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

Technical Report

June 2016

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Document Quality Control

Document History

Version:	2	Status:	Preliminary
Date:	November 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.

Physiographics of Southland

Part 1:

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Technical Chapter 1:

Precipitation

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Document Quality Control

Environment Southland Division:	Environmental Information		
Report reference:	Title: Technical Chapter 1: Precipitation		No: 2016/3
Prepared by:	Rodway, E., Rissmann, C., Beyer, M., Marapara, T. R., Hodgetts, J.		
Key Technical Reviewers:	Daughney, C., Hughes, B., Horton, T.		
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Approved for issue by:	Graham Sevicke-Jones Director, Science and Information		
Date issued:	1 June 2016	Project Code:	4065.1446

Document History

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Technical Chapters

Supporting geochemical and hydrological analysis

These Technical Notes aim to support the conceptual model and maps of hydrochemistry affecting the key driver maps presented in the main chapters of this report. It is the intention of the authors that the following Technical Chapters are not viewed in isolation. Rather each chapter contributes essential detail in building a regional view of the key drivers governing the hydrochemistry of regional ground and surface waters and hence regional water quality outcomes. Whereas some Technical Chapters elucidate and develop a map of a key hydrochemical driver (i.e., recharge mechanism, precipitation source and composition, landform type and age along with parent material composition and redox controls), others build upon the conceptual framework for accurately interpreting the spatial variation in regional hydrochemistry. Most Technical Chapters are structured as introduction, methods, results, conclusion to help guide the reader through the extensive and complex analysis carried out in this study on a variety of samples.

TC1 Southland Precipitation

TC1.1 Introduction

In maritime environments such as New Zealand, marine derived salts dominate the chemical composition of precipitation that falls on the land surface (Nichol et al., 1997; Rosen, 2001). Marine aerosols are created when bubbles produced by breaking waves burst on the water surface producing salt aerosols that ascend into the atmosphere. They are sequestered into the forming cloud mass or scrubbed out of the atmosphere in falling precipitation. As a consequence, over the ocean or in coastal settings, the major ion composition of precipitation is similar, albeit far more dilute, to that of seawater.

The concentration and composition of dissolved marine salts within the cloud mass can change dramatically with distance from the ocean or with elevation as does precipitation volume. Marine salts are 'rained out' as the cloud mass moves inland, resulting in progressively more dilute precipitation. We found that the composition and concentration of aerosols of precipitation samples varies greatly across Southland. The most prominent controls over variation in chemical signature (and precipitation volume) are altitude and secondly distance from the coast, expressed as latitude.

We demonstrate that precipitation composition, primarily Na and Cl load, is strongly influenced by marine aerosol rainout. The spatial variability in the concentration of Na and Cl is primarily driven by precipitation volume. Further, we note that altitude and latitude determine the fractionation of the stable isotopes of water (δ^{18}O-H_2O and δ^2H-H_2O) that are key indicators of water source. Both Cl and the stable isotopes of water are considered 'ideal' tracers of water source due to their conservative behaviour. Therefore we identified precipitation 'types' (with significantly different aerosol loads and compositional signatures) and the drivers responsible for variability in precipitation type. We compared precipitation composition against that of surface and shallow groundwater with a view to a more resolved assessment of water origin and source in TC 2. As an outcome of this chapter, we developed a map of regional precipitation characteristics including source and marine aerosol load.

TC1.2 Precipitation characteristics

To assess the characteristics of Southland's precipitation, we examined the spatial distribution of regional precipitation volume, illustrated in Figure 1-1. Further, we examined the chemical signature of a total of 113 precipitation (rain, hail and snow) samples that have been collected across Southland over a five year period (2011 – 2015). Table 1-1 summarises the major components of Southland's precipitation.

As expected, Southland precipitation volumes vary greatly spatially with Fiordland receiving the highest precipitation volumes (> 4000mm/year) and lowland and northern Southland receiving the lowest precipitation volumes. It is apparent from Figure 1-1 that the spatial distribution of precipitation volumes is strongly influenced by altitude due to orographic rainfall (i.e. the higher altitude areas receive higher volumes of precipitation), and prevailing wind direction in combination with topography resulting in rain shadow effects (i.e. lowest precipitation volumes in northern Southland).

Southland precipitation exhibits major ion compositions similar to that of seawater, variably dilute Na-Cl waters, with marine-derived aerosols decreasing in magnitude from Cl > Na > SO$_4$ > Mg. Other major ions such as Ca and K constitute less than 5% of the total dissolved ions.
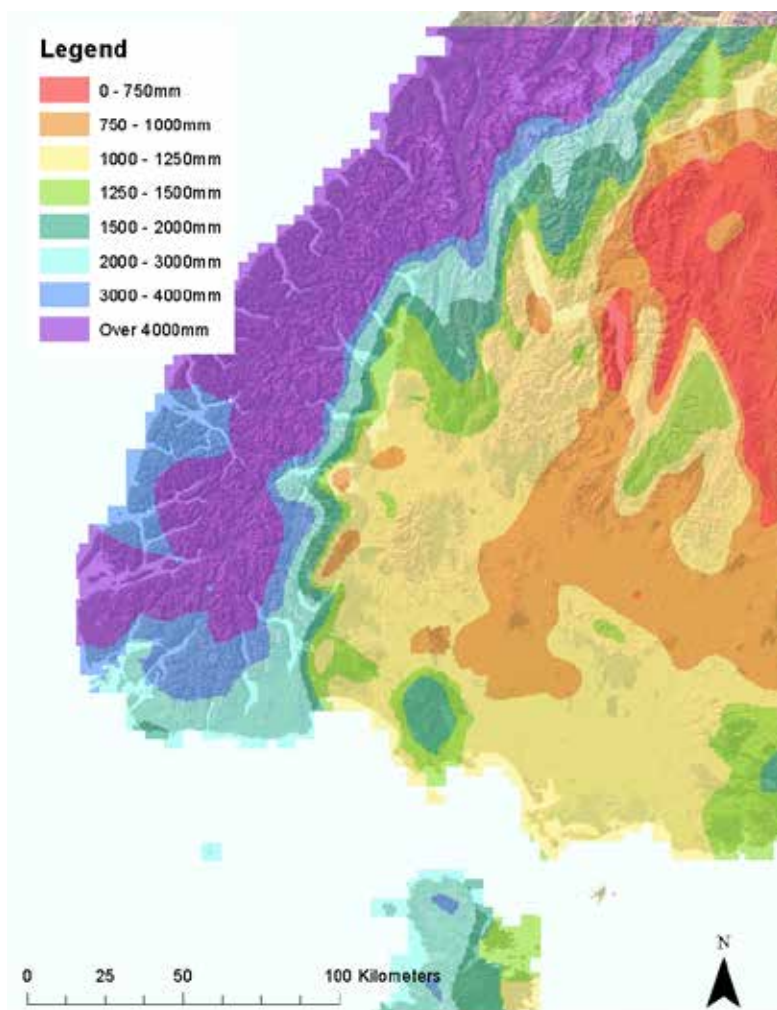
Figure 1-1: Spatial distribution of yearly precipitation volumes across Southland using data from 1960 to 2010

Table 1-1: Median and Standard Deviation (SD) values for selected analytes for all Southland precipitation samples, 'Total' refers to total concentration i.e. determined in unfiltered samples. 'Dissolved' refers to dissolved concentration i.e. determined in filtered water samples.

Analytes	n	Median	SD
Alkalinity as HCO$_3$(Total) [mg/L]	91	2.50	1.11
Calcium (Dissolved) [mg/L]	112	0.38	0.48
Chloride (Total) [mg/L]	112	2.70	6.79
Conductivity (Lab) [uS/cm]	109	15.00	23.88
Iron (Dissolved) [mg/L]	74	0.02	0.01
Magnesium (Dissolved) [mg/L]	112	0.25	0.47
Nitrogen (Total) [mg/L]	92	0.11	0.13
Phosphorus (Total) [mg/L]	82	0.01	0.06
Potassium (Dissolved) [mg/L]	112	0.18	0.16
Sodium (Dissolved) [mg/L]	112	1.77	3.97
Sulphate (Total) [mg/L]	112	0.90	0.98
pH (Lab)	99	5.80	0.36
Isotope Delta ^{18}O-H$_2$O [ppt VSMOW]	23	-5.40	4.17

All of Southland's precipitation data falls along the Sea Water Dilution Line (SWDL) indicating a major ion composition that is similar to that of seawater across the entire concentration range (Figure 1-2,

Figure 1-3 and Figure 1-4), although there is evidence of a minor (<1 mg/L) terrigenous component for Ca, probably associated with airborne clays as dust (Figure 1-5). A similar relationship of chloride and sodium, with most samples plotting near the SWDL, is also found for Southland's surface and groundwater (TC 1.5, Figure 1-12).

The composition of snow and rain samples varies greatly across Southland. For example, electrical conductivity (EC), as an indicator of the amount of dissolved salts in water, varies between <0.05 – 134 µS/cm (Table 1-1). Not surprisingly, the samples with the lowest conductivity correspond to the highest and most inland sites within the northern mountains and those with the highest conductivity predominantly occur at low altitude and are closest to the southern coast (Figure 1-10) mirroring spatial patterns in precipitation volumes (Figure 1-1). Importantly, ion ratios also change as a result of differing rainout mechanisms of marine derived aerosols, in particular for Na, Cl and SO_4 and Ca.
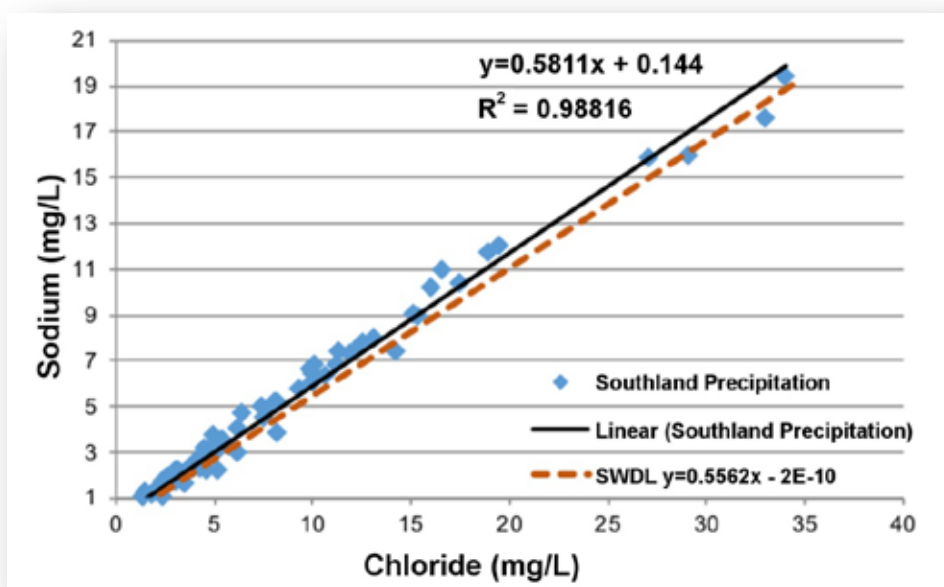

Figure 1-2: Chloride vs. sodium for all Southland precipitation samples as compared to the Sea Water Dilution Line SWDL.
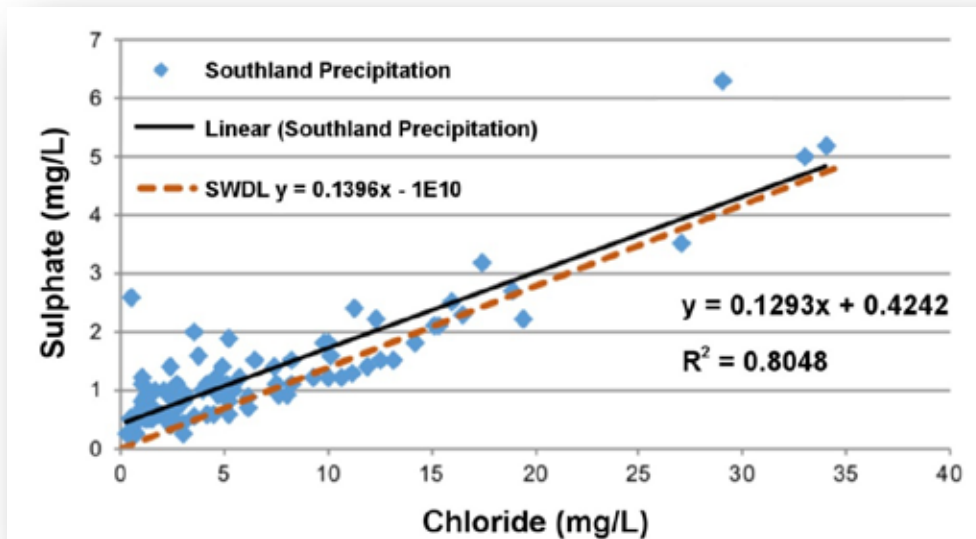
Figure 1-3: Chloride vs. sulphate for all Southland precipitation samples as compared to the SWDL.
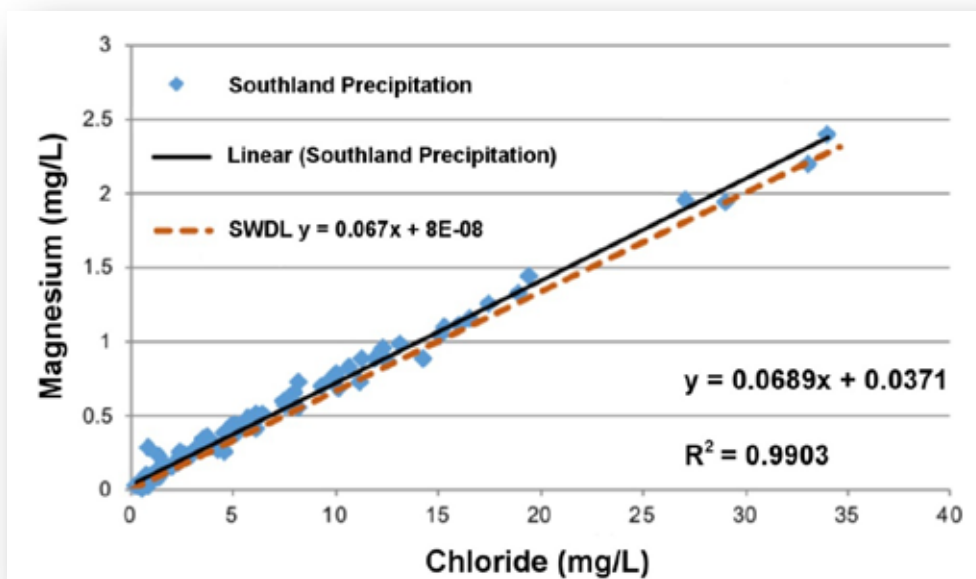

Figure 1-4: Chloride vs. magnesium for all Southland precipitation samples as compared to the SWDL.
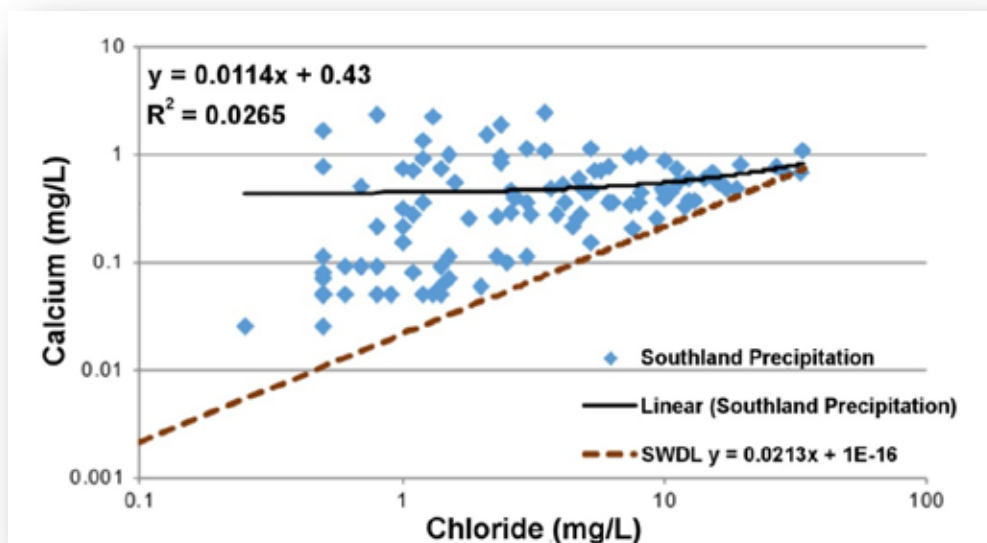
Figure 1-5: Chloride vs. Calcium for all Southland precipitation samples compared to the SWDL.

TC1.3 Drivers of variability

To identify covariance among chemical parameters and infer drivers of variability in the composition i.e., concentration of marine aerosols and major ion ratios of Southland's precipitation, Principal Component Analysis (PCA) was applied to 113 samples. The parameters considered in the PCA were Ca, Cl, K, Na SO_4, Mg, northing and elevation, for further detail on the PCA methods see Appendix C.

Multiple combinations of variables were trialled within the PCA in an attempt to find the best explanation of variance. Alkalinity was not included as a variable as all snow samples show relatively elevated alkalinities and isotopic δ^{13}C-DIC signatures[1] (-24.5 to -19.4 ‰ VPDB) typical of a soil respired CO_2 source. Soil derived δ^{13}C-DIC signatures for snowpack samples taken from high altitude sites (up to 1756 m RSL) are especially remarkable where the accumulated snow pack overlies scree and talus, indicating a soil respired CO_2 flux accumulating within the overlying snow pack. A strong linear relationship between sample alkalinity and δ^{13}C-DIC is consistent with a greater soil respired CO_2 contribution for the most depleted samples (Figure 1-6). Isotopically heavier values coincide with lower alkalinity values indicating the mixing between atmospheric and soil respired CO_2 sources. There is no evidence of a relationship between altitude and δ^{13}C-DIC.

Principal Component Analysis identified only one significant component with an Eigenvalue >1 over variance within the data that explains 72% of the variance in the composition of marine aerosols in Southland's precipitation (Table 1-2). Component 1 exhibits a negative loading for northing and elevation and positive loading for all other variables, except easting, indicating decreasing concentrations of major ions with increasing elevation (Table 1-3). Easting was found to have no significant effect over variance. Northing and elevation were found to be highly co-correlated and explained variance within the data to the same extent. This reflects the general increase in altitude with distance north of the southern coast.

These findings are consistent with the well-recognised and documented effects of altitude and distance inland from the coast on marine aerosol rainout (Ballance and Duncan, 1985; Nichols et al.,

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[1] δ^{13}C-DIC has been used as a tracer to distinguish sources of C e.g. in HCO3 or alkalinity, specifically to distinguish microbially respired and weathering induced C sources [USGS, 2016].

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1997; Haberecht and Kear, 2005; Guan et al., 2010). As previously stated, the concentration of dissolved marine salts within the cloud mass can change dramatically with distance from the ocean or with elevation. Salts are 'rained out' as the cloud mass moves inland resulting in progressively more dilute precipitation. Similarly, intense rainout of marine salts occurs where mountain ranges cause orographic forcing of the cloud mass. Accordingly, low altitude coastal precipitation typically has a much higher dissolved salt load than high altitude precipitation that has traversed mountain ranges and/or travelled considerable distances inland.
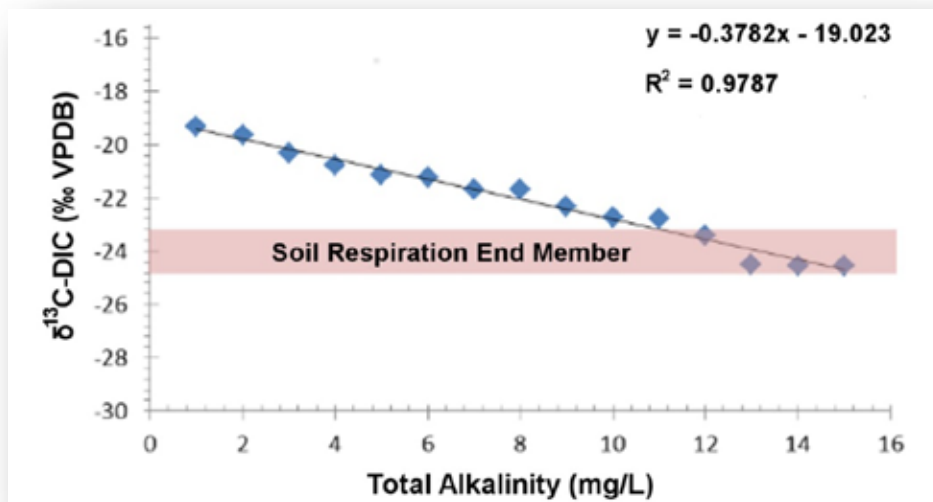

Figure 1-6: Strong linear relationship between the δ^{13}C-DIC and Total Alkalinity for Southland snow samples collected from accumulated snowpack.

Table 1-2: Summary of PCA results. PCA confirms only one significant component (eigenvalue > 1) and that this explains 72% of the data variance. Component 2 is included to show its non-significance.

Component No.	Eigenvalue	Cumulative Variance	Percent	Cumulative Percent
1	5.770	5.770	0.721	0.721
2	0.768	6.539	0.096	0.817

Table 1-3: Eigenvectors for each of the variables considered within the PCA.

Variables	Component 1	Component 2
Northing	-0.330	0.462
Elevation	-0.312	0.547
Calcium	0.293	0.514
Chloride	0.391	0.023
Magnesium	0.402	-0.017
Sodium	0.385	-0.133
Sulphate	0.344	0.267
Potassium	0.357	0.364

Scatter plots of EC vs. altitude (mRSL) and EC vs. northing (m) confirm this mechanism indicating quasi exponential trends of marine aerosol rainout, with altitude having the strongest control over the EC of the data set (Figure 1-7 and Figure 1-8). The magnitude of the decline in EC with elevation and northing is considerably larger than that previously reported by Nichol et al., (1997) who observed dissolved salt loads 5 to 10 times greater for coastal sites relative to inland sites in New Zealand. The sample with the lowest EC value (Moffat Peak snow sample, 0.05 µS/cm, altitude 1,756 m) being

2,680 times lower than the sample with the highest EC (Waituna at Lawson Road, 134 µS/cm, altitude 20 m, several km from the southern coast).
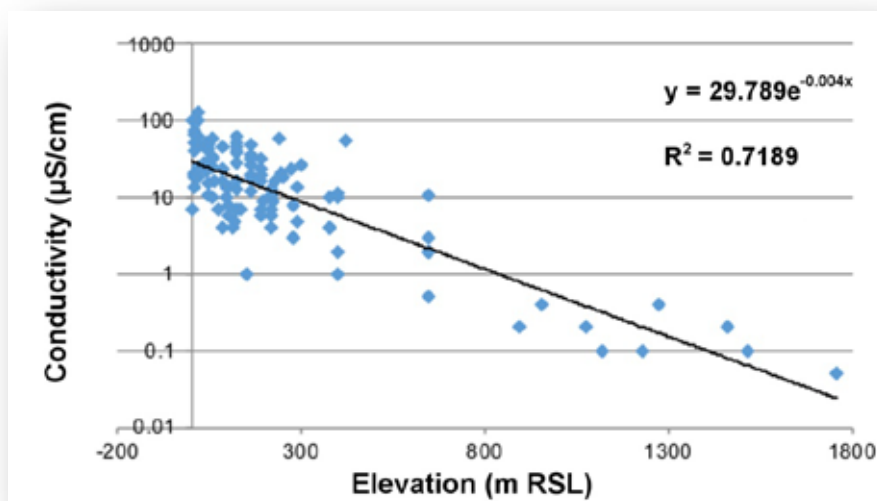
Figure 1-7: Relationship between electrical conductivity and elevation for Southland precipitation.
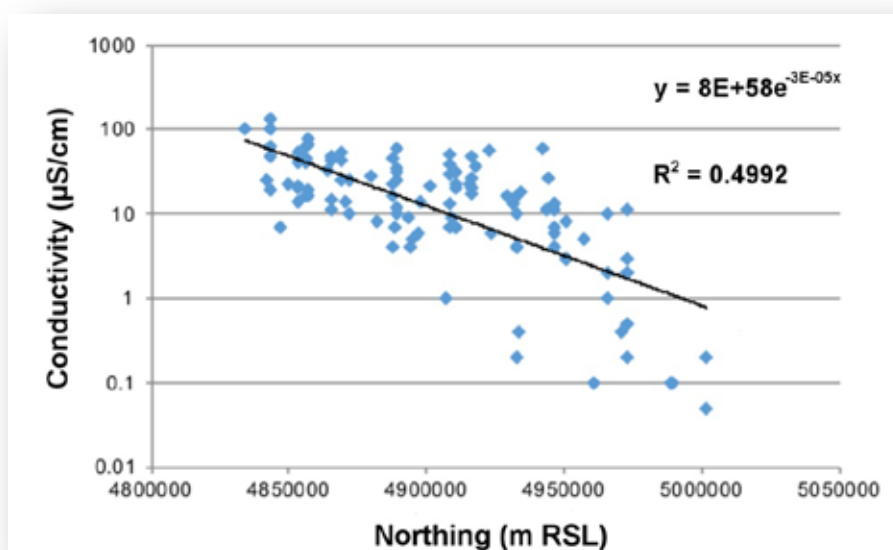
Figure 1-8: Relationship between northing as a proxy for distance from the coast and electrical conductivity for Southland precipitation.

TC1.4 Precipitation types

To identify different 'types' of precipitation, with significantly different major ion ratios and marine aerosol concentration in Southland, Hierarchal Cluster Analysis (HCA) was carried out on 113 precipitation samples. The parameters considered within the HCA were Ca, Cl, K, Na SO_4 and Mg, for further detail on the HCA methods see Appendix C.

HCA identified 2 and 3 clusters at the 600 and 200 phenon lines, respectively (Figure 1-9). At the 600 phenon line two broad clusters or 'types' of precipitation are evident, in the following referred to as Type 1 and Type 2 precipitation. Type 1 constitutes 71% of the data and Type 2 29%.
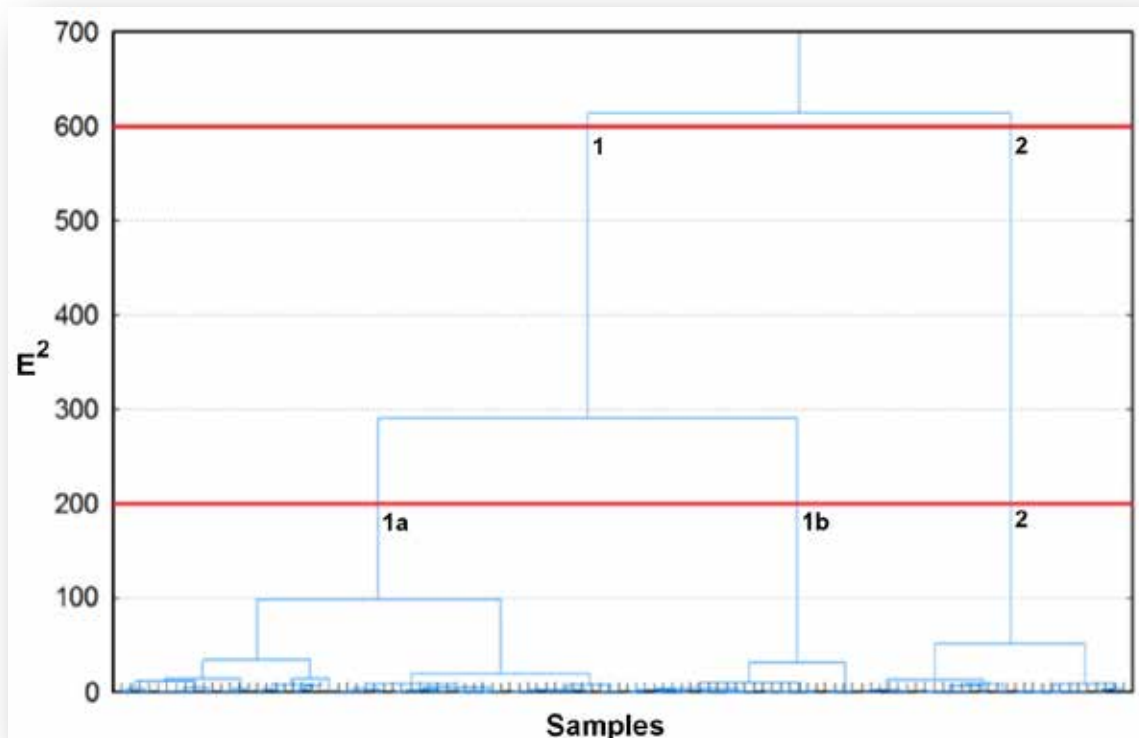
Figure 1-9: Dendrogram of Southland precipitation samples identifying cluster memberships at the 600 and 200 phenon lines, (red lines). Where the distance measured is the square of the Euclidian distance.

Table 1-4: Summary hydrochemistry statistics for each of the clusters identified at the 200 phenon level. * $\delta^{18}O$ values for the 1a cluster are highly influenced by sampling during a single summer precipitation event resulting in relatively enriched values.

Cluster	1a		1b		2	
	Median	SD	Median	SD	Median	SD
Elevation (mRSL)	147	135	53	90	389	499
Alkalinity (Bicarbonate) (mg/L as CaCO$_3$)	2.60	1.43	2.70	0.56	2.30	0.30
Calcium (Dissolved) (mg/L)	0.48	0.55	0.54	0.19	0.06	0.03
Chloride (Total) (mg/L)	2.85	2.16	12.80	7.46	0.75	0.69
Conductivity (Lab) (µS/cm)	16.00	14.26	51.00	22.69	2.50	3.85
Iron (Dissolved) (mg/L)	0.02	0.01	0.02	0.01	0.02	0.00
Magnesium (Dissolved) (mg/L)	0.25	0.16	0.92	0.50	0.07	0.06
Nitrogen (Total) (mg/L)	0.15	0.16	0.11	0.12	0.11	0.08
Phosphorus (Total) (mg/L)	0.02	0.09	0.00	0.02	0.00	0.00
Potassium (Dissolved) (mg/L)	0.18	0.13	0.37	0.14	0.05	0.03
Sodium (Dissolved) (mg/L)	1.79	1.38	7.70	3.96	0.59	0.54
Sulphate (Total) (mg/L)	0.90	0.41	1.95	1.32	0.50	0.12
pH (Lab) (pH units)	5.90	0.41	6.00	0.27	5.70	0.21
$\delta^{18}O$ (‰ VSMOW) *	-2.08	1.99	-7.36	0.00	-9.32	2.04
Ca/Cl ratio	0.168	-	0.042	-	0.080	-
SO$_4$/Cl ratio	0.316	-	0.152	-	0.667	-
CaHCO$_3$/Cl ratio	0.912	-	0.211	-	3.067	-

Type 1 precipitation is characterised by a mean EC of 29.7 μS/cm and mean Cl and Na concentrations of 7.2 and 4.3 mg/L, respectively, a mean altitude (135 m RSL) and has a less northern, inland aspect relative to Type 2 (Table 1-4).

Type 2 precipitation has a more dilute signature than Type 1 waters with a mean EC of 3.8 μS/cm (~8 times lower than Type 1) and Cl and Na concentrations of 1.0 and 0.7 mg/L, respectively. The mean altitude of Type 2 precipitation is 578 m RSL (median of 389 m RSL).

Importantly, ion ratios also differ for Type 1 and Type 2 precipitation suggesting differing rainout mechanisms, specifically of Cl, Na and SO_4 for Type 1 and Type 2 precipitation and terrigenous sources of Ca and alkalinity probably associated with airborne clays. Figure 1-10 illustrates the spatial distribution of the precipitation types in Southland at the 200 phenon line.

As indicated by its unique signature and distinct spatial distribution in Southland, Type 1 precipitation can be associated with the low to medium elevation areas of Southland and with coastal precipitation that appears to be channelled northward from the coast up incised river valleys of the Waiau and Mataura rivers. Type 1 precipitation also occurs across the large, low lying area of the south central and south eastern plains and the coastal Catlins (Figure 1-10). The south central and eastern plains, as well as the Catlins, are all exposed to the prevailing south-westerly air flow off the sea. Type 1 precipitation is also evident within the lowest lying portions of the Te Anau basin and the Waimea Plains.

Type 2 precipitation can be predominantly associated with the inland hill country and mountains of northern Southland. These waters are very dilute when compared to Type 1 waters. Several precipitation samples from low lying areas of Southland are classified as Type 2 waters; these are all snow samples collected from a single storm event (6–8 July, 2015).

At the 200 phenon line HCA identified three clusters or 'types' of precipitation. Type 2 waters are undifferentiated and represent the dilute high altitude precipitation described above. Type 1a and 1b waters provide resolution between the precipitation of the lowest altitude coastal regions and slightly more elevated inland areas (Figure 1-10). Type 1b precipitation is characterised by the highest concentrations of marine derived aerosols. Mean EC, Cl and Na concentrations are 56.9 μS/cm, 15.48 mg/L and 9.34 mg/L, respectively. In comparison, the mean EC, Cl and Na concentrations for Type 1a are 18.5 μS/cm, 3.32 mg/L and 2.00 mg/L, respectively. Mean elevations for Type 1a and Type 1b are 157 and 88 m RSL respectively. Due to differing precipitation sources and weather systems, the type of precipitation at any given site can vary between Type 1 and 2. This variation can be seen in some of the monthly rainfall collection sites, particularly in close proximity to high elevation areas, such as the Garvie Mountains, Umbrella Mountains and the Takitimu Mountains (Figure 1-10). Specifically, high intensity winter rainfall corresponds to high salt load, which is consistent with higher surface roughness, driving elevated marine aerosol load.

In summary, analysis of Southland's precipitation data has highlighted that spatial variation of hydrochemical signatures exist and can be linked to different precipitation sources. The most prominent controls over variation in chemical signature are the altitude and distance from the coast (i.e. latitude) -the key variable being a dramatic shift in the concentration of marine aerosols with altitude and distance from the coast.

We observed a large magnitude, quasi-exponential marine aerosol rainout effect in Southland precipitation resulting in high marine aerosol loads in the southern coastal regions and extremely low aerosol loads in the high altitude northerly areas of Southland. These highly spatially contrasting

differences in marine aerosol load play a major role in the hydrochemistry of Southland waters, as will be shown subsequently.

On the basis of the above findings, we mapped the areas that are likely to be dominated by Type 1b rainfall (red), Type 1a (yellow) and Type 2 (green). These categories were defined on the basis of upper and lower quartile elevation values for each cluster. The patterns elucidated in this map are similar to the ones defined through assessment of regional ground and surface water chemistry in the following (TC 2).
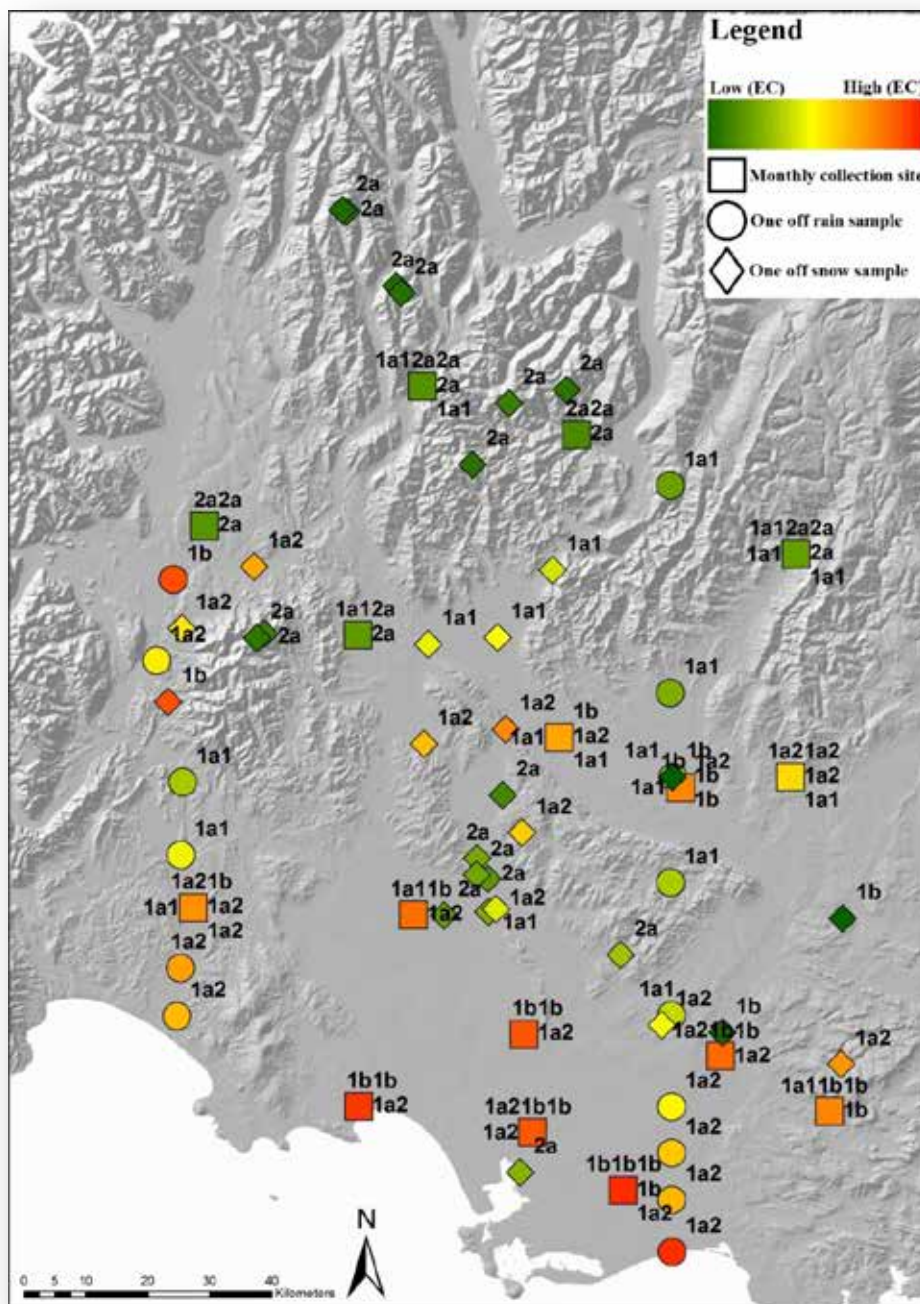

Figure 1-10: Map of Southland showing individual precipitation samples which are coloured according to conductivity, see legend, and labelled with the precipitation type at the 200 phenon level. The shape of the samples defines the type of sample, i.e. squares are monthly rainfall collection stations, circles are one off rainfall samples and diamonds are one off snow samples.

Specifically, we will show that differences in the composition of precipitation, in particular marine aerosol load, play a major role in Southland ground and surface water composition. Across the majority of lowland Southland, the concentration of marine aerosol derived Na and Cl overwhelm land use and endogenous soil and rock weathering. The endogenous sources have a significant effect only in high altitude alpine areas dominated by dilute Type 2a precipitation. With respect to the stable isotopes of water precipitation, signatures are retained. Understanding the relationship between precipitation source and subsequent hydrochemical signatures of regional waters is fundamental.
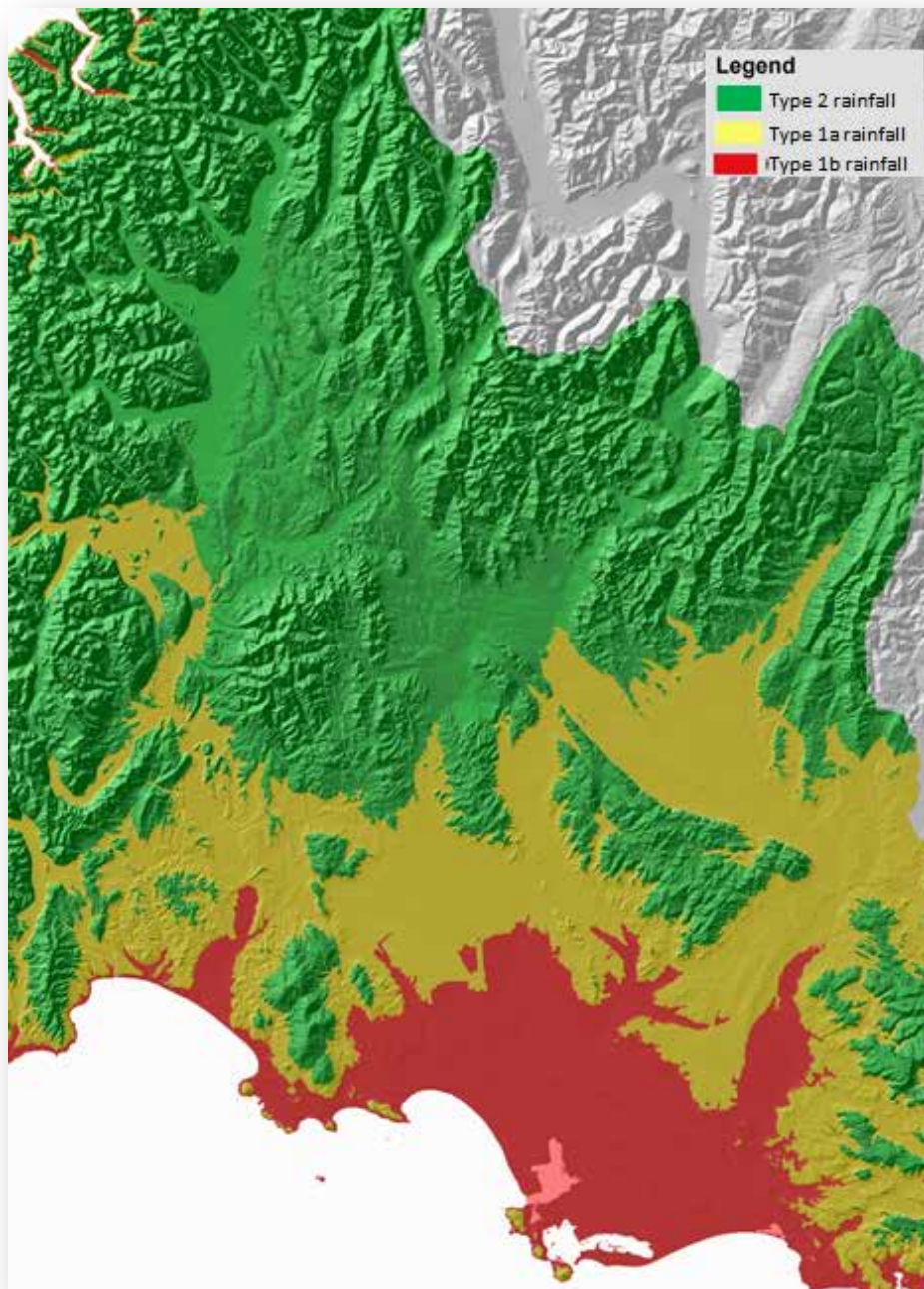
Figure 1-11: Map of Southland showing area likely to be dominated by Type 1b rainfall (red), Type 1a (yellow) and Type 2 (green). Map is coloured according to upper and lower quartile elevation values for each cluster. Area of elevation below the lower quartile of Type 1b was assigned to Type 1b and area above the upper quartile of Type 2 was assigned to Type 2. Note the interquartile ranges for clusters 1a and 1b overlap considerably.

TC1.5 Precipitation Source Signatures in Regional Ground and Surface Waters

Across Southland, a total of 2,546 groundwater samples at 403 sites and a total of 19,097 surface water samples at 339 sites have been collected since 1986 and 1975, respectively. However, not until comparatively recently, 2011, has an extended hydrochemical suite been applied uniformly across the region, measuring the same key analytes for both ground and surface water. Figure 1-12 shows that ground and surface waters plot along the SWDL indicating chemistry very similar to that of precipitation. However, it is important to note that because of the concentration of marine aerosolic Na and Cl by evapotranspiration, Na and Cl concentrations are much higher in regional ground and surface waters than in precipitation occurring at the same altitude, compare Figure 1-10 to Figure 1-13.

Dilute groundwater samples plot above the SWDL indicating minor Na enrichment in both ground and surface water (further assessed in TC 5.2). This is a result of soil, and/ or rock interaction. The contribution from epigenic mineral weathering is most apparent for dilute high altitude waters whereas the weathering related signature is swamped by marine aerosolic Na across low altitude areas.
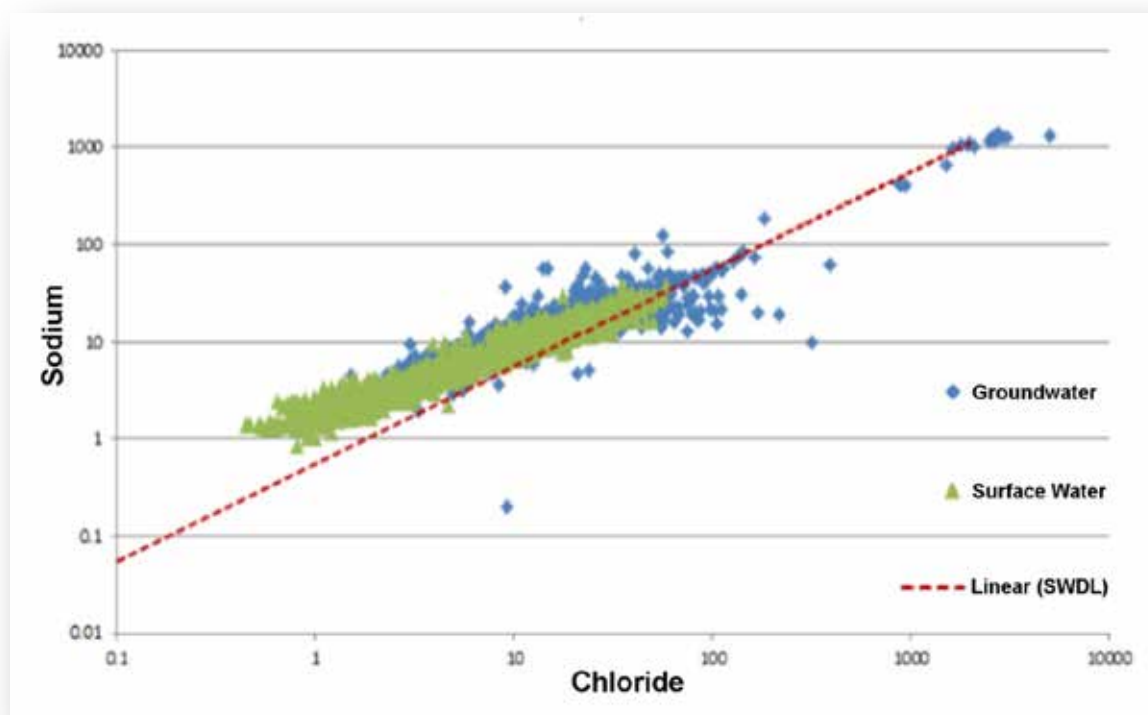
Figure 1-12: Chloride vs. sodium for Southland groundwater and surface waters as compared to the SWDL (sea water dilution line).

When assessing the spatial distribution of $\delta^{18}O$-H_2O values, Cl and Na concentrations, and EC in ground and surface water in Figure 1-13and Figure 1-14, one can observe similar patterns to those observed for precipitation (presented in TC 1).

TC1.5.1 Cl concentrations in ground and surface water
Figure 1-13 illustrates the spatial distribution of Cl concentrations in ground and surface water across the Southland Region. The figure shows a pronounced, albeit generalised, inland gradient in

concentration, which follows the marine aerosolic loading observed in precipitation (see Figure 1-10 and Figure 1-11). Also apparent is that altitude plays an important role over the relative concentration of Cl for the Waimea Plains and other inland areas of northern Southland that constitute topographic lows and show therefore a greater incidence of Type 1 recharge. The gradient in Cl concentration is unrelated to increased precipitation volume as demonstrated by analysis of alpine soils leachate in TC4.
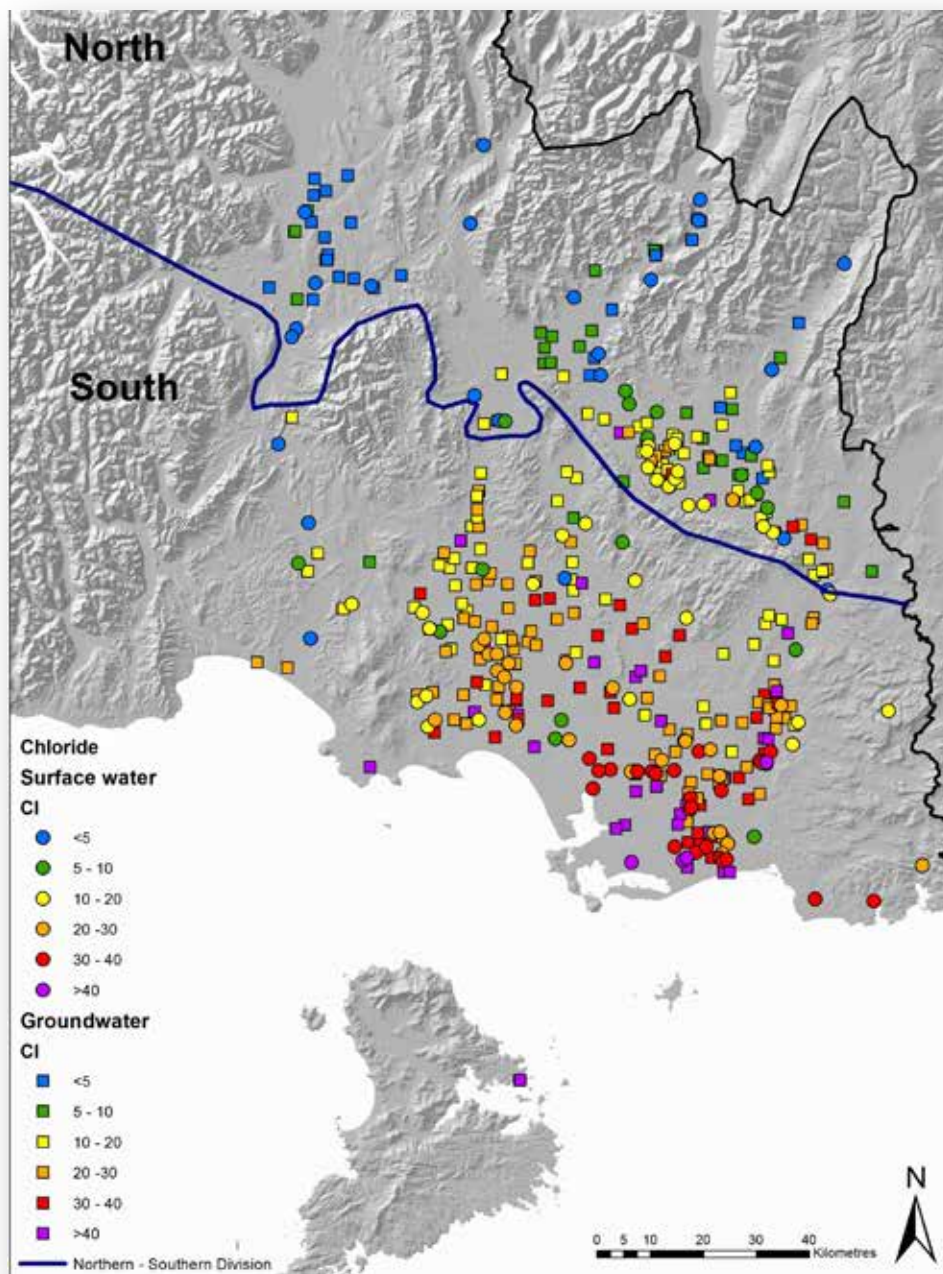

Figure 1-13: Plot of median Cl concentration for Southland ground and surface waters. Note the strong transition in source signature that also mimics that of precipitation for the region. Differences are particularly apparent between northern and southern Southland.

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TC1.5.2 Cl:δ^{18}O-H$_2$O ratio of surface and groundwater

Figure 1-14 shows a similar spatial variation for the Cl:δ^{18}O-H$_2$O ratio of surface and groundwater across the region. Inland waters exhibit low Cl concentrations and depleted δ^{18}O-H$_2$O signatures while coastal waters show elevated Cl concentrations and less depleted δ^{18}O-H$_2$O values, with the isotopic signature of alpine precipitation carried down to the lower reaches of the main stem rivers. Na:δ^{18}O ratios across Southland show a similar pattern with some anomalies (particularly in the alpine regions) due to the low marine aerosolic Na and Cl load of precipitation falling in high altitude inland areas. Consequently, at high altitudes Na is predominantly derived from weathering resulting in a divergence from the SWDL for dilute high altitude waters (see Figure 1-2 and TC 3.1). At low altitudes the minor Na contribution from weathering is swamped by the much larger marine aerosolic load.

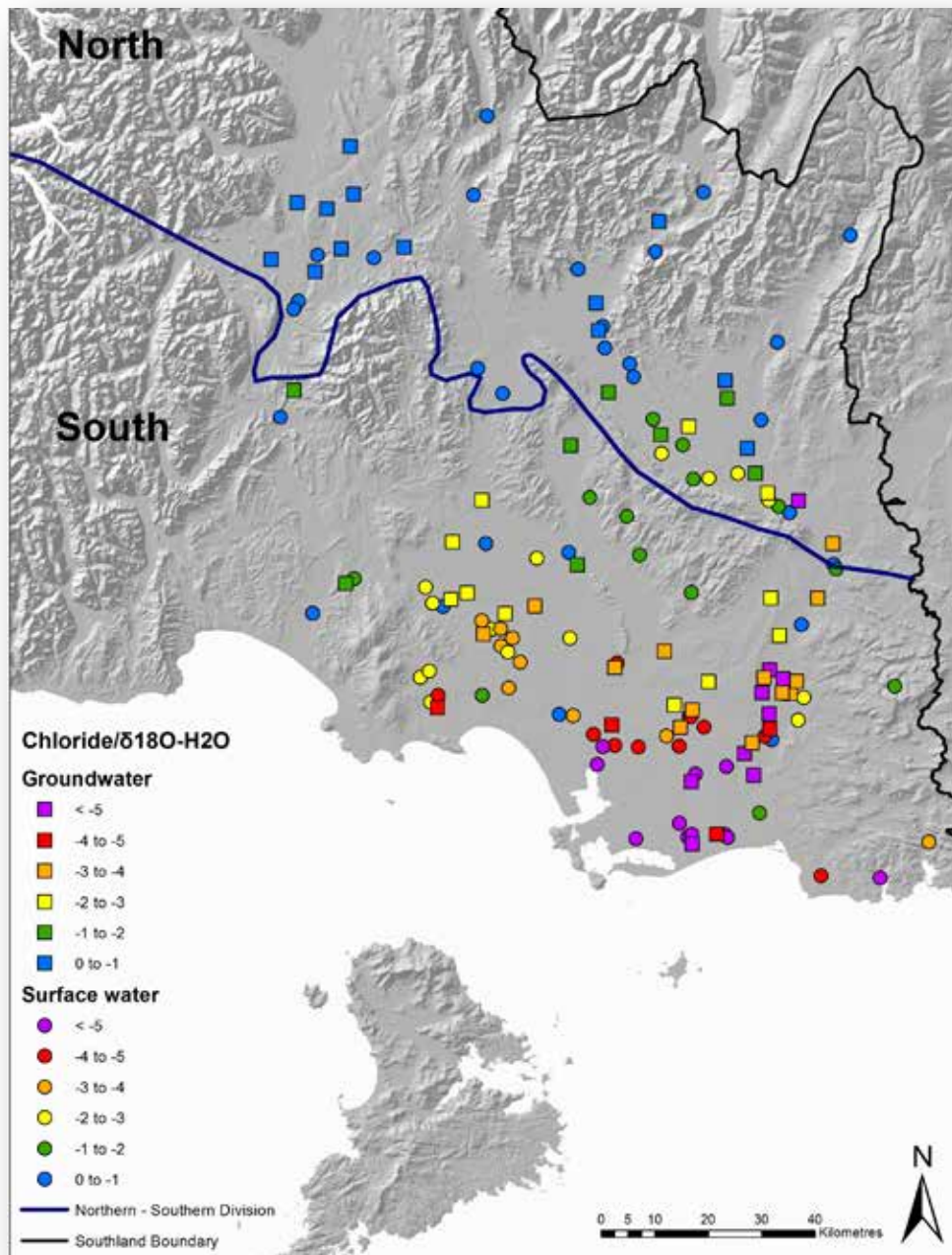**Figure 1-14: Plot of median Cl/δ^{18}O-H$_2$O ratio for Southland ground and surface waters. Note the strong transition in source signature that also mimics that of precipitation for the region. Differences are particularly apparent between northern and southern Southland.**

TC1.5.3 PCA of surface and groundwater composition

PCA, using the same variable as for PCA of precipitation presented previously, namely northing, elevation, Ca, Cl, Mg, Na, SO_4 and K, confirmed that Na and Cl concentrations in ground and surface water are mainly affected by precipitation patterns. For ground and surface water, component 1, a major component, was found to explain 44% and 62% of the variation in the data, in Table 1-5 and Table 1-7 respectively.

Component 1 is strongly correlated with northing, elevation, Cl and Na and also δ^{18}O-H_2O when included in the PCA, indicating the effect of more dilute precipitation at higher altitudes and further inland on ground and surface water signatures (Table 1-5 and Table 1-8).

Component 2 accounts for 18 and 15% of the variance in ground and surface waters, respectively, and is strongly correlated with Ca, Mg, K and SO_4 indicating the effect of soil zone and rock processes on ground and surface water chemistry (Table 1-5 and Table 1-8). Notably, Southland surface waters exhibit significant weightings for Ca, Mg, K and SO_4 with elevation and northing, whereas groundwaters do not. This reflects greater volumetric dilution for northern surface waters and possibly less interaction with evolved soils within alpine riverine recharge (TC3 – 6, 7).

Component 3 is strongly influenced by the variable depth, when including depth in the PCA of groundwater, possibly indicating Mg and K enrichment with increasing depth as a result of ion exchange (Table 1-5 and Table 1-8). For groundwater, the third component strongly correlates with Mg and K.

Of key relevance is that the conservative tracers of water source i.e., Cl and the stable isotopes of water, determine the same regional signatures for ground and surface waters. However, as expected varying interaction with the regolith modifies the weak marine Ca, Mg, K and SO_4 signatures of regional precipitation.

Table 1-5: PCA results for Southland groundwater. PCA confirms one significant component (eigenvalue > 1) which explains 44% of the data variance. Component 2 and 3 are significantly less significant than component 1 (eigenvalue close to 1).

Component No.	Eigenvalue	Percent	Cumulative %
1	3.492	43.65	43.65
2	1.439	17.99	61.64
3	1.114	13.85	75.49

Table 1-6: Eigenvectors for each of the variables considered within the PCA for Southland's groundwater.

Variables	Component 1	Component 2	Component 3
Northing	0.493	0.195	-0.086
Elevation	0.491	0.094	-0.029
Calcium	-0.161	0.400	-0.256
Chloride	-0.487	-0.067	0.055
Magnesium	-0.153	0.428	-0.606
Sodium	-0.444	-0.202	-0.080
Sulphate	-0.157	0.641	0.128
Potassium	-0.090	0.392	0.730

Table 1-7: PCA results for Southland surface water. PCA confirms one significant component (eigenvalue > 1) which explains 62% of the data variance. Component 2 is significantly less significant than component 1 (eigenvalue close to 1).

Component No.	Eigenvalue	Percent	Cumulative %
1	4.923	61.54	61.54
2	1.179	14.74	76.28

Table 1-8: Eigenvectors for each of the variables considered within the PCA for Southland's surface water.

Variables	Component 1	Component 2
Northing	0.370	0.439
Elevation	0.337	0.360
Calcium	-0.277	0.591
Chloride	-0.412	-0.142
Magnesium	-0.307	0.513
Sodium	-0.410	-0.073
Sulphate	-0.368	0.189
Potassium	-0.324	-0.057

TC1.5.4 Contouring of Cl, Na and delta 18O

On the basis of the above findings, we conclude that Southland's surface and groundwater recharge primarily originates from rain or snowmelt, and can be characterised in terms of two primary sources:

➢ high altitude Type 2 precipitation from elevated inland alpine[2] and hill country headwaters, characterised by low marine aerosolic solute concentrations and isotopically most negative δ^{18}O-H$_2$O signatures[3]; and

➢ Type 1 precipitation across flatter, low elevation land across the Southland Plains and inland basins associated with predominantly land surface recharge (LSR). These waters contain greater marine aerosolic Na and Cl and have more positive δ^{18}O-H$_2$O values.

As a consequence of differing recharge sources, southern and northern ground and surface waters exhibit significantly different (t-test, $p < 0.05$) δ^{18}O-H$_2$O, Cl, Na and EC signatures (Table 1-9 and Table 1-10). Generally, Southland's northern surface and groundwater exhibit lower Cl and Na concentrations, as well as lower EC and more negative δ^{18}O-H$_2$O values, than Southland's northern ground and surface water, which retain the signature of Type 2 precipitation. Southland's southern ground and surface waters retain the signature of Type 1 precipitation and generally exhibit a wider range of signatures indicating the effect of differing recharge mechanisms, e.g. river recharge (RR) , land surface recharge (LSR) or both, on their chemical composition.

As groundwaters represent the weighted mean of recharge (Fritz and Clark, 1993), source plots of Cl, Na, δ^{18}O-H$_2$O and EC can be used to refine our knowledge of the spatial patterns in regional precipitation and hence water source as depicted in contour plot Figure 1-15 and Figure 1-16. As discussed previously, marine aerosolic load is a key driver of Na and Cl concentrations regionally and

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[2] Alpine and hill country recharge was distinguished based on δ^{18}O-H$_2$O signatures of precipitation presented previously. The boundary is 800m, i.e. above 800m recharge is considered as alpine recharge. The boundary of 800m identified as the lowest mean altitude for alpine waters on the basis of δ^{18}O-H$_2$O signatures also coincides with the tree line or 0 degree isotherm for some areas of Southland [Wardle, 1984; Adams and Adams, 1973].

[3] These waters still show considerable concentration of solutes relative to precipitation, which indicates a high degree of soil zone influence.

as such critically important for understanding regional variability in hydrochemical signatures of ground and surface waters.

Contouring of Na and Cl concentrations and δ^{18}O-H$_2$O values in oxic and under-saturated surface and groundwater, clearly identified areas that receive coastal precipitation with the highest concentration of Cl and Na and most positive δ^{18}O-H$_2$O values, these include the two upper contour bands with >34mg/L Cl, >22 mg/L Na and >-7.4 δ^{18}O-H$_2$O. Also apparent is the extension of a SW to SE band of coastal precipitation that extends inland mirroring the prevailing wind and precipitation patterns. Excursion of marine derived precipitation inland is restricted by hill and mountain ranges such as the Hokonui Hills. Areas of highest elevation and areas that lie most inland receive most dilute precipitation. In combination with mapping of dominant recharge mechanism (LSR, RR and mixed recharge), Figure 1-15 and Figure 1-16 aid the establishment of a recharge source and mechanism map in TC2, which will help us predict the chemistry of Southlands freshwater.

Table 1-9: δ^{18}O-H$_2$O, Cl, Na and EC signatures (mean, median and stand deviation) for southern and northern Southland groundwater, concentration/values for each parameter are significantly different in northern and southern waters ($p<0.05$, T-test, F-test confirmed that the populations have unequal variance); *the boundary between northern and southern samples is illustrated in Figure 1-13

Groundwater	δ^{18}O-H$_2$O [ppt VSMO]		Sodium [mg/L]		Chloride [mg/L]		Conductivity [µS/cm]	
Region*	North	South	North	South	North	South	North	South
Sample size	84	21	657	129	657	129	655	129
Mean	-9.42	-7.31	4.01	12.41	3.57	18.22	66.17	173.81
Median	-9.45	-7.18	3.03	10.23	2.06	13.97	55.00	111.87
SD	0.93	0.70	3.15	5.31	4.29	9.42	45.43	126.52

Table 1-10: δ^{18}O-H$_2$O, Cl, Na and EC signatures (mean, median and stand deviation) for southern and northern Southland surface water; concentration/values for each parameter are significantly different in northern and southern waters ($p<0.05$, T-test, F-test confirmed that the populations have unequal variance).

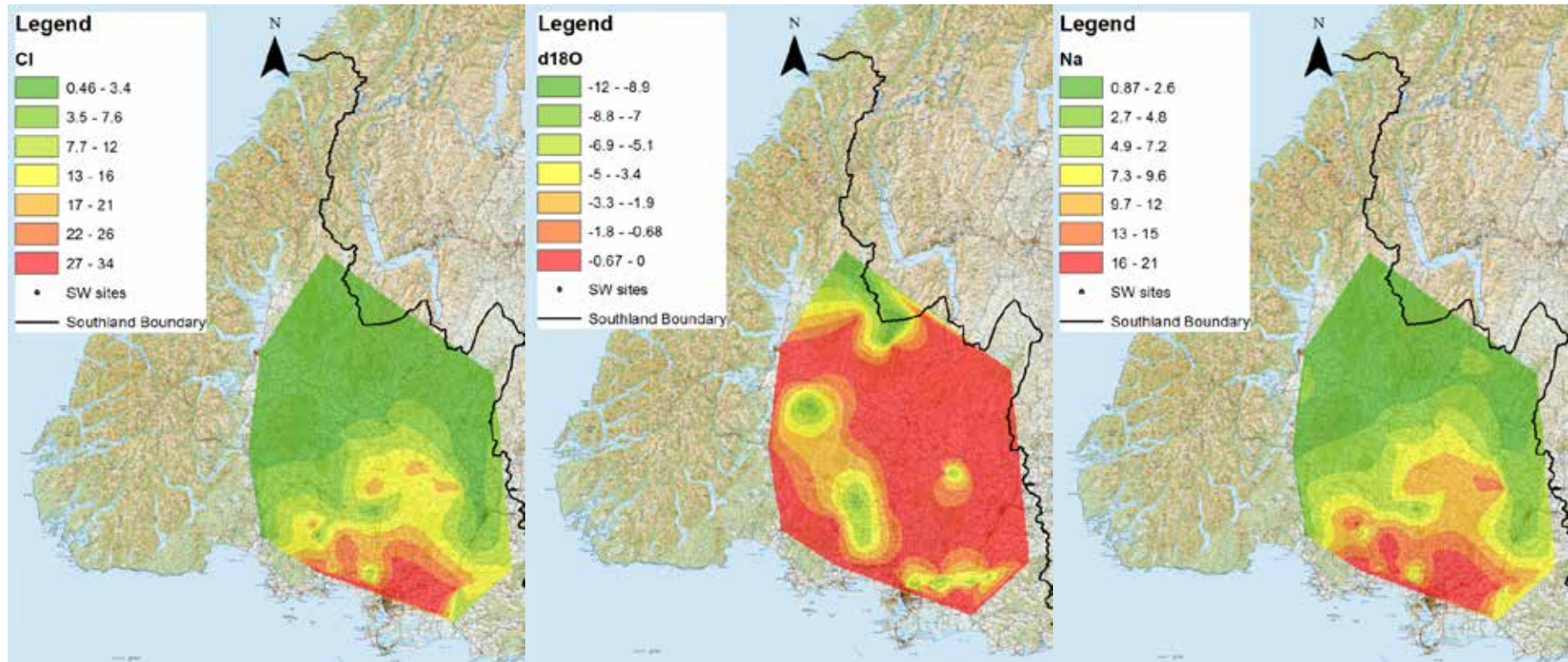| Surface Water	δ^{18}O-H$_2$O [ppt VSMO]		Sodium [mg/L]		Chloride [mg/L]		Conductivity [µS/cm]	
Region	North	South	North	South	North	South	North	South
Sample size	119	252	962	2212	962	2212	960	2212
Mean	-8.98	-7.28	6.35	14.91	6.67	22.19	90.78	174.98
Median	-9.19	-7.21	3.69	15.20	2.93	21.91	68.00	179.00
SD	1.17	1.03	5.09	5.99	7.14	11.03	61.00	72.87

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Figure 1-15: Cl (upper) and Na, (middle) contours in surface water to distinguish areas that receive coastal, inland and alpine/hill country recharge. The contours were established using nearest neighbour interpolation (grid size 400m). Oxic and under-saturated surface water (SI < 0) with respect to calcite minerals only were used to exclude groundwater that had been significantly altered by weathering reactions.
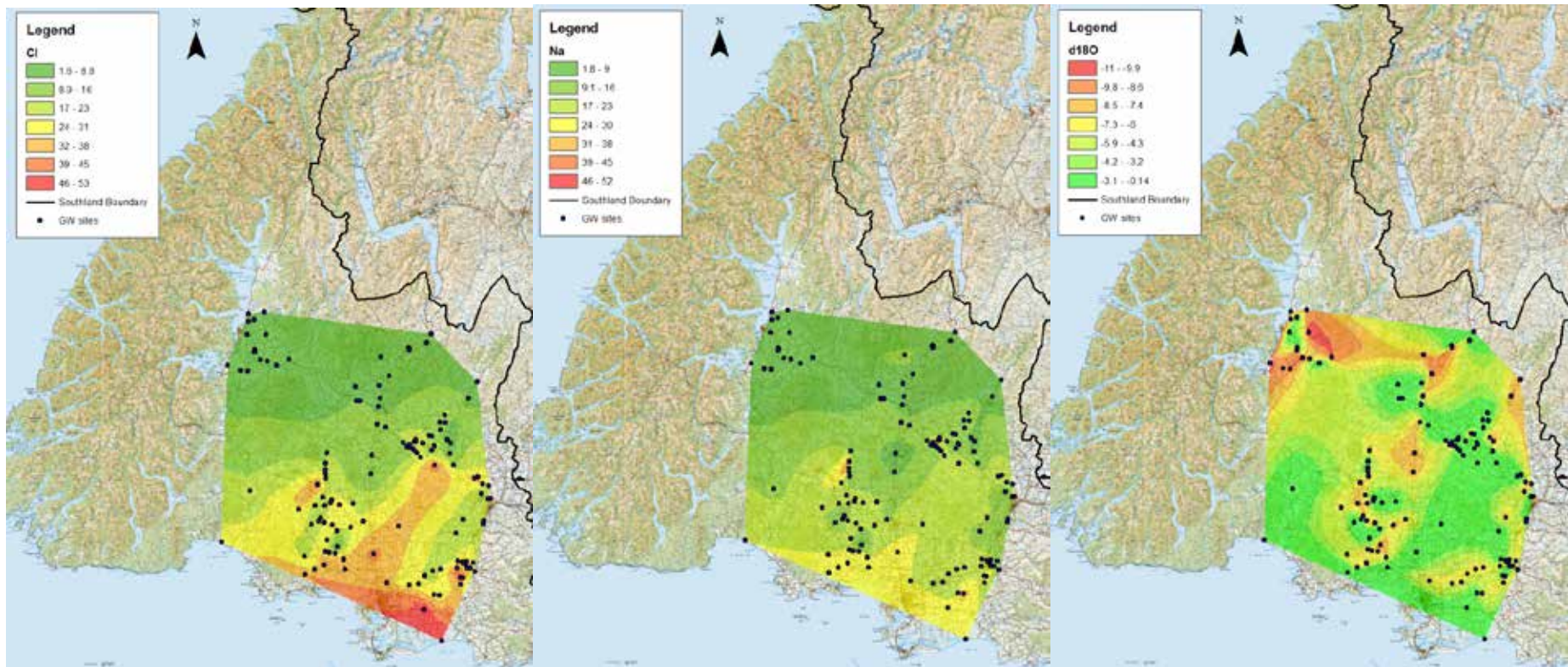
Figure 1-16: Cl (left), Na, (middle) and ¹⁸O (right) contours in groundwater to distinguish areas that receive coastal, inland and alpine/hill country recharge. The contours were established using nearest neighbour interpolation (grid size 400m). Oxic and under-saturated groundwater (SI < 0) with respect to calcite minerals only were used to exclude groundwater that had been significantly altered by weathering reactions.

TC1.6 Summary

We have shown that in Southland, Cl, Na, δ^{18}O-H_2O and δ^{2}H-H_2O play a critical role in clarifying the origin of Southland's surface and shallow groundwater resources. These metrics can be used to determine water source and precipitation origin at any one point. Specifically, we found that the spatial distribution of δ^{18}O-H_2O values, Cl and Na concentrations, and EC in ground and surface water follow similar patterns to those observed for precipitation. PCA confirmed that Na and Cl concentrations and ratios and other major ions such as SO_4 in ground and surface water are mainly affected by precipitation patterns. Our findings are in line with other studies that showed major ion chemistry, such as the concentration of Cl and Na, and isotopic signatures, such as δ^{18}O-H_2O and δ^{2}H-H_2O, are robust tracers of recharge source(s) of ground and surface water (e.g. Fritz and Clark, 1993; Kendal and McDonell, 1998; Böhnke et al, 2002; Zhang et al., 2005; Guggenmos et al., 2011).

As a key output of this chapter a regional precipitation source map was developed on the basis of Cl, Na and δ^{18}O signatures in precipitation, groundwater and surface water. This map is used in combination with other driver maps developed in the subsequent chapters to predict freshwater composition in Southland.
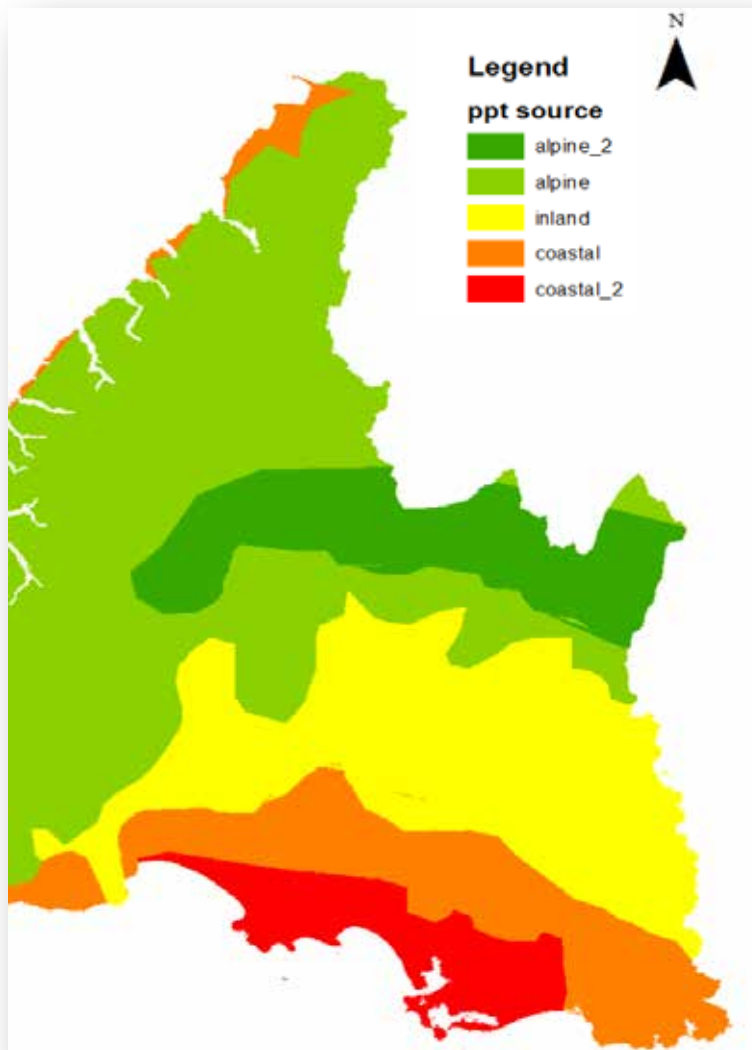

Figure 1-17: precipitation source map of Southland region with alpine 2 precipitation being the most dilute, followed by alpine, inland, coastal and coastal 2 (in order of increasing solute concentration).