainly of unreactive quartz, chert and feldspar and are characterised by high permeability. Krantz and Powars (2000) assigned intermediate potential for denitrification for geological units with variable composition, and hence a variable ability to attenuate nitrate. Examples of sediments with intermediate potential for denitrification include sand and silty sand with variable amounts of glauconite and pyrite. Rissmann (2011) classified the rocks in the Southland groundwater management zone, South Island, New Zealand, following the classification of Krantz and Powars (2000), into high, intermediate and low according to their potential for denitrification. Close et al. (2016) assigned scores (1 to 5) to soils and rocks, in the Waikato and Canterbury regions in New Zealand, according to their redox potential. Close et al. (2016) assigned low scores to rocks and soils that are highly likely to be inert (unreactive) and therefore will be associated with oxidizing conditions; and high scores to soils and rocks that are more reactive and hence are characterised by reducing conditions. In the classification of Close et al. (2016), rocks with high scores (i.e. reducing conditions) include mudstone, lignite and peat; and rocks with low scores (i.e. oxidising conditions) include dacite and gravel.

We have classified different soils and rocks in the Tararua and Rangitikei catchments into three categories according to their likely potential nitrogen attenuation capacity. These categories were high, medium and low attenuation capacities. For the soils, the Fundamental Soil Layer (FSL; Newsome et al., (2008)) was used to classify the soils into three attenuation categories based on soil texture, drainage class and carbon content (Table 5.1). For the rock types, the QMAP (Heron, 2014) was used to classify the rocks into three nitrogen attenuation factor categories based on their geological material characteristics (Table 5.1). These soils and rock classes were assigned different nitrogen attenuation factors ranging from 0.1 – 0.30 for the low category (e.g. stony sandy loam, sand, and sand & stony gravel, carbon class 5, drainage classes 4 and 5, gravels), 0.35 – 0.65 for the medium category (e.g. sandy loam and loam, carbon classes 3 and 4, drainage class 3, sandstone and limestone), and 0.70 – 0.95 for the high category (e.g. heavy silt loam, clay loam and peaty loam, carbon classes 1 and2, drainage classes 1 and 2, mudstone and peat) (Table 5.1). We assigned low nitrogen attenuation capacity for soils with less proportion of compounds that can attenuate nitrogen (such as organic matter), coarse texture, well drainage and lower carbon content. These soils are highly likely to have faster water movement and hence shorter residence times and therefore less time for denitrification. On the other hand, we assigned a high nitrogen attenuation factor for soils with higher proportions of compounds that can attenuate nitrogen (such as organic matter), heavy texture, poor drainage and high carbon content. These soils are highly likely to have slower water movement and hence longer residence time, and therefore enough time for denitrification to occur. This classification was based on a number of studies. For example, Gaines and Gaines (1994) showed that soils with silt, clay and organic matter and fine texture (such as sandy clay loam and clay loams) have higher cation exchange capacity and slow water movement and therefore have higher potential for denitrification. On the other hand, Gaines and Gaines (1994) showed that soils with lower proportions of silt, clay and organic matter and coarse texture have lower cation exchange capacity and faster water movement, and therefore have lower potential for denitrification. Other studies have highlighted the association between soils with coarse texture and the less likely potential for denitrification (e.g. Korom et al., 2012; Rivas et al., 2017). A number of studies have highlighted the relationship between soil drainage and the potential for denitrification (e.g. Burkart and Stoner, 2008; Griffith et al., 1997; Howard and Falck, 1986; Jahangir et al., 2012c; Meynendonckx et al., 2006; Mueller et al., 1997; Nolan, 2001; Rivas et al., 2017; Spalding and Exner, 1993). Well-drained soils have a lower potential for denitrification and poorly drained soils have a higher potential for denitrification. Regarding carbon content, a number of studies showed that denitrification is a function of soil carbon content (e.g. Weier et al. 1993), with higher denitrification rates occurring in soils with higher carbon content (Adelman and Tabidian, 1996; Webster and Goulding, 1989).

We classified rocks into three classes (high, medium and low potential for denitrification) according to the proportions of compounds that are chemically reactive (e.g. glauconite, pyrite and/or organic matter), and hence should attenuate nitrogen following other studies (e.g. Krantz and Powars, 2000). Also, in our rock classification, we have accounted for the hydraulic conductivity, which was found by a number of studies to be associated with the potential for denitrification. For example, a number of studies showed that rocks with higher hydraulic conductivities are highly likely to have less potential for denitrification, while rocks with lower hydraulic conductivities are highly likely to have higher potential for denitrification (Fenton et al., 2009; Jahangir et al., 2012b; Jahangir et al., 2012c; Rivas et al., 2017).

Table 5.1: Estimates of nitrogen attenuation categories assigned to different soils and rocks types in the Tararua and Rangitikei catchments. The soil drainage classes range from 1 (well drained) to 5 (poorly drained); and soil carbon classes range from 1 (20-40 % TC "g C/100 g soil") to 5 (0.1-1.9 % TC "g C/100 g soil") in the Fundamental Soil Layer "FSL" (Newsome et al., 2008).

***AF* class**	***AF* value**	**Soils**	**Rocks**
Low	0.1 – 0.30	e.g. Stony sandy loam, sand and stony gravel Carbon class 5 Drainage classes 4 and 5	e.g. Gravel
Medium	0.35 – 0.70	e.g. Sandy loam and loam Carbon classes 3 and 4 Drainage class 3	e.g. Sandstone and limestone
High	0.70 – 0.95	e.g. Heavy silt loam, clay loam and peaty loam Carbon classes 1 and 2 Drainage classes 1 and 2	e.g. Mudstone and peat

5.3.5.3 Influence of different soils and/or rocks on predicting land-based nitrogen loads to rivers

To evaluate the influence of the attenuation capacities of the different soils and/or rock types on the prediction of land-based SIN loads, we developed and analysed four versions of the hydrogeologic based model (Equation 5.2), described in Equations 5.3 to 5.6 as follows:

Model 1 (Uniform nitrogen attenuation factor)

$$River\ SIN\ load\ = m \sum_{i=1}^{n} A_i * N_i * (1 - AF_{N\,0.5}) \qquad (5.3)$$

Model 2 (Variable nitrogen attenuation factor using soils only "FSL")

$$River\ SIN\ load\ = m \sum_{i=1}^{n} A_i * N_i * (1 - AF_{N\,ST}) \tag{5.4}$$

Model 3 (Variable nitrogen attenuation factor using rocks only "QMAP")

$$River\ SIN\ load\ = m \sum_{i=1}^{n} A_i * N_i * (1 - AF_{N\,RT}) \tag{5.5}$$

Model 4 (Variable nitrogen attenuation factor using soils and rocks "FSL and QMAP")

$$River\ SIN\ load\ = m \sum_{i=1}^{n} A_i * N_i * (1 - AF_{N\,RT})(1 - AF_{N\,ST}) \tag{5.6}$$

where:

$\boldsymbol{m}$ = Conversion factor;

$\boldsymbol{A_i}$ = Area of land use type (km^2);

$\boldsymbol{N_i}$ = Root-zone nitrogen loss rate for land use type (kg-N ha^{-1} yr^{-1});

$\boldsymbol{AF_N}$ = Nitrogen attenuation factor. $\boldsymbol{AF_{N\,0.5}}$ indicates fixed uniform attenuation factor of 0.5; $\boldsymbol{AF_{N\,ST}}$ and $\boldsymbol{AF_{N\,RT}}$ indicates variable nitrogen attenuation factor for different soil and rock types, respectively.

These four models did not account for the instream-nitrogen uptake (Equation 5.2) as it was assessed as relatively insignificant in explaining reductions in nitrogen flows from the root zone to the rivers in Tararua and Rangitikei catchments (see Section 5.4.3.1 below). Model 1

(Equation 5.3) used a uniform nitrogen attenuation factor of 0.5. This value was chosen based on a number of studies in New Zealand, that suggested this fixed value (e.g. Clothier et al., 2007; Roygard and Clark, 2012), in absence of detailed measurements and/or locally calibrated models assessing spatially variable nitrogen attenuation capacity of different soils and rock types. Our other three models, Models 2, 3 and 4, were developed to evaluate the influence of variable nitrogen attenuation capacities for soils only (Model 2; Equation 5.4); or rock types only (Model 3; Equation 5.5); or a combination of both soils and rock types (Model 4; Equation 5.6).

Predictions of average annual river SIN loads predicted in this manner (i.e. Models 1 – 4, Equations 5.3 – 5.6) were compared with the average annual loads of SIN (t yr^{-1}) measured at selected 15 and 5 sites (Fig. 5.3), in the Tararua and Rangitikei catchments, respectively. We used the root mean square error (RMSE), coefficient of mass residual (CRM), index of agreement (IoA) and model efficiency (EF) as model performance evaluation indices, described in Equations 5.7 to 5.10 as follows:

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(P_i - M_i)^2} \tag{5.7}$$

$$CRM = \frac{\sum_{i=1}^{N} P_i - \sum_{i=1}^{N} M_i}{\sum_{i=1}^{N} M_i} \tag{5.8}$$

$$IoA = 1 - \frac{\sum_{i=1}^{N}(P_i - M_i)^2}{\sum_{i=1}^{N}(|M_i - M| + |P_i - M|)^2} \tag{5.9}$$

$$EF = \frac{\sum_{i=1}^{N}(M_i - M)^2 - \sum_{i=1}^{N}(P_i - M_i)^2}{\sum_{i=1}^{N}(M_i - M)^2} \tag{5.10}$$

where:

N = Number of observations (sites);

P_i = Predicted river SIN load value at the ith site;

M_i = Measured river SIN load value of the ith site; and

M = Mean of measured river SIN load values.

The RMSE (Equation 5.7) estimates the average absolute error between predicted and measured values, and lower values suggest a better performance of a model. However, RMSE does not account for the relative size and nature of the error. On the other hand, CRM (Equation 5.8) evaluates the relative size and nature of the error. A negative CRM value indicates under prediction of the model whereas a positive value indicates over prediction. The IoA (Equation 5.9) estimates the agreement between predicted and measured values. The closer the value of IoA to 1 indicates a significant match between predicted and measured values (Willmott, 1982). The EF (Equation 5.10) estimates the error relative to the natural variability of the measured values. EF varies from - ∞ to 1, and EF values > 0.5 are considered acceptable (Helwig et al., 2002; Wang et al., 2006).

Apart from using ArcGIS 10.4.1® for extracting the spatial data (areal percentage of main rocks, sub rocks, and soil texture, drainage and carbon classes), the entire analysis was completed in R software (Appendix C) version 3.4.2 (R Core Team, 2017).

5.4 Results and discussion

5.4.1 Spatial variation of nitrogen attenuation factor

Figure 5.4 presents the spatial variation of nitrogen attenuation factor AF_N quantified by comparing estimates of average annual nitrogen losses from the root zone (i.e. the nitrogen leached from the root zone in different land uses in the catchment) and the measured loads of SIN loads across different sub-catchments in the Tararua (Fig. 5.4a) and Rangitikei (Fig. 4b) catchments. The estimated AF_N varied from 0.14 (Makuri at Tuscan Hills) to 0.77 (Tiraumea at Ngaturi), with an average of 0.58 for the whole Tararua catchment (Fig. 5.4a). Similarly, the AF_N varied from 0.69 (Rangitikei at McKelvies) to 0.94 (Rangitikei at Pukeokahu) with an average of 0.84 for the whole Rangitikei catchment (Fig. 5.4b). This suggests that about 58% and 84% of leached nitrogen from the root zone, in Tararua and Rangitikei catchments respectively, is attenuated along its flow pathways from the farms to the rivers. Quantification of nitrogen attenuation capacity in this manner (Equation 5.1), however, assumes that there are no changes in inorganic nitrogen storages between the root zone and receiving rivers. This assumption is acceptable, since the AF_N values presented here were quantified by comparing estimates of average annual values (t yr^{-1}) of root zone nitrogen losses and river SIN loads. In this study, the average annual river SIN loads (t yr^{-1}) were estimated using mean daily river flows (m^3 day^{-1}) and monthly measurements of (SIN) concentrations (mg L^{-1}) over 8 years (2009 to 2016) in both the Tararua and Rangitikei catchments. This is a sufficiently long period when considering the mean residence time (MRT) of water, based on tritium dating, to be 5 and 3 years in the Tararua and Rangitikei catchments, respectively (Morgenstern et al., 2014).

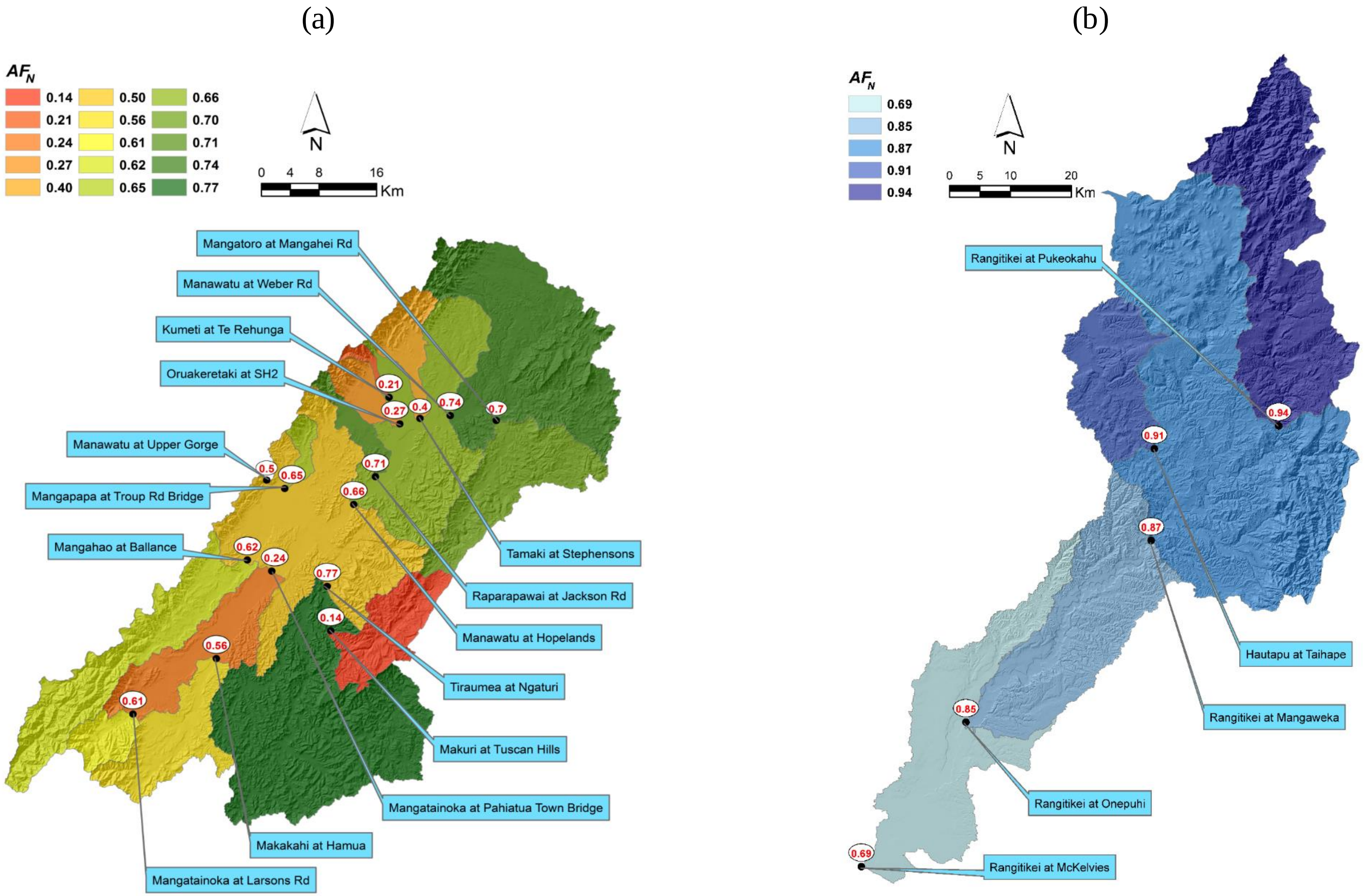

Fig. 5.4. Spatial distribution of the nitrogen attenuation factor for (a) 15 sub-catchments in the Tararua catchment; and (b) 5 sub-catchments in the Rangitikei catchment.

Figure 5.5 reproduces the quantification of AF_N (Equation 5.1) including 95% confidence interval computed using parametric bootstrapping. Figure 5.5 suggests that spatial variability observed in the AF_N values could not be totally attributed to the levels of uncertainty in the average annual estimates of root zone nitrogen losses and river SIN loads across sub-catchments in the study catchments. The AF_N values quantified for Rangitikei sub-catchments were relatively higher (with lower variance) than the Tararua sub-catchments (Fig. 5.5). This could be due to the higher nitrogen attenuation capacity in Rangitikei sub-catchments, due to the availability of electron donors and the dominance of reducing conditions conducive to potential attenuation.

In-field push-pull tests (Istok, 2013) in the Tararua and the lower Rangitikei catchments (Aldrin Rivas, personal communication, 2018; Collins et al., 2017) showed a variable rate in denitrification in shallow groundwater. Yet, these in-field push-pull tests showed that the lower Rangitikei catchment has higher capacity for denitrification than the Tararua catchment. In the Tararua catchment, the denitrification rate varies from 0.04 mg N L^{-1} h^{-1} to a maximum of 0.18 mg N L^{-1} h^{-1} (Aldrin Rivas, personal communication, 2018). On the other hand, in the lower Rangitikei catchment, Collins et al., (2017) found that the denitrification rate varies from 0.04 mg N L^{-1} h^{-1} to a maximum of 1.57 mg N L^{-1} h^{-1}.

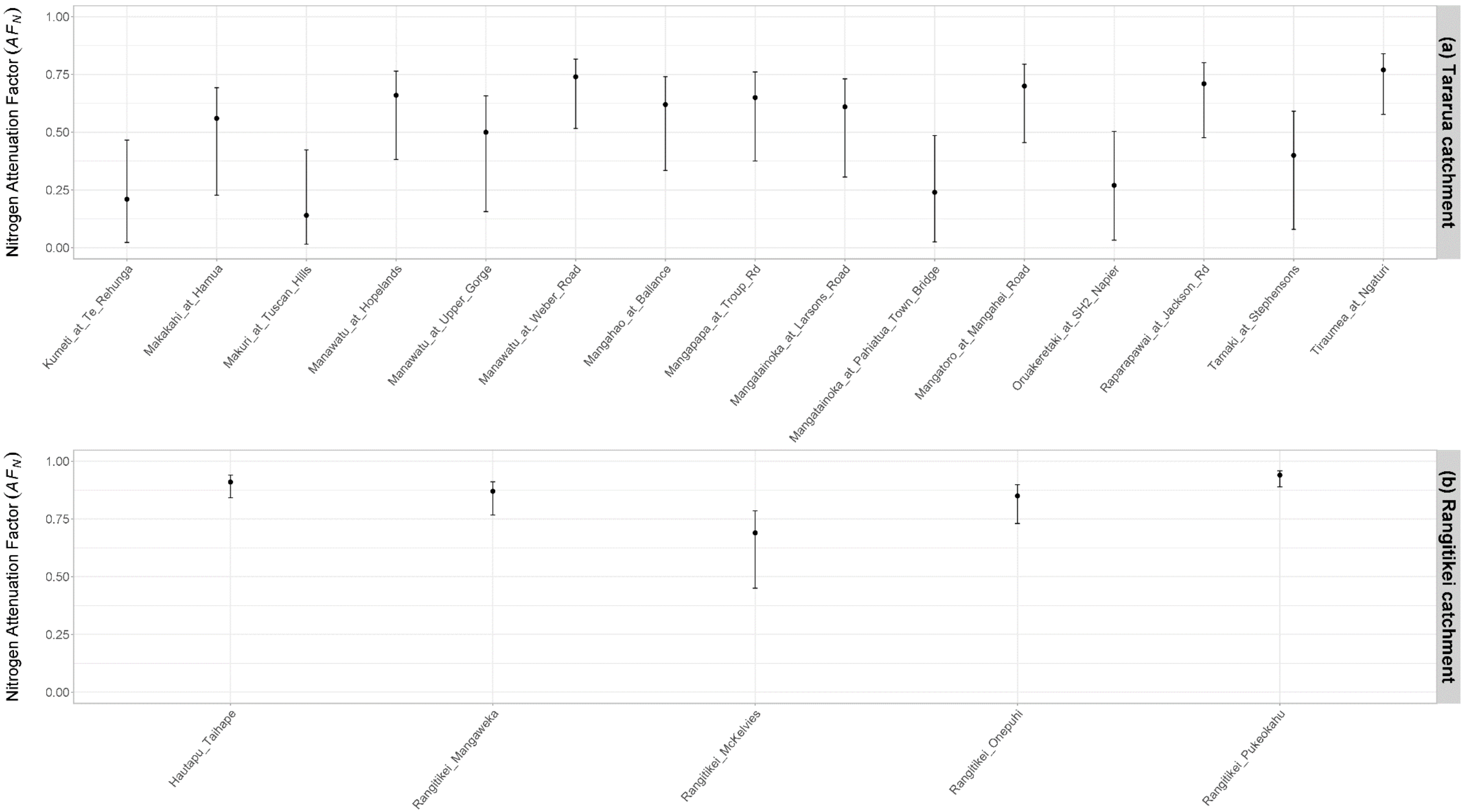

Fig. 5.5. Nitrogen attenuation factor (AF_N) with bars representing the 95% confidence interval by parametric bootstrap (Efron and Tibshirani, 1993) for the sites in (a) the Tararua catchment; and (b) the Rangitikei catchment.

Regardless of the different sources of the uncertainties that are associated with the quantification of sub-catchment nitrogen attenuation capacity, the redox status of groundwater wells was found to closely match the spatial variability of AF_N values across Tararua sub-catchments (Fig. 5.6).

Based on a groundwater survey in the Tararua catchment, Rivas et al., (2017) found that around 18% of the wells were assessed as reducing wells (DO < 1 mg L^{-1} and oxidation–reduction potential ORP 'Eh' < 150 mV). These wells with reducing conditions suggest potential attenuation through denitrification (Fig. 5.6). The groundwater wells with reducing conditions were found to be mainly located in sub-catchments with higher AF_N values. None of the wells classified as reducing were located in a sub-catchment that had nitrogen attenuation factor less than 0.5. Similarly, Collins et al., (2017) found out that all groundwater wells surveyed were categorised as anoxic (reduced; DO < 1 mg L^{-1}) in lower (coastal) parts of Rangitikei catchment. This suggest that the subsurface environment in the lower Rangitikei catchment is conducive to potential attenuation through denitrification.

However, more catchment-scale groundwater surveys and field-scale experiments, that are spatially and temporally distributed, are needed to confirm the spatial variability of nitrogen attenuation across Tararua and Rangitikei sub-catchments. Our analysis presented in Figures 5.4-5.6 suggest that the nitrogen attenuation factor AF_N could be used as a catchment descriptor to indicate the capacity of a catchment to attenuate nitrogen. A lower value of AF_N from 0.1 to 0.3 suggests that groundwater is highly likely not to be conducive to attenuation through denitrification. Conversely, a higher value of AF_N from 0.70 to 0.95 suggests that groundwater is highly likely to be reduced in the study area, and therefore conducive to potential attenuation through denitrification.

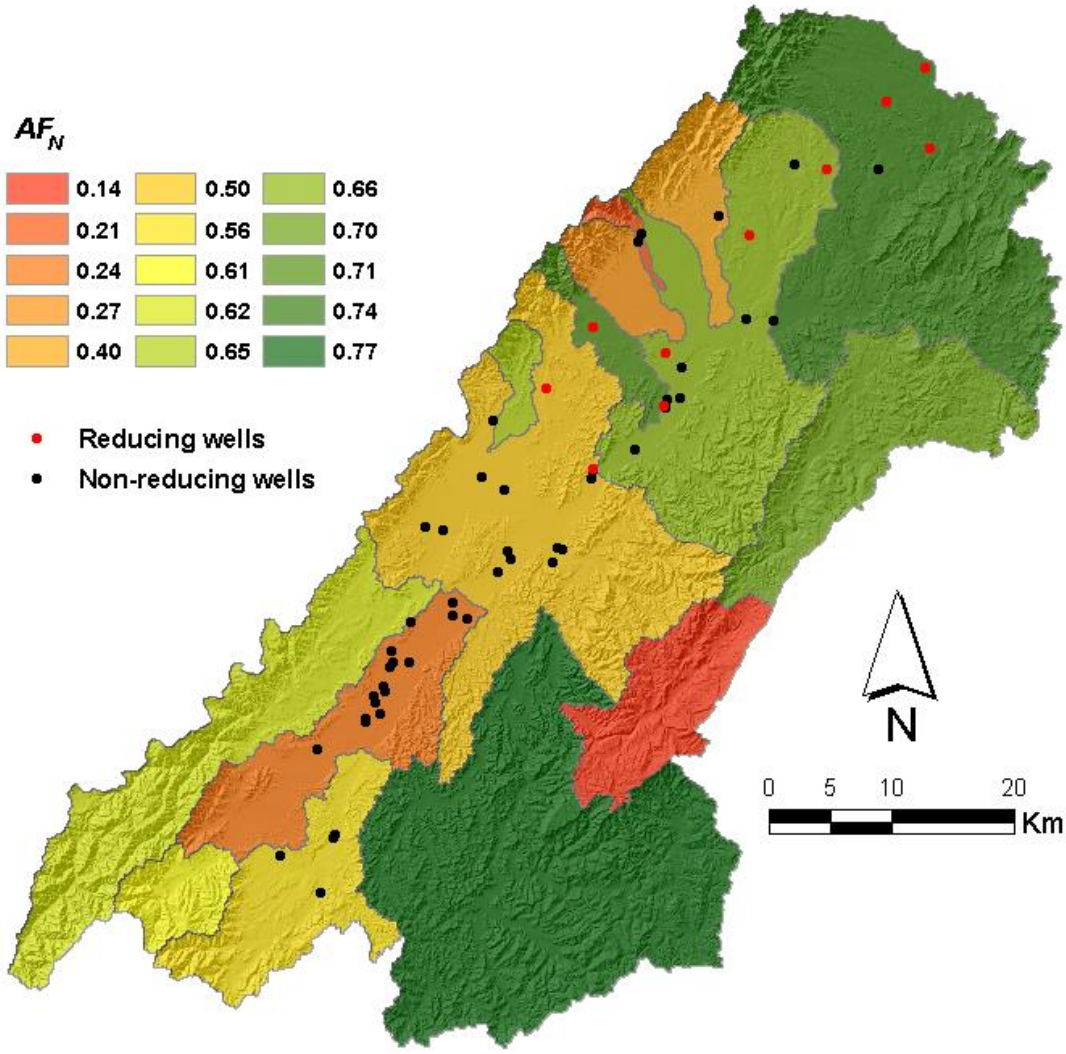

Fig. 5.6. Spatial distribution of the nitrogen attenuation factor values along with redox status of the groundwater; (Rivas et al., 2017) in the Tararua sub-catchments. The non-reducing wells are characterised by dissolved oxygen (DO) ≥ 1 mg L^{-1} and oxidation reduction potential 'ORP' (Eh) ≥ 150 mV, While the reduced wells are characterised by DO < 1 mg L^{-1} and Eh < 150 mV.

5.4.2 Relationship between nitrogen attenuation factor and catchment characteristics

Catchment characteristics such as soils and underlying geological rocks could affect water flow pathways, its travel times and chemistry, affecting nitrogen flow and its potential attenuation in subsurface environment. Figure 5.7 reproduces the results of PLSR analysing the direction and magnitude of the relationship between the spatial variations of soils ad rock characteristics and nitrogen attenuation factor AF_N values across the 15 Tararua sub-catchments (Fig. 5.4a). In Figure 5.7, a positive value of the correlation loadings for the first PLSR component indicates a positive correlation between the independent variable (catchment characteristics) and AF_N values, and vice-versa. The magnitude of the relationship is indicated by the magnitude of the PLSR correlation loading value. The higher the PLSR correlation loading value the stronger the relationship between the variables analysed.

Figure 5.7 shows that the AF_N is related negatively with well-drained soils and gravels, but related positively with imperfectly drained soils and mudstone across Tararua sub-catchments. Our results correspond with the findings of other studies (e.g. Burkart and Stoner, 2008; Griffith et al., 1997; Howard and Falck, 1986; Jahangir et al., 2012c; Meynendonckx et al., 2006; Mueller et al., 1997; Nolan, 2001; Rivas et al., 2017; Spalding and Exner, 1993) that highlighted the lower potential of well-drained soils for denitrification and the higher potential of imperfectly drained soils for denitrification. This has been attributed to the faster water movement in well-drained soils and hence the less time for geochemical reactions to occur and the vice versa for imperfectly drained soils. Also, our results, for rocks, match the findings by a number of studies (e.g. Fenton et al., 2009; Jahangir et al., 2012b; Jahangir et al., 2012c; Rivas et al., 2017). These studies showed that rocks with a higher hydraulic conductivity are highly likely to have a lower potential for denitrification due to the faster flow and shorter residence time that suggests less time for denitrification, and vice versa for rocks with lower conductivities.

These PLSR results, in general, show a strong match with our classifications of soils and rocks into different categories according to their likely nitrogen attenuation capacity (Table 5.1). We classified gravels as low nitrogen attenuation category. This means that sub-catchments with a higher proportion of gravels are more likely to have a lower AF_N than sub-catchments with less proportion of gravels in the underlying geology. This was substantiated by the PLSR results (Fig. 5.7) that showed negative relationship between the proportions of gravels and the AF_N values across Tararua sub-catchments. Similarly, we classified mudstone as high nitrogen attenuation category (Table 5.1), and the PLSR results (Fig. 5.7) clearly showed a positive relationship between the proportions of mudstone and the AF_N values across Tararua sub-catchments. Thus, PLSR results showed that many of the catchment characteristics, e.g. main rock types, soil drainage and carbon classes, have the similar relationship with the AF_N values as assessed in our classification of different soils and rocks types according to their likely nitrogen attenuation potential (Section 5.3.5.2, Table 5.1). However, the soil texture showed a relationship with the AF_N that was inconsistent, as assessed in Table 5.1. For example, silt loam texture was classified (Table 5.1) in the high nitrogen attenuation category, but it showed a negative relationship with the AF_N in the PLSR results (Fig. 5.7). This could have resulted from the large proportions of soils with well drainage, and low/average carbon content (i.e. carbon content classes 3 to 5) that are classified as silt loam in the Fundamental Soil Layer across sub-catchments with lower AF_N values in the study area. The soil drainage and carbon classes were assessed as having a similar relationship with the AF_N values in both the PLSR results (Fig. 5.7) and their classification into different nitrogen attenuation capacities (Table 5.1). Overall, the PLSR results (Fig. 5.7) support the classification of different soils and rock types into spatial variable nitrogen attenuation categories (Table 5.1) in the study sub-catchments.

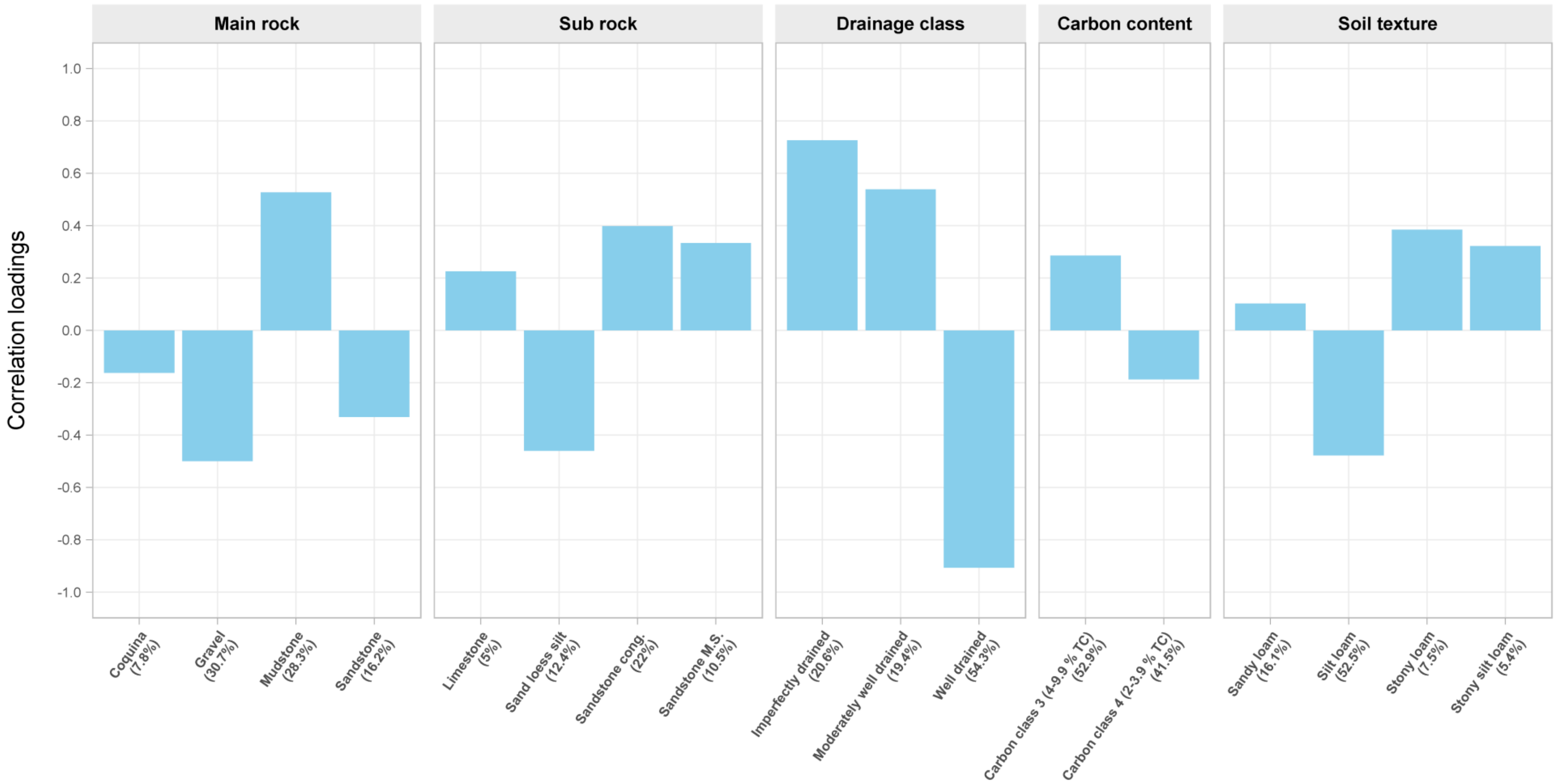

Fig. 5.7. Partial least squares regression (PLSR) correlation loadings between spatial variations of nitrogen attenuation capacity AF_N values (dependent variable) and different soils and rocks characteristics (independent variables) across Tararua sub-catchments.

5.4.3 Prediction of land-based river N loads

Using the classification of different soils and underlying geology into variable nitrogen attenuation capacities (Table 5.1), the hydrogeologic model (Equation 5.2) was applied to evaluate predictions of land-based average annual SIN loads (t yr^{-1}) across both Tararua and Rangitikei sub-catchments (Fig. 5.3).

5.4.3.1 Instream uptake

Application of the hydrogeologic model (Equation 5.2) required quantification and assessment of the potential in-stream N uptake/transformation in stream and rivers. In absence of accurate measurements and/or locally calibrated models, we used the simple model developed by Singh et al. (2017b) to quantify the potential in-stream N uptake in the study catchments (Appendix B). The estimates of potential in-stream N uptake accounted for a maximum of 3% and 5.7% of the estimates of root zone N losses in the Tararua and Rangitikei catchments, respectively. This highlights that potential in-stream N uptake values are relatively insignificant as compared with the estimates of root zone N losses in both study catchments (Appendix B). It suggests that in-stream N uptakes are not major contributors to the estimates of 58% and 84% reductions in nitrogen loads between the root zone and the river loads in Tararua and Rangitikei catchments, respectively (Fig. 5.4).

Given the high level of uncertainty, and its relatively small magnitude, the in-stream N uptake was not accounted for in the subsequent analyses of the hydrogeologic model (Equation 5.2) to predict land-based average annual river SIN loads across the Tararua and Rangitikei sub-catchments.

5.4.3.2 *Influence of different soils and/or rocks on river SIN loads*

A series of four models (Equations 5.3 – 5.6) were applied to evaluate the spatial effects of both soil types and/or underlying geologies on spatial nitrogen attenuation capacity and prediction of land-based average annual river SIN loads across Tararua and Rangitikei sub-catchments (Fig. 5.8&5.9). Model 1 (Equation 5.3) used a uniform nitrogen attenuation factor of 0.5 and clearly over-predicted the river SIN loads for all Rangitikei sub-catchments (Fig. 5.9); and for most of Tararua sub-catchments (Fig. 5.8). Using Model 1, the differences between the predicted and measured river SIN loads varied from 1.1 to 182.6 t yr^{-1} with an overall over-prediction of 375.8 t yr^{-1} (20%) for the whole Tararua catchment, and varied from 99.5 to 425.3 t yr^{-1} with an overall over-prediction of 1158.7 t yr^{-1} (207%) for the whole Rangitikei catchment. Model 2 (Equation 5.4) used a spatially variable AF_N for soils only, and resulted in higher over-estimation of river SIN loads across Tararua and Rangitikei sub-catchments. Using the Model 2, the differences between the predicted and measured river SIN loads varied from 1.1 to 336.2 t yr^{-1} with an overall over-prediction of 1156.7 t yr^{-1} (63%) for the whole Tararua catchment, and varied from 98.8 to 460.1 t yr^{-1} with an overall over-prediction of 1291.4 t yr^{-1} (231%) for the whole Rangitikei catchment. However, Model 3 which used a spatially variable AF_N for rocks only, resulted in improved predictions for river SIN river loads, in comparison to the Models 1 and 2. Model 4, which used a spatially variable AF_N for both soils and rocks types, resulted in better predictions of river SIN loads across most of Tararua (Fig. 5.8) and Rangitikei (Fig. 5.9) sub-catchments. The differences between the predicted and measured river SIN loads varied from 0.6 to -132.5 t yr^{-1} with an overall under-prediction of -87.4 t yr^{-1} (-5%) for the whole Tararua catchment, and varied from 7.3 to 51.7 t yr^{-1} with an overall over-prediction of 111.4 t yr^{-1} (+20%) for the whole Rangitikei catchment.

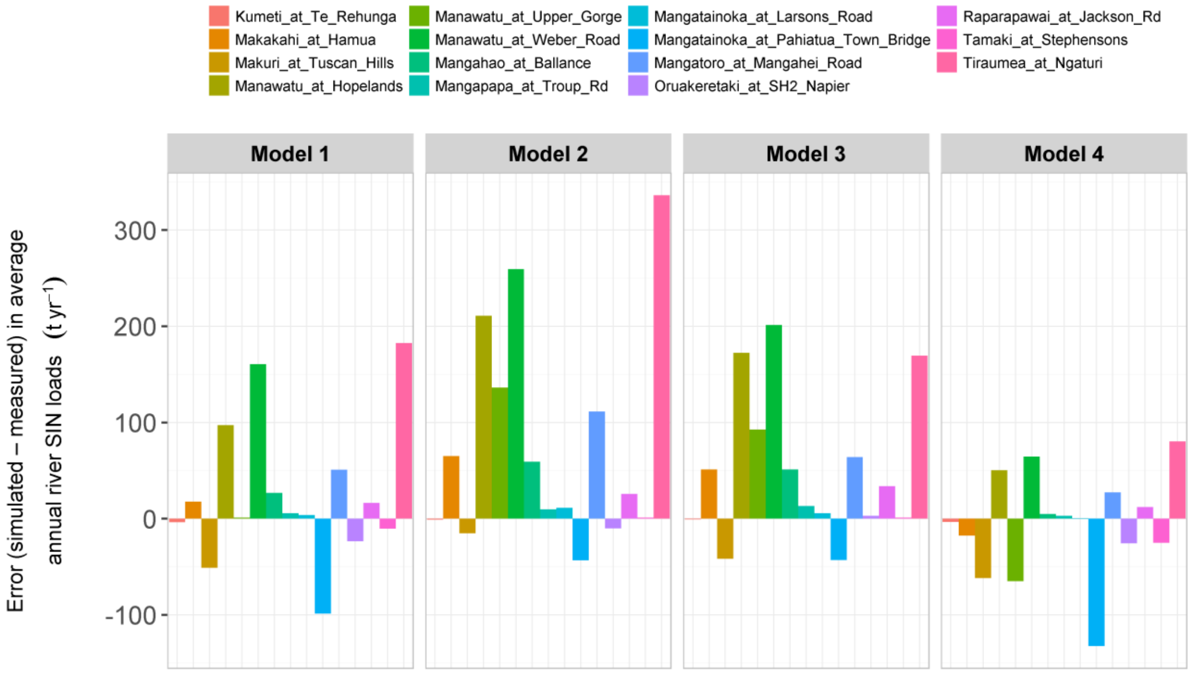

Figure 5.8. The error (simulated – measured) in average annual river SIN loads (t yr^{-1}) for different models (Model 1 = uniform 0.5 AF_N; Model 2 = spatially variable AF_N for soils only; Model 3 = spatially variable AF_N for rocks only; and Model 4 = spatially variable AF_N for soils and rocks) across Tararua sub-catchments.

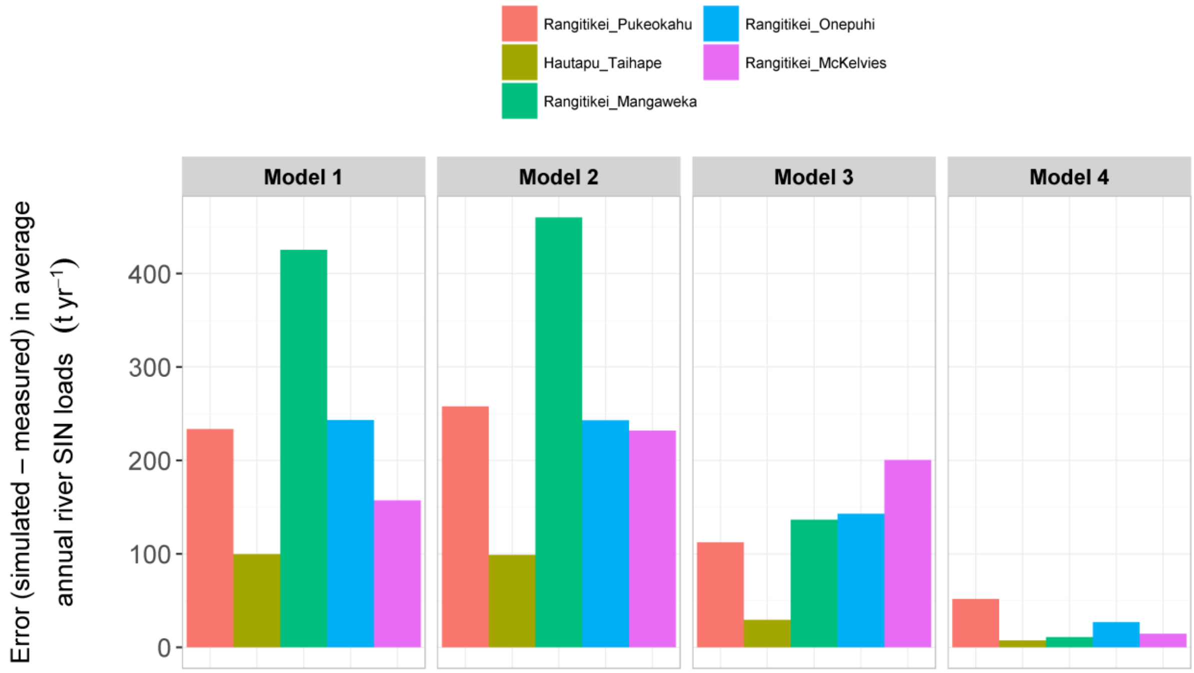

Figure 5.9. The error (simulated – measured) in t yr^{-1} for different models (Model 1 = uniform 0.5 AF_N; Model 2 = spatially variable AF_N for soils only; Model 3 = spatially variable AF_N for rocks only; and Model 4 = spatially variable AF_N for soils and rocks) for the sites in the Rangitikei Catchment.

Tables 5.2 and 5.3 reproduce the results of model performance measures (Equations 5.7-5.10), comparing the predicted and measured average annual river SIN loads across Tararua and Rangitikei sub-catchments, respectively. These four statistical measures show that regardless of the different sources of uncertainty associated with the models used, Model 4 resulted in better estimates than other models. Model 4 resulted in the lowest RMSE (52.45 t yr^{-1} and 27.51 t yr^{-1} for Tararua and Rangitikei catchments, respectively) and smallest CRM (-0.05 and 0.20 for Tararua and Rangitikei catchments, respectively) (Tables 5.2 and 5.3). Furthermore, the Model 4 resulted in EF values closest to 1 and acceptable (>0.5) (Helwig et al., 2002; Wang et al., 2006) for Tararua (EF = 0.75) and Rangitikei (EF = 0.90) catchments. Also, the highest values of IoA (0.93 and 0.97 for Tararua and Rangitikei sub-catchments, respectively) confirmed that the Model 4 performed better than any other model (Tables 5.2 and 5.3).

Figures 5.8 and 5.9 clearly highlight the effects of different hydrogeologic settings on nitrogen flows and its potential attenuation from farms to streams and rivers. The predictions of land-based river SIN loads were markedly better when the spatial effects of both soil types and underlying geologies (Model 4) were accounted for in modelling nitrogen flows and its potential attenuation in the subsurface environment.

Table 5.2. Model evaluation parameters (RMSE = root mean square error; CRM = coefficient of mass residual; EF = model efficiency; and IoA = index of agreement) for the different models (Model 1 = uniform 0.5 AF_N; Model 2 = spatially variable AF_N for soils only; Model 3 = spatially variable AF_N for rocks only; and Model 4 = spatially variable AF_N for soils and rocks only) used to predict nitrogen river loads in the Tararua catchment.

Model evaluation parameters	**Models**			
	Model 1	Model 2	Model 3	Model 4
RMSE	75.52	133.32	90.11	52.45
CRM	0.20	0.63	0.42	-0.05
EF	0.49	-0.59	0.28	0.75
IoA	0.89	0.78	0.87	0.93

Table 5.3. Model evaluation parameters (RMSE = root mean square error; CRM = coefficient of mass residual; EF = model efficiency; and IoA = index of agreement) for the different models (Model 1 = uniform 0.5 AF_N; Model 2 = spatially variable AF_N for soils only; Model 3 = spatially variable AF_N for rocks only; and Model 4 = spatially variable AF_N for soils and rocks only) used to predict nitrogen river loads in the Rangitikei catchment.

Model evaluation parameters	**Models**			
	Model 1	Model 2	Model 3	Model 4
RMSE	256.58	283.09	136.23	27.51
CRM	2.07	2.31	1.11	0.20
EF	-7.89	-9.82	-1.50	0.90
IoA	0.43	0.42	0.73	0.97

5.5 Conclusions

Excessive applications of fertilizer, intensive cropping, pastoral grazing and associated animal urine patches, plus farm effluent spreading have the potential to increase nutrient leaching and/or runoff from agricultural soils (Di and Cameron, 2002; Wang et al., 2004). Researchers and managers are devoting significant investments and efforts to develop and apply farm nutrient budgeting tools, such as OVERSEER® model (Wheeler et al., 2003), to account and manage for the leaching of nitrogen from farming systems. However, these models only account for nitrogen flows into and within the farm boundaries and can only predict nitrogen losses from the root zone. The NPS-FM is, however, focussed on water quality in the receiving water bodies. Therefore, implementation of the NPS-FM requires some assessment of the link between the farms and receiving rivers.

In this study, accounting of nitrogen flows in the Tararua and Rangitikei catchments showed that the measured loads of soluble inorganic nitrogen (SIN) into the rivers are significantly smaller than the estimates of nitrogen loads from the root zones of farming systems. Our findings showed that this nitrogen attenuation capacity quantified as a nitrogen attenuation factor, AF_N, varied from 0.14 to 0.77 across 15 Tararua sub-catchments, and from 0.69 to 0.94 across 5 Rangitikei sub-catchments (Fig. 5.4). The overall average AF_N for Tararua and Rangitikei catchments were estimated at 0.58 and 0.84, respectively. This indicates that about 58% and 84% of nitrogen leached, from root zone, is being attenuated in the subsurface in Tararua and Rangitikei catchments, respectively. This clearly highlights that nitrogen attenuation in the subsurface is not constant everywhere, as it is a function of catchment characteristics that vary spatially as well.

With a PLSR analysis, we have found that the AF_N has a negative relationship with proportions of well-drained soils and gravels geology across Tararua sub-catchments (Fig. 5.7). Conversely, the AF_N had a positive relationship with poorly drained soils and mudstone across the sub-catchments.

We further analysed the spatial effects of soils and the underlying geology characteristics on modelling of the spatial variation of nitrogen attenuation capacity and prediction of land-based river SIN loads across Tararua and Rangitikei sub-catchments. A series of simple hydrogeologic-based model versions were evaluated to predict average annual river SIN loads, based on either uniform or spatially variable nitrogen attenuation capacity of the subsurface. The model that accounted for the spatial distribution of nitrogen attenuation capacities of soils and rocks resulted in markedly better predictions of river SIN loads across both Tararua and Rangitikei sub-catchments (Fig. 5.8&5.9). This clearly highlights that the likely influence of catchments characteristics such as soils and rock types on attenuating nitrogen in the subsurface should be mapped and accounted for in predicting land-based nitrogen loads streams and rivers in agricultural catchments. This new information and knowledge will provide the basis of the modelling and planning tools required to aligning spatially intensive land use practices with high nitrogen attenuation pathways. This ‘matching landuse with land suitability’ will result in reducing nitrogen loads (from non-point sources) to rivers, which in turn, will reduce the incidence and extent of nuisance periphyton growth or nitrate toxicity in rivers.

Yet still further research is needed to understand better the effects of catchment characteristics on spatial variations of nitrogen attenuation capacity in subsurface environment in agricultural catchments. There remained uncertainty in the Model 4, which combines both the nitrogen attenuation capacities of the soils and underling geology to predict average annual river SIN loads (Equation 5.6). This stems from varying estimates of average nitrogen leaching (kg N ha^{-1} yr^{-1}) from the root zone for different land use types; the areas (ha) of different land use types; and the classification of different soils and rocks into three (high, medium and low) nitrogen attenuation categories (Table 5.1). This classification of different soils and rocks into different nitrogen attenuation categories, based on their likelihood of nitrogen attenuation potential, could be further improved by conducting detailed field surveys to check the redox status and denitrification potential of groundwater under combinations of different soils and rock types in agricultural landscape. We propose that further research be carried out in mapping and accounting of spatial nitrogen attenuation capacity to become the corner stone for formulating future land use planning and nutrient management strategies for targeted and effective water quality outcomes in sensitive agricultural catchments.

5.6 Acknowledgments

This study is a part of a wider collaborative research programme between Massey University School of Agriculture and Environment, Fertilizer and Lime Research Centre (FLRC) and Horizons Regional Council (HRC). DairyNZ and HRC funded and provided information for this study. This funding and in-kind support is greatly appreciated. We thank Dr. Alan Palmer, School of Agriculture and Environment at Massey University, for his feedback regarding classification of soils and rocks according to their attenuation capacities.

Chapter 6: Synthesis and recommendations

6.1 Problem statement

As the world population increases, agriculture must meet the growing demand for food. However, intensive agriculture activities have detrimental impacts on water quality (Foley et al., 2005; Tilman et al., 2002) through the leaching of farm nutrients, mainly nitrogen and phosphorus, to receiving water bodies (Di and Cameron, 2002; Harding et al., 1999; Hooda et al., 2000; Wilcock et al., 2006). Elevated levels of farm nutrients (N and P) in freshwaters can cause severe environmental impacts such as eutrophication, algal blooms and loss of aquatic biodiversity (Carpenter et al., 1998; Gillingham and Thorrold, 2000). Also, drinking water enriched in nitrate can cause methaemoglobinaemia, especially in infants (Ward et al., 2005).

The concerns about the negative repercussions of elevated nutrient levels are being translated into policy and management actions worldwide, which aim to protect water resources. Among these policies are; for example the European Union Water Directive Framework (European Community, 2000); the Total Maximum Daily Load (TMDL) program under the Clean Water Act (CWA) in the United States (USEPA, 1999); and the National Policy Statement for Freshwater Management (NPS-FM), in New Zealand (Ministry for the Environment, 2014). In response to the NPS-FM, Regional Councils are required to set water quality limits to meet freshwater objectives (Ministry for the Environment, 2014).

For these management programs to be effective, a sound understanding of the fate of nutrients as they are transported from farms to rivers is required. The appropriate scale for effective management of diffuse (non-point sources) pollution is the catchment scale (Howard-Williams et al., 2010). Furthermore, accurate estimates of river loads are essential for water quality management at a catchment scale (Guo et al., 2002; Lee et al., 2016; Zamyadi et al., 2007). Hence, the NPS-FM requires Regional Councils to set a freshwater-quality accounting system, each five years, for relevant contaminant loads (measured, modelled or estimated) at a freshwater management unit (catchment) scale (Ministry for the Environment, 2014). Effective implementation of the NPS-FM requires not only a focus on the water quality in receiving water bodies but also a sound understanding of the sources (land use) and the link (transport factor) for contaminant flows between land (farms) and receiving water bodies (rivers and lakes).

The literature review (Chapter 2) suggested that, upon leaching from the root zone, the water soluble nitrate is attenuated, mainly through subsurface denitrification, on its journey from different land units to rivers and streams (Rivett et al., 2007). A number of studies have shown that subsurface denitrification is influenced by catchment characteristics such as soil and rock properties, flow pathway length, residence time, and consequently the time and environment conducive for the biogeochemical reactions which attenuate nitrate (Fenton et al., 2009; Jahangir et al., 2012b; McAleer et al., 2017; Vidon and Hill, 2004; Wu et al., 2018). The spatial variability of catchment characteristics suggests nitrate attenuation capacities will vary accordingly, with different catchments having different nitrate attenuation capacities. There has been very limited research on nitrate attenuation capacity of New Zealand's agricultural landscape (e.g. around 45% by Woodward et al. (2013) in a small Toenepi stream catchment in the Waikato region and around 50% by Clothier et al. (2007) in the Manawatu at Hopelands catchment). This uniform attenuation (50%) has been adopted by Horizons Regional Council's One Plan (e.g. Ledein et al., 2007). In contrast to this value, the limited recent research in New Zealand and worldwide suggests that nitrate attenuation is spatially variable in the subsurface environment (Collins et al., 2017; Hansen et al., 2014, 2009; Jahangir et al., 2012b; McAleer et al., 2017; Rivas et al., 2017; Stenger et al., 2014, 2008). Few studies (e.g. Hansen et al., 2014, 2009) have quantified the spatial distribution of nitrate attenuation in the subsurface. These limited studies used models that are data-intensive and the required data is unlikely to be available for their wider applications across catchments. The parameters that are routinely monitored by water regulatory authorities (e.g. Regional Councils) are very limited (mainly flow and water quality parameters) with infrequent sampling (e.g. monthly for water quality parameters due to the cost of sampling and analysis).

A few recent field-based studies have shown variable nitrate attenuation conditions in New Zealand catchments (Collins et al., 2017; Rivas et al., 2017; Stenger et al., 2014, 2008). However, no study has yet evaluated the relationship between different catchment characteristics and the spatial distribution of nitrate attenuation across New Zealand catchments. In addition, no study has evaluated the influence of catchment characteristics on river soluble inorganic nitrate (SIN) concentrations, stratified by flows, and using robust statistical analysis that account for collinearity between predictors. Despite the importance of river load estimation, as highlighted in the NPS-FM, no study in New Zealand has evaluated the uncertainty associated with annual river load quantification as a function of load estimation method and sampling frequency.

This thesis used large water quality records and robust statistical methods to investigate the influence of different catchment characteristics (including subsurface hydrogeology) on river SIN concentrations at different flows (all flows, highest 25% flows and lowest 25% flows) at 15 sites in the Tararua catchment (3192 km^2), located in lower parts of North Island, New Zealand. The findings highlighted that hydrological indices and subsurface hydrogeological characteristics supersede the land-use influence on the river SIN concentrations. The thesis developed and applied a framework, which is not data intensive, to quantify the capacity of the catchment to attenuate nitrogen in the subsurface environment. The thesis defined this nitrogen attenuation capacity as nitrogen attenuation factor (AF_N), quantified through linking the estimates of average annual leaching losses of nitrogen from the root zone under the different land uses with the measured average annual loads of river SIN at a sub-catchment scale. By definition, the AF_N could vary theoretical between 0 and 1, '0' means no attenuation and '1' means complete (100%) attenuation. The AF_N was found to be highly spatially variable, ranging from 0.14 to 0.94, across the Tararua and Rangitikei sub-catchments. The AF_N was further assessed in terms of its uncertainty associated with the river SIN loads as function of water quality sampling frequency and river load estimation methods, and estimates of annual nitrogen losses from the root zone from various land uses. In doing so, five river load calculation methods and four water quality sampling frequencies were applied to quantify uncertainty in estimates of average annual river SIN loads. The results showed that flow-stratified (FS) method using a monthly sampling frequency had the lowest bias when comparing with the 'true' load (quantified based on the daily water quality sampling) at the Manawatu River Teachers College site, and therefore was used in the quantification of AF_N for other sub catchments in the Tararua and Rangitikei catchments. The robust statistical analysis of the relationship between the AF_N and catchment characteristics, and of the uncertainty associated with the AF_N quantification, supports the definition and applicability of AF_N as a catchment descriptor to quantify a catchment/sub-catchment nitrogen attenuation capacity.

The thesis further developed and applied a simple hydrogeologic-based model, evaluating the potential of using spatially variable estimates of nitrogen attenuation capacities of different soils and rocks and the estimates of nitrogen leaching losses from the root zone under different land uses, to predict average annual river SIN loads at sub-catchment scales. Four versions of the model (uniform nitrogen attenuation, spatially variable nitrogen attenuation based on: soils only; rocks only; and both soils and rocks) were developed and compared. The results highlighted that accounting for the spatially variable nitrogen attenuation capacities of both soils and rocks resulted in markedly better predictions of average annual river SIN loads in the Tararua and Rangitikei sub-catchments. This gained new knowledge and modelling capability will be instrumental for effective and targeted water quality management not only across similar agricultural landscapes in New Zealand but also worldwide.

The following sections further synthesise the thesis findings and recommendations for the future research in the study area.

6.2 Land use influence on river soluble inorganic nitrogen is outweighed by other catchment characteristics

Large datasets of catchment characteristics and water quality records along with robust statistical analysis (PLSR) were used to evaluate the relationship between a unique set of catchment characteristics (including subsurface characteristics such as soils and rocks) and river SIN concentrations stratified by flows in the Tararua catchment (Chapter 3). The results suggested that the influence of land use on SIN in the stream and rivers of the Tararua catchment is outweighed by other catchment characteristics such as soil characteristics and hydrological indices. The results suggested that different land use types influence river SIN concentrations as a function of flow category; with dairy being the only land use type that showed a positive influence (variable influence on projection VIP >1) on river SIN at the highest 25% flows. Conversely, sheep and/or beef was the land use type that showed a positive influence (VIP >1) on river SIN concentrations at the lowest 25% flows. In a recent study, Julian et al. (2017) found that high producing pasture was strongly correlated to river oxidised nitrogen concentrations across 77 catchments in New Zealand. The new findings of analysis presented here suggest that freshwater managers and policy makers should account for the observed variability and influence of different land uses at different flows for targeted and effective management of water quality outcomes.

The results of this study also suggested that, regardless of the flow category, the base flow index and the presence of well-drained soils were among the most influential variables on river SIN concentrations. The results suggested that catchments with larger proportions of well-drained soils, coquina and gravel lead to greater soil water percolation rates, nitrogen leaching and faster groundwater movement. Consequently, groundwater in these catchments will have faster groundwater recharge and flow and less residence time, hence less potential for geochemical reaction to attenuate nitrogen through subsurface denitrification. The positive regression coefficients between catchment characteristics that result in faster groundwater movement (such as well-drained soils, coquina and gravel) and river SIN concentrations reflect the limited opportunity for attenuation as the nitrate moves rapidly from farm systems to receiving water bodies.

The findings of this study clearly suggest that effective and targeted management of diffuse (non-point) sources at a catchment scale should not be based only on land use types (the sources factor). The results suggest that policy makers should also account for other catchment characteristics (the transport factor) for targeted and effective management of water quality at a catchment scale. Therefore, the next step is to link land use nitrogen leaching losses with diffuse 'non-point source' river loads to quantify the capacity of different catchments (transport factor) to attenuate nitrogen (as a function of their unique subsurface soil and rock characteristics) in the subsurface environment.

6.3 Nitrogen attenuation factor is highly spatially variable

The review of existing literature showed that only limited studies worldwide, particularly in New Zealand, have simulated the spatial distribution of attenuation (denitrification) in the subsurface. These limited studies used complex models that are data-intensive. The data required for these models might be available for certain small catchments but would not be available for most catchments. Therefore, as noted above, there is a need for a simple approach that makes use of limited available data to quantify nitrate attenuation capacity on a catchment scale, which will, in turn, inform effective and spatially targeted management of water quality.

A simple approach, that is not data-intensive, was developed and used in this study (Chapter 5) to quantify the capacity of a catchment to attenuate nitrogen, defined as the nitrogen attenuation factor. The nitrogen attenuation factor was quantified by comparing the estimates of average annual leaching losses of nitrogen from the root zone under the different land uses with the measured average annual loads of river SIN at a sub-catchment scale. The nitrogen attenuation factor, AF_N, defined as the average annual root zone nitrogen leaching losses minus the average annual SIN river loads, divided by the average annual root zone nitrogen leaching losses. According to this definition, the AF_N varies from 0 (no nitrogen attenuation) to 1 (full nitrogen attenuation) in the study catchment. For example, a value of AF_N = 0.75 can be interpreted as "75% of the nitrogen leached from the root zone is attenuated (reduced) in its flow pathways from farms to river". In other words, it means that only 25% of the nitrogen leached from the root zone reaches the river. This definition and analysis was applied to 15 and 5 sub-catchments in the Tararua and Rangitikei catchments, respectively.

The results of this study (Chapter 5) showed that nitrogen attenuation factor is highly variable as it ranges from 0.14 to 0.94 across the study sub-catchments. The new findings of this study were in contrast to the earlier findings of uniform attenuation factor (0.5) in agricultural catchments (e.g. Clothier et al. (2007)).

The simple definition and quantification of nitrogen attenuation factor was further subjected to a robust uncertainty analysis evaluating its application as a sub-catchment descriptor. In order to assess the uncertainty associated with the nitrogen attenuation factor, the uncertainty in annual river SIN load must be quantified (as it is one of the main components of the nitrogen attenuation factor).

6.4 Flow-stratified load estimation method has the lowest bias for annual river SIN loads using monthly sampling frequency

To quantify the uncertainty in annual river SIN loads as a function of load estimation methods and sampling frequency, five load estimation methods and four sampling frequencies were studied (Chapter 4). One year (May, 2010 to April, 2011) of daily measurements of river flow and SIN concentrations as measured at the Manawatu at Teachers College monitoring site was used. The site is located downstream of the Tararua catchment. It was selected, to conduct the analysis, for having the highest sampling frequency of water quality measurements and for being representative of the river and stream in the Tararua and Rangitikei catchments. Being the first study to be conducted in New Zealand, and among the very limited number of studies worldwide for medium size catchments in temperate climate, this study provides water regulatory authorities with insights into the required sampling frequency and load estimation method(s) to quantify river annual load estimates within the acceptable range of uncertainty (Chapter 4). For example, in New Zealand, most Regional Councils monitor river water quality parameters on monthly basis. Therefore, if the accuracy and precision of 80% (i.e. RMSE = 20%) of the estimated loads is considered an acceptable threshold for Regional Councils, this means a monthly sampling frequency for SIN, using FW, RE and FS methods, is sufficient to estimate accurate and precise loads within the acceptable threshold.

The results of this study showed that methods that do not account for flow at the time of sampling, such as global mean (GM), will result in imprecise and inaccurate estimates of average annual river loads of SIN regardless of the sampling frequency. Also, the results showed that methods that rely on the flow-concentration relationship (such as rating curve 'RC') will overestimate average annual loads for water quality parameters that show a dilution effect (such as SIN) at flow peaks. Thus, the findings showed that it is not recommended to use RC or GM for river SIN load estimation for catchments with flow regime and flow-concentration relationship similar to the study site.

The results highlighted that the flow-stratified (FS) method has the lowest bias for SIN using monthly sampling frequency, and a similar root-mean square error (RMSE) to the flow-weighted (FW) and ratio estimator (RE) methods. The flow-stratified (FS) method combined with the monthly sampling frequency resulted into a bias of 0.9% and RMSE of 12% in quantification of average annual river SIN load at the study site. This quantification of the uncertainty associated with the river SIN loads allowed the quantification of the uncertainty associated with the nitrogen attenuation factor as will be discussed in the next section.

6.5 Uncertainty in nitrogen attenuation factor will not prevent its use as a catchment descriptor

A parametric bootstrap was used to estimate the uncertainty in the nitrogen attenuation factor estimates as a function of the uncertainties in its two components, i.e. the average annual root zone nitrogen leaching losses and average annual river SIN loads. The 95% confidence interval was quantified as the 0.025 and 0.975 quantiles of the parametric bootstrap distribution (Chapter 5).

The standard errors of average annual root zone nitrogen leaching losses and river SIN loads used in the parametric bootstrap were 23% (Ledgard and Waller, 2001) and 2% (based on uncertainty analysis in Chapter 4), respectively.

The 95% confidence intervals computed by the parametric bootstrap 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. Also, the redox status for groundwater wells across Tararua sub-catchments (Rivas et al., 2017) was found to closely match the spatial variability of the values of the nitrogen attenuation factor. None of the Tararua groundwater wells classified as reducing were located in a sub-catchment that had a nitrogen attenuation factor less than 0.5. Also, in the lower (coastal) parts of the Rangitikei catchment, all groundwater wells were found to be anoxic (reduced) (Collins et al., 2017) aligning with the higher (0.69) nitrogen attenuation factor quantified in the lower Rangitikei catchment.

This suggests that nitrogen attenuation factor could be used as a catchment descriptor to indicate the capacity of a catchment to attenuate nitrogen. A small nitrogen attenuation factor (0.1 to 0.3) suggests that groundwater is not likely to be conducive to attenuation through subsurface denitrification. On the other hand, a larger nitrogen attenuation factor (0.70 to 0.95) suggests that groundwater is highly likely to be reduced, and therefore conducive to potential attenuation of nitrate through subsurface denitrification.

Given this high spatial variability in the nitrogen attenuation factor, the next step is a sound understanding of catchment characteristics that influence this variability.

6.6 Variability of nitrogen attenuation factor is a function of sub-catchment characteristics

There is, to my knowledge, no study that evaluates the relationship between the capacity of catchments to attenuate nitrogen (nitrogen attenuation factor) and catchment characteristics in New Zealand landscape. To better understand this relationship, PLSR was used to evaluate the magnitude and direction of the relation between the nitrogen attenuation factor and catchment characteristics such as; soil texture, soil drainage class, soil carbon content, and main- and sub-rocks across Tararua sub-catchments (Chapter 5). The results showed that the nitrogen attenuation factor of the Tararua sub-catchments has a positive relationship with poorly drained soils and mudstone, whereas it has a negative relationship with well-drained soils and gravel. This suggests that catchments with higher proportions of well-drained soils and gravel will allow faster groundwater recharge and movement, less residence time in the subsurface and hence less time for subsurface denitrification to occur. Therefore, catchments with higher proportions of well-drained soils and gravels are highly likely to have lower nitrogen attenuation factors. The next step is to evaluate the potential to use the attenuation factor, as determined by subsurface catchment characteristics (soils and rocks), to predict diffuse (non-point sources) river SIN loads.

6.7 Accounting for soils and rock attenuation capacities in a hydrogeologic-based model resulted in markedly better predictions of river SIN loads

A novel but simple hydrogeologic-based model was developed that links the source (nitrogen leaching losses from root zone for different land uses) with the nitrogen attenuation factor (attenuation capacities of subsurface catchment characteristics) to predict river SIN loads (Chapter 5). Four different versions of the model (uniform nitrogen attenuation, variable nitrogen attenuation based on soils only; variable nitrogen attenuation based on rocks only; and variable nitrogen attenuation based on both soils and rocks) were developed and evaluated through comparisons between the predicted and measured average annual river SIN loads in the Tararua and Rangitikei sub-catchments. The model that accounted for the spatial variability in the nitrogen attenuation capacities of both soils and rocks resulted in markedly better predictions of average annual river SIN loads across the Tararua and Rangitikei sub-catchments.

This clearly highlights that the likely influence of catchment characteristics such as soils and rock types on attenuating nitrogen in the subsurface should be identified, mapped and used to predict the land-based nitrogen loads to streams and rivers in agricultural catchments.

6.8 Implications for water quality management

In New Zealand, management of diffuse (non-point) sources is mainly through nutrient budgeting tools (e.g. OVERSEER®, Wheeler et al. (2003)) that estimate nitrogen losses from farming systems (Roygard et al., 2012). Similarly, in Europe, management of diffuse pollution is based on controlling nitrogen leaching from farming systems. The results presented in this thesis, Chapter 3, highlight that catchment characteristics (such as hydrological indices, soil and underlying hydrogeological characteristics) outweighed the influence of land use on the river SIN concentrations at different flows in the Tararua catchment. This suggests that water regulatory authorities should account not only for land use but also for other catchment characteristics (soils, rocks and hydrological indices) in their plans for effective and targeted water quality management at a catchment scale. Also, the results highlight that catchment characteristics that lead to faster groundwater recharge and flow (e.g. well-drained soils and gravels) have a positive regression coefficients with the river SIN concentrations (Chapter 3), suggesting unconducive environment for nitrate attenuation (less residence time and oxic groundwater conditions). Thee sub-catchments with the faster flow characteristics (i.e. less residence time) are highly likely be more responsive to water quality management plans by the Regional Councils. The results (Chapter 3) further showed the temporal influence of subsurface hydrogeologic settings below different land-use types on the river SIN concentrations. Subsurface hydrogeologic setting characterized by the faster flow (shorter flow paths and less residence time due to larger proportions of well-drained soils and gravels), associated with dairy land use was found to influence the river SIN concentrations at the highest 25% flows in the Tararua sub-catchments. Accounting for these insights will help Regional Councils in their policy and planning for better, more effective and targeted SIN management in agricultural catchments. A robust analysis of different water sampling frequency and river load estimation method(s) also provides the Regional Councils insights for monitoring and quantification of annual river loads (and, nitrogen attenuation capacity) within the acceptable range of uncertainty (Chapter 4). The results highlight as one month (September, 2010) accounted for around 50% of the total annual loads for TP and TSS at the Manawatu Teachers College site in year 2010/2011. Hence, the river flow-based sampling will highly likely result in less uncertain estimates of annual river loads; especially for particles such as TSS and TP. The analysis also suggested that, for a catchment with similar characteristics (flow-concentration relationship), river load calculations that rely on the flow-concentration relation such as rating curve (RC) will result in overestimate of annual river loads for water quality parameters that show a dilution effect (such as SIN) at flow peaks. Hence, the use of RC method for estimation of river SIN load in catchments with a similar flow-concentration relationship by water regulatory authorities is not recommended.

The framework, developed and applied in this thesis, to quantify nitrogen attenuation factor could be adopted by Regional Councils to quantify and use the spatial variable instead a uniform nitrogen attenuation factor in their considerations for water quality management across agricultural catchments. The hydrogeologic-based model (Chapter 5), that accounted for the spatially variable nitrogen attenuation capacities of soils and rocks, resulted in markedly better predictions of the river SIN loads across both the Tararua and Rangitikei sub-catchments. In the short term, water regulatory authorities and policy makers should focus on sub-catchments with lower nitrogen attenuation factors (lower capacity to attenuate nitrogen). This could be achieved through a number of procedures including, but not limited to, additional high resolution measurements and mapping (both spatially and temporally) of nitrate attenuation in the subsurface environment. Water regulatory authorities should take the nitrogen attenuation capacities of soils and rocks into account when issuing new consents, especially in sensitive catchments with smaller nitrogen attenuation factors.

Accounting for hydrogeologic influences on subsurface nitrogen attenuation will provide the basis for water regulatory authorities to align spatially intensive land-use practices with high nitrogen attenuation pathways. This is expected to result in reducing river SIN loads (from non-point sources), which in consequence will result in reducing the incidence and extent of nuisance periphyton growth or nitrate toxicity in freshwater ecosystems.

The hydrogeologic-based model (Chapter 5) suggests that a number of scenarios can be conducted to account for, and take advantage of, the spatial variability of nitrogen attenuation capacities of different hydrogeologic settings (soils and rocks types) across agricultural catchments. These scenarios could be; de-intensifying the land use where soils and rocks have lower capacities for nitrogen attenuation; intensifying the land use where soils and rocks have higher capacities for nitrogen attenuation; and a combination of these two scenarios. The objective of the latter scenarios would be to evaluate the potential for increasing agricultural productivity (i.e. increase leaching) while reducing the environmental impacts (e.g. river load) through spatial alignment of land use with land suitability.

This concept has undergone preliminary evaluation for the Rangitikei catchment (Horne et al., 2017; Singh et al., 2017a, 2017b). I was among the co-authors of the aforementioned published reports and conference papers, and I wrote the code for the data analysis. This preliminary analysis showed that by reducing nitrate leaching losses in areas of low nitrogen attenuation capacities (i.e. hydrogeologic units that have either low/low, low/medium or medium/low nitrogen attenuation capacities for soils and rocks) and increasing nitrate leaching in areas with higher attenuation capacities (i.e. hydrogeologic units that have either high/high, high/medium or medium/high nitrogen attenuation capacities for soils and rocks) it is possible to have a net intensification in agricultural land use and a decrease in the average annual river SIN load in the Rangitikei catchment.

To further this analysis, there is a need for higher resolution measurements and mapping of nitrogen attenuation capacity of different soil and rock types across agricultural landscape. Also, additional field measurements are essential to investigate the redox status of groundwater wells and its relation with soils and rocks. These high-resolution measurements and maps will inform better classification of nitrogen attenuation capacities of soils and rocks, facilitating spatial alignment of land use with land suitability for targeted and effective water quality outcomes.

6.9 Future research recommendations

The key findings of this study suggest a number of actions that are required in future studies if greater insights into effective and targeted water quality management at a catchment scale are to be achieved. These aspects are summarized below:

- *Increasing the sample size to get better insights into the relationship between catchment characteristics and both river soluble inorganic nitrogen (SIN) concentration and nitrogen attenuation factor*

In the partial least squares regression (PLSR), 15 observations (sites), in the Tararua catchment (Chapters 3 and 5), were used to investigate the relationship between catchment characteristics and both river SIN concentrations and nitrogen attenuation factor. PLSR is robust in dealing with dataset with smaller number of observations compared to number of predictors (independent variables). However, increasing the sample size would be expected to result in better understanding of the complex relationship between catchment characteristics and both river SIN concentrations and nitrogen attenuation factor, by increasing statistical power and decreasing uncertainty. Therefore, it is recommended to conduct further studies to investigate this complex relationship for a larger number of catchments across New Zealand.

- *Using higher resolution GIS layers for catchment characteristics*

In this study, the 1:250 000 Geological Map of New Zealand, called QMAP "for Quarter-million MAP" was used to extract the areal percentage of main rocks and subrocks in the study catchments. Also, the 1:50 000 Fundamental Soil Layer "FSL" was used to extract the areal percentage of soil properties across the study catchments. Well-informed decision making requires accurate and higher resolution datasets. Higher resolution GIS layers, especially for soils, are essential for scenario analysis of land use (intensification and/or de-intensification) on a farm scale (Section 6.8). Therefore, future studies are recommended to use and/or map catchment characteristics, such as land use, soils and rocks, at a higher resolution.

- *Accounting for the temporal changes in land use*

In this study, due to data limitations, it was assumed that there was no changes in the land use over the 8 years (2009-2016) used in the analysis. Future studies are recommended to investigate the temporal changes in the land use upon quantification of the nitrogen attenuation factor and the influence of changes in land use on river SIN concentrations and loads.

- *Further detailed temporal and spatial field measurements to investigate the redox status of groundwater and its relationship with different soil and rock types*

In this study, to reduce the uncertainty associated with the hydrogeologic-based model that accounts for nitrogen attenuation capacities of soils and rocks in the prediction of river nitrogen loads, additional detailed field measurements will be required. These detailed spatial and temporal field measurements should investigate the redox status of groundwater across different combinations of soils and rocks in the agricultural landscape. This will be essential to refine the classification of soils and rocks into different classes according to their nitrogen attenuation capacities.

- *Field measurements to measure the hydraulic conductivity across different rocks and the potential for denitrification*

The findings of this study highlighted that permeable rocks such as gravel have negative relationship with nitrogen attenuation capacity and positive relationship with river SIN concentrations. A number of studies suggested the negative relationship between permeability and the potential for denitrification (Jahangir et al., 2012b, 2012c; Orr et al., 2016; Rivas et al., 2017). Yet, further field measurements are required to investigate the relationship between the hydraulic conductivity of different rocks and the potential for denitrification, particularly in New Zealand. This information will help refine the classification of rocks into classes according to their nitrogen attenuation.

- *Longer flow and water quality records at different sites to quantify the uncertainty in annual river SIN loads*

In this study, due to data limitation, one year of flow and water quality data (2010-2011) was used to quantify the uncertainty in annual river loads as a function of sampling frequency and load estimation methods. This year was found to be representative of the flow data for 20 years at this site. Use of longer records of flow and water quality measurements at a number of sites, in New Zealand's agricultural landscape is recommended to confirm the quantification of uncertainty in annual river loads.

- *Field measurements of nitrogen leaching for different land use types and comparing it to modelled N-leaching by OVERSEER®*

Additional field measurement of nitrogen leaching under different land use types are required. These measurements should be compared with modelled N-leaching by OVERSEER® to quantify the uncertainty associated with modelled OVERSEER® estimates. This will be essential to refining the uncertainty associated with the nitrogen attenuation factor and the hydrogeologic-based model to predict river loads.

- *Additional measurements to better estimate the in-stream uptake*

According to the finding of this study, in-stream attenuation is not significant compared to either average annual root zone load or river SIN load in the Tararua and Rangitikei sub-catchments. Therefore, it was not considered in the hydrogeologic-based model. Yet, the model used to estimate the instream nitrogen attenuation could be improved by high-resolution measurements to investigate in-stream nutrient cycling and periphyton growth to better quantify nitrogen flows and attenuation in agricultural landscape.

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Appendices

Appendix A: Supporting materials for chapter 3

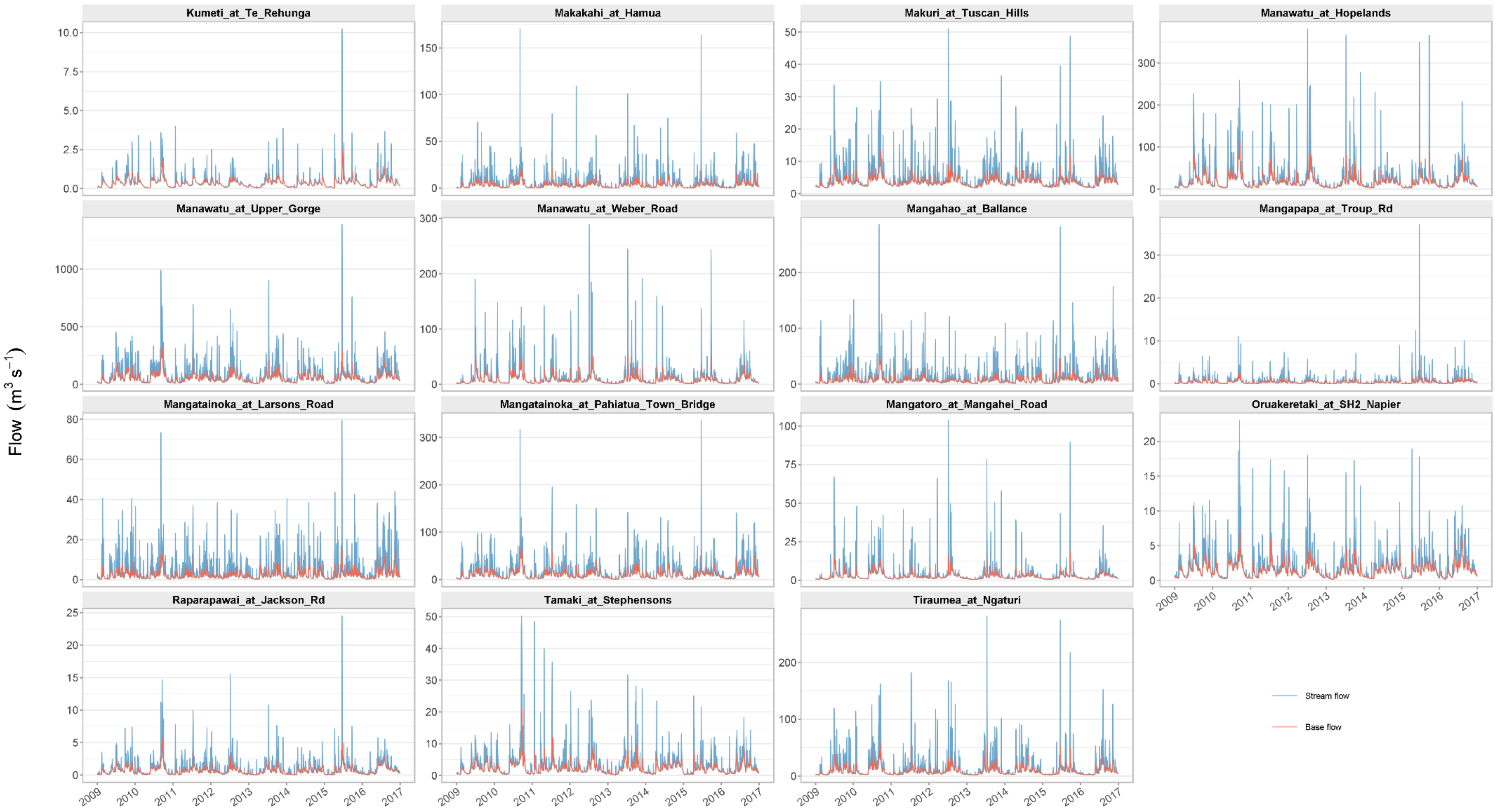

Fig. A.1. Base flow (red) and stream flow (light blue) (m^3 s^{-1}) at15 monitoring sites in the Tararua catchment.

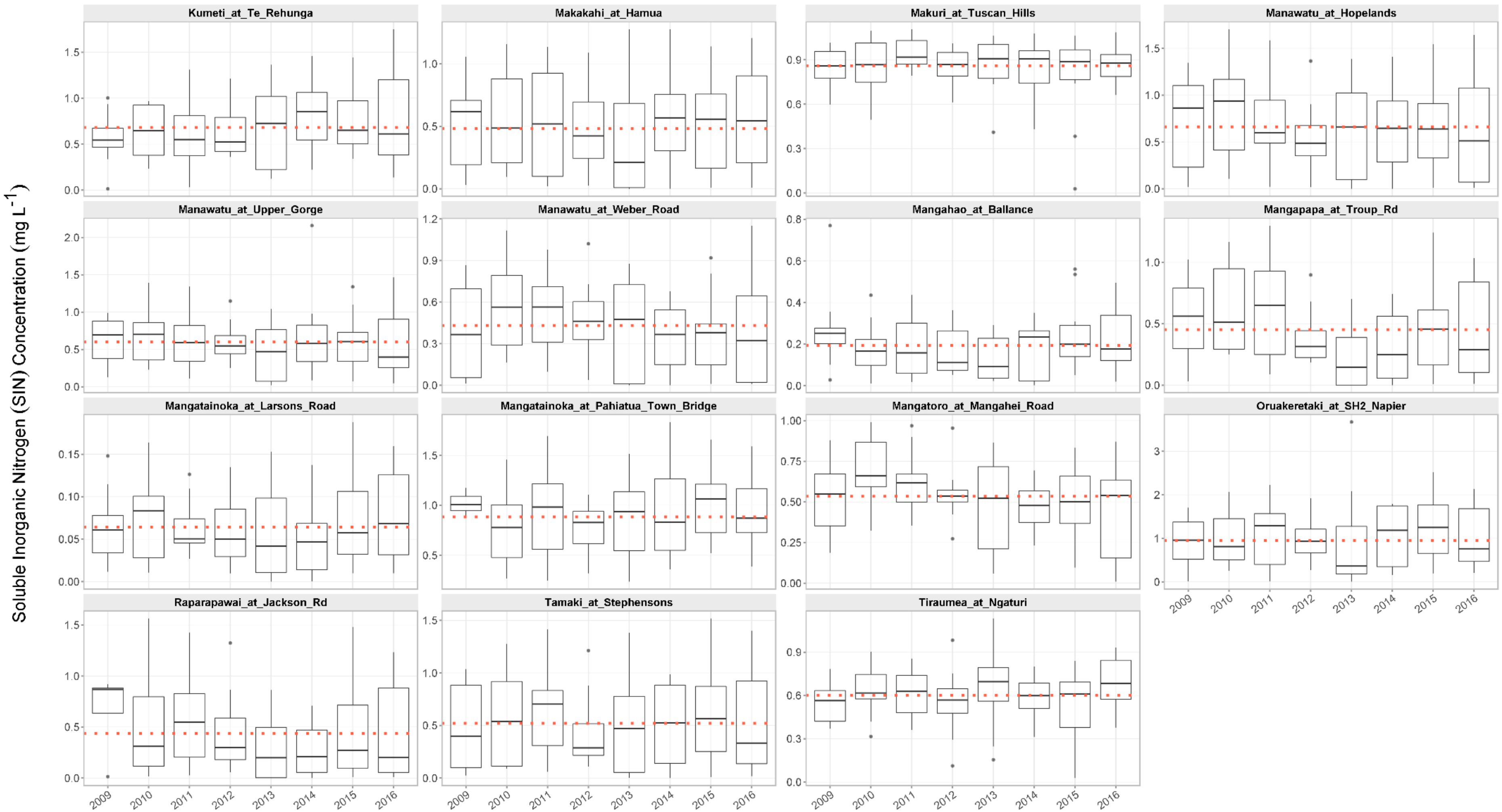

Fig. A.2. Temporal changes in SIN concentrations (mg L^{-1}) measured at the monitoring sites in the Tararua catchment for 8 years (from Jan., 2009 to Dec., 2016). Dashed red line represents mean SIN concentrations (mg L^{-1}) at each monitoring site for 8 years.

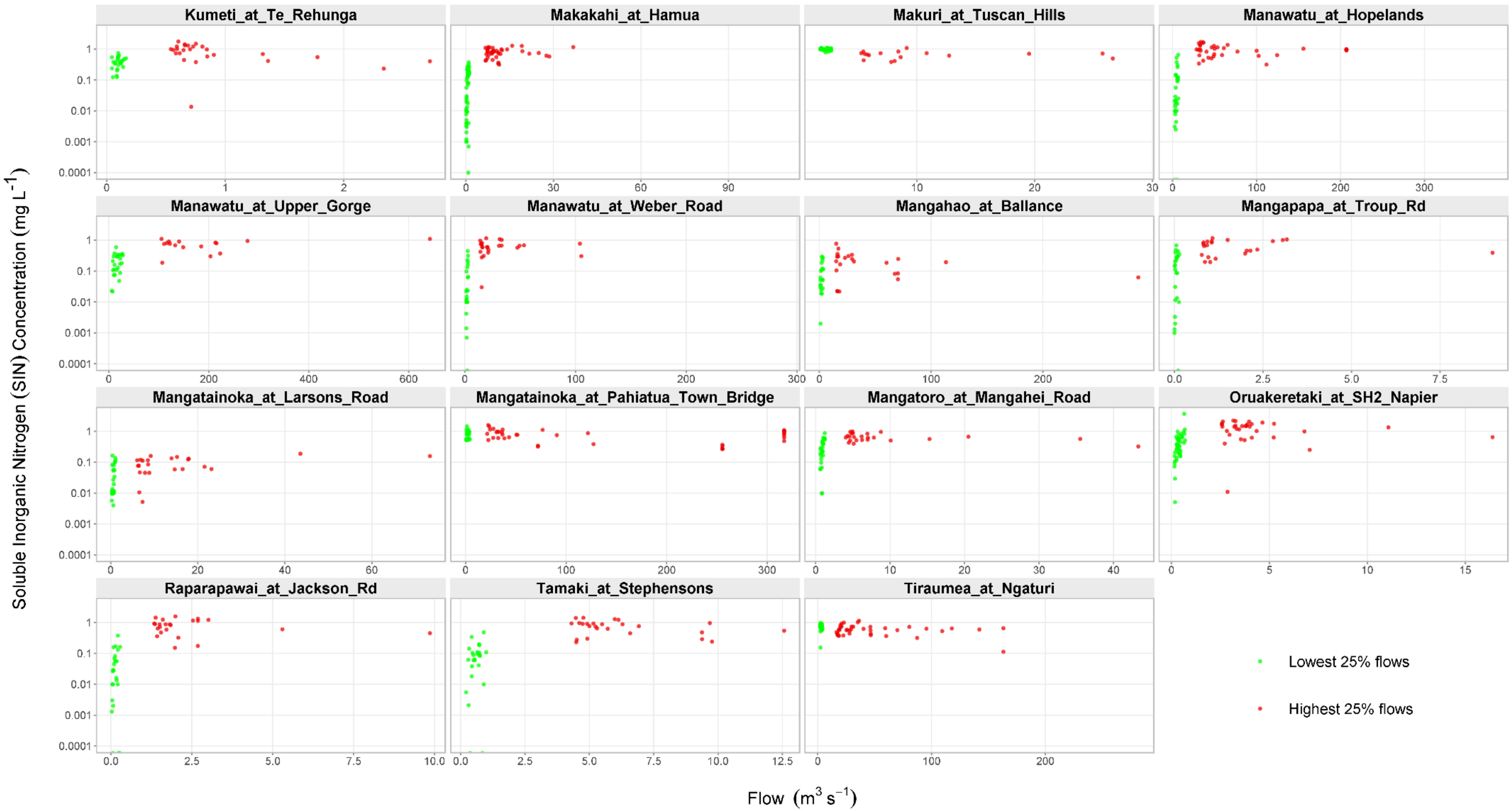

Fig. A.3. Relationship between river flow (m^3 s^{-1}) and SIN concentration (mg L^{-1}) measured at the monitoring sites in the Tararua catchment for 8 years (from Jan., 2009 to Dec., 2016). The colour of the data is according to the flow quantiles with lowest 25% flows and highest 25% flows represented by green and red, respectively.

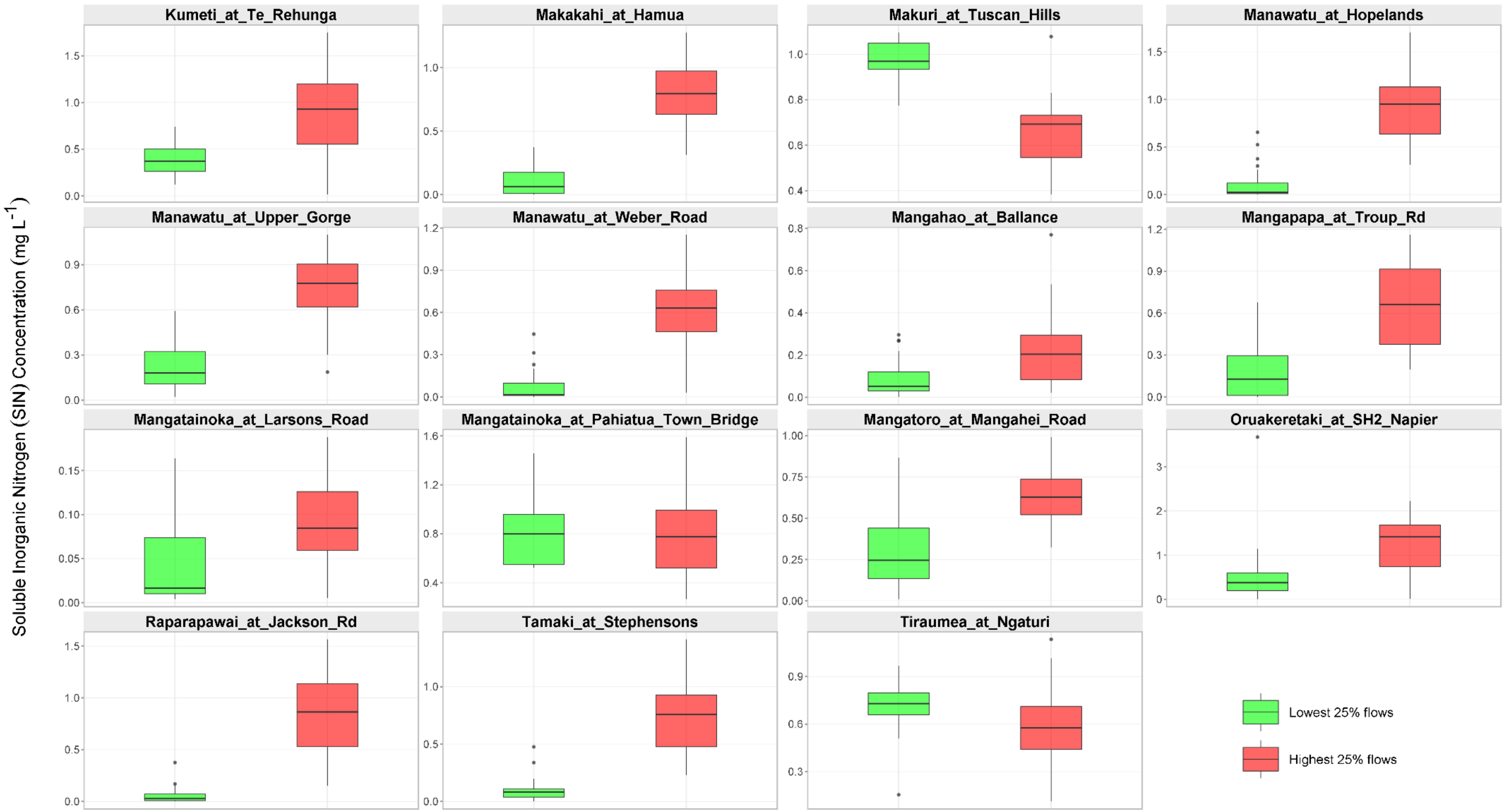

Fig. A.4. Temporal changes in SIN concentrations (mg L^{-1}) measured at the monitoring sites in the Tararua catchment for 8 years (from Jan., 2009 to Dec., 2016) at the highest 25% flows (red) and lowest 25% flows (green).

Table A.1. Summary statistics of soluble inorganic nitrogen (SIN) concentration (mg L^{-1}) measured at the 15 monitoring sites (Fig. 3.1) in the Tararua catchment for 8 years (from Jan., 2009 to Dec., 2016) at all flows, highest 25% flows and lowest 25% flows

Site	Flow category	n	mean	median	min	max	sd
Kumeti_at_Te_Rehunga	All flows	96	0.7	0.6	0.01	1.8	0.4
	Highest 25% flows	26	0.9	0.9	0.01	1.8	0.4
	Lowest 25% flows	25	0.4	0.4	0.1	0.7	0.2
Makakahi_at_Hamua	All flows	194	0.5	0.5	0	1.3	0.4
	Highest 25% flows	39	0.8	0.8	0.3	1.3	0.3
	Lowest 25% flows	52	0.1	0.1	0	0.4	0.1
Makuri_at_Tuscan_Hills	All flows	96	0.9	0.9	0.03	1.1	0.2
	Highest 25% flows	17	0.7	0.7	0.4	1.1	0.2
	Lowest 25% flows	26	1	1	0.8	1.1	0.1
Manawatu_at_Hopelands	All flows	135	0.7	0.6	0	1.7	0.4
	Highest 25% flows	36	0.9	0.9	0.3	1.7	0.4
	Lowest 25% flows	30	0.1	0.02	0	0.7	0.2
Manawatu_at_Upper_Gorge	All flows	96	0.6	0.6	0.02	2.2	0.4
	Highest 25% flows	16	0.7	0.8	0.2	1.1	0.3
	Lowest 25% flows	25	0.2	0.2	0.02	0.6	0.1
Manawatu_at_Weber_Road	All flows	96	0.4	0.4	0	1.2	0.3
	Highest 25% flows	24	0.6	0.6	0.03	1.2	0.3
	Lowest 25% flows	25	0.1	0.02	0	0.4	0.1
Mangahao_at_Ballance	All flows	98	0.2	0.2	0.002	0.8	0.1
	Highest 25% flows	23	0.2	0.2	0.02	0.8	0.2
	Lowest 25% flows	21	0.1	0.1	0.002	0.3	0.1
Mangapapa_at_Troup_Rd	All flows	96	0.5	0.4	0	1.3	0.3
	Highest 25% flows	22	0.6	0.7	0.2	1.2	0.3
	Lowest 25% flows	26	0.2	0.1	0	0.7	0.2

Mangatainoka_at_Larsons_Road	All flows	112	0.1	0.1	0	0.2	0.05
	Highest 25% flows	23	0.1	0.1	0.005	0.2	0.05
	Lowest 25% flows	26	0.04	0.02	0.004	0.2	0.05
Mangatainoka_at_Pahiatua _Town_Bridge	All flows	118	0.9	0.9	0.2	1.8	0.4
	Highest 25% flows	37	0.8	0.8	0.3	1.6	0.3
	Lowest 25% flows	22	0.8	0.8	0.5	1.5	0.3
Mangatoro_at_Mangahei_Road	All flows	96	0.5	0.6	0.01	1	0.2
	Highest 25% flows	24	0.6	0.6	0.3	1	0.2
	Lowest 25% flows	26	0.3	0.2	0.01	0.9	0.2
Oruakeretaki_at_SH2_Napier	All flows	143	0.9	0.9	0.005	3.7	0.6
	Highest 25% flows	32	1.3	1.4	0.01	2.2	0.6
	Lowest 25% flows	44	0.5	0.4	0.005	3.7	0.6
Raparapawai_at_Jackson_Rd	All flows	89	0.4	0.3	0	1.6	0.4
	Highest 25% flows	23	0.8	0.9	0.2	1.6	0.4
	Lowest 25% flows	24	0.1	0.03	0	0.4	0.1
Tamaki_at_Stephensons	All flows	97	0.5	0.5	0	1.5	0.4
	Highest 25% flows	25	0.8	0.8	0.2	1.4	0.4
	Lowest 25% flows	25	0.1	0.1	0	0.5	0.1
Tiraumea_at_Ngaturi	All flows	179	0.6	0.6	0.03	1.1	0.2
	Highest 25% flows	39	0.6	0.6	0.1	1.1	0.2
	Lowest 25% flows	43	0.7	0.7	0.2	1	0.1

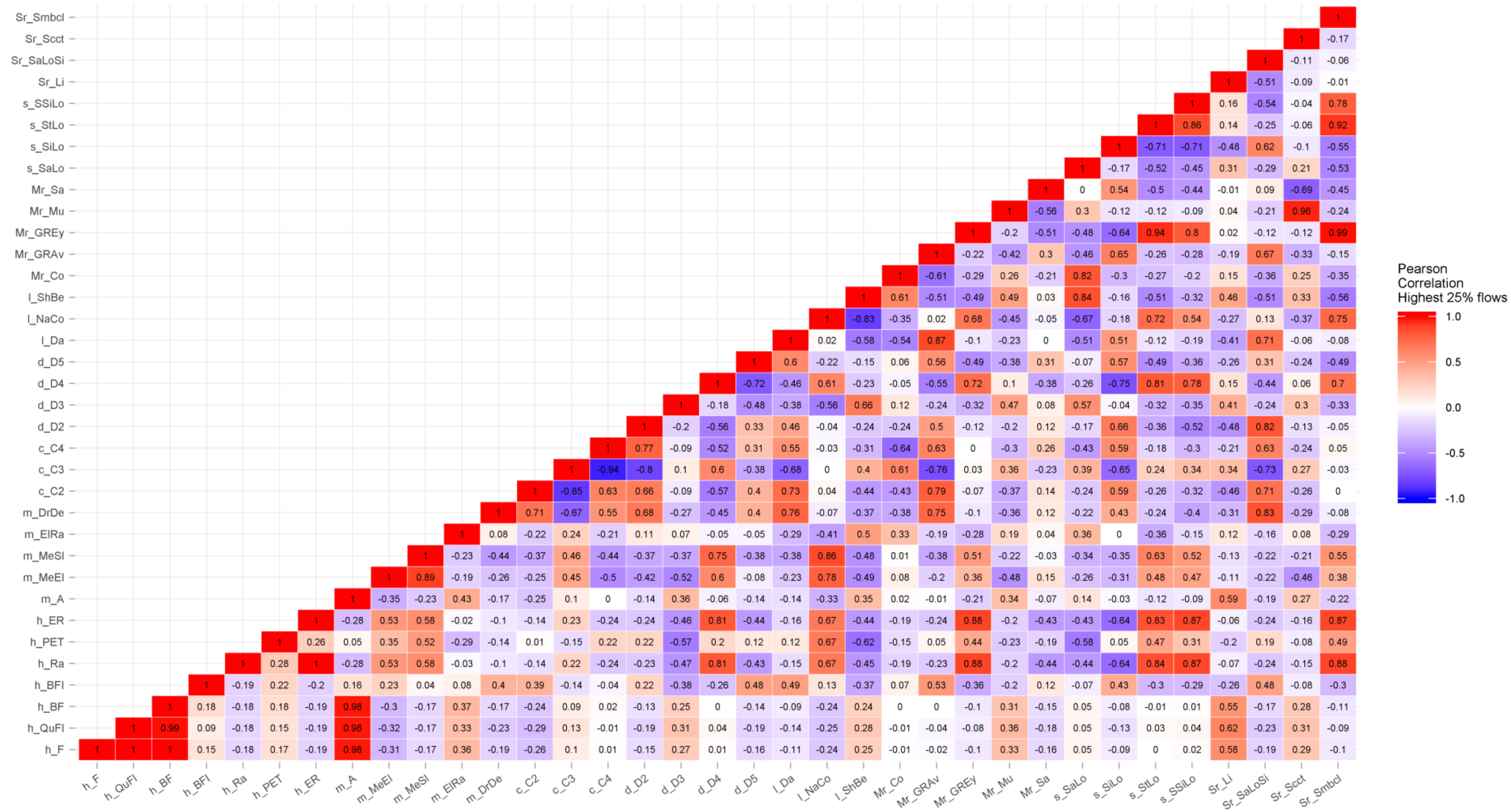

Fig. A.5. Pearson correlation between independent variables (catchment characteristics) at the highest 25% flows in the Tararua catchment. The magnitude and direction of the co-dependence are indicated by the different colours and their intensity.

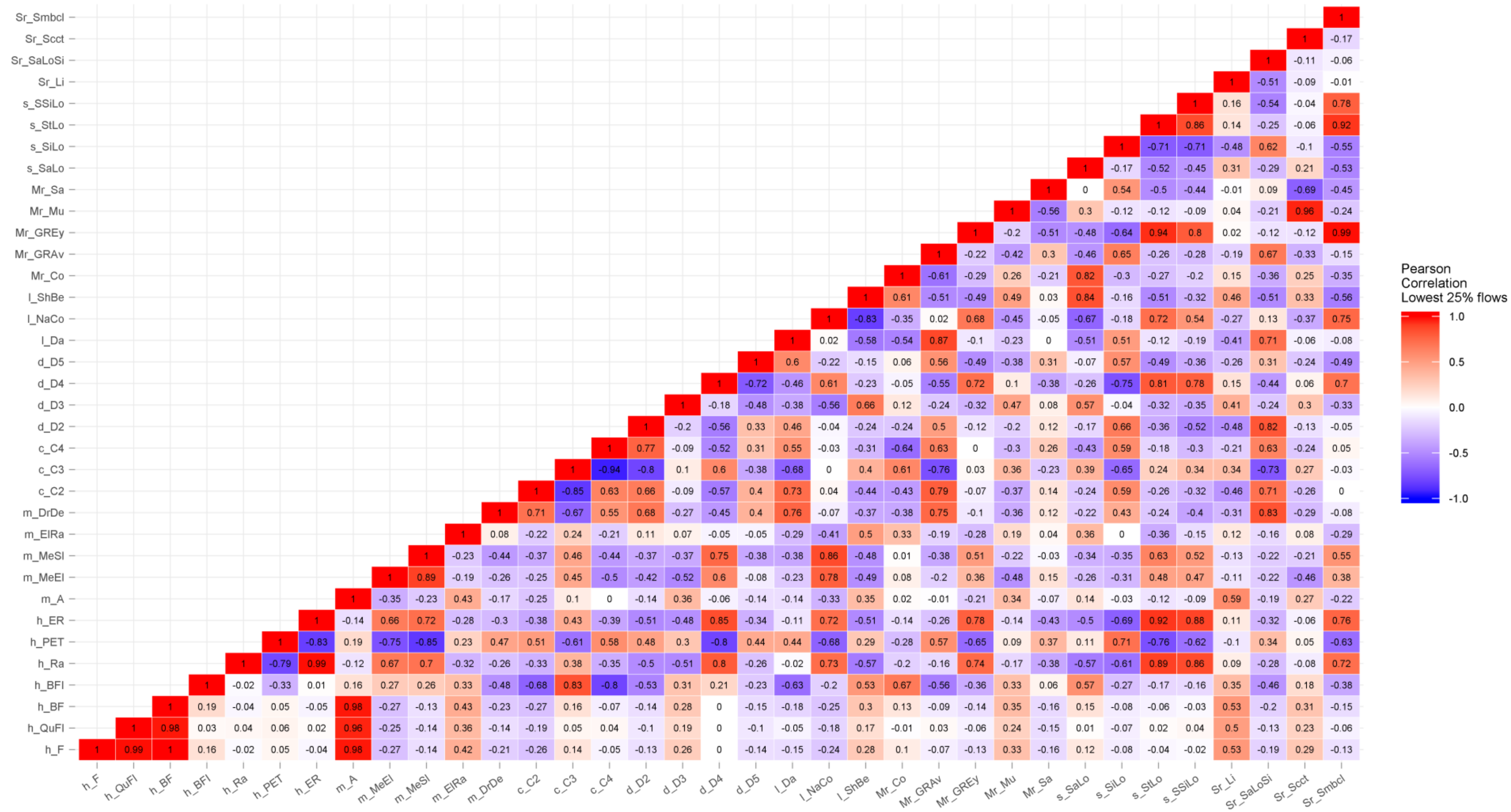

Fig. A.6. Pearson correlation between independent variables (catchment characteristics) at the lowest 25% flows in the Tararua catchment. The magnitude and direction of the co-dependence are indicated by the different colours and their intensity.

Fig. A.7. Variable influence on projection (VIP) and regression coefficients for catchment characteristics for the first component, the first two components, the first three components and the first four components (at all flows). The dashed lines in the regression coefficients differentiate between positive and negative directions whereas dashed line in the VIP (VIP =1) is to highlight the important independent variables located above the line.

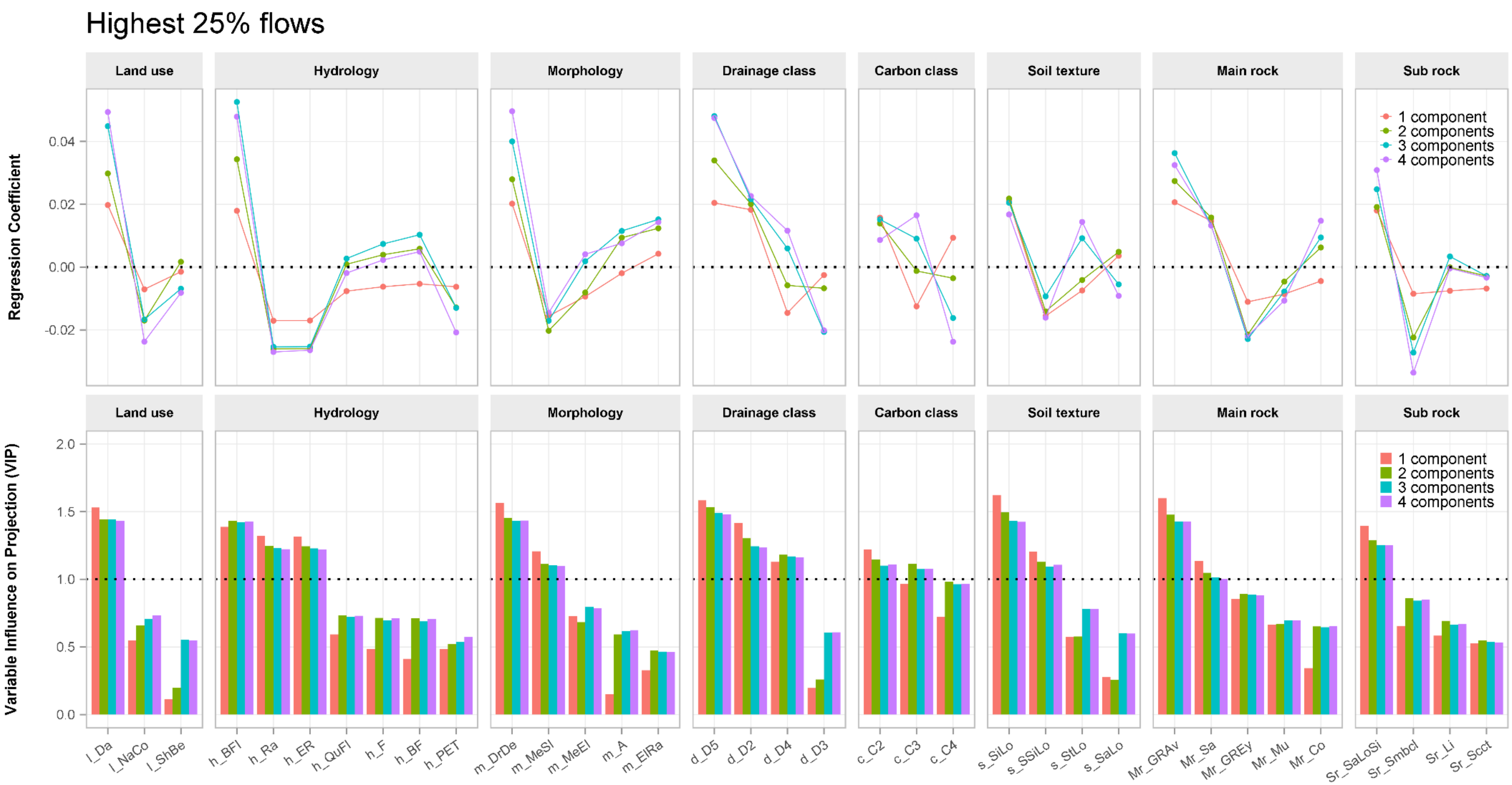

Fig. A.8. Variable influence on projection (VIP) and regression coefficients for catchment characteristics for the first component, the first two components, the first three components and the first four components (at the highest 25% flows). The dashed lines in the regression coefficients differentiate between positive and negative directions whereas dashed line in the VIP (VIP =1) is to highlight the important independent variables located above the line.

Fig. A.9. Variable influence on projection (VIP) and regression coefficients for catchment characteristics for the first component, the first two components and the first three components (at the lowest 25% flows). The dashed lines in the regression coefficients differentiate between positive and negative directions whereas dashed line in the VIP (VIP =1) is to highlight the important independent variables located above the line.

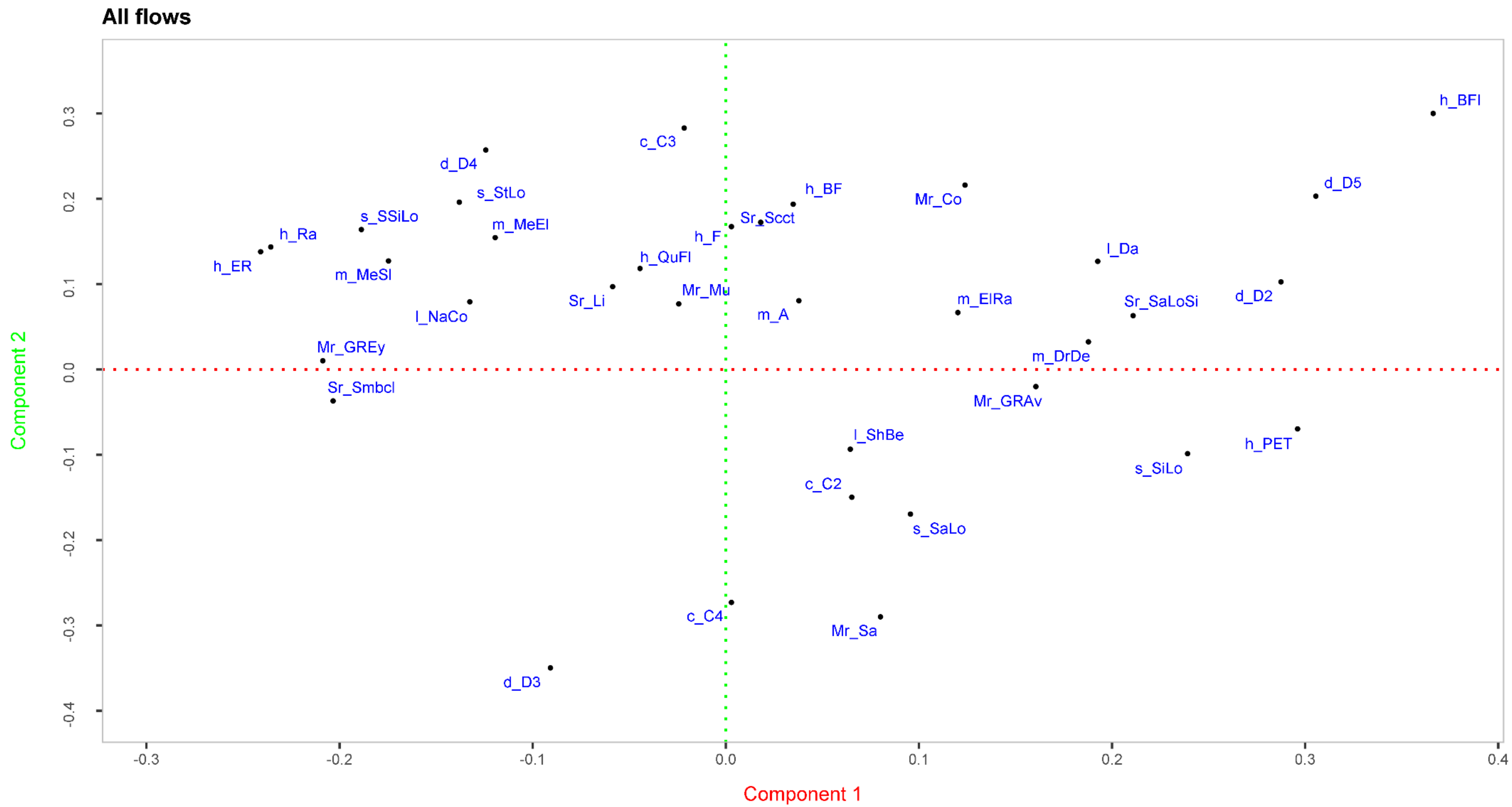

Fig. A.10. Loading weights (scatter) for the first and second PLSR components for the independent variables of the Tararua catchment (at all flows).

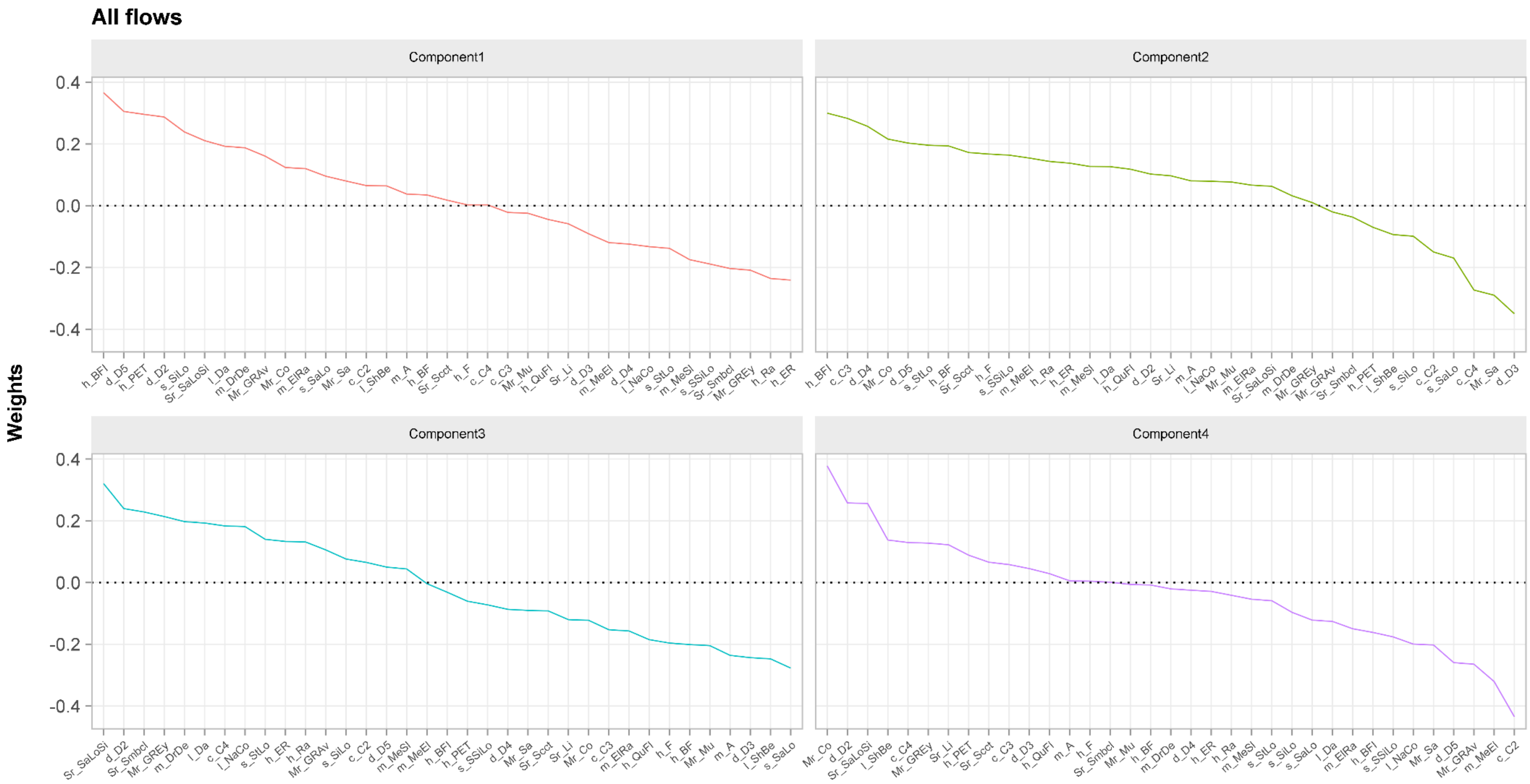

Fig. A.11. Loading weights (spectral) for component 1, component 2, component 3 and component 4 of the PLSR for the independent variables of the Tararua catchment (at all flows).

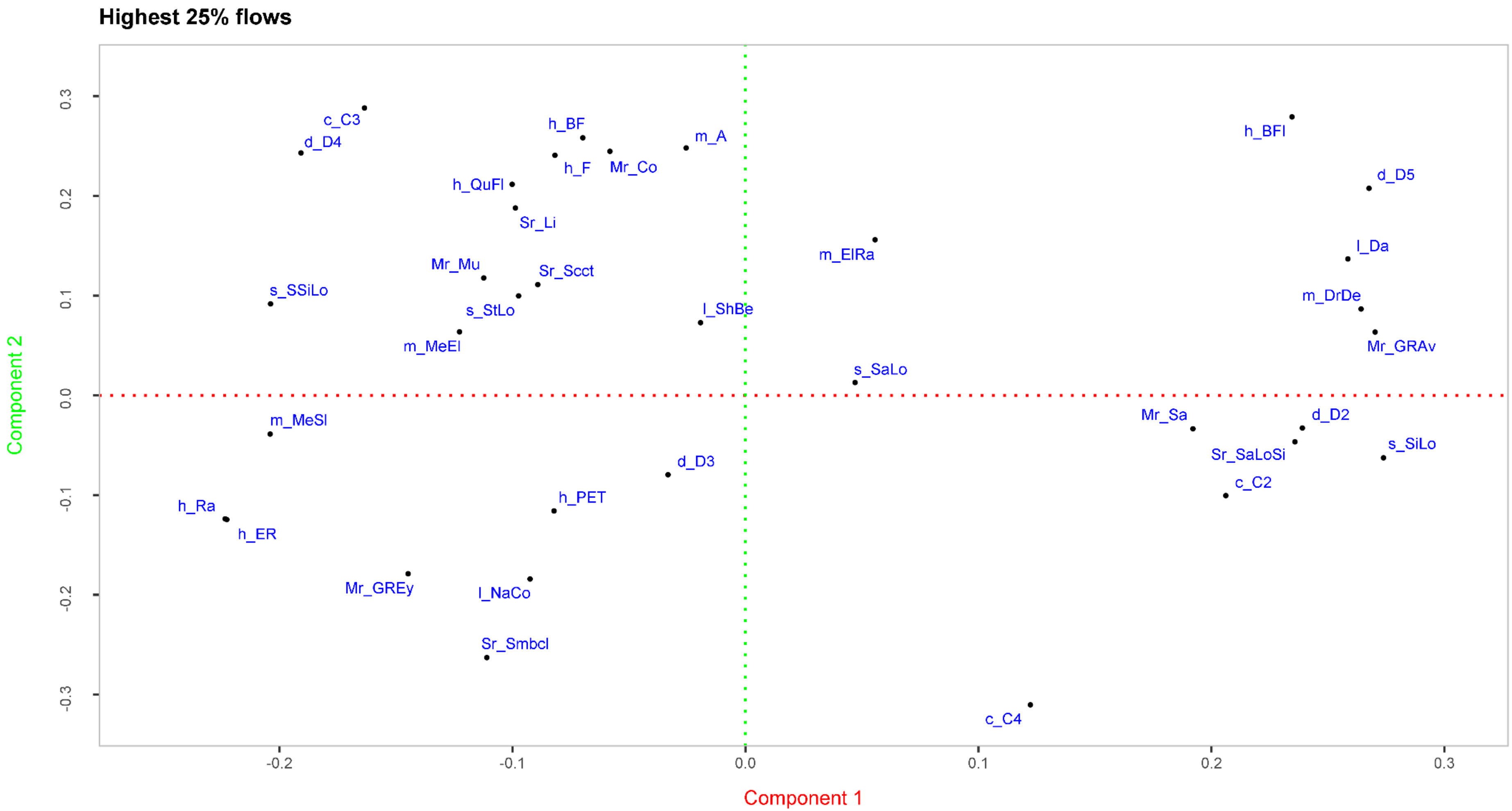

Fig. A.12. Loading weights (scatter) for the first and second PLSR components for the independent variables of the Tararua catchment (at the highest 25% flows).

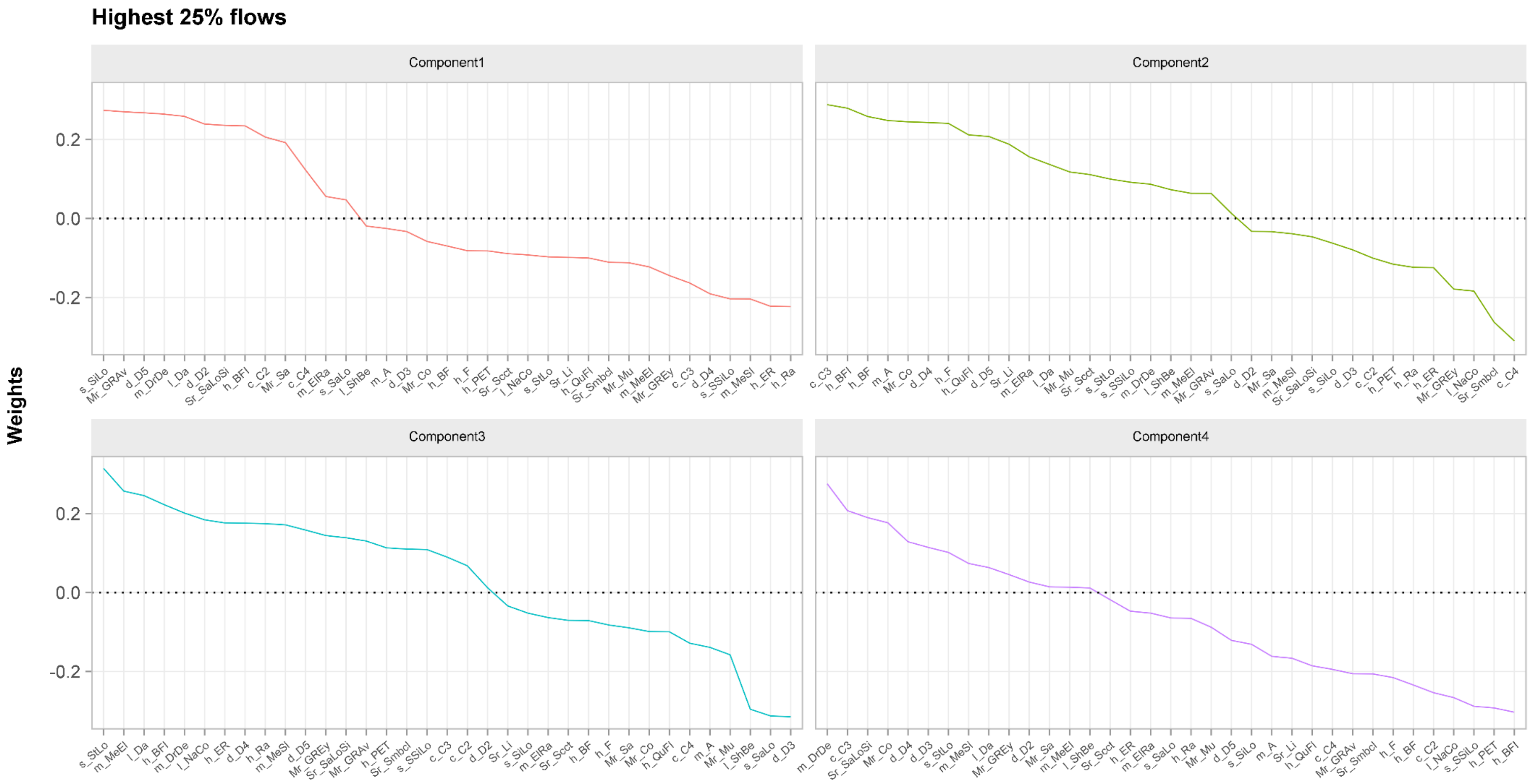

Fig. A.13. Loading weights (spectral) for component 1, component 2, component 3 and component 4 of the PLSR for the independent variables of the Tararua catchment (at the highest 25% flows).

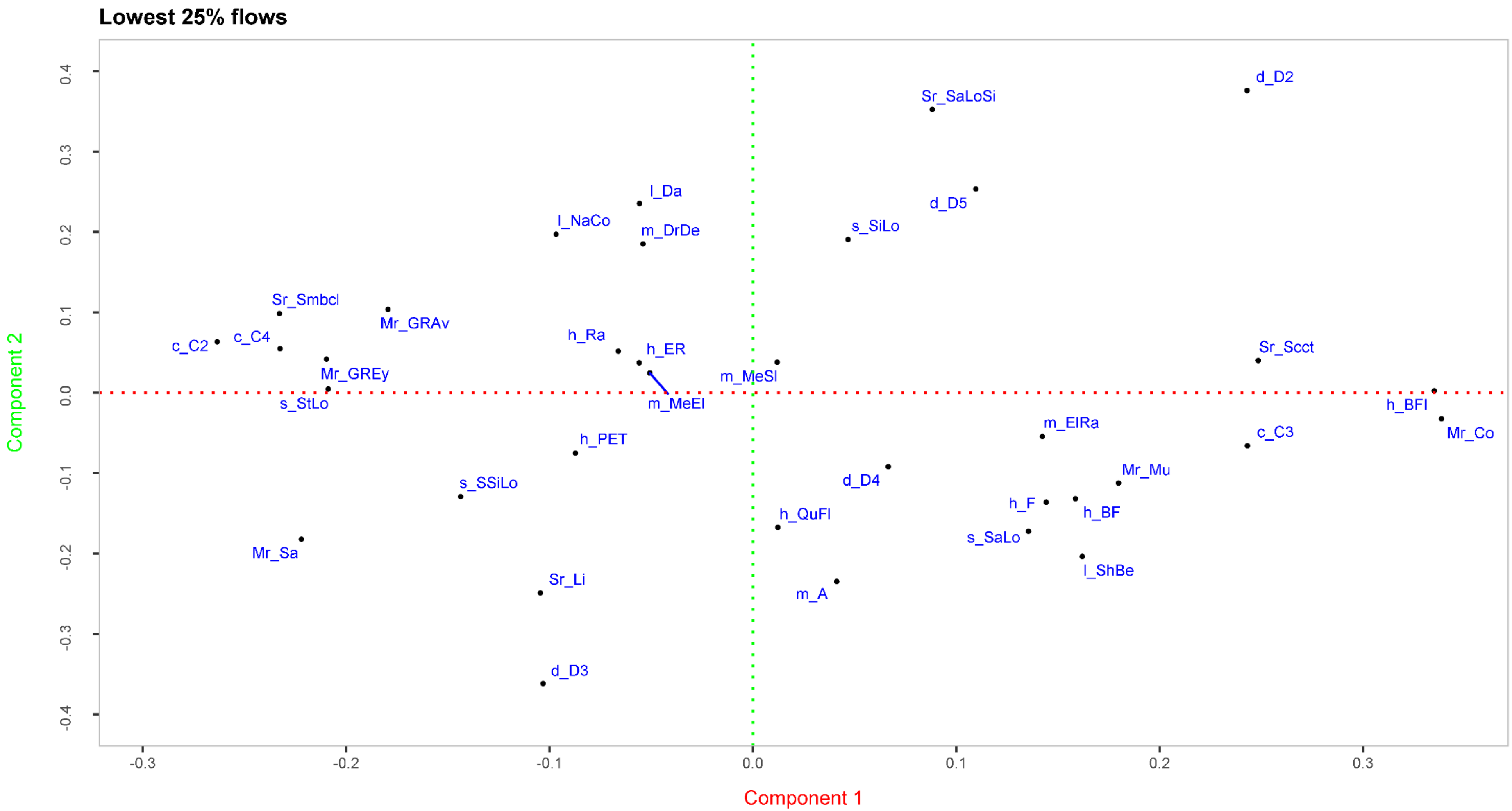

Fig. A.14. Loading weights (scatter) for the first and second PLSR components for the independent variables of the Tararua catchment (at the lowest 25% flows).

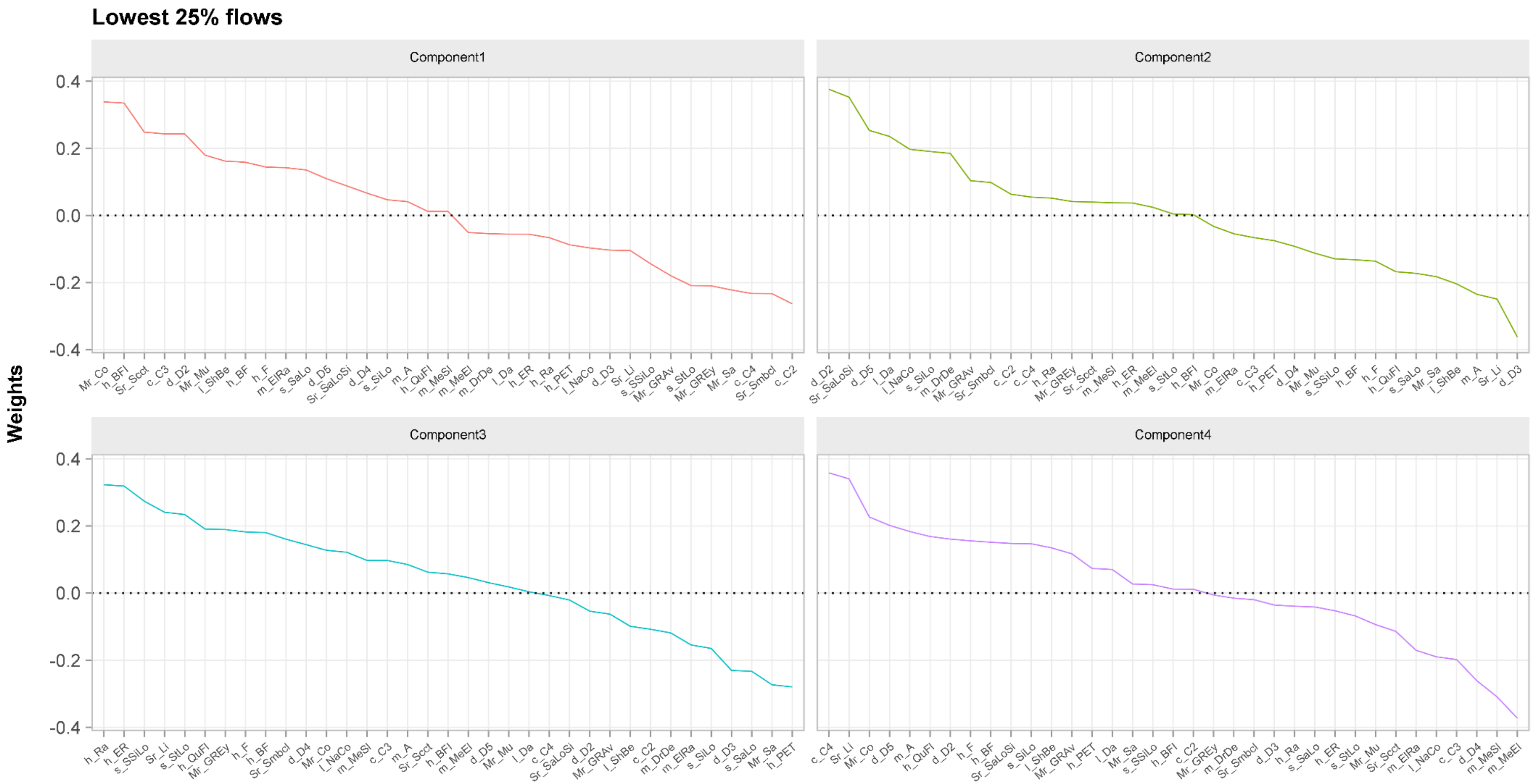

Fig. A.15. Loading weights (spectral) for component 1, component 2, component 3 and component 4 of the PLSR for the independent variables of the Tararua catchment (at the lowest 25% flows).

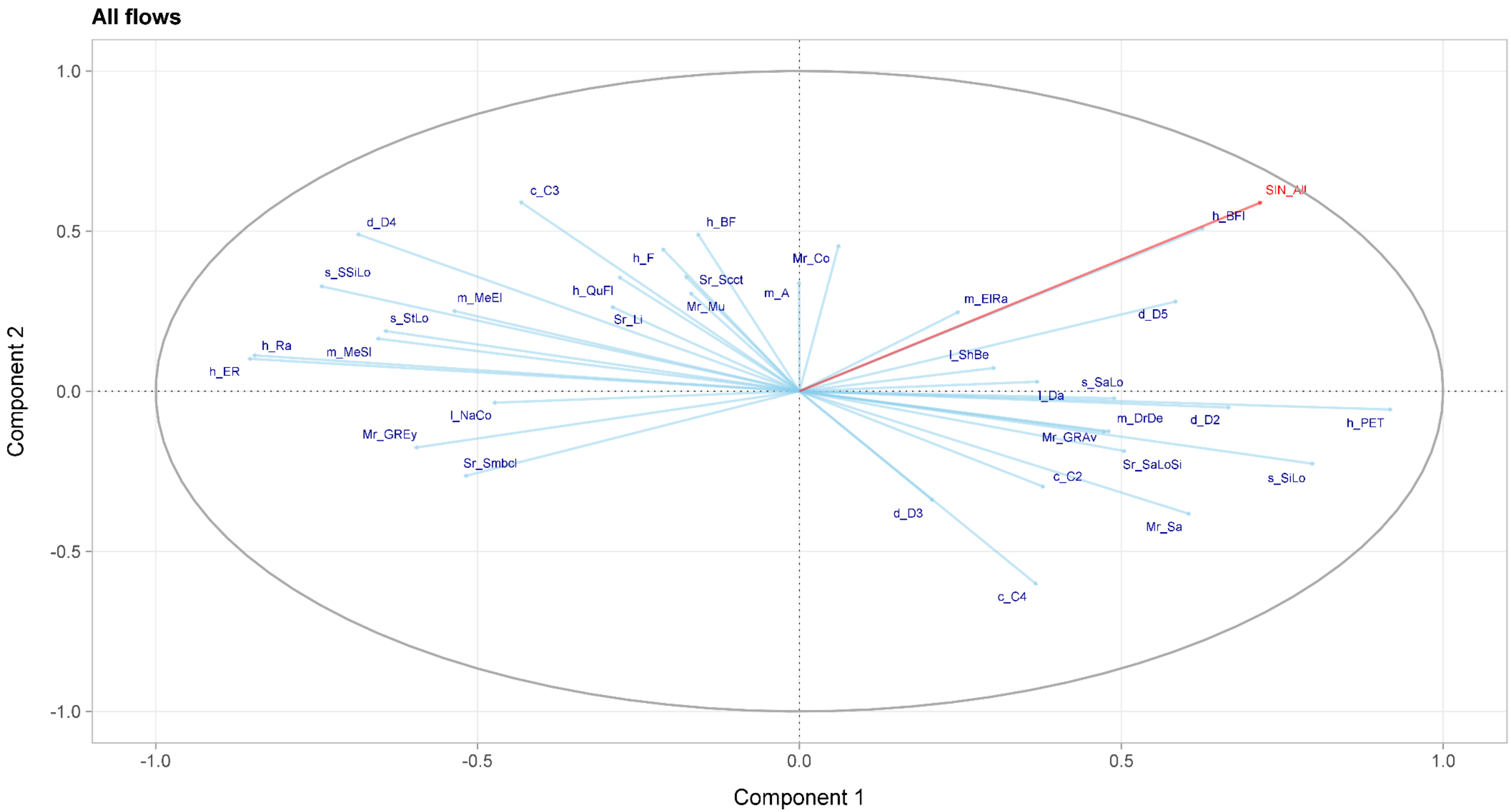

Fig. A.16. Loading correlations (scatter) for component 1and component 2 of the PLSR for the independent variables of the Tararua catchment (at all flows).

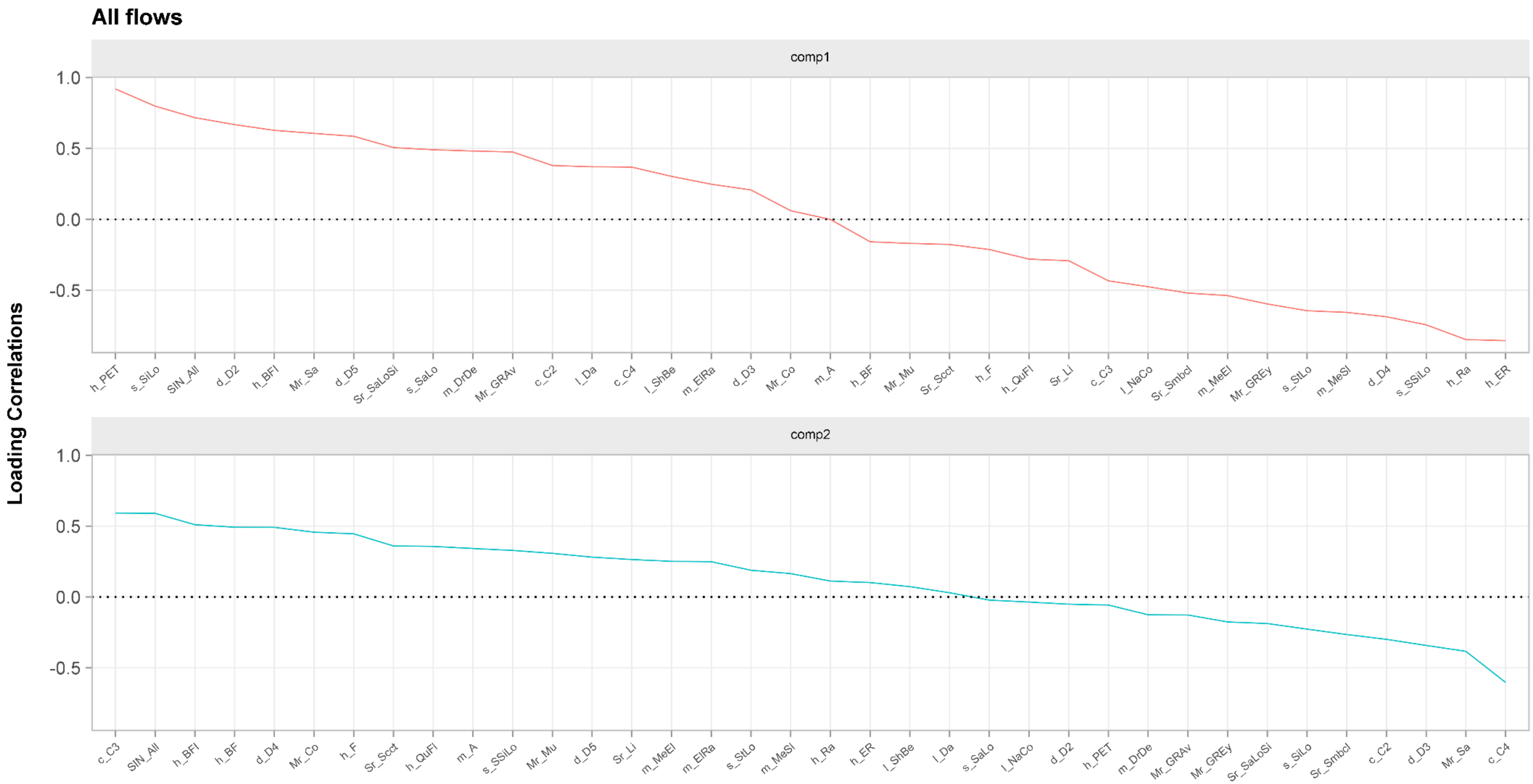

Fig. A.17. Loading correlations (spectral) for component 1and component 2 of the PLSR for the independent variables of the Tararua catchment (at all flows).

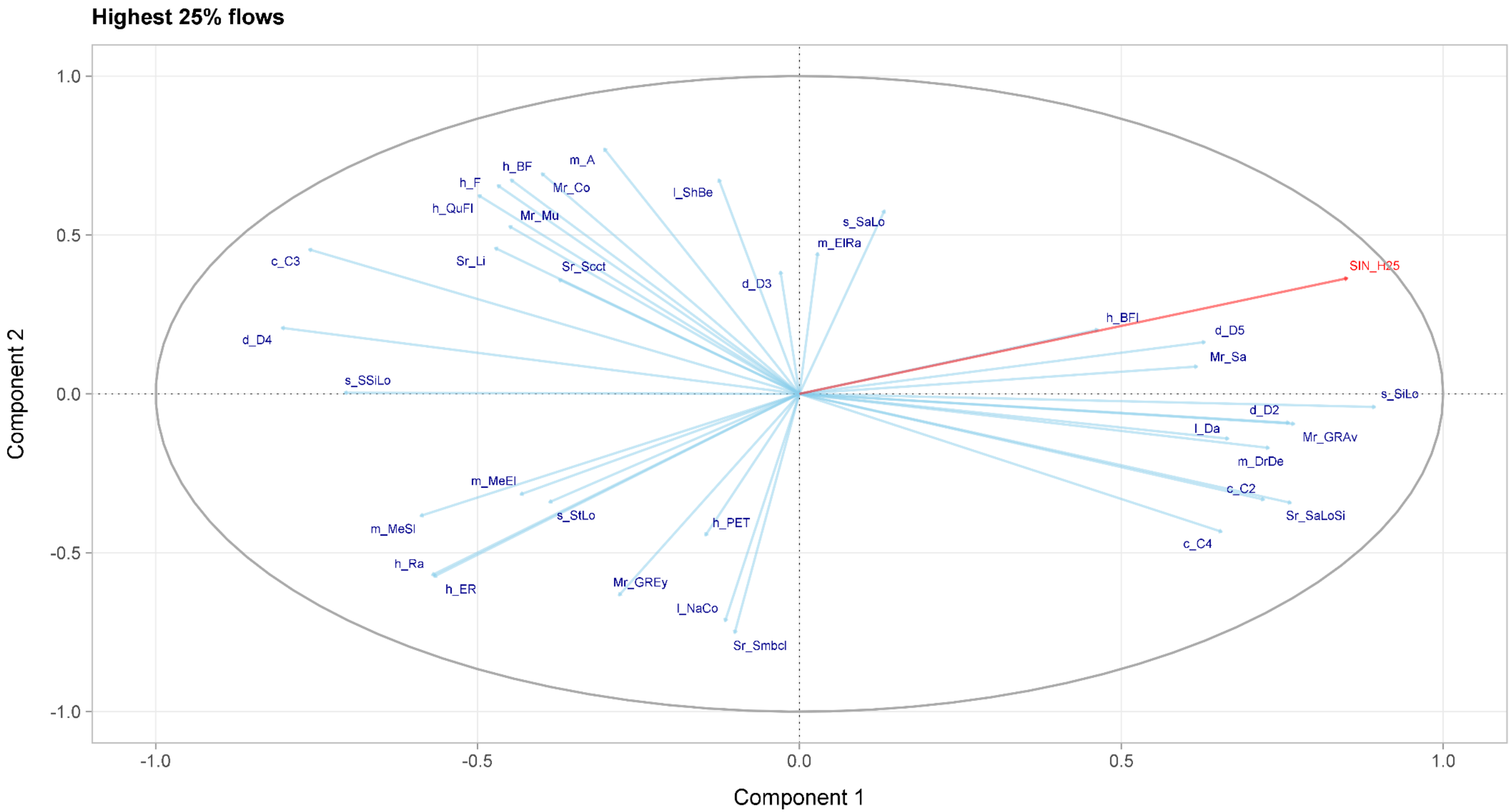

Fig. A.18. Loading correlations (scatter) for component 1and component 2 of the PLSR for the independent variables of the Tararua catchment (at the highest 25% flows).

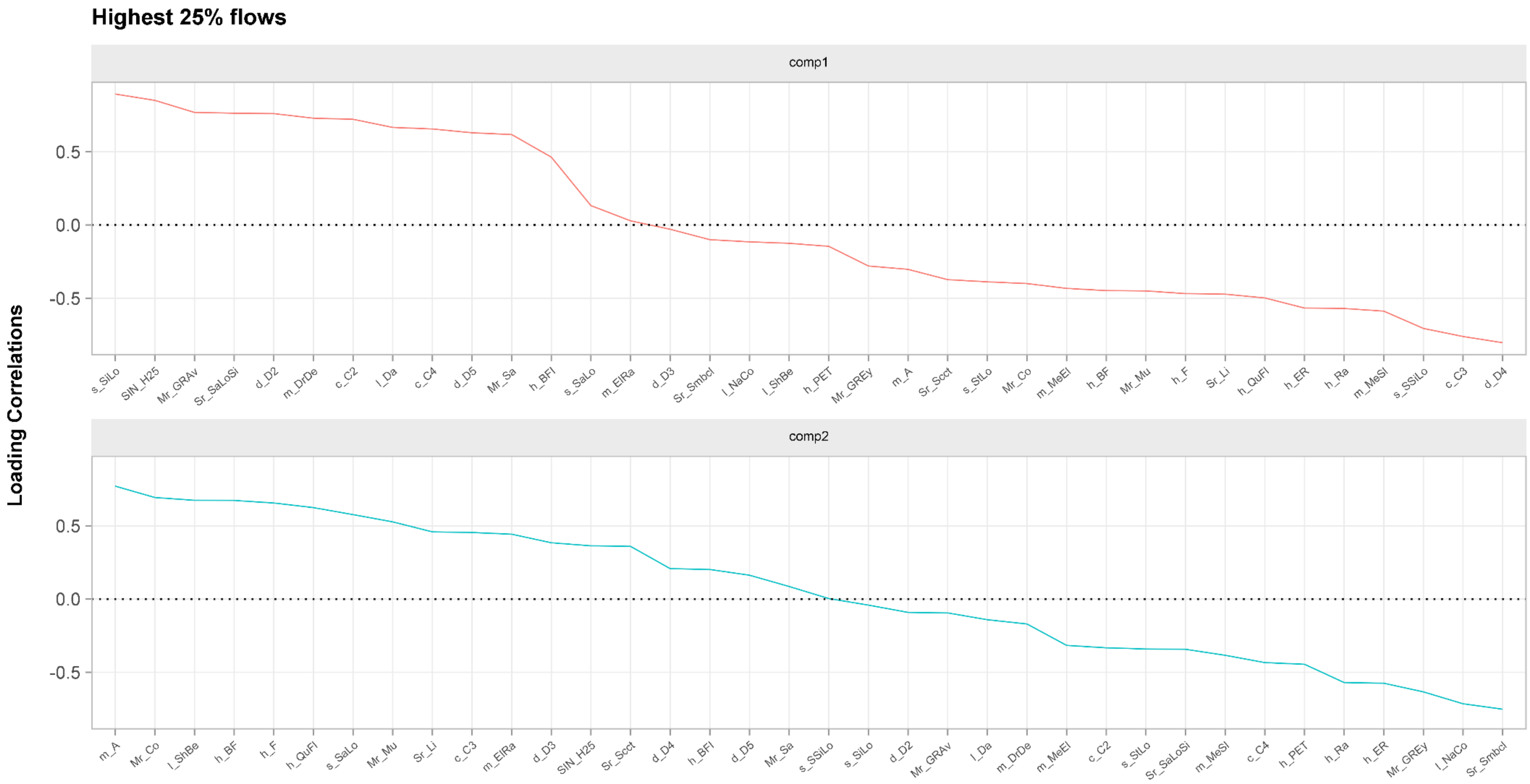

Fig. A.19. Loading correlations (spectral) for component 1and component 2 of the PLSR for the independent variables of the Tararua catchment (at the highest 25% flows).

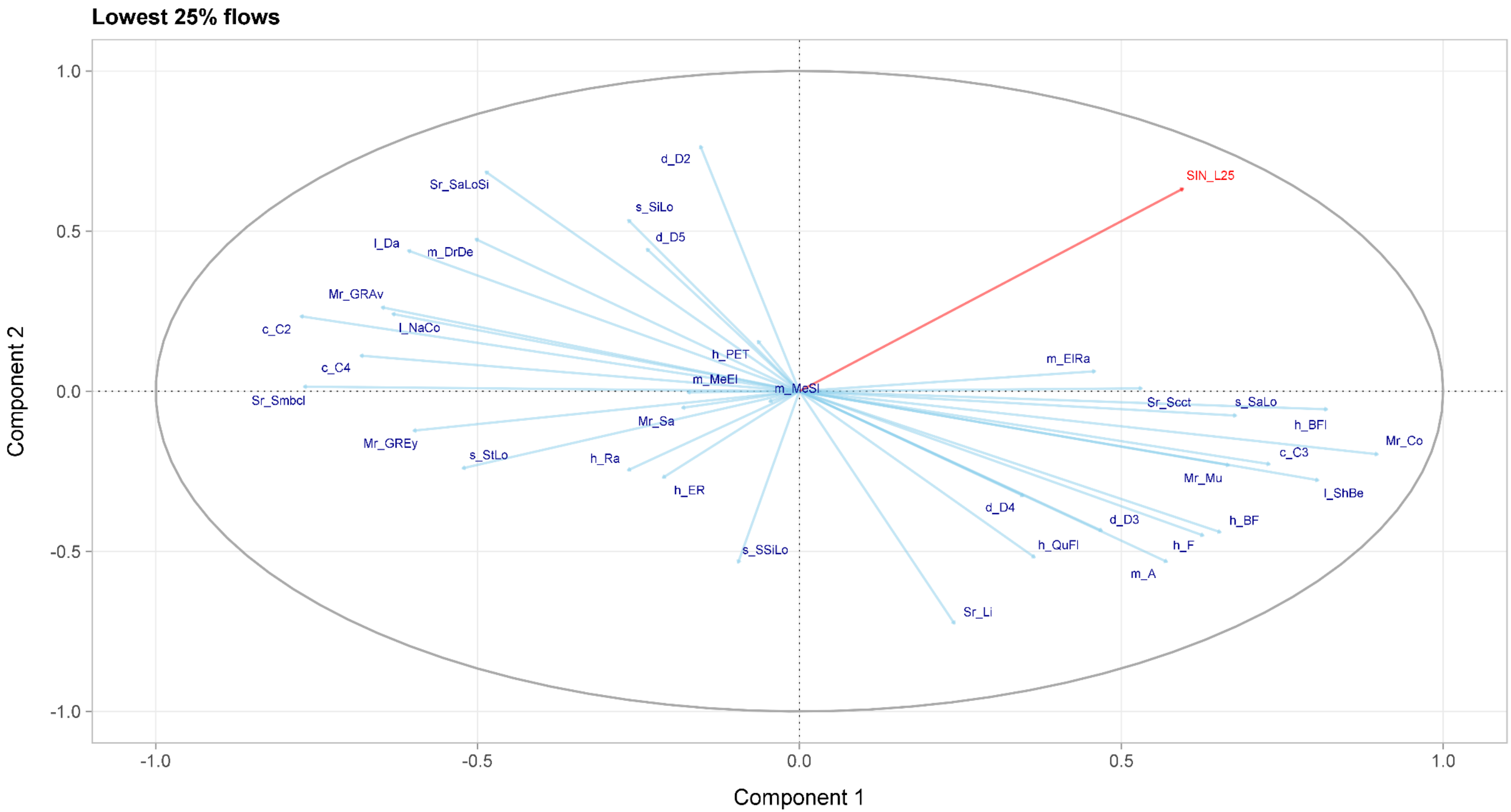

Fig. A.20. Loading correlations (scatter) for component 1and component 2 of the PLSR for the independent variables of the Tararua catchment (at the lowest 25% flows).

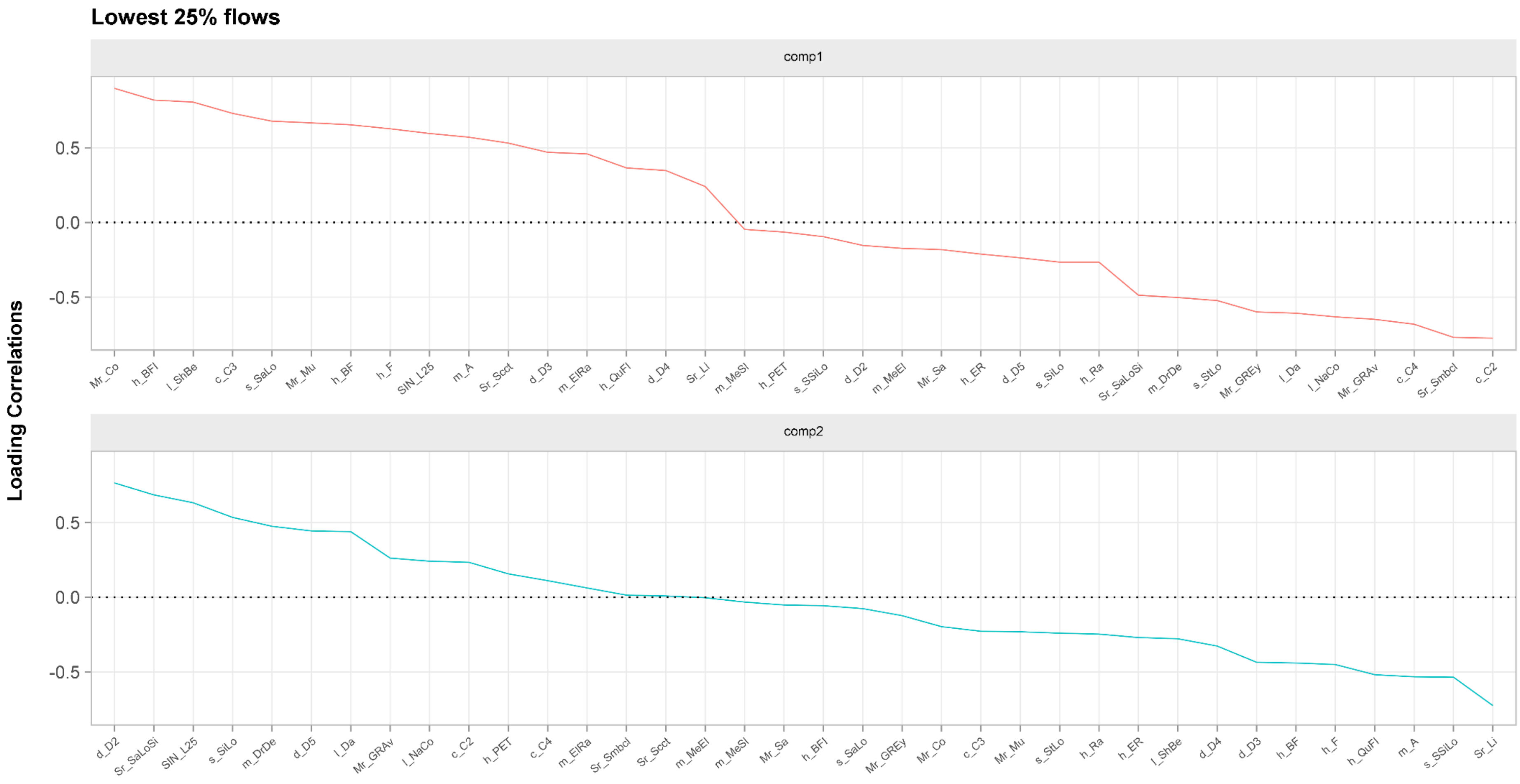

Fig. A.21. Loading correlations (spectral) for component 1and component 2 of the PLSR for the independent variables of the Tararua catchment (at the lowest 25% flows).

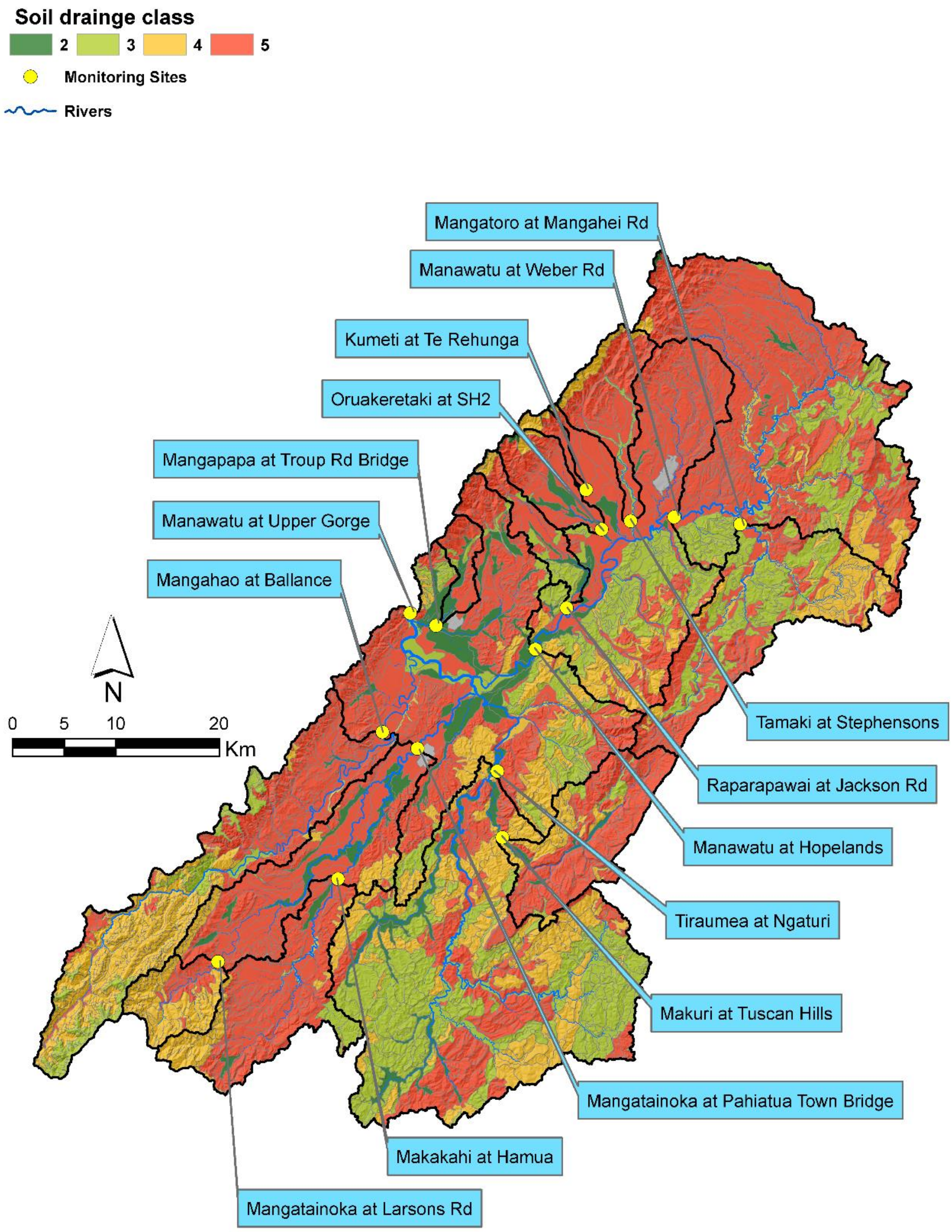

Fig. A.22. Soil drainage classes in the Tararua catchment.

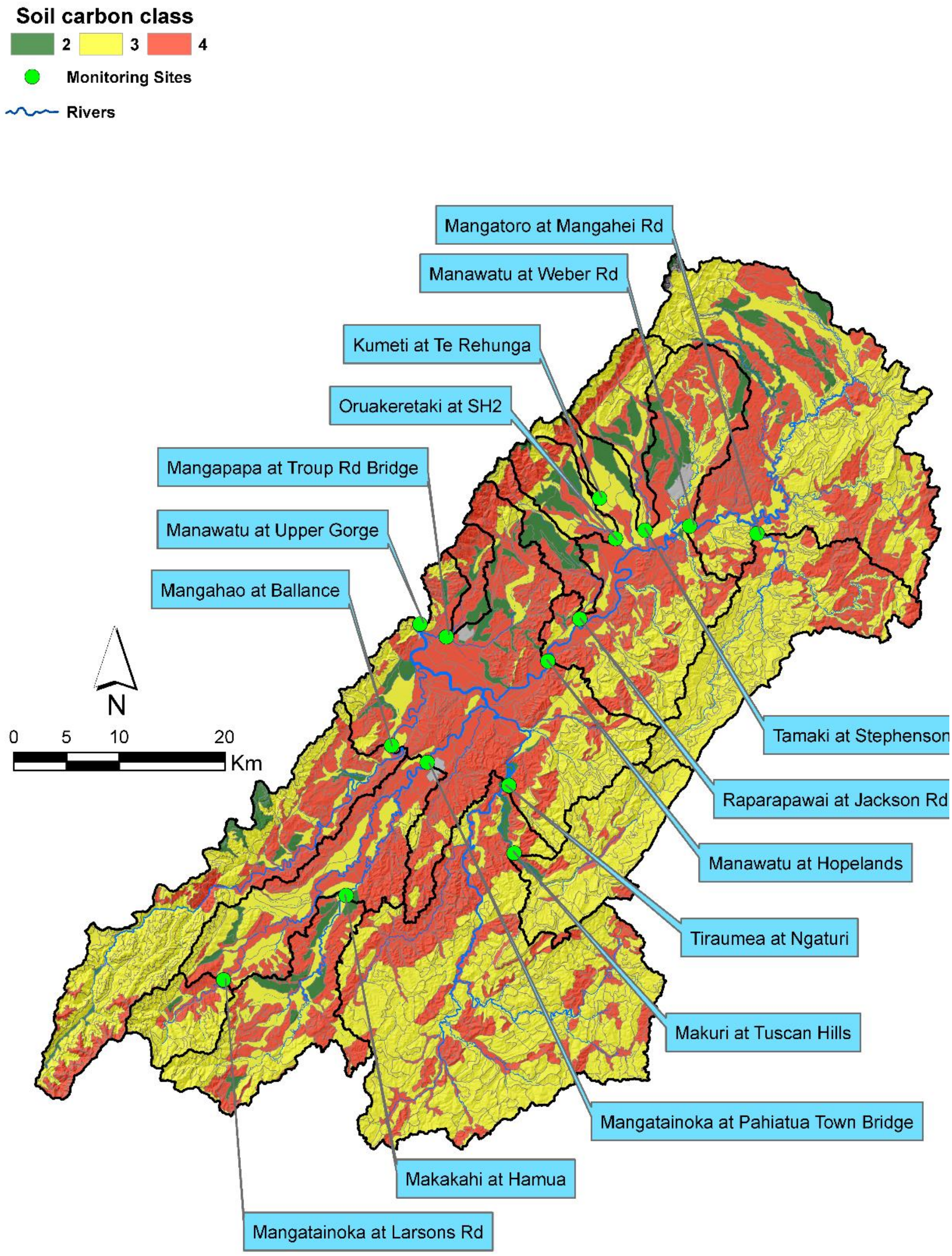

Fig. A.23. Soil carbon classes in the Tararua catchment.

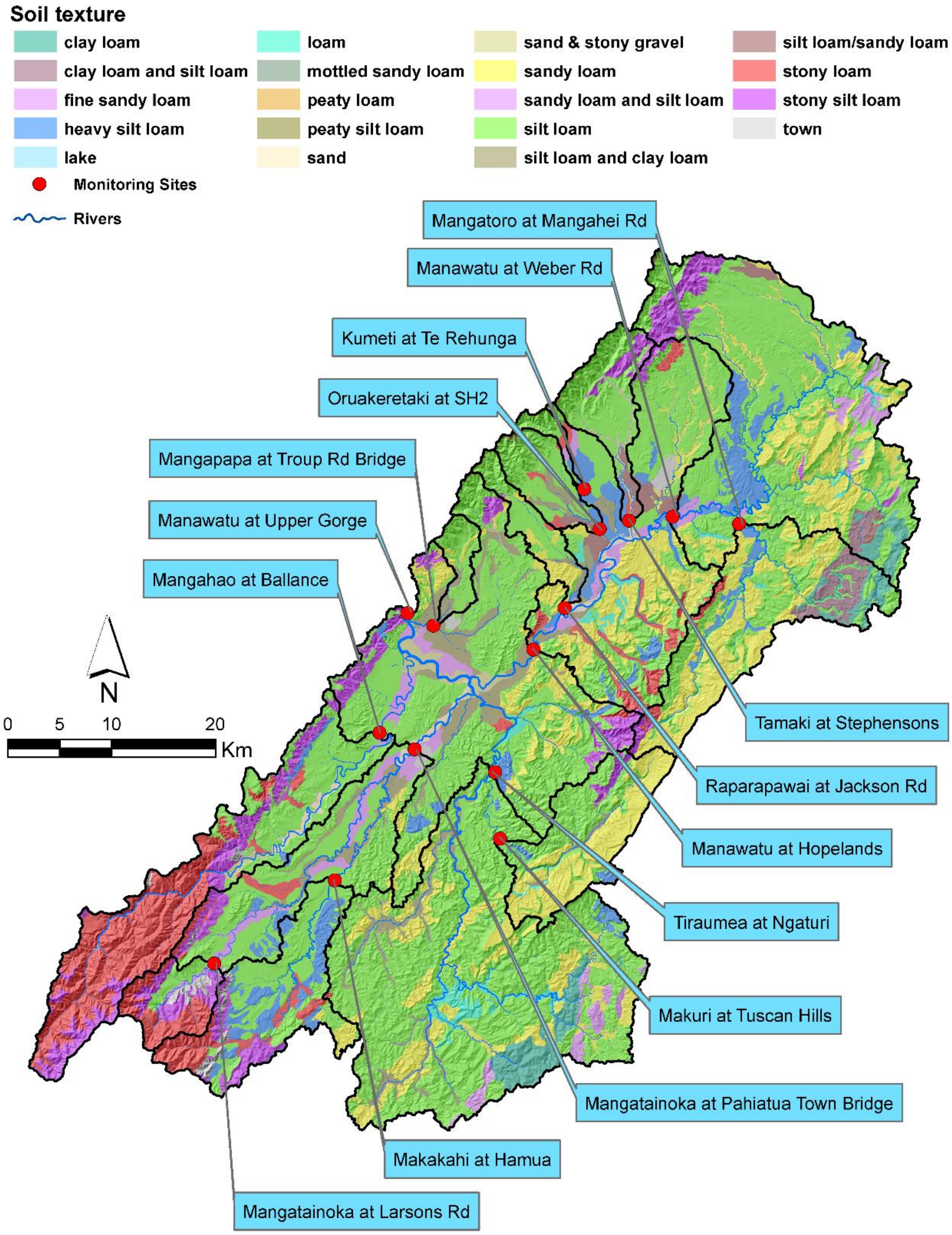

Fig. A.24. Soil textures in the Tararua catchment.

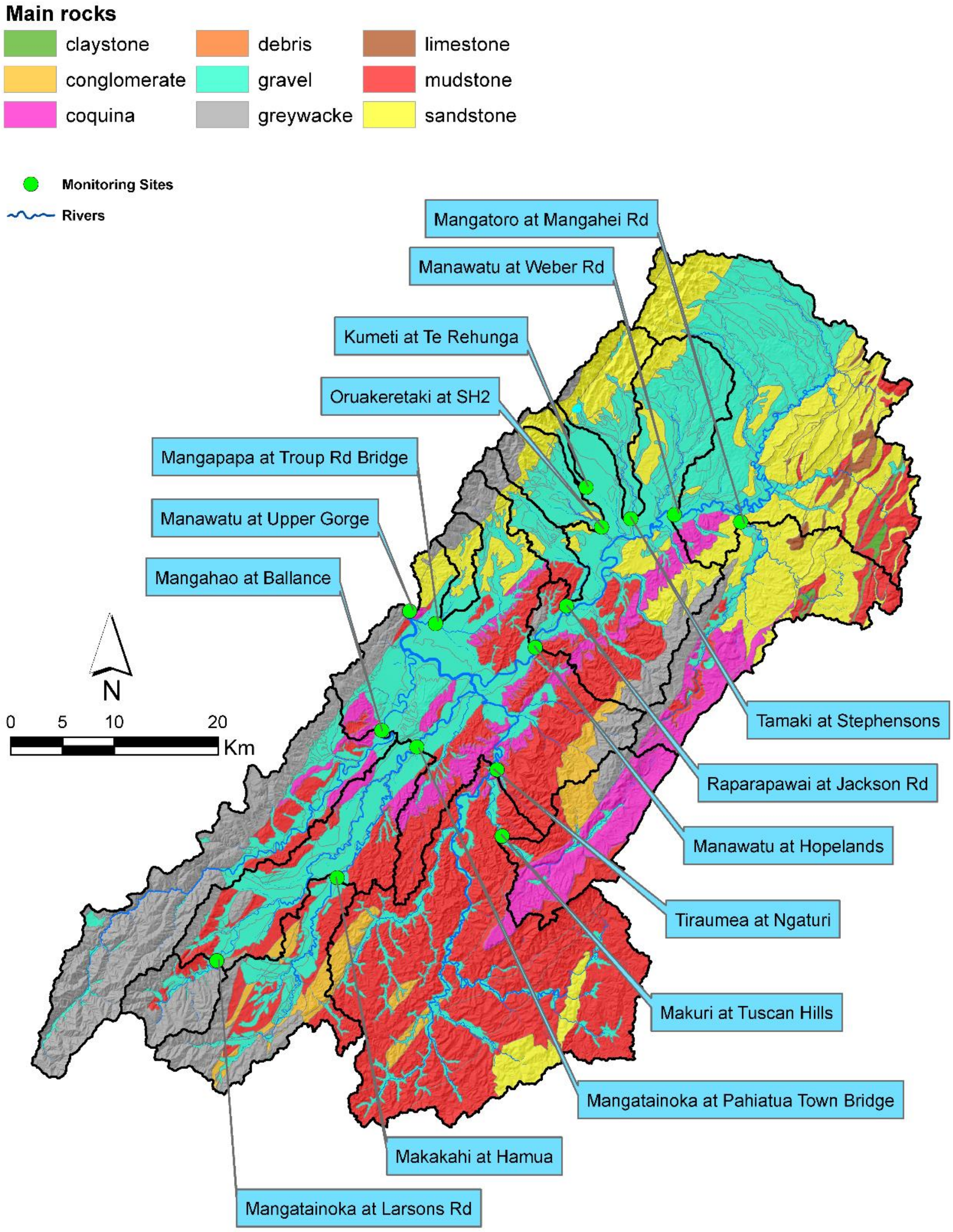

Fig. A.25. Main rocks in the Tararua catchment.

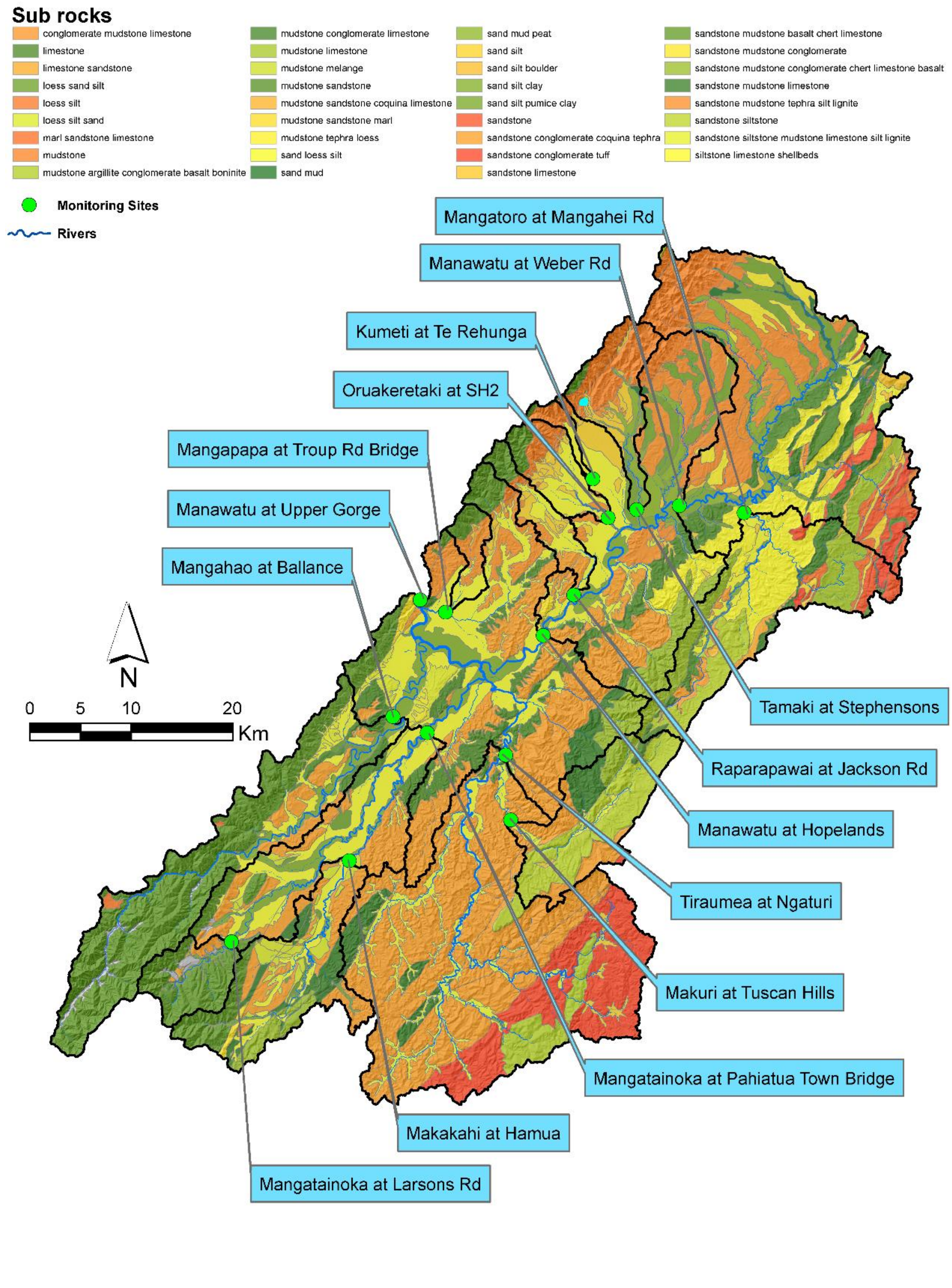

Fig. A.26. Sub rocks in the Tararua catchment.

Appendix B: Supporting materials for chapter 5

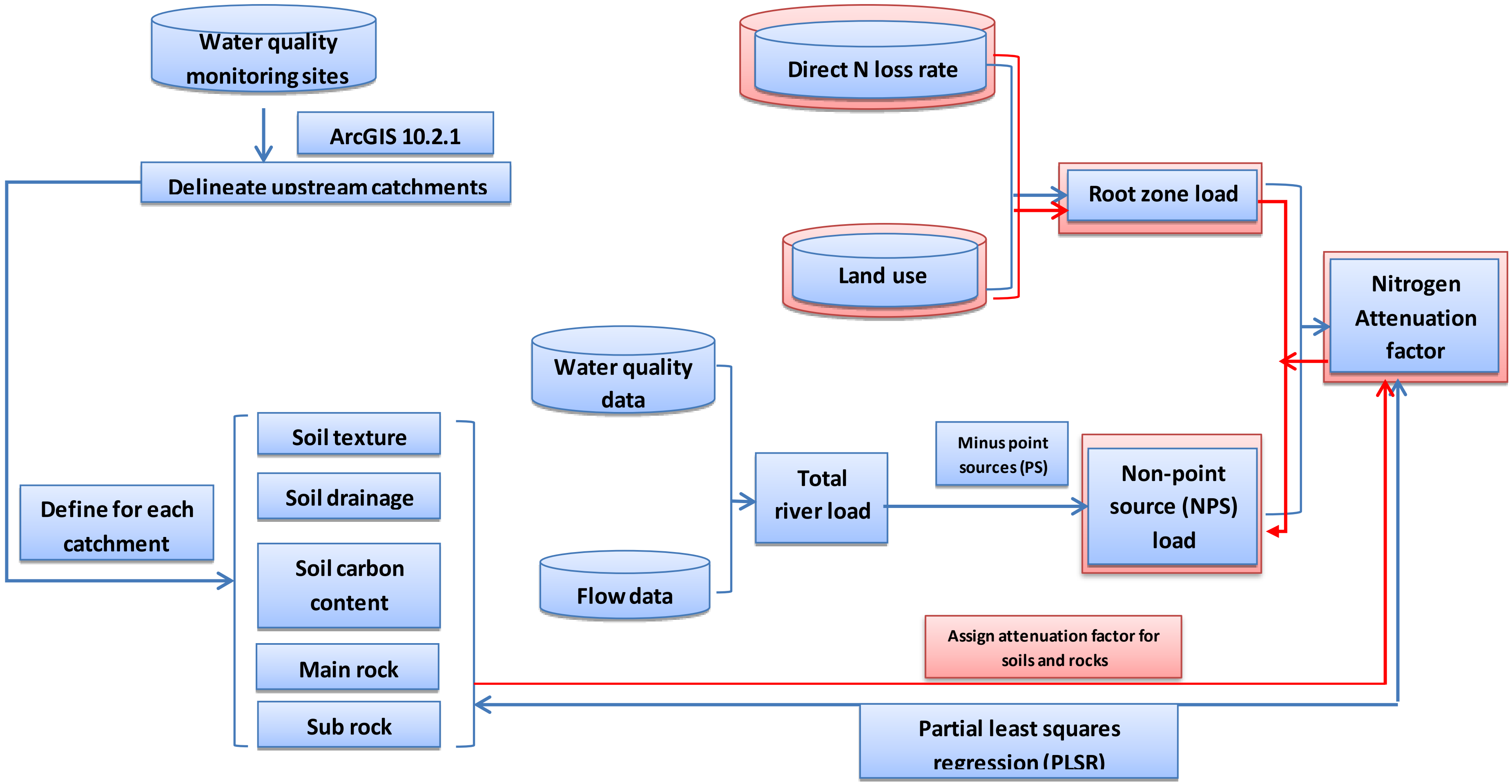

Fig. B.1. A flowchart for the data processing and analysis used to quantify the nitrogen attenuation factor in the Tararua and Rangitikei sub-catchments, Partial least squares regression analysis between nitrogen attenuation factor and catchment characteristics in the Tararua sub-catchment and predicting river load based on the nitrogen attenuation capacities for soils and rocks. The red colour used to indicate the data and analysis used for predicting river load.

Delta Method

To assess uncertainty in quantification of AF_N as a function of its two components, the $N_{Root\ zone}$ and $N_{river\ load}$ (Equation B.1), we used the delta method (Rice, 2007) to calculate the variance of log ($\frac{AF_N}{1- AF_N}$), as described below:

$$Var(G) = \sigma_X^2 \left(\frac{\partial g(\mu)}{\partial x}\right)^2 + \sigma_Y^2 \left(\frac{\partial g(\mu)}{\partial y}\right)^2 + 2\sigma_{XY} \left(\frac{\partial g(\mu)}{\partial x}\right) \left(\frac{\partial g(\mu)}{\partial y}\right) \qquad \text{(B.1)}$$

Where:

G = log $\frac{AF_N}{1- AF_N}$;

X = the root zone N leaching, $N_{Root\ zone}$;

Y = The river SIN load, $N_{river\ load}$;

σ_X and σ_y = standard error of the root zone N leaching, $N_{Root\ zone}$; and the river SIN load, $N_{river\ load}$, respectively.

In this study, we estimated and used the standard errors of root zone load, $N_{Root\ zone}$, and river SIN loads $N_{river\ load}$ to be 23% and 2%, respectively, in delta method calculation (Equation B.1) to assess uncertainty in AF_N for selected sites in both Tararua and Rangitikei catchments. The standard error in root zone N leaching $N_{Root\ zone}$ was based on the estimate by Ledgard and Waller (2001), and in river SIN loads $N_{river\ load}$ was based on the estimate by Elwan et al., (2018). The standard errors were calculated at the logit scale using the delta method, and used to calculate the 95% confidence interval at the logit scale. The boundaries of the confidence interval were then back-transformed to the original scale.

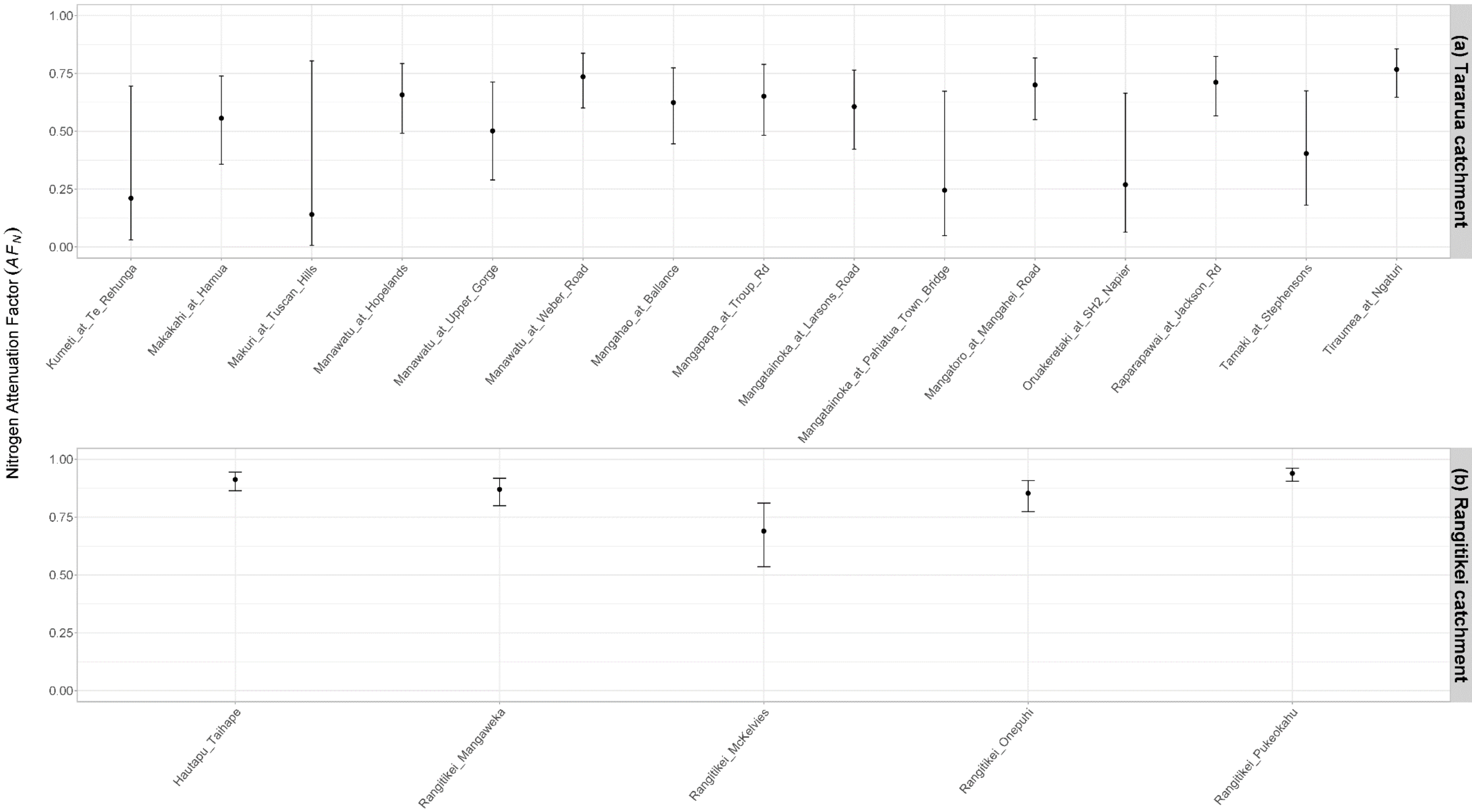

Fig. B.2. Nitrogen attenuation factor (AF_N) and bars represent the 95% confidence interval using the delta method (Rice, 2007) for the sites in (a) the Tararua catchment; and (b) the Rangitikei catchment.

Table B.1. Nitrogen attenuation factor, AF_N, and associated standard errors, SE, calculated using delta method for 15 and 5 sites in the Tararua and Rangitikei catchments, respectively.

Catchment	Sub-catchment	AF_N	SE
Tararua catchment	Kumeti_at_Te_Rehunga	0.21	0.18
	Makakahi_at_Hamua	0.56	0.10
	Makuri_at_Tuscan_Hills	0.14	0.20
	Manawatu_at_Hopelands	0.66	0.08
	Manawatu_at_Upper_Gorge	0.50	0.12
	Manawatu_at_Weber_Road	0.74	0.06
	Mangahao_at_Ballance	0.62	0.09
	Mangapapa_at_Troup_Rd	0.65	0.08
	Mangatainoka_at_Larsons_Road	0.61	0.09
	Mangatainoka_at_Pahiatua_Town_Bridge	0.24	0.17
	Mangatoro_at_Mangahei_Road	0.70	0.07
	Oruakeretaki_at_SH2_Napier	0.27	0.17
	Raparapawai_at_Jackson_Rd	0.71	0.07
	Tamaki_at_Stephensons	0.40	0.14
	Tiraumea_at_Ngaturi	0.77	0.05
Rangitikei catchment	Rangitikei_Pukeokahu	0.94	0.01
	Hautapu_Taihape	0.91	0.02
	Rangitikei_Mangaweka	0.87	0.03
	Rangitikei_Onepuhi	0.85	0.03
	Rangitikei_McKelvies	0.69	0.07

In-stream uptake

Singh et al., (2017) developed a simple model to estimate potential dissolved inorganic nitrogen uptake by periphyton in streams and rivers, as follows:

$$N_{up} = m * (f_n * AI * P) * (f_p * W) \quad \text{(B.2)}$$

Where:

$\boldsymbol{N_{up}}$	= In-stream N uptake (t yr^{-1});
$\boldsymbol{m}$	= Conversion factor;
$\boldsymbol{W}$	= Wetted area of stream/river bed (m^2);
$\boldsymbol{f_p}$	= Periphyton cover fraction (-);
$\boldsymbol{P}$	= Periphyton growth (mg C*hl-a*/m^2);
$\boldsymbol{AI}$	= Autotrophic Index (i.e. ratio of periphyton biomass "ash-free dry mass" to *Chl-a*) (-); and
$\boldsymbol{f_n}$	= Periphyton biomass N content fraction (-).

To estimate the average wetted area of streams and rivers bed (*W)* for each sub-catchment in the study areas, the channels length (m) were multiplied by the estimate of wetted perimeter (m) for stream orders larger than one (Singh et al., 2017). The average stream wetted perimeters for each stream order were based on field measurements conducted by HRC in the study areas. A value of 0.60 was used for the average periphyton cover fraction f_p based on long-term periphyton measurements in the study areas (Kilroy et al., 2016). *Chlorophyll-a* (*Chl-a*) measurements account mostly for the autotrophic growth *P* (periphyton algae) in streams and rivers (Biggs and Kilroy, 2000). A total of 600 – 800 mg *chl-a*/m^2 of potential periphyton growth (***P***) were estimated per year assuming a maximum of 3-4 accruals of 200 mg *chl-a*/m^2. The autotrophic index *AI* is the ratio of periphyton biomass (ash-free dray mass) to *Chl-a* measurements. According to Biggs and Kilroy (2000), algae-dominated periphyton communities include 1-2% of *Chl-a* resulting in *AI* values of 50 -100. Larger *AI* values (>400) indicate the influence of organic pollution (non-autotrophic matter) on the periphyton communities. There were neither measurements for periphyton biomass (ash-free dry mass), nor *AI* in the study areas. A sensitivity analysis, therefore, was done using *AI* that ranged from 50 to 400 to evaluate the potential amount of in-stream N uptake in the study areas. A value of 0.05 was used for periphyton biomass N content fraction (Kilroy, personnel communication, 2016).

Appendix C: R codes

```r
log10_whole <- df_whole %>%
  tidyr::gather("id", "value", 3:37) %>%
  dplyr::left_join(., check_normality_df_whole) %>%
  dplyr::group_by(id) %>%
  mutate(logvalue = ifelse(p.value < 0.05 & value != 0 , log10(value), value)) %>%
  mutate(log1pvalue = ifelse(p.value < 0.05 , log1p(value), value))

log10_whole_wide <- log10_whole %>%
  dplyr::select(site, SIN_All, id, logvalue) %>%
  tidyr::spread(id, logvalue)

write.csv(log10_whole_wide, "df_log10whole_2018.csv")

df_log10whole <-  read.csv("df_log10whole_2018.csv")
df_log10whole <-  df_log10whole[, -1]

y_whole <- as.matrix(df_log10whole[,2])
x_whole <- as.matrix(df_log10whole[,3:37])
plsr_whole <- mvr(y_whole  ~ x_whole ,
                  ncomp = 10,
                  method = "oscorespls" ,
                  validation = "LOO",
                  scale = T)
summary(plsr_whole)
plot(RMSEP(plsr_whole), legendpos = "topright")
plot(R2(plsr_whole))
CV_RMSEP_whole <-  RMSEP(plsr_whole)$val[1, 1, -1]

r2_whole <- R2(plsr_whole)$val[, , -1]
cumsum_y_whole <- 100 * drop(R2(plsr_whole, estimate = "train",
                                intercept = FALSE)$val)
cumsum_y_whole

individual_whole = cumsum_y_whole - lag(cumsum_y_whole, default = 0)
summary_pls_whole_csv <-  as.data.frame(cbind(individual_whole,
                                             cumsum_y_whole,
                                             CV_RMSEP_whole
                                             ))
coef_whole <-  as.data.frame(coef(plsr_whole, ncomp = 1:4))
names(coef_whole) <- c("Comp 1", "Comp 2", "Comp 3", "Comp 4")

#reference http://mevik.net/work/software/VIP.R
VIP <- function(object) {
  if (object$method != "oscorespls")
    stop("Only implemented for orthogonal scores algorithm.  Refit with 'method = \"oscorespls\"'")
  if (nrow(object$Yloadings) > 1)
    stop("Only implemented for single-response models")

  SS <- c(object$Yloadings)^2 * colSums(object$scores^2)
  Wnorm2 <- colSums(object$loading.weights^2)
  SSW <- sweep(object$loading.weights^2, 2, SS / Wnorm2, "*")
  sqrt(nrow(SSW) * apply(SSW, 1, cumsum) / cumsum(SS))
}
```

Fig. C.1. Part of the R code used in the data analysis for Chapter 3.

```r
Fwday
fort<-levels(as.factor(dataFIN5m$Fortnight))
Fwfort<-cbind(rep("Fw", 84), rep("Fortnightly", 84),rep(fort, each=6), rep(c("NO3" ,"SIN" ,"TN" , "DRP", "TP", "TSS"), 14), rep(0,84))
for (i in 1:length(Fwfort[,1])) {
  Fwfort[i,5]<-Fw(data=dataFIN5m[dataFIN5m$Fortnight==Fwfort[i,3],], meas=Fwfort[i,4])
}
Fwfort[1:10,]
mont<-levels(as.factor(dataFIN5m$Monthday))
Fwmont<-cbind(rep("Fw", 186), rep("Monthly", 186),rep(mont, each=6), rep(c("NO3" ,"SIN" ,"TN" , "DRP", "TP", "TSS"), 31), rep(0,186))
for (i in 1:length(Fwmont[,1])) {
  Fwmont[i,5]<-Fw(data=dataFIN5m[dataFIN5m$Monthday==Fwmont[i,3],], meas=Fwmont[i,4])
}
Fwmont[1:10,]

Fwdat<-rbind(Fwday,Fwfort,Fwmont)
summary(Fwdat)

RE <-function (data, meas) {
  qbar<-mean(data$Flow)
  lbar<-mean(data$Flow*data[,meas])
  sq2<-1/(length(data[,meas])-1)*sum((data$Flow-qbar)^2)
  slq<-1/(length(data[,meas])-1)*sum((data$Flow-qbar)*(data$Flow*data[,meas]-lbar))
  qt<-sum(dataFIN5m$Flow)
  qt*lbar/qbar*(1+(1/365)*(slq/(lbar*qbar)))/(1+(1/365)*(sq2/(qbar^2)))
}
days<-levels(as.factor(dataFIN5m$weekday))
REday<-cbind(rep("RE", 42), rep("weekly", 42),rep(days, each=6), rep(c("NO3" ,"SIN" ,"TN" , "DRP", "TP", "TSS"),7), rep(0,42))
for (i in 1:length(REday[,1])) {
  REday[i,5]<-RE(data=dataFIN5m[dataFIN5m$weekday==REday[i,3],],  meas=REday[i,4])
}
REday

fort<-levels(as.factor(dataFIN5m$Fortnight))
REfort<-cbind(rep("RE", 84), rep("Fortnightly", 84),rep(fort, each=6), rep(c("NO3" ,"SIN" ,"TN" , "DRP", "TP", "TSS"), 14), rep(0,84))
for (i in 1:length(REfort[,1])) {
  REfort[i,5]<-RE(data=dataFIN5m[dataFIN5m$Fortnight==REfort[i,3],], meas=REfort[i,4])
}
REfort[1:10,]

mont<-levels(as.factor(dataFIN5m$Monthday))
REmont<-cbind(rep("RE", 186), rep("Monthly", 186),rep(mont, each=6), rep(c("NO3" ,"SIN" ,"TN" , "DRP", "TP", "TSS"), 31), rep(0,186))
for (i in 1:length(REmont[,1])) {
  REmont[i,5]<-RE(data=dataFIN5m[dataFIN5m$Monthday==REmont[i,3],], meas=REmont[i,4])
}
REmont[1:10,]

REdat<-rbind(REday,REfort,REmont)
summary(REdat)
byquantile <-function (data, dat, n, meas) {
  dat$qflow<-(n+1) - as.integer(cut(dat$Flow, quantile(dat$Flow, probs=0:n/n, type = 5), include.lowest=TRUE))
  df1<-aggregate(Flow~qflow, data=dat, FUN=mean)
  df2<-merge(dat[, c("Date", "qflow")], data, by="Date")
  df3<-aggregate(df2[,meas]~df2$qflow, FUN=mean)
```

Fig. C.2. Part of the R code used in the data analysis for Chapter 4.

```r
                  Eketahuna_STP_at_Secondary_oxpond_waste,
                  Fonterra_Pahiatua_wastewater,
                  Norsewood_STP_at_oxpond_waste,
                  Ormondville_STP_at_2nd_oxpond_waste ,
                  Pahiatua_STP_at_Tertiary_oxpond_waste,
                  PPCS_Oringi_STP_at_oxpond_waste,
                  Woodville_STP_at_Secondary_oxpond_waste
  ) %>%
  dplyr::filter(Date > "2008-12-31") %>%
  dplyr::filter(Date < "2017-01-01")
ps_flow_2017_tararua_long <- ps_2017_flow_tararua %>%
  tidyr::gather("site", "flow", 2:10)
levels(ps_flow_2017_tararua_long$site)
ps_flow_2017_tararua_long$site <- factor(ps_flow_2017_tararua_long$site)
ggplot(ps_flow_2017_tararua_long, aes (x = Date, y = flow)) +
  geom_line()+
  facet_wrap(~site)
ps_flow_2017_tararua_percentile <- ps_flow_2017_tararua_long %>%
  dplyr::mutate(year =     factor(format(Date, "%Y")),
                month =    factor(format(Date, "%m")),
                season =ifelse(month%in%c("06", "07", "08"), "Winter",
                               ifelse(month%in%c("09", "10", "11"), "Spring",
                                      ifelse(month%in%c("12", "01", "02"), "Summer",
                                             ifelse(month%in%c("03", "04", "05"), "Autumn", NA)))),
                season = factor(season, levels=c("Summer", "Autumn", "Winter", "Spring"))) %>%
  dplyr::group_by(site) %>%
  dplyr::mutate(flowdeciles_10 = 11 - as.integer(cut(flow,
                                                     quantile(flow,
                                                              probs=0:10/10,
                                                              type = 5,
                                                              na.rm = T),
                                                     include.lowest=TRUE)),
                flowdeciles_20 = 21 - as.integer(cut(flow,
                                                     quantile(flow,
                                                              probs=0:20/20,
                                                              type = 5,
                                                              na.rm = T),
                                                     include.lowest=TRUE)),
                flowdeciles_10 = factor(flowdeciles_10, levels = c("1","2", "3", "4", "5", "6", "7", "8", "9", "10")),
                flowdeciles_20 = factor(flowdeciles_20, levels = c("1","2", "3", "4", "5", "6", "7", "8", "9", "10",
                                                                    "11", "12", "13", "14", "15", "16", "17", "18", "19", "20")),
                highlow_20per = ifelse(flowdeciles_10%in%c("1", "2"), "High_Flows",
                                       ifelse(flowdeciles_10%in%c("9", "10"), "Low_Flows", NA)),
                highlow_25per = ifelse(flowdeciles_20%in%c("1", "2", "3", "4", "5"), "High_Flows",
                                       ifelse(flowdeciles_20%in%c("16","17", "18", "19", "20"), "Low_Flows", NA)),
                highlow_20per = factor(highlow_20per, levels = c("Low_Flows", "High_Flows")),
                highlow_25per = factor(highlow_25per, levels = c("Low_Flows", "High_Flows")),
                fixed_flow_m3_d = ifelse(site == "Dannevirke_STP_at_microfiltered_oxpond" ,  3082.00,
                                         ifelse(site == "DB_Breweries_at_Industrial_wastewater" ,  389.80,
                                                ifelse(site == "Eketahuna_STP_at_Secondary_oxpond_waste" ,  336.00,
                                                       ifelse(site == "Fonterra_Pahiatua_wastewater" ,  1014.00,
                                                              ifelse(site == "Norsewood_STP_at_oxpond_waste" ,  50.00,
                                                                     ifelse(site == "Ormondville_STP_at_2nd_oxpond_waste" , 100.00,
```

Fig. C.3. Part of the R code used in the data analysis for Chapter 5.

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STATEMENT OF CONTRIBUTION
TO DOCTORAL THESIS CONTAINING PUBLICATIONS

(To appear at the end of each thesis chapter/section/appendix submitted as an article/paper or collected as an appendix at the end of the thesis)

We, the candidate and the candidate's Principal Supervisor, certify that all co-authors have consented to their work being included in the thesis and they have accepted the candidate's contribution as indicated below in the *Statement of Originality*.

Name of Candidate: Ahmed Elwan

Name/Title of Principal Supervisor: Dr. Ranvir Singh

Name of Published Research Output and full reference:

Elwan, A., Singh, R., Patterson, M., Roygard, J., Horne, D., Clothier, B., & Jones, G. (2018). Influence of sampling frequency and load calculation methods on quantification of annual river nutrient and suspended solids loads. Environmental Monitoring and Assessment, 190(2). doi:10.1007/s10661-017-6444-y

In which Chapter is the Published Work: Chapter 4

Please indicate either:

- The percentage of the Published Work that was contributed by the candidate: 90%

  and / or

- Describe the contribution that the candidate has made to the Published Work:

  Ahmed carried out the data analysis, results and discussion, and drafted this article. His co-authors (main- and co-supervisors) contributed with their comments and suggestions on the draft article, interpretations of its results and discussion. Ahmed handled the submission, review and publication process of the article.

Ahmed Elwan Digitally signed by Ahmed Elwan Date: 2018.07.23 09:26:50 +12'00' | 23/07/2018

Candidate's Signature | Date

Ranvir Singh Digitally signed by Ranvir Singh Date: 2018.07.23 10:13:12 +12'00' | 23/07/2018

Principal Supervisor's signature | Date