

Physiographics of Southland

Part 1:

Delineation of key drivers of regional hydrochemistry and water quality

Technical Report

June 2016

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Physiographics of Southland

Part 1:

Delineation of key drivers of regional hydrochemistry and water quality


Technical Chapter 4:

Relationship between Soil Chemistry and Soil Water Chemistry

June 2016

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TC4 Relationship between Soil Chemistry and Soil Water Chemistry

TC4.1 Introduction

The chemical characteristics of Southland soils and the association of soil chemical characteristics against soil order have been explored in the previous chapter (TC 3). In this chapter we look at the general relationships between soil chemical properties and infiltrating precipitation. Specifically, we assess how soil chemical characteristics influence the major ion composition of infiltrating precipitation. This was carried out through leaching tests of soil samples and analysis of soil water (soil solution) and soil drainage water. The locations of sampling sites are illustrated in Figure 4-1. The sampling sites are either at, or close to soil quality monitoring sites established through Southland's State of the Environment (SoE) monitoring programme.

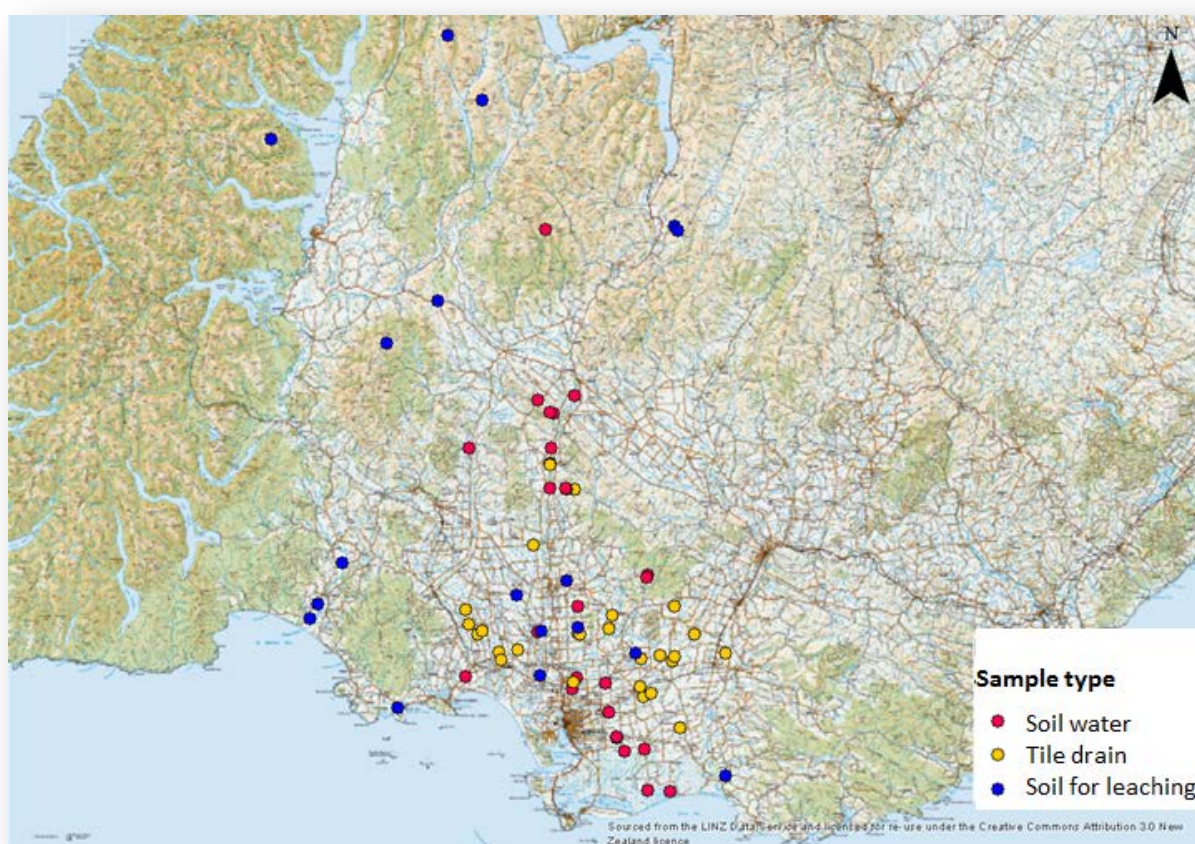


Figure 4-1: Sampling locations to investigate relationship between soil chemistry and infiltrating water. The location of soil samples that were used for leaching experiments are illustrated in addition to the location of soil drainage and soil water samples.

As noted in the previous chapter (TC 3), precipitation is a dilute Na-Cl type fluid where $\text{Cl} > \text{Na} > \text{SO}_4 > \text{Mg}$ and Ca and K generally constitute less than 5% of the total dissolved solute (or TDS) load. At high altitude inland sites the Total Dissolved Solid (TDS) concentration of the snow pack is $< 0.05 \text{ mg/Kg}$, whereas TDS of coastal precipitation is as high as c. 90 mg/Kg (Conductivity values $< 0.05 - 140 \mu\text{S/cm}$).

Findings in this section indicated that the soil zone has a considerable impact on Southland's freshwater chemistry. This is important information for subsequent chapters where we demonstrate

that the soil zone is the major source of alkalinity for Southland's oxidised and/or weakly reduced ground- and surface waters that are under-saturated with respect to carbonate minerals.

TC4.2 Leaching Trial

Method

Twenty representative soils from across the Southland region were leached following USEPA (1994) guidelines. The sample locations are illustrated in Figure 4-1. Each soil sample was a composite of A, B, and C horizons. Synthetic Precipitation Leaching Procedure (SPLP) was employed to simulate leaching of soil materials by precipitation (USEPA, 1994), and was undertaken by Hills Laboratories. Soil samples were air dried and a 100 g sub-sample gently shaken with 2,000 ml of deionised water for a duration of 18 hours to allow for leaching of the soil components. The leachate was then analysed for major ions (e.g., concentrations of Ca, Si, and Na, pH, and EC). The same soils were also analysed for traditional soil chemical metrics (i.e., BS%, CEC, C% etc.) using standard methods, and undertaken by Hills Laboratories.

The deionised water used as a leaching solution had a pH of c. 5.8 and conductivity on the order of 1 $\mu\text{S}/\text{cm}$. This suggests that the deionised water used for soil leaching was in equilibrium with atmospheric CO_2 , and dissociation of dissolved atmospheric CO_2 to H^+ and HCO_3^- ions occurred (Plummer and Busenberg, 1982). For comparison, the composition of the most dilute Southland precipitation samples is similar to that of deionised water with a conductivity of 0.05 – 0.20 $\mu\text{S}/\text{cm}$ and a pH of 5.5 – 6.2.

Results

As expected, strong relationships between soil chemical characteristics and leachate chemistry were found (illustrated in Figure 4-2 and Figure 4-3, $r^2 > 0.86$), although the hydrochemical composition of soil leachate differed substantially for the distinct soil types as illustrated in Figure 4-8. Further study of soil waters (TC 5) suggests similar trends and relationships to those found in this section, supporting our findings and conclusions. The key observations, which are in line with findings of Robertson et al. (1999) and Mengel (2011) include:

- Despite using deionised water that was free of Na and Cl, Na and Cl concentrations in soil leachate were higher than Ca concentrations for all but one soil, supporting the concept of evaporative concentration of these ions within the soil profile during recharge (Figure 4-8).
- A strong positive correlation of soil pH and BS% was found, indicating the control of soil BS% over soil pH (Figure 4-2). The pH of deionised water (5.8 ± 0.4) which was used to simulate precipitation increased by a minimum of 0.9 pH units following equilibration with the soil (the median pH increase was 1.55 pH units; the maximum increase was 2.5 pH units).
- Both TDS and EC of leached waters are positively correlated with the sum of exchangeable bases ($r^2 = 0.53$, relationship not shown here) indicating as the concentration of exchangeable bases increase so does the TDS concentration of the leached water.
- Both dissolved Ca and Mg concentration in leachate are strongly positively correlated ($r^2 > 0.86$) with soil BS% following a near exponential relationship (Figure 4-2 and Figure 4-3). This can be explained by leaching of these cations from the soil through infiltration of dilute precipitation (i.e. under-saturated with respect to all minerals).
- Na does not show a strong correlation with BS% ($R^2 = 0.01$, relationship not illustrated here). This may indicate that Na is not well retained within the soil as a result of its larger hydrated

radius compared to the radius of hydrated Mg or Ca (Lasaga, 1984; McLaren and Cameron, 2005).

- Dissolved Si is weakly negatively correlated with soil BS% ($r^2=0.19$). This probably reflects the higher solubility of Si at higher pH (relationship not shown here).
- Soil C% is strongly positively correlated with dissolved organic carbon (DOC) in leachate (Figure 4-3, $r^2=0.82$) as is soil CEC and DOC ($r^2=0.64$, relationship not presented here). Although we only analysed a small amount of samples and the correlation is not very strong, similar relationships were also found during analysis of a larger hydrochemical data set and the soil dataset (presented in in TC 3 and TC 5) indicating higher DOC in waters from areas of wetland soils which have a high C% and high CEC.
- The composition of alpine soils was considerably different than that of all other soils sampled at lower altitudes (Figure 4-8). Alpine soil leachate contained low dissolved ion concentrations; in particular K, Cl, F, and DRP were all below detection. Only Na, SiO₂, DOC, Mg, Ca, and alkalinity were detectable in alpine soil leachate. The very low/non-detectable Cl and Br concentrations in alpine soil leachate further supports that alpine soils receive very dilute precipitation and/or receive relatively high amounts of precipitation (i.e. the marine Cl signature is lost; TCs 1 and 2). The detectable Na (and other elements) in soil leachate must have therefore originated from the soil (e.g. from weathering) as opposed to being sourced from precipitation.
- Nitrate and phosphate concentrations in leachate of alpine soils were much lower (in fact below detection limit) than in leachate of all other (lower altitude) soils suggesting that anthropogenic effects are significantly lower in alpine areas than at lower altitudes. This is supported by the observation that high altitude land is seldom used for agricultural purposes as opposed to lower altitude land.

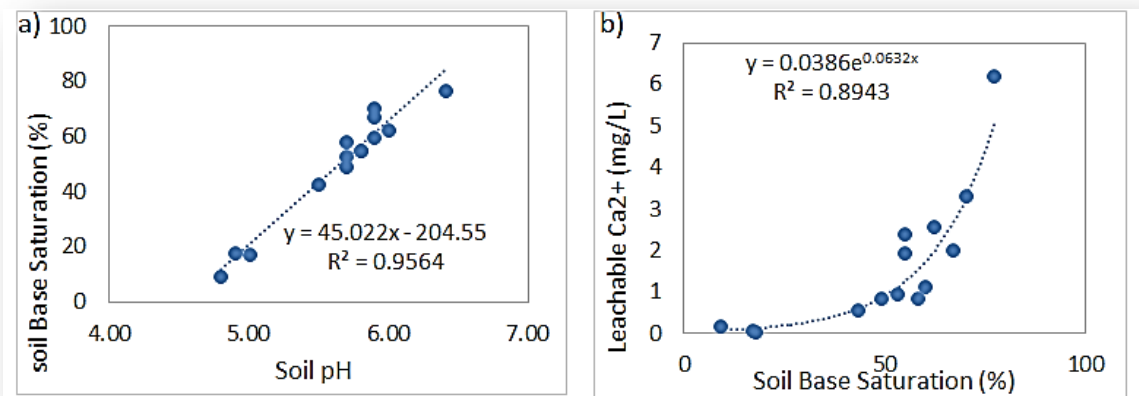


Figure 4-2: a) Correlation between soil pH and BS% for soils in leaching trial, b) Soil BS% vs. Ca in leachate.

In summary, the soil leachate experiments suggested that Na and Cl concentrations in leachate exceeded those of Ca for the majority of analysed soils. This supports the concept of evaporative concentration of these ions within the soil profile. As noted in TC 1 and TC 2, the concentration of Na and Cl declines exponentially with distance from the coast and altitude (in addition to increasing precipitation volumes with distance from the coast). This pattern was also observed in soil Na concentrations (TC 3). Accordingly, soils in close proximity to the sea receive high marine aerosol loads and therefore leach more Cl and Na, whereas marine aerosolic Cl and Br were below detection

in alpine soils. Overall, trends in leachate chemistry demonstrated a reasonable correlation between soil chemical properties and reflect the rapid evolution of precipitation as it comes into contact with soil materials due to simple ion exchange and solubilisation reactions.

However, we note that the small sample size of this simple laboratory trial only provides generalised insight into the relationships between soil chemistry and resulting drainage water composition, further study of soil waters (presented in TC 4.3) show similar trends and relationships to support the findings of this section.

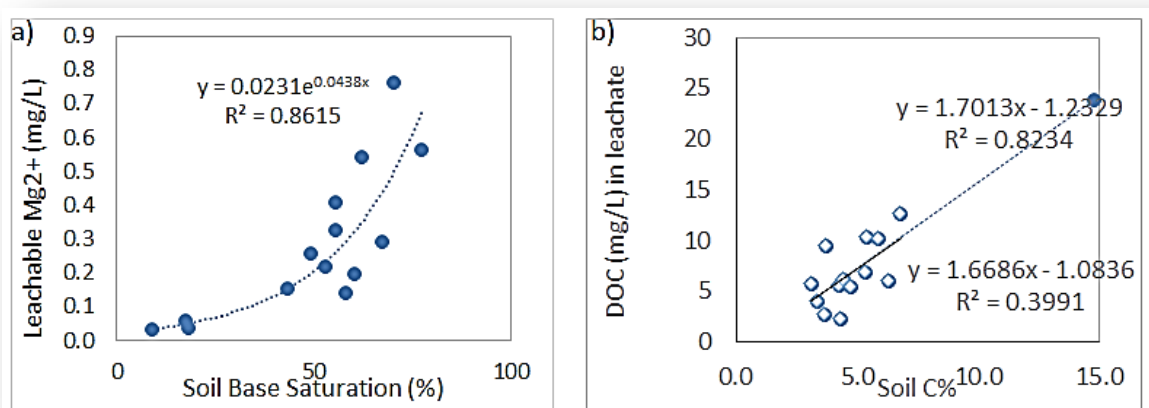


Figure 4-3: a) Soil BS% vs. Mg²⁺ in leachate; b) Soil organic C % vs. DOC in leachate (note the relationship is still significant when the highest C% and DOC value is removed).

Method

A total of 40 soil water samples were collected from 14 reserve areas using Teflon suction cups. Figure 4-1 illustrates the soil water sampling locations and Figure 4-9 shows an example of the suction cup sampling in the field. There is no recent (*c.* 50 years) history of land use at these sites. The most coastal site is associated with peat wetland reserve within the Waituna Catchment and the most inland site occurs at Dunsdale Reserve within the Hokonui Hills. Soil suction cup water samples were not collected from high altitude sites as the soil layer in these areas is generally very thin to non-existent.

The excess or deficit of suction cup soil water solutes relative to mean seawater was calculated using Eqn. 1.

$$F_c = (C/Cl)_{\text{sample}} / (C/Cl)_{\text{seawater}} \quad (\text{Eqn. 1})$$

where F_c is the Fractionation Factor, and C is the concentration of a given species (e.g. Na). Fractionation is determined in relation to Cl, since Cl is considered a conservative species. A $F_c > 1$ indicates excess of the given species over the marine source, whereas a $F_c < 1$ indicates a deficit of the given species relative to the marine source.

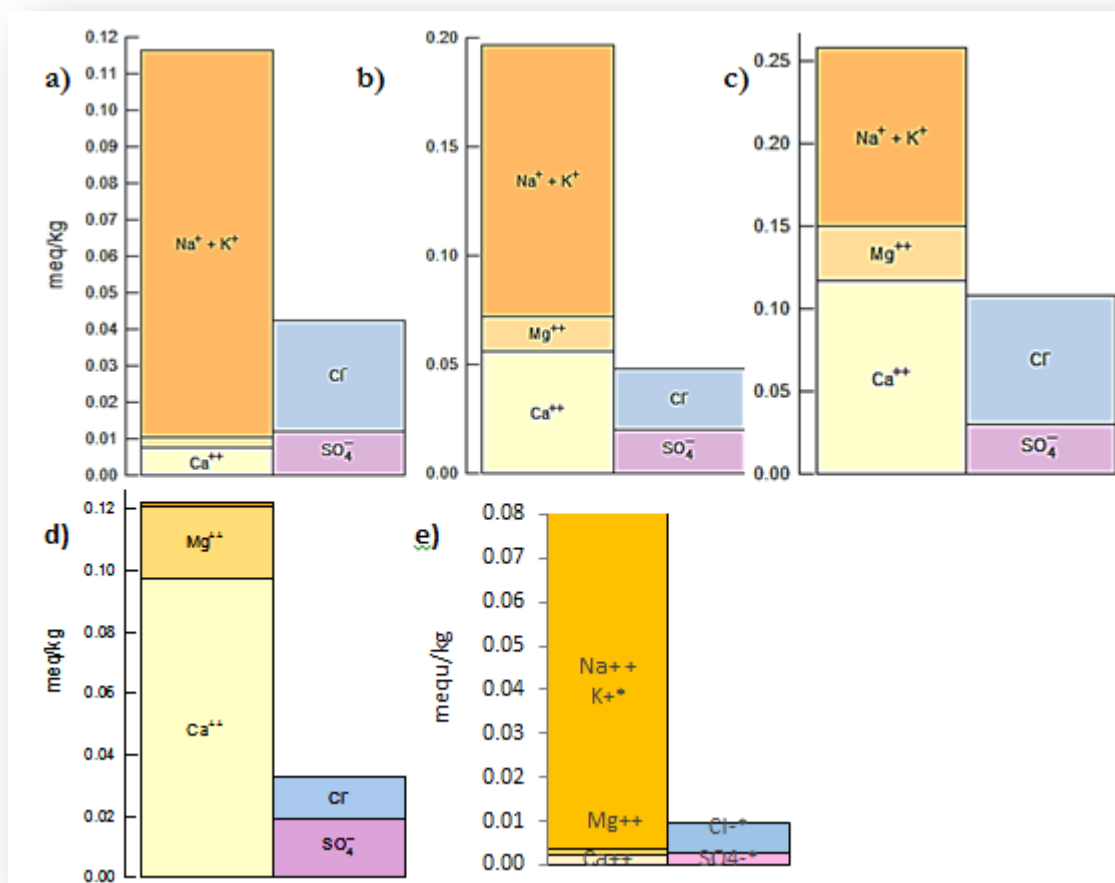


Figure 4-4: Composition of soil water leachate for three distinct soil types. a) Native tussock reserve; b) Papatotara intensive on Allophanic soils; c) Oreti Plains Dairy on Brown Soils, and; d) Wallacetown Dairy on Pallic Soils. BS% increases from a – d (9% - 70%), (e) alpine soils indicates concentration was below detection, to illustrate took 0.5 times the limit of detection

TC4.3 Soil Suction Cup Waters

Results

The analysed soil water samples show a considerable range in major element composition (summarised in Table 4-1). Soil water Cl ranges between 26 – 360 mg/L from the most inland to the most coastal site, respectively, with a median of 94 mg/L. Na concentrations have a median value of 57.5 mg/L and range from 8.9 to 70.0 mg/L from the most inland to the most coastal site, respectively. Soil water samples from the top soils (0.05 – 0.3 m BGL) of reserve sites show elevated Na and Cl relative to those of precipitation occurring at the same location (Table 4-2). This suggests enrichment of Cl and Na concentration in the soil through evapotranspiration of infiltrating precipitation.

More specifically, the elevated concentration of both Na and Cl in soil water suggest evaporative enrichment of marine aerosols within the upper layers of the soil, which would be flushed to depth during a heavy rainfall event. Accumulation of marine aerosols within the upper layers of soils is a commonly observed feature in humid environments and results in seasonal pulses of elevated EC waters to aquifers and streams (Drever, 1997; Langmuir, 1997; Daughney et al., 2015). Whilst evapotranspiration concentrates salts within Southland soils, salinisation is not a problem due to abundant flushing of salts from the topsoil to depth during winter recharge events.



Figure 4-5: Example of Teflon suction cup deployment in a Southland soil. The steel plate is hammered into the soil and an awl (a narrow diameter spike) of slightly smaller diameter than the suction cup is made through drill holes within the plate. A paste of soil and deionised water is used to seal the cups and suction is applied and left for 18 – 24 hours before collection.

Table 4-1: Summary of major hydrochemistry of soil waters sampled using suction cups.

Parameter	Alkal tot	Ca	DOC	Cl	Fe	Mg	DO	K	Si	Na	SO ₄	pH	EC
unit	mg/L											μS/cm	
average	22.3	13.6	7.9	52.0	0.54	6.0	6.8	2.2	13.0	24.9	19.2	5.9	242
median	19.8	15.0	6.5	31.0	0.26	5.0	7.1	1.0	10.9	18.5	19.1	6.2	229
SD	18.9	9.1	5.9	69.5	0.95	3.5	2.4	3.2	8.1	19.1	11.9	1.0	108

Table 4-2: Comparison of Na and Cl concentrations from coastal and inland precipitation and soil moisture results. The coastal sample location refers to the Waituna Catchment, and the inland sample location refers to the Dunsdale Reserve.

Location	Precipitation		Soil moisture sample	
	Median Na [mg/L]	Median Cl [mg/L]	Median Na [mg/L]	Median Cl [mg/L]
Coastal (Waituna Catchment)	9.3	15.5	63	38
Inland (Dunsdale Reserve)	4.3	7.2	13.9	23.5

For most topsoil waters, irrespective of the concentration of the salts, there is little enrichment in Na, Mg, or K relative to seawater (see median F_c (Eqn. 1) for selected species in Table 4-3) suggesting a dominantly marine aerosolic origin. For acidic organic soils, Ca is enriched relative to mean seawater but only slightly in contrast to the enrichment associated with mineral soils (Gley and Brown) of higher BS% where Ca is strongly enriched within the topsoil relative to mean seawater (F_c up to 100). This phenomenon can be explained by ion exchange (Ca replacing Na in soil) and/or weathering of soil.

Two soil water samples of acidic organic soil waters (sampled from 0.15 m BGL) from the Awarua Wetlands are depleted in Na relative to mean seawater. Depletion of salts just below the topsoil layer is a common feature caused by evaporative draw or wicking, which is especially pronounced in peat. These samples also show depletion in Ca and Mg relative to mean seawater. Although data is limited, soil water samples from the same locations but at greater depths (0.35 – 0.65 m BGL) show a decline in the concentration of Cl, but an increase in Na, Mg, and K with depth (Figure 4-10).

At Dunsdale Reserve, concentrations of Ca, Mg, and K in soil water also increase with depth (from 0.1 to 1.4 m BGL) (Figure 4-10). Similarly, excess of these species relative to mean seawater also increase with depth at other sites. These findings indicate an increase in Ca, Mg, and K due to contributions from the soil associated with ion exchange. Note, the effect of precipitation source on these cations is only significant in the first few centimetres of the soil (presented above).

Table 4-3: Summary statistics for the fractionation factor (Fc) of Na, K, Mg, Ca, and SO₄ in soil water samples.

	Valid Cases	Mean	Median	SD	Minimum	Maximum	Range
Fc Na	83	1.06	1.03	0.36	0.20	2.24	2.04
Fc K	83	7.99	2.53	16.93	0.02	103.03	103.01
Fc Mg	83	2.48	1.96	1.65	0.42	8.79	8.37
Fc Ca	83	24.50	21.99	19.45	0.11	110.76	110.65
Fc SO ₄	83	4.13	3.27	2.98	0.07	14.75	14.68

Soils with a relatively high mineral content (i.e. Brown soils) exhibit K excess relative to mean seawater, whereas waters from organic soils do not - again indicating the role of mineral weathering and phyllosilicate clay development. At Dunsdale Reserve, K concentrations appear to be most elevated within the topsoil but show only a minor excess relative to seawater. Calcium excess is highest for mineral soils and is lowest for undeveloped organic and/or highly leached soils. Sodium concentrations decline as Ca increases reflecting both an increase in mineral content and BS% of these soils by soil subgroup i.e., Organic > Gley hill country > mineral Brown lowland soils.

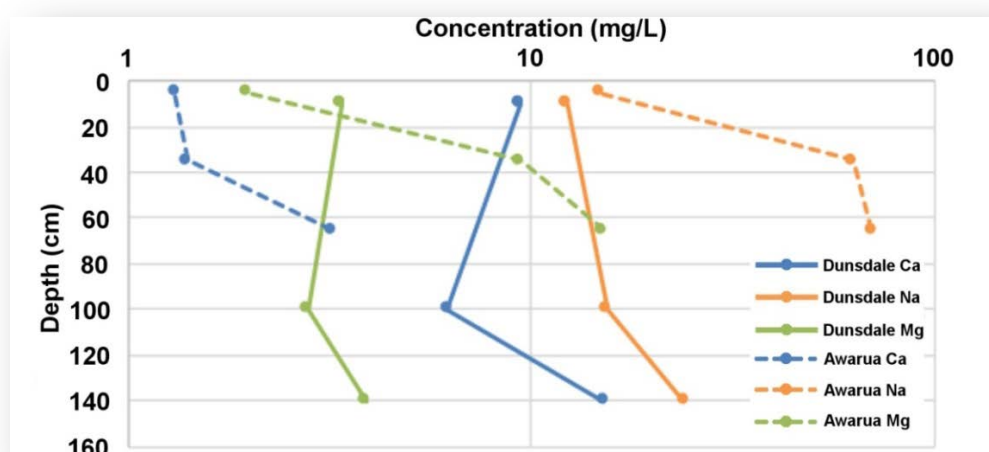


Figure 4-6: Concentration of Ca, Mg, and Na as a function of soil depth (cm BGL) from Dunsdale Reserve and Awarua Wetlands.

Although alkalinity data is limited, a general increase with depth was found in the soil water samples. Alkalinity was below the detection level for highly acidic organic soils (pH <4.5). Only two soil water samples have been analysed for the stable isotope composition for dissolved inorganic carbon ($\delta^{13}\text{C-DIC}$), with values of -19.2 and -21.4‰, V-PDB. Both signatures suggest a predominantly C3 soil organic

carbon source. Minor enrichment may reflect degassing during filtration through the membrane of the Teflon suction cup or enrichment due to diffusive transport of the isotopologues of CO₂ through the porous media of the soil (see Rissmann et al., 2012 and references therein). Where soils become more reducing with depth, alkalinity increases in response to bacterial oxidation of organic matter linked to electron acceptor reduction (i.e., heterotrophic oxidation of soil organic matter).

Soil water pH for the few sites ranges from 3.6 – 6.6, increasing from acidic organic soils to mineral Brown soils. Soil water pH increases with depth at all sites although as expected the magnitude of increase is greatest for mineral soils of high BS%.

In summary, soil water analysis suggested that evapotranspiration and ion exchange lead to elevated concentration of Na, Ca, and Cl in soil water in the uppermost centimetres (c. 0 – 40 cm) of the soil profile (particularly at sites that are located in close proximity to the coast which receive high marine aerosolic load in precipitation). Na, Ca and Mg found at greater depth in the soil profile are more likely sourced from weathering than precipitation. This suggests that tile drainage water is likely to carry the precipitation signature than soil signature. This is further assessed in the subsequent sections (TC 4.4 and TC 4.5).

TC4.4 Mole-pipe (Tile) Drainage Waters

Methods

In this section, we elucidate the origin of dissolved solutes in drainage water. Specifically we distinguish between evaporative input, ion exchange, and soil/rock-water interaction (and land use inputs). Soil waters (n = 79) were collected from mole-pipe drainage (tiles) at 67 sites across Southland (Figure 4-1). The partial pressure of CO₂ (pCO₂) for tile waters was determined according to Eqn. 2.

$$p\text{CO}_2 = C_T \alpha_0 / K_H \quad (\text{Eqn. 2}) \quad (\text{after Stumm and Morgan (1981)})$$

where C_T is the total DIC concentration (mol C l⁻¹) in the sample, α_0 is the ionisation fraction between CO₂ and H₂CO₃ and K_H is the Henry's Law equilibrium constant for CO₂ in water.

Results

In Table 4-4 the chemical composition of the tile drain samples is summarised. The conductivity of tile water ranges between 21.0 - 443.0 μS/cm. A median of 223.0 μS/cm indicates conductivity is highly elevated relative to the median for low altitude (< 300 m RSL) precipitation (i.e., 22 μS/cm; n = 79) across Southland.

Sodium and Cl concentrations for tile drain waters range between 0.1 – 30.8 mg/L and 5.2 – 64.7 mg/L with median values of 17.4 and 29.0 mg/L, respectively. These median Na and Cl concentrations are high relative to those of lowland precipitation sites (4.3 and 7.2 mg/L, respectively, n = 82) and coastal precipitation sites (9.3 and 15.5 mg/L, respectively, n = 37). As with suction cup soil waters, the high concentrations of Na and Cl relative to that of precipitation reflect evaporative enrichment of both marine aerosols and to a lesser extent anthropogenic Na and Cl within the soil zone.

Anthropogenic contributions of Na and Cl are most evident for tile drainage associated with intensive wintering and dairy effluent irrigation. Specifically, a log cumulative probability plot of Cl exhibits two major inflection points at c. 30 and 40 mg/L (Figure 4-8). Inflection points in cumulative probability plots can be used to identify populations of samples with distinct signatures and ultimately define specific thresholds for each sub-population (more information on this technique is given in Appendix C). The 30 mg/L inflection point reflects the upper limit for natural background for southern

Southland whereas beyond the 40 mg/L threshold significant anthropogenic Cl input coincides with elevated K, Na, Ca, Mg, SO₄, and *E.coli* levels. These threshold values are similar to those determined for shallow unconfined groundwater in southern Southland (Rissmann et al., 2012).

The log-probability plot of sodium shows a similar pattern to that of Cl with a median of 17.2 mg/L and a range of 0.14 – 30.8 mg/L (Figure 4-12). The 20 mg/L inflection point indicates the upper limit for natural background concentration for the Southland tile water dataset beyond which anthropogenic Na input becomes important. As with Cl, tile waters that exceed the 20 mg/L threshold also have elevated K, Na, Ca, Mg, SO₄, and *E.coli* levels. Again, the threshold value for Na is similar to that determined for shallow unconfined groundwater in southern Southland (Rissmann et al., 2012).

Table 4-4: Summary of major hydrochemistry of soil drain waters.

Parameter	Alkal. (tot.)	Ca	DOC	Cl	Fe	Mg	DO	K	SiO ₂	Na	SO ₄	pH	EC
unit	mg/L												μS/cm
average	29.6	16.7	6.7	29.2	0.23	5.4	7.2	1.9	15.1	17.1	19.6	6.1	230
median	26.5	16.7	5.3	29.0	0.11	4.8	7.3	1.1	14.7	17.3	19.1	6.3	217
SD	14.8	7.2	4.7	11.2	0.50	2.6	2.3	2.2	8.5	5.3	9.7	0.9	74

Figure 4-13 depicts the increase in K with Cl concentration for tile drain waters suggesting a high degree of variance in K concentration beyond the Cl threshold of 40 mg/L. Tile drain samples with Cl concentrations in excess of 40 mg/L have the highest median K, Ca, Mg, and SO₄ concentrations and coincide with sites of intensive winter grazing or farm dairy effluent irrigation (Table 4-5).

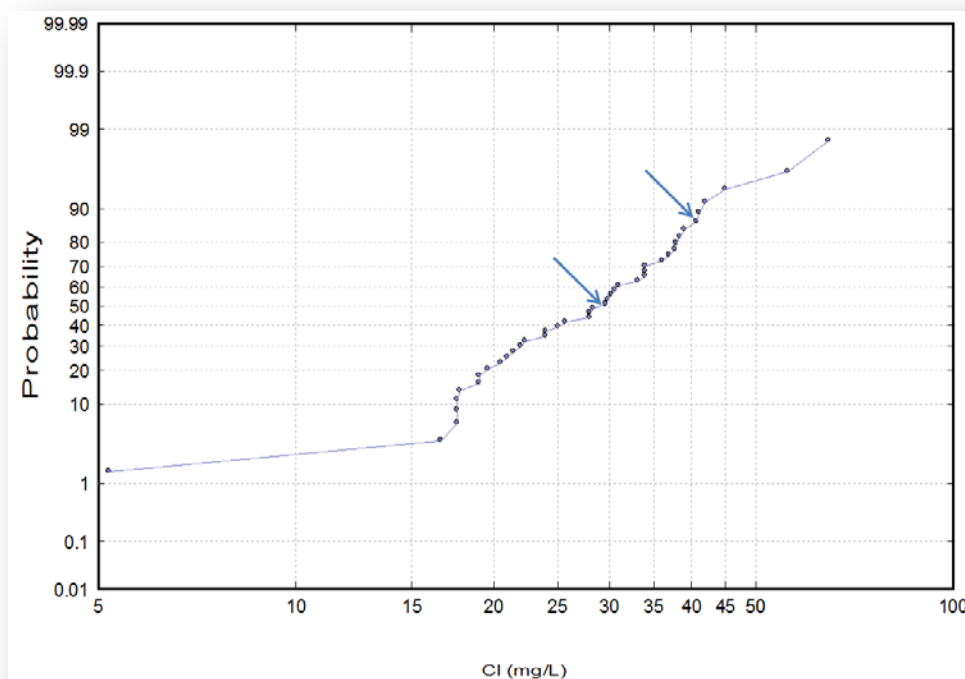


Figure 4-7: Cumulative probability plot of Cl (mg/L) for tile drain waters. Two major inflection points depicted by arrows occur at c. 30 and c. 40 mg/L, respectively. The 30 mg/L inflection point reflects the upper limit for natural background for Southland, whereas beyond 40 mg/L, a significant anthropogenic Cl input is evident (Rissmann et al., 2012). The one tile water with a very low Cl concentration is from Mathews Rd_The Bastion_Tile Drain and is probably associated with a piped spring.

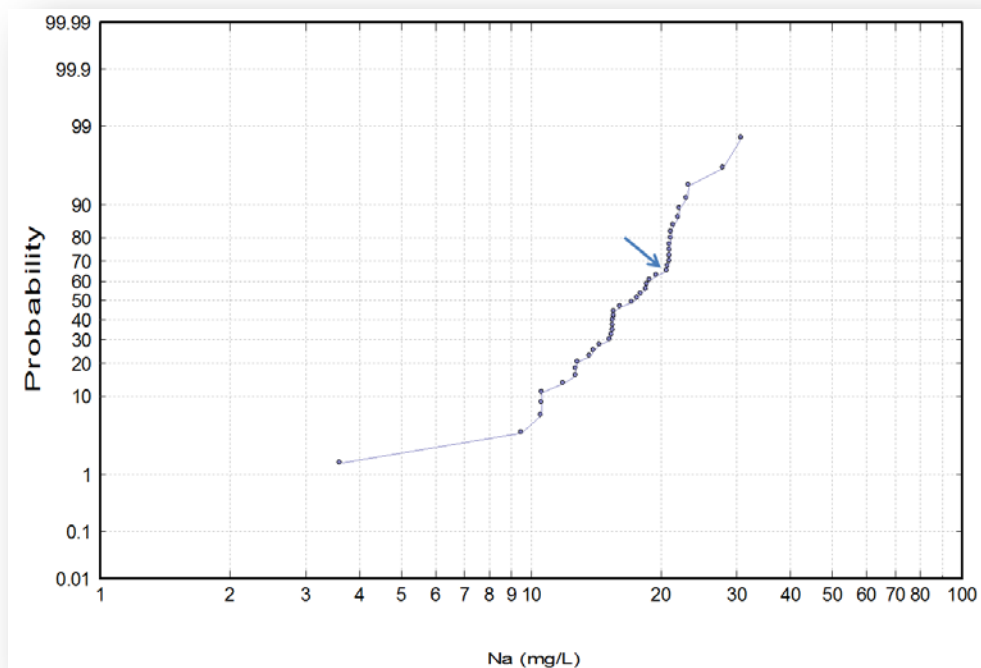


Figure 4-8: Cumulative probability plot of Na (mg/L) for tile drain waters. One major inflection point depicted by the arrows occurs at 25 mg/L. The 25 mg/L inflection point reflects the upper limit for natural background for Southland beyond which a significant anthropogenic Na input is evident (Rissmann et al., 2012).

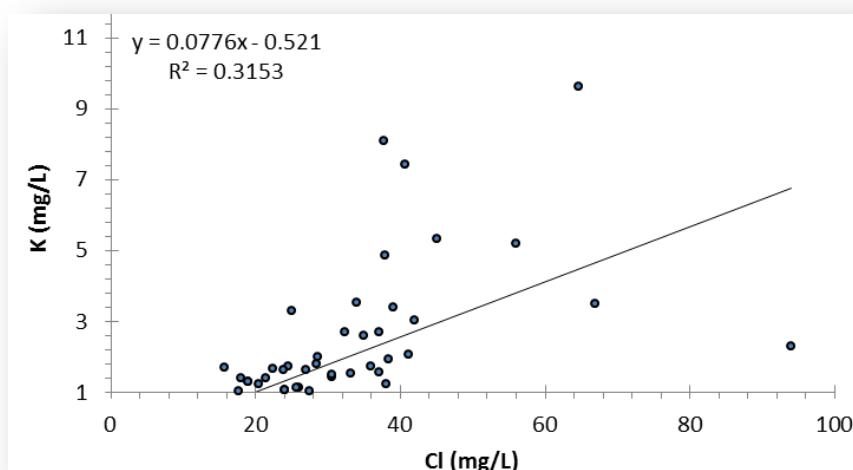


Figure 4-9: Relationship between Cl and K for Southland tile drainage waters. Cl and K show a reasonable correlation below the 40 mg/L Cl threshold beyond which the variance is large, probably reflecting localised soil controls over K regulation (i.e., organic soils vs. clay rich soils).

The excess or deficit of tile water solutes relative to mean seawater (e.g., enrichment factor F_c , Eqn 1) for Southland tile drain waters are summarised in Table 4-5. The median value for Na shows no enrichment above that of mean seawater. However, there is some minor variance from 0.8 – 1.6 F_c . Of the 26% of tile drain waters with a small Na excess (i.e. ≥ 1.3), all have high clay contents and some also have base rich parent materials suggesting a minor endogenous Na source associated with mineral weathering. Interestingly, tile waters with a Na deficit relative to mean seawater are all

associated with intensive wintering sites that have Cl and Na concentrations above the respective threshold limits determined above.

Table 4-5: Excess (>1) or deficit (<1) over mean seawater for Southland tile waters.

	N	Mean	Median	SD	C.V.	Min.	Max.	Range
Fc Na	42	1.1	1.0	0.2	0.2	0.8	1.6	0.8
Fc Ca	41	27.8	26.5	11.6	0.4	4.1	50.2	46.1
Fc Mg	42	3.0	2.2	1.8	0.6	1.1	8.8	7.6
Fc K	42	2.9	2.4	2.3	0.5	0.3	10.7	10.4
Fc SO ₄	41	5.1	4.6	2.6	0.5	1.1	9.7	8.6

Excluding tile waters with Cl concentrations in excess of 40 mg/L and recalculating the excess or deficit for all major ions relative to mean sea water, makes little difference to median enrichment values – with only minor decreases in Mg and K and a slight increase in Ca enrichment. This pattern suggests that Na concentrations in tile waters for the most part are dominated by marine aerosols. A similar pattern of minor enrichment in Na relative to mean seawater is observed for ground and surface waters across Southland, again indicating a predominantly aerosolic origin (see TC 2).

Of the major cations, Ca shows by far the greatest magnitude of enrichment (median $F_c = 26.5$), relative to mean seawater, with a range of 4.1 - 50.2. Tile waters associated with organic soils show the lowest enrichment and base rich mineral soils occurring within catchments with known carbonate or mafic parent materials the highest (Figure 4-14). Again this reflects the relationship between soil BS% and the abundance of exchangeable Ca (see lab leaching trial presented in TC 4.1).

Concentrations of Ca for Southland tile drain waters range between 0.5 – 36.2 mg/L with a median value of 17.0 mg/L. Enrichment of Ca generally increases with increasing Ca concentration, although there is some data scatter (Figure 4-14). Elevated Ca F_c values relative to Ca concentration are associated with Melanic soils formed in carbonate rock. These may reflect a difference in proportion of exchangeable Ca to solid state (carbonate) Ca for those samples.

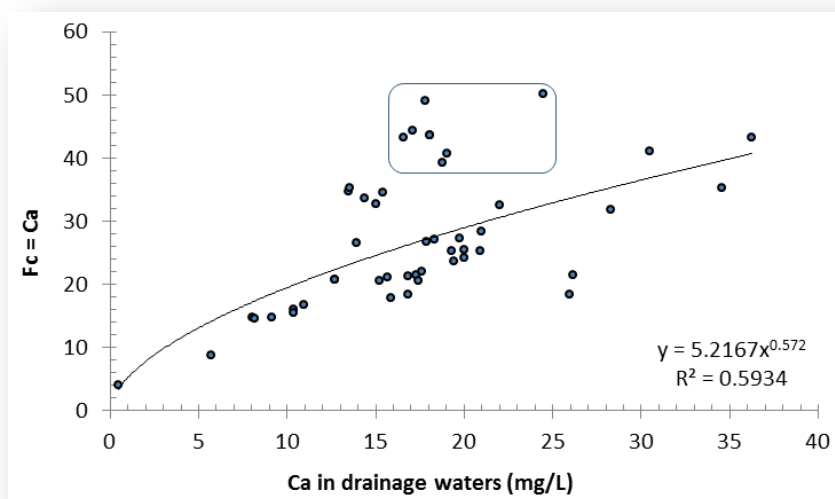


Figure 4-10: Correlation between Ca excess relative to mean seawater (F_c Ca) and Ca concentration in tile drain waters. Waters within the rectangular space originate from catchments with known carbonate rock. The fact that F_c is elevated relative to Ca in drainage waters may reflect a difference between the proportion of exchangeable Ca to solid state Ca (i.e. carbonate).

Median Mg, K, and SO₄ show enrichment factors that are small relative to that of Ca (Table 4-5). Again the ranges for Mg, K, and SO₄ enrichment factors are wide with the most enriched waters associated with soils of high BS% and mafic parent materials (i.e., Braxton and Makarewa soils). Of these three species, SO₄ shows the highest enrichment relative to mean seawater (Fc=4.6), and a median concentration of 19.1 mg/L with a range of 0.8 - 50.0 mg/L (Table 4-5). Ca and SO₄ enrichment factors are also highly correlated, occurring along a continuum between depleted organic and weathered acidic mineral soils and soils of high BS% and mafic parent materials (Figure 4-15).

Magnesium concentrations range between 0.06 - 12.1 mg/L with a median value of 4.5 mg/L. Potassium ranges between 0.1 - 9.6 mg/L with a median of 1.1 mg/L suggesting strong regulation by phyllosilicate. However, anomalous K concentrations (>3.0 - 6.0 mg/L) also occur, and are associated with drainage from areas of organic soils or soils with low phyllosilicate abundance that are less able to buffer high K loadings from animal urine and fertiliser application (Figure 4-13).

Not surprisingly, the relative median concentrations of Ca > Mg > K in tile waters are similar in proportion to the relative abundances of exchangeable ions on soil exchange sites (McLaren and Cameron, 2005). However, as anticipated, Na does not follow the proportionate relationship of exchangeable Na within the soil, with most soils having very limited stores of Na. Although data are limited in this assessment, the general patterns of enrichment for Ca, Mg, K, and SO₄ for Southland soil waters are similar to those observed for regional ground and surface waters (TC 2).

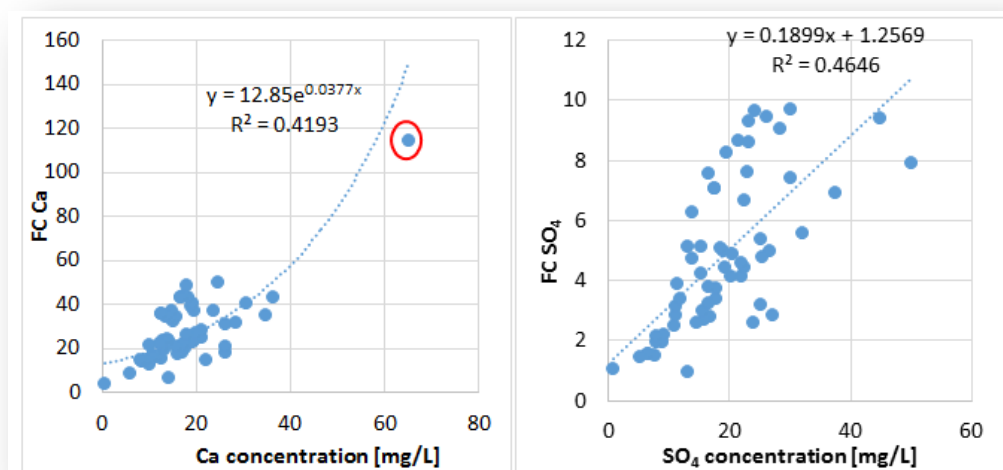


Figure 4-11: Strong positive correlation between a) Ca, and b) SO₄ enrichment factors; the circled sample in plot a) is a mafic soil.

Tile water pH ranges between 4.2 and 8.5 with a median of 6.4. Alkalinity is highest in soil waters with the most reduced signatures (i.e. lowest concentration of oxidised species, such as DO and highest concentration of reduced species, such as Fe(II) and Mn(II)), probably due to heterotrophic oxidation of organic matter. The process and impact of heterotrophic oxidation of organic matter on water quality, in particular alkalinity and pH, is further discussed in TC4.5. Due to the small pH range observed in this study, the correlation between pH and alkalinity is poor; although as a general rule alkalinity is lower for more acidic waters. All soil waters are strongly under-saturated with respect to calcite (CaCO₃) (Figure 4-16).

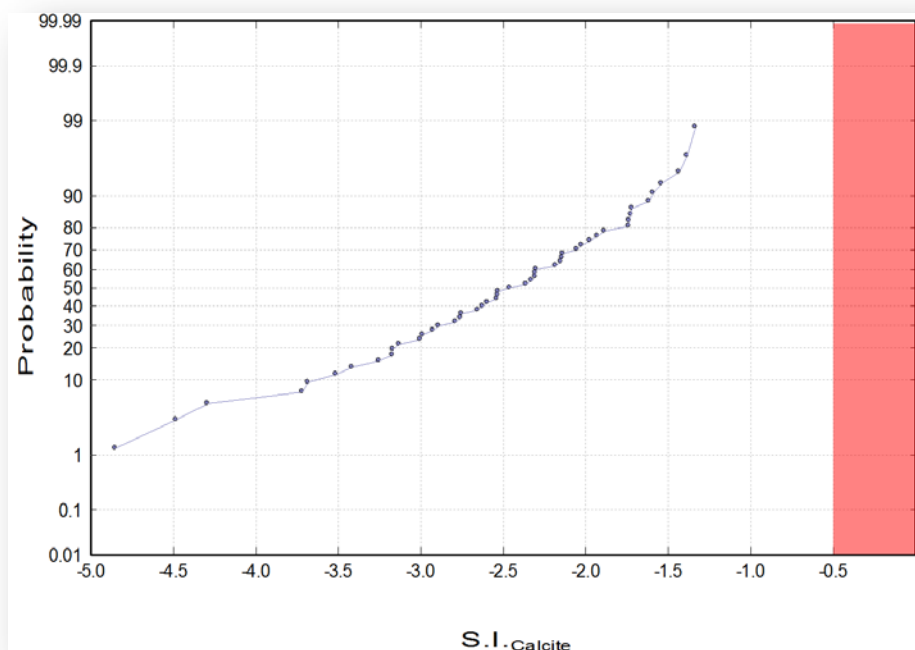


Figure 4-12: Cumulative probability plot of calcite ($\log Q/K \text{CaCO}_3$) Saturation Indices (S.I.) for Southland soil waters. The pink rectangle denotes the zone of equilibrium for calcite with S.I. < -0.5 indicating under-saturation and > 0.5 indicating super-saturation. All samples are under-saturated with respect to carbonate minerals.

The $\delta^{13}\text{C}$ -DIC values of tile drain waters range between -0.1 and -27.8‰ ($n = 35$) with a median value of -18.3‰ (Table 4-6). The $\delta^{13}\text{C}$ -DIC signatures are similar to these found in suction cup soil waters, presented in previously in TC 4.2. Both the suction cup and tile drain soil water $\delta^{13}\text{C}$ -DIC values cluster towards the C3 plant end-member of -24‰ (Boutton, 1996; Amundsen, 2001). The median values for both (i.e. -19.3‰) are similar to the medians of -19.8‰ ($n = 108$) and -19.5‰ ($n = 142$) for northern and southern groundwater, respectively, that are under-saturated with respect to calcite (TC 2). These findings suggest soil respiration processes are the dominant source of alkalinity in soil waters.

Table 4-6: Summary of tile drainage water signature

Parameter	n	Mean	Median	SD	C.V.	Min.	Max.	Range
pH	74	6.1	6.3	0.7	0.1	4.2	7.4	3.2
Water Temp (Field) (°C)	42	10.0	9.3	2.1	0.2	7.5	16.0	8.5
CO ₂ (g) (fug)	37	0.0052	0.0047	0.0028	0.5442	0.0012	0.0112	0.0099
Alkalinity as HCO ₃ (Total) (mg/L)	42	30.0	26.5	15.1	0.5	2.4	71.4	69.0
Alkalinity (carb) (mg/L)	42	0.21	0.03	0.24	1.13	0.002	0.50	0.50
Alkalinity (Bicarbonate) (mg/L)	39	29.3	27.0	14.8	0.5	2.4	71.3	68.9
Dissolved Iron (mg/L)	38	0.23	0.11	0.51	2.27	0.01	3.14	3.13
Dissolved Manganese (mg/L)	38	0.103	0.035	0.305	2.974	0.001	1.905	1.903
$\delta^{13}\text{C}$ -DIC (pptv VMSO)	35	-17.4	-18.3	4.9	-0.3	-27.8	-8.8	19.0

The more positive $\delta^{13}\text{C}$ -DIC value in soil tile drain water than that of the C3 end-member may be a result of the degassing of CO₂ as soil waters exit the soil profile and drain into the open void of a tile (Mulder and Cresser, 1994; Boutton, 1996; Doctor et al., 2008). This is supported by the more negative $\delta^{13}\text{C}$ -DIC values (i.e., -21.4 and -19.2 ‰) of two soil suction cup samples that appear to be less influenced by degassing. Hendy (1971) reported that the isotopic fractionation of HCO₃ due to CO₂ loss becomes significant when the pCO₂ of the solution is greater than twice that of the

atmosphere. Doctor et al. (2007) reported an enrichment of c. 3 ‰ as pCO₂ values dropped from 5.9 to 1.9 times that of the atmosphere within the stream waters of the Sleepers River catchment, Vermont.

The mean pCO₂ for tile waters (i.e., 0.0047 atm.; n = 37) was evaluated according to Stumm and Morgan (1981) in Eqn. 2. We note that soil waters have pCO₂ values that are at least twice that of the atmosphere (1.8 – 50 times atmosphere), and so a net positive flux of soil zone CO₂ to the atmosphere and associated isotopic fractionation is likely. However, it is difficult to detect any clear trends with respect to δ¹³C-DIC enrichment relative to pCO₂ within the soil water dataset. This probably reflects the nature of end of tile sampling with no down profile sampling of soil δ¹³C-DIC prior to interception by the tile and no longitudinal sampling along the length of a tile. Other sources of fractionation may include enrichment of CO₂ isotopologues during diffusion through the porous matrix of the soil by up to +4.4‰ (Rissmann et al., 2012b) or mixing with isotopically more positive atmospheric CO₂ (i.e., c. -7.0‰), although evidence for a positive flux would suggest that an atmospheric source is unlikely.

A positive shift in δ¹³C-DIC due to soil zone carbonic acid dissolution of carbonate within the soil zone is unlikely given historical pH values for the majority of Southland soils are very low (i.e., pH <5.0). In addition, the presence of predominantly felsic parent materials and soil laboratory analysis has demonstrated that Southland soils seldom, if ever, have any free CaCO₃ (DSRI, 1968; O'Byrne, 1986). Even in areas of limestone outcrop free CaCO₃ normally comprises <1 wt. % of the top and subsoil (DSRI, 1986). Furthermore, people sampling soil waters in carbonate terrains commonly note that soil zone alkalinity most often has a soil respiration δ¹³C-DIC signature and that only after infiltration to the underlying carbonate aquifer does soil carbonic acid driven water-rock interaction shift the δ¹³C-DIC towards more positive (i.e., -13‰, V-PDB) values (Doctor et al., 2008).

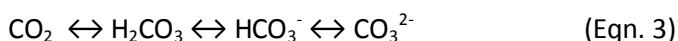
In conclusion, although limited data is available, the median δ¹³C-DIC of Southland soil waters suggests that soil organic matter (and not weathering) is the dominant source of alkalinity for Southland soil waters, at least for >90% of the area for which carbonate rock is absent. This observation is consistent with a dominance of moderately weathered soils, a history of acidic soils and predominantly felsic soil parent materials. These findings also suggest that Ca in soil water and drainage water do not originate from calcite weathering, but are likely sourced from ion exchange with Na originating from evapotranspiration of infiltrating precipitation.

TC4.5 Alkalinity of Southland Soil Waters

As demonstrated in the preceding sections, the soil zone has a significant effect on the hydrochemistry of Southland's soil water. Chemical analysis indicates that the source of alkalinity in Southland's soil water is soil organic matter (on the basis of similar δ¹³C-DIC values in soil water, surface and groundwater). In this section, we show that alkalinity generation within Southland's soils is not limited by the abundance of microbially respired CO₂ and that pH is the chief control over HCO₃⁻ alkalinity generation in Southland soil. In TC 5 we demonstrate that the soil zone determines the alkalinity and major ion concentration of shallow oxidised ground and surface waters for the vast majority of Southland for which carbonate rock is absent. We also show that we can predict the alkalinity of Southland's soil, ground and surface waters (that are oxidized and under-saturated with respect to carbonate minerals) from soil pH using carbonate equilibria relationships.

Alkalinity is defined as the capacity of water for neutralising an acid solution or the buffering capacity of water. Since the main contributors to alkalinity in natural environments are carbonate species

(bicarbonate and carbonate)¹, total (or carbonate) alkalinity is also defined as the amount of strong acid required to titrate water to pure carbonic acid. The abundance of bicarbonate and carbonate ions in water is dependent on pH, pCO₂, and temperature as illustrated in Figure 4-17 to Figure 4-19. For example, with increasing pH, carbonate equilibrium is moved towards the left, producing more CO₂ and carbonic acid compared to bicarbonate and carbonate, consequently decreasing alkalinity (Eqn. 3, not balanced).



(carbon dioxide ↔ carbonic acid ↔ bicarbonate ↔ carbonate)

Soil water tends to have high levels of DIC² due to high pCO₂ within the soil zone (Mulder and Cresser, 1994; Boutton, 1996; Sposito, 2008). Generally, soil temperature and availability of water govern metabolic rates and hence plant growth including magnitude of root respiration (Figure 4-21) and microbial activity such as heterotrophic oxidation of soil organic matter (e.g. Boone et al., 1998; Kirschbaum, 2006). As a consequence, generally, lower soil CO₂ production rates occur during the winter months when soils are cooler. CO₂ production is typically highest within the topsoil but pCO₂ peaks within the subsoil due to less exchange with (or loss to) the atmosphere (Figure 4-21).

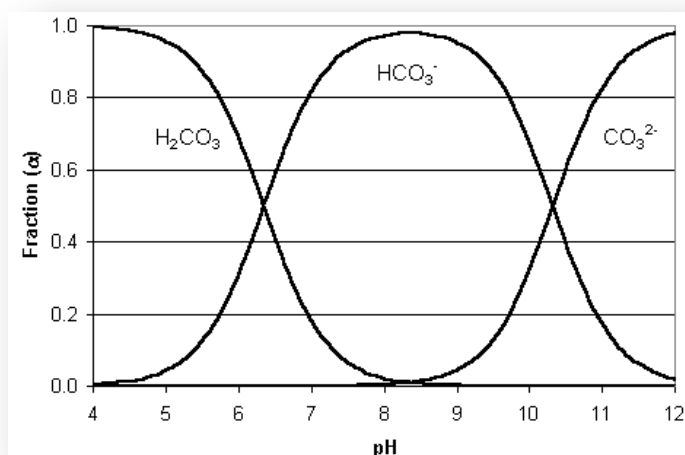


Figure 4-13: pH dependent carbonate speciation in water (after Plummer and Busenberg, 1982).

¹ A minor and often negligible contribution to alkalinity have silicates, borates, phosphates, ammonia, and organic acids and bases. These become only important if they appear in (unnaturally) elevated concentration, e.g. in the outflow of waste treatment plants.

² DIC is the sum of H₂CO₃ + HCO₃⁻ + CO₃²⁻

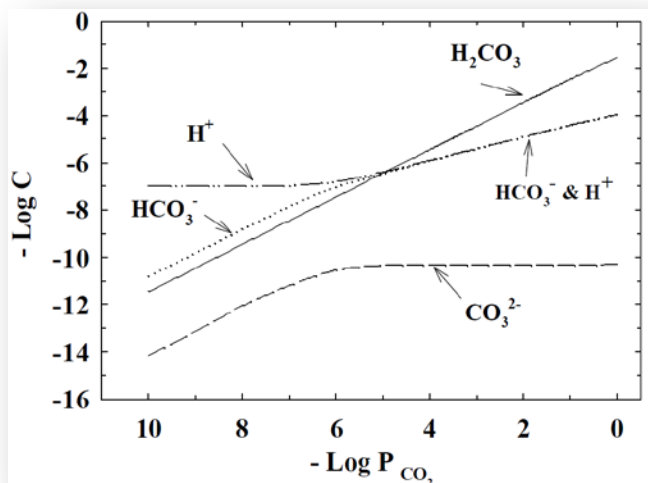


Figure 4-14: Effect of carbon dioxide partial pressure ($p\text{CO}_2$) on the solution concentration of carbonate species in the CO_2 -water system (modified from McBride, 1994).

In Southland, most soils are at or are close to soil moisture field capacity from May to August (Wilson et al., 2014; Chanut, 2014). Soil temperatures during the months of greatest soil drainage are relatively uniform across the region with mean temperatures ranging between 7.05°C – 7.10°C at 0.1 m depth for 19 of Environment Southland’s 20 soil moisture sites. Over the same time period, the median temperature for all groundwater ranged between 3.7 and 12.6°C with a mean of 7.1°C and a median of 6.8°C . On the basis of these observations, it is expected that soil moisture and soil temperature during May to August are not limiting CO_2 production in the soil zone across the region.

Direct measurement of soil CO_2 concentration profiles were made at four regional soil moisture sites and at two locations at Environment Southland during August 2015. CO_2 concentrations were measured within the atmosphere (c. 1 m above the soil surface) and at 0.2, 0.4, and 0.6 m depth using a Li-COR LI820 Infrared Gas Analyser and a soil gas sampling probe following the method of Rissmann (2014). Soil $p\text{CO}_2$ concentrations for the six measurement sites ranged between 375 – 14,295 ppmV (3.75×10^{-4} – 0.015 atm) and show a general picture of increasing CO_2 with depth with a mean $p\text{CO}_2$ of 0.0047 atm or $4.7 \mu\text{atm}$ (Figure 4-21 and Figure 4-22). The mean $p\text{CO}_2$ value for soil gas profiles is similar to that of soil waters (i.e., 0.0047 atm.; $n = 37$) and that of oxic groundwaters that are under-saturated with respect to carbonate minerals³ (median = 0.0038 atm.; $n = 513$) calculated using Equation 2 (TC 4.3).

³ Reducing groundwater were excluded as heterotrophic reduction of terminal electron acceptors produces additional alkalinity under favourable pH conditions.

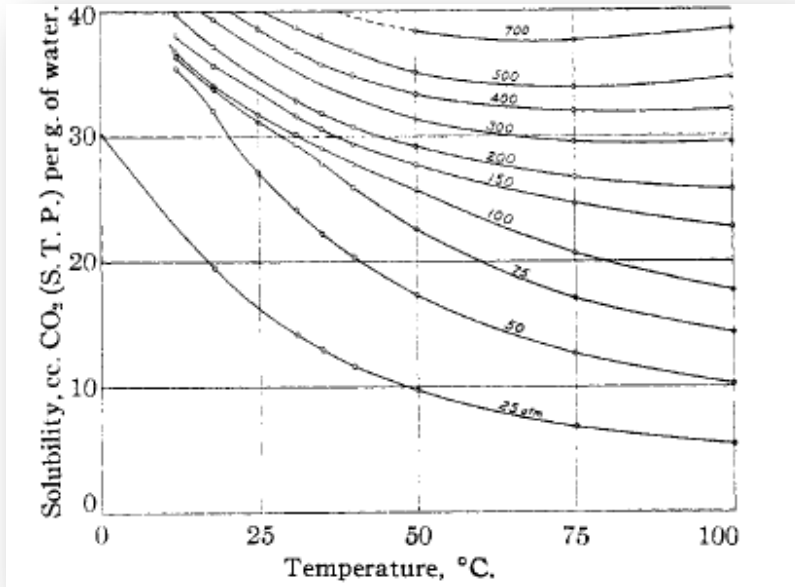


Figure 4-15: Effect of temperature on CO₂ solubility [Wiebe and Gaddy, 1940]

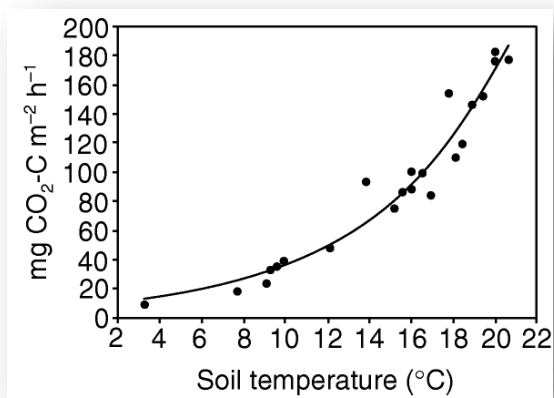


Figure 4-16: Relationship between mean daily CO₂ flux (calculated) from 'roots' and soil temperature at 5cm depth (Boone et al., 1998).

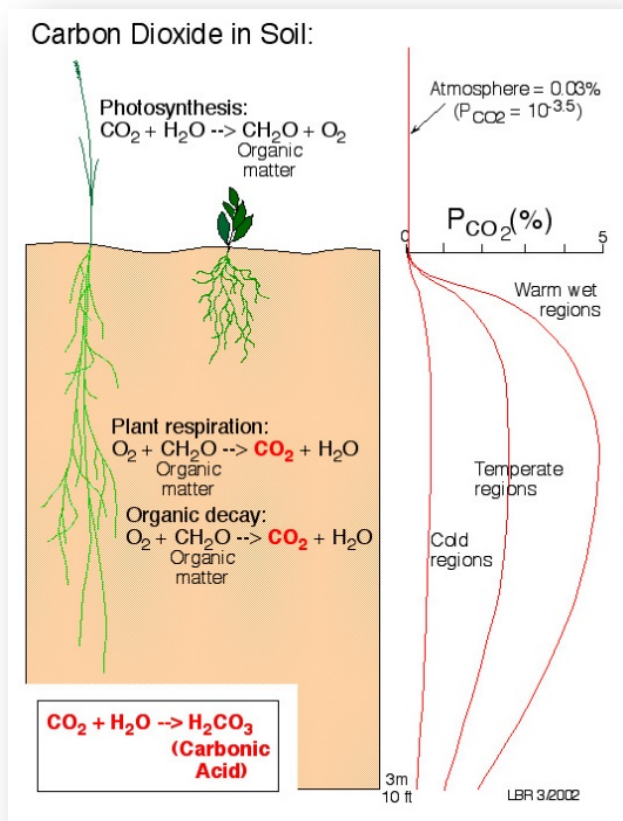


Figure 4-17: Schematic of CO₂ and H₂CO₃ (carbonic acid) population in the soil zone (Railsback, 2012).

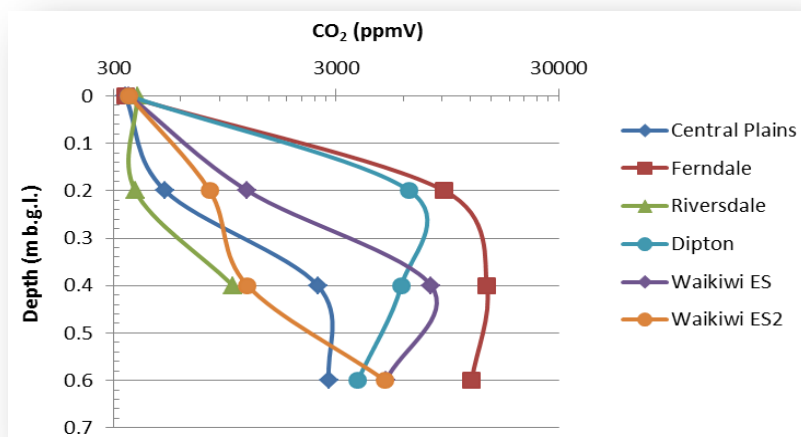


Figure 4-18: CO₂ concentration profiles (ppmV) for six soils in Southland, measured August, 2015.

Soil pH is typically measured by a pH electrode in 1:5 slurry of field moist soil to deionised water. Averaged horizon depth-weighted pH measurements for 583 Southland soils range between 3.4 and 7.8 with a median pH of 5.8 (TC 3). The relatively wide range in soil pH paired with an abundance of CO₂ and relatively consistent soil temperatures across Southland, suggests that alkalinity production within recharge waters is primarily limited by soil and unsaturated zone pH. For example, in acidic soils, alkalinity concentrations are expected to be considerably lower than in basic soils (Figure 5-17).

Method

Using the 583 discrete measures of soil pH and Southland specific soil temperature and pCO₂ values noted above, we calculated the theoretical alkalinity of soil waters through application of the carbonate equilibria equations of Plummer and Busenberg (1982) to produce a range of theoretical alkalinity curves (HCO₃⁻ + CO₃²⁻) for Southland soil water (Figure 5-23). For comparison, measured soil-, ground-, and surface water alkalinities are plotted against theoretical soil alkalinity curves in Figure 5-24.

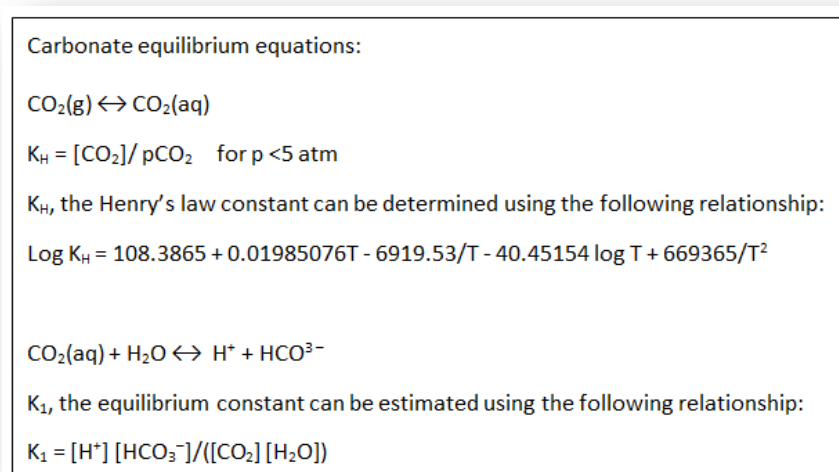


Figure 4-19: Carbonate equilibrium equations (after Plummer and Busenberg, 1982).

Results

Figure 4-21 shows that the majority of alkalinities measured for soil water fell between the theoretical alkalinities determined for mean soil gas pCO₂ (of 0.0047 atm) and atmospheric pCO₂. With the exception of very acidic soil waters (<4.5 pH units from peat wetland soils) that have no detectable bicarbonate or carbonate alkalinity (<0.5 mg/L), the prediction of soil water alkalinity using carbonate equilibria relationships was reasonable. Overall, the measured alkalinity of soil waters was slightly lower than the predicted alkalinity. This may reflect the small soil gas sample size and/or potential underestimation of soil pCO₂ and/or (most likely) the recognised tendency for simple carbonate equilibria calculations of the CO₂-H₂O system to overestimate actual soil water alkalinity due to other sources of alkalinity consuming acidity within soil systems that were not accounted for (see also Thaysen et al., 2014).

Table 4-7: Soil CO₂ concentrations (ppmV) for Southland Soils.

Depth	No.	Mean	Median	SD	C.V.	Min.	Max.	Range
Atmosphere	6	353	353	16	0.05	339	383	45
0.2 m	6	3083	1006	3770	1.22	375	9200	8825
0.4 m	6	4986	3751	4974	1.00	1033	14295	13262
0.6 m	5	6350	5000	3813	0.60	2788	12193	9405
All soil	17	4716	3754	4204	0.89	375	14295	13920

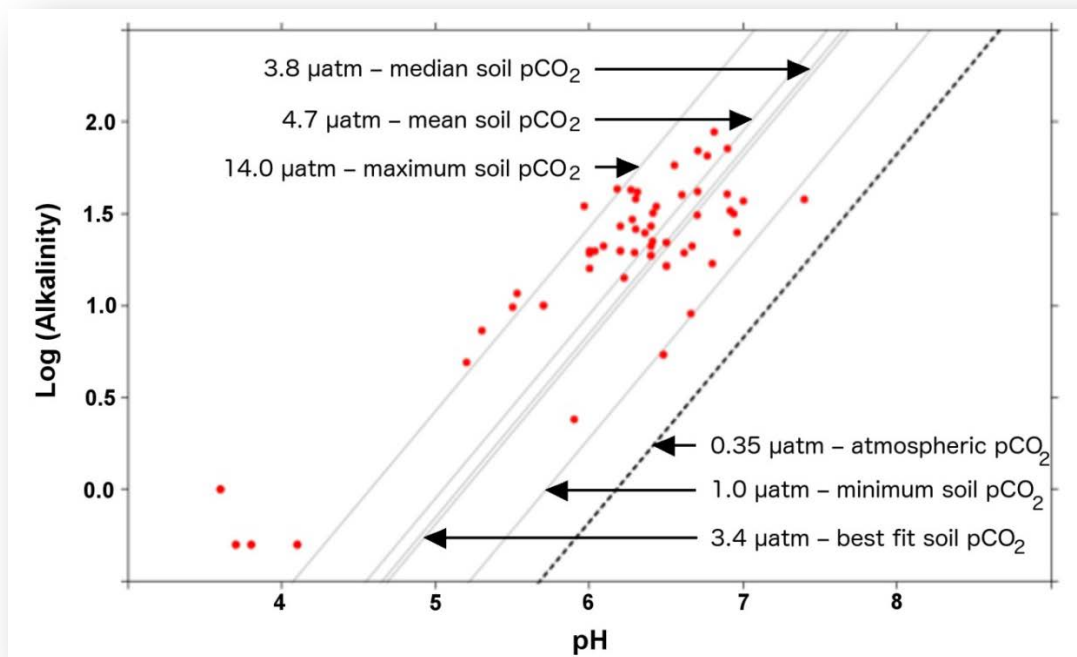


Figure 4-20: Log Total Alkalinity vs. pH plot for Southland soil waters. Acidic soil waters (pH < 4.5) have no bicarbonate or carbonate alkalinity. The majority of soil waters fall between the 1.0 and 4.7 μatm range for CO_2 partial pressure. pCO_2 isolines are modelled using a recharge temperature of 7°C estimated from soil and shallow groundwater measurements (note, a change in temperature of +/-1 °C does not considerably affect pCO_2 values).

On the basis of these findings, we proposed using the pCO_2 range of 0.001 – 0.0047 atm. to predict the upper and lower bounds of theoretical soil recharge water alkalinities for Southland, respectively. We note that a mean pCO_2 of 0.0034 atm. generated similar mean and median alkalinity values to the soil water data set (i.e., actual mean and median = 27.3 ± 7.3 and 22.4 ± 6.3 mg/L, C.I.; $p = 0.05$; modelled = 25.4 ± 1.3 and 24.1 ± 0.5 mg/L, C.I.; $p = 0.05$), which supported the choice of a pCO_2 range of 0.001 – 0.0047 atm. to predict the upper and lower bounds of theoretical soil water alkalinities, respectively.

To confirm whether the source of alkalinity in ground- and surface- water in Southland is soil alkalinity (as suggested by the similarity of $\delta^{13}\text{C}$ -DIC values in soil, ground and surface water indicating a consistent soil organic carbon source, presented in TC 2), we compared the estimated theoretical soil alkalinities with alkalinities measured in ground- and surface- water (Figure 5-25 and Figure 5-26)⁴. Theoretical soil water alkalinity and that of oxic non-carbonate groundwaters were similar, supporting the concept that the soil zone is the dominant source of alkalinity in Southland's water. This also supports that other sources, e.g. from dissolution of aquifer material (i.e. carbonates), do not likely contribute considerably to the alkalinity in most regional ground and surface waters. Specifically, the majority of Southland groundwaters fell between the 1.0 and 4.7 μatm pCO_2 range determined for the soil zone.

⁴ Oxidised surface and groundwater that are under-saturated with respect to calcite.

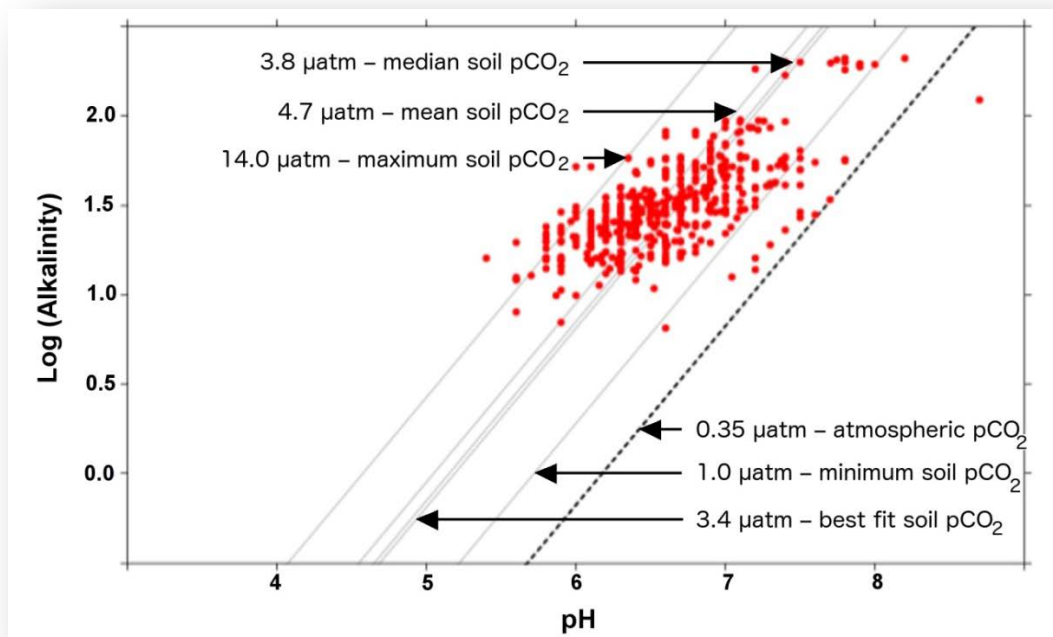


Figure 4-21: Log Total Alkalinity vs. pH plot for oxic groundwater that are under-saturated with respect to calcite (<-1.0). The majority of groundwaters fell between the 1.0 and 4.7 μatm range for pCO_2 . pCO_2 isolines are modelled from Southland soil temperature, pCO_2 , and pH values.

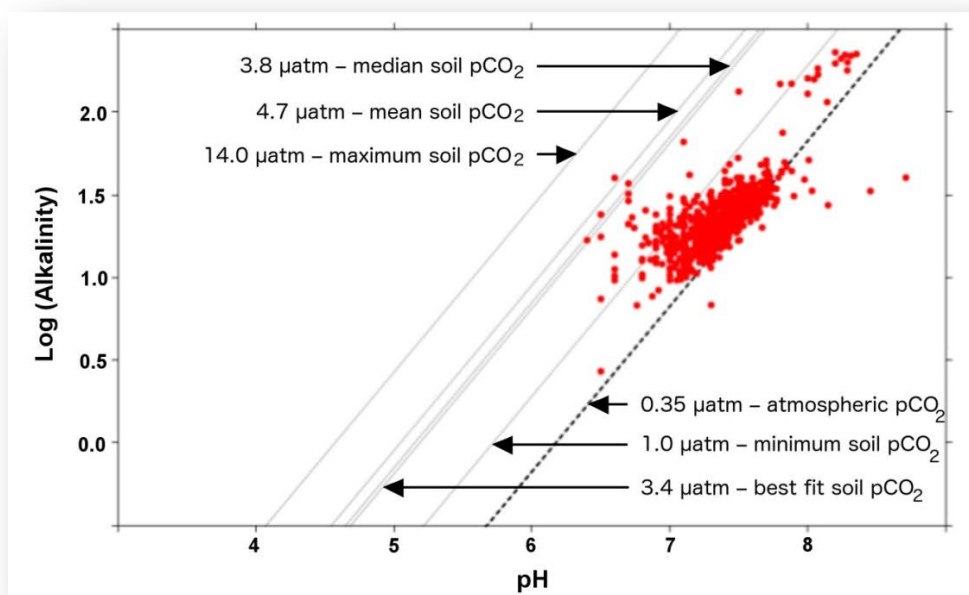


Figure 4-22: Log Total Alkalinity vs. pH plot for oxic surface waters that were under-saturated with respect to calcite (<-1.0). The majority of surface waters fell between the 1.0 and 4.7 μatm range for pCO_2 . pCO_2 isolines are modelled from Southland soil temperature, pCO_2 , and pH values.

Finally, Figure 4-24 is a contour plot (nearest neighbour) of predicted soil water alkalinities based on the 558 soil profile sites (using the pCO_2 range of 0.001 – 0.0047 atm., horizon weighted mean soil pH (specific for each site) and the mean winter (May – August) recharge temperature of $7.0 \pm 0.5^\circ\text{C}$). As shown, in most instances, with the exception of very acidic organic soils, alkalinity generation within

the soil zone was more than sufficient to account for the concentrations observed in regional ground- and surface- waters (TC 5). As expected, pH was the key control over the speciation of inorganic carbon and generation of alkalinity in soil water. This was further supported by the strong correlation of soil BS% and theoretical alkalinity in Southland soils (Figure 4-25), which confirmed the control of BS% over pH as noted in TC 3 and TC 8.

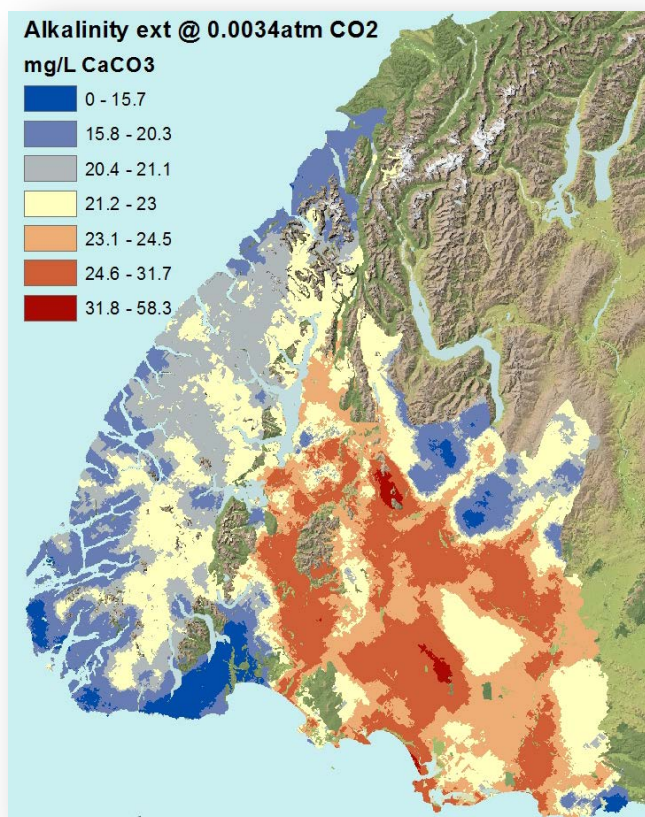


Figure 4-23: Predicted alkalinities for Southland using carbonate equilibrium relationships, a $p\text{CO}_2$ range of 0.001 – 0.0047 atm., horizon weighted mean soil pH (specific for each site), and the mean winter (May – August) recharge temperature of $7.0 \pm 0.5^\circ\text{C}$.

TC4.6 Summary

In summary, laboratory leaching trials, field suction cup analysis and assessment of tile drain water samples from across Southland suggested that evaporative concentrations of marine aerosolic Na and Cl play an important role over the hydrochemical evolution of Southland’s soil waters. The concentration of salts by evapotranspiration is a well-recognised phenomenon resulting in median soil water concentrations for Na and Cl that are four times higher than the mean for precipitation across lowland Southland.

Whilst evapotranspiration concentrates salts, soil salinisation does not occur due to Southland’s humid climate and frequent flushing of concentrated salts from the topsoil to depth during recharge events. On the basis of our findings, we suggest that seasonal flushing of soil zone salts, especially Na and Cl, concentrated by evapotranspiration, results in pulses of high EC recharge either to ground- or surface- waters as demonstrated by a number of studies within the Southland region (Houlbrooke and Monaghan, 2009; Cameron et al., 2014). Patterns of seasonal flushing of high salt content in soil zone waters, was apparent in a number of continuous data records (ES unpublished data).

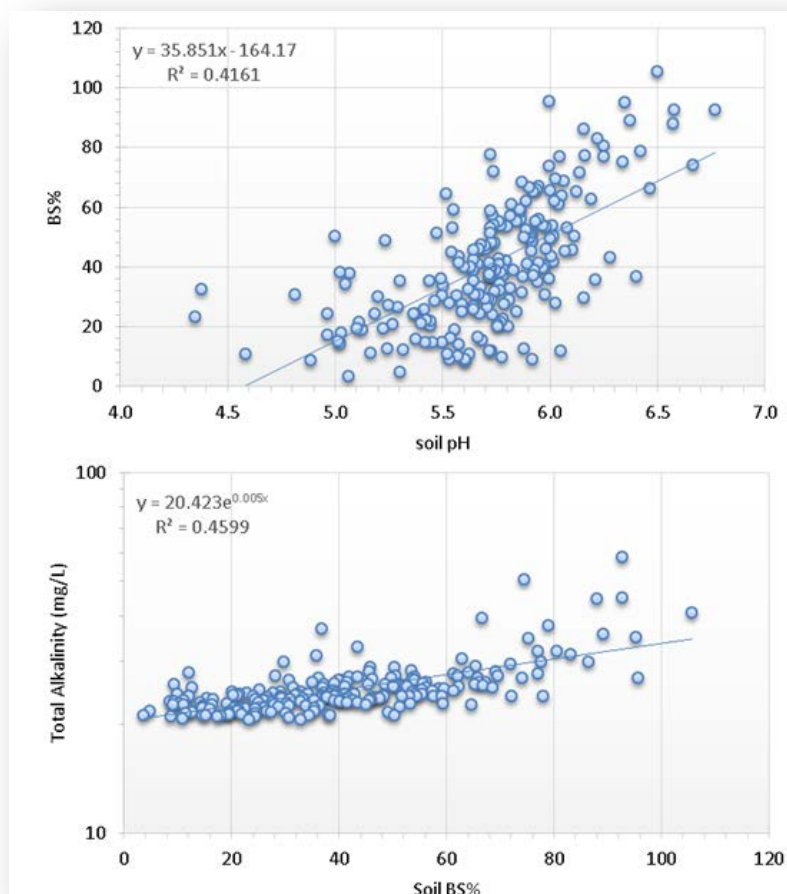


Figure 4-24: Relationship between: a) Southland soil pH and BS%; and b) Southland soil BS% and modelled Total Alkalinity.

We found that generally, Na and Cl concentrations in Southland soil waters were dominated by marine aerosolic inputs. Although anthropogenic sources of Na and Cl were ubiquitous, they are often swamped by the much larger contribution from marine aerosolic rainout. Specifically, Na in soil waters were primarily of a marine aerosolic origin but did exhibit a minor contribution from epigenic mineral weathering and subsequent ion exchange. Therefore, as with other temperate maritime regions, the Na and Cl content of Southland soil waters were mainly derived from wet and dry deposition of marine aerosols that subsequently become concentrated within the upper portion of the soil profile due to evapotranspiration. However, there were instances when high loadings from intensive land use made an additional contribution to the Na and Cl concentrations of soil waters. Furthermore, in high altitude inland catchments, marine aerosolic loadings were negligible and mineral weathering was the main source of Na.

Ca was by far the most enriched major ion relative to precipitation, which is consistent with a dominantly epigenic source coupled to mineral weathering and subsequent ion exchange. Sulphate, along with Mg and K, showed significant enrichment relative to mean seawater. The relative abundance of Ca, Mg, and K in soil waters showed a similar pattern to that of exchangeable ions on soil exchange sites, whereas Na and Cl concentrations did not.

Finally, the alkalinity of DIC of soil zone waters exhibited a strong soil organic carbon (C3) origin with little evidence for contribution from calcite or carbonate weathering, which is consistent with the findings of other studies (Clark and Fritz, 1997; Doctor et al., 2008 and references therein). Our data

suggested that the soil zone is often the main source of alkalinity in oxic ground- and surface- waters and we demonstrated that it is possible to predict the relative magnitude of alkalinity generated within the soil zone using Southland specific data and carbonate equilibria. These findings are important for subsequent chapters where we demonstrate that the soil zone is the major source of alkalinity for Southland's oxidised and/or weakly reduced ground- and surface- waters that are under-saturated with respect to carbonate minerals.