Physiographics of Southland

Part 1: Delineation of key drivers of regional hydrochemistry and water quality

Technical Report

June 2016

Rissmann, C., Rodway, E., Beyer, M., Hodgetts, J., Snelder, T[a]., Pearson, L., Killick, M., Marapara, T.R., Akbaripasand, A., Hodson, R., Dare, J., Millar, R., Ellis, T., Lawton, M., Ward, N., Hughes, B[a]., Wilson, K[b]., McMecking, J., Horton, T[c]., May, D., Kees, L.

[a]LWP Ltd, [b]Landpro Ltd, [c]Geological Sciences, University of Canterbury

Publication No. 2016/3

Version 2 - Preliminary

Document Quality Control

Environment Southland Division:	Environmental Information		
Report reference:	Title: Physiographics of Southland Part 1: Delineation of key drivers of regional hydrochemistry and water quality	No: 2016/3	
Prepared by:	Rissmann, C., Rodway, E., Beyer, M., Hodgetts, J., R., Snelder, T., Pearson, L., Killick, M., Marapara, T. R., Akbaripasand, A., Hodson, R., Dare, J., Millar, R., Ellis, T., Lawton, M., Ward, N., Hughes B., Wilson K., McMecking, J., Horton, T., May, D., Kees, L.		
Illustrations by:	Hodgetts, J.	**Maps produced by:**	Rodway, E., Beyer, M.
Reviewed by:	Peter Almond[1], Troy Baisden[2], Vincent Bidwell[3], Chris Daughney[2], Bill Dyck[4], Allan Hewitt[5], Clive Howard-Williams[6], Scott Larned[6], Matthew Leybourne[7], Mike Scarsbrook[8], Hanspeter Schreier[9], Ranvir Singh[10], Trevor Webb[5], Jenny Webster-Brown[11]; Southland Science Technical Advisory Group[12]. 1. Soils and Physical Sciences, Lincoln University 2. GNS Science 3. Vincent Bidwell Consulting 4. Bill Dyck Ltd 5. Landcare Research 6. NIWA 7. Department of Earth Sciences, Laurentian University 8. Dairy New Zealand 9. Professor Emeritus, Land and Water Systems, University of British Columbia 10. Massey University, Institute of Natural Resources 11. Waterways Centre for Freshwater Management, University of Canterbury and Lincoln University 12. Southland Science Technical Advisory Group comprised of National and International Experts advising on the Southland Science Programme. Members: Dr Clive Howard-Williams, NIWA; Dr Chris Daughney, GNS; Dr Murray Close, ESR; Dr Cath Moore, GNS/ESR; Dr Liz Wedderburn, AgResearch; Prof. Jenny Webster-Brown, University of Canterbury; Associate Prof. Peter Almond, Lincoln University; Dr Mike Scarsbrook, DairyNZ; Dr Vince Bidwell (independent consultant); Bill Dyck, Envirolink Coordinator.		
Approved for issue by:	Graham Sevicke-Jones Director, Science and Information		
Date issued:	1 June 2016	Project Code:	4065.1446

Document History

Version: 1	**Status:** Preliminary
Date: June 2016	**Doc ID:**
Disclaimer:	This report has been prepared in good faith within time and budgetary limits. Due to time constraints we have not been able to incorporate all review feedback. These limitations will be addressed in a later review and a subsequent version published.

Version: 2	**Status:** Preliminary
Date: November 2016	**Doc ID:**
Notes:	Text and figure amended on page 15 to reflect the fact that the previous Physiographics of Southland Part 2 and Part 3 reports have been combined into a new single Part 2 report.
Disclaimer:	This report has been prepared in good faith within time and budgetary limits. Due to time constraints we have not been able to incorporate all review feedback. These limitations will be addressed in a later review and a subsequent version published.

Disclaimer

Environment Southland uses reasonable endeavours but does not warrant that this information is current, complete or accurate. Professional or specialist advice should be obtained before taking or refraining from taking any action on the basis of this information. To the extent permitted by law, Environment Southland will not be liable for any loss, liability or costs suffered or incurred as a result of any reliance placed on this information.

Citation of documents should be in the form:

Physiographics of Southland (2016). *Part 1: Delineation of key drivers of regional hydrochemistry and water quality.*
Environment Southland publication number: 2016/3
ISBN: 978-0-909043-16-2 (online)

Physiographics of Southland (2016): *Development and application of a classification system for managing land use effects on water quality in Southland*.
Environment Southland publication number: 2016/11
ISBN: 978-0-909043-17-9 (online)

Abstract

The key aim of this work was to better understand and estimate spatial variation in freshwater hydrochemistry at a regional scale in Southland, New Zealand using a physiographic approach. We developed a semi-quantitative, mechanistic conceptual model to estimate the hydrochemical variation in ground- and surface waters and shallow, soil influenced groundwater on the basis of four key drivers: (i) precipitation source; (ii) recharge mechanism and water source; (iii) combined soil and geological redox potential, and; (iv) the combination of geomorphic setting and substrate (rock or biological sediment) composition. We applied a multi-element, multi-isotope approach to 28,548 individual samples to identify critical characteristics of existing spatial frameworks (for soil, geology, topography, hydrology and hydrogeology) to resolve key spatial drivers over the hydrochemical variation of surface water and shallow, soil influenced groundwater. The model was validated through stratification of hydrochemical data using maps spatially depicting variance in key drivers, and independent empirical modelling. Empirical testing indicated a strong estimation capacity for surface water hydrochemistry, but was weaker for groundwater. Nonetheless, the patterns of hydrochemical response for groundwater were still consistent with the model. Furthermore, given a regional, median base flow index of 0.47 the strong performance of the model for surface water indicates the characterisation of young, soil zone influenced groundwater across Southland is robust. We conclude that the conceptual model is a sound platform for understanding and explaining the spatial controls over hydrochemistry outcomes in Southland. This work provides a spatially resolved platform for the development of a risk based framework for regional landuse. Future work will look at the use of the key drivers as a basis for modelling of transient water and nutrient flux.

Executive Summary

Why is the delineation of key drivers of hydrochemistry important?

The controls over and signatures of Southland's freshwater were studied to help understand the setting and suite of key drivers that govern regional scale variation in freshwater hydrochemistry, including water quality. Specifically, this work focuses on characterising the controls (key drivers) over surface and shallow soil zone influenced groundwater composition based on a physiographic approach. It makes no attempt to estimate exact compositions but rather estimate general trends, magnitudes and patterns in regional freshwater composition. Further, this study makes no attempt to theorise the composition and/or water quality of deeper groundwaters associated with semi-confined or confined aquifers that are poorly coupled to the soil zone (Figure 1). The latter is an important frame of reference for this work as surface water is by definition a mix of soil water and groundwater drainage. The ability to estimate surface water composition is therefore considered a robust test of the performance of our approach.

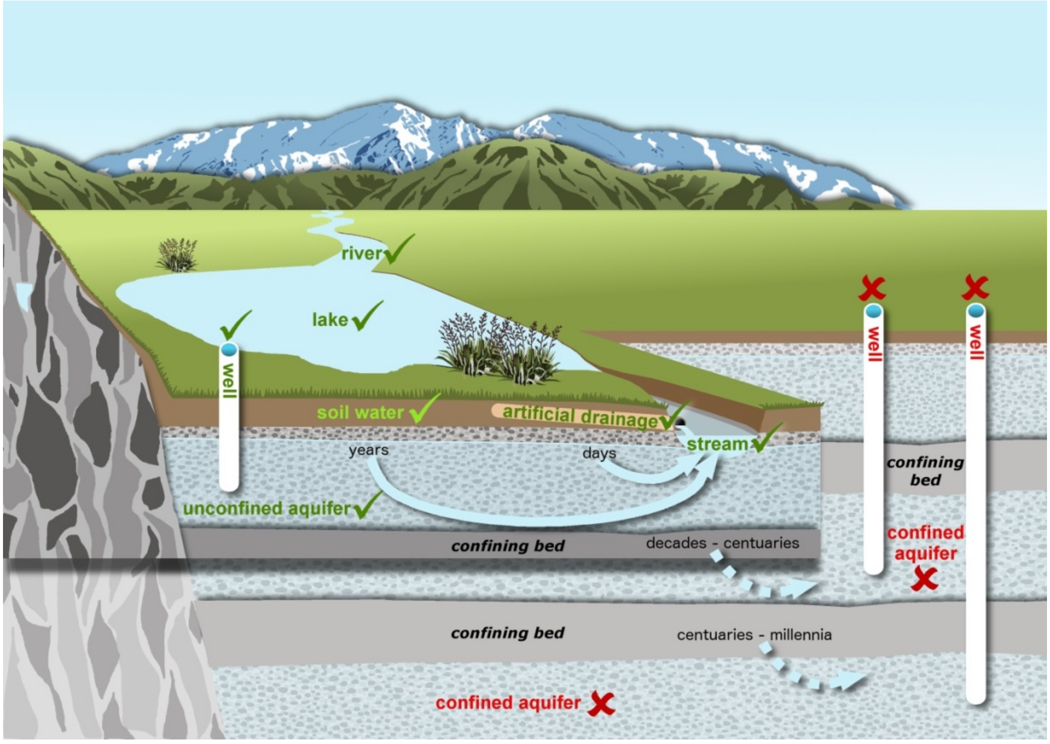

Figure 1: Diagram depicting what constitutes shallow, hydrologically connected ground- and surface water in this study (green ticks are included, red crosses are excluded).

How were the key drivers delineated?

To identify and explain the drivers of spatial variation, data for precipitation (rain, hail and snow), soil, soil water, ground- and surface water were analysed and cross-referenced against existing spatial frameworks of topography, geomorphology, hydrology, hydrogeology and soils. This included classifying waters with common origins and identification of the controls or 'drivers' over hydrochemical variation.

The drivers specific to the Southland context were identified as: precipitation source and composition; recharge mechanism(s) and water source; geomorphic setting and substrate (rock and biological sediments including soils) composition, and; redox control (combined soil zone and geological reduction potential (CRP)). The drivers were then mapped, which when combined, allowed for estimation of spatial variability in regional hydrochemistry of surface and local soil zone influenced groundwaters (Figure 2).

The conceptual model is defined as a semi-quantitative, mechanistic model[1] that aims to simulate hydrochemical variation in surface water and young, soil influenced groundwater at any point in the landscape. Accordingly, this model operates across multiple scales, for example regional, low and high order drainage basin or river catchments.

We consider the ability to approximate expected surface water composition the best test of the performance of the method as surface waters are inherently a mix of soil water and young hydrologically connected groundwater. Accurate estimation of surface water composition infers a sound characterisation of the drivers of variation in soil water and shallow hydrologically connected groundwater.

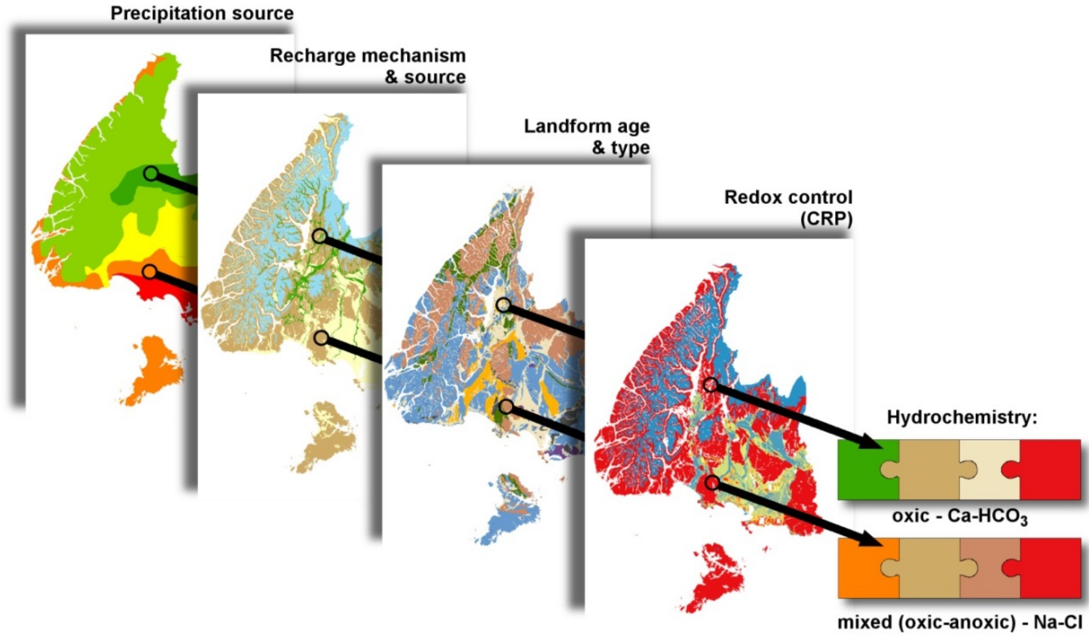

Figure 2: Diagram depicting how this conceptual model uses the combination of four key drivers to estimate hydrochemistry at a given location.

---

[1] Using the computation, complexity, and level of organisation model classification framework of Hoosbeek and Bryant (1992).

The conceptual model was validated through stratification of chemistry data by key drivers and empirical modelling (machine learning approach). Both sets of results validated the conceptual model's ability to simulate spatial variability in hydrochemistry and water quality metrics of regional surface waters.

What are the main findings?

The empirical testing of the performance of the model demonstrated a strong ability to estimate hydrochemistry for surface waters. Estimation of groundwater hydrochemical composition from drivers was weaker than for surface water although the ability to estimate general hydrochemical setting (i.e., redox and recharge mechanism and water source) was strong. Further, the response in the data was consistent with the underlying drivers of groundwater variability.

The strong performance of the model in regards to surface water indicates a robust characterisation of young, soil zone influenced groundwater across Southland. The latter is consistent with both regional, national and international studies indicating that regional groundwater data is not always indicative of the shallow, soil zone connected system due to limitations associated with poor constraint over well characteristics, such as depth and screen interval, poor installation; discrete sampling of a small proportion of a hydrologically connected aquifer; the spatial distribution of semi-confining and/or confining layers; topographic relief and composition of shallow basement geology and time. As expected and as widely recognised due to the integration of flow paths, surface waters provided perhaps the best picture of the hydrochemical composition of shallow soil influenced groundwaters, particularly under low flow conditions.

In conclusion, the mechanistic basis of this approach and its strong performance regarding estimation of surface water hydrochemistry means it is a sound platform for understanding and explaining the spatial controls over hydrochemistry and water quality outcomes. Future work will look at the use of the key drivers as a basis for transient models attempting to simulate water flow and nutrient flux in time. Further, this work provides a spatially resolved platform for the development of a risk based framework for landuse across Southland.

Contents

Figures

Tables

1. Introduction

1.1 Scope

This work is part of the Physiographics of Southland project, which forms part of Environment Southland’s *Water and Land 2020 & Beyond* (WAL2020) project. The aim of WAL2020 is to manage Southland’s freshwater (including rivers, lakes, wetlands and groundwater). The WAL2020 project incorporates Environment Southland’s response to the National Policy Statement for Freshwater Management 2012 (NPSFM), which requires all regional councils in New Zealand to maintain and improve water quality in their regions.

The size and complexity of the Physiographics of Southland project resulted in the body of work being divided into two separate reports (Figure 1-1). This work forms Part 1 of the Physiographics of Southland project, which aims to develop a conceptual mechanistic understanding of the drivers governing hydrochemical variation in Southland’s, surface and shallow, locally soil-influenced groundwater. The conceptual mechanistic understanding underpins land and water quality management actions.

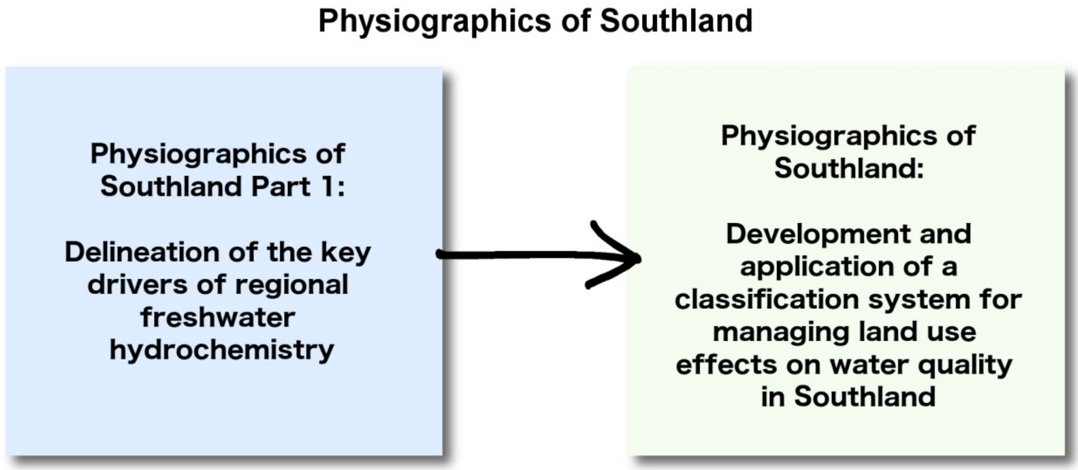

Figure 1-1: The Physiographics of Southland project has been divided into separate science reports.

Part 1 is focussed on estimating the hydrochemistry of surface water and hydrologically coupled soil-influenced groundwaters (Figure 1-2). The rationale for this restricted focus, is that across Southland those groundwaters that are poorly coupled to the soil environment show little if any signs of anthropogenic contamination, are poorly connected to the surface water network and as such make little contribution to surface water composition. Under this focus, surface water is defined as a mix of soil water from overland, lateral matrix flow and artificial bypass flow, and hydrologically coupled, soil-influenced groundwaters.

The objective of this report is to elucidate the relationships between hydrochemical signatures and driver assemblages for Southland's surface and shallow groundwaters. Explicitly, hydrochemical and biogeochemical signatures of soils and water are used in conjunction with existing spatial frameworks including the River Environment Classification (REC), regional Digital Elevation Model (DEM, 8 m), Qmap geological series (various tiles), soils layers (TopoClimate South, Wallace County Soils Map, S-map and LRI) and Southland's groundwater hydrogeological framework (Hughes, 2003, 2016) to elucidate drivers and driver assemblages that govern the variance in regional hydrochemical signatures of surface waters and soil influenced groundwaters.

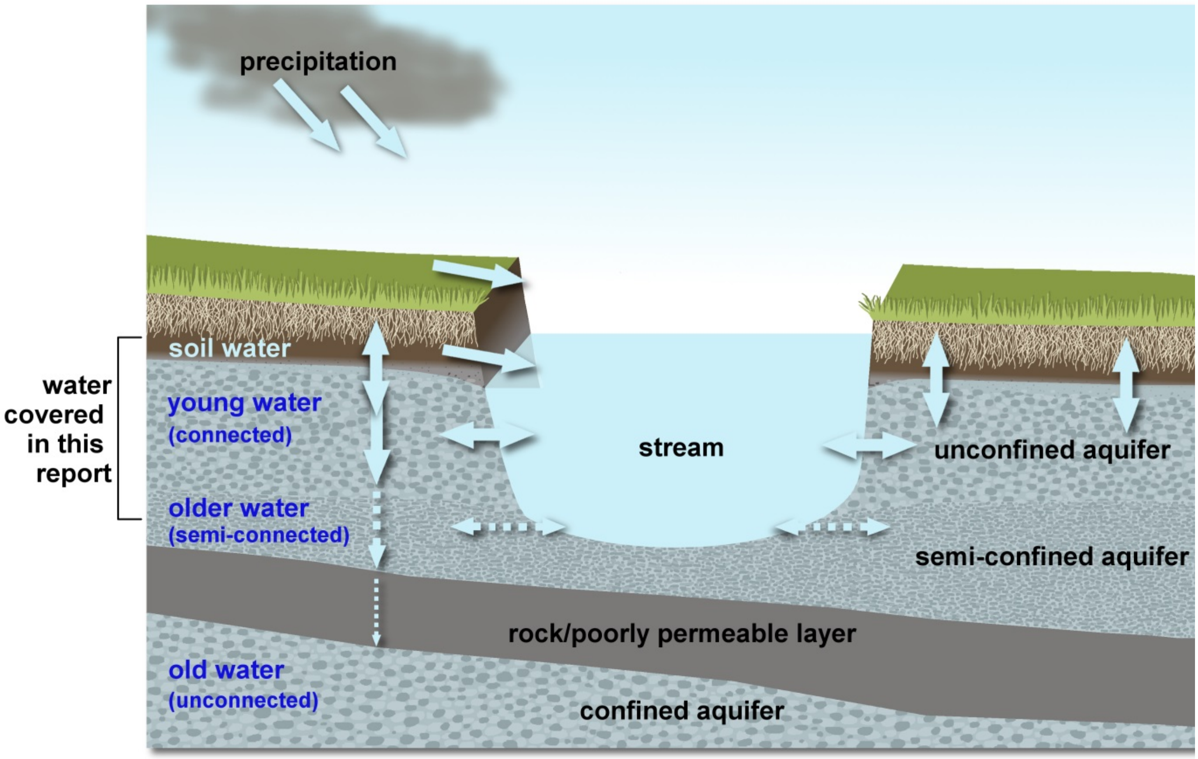

Figure 1-2: Illustration showing the connectivity of subsurface water resources, including soil water, surface and shallow groundwater. In this study, we are interested in shallow groundwater, surface water and soil water that are directly connected to the surface, as they are directly impacted by surface processes.

We refer to the approach taken in this report as a 'Bottom Up' approach as it based on letting the water chemistry inform and calibrate an understanding of which drivers are important determinants of hydrochemical signatures as well as the underlying mechanisms of influence. Specifically, the hydrochemical fingerprint of a water sample interpreted in conjunction with the relevant spatial framework, such as soils or geology, enables the water source, recharge mechanisms and range of physical, chemical and biogeochemical processes to be resolved. The influence of a given driver or assemblage of drivers varies in space and in time. With respect to time, this work utilises median concentrations or isotopic values for a given site, some of which have up to 50 replicates, and as such this work does not attempt to provide a rate or time integrated model.

The understanding of the spatial variation in drivers of hydrochemical outcomes and the interaction between driver assemblages provides the basis for classifying and mapping unique driver assemblages that then form the basis for the mapping of physiographic units. The key point of difference of this work is the direct measurement of regional precipitation, soil, soil water and ground- and surface water, which is used to inform and calibrate a spatially refined understanding of regional drivers of hydrochemistry.

1.2 Report structure

This report is divided into three main sections (Figure 1-3):

1. Report Body Chapters
2. Technical Chapters – supporting information
3. Appendices and Glossary

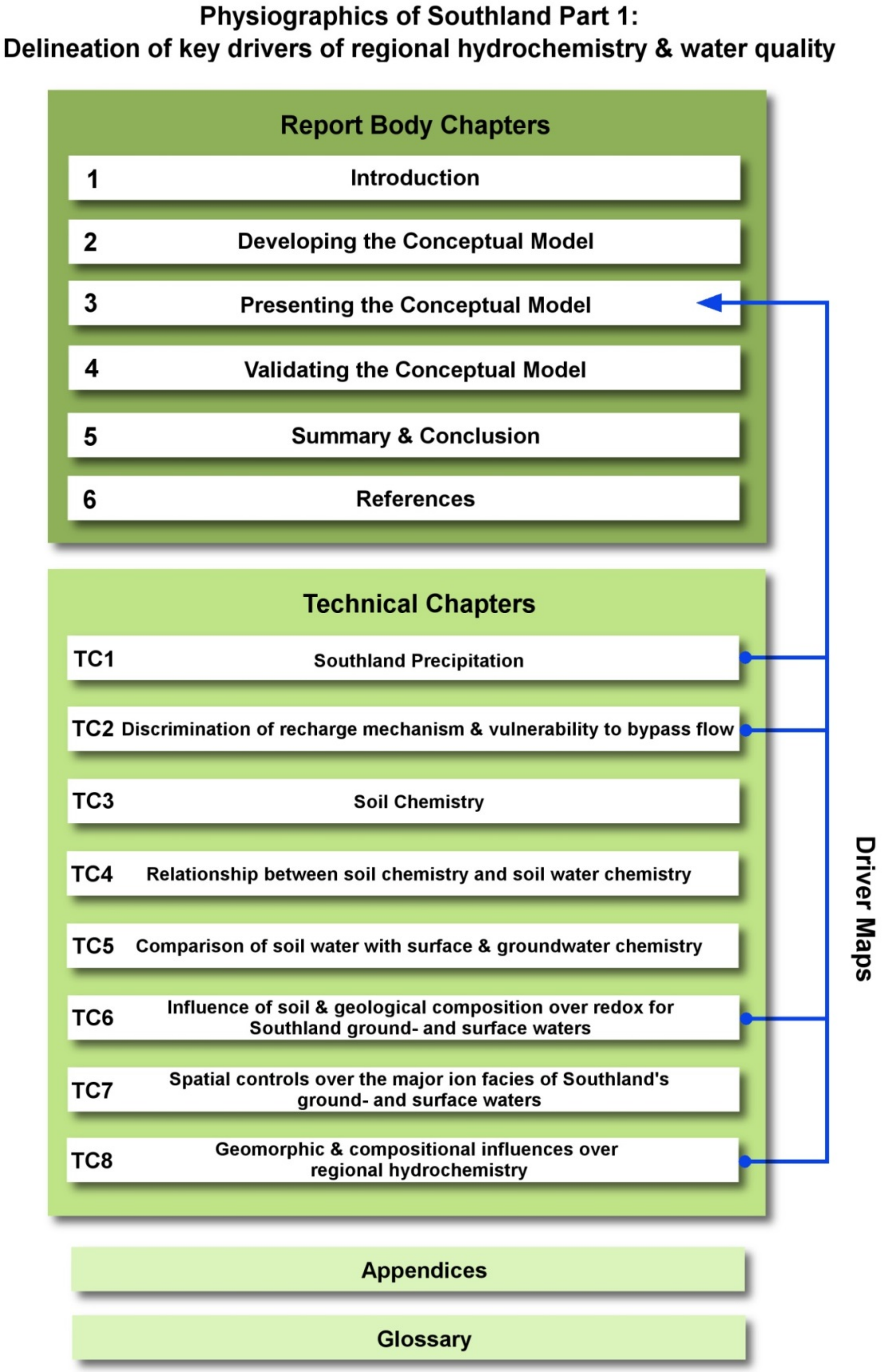

Figure 1-3: Diagram outlining the document structure and relationship between Technical Chapters and the main report body. Note that all eight Technical Chapters feed into Chapter 3 (and 4) of the main report – Validating the Conceptual Model.

1.2.1 Report body

The main report body is composed of five chapters:

Chapter 1 provides a brief introduction to current freshwater quality and quantity issues in Southland and outlines the aim and purpose of this study.

Chapter 2 presents the conceptual model, which was developed through elucidation of key drivers through a spatially explicit framework developed within a GIS platform.

Chapter 3 outlines the four main driver maps: precipitation source; recharge mechanism; landform age and type; and combined reduction potential (CRP), and how these have been established.

Chapter 4 outlines how the validity of the conceptual model is tested. Specifically, a GIS based stratification of the regional hydrochemical data set was used to assess whether systematic characterisation of key drivers can be used to explain both the spatial patterns in major ion facies, general redox category and multivariate classification schemes that have been applied to the same data set. The predictive capability of the conceptual model was subsequently evaluated through regional chemistry data (using a range of different hydrochemical metrics).

Chapter 5 presents the summary and conclusion, and recommendations for future work.

1.2.2 Technical chapters

Technical Chapters underpin the application and testing of the conceptual model and are the means through which key drivers were identified and conceptual understanding progressed. The Technical Chapters elucidate in considerable detail the mechanistic nature of each of the key drivers that forms the basis of Chapter 3, as well as validation of the conceptual model, outlined in Chapter 4.

1.2.3 Appendices, Glossary and References

Appendices provide further information on the work presented in the main report and Technical Chapters. Specifically, the appendices provide detailed information on national and international studies of drivers of hydrochemistry (Appendix A), hydrochemical metrics and methods used in this study (Appendix B and C, respectively), capture zone capture zone delineation for surface and groundwater sites (Appendix D), clustering of groundwater chemical data (Appendix E), validation of the conceptual model (Appendix F) and the datasets employed in this study (Appendix G).

Glossary

References

1.3 Setting the scene

1.3.2 Regional setting

Southland is New Zealand's second largest region, occupying 12.5% of the total land area of New Zealand (approximately 3.2 million hectares). It extends from Awarua Point (Tasman Sea) on the West Coast to Brothers Point (Pacific Ocean) on the East Coast and also includes Stewart Island, which lies to the south of Foveaux Strait (Figure 1-4).

Southland is characterised by its diverse geological landscapes, climate and soils. The climate is heavily influenced by topography and prevailing weather systems, making it one of the most variable climatic regions in New Zealand. Soil types reflect the recent climate history of the region, and the geological terrains that range from ancient intrusive complexes in the west to younger sedimentary sequences in the east and schist to the north.

Public conservation land makes up 53% of the Southland Region, most of which occurs in two national parks: Fiordland National Park and Rakiura National Park (Stewart Island). The majority of the remaining land (76%) has been developed for pastoral agriculture; an activity that has significantly intensified and expanded in the last 150 years (Ledgard, 2013).

Figure 1-4: Map showing extent of the Southland Region.

Over the course of human occupation of Southland, the biggest land cover change has been the loss of indigenous forest, shrubland and wetlands, and their subsequent replacement by agricultural farming systems. This change has disproportionately affected lowland ecosystems, as wetlands and forests now occupy less than 10% of their original area (Ledgard, 2013).

Deforestation and intensification of land use have had significant implications for Southland's freshwater resources.

1.3.2 Water quality issues in Southland

Southland's primary production economy is dependent on both the quantity and quality of water available in the region. The contaminants affecting water quality in Southland have changed over time both in terms of their impact and their source. For example, sediment was once the main cause of degraded water quality sourced from land clearance and development. Point source discharges of industrial effluents, community wastewater and dairy farm effluents were once an important contributor to degraded water quality in Southland (Hodson, 2014). However, greater regulatory control of such point source discharges followed the introduction of the Resource Management Act (RMA) 1991, and their impact in Southland was greatly reduced. Improvements in technologies for the treatment and disposal of point source discharges have also helped with many industrial, community and agricultural effluents now discharged to land rather than surface water (Hodson, 2014).

Up until the mid-20th century, agricultural land use was of low intensity (Ledgard, 2013), and diffuse pollution was not a major factor affecting rural water quality. However, today the primary driver of reduced water quality in Southland is the diffuse pollution of waterways by sediment, nutrients and faecal bacteria (Snelder et al., 2014). The combination of farm productivity increases, such as irrigation, pasture development, and intensive farming systems, and positive dairy market conditions has resulted in land use change and intensification. Intensification has primarily occurred in the lowland plains and the inland basins of Southland (Ledgard, 2013).

The conversion of land to dairying and dairy support grazing, in particular, can be linked to increasing nitrogen, phosphorus, sediment and faecal contamination of water. Increases in dairy grazing and irrigated land for dairy grazing and feed have also increased nitrogen levels in ground- and surface waters regionally. In addition, increases in tile drainage have facilitated contaminant loss to surface waters, by by-passing the deeper soils and riparian zones that can otherwise reduce contaminant loads (Monaghan et al. 2002; Monaghan and Smith, 2012; Cameron et al., 2014; Monaghan et al., 2014).

The routine monitoring of water in Southland has demonstrated an on-going decline in its spatial extent, quantity and quality (SoE 2010; Rissmann, 2012; Snelder et al., 2014; Moreau and Hodson, 2015). At a regional level, water quality has declined in developed areas, with higher nitrate concentrations and loading to surface and groundwaters across the region (Environment Southland and Te Ao Marama Inc., 2011; Rissmann, 2012; Snelder et al., 2014; Moreau and Hodson, 2015). Catchments with the highest proportions of intensive land use, such as the lowland plains and inland basins, also tend to show the highest levels of nitrate, phosphorus, *E. coli*, and sediment in their waterways.

The data also shows spatial and temporal variations in water quality across the region, despite equivalent landuse history and intensity, highlighting that the drivers for regional variability in water quality are not well understood.

1.3.3 Variation in water quality

Often, water quality is variable in both space and time. Spatial and temporal variability in water quality occurs despite similar or identical land use and intensity (Figure 1-5). Different water quality outcomes for the same or similar intensity of land use can result from different:

- physical factors, such as flow and recharge mechanism; and/or
- biogeochemical factors, such as substrate composition and chemistry.

For example, the same type and level of intensity of land use over deep free draining gravels versus heavy (fine textured and imperfectly drained) soils will result in very different water quality outcomes. Specifically, rapidly draining gravels tend to have high groundwater nitrate leaching rates, whereas slowly permeable and imperfectly to poorly drained heavy soils do not.

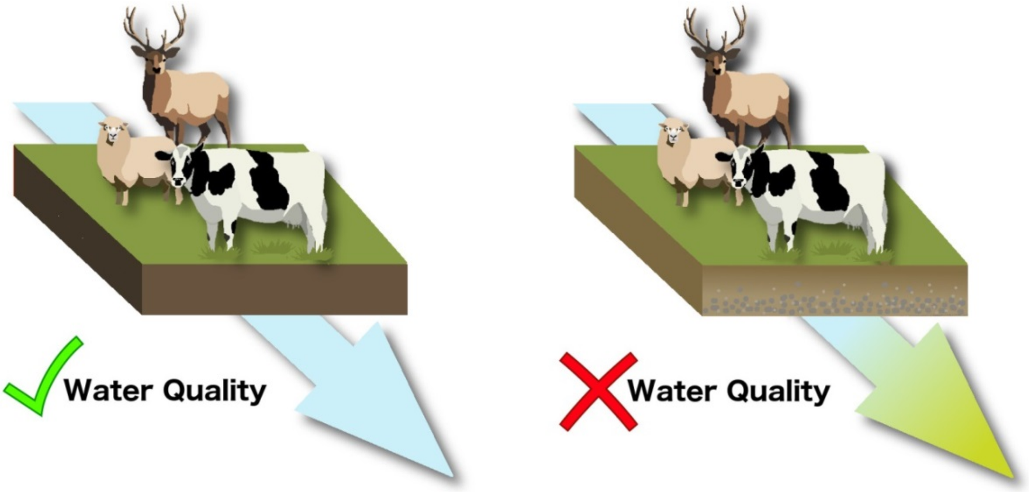

Figure 1-5: Areas of similar land use and intensity can have very different water quality outcomes depending on the biophysical setting/context. In this example, differences in soil hydraulic properties result in different water quality outcomes. Poorly draining soil is depicted on the left, and well-draining soil on the right.

The difference between rapidly draining gravel soils and imperfectly drained fine textured soils is but one example of a number of key controls and varied assemblages of key controls or 'drivers' that determine different water quality outcomes.

This report assesses the role that different assemblages or combinations of physical and biogeochemical drivers have over hydrochemistry[2] and in particular, water quality[3]. In doing so we provide a spatially resolved process based understanding of the factors governing hydrochemical and water quality outcomes.

---

[2] Hydro(geo)chemistry refers to the study of geological and chemical interactions within the natural environment that in conjunction with land use determine water quality and ecosystem health outcomes.

[3] Importantly, we consider water quality, at least chemical water quality metrics, as component of the much broader study of hydrochemistry.

2. Developing the Conceptual Model

2.1 Introduction

Generally, a **conceptual model** is a simplified representation of natural processes. Conceptual models are often used to better understand the underlying natural phenomena and processes and to study possible responses of these to changes in the environment. As such, the primary objective of a conceptual model is to convey the fundamental principles and basic functionality of the system that it represents. In addition, a conceptual model must be developed in such a way as to provide an easily understood system interpretation for users.

This study aims to develop a conceptual model to explain variability of regional freshwater composition. As such, this model (as with any conceptual model) attempts to satisfy the following objectives:

1. Enhance the understanding of the drivers of regional freshwater hydrochemistry, including water quality
2. Facilitate efficient transfer of knowledge of system details between stakeholders, including farmers, regional authorities and policy makers
3. Provide a point of reference for system designers to extract system specifications and parameters
4. Document the system for future reference, as the model may be applicable to other regions to some extent.

Using the *computation*, *complexity*, and *level of organisation* framework of Hoosbeek and Bryant (1992) the conceptual model presented here is defined as being semi-quantitative and mechanistic, and aims to simulate hydrochemical variation in surface water and young, hydrologically connected groundwater at any point in the landscape.

The semi-quantitative aspect relates to the sampling and analytical determination of relevant isotopic, inorganic and organic chemical species associated with regional precipitation, soil, soil waters, surface and ground water in addition to the calculation of various geochemical and isotopic metrics, such as redox state and process, mineral saturation indices, and isotopic determination of recharge altitude.

The model is defined as mechanistic as it is based on derivation of the fundamental processes and relevant importance of these processes in governing spatial variation in hydrochemical signatures. For example, some of the processes and fundamental drivers of spatial variation in freshwater hydrochemistry in Southland include: processes controlling the marine aerosol load of precipitation; the isotopic fractionation of the stable isotopes of H_2O and $\delta^{13}C$ of Dissolved Inorganic Carbon (DIC);

bacterially mediated redox succession; and weathering and associated physiochemical processes such as ion exchange and pH buffering.

The level of complexity of the model or organisational hierarchy is specific to the need to estimate the spatial patterns in hydrochemical signatures of Southland's surface and hydrologically connected, soil influenced groundwater. On this point, water is viewed as the 'weighted mean' of its interactions along a flow path(s) that includes the variance in materials and both physical and biogeochemical processes. Water is deposited as precipitation across a large area but accumulates in a far smaller area either as a flowing stream or as a shallow aquifer (Figure 2-1). It is therefore an accumulation of volume derived from a wider area and carries with it a range of signatures at any collection point. To predict the signature of a water sample at a given location, the model must honour the flow paths and spatial variation in materials and associated reactions occurring across the zone of capture.

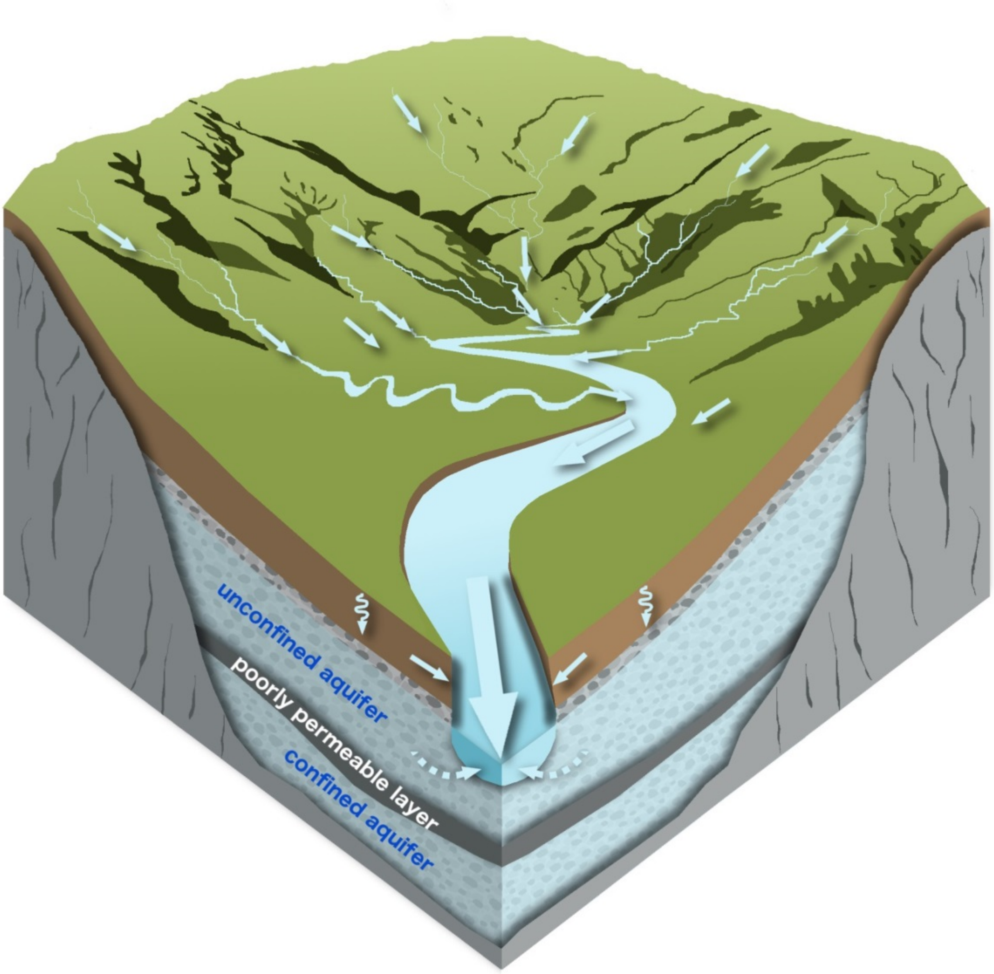

Figure 2-1: Illustrates a hypothetical capture zone, showing how water is deposited as precipitation across a large area but accumulates in a much smaller area either as a flowing stream or as a shallow unconfined aquifer.

As such, the conceptual model uses a physiographic approach meaning it links the physical setting (e.g. topography, soil characteristics) to spatial variability in freshwater hydrochemistry. Importantly, the ability to build a mechanistic model capable of simulating spatial variation in hydrochemical signatures requires a fundamental understanding of the underlying processes and their relative significance. As such this physiographic approach eschews so called ‘black box’ or empirical models that do not honour or understand the underlying processes or ‘mechanisms’ responsible for spatial variation.

Finally, the conceptual model is not a rate model. It does not simulate changes in a variable as a function of time; rather it simulates changes in the concentration of median chemical species or isotopic signatures in space. Future work is designed to use this conceptual model as a framework for simulating concentration and isotopic signature change as a function of time.

2.2 Understanding the drivers of hydrochemical variation

Identifying the key drivers of hydrochemistry for a region, and understanding why these key drivers vary in space, is critical to explaining variation in freshwater hydrochemistry, and therefore water quality. The main objective of this section is to elucidate the current understanding around the relationships between hydrochemical signatures and driver assemblages for surface water and hydrologically connected groundwater in Southland, and other locations.

Figure 2-2 illustrates the major processes occurring in the subsurface that alter hydrochemistry. It is well established that the dynamics of these processes and resultant hydrochemistry are generally driven by both fluctuations in natural conditions or processes, and anthropogenic impacts (Fritz and Clark, 1997; Drever, 1997; Kendall and Caldwell 1998; Gueler et al., 2004; McMahon and Chapelle, 2008; Jiang et al., 2009; Dinka et al., 2015; Daughney et al., 2015). These so called ‘drivers’ of hydrochemical variation include:

1. altitude;
2. proximity to coast;
3. recharge mechanism;
4. substrate composition (soils and geology[4]); and
5. redox processes

The drivers listed above influence solute concentrations through hydrolysis, precipitation, sorption, complexation and ion exchange reactions as well as isotopic fractionation and redox reactions (Wangersky et al., 1994; Fritz and Clark, 1997; Drever, 2005; Sposito, 2008).

---

[4] In Southland we expect the soil zone to be a more important driver than geology, because the majority of Southland’s soils are in direct contact with the shallow, unconfined groundwater system and the signature of soil drainage is readily imprinted (median static water level of -2.75 m b.g.l. (n = 1,750 wells) for unconfined aquifers and a median depth of pedogenic differentiation is at least 2 m under Southland’s cool, humid, temperate climate). Furthermore, those areas with a deeper, pedogenically undifferentiated, unsaturated zone are comprised of inert silicate minerals.

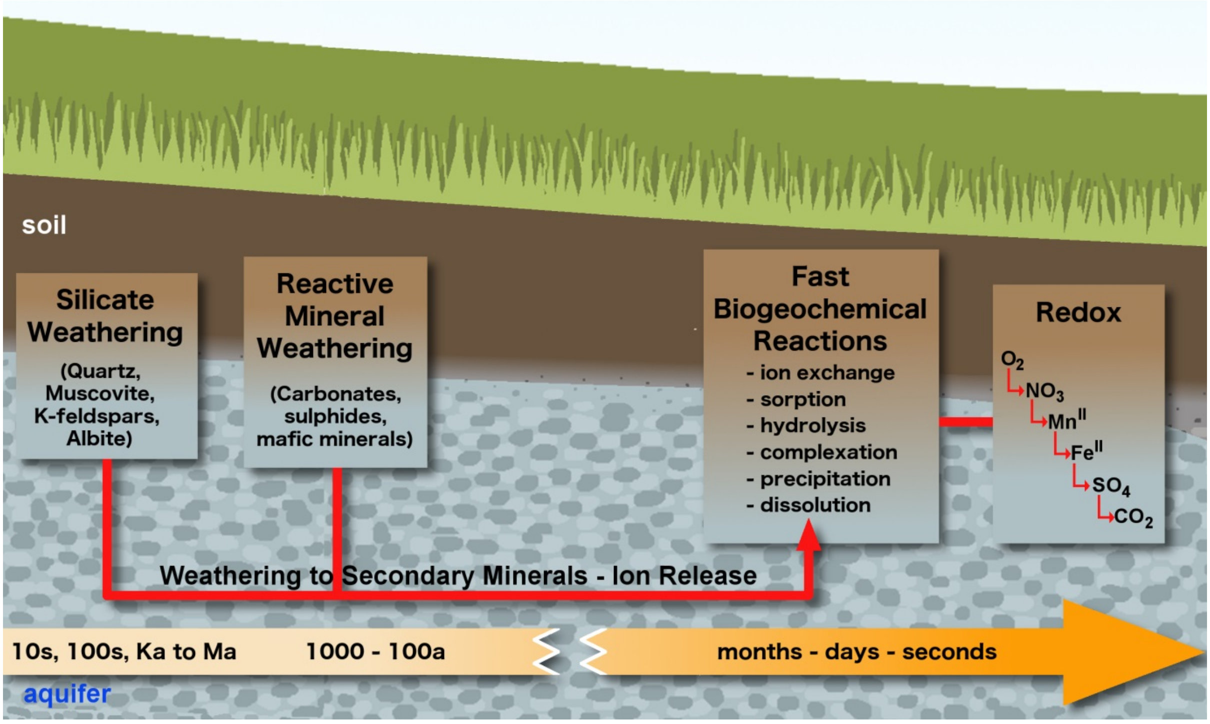

Figure 2-2: Schematic of major processes in soil and aquifer and their time scale. Key is the role of rapid geochemical process, such as but not limited to, ion exchange, complexation, precipitation, dissolution and sorption. Units Ka and Ma refer to kilo (103) annum and mega (106) annum, respectively.

These drivers of hydrochemistry naturally vary in space, and some in time. Therefore, the hydrochemical signature of water also varies with space and time. As a result, different assemblages of key drivers tend to result in distinct hydrochemical signatures. Ergo, where the assemblage of key drivers is similar, we see compositionally similar waters. Where the assemblages of drivers are different, water composition is different.

Note that land use cover and land management intensity are also important drivers of some hydrochemical signatures. Although not directly explored in this report, they are naturally important factors in the spatial drivers studied here. For example, from the assessment of landuse patterns across Southland and elsewhere in New Zealand it is evident that land use history and intensity are well correlated with geomorphic or 'physiographic' domains (de Klein et al., 2006; McDowell, 2008; Lynn et al., 2009; Rissmann, 2012; Ledgard, 2013; Snelder et al., 2014). This is due primarily to climatic and physical constraints over primary production (Lynn et al., 2009). Specifically, in Southland, little if any high intensity landuse occurs across the majority of alpine and bedrock/hill country areas of Southland. The majority of high intensity landuse is associated with lowland and some bedrock/hill country areas.

- In the following section we provide a brief review of national and international literature regarding the drivers of hydrochemical variation of water. Specifically, in the context of the Southland region, we review the effect of five natural key drivers (altitude; proximity to coast; recharge mechanism; substrate composition (i.e. soils and geology); and redox processes) on:

- Major ion composition - excluding redox sensitive species
- Redox species - D.O., NO_3, Mn(II), Fe(II)
- Isotope fractionation

2.2.1 Major ion composition

Major ion composition (excluding redox sensitive species) in freshwater is predominantly affected by recharge mechanism, landform type and age, proximity to the coast and topography. Each is described in detail in the sections below.

2.2.1.1 Recharge mechanism

Recharge mechanism determines the degree of interaction precipitation has with the subsurface of the earth (regolith). Generally, surface and groundwaters are mainly recharged by precipitation, which infiltrates and percolates through the soil (also referred to as **Local Recharge**); and/or water running across the land surface as overland flow (runoff).

Factors that influence whether local recharge or overland flow is the dominant mechanism at a particular location include the hydrological properties of soil and raw geomorphic surfaces, and climatic factors such as rainfall volume and intensity.

Waters that percolate through well-developed soils or regolith often have profoundly different chemistry to those that skim the surface or run across poorly permeable substrates including bare rock and raw geomorphic surfaces (Moldan and Cerny, 1994; Wangersky et al., 1994; Greyson and Bloschl, 2001; Vertessy et al., 2001; Bundi, 2010).

Recharge associated primarily with overland flow from steep or poorly permeable surfaces, such as alpine and steep bedrock/hill country catchments, flow to collection points and may be transported large distances from their origin. Ground- and surface waters recharged by drainage from distant sources that is conveyed through rivers and streams is referred to as **Distal Recharge**.

Different recharge pathways result in significant variation in the opportunity for water to interact with the regolith. Therefore, recharge pathway is an important factor in the concentration of major ions and chemical composition of water (Moldan and Cerny, 1994; Fritz and Clark, 1997; Blasch and Bryson, 2007).

Generally, in areas of variable topographic relief, solute concentrations from areas of local Land Surface Recharge (LSR) tend to be higher than those recharged by overland flow from high or higher altitude alpine or bedrock/hill country settings (Gat, 1980; Fritz and Clark, 1993; Drever, 1997; Bundi, 2010). This reflects a number of processes of which the opportunity for greater interaction with the regolith and higher rates of evapotranspiration are key.

2.2.1.2 Landform age and type

Landform age and type govern substrate composition and weathering rates, which impact freshwater hydrochemical composition (Giller and Malmqvits, 2004; Desonie, 2007). For context, the weathering rates of major silicate minerals are summarised in Table 2-1 (for a standard mineral size of 1mm^3, a pH of 5 and a temperature of 25°C) (Table 2-1). Immediately apparent is the slow reaction rates for quartz, feldspars (K-feldspar and albite) and micas (muscovite) that make up a large proportion of Southland's geology. Of these minerals, quartz and muscovite mica are largely insoluble whereas albite (Na-feldspar) is the most reactive. Even so, geological time spans of tens of thousands of years are required for appreciable albite weathering, especially under the cool temperate climate of Southland (Table 2-1).

In addition to the slow weathering rates of the bulk of silicate minerals, infiltrating water moves relatively rapidly through the unsaturated zone and shallow aquifers across Southland (Wilson et al., 2014; Chanut, 2014; Daughney et al., 2015). As a result, the contact time between the infiltrating water and rock minerals is insufficient for any significant instantaneous dissolved load from direct water-rock reaction of silicates to be inherited by the reacting water.

However, advanced weathering of stable landforms is manifest as soil cover and regolith (McBride, 1994; Drever, 2005; Sposito, 2008). The soil zone is more weathered than most unsaturated zones and aquifer systems, due to the near continuous replenishment of carbonic acid. This is due to high partial pressures of CO_2 within the soil zone, and concomitant supply of organic acids. The latter drive the weathering of primary silicate minerals as depicted in Figure 2-2.

As silicates gradually weather to clays, a portion of the cations and some anions released from primary silicates migrate to sites of electrostatic charge associated with clay minerals and organic matter (McBride, 1994; Drever, 2005; Sposito, 2008). The attraction of ions to solid phase clay and organic matter provides a reservoir of ions ready for fast exchange with dilute recharge waters. Other, less surface reactive ions, move directly into solution and are flushed from the unsaturated zone to the underlying groundwater table during recharge events.

Other rapid geochemical reactions that influence the hydrochemical evolution of freshwaters include hydrolysis (including acid-base reactions), complexation, precipitation and sorption reactions, which are often most significant within the soil zone (McBride, 1994; Drever, 2005; Sposito, 2008).

Table 2-1: Mean Lifetime of a 1-mm^3 mineral crystal predicted from chemical kinetics of water-rock interaction at pH 5 and T = 298 K (Lasaga, 1984).

Mineral	Lifetime [years]
Quartz	34,000,000
Muscovite	27,000,000
K-feldspar	520,000
Albite	80,000
Diopside	6,800
Nepheline	211
Anorthite	112

Due to the long-time spans required for silicate weathering, we generally do not see a significant increase/change in solute concentration of key major ions in young soil- or groundwaters associated with relatively inert landforms, with the key exception of silica (Fritz and Clark, 1993; Freeze and Cherry, 1997). The compositional modifications we do see are due predominately to the aforementioned rapid biogeochemical reactions. However, direct water-rock interactions between highly reactive substrates such as carbonate are locally important modifiers of water chemistry.

Studies of the chemical kinetics of water-rock interaction reveal carbonate weathering rates that are 6 orders of magnitude faster than silicates (Lasaga, 1984). Soil zone recharge waters that subsequently interact with highly reactive carbonate aquifers or soils undergo rapid changes in composition. Specifically, these waters often have high concentrations of Ca and HCO_3 and have high alkalinity (Drever, 2005; Doctor et al., 2008; Scott and Pain, 2009).

Therefore, across Southland it is primarily rapid geochemical reactions and reactive rock or substrate that are responsible for rapid shifts in solute composition and hydrochemical make up of young freshwaters.

2.2.1.3 Proximity to the coast

Proximity to the coast governs the marine aerosolic load (Cl and Na concentrations) of precipitation, which plays an important role over freshwater composition. Specifically, the distance from or the altitude above sea level, strongly influences the variation in marine aerosol load and solute load of precipitation, and subsequently hydrochemical composition (Nichol et al., 1997; Fritz and Clark, 1997; Legrand and Puxbaum, 2007; Lewis and Schwartz, 2009; Salvador et al., 2010).

Generally, areas that are close to the sea are irrigated by maritime air masses that contain significant quantities of marine derived Na and Cl, and relatively low concentration of Ca, K, SO_4 and Mg (Fritz and Clark, 1997; Legrand and Puxbaum, 2007; Lewis and Schwartz, 2009).

For example, in inland and high altitude settings the marine aerosolic load is often small due to:

1. the tendency for marine aerosols to be concentrated near the coast;
2. aerosol scrubbing by falling precipitation;
3. physical barriers to marine aerosol incursion, such as hills or mountain ranges, and;
4. the rapid rainout of marine aerosols entrained within the cloud mass during a precipitation event and or in response to orographic forcing.

Orographic forcing by mountain ranges and subsequent intense rainout of marine salts, results in low marine aerosolic loads in these areas, and is a consistent pattern around the globe. In contrast, lowland areas in maritime settings often receive higher marine aerosol loads than alpine and/or inland settings (Nichol et al., 1997; Fritz and Clark, 1997; Legrand and Puxbaum, 2007; Lewis and Schwartz, 2009). See sections below for detail about alpine, sub-alpine and hill country and low altitude settings.

2.2.1.4 Topography

Topography governs climate, erosion rates and processes, biomass accumulation and hence freshwater composition (Fritz and Clark, 1993).

2.2.1.4.1 Alpine

Alpine settings have low concentrations of solutes due to low marine aerosol load, high precipitation volumes, and thin or incipient soil or regolith development. Specifically, high flushing rates, moderate to low secondary clay development, and limited biomass accumulation results in low dissolved solute concentrations inlcudining Dissolved Organic Carbon (DOC), low alkalinity, and poor pH buffering (Nichol et al., 1997; Borowiak et al., 2006; Bona et al., 2007; Noges, 2009; Bundi, 2010; Goudie, 2013).

2.2.1.4.2 Sub-alpine and Hill Country

Sub-alpine or hill country areas of elevated relief underlain by rock, also receive high volumes and instances of high intensity precipitation (Macara, 2013). However, slope to length ratios are on average larger than in alpine areas, precipitation volume lower and plant cover more extensive (Renard, 1997; Macara, 2013).

Accordingly, soil and regolith development is more advanced, although soil cover is generally thin and overlies colluvium and fractured rock. Water interacting with soils formed under forest or sub-alpine plant communities, thin colluvium and fractured rock is more evolved. Water has higher solute concentration than that of alpine areas, as it has greater opportunity to interact with secondary minerals (including sesquioxides) and organic compounds.

2.2.1.4.3 Low altitude

In low altitude (<400m.a.s.l) flat lying areas of Southland, precipitation rates are lower, the climate more benign and landforms more stable (Turnbull and Allibone, 2003; Environment Southland, 2002; Macara, 2013). Under this setting, soils are more evolved and often thicker, precipitation rates are lower and evapotranspiration rates are higher. Precipitation falling across this area interacts with more evolved soils and regolith. In conjunction with higher rates of evapotranspiration, this results in significant concentration of solutes within the soil zone during the growing season. The concentration of solutes through evapotranspiration within the soil profile is a well-documented phenomenon that equates to significant pulses of solutes during the recharge season to hydrologically connected water bodies (Fritz and Clark, 1997; Chapin et al., 2011; Goyal and Harmsen, 2014).

2.2.2 Redox sensitive species

The concentration of redox sensitive species in freshwater is determined to varying degrees by substrate composition, soil and/or subsurface hydrology, and topography.

2.2.2.1 Substrate composition

In natural waters and soils, redox reactions are largely catalysed by bacteria, which gain energy by facilitating the transfer of electrons from organic matter to an electron acceptor. This process results in the breakdown of organic matter into its constituent elements of carbon, oxygen, nitrogen, phosphorus and some minor trace elements. It also results in the consumption of the electron acceptor and a net energy release for the micro-organism.

Organic carbon is the principal electron donor in most freshwater systems (Bernal, 2008; Andersen, 2009; Traneyek et al., 2011). Since organic carbon is an electron source and is seldom limited in temperate climate soils (Environment Southland, 2002; Collins and Kuehl, 2000; Bernal, 2008; Fissore et al., 2009), redox processes and the concentrations of redox sensitive species are primarily impacted by soil hydrology particularly drainage class (e.g. Rupp et al., 2004; Shenker et al.,2005; Mitsch and Gosselink, 2007; Bernal, 2008; Peralta et al., 2013; Stenger et al., 2013). Well drained soils often have low organic carbon content and are oxidising, while poorly drained soils accumulate high organic carbon content and are reducing (Mitsch and Gosselink, 2007).

Micro-organisms gain energy by catalysing the transfer of electrons from donor (almost always organic matter) to an electron acceptor, therefore they tend to favour the acceptor that supplies them with the largest amount of energy. Of the possible terminal electron acceptors, oxygen provides the greatest amount of energy and is therefore preferentially used by micro-organisms. However, groundwater and/or soil water can be isolated from the atmosphere, which results in consumption of oxygen. Flowing or wind mixed surface waters are seldom decoupled from an atmospheric supply of oxygen. Once oxygen has been depleted from water, the decay of organic matter continues through a succession of reactions that represent a progressively lower tendency of the water to remove electrons from organic matter. Once oxygen has been consumed, micro-organisms move onto the next most energetically favourable electron acceptor, nitrate (NO_3^-), followed by manganese (Mn^{4+} also referred to as Mn(IV)), ferric iron (Fe^{3+} also referred to as Fe(III)), sulphate (SO_4^{2-}) and eventually carbon dioxide (CO_2). This order of preferential electron acceptor utilisation is referred to as the ecological succession of terminal electron-accepting processes:

$O_2 > NO_3 > Mn(IV) > Fe(III) > SO_4 > CO_2$

2.2.2.2 Subsurface hydrology and recharge mechanism

Soils, or more generally subsurface hydrology and recharge mechanism, are important determinants in the development of reduction conditions that favour denitrification and other redox processes (Krantz and Powers, 2002; McMahon and Chappelle, 2009; Rissmann, 2011; Rissmann et al. 2012; Killick et al., 2014).

Within poorly drained soils there is often sufficient residence time for the evolution of reducing conditions, which results in the ecological succession of terminal electron-accepting processes including NO_3 reduction (denitrification) (Figure 2-3). This is possible because, under saturated soil or subsoil conditions the diffusivity of atmospheric oxygen is reduced by 10,000 fold, which effectively decouples the soil or subsurface from the atmospheric supply of molecular oxygen (Moncayo, 2003).

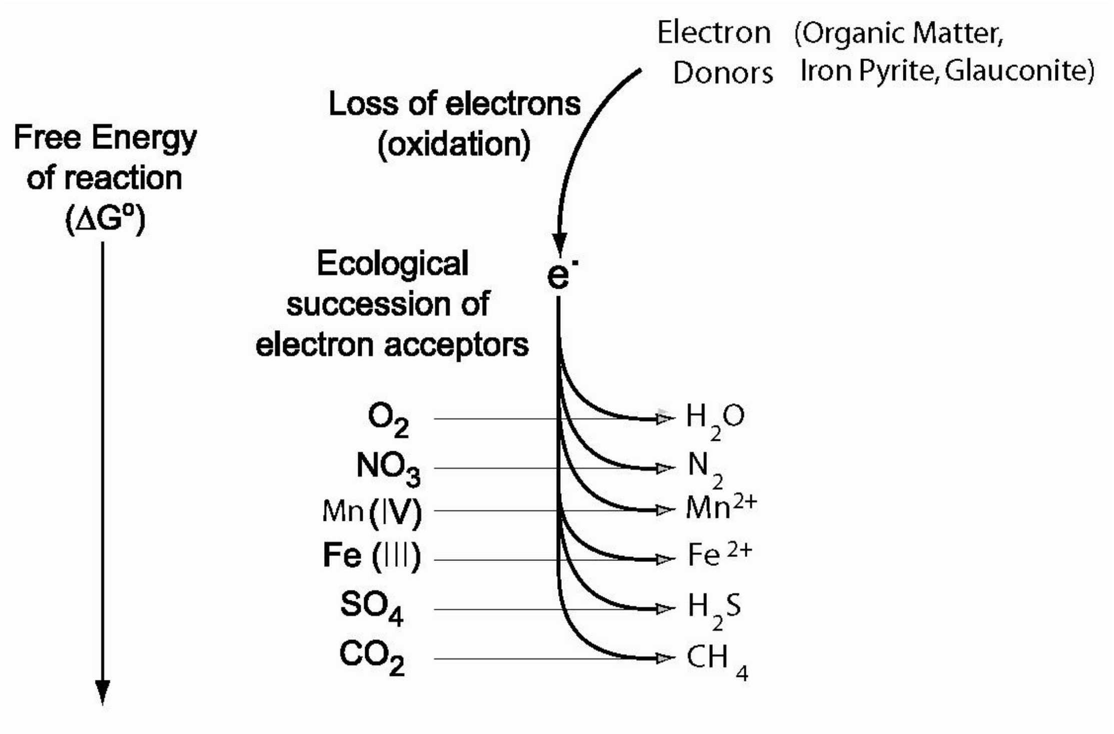

Figure 2-3: Ecological succession of electron-accepting processes and sequential production of final products in natural waters. A decrease in free energy available to micro-organisms occurs as each successive electron acceptor is consumed. Typically organic matter (organic carbon) is by far the most common electron donor in groundwater but iron pyrite and glauconite may be locally significant (modified from McMahon and Chappelle, 2008).

In areas of natural bypass (soil cracks), artificial drainage or in well drained and/or rapidly permeable soils, the decoupling of the soil or subsurface from atmospheric oxygen is less common and accordingly the evolution of reducing conditions and associated denitrification is also less common (Fiedler, 2000; Mitsch and Gosselink, 2007; Schüring et al., 2013).

Various studies in New Zealand and Southland have demonstrated the increase in contaminants, pathogens and in particular redox-sensitive species such as nitrate and phosphate, in bypass flow environment (e.g. McLeod et al., 1998; Aislabie et al., 2001; Monaghan and Smith 2004; Houlbrooke et al., 2008, McLeod et al., 2008; Monaghan et al., 2016). Internationally, a number of studies have also demonstrated the importance of by-pass flow as an pathway of water contamination (e.g. Scott et al., 1998; Watson et al., 2000; Oliver, 2003; Martins et al., 2013; Oliver et al., 2013; Peukert et al., 2014; Zhang et al., 2015, among others).

2.2.2.3 Topography

Topography governs plant growth and ultimately organic carbon biomass. For example, high altitude areas (alpine, 800 m a.s.l) do not support much plant growth and have low carbon biomass, due to low temperatures, more extreme climatic conditions and thin soils (Salmon, 1992; Turnbull and Allibone, 2003; Macara, 2013).

The scarce vegetation in alpine areas results in low levels of organic carbon, which is the key electron donor for reduction. Therefore, attenuation of contaminants through biological redox processes (e.g. denitrification) is limited relative to hill country and lowland areas (Bundi, 2010). In mid-altitude areas (~400-800 m a.s.l) temperatures are more favourable for plant growth, which increases the levels of organic carbon. In turn, this facilitates reduction processes and associated reduction of nitrogen (McColl et al., 1977; Lambert et al., 1985, 1986, 2000, 2003; Blaschke et al., 1992; Andersen, 2003).

2.2.3 Stable isotope composition

Freshwater isotope composition ($\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O) is predominantly affected by topography. However, $\delta^{13}C$-DIC values for freshwater are predominantly affected by recharge mechanism. The impacts of topography and recharge mechanism on stable isotope composition are outlined below.

2.2.3.1 Topography

Topography governs altitude and accordingly the fractionation of the stable isotopes of oxygen and hydrogen ($\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O). These ideal hydrological tracers become increasingly negative with altitude and to a lesser extent with distance inland (latitude) (Clark and Fritz, 1997; Kendall and McDonell, 1999; Strang et al., 2010).

Fractionation is driven by temperature changes during rainout. Consequently, low altitude coastal areas receive precipitation with more positive $\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O signatures and high altitude areas receive more negative $\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O signatures. Therefore, it is possible to calculate the altitude of rainout of a water sample from measurement of $\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O signatures (Clark and Fritz, 1997; Kendall and McDonell, 1999).

Topography is also linked to recharge source. The effect of recharge source on stable isotope composition is described in the following.

2.2.3.2 Recharge mechanism

Recharge mechanism plays an important role in governing what water interacts with at it travels through the landscape.

For example, waters that percolate through the soil interact with large quantities of soil respired CO_2. Therefore, the resultant recharge water inherits the signature of soil zone carbon ($\delta^{13}C$-DIC of -28 to -20%, V-PDB). In contrast, waters that have little opportunity to interact with soils tend to have more positive $\delta^{13}C$-DIC values and low concentrations of Dissolved Inorganic Carbon (DIC) (Fritz and Clark, 1997; Kendall and McDonnell, 1999; Kendall et al., 2014).

Groundwaters in non-volcanically active areas without significant carbonate aquifers, commonly exhibit δ^{13}-DIC signatures that are consistent with soil respired CO_2 and are readily distinguished from surface waters in the same areas (Fritz and Clark, 1997; Kendall and McDonnell, 1999; Kendall et al., 2014). Surface waters tend to have more positive $\delta^{13}C$-DIC signatures due to in-stream processes, such as CO_2 degassing of carbon rich baseflow and carbon uptake by aquatic organisms. Therefore, it is often possible to distinguish between LSR derived recharge and river derived recharge for ground- and surface waters (Clark and Fritz, 1997; Drever, 1997; Kendall and Caldwell, 1998; Kendall and McDonell, 1999; Blasch and Bryson, 2007; Guggenmos et al., 2011; King et al., 2015; Scott, 2015).

2.2.4 Summary

As detailed above, national and international studies (Fritz and Clark, 1997; Drever, 1997; Kendall and Caldwell 1998; Gueler et al., 2004; McMahon and Chapelle, 2008; Jiang et al., 2009; Dinka et al., 2015; Daughney et al., 2015) have shown that the key drivers of hydrochemical variation of freshwater include:

1. altitude;
2. proximity to coast;
3. recharge mechanism;
4. substrate composition (i.e. soils and geology); and
5. redox processes

This study aims to elucidate the relationships between hydrochemical signatures and driver assemblages for Southland’s surface and shallow groundwaters. The following section presents the methods used to develop a conceptual understanding of the drivers of regional freshwater chemistry.

2.3 Methods

2.3.1 Area of focus and scope

This work focuses on characterising the controls over shallow, soil zone influenced ground- and surface water. It makes no attempt to estimate the composition and/or water quality of deeper groundwaters associated with semi-confined or confined aquifers as these are often poorly connected to the shallow surface water network (Figure 2-4).

It is important to recognise that surface water flow is derived primarily from shallow soil drainage and shallow hydrologically connected groundwater (Figure 2-5). During periods of low flow the water running in a stream or river may be 100% groundwater. However, during high flow events, soil water runoff as lateral, bypass and overland flow dominate volumetrically.

Groundwaters that are not well connected to the surface water hydrological system generally play little role in surface water composition and quality. They are often less impacted by landuse and/or show little relationship, in terms of chemical composition, to shallow surficial soils and geology (Freeze and Cherry, 1997; Fetter, 1994; Green and Wang, 2008; Rissmann, 2012; Woodward et al. 2013, 2016; Daughney et al., 2015).

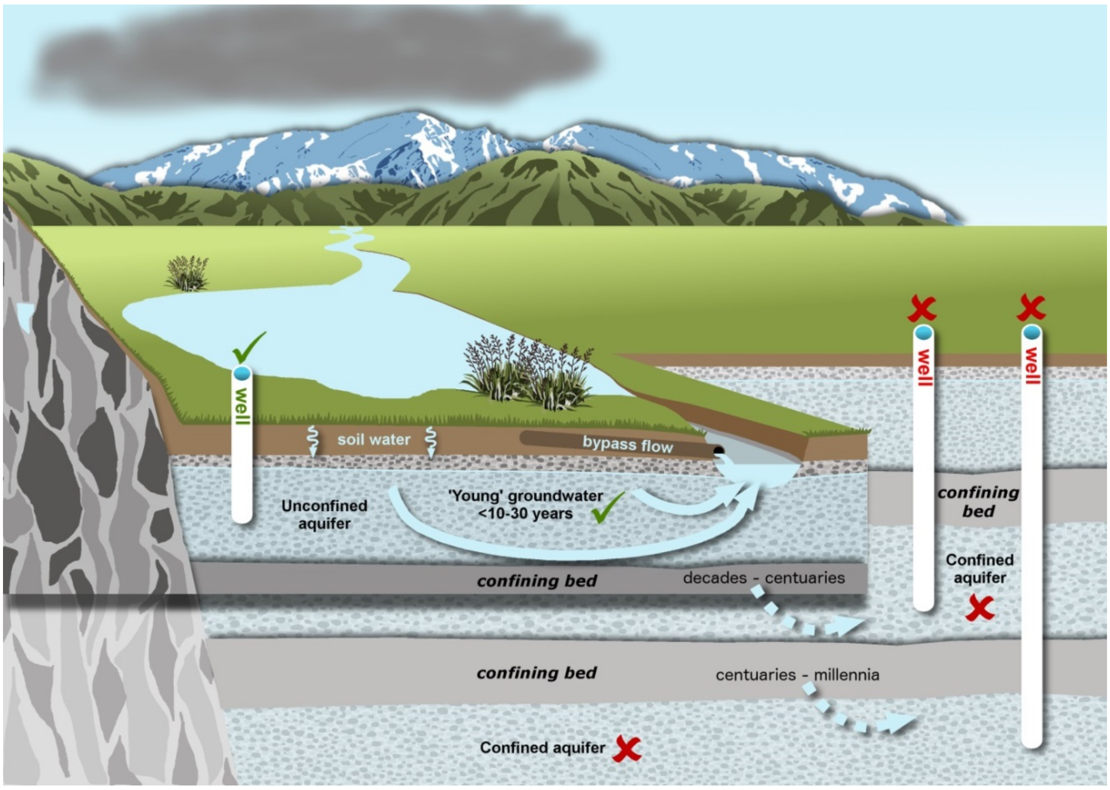

Figure 2-4: This work only focuses on characterising the controls over shallow hydrologically connected ground- and surface water. Wells drawing 'young' water from hydrologically connected unconfined aquifers were included in this work as the sampled groundwater is strongly hydrologically connected to surface water. Wells drawing from deeper, semi confined and confined aquifers were not included.

Variability in surface water composition and quality is determined primarily by shallow, soil-influenced groundwaters and soil water drainage. Therefore, in order to estimate the hydrochemistry and water quality of surface waters, a strong understanding of the controls over the hydrochemical composition of soil water and shallow hydrologically connected groundwater is critical.

Variability of drivers with temporal characteristics, such as precipitation source, was not directly considered in this study, as we predominantly used median data in our analysis. However, at some sites temporal variability in water chemistry is further explored to better refine water origins and chemical composition. Further, this study does not attempt to estimate exact freshwater composition at any given site in the region, but rather aims to estimate regional patterns and spatial trends in hydrochemical variation.

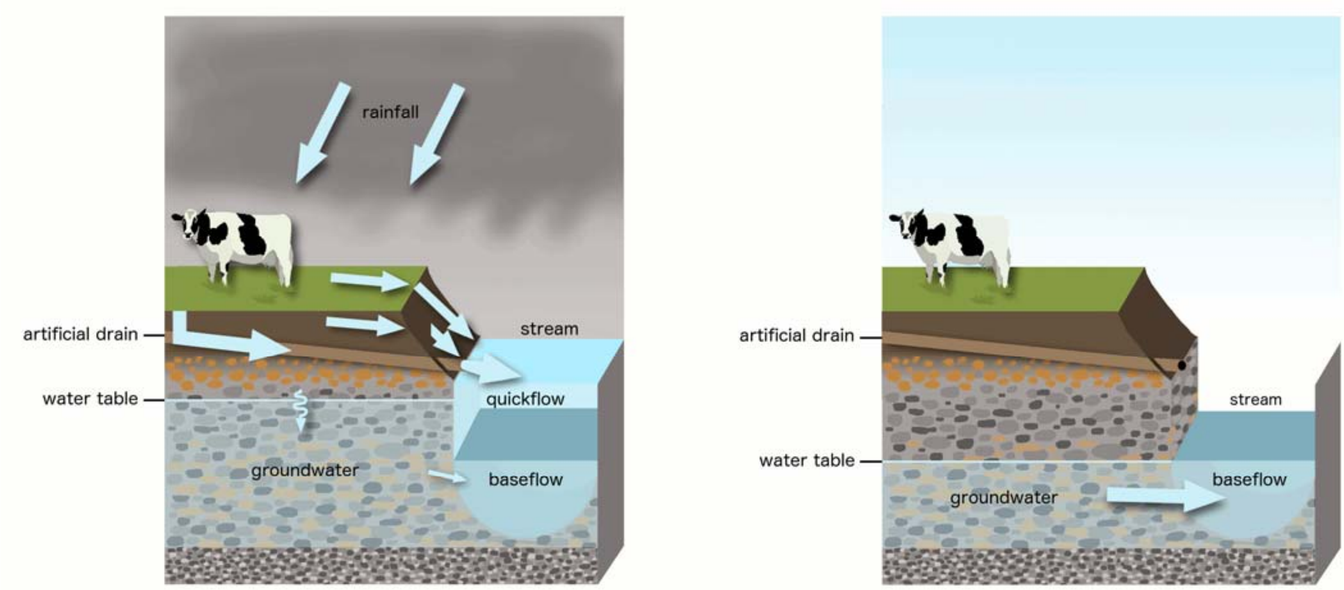

Figure 2-5: Connectivity of surface and groundwater and varying contribution of recharge sources during periods of high flow (LEFT) and low flow (RIGHT). The figure illustrates that surface water flow is derived primarily from shallow soil drainage and shallow hydrologically connected groundwater. During periods of low flow the stream or river may be recharged entirely from groundwater. During high flow events, recharge may occur primarily from soils runoff, bypass and overland flow.

2.3.2 Data and methods employed

2.3.2.1 Sampling sites and parameters

Isotopic and biogeochemical measurements were used as the basis for discovering patterns of chemical transformation in regional freshwater and to establish the main ‘drivers’ that determine the chemical fingerprint of each water sample. Specifically, we looked at the isotopes $\delta^{13}C$-DIC, $\delta^{18}O$-H_2O, $\delta^{2}H$-H_2O; and the State of the Environment (SoE) hydrochemistry suite (Table 2-2).

A total of 20,226 surface water samples, 8,023 groundwater and 28 spring samples, and 67 soil water samples, 102 tile drain, and 102 precipitation samples (including rain, snow and rain/hail samples) were analysed for the above parameters in this study. The sampling locations are illustrated in (Figure 2-6). A further, c. 500 soil profiles with soil chemical measures for multiple horizons were made available through the TopoClimate South soil mapping project. Laboratory leaching of soils with deionised water revealed additional information regarding the influence of soil chemical variability over soil water composition.

Water samples were taken from a mixture of regular monitoring sites, one off investigations and specific samples to fill data gaps. Again, our key focus was on understanding the controls over young, hydrologically connected ground- and surface waters and young, soil-influenced groundwater.

To eliminate bias towards cause-effect-relationships when providing context to the hydrochemistry data, water samples were continuously cross-referenced to natural settings such as soil properties and precipitation. This process of cross-referencing has evolved over the last 20 years, taking time to build up a foundation knowledge base.

2.3.2.2 Additional data employed

As with any discipline or method, integration of observations with established physical models such as soil, geological and hydrological frameworks, provides the strongest basis for any unified and regional-scale conceptual mechanistic model of hydrochemical evolution. Accordingly, established knowledge of regional climate, topography, hydrology, hydrogeology, soil hydrology and geology provided the physical constructs or setting for application and interpretation. Some of the key regional scale physical representations of Southland utilised in this study include:

- Regional scale Digital Elevation Model (DEM) resampled to 8 m;
- Regional scale River Environment Classification (REC) network re-issued to comply with the 8 m DEM;
- Regional and sub-regional scale soil maps including soil hydrology associated with the Wallace County, LRI and Topoclimate soil surveys;
- Regional and sub-regional scale geological maps, and;
- Regional scale groundwater zones and aquifer types and characteristics.

2.3.2.3 Characterisation methods

Widely used and acknowledged scientific methods were used to identify and characterise outliers, variation within the data and spatial relationships, classify waters with common origins and identify drivers of water composition. Hydrochemical variables, abbreviations and units used in this report are listed in Table 2-2. Sample locations and types are shown in Figure 2-6. Some of the methods we used include:

- **Hierarchical cluster analysis** (HCA; Daughney et al., 2015), was used to assess similarity of data and data sub-sets. Specifically, HCA was mainly run on selected analytes for a range of samples to identify waters that have similar origin and/or have undergone similar processes.

- **Principal component analysis** (PCA; Daughney et al., 2015), was used to identify and visualise linear patterns and trends between multiple hydrochemical variables. For example, PCA identifies low D.O. concentrations occur in conjunction with high DOC and Fe(II) concentrations. This allowed us to identify possible causes of variability of the data, for example, where organic carbon is elevated and D.O. is low due to redox succession.

- **Correlation analysis** (Freedman, 2005), is similar to PCA but reveals linear relationships between a pair of variables. Correlation analysis is a method indicating the strength and direction of the linear relationship. For example, DOC and Fe(II) concentrations are strongly positively correlated.

- **Analysis of variance** (ANOVA; Freedman, 2005), were used to determine whether there were differences between mean values of the variables when grouped by an explanatory factor. In combination with correlation analysis, ANOVA was used to identify associations between variables and explanatory factors and infer similarity in the causative mechanism(s). For example, statistical testing confirms that Cl concentrations are significantly different in coastal settings than those in alpine settings. This suggests that alpine and coastal setting have different Cl sources**.**

- **Cumulative probability plots** (Sinclair, 1974; Reimann et al., 2005), were used to identify outliers and to assess the robustness of estimation methods used for missing hydrochemical data. Cumulative probability plots were also used to support the identification of distinct populations within a dataset, for example populations that are likely to be representative of direct contamination or a result from differing processes.
- **Hydrogeochemical indices,** were used to characterise freshwater composition at coarser grain/spatial resolution than defined by individual observations of ion concentrations and ion ratio variables. They were also used to identify the state of reactions. Metrics included:
  - **Mineral saturation indices,** were used to characterise the state of mineral dissolution reactions, such as saturation or under-saturation. These can play an important role in governing the hydrochemistry of surface water and groundwater.
  - **Redox assignments,** were used to characterise the state of redox succession of electron-accepting processes. Redox processes play an important role in the attenuation and removal of contaminants such as nitrate.
  - **Stable isotopic mixing models and recharge calculations,** were used to compute approximate recharge altitude for waters, decipher volumetric mixing of endmembers associated with different water source and differing alkalinity sources.
  - **Carbonate Equilibria,** equations and field data (pH, pCO_2 and temperature) were used to constrain recharge alkalinity.

Further detail on the above and additional hydrochemical metrics can be found in Appendix B, which also describes why the specific methodologies were used. Further detail on the other characterisation methods, in addition to further information on the employed dataset and hydrochemical metrics, can be found in Appendix C.

Table 2-2: Hydrochemical variables or more commonly referred to as hydrochemical variables, abbreviations and units used in this report.

Type	Abbrev.	Units	Parameter Name	Notes
Major Inorganic Constituents	Ca	mg/L [1]	Dissolved Calcium [2]	[1] mg/L = milligrams per litre (equivalent to grams per cubic meter and also equivalent to parts per million). [2] Most samples collected by Environment Southland are filtered prior to analysis, and hence analytical results reflect dissolved rather than
	Cl	mg/L	Dissolved Chloride	
	DIC	mg/L	Dissolved Inorganic Carbon [3]	
	HCO_3	mg $CaCO_3$/L [4]	Dissolved Bicarbonate Alkalinity [4]	
	K	mg/L	Dissolved Potassium	
	Mg	mg/L	Dissolved Magnesium	
	Na	mg/L	Dissolved Sodium	
	SO_4	mg/L	Dissolved Sulphate	

Type	Abbrev.	Units	Parameter Name	Notes
	SiO_2	mg/L	Dissolved Silica	total concentrations. [3] DIC is the sum of dissolved CO_2, H_2CO_3, HCO_3 and CO_3. [4] Alkalinity quantifies the acid-neutralising capacity of a water sample, which is typically reported in mg $CaCO_3$ per litre. Multiply by 0.82 to convert concentration from mg $CaCO_3$/L to mg HCO_3/L. [5] The Becquerel (Bq) is the SI unit of radioactivity; 1 Bq represents the decay of one nucleus per second. [6] mg N/L means that the reported concentrations only reflect the weight of nitrogen within the compound. [7] TON = NO_3 + NO_2 [8] mg P/L means that the reported concentrations only reflect the weight of phosphorus within the compound. [9] The δ notation relates the isotope ratio of the sample to the isotope ratio of a standard and is reported in parts per thousand (‰), e.g.: $\delta^2H = \left[\frac{(^2H/^1H)_{sample}}{(^2H/^1H)_{standard}} - 1\right] \times 1000$ [10] Standards used for isotope ratios are Vienna Standard Mean Ocean Water (VSMOW), Vienna Pee Dee Belemnite (VPDB), and boric acid Standard Reference Material 951 (SRM 951). [11] Colony forming units per 100 millilitres, which provides an indication of the number of viable cells.
Minor Inorganic Constituents	As	mg/L	Dissolved Arsenic	
	B	mg/L	Dissolved Boron	
	Br	mg/L	Dissolved Bromide	
	Cd	mg/L	Dissolved Cadmium	
	CH_4	mg/L	Dissolved Methane (gas)	
	CO_2	mg/L	Dissolved Carbon Dioxide (gas)	
	F	mg/L	Dissolved Fluoride	
	Fe(II)	mg/L	Dissolved Iron	
	H_2S	mg/L	Dissolved Sulphide	
	I	mg/L	Dissolved Iodide	
	Mo	mg/L	Dissolved Molybdenum	
	Mn(II)	mg/L	Dissolved Manganese	
	Rn	Bq/L	Dissolved Radon-222 (gas)	
	Zn	mg/L	Dissolved Zinc	
Nutrients	TON	mg N/L [6]	Total Oxidised Nitrogen [7]	
	NO_3	mg N/L	Dissolved Nitrate	
	NO_2	mg N/L	Dissolved Nitrite	
	NH_4	mg N/L	Dissolved Ammonical Nitrogen	
	TKN	mg N/L	Total Kjeldahl Nitrogen	
	TN	mg N/L	Total Nitrogen	
	PO_4	mg P/L [8]	Dissolved Reactive Phosphorus	
	TDP	mg P/L	Total Dissolved Phosphorus	
	TP	mg P/L	Total Phosphorus	
	DOC	mg/L	Dissolved Organic Carbon	
	TOC	mg/L	Total Organic Carbon	
Isotopes	$\delta^2H\_H_2O$ [9]	‰ VSMOW [10]	^2H to ^1H isotope ratio in water	
	$\delta^{18}O\_H_2O$	‰ VSMOW	^{18}O to ^{16}O isotope ratio in water	
	$\delta^{18}O\_DIC$	‰ VSMOW	^{18}O to ^{16}O isotope ratio in DIC	
	$\delta^{13}C\_DIC$	‰ VPDB	^{13}C to ^{12}C isotope ratio in DIC	
	$\delta^{11}B$	‰ SRM 951	^{11}B to ^{10}B isotope ratio in BO_3	
Biological	E. coli	cfu/100 mL [11]	Escherichia coli	
	Entero	cfu/100 mL	Enterococci	
	FC	cfu/100 mL	Faecal coliforms	
	TC	cfu/100 mL	Total coliforms	
Other Parameters	Clarity	m	Visual clarity	[11] Microsiemens per meter. [12] Simulations of river flow and flow percentiles are based on Griffiths and Horrell (2012). [13] Nephelometric turbidity units.
	D.O.Field	mg/L	Dissolved Oxygen (Field Meas.)	
	D.O.Lab	mg/L	Dissolved Oxygen (Lab Meas.)	
	EC	µS/cm [11]	Electrical Conductivity	
	Flow	m^3/s	Recorded River Flow	
	Flow%	%	Recorded River Flow Percentile	
	FlowSim	m^3/s	Simulated River Flow [12]	
	FlowSim%	%	Simulated River Flow Percentile	

Type	Abbrev.	Units	Parameter Name	Notes
	FlowVirt	m^3/s	Virtual River Flow	
	ORP	mV	Oxidation-Reduction Potential	
	pHField	pH units	pH (Field Meas.)	
	pHLab	pH units	pH (Lab Meas.)	
	SS	mg/L	Suspended Solids	
	SSV	mg/L	Volatile Suspended Solids	
	Temp	°C	Water Temperature	
	Turb	NTU [13]	Turbidity	

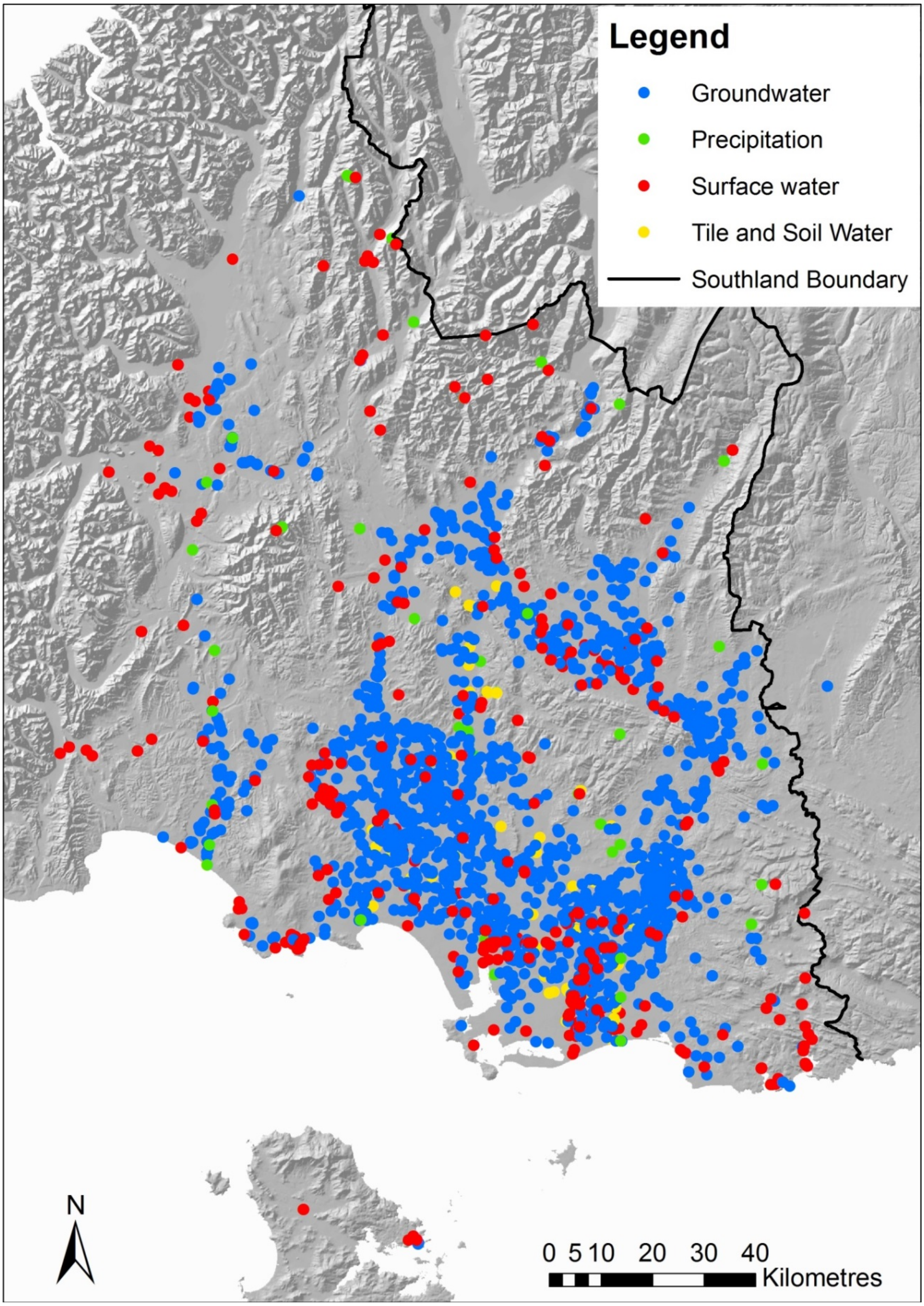

Figure 2-6: Sampling locations and types of this study, showing a general distribution of samples across Southland. For maps showing greater detail of sample distribution and type see the Technical Chapters.

2.3.2.4 Capture Zones

The hydrochemical drivers associated with a particular site were quantified according to the extent of delineated capture zones (Figure 2-7). Surface water capture zones (or more traditionally watersheds) were based on REC (River Environment Classification) delineations, which are represented by polygons in a GIS layer (see detail in Appendix D1). Surface water sites without previously characterised (REC) capture zones were not included in our analysis. Groundwater capture zones were defined according to a simple hydromorphic approach (Figure 2-7, detailed in Appendix D2).

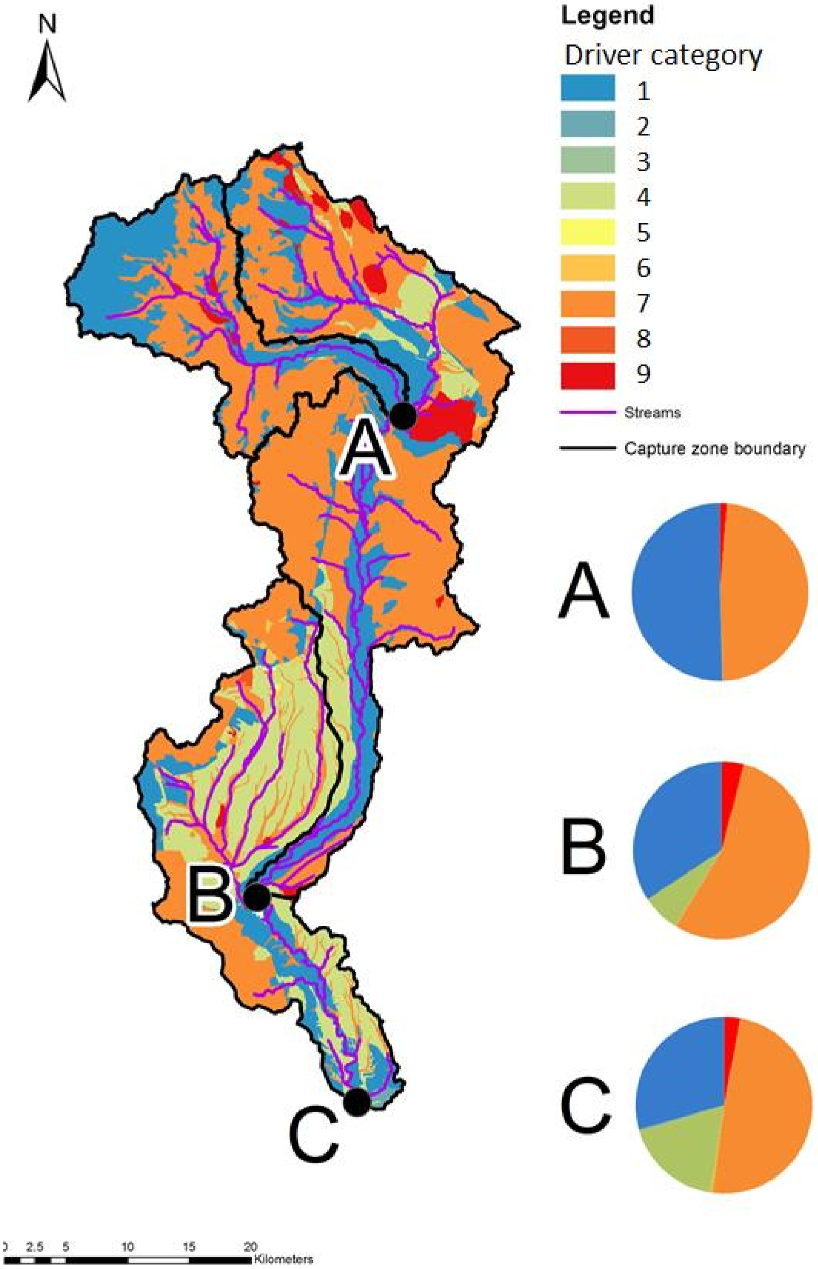

Figure 2-7: Example of key driver assemblage (A, B, C) in capture zones of assorted surface water sites in the Waimea catchment. Pie charts symbolize the proportion (area) associated with key driver categories within the capture zone.

For groundwater capture zone delineation we used the elongated parabola method, assuming uniform flow and an ArcGIS tool developed by GNS Science (Toews et al., 2013). Specifically, each groundwater site was intersected with pre-existing groundwater zones (Hughes, 2003; 2016; Figure 2-8) and groundwater management zone specific flow lines. Well or bore depth, in conjunction with static water level data, was then used to constrain aquifer confinement for each groundwater zone.

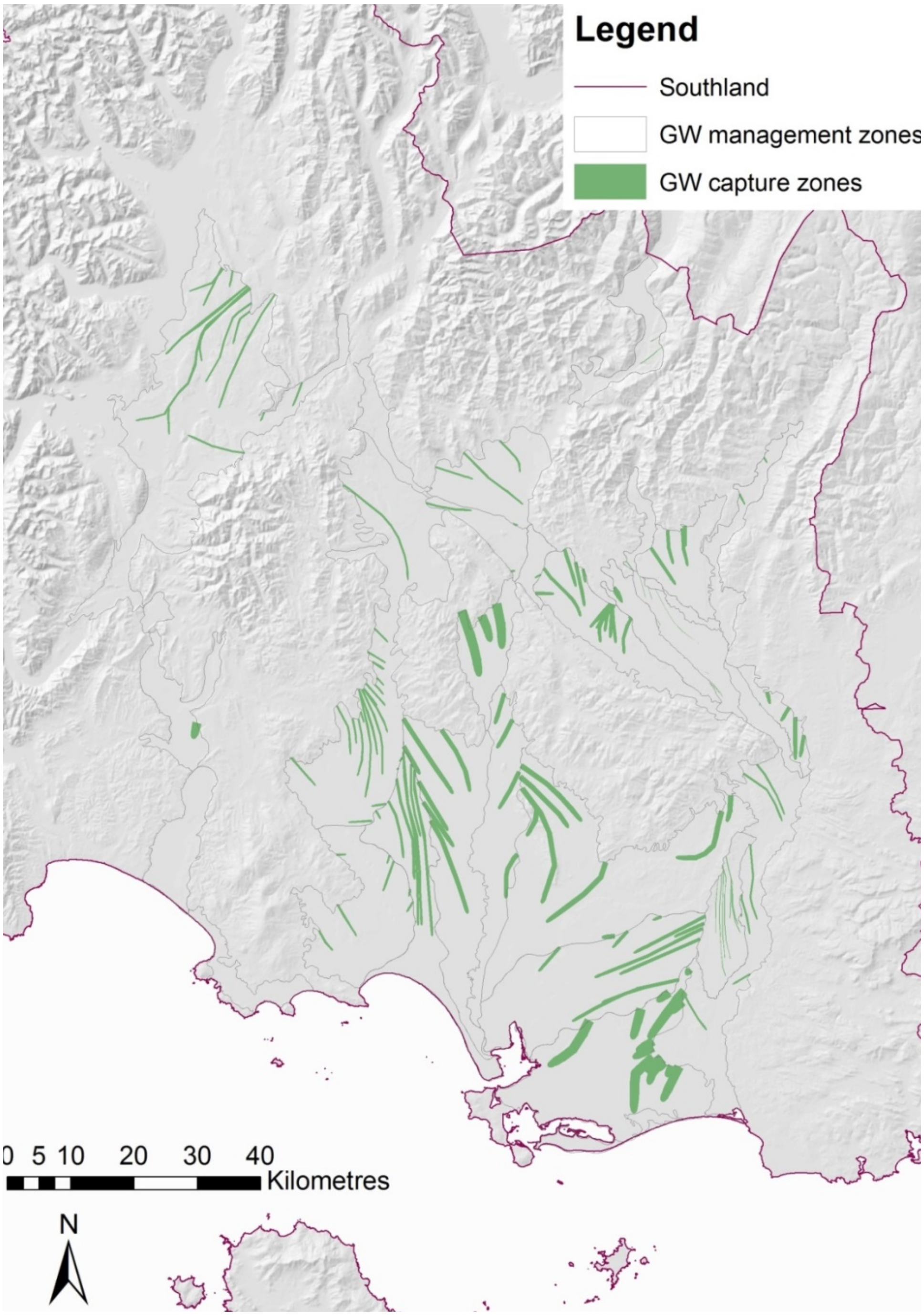

Figure 2-8: Groundwater management zones and delineated groundwater capture zones. The thickness of the capture zones is a function of hydraulic conductivity, porosity, and saturated aquifer thickness.

We note that although these simplistic ‘capture zones’ help constrain the general hydromorphic setting of a groundwater site, they are crude relative to evolved capture zone analysis, such as those developed using complex groundwater models. In addition to the use of capture zones, we considered an hydromorphic assessment of Hughes (2006) to provide some general constraint over the (i) groundwater zone (Figure 2-8); (ii) aquifer type; (iii) confined aquifer depth, (iv) potential for bypass flow, (v) river influence, and (vi) river connectivity for a given site. The latter assessment provides important hydrogeological context to well sites and capture zones.

2.3.3 Determining the main drivers

Following the assessment of relationships and spatial patters in freshwater chemistry, we considered a range of factors to confirm the following as the main drivers for variability in freshwater chemistry in the Southland region: 1. altitude, 2. proximity to coast, 3. recharge mechanism, 4. substrate composition (i.e. soils and geology), and 5. redox processes.

First, we looked at the origin of water within rivers and aquifers regionally, including the mechanism of recharge (this is detailed in TC 1 and 2). Second,the factors governing regional soil chemical variability were assessed and the role of this variability over the hydrochemical composition of soil waters, and regional surface and groundwater (this is detailed in TC 3, 4 and 5). Third, we looked at the role and spatial controls of soil and geological materials in determining the redox category, Terminal Electron Accepting Process (TEAP), and ultimately the fate of contaminants such as nitrate, at a regional scale (detailed in TC 6). Subsequently, the governing factors or drivers determining the spatial pattern of major ion facies of Southland’s ground- and surface waters were determined (detailed in TC 7). Finally, we looked at the influence of geological factors over the spatial variation in soil chemistry and the hydrochemical signatures (i.e., Ca, Mg, pH and alkalinity) of ground- and surface waters (detailed in TC 8).

2.3.3.1 Water origin and recharge mechanism

Overall, analysis of precipitation chemistry (detailed in TC1) and freshwater chemistry (detailed in TC2), suggested that patterns in precipitation control regional freshwater major ion composition, specifically Cl and Na concentration. We found marine aerosolic load and recharge source, whether proximal or distal, are influencing factors.

2.3.3.2 Regional soil chemical variability

Analysis of soil water and freshwater, and comparison to soil chemistry and geology, confirmed that landform type, rock and sediment composition are the dominant control over the chemical composition of soil, soil water and ultimately freshwater in Southland (detailed in TC3, TC4, TC5, TC6 and TC8). Analysis of major ions in soil water confirmed that soils play a critical role in the evolution of soil water and ultimately have a significant impact on both ground- and surface waters (detailed in TC4).

We concluded that soil pH, BS (base saturation) and C (carbon content) are regionally the most important soil chemical characteristics and that P-retention is locally significant. Furthermore, comparison of the chemical composition of soil water with that of surface and groundwater (detailed in TC5) revealed that the bulk of chemical constituents in Southland's freshwater are inherited from water percolating through the soil and unsaturated zone. This is in contrast with many other studies that show chemical constituents are more strongly associated with the aquifer or saturated zone (e.g. Guggenmos et al., 2011; Beyer et al., 2015).

2.3.3.3 Spatial controls

The hydrochemical signatures of surface water and soil influenced groundwater samples showed distinct spatial groupings or patterns (Daughney et al., 2015; This work). The relationship between similar groups of waters and their hydrochemical signatures were interrogated against information provided by existing spatial frameworks and through measurement of precipitation and soil water. Through this process it was possible to discriminate the assemblages of key drivers in each setting that give rise to specific hydrochemical signatures.

Specifically, an assessment of the spatial distribution of major ion facies in soil zone influenced ground- and surface water (detailed in TC7) confirmed that cation facies, such as Ca and to a lesser degree soil zone Mg, are controlled by a threshold relationship between marine aerosolic Na in precipitation and spatial variations in soil BS. For example, in coastal areas of high marine aerosol flux, marine Na loading locally overwhelm Ca and Mg on soil exchange sites, resulting in Na dominated waters. Conversely, in alpine and inland areas low marine aerosol load results in Ca (or Mg) dominated waters. Furthermore, anion facies are also controlled by a threshold relationship between marine aerosolic Cl in precipitation and the influence of geomorphic age and substrate composition over soil pH. Specifically, geological composition, such as rock or biological sediment type, influences pH and the subsequent speciation of inorganic carbon, and more specifically alkalinity. In areas of relatively elevated soil pH, alkalinity concentrations may be high relative to the marine aerosol load of Cl, resulting in dilute waters dominated by HCO_3 anion facies. Alternatively, in Alpine areas marine Cl loading is so low as to be negligible that even relatively minor alkalinity generation dominates the major anion facies of these waters. Variation in soil chemistry is therefore governed primarily by landform age and the chemical composition of the rock and/or sediments the soil has formed in (detailed in TC3 and TC4).

2.3.3.4 Spatial patterns of major ion facies

Analysis of precipitation chemistry (detailed in TC1) and freshwater chemistry (detailed in TC2), confirmed that patterns in precipitation and recharge source control major ion composition, particularly Cl and Na concentration, of freshwater in the region.

Landform type, geomorphic surface age and rock and sediment composition were found to be the dominant control over the chemical composition of soil. In combination, they influence the major ion composition, and in some instances the concentration of redox sensitive species, of soil water (detailed in TC3, TC4, TC5, TC6 and TC8). Further, analysis of major ions in soil water confirmed that variation in soil chemical characteristics govern the chemical variability of soil water and ultimately have a significant impact on the composition of ground- and surface waters (detailed in TC5).

2.3.3.5 Influence of geological factors

Relatively little post-percolation evolution of hydrochemistry occurs within Southland groundwaters, with the exception of areas of highly reactive carbonate rocks and where shallow unconfined aquifers are influenced by reducing lithologies or biological sediments. Limited post-infiltration recharge evolution of regional groundwater reflects predominantly inert lithologies and ground-water residence times that are too short for significant *in-situ* water-rock interaction to occur (TC5).

3. Presenting the Conceptual Model

3.1 Introduction

We developed a conceptual understanding of the evolution of regional freshwater chemistry through the assessment of a total of 28,548 water samples and the employment of acknowledged scientific methods (detailed in the subsequent section). Specifically, we looked at the chemical and isotopic signatures in precipitation, soil water, mole-pipe drainage waters, ground-, spring water and surface water.

On the basis of this analysis, we hypothesised that we can estimate water chemistry on the basis of the assemblage of four key drivers. These Southland specific key drivers of regional freshwater chemistry, in no particular hierarchy, are:

1. Precipitation source;
2. Recharge mechanisms and source;
3. Geomorphic age and substrate composition; and
4. Redox control (combined reduction potential of soil and geology - CRP).

Spatial variation in each key driver was characterised by a range of driver categories, and at any site a unique combination of key driver categories is present. Figure 3-2 illustrates the conceptual model developed in this study. The key drivers are symbolised as jigsaw puzzle pieces and their colouring represents the category of key driver, e.g. yellow colour for the precipitation source represents an inland precipitation source, as opposed to other categories such as coastal or alpine. Note that the colours match those represented in the Driver Maps, detailed in section 3.2.

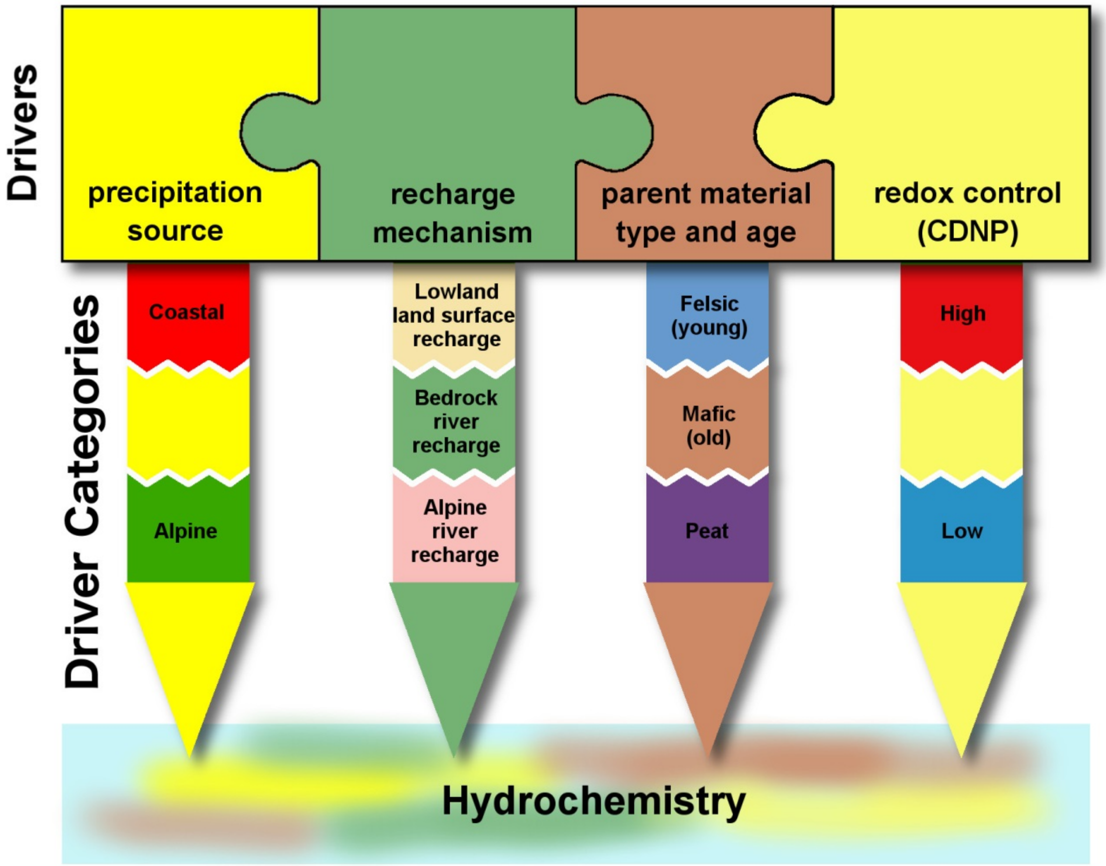

Figure 3-1: Jigsaw puzzle analogy illustrating the effect of drivers on water quality in Southland. Unique combinations of drivers lead to a unique water composition. Driver categories use colours depicted in the Driver Maps in section 3. However, drivers have varying numbers of categories, therefore for simplicity, we have only shown three categories per driver.

Each key driver and driver category has a specific impact on freshwater composition. For example, highly concentrated coastal precipitation will add a high Cl and Na load to freshwater. Waters with a coastal precipitation source are therefore often, but not always, of Na-Cl type. Modifiers of Na-Cl dominance may include substrates (soil and geology) that contains very high concentrations of labile/reactive Ca and Mg or high pH buffering capacity. As such, it is the unique combination and hierarchy of key driver categories with the capture zone of a site that results in a unique hydrochemical composition.

The role of each of these drivers as key controls over surface water and shallow, soil-influenced groundwater is consistent with the international peer reviewed literature as outlined in Chapter 2.2 and detailed in Appendix A. The point of difference of our approach is the use of chemical and isotopic data of soil and water to inform our understanding of key drivers. This departs from the more traditional geomorphic analysis of landscapes, empirical models of soil nutrient loss or nutrient transport, which is generally applied in the literature. The identification of regional key drivers and development of key driver maps in this study is further detailed in section 3.2.

Spatial variation for each driver is depicted as a map, which when combined form layers of information that define each site's specific driver assemblage. Therefore, the maps provide a spatial platform for intersecting and subsequently classifying hydrochemical data. Using the understanding of drivers to spatially group hydrochemical data tests the capacity to estimate spatial variation in hydrochemistry (Chapter 4).

Figure 3-2 is a simplified illustration of how the driver maps are combined to estimate different water quality outcomes in two separate locations, 1) an inland location near Te Anau and 2) a more coastal location near Otautau.

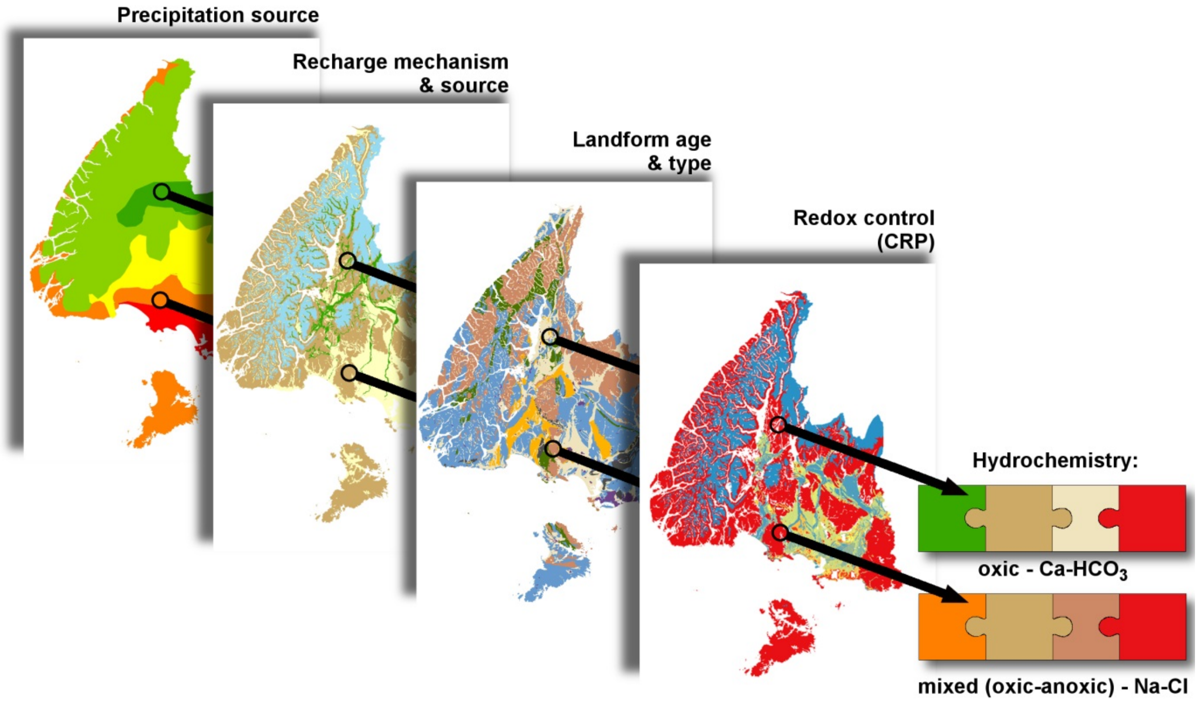

Figure 3-2: Two examples of how the conceptual model works for specific locations. The upper example location near Te Anau shows that the combination of key drivers specific to that location result in an oxic – Ca-HCO3 water type. The combination of key drivers for lower example location near Otautau results in a mixed (oxic-anoxic) – Na-Cl water type.

3.2 Mapping of key drivers

This section details how the key drivers of Southland freshwater chemistry have been determined on the basis of relationships and spatial patterns in hydrochemistry.

3.2.1 Precipitation Source Driver

In this section we discuss the identification and mapping of regional precipitation sources. More detail on the development of this driver map can be found in TC 1.

Analysis of precipitation samples for Southland revealed spatial variation in chemical signatures that can be linked to different precipitation sources. We found that altitude and distance from the coast (latitude) are the dominant controls over variation in the solute load of precipitation in Southland. We observed a large magnitude, quasi-exponential marine aerosol rainout effect resulting in high marine aerosol loads in the southern coastal regions and extremely low (below analytical detection limit) aerosol loads in the high altitude northern areas of Southland.

Analysis of groundwater and surface water chemistry revealed a similar picture. We found a pattern of chemical freshwater composition that clearly uncovers the spatial origin of the initial precipitation. Signatures of, Na, Cl and/or $\delta^{18}O\text{-}H_2O$ in regional ground- and surface waters closely resemble the solute load gradients of regional precipitation.

In close proximity to the coast, the high marine aerosolic Na and Cl input overwhelms the effects of endogenous sources of Na (or Cl) associated with feldspar or similar mineral weathering. Effects of geology and soil on freshwater composition are more prominent in high altitude and/or northern inland locations due to very dilute precipitation occurring at these sites. These spatially highly contrasting differences in marine aerosol load play a major role in the hydrochemistry of Southland's ground- and surface waters.

Based on this, we defined and mapped five categories for precipitation source. The five precipitation source categories are:

1. **Alpine precipitation**, very dilute precipitation, above 800m altitude.
2. **Sub-alpine precipitation**, below 800m, but above ~ 300m, i.e. slightly less dilute than above
3. **Coastal precipitation**, highly concentrated precipitation, composition close to that of seawater, occurring in close proximity to the coast.
4. **Inland precipitation with little coastal influence**, more concentrated than sub-alpine and alpine precipitation, but less concentrated than coastal precipitation, occurring particularly in northern Southland inland plains.
5. **Inland precipitation with significant coastal influence**, more concentrated than inland precipitation with significant coastal influence occurring in lowland southern Southland at some distance to the sea.

The spatial extent of each category across Southland is depicted in Figure 3-3. The map was established on the basis of Cl, Na and $\delta^{18}O\text{-}H_2O$ contours and thresholds identified through Hierarchical Cluster Analysis (HCA) of precipitation and freshwater chemistry data (Table 3-1).

Table 3-1: Summary of thresholds of indicator species to define precipitation source categories in Southland. These categories define proximal precipitation source for surface and groundwater.

Precipitation source	**Cl threshold [mg/L]**	**Na threshold [mg/L]**	**$\delta^{18}O\text{-}H_2O$ threshold [pptv VSMO]**
Alpine2 (most dilute)	LOW(<4)	LOW(<3)	LOW(<-9.3)
Alpine	MOD LOW (3 to 8)	MOD LOW(3 to 5)	MOD LOW(9.3 to-8)
Inland	MOD(8 to 16)	MOD(5 to 10)	MOD (-8 to -7.4)
Coastal	MOD HIGH (16 to 27)	MOD HIGH (10 to 16)	MOD HIGH (>7.4)
Coastal 2 (least dilute)	HIGH(>27)	HIGH(>16)	HIGH (> - 7.4)

Although the map identifies distinct areas of precipitation source types of differing composition, the change in composition is rather gradual. For further study in other regions, we recommend integrating gradual precipitation type bounds, although using absolute bounds did not seem to be an issue in Southland as demonstrated in Chapter 4.

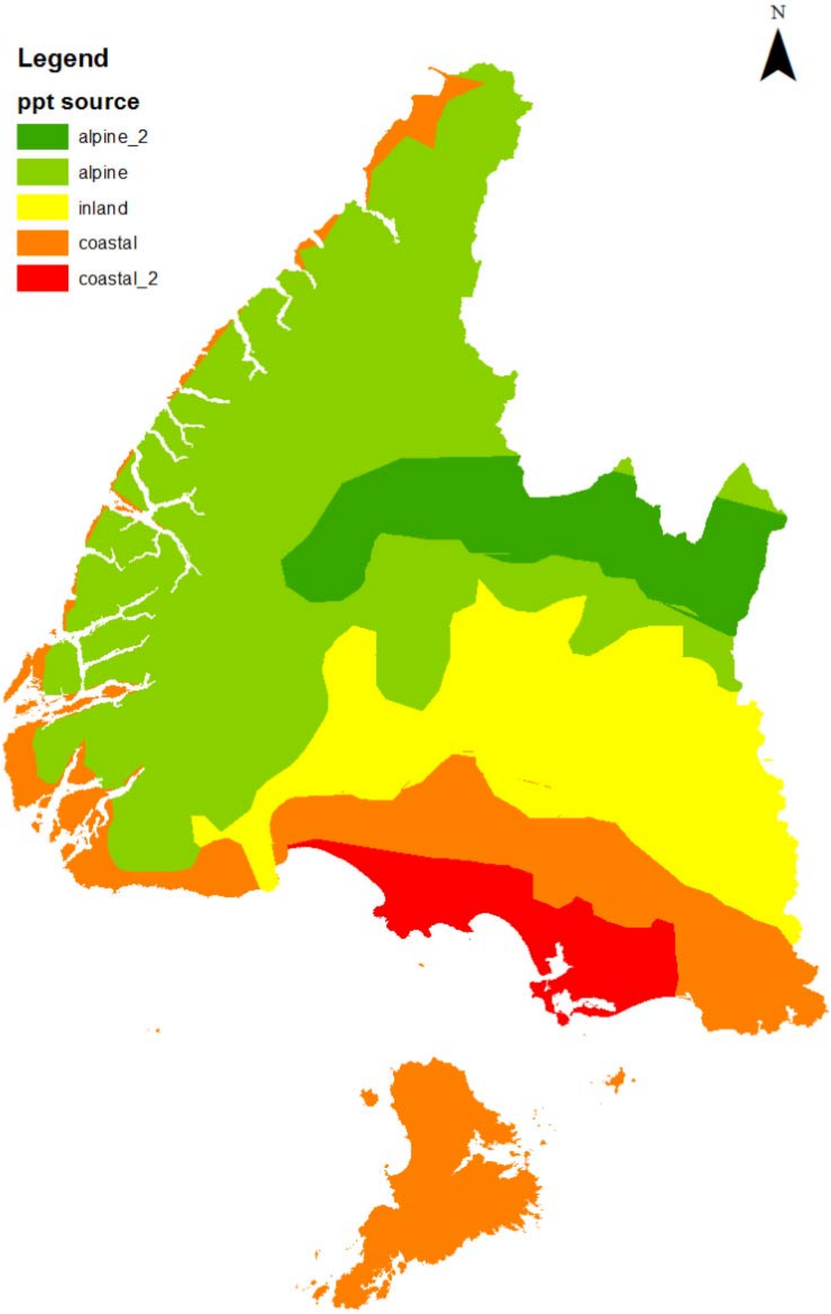

Figure 3-3: Patterns of precipitation source in Southland region with alpine 2 precipitation being the most dilute, followed by alpine, inland, coastal and coastal 2 (in order of increasing solute concentration).

3.2.2 Recharge Mechanism and Source Driver

In this section, we discuss the identification and mapping of recharge mechanisms and source as a key driver of regional freshwater composition. For more detail see TC 2.

Assessment of surface and groundwater composition revealed that in addition to precipitation source, recharge mechanism and water source have significant impacts on regional freshwater chemistry. Assessment of the relationship between $\delta^{18}O-H_2O$ and both Cl and EC in Southland's ground- and surface waters showed distinct patterns of Na, Cl, EC and/or $\delta^{18}O-H_2O$ signatures. These can be linked to five principal precipitation sources (described in section 3.2.1) and three recharge mechanisms (local, distal and mixed recharge). Recharge mechanisms and sources were defined according to the domain in which the water originates: River Recharge (RR), Land Surface Recharge (LSR) and Mixed recharge (Alpine-LSR, Bedrock-LSR, Alpine-Bedrock-LSR).

3.2.2.1 Recharge mechanisms – local, distal and mixed

Local recharge is where the water source (precipitation) and the resultant recharge area occur within the same recharge domain and the recharge does not move large distances outside of the recharge domain. Hereafter, we refer to local recharge as 'Land Surface Recharge. '

Distal recharge is where the water source (precipitation) and the resultant recharge area(s) occur within different domains. The water has moved a long distance from its point of origin. Hereafter, we refer to distal recharge as 'River or Riverine Recharge'. The water in the main stems of major rivers in Southland originates in alpine and bedrock areas and travels into lowland areas. Hereafter we refer to these distal recharge sources of regional freshwater as 'Alpine River Recharge' and 'Bedrock River Recharge'. Where 'Bedrock' again encompasses but is not limited to the traditional, land use capability classification of 'Hill Country'.

Generally, recharge of freshwater comprises varying portions of both distal and local recharge, and is therefore 'mixed'. In reality, pure distal recharge is unlikely to exist given that local recharge will to some extent always be present at any given site in the region (except for confined freshwater bodies, which are not considered in this study). As such, regional freshwaters will to some extent carry signatures of both distal and local recharge.

3.2.2.2 Flow pathways

In addition to local or distal recharge mechanisms there are also *rapid* and *slow* flow pathways along which recharge moves. Overland flow is an example of a rapid flow path, which is most common in steep areas with minimal soil cover or areas where soils are slowly permeable. Slower flow paths are normally associated with deep percolation of recharge waters to underlying aquifers and eventual discharge through the surface water network as baseflow.

Rapid flow paths typically predominate in alpine or bedrock country catchments, which do not have significant aquifer systems for slower transport of meaningful volumes of water. Artificial subsoil drainage and open drains facilitate rapid flow in less steep areas. Rapid flow is also associated with natural structures such as shrink-swell clays or other pedogenic structures within soils that rapidly conduct recharge to either a poorly permeable subsoil layer or in some instances an aquifer. In areas influenced by vertical cracking the bulk of the soil zone may be bypassed during recharge.

In TC 2 we identify both the recharge mechanism and source domains, including natural bypass flow (i.e., not artificially mediated bypass such as mole-pipe drainage), across Southland on the basis of hydrochemistry indicators and explore the impact of these on freshwater composition. We showed that in alpine and hill country (hereafter 'bedrock') areas surface waters are recharged proximally through shallow subsurface or overland flow, and then discharge down gradient through the river network. Significant groundwater resources in these areas do not exist. In lower altitude areas, such as Southland's lowland plains, the majority of ground- and surface waters are recharged proximally through land surface recharge. However, aquifers adjacent to streams or main stem rivers that receive alpine or bedrock recharge exhibit a mixed recharge signature. For Southland's main stem rivers the amount of LSR increases in the downstream direction.

3.2.2.3 Recharge domains

The following four main recharge categories/domains have been identified for Southland based upon precipitation source (marine aerosol load), stable isotope estimation of recharge altitude and recharge mechanism:

1. **Alpine River Recharge (ARR)** – originating from high altitude (> 800 m RSL) areas, waters generally show the lowest variation in chemical composition, no significant areas of groundwater resource; and

2. **Bedrock River Recharge (BRR)** – originating from mid to high altitude (< 800 m RSL) bedrock catchments both coastal and inland; similarly to alpine river recharged waters, these waters show low variation in chemical composition; although proximity to the coast greatly influences the concentrations of Na and Cl in these waters.

   We observed that bedrock derived streams that are disconnected to alpine areas carry a different signature than bedrock derived streams that receive alpine input (often a switch between the 'alpine and bedrock signature' occurs in response to presence/absence of alpine input). This suggests that in Southland we can distinguish between pure BRR that is disconnected from alpine areas ('bedrock 2') and BRR that receives some proportion of ARR ('bedrock 1'):

   a. **Bedrock 1** - BRR that receives an alpine input, and
   b. **Bedrock 2** - pure BRR that does not receive an alpine input (e.g. Catlins, Hokonui Hills).

3. **Land Surface Recharge (LSR)** coastal and inland – precipitation percolating through lowland soils (< 300 m RSL), associated with constructional landforms that are mainly Quaternary aged alluvial and alluvial/aeolian landforms; waters show generally the highest variability in Na, Cl, EC and $\delta^{18}O-H_2O$ signatures, reflecting spatial heterogeneity in precipitation source and the chemical and physical composition of soils and geology. Some areas subject to LSR are affected by natural bypass flow, such as the development of preferential flow pathways via cracking of fine textured

soils. In some settings this allows bypass of the soil zone resulting in delivery of oxidised water to the underlying aquifers.

4. **Mixed recharge** - distal hill country or alpine RR in addition to proximal LSR (inland and coastal) across the low altitude plains in close proximity to major stem rivers.

To discriminate between these recharge categories, threshold values of conservative tracers $\delta^{18}O$-H_2O, δ^2H-H_2O, Na, Cl and EC, and elevation can be used (summarised in Table 3-2). It is possible to further discriminate land surface recharge from carbonate influenced recharge by combining values for conservative tracers with carbonate saturation data and/or alkalinity values.

We note that waters that are characterised as alpine and bedrock/hill country recharged exhibit the lowest variation in chemical composition, are therefore easiest to distinguish from waters that are recharged through LSR or mixed recharge.

Waters that are characterised as LSR show the greatest variability in composition, which likely reflects the heterogeneous chemistry of soil and geology of lowland Southland. In addition, precipitation in these areas can range from dilute in close proximity to high altitude areas, to highly concentrated in Na and Cl in close proximity to the coast.

Distinguishing LSR waters from waters that received mixed recharge is difficult as even a small amount of land surface recharge can have a large impact on solute chemistry (Table 3-2). However, through the application of hydrodynamic capture zones and the assumption that mixed recharge is limited to areas of active floodplains with fluvial recent soils, it is possible to distinguish between groundwaters that receive mixed recharge from those that receive land surface recharge based on their location.

LSR waters can also be impacted by the presence of bypass flow. Areas of Southland that have soils vulnerable to bypass flow were mapped to distinguish between areas vulnerable to shallow, deep, and artificial bypass flow. Specifically, we discriminate areas where there is deep soil cracking that intersects an aquifer, areas where shallow cracking intersects the subsoil but not the aquifer, and areas with shallow lateral bypass flow that is facilitated by artificial drainage.

In addition to recharge mechanism, we also found that water source or origin is an important driver of surface water composition (TC2, 6 - 7). For example, streams that originate in alpine environments generally carry their alpine (dilute, oxic) signature all the way down into the lowland, although significant land surface recharge may occur. It is therefore important to consider the stream source for prediction of surface water composition in Southland.

Table 3-2: Summary of thresholds of indicator species to discriminate recharge sources and recharge mechanisms categories of Southland surface and ground water. *We distinguish bedrock 1 (connected to alpine) and bedrock 2 (disconnected to alpine) on the basis of connectedness to alpine areas using REC capture zones.

Recharge Source Indicator Species	Alpine River Recharge	Hill country/ bedrock River Recharge*	Land surface recharge across lowland plains	Mixed recharge across lowland plains
Electrical Conductivity	Low (<80 µS/cm)	Mod. (<100 µS/cm)	High (80 to 120 µS/cm)	Mod to low
Cl concentration	Low (<8 mg/L)	Mod. (<15 mg/L)	High (15 to 25 mg/L)	Mod to low (5 to 15 mg/L in North; 15 to 30 mg/L in South)
Na concentration	Low (<5 mg/L)	Mod. (<8 mg/L)	High (10 to 20 mg/L)	Mod to low (5 to 15 mg/L in North, 13 to 25 mg/L in South)
$\delta^{18}O-H_2O$	Low (<-9.3 pptv VSMO)	Mod. (<-7.4 pptv VSMO)	High (-7 to -8 pptv VSMO	Mod to low
Elevation/ Topography	Mountainous >800 m RSL	Elevated bedrock 500-800 m RSL	<500m RSL	<500m RSL

The recharge domains and recharge sources were subsequently mapped as key drivers for prediction of regional water chemistry. The map was established based on: the thresholds summarised in Table 3-1; information on regional hydrology (REC) and hydrogeology occurring as groundwater zones (Hughes, 2003, 2016); recharge elevation calculated from $\delta^{18}O-H_2O$, and; discrimination between alluvium and bedrock and soil properties.

Alpine areas > 800m were defined based on:

(i) the lowest mean recharge altitude determined from $\delta^{18}O-H_2O$ of alpine sourced streams that coincides with the altitude of the tree line across some parts of Southland;
(ii) bedrock not alluvium, and;
(iii) alpine plant communities and/or raw geomorphic surfaces.

Hill country/bedrock (sub-alpine rolling land) below 800 m RSL was defined according to:

(i) $\delta^{18}O-H_2O$ recharge elevation calculations and ecological factors associated with vegetative cover, and;
(ii) bedrock not alluvium.

Bedrock catchments were further subdivided into those with an alpine component (Bedrock 1) and those without (Bedrock 2) on the basis of connection or otherwise to alpine (>800m) areas. The Hokonui Hills and Catlins are two examples of type 2 Bedrock/Hill Country that have no alpine catchment area.

The remaining areas not defined as Alpine or Bedrock/Hill Country are all characterised by lowland alluvium and host shallow aquifer systems (Table 3-2). Across the majority of this area land surface recharge is the dominant recharge mechanism (Figure 3-4). However, where aquifers occur in close proximity to streams with alpine or bedrock head waters they exhibit a mixed recharge signature. In particular, areas of recent and raw soils (using Topoclimate) that are connected to a stream with alpine source were defined as mixed recharge[5].

Following map completion we defined stream/surface water source. We used RECversion 3, which is based on a resampled regional 8 m DEM to identify streams originating with within alpine, bedrock and lowland areas (Figure 3-4 to Figure 3-7). The bypass map established on the basis of soil properties was added to the recharge domain map (Figure 3-4). Combining the maps provides a spatially explicit picture of hydrogeological, soil hydrological, recharge mechanisms and water source that constitutes a key driver over hydrochemical variation.

---

[5] Specifically, the following mapping rules were used: TCS - NZSC Order and Group = Recent Fluvial Soils; excluding the 'Waiau' soil Series in the Lower Waiau Catchment. Also excluding recent fluvial soils that are not within an active floodplain (defined by terraces) or do not have an alpine source (> 800 m asl) (DEM, REC) AND Qmap - Map Unit = All alluvium hydrologically connected to an alpine source (> 800 m asl, DEM, REC) (where no soil information exists).

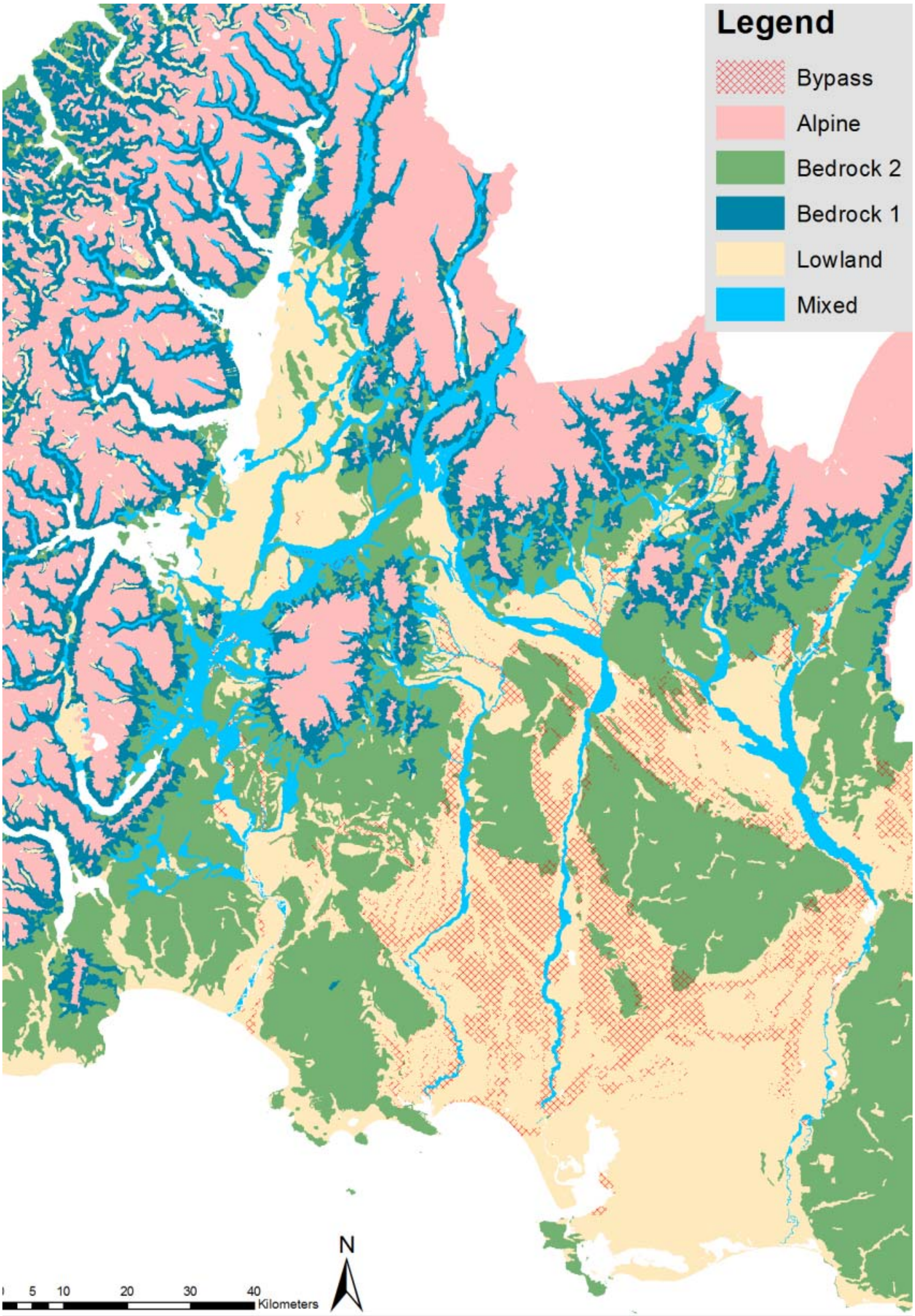

Figure 3-4: Recharge domains (Alpine RR; Bedrock RR; Lowland LSR, and; Mixed Alpine RR and Lowland RR) and areas of bypass flow.

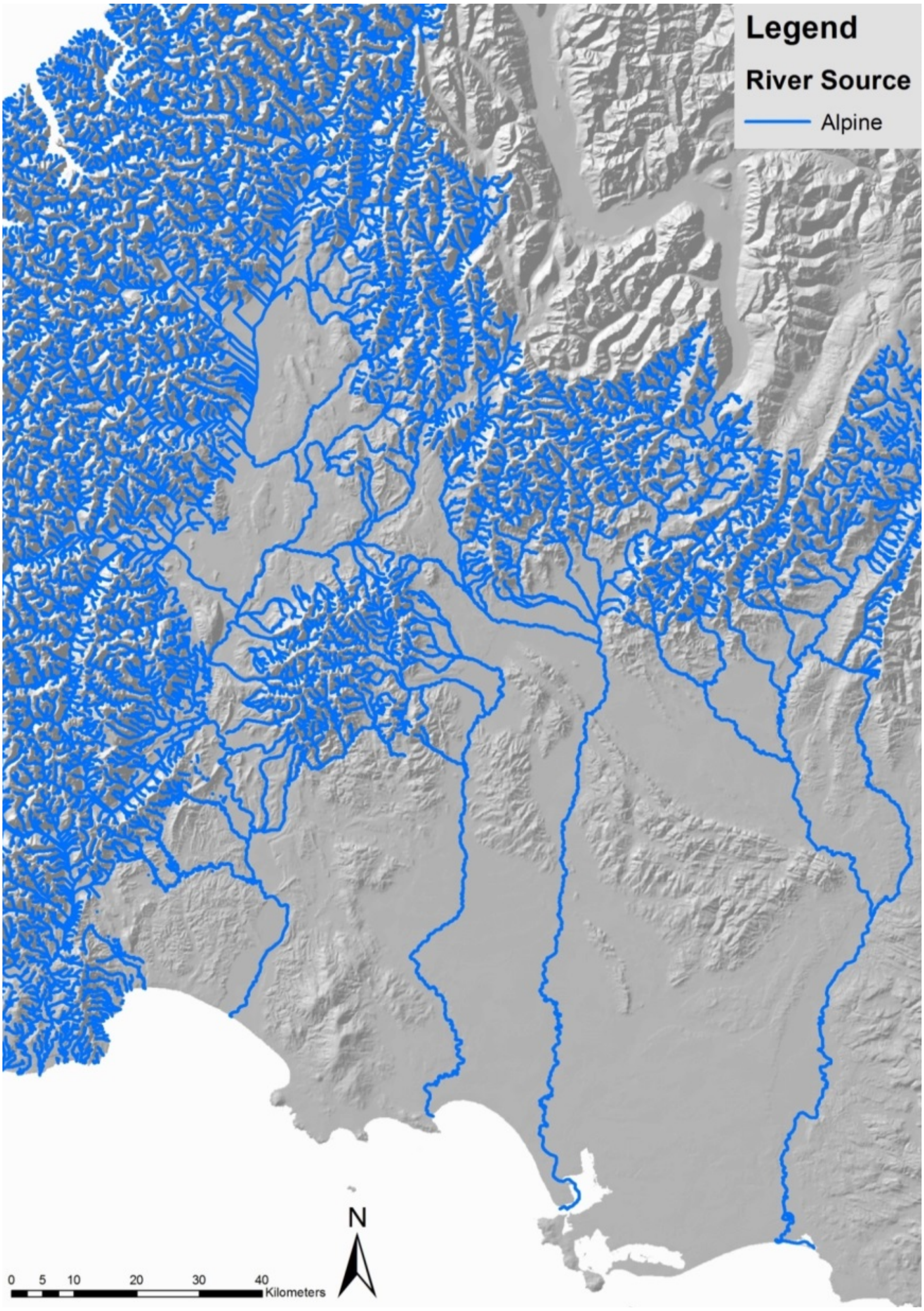

Figure 3-5: Alpine sourced river network from REC.

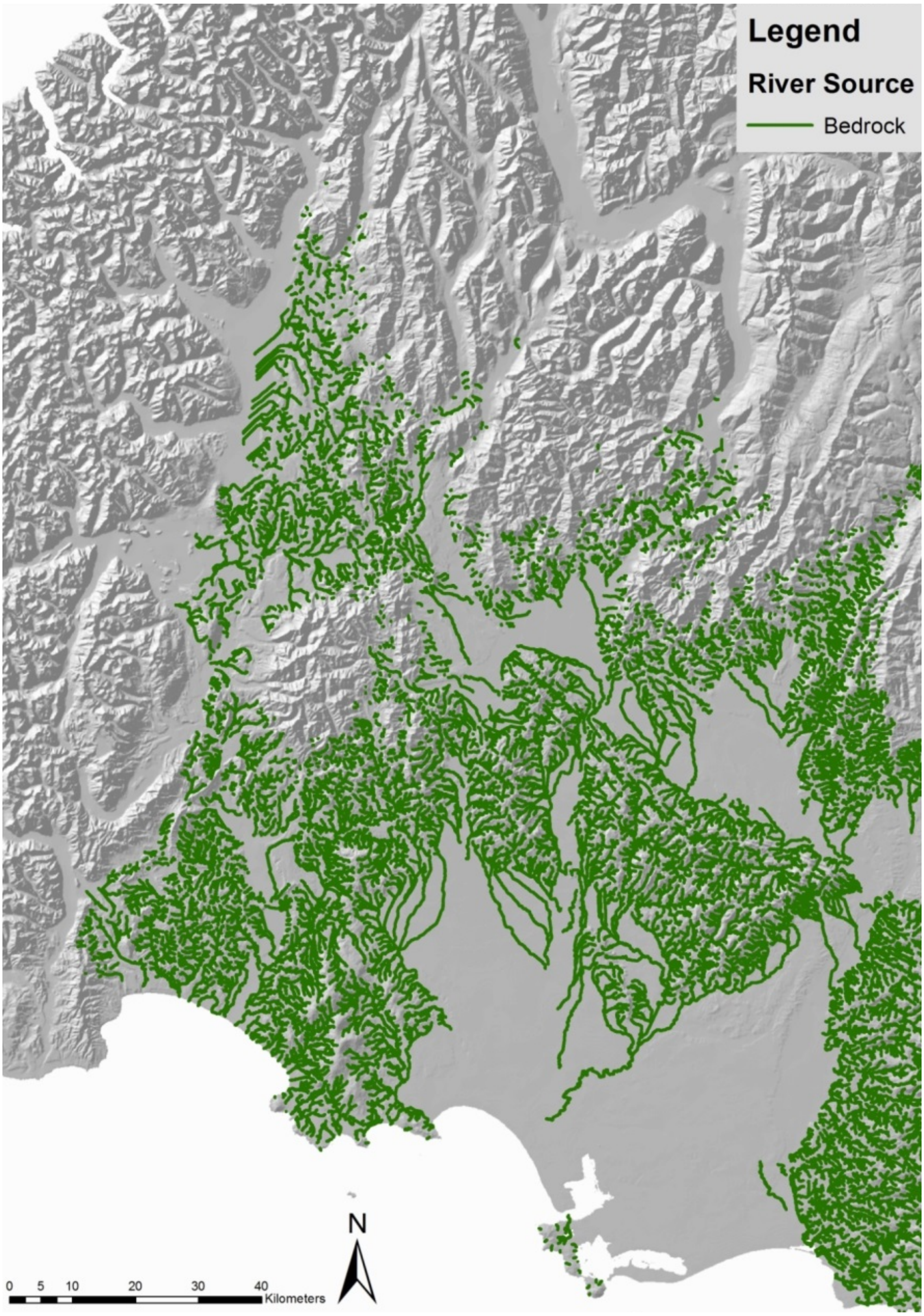

Figure 3-6: Bedrock sourced river network from REC.

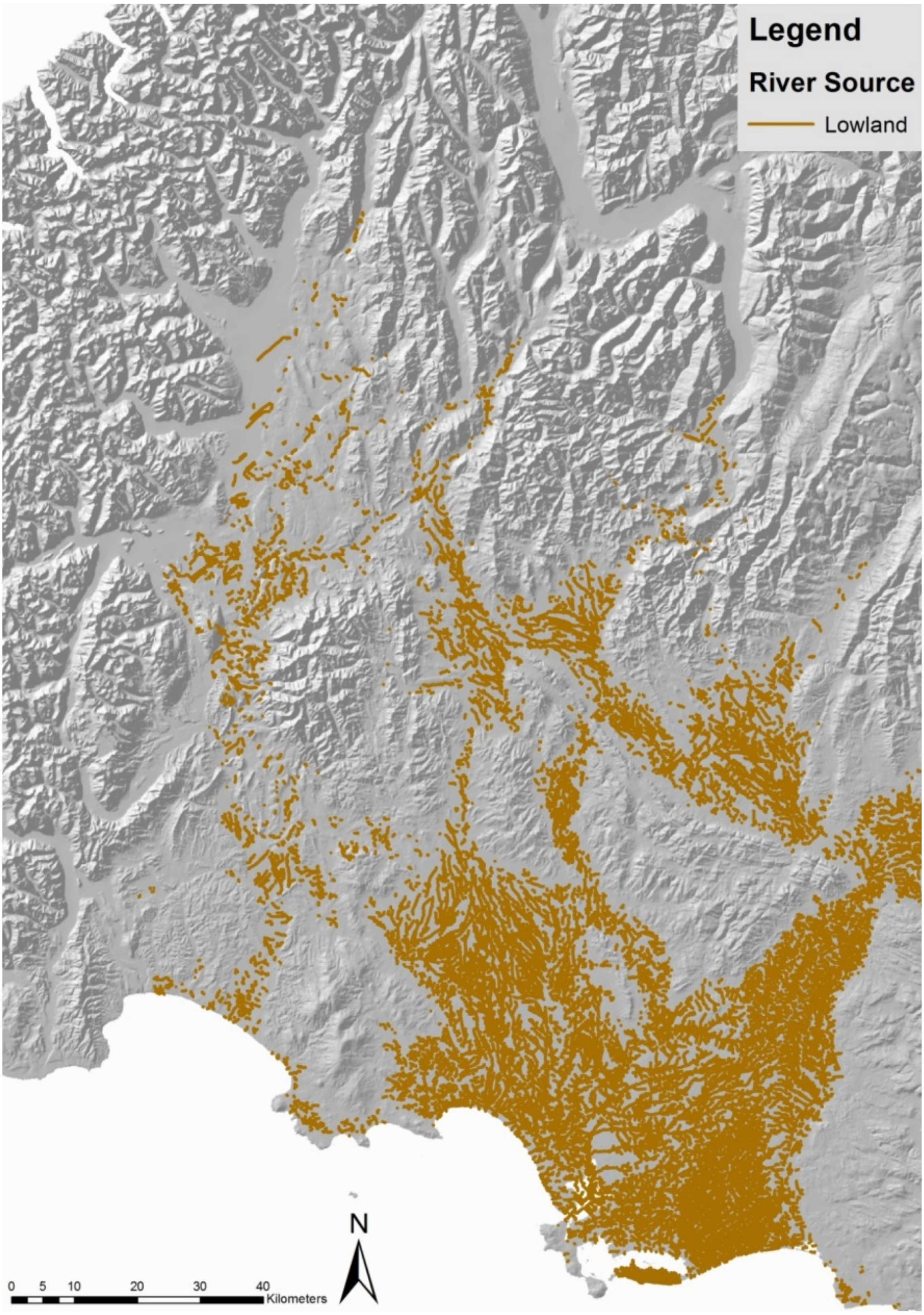

Figure 3-7: LSR sourced river network from REC.

3.2.3 Redox Driver (Combined Reduction Potential – CRP)

In this section we discuss the development of a regional redox categories and driver map. More detail on the development of the map can be found in TC 6. This map is based solely on substrate response and does not include consideration of hydrology.

We assessed the reduction potential for Southland soils and aquifers using different indicators. We used the qualitative soil and geological 'denitrification' assessments and developed maps of Killick et al. (2015) and Rissmann (2011), respectively. These assessments are inclusive of soil and aquifer hydrology[6]. The maps formed a basis for an integrated (combined) assessment of soil and geological reduction potential through assessment of the redox sensitive species DO, total oxidisable nitrogen (TON), Mn(II), Fe(II) and SO_4. Although TON is an important contaminant, an understanding of redox setting cannot be made on the basis of TON alone.

Due to the nature of the assessments of soil zone and geological denitrification potential by Killick et al. (2015) and Rissmann (2011), we consider both inferred denitrification potentials are a reasonable proxy for the broader assessment of 'reduction potential' of soil and geology, respectively[7]. Particularly, the combined assessment provides information on the ecological succession of terminal electron accepting species including redox category (e.g. oxic, mixed, anoxic) and redox process (e.g. O_2, NO_3, Mn(IV) reducing).

We then studied the relationship between estimated and observed redox indicators for groundwaters and surface waters. Notably, we demonstrated that redox sensitive parameters in regional waters vary according to the strength of reduction in the soil zone and/or underlying geology. Underlying geology includes: water bearing sediments, which can loosely be referred to as 'aquifers'; the undifferentiated vadose zone; and the stream hyporeic zone. Specifically, the concentration of redox sensitive species, general redox category and redox process for regional ground- and surface water change in a predictable manner with both soil and geological reduction potential. However, only through incorporation of recharge drivers were redox signatures strongly resolved (see Chapter 4 Stratification and validation section).

---

[6] Soil permeability and drainage status ('hydrology') is a chief determinant of overredox conditions within the soil zone as well as the pathway(s) water takes (demonstrated in TC 5 to 8). Redox signatures are well correlated with soil hydrology defined by soil drainage class (shown in TC 5 and 8). The pathway water takes also influences water composition (demonstrated in TC 5 – 7). Overland flow, lateral subsurface soil water movement including artificial subsurface drainage, vertical bypass flow impart different signatures to water composition (shown in TC 2 – 8).

[7] Specifically, where reduction potential refers to the broader redox process associated with the ecological succession of terminal electron accepting processes with an emphasis on D.O., Total Oxidisable Nitrogen (TON = NO_3^- + NO_2^-), Mn(II), Fe(II), SO_4^{2-} and CO_2 reduction as well as electron donor abundance (mainly organic carbon). Denitrification potential is more restrictive and refers exclusively to the removal of oxidised forms of nitrogen (TON) from nutrient cycling due to conversion either to nitrous oxides or N_2 gas. We note that consideration of the broader redox setting is a more robust approach to understanding the controls over redox state and process in surface and shallow ground waters across Southland.

A key finding of this chapter is that the soil zone exerts by far the greatest control over the variability in regional soil influenced ground- and surface water redox signatures. The soil zone control over oxidisable constituents, such as nitrate, relates to both deep vertical percolation but also shallow soil zone lateral discharges mediated by interflow or subsurface artificial drainage, such as mole-pipe drainage.

We conclude that the pattern in substrate mediated reduction potential requires the inclusion of both soil and geological substrates. Further, we note that the soil zone is the key control over shallow groundwater redox signatures for c. 90% of Southland's alluvial aquifer systems. Only a small proportion, c. 10%, of soil influenced aquifers, are significantly influenced by reducing aquifer materials. By comparison the majority of deeper tertiary aquifers are reducing.

On the basis of these findings, the following 12 categories were defined for redox control/combined reduction potential (CRP) of soil and geology:

- Alpine Low over Low
- Low over Intermediate
- Low over High
- Moderate over Low
- Moderate over Intermediate
- Moderate over High
- Low over Low
- High over Low
- Bedrock 1 High over Low
- Bedrock 2 High over Low
- High over Intermediate
- High over High

Figure 3-8 depicts combined reduction potential (CRP) of Southlands soil and geology, which is used as a spatially explicit presentation of substrate control over redox.

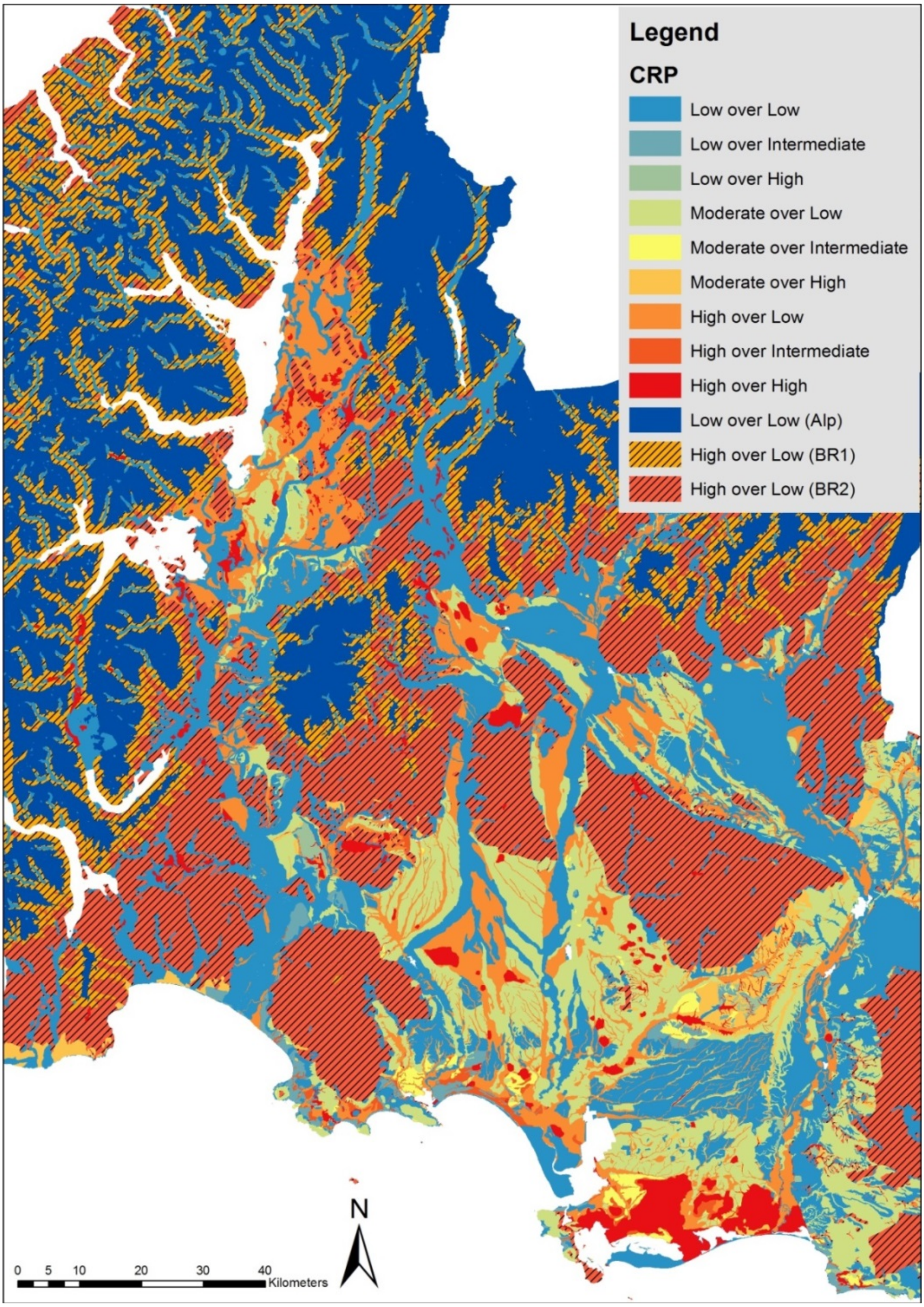

Figure 3-8: Map of combined reduction potential (CRP).

3.2.4 Geomorphic and Compositional Driver

Assessment of the chemical variation in Southland's soil and its major determinants[8] revealed that the main factors governing soil chemical variation across Southland are[9] (TC 3):

1. soil weathering (landform age);
2. parent materials;
3. drainage class;
4. retention/adsorption of P; and
5. an undetermined control over exchangeable bases.

On the basis of our analysis, we concluded that the spatial variation in chemistry of Southland soils is determined primarily (65% of the variation) by the age and degree of weathering of a soil (TC3). In turn, this is positively correlated with geomorphic land surface age and the parent material of the soils.

Other important factors determining spatial variability in soil chemistry included clay formation, exchangeable bases, and position in the landscape, for example, low-lying areas with high water table versus elevated areas with low water table. However, when combined these factors only explained <20% of the variance in soil chemical data. Significantly, we note that there was not a strong correlation between soil order or suborder and soil chemistry and composition.

Through assessment of soil water composition (in TC 4), we established the important correlation between soil BS, pH and soil water hydrochemical composition. We also demonstrated how the alkalinity of shallow, soil influenced groundwater can be estimated from soil pH and the partial pressure of soil zone CO_2.

Further we demonstrated the key relationships between soil water hydrochemistry and regional surface (in TC5). We found no statistically significant difference in Ca and alkalinity concentration between soil waters and oxidised, under-statured (with respects to carbonate minerals) ground- and surface waters regionally suggesting that the soil zone is the main source of alkalinity in regional freshwater suggesting a predominantly soil zone origin for these species. The latter is an important observation. If significant post infiltration water-rock interaction was occurring, an increase in Ca and alkalinity would be evident (TC4 and 5).

Collectively, the work of TC 3 to TC 5 demonstrates the coupled relationship between geomorphic surface age and substrate composition over the Ca, Mg, pH and alkalinity profiles of regional soil, soil waters, surface water and soil-influenced groundwaters.

On the basis of the above findings and the understanding developed in TC 3 to 5 (and TC 7) we classified spatial frameworks of geomorphic surface age and substrate composition into meaningful

---

[8] Using data available through Topoclimate South, Wallace County Soil Survey and the General Survey of the Soils of the South Island and a number of statistical techniques

[9] See TC4, A5, and A6 for more detail.

categories that govern spatial variance in Ca, Mg, pH and alkalinity profiles of regional soil[10], soil waters, surface water and soil-influenced groundwaters (in TC 8). Specifically, we developed a regional scale map of geomorphic surface age and compositional assemblages as key drivers of regional freshwater composition(in TC 8).

We used existing frameworks (i.e., QMAP and TopoClimate/S-Map) to classify geomorphic surface age and substrate composition according to their influence over the hydrochemical variation in Ca and Mg abundances and pH buffering of regional freshwaters (TC8). Developing a regional scale map of rock and sediment provenance required combination of local geological knowledge in addition to existing spatial frameworks. Specifically, the spatial frameworks important to classification of the drivers of hydrochemical variation in Ca and Mg abundance, pH and alkalinity across Southland are the S-Map parent material source layer, QMAP and TopoClimate, where S-Map provides an indication of soil parent material composition. QMAP also provides an estimate of depositional landform age which serves as a proxy for geomorphic surface age.

Figure 3-9 and Figure 3-10 depict the landform type and age of surface and subsurface geology in the Southland region that serve to estimate major ion composition of regional freshwater (TC8). For the purpose of this report, Southland's geological landscape has been divided into eight distinct categories according to landform type/composition and 6 categories according to landform age:

Landform Type/Composition:

- Clastics
- Felsic
- Mafic
- Carbonate
- Peat
- Lignite/Carbonaceous
- Undifferentiated clastics
- Intermediate (between felsic and mafic)

Landform Age:

- Q1
- Q2-4
- Q5-Q7
- Q8-Q10
- Q11-Pl
- Erosive

---

[10] Where alkalinity refers to soil alkalinity generating potential.

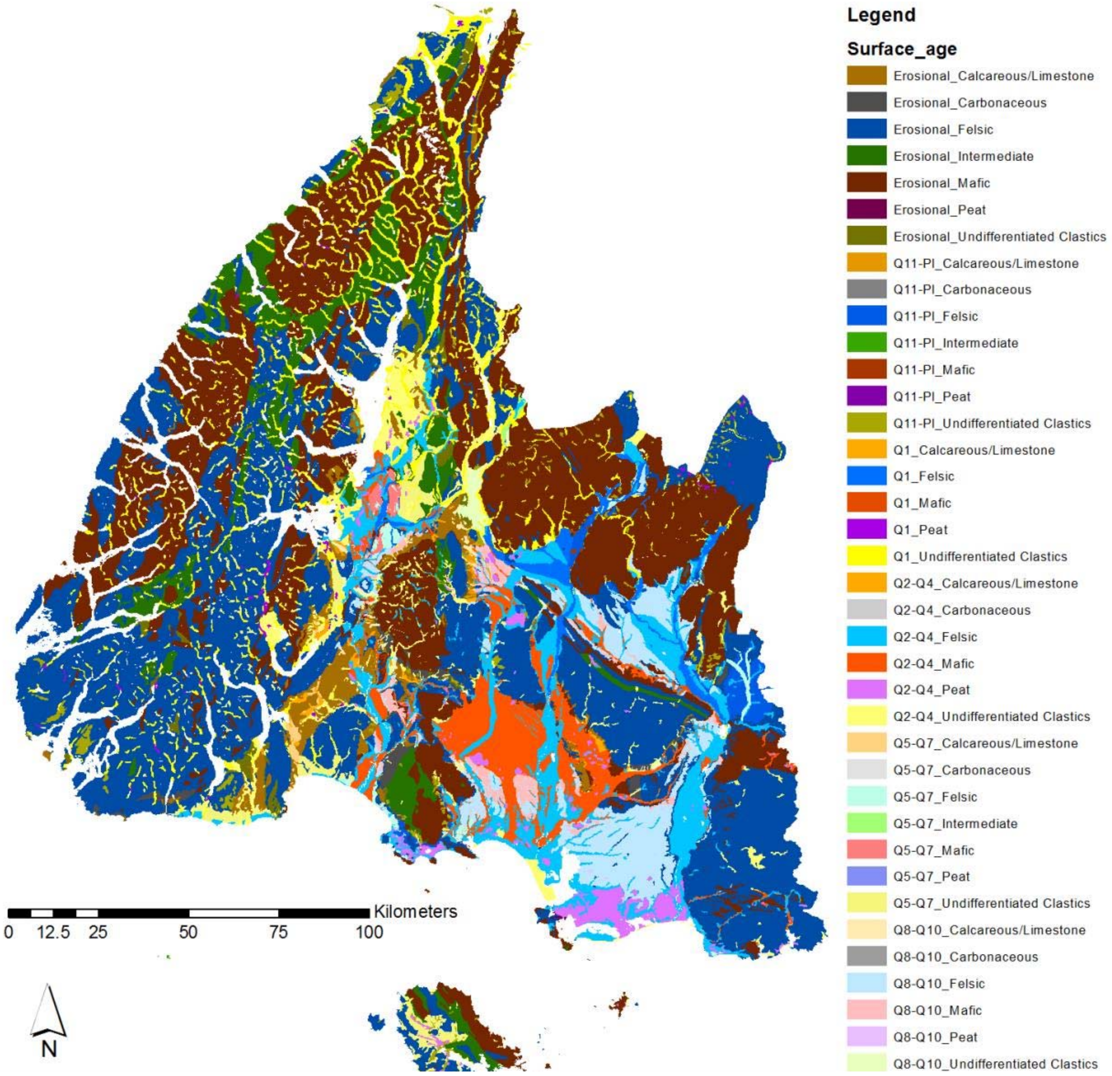

Figure 3-9: Spatial variation in the main rock and sediment compositional types across Southland, including landform type and age, for surface geology.

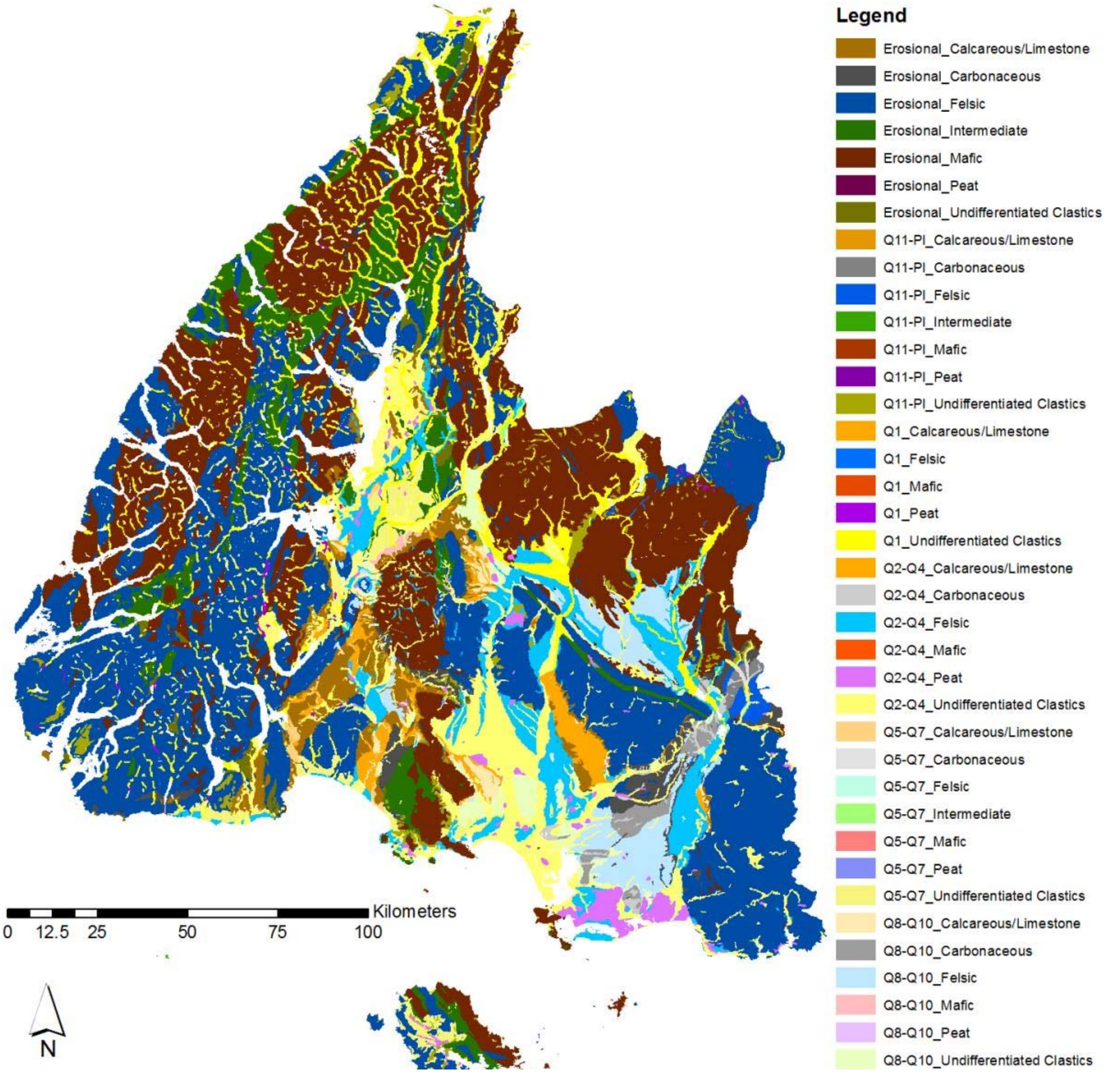

Figure 3-10: Spatial variation in the main rock and sediment compositional types across Southland, including landform type and age, for subsurface geology.

3.3 Summary

In this section we have described the development of regional driver maps of freshwater hydrochemistry. These were: 1) precipitation source, 2) recharge mechanism and source, 3) landform age and type, and 4) redox control (CRP). On the basis of the developed driver maps, we hypothesise that the hydrochemistry of surface water and regional soil-influenced groundwater can be estimated from the assemblage of key drivers associated with a given capture zone for surface water and soil influenced groundwater.

Possible combinations of driver categories for surface water are illustrated in Figure 3-11, and groundwater in Figure 3-12. Each combination of key driver assemblage will result in a unique freshwater composition. Due to the spatial extent of the key driver categories (depicted Figure 3-3 to Figure 3-8), some assemblages do not occur at any given site. These include the combinations of, alpine river recharge and coastal precipitation, and land surface recharge and alpine2 (the most dilute) precipitation.

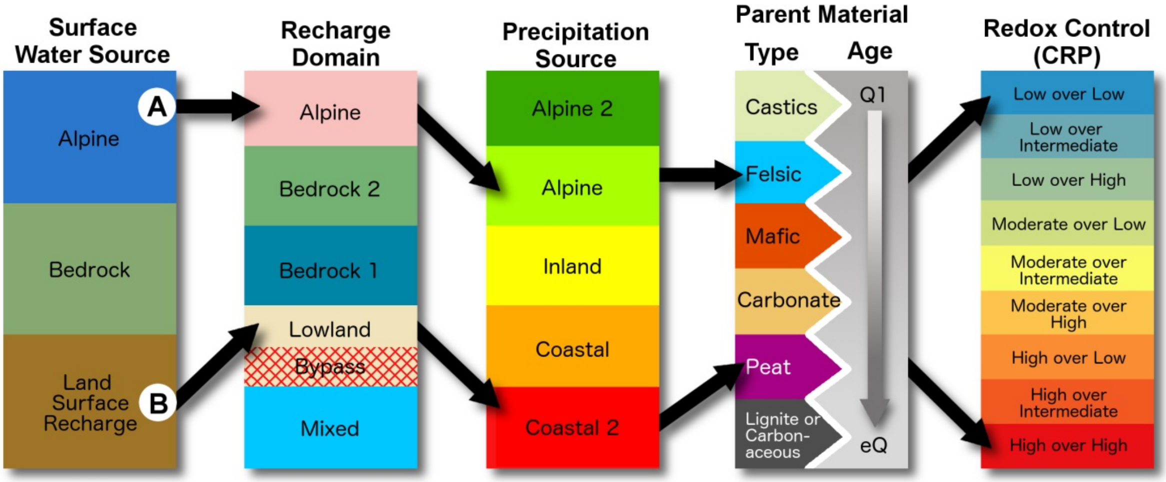

Figure 3-11: Key driver assemblages for surface water. Key driver assemblage for example A is expected to result in the following surface water properties: most dilute of all surface waters (lowest EC), highly oxic, of type Ca-HCO$_3$ and most negative δ^{18}O-H$_2$O of all surface waters. Surface water of example B is expected to have the following properties: highly concentrated (highest EC) of all surface waters, of type Na-Cl, highly reduced and of highest δ^{18}O-H$_2$O values.

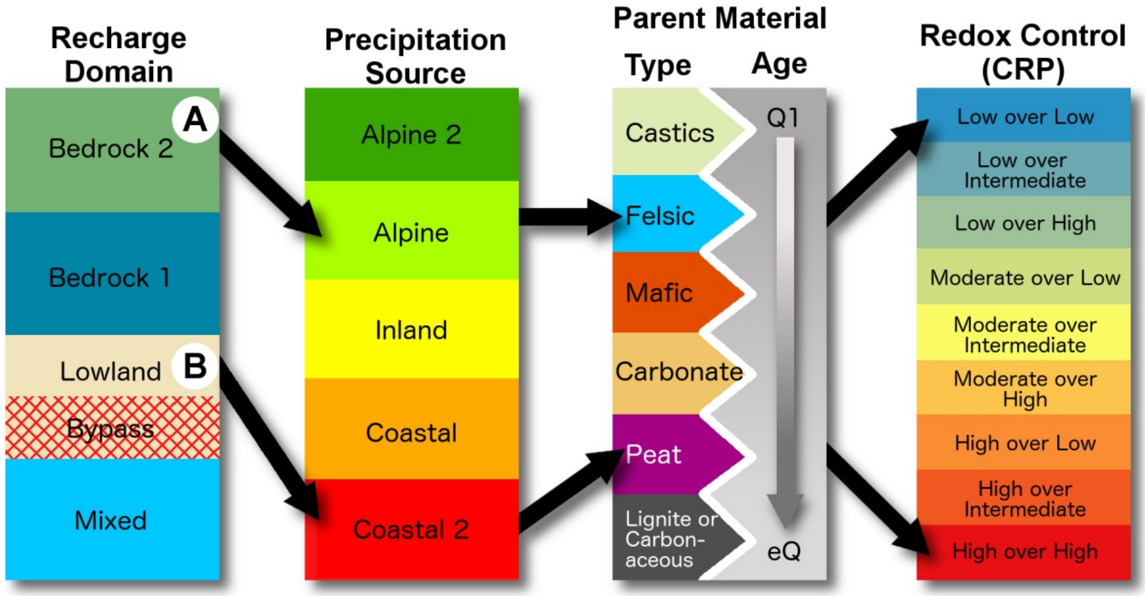

Figure 3-12: Key driver assemblages for groundwater. Key driver assemblage for example A is expected to result in the following groundwater properties: most dilute of all groundwaters (lowest EC), highly oxic, of type Ca-HCO$_3$ and most negative δ^{18}O-H$_2$O of all groundwaters. Groundwater of example B is expected to have the following properties: highly concentrated (highest EC) of all groundwaters, of type Na-Cl, highly reduced and most positive δ^{18}O-H$_2$O values.

Summaries of expected freshwater composition for combinations of existing driver categories are given in Table 3-3 and Table 3-4. Table 3-3 provides a summary of dominant combinations of driver categories and expected surface water (SW) composition in the Southland region. Table shows site specific driver assemblages for groundwater.

For simplification, freshwater composition is represented by water type and redox state only in Table 3-3 and Table 3-4. Whilst it appears that non-unique outcomes can be achieved in the below table, compositional differences are apparent when looking at more detailed composition such as major/minor ions (ion ratios), mineral, saturation indices and/or stable isotopes (see also TC7). Only key variables are shown in the table, the ‘other characteristics’ column attempts to summarise/highlight more detailed compositional differences.

Table 3-3: Summary of existing combinations of driver categories and expected surface water (SW) composition in the Southland region. Only key variables are shown in the table, the 'other characteristics' column attempts to summarise/highlight more detailed compositional differences. Parent material age is not included and is not expected to have a significant impact on SW composition at this level of detail. The impact of redox control (CRP) on SW composition is captured in 'other categories' column, * dominant in CZ.

Recharge mechanism in capture zone		Ppt source*	Parent material composition*	Expected characteristics of water			
Source	**Recharge Domain***			**EC**	**Major ions**	**Redox**	**Other characteristics**
Alpine	Predominantly alpine river recharge (ARR)	Any	Any	Most dilute of all SWs	Ca-HCO_3(minor $MgHCO_3$)	Oxic	Most negative $\delta^{18}O$ of all SWs
Alpine	Predominantly bedrock (2) river recharge (BRR)	Any	Any	Less dilute than above	Ca-HCO_3(minor $MgHCO_3$)	Oxic	More positive $\delta^{18}O$ than above
Alpine	Predominantly LSR	Any	Any	Highest EC of all alpine sourced SW	Ca-HCO_3	Oxic	More positive $\delta^{18}O$ than above
Bedrock	Predominantly BRR	Inland	Any	Lowest EC of all bedrock derived SWs	Na- HCO_3-Cl	Oxic	Higher dissolved Fe(II), Mn(II) and TOC (Fe > 0.1 mg/L; TOC > 8mg/L) and lower TON (TON<1 mg/L) than alpine sourced SWs; more dilute and composition close to that of alpine sourced water if BRR 2 recharged than when BRR 1 recharged
Bedrock	Predominantly BRR	Coastal	Any	Higher EC than above	Na-Cl-HCO3	Oxic	Higher Na and Cl than above; more dilute and composition close to that of alpine sourced water if BRR 2 recharged than when BRR 1 recharged
Bedrock	Predominantly LSR	Any	Any, except carbonate	Higher EC than above	Ca-Cl	Oxic	Higher Ca, Mg, K, SO4, alkalinity and TON, plus lower Fe(II), Mn(II) and TAN than above
Bedrock	Predominantly LSR	Any	Any, carbonate	Highest EC of all bedrock derived SWs	Ca-HCO_3	Oxic	Highest Ca, HCO3 and alkalinity of all bedrock sourced SWs
Lowland LSR	Entirely LSR	Any	Any, carbonate	Highest EC of all SWs	Ca-HCO_3	Oxic	Highest alkalinity, Ca and HCO3 concentration of all lowland LSR SWs
Lowland LSR	Entirely LSR	Any	Predominantly mafic, some	Similar to above	Ca-HCO_3	Oxic	Higher concentration of oxidized species (e.g. TON) and lowest concentration of reduced species (e.g.

Recharge mechanism in capture zone		Ppt source*	Parent material composition*	Expected characteristics of water			
Source	Recharge Domain*			EC	Major ions	Redox	Other characteristics
			peat, no carbonate				Fe(II)) - likely increasing and decreasing, respectively with increasing proportion of LL CRP in capture zone
Lowland LSR	Entirely LSR	Any	Predom. mafic, no peat, no carbonate	Similar to above	Ca-Cl	Oxic	Elevated DRP, DOC, TOC, Mn(II), Fe(II) than above
Lowland LSR	Entirely LSR	Any	Predominantly felsic, some peat, no carbonate	Similar to above	Na-Cl	Oxic	Higher concentration of oxidized species (e.g. TON) and lowest concentration of reduced species (e.g. Fe(II)) – likely increasing and decreasing, respectively with increasing proportion of LL CRP in capture zone
Lowland LSR	Entirely LSR	Any	Predominantly felsic, no peat, no carbonate	Similar to above	Na-Cl	Oxic	Elevated DRP, DOC, TOC, Mn(II), Fe(II) than above (likely increasing with proportion of peat in capture zone)
Lowland LSR	Entirely LSR, bypass (Central plains)	Any	Any,	Similar to above	Various	Oxic	Oxidising characteristics, such as elevated TON and low Mn(II) and Fe(II) concentrations

Table 3-4: Summary of existing combinations of driver categories and expected groundwater (GW) composition in the Southland region. Only key variables are shown in the table. The 'other characteristics' column attempts to summarize/highlight more detailed compositional differences. Parent material age is not included and is not expected to have a significant impact on GW composition at this level of detail, * present at site.

Recharge mechanism in capture zone*	Ppt source*	Parent material composition*	CRP*	Expected Characteristics of water			
				EC	Major ions	Redox state	Other characteristics
Large proportion of ARR	Predominantly alpine or inland	Any, no carbonate or peat present	Predom. LL or HL/HH with bypass	Most dilute of all mixed recharge GWs	Ca-HCO_3	Oxic	Most negative $\delta^{18}O$-H_2O values, very dilute, very oxic
Large proportion of ARR	Predominantly alpine or inland	Any, no carbonate or peat present	Predominantly HL	Similar to above	Ca-HCO_3	Oxic or mixed	Same as above with higher concentration of reduced species (e.g. Fe(II), Mn(II)) and lower concentration of oxidized species (e.g. DO) than above
Large proportion of ARR	Predominantly coastal	Any, no carbonate or peat present	Predominantly LL or HL/HH with presence of bypass	Higher EC than above	Ca-Cl or Na-Cl	Oxic	Higher concentration of Cl and Na and more positive $\delta^{18}O$-H_2O than above, , higher Na and Cl concentrations increasing with increasing proportion of coastal ppt source in the capture zone
Large proportion of ARR	Predominantly coastal	Any, no carbonate or peat present	Predominantly HL	Similar to above	Ca-Cl or Na-Cl	Oxic or mixed	Same as above, with higher concentration of reduced species (e.g. Fe(II), Mn(II)) & lower concentration of oxidized species (e.g. D.O.) than above
Large proportion of BRR	Predominantly inland	Any, no carbonate or peat present	Predominantly LL or HL/HH with presence of bypass	Slightly higher EC than predominantly ARR, but still relatively dilute	Ca/Na/Mg-HCO_3, dependent on parent material	Oxic to mixed	Reducing signature due to large proportion of BRR, despite predominantly oxidizing geology and soil
Large proportion of BRR	Predominantly inland	Any, no carbonate or peat present	Predominantly HL	Similar to above	Ca/Na/Mg/Fe-HCO_3, dependent on parent material	Mixed to anoxic	Even higher concentration of reduced species (e.g. Fe(II), Mn(II)) & lower concentration of oxidized species (e.g. D.O.) than above - strongly reducing
Large	Predomi-	Any, no	Predominantly	Higher than	Ca/Na/Mg -HCO_3	Oxic to mixed	Reducing signature due to large

Recharge mechanism in capture zone*	Ppt source*	Parent material composition*	CRP*	Expected Characteristics of water			
				EC	Major ions	Redox state	Other characteristics
proportion of BRR	nantly coastal	carbonate or peat present	LL or HL/HH with presence of bypass	above	(/Cl if proportion of LSR with coastal ppt is large enough), dependent on parent material		proportion of BRR, despite predominantly oxidizing geology and soil, higher Na and Cl concentrations increasing with increasing proportion of coastal ppt source in the capture zone
Large proportion of BRR	Predominantly coastal	Any, no carbonate or peat present	Predominantly HL	Similar to above	Similar to above	Anoxic or mixed	Same as above with higher concentration of reduced species (e.g. Fe(II), Mn(II)) & lower concentration of oxidized species (e.g. D.O.) than above
Large proportion of LSR	Predominantly inland	Any, no carbonate or peat present	Predominantly LL or HL/HH with presence of bypass	Higher than ARR and BRR dominated	Ca/Na/Mg-HCO_3, dependent on parent material	Oxic	Higher Cl, Na, SpC and more positive $\delta^{18}O$-H_2O than above; Higher Ca, Mg, pH and alkalinity than above (likely increasing with increasing proportion of mafic geology in capture zone), increasing Na and Cl concentrations with increasing proportion of coastal ppt source in the capture zone
Large proportion of LSR	Predominantly inland	Any, no carbonate or peat present	Predominantly HL	Similar to above	Similar to above, potentially Fe(II) as dominant cation if strongly reducing	Mixed to anoxic	Same as above with higher concentration of reduced species (e.g. Fe(II), Mn(II)) & lower concentration of oxidized species (e.g. D.O.) than above
Large proportion of LSR	Predominantly coastal	Any, no carbonate or peat present	Predominantly LL or HL/HH with presence of bypass	Highest EC of all mixed recharge GWs	Ca/Na/Mg-Cl , dependent on parent material	Oxic	Higher Cl, Na, SpC and more positive $\delta^{18}O$-H_2O than above; Higher Ca, Mg, pH and alkalinity than above (likely increasing with increasing proportion of mafic geology in capture zone), increasing Na and Cl load with increasing proportion of coastal ppt in capture zone

Recharge mechanism in capture zone*	Ppt source*	Parent material composition*	CRP*	Expected Characteristics of water			
				EC	Major ions	Redox state	Other characteristics
Large proportion of LSR	Predominantly coastal	Any, no carbonate or peat present	Predominantly HL	Similar to above	Similar to above	Mixed to anoxic	Same as above with higher concentration of reduced species (e.g. Fe(II), Mn(II)) & lower concentration of oxidized species (e.g. D.O.) than above
Mixed, any proportion of LSR, BRR and ARR	Any	Any, presence of carbonate	Predominantly LL or HL/HH with presence of bypass	Relatively high, depending on ppt source	Ca-HCO_3	Oxic	Highest Ca, HCO_3 and alkalinity of all mixed recharged GWs, saturated with respect to calcite, increasing Na and Cl concentrations with increasing proportion of coastal ppt source in the capture zone
Mixed, any proportion of LSR, BRR and ARR	Any	Any, presence of carbonate	Predominantly HL or HH	Similar to above	Ca-HCO_3	Mixed to anoxic	Same as above with higher concentration of reduced species (e.g. Fe(II), Mn(II)) & lower concentration of oxidized species (e.g. D.O.) than above
Mixed, any proportion of LSR, BRR and ARR	Any	Any, presence of peat or lignite, marine terraces	Predominantly LL or HL/HH with presence of bypass	Various, dependent on ppt source	Na/Mg/Ca - HCO_3/Cl, dependent on parent material and proportion of coastal ppt	Mixed to anoxic	Reducing, despite presence of oxidizing geology/soil, increasing Na and Cl load with increasing proportion of coastal ppt in capture zone
Mixed, any proportion of LSR, BRR and ARR	Any	Any, presence of peat or lignite, marine terraces	Predominantly HL or HH	Similar to above	Similar to above, potentially Fe(II) as dominant cation if strongly reducing and small proportion of coastal ppt	Anoxic	Same as above with even higher concentration of reduced species (e.g. Fe(II), Mn(II)) & lower concentration of oxidized species (e.g. D.O.) than above - Strongly reducing
LSR dominated	Predominantly coastal	Any, no carbonate or peat present	Predominantly LL or HL/HH with presence	Highest of all GWs	Na-Cl	Mixed to anoxic	Higher concentration of Cl and Na and more positive δ^{18}O-H_2O than above, increasing Na and Cl load with

Recharge mechanism in capture zone*	Ppt source*	Parent material composition*	CRP*	Expected Characteristics of water			
				EC	Major ions	Redox state	Other characteristics
			of bypass flow				increasing proportion of coastal ppt in capture zone
LSR dominated	Predominantly coastal	Any, no carbonate or peat present	Predominantly HL or HH	Similar to above	Na/Fe-Cl	Anoxic/mixed	Same as above, plus very high Fe(II), moderately reducing,
LSR dominated	Predominantly inland	Any, no carbonate or peat present	Predominantly LL or HL/HH with presence of bypass flow	Lowest of all LSR GW, but higher than mixed recharged GWs	Na/Mg/Ca-HCO$_3$ dependent on parent material	Mixed to anoxic	Reducing, despite presence of oxidizing geology/soil
LSR dominated	Predominantly inland	Any, no carbonate or peat present	Predominantly HH or HL	Similar to above	Na/Mg/Ca (/Fe)-HCO$_3$, dependent on parent material	Anoxic	Same as above with even higher concentration of reduced species (e.g. Fe(II), Mn(II)) & lower concentration of oxidized species (e.g. D.O.) than above
LSR dominated	Predominantly coastal	Any, with presence of peat	any	Various, dependent on ppt source	Na/Fe-Cl	Anoxic/mixed	Very high Fe(II), strongly reducing, increasing Na and Cl concentrations with increasing proportion of coastal ppt source in the capture zone
LSR dominated	Any	Any, with presence of carbonate	Predominantly HH or HL	Relatively high, depending on ppt source	Ca-HCO$_3$	Anoxic/mixed	Saturated with respect to calcite, but still strongly reducing signature, increasing Na and Cl concentrations with increasing proportion of coastal ppt source in the capture zone
LSR dominated	Any	Any, with presence of carbonate	Predominantly LL or HL/HH with presence of bypass flow	Relatively high, depending on ppt source	Ca-HCO$_3$	Oxic	Same as above with higher concentration of reduced species (e.g. Fe(II), Mn(II)) & lower concentration of oxidized species (e.g. D.O.) than above

4. Validating the conceptual model

4.1 Introduction

The aim of this chapter is to assess how well the conceptual model of hydrochemical drivers estimates the spatial variation in surface water and soil-influenced groundwater hydrochemical setting across Southland. To do this we applied two approaches to validate and test the performance of the conceptual framework developed in TCs 1 to 8 and as summarised in Chapter 3 of this report. These approaches are:

(i) A **statistical modelling approach** to assesses objectively (without human influence) whether observed patterns in hydrochemistry and drivers are consistent with the conceptual model, and

(ii) A manual **hierarchal stratification** of spatial data according to hydrochemical drivers. This manual approach was guided by expert knowledge of the mechanistic controls as elucidated by the conceptual model (Chapter 3).

The same data sets were used for both the statistical model and manual hierarchal stratification (hereafter 'hierarchal stratification'). The purpose of each analysis was two-fold: (i) To examine the nature of the underlying relationships to assess whether these are consistent with theoretical considerations. Consistency between objectively determined relationships and theoretical considerations supports the technical assessment of cause-effect relationship and supports the conceptual model as a basis for understanding the spatial variation of hydrochemistry and water quality, and; (ii) assess as to whether the data derived drivers of hydrochemistry have utility as estimators of observed hydrochemical setting. Demonstration of objective predictions supports the use of mapped driver information to understand hydrochemical and water quality variation across the region.

The performance of the conceptual model through both statistical modelling and hierarchal stratification was assessed against groups of sampling sites defined by general hydrochemical setting and Hierarchal Cluster Analysis (HCA) as well as a range of hydrochemical metrics (i.e., major ion facies and redox assignments). Detailed data on the chemical and isotopic composition of freshwater, including major ion concentrations, mineral saturation indices, redox sensitive species and redox metrics (ORP) provided finer grained resolution than HCA clusters on their own. Accordingly, the model was also tested against a larger suite of hydrochemical variables including stable isotopes, major ions, trace ions and organic constituents.

4.2 Method

In this section we briefly describe quality control (QA/QC) and spatial intersection of hydrochemical data used for validation. More detail regarding QA/QC protocols and delineation of surface water capture zones is provided in the Appendices C1 and D1, respectively.

4.2.1 Data intersection for validation

4.2.1.1 QA/QC of Data

We used cumulative probability plots (Appendix C 1) and HCA single linkage to identify samples with anomalous hydrochemical signatures (contaminated sites or potentially erroneous data). This included identification of ground and surface water sites associated with direct contamination by animal wastes and sites of known contamination[11]. Any bores known to be influenced by poor well head protection were also removed following the water quality assurance protocol outlined in Appendix C1. Applying the quality assurance protocol removed the majority of anomalous groundwater facies (e.g. Ca-SO_4, Mg-SO_4, Mg-Cl, NO_3-SO_4), leaving 225 groundwater sites with median hydrochemical data. Of the 225 groundwater sites, 32 were associated with semi-confined or confined aquifers as defined by Environment Southland's wells database and as such were excluded from subsequent analysis. Selecting only well constrained bores associated with unconfined or water table aquifers resulted in a total of 193 groundwater sites. The number of surface water sites available for assessment were restricted to those with delineated capture zones (n = 93). Surface water capture zones were based on REC classification polygons (see detail in section 2.3.2 and Appendix D1).

Of the final 93 surface water and 193 groundwater sites, the number of hydrochemical analytes (hereafter 'variables') ranged between 35 – 50+. These included a hydrochemical ion or solute suite, varying stable isotope and radiogenic (tritium) measures and field parameters (DO, Temp., pH, EC, ORP). A number of the sites had >30 replicates, while some groundwater sites only had one. The median values of each analyte were used for sites with more than one sample. Hydrochemical metrics were calculated from hydrochemical data to provide: (i) major ion facies, (ii) general redox state and redox process (TEAP); (iii) mineral saturation indices, and; (iv) a more general characterisation of hydrochemical composition based on hierarchical cluster analysis (HCA) of the individual hydrochemical variables (section 4.2.1.2 and Appendix E). For groundwater sites an assessment of the general hydrochemical setting was also made as per the hydrochemical variables (Daugghney et al., 2015; Appendix E).

The hydrochemical variables that characterise the data were placed into four general categories:

1. Hydrological tracers: $\delta^{18}O$-H_2O, $\delta^{2}H$-H_2O, $\delta^{13}C$-DIC, Cl, Br, I, F, SO_4 and Na
2. Soil-water-rock interaction tracers: Ca, Mg, K, Na, SO_4, Si, Alkalinity, $\delta^{13}C$-DIC, DOC, TOC and pH
3. Redox indicators: DO, TN, TON, Mn(II), Fe(II), SO_4, and ancillary indicators DOC, TOC, TAN, DRP

---

[11] For example, community sewage scheme monitoring sites; septic contaminated groundwaters; Taha Crawfords site.

4. Water quality metrics: TN, TON, TP, DRP, SS, SSV, TAN, clarity, turbidity, *E.coli*

Note that some hydrochemical variables fall into more than one category due to multiple interactions and/or origins. Hydrological tracers are those species that are often good indictors of water source and recharge mechanism, including precipitation and associated aerosol load. Soil-water-rock indicators relate to changes occurring during the passage and subsequent interaction of water with soil, biology and geology. Redox indicators are also an artefact of interaction with soil, biology and geology but also provide important information on the redox conditions (state and process) within the site of drainage or within an aquifer. Water quality metrics are specific to our understanding of ecosystem, animal and human health. Groundwater data do not routinely contain measures of SS, SSV, clarity or turbidity so these metrics were excluded from the regional groundwater data set used for this assessment.

4.2.1.2 Hierarchical cluster analysis

As noted earlier, the performance of the conceptual model was assessed against predefined measures: (i) general hydrochemical setting (groundwater); (ii) empirically derived Hierarchal Clusters; (iii) redox assignments, and; (iv) major ion facies. For surface waters we used the HCA clusters defined in Daughney et al. (2015).

We chose to aggregate the Level 4 clusters to define the following five aggregated categories or 'general hydrochemical setting' defined primarily by recharge mechanism/water source and redox signatures that correlate with the main regional settings (i.e., alpine, inland basins, lowland etc) :

1. River influenced clusters: 1B0b, 1C1b, 1C2a, 1C2b
2. Oxidised, LSR clusters: 1C1a, 2B0a, and 2B0b
3. Weakly reducing clusters, LSR: 2a2a, 2a2b, 2a2c (all associated with reducing soils)
4. Organic carbon/reducing clusters, LSR: 3B1o, 3B2a, 3B2b
5. Carbonate influenced, LSR: 2A10

For groundwater, we found the HCA clusters defined in Daughney et al. (2015) did not provide sufficient resolution over groundwater origin and consequently hydrochemical setting. The poorer resolution of HCA clusters for groundwater reflects the combination of surface and groundwater data set for the HCA run and the use of only 10 variables (Daughney et al., 2015). For these reasons we re-clustered the groundwater data separately and included an additional 5 variables including $\delta^{18}O\text{-}H_2O$, one of the stable isotopes of water (Table 4-1), from which 3 general categories or 'general hydrochemical settings' were defined (Table 4-2; further detailed in Appendix E). Assessment of drivers against new cluster memberships and general hydrochemical setting gave much clearer, hydrochemically/genetically sensible results and a good to strong, fitted miss-classification rate (see section 4.3.1.2 Groundwater).

An ability to estimate the general hydrochemical setting for groundwater is important as redox in conjunction with water source and recharge mechanism are the two chief determinants of water quality outcomes (variation) in areas of intensive landuse in Southland and New Zealand (TC1-8 and Daughney, 2005, Daughney and Reeves, 2005, Daughney et al., 2010; Rissmann et al., 2012;

Daughney et al., 2015). As defined above, general hydrochemical setting is a factor of recharge mechanism and water source and includes discrimination between river influence and land surface recharged aquifers and redox setting (TC 1 - 8). Modifiers such as geomorphic age and substrate composition along with variation and marine aerosol load introduce extra resolution of hydrochemical metrics such as major ion facies (i.e., whether a water is a $Ca\text{-}HCO_3$ or Na-Cl water), which although useful for understanding water provenance are not essential for explaining spatial variation in water quality (TC 5 - 8).

Table 4-1: Cluster summary. The 6 general hydrochemical settings (clusters or classes) for regional unconfined aquifer systems resolved from HCA. Each cluster corresponds to 6 regionally significant hydrochemical settings.

HCA Clust	Recharge	Redox	Key characteristics	General location	n
1	River	Oxidising	Very dilute waters. Low alkalinity, low TON, $Ca\text{-}HCO_3$ and $Mg\text{-}HCO_3$ waters of low Cl; very high DO	Northern and southern groundwaters, occuring in riparian aquifers, inland or alpine precipitation, derived from high altitude rivers.	25
2	Land Surface Recharge	Oxidising	Groundwaters of elevated EC and mod-low TON. High TOC and dominantly, $Ca\text{-}HCO_3$ waters	Northern eastern and south central (west of Oreti) Southland in association with areas of reducing soils.	56
3	Land Surface Recharge	Weakly Reducing	Predominantly Na-Cl waters. Slightly elevated Fe(II), TOC and low TON consistent with weak reduction in soil zone and/or aquifer.	Mainly southeastern, Kamahi and Waikiwi Tce Formations with fewer south-western occurrences.	43
4	Land Surface Recharge	Strongly Reducing	Very low TON, high dissolved Fe, relative elevated TAN (ammonification of organic matter) and organic carbon	Most prevalent at distal end of Mataura Catchment in conjunction with marine terraces, peat wetlands and variably lignite measures. Also occurring in places across southeast of Mataura River to Coastal Longwoods. Few occurrences in northern Southland.	32
5	Land Surface Recharge	Strongly Oxidising	Characterised by very high TON (median 13.5 mg/L) but low SO_4 due to anion retention in aluminium oxide rich soils associated with the oldest geomorphic surfaces in Southland. Mainly, Na-Cl waters.	Predominantly across northern Southland in association with old remnant surfaces including Balfour, Wendonside and Knapdale areas	19
6	Land Surface Recharge	Strongly Oxidising	Waters are strongly oxidising with strongly elevated TON, Ca, SO_4, K consistent with soil zone contamination due to natural vertical bypass.	North-eastern and southern lowland	18

Table 4-2: Generalised set of 3 hydrochemical settings for regional unconfined aquifers based solely on recharge and redox.

Category	Recharge	Redox	General location	HCA cluster (s)	n
1	Land Surface Recharge	Oxidising	Present across northern and southern Southland. However absent across large areas of south-eastern Southland	2,5,6	93
2	Land Surface Recharge	Reducing	Predominantly occurring in the southeast, south of the Waimea Valley and across the historical floodplain of the Matura River. Interspersed with oxidising groundwaters predominantly across southwestern Southland and less predominantly across northern Southland	3,4	75
3	River	Oxidising	Southland's northern, inland basins (Te Anau, Fiver Rivers, Upper Mataura, Upper Waikaia and parts of the Waimea Valley that are hydrologically connected to alpine rivers) and associated alpine range fronts as well as riparian aquifers adjacent to main stem rivers.	1	25

The pattern of general hydrochemical settings for Southland's unconfined aquifer systems provides a regional spatial hydrochemical framework for Southland's unconfined aquifer systems that correspond to distinct spatial distributions.

4.2.1.3 Intersection

Following data quality assurance, hierarchal clustering, surface water capture zone delineation and groundwater hydrochemical setting assessment each site and its associated capture zone was intersected with the four driver maps developed in TCs 1 to 8. These data were used as predictors in the statistical modelling and for the manual hierarchal stratification of the sites. For the groundwater sites six predictors were available, all of which were categorical (Table 4-3). For surface water sites 29 predictors were available, four of which were categorical (Table 4-4).

Table 4-3: Groundwater predictors.

Predictor	Number of Categories	Categories
Recharge Domain	2	Land Surface Recharge(LSR),Mixed Alpine River Recharge and Land Surface Recharge
Combined Soil geological reduction potential (CRP)	6	Low over VeryLow-Low, High over Very Low-Low, Moderate over Very Low-Low, No Data, High over High-Very High, Bedrock
Parent Material Age and Composition	14	Q2-Q4 Mafic, Q1-Q2 Felsic, Q6-eQ Felsic,Q4-Q6 Clastic sediments, Q1-2 Peat, Q1-Q2 Peat, Q4-Q6 Felsic, Q2-Q4 Felsic, Q1-Q2 Mafic, Q4-Q6 Mafic, Q6-eQ Mafic, >QFelsic, Q2-Q4 Clastic sediments, Q1-Q2 Clastic sediments
Precipitation Source	5	Alpine, Alpine2, Coastal, Coastal2, Inland
Vertical Bypass Flow	2	N,Y
Carbonate Rock Presence	2	N,Y

Table 4-4: Surface water predictors.

Predictor	Number of Categories	Categories (categorical predictors) or range (continuous predictors)
River Source	3	Bedrock, Alpine, Lowlands
Alpine River Recharge	NA	0 to 85.4
Hill Bedrock River Recharge	NA	1.4 to 100
Land Surface Recharge	NA	0.7 to 100
Mixed Alpine Land Surface Recharge	NA	0 to 19
Alpine	NA	1.5 to 83.8
Alpine2	NA	12.9 to 96
Coastal	NA	0 to 100
Coastal2	NA	0 to 100
Inland	NA	0 to 100
Clastics	NA	0.1 to 50.5
Carbonate	NA	0 to 24.5
Lignite	NA	0 to 0.6
Q1-Q4 Feslic	NA	0 to 85.1
Q1-Q4 Mafic	NA	0 to 100
Peat	NA	0 to 100
Erosional Felsic	NA	0.3 to 100
Erosional Mafic-Ultramafic	NA	0 to 98.5
Q4-Q6 Felsic	NA	0 to 65.5
Q4-Q6 Mafic-Ultramafic	NA	0 to 31.1
Q6-eQ Felsic	NA	0 to 100
Q6-eQ Mafic-Ultramafic	NA	0 to 26.7
LL	NA	0.5 to 94.6
ML	NA	0 to 71.6
HH	NA	0 to 89.1
HL	NA	0.1 to 84.9
Some Carbonate	2	Y,N
PPT Alpine Spill-over	2	N,Y
Bypass Flow	2	N,Y

4.2.3 Statistical modelling approach

Statistical modelling was based on Random Forest (RF) models. RF models are a machine learning modelling method that has numerous useful properties including modelling categorical or continuous responses, using categorical or continuous predictors, detecting and fitting non-linear responses and high order interactions, and requiring no distributional assumptions (Breiman, 2001; Cutler et al. 2007).

A RF model is an ensemble of individual Classification and Regression Trees (CART; Breiman et al. 1984). RF model predictions are based on the predictions averaged over all CART models (a forest). An important feature of RF models is that each tree is grown with a bootstrap[12] sample of the training data. In addition, at each node a random subset of the predictors is made available to define

---

[12] This technique allows estimation of the sampling distribution of almost any statistic using random sampling methods. It is a form of resampling.

the split. Introducing these random components and then averaging over the forest increases prediction accuracy while retaining the numerous useful properties of CART.

RF models were fitted to various responses representing characteristics of both surface and groundwater. These responses were a mix of categorical variables, such as the HCA classes, and continuous variables such as $\delta^{13}C$-DIC and $\delta^{18}O$-H_2O.

Model parsimony is desirable for interpretation of the underlying relationship. For all models the predictor dataset was reduced using backwards elimination to produce the most parsimonious model. For the groundwater models this was the model that achieved maximum predictive performance. Surface water models had a larger suite of predictors than the groundwater models and a more aggressive reduction strategy was used. We used the ‘1 standard error rule’ (Breiman et al., 1984) to select the reduced model with the highest prediction performance that was not different, within the error generated from the cross-validation process, from the model with the best performance. Retained predictors can be considered to be making significant contributions to the model.

The performance of each model was reported for categorical responses as the ‘cross validated miss-classification rate’ and Cohen’s Kappa, and the ‘fitted miss-classification rate’ and Kappa Cohen’s kappa (K) measures inter-rater agreement for categorical items. It is a more robust measure than misclassification rate because K takes into account the agreement occurring by chance. Fleiss, (1981) provided guidelines for assessing the value of K suggesting values more than 0.75 are excellent, 0.40 to 0.75 is fair to good, and below 0.40 as poor. For continuous responses, model performance is reported as the cross validated and fitted r^2 values.

The underlying model structure was described by a measure of predictor variable importance and partial plots. When fitting a RF model, predictions are made for each tree on the observations that are excluded from the bootstrap or out-of-bag (OOB) samples. To assess the importance of a specific predictor variable, the values of the variable are randomly permuted for the OOB observations, and predictions are obtained from the tree for these modified data. The difference between the prediction accuracy (miss-classification rate or r^2) for the modified and original OOB data, divided by the standard error, measures the importance of each variable (Cutler et al. 2007).

Partial dependence plots show the marginal effect of a variable on the response after accounting for the average effects of the other variables in the model. These plots do not perfectly represent the effects of each variable, particularly when predictors are highly correlated or strongly interacting, but provide useful information for interpretation (Breiman, 2001). We also note that, because estimating a RF model involves randomly selecting observations and predictors throughout the fitting process, successive models fitted to the same data set will exhibit subtle differences in structure and diagnostics such as total explained deviance, mean square error, partial dependence plots, and the rank order of predictors of similar importance.

4.2.4 Manual hierarchical stratification of spatial hydochemical data according to hydrochemical drivers

Manual hierarchical stratification proceeds by sorting hydrochemical data for surface water and for groundwater by hydrochemical driver membership within an excel spreadsheet. Due to the natural spatial variability in freshwater chemistry, in addition to a large water data set and a large number of possible combinations of drivers, a spatially (GIS) based approach to classifying the hydrochemical data made the most sense. Figure 4-1 diagrammatically depicts the stratification approach. For example, data were sorted by recharge mechanism into land surface recharge and water source. Conceptually, as data are stratified by each driver, the hydrochemical variation in the data set should be reduced until the data formed clusters of homogenous subgroups characterised by similar driver assemblages. Ergo, where the assemblages of drivers were similar we saw similar water composition.

Most often, but not always, recharge was the first driver the data was sorted by followed variably by Precipitation Source, Combined Redox Potential (CRP) and Geomorphic age and Substrate Composition. Surface water and groundwater were stratified separately. Accordingly, stratification proceeded in a hierarchal fashion as depicted in Figure 4-1. If the hydrochemical drivers are mechanistically well defined we would expect increasing homogeneity of pre-defined hydrochemical characteristics as each successive driver group is isolated. Key metrics of success include the uniformity or otherwise of predefined general hydrochemical setting, empirical clusters (HCA), and a range of pre-defined hydrochemical metrics (i.e., hydrochemical facies, redox category) produced by successive stratification by regional drivers - essentially, a manual hierarchical clustering of hydrochemical signatures by driver assemblages.

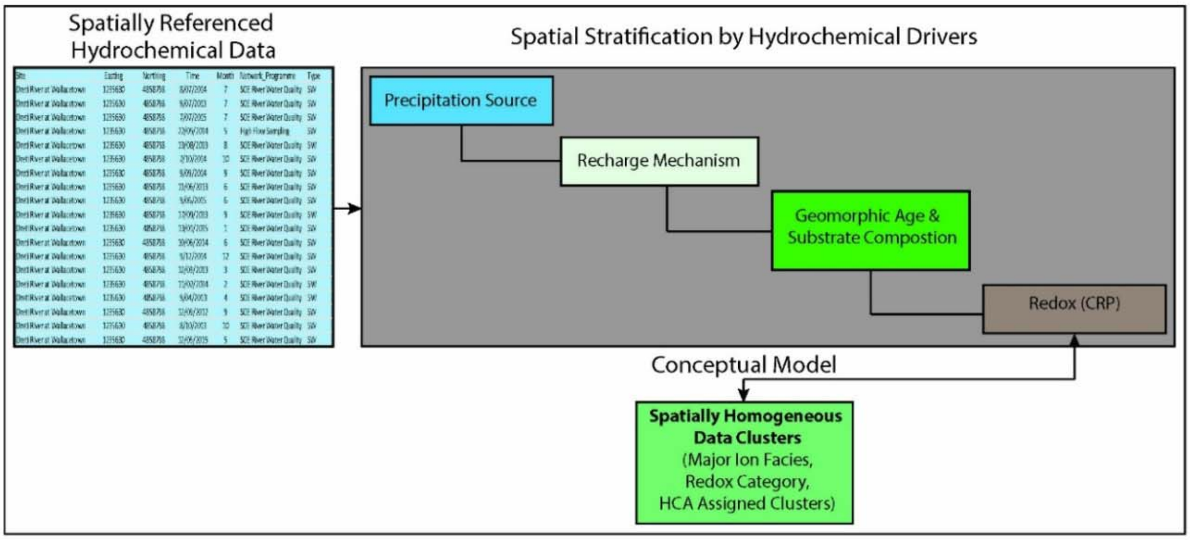

Figure 4-1: Conceptual diagram of idealised hydrochemical data stratification approach for surface water. Elucidated hydrochemical drivers are used to stratify/classify hydrochemical data sets. With each driver hydrochemical variation is reduced until the data is stratified into homogenous subgroups characterised by similar driver assemblages. However, the hierarchy of drivers, as displayed in this figure, are not fixed and vary between assemblages.

Significantly, the order of importance or degree of influence of each driver should between sites. Specifically, for a capture zone that shows major variance in redox but not in precipitation or recharge mechanism, we would expect redox category to exhibit more influence. Alternatively, geomorphic age and substrate composition and redox settings for a capture zone may be very similar but precipitation source and/or recharge mechanism may vary. Furthermore, hydrochemical variables for the same site respond to different drivers. For example, the stable isotopes of water are governed by precipitation source whereas the concentration of dissolved Fe by redox drivers and at times local hydrological factors. These are but a few examples of how driver influence may vary for a given site and/or associated capture zone.

4.3 Results

The results section is broken down into two main sections, validation through statistical models, and manual hierarchical stratification. Each section discusses results for surface and groundwater separately.

4.3.1 Statistical models

4.3.1.1 Surface water

The reduced models of the four classifications had a fitted miss-classification rates of between 2% and 20% and out-of-bag (OOB, i.e. independent predictions) miss-classification rates of between 9 and 27% (Table 4-5). OOB and fitted Kappa value ranged between 0.6 and 0.97 indicating good to excellent model performance. These results indicate a strongly consistent relationship between drivers and HCA classes and reasonable ability to predict HCA class (i.e. general hydrochemical composition) as a function of the drivers. The reduced models of the five classifications retained between two and nine predictors indicating that membership of classes is dependent on multiple predictors (Table 4-5). This supports an underlying hypothesis postulated by the conceptual model that aspects of hydrochemical character are associated with a complex mix of drivers (i.e. driver assemblages).

Partial dependence of each of the eight HCA classes on the 8 most important predictors are shown as an example in Figure 4-2 and their hydrochemical characteristics are shown in Table 4-6. The plots show the effect of the 8 most important predictors (X-axis) on the probability a site belongs to Class 1 (Y-axis). The values on the Y-axis of these plots are logit[13] transformed probabilities. They should be interpreted as the marginal effect of the predictor on the response (which here is the probability of belonging to a particular class).

---

[13] The logit function is the inverse of the sigmoidal "logistic" function or logistic transform used in mathematics, especially in statistics. When the function's parameter represents a probability p, the logit function gives the log-odds, or the logarithm of the odds p/(1 − p).

Table 4-5: Number of predictors retained and performance of the five surface water classifications. Model performance is the out-of-bag (OOB) misclassification rate and the misclassification rate of the fitted model and the OOB and fitted Kappa values.

Classification	Number of predictors	OOB Misclassification (%)	Fit Misclassification (%)	OOB Kappa	Fit Kappa
HCA	9	27	2	0.7	1.0
General_Redox	2	9	9	0.8	0.8
Redox_Proc	3	26	20	0.6	0.7
WaterTypeS	3	20	14	0.7	0.8
Water_Type	9	45	1	0.5	1.0

Where General Redox = redox state (oxic, suboxic, mixed (oxic-anoxic), anoxic and other variations); Redox Process = the terminal electron accepting process (O_2-reduction, NO_3-reduction, Mn(II)-reduction, Mn(IV)-reduction and so forth); Water TypeS = short water type or major ion facies which is a presentation of the major ion facies by major cation and anion populated on a milliequivalent basis; Water Type = long water type or major ion facies which is a presentation of the major ion facies for all cations and anions that make up more than 10% of the ion balance on a milliequivalent basis.

The plot indicates (for example) that the probability of a site belonging to HCA class 1A0 increases with increasing values of Land_Surface_Recharge and generally decreases with increasing values of the other 7 predictors (Figure 4-2). Relative to the other classes, class 1A0 of the HCA classification had low conductivity, high chloride and sodium, low dissolved oxygen and total organic nitrogen and high values of $\delta^{18}O-H_2O$ and $\delta^{2}H-H_2O$ (see Appendix E). Similarly, the probability of a site belonging to HCA class 2B0 increases with increasing values of Land_Surface_Recharge, HL (Combined Reduction Potential category), and Q1_Q4_Mafic (geomorphic age and composition) but decreases with increasing values of the other five predictors (Figure 4-2). Class 2B0 was characterised by high conductivity, high chloride and sodium, very high TON and medium values of $\delta^{18}O-H_2O$ and $\delta^{2}H-H_2O$ (see Appendix E).

Thirty two continuous hydrochemical response variables were modelled (Table 4-6). Model performance varied across the modelled responses from reasonable to very good (Table 4-6). Between two and 20 predictors were included in the reduced models and the order of importance of the individual predictors varied for each variable (Table 4-6). This supports an underlying hypothesis postulated by the conceptual model that aspects of hydrochemical character are associated with a complex mix of drivers (i.e. driver assemblages).

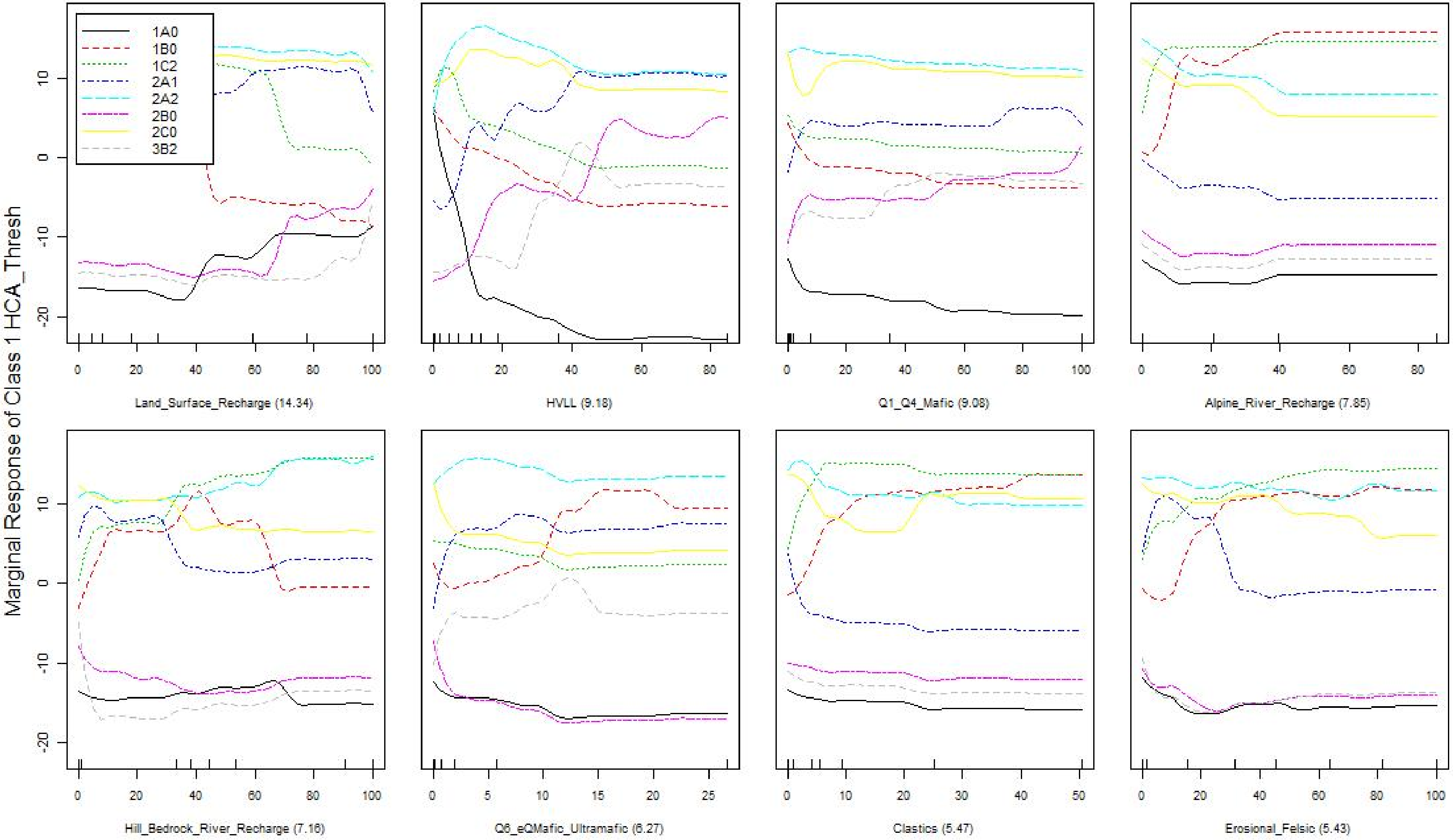

Figure 4-2: Partial Dependence of each of the eight surface water HCA classes on the 8 most important predictors. The lines show the probability of class membership for given values of each predictor (i.e. the change in probability along the predictor gradient when all other predictors in the model are held at their respective mean values). The ticks on the x-axis represent centiles in increments of ten of the predictor data. The lines have been smoothed to reduce noise to aid interpretation.

Partial plots for the selected responses are shown in Figure 4-3. These plots indicate relationships between the predictors (representing the drivers) and responses (hydrochemistry) that are consistent with the conceptual model. For example, the value of δ^{13}C-DIC decreases with increasing values of Land_Surface_Recharge and HL (Figure 4-3 black line), which are the only two predictors that were included in the reduced model for this variable (Table 4-6). The pattern is consistent with hydrochemical theory and reflects an increasing contribution of more negative soil zone recharge as the proportion of land surface recharge increases (TC1 – 7). Rivers with a dominant or significant Alpine or Hill Country source show more positive δ^{13}C-DIC values due to strong head water degassing and in the instance of Alpine derived streams lower organic carbon biomass in the recharge environment (TC2-8). Further, soils and waters with high reduction potential exhibit the most negative δ^{13}C-DIC values of regional waters due to enhanced heterotrophic reduction of organic carbon (TC4).

Similarly, the conductivity of surface waters increases with increasing values of Land_Surface_Recharge and Mixed_ Alpine_River_Recharge and Q1_Q4_Mafic (Figure 4-3). Again, these patterns are consistent with driver theory and reflect greater solute concentrations associated with lowland LSR due to both higher marine aerosol inputs but also more intense evapotranspirative concentration of salts within soils of lowland areas. The increase in conductivity due to an increase in Q1_Q4_Mafic likely reflects the greater endogenous solute load associated with young mafic alluvial soils (and geology) that have high Base Saturation, pH (hence alkalinity) and consequently higher dissolved solute supply and ensuing conductivity.

Table 4-6: Number of variables retained by the RF models for the individual surface water hydrochemical variables and model performance.

Variable	Number of Retained variables	Cross validated r^2	Fitted r2
δ^{13}C-DIC	2	68	68
δ^{18}O-H_2O	20	92	93
δ^{2}H-H_2O	20	93	93
Cl	14	94	94
Br	20	86	86
SO_4	5	81	82
Na	14	91	91
EC	14	79	80
Ca	20	58	59
Mg	10	86	86
K	20	67	67
SiO_2	10	74	75
Alk Tot	14	54	55
Alk HCO_3	14	51	51
DOC	5	81	84
pH (Field)	20	48	48
DO (Field)	5	38	38
TON	5	76	77
Mn(II)	14	71	71
Fe(II)	7	75	76
TAN	10	46	46
SS	20	33	33

Variable	Number of Retained variables	Cross validated r^2	Fitted r2
DRP	10	32	33
SSV	20	62	62
Clarity	14	72	73
E. coli	7	38	38
ORP	2	37	38
I	14	76	76
F	10	64	64
Turb	14	50	50
Temp	5	36	36
δ^{13}C-DIC	2	68	68

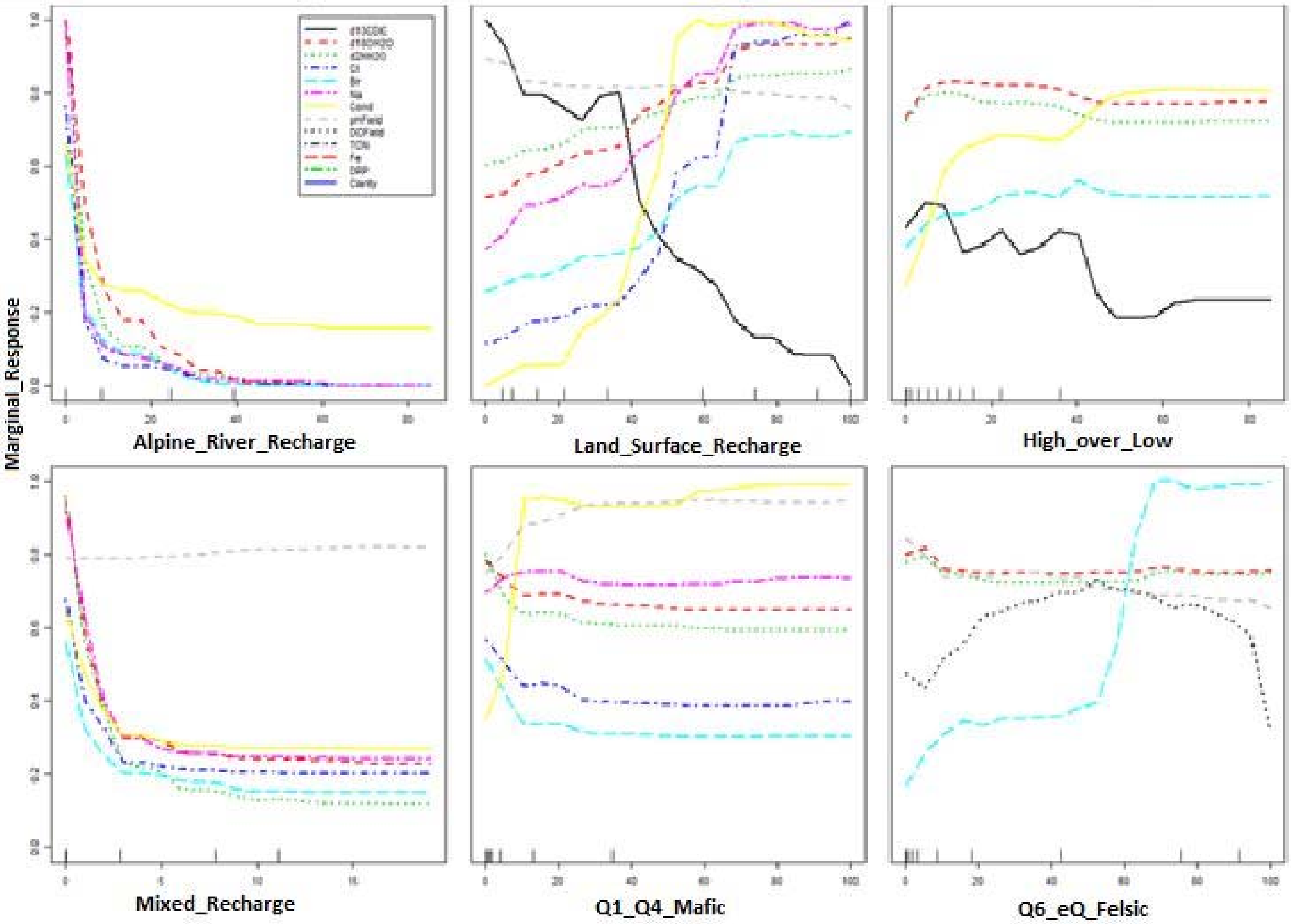

Figure 4-3: Partial plot for reduced model for selected individual surface water hydrochemical variables. The Y-axis represents the marginal effects of each predictor on the absolute value of the response (i.e. the change in probability along the predictor gradient when all other predictors in the model are held at their respective mean values). The ticks on the x-axis represent centiles in increments of ten of the predictor data. The lines have been smoothed to reduce noise to aid interpretation.

4.3.1.2 Groundwater

The reduced random forest models of the classifications had a fitted miss-classification rates of between 18% and 28% and fitted Kappa values ranged from 0.4 to 0.7, indicating the models had fair to good fits (Table 4-7). This included fitted Kappa values of 0.6 to 0.7 for groundwater hydrochemical clusters and general hydrochemical setting indicating a good to strong performance (e.g., general water source, recharge mechanism and redox setting; Appendix E). Out-of bag (OOB, i.e. independent predictions) miss-classification rates ranged between 31% and 50% and OOB Kappa values ranged between 0.2 and 0.5. These results indicate consistency in the relationships between drivers and classes but a weak ability the predict class for a new (i.e. independent data) as a function of the drivers.

The reduced models of the categorical responses retained between eight and ten predictors (Table 4-7). This indicates that membership of classes was significantly associated with several predictors and that multiple drivers (i.e. driver assemblages) are associated with particular hydrochemical outcomes.

The partial dependence plots for each of the groundwater classification models indicate many associations between driver gradients and hydrochemical outcomes that are consistent with prior expectations indicated by the conceptual model. An example of partial dependence of Class 4 of the six-class HCA classification (Cluster 6) on the 6 most important predictors is shown in Figure 4-4. Class 4 is characterised by high values for conductivity, Cl, Na, DOC $\delta^{18}O\text{-}H_2O$ and $\delta^{2}H\text{-}H_2O$ and low values for TON and DOField Table 4-1. The full details of the hydrochemical characteristics of all classes are shown in Appendix E. The plots show the effect of the 6 most important predictors (X-axes) on the probability a site belongs to Class 4 (Y-axis). The values on the Y-axis of these plots are logit transformed probabilities. They should be interpreted as the marginal effect of the predictor (here always a category) on the response (which here is the logit transformed probability of belonging to a particular class).

Table 4-7: Number of predictors retained and performance of the five groundwater classifications. Model performance is the out-of-bag (OOB) misclassification rate and the misclassification rate of the fitted model and the OOB and fitted Kappa values.

Classification	Number of predictors	OOB Misclassification (%)	Fit Misclassification (%)	OOB Kappa	Fit Kappa
4 hydrochemical clusters	8	40	26	0.4	0.6
6 hydrochemical clusters	10	50	22	0.4	0.7
General Redox Category	8	31	18	0.5	0.7
General hydrochemical Setting	10	50	22	0.4	0.7

The top left plot in Figure 4-4 indicates there is a marked difference in the probability of membership associated with the predictor PPTSource. This indicates that, all other things being equal, a site has a low probability of belonging to Class 4 if PPTSource is in the Alpine and Alpine2 categories. Further, a site has a higher probability of belonging to Class 4 if PPT Source is Coastal or Coastal2 category.

Similarly, a site has lower probability of belonging to Class 4 if SubSurface is UndiffClasstics, GeomorphicAge is Q1, SoilRP is Low and CRPdomain is Low/Low. The latter pattern is consistent with this particular assemblage of drivers correlating with dilute and oxidising groundwaters across Southland whereas cluster 4 waters are pre-defined as “strongly reducing, organic carbon rich, coastal, land surface recharge groundwaters” with attendant chemical metrics (i.e., high dissolved Fe, low DO, high Na and Cl and high both DOC and TOC). Class 4 groundwaters are most prevalent at distal end of Mataura Catchment in conjunction with reducing aquifers (i.e., marine terraces, peat wetlands and variably lignite measures).

The performance of the models fitted to 24 individual hydrochemical continuous variables varied from reasonable (e.g. $r^2 > 40\%$) to poor ($r^2 < 10\%$) (Table 4-8). The number of predictors included in the reduced models for individual groundwater hydrochemical variables and the order of importance of the predictors varied from one (e.g. TAN and DRP; Table 4-8) to 13 (e.g. TON, TN, and $AlkHCO_3$; Table 4-8) depending on the variable.

Examples of partial dependence for two hydrochemical variables (Cl and TON) are shown in Figure 4-5and Figure 4-6. The plots show the effect of the 6 most important predictors (X-axis) on the absolute value of the response variable (Y-axis). They should be interpreted as the marginal effect of the predictor (here always a category) on the absolute value of the response.

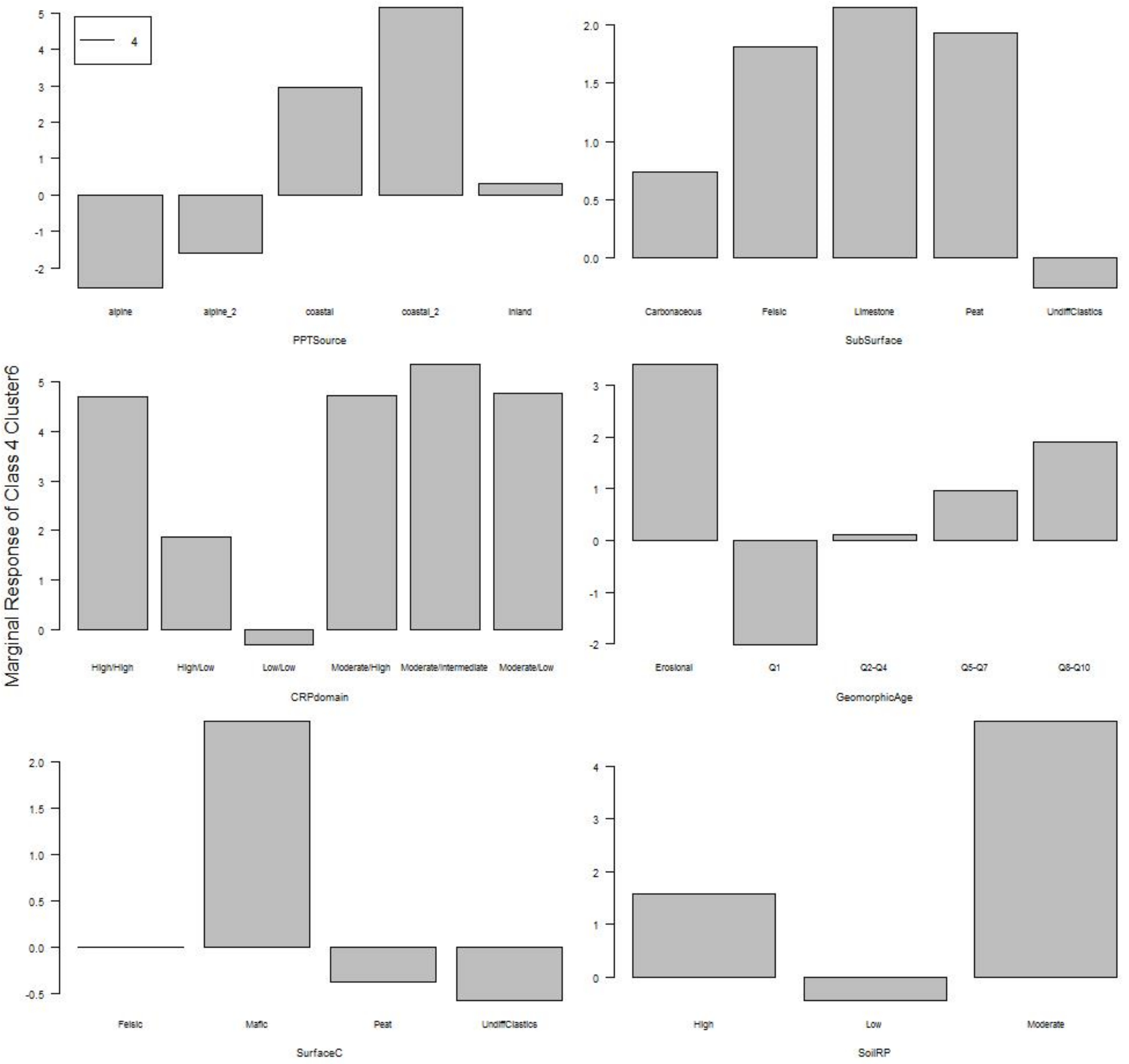

Figure 4-4: Partial Dependence of Class 4 of the six-class HCA groundwater classification of the groundwater sites on the 6 most important predictors. The bars indicate the marginal effects of each variable's category on the class logit transformed probability.

The value of the response variable Cl varies over all sites from 0.9 to 41 with a mean value of 19.6 (see Appendix E). The top left plot in Figure 4-5 indicates there is a marked difference in the value of Cl associated with the 5 category predictor PPT Source. This indicates that, all other things being equal, a site has a Cl value of greater than 25 if PPT Source is in the Coastal or Coastal2 category. If PPT Source is the Alpine and Alpine2 categories, all other things being equal, values of Cl are less than 20. These patterns are consistent with low marine aerosol loads associated with alpine precipitation and rivers or streams originating from these areas and higher marine aerosol loads in close proximity to the sea (TC1 and 2). Similarly, a site has higher values of Cl if River Connectivity is Low, Aquifer Type is Lowland, there is Vertical Bypass and Redox is High/Low. The latter patterns are consistent with: (i) limited dilution of lowland aquifers by low Cl river waters sourced from alpine or bedrock/hill country areas (TC1 and 2); (ii) the bypassing of the filtering capacity of the soil which equates to higher Cl and other anthropogenic inputs from animal wastes (TC1-2, 4-5), and; a higher proportion of High over Low CRP assemblages in lowland coastal areas the also receive high marine derived Cl inputs.

Table 4-8: The number of predictors included in the reduced random forest models for the 23 individual hydrochemical continuous variables and OOB and fitted performance (r2) of the models.

Response	Number of predictors	OOB r^2	Fitted r^2
pH (Field)	9	15	17
EC	9	31	31
Cl	4	50	51
Cl/Br	3	26	26
DO(Field)	13	6	9
TON	13	26	26
Mn(II)	1	0	0
Fe(II)	9	24	25
SO_4	13	19	19
TON	1	-2	1
DOC	13	6	11
TOC	1	11	12
Alk Tot	6	15	16
Alk HCO_3	13	11	14
Ca	6	19	19
K	1	6	6
SiO_2	3	24	24
Na	1	45	45
Mg	9	27	27
TN	13	29	30
DRP	1	1	1
$\delta^{13}C$-DIC	6	11	11
$\delta^{18}O-H_2O$	1	38	38
$\delta^{2}H-H_2O$	2	43	44

The value of the response variable TON varies over all sites from 0 to 6.5 with a mean value of 1.3 (see Appendix E).The top left plot in Figure 4-6 indicates there is a marked difference in the value of TON associated with the 5 category predictor PPT Source. This indicates that, all other things being equal, a site has a TON value of greater than 5 or 6 if PPT Source is in the Coastal or Inland categories respectively. If PPT Source is the Alpine and Alpine2 categories, all other things being equal, values of TON are less than 4. Similarly, a site has higher values of TON if Geomorphic Age is Q2-Q4 and River Influence is Low. As regional precipitation contains next to no TON (TC1) this PPT Source appears to be acting as a spatial substitute for landuse intensity with both Alpine categories occurring in mountainous areas and both Coastal PPT source bands across highly developed lowland plains of Southland. The Inland precipitation category contains both pristine and intensive land uses. Low River influence equates to low flushing rates and young Q2-Q4 alluvial deposits across lowland Southland have a higher propensity for bypass flow both of which favour higher TON concentrations.

The second left plot in Figure 4-6 indicates there is a marked difference in the value of TON associated with the 6 category predictor Combined Redox Potential (CRP). This indicates that, all other things being equal, a site has a TON value of greater than >5 - 6 mg/L if CRP domain is Low over Low reflecting limited denitrification in soil or geological (aquifer) material. If CRP domain has a reducing component (High, Intermediate or Moderate) in either or both the soil or geology than all other things being equal, values of TON are < 4 mg/L. The latter is strongly consistent with reduction induced denitrification resulting in lower TON concentrations for sites with reducing soils and/or geology as demonstrated in TC6. Similarly, a site has higher values of TON if River Connectivity is Low, consistent with both limited flushing of aquifers and low median N concentration in river waters relative to groundwaters. Again, these patterns (conceptual model response) are consistent with the conceptual model outlined in TCs 1 – 8 and Chapter 3 above.

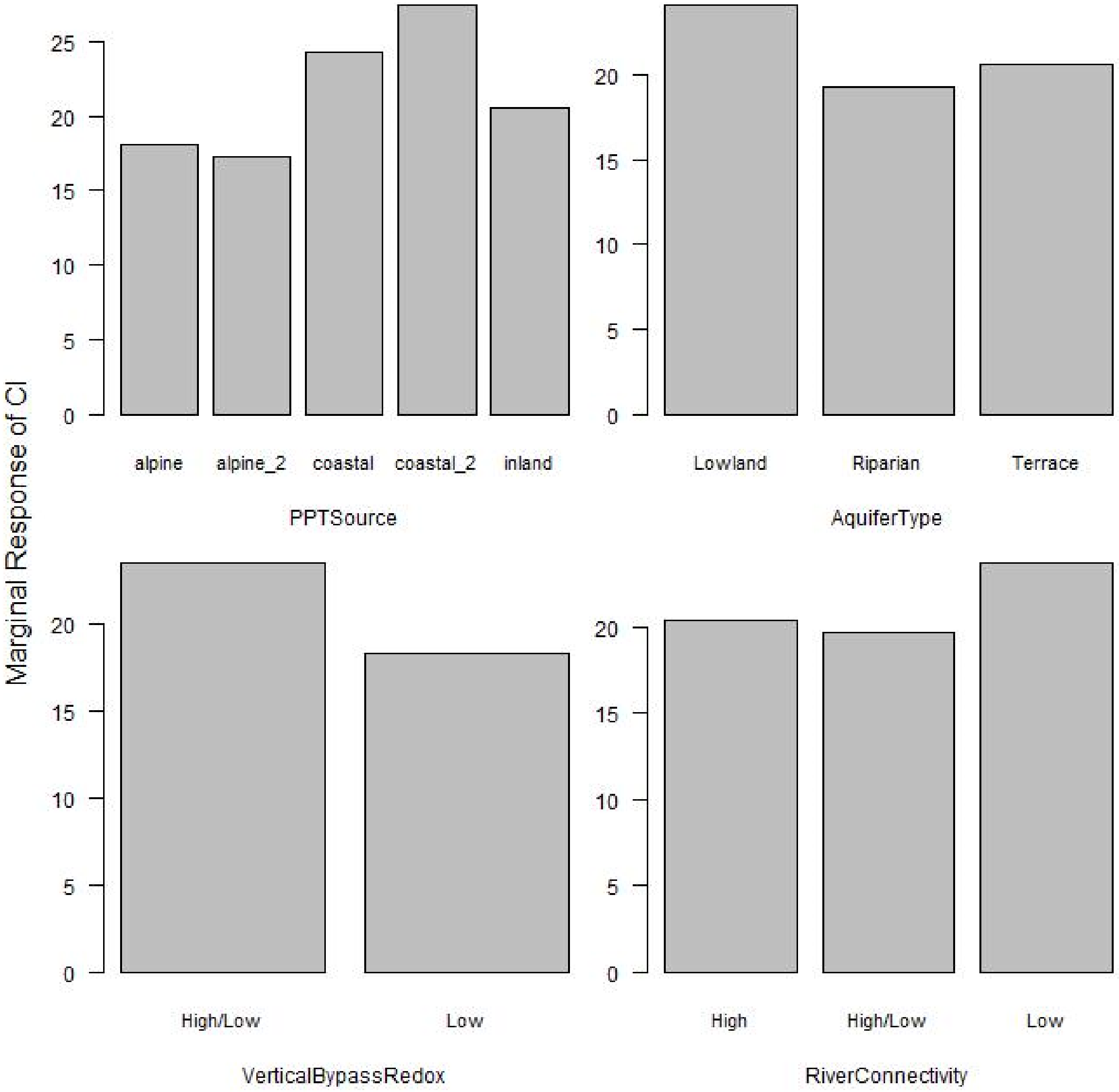

Figure 4-5: Partial Dependence of one of the 23 individual groundwater hydrochemical variables (Cl) on the four predictors that were included in the reduced model (note that these predictors are all categorical). The bars show the marginal effects of each variable's category on the absolute value of the response.

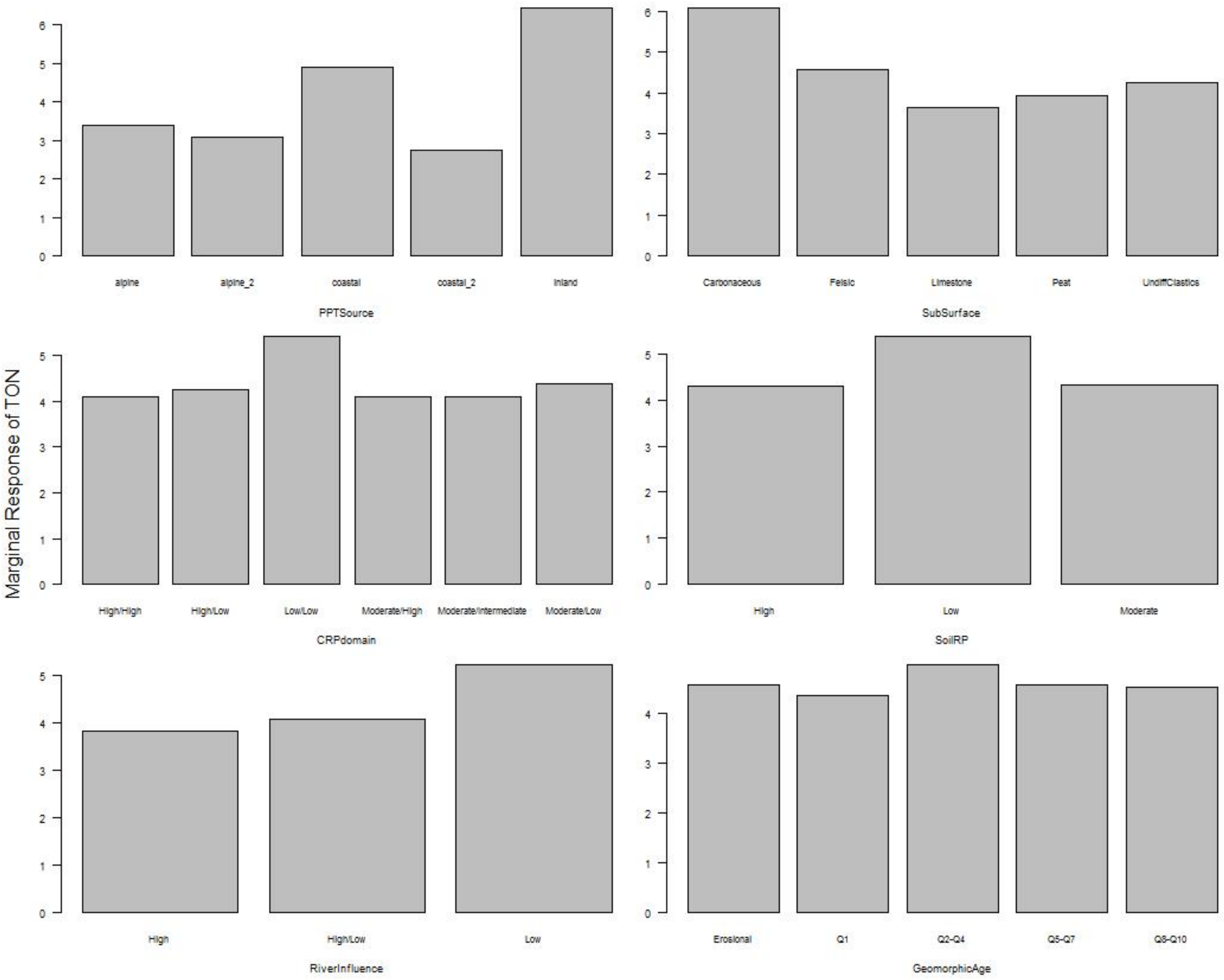

Figure 4-6: Partial Dependence of one of the 23 individual groundwater hydrochemical variables (TON) on the six most important predictors that were included in the reduced model (note that these predictors are all categorical). The bars show the marginal effects of each variable's category on the absolute value of the response.

4.3.2 Summary of validation through statistical modelling

The statistical modelling tested the relationships between observed hydrochemistry and drivers postulated by the conceptual model. Despite the relatively small test datasets, all the models achieved statistical significance, however, the models performance was variable (i.e. models explained differing amounts of variation). In general, model performance was better for the surface water than the groundwater data. At a hydrochemical level, the strong performance of surface water hydrochemical metrics indicates the conceptual model is a strong estimator of shallow, soil-influenced groundwater which constitutes a significant proportion of the total stream flow as base flow.

Model fitting used variable reduction to reduce the predictors selected by the models to the most parsimonious set. While some models selected only a subset of predictors, the reduced models generally included a number of predictors. In particular, various models predicted classes that represented groups of sites with similar hydrochemical characteristics. That models generally included many predictors, supports an underlying hypothesis postulated by the conceptual model that aspects of hydrochemical character are associated with a complex mix of drivers (i.e. driver assemblages).

We used partial plots to reveal the associations between surface and groundwater hydrochemical characteristics and the model predictors. The model predictors represented the drivers of hydrochemistry postulated by the conceptual model. We found that the partial plots described associations between hydrochemistry and drivers that are consistent with the conceptual model.

There are a large number of relationships between predictors and hydrochemical response that are revealed by the models. Many inferences can be made from these relationships about the validity of the conceptual model. This report has not exhaustively assessed these in the interests of brevity. However, Appendix F contains more details about these and additional supplementary material has been provided, particularly showing more partial plots.

4.3.3 Manual hierarchal stratification of spatial hydrochemical data according to hydrochemical drivers

In the following, we demonstrate that hierarchal stratification of surface water hydrochemical data by key drivers proves to be highly accurate, consistently clustering waters of similar hydrochemical composition into homogenous subgroups. The effectiveness of hierarchal stratification by key hydrochemical drivers is seen as evidence for the validity of this approach and provides a strong platform for a simplified conceptual model of regional controls over surface water hydrochemistry and water quality based on the drivers outlined above. Significantly, lowland LSR surface waters require a higher degree of stratification and Alpine River Recharged waters the least.

4.3.3.1 Surface waters

Stratification by river source, classified the 93 surface water sites with both capture zone data and HCA cluster memberships into four subgroups containing differing number of sites, specifically, 29 sites with an Alpine, 26 with a Bedrock, and 38 with a Lowland, Land Surface recharge (LSR) source.

4.3.3.1.1 Alpine derived rivers and streams

Twenty nine sites were associated with rivers with an Alpine River Recharge (ARR) source and include all of Southland's main stem rivers. Sorting the fraction of ARR within the capture zone of each site by largest to smallest ordered the hydrochemical data from the most to the least ARR influenced (Table 4-9). Specifically, the most ARR influenced sites were dilute, oxic, Ca-HCO_3 waters with the isotopically most negative $\delta^{18}O$-H_2O values and a 1B0 cluster membership. These sites had a high proportion of their capture zone, c. ≥40%, within the ARR domain and accordingly receive predominantly alpine precipitation (Table 4-9). Specifically, 1B0a waters were generally more dilute than 1B0b waters, which can be related to 1B0a having < 2% LSR and 1B0b having between 2 and 10% LSR.

As the proportion of ARR declined and either Bedrock River Recharge (BRR) and/or Land Surface Recharge (LSR) increased, there was a generalised increase in conductivity, Na and Cl concentrations and a shift in $\delta^{18}O\text{-}H_2O$ values towards more positive values. Significantly, the sites for which Cl is a major ion all had at least 10% LSR within their respective capture zone in addition to up to 10% coastal precipitation. Sorting the fraction of the capture zone by LSR from largest to smallest also neatly ordered the hydrochemical data and indicated that when the proportion of LSR of an ARR derived stream exceeded c. 10% there was a pronounced change in hydrochemistry. These findings confirm that it only takes a little LSR within the capture zone of an ARR derived stream to considerably modify ARR derived hydrochemistry (TC 2).

For this particular assemblage of key drivers the increase in Na, Cl and $\delta^{18}O\text{-}H_2O$ as the proportion of ARR within a capture zone declined, coinciding with a generalised change in pre-defined clusters from 1B0a > 1B0b > 1C2a > 1C2b > 2A2c as the solute contribution from BRR and LSR increased. Specifically, the change from: (i) 1B0a to 1B0b clusters was associated with an increase in the proportion of BRR; (ii) 1B0a/1B0b to 1C2a occurred as the proportion of LSR exceeds 10%; (iii) 1C2b waters differed from 1C2a waters in that the former had a higher proportion of BRR, and; (iv) 1C2a/1C2b > 2A2c facies reflected negligible ARR and greater BRR and most importantly LSR derived solute inputs associated with young mafic soils and geology.

In conclusion, stratification by river source and the fraction of recharge domain within the capture zone of a site clearly identified ARR dominated sites and logically ordered alpine river sites into a continuum according to the degree of influence associated with BRR and LSR. Stratification demonstrated that the longitudinal shift in hydrochemistry of ARR derived streams is explainable. As a metric of the success of the stratification we note that at a categorical level the variance in hydrochemistry is 100% resolvable following stratification by river source, recharge mechanism, precipitation source, redox control (i.e. CRP) and geology. More detail on the specific characteristics of Daughney et al. (2015) clusters and how variability in hydrochemistry can be explained can be found in Appendix E and Appendix F, respectively.

4.3.3.1.2 Bedrock derived streams and rivers

Stratifying surface waters by Bedrock River Recharge (BRR) source identified 26 sites that also had cluster assignments. All of these sites had a source associated within currently or historically forested bedrock outcrop, occur below 800 m RSL and had no Alpine River Recharge (ARR) within their capture zone. Further stratifying by the proportion of BRR or LSR within the capture zone of each site ordered the hydrochemical data from the most to the least BRR influenced. As the proportion of BRR declined and LSR increased, there was a generalised shift in hydrochemistry and pre-defined clusters.

Changes in stream chemistry as the proportion of LSR within a capture zone increased, coincided with a shift in hydrochemical facies from the BRR dominated 1C2a/1C2b to the 2A2c water type (Table 4-9 and Table 4-10). Specifically, 2A2c surface waters were consistent with LSR from lowland areas of Southland (Daughney et al., 2015). Of the LSR influenced streams, stratification by geology revealed a significant carbonate headwater source for Tussock Creek and Opouriki[14] streams, both of which are associated with the carbonate dominated 2A1o facies of Daughney et al. (2015). Although the Winton, Bogburn and sites on the lower Longridge show some association with carbonate rock the influence is relatively minor. Accordingly, it is necessary to stratify at the geological and redox (CRP) level to make sense of the changes in major ion facies, redox characteristics and site cluster memberships for BRR derived streams (Table 4-10).

Sites with >75% BRR (or <25%LSR) within their capture zone were characterised by a relatively homogenous hydrochemistry. Specifically, Na-Ca-Mg-HCO_3/Cl facies all had neutral pH (>7.1), elevated Fe(II) (>0.2 mg/L) and TOC (>8 mg/L) but low TON (<1.0 mg/L) concentrations and predominantly 1C2b cluster memberships with a few 1C2a (Table 4-10)[15]. (These 1C2a waters differed from the ARR derived 1C2a waters discussed above). This indicated a relatively uniform redox setting at the recharge level consistent with reducing conditions in thin soils and colluvium overlying fractured bedrock (TC 4 - 7).

---

[14] Although carbonate is not present on the surface, it is present in the shallow subsurface.

[15] The only BRR dominated site that does not have a 1C2a or 1C2b designation is North Peak Stream at Waimea Valley Road (i.e. 2A2a). However, this site still showed characteristics consistent with a BRR origin as detailed in Appendix F.

Table 4-9: Southland surface water hydrochemical data for Alpine River Recharge (ARR) sourced sites. Stratification by proportion of the catchment in ARR and precipitation source (PPT Source) sorts the data into a natural continuum (see text for commentary). Where BRR = Bedrock River Recharge ('Hill Country' derived streams); LSR = Land Surface Recharge.

WQSiteName	HCA 4th thresh.	Water Type	Hydrochemistry							Recharge domain					ppt source		
			TOC (mg/L)	Cl (mg/L)	EC (uS/cm)	Fe (mg/L)	Mn (mg/L)	Na (mg/L)	$\delta^{18}O-H_2O$	Alpine (%)	Bedrock (%)	Bedrock1 (%)	Lowland (%)	Mixed (%)	Alpine	Coastal	inland
Waikaia River u/s Piano Flat	1B0a	Ca-Na-Mg-HCO_3	0.60	1.59	29.60	0.04	0.001	2.10	-9.83	84.0%	5.6%	8.8%	0.0%	0.0%	98.6%	0.0%	0.0%
Mararoa River at South Mav. Lk	1B0a	Ca-Na-Mg-HCO_3	0.62	0.93	32.90	0.03	0.000	1.65	-9.90	75.4%	1.2%	11.6%	1.4%	6.6%	99.7%	0.0%	0.0%
Oreti River at Three Kings	1B0a	Ca-Na-Mg-HCO_3	0.60	1.20	32.75	0.04	0.001	2.10	-9.85	66.6%	0.9%	12.6%	0.7%	19.0%	99.7%	0.0%	0.0%
Waikaia River at Waikaia	1B0b	Ca-Na-Mg-HCO_3	12.13	2.50	44.60	0.06	0.007	3.10	-9.38	51.4%	28.5%	14.0%	3.2%	2.5%	97.9%	0.0%	1.7%
Mataura River at Garston	1B0b	Ca-Na-Mg-HCO_3	0.95	1.53	48.00	0.03	0.002	2.80	-9.96	46.6%	8.7%	28.2%	6.6%	8.2%	98.2%	0.0%	0.0%
Mararoa River at The Key	1B0b	Ca-Na-Mg-HCO_3	0.99	1.60	50.70	0.03	0.001	2.40	-9.79	45.2%	17.8%	14.2%	4.4%	16.4%	99.8%	0.0%	0.0%
Waikaia River at Waipounamu Bdg Rd	1B0b	Ca-Na-Mg-HCO_3	12.00	3.10	52.66	0.05	0.005	3.60	-9.24	42.3%	30.3%	14.1%	8.8%	4.1%	80.7%	0.0%	19.1%
Waiau River at Duncraigen Rd	1B0b	Ca-Na-Mg-HCO_3	1.09	2.00	63.00	0.04	0.002	2.80	-9.49	41.0%	7.2%	18.8%	13.6%	10.2%	99.9%	0.0%	0.0%
Waiau River at Sunnyside	1B0b	Ca-Na-Mg-HCO_3	1.00	2.16	54.00	0.03	0.001	2.90	-9.41	40.1%	8.3%	18.5%	12.9%	11.7%	96.1%	0.0%	3.9%
Upukerora River at Te Anau Milf. Rd	1B0b	Ca-Na-Mg-HCO_3	1.10	2.20	88.30	0.04	0.002	3.19	-8.87	39.3%	7.3%	13.8%	24.8%	14.6%	100.0%	0.0%	0.0%
Mataura River at Parawa	1B0b	Ca-Na-Mg-HCO_3	1.02	2.02	54.65	0.04	0.005	3.17	-9.62	37.8%	15.7%	26.1%	9.4%	8.5%	97.4%	0.0%	0.2%
Waiau River at Tuatapere	1C2a	Ca-Na-Mg-HCO_3	9.77	4.37	81.75	0.06	0.005	4.87	-8.70	34.0%	17.0%	16.4%	14.4%	11.1%	81.4%	3.3%	15.3%
Oreti River at Lumsden Bridge	1C2a	Ca-Na-Mg-HCO_3	1.09	2.29	59.50	0.04	0.002	3.10	-9.65	32.6%	16.9%	17.0%	17.9%	15.4%	73.5%	0.0%	26.4%
Aparima River at Dunrobin	1B0b	Ca-Na-Mg-HCO_3	0.99	2.00	59.00	0.03	0.001	3.39	-9.65	30.0%	26.4%	21.3%	10.6%	11.7%	60.9%	0.0%	39.1%
Mararoa River at Weir Road	1B0b	Ca-Na-Mg-HCO_3	1.10	2.10	64.00	0.04	0.002	2.89	-9.26	30.0%	16.2%	13.1%	21.3%	18.3%	99.9%	0.0%	0.0%
Mataura River at Otamita Bdg	1C2a	Ca-Na-Mg-HCO_3	14.24	4.42	69.35	0.06	0.005	5.10	-8.89	27.7%	30.2%	14.9%	19.6%	6.8%	64.0%	0.0%	35.3%
Mataura River at Gore	1C2a	Ca-Na-Mg-HCO_3-Cl	12.70	5.30	74.00	0.07	0.006	5.70	-8.66	26.2%	30.4%	14.0%	21.5%	7.1%	60.4%	0.0%	39.0%
Oreti River at Centre Bush	1C2a	Ca-Mg-Na-HCO_3-Cl	1.30	4.68	73.00	0.05	0.004	4.66	-8.93	23.2%	25.7%	12.2%	25.2%	13.5%	52.5%	0.0%	47.4%
Mataura River 200m d/s Mataura Bdg	1C2b	Ca-Na-Mg-HCO_3-Cl	13.06	6.59	86.10	0.09	0.008	6.55	-8.44	22.2%	33.9%	12.0%	24.8%	6.1%	52.0%	0.0%	47.3%
Irthing Stream at Ellis Road	1C2a	Ca-Na-Mg-HCO_3	12.74	4.71	77.50	0.05	0.004	4.81	-8.91	18.3%	27.1%	20.8%	24.1%	9.7%	66.0%	0.0%	34.0%
Mataura River at Mataura Isl. Bdg	1C2b	Ca-Na-Mg-HCO_3-Cl	12.00	9.00	99.30	0.13	0.011	8.47	-8.14	17.9%	39.7%	9.7%	25.4%	5.0%	42.0%	6.8%	49.3%

Mataura River at Gorge Road	1C2b	Na-Ca-Mg-HCO_3-Cl	13.29	10.35	101.05	0.15	0.016	9.19	-7.79	17.5%	39.1%	9.5%	26.7%	5.0%	41.0%	8.8%	48.2%
Oreti River at Wallacetown	1C2a	Ca-Na-Mg-HCO_3-Cl	12.00	6.92	94.05	0.09	0.006	6.30	-8.50	17.5%	24.6%	9.1%	37.2%	11.4%	39.5%	10.8%	49.6%
Whitestone River d/s Manap.-Hills.	1B0b	Mg-Ca-Na-HCO3	1.09	2.70	85.60	0.05	0.002	3.31	-9.21	15.3%	15.6%	16.5%	34.4%	18.1%	100.0%	0.0%	0.0%
Aparima River at Otautau	1C2a	Ca-Na-Mg-HCO_3	1.30	5.17	98.00	0.06	0.004	5.90	-8.64	9.5%	34.3%	9.2%	36.8%	10.1%	17.5%	6.3%	76.3%
Aparima River at Thornbury	2A2c	Ca-Na-Mg-HCO_3-Cl	4.90	10.88	126.00	0.08	0.008	8.85	-7.84	6.5%	33.1%	6.3%	46.2%	7.7%	12.0%	33.5%	54.5%
Aparima River at Wreys Bush	1C2a	Ca-Na-Mg-HCO_3-Cl	1.30	5.90	78.65	0.05	0.002	5.84	-8.40	0.3%	56.2%	2.0%	32.5%	9.0%	0.0%	3.3%	96.7%
Waikaka Stream at Gore	2A2c	Na-Ca-Mg-HCO_3-Cl	11.03	15.64	139.25	0.41	0.031	12.75	-7.53	0.1%	53.0%	1.1%	44.3%	0.0%	6.6%	0.0%	92.0%
Orauea River at Orawia Pukemaori Rd	2A2c	Ca-Na-Mg-HCO_3-Cl	12.00	14.00	179.80	0.26	0.022	13.49	-7.52	0.0%	72.0%	1.0%	26.6%	0.0%	0.0%	30.2%	69.8%

Stratifying by precipitation source discriminated between 1C2b waters derived from coastal Bedrock catchments with Cl and those derived from inland and northern BRR sites with lower Cl. That is, there was a shift from Na-Cl-HCO_3 to Na-HCO_3-Cl facies as marine aerosol input declines with distance from the coast (Table 4-10). Within this cohort, the two 1C2a waters at Waimea Tributary at McCale Road and Waimea Stream at Old Balfour Road, are a special case being the most inland and dilute BRR derived waters associated with the spill over of isotopically ($\delta^{18}O$-H_2O) and marine solute depleted precipitation from the northern mountains (TC 1 and 2).

Where the proportion of BRR within a site capture zone fell below 75%, and/or LSR was greater than 25%, there was a pronounced change in hydrochemistry. In particular, conductivity and the concentration of Ca, Mg, K, SO_4, Alkalinity and TN increase and dissolved Mn(II), Fe(II) and TAN decreased (Table 4-10). This shift could be interpreted as reflecting greater land use intensity. However, this shift primarily reflects a definitive shift in redox control and geology (as demonstrated in TCs 3 to 8). Specifically, stratifying by geology elucidated a strong association between young constructional landforms (Q2-4) and/or proportion of mafic surficial geology, and Ca-Cl and Ca-HCO_3 waters for those sites with a high (>25%) LSR proportion (TC 3, 4 and 7)[16]. Stratifying by CDNP, we noted that as the proportion of LSR increased, so too did the proportion of moderately reducing and oxidising soils over oxidising aquifers (Moderate over Low and Low over Low; TC 6). The change from dominantly strongly reducing BRR to more weakly reducing LSR was accompanied by a decrease in TAN, Mn(II) and Fe(II)concentrations and an increase in TON.

In conclusion, stratification by river source, the fraction of recharge domain, geology and precipitation source within the capture zone of a site clearly identified BRR dominated sites as well as logically ordering sites according to the degree of influence associated with LSR. Specifically: (i) 1C2a (dilute inland) and 1C2b sites were most characteristic of BRR; (ii) 2A2c BRR derived surface waters had a significant LSR component, and; (iii) 2A1o waters were influenced by carbonate. Stratification also demonstrated that the longitudinal shift in hydrochemistry of BRR derived streams is explainable. As a metric of the success of the stratification we note that at a categorical level the variance in hydrochemistry is 100% resolvable following stratification by river source, recharge mechanism, precipitation source, geology and redox (CRP). More detail on the specific characteristics of Daughney et al. (2015) clusters and how variability in hydrochemistry can be explained can be found in Appendix E and Appendix F, respectively.

---

[16] We note from TC3 and TC4 that recent soils (Q1 – Q4) are associated with high BS and exchangeable Ca relative to older soils and older constructional landforms.

Table 4-10: Southland surface water hydrochemical data for Bedrock River Recharge (BRR) sourced sites. Sorting by the proportion of BRR within their capture zone reveals a relatively homogenous hydrochemistry for sites with ≥ 75% BRR within their capture zone. Specifically, Na-Ca-Mg-HCO_3/Cl facies, circumneutral pH, elevated Fe(II) and TOC but low TON and predominantly 1C2b/1C2a cluster memberships indicating a relatively uniform redox setting at the recharge level consistent with reducing conditions in thin soils and colluvium overlying fractured bedrock.

			Hydrochemistry								Recharge domain		CRP	
WQSiteName	HCA 4th threshold	Water_Type	TOC (mg/L)	Cl (mg/L)	EC (uS/cm)	Fe (mg/L)	Mn (mg/L)	TN (mg/L)	pH	Na (mg/L)	BRR	LSR	High over High	Low over Low
Mimihau Stream Tributary at Venlaw Forest	1C2b	Na-Ca-Mg-Cl-HCO_3	12.00	11.30	87.00	0.04	0.002	0.34	7.33	7.90	100.0%	0.0%	0.0%	0.0%
North Peak Stream at Waimea Valley Rd	2A2a	Na-Ca-Mg-HCO_3-Cl	10.87	12.70	147.00	0.23	0.021	0.99	6.68	12.70	98.5%	1.5%	0.0%	17.6%
Dunsdale Stream at Dunsdale Reserve	1C2b	Na-Ca-Mg-HCO_3-Cl	12.00	12.81	118.95	0.06	0.003	0.29	7.31	9.85	97.3%	2.7%	0.0%	2.7%
Waikopikopiko Stream at Haldane CurioBay	1C2b	Na-Ca-Cl-HCO_3	12.78	30.78	157.55	0.20	0.012	0.36	6.79	18.07	95.9%	4.1%	0.0%	3.6%
Mimihau Stream at Wyndham	1C2b	Na-Ca-Mg-Cl-HCO_3	11.71	14.40	117.00	0.20	0.013	1.17	6.51	11.30	95.1%	4.5%	0.1%	14.4%
Makarewa River at Lora Gorge Road	1C2b	Na-Ca-Mg-HCO_3-Cl	12.00	12.90	129.10	0.21	0.013	0.98	6.71	12.10	94.1%	5.9%	0.0%	5.9%
Otamita Stream at Mandeville	1C2b	Na-Ca-Mg-HCO_3-Cl	11.34	11.61	112.40	0.21	0.011	1.17	6.38	11.50	93.3%	6.7%	0.6%	6.5%
Otapiri Stream at Otapiri Gorge	1C2b	Na-Ca-Mg-HCO_3-Cl	12.00	10.90	105.70	0.22	0.011	0.95	6.59	10.90	93.1%	6.9%	2.8%	7.4%
Waimea Stream at Old Balfour Road	1C2a	Na-Ca-Mg-HCO_3-Cl	11.49	7.90	93.70	0.15	0.010	0.85	6.70	8.40	90.7%	9.3%	0.0%	11.9%
Tokanui River at Fortrose Otara Road	2A2c	Na-Ca-Mg-Cl-HCO_3	10.49	30.86	191.20	0.39	0.032	1.57	6.33	22.00	90.7%	9.3%	0.0%	6.8%
Waikawa River at Progress Valley	1C2b	Na-Ca-Mg-Cl-HCO_3	11.26	20.40	144.00	0.32	0.021	1.07	6.35	15.32	88.0%	11.5%	1.1%	12.0%
Pourakino River at Ermedale Road	1C2b	Na-Ca-Mg-Cl-HCO_3	12.00	16.55	109.05	0.24	0.013	0.26	6.70	11.51	81.7%	18.3%	0.0%	11.0%
Mokoreta River at Wyndham River Rd	1C2b	Na-Ca-Mg-Cl-HCO_3	11.49	17.30	124.00	0.18	0.011	1.52	6.51	13.10	76.6%	6.3%	0.3%	9.6%
Pourakino River at Traill Road	1C2b	Na-Ca-Mg-Cl-HCO_3	12.74	19.60	119.50	0.28	0.018	0.38	6.75	12.72	75.1%	24.9%	0.0%	9.5%
Bog Burn d/s Hundred Line Road	2A2c	Ca-Na-Mg-Cl-HCO_3	9.37	19.10	182.00	0.34	0.022	1.51	6.46	15.02	56.4%	43.6%	0.0%	0.1%
Winton Stream at Lochiel	2C0b	Ca-Na-Mg-HCO_3-Cl	8.04	23.00	252.90	0.27	0.037	2.40	6.85	17.15	49.8%	48.6%	0.0%	4.0%
Otautau Stream at Waikouro	2A2c	Ca-Na-Mg-HCO_3-Cl	11.90	19.65	218.55	0.28	0.046	1.25	7.09	15.00	46.7%	53.3%	0.9%	24.7%

Makarewa River at Wallacetown	2A2c	Ca-Na-Mg-Cl-HCO_3	11.86	22.04	192.20	0.36	0.035	1.81	6.17	15.60	40.8%	59.2%	3.8%	10.6%
Opouriki Stream at Tweedie Road	2A1o	Ca-Na-Mg-HCO_3-Cl	4.46	28.15	287.00	0.18	0.046	2.20	6.94	18.50	39.6%	60.4%	0.0%	57.2%
Longridge Stream at Sandstone	2A2c	Ca-Na-Mg-Cl-HCO_3	5.69	17.76	175.55	0.11	0.011	3.90	6.41	14.49	33.9%	65.6%	0.0%	31.3%
Waimea Stream at Murphy Road	2A2c	Ca-Na-Mg-Cl-HCO_3	5.84	17.00	156.60	0.18	0.018	2.30	6.36	12.36	33.6%	65.9%	0.0%	24.1%
Otautau Stream at Otautau-Tuatapere Rd	2A2c	Ca-Na-Mg-HCO_3-Cl	12.00	19.20	204.40	0.28	0.040	1.36	6.81	15.48	33.1%	66.6%	0.5%	10.5%
Waimea Stream at Mandeville	2A2c	Ca-Na-Mg-HCO_3-Cl	5.70	19.21	191.65	0.14	0.015	3.60	6.44	15.04	32.9%	66.9%	0.0%	33.5%
Waimea Stream at Nine Mile Road	2A2c	Ca-Na-Mg-Cl-HCO_3	5.56	19.18	190.50	0.13	0.014	4.00	6.45	15.04	32.8%	66.9%	0.1%	31.2%
Tussock Creek at Cooper Road	2A1o	Ca-Na-HCO_3-Cl	5.34	28.94	465.00	0.10	0.029	2.05	7.64	19.77	32.6%	67.4%	0.0%	19.1%
Sandstone Stream at Kingston Crossing Rd	2A2c	Ca-Na-Mg-Cl-HCO_3	7.51	24.00	192.90	0.33	0.029	2.55	6.39	16.93	1.4%	98.6%	0.0%	46.6%

Table 4-11: Southland surface water hydrochemical data for Bedrock River Recharge (BRR) sourced sites sorted by the proportion of Erosive Felsic geology within a capture zone. North Peak Stream at Waimea Valley Rd is unique in having a capture zone comprised of 100% 'mafic geologies.' The later gives rise to higher pH, Ca and Mg and cluster membership (2A2a). Carbonate influenced waters, 2A1o membership, are associated with areas of carbonate rock within the capture zone. However, the subsurface extent and hence degree of influence of carbonate rock is not well known regionally and may only be inferred from hydrochemistry (i.e., saturation indices, δ^{13}C-DIC, Ca and Alkalinity) until better geological maps are derived.

			Hydrochemistry				Surficial	Subsurf.	Erosive		Alluvium		
WQSiteName	**HCA 4th threshold**	**Water_Type**	**AlkHCO$_3$ (mg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**pH**	**Carbo-nate**	**Carbo-nate**	**Felsic**	**Mafic**	**Felsic**	**Mafic**	**Alluvium total**
Mimihau Stream Tributary at Venlaw Forst	1C2b	Na-Ca-Mg-Cl-HCO$_3$	20.9	5.1	2.2	7.3	0.0%	0.0%	100.0	0.0	0.0	0.0	0.0%
Dunsdale Stream at Dunsdale Reserve	1C2b	Na-Ca-Mg-HCO$_3$-Cl	33.9	8.3	3.0	7.3	0.0%	0.0%	97.3	0.0	0.0	0.0	2.7%
Waikopikopiko Stream at Haldane CurioBay	1C2b	Na-Ca-Cl-HCO$_3$	22.0	5.5	3.0	6.8	0.0%	0.0%	95.9	0.0	0.5	0.0	4.1%
Makarewa River at Lora Gorge Road	1C2b	Na-Ca-Mg-HCO$_3$-Cl	33.0	8.9	3.3	6.7	0.0%	0.0%	94.1	0.0	0.0	0.0	5.9%
Mimihau Stream at Wyndham	1C2b	Na-Ca-Mg-Cl-HCO$_3$	27.0	7.5	2.8	6.5	0.0%	2.3%	89.8	0.0	1.5	0.7	4.9%
Tokanui River at Fortrose Otara Road	2A2c	Na-Ca-Mg-Cl-HCO$_3$	33.4	9.7	4.1	6.3	0.0%	0.0%	80.8	0.0	5.3	3.9	9.3%
Otamita Stream at Mandeville	1C2b	Na-Ca-Mg-HCO$_3$-Cl	30.9	7.9	2.8	6.4	0.0%	0.0%	78.2	12.6	1.0	1.5	6.6%
Mokoreta River at Wyndham River Road	1C2b	Na-Ca-Mg-Cl-HCO$_3$	26.1	6.9	2.9	6.5	0.0%	0.2%	76.1	0.0	1.2	0.1	22.9%
Waikawa River at Progress Valley	1C2b	Na-Ca-Mg-Cl-HCO$_3$	27.0	7.2	3.1	6.4	0.0%	0.0%	75.6	0.0	6.3	3.5	11.9%
Otapiri Stream at Otapiri Gorge	1C2b	Na-Ca-Mg-HCO$_3$-Cl	29.3	7.3	2.7	6.6	0.0%	0.0%	74.1	16.5	0.6	0.0	6.8%
Bog Burn d/s Hundred Line Road	2A2c	Ca-Na-Mg-Cl-HCO$_3$	38.2	13.3	5.1	6.5	0.0%	0.0%	55.8	0.0	5.7	37.6	43.6%
Makarewa River at Wallacetown	2A2c	Ca-Na-Mg-Cl-HCO$_3$	34.9	14.4	4.3	6.2	4.6%	16.3%	43.1	1.6	12.0	25.2	43.4%
Winton Stream at Lochiel	2C0b	Ca-Na-Mg-HCO$_3$-Cl	64.3	23.0	6.2	6.9	4.3%	36.2%	41.8	0.0	20.5	27.1	50.2%
North Peak Stream at Waimea Valley Rd	2A2a	Na-Ca-Mg-HCO$_3$-Cl	38.0	10.3	3.7	6.7	0.0%	0.0%	38.3	4.1	0.0	1.5	1.5%
Longridge Stream at Sandstone	2A2c	Ca-Na-Mg-Cl-HCO$_3$	37.1	14.5	5.3	6.4	0.0%	0.4%	33.0	0.0	64.2	1.5	66.1%
Waimea Stream at Nine Mile Road	2A2c	Ca-Na-Mg-Cl-HCO$_3$	40.2	14.3	6.0	6.5	0.0%	0.1%	17.2	0.5	51.0	16.1	67.2%
Waimea Stream at Mandeville	2A2c	Ca-Na-Mg-HCO$_3$-Cl	41.5	15.4	5.6	6.4	0.0%	0.1%	15.0	0.2	50.5	16.3	67.1%

Waimea Stream at Murphy Road	2A2c	Ca-Na-Mg-Cl-HCO_3	32.8	13.3	4.6	6.4	0.0%	0.0%	14.0	0.0	55.2	10.9	66.4%
Otautau Stream at Otautau-Tuatapere Rd	2A2c	Ca-Na-Mg-HCO_3-Cl	49.0	16.0	5.6	6.8	0.2%	4.0%	13.6	0.0	5.6	54.6	65.0%
Opouriki Stream at Tweedie Road	2A1o	Ca-Na-Mg-HCO_3-Cl	62.3	23.0	5.5	6.9	0.0%	14.7%	13.2	0.0	50.0	10.4	60.4%
Waimea Stream at Old Balfour Road	1C2a	Na-Ca-Mg-HCO_3-Cl	27.3	7.3	2.5	6.7	0.0%	0.0%	12.9	0.0	7.4	2.0	9.3%
Tussock Creek at Cooper Road	2A1o	Ca-Na-HCO_3-Cl	163.1	61.4	6.2	7.6	24.5%	39.8%	7.3	0.0	12.8	52.0	67.4%
Otautau Stream at Waikouro	2A2c	Ca-Na-Mg-HCO_3-Cl	60.7	18.0	6.8	7.1	0.0%	2.8%	5.3	0.0	7.2	38.6	53.3%
Pourakino River at Traill Road	1C2b	Na-Ca-Mg-Cl-HCO_3	24.5	7.2	2.7	6.7	1.4%	1.7%	0.8	15.1	10.9	5.3	24.9%
Sandstone Stream at Kingston Crossing Rd	2A2c	Ca-Na-Mg-Cl-HCO_3	44.1	16.6	5.2	6.4	0.0%	0.0%	0.5	0.0	97.7	0.9	98.6%
Pourakino River at Ermedale Road	1C2b	Na-Ca-Mg-Cl-HCO_3	23.4	5.9	2.6	6.7	2.3%	2.5%	0.4	25.5	7.4	0.8	18.3%

Table 4-12: Southland surface water hydrochemical data for Bedrock River Recharge (BRR) sourced sites. Data sorted by major ion facies reveals an association between precipitation source and major ion facies. Stratifying by precipitation source discriminates between 1C2b waters derived from coastal BRR catchments with Cl and those derived from inland and northern BRR sites with lower Cl (i.e., a shift from Na-Cl-HCO$_3$ to Na-HCO$_3$-Cl facies as marine aerosol input declines with distance from the coast). Within this cohort, the 1C2a membership for the Waimea Stream at Old Balfour Road is associated with a significant Alpine precipitation source.

	HCA 4th		Hydrochemistry				Recharge domain		ppt source		
WQSiteName	**threshold**	**Water_Type**	**Cl (mg/L)**	**EC (mg/L)**	**Na (mg/L)**	**δ^{18}O-H_2O**	**BRR**	**LSR**	**Alpine**	**Coastal**	**Inland**
North Peak Stream at Waimea Valley Road	2A2a	Na-Ca-Mg-HCO$_3$-Cl	12.70	147.00	12.70	-7.59	98.5%	1.5%	0.0%	0.0%	100%
Dunsdale Stream at Dunsdale Reserve	1C2b	Na-Ca-Mg-HCO$_3$-Cl	12.81	118.95	9.85	-7.96	97.3%	2.7%	0.0%	0.0%	100%
Makarewa River at Lora Gorge Road	1C2b	Na-Ca-Mg-HCO$_3$-Cl	12.90	129.10	12.10	-7.72	94.1%	5.9%	0.0%	0.0%	100%
Otamita Stream at Mandeville	1C2b	Na-Ca-Mg-HCO$_3$-Cl	11.61	112.40	11.50	-7.95	93.3%	6.7%	0.0%	0.0%	100%
Otapiri Stream at Otapiri Gorge	1C2b	Na-Ca-Mg-HCO$_3$-Cl	10.90	105.70	10.90	-7.99	93.1%	6.9%	0.0%	0.0%	100%
Waimea Stream at Old Balfour Road	1C2a	Na-Ca-Mg-HCO$_3$-Cl	7.90	93.70	8.40	-8.37	90.7%	9.3%	30.1%	0.0%	69.9%
Mimihau Stream Tributary at Venlaw Forst	1C2b	Na-Ca-Mg-Cl-HCO$_3$	11.30	87.00	7.90	-8.05	100%	0.0%	0.0%	0.0%	100%
Mimihau Stream at Wyndham	1C2b	Na-Ca-Mg-Cl-HCO$_3$	14.40	117.00	11.30	-7.60	95.1%	4.5%	0.0%	0.4%	99.2%
Tokanui River at Fortrose Otara Road	2A2c	Na-Ca-Mg-Cl-HCO$_3$	30.86	191.20	22.00	-7.05	90.7%	9.3%	0.0%	100.0%	0.0%
Waikawa River at Progress Valley	1C2b	Na-Ca-Mg-Cl-HCO$_3$	20.40	144.00	15.32	-7.12	88.0%	11.5%	0.0%	99.5%	0.0%
Pourakino River at Ermedale Road	1C2b	Na-Ca-Mg-Cl-HCO$_3$	16.55	109.05	11.51	-7.36	81.7%	18.3%	0.0%	100.0%	0.0%
Mokoreta River at Wyndham River Road	1C2b	Na-Ca-Mg-Cl-HCO$_3$	17.30	124.00	13.10	-7.79	76.6%	6.3%	0.0%	45.7%	37.2%
Pourakino River at Traill Road	1C2b	Na-Ca-Mg-Cl-HCO$_3$	19.60	119.50	12.72	-7.23	75.1%	24.9%	0.0%	100.0%	0.0%
Waikopikopiko Stream at Haldane CurioBay	1C2b	Na-Ca-Cl-HCO$_3$	30.78	157.55	18.07	-6.67	95.9%	4.1%	0.0%	100.0%	0.0%
Winton Stream at Lochiel	*2C0b*	*Ca-Na-Mg-HCO$_3$-Cl*	*23.00*	*252.90*	*17.15*	*-6.89*	*49.8%*	*48.6%*	*0.0%*	*20.5%*	*79.5%*
Otautau Stream at Waikouro	*2A2c*	*Ca-Na-Mg-HCO$_3$-Cl*	*19.65*	*218.55*	*15.00*	*-7.22*	*46.7%*	*53.3%*	*0.0%*	*100.0%*	*0.0%*
Opouriki Stream at Tweedie Road	*2A1o*	*Ca-Na-Mg-HCO$_3$-Cl*	*28.15*	*287.00*	*18.50*	*-6.76*	*39.6%*	*60.4%*	*0.0%*	*100.0%*	*0.0%*
Otautau Stream at Otautau-Tuatapere Rd	*2A2c*	*Ca-Na-Mg-HCO$_3$-Cl*	*19.20*	*204.40*	*15.48*	*-7.40*	*33.1%*	*66.6%*	*0.0%*	*90.6%*	*9.4%*

Waimea Stream at Mandeville	2A2c	Ca-Na-Mg-HCO_3-Cl	19.21	191.65	15.04	-7.32	32.9%	66.9%	1.5%	0.0%	98.5%
Bog Burn d/s Hundred Line Road	2A2c	Ca-Na-Mg-Cl-HCO_3	19.10	182.00	15.02	-7.39	56.4%	43.6%	0.0%	0.0%	100%
Makarewa River at Wallacetown	2A2c	Ca-Na-Mg-Cl-HCO_3	22.04	192.20	15.60	-7.02	40.8%	59.2%	0.0%	45.1%	54.9%
Longridge Stream at Sandstone	2A2c	Ca-Na-Mg-Cl-HCO_3	17.76	175.55	14.49	-7.42	33.9%	65.6%	0.0%	0.0%	100%
Waimea Stream at Murphy Road	2A2c	Ca-Na-Mg-Cl-HCO_3	17.00	156.60	12.36	-7.80	33.6%	65.9%	7.3%	0.0%	92.7%
Waimea Stream at Nine Mile Road	2A2c	Ca-Na-Mg-Cl-HCO_3	19.18	190.50	15.04	-7.41	32.8%	66.9%	1.7%	0.0%	98.3%
Sandstone Stream at Kingston Crossing Rd	2A2c	Ca-Na-Mg-Cl-HCO_3	24.00	192.90	16.93	-7.29	1.4%	98.6%	0.0%	0.0%	100%
Tussock Creek at Cooper Road	2A1o	Ca-Na-HCO_3-Cl	28.94	465.00	19.77	-6.64	32.6%	67.4%	0.0%	100.0%	0.0%

4.3.3.1.3 Lowland – Land Surface Recharge (LSR), Streams and Rivers

Sites classified as having a lowland-LSR source constituted the largest and most varied category of Southland surface waters (n = 38 sites; Table 4-13). These surface waters were generally more mineralised (at their source) than ARR and BRR derived streams. Only one site, Sandstone Stream at Kingston Crossing Rd, also had a minor (1.4% of the catchment area) BRR component within its capture zone. None of the sites had ARR within the capture zone.

Stratifying by geology neatly ordered the hydrochemical data in terms of major ion facies. Specifically, sorting from largest to smallest the proportion of mafic geology and carbonate rock within a capture zone resulted in all Ca-HCO_3 waters (n = 8) being grouped first along with one Ca-Cl water. As the proportion of mafic alluvium within the capture zone fell below c. 40%, Na-Cl (mainly Na-Ca-Mg-Cl-HCO_3; n = 32) waters predominated. The Ca-HCO_3 waters were all 2A1o waters whereas Na-Cl waters were mainly 2C0b and 2C0a with few 2A2c waters (Table 4-13).

Of the eight sites with Ca-HCO_3 facies, seven showed an association with carbonate rock of the Isla Bank aquifer system (i.e., six sites on Waimatuku Stream, Middle Creek at Argyle - Otahuti Road and Ayr Creek at Argyle Otahuti Road) and all shared a 2A1o cluster membership and time series records for these sites all exhibit periods of saturation with respect to calcite. The Isla Bank limestone aquifer occurs immediately south of Bayswater Bog and lies up gradient of, and adjacent to, the aforementioned creeks. Springs and seeps drain from the carbonate aquifer and impart a significant carbonate signature to the lower reaches of the Waimatuku stream, Middle and Ayr creeks (Table 4-13). The only site with Ca-HCO_3 facies that did not have 2A1o cluster membership was the Waimatuku Stream d/s Bayswater Bog site. Stratifying by geology identified a large peat component (41%) within the capture zone of this site and an associated 3A2a cluster membership (Table 4-14). This site had elevated median DOC, TOC, Mn(II) and Fe(II) concentrations relative to the aforementioned sites. Finally, Waimatuku Stream Tributary at Otautau exhibited Ca-Cl facies and was under saturated with respects to calcite, had lower Ca, Mg and alkalinity and a cluster membership 2B0a. This site occurs up gradient of the Isla Bank carbonate aquifer system.

Of the remaining sites (n = 29), 26 were Na-Cl and three were Ca-Cl (Ca-Na-Mg-Cl-HCO_3) waters. The Na-Cl facies are associated with dominance by felsic geology and peat and a predominantly coastal precipitation source. The sites with Ca-Cl waters had marginally higher Ca relative to Na but little other difference to the Na-Cl dominated sites, and were not differentiated on the basis of cluster membership.

At a redox level the proportion of reducing soils and aquifers within a capture zone played an important role over the hydrochemistry of lowland LSR streams (Table 4-15). Stratifying by redox category (CRP) within each respective capture zone produced a redox continuum within the data set. Specifically, the sites with the highest proportion of reducing soils and aquifers (i.e., mainly peat) with their capture zones also had the highest TOC, DOC, Mn(II), Fe(II), TAM and lowest TON concentrations. Those with the great proportion of oxidising soils over oxidising aquifers (LL, CRP category) had the highest concentration of TON and the lowest concentration of reduced species (TC6). Importantly, sites with a high proportion of peat within the capture zone showed the most reduced signatures but also the most elevated TP and DRP concentrations of all regional surface waters. This observation is consistent with the limited capacity of peat soils to retain P (Rissmann et al., 2012; McDowell, 2014).

Only sites from with the Central Plains area (Waimatuku, Middle Creek and Ayr Creek) deviated from the general trend. Specifically, despite strongly reducing soils these sites all showed oxidising characteristics such as elevated TON and low Mn(II) and Fe(II) concentrations. For all of the sites within the Central Plains area there is strong evidence for macropore cracking during the summer months and the bypass of the reducing soil zone by autumn recharge (Table 4-15). Sorting by bypass resolved these waters.

Table 4-13: Hydrochemical data and pre-defined cluster membership for lowland-LSR derived streams. Stratifying by geology (in this case mafic alluvium) orders the hydrochemical data in terms of major ion facies. See text for discussion.

	HCA 4th		Surficial geology							Subsurf. geology
WQSiteName	Threshold	Major ion facies	Carbonate	Carbonaceous	Felsic	Intermediate	Mafic	Peat	Clastics	Carbonate
Middle Creek at Otahuti	2A1o	Ca-Mg-Na-HCO_3-Cl	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%
Waimatuku Stream Tributary at Otautau Dr	2B0a	Ca-Na-Mg-Cl-HCO_3	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%	1.3%
Waimatuku Tributary at Robertson Road	2B0a	Ca-Mg-Na-HCO_3-Cl	0.0%	0.0%	0.0%	0.0%	99.7%	0.3%	0.0%	0.3%
Middle Creek at Argyle - Otahuti Road	2A1o	Ca-Mg-Na-HCO_3-Cl	0.0%	0.0%	0.6%	0.0%	98.6%	0.9%	0.0%	0.0%
Ayr Creek at Argyle Otahuti Road	2A1o	Ca-Na-Mg-HCO_3-Cl	3.0%	0.0%	3.4%	0.0%	87.0%	6.6%	0.0%	20.7%
Waimatuku Stream at Robertson Road	2A1o	Ca-Mg-Na-HCO_3-Cl	0.5%	0.0%	0.4%	0.0%	77.4%	21.7%	0.0%	19.7%
Waimatuku Stream at Isla Bank-Fairfax Rd	2A1o	Ca-Mg-Na-HCO_3-Cl	2.0%	0.0%	38.8%	0.0%	59.2%	0.0%	0.0%	46.0%
Waimatuku Stream d/s Bayswater Bog	3B2a	Ca-Na-Mg-HCO_3-Cl	0.0%	0.0%	0.0%	0.0%	59.1%	40.9%	0.0%	25.7%
Waimatuku Stream at Fraser Road	2A1o	Ca-Na-Mg-HCO_3-Cl	0.0%	0.0%	57.7%	0.0%	37.9%	4.3%	0.0%	56.9%
Waikiwi Stream at North Road	2A2c	Na-Ca-Mg-Cl-HCO_3	0.0%	0.0%	94.1%	0.0%	5.5%	0.4%	0.0%	0.0%
Oteramika Stream at Seaward Downs	2C0b	Na-Ca-Mg-Cl-HCO_3	0.0%	0.0%	98.8%	0.0%	0.7%	0.0%	0.0%	0.0%
Otepuni Creek at Nith Street	2A2c	Na-Ca-Mg-Cl-HCO_3	0.0%	0.0%	71.9%	0.0%	0.1%	0.6%	0.0%	0.0%
Waihopai River Dacre Catchment Outlet	2A2c	Na-Ca-Mg-Cl-HCO_3	0.0%	0.0%	98.2%	0.0%	0.1%	1.7%	0.0%	0.0%
Waihopai River u/s Queens Drive	2C0b	Na-Ca-Mg-Cl-HCO_3	0.0%	0.0%	98.0%	0.0%	0.0%	0.3%	0.1%	0.0%
Waihopai River 20 m us Waihopai Dam	2C0b	Na-Ca-Mg-Cl-HCO_3	0.0%	0.0%	66.4%	0.0%	0.0%	0.0%	1.4%	0.0%
Waihopai River d/s Kennington	2A2c	Na-Ca-Cl-SO_4	0.0%	0.0%	99.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Moffat Creek 900m d/s Moffat Road	2C0a	Na-Ca-Mg-Cl	0.0%	0.0%	50.4%	0.0%	0.0%	48.9%	0.0%	0.0%
Carran Creek 800m u/s Waituna Lagoon Rd	2C0a	Na-Ca-Mg-Cl	0.0%	0.0%	37.7%	0.0%	0.0%	59.2%	0.0%	0.0%
Carran Creek west d/s Waituna Gorge Rd	2C0a	Na-Ca-Mg-Cl	0.0%	0.0%	98.2%	0.0%	0.0%	1.8%	0.0%	0.0%
Moffat Creek 20m u/s Hanson Road	2C0a	Na-Ca-Mg-Cl	0.0%	0.0%	95.9%	0.0%	0.0%	4.1%	0.0%	0.0%

			Surficial geology							Subsurf. geology
WQSiteName	**HCA 4th Threshold**	**Major ion facies**	**Carbonate**	**Carbonaceous**	**Felsic**	**Intermediate**	**Mafic**	**Peat**	**Clastics**	**Carbonate**
Waihopai River us Longbush S Rd	2C0b	Na-Ca-Cl-HCO_3	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Carran Creek 1km d/s Waituna Gorge Rd	2C0a	Na-Ca-Mg-Cl	0.0%	0.0%	95.9%	0.0%	0.0%	4.1%	0.0%	0.0%
Moffat Creek at Moffat Road	2C0a	Na-Ca-Mg-Cl	0.0%	0.0%	53.7%	0.0%	0.0%	46.3%	0.0%	0.0%
Spurhead Creek 1	2C0b	Na-Ca-Mg-Cl-HCO_3	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Carran Creek east u/s Waituna Gorge Rd	2C0a	Na-Ca-Mg-Cl	0.0%	0.0%	95.1%	0.0%	0.0%	4.9%	0.0%	0.0%
Waituna Creek at Marshall Road	2C0b	Na-Ca-Cl-SO_4	0.0%	0.0%	86.3%	0.0%	0.0%	13.7%	0.0%	0.0%
Moffat Creek Sth branch 1.2km u/s Miller Rd	2C0a	Na-Mg-Ca-Cl	0.0%	0.0%	40.7%	0.0%	0.0%	59.3%	0.0%	0.0%
Waituna Creek 5m upstream NE trib. Confl.	2C0b	Ca-Na-Mg-Cl-SO_4	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Waihopai South Branch at Woodlands South	2C0b	Na-Ca-Mg-Cl-HCO_3	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Waihopai South Branch at Waituna Morton	2C0b	Na-Ca-Mg-Cl-HCO_3	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Carran Creek 3km u/s Waituna Lagoon Rd	2C0a	Na-Ca-Cl	0.0%	0.6%	5.3%	0.0%	0.0%	94.2%	0.0%	0.0%
Carran Creek trib.1km u/s Waituna Lag.Rd	1A0o	Na-Cl	0.0%	0.0%	2.5%	0.0%	0.0%	97.5%	0.0%	0.0%
Mokotua Stream at Awarua	1A0o	Na-Cl	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%
Waihopai River 1.5 km us Walker Road	2C0b	Na-Ca-Mg-Cl-HCO_3	0.0%	0.0%	98.8%	0.0%	0.0%	1.2%	0.0%	0.0%
Waihopai River 100m d/s Evans Road	2C0b	Na-Ca-Mg-Cl-HCO3	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Waihopai River at kennington Road	2C0b	Na-Ca-Mg-Cl-HCO_3	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Waituna Creek 1m upstream Rimu Seaward	2C0b	Ca-Na-Mg-Cl-HCO_3	0.0%	0.0%	99.6%	0.0%	0.0%	0.4%	0.0%	0.0%
Waituna Creek at White Pine Road	2A2c	Ca-Na-Cl-SO_4	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Table 4-14: Stratifying by geology and in this instance the proportion of peat within a sites capture zone discriminates between cluster memberships. See text for discussion.

			Carbonate presence		Surficial geology						
WQSiteName	HCA 4th threshold	Major ion facies	Carbonate surface	Carbonate subsurface	Peat	Erosive felsic	Erosive mafic	Alluvium felsic	Alluvium mafic	Alluvium total	Clastics
Mokotua Stream at Awarua	1A0o	Na-Cl	0.00%	0.00%	100.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%
Carran Creek tributary 1km u/s Waituna Lagoon Rd	1A0o	Na-Cl	0.00%	0.00%	97.51%	0.00%	0.00%	2.49%	0.00%	100.00%	0.00%
Carran Creek 3km u/s Waituna Lagoon Road	2C0a	Na-Ca-Cl	0.00%	0.00%	94.16%	0.00%	0.00%	5.26%	0.00%	100.00%	0.00%
Moffat Creek Sth branch 1.2km u/s Miller Road	2C0a	Na-Mg-Ca-Cl	0.00%	0.00%	59.28%	0.00%	0.00%	40.72%	0.00%	100.00%	0.00%
Carran Creek 800m u/s Waituna Lagoon Road	2C0a	Na-Ca-Mg-Cl	0.00%	0.00%	59.18%	0.00%	0.00%	37.70%	0.00%	100.00%	0.00%
Moffat Creek 900m d/s Moffat Road	2C0a	Na-Ca-Mg-Cl	0.00%	0.00%	48.89%	0.00%	0.00%	50.39%	0.00%	100.00%	0.00%
Moffat Creek at Moffat Road	2C0a	Na-Ca-Mg-Cl	0.00%	0.00%	46.31%	0.00%	0.00%	53.69%	0.00%	100.00%	0.00%
Waimatuku Stream d/s Bayswater Bog	3B2a	Ca-Na-Mg-HCO_3-Cl	0.00%	25.74%	40.89%	0.00%	0.00%	0.00%	59.11%	100.00%	0.00%
Waimatuku Stream at Robertson Road	2A1o	Ca-Mg-Na-HCO_3-Cl	0.50%	19.67%	21.66%	0.00%	0.00%	0.41%	77.44%	100.00%	0.00%
Waituna Creek at Marshall Road	2C0b	Na-Ca-Cl-SO_4	0.00%	0.00%	13.71%	0.48%	0.00%	85.82%	0.00%	99.50%	0.00%
Ayr Creek at Argyle Otahuti Road	2A1o	Ca-Na-Mg-HCO_3-Cl	3.04%	20.73%	6.60%	0.00%	0.00%	3.35%	87.00%	100.00%	0.00%
Carran Creek east branch u/s Waituna Gorge Road	2C0a	Na-Ca-Mg-Cl	0.00%	0.00%	4.86%	0.00%	0.00%	95.14%	0.00%	100.00%	0.00%
Waimatuku Stream at Fraser Road	2A1o	Ca-Na-Mg-HCO_3-Cl	0.00%	56.93%	4.34%	0.00%	0.00%	57.73%	37.93%	100.00%	0.00%
Moffat Creek 20m u/s Hanson Road	2C0a	Na-Ca-Mg-Cl	0.00%	0.00%	4.15%	0.00%	0.00%	95.85%	0.00%	100.00%	0.00%
Carran Creek 1km d/s Waituna Gorge Road	2C0a	Na-Ca-Mg-Cl	0.00%	0.00%	4.08%	0.00%	0.00%	95.92%	0.00%	100.00%	0.00%
Carran Creek west branch d/s Waituna Gorge Road	2C0a	Na-Ca-Mg-Cl	0.00%	0.00%	1.83%	0.00%	0.00%	98.17%	0.00%	100.00%	0.00%
Waihopai River Dacre Catchment Outlet	2A2c	Na-Ca-Mg-Cl-HCO_3	0.00%	0.00%	1.74%	0.00%	0.00%	98.20%	0.06%	100.00%	0.00%
Waihopai River 1.5 km u/s Walker Road	2C0b	Na-Ca-Mg-Cl-HCO_3	0.00%	0.00%	1.22%	0.00%	0.00%	98.78%	0.00%	100.00%	0.00%
Middle Creek at Argyle - Otahuti Road	2A1o	Ca-Mg-Na-HCO_3-Cl	0.00%	0.00%	0.86%	0.00%	0.00%	0.57%	98.57%	100.00%	0.00%

			Carbonate presence		Surficial geology						
WQSiteName	HCA 4th threshold	Major ion facies	Carbonate surface	Carbonate subsurface	Peat	Erosive felsic	Erosive mafic	Alluvium felsic	Alluvium mafic	Alluvium total	Clastics
Otepuni Creek at Nith Street	2A2c	Na-Ca-Mg-Cl-HCO$_3$	0.00%	0.00%	0.59%	0.00%	0.00%	71.92%	0.14%	100.00%	0.00%
Waikiwi Stream at North Road	2A2c	Na-Ca-Mg-Cl-HCO$_3$	0.00%	0.00%	0.42%	0.00%	0.00%	94.12%	5.46%	100.00%	0.00%
Waituna Creek 1m upstream Rimu Seaward Downs Rd	2C0b	Ca-Na-Mg-Cl-HCO$_3$	0.00%	0.00%	0.37%	0.00%	0.00%	99.63%	0.00%	100.00%	0.00%
Waihopai River u/s Queens Drive	2C0b	Na-Ca-Mg-Cl-HCO$_3$	0.00%	0.00%	0.28%	1.31%	0.00%	96.74%	0.01%	98.69%	0.05%
Waimatuku Tributary at Robertson Road	2B0a	Ca-Mg-Na-HCO$_3$-Cl	0.00%	0.29%	0.26%	0.00%	0.00%	0.00%	99.74%	100.00%	0.00%
Middle Creek at Otahuti	2A1o	Ca-Mg-Na-HCO$_3$-Cl	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	100.00%	0.00%
Waimatuku Stream Tributary at Otautau Dr	2B0a	Ca-Na-Mg-Cl-HCO$_3$	0.00%	1.34%	0.00%	0.00%	0.00%	0.00%	100.00%	100.00%	0.00%
Waimatuku Stream at Isla Bank-Fairfax Rd	2A1o	Ca-Mg-Na-HCO$_3$-Cl	2.01%	46.05%	0.00%	1.38%	0.00%	37.46%	58.63%	97.78%	0.00%
Oteramika Stream at Seaward Downs	2C0b	Na-Ca-Mg-Cl-HCO$_3$	0.00%	0.00%	0.00%	14.33%	0.00%	84.45%	0.69%	85.67%	0.00%
Waihopai River 20 m us Waihopai Dam	2C0b	Na-Ca-Mg-Cl-HCO$_3$	0.00%	0.00%	0.00%	0.00%	0.00%	66.40%	0.00%	100.00%	1.40%
Waihopai River d/s Kennington	2A2c	Na-Ca-Cl-SO$_4$	0.00%	0.00%	0.00%	0.00%	0.00%	99.02%	0.00%	100.00%	0.00%
Waihopai River us Longbush S Rd	2C0b	Na-Ca-Cl-HCO$_3$	0.00%	0.00%	0.00%	0.27%	0.00%	99.73%	0.00%	99.73%	0.00%
Spurhead Creek 1	2C0b	Na-Ca-Mg-Cl-HCO$_3$	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	100.00%	0.00%
Waituna Creek 5m upstream NE tributary confluence	2C0b	Ca-Na-Mg-Cl-SO$_4$	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	100.00%	0.00%
Waihopai South Branch at Woodlands South	2C0b	Na-Ca-Mg-Cl-HCO$_3$	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	100.00%	0.00%
Waihopai South Branch at Waituna Morton	2C0b	Na-Ca-Mg-Cl-HCO$_3$	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	100.00%	0.00%
Waihopai River 100m d/s Evans Road	2C0b	Na-Ca-Mg-Cl-HCO$_3$	0.00%	0.00%	0.00%	19.54%	0.00%	80.46%	0.00%	80.46%	0.00%
Waihopai River at kennington Road	2C0b	Na-Ca-Mg-Cl-HCO$_3$	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	100.00%	0.00%
Waituna Creek at White Pine Road	2A2c	Ca-Na-Cl-SO$_4$	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	100.00%	0.00%

Table 4-15: Hydrochemical data and pre-defined cluster membership for lowland-LSR derived streams. Stratifying by redox (CDNP) category produces a redox continuum within the data set. Specifically, the sites with the highest proportion of reducing soils and aquifers (i.e., mainly peat) with their capture zones also have the highest TOC, DOC, Mn(II), Fe(II) and the lowest TON concentrations.

WQSiteName	HCA 4th threshold	Major ion facies	Hydrochemistry						Peat presence	CRP			Bypass likely
			DOC (mg/L)	TOC (mg/L)	Fe (mg/L)	Mn (mg/L)	TON (mg/L)	DO (mg/L)		High over High	Low over Low	Moderate over Low	
Mokotua Stream at Awarua	1A0o	Na-Cl	30.20	32.71	1.04	0.01	0.01	8.24	100.0%	100.0%	0.0%	0.0%	0.0%
Carran Creek 3km u/s Waituna Lagoon Road	2C0a	Na-Ca-Cl	17.80	20.00	0.53	0.04	0.36	9.44	94.2%	98.0%	0.0%	0.7%	0.0%
Carran Creek tributary 1km u/s Waituna Lagoon Rd	1A0o	Na-Cl	28.50	29.50	0.64	0.01	0.01	8.03	97.5%	97.5%	0.0%	0.0%	0.0%
Carran Creek 800m u/s Waituna Lagoon Road	2C0a	Na-Ca-Mg-Cl	16.00	18.20	0.79	0.05	0.26	9.40	59.2%	78.0%	0.0%	5.7%	0.0%
Waimatuku Stream d/s Bayswater Bog	3B2a	Ca-Na-Mg-HCO$_3$-Cl	7.96	8.04	0.44	0.06	1.42	9.54	40.9%	45.7%	0.0%	12.0%	47.0%
Moffat Creek Sth branch 1.2km u/s Miller Road	2C0a	Na-Mg-Ca-Cl	24.00	25.00	0.76	0.03	0.30	11.06	59.3%	37.5%	0.0%	0.0%	0.0%
Moffat Creek at Moffat Road	2C0a	Na-Ca-Mg-Cl	20.96	25.50	1.30	0.06	0.64	9.21	46.3%	36.3%	0.0%	8.6%	0.0%
Moffat Creek 900m d/s Moffat Road	2C0a	Na-Ca-Mg-Cl	20.66	27.67	1.41	0.09	1.37	9.30	48.9%	32.1%	0.0%	7.1%	0.0%
Waimatuku Stream at Robertson Road	2A1o	Ca-Mg-Na-HCO$_3$-Cl	4.27	5.36	0.20	0.03	2.50	10.33	21.7%	24.4%	6.8%	7.0%	64.4%
Waituna Creek at Marshall Road	2C0b	Na-Ca-Cl-SO$_4$	9.15	12.62	0.34	0.04	1.73	10.97	13.7%	12.2%	25.6%	43.4%	0.0%
Waihopai River 100m d/s Evans Road	2C0b	Na-Ca-Mg-Cl-HCO$_3$	4.84	5.70	0.20	0.02	2.40	12.27	0.0%	9.5%	75.7%	4.4%	0.0%
Ayr Creek at Argyle Otahuti Road	2A1o	Ca-Na-Mg-HCO$_3$-Cl	4.85	4.37	0.05	0.03	2.50	9.92	6.6%	9.0%	6.4%	42.3%	80.3%
Carran Creek east branch u/s Waituna Gorge Road	2C0a	Na-Ca-Mg-Cl	17.70	18.00	0.42	0.04	0.54	8.84	4.9%	4.7%	2.2%	72.7%	0.0%
Waimatuku Stream at Fraser Road	2A1o	Ca-Na-Mg-HCO$_3$-Cl	4.21	5.47	0.07	0.01	2.80	11.90	4.3%	4.2%	43.8%	29.2%	29.7%

			Hydrochemistry							CRP			
WQSiteName	HCA 4th threshold	Major ion facies	DOC (mg/L)	TOC (mg/L)	Fe (mg/L)	Mn (mg/L)	TON (mg/L)	DO (mg/L)	Peat presence	High over High	Low over Low	Moderate over Low	Bypass likely
Carran Creek 1km d/s Waituna Gorge Road	2C0a	Na-Ca-Mg-Cl	14.60	15.65	0.42	0.05	0.87	11.27	4.1%	3.9%	1.6%	67.3%	0.0%
Carran Creek west branch d/s Waituna Gorge Road	2C0a	Na-Ca-Mg-Cl	15.30	16.25	0.59	0.05	0.25	9.94	1.8%	1.8%	0.0%	51.7%	0.0%
Middle Creek at Argyle - Otahuti Road	2A1o	Ca-Mg-Na-HCO_3-Cl	3.57	5.12	0.03	0.01	6.50	11.32	0.9%	1.1%	22.3%	7.9%	72.5%
Waihopai River u/s Queens Drive	2C0b	Na-Ca-Mg-Cl-HCO_3	5.07	7.96	0.22	0.03	2.40	11.46	0.3%	0.8%	70.0%	15.4%	0.0%
Waimatuku Tributary at Robertson Road	2B0a	Ca-Mg-Na-HCO_3-Cl	1.95	5.13	0.07	0.01	5.70	8.93	0.3%	0.3%	29.9%	14.6%	69.9%
Waihopai River us Longbush S Rd	2C0b	Na-Ca-Cl-HCO_3	5.67	9.18	0.23	0.03	2.55	11.86	0.0%	0.2%	53.0%	36.7%	0.0%
Waikiwi Stream at North Road	2A2c	Na-Ca-Mg-Cl-HCO_3	4.96	5.81	0.23	0.03	2.71	11.25	0.4%	0.0%	72.0%	14.6%	7.0%
Moffat Creek 20m u/s Hanson Road	2C0a	Na-Ca-Mg-Cl	24.00	25.00	0.95	0.04	0.28	9.25	4.1%	0.0%	0.0%	68.8%	0.0%
Otepuni Creek at Nith Street	2A2c	Na-Ca-Mg-Cl-HCO_3	8.12	11.20	0.33	0.03	1.34	12.10	0.6%	0.0%	5.1%	57.4%	0.0%
Waituna Creek at White Pine Road	2A2c	Ca-Na-Cl-SO_4	9.20	13.51	0.28	0.04	2.25	9.45	0.0%	0.0%	11.1%	72.6%	0.0%
Waimatuku Stream Tributary at Otautau Dr	2B0a	Ca-Na-Mg-Cl-HCO_3	5.26	4.68	0.19	0.01	6.00	9.82	0.0%	0.0%	15.1%	0.0%	84.9%
Middle Creek at Otahuti	2A1o	Ca-Mg-Na-HCO_3-Cl	3.57	5.49	0.04	0.00	3.20	13.69	0.0%	0.0%	18.3%	15.0%	81.8%
Waihopai River 20 m us Waihopai Dam	2C0b	Na-Ca-Mg-Cl-HCO_3	4.76	5.91	0.23	0.02	2.40	11.75	0.0%	0.0%	36.4%	0.0%	0.0%
Waimatuku Stream at Isla Bank-Fairfax Rd	2A1o	Ca-Mg-Na-HCO_3-Cl	3.96	5.47	0.11	0.02	2.95	12.39	0.0%	0.0%	36.5%	19.5%	58.7%
Oteramika Stream at Seaward Downs	2C0b	Na-Ca-Mg-Cl-HCO_3	7.64	11.93	0.34	0.03	1.48	12.24	0.0%	0.0%	45.3%	40.1%	35.7%
Waituna Creek 1m upstream Rimu	2C0b	Ca-Na-Mg-Cl-HCO_3	5.40	6.57	0.23	0.02	1.89	10.77	0.4%	0.0%	47.6%	40.6%	0.0%

			Hydrochemistry							CRP			
WQSiteName	**HCA 4th threshold**	**Major ion facies**	**DOC (mg/L)**	**TOC (mg/L)**	**Fe (mg/L)**	**Mn (mg/L)**	**TON (mg/L)**	**DO (mg/L)**	**Peat presence**	**High over High**	**Low over Low**	**Moderate over Low**	**Bypass likely**
Seaw. Downs Rd													
Waituna Creek 5m upstream NE tributary confluenc	2C0b	Ca-Na-Mg-Cl-SO_4	3.70	4.80	0.17	0.04	1.66	11.46	0.0%	0.0%	55.2%	37.0%	0.0%
Waihopai River d/s Kennington	2A2c	Na-Ca-Cl-SO_4	8.83	13.05	0.24	0.04	2.00	10.63	0.0%	0.0%	56.3%	15.2%	0.0%
Waihopai River 1.5 km us Walker Road	2C0b	Na-Ca-Mg-Cl-HCO_3	5.90	9.37	0.26	0.03	2.10	11.09	1.2%	0.0%	59.7%	28.3%	0.0%
Waihopai South Branch at Waituna Morton	2C0b	Na-Ca-Mg-Cl-HCO_3	5.30	8.56	0.30	0.03	1.54	10.23	0.0%	0.0%	74.6%	11.1%	0.0%
Waihopai South Branch at Woodlands South	2C0b	Na-Ca-Mg-Cl-HCO_3	6.08	9.07	0.24	0.03	2.50	11.42	0.0%	0.0%	77.4%	10.7%	0.0%
Spurhead Creek 1	2C0b	Na-Ca-Mg-Cl-HCO_3	5.91	9.02	0.24	0.03	1.95	11.68	0.0%	0.0%	80.6%	4.8%	0.0%
Waihopai River Dacre Catchment Outlet	2A2c	Na-Ca-Mg-Cl-HCO_3	4.52	5.42	0.18	0.02	2.30	11.89	1.7%	0.0%	85.5%	2.7%	0.61%
Waihopai River at Kennington Road	2C0b	Na-Ca-Mg-Cl-HCO_3	4.69	5.73	0.20	0.02	2.50	12.34	0.0%	0.0%	94.6%	0.0%	0.0%

4.3.3.1.4 Surface water hierarchical stratification summary

In summary, manual hierarchical stratification of surface water hydrochemical data by key hydrochemical drivers proved to be highly accurate, consistently clustering waters of similar hydrochemical composition into homogenous subgroups. Furthermore, stratification provided further insight into the role of hydrochemical drivers of hydrochemical and water quality variation for regional surface waters. The effectiveness of hierarchical stratification by key hydrochemical drivers is seen as evidence for the validity of this approach and provides a strong platform for a simplified conceptual model of regional controls over surface water hydrochemistry and water quality based on the drivers outlined above. Significantly, lowland LSR surface waters require a higher degree of stratification and Alpine River Recharged waters the least.

Although validation through the empirical approach, presented in the preceding sections indicated that not all of the variability in hydrochemistry could be explained by our conceptual model, stratification by key drivers resolved and explained these inconsistencies. Stratification by key drivers suggests that our conceptual model is capable of explaining variation in regional surface water chemistry and hence estimating regional surface water chemistry with a high degree of certainty at any point in the region.

4.3.3.3 Manual hierarchical stratification of spatial groundwater hydrochemical data according to hydrochemical drivers

We stratified the groundwater data by recharge driver domain, either as Mixed (ARR-BRR-LSR) or Lowland - LSR. We subsequently stratified by Combined Reduction Potential (CRP). For all recharge domains, CRP appeared to exert the strongest control over the spatial variation in groundwater hydrochemistry and HCA clusters. That redox conditions exerts the strongest control over groundwater hydrochemistry is not surprising given it is often one of the most dominant factors governing the chemical variability of national groundwater systems including those of Southland (Rissmann et al., 2012; Daughney, et al., 2015). Further, as demonstrated in TC6, CRP is a strong predictor of redox sensitive species, primarily DO, Mn(II), Fe(II) and TON.

4.3.3.3.1 River influenced waters

Stratification by recharge mechanism helped distinguish LSR influenced waters from waters that carry a riverine signature for both point and capture zone intersected data.

Specifically, sorting by mixed recharge for point intersected data, successfully identified 10 out of 15 river influenced groundwaters (i.e. waters associated with cluster 1; Table 4-16). Four of the remaining five groundwaters were associated with HCA cluster 2 (oxidising) and occur in riverine or terrace aquifers with high river influence and high connectivity. These waters had compositions that resemble riverine waters as opposed to land surface recharged waters. Specifically, these waters had relatively high concentrations of DO and low DOC and EC, similar to those observed for groundwaters associated with the riverine cluster (i.e. HCA cluster 1). The remaining groundwater (x1) is associated with cluster 3 (weakly reducing, LSR, coastal). Although this water had an oxic signature (as opposed to a reducing signature), EC was higher and $\delta^{18}O-H_2O$ more positive than riverine influenced waters suggesting this site has been misclassified. Overall, stratification by recharge domain successfully identified 93% of the river influenced waters (success rate of 93%).

All river influenced waters have HCO_3 as their major anion and are very dilute (i.e. have low EC). The majority of waters (79%) are of type Ca-HCO_3 which can be related to their alpine source, where young felsic parent material dominates. Stratification by surface/subsurface geology generally identifies Ca-HCO_3 waters (young felsic parent geology) and Mg- HCO_3 waters (mafic parent material), but often subsurface and or surface geology is not defined (i.e. undifferentiated Clastics). This can be resolved with better definition of surface and subsurface geology (e.g. inclusion of carbonate rock). Further, we expect that we can resolve the estimation of major ions based on surface and subsurface geology better with use of groundwater capture zones.

4.3.3.3.2 LSR waters

River influenced waters

The largest number of sites (178 of 193) were associated with Lowland LSR. Fourteen of the 178 sites showed clear evidence for river influence (i.e. have cluster 1 assignment). These sites were associated with riverine or terrace aquifers with high river influence and connectivity (TC2). Although these waters did not get picked up through stratification by general recharge domain (i.e. were misclassified, Table 4-17), sorting by hydrodynamic setting resolved a high potential for river influence and degree of river connectivity.

Overall, stratification by recharge domain had a success rate of 91.5%. However, consideration of groundwater hydrodynamic setting, which is part of the recharged river, in particular river influence and connectivity, successfully identified all river influenced waters (success rate of 100%).

All river influenced waters have HCO_3 as their major anion and have low EC (i.e. are very dilute). Stratification by surface/subsurface geology successfully identifies Ca-HCO_3 waters (young felsic parent material) and Mg-HCO_3 waters (mafic parent material).

Following removal of river influenced waters, point intersected data (of 164 sites) were sorted by CRP, specifically by high reduction potential (High over High, Moderate over High and Moderate over Intermediate CRP), moderate soil reduction potential (Moderate over Low CRP), high soil reduction potential (High over Low CRP) and low reduction potential (Low over Low CRP, Table 4-18), successfully identified reducing and oxidising groundwaters as demonstrated below.

Redox state

High over High, Moderate over High and Moderate over Intermediate CRP

All but one of the seven samples associated with high reduction potential were classified as reducing (5 of them were associated with cluster 4 = strongly reducing, and 1 of the samples was associated with cluster 3 = weakly reducing). These samples exhibited low concentrations of TON, high Fe(II) and Mn(II), and low ORP levels (Table 4-19).

One sample showed a clear oxidising signature and has cluster assignment 2 (weakly oxidising). We note that subsurface geology was undefined (Undiff. Clastics) at this site, hence we expect that CRP is not well defined at this location.

Considering this site's misclassification is explainable, the success rate of stratification by high reduction potential (i.e. High over High, Moderate over High and Moderate over Intermediate CRP) is 86 to 100%.

Moderate over Low CRP

Stratification by Moderate over Low CRP correctly identified 40 of 56 (71%) samples with a reducing or mixed redox (oxic-anoxic) signature (Table 4-20).

The remaining 16 groundwaters were weakly oxidising, with moderately high levels of DO, TON and moderately low levels of Fe(II) and were mainly associated with cluster 2 and 3 (weakly oxidising and weakly reducing, respectively). All of these (oxidising) samples are associated with hydrodynamic settings (TC2) with high bypass flow potential (6 sites) and/or were either associated with areas where bypass flow is highly likely (10 samples). Hence the oxidising signature of these waters could be explained by bypass flow (bypass of the reducing subsoils and unsaturated zone).

Considering the misclassification of oxic samples can be explained by presence of bypass flow, sorting by Moderate over Low CRP had a success rate of 100%.

High over Low CRP

Stratification by High over Low CRP initially identified 20 of 35 (57%) samples that were classified as reducing (anoxic) or mixed (oxic-anoxic) which matches what we would expect in a High over Low CRP environment. These samples were primarily associated with reducing clusters (4 and 3, 10 samples), but also with weakly oxidising clusters (2, 8 samples) (Table 4-21). Two samples had cluster assignment 6 (strongly oxidising), which did not match the general redox state of mixed (oxic-anoxic). However, both samples have elevated Mn(II) concentrations suggesting at least mixed redox state (if not anoxic).

The remaining 15 samples exhibited an oxidising signature, with high concentrations of DO and TON, and low concentrations of dissolved Fe and high ORP. These samples were mainly associated with oxidising clusters 2 and 6 (13 samples). Two samples had cluster 3 assignment (weakly reducing). All of these samples were associated with high hydrodynamic settings characterised by high bypass risk, hence explaining the occurrence of oxic waters associated with High over Low CRP.

Considering the misclassification of oxic samples can be explained by presence of bypass flow, stratification by High over Low CRP had a success rate of 91% in terms of groundwater redox characteristics.

Low over Low CRP

Table 4-18 shows that 17 of 66 (26%) samples associated with Low over Low CRP were classified as oxidising (of varying cluster assignment i.e. cluster 2>6>5>1, Table 4-18). These samples clearly showed an oxidising signature, with elevated concentrations of DO and TON, high ORP and very low Mn(II) and Fe(II) levels.

Of the remaining 49 samples, 45 showed a mixed (oxic-anoxic) signature as defined by redox assignment. However, as noted in TC6, threshold redox assignments are poor at picking up subtle differences in the concentrations of redox sensitive species. Actually, 23 samples had an oxidising as opposed to a mixed (or reducing) signature as evident from the concentrations of redox sensitive species (generally low concentrations of Fe(II) and Mn(II) and high TON) and association with weakly or strongly oxidising HCA clusters (16 samples had cluster 5 or 6 assignment and 7 samples had cluster 2 assignment). The mixed redox signatures for remaining 21 samples with cluster assignment 3 (weakly reducing) can be related to the presence of both oxidising and reducing species as a result of mixing of water (as demonstrated in TC 6). We note that consideration of capture zone data could resolve this.

In addition to the above, 8 sites with mixed redox assignment had undefined subsurface geology (Undiff. Clastics) suggesting that CRP is not well defined at these particular sites, this includes 1 site associated with cluster 4 (strongly reducing).

The remaining four groundwaters showed a reducing signature. These groundwaters exhibited clear evidence of reduction with negative ORP, low TON and D.O levels, and high Fe(II) and Mn(II) concentrations. Two of these samples had undefined subsurface geology (Undiff. Clastics). Again, we expect that CRP is not well defined at these particular sites. This can be resolved with better definition of subsurface geology (e.g. through inclusion of reducing aquifers and carbonate rock).

The reducing signature of the remaining two groundwaters could not be easily explained. We suggest that these sites have been misclassified.

Considering the misclassification of mixed and reducing samples is explainable (as shown above), overall sorting by Low over Low CRP had a success rate of 97%. When considering all sites of mixed or anoxic redox state that showed clear evidence of reduction (i.e. 26 samples) as misclassified, the success rate decreased to 61%.

Table 4-16: Stratification by recharge mechanisms. Mixed recharge highlights all river influenced waters of cluster membership 1, four sites are associated with cluster 2 (oxidising). These occur in braided river aquifers. One site(in italics) associated with cluster 3 (weakly reducing) shows clear signs of land surface recharge – suggesting it has been misclassified.

Site	GW Zone	Aquifer type	River Influence	Connectivity	HCA Cluster	Water type	General Redox Category	EC [uS/cm]	DO Field [mg/L]	TON [mg/L]	Fe(II) [mg/L]	DOC [mg/L]	Surface Geology	Subsurface Geology
D43/0041	Te Anau	Terrace	High	Low/High	1	Mg-HCO_3	Oxic	99.8	1.6	0.5	0.1	1.1	Undiff. Clastics	Undiff. Clastics
D43/0052	Te Anau	Terrace	High	Low/High	1	Mg-HCO_3	Mixed(oxic-anoxic)	90.7	5.7	1.6	0.1	1.1	Felsic	Undiff. Clastics
D43/0053	Te Anau	Terrace	High	Low/High	2	Ca-HCO_3	Oxic	126.0	6.6	2.0	0.0	0.7	Mafic	Undiff. Clastics
D43/0064	Te Anau	Terrace	High	Low/High	1	Ca-HCO_3	Mixed(oxic-anoxic)	186.4	7.1	4.5	0.1	0.6	Mafic	Undiff. Clastics
E44/0007	Oreti	Riparian	High	High/Low	2	Ca-HCO_3	Oxic	207.5	3.9	6.5	0.1	2.3	Felsic	Felsic
E44/0066	Upper Aparima	Terrace	High	High/Low	2	Ca-HCO_3	Oxic	192.6	14.3	3.0	0.1	4.1	Felsic	Undiff. Clastics
D43/0004	Te Anau	Terrace	High	Low/High	1	Ca-HCO_3	Mixed(oxic-anoxic)	143.0	8.6	2.6	0.1	0.7	Felsic	Undiff. Clastics
D43/0026	Te Anau	Terrace	High	Low/High	1	Ca-HCO_3	Oxic	56.9	2.3	0.3	0.1	1.2	Undiff. Clastics	Undiff. Clastics
D43/0060	Te Anau	Terrace	High	Low/High	1	Ca-HCO_3	Oxic	107.0	3.1	0.6	0.1	1.0	Felsic	Undiff. Clastics
D43/0117	Te Anau	Terrace	High	Low/High	1	Ca-HCO_3	Oxic	87.2	4.3	0.3	0.1	1.0	Undiff. Clastics	Undiff. Clastics
D43/0119	Te Anau	Terrace	High	Low/High	1	Ca-HCO_3	Oxic	114.3	3.6	0.6	0.1	0.8	Felsic	Undiff. Clastics
F43/0021	Upper Mataura	Riparian	High	High/Low	1	Ca-HCO_3	Mixed(oxic-anoxic)	125.9	8.5	3.9	0.1	0.9	Felsic	Undiff. Clastics
F44/0042	Waipounamu	Riparian	High	Low	1	Ca-HCO_3	Oxic	115.0	7.6	2.9	0.1	0.3	Felsic	Felsic
F44/0123	Cattle Flat	Riparian	High	High	2	Na-HCO_3	Mixed(oxic-anoxic)	88.0	8.8	1.5	0.6	0.8	Felsic	Undiff. Clastics
F45/0576	*Knapdale*	*Lowland*	*Low*	*Low*	*3*	*Ca-SO_4*	*Mixed(oxic-anoxic)*	*231.0*	*6.2*	*5.6*	*0.2*	*0.9*	*Felsic*	*Undiff. Clastics*

Table 4-17: River influenced groundwaters (i.e. cluster 1 assignment) that did not get picked up through stratification by recharge domain. All sites are associated with Riparian or Terrace aquifers and high river influence and connectivity.

Site	GW Zone	Aquifer type	River Influence	Connectivity	HCA Cluster	Water type	General Redox Category	EC [uS/cm]	DO [mg/L]	TON [mg/L]	Fe(II) [mg/L]	$\delta^{18}O-H_2O$ [pptv VSMO]	Surface Geology	Subsurface Geology
D43/0001	Te Anau	Terrace	High	Low/High	1	$Mg-HCO_3$	Oxic	104.8	9.2	2.2	0.0	-10.2	Mafic	Undiff.Clastics
E44/0350	Upper Aparima	Terrace	High	High/Low	1	$Ca-HCO_3$	Oxic	119.0	6.9	0.4	0.1	-9.4	Mafic	Felsic
D43/0030	Te Anau	Terrace	High	Low/High	1	$Ca-HCO_3$	Oxic	137.2	5.2	2.9	0.1	-10.0	Felsic	Felsic
D43/0067	Te Anau	Terrace	High	Low/High	1	$Ca-HCO_3$	Oxic	37.2	8.7	0.4	0.0	-10.6	Felsic	Undiff. Clastics
E44/0087	Five Rivers	Riparian	High	High/Low	1	$Ca-HCO_3$	Oxic	89.1	4.8	1.0	0.1	-8.9	Felsic	Undiff.Clastics
E44/0173	Five Rivers	Riparian	High	High/Low	1	$Ca-HCO_3$	Mixed(oxic-anoxic)	138.5	7.1	6.1	0.2	-8.5	Felsic	Undiff.Clastics
E44/0232	Five Rivers	Riparian	High	High/Low	1	$Ca-HCO_3$	Mixed(oxic-anoxic)	127.5	6.1	3.8	0.2	-8.5	Felsic	Felsic
E45/0353	Lower Oreti	Lowland	High	Low/High	1	$Ca-HCO_3$	Oxic	120.0	1.6	1.0	0.0	-9.9	Felsic	Calcareous/ Limestone
E45/0406	Upper Aparima	Terrace	High	High/Low	1	$Ca-HCO_3$	Mixed(oxic-anoxic)	158.0	9.2	2.3	0.2	-9.9	Felsic	Undiff.Clastics
F43/0009	Upper Mataura	Riparian	High	High/Low	1	$Ca-HCO_3$	Mixed(oxic-anoxic)	117.6	8.5	3.9	0.1	-9.1	Felsic	Undiff.Clastics
F44/0005	Riversdale	Riparian	High	High/Low	1	$Ca-HCO_3$	Oxic	132.8	7.2	4.2	0.0	-9.0	Felsic	Felsic
F44/0055	Riversdale	Riparian	High	High/Low	1	$Ca-HCO_3$	Oxic	103.5	7.4	2.2	0.1	-9.5	Felsic	Felsic
F44/0291	Wendon	Terrace	High/Low	Low	1	$Ca-HCO_3$	Oxic	43.0	10.8	0.8	0.1	-10.0	Felsic	Undiff.Clastics
F44/0326	Riversdale	Riparian	High	High/Low	1	$Ca-HCO_3$	Oxic	144.3	6.7	4.6	0.0	-9.1	Felsic	Felsic

Table 4-18: Stratification by Low over Low CRP. The majority of sites (32 of 47 samples) are classified as oxidising.

Site	DEPTH [m]	GW Zone	Aquifer TYPE	River Influence	Connectivity	Bypass-Redox	HCA Cluster	General Redox Category	TON [mg/L]	Fe [mg/L]	DO Field [mg/L]	DOC [mg/L]	TOC [mg/L]	Surface geology	Subsurface geology
E44/0526		Longridge	Terrace	Low	Low	High/Low	2	Oxic	12.08	1.93	0.04	1.89	12.00	Felsic	Felsic
E45/0010	9.5	Upper Aparima	Terrace	High	High/Low	High/Low	2	Oxic	7.30	7.7	0.07	1.84	4.00	Mafic	Undiff. Clastics
E45/0011	7.5	Central Plains	Lowland	Low	Low	High/Low	2	Oxic	7.00	11.25	0.02	1.46	4.01	Mafic	Undiff. Clastics
E45/0250	5.5	Upper Aparima	Terrace	High	High/Low	High/Low	2	Oxic	8.50	5.9	0.06	1.61	25.56	Mafic	Undiff. Clastics
E46/0099	10.5	Lower Oreti	Lowland	High	Low/High	High/Low	2	Oxic	3.34	5.2	0.10	1.17	25.83	Felsic	Felsic
E46/0575		Waimatuku	Lowland	Low	Low	High/Low	2	Oxic	4.32	8.2	0.09	2.10	26.00	Felsic	Undiff. Clastics
F45/0614	6.38	Riversdale	Riparian	High	High/Low	Low	2	Oxic	12.54	5.9	0.09	4.07	5.90	Felsic	Felsic
E44/0008	5.6	Waimea Plains	Lowland	Low	Low	High/Low	5	Oxic	9.30	9.5	0.08	0.64	8.49	Felsic	Felsic
E44/0009	10.5	Waimea Plains	Lowland	Low	Low	High/Low	5	Oxic	9.20	7.8	0.04	0.88	8.33	Felsic	Felsic
E44/0014	8.66	Five Rivers	Riparian	High	High/Low	High/Low	5	Oxic	9.17	7.3	0.07	0.88	16.61	Felsic	Felsic
F44/0040	9.23	Wendonside	Terrace	Low	Low	Low	5	Oxic	9.47	9.1	0.07	0.83	8.33	Felsic	Felsic
E45/0055	7	Central Plains	Lowland	Low	Low	High/Low	6	Oxic	8.75	7.3	0.07	1.97	3.92	Felsic	Undiff. Clastics
E45/0537		Upper Aparima	Terrace	High	High/Low	High/Low	6	Oxic	7.17	13.9	0.06	1.61	4.00	Felsic	Undiff. Clastics
F44/0379		Riversdale	Riparian	High	High/Low	Low	6	Oxic	6.68	16.002	0.00	2.40	4.00	Felsic	Felsic
F46/0456	12	Edendale	Terrace	Low	Low	High/Low	6	Oxic	7.06	10.65	0.08	1.27	9.71	Felsic	Felsic
F46/0847	17	Edendale	Terrace	Low	Low	High/Low	6	Oxic	9.20	9.9	0.05	0.64	4.01	Felsic	Felsic
F44/0039	35	Wendonside	Terrace	Low	Low	Low	1	Oxic	8.65	4.15	0.07	0.75	14.37	Felsic	Felsic
D45/0298	10	Waiau	Terrace	Low	Low	Low	2	Mixed(oxic-anoxic)	1.20	3.1	0.03	1.26	25.80	Mafic	Undiff. Clastics
E45/0034	17	Lower Oreti	Lowland	High	Low/High	High/Low	2	Mixed(oxic-anoxic)	0.74	0.001	0.14	0.88	3.95	Felsic	Felsic
E45/0088	6	Upper Aparima	Terrace	High	High/Low	High/Low	2	Mixed(oxic-anoxic)	4.94	3.3	0.32	0.98	26.00	Mafic	Undiff. Clastics

Site	DEPTH [m]	GW Zone	Aquifer TYPE	River Influence	Connectivity	Bypass-Redox	HCA Cluster	General Redox Category	TON [mg/L]	Fe [mg/L]	DO Field [mg/L]	DOC [mg/L]	TOC [mg/L]	Surface geology	Subsurface geology
E45/0402	8	Dipton	Terrace	Low	High/Low	High/Low	2	Mixed(oxic-anoxic)	7.81	4.3	0.33	1.30	7.59	Felsic	Undiff. Clastics
E45/0456	6.5	Upper Aparima	Terrace	High	High/Low	High/Low	2	Mixed(oxic-anoxic)	6.26	2.974	0.19	1.70	11.06	Mafic	Undiff. Clastics
F45/0350	5	Riversdale	Riparian	High	High/Low	Low	2	Mixed(oxic-anoxic)	6.73	2.7	0.06	0.55	7.48	Felsic	Felsic
F45/0475	18	Knapdale	Lowland	Low	Low	High/Low	2	Mixed(oxic-anoxic)	4.58	10.7	0.10	0.25	26.00	Felsic	Felsic
D45/0164	23.5	Blackmount	Terrace	Low	Low	High/Low	5	Mixed(oxic-anoxic)	8.38	12.6	0.14	1.30	5.28	Mafic	Felsic
E44/0036	6	Waimea Plains	Lowland	Low	Low	High/Low	5	Mixed(oxic-anoxic)	9.60	12.7	0.11	0.67	8.28	Felsic	Felsic
E44/0167		Waimea Plains	Lowland	Low	Low	High/Low	5	Mixed(oxic-anoxic)	9.72	16.3	0.14	0.77	8.09	Felsic	Felsic
E44/0198	6.5	Castlerock	Terrace	Low	Low	High/Low	5	Mixed(oxic-anoxic)	8.96	18.97954	0.15	1.05	5.74	Felsic	Felsic
E44/0236	12.5	Waimea Plains	Lowland	Low	Low	High/Low	5	Mixed(oxic-anoxic)	9.50	19.1	0.12	0.67	8.28	Felsic	Felsic
E44/0369		Waimea Plains	Lowland	Low	Low	High/Low	5	Mixed(oxic-anoxic)	9.50	15.5	0.14	0.77	8.09	Felsic	Felsic
E44/0377	7.7	Waimea Plains	Lowland	Low	Low	High/Low	5	Mixed(oxic-anoxic)	10.00	19.3	0.13	0.66	8.18	Felsic	Felsic
E44/0417		Waimea Plains	Lowland	Low	Low	High/Low	5	Mixed(oxic-anoxic)	8.94	7.2	0.26	1.09	6.39	Felsic	Felsic
E44/0418		Waimea Plains	Lowland	Low	Low	High/Low	5	Mixed(oxic-anoxic)	9.30	10.2	0.11	0.78	8.17	Felsic	Felsic
E44/0457		Waimea Plains	Lowland	Low	Low	High/Low	5	Mixed(oxic-anoxic)	9.84	15.6	0.14	0.67	8.18	Felsic	Felsic
F44/0018	10	Wendonside	Terrace	Low	Low	Low	5	Mixed(oxic-anoxic)	9.49	14.8	0.14	0.67	8.18	Felsic	Felsic
F44/0139	27	Wendonside	Terrace	Low	Low	Low	5	Mixed(oxic-anoxic)	9.82	13.5	0.11	0.62	18.39	Felsic	Felsic
F45/0343	11.2	Knapdale	Lowland	Low	Low	High/Low	5	Mixed(oxic-anoxic)	8.76	13.47	0.12	1.09	8.19	Felsic	Carbonaceous
E46/0895	8.5	Makarewa	Lowland	Low	Low	High/Low	6	Mixed(oxic-anoxic)	7.00	31.5	0.12	1.41	3.98	Felsic	Carbonaceous
F45/0167	4.3	Riversdale	Riparian	High	High/Low	Low	6	Mixed(oxic-anoxic)	4.63	7.95	0.13	2.25	12.85	Felsic	Felsic
F45/0172	4.6	Croydon	Riparian	High	High/Low	High/Low	6	Mixed(oxic-anoxic)	5.62	16.95	0.10	1.75	3.98	Felsic	Carbonaceous
D46/0115	24	Lower Aparima	Terrace	High	Low/High	High/Low	3	Mixed(oxic-anoxic)	8.10	2.7	0.31	0.25	6.39	Felsic	Undiff. Clastics

Site	DEPTH [m]	GW Zone	Aquifer TYPE	River Influence	Connectivity	Bypass-Redox	HCA Cluster	General Redox Category	TON [mg/L]	Fe [mg/L]	DO Field [mg/L]	DOC [mg/L]	TOC [mg/L]	Surface geology	Subsurface geology
E45/0596	12.5	Upper Aparima	Terrace	High	High/Low	High/Low	3	Mixed(oxic-anoxic)	3.33	0.004	2.00	2.65	12.80	Felsic	Undiff. Clastics
E46/0097	8	Waihopai	Lowland	Low	Low	Low	3	Mixed(oxic-anoxic)	6.67	6.3	0.14	0.70	8.10	Felsic	Undiff. Clastics
E46/0259	9	Waihopai	Lowland	Low	Low	Low	3	Mixed(oxic-anoxic)	9.24	2.4	0.21	2.30	17.97	Felsic	Carbonaceous
E46/0299	12	Waihopai	Lowland	Low	Low	Low	3	Mixed(oxic-anoxic)	3.90	4.8	2.45	0.25	12.40	Felsic	Felsic
E46/0320	2.85	Waihopai	Lowland	Low	Low	Low	3	Mixed(oxic-anoxic)	8.12	4.6	0.26	0.57	7.35	Felsic	Felsic
F45/0170	4	Lower Mataura	Lowland	High	Low	High/Low	3	Mixed(oxic-anoxic)	6.73	5.5	0.16	1.08	5.13	Felsic	Felsic
F45/0253	15	Makarewa	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	8.55	2.8	1.31	1.37	18.02	Felsic	Felsic
F46/0183	20	Waihopai	Lowland	Low	Low	Low	3	Mixed(oxic-anoxic)	8.93	1.61	0.13	2.30	18.97	Felsic	Carbonaceous
F46/0185	14	Edendale	Terrace	Low	Low	High/Low	3	Mixed(oxic-anoxic)	6.83	9.15	0.12	0.70	4.01	Felsic	Felsic
F46/0186	7.3	Lower Mataura	Lowland	High	Low	High/Low	3	Mixed(oxic-anoxic)	3.01	3.6	4.71	1.85	12.78	Felsic	Felsic
F46/0193	12.5	Edendale	Terrace	Low	Low	High/Low	3	Mixed(oxic-anoxic)	8.53	8.85	0.13	0.71	4.02	Felsic	Felsic
F46/0194	12	Edendale	Terrace	Low	Low	High/Low	3	Mixed(oxic-anoxic)	8.10	8	0.85	0.88	5.02	Felsic	Felsic
F46/0239		Edendale	Terrace	Low	Low	High/Low	3	Mixed(oxic-anoxic)	7.69	6.25	0.23	0.81	5.66	Felsic	Felsic
F46/0522	26	Waihopai	Lowland	Low	Low	Low	3	Mixed(oxic-anoxic)	1.75	0.33	1.29	1.99	1.80	Felsic	Felsic
F46/0702	12.5	Waihopai	Lowland	Low	Low	Low	3	Mixed(oxic-anoxic)	7.07	3.1	0.18	0.50	18.80	Felsic	Felsic
F46/0802	5.5	Waihopai	Lowland	Low	Low	Low	3	Mixed(oxic-anoxic)	5.35	1.38	0.03	12.13	13.00	Felsic	Felsic
F46/0820	17.5	Waihopai	Lowland	Low	Low	Low	3	Mixed(oxic-anoxic)	6.70	2.1	0.17	1.62	18.26	Felsic	Carbonaceous
F47/0114	10.4	Awarua	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	3.16	0.019	6.80	8.58	26.60	Felsic	Felsic
F47/0251		Awarua	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	9.24	0.67	0.13	2.30	17.97	Felsic	Felsic
F47/0252	7	Awarua	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	3.69	3.8	0.19	1.40	12.80	Felsic	Felsic
D45/0276	31	Blackmount	Terrace	Low	Low	High/Low	4	Mixed(oxic-anoxic)	6.44	0.10267	0.20	1.51	10.36	Mafic	Undiff. Clastics

Site	**DEPTH [m]**	**GW Zone**	**Aquifer TYPE**	**River Influence**	**Connectivity**	**Bypass-Redox**	**HCA Cluster**	**General Redox Category**	**TON [mg/L]**	**Fe [mg/L]**	**DO Field [mg/L]**	**DOC [mg/L]**	**TOC [mg/L]**	**Surface geology**	**Subsurface geology**
E45/0608	*6*	*Upper Aparima*	*Terrace*	*High*	*High/Low*	*High/Low*	*3*	*Mixed(anoxic)*	*0.01*	*0.74*	*1.73*	*2.20*	*0.92*	*Felsic*	*Undiff. Clastics*
E44/0075	*4.43*	*Waimea Plains*	*Lowland*	*Low*	*Low*	*High/Low*	*4*	*Anoxic*	*0.47*	*0.001*	*0.22*	*0.25*	*9.70*	*Felsic*	*Undiff. Clastics*
F46/0434	*4.85*	*Edendale*	*Terrace*	*Low*	*Low*	*High/Low*	*4*	*Anoxic*	*0.12*	*0.009*	*9.10*	*1.04*	*3.76*	*Felsic*	*Felsic*
F46/0800	*16*	*Lower Mataura*	*Lowland*	*High*	*Low*	*High/Low*	*4*	*Anoxic*	*0.28*	*0.035*	*4.00*	*1.10*	*3.25*	*Felsic*	*Felsic*

Table 4-19: Stratification by High over High, Moderate over High and Moderate over Intermediate CRP successfully identifies reducing groundwaters.

Site	DEPTH [m]	GW Zone	Aquifer TYPE	River Influence	Con-nectivity	Bypass-Redox	HCA Cluster	General Redox Category	TON [mg/L]	Fe [mg/L]	DO Field [mg/L]	DOC [mg/L]	TOC [mg/L]	Surface geology	Subsurface geology
F47/0253	7.35	Awarua	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	0.61	0.069	3.60	1.02	3.71	Peat	Peat
E47/0155	12	Awarua	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	2.41	0.028	11.00	1.80	4.22	Felsic	Felsic
E47/0250	14.2	Awarua	Lowland	Low	Low	High/Low	4	Anoxic	0.03	0.011	14.90	0.92	3.71	Felsic	Felsic
F46/0382	8.2	Makarewa	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	4.79	0.18908	6.90	4.69	21.89	Felsic	Carbonaceous
F47/0201	11.8	Awarua	Lowland	Low	Low	High/Low	4	Anoxic	0.01	0.032	26.00	10.15	12.76	Peat	Carbonaceous
F47/0256	6	Awarua	Lowland	Low	Low	High/Low	4	Anoxic	0.40	0.0175	21.00	13.59	13.07	Felsic	Peat

Table 4-20: Stratification by Moderate over Low CRP successfully identifies anoxic and mixed (oxic-anoxic) waters.

Site	DEPTH [m]	GW Zone	Aquifer TYPE	River Influence	Con-nectivity	Bypass-Redox	HCA Cluster	General Redox Category	TON [mg/L]	Fe [mg/L]	DO Field [mg/L]	DOC [mg/L]	TOC [mg/L]	Surface geology	Subsurface geology
F46/0480	14	Lower Mataura	Lowland	High	Low	High/Low	3	Anoxic	0.04	0.016	4.60	0.87	2.31	Felsic	Felsic
D45/0137	25.1	Upper Aparima	Terrace	High	High/Low	High/Low	4	Anoxic	0.03	0.049	1.94	0.25	1.06	Mafic	Undiff.Clastics
E46/0472	15.7	Makarewa	Lowland	Low	Low	High/Low	4	Anoxic	0.12	0.036	6.40	1.59	1.04	Mafic	Felsic
E47/0079		Awarua	Lowland	Low	Low	High/Low	4	Anoxic	0.01	0.005	9.50	1.03	3.45	Felsic	Felsic
F45/0169	14	Lower Mataura	Lowland	High	Low	High/Low	4	Anoxic	0.02	0.20493	3.90	2.10	1.04	Felsic	Felsic
F46/0677	8	Awarua	Lowland	Low	Low	High/Low	4	Anoxic	0.45	0.023	12.00	3.03	24.38	Felsic	Felsic
F47/0149		Awarua	Lowland	Low	Low	High/Low	4	Anoxic	0.15	0.02	19.90	0.60	5.87	Felsic	Undiff.Clastics
D45/0046	4.5	Upper Aparima	Terrace	High	High/Low	High/Low	2	Mixed(anoxic)	0.19	1.19	0.15	0.73	22.14	Mafic	Undiff. Clastics
E44/0010	6.7	Waimea Plains	Lowland	Low	Low	High/Low	4	Mixed(anoxic)	0.26	0.74	1.30	2.51	12.00	Felsic	Felsic
D45/0039	6	Upper Aparima	Terrace	High	High/Low	High/Low	2	Mixed(oxic-anoxic)	8.63	4.2	0.25	0.73	26.00	Mafic	Undiff. Clastics
D45/0185	62.6	Upper Aparima	Terrace	High	High/Low	High/Low	2	Mixed(oxic-anoxic)	5.44	0.28	1.55	0.41	7.56	Mafic	Undiff. Clastics
E44/0420		Waimea Plains	Lowland	Low	Low	High/Low	2	Mixed(oxic-anoxic)	1.91	10.7	0.25	2.07	24.87	Felsic	Felsic
E45/0113	3.4	Central Plains	Lowland	Low	Low	High/Low	2	Mixed(oxic-anoxic)	5.73	8	0.20	0.25	22.73	Mafic	Undiff. Clastics
E45/0289	6.5	Upper Aparima	Terrace	High	High/Low	High/Low	2	Mixed(oxic-anoxic)	10.49	5.5	0.21	0.54	26.00	Mafic	Undiff. Clastics
E46/0093	7	Waimatuku	Lowland	Low	Low	High/Low	2	Mixed(oxic-anoxic)	5.24	5.2	0.23	1.13	26.00	Mafic	Undiff. Clastics
E46/0846		Makarewa	Lowland	Low	Low	High/Low	2	Mixed(oxic-anoxic)	6.80	6.3	0.18	0.25	26.00	Felsic	Felsic
E46/0858	6.5	Central Plains	Lowland	Low	Low	High/Low	2	Mixed(oxic-anoxic)	4.52	5	0.22	1.40	26.00	Felsic	Undiff. Clastics
F45/0455	12	Croydon	Riparian	High	High/Low	High/Low	2	Mixed(oxic-anoxic)	8.07	1.66	0.28	0.53	0.91	Mafic	Carbonaceous
E44/0047	10	Waimea Plains	Lowland	Low	Low	High/Low	5	Mixed(oxic-anoxic)	9.60	15.2	0.12	0.67	8.23	Felsic	Felsic
E45/0121	9.25	Waimea Plains	Lowland	Low	Low	High/Low	5	Mixed(oxic-anoxic)	8.69	7.1	0.26	1.09	6.39	Felsic	Felsic

Site	DEPTH [m]	GW Zone	Aquifer TYPE	River Influence	Con-nectivity	Bypass-Redox	HCA Cluster	General Redox Category	TON [mg/L]	Fe [mg/L]	DO Field [mg/L]	DOC [mg/L]	TOC [mg/L]	Surface geology	Subsurface geology
E44/0046	8	Waimea Plains	Lowland	Low	Low	High/Low	6	Mixed(oxic-anoxic)	9.19	21	0.12	1.31	3.95	Felsic	Felsic
E46/0906	6.5	Central Plains	Lowland	Low	Low	High/Low	6	Mixed(oxic-anoxic)	6.24	21.305	0.15	1.44	3.97	Felsic	Undiff. Clastics
D45/0004	12	Upper Aparima	Terrace	High	High/Low	High/Low	3	Mixed(oxic-anoxic)	7.98	0.94	0.82	1.59	17.37	Mafic	Undiff. Clastics
D45/0063	13.7	Upper Aparima	Terrace	High	High/Low	High/Low	3	Mixed(oxic-anoxic)	11.30	2.2	0.39	1.69	18.15	Mafic	Felsic
E45/0119	4.57	Makarewa	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	3.51	1.67	0.18	0.25	1.83	Mafic	Calcareous/ Limestone
E46/0440	20	Lower Aparima	Terrace	High	Low/High	High/Low	3	Mixed(oxic-anoxic)	3.71	1.67	0.26	2.42	6.47	Mafic	Undiff. Clastics
F46/0184		Lower Mataura	Lowland	High	Low	High/Low	3	Mixed(oxic-anoxic)	5.45	4.65	1.42	1.83	12.80	Felsic	Felsic
F46/0693	12.5	Awarua	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	4.82	1.225	0.52	1.35	6.73	Felsic	Felsic
F47/0099	8.9	Awarua	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	8.13	2.47	0.16	12.05	10.57	Felsic	Felsic
F47/0101	9.15	Awarua	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	1.94	0.36	0.31	19.40	27.37	Felsic	Felsic
E45/0064	6	Lower Oreti	Lowland	High	Low/High	High/Low	4	Mixed(oxic-anoxic)	3.94	0.017	0.11	1.50	22.26	Felsic	Felsic
E45/0120	6	Makarewa	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	5.31	0.001	1.26	0.25	7.35	Mafic	Felsic
E45/0575	8	Makarewa	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	6.06	1.725	2.30	2.05	14.98	Mafic	Calcareous/ Limestone
E45/0628	5	Lower Oreti	Lowland	High	Low/High	High/Low	4	Mixed(oxic-anoxic)	0.71	0.9	0.33	4.60	1.11	Felsic	Calcareous/ Limestone
E46/0013	7.5	Makarewa	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	1.32	0.70581	3.41	2.01	12.00	Mafic	Felsic
E46/0095	33	Central Plains	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	0.79	0.022	10.60	0.80	20.79	Mafic	Undiff. Clastics
E46/0505	6.5	Makarewa	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	3.10	0.957	4.20	2.07	11.41	Mafic	Undiff. Clastics
F46/0278	12	Awarua	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	1.20	0.045	0.11	1.30	25.07	Felsic	Felsic

Site	DEPTH [m]	GW Zone	Aquifer TYPE	River Influence	Con-nectivity	Bypass-Redox	HCA Cluster	General Redox Category	TON [mg/L]	Fe [mg/L]	DO Field [mg/L]	DOC [mg/L]	TOC [mg/L]	Surface geology	Subsurface geology
F46/0688	11.22	Awarua	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	3.68	0.48	8.50	10.64	25.01	Felsic	Felsic
F47/0145	7.9	Awarua	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	0.63	0.1715	0.14	2.88	1.94	Felsic	Undiff. Clastics
D45/0163	10	Upper Aparima	Terrace	High	High/Low	High/Low	2	Oxic	7.02	2.3005	0.05	1.79	5.18	Mafic	Felsic
D45/0193	6	Upper Aparima	Terrace	High	High/Low	High/Low	2	Oxic	10.24	3	0.05	0.94	25.80	Mafic	Undiff. Clastics
E44/0067	4.6	Castlerock	Terrace	Low	Low	High/Low	2	Oxic	8.74	3.1	0.04	3.80	5.90	Felsic	Felsic
E45/0012	18	Central Plains	Lowland	Low	Low	High/Low	2	Oxic	5.22	3.75	0.04	0.69	26.00	Mafic	Felsic
E45/0111	6.8	Central Plains	Lowland	Low	Low	High/Low	2	Oxic	7.69	14.8	0.10	1.16	4.16	Mafic	Felsic
E46/0094	13.5	Waimatuku	Lowland	Low	Low	High/Low	2	Oxic	2.60	1.59	0.09	1.03	25.98	Mafic	Undiff. Clastics
E46/0200	7	Central Plains	Lowland	Low	Low	High/Low	2	Oxic	7.39	1.3	0.05	1.14	0.91	Mafic	Undiff. Clastics
E46/0460	27.5	Lower Aparima	Terrace	High	Low/High	High/Low	2	Oxic	5.48	0.58	0.08	1.60	25.99	Mafic	Calcareous/ Limestone
E46/0514		Lower Aparima	Terrace	High	Low/High	High/Low	2	Oxic	1.09	0.98	0.08	0.25	25.97	Mafic	Undiff. Clastics
E46/0627	15.6	Waimatuku	Lowland	Low	Low	High/Low	2	Oxic	8.67	4.7	0.05	1.80	5.15	Mafic	Undiff. Clastics
E46/0740	22.2	Central Plains	Lowland	Low	Low	High/Low	2	Oxic	2.24	1.315	0.10	1.00	20.24	Mafic	Undiff. Clastics
E46/0432	6.15	Waimatuku	Lowland	Low	Low	High/Low	6	Oxic	7.23	9.610025	0.09	1.07	4.09	Mafic	Undiff. Clastics
E46/0406	23	Lower Aparima	Terrace	High	Low/High	High/Low	3	Oxic	14.95	0.116	0.04	2.20	12.00	Mafic	Calcareous/ Limestone
F46/0359	12.35	Edendale	Terrace	Low	Low	High/Low	3	Oxic	6.66	7.2	0.03	0.62	7.85	Felsic	Felsic
F46/0445	3.4	Lower Mataura	Lowland	High	Low	High/Low	3	Oxic	8.16	7.6	0.10	0.51	4.02	Felsic	Felsic
F46/0854	12	Makarewa	Lowland	Low	Low	High/Low	3	Oxic	9.91	0.72	0.03	3.61	4.31	Felsic	Felsic

Table 4-21: Stratification by High over Low CRP successfully identifies anoxic and mixed (oxic-anoxic) waters.

Site	DEPTH [m]	GW Zone	Aquifer TYPE	River Influence	Connectivity	Bypass-Redox	HCA Cluster	General Redox Category	TON [mg/L]	Fe [mg/L]	DO Field [mg/L]	DOC [mg/L]	TOC [mg/L]	Surface geology	Subsurface geology
E47/0124	28	Awarua	Lowland	Low	Low	High/Low	4	Anoxic	0.20	0.05827	14.20	1.40	5.87	Felsic	Undiff.Clastics
F47/0259	30	Awarua	Lowland	Low	Low	High/Low	4	Anoxic	0.01	0.026	34.00	1.04	3.76	Felsic	Carbonaceous
D43/0007	45.5	Te Anau	Terrace	High	Low/High	Low	2	Mixed(oxic-anoxic)	7.64	1.855	0.25	0.79	11.85	Felsic	Undiff.Clastics
D43/0062	42	Te Anau	Terrace	High	Low/High	Low	2	Mixed(oxic-anoxic)	8.13	1.96	0.30	0.77	11.72	Felsic	Undiff.Clastics
D43/0099	13	Te Anau	Terrace	High	Low/High	Low	2	Mixed(oxic-anoxic)	5.78	1.585	0.13	0.69	0.95	Felsic	Undiff.Clastics
D43/0115		Te Anau	Terrace	High	Low/High	Low	2	Mixed(oxic-anoxic)	2.06	0.64	0.15	1.18	6.61	Felsic	Undiff. Clastics
D45/0105	15	Upper Aparima	Terrace	High	High/Low	High/Low	2	Mixed(oxic-anoxic)	10.63	0.69	0.12	4.16	12.00	Mafic	Undiff.Clastics
E44/0044	25.2	Dipton	Terrace	Low	High/Low	High/Low	2	Mixed(oxic-anoxic)	3.09	0.015	0.11	1.54	6.57	Felsic	Felsic
E44/0359	19.5	Longridge	Terrace	Low	Low	High/Low	2	Mixed(oxic-anoxic)	8.22	1.5	0.20	0.95	1.55	Felsic	Felsic
E45/0447	2.5	Waimatuku	Lowland	Low	Low	High/Low	2	Mixed(oxic-anoxic)	2.70	7.1	0.44	2.70	26.00	Mafic	Undiff. Clastics
E45/0047	7.3	Lower Oreti	Lowland	High	Low/High	High/Low	6	Mixed(oxic-anoxic)	3.47	3.819	0.08	1.35	12.50	Felsic	Calcareous/ Limestone
E45/0126	3.38	Dipton	Terrace	Low	High/Low	High/Low	6	Mixed(oxic-anoxic)	0.85	6.5	0.02	2.30	14.91	Felsic	Undiff.Clastics
E46/0110	4.57	Waimatuku	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	8.32	0.967385	0.67	8.65	15.93	Mafic	Undiff.Clastics
F45/0168	6	Knapdale	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	4.15	3.2	0.32	2.49	12.06	Felsic	Felsic
F46/0262	11.9	Awarua	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	9.54	0.47	0.20	2.32	4.78	Felsic	Felsic
F47/0275		Awarua	Lowland	Low	Low	High/Low	3	Mixed(oxic-anoxic)	10.57	0.001	1.26	6.16	9.11	Felsic	Carbonaceous
E45/0221	12	Central Plains	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	0.76	0.0045	5.58	0.79	16.60	Felsic	Undiff. Clastics
E46/0156	6.5	Waimatuku	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	0.78	1.195	1.97	2.68	20.01	Mafic	Undiff. Clastics
E46/0926		Waimatuku	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	2.24	0.169	2.97	1.23	9.84	Mafic	Undiff. Clastics

Site	DEPTH [m]	GW Zone	Aquifer TYPE	River Influence	Con-nectivity	Bypass-Redox	HCA Cluster	General Redox Category	TON [mg/L]	Fe [mg/L]	DO Field [mg/L]	DOC [mg/L]	TOC [mg/L]	Surface geology	Subsurface geology
F47/0138	16	Awarua	Lowland	Low	Low	High/Low	4	Mixed(oxic-anoxic)	2.25	0.0065	5.17	1.52	14.17	Felsic	Carbonaceous
D45/0005	4	Upper Aparima	Terrace	High	High/Low	High/Low	2	Oxic	2.70	3.1	0.07	1.00	25.94	Mafic	Undiff. Clastics
D45/0028	4.8	Upper Aparima	Terrace	High	High/Low	High/Low	2	Oxic	9.18	6	0.06	2.50	5.85	Mafic	Undiff. Clastics
E44/0035	11.5	Waimea Plains	Lowland	Low	Low	High/Low	2	Oxic	6.70	0.85	0.07	1.37	1.10	Felsic	Felsic
E44/0172	6	Waimea Plains	Lowland	Low	Low	High/Low	2	Oxic	4.14	9.55	0.09	1.61	19.22	Felsic	Felsic
E45/0330	15	Central Plains	Lowland	Low	Low	High/Low	2	Oxic	8.30	11.8	0.06	2.60	4.23	Mafic	Undiff. Clastics
E45/0423	8	Waimatuku	Lowland	Low	Low	High/Low	2	Oxic	8.53	8.8	0.05	2.00	4.17	Mafic	Undiff. Clastics
E46/0237	5.5	Waimatuku	Lowland	Low	Low	High/Low	2	Oxic	5.03	3.1	0.08	2.30	12.17	Mafic	Undiff. Clastics
E46/0744	21.7	Waimatuku	Lowland	Low	Low	High/Low	2	Oxic	9.93	9.7	0.05	2.20	5.15	Mafic	Undiff. Clastics
E45/0213	5	Upper Aparima	Terrace	High	High/Low	High/Low	6	Oxic	7.58	10.6345	0.09	2.10	4.12	Mafic	Undiff. Clastics
E45/0330	12	Central Plains	Lowland	Low	Low	High/Low	6	Oxic	7.47	13.7	0.03	1.75	3.93	Mafic	Undiff. Clastics
E45/0330	3	Central Plains	Lowland	Low	Low	High/Low	6	Oxic	7.22	12.3	0.06	1.61	4.00	Mafic	Undiff. Clastics
E45/0330	6	Central Plains	Lowland	Low	Low	High/Low	6	Oxic	7.27	13.35	0.04	1.86	3.93	Mafic	Undiff. Clastics
E45/0330	9	Central Plains	Lowland	Low	Low	High/Low	6	Oxic	7.47	13.7	0.03	1.98	3.93	Mafic	Undiff. Clastics

Major ions

Following removal of river influenced waters, sorting point intersected data (of 164 sites) by geology and precipitation source, successfully identified major ion facies groundwaters as demonstrated below.

Generally, the number of Na-Cl type samples and samples associated with Na or Cl as their major cation/anion, respectively, was higher for sites that receive coastal precipitation, i.e. higher marine Na and Cl load (Table 4-22). Further, sites that receive alpine precipitation were the most dilute and of type Ca-HCO_3.

Stratifying by geology, specifically carbonate/limestone subsurface geology successfully identifies two carbonate influenced waters of Ca-HCO_3 type (with relatively high Ca and HCO_3 alkalinity). Additional carbonate influenced waters not identified due to lack of detailed information on carbonate.

Generally, the dominant anion (whether Cl or HCO_3) is driven by the precipitation source and the dominant cation is largely driven by geology (and by precipitation source) (TC7). Specifically, sites with alpine or inland precipitation have HCO_3 as dominant anion. Sites that receive coastal precipitation have Cl as their major anion (except for carbonate influenced waters where HCO_3 dominates the marine Cl load) (Table 4-22).

Groundwater samples associated with older felsic (>Q6) geology generally have Na as dominant cation (TC7). Sites associated with younger felsic (Q1 to Q4) geology where coastal precipitation does not overwhelm the geological signature generally have Ca as the dominant cation (TC7). Groundwaters associated with mafic geology generally have Ca or Mg as dominant cation (TC7; Table 4-22).

Table 4-22: Stratification by 1) precipitation source (colour code represents precipitation source), 2) surface geology, 3) subsurface geology and 4) geomorphic age.

Site	DEPTH [m]	GW Zone	Aquifer TYPE	River Influence	Connectivity	Bypass-Redox	HCA Cluster	Water type	General Redox Category	EC [uS/cm]	Alk HCO$_3$ [mg'L]	Ca [mg/L]	PPT Source	Surface Geology	Subsurface Geology	Geom. Age
D43/0062	42	Te Anau	Terrace	High	Low/High	Low	2	Ca-HCO$_3$	Mixed(oxic-anoxic)	163.7	62.0	15.4	alpine_2	Felsic	Undiff. Clastics	Q2-Q4
D43/0099	13	Te Anau	Terrace	High	Low/High	Low	2	Ca-HCO$_3$	Mixed(oxic-anoxic)	158.4	53.8	14.1	alpine_2	Felsic	Undiff. Clastics	Q2-Q4
D43/0115		Te Anau	Terrace	High	Low/High	Low	2	Ca-HCO$_3$	Mixed(oxic-anoxic)	216.3	84.0	28.0	alpine_2	Felsic	Undiff. Clastics	Q2-Q4
D43/0007	45.5	Te Anau	Terrace	High	Low/High	Low	2	Mg-HCO3	Mixed(oxic-anoxic)	152.7	58.0	13.4	alpine_2	Felsic	Undiff. Clastics	Q2-Q4
E45/0047	7.3	Lower Oreti	Lowland	High	Low/High	High/Low	6	Ca-HCO$_3$	Mixed(oxic-anoxic)	294.5	59.2	23.7	inland	Felsic	**Calcareous/ Limestone**	Q2-Q4
E45/0628	5	Lower Oreti	Lowland	High	Low/High	High/Low	**4**	Ca- HCO$_3$	Mixed(oxic-anoxic)	198.4	62.0	19.1	inland	Felsic	**Calcareous/ Limestone**	Q2-Q4
F46/0382	8.2	Makarewa	Lowland	Low	Low	High/Low	**4**	Na- HCO$_3$	Mixed(oxic-anoxic)	195.9	42.0	8.7	inland	Felsic	Carbonaceous	Erosional
F45/0343	11.2	Knapdale	Lowland	Low	Low	High/Low	5	Ca-Cl	Mixed(oxic-anoxic)	227.5	22.6	15.1	inland	Felsic	Carbonaceous	Q2-Q4
F45/0172	4.6	Croydon	Riparian	High	High/Low	High/Low	6	Ca-Cl	Mixed(oxic-anoxic)	362.4	26.0	28.3	inland	Felsic	Carbonaceous	Q2-Q4
E44/0067	4.6	Castlerock	Terrace	Low	Low	High/Low	2	Ca- HCO$_3$	Oxic	197.0	56.0	13.2	inland	Felsic	Felsic	Q2-Q4
F45/0350	5	Riversdale	Riparian	High	High/Low	Low	2	Ca- HCO$_3$	Mixed(oxic-anoxic)	195.0	59.0	13.3	inland	Felsic	Felsic	Q2-Q4
F44/0379		Riversdale	Riparian	High	High/Low	Low	6	Ca- HCO$_3$	Oxic	324.7	62.0	25.0	inland	Felsic	Felsic	Q2-Q4
E45/0034	17	Lower Oreti	Lowland	High	Low/High	High/Low	2	Na- HCO$_3$	Mixed(oxic-anoxic)	207.9	89.0	15.4	inland	Felsic	Felsic	Q2-Q4
F45/0169	14	Lower Mataura	Lowland	High	Low	High/Low	**4**	Na- HCO$_3$	Anoxic	212.0	80.0	13.0	inland	Felsic	Felsic	Q2-Q4
F46/0434	4.85	Edendale	Terrace	Low	Low	High/Low	**4**	Na- HCO$_3$	Anoxic	216.6	70.0	12.4	inland	Felsic	Felsic	Q2-Q4
E44/0044	25.2	Dipton	Terrace	Low	High/Low	High/Low	2	Mg- HCO$_3$	Mixed(oxic-anoxic)	249.2	116.0	20.0	inland	Felsic	Felsic	Q2-Q4
F45/0475	18	Knapdale	Lowland	Low	Low	High/Low	2	Na-Cl	Mixed(oxic-anoxic)	280.0	36.0	16.3	inland	Felsic	Felsic	Q2-Q4
E44/0014	8.66	Five Rivers	Riparian	High	High/Low	High/Low	5	Na-Cl	Oxic	147.7	18.0	9.6	inland	Felsic	Felsic	Q2-Q4
E44/0417		Waimea Plains	Lowland	Low	Low	High/Low	5	Na-Cl	Mixed(oxic-anoxic)	171.0	22.8	10.5	inland	Felsic	Felsic	Q2-Q4
F44/0040	9.23	Wendonside	Terrace	Low	Low	Low	5	Na-Cl	Oxic	168.0	25.0	10.4	inland	Felsic	Felsic	Q2-Q4
F46/0193	12.5	Edendale	Terrace	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	249.4	17.5	17.4	inland	Felsic	Felsic	Q2-Q4
F46/0239		Edendale	Terrace	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	151.9	13.0	9.2	inland	Felsic	Felsic	Q2-Q4

F46/0445	3.4	Lower Mataura	Lowland	High	Low	High/Low	3	Na-Cl	Oxic	215.2	12.2	13.5	inland	Felsic	Felsic	Q2-Q4
F45/0614	6.38	Riversdale	Riparian	High	High/Low	Low	2	Ca-Cl	Oxic	187.0	29.0	12.3	inland	Felsic	Felsic	Q2-Q4
F45/0167	4.3	Riversdale	Riparian	High	High/Low	Low	6	Ca-Cl	Mixed(oxic-anoxic)	226.2	30.0	18.5	inland	Felsic	Felsic	Q2-Q4
F45/0168	6	Knapdale	Lowland	Low	Low	High/Low	3	Ca-Cl	Mixed(oxic-anoxic)	205.8	28.5	15.2	inland	Felsic	Felsic	Q2-Q4
F45/0170	4	Lower Mataura	Lowland	High	Low	High/Low	3	Ca-Cl	Mixed(oxic-anoxic)	200.0	28.5	15.3	inland	Felsic	Felsic	Q2-Q4
F45/0248	2	Lower Mataura	Lowland	High	Low	High/Low	3	Ca-Cl	Oxic	186.7	22.0	13.9	inland	Felsic	Felsic	Q2-Q4
F46/0186	7.3	Lower Mataura	Lowland	High	Low	High/Low	3	Ca-Cl	Mixed(oxic-anoxic)	185.9	30.0	14.1	inland	Felsic	Felsic	Q2-Q4
E44/0198	6.5	Castlerock	Terrace	Low	Low	High/Low	5	Ca	Mixed(oxic-anoxic)	252.1	15.4	22.9	inland	Felsic	Felsic	Q2-Q4
E44/0526		Longridge	Terrace	Low	Low	High/Low	2	Ca- HCO_3	Oxic	117.0	42.0	10.2	inland	Felsic	Felsic	Q8-Q10
F46/0854	12	Makarewa	Lowland	Low	Low	High/Low	3	Ca- HCO_3	Oxic	147.5	46.0	14.0	inland	Felsic	Felsic	Q8-Q10
E44/0035	11.5	Waimea Plains	Lowland	Low	Low	High/Low	2	Na- HCO_3	Oxic	175.7	59.8	10.2	inland	Felsic	Felsic	Q8-Q10
E44/0359	19.5	Longridge	Terrace	Low	Low	High/Low	2	Na- HCO_3	Mixed(oxic-anoxic)	158.0	52.2	9.0	inland	Felsic	Felsic	Q8-Q10
E44/0010	6.7	Waimea Plains	Lowland	Low	Low	High/Low	**4**	Na- HCO_3	Mixed(anoxic)	276.4	68.8	15.6	inland	Felsic	Felsic	Q8-Q10
E44/0420		Waimea Plains	Lowland	Low	Low	High/Low	2	Na-Cl	Mixed(oxic-anoxic)	266.6	47.9	13.5	inland	Felsic	Felsic	Q8-Q10
E44/0008	5.6	Waimea Plains	Lowland	Low	Low	High/Low	5	Na-Cl	Oxic	167.8	14.2	8.8	inland	Felsic	Felsic	Q8-Q10
E44/0009	10.5	Waimea Plains	Lowland	Low	Low	High/Low	5	Na-Cl	Oxic	182.3	32.0	9.0	inland	Felsic	Felsic	Q8-Q10
E44/0036	6	Waimea Plains	Lowland	Low	Low	High/Low	5	Na-Cl	Mixed(oxic-anoxic)	192.1	20.0	9.9	inland	Felsic	Felsic	Q8-Q10
E44/0047	10	Waimea Plains	Lowland	Low	Low	High/Low	5	Na-Cl	Mixed(oxic-anoxic)	229.8	18.3	11.2	inland	Felsic	Felsic	Q8-Q10
E44/0167		Waimea Plains	Lowland	Low	Low	High/Low	5	Na-Cl	Mixed(oxic-anoxic)	227.1	17.1	12.8	inland	Felsic	Felsic	Q8-Q10

E44/0236	12.5	Waimea Plains	Lowland	Low	Low	High/Low	5	Na-Cl	Mixed(oxic-anoxic)	259.0	18.3	10.7	inland	Felsic	Felsic	Q8-Q10
E44/0377	7.7	Waimea Plains	Lowland	Low	Low	High/Low	5	Na-Cl	Mixed(oxic-anoxic)	254.0	8.5	13.3	inland	Felsic	Felsic	Q8-Q10
E44/0418		Waimea Plains	Lowland	Low	Low	High/Low	5	Na-Cl	Mixed(oxic-anoxic)	177.0	19.6	9.4	inland	Felsic	Felsic	Q8-Q10
E44/0457		Waimea Plains	Lowland	Low	Low	High/Low	5	Na-Cl	Mixed(oxic-anoxic)	231.3	17.5	11.1	inland	Felsic	Felsic	Q8-Q10
E45/0121	9.25	Waimea Plains	Lowland	Low	Low	High/Low	5	Na-Cl	Mixed(oxic-anoxic)	179.8	23.0	8.8	inland	Felsic	Felsic	Q8-Q10
F44/0018	10	Wendonside	Terrace	Low	Low	Low	5	Na-Cl	Mixed(oxic-anoxic)	197.2	17.1	10.7	inland	Felsic	Felsic	Q8-Q10
F44/0139	27	Wendonside	Terrace	Low	Low	Low	5	Na-Cl	Mixed(oxic-anoxic)	171.0	17.7	11.5	inland	Felsic	Felsic	Q8-Q10
F45/0253	15	Makarewa	Lowland	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	139.6	30.0	7.3	inland	Felsic	Felsic	Q8-Q10
E44/0172	6	Waimea Plains	Lowland	Low	Low	High/Low	2	Ca-Cl	Oxic	310.3	40.8	22.6	inland	Felsic	Felsic	Q8-Q10
E44/0369		Waimea Plains	Lowland	Low	Low	High/Low	5	Ca-Cl	Mixed(oxic-anoxic)	280.9	21.0	18.6	inland	Felsic	Felsic	Q8-Q10
E44/0046	8	Waimea Plains	Lowland	Low	Low	High/Low	6	Ca-Cl	Mixed(oxic-anoxic)	310.0	25.9	23.5	inland	Felsic	Felsic	Q8-Q10
E45/0126	3.38	Dipton	Terrace	Low	High/Low	High/Low	6	Ca- HCO_3	Mixed(oxic-anoxic)	293.0	73.0	23.0	inland	Felsic	Undiff. Clastics	Q2-Q4
E45/0596	12.5	Upper Aparima	Terrace	High	High/Low	High/Low	3	Na- HCO_3	Mixed(oxic-anoxic)	309.9	117.0	14.2	inland	Felsic	Undiff. Clastics	Q2-Q4
E45/0608	6	Upper Aparima	Terrace	High	High/Low	High/Low	3	Na- HCO_3	Mixed(anoxic)	275.5	76.0	9.2	inland	Felsic	Undiff. Clastics	Q2-Q4
E45/0221	12	Central Plains	Lowland	Low	Low	High/Low	**4**	Na- HCO_3	Mixed(oxic-anoxic)	358.5	95.8	18.6	inland	Felsic	Undiff. Clastics	Q2-Q4
E45/0402	8	Dipton	Terrace	Low	High/Low	High/Low	2	Ca-Cl	Mixed(oxic-anoxic)	134.0	23.0	10.9	inland	Felsic	Undiff. Clastics	Q2-Q4
E45/0537		Upper Aparima	Terrace	High	High/Low	High/Low	6	Ca-Cl	Oxic	339.0	32.5	26.1	inland	Felsic	Undiff. Clastics	Q2-Q4
E44/0075	4.43	Waimea Plains	Lowland	Low	Low	High/Low	**4**	Ca- HCO_3	Anoxic	330.0	150.0	31.0	inland	Felsic	Undiff. Clastics	Q8-Q10

F45/0455	12	Croydon	Riparian	High	High/Low	High/Low	2	Na- HCO_3	Mixed(oxic-anoxic)	153.0	47.0	8.6	inland	Mafic	Carbonaceous	Q2-Q4
E45/0012	18	Central Plains	Lowland	Low	Low	High/Low	2	Ca- HCO_3	Oxic	244.9	81.0	17.5	inland	Mafic	Felsic	Q2-Q4
D45/0164	23.5	Blackmount	Terrace	Low	Low	High/Low	5	Ca- HCO_3	Mixed(oxic-anoxic)	276.4	44.7	21.1	inland	Mafic	Felsic	Q2-Q4
E45/0111	6.8	Central Plains	Lowland	Low	Low	High/Low	2	Ca-Cl	Oxic	329.6	78.0	32.0	inland	Mafic	Felsic	Q2-Q4
D45/0185	62.6	Upper Aparima	Terrace	High	High/Low	High/Low	2	Ca- HCO_3	Mixed(oxic-anoxic)	222.6	107.0	19.8	inland	Mafic	Undiff. Clastics	Q2-Q4
E45/0088	6	Upper Aparima	Terrace	High	High/Low	High/Low	2	Ca- HCO_3	Mixed(oxic-anoxic)	223.0	59.0	17.0	inland	Mafic	Undiff. Clastics	Q2-Q4
E45/0113	3.4	Central Plains	Lowland	Low	Low	High/Low	2	Ca- HCO_3	Mixed(oxic-anoxic)	327.6	73.0	23.0	inland	Mafic	Undiff. Clastics	Q2-Q4
E45/0250	5.5	Upper Aparima	Terrace	High	High/Low	High/Low	2	Ca- HCO_3	Oxic	218.1	45.0	19.2	inland	Mafic	Undiff. Clastics	Q2-Q4
E45/0330_15	15	Central Plains	Lowland	Low	Low	High/Low	2	Ca- HCO_3	Oxic	372.0	85.0	28.0	inland	Mafic	Undiff. Clastics	Q2-Q4
D45/0276	31	Blackmount	Terrace	Low	Low	High/Low	**4**	Ca- HCO_3	Mixed(oxic-anoxic)	320.0	151.3	56.0	inland	Mafic	Undiff. Clastics	Q2-Q4
E45/0456	6.5	Upper Aparima	Terrace	High	High/Low	High/Low	2	Na-Cl	Mixed(oxic-anoxic)	218.3	27.2	14.3	inland	Mafic	Undiff. Clastics	Q2-Q4
E45/0213	5	Upper Aparima	Terrace	High	High/Low	High/Low	6	Ca-Cl	Oxic	331.6	38.9	26.4	inland	Mafic	Undiff. Clastics	Q2-Q4
E45/0330_12	12	Central Plains	Lowland	Low	Low	High/Low	6	Ca-Cl	Oxic	328.1	38.0	22.0	inland	Mafic	Undiff. Clastics	Q2-Q4
E45/0330_3	3	Central Plains	Lowland	Low	Low	High/Low	6	Ca-Cl	Oxic	316.5	34.0	25.2	inland	Mafic	Undiff. Clastics	Q2-Q4
E45/0330_6	6	Central Plains	Lowland	Low	Low	High/Low	6	Ca-Cl	Oxic	321.0	33.0	27.0	inland	Mafic	Undiff. Clastics	Q2-Q4
E45/0330_9	9	Central Plains	Lowland	Low	Low	High/Low	6	Ca-Cl	Oxic	313.5	36.0	26.0	inland	Mafic	Undiff. Clastics	Q2-Q4
D45/0163	10	Upper Aparima	Terrace	High	High/Low	High/Low	2	Na- HCO_3	Oxic	139.5	33.7	10.7	coastal	Mafic	Felsic	Q2-Q4
D45/0193	6	Upper	Terrace	High	High/Low	High/Low	2	Na- HCO_3	Oxic	187.9	58.0	12.0	coastal	Mafic	Undiff. Clastics	Q2-Q4

		Aparima														
E45/0289	6.5	Upper Aparima	Terrace	High	High/Low	High/Low	2	Na- HCO_3	Mixed(oxic-anoxic)	214.2	50.0	14.9	coastal	Mafic	Undiff. Clastics	Q2-Q4
E46/0740	22.2	Central Plains	Lowland	Low	Low	High/Low	2	Na- HCO_3	Oxic	254.8	80.1	14.4	coastal	Mafic	Undiff. Clastics	Q2-Q4
D45/0004	12	Upper Aparima	Terrace	High	High/Low	High/Low	3	Na- HCO_3	Mixed(oxic-anoxic)	144.0	41.5	7.3	coastal	Mafic	Undiff. Clastics	Q2-Q4
F46/0262	11.9	Awarua	Lowland	Low	Low	High/Low	3	Na- HCO_3	Mixed(oxic-anoxic)	151.8	43.5	7.9	coastal	Felsic	Felsic	Q8-Q10
E45/0575	8	Makarewa	Lowland	Low	Low	High/Low	**4**	Na- HCO_3	Mixed(oxic-anoxic)	231.3	62.6	12.4	coastal	Mafic	Calcareous/Limestone	Q2-Q4
E46/0013	7.5	Makarewa	Lowland	Low	Low	High/Low	**4**	Na- HCO_3	Mixed(oxic-anoxic)	309.5	86.4	16.6	coastal	Mafic	Felsic	Q2-Q4
E46/0095	33	Central Plains	Lowland	Low	Low	High/Low	**4**	Na- HCO_3	Mixed(oxic-anoxic)	358.1	97.0	16.5	coastal	Mafic	Undiff. Clastics	Q8-Q10
E46/0472	15.7	Makarewa	Lowland	Low	Low	High/Low	**4**	Na- HCO_3	Anoxic	217.5	75.0	12.4	coastal	Mafic	Felsic	Q8-Q10
E46/0505	6.5	Makarewa	Lowland	Low	Low	High/Low	**4**	Na- HCO_3	Mixed(oxic-anoxic)	223.1	54.0	14.6	coastal	Mafic	Undiff. Clastics	Q2-Q4
E46/0926		Waimatuku	Lowland	Low	Low	High/Low	**4**	Na- HCO_3	Mixed(oxic-anoxic)	336.5	93.9	17.2	coastal	Mafic	Undiff. Clastics	Q2-Q4
D46/0031	19	Waiau	Terrace	Low	Low	Low	2	Na- HCO_3	Oxic	211.0	59.0	9.2	coastal_2	Undiff. Clastics	Undiff. Clastics	Q5-Q7
E46/0094	13.5	Waimatuku	Lowland	Low	Low	High/Low	2	Na- HCO_3	Oxic	280.0	84.0	15.5	coastal_2	Mafic	Undiff. Clastics	Q2-Q4
E46/0460	27.5	Lower Aparima	Terrace	High	Low/High	High/Low	2	Na- HCO_3	Oxic	243.2	66.0	12.3	coastal_2	Mafic	Calcareous/ Limestone	Q8-Q10
E46/0627	15.6	Waimatuku	Lowland	Low	Low	High/Low	2	Na- HCO_3	Oxic	390.2	105.0	24.0	coastal_2	Mafic	Undiff. Clastics	Q2-Q4
E46/0406	23	Lower Aparima	Terrace	High	Low/High	High/Low	3	Na- HCO_3	Oxic	170.7	50.0	9.2	coastal_2	Mafic	Calcareous/ Limestone	Q8-Q10
F46/0480	14	Lower Mataura	Lowland	High	Low	High/Low	3	Na- HCO_3	Anoxic	319.5	123.0	24.0	coastal_2	Felsic	Felsic	Q8-Q10
E47/0124	28	Awarua	Lowland	Low	Low	High/Low	**4**	Na- HCO_3	Anoxic	297.0	116.0	17.7	coastal_2	Felsic	Undiff. Clastics	Q8-Q10
F46/0677	8	Awarua	Lowland	Low	Low	High/Low	**4**	Na- HCO_3	Anoxic	237.1	56.0	6.9	coastal_2	Felsic	Felsic	Q8-Q10
F46/0800	16	Lower Mataura	Lowland	High	Low	High/Low	**4**	Na- HCO_3	Anoxic	183.6	58.0	9.0	coastal_2	Felsic	Felsic	Q2-Q4
F47/0149		Awarua	Lowland	Low	Low	High/Low	**4**	Na- HCO_3	Anoxic	278.0	100.0	14.0	coastal_2	Felsic	Undiff. Clastics	Q8-Q10

D45/0005	4	Upper Aparima	Terrace	High	High/Low	High/Low	2	Ca- HCO_3	Oxic	279.0	92.0	26.0	coastal	Mafic	Undiff. Clastics	Q2-Q4
D45/0028	4.8	Upper Aparima	Terrace	High	High/Low	High/Low	2	Ca- HCO_3	Oxic	234.0	50.0	23.0	coastal	Mafic	Undiff. Clastics	Q2-Q4
D45/0046	4.5	Upper Aparima	Terrace	High	High/Low	High/Low	2	Ca- HCO_3	Mixed(anoxic)	203.4	84.0	17.8	coastal	Mafic	Undiff. Clastics	Q2-Q4
D45/0105	15	Upper Aparima	Terrace	High	High/Low	High/Low	2	Ca- HCO_3	Mixed(oxic-anoxic)	283.1	119.0	23.0	coastal	Mafic	Undiff. Clastics	Q2-Q4
D45/0298	10	Waiau	Terrace	Low	Low	Low	2	Ca- HCO_3	Mixed(oxic-anoxic)	227.2	69.0	18.9	coastal	Mafic	Undiff. Clastics	Q2-Q4
E45/0010	9.5	Upper Aparima	Terrace	High	High/Low	High/Low	2	Ca- HCO_3	Oxic	297.8	60.0	27.0	coastal	Mafic	Undiff. Clastics	Q2-Q4
E45/0423	8	Waimatuku	Lowland	Low	Low	High/Low	2	Ca- HCO_3	Oxic	322.0	71.0	27.0	coastal	Mafic	Undiff. Clastics	Q2-Q4
E45/0447	2.5	Waimatuku	Lowland	Low	Low	High/Low	2	Ca- HCO_3	Mixed(oxic-anoxic)	311.5	68.0	24.0	coastal	Mafic	Undiff. Clastics	Q2-Q4
E46/0093	7	Waimatuku	Lowland	Low	Low	High/Low	2	Ca- HCO_3	Mixed(oxic-anoxic)	231.3	54.5	17.8	coastal	Mafic	Undiff. Clastics	Q2-Q4
E46/0237	5.5	Waimatuku	Lowland	Low	Low	High/Low	2	Ca- HCO_3	Oxic	289.0	85.0	26.0	coastal	Mafic	Undiff. Clastics	Q2-Q4
E46/0744	21.7	Waimatuku	Lowland	Low	Low	High/Low	2	Ca- HCO_3	Oxic	315.6	71.0	27.0	coastal	Mafic	Undiff. Clastics	Q2-Q4
E45/0064	6	Lower Oreti	Lowland	High	Low/High	High/Low	**4**	Ca- HCO_3	Mixed(oxic-anoxic)	293.8	109.0	22.0	coastal	Felsic	Felsic	Q2-Q4
E45/0120	6	Makarewa	Lowland	Low	Low	High/Low	**4**	Ca- HCO_3	Mixed(oxic-anoxic)	611.0	270.0	87.0	coastal	Mafic	Felsic	Q2-Q4
E46/0156	6.5	Waimatuku	Lowland	Low	Low	High/Low	**4**	Ca-HCO_3	Mixed(oxic-anoxic)	334.1	80.0	26.7	coastal_2	Mafic	Undiff. Clastics	Q2-Q4
F46/0278	12	Awarua	Lowland	Low	Low	High/Low	**4**	Ca-HCO_3	Mixed(oxic-anoxic)	338.4	137.0	38.0	coastal_2	Felsic	Felsic	Q8-Q10
D45/0137	25.1	Upper Aparima	Terrace	High	High/Low	High/Low	**4**	Mg- HCO_3	Anoxic	282.0	129.0	22.0	coastal	Mafic	Undiff. Clastics	Q2-Q4
E45/0055	7	Central Plains	Lowland	Low	Low	High/Low	6	Ca-SO4	Oxic	240.0	27.0	18.7	coastal	Felsic	Undiff. Clastics	Q2-Q4
E45/0011	7.5	Central Plains	Lowland	Low	Low	High/Low	2	Ca-Cl	Oxic	303.5	45.0	22.0	coastal	Mafic	Undiff. Clastics	Q2-Q4
E46/0895	8.5	Makarewa	Lowland	Low	Low	High/Low	6	Ca-Cl	Mixed(oxic-anoxic)	428.0	24.3	21.5	coastal	Felsic	Carbonaceous	Q8-Q10
E46/0906	6.5	Central Plains	Lowland	Low	Low	High/Low	6	Ca-Cl	Mixed(oxic-anoxic)	477.0	25.0	30.0	coastal	Felsic	Undiff. Clastics	Q2-Q4
F46/0456	12	Edendale	Terrace	Low	Low	High/Low	6	Ca-Cl	Oxic	243.5	28.7	17.4	coastal	Felsic	Felsic	Q2-Q4
F46/0184		Lower	Lowland	High	Low	High/Low	3	Ca-Cl	Mixed(oxic-anoxic)	202.8	21.0	17.1	coastal	Felsic	Felsic	Q2-Q4

		Mataura														
F46/0194	12	Edendale	Terrace	Low	Low	High/Low	3	Ca-Cl	Mixed(oxic-anoxic)	202.0	15.0	13.7	coastal	Felsic	Felsic	Q2-Q4
E46/0575		Waimatuku	Lowland	Low	Low	High/Low	2	Ca-Cl	Oxic	324.1	65.0	22.0	coastal_2	Felsic	Undiff. Clastics	Q2-Q4
E46/0432	6.15	Waimatuku	Lowland	Low	Low	High/Low	6	Ca-Cl	Oxic	298.5	34.2	19.9	coastal_2	Mafic	Undiff. Clastics	Q2-Q4
F46/0693	12.5	Awarua	Lowland	Low	Low	High/Low	3	Ca-Cl	Mixed(oxic-anoxic)	190.1	45.0	18.8	coastal_2	Felsic	Felsic	Q8-Q10
F47/0101	9.15	Awarua	Lowland	Low	Low	High/Low	3	Ca-Cl	Mixed(oxic-anoxic)	188.0	60.0	26.0	coastal_2	Felsic	Felsic	Q8-Q10
D45/0039	6	Upper Aparima	Terrace	High	High/Low	High/Low	2	Na-Cl	Mixed(oxic-anoxic)	253.3	35.0	18.1	coastal	Mafic	Undiff. Clastics	Q2-Q4
E46/0099	10.5	Lower Oreti	Lowland	High	Low/High	High/Low	2	Na-Cl	Oxic	272.2	50.0	10.8	coastal	Felsic	Felsic	Q2-Q4
E46/0846		Makarewa	Lowland	Low	Low	High/Low	2	Na-Cl	Mixed(oxic-anoxic)	234.0	48.0	12.2	coastal	Felsic	Felsic	Q2-Q4
E46/0858	6.5	Central Plains	Lowland	Low	Low	High/Low	2	Na-Cl	Mixed(oxic-anoxic)	164.0	50.0	12.2	coastal	Felsic	Undiff. Clastics	Q2-Q4
F46/0847	17	Edendale	Terrace	Low	Low	High/Low	6	Na-Cl	Oxic	344.7	16.1	17.0	coastal	Felsic	Felsic	Q2-Q4
D45/0063	13.7	Upper Aparima	Terrace	High	High/Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	113.4	23.0	4.9	coastal	Mafic	Felsic	Q2-Q4
E45/0119	4.57	Makarewa	Lowland	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	186.3	42.0	9.3	coastal	Mafic	Calcareous/ Limestone	Q2-Q4
E46/0110	4.57	Waimatuku	Lowland	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	177.1	13.9	4.8	coastal	Mafic	Undiff. Clastics	Q2-Q4
E46/0259	9	Waihopai	Lowland	Low	Low	Low	3	Na-Cl	Mixed(oxic-anoxic)	123.0	14.0	4.3	coastal	Felsic	Carbonaceous	Q8-Q10
E46/0299	12	Waihopai	Lowland	Low	Low	Low	3	Na-Cl	Mixed(oxic-anoxic)	168.0	9.9	8.7	coastal	Felsic	Felsic	Q8-Q10
E46/0320	2.85	Waihopai	Lowland	Low	Low	Low	3	Na-Cl	Mixed(oxic-anoxic)	169.8	19.8	6.0	coastal	Felsic	Felsic	Q8-Q10
F46/0183	20	Waihopai	Lowland	Low	Low	Low	3	Na-Cl	Mixed(oxic-anoxic)	125.6	15.9	4.0	coastal	Felsic	Carbonaceous	Q8-Q10
F46/0185	14	Edendale	Terrace	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	294.6	21.0	18.0	coastal	Felsic	Felsic	Q2-Q4
F46/0359	12.35	Edendale	Terrace	Low	Low	High/Low	3	Na-Cl	Oxic	221.6	19.7	9.3	coastal	Felsic	Felsic	Q2-Q4
F46/0522	26	Waihopai	Lowland	Low	Low	Low	3	Na-Cl	Mixed(oxic-anoxic)	160.0	38.0	7.1	coastal	Felsic	Felsic	Q8-Q10
F46/0702	12.5	Waihopai	Lowland	Low	Low	Low	3	Na-Cl	Mixed(oxic-anoxic)	148.0	21.0	5.8	coastal	Felsic	Felsic	Q8-Q10
F46/0820	17.5	Waihopai	Lowland	Low	Low	Low	3	Na-Cl	Mixed(oxic-anoxic)	154.6	32.0	6.6	coastal	Felsic	Carbonaceous	Q8-Q10
E46/0200	7	Central Plains	Lowland	Low	Low	High/Low	2	Na-Cl	Oxic	196.8	51.0	11.2	coastal_2	Mafic	Undiff. Clastics	Q8-Q10
E46/0514		Lower Aparima	Terrace	High	Low/High	High/Low	2	Na-Cl	Oxic	202.0	52.0	9.6	coastal_2	Mafic	Undiff. Clastics	Q8-Q10

D46/0115	24	Lower Aparima	Terrace	High	Low/High	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	191.0	37.0	7.8	coastal_2	Felsic	Undiff. Clastics	Q8-Q10
E46/0097	8	Waihopai	Lowland	Low	Low	Low	3	Na-Cl	Mixed(oxic-anoxic)	193.8	19.6	7.0	coastal_2	Felsic	Undiff. Clastics	Q8-Q10
E46/0440	20	Lower Aparima	Terrace	High	Low/High	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	226.0	24.2	6.6	coastal_2	Mafic	Undiff. Clastics	Q8-Q10
F46/0761	12.5	Awarua	Lowland	Low	Low	High/Low	3	Na-Cl	Oxic	190.1	50.0	8.9	coastal_2	Felsic	Felsic	Q8-Q10
F46/0802	5.5	Waihopai	Lowland	Low	Low	Low	3	Na-Cl	Mixed(oxic-anoxic)	231.7	29.0	9.7	coastal_2	Felsic	Felsic	Q8-Q10
F47/0099	8.9	Awarua	Lowland	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	170.0	37.9	13.8	coastal_2	Felsic	Felsic	Q8-Q10
F47/0114	10.4	Awarua	Lowland	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	198.0	56.0	9.5	coastal_2	Felsic	Felsic	Q8-Q10
F47/0251		Awarua	Lowland	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	147.5	14.5	5.9	coastal_2	Felsic	Felsic	Q8-Q10
F47/0252	7	Awarua	Lowland	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	240.3	25.0	14.3	coastal_2	Felsic	Felsic	Q8-Q10
F47/0253	7.35	Awarua	Lowland	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	198.5	34.0	7.6	coastal_2	Peat	Peat	Q2-Q4
F47/0275		Awarua	Lowland	Low	Low	High/Low	3	Na-Cl	Mixed(oxic-anoxic)	218.3	67.0	12.4	coastal_2	Felsic	Carbonaceous	Q8-Q10
E47/0079		Awarua	Lowland	Low	Low	High/Low	**4**	Na-Cl	Anoxic	335.0	71.0	14.5	coastal_2	Felsic	Felsic	Q8-Q10
E47/0155	12	Awarua	Lowland	Low	Low	High/Low	**4**	Na-Cl	Mixed(oxic-anoxic)	324.3	32.0	7.9	coastal_2	Felsic	Felsic	Q2-Q4
E47/0250	14.2	Awarua	Lowland	Low	Low	High/Low	**4**	Na-Cl	Anoxic	272.9	38.0	4.3	coastal_2	Felsic	Felsic	Q2-Q4
F46/0688	11.22	Awarua	Lowland	Low	Low	High/Low	**4**	Na-Cl	Mixed(oxic-anoxic)	257.0	62.0	12.5	coastal_2	Felsic	Felsic	Q8-Q10
F47/0138	16	Awarua	Lowland	Low	Low	High/Low	**4**	Na-Cl	Mixed(oxic-anoxic)	219.2	45.1	9.0	coastal_2	Felsic	Carbonaceous	Q8-Q10
F47/0145	7.9	Awarua	Lowland	Low	Low	High/Low	**4**	Na-Cl	Mixed(oxic-anoxic)	214.6	41.5	10.8	coastal_2	Felsic	Undiff. Clastics	Q8-Q10
F47/0201	11.8	Awarua	Lowland	Low	Low	High/Low	**4**	Na-Cl	Anoxic	242.6	30.0	3.2	coastal_2	Peat	Carbonaceous	Q2-Q4
F47/0256	6	Awarua	Lowland	Low	Low	High/Low	**4**	Na-Cl	Anoxic	260.8	52.0	4.7	coastal_2	Felsic	Peat	Q2-Q4
F47/0259	30	Awarua	Lowland	Low	Low	High/Low	**4**	Na-Cl	Anoxic	400.0	43.0	19.9	coastal_2	Felsic	Carbonaceous	Q8-Q10

4.3.3.3.3 Groundwater summary

We demonstrated that manual hierarchical stratification of regional groundwater hydrochemical data by regional drivers produced relatively homogenous hydrochemical subsets, despite greater uncertainty regarding subsurface geology. In particular, we found manual stratification was effective at predicting pre-defined hydrochemical cluster membership and general hydrochemical setting and/or redox and recharge signatures (Figure 4-7). The ability to predict recharge and redox signatures with a high degree of confidence is particularly relevant to controls over TON concentrations in regional aquifer systems. However, unlike surface water sites it was difficult to estimate with high precision solute or isotopic concentrations although relative absolute concentrations and isotopic signatures were well defined as supported by a strong ability to estimate redox signatures.

The stronger performance of the manual stratification to estimate pre-defined redox signatures, recharge source and mechanism, groundwater cluster membership and general hydrochemical setting relative to the empirical approach is perhaps feature of greater flexibility. Specifically, it is possible to selectively apply modifiers (driver attributes) of hydrochemical setting on the basis of expert or pre-knowledge of the setting. For example, attributes of hydrodynamic setting such as bypass flow or river connectivity can be viewed and applied as a modifier. Further, only predictors (drivers) that are hydrochemically relevant are selected.

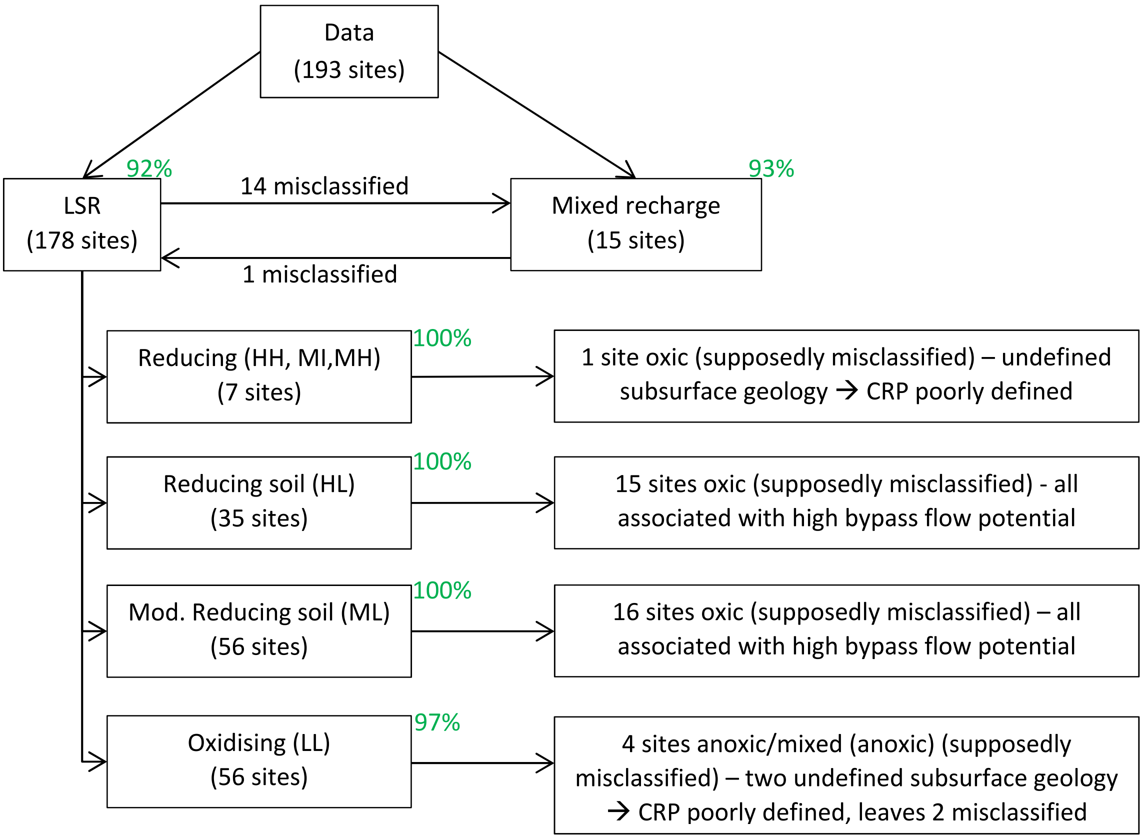

Figure 4-7: Schematic of groundwater stratification by recharge domain and CRP.

4.3.4 Summary of Manual Stratification

Manual stratification of regional surface water hydrochemical data by key drivers was considered highly successful (success rate ranged from 75 to 100% for groundwater and variation in surface water chemistry was 100% resolvable). Manual stratification produced relatively homogenous groupings of pre-defined general hydrochemical setting and empirically defined cluster membership for both surface and ground waters.

Overall, stratification by drivers work best for surface water with a high success rate and an ability to estimate with a degree of precision the majority of solute concentrations and stable isotopic signatures across regional sites. Furthermore, it was possible to resolve and estimate longitudinal changes in median hydrochemical signatures for streams and rivers with two or more sites. For groundwater however, it was hard to resolve with a high degree of precision absolute solute concentrations although predefined general hydrochemical setting, cluster membership and/or redox and recharge signatures were well resolved.

An ability to estimate the general hydrochemical setting for groundwater is important as redox in conjunction with water source and recharge mechanism are the two chief determinants of water quality outcomes (variation) in areas of intensive landuse in Southland and New Zealand (TC1-8 and Daughney, 2005, Daughney and Reeves, 2005, Daughney et al., 2010; Rissmann et al., 2012; Daughney et al., 2015). For this reason we consider the performance of regional drivers to estimate hydrochemical setting, the 6 main regional hydrochemical clusters highly successful.

The ability to resolve and then estimate surface water hydrochemistry according to spatial maps of regional drivers provided a strong conceptual basis for an integrated ‘top-down’ approach to mapping controls over regional water quality outcomes for surface water. Specifically, integration of key driver assemblages into one mapping based platform holds considerable promise for understanding spatial variation in surface water quality.

5. Summary and Conclusion

5.1 Summary

5.1.1 Background

This report documents research on the controls over surface water and shallow soil-influenced, groundwater hydrochemistry. The research stems from four years of collecting hydrochemical data and the observation of spatial differences across given areas and querying why there were differences or similarities in hydrochemistry between sites, sub-regions, and catchments.

With increased data collection, understanding of regional hydrochemistry evolved through an informal and *ad hoc* interrogation of the relationships between soils, geology, hydrology and local climate zones. A number of regional and local studies during this time further developed our understanding of the nature of the underlying controls (Rissmann, 2011; Rissmann, 2012; Rissmann et al., 2012; Daughney et al., 2015; Rekker and Wilson, 2016). Ergo, hydrochemistry was used to determine characteristics of our various regional frameworks that correlated with the observed hydrochemical signatures.

A key finding was the importance of the soil zone over both surface water and unconfined groundwater hydrochemistry, and water quality in general. The importance of the soil zone over shallow groundwater hydrochemistry and quality is highlighted by a median static water level of -2.75 m b.g.l. (n = 1,750 wells) for Southland's unconfined aquifers and a median depth of pedogenic differentiation is at least 2 m under Southland's cool, humid, temperate climate. Therefore, the majority of Southland's soils are in direct contact with the shallow, unconfined groundwater system and the signature of soil drainage is readily imprinted. Furthermore, those areas with a deeper, pedogenically undifferentiated, unsaturated zone are comprised of inert silicate minerals.

Surface water is by definition a mix of soil water and groundwater drainage, the majority of which is associated with young, unconfined and soil influenced aquifers. Southland's semi-confined and confined aquifer systems are often poorly coupled to both the soil zone and surface water network. Importantly, these aquifers show little evidence for anthropogenic contamination. It is the fluxing of young, soil-influenced groundwaters to stream channels that are often noted as the main pathway of nitrogen to stream networks both nationally (e.g. Woodward et al., 2013, 2016) and internationally (e.g. Green and Wang, 2008).

5.1.2 Developing a conceptual model

Based on the knowledge gained above, the key objective of the Physiographic Programme was to build a regional scale conceptual model of how and why we see spatial variation in regional hydrochemistry. More specifically, we wanted to define the reasons for why hydrochemical signatures of surface water and shallow, soil-influenced groundwater vary in space as a platform for better understanding of water quality outcomes.

As the data collection and learning advanced, the concept of a mechanistic conceptual model depicting how and why hydrochemistry varied in space was envisioned. Accordingly, a series of simplified driver assemblages were produced as a proof of concept before the development of a physiographic work stream.

The role of hydrochemical analysis was to first identify spatial patterns in hydrochemical signatures and use these signatures in conjunction with the spatial knowledge provided by existing regional frameworks to inform an iterative loop. Specifically, hydro-biogeochemical data enabled identification of the critical characteristics of existing spatial frameworks (i.e., Soil (TopoClimate and S-Map), hydrology (REC), hydrogeology, geomorphology and geology (Qmap)) and identify key drivers of spatial variation in hydrochemical signatures.

The four key drivers governing hydrochemical variation of surface waters and shallow, soil-influence groundwaters across Southland were resolved as:

1. precipitation source and composition;
2. recharge mechanism(s) and water source;
3. geomorphic setting and substrate (rock and biological sediments including soils) composition, and;
4. redox control (combined soil zone and geological reduction potential (CRP)).

Technical chapters within this report provide a data driven justification for identification of the four key drivers responsible for hydrochemical variation.

Once the drivers were established, regional ground- and surface water capture zones were then intersected with the map of each driver. This was based on the hypothesis that through combining the drivers of hydrochemical variation it should be possible to estimate with a degree of certainty the measured composition of a stream or shallow, soil-influenced groundwater. The resulting conceptual model was then defined as semi-quantitative and mechanistic. It aimed to simulate hydrochemical variation in surface water and young, soil influenced groundwater at any point in the landscape across multiple scales.

5.1.3 Validation of the model

The conceptual model was then validated through stratification of chemistry data by key drivers and empirical modelling, which is a machine learning approach. Both sets of results validated the conceptual model’s ability to simulate spatial variability in hydrochemistry and water quality metrics of regional surface waters.

The empirical testing of the performance of the model demonstrated a strong ability to estimate hydrochemistry for surface waters. Estimation of groundwater hydrochemical composition from drivers was weaker than for surface water, although the response in the data was consistent with the underlying drivers. Further, the strong performance of the model in regards to surface water indicates a robust characterisation of young, soil zone influenced groundwater across Southland. The latter is consistent with both regional, national and international studies indicating that regional groundwater data is not always indicative of the shallow, soil zone connected system due to limitations associated with poor constraint over: well characteristics, such as depth and screen interval, and poor installation; the spatial distribution of semi-confining and/or confining layers; topographic relief on and composition of shallow basement geology. Accordingly, and as widely recognised, surface waters provide perhaps the best picture of the hydrochemical composition of shallow soil influenced groundwaters, particularly under low flow conditions.

5.2 Conclusion

The mechanistic basis of this approach and its strong performance regarding estimation of surface water hydrochemistry means it is a sound platform for understanding and explaining the spatial controls over hydrochemistry and as such water quality outcomes. A model was developed based on dataset included chemical and isotopic signatures of precipitation, soil, soil water, ground- and surface water chemistry. Integration of hydrochemistry and key spatial frameworks proved to be a powerful contextual learning tool.

This work provides a spatially resolved platform for the development of a risk based framework for landuse across Southland. Future work will look at the use of key drivers as a platform for transient models attempting to simulate water flow and nutrient flux in time.

5.3 Recommendations for Future Work

On the basis of our findings, the following recommendations for future work were drawn:

- To improve the prediction of groundwater chemistry based on key drivers, it would be valuable to better define the boundary between Mixed and Land Surface Recharge dominated groundwater. This may be carried out through assessment of EC or other hydrochemical parameters in groundwaters as a function of distance to a stream, particularly for groundwaters that are located adjacent to the main stem rivers in northern Southland. Alternatively, or in addition, capture zones could be refined for each groundwater site.
- In addition to the above, better resolution of subsurface geology, specifically reducing aquifers and carbonate rock is recommended to better estimate freshwater quality. For example, inclusion of the carbonate rock occurring in Isla Bank or areas fringing the Coastal Longwoods in the regional geological map, would benefit the prediction of freshwater quality in Southland. These are currently not mapped because they do not outcrop at the surface.
- To better acknowledges spatial and temporal variability of drivers (e.g. Gueler and Thymes, 2004), the use of other clustering techniques, such as fuzzy clustering, is recommended.
- To better estimate redox control, we recommend to consider soil hydrology and bypass flow. To get a better understanding of deep and shallow bypass flow and its impact on water composition, in particular redox processes, we recommend targeted sampling and analysis of freshwater in affected areas.

6. References

A B C D E F G H I J K L M
N O P Q R S T U V W X Y Z

Adams and Adams, 1973; New Zealand Alpine Plants; Publisher REED.

Aislabie, J., Smith, J.J., Fraser, R., McLeod, M., 2001. Leaching of bacterial indicators of faecal contamination through four New Zealand soils. Aust. J. Soil Res., 39: 1397-1406

Aislabie, J., McLeod, M., Ryburn, J., McGill, A., Thornburrow, D., 2011. Soil type influences the leaching of microbial indicators under natural rainfall following application of dairy shed effluent. Soil Research 49(3) 270-279

Andersen, H.E., 2003. Hydrology, nutrient processes and vegetation in floodplain wetlands. PhD thesis. National Environmental Research Institute, Denmark. http://afhandlinger.dmu.dk

Ballance, J.A., Duncan, J.R., 1985. Wind borne transport and deposition of sea salt in New Zealand. New Zealand journal of technology 1: 239-244

Bernal, B., 2008. Carbon pools and profiles in wetland soils: The effect of climate and wetland type. The Ohio State University.

Blasch, K.W., Bryson, J.R., 2007. Distinguishing Sources of Ground Water Recharge by Using δ2H and δ18O. Ground Water 45, 294-308.

Blaschke, P.M., N.A. Trustrum., R.C. DeRose., 1992. Ecosystem processes and sustainable land use in New Zealand steeplands. Agriculture, Ecosystems and Environment 41:153-178.

Böhnke, R., Geyer, S., Kowski, P., 2002. Using environmental isotopes 2H and δ18O-H2O for identification of infiltration processes in floodplain ecosystems of river Elbe. Isotopes in Environmental and Health Studies 38: 1–13.

Boone, R.D.; Nadelhoffer, K.J.; Canary J.D., Kaye. J.P., 1998. Roots exert a strong influence on the temperature sensitivity of soil respiration. Nature 396: 570-572, doi:10.1038/25119.

Boutton, R.W., 1996. Stable carbon isotope ratios of soil organic matter and their use as indicators of vegetation and climate change. In: Mass Spectrometry of Soils (Eds Boutton, T.W and Yamasaki, S), pp. 47–82. Marcel Dekker, New York.

Brantley, S.L., 2008. Chapter 5: Kinetics of Mineral Dissolution. Pennsylvania State University, Centre for Environmental Kinetics Analysis, Earth and Environmental Systems Institute, Pp 60.

Bundi, U., Peter, A., Robinson, C. T., Schädler, B., Truffer, B., Vollenweider, S., Weingartner, R., 2010. Alpine Waters: Springer Berlin Heidelberg.

Cameron, K.C., Di, H.J., Roberts, A., Beale, N., Weir, J., Borrie, N., 2014. Monitoring Effects of Southland Demonstration Farm on Stream Water Nitrate. Nutrient management for the farm, catchment and community.

Champ, D.R., Gulens,J., Jackson, R.E.. 1979. Oxidation-reduction sequences in groundwater flow systems. Canadian Journal of Earth Sciences 16, no. 1: 12–23

Chanut, P., 2014. Seasonality of land surface recharge in Southland. Environment Southland, Invercargill. Pp28.

Chanut, P., Ledgard, G., Rissmann, C., Wilson, S., 2014. Estimating Time Lags for Nitrate Response in Shallow Southland Groundwater, Technical Report. Environment Southland publication No 2014-13, Invercargill. 51p.

Chapin, F. S., Chapin, M. C., Matson, P. A., Vitousek, P., 2011. Principles of Terrestrial Ecosystem Ecology: Springer New York.

Chinn, T, 1979. How wet is the wettest of the wet West Coast. New Zealand Alpine Journal 32: 86

Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Taylor & Francis.

Clayden, B., Webb, T.H., 1994. Criteria for defining the soil form – the fourth category of the New Zealand soil classification, Landcare Research Science Series 3. 36 p.

Cloutier, V., Lefebvre, R., Therrien, R., Savard, M. M., 2008. Multivariate statistical analysis of geochemical data as indicative of the hydrogeochemical evolution of groundwater in a sedimentary rock aquifer system, J. Hydrol., 353, 294–313.

Clow, D.W., Drever, J.I., 1996. Weathering rates as a function of flow through an alpine soil. Chemical Geology 132: 131-141.

Crews, T.E., Kitayama, K., Fownes, J.H., Riley, R.H., Herbert, D.A., Mueller-Dombois, D., Vitousek, P.M., 1995. Changes in soil phosphorus fractions and ecosystem dynamics across a long chronsequence in Hawaii, Ecology, July 1995 v76 n5 p1407 (18).

Daughney, C., 2004. Review of the Environment Southland Baseline Groundwater Quality Monitoring Programme. GNS Client Report 2004/68. 75 p. and 20 appendices.

Daughney, C.J., Reeves, R.R., 2005. Definition of Hydrochemical Facies in the New Zealand National Groundwater Monitoring Programme. J. Hydrol. (NZ) 44: 105-130.

Daughney, C.J., Reeves, R., 2006. Analysis of Long-Term Trends in New Zealand’s Groundwater Quality based on data from the National Groundwater Monitoring Programme. J. Hydrol. (NZ). 45: 41-62.

Daughney, C.J., 2008. Multivariate statistical methods for assessment of groundwater chemistry in the Waiareka and Deborah Aquifers, Otago. GNS Science Report 2008/125. 31 p.

Daughney, C.J., 2009. Hydrochemical Classification of Groundwater and River State of the Environment Monitoring Sites in the Greater Wellington Region. GNS Science Report 2009/68. 62 p.

Daughney, C., Meilhac, C., Zarour, H., 2009. Spatial and temporal variations and trends in groundwater quality in the Manawatu-Wanganui Region. GNS Science Report 2009/02. 146p.

Daughney, C., Randall, M., 2009. National groundwater quality indicators update: State and trends 1995-2008. GNS Science Consultancy Report 2009/145. 60 p.

Daughney, C.J., Morgenstern, U., van der Raaij, R., Reeves, R.R., 2010. Discriminant analysis for estimation of groundwater age from hydrochemistry and well construction: application to New Zealand aquifers. Hydrogeology J. 18: 417-428.

Daughney, C., Rissmann, C., Friedel, M., Morgenstern, U., Hodson, R., van der Raaij, R., Rodway, E., Martindale, H., Pearson, L., Townsend, D., Kees, L., Moreau, M., Millar, R., Horton, T., 2015. Hydrochemistry of the Southland Region, GNS Science Report 2015/24.

Davie, T., 2002. Fundamentals of Hydrology. 2nd edition published by Taylor & Francis.

De Klein, C.A.M., Smith, L.C., Monaghan, R.M., 2006. Restricted autumn grazing to reduce nitrous oxide emissions from dairy pastures in Southland, New Zealand. In: McDowell, R.W. (ed). Environmental Impacts of Pasture-based farming. Agriculture, Ecosystems and Environment 112, 172-199.

Demlie, M., Wohnlich, S., Wisotzky, F., Gizaw, B., 2007. Groundwater recharge, flow and hydrogeochemical evolution in a complex volcanic aquifer system, central Ethiopia, Hydrogeol. J., 15, 1169–1181.

Desonie, D. 2007. Hydrosphere: Freshwater Systems and Pollution. Infobase Publishing.

Dinka, M.O., Loiskandl, W., Ndambuki, J.M., 2015. Hydrochemical characterization of various surface water and groundwater resources available in Matahara areas, Fantalle Woreda of Oromiya region. Journal of Hydrology: Regional Studies 3, 444-456.

Doctor, D.H., Kendall, C., Sebestyen, S.D., Shanley, J.B., Ohte, N., Boyer, E.W., 2008. Carbon isotope fractionation of dissolved inorganic carbon (DIC) due to outgassing of carbon dioxide from a headwater stream, Hydrol. Process. 22, #14, DOI: 10.1002/hyp.6833.

Donath, F.M., Daughney, C.J., Morgenstern, U., Cameron, S.G., Toews, M.W., 2014. Hydrochemical interpretation of groundwater-surface water interactions at regional and local scales, Lake Rotorua catchment, New Zealand. J. Hydrol. (NZ), in press.

Drever, J.I., 1997. The geochemistry of natural waters, surface and ground water environments third edition. Prentice Hall.

Drever, J. I., 2002. The Geochemistry of Natural Waters: Surface and Groundwater Environments, pp. 114–116, Prentice Hall, Upper Saddle River, N. J.

Drever, J.I., 2005. Surface and Ground Water, Weathering, and Soils: Treatise on Geochemistry, Second Edition. Elsevier Science.

DSIR., 1968. General survey of the soils of South Island, New Zealand. New Zealand Department of Scientific and Industrial Research, Soil Bureau Bulletin 27.

Elwan, A., Singh, R., Horne, D., Roygard, J., Clothier, B., 2015. Nitrogen attenuation factor: Can it tell a story about the journey of nitrogen in different subsurface environments? In: *Moving farm systems to improved attenuation*. (Eds L.D. Currie and L.L Burkitt). http://flrc.massey.ac.nz/publications.html.

Encyclopaedia of Soil Science, Second Addition., 2006. The Ohio State university, Columbus, Ohio, U.S.A. CRC Press.

Environment Southland and Te Ao Marama Inc., 2011. Our Ecosystems: How healthy is the life in our water and our freshwater ecosystems? Part 2 of Southland Water 2010: Report on the State of Southland's Freshwater Environment. Environment Southland. Invercargill. Publication number 2011/7 ISBN 0-90943-45-0

Environment Southland., 2002. Crops For Southland – Report by Venture Southland and Environment Southland (Topoclimate soils database).

Essington, M. E., 2015. Soil and Water Chemistry: An Integrative Approach, Second Edition: CRC Press.

Fiedler, S., 2000. In situ longterm measurement of redox potential in redoximorphic soils. In: Schuring, J., Schulz, H.D., Fischer, W.R., Bottecher, J., Duijnisved, W.H.M (eds). Redox: Fundamentals, Processes and Applications

Freedman, D, A., 2005. Statistical Models: Theory and Practice, Cambridge University Press.

Frossard, E., Brossard, M., Hedley, M.J., Metherell,A., 1995. Phosphorus in the Global Environment, Transfers, Cycles and Management. Chapter 7 article title: Reactions Controlling the Cycling of P in Soils. Edited by Teissen, H.

Gabler, R.E., Petersen, J.F., Petersen, L., Trapasso, M., 2007. Essentials of Physical Geography. Eight Edition.

Gat, J.R., 1980. The relationship between surface and subsurface waters: water quality aspects in areas of low precipitation. Hydrological Sciences Bulletin 25, 257-267.

Gill, W.B., Cole, C.V., 1981. Comparative Asspects of Cycling of Organic C, N, S and P through Soil Organic Matter. Geoderma, 26: pp 267-286.

Giller, P.S., Malmqvist, B., 2004. The biology of streams and rivers. Oxford university Press.

Goudie, A., 2013. Encyclopedia of Geomorphology. Taylor & Francis.

Goyal, M. R., Harmsen, E. W., 2013. Evapotranspiration: Principles and Applications for Water Management: Apple Academic Press.

Green, M. B., Wang, D., 2008. Watershed flow paths and stream water nitrogen-to-phosphorus ratios under simulated precipitation regimes. Water Resources Research, 44(12)

Greenwood, P.B. 1999. Irrigation of farm dairy effluent in Southland. Report to the Southland Regional Council. Soil Work Ltd Report SW-MR-0196.

Guan, H., Love, A. J., Simmons, C.T, Makhnin O., Kayaalp, A.S., 2010. Factors influencing chloride deposition in a coastal hilly area and application to chloride deposition mapping. Hydrol Earth Syst Sci 14(5):801-813 doi:10.5194/hess-14-801-2010

Guggenmos, M.R., Daughney, C.J., Jackson, B.M., Morgenstern, U., 2011. Regional-scale identification of groundwater-surface water interaction using hydrochemistry and multivariate statistical methods, Wairarapa Valley, New Zealand. Hydrol. Earth Syst. Sci. 15: 3383-3398.

Güler, C., Thyne, G.D., McCray, J.E., Turner, A.K., 2002. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. Hydrogeology Journal 10:455–474.

Güler, C., Thyne, G.D., 2004. Delineation of hydrochemical facies distribution in a regional groundwater system by means of fuzzy c-means clustering, Water Resour. Res., 40, 1–11.

Haberecht, P.W., Kear, G., 2005. Stormy seas, Salt deposition and Environmental corrosivity- a discussion. Conference paper, No 113, presented at 16th International Corrosion Congress

Hamblin, W.K. and Christiansen, E.H. (2004) Earth’s Dynamic Systems. Upper Saddle River, N.J.: Pearson, Prentice Hall, 2004. 740p.

Heron, D.W., 2014. Geological Map of New Zealand 1:250 000. GNS Science.

Hewitt, A.E., 1993. New Zealand soil classification. Landcare Research Science Series. Lincoln Landcare Research.

Hitchcock, M.K., 2014. Characterising the surface and groundwater interactions in the Waimatuku Stream, Southland. University of Otago, Dunedin. Pp180.

Houldroke, D.J., Monaghan, R.M., 2009. The Influence of soil drainage characteristics on contaminant leakage risk associated with the land application of farm dairy effluent. Agresearch, prepared for Environment Southland, pp 32.

Huggett, R., 2007. Fundamentals of geomorphology. Routledge.

Hughes, B., 2012. Knapdale Groundwater Zone Technical Report. Environment Southland, Invercargill. 42p.

Hughes, B., Ledgard, G., 2012. Hill Country Development Technical Report. Environment Southland publication No 212-08, Invercargill. 46p.

Hughes, B., Ledgard, G., Ogilvie, H., Rissmann, C., 2013. On-site Wastewater Groundwater Quality Risk. Environment Southland, Invercargill. 20p.

Jahangir, M., Khalil, M.I., Johnston, P., Cardenas, L.M., Hatch, D.J., Butler, M., Richards, K.G., 2012. Denitrification potential in subsoils: A mechanism to reduce nitrate leaching to groundwater. Agriculture, Ecosystems & Environment, 147, 13-23.

Jiang, Y., Wu, Y., Groves, C., Yuan, D., Kambesis, P., 2009. Natural and anthropogenic factors affecting the groundwater quality in the Nandong karst underground river system in Yunan, China. Journal of Contaminant Hydrology 109, 49-61.

Jobbagy, E.G., Jackson, R.B., 2001. The distribution of soil nutrients with depth: Global patterns and the imprint of plants. Department of Botany, Duke University, Durham, NC 27708, NC, USA. Pp28.

Jurgens, B.C., McMahon, P.B., Chapelle, F.H., Eberts, S.M., 2009. An Excel workbook for identifying redox processes in ground water. USGS Open File Report 2009-1004, USGS, Sacramento, California.

Kendall, C., Caldwell, E.A., 1998. Fundamentals of Isotope Geoichemistry. In: Kendall c., McDonnell , J.J (eds.), Isotope Tracers in Catchment Hydrology. Elsevier Science B.V., Amsterdam. Pp. 41-86.

Kendall, C., McDonell, J.J., 1998. Isotope Tracers in catchment hydrology. Elsevier, Amsterdam.

Killick, M., Stenger., R., Rissmann, C., 2014. Estimating soil zone denitrification potential for Southland, Environment Southland and Lincoln Agritech Ltd, Invercargill. 29p.

Killick, M., Stenger, R., Rissmann, C., 2015. Estimating soil zone denitrification for Southland. Environment Southland Technical Report.

Kirschbaum, M.U.F., 2006. The temperature dependence of organic-matter decomposition—still a topic of debate. Soil Biol. Biochem. 38: 2510–2518.

Krantz, D.E., Powars, D.S.,2002. Hydrogeologic setting and potential for denitrification in

groundwater, Coastal Plain of Southern Maryland: U.S. Geological Survey Water-Resources Investigations Report 00-4051.

Kumar, M., Ramanathan, A., Keshari, A.K., 2009. Understanding the extent of interactions between groundwater and surface water through major ion chemistry and multivariate statistical techniques, Hydrol. Process, 23, 297–310.

Lambert, M.G., Devantier, B.P., Nes, P., Penny, P.E., 1985. Losses of nitrogen, phosphorus, and sediment in runoff from hill country under different fertiliser and grazing management regimes. New Zealand Journal of Agricultural Research 28:371.

Lambert, M.G., Clark, D.A., 1986. Effects of late-autumn nitrogen application on hill country pastures and sheep production. Proceedings of the New Zealand Grassland Association, 47:211-215.

Lambert, M.G., Mackay, A.D., Costall, D.A., Clark, D.A., 2000. Effects of fertiliser application on nutrient status and organic matter content of hill soils. New Zealand Journal of Agricultural Research 43:127-138.

Lambert, M.G., MacKay, A.D., Devantier, B.P., McDougall, D.B., Barker D.J., Park-Ng., Z. A., 2003. Redefining the production potential of hill pastures using fertiliser nitrogen. Proceedings of the New Zealand Grassland Association 65, 35-40.

Landcare Research., 2016. Landcare Research, New Zealand. S-map Online http://smap.landcareresearch.co.nz. Date last accessed: 27.04.2016.

Langmuir, D., 1997. Aqueous Environmental Geochemistry. Prentice-Hall, New Jersey.

Lasaga, A., 1984. Chemical Kinetics of Water-Rock Interactions. Journal of Geophysical Research, vol. 89, no. B6, pages 4009-4025, June 10, 1984.

Ledgard, G., 2013. Nitrogen, Phosphorus and Sediment losses from rural land uses in Southland, Technical Report. Environment Southland publication No 2013-7, Invercargill. 25p.

Ledgard, G., 2013. Land Use Change in the Southland region. Environment Southland publication No 2013-13, Invercargill. 80p.

Ledington, S., 2011. Instream Flow Requirements for the Irthing Stream. Environment Southland, publication No 2011-01. 22p.

Lerman, A., Meybeck, M., (Editors). Physical and Chemical Weathering in Geochemical Cycles. NATO ASI Series. Series C: Mathmatical and Physical Sciences – Vol. 251. Luwer Academic Publishers.

Letkeman, L.P., Tiessen, H., Campbell, C.A., 1996. Humic Substances in Terrestrial Ecosystems. Chapter 11, article title: Dynamics of Organic Phosphorus in Soils under Natural and Agricultural Ecosystems. Edited by; Alessandro Piccolo.

Lewis, E.R., Schwartz, S.E., 2004. Sea Salt Aerosol Production: Mechanisms, Methods, Measurements, and Models - A Critical Review. Wiley.

Macara, G.R., 2013. The climate and weather of Southland. 2nd edition. NIWA SCIENCE AND TECHNOLOGY SERIES NUMBER 63

Mager, S.M. & Diack, E.E, 2014. Geomorphological and climatic influences on the hydrochemical facies of Southern Alps rivers. New Zealand Hydrological Society Conference.

Magesan, G.N., Dalgety, J., Lee, R., Luo, J., van Oostrom, A.J. 1999. Preferential flow and water quality in two New Zealand soils previously irrigated with wastewater. Journal of Environmental Quality 28, 1428-1532

Martins, J.M.F., Majdalani, S., Vitorge, E., Desaunay, A., Navel, A., Guine, V., Daian, J.F., Vince, E., Denis, H., Gaudet, J.P., 2013. Role of macropore flow in the transport of Escherichia coli cells in undisturbed cores of a brown leached soil. Environmental Science: Processes & Impacts 15, 347-356.

McBride, M.B., 1994. Environmental Chemistry of Soils. Oxford University Press.

McBride, M.B., 1998. Growing food crops on sludge-amended soils: Problems with the U.S. Environmental Protection Agency method of estimating toxic metal transfer. Environmental Toxicology and Chemistry 17(11):2274-2281

McColl, R.H.S., White, E., Gibson., A.R,. 1977. Phosphorus and nitrate runoff in hill pasture and forest catchments, Taita, New Zealand. New Zealand Journal of Marine and Freshwater Research 11:729-744.

McDowell, R.W., Monaghan, R.M., 2014. Extreme Phosphorus Losses in Drainage from Grazed Dairy Pastures on Marginal Land. Journal of Environmental Quality.

McLaren, R. G., Cameron, K. C., 2005. Soil science: an introduction to the properties and management of New Zealand soils (2nd Ed). Auckland, New Zealand: Oxford University Press. 314 pp.

McLeod, M., Aislabie, J., Ryburn, J. and McGill, A., 2008. Regionalizing potential for microbial bypass flow through New Zealand soils. Journal of Environmental Quality, 37(5), pp.1959-1967.

McMahon, P.B., Chapelle, F.H., 1991. Microbial production of organic acids in aquitard sediments and its role in aquifer geochemistry.

McMahon, P. B., Chapelle, F. H., 2008. Redox Processes and Water Quality of Selected Principal Aquifer Systems. Ground Water, 46(2), 259-271.

McNeil, V.H., Cox, M.E., Preda, M., 2005. Assessment of chemical water types and their spatial variation using multi-stage cluster analysis, Queensland, Australia, J. Hydrol, 310, 181–200.

Merz, S.K., 2004. Northern Southland Groundwater Model. Report prepared for Environment Southland.

Mengel, D.D., 2011. Fundamentals of Soil Cation Exchange Capacity. Department of Agronomy, Purdue University.

Milne, J.D.G., Clayden, B., Singleton, P.L., Wilson, A.D., 1995. Soil description. Lincoln, Manaaki Whenua Press. 157p

Monaghan, R.M., Paton, R.J., Drewry, J.J., 2002. Nitrogen and phosphorus losses in mole and tile drainage from a cattle-grazed pasture in eastern Southland, New Zealand. Journal of Agricultural Research, 45:3, 197-205.

Monaghan, R.M., Smith, L.C., Muirhead, R.W. (in press) Pathways and loads of N, P, sediment and Escherichia coli transfers from a grazed dairy pasture to water. Agriculture, Ecosystems and Environment.

Monaghan. R., Smith. C., 2013. Comparing Overseer estimates of N leaching from grazed winter forage crops with results from Southland trail sites. Agresearch report prepared for Environment Southland, Southland, New Zealand. Pp9.

Monaghan, R., 2014. The influence of land use and soil properties on contaminant accumulation and loss from farming systems. Argresearch, report prepared for Environment Southand, pp 55.

Moncayo, F,H,O., 2003. Oxygen transport in waterlogged soils, Part II. Diffusion coefficients

Moreau, M., Hodson, R., 2014. Trends in Southland’s water quality: a comparison between national and Southland’s monitoring sites for groundwater and rivers, GNS Science Consultancy Report 2014/16.

Morgenstern, U., Brown, L., Begg, J., Daughney, C., Davidson, P., 2009. Linkwater catchment groundwater residence time, flow pattern, and hydrochemistry trends. GNS Science Report 2009/08. 47 p.

Morgenstern, U., Daughney, C.J., 2012. Groundwater age for identification of baseline groundwater quality and the impacts of land-use intensification - The National Groundwater Monitoring Programme of New Zealand. J. Hydrol. 456-457: 79-93.

Mulder, J., Cresser, M.S., 1994. Soil and soil solution chemistry. In Biogeochemistry of Small Catchments: A Tool for Environmental Research, Edited by: Moldan, B and Cerny, J. 107–131. John Wiley & Sons Ltd., Chichester, UK.

Nahon, D., 1991. Introduction to the petrology or soils and chemical weathering. Wiley.

Nichols, S. E., Harvey, M.J. Boyd, I.S., 1997. Ten years of rainfall chemistry in New Zealand. pp 30.

O'Byrne, T.N., 1986. Soils of part Wallace County, South Island, New Zealand. NZ Soil Bureau.

Ohte N., Dahlgren R.A., Silva S.R., Kendall C., Kratzer C.R., Doctor D.H., 2007. Sources and transport of algae and nutrients in a Californian river in a semi-arid climate. Freshwater Biology 52, p. 2476–2493

Oliver, D.M., Heathwaite, L.A., 2013. Pathogen and Nutrient transfer through and across agricultural soils. In: Meyers (ed). Encyclopedia of Sustainability Science and Technology.

Oliver, D. M., Clegg, C. D., Haygarth, P. M., Heathwaite, A. L., 2003. *Determining hydrological pathways for the transfer of potential pathogens from grassland soils to surface waters*. 36-41.

Olson, J, R., 2012. The Influence of Geology and Other Environmental Factors on Stream Water Chemistry and Benthic Invertebrate Assemblages. *All Graduate Theses and Dissertations.* Paper 1327

Pearson, L., 2015. Artificial subsurface drainage in Southland. Environment Southland Technical Report.

Peralta, A. L.; Ludmer, S.; Kent, A. D., 2013. Hydrologic history influences microbial community composition and nitrogen cycling under experimental drying/wetting treatments. Soil Biology and Biochemistry Vol.66, pp.29-37

Peukert, S., Griffith, B.A., Murray, P.J., Macleod, C.J.A., Brazier, R.E., 2014. Intensive Management in Grasslands Causes Diffuse Water Pollution at the Farm Scale. Journal of Environmental Quality 43.

Physical and Chemical Weathering in Geochemical Cycles. Edited by A. Lerman and M. Meybeck. NATO ASI Series. Series C: Mathmatical and Physical Sciences – Vol. 251. Luwer Academic Publishers.

Plummer, L. and N. E. Busenberg. “The Solubilities of calcite, aragonite and vaterite in CO2 – H2 O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO3 – CO2 – H2 O.” Geochimica et Geochimica Acta 46 (1982):1011–1040

Raiber, M., White, P.A., Daughney, C.J., Tschritter, C., Davidson, P., Bainbridge, S., 2012. Three-dimensional geological modeling and multivariate statistical analysis of water chemistry data to analyse and visualise aquifer structure and groundwater composition in the Wairau Plain, Marlborough District, New Zealand. J. Hydrol. 436-437: 13-34.

Reily, J.A., Steinhorst, R.K., Winter, G.V., and Williams, R.E., 1990. Statistical analysis of the hydrochemistry of ground waters in Colombia River Basalts, J. Hydrol, 119, 245–262.

Reimann, C., Filzmoser, P., Garrett, R.G., 2005. Background and threshold: critical comparison of methods of determination. Science of the Total Environment: Vol. 346, No. 1-3, pp. 1-16.

Renard, K.G., Service, U.S.A.R., 1997. Predicting Soil Erosion by Water: A Guide to Conservation Planning with the Revised Universal Soil Loss Equation (RUSLE). U.S. Department of Agriculture, Agricultural Research Service.

Rissmann, C., 2011. Regional Mapping of Groundwater Denitrification Potential and Aquifer Sensitivity, Technical Report. Environment Southland publication No 2011-12, Invercargill. 40p

Rissmann, C., 2012. Groundwater Quality Survey Results for Lower Waiau Nitrate Survey. Environment Southland, Invercargill. 11p.

Rissmann, C., 2012. The Extent of Nitrate in Southland Groundwaters Regional 5 Year Median (2007-2012 (June)) Technical Report. Environment Southland publication No 2012-09, Invercargill. 24p.

Rissmann, C., Wilson, K.L., Hughes, B.N., 2012. Waituna Catchment Groundwater Resources, Technical Report. Environment Southland publication No 2012-04, Invercargill. 92p.

Rissmann, C., Hodson, R., Meijer, K., 2013. Role of baseflow and catchment geology over the surface water biogeochemistry of the Waituna Catchment – Redox gradients and nutrient speciation. New Zealand Hydrological Society Conference, 2013.

Rissmann, C., Leybourne, M., Benn, C., Christenson, B., 2015. The origin of solutes with in the groundwaters of a high Andean aquifer. Chem. Geol., 396: 164-181/

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

Robert E., Gabler, J.F. Petersen, L., Trapasso, M., 2007. Essentials of Physical Geography. Eighth Edition

Rosen, M.R., 2001. Hydrochemistry of New Zealand's aquifers. Groundwaters of New Zealand, pp 77-110

Rupp, H., Meissner, R., Leinweber, P., 2004. Effects of extensive land use and re-wetting on diffuse phosphorus pollution in fen areas — results from a case study in the Dromling catchment, Germany. Journal of Plant Nutrition and Soil Science 167, 408–416

Salmon, J. T., 1992. A Field Guide to the Alpine Plants of New Zealand: Godwit.

Salvador, P., Artíñano, B., Pio, C., Afonso, J., Legrand, M., Puxbaum, H., Hammer, S., 2010. Evaluation of aerosol sources at European high altitude background sites with trajectory statistical methods. Atmospheric Environment, 44(19), 2316-2329.

Sanyal, S.K., Dedatta., 1991. Organic Phosphorus.

Schmidt, J., Almond, P.C., Basher, L., Carrick, S., Hewitt, A.E., Lynn, I.H., Webb, T.H., 2005. Modelling loess landscapes for the South Island, New Zealand, based on expert knowledge. New Zealand Journal of Geology and Geophysics, 48(1): 117-133.

Schüring, J., Schulz, H. D., Fischer, W. R., Böttcher, J., Duijnisveld, W. H. M., 2013. Redox: Fundamentals, Processes and Applications: Springer Berlin Heidelberg.

Scott, K., Pain, C., 2009. Regolith Science. CSIRO PUBLISHING.

Scott, C.A., Geohring, L.D., Walter, M.F., 1998. Water quality impacts of tile drains in shallow, sloping, structured soils as affected by manure application. Applied Engineering in Agriculture, 14 (6): 599-603.

Scotter, D.R., Clothier, B.E., Turner, M.A., 1979. The soil water balance in a Fragiaqualf and its effect on pasture growth in central New Zealand. Australian Journal of Soil Research 17, 455-465.

Shenker, M., Seitelbach, S., Brand, S., Haim, A., Litaor, M.I., 2005. Redox reactions and phosphorus release in reflooded soils of an altered wetland. European Journal of Soil Science 56, 515–525.

Sinclair, A.J., 1974. Selection of threshold values in geochemical data using probability graphs. Journal of Geochemical Exploration: Vol. 3, No. 2, pp. 129–149.

Sinclair, A.J., 1991. A fundamental approach to threshold estimation in exploration geochemistry: probability plots revisited. Journal of Geochemical Exploration: Vol. 41, No. 1-2.

Singh, R., Horne, D., 2014. Southland subsurface drainage management – exploring the way forward. Environment Southland Meeting, 29-30th May, 2014, Invercargill, New Zealand.

Singh, R., Rivas, A. Espanto, P., Elwan, A., Horne, D., Roygard, J., Matthews, A., Clothier, B., 2014. Assessment of transport and transformation of nitrogen in the subsurface environment of Manawatu River catchment – work-in-progress. In: Nutrient management for the farm, catchment and community. (Eds Currie, L.D. and Christensen, C.L.). http://flrc.massey.ac.nz/publications.html. Occasional Report No. 27. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand, 11 pp.

Smith, L.C., Monaghan, R.M., 2003. Nitrogen and phosphorus losses in overland flow from a cattle-grazed pasture in Southland. New Zealand Journal of Agricultural Research, 46(3): 225-237.

Snelder, T., Fraser, C., Hodson, R., Ward, N., Rissmann, C., Hicks, A., 2014. Regional Scale Stratification of Southland’s Water Quality- Guidance for Water and Land Management. Aqualinc, prepared for Southland Regional Council, Report # C13055/02 pp90.

Sposito, B.G., 2008. The Chemistry of Soils. Oxford University Press, USA.

Stenger. R., Clague, J., Woodward, S., Moorhead. B., Wilson, S., Shokri, A., Wohling, T., Canard, H., 2013. Denitrification – the key component of a groundwater system's assimilative capacity for nitrate. In: *Accurate and efficient use of nutrients on farms*. (Eds L.D. Currie and C L. Christensen). http://flrc.massey.ac.nz/publications.html. Occasional Report No. 26. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand, 11 pp.

Stenger. R., Clague, J., Woodward, S., Moorhead. B., Wilson, S., Shokri, A., Wohling, T., Canard, H., 2014. Rootzone losses are just the beginning. In: Nutrient management for the farm, catchment and community. (Eds L.D. Currie and C.L.Christensen). http://flrc.massey.ac.nz/publications.html. Occasional Report No. 27. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand, 8 pp.

Stevenson, F.J., 1986. Cycles of Soil: Carbon, Nitrogen, Phosphorus, Sulphur, Micronutrients. John Wiley and Sons.

Stevenson, F.J., 1994. Humus Chemistry, Genesis, Composition, Reactions: 2nd Edition.

Stumm, W., Morgan, J.J., 1981. Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters. New York: Wiley-Interscience. 780 p

Sun, L., Leybourne, M.I., Rissmann, C., Olariu, J.S., Lake Study Group., 2014. Geochemistry of a large impoundment, Part I: solute sources, mixing dynamics, and seasonal anoxia.

Summerfield, M.A., 2000. Geomorphology and global tectonics. Wiley.

Syers, J.K., Walker, T.W., 1969. Phosphorus Transformations and a Chronosequence of Soils Developed on a Wind-blown Sand in New Zealand. Journal of Soil Science: vol 20 i) Total and Organic Phosphorus (p53-57) Inorganic Phosphorus (p308-318).

Syers, S.K., Adams, J.A., Walker, T.W., 1970. Accumulation of Organic Matter in a Chronosequence of Soils Developed on Wind blow and New Zealand. Journal of Soil Science, Vol 21.

Taboada, M.A., 2003. Soil Shrinkage Characteristics in Swelling Soils. Lecture given at the College on Soil Physics, Trieste, 3-21 March, Buenos Aires, Argentina.

Thaysen, E., Jacques, D., Laloy, E., 2013. CO2 fluxes to aquifers beneath cropland: merging measurements and modeling, Hydrus conference, Praha, Czech Republic. Oral Presentation and conference paper.

Thaysen, E.M., Jessen, S., Ambus, P., Beier, C., Postma, D., Jakobsen I., 2014. Mesocosm approach to quantification of carbon dioxide fluxes across the vadose zone. Biogeosciences 11: 1077–1084.

Toner, C.V., Sparks, D.L., Carski, T.H., 1989. Anion exchange chemistry of Middle Atlantic soils: charge properties and nitrate retention kinetics. Soil Science Society of America Journal 53.4: 1061-1067.

Tratnyek, P.G., Grundl, T.J., Haderlein, S.B. (editors). 2012. Aquatic Redox Chemistry. American Chemical Society symposium series 1071; Oxford University Press, 20.

Turnbull, I.M. (compiler), 2000: Geology of the Wakatipu area: scale 1:250,000. Lower Hutt: Institute of Geological & Nuclear Sciences. Institute of Geological & Nuclear Sciences 1:250,000 geological map 18. 72 p. + 1 folded map

Turnbull, I.M., Allibone, A.H. (compilers), 2003: Geology of the Murihiku area: scale 1:250,000. Lower Hutt: Institute of Geological & Nuclear Sciences Limited. Institute of Geological & Nuclear Sciences 1:250,000 geological map 20. 74 p. + 1 folded map

Turnbull, I.M.; Allibone, A.H.; Jongens, R. (compilers), 2010: Geology of the Fiordland area: scale 1:250,000. Lower Hutt: GNS Science. Institute of Geological & Nuclear Sciences 1:250,000 geological map 17. 97 p. + 1 folded map

US Epa method http://www3.epa.gov/epawaste/hazard/testmethods/sw846/ pdfs/1312.pdf, Accessed 2.11.15

Velde, B.B., Meunier, A., 2008. The Origin of Clay Minerals in Soils and Weathered Rocks: With 23 Tables. Springer Science & Business Media.

Vroblesky, D.A., Chapelle, F.,1994. Temporal and spatial changes of terminal electron-accepting processes in a petroleum hydrocarbon-contaminated aquifer and the significance for contaminant biodegradation. Water Resources Research, 30, (5), pp. 1561–1570.

Walker, T.W., Syers, J.K., 1976. The fate of phosphorus during pedogenesis. Geoderma, 15: 1-19.

Wardle, J., 1984. New Zealand Beeches – Ecology Utilisation and Management; Pub: NZ Forestry Service.

Watson, C.J., Jordan, C., Lennox, S.D., Smith, R.V., Steen, R.W.J., 2000. Inorganic Nitrogen in Drainage Water from Grazed Grassland in Northern Ireland. Journal of Environmental Quality 29.

Watters, W. A., 1952. The geology of the Eastern Hokonui Hills, Southland, NZ. Transactions of the Royal Society of New Zealand. Vol. 79.

Weathering and Landscape Evolution. Proceedings of the 35th Binghampton Symposium in Geomorphology. October, 2004. Edited by A. Turkington, J. Phillips and S. Campbell.

Webb, T., Hewitt, A., Lilburne, L., McLeod, M., 2010. Mapping of vulnerability of nitrate and phosphorus leaching, microbial bypass flow, and soil runoff potential for two areas of Canterbury.

Wells, N. 1973. The properties if New Zealand soils in relation to effluent disposal. Geoderma 10, 123-130.

Wiebe, R., Gaddy, V.L., 1940. The Solubility of Carbon Dioxide in Water at Various Temperatures from 12 to 40 and at Pressures to 500 Atmospheres. Critical Phenomena*J. Am. Chem. Soc., 62: 815, **doi:**10.1021/ja01861a033.

Wilson, K., 2011. Riversdale Groundwater Management Zone, Technical Report. Environment Southland, Invercargill. 47p.

Wilson, K., 2011. State of the Environment: Groundwater Quantity, Technical Report. Environment Southland, Invercargill. 96p.

Woodward, S.J.R., Stenger, R., Bidwell, V.J., 2013. Dynamic analysis of stream flow and water chemistry to infer subsurface water and nitrate fluxes in a lowland dairying catchment. Journal of Hydrology, 505: 299-311.

Woodward, S.J.R., Barker, D.J., Zyskowski, R.F., 2001. A practical model for predicting soil water deficit in New Zealand pastures. New Zealand Journal of Agricultural Research 44, 91-109.

Zhang, W., Tang, X.-Y., Weisbrod, N., Zhao, P., Reid, B.J. 2015. A coupled field study of subsurface fracture flow and colloid transport. Journal of Hydrology 524, 476-488.

Zhang Y, Wu Y, Su J, Wen X, Liu F., 2005. Groundwater replenishment analysis by using natural isotopes in Ejina Basin, Northwestern China. Environmental Geology 48: 6–14.

Zobrist, J., Drever, J.I., 1990. Weathering processes in alpine watersheds sensitive to acidification. In: Johannessen, M., Mosello, R., Barth, H (Eds). Acidification Processes in Remote Mountain Lakes, CEC Brussels (Belgium), p. 149 -161.

6.1 Websites

http://www.cropssouthland.co.nz/topoclimate.asp

http://www.topoclimate-south.co.nz/

http://www.venturesouthland.co.nz/Economic-Development/Regional-Projects/Agriculture-and-Food/Topoclimate

https://www.soils.landcareresearch.co.nz/contents/index.aspx

6.2 Geology data

Geology data was sourced from the digital 1:250,000 geological map coverage produced by the Institute of Geological and Nuclear Sciences:

http://www.gns.cri.nz/Home/Our-Science/Earth-Science/Regional-Geology/Geological-Maps/1-250-000-Geological-Map-of-New-Zealand-QMAP

Background geological references cited include:

Isaac, M.J., Lindqvist, J.K., 1990. Geology and lignite resources of the East Southland Group, New Zealand. New Zealand Geological Survey Bulletin 101.

Rodway, E.M., 2012. Ti-in-Quartz Geothermometry and Sediment Provenance in the Western Southland Basins. A thesis submitted for the degree of Master of Science, University of Otago, Dunedin, New Zealand. 173 p.

Turnbull, I.M., 1995. Geology of the Monowai – Waitutu area. Scale 1:50 000. Institute of Geological and Nuclear Sciences geological map 19. Lower Hutt, Institute of Geological and Nuclear Sciences. 2 sheets & 68p.

Turnbull, I.M., 2000. Geology of the Wakatipu Area. Lower Hutt, Institute of Geological & Nuclear Sciences Ltd. Institute of Geological and Nuclear Sciences 1:250,000 geological map 18. 1 sheet and 72 p.

Turnbull, I.A., Allibone, A.H., 2003. Geology of the Murihiku Area. Institute of Geological & Nuclear Sciences 1:250,000 geological map 20. 1 sheet and 74 p. Lower Hutt, Institute of Geological and Nuclear Sciences Ltd.

Turnbull, I.M., Allibone, A.H., Jongens, R., 2010. Geology of the Fiordland Area. Institute of Geological & Nuclear Sciences 1:250,000 geological map 17.

6.3 Hydrology Data and Sources

Hydrology data was sourced from the Environment Southland environmental data archive (rainfall, soil moisture, stream flow) and the NIWA virtual climate station (VCN) network (rainfall and evapotranspiration).

Background hydrology references include:

Hitchcock, K.M., 2014. Characterising the surface and groundwater interactions in the Waimatuku Stream, Southland. A thesis submitted in partial fulfilment for the degree of Master of Science in Geography at the University of Otago, Dunedin, New Zealand.

Hughes, B., 2003. Mid-Mataura Water Resource Zone. Unpublished Environment Southland Report. 17p.

Hughes, B., 2003. Upper Mataura Water Resource Zone. Unpublished Environment Southland Report. 11p.

Lincoln Environmental, 2003. Southland Water Resources Study - Stages 1 to 3. Report No 4597/1. Prepared for Venture Southland, September 2003.

Wilson, K., 2008. Surface Water and Groundwater Relationships in the Mataura Catchment above Gore. Environment Southland Publication No. 2008-03.

6.4 Hydrogeology Data and Sources

Hydrogeology data was sourced from the Environment Southland Wells database (bore logs, manual groundwater level measurements, aquifer hydraulic properties) and the Environment Southland environmental data archive (automatic groundwater level monitoring data).

Background hydrogeological references include:

Blakemore, H.N., 2006. A geophysical study of the Oreti Basin groundwater system. Thesis submitted for the degree of Master of Science of the University of Otago, Dunedin, New Zealand.

Chanut, P., 2014. Seasonality of land surface recharge in Southland. Environment Southland Report, April 2014.

Durie, M.A., 2001. Hydrogeology of the Eastern Southland Plains, New Zealand. A thesis submitted in partial fulfilment of the requirements for the degree of Master of Science in Engineering Geology at the University of Canterbury

Environment Southland; 2006. Groundwater Management Zone information sheets. http://www.es.govt.nz/environment/water/groundwater/management-zones/

Güler, C., Thyne, G.D., McCray, J.E., Turner, A.K., 2002. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. *Hydrogeology Journal* 10:455, pp 455-474

Hughes, B., 2003. Proposed Framework for Groundwater Allocation in the Southland Region. Draft report to Environment Southland, June 2003.

Hughes, B., 2012. Knapdale groundwater zone technical report. Report prepared for Environment Southland, June 2012.

Lincoln Environmental, 2003. Southland Water Resources Study - Stages 1 to 3. Report No 4597/1. Prepared for Venture Southland, September 2003.

Liquid Earth, Aqualinc Research, Harris Consulting, 2011. Mataura Catchment Strategic Water Study. Report prepared for Environment Southland.

Phreatos Limited, 2007. Mid-Mataura Groundwater Model. Report prepared for Environment Southland.

Rissman, C., Wilson K., Hughes, B., 2012. Waituna Catchment Groundwater Resource. Environment Southland Publication No. 2012-04, May 2012.

SKM, 2005. Hydrogeology of the Oreti Basin. Report prepared for Environment Southland, July 2005.

SKM, 2008. Management of Confined Aquifers in the Southland Region. Report prepared for Environment Southland, February 2008.

Wilson, K., 2010. Groundwater Report on the Balfour Groundwater Quality Study. Environment Southland Report, July 2010.

Wilson, K., 2010. Edendale Groundwater Management Zone Technical Report. Environment Southland Report, October 2010.

Wilson, K., 2011. State of the Environment: Groundwater Quantity Technical Report. Report prepared for Environment Southland, February 2011.

Wilson, K., 2011. Riversdale Groundwater Management Zone Technical Report. Environment Southland Report, October 2011.

Wilson, S., Chanut, P., Rissman, C., Ledgard, G., 2014. Estimating Time Lags for Nitrate Response in Shallow Southland Groundwater. Environment Southland Publication No. 2014-03, April 2014.