

# **Physiographics of Southland**

## **Part 1:**

### **Delineation of key drivers of regional hydrochemistry and water quality**

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## **Technical Report**

June 2016

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# **Physiographics of Southland**

## **Part 1:**

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#### **Technical Chapter 5:**

#### **Comparison of Soil Water with Surface water and Groundwater Chemistry**

June 2016

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## TC5 Comparison of Soil Water with Surface water and Groundwater Chemistry

### TC5.1 Introduction

In this chapter we demonstrate that the majority of chemical constituents in Southland's groundwater and surface waters are inherited when recharge waters that move through the soil zone. We demonstrate that with the exception of highly reactive carbonate rocks and rapid redox reactions, little post-infiltration evolution of Southland's waters occurs. These observations are consistent with theoretical perspectives on water evolution in temperate, humid climates, dominated by silicate rocks in which carbonate free soils, alluvium, and bedrock have little acid buffering capacity and mineral assemblages take long time periods to weather (Lasaga, 1984; Rissmann et al., 2012a; Clark and Fritz, 1997; Doctor, 2015).

### TC5.2 Methods

The chemistry of surface water and groundwater were compared with that of soil to investigate the importance of soil (and other) processes on groundwater and surface water chemistry. Southern and northern surface water and groundwater were studied separately as they have significantly different chemical compositions (refer to TC 2 for further detail on the categorisation of waters). Redox state for groundwater, surface water and soil waters were defined using the USGS workbook (Jürgen et al., 2009) which is based on the method of McMahon and Chappelle (2008). It is noted that the redox assignment framework of McMahon and Chappelle (2008) is designed specifically to assess the redox status of aquifer systems. We also note that this framework should be used with caution, because it has been developed without consideration for the role of the soil zone over groundwater redox status.

To assess the influence of carbonate rocks on groundwater and surface water chemistry, calcite saturation was determined. For a meaningful comparison of surface water and groundwater chemistry with soil water chemistry, the dataset was restricted to southern surface water and groundwater, due to the majority of soil waters being collected in southern Southland. Additionally, groundwater and surface water samples exhibiting a calcite saturation index(SI) > -1.0 were excluded from this analysis, because of the influence of carbonate rock or shell bed interactions on their composition. Surface water samples with northern head waters were also excluded, because they are expected to show a mixed Alpine-Lowland signature. This resulted in a reduction in the number of southern sites from 111 to 74 for groundwater and from 66 to 40 for surface water.

The soil water dataset consisted of 119 samples (83 individual sites), that were a mixture of tile drain samples and soil suction cup waters, all but one was collected in southern Southland (Figure 4-1). Twenty of these samples were seasonal repeats, one winter and one summer, except at two sites within the Waituna Catchment, where three and four repeats were included.

The **southern oxic groundwater** dataset consisted of 254 samples (74 individual sites). There were 25 sites for which more than one sample had been collected. The maximum number of analyses at a given site was 18 (F45/0183).

The **southern oxic surface water** dataset consisted of 331 samples (40 individual sites). There were 23 sites at which more than one sample was collected. The maximum number of analyses for a given site was 33 (Waiau River at Sunnyside).

### TC5.3 Results

#### TC5.3.1 Data subsetting using calcite saturation indices and redox state

A cumulative probability plot of calcite ( $\text{CaCO}_3$ ) Saturation Indices (SI) for southern groundwater (Figure 5-1), indicates a number of inflection points or thresholds corresponding to distinct SI populations (the use of cumulative probability plots is further detailed in Appendix A1). The pink rectangle denotes the zone of equilibrium with calcite with  $\text{SI} < -0.5$  indicating under-saturation and with  $\text{SI} > +0.5$  indicating super-saturation. An inflection at c.  $-1.0$  suggests the influence of carbonate rocks can be seen even in under-saturated waters. The waters with  $\text{SI} > -1.0$  have a high incidence of carbonate rock or shell beds reported in bore log data (as further discussed in TC 7). They also exhibit elevated Ca, Total Alkalinity, Carbonate alkalinity, and EC relative to  $< -1.0$  waters. The cumulative probability plot of calcite S.I. for northern groundwater shows fewer carbonate-influenced waters (inflection at  $-0.5$ ; Figure 5-2).

The cumulative probability plot of  $\text{SI}(\text{CaCO}_3)$  for oxic southern surface waters (Figure 5-3) is similar to that of oxic southern groundwater for which the influence of carbonate rocks can be seen at SI of  $> -1.0$ . A similar plot for oxic northern surface waters shows fewer carbonate-influenced waters with an inflection at  $-0.5$  (Figure 5-4), which is similar to the northern groundwater plot. Overall, the influence of carbonate rocks appears to be greater in southern Southland than northern Southland. Specifically, the majority of southern surface water samples with  $\text{SI} > -1.0$  are associated with known areas of carbonate rock (i.e., Waimatuku and Isla Bank, Tussock Creek, Bogburn, Winton Stream, Opouriki, Middle Creek, and Orauea streams/rivers).

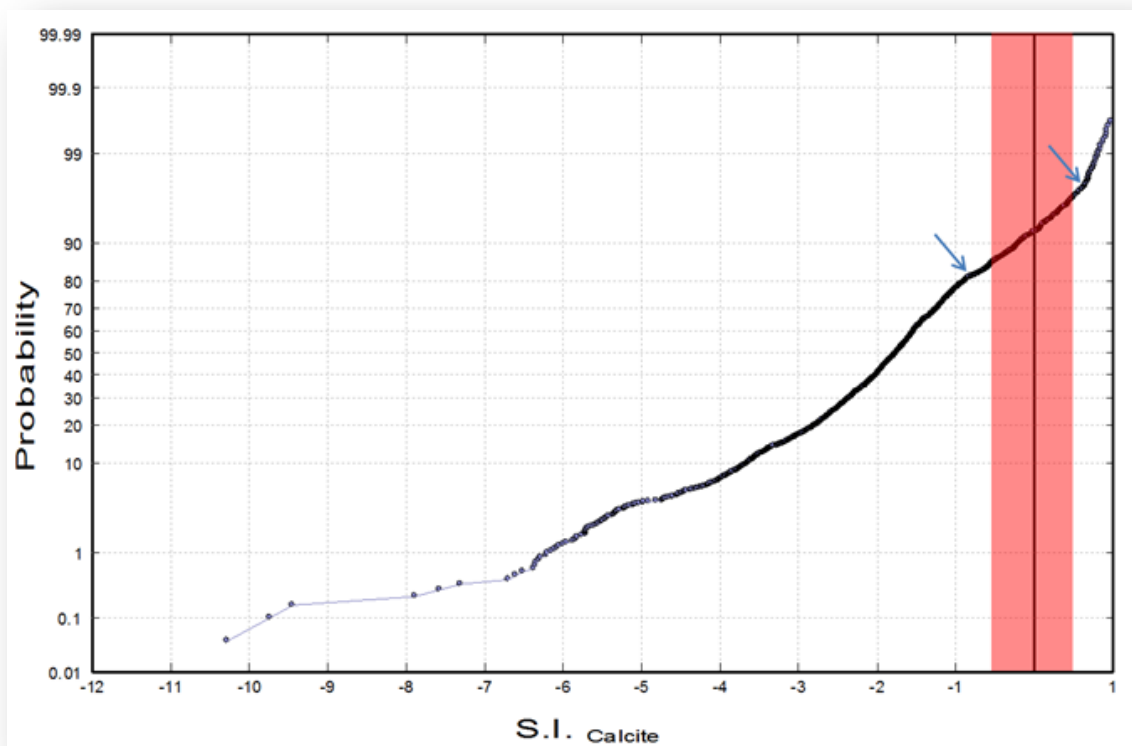


Figure 5-1: Cumulative probability plot of calcite ( $\text{CaCO}_3$ ) Saturation Indices (SI) for southern groundwater. The pink rectangle denotes the zone of equilibrium with  $\text{CaCO}_3$  with  $\text{SI} < -0.5$  indicating under-saturation and those  $> 0.5$  indicating super-saturation. Blue arrows indicate important inflections or threshold values in the data.

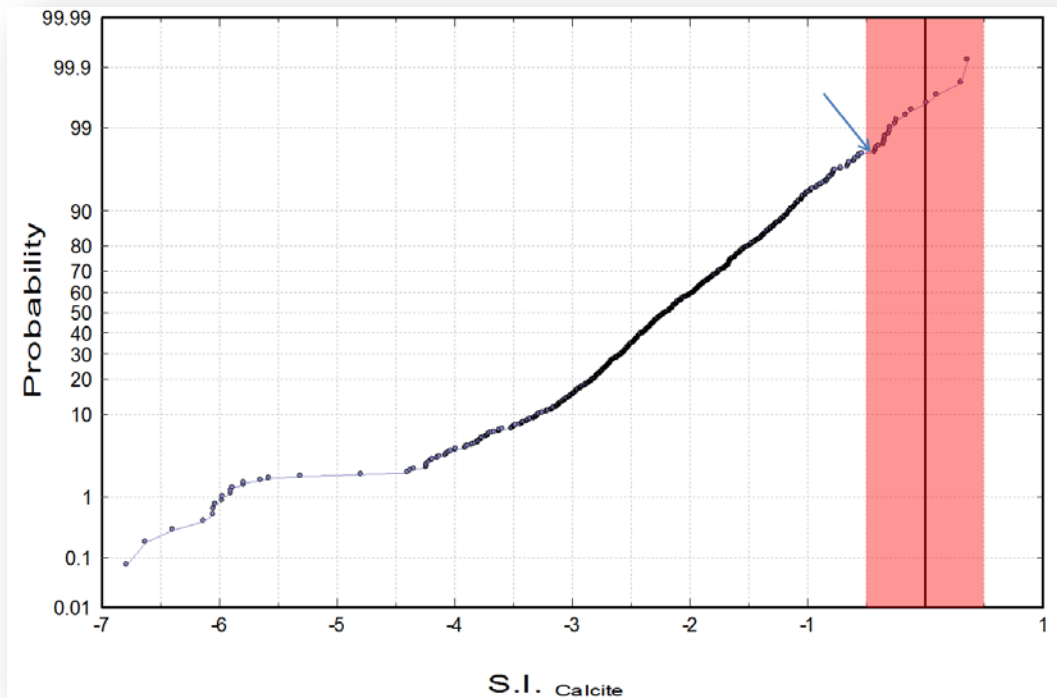


Figure 5-2: Cumulative probability plot of calcite ( $\text{CaCO}_3$ ) Saturation Indices (SI) for northern groundwater. The pink rectangle denotes the zone of equilibrium with  $\text{CaCO}_3$  with SI < -0.5 indicating under-saturation and those > 0.5 indicating super-saturation. Blue arrow indicates important inflection or threshold value in the data.

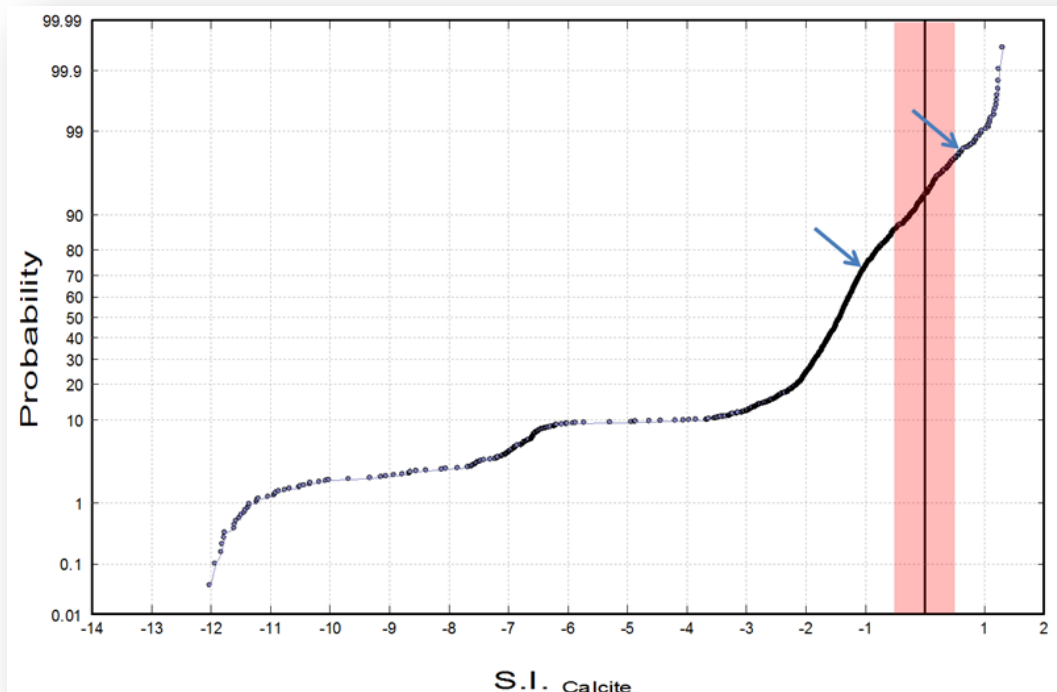


Figure 5-3: Cumulative probability plot of calcite ( $\text{CaCO}_3$ ) Saturation Indices (SI) for southern surface waters. The pink rectangle denotes the zone of equilibrium with  $\text{CaCO}_3$  with SI < -0.5 indicating under-saturation and those > 0.5 supersaturation. Blue arrows indicate important inflection or threshold values in the data. Southern groundwater and surface waters show similar populations and thresholds.



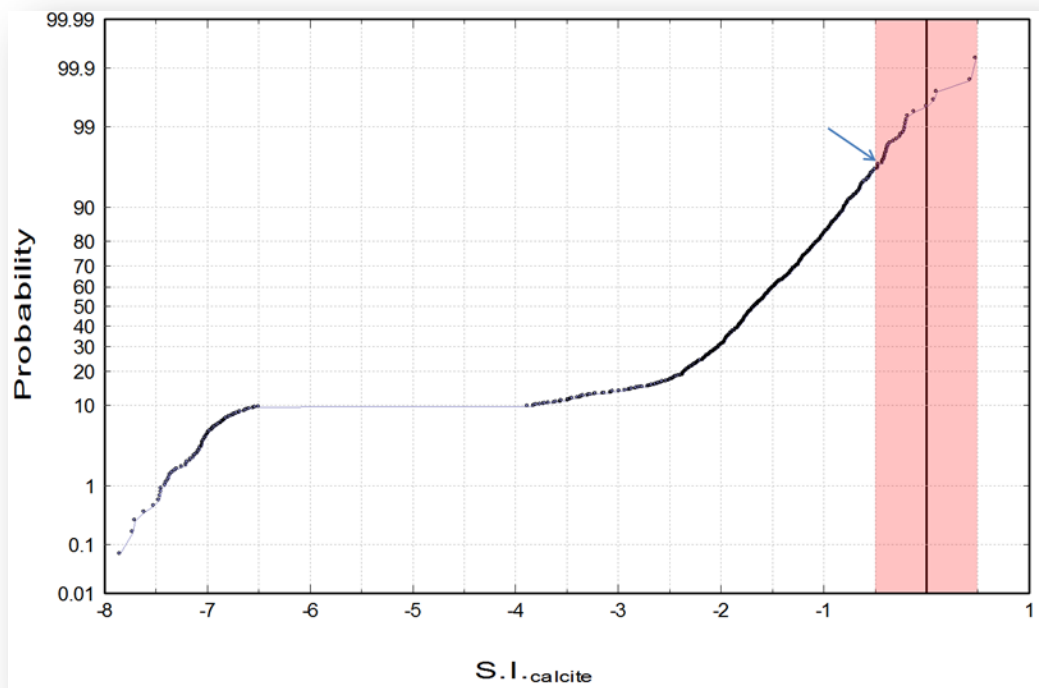


Figure 5-4: Cumulative probability plot of calcite ( $\text{CaCO}_3$ ) Saturation Indices (SI) for northern surface waters. The pink rectangle denotes the zone of equilibrium with calcite with  $\text{SI} < -0.5$  indicating undersaturation and those  $> 0.5$  indicating supersaturation. Blue arrow indicates important inflection or threshold value in the data. The points with the most under-saturated waters are all associated with high altitude streams. With the exception of high altitude samples, northern ground- and surface- waters show similar populations and thresholds.

### TC5.3.2 Soil water vs. shallow groundwater and surface water

The major hydrochemistry from soil water, groundwater and surface waters is illustrated in Figure 5-5 and Figure 5-6. Median concentration of selected hydrochemistry parameters are summarised in Table 5-1. The parameters that are statistically significantly different between ground or surface water and soil water are highlighted (Wilcoxon  $p$ -value  $< 0.05$ ).

Stable isotope ratios ( $\delta^{18}\text{O}\text{-H}_2\text{O}$  and  $\delta^2\text{H}\text{-H}_2\text{O}$ ) are similar in soil waters and oxic southern groundwater that are under-saturated with calcite, hereafter referred to as “oxic southern groundwater” (Table 5-1). This supports a similar origin and/or similar processes controlling the chemistry of soil water and oxic southern groundwater and rules out strong altitudinal effects over groundwater that can influence major ion composition (TC 7). Boron isotope values ( $^{11}\text{B}\text{-B}$ ), the median  $\text{Cl}/\text{Br}$  ratio and the concentrations of conservative ions,  $\text{Br}$  and  $\text{Cl}$ , are also similar in oxic southern groundwater and soil water (Wilcoxon  $p$ -value  $< 0.05$ ). These findings again support similar controlling factors or water provenance and solute sources of soil water and oxic southern groundwater.

Median concentrations of  $\text{Na}$ ,  $\text{K}$ ,  $\text{Mg}$ ,  $\text{Ca}$ ,  $\text{Cl}$ , and alkalinity are also very similar in soil and southern groundwater (Wilcoxon  $p$ -value  $< 0.05$ ; Figure 5-5). Median  $\text{Ca}$ ,  $\text{pCO}_2$  values, and alkalinity is not significantly higher in groundwater than in the soil (Table 5-1), although the southern groundwaters are slightly more alkaline (+ 0.3 pH units) compared to soil water. In addition, the median  $\delta^{13}\text{C}\text{-DIC}$  of -19.1‰ for southern oxic groundwater subset is similar to that of soil waters (i.e., -19.8‰) supporting a dominant C3 soil zone organic carbon signature (TC 2, TC 3 and TC 4). Furthermore, for oxidised non-carbonate groundwater, the similarity between soil water and groundwater alkalinity, major

ions, and  $\delta^{13}\text{C}$ -DIC signatures is consistent with the limited acid buffering potential of silicate minerals, relative to carbonate rock, for which consumption of soil zone carbonic acid during water-rock interaction generally occurs at a very slow rate (Lasaga, 1984).

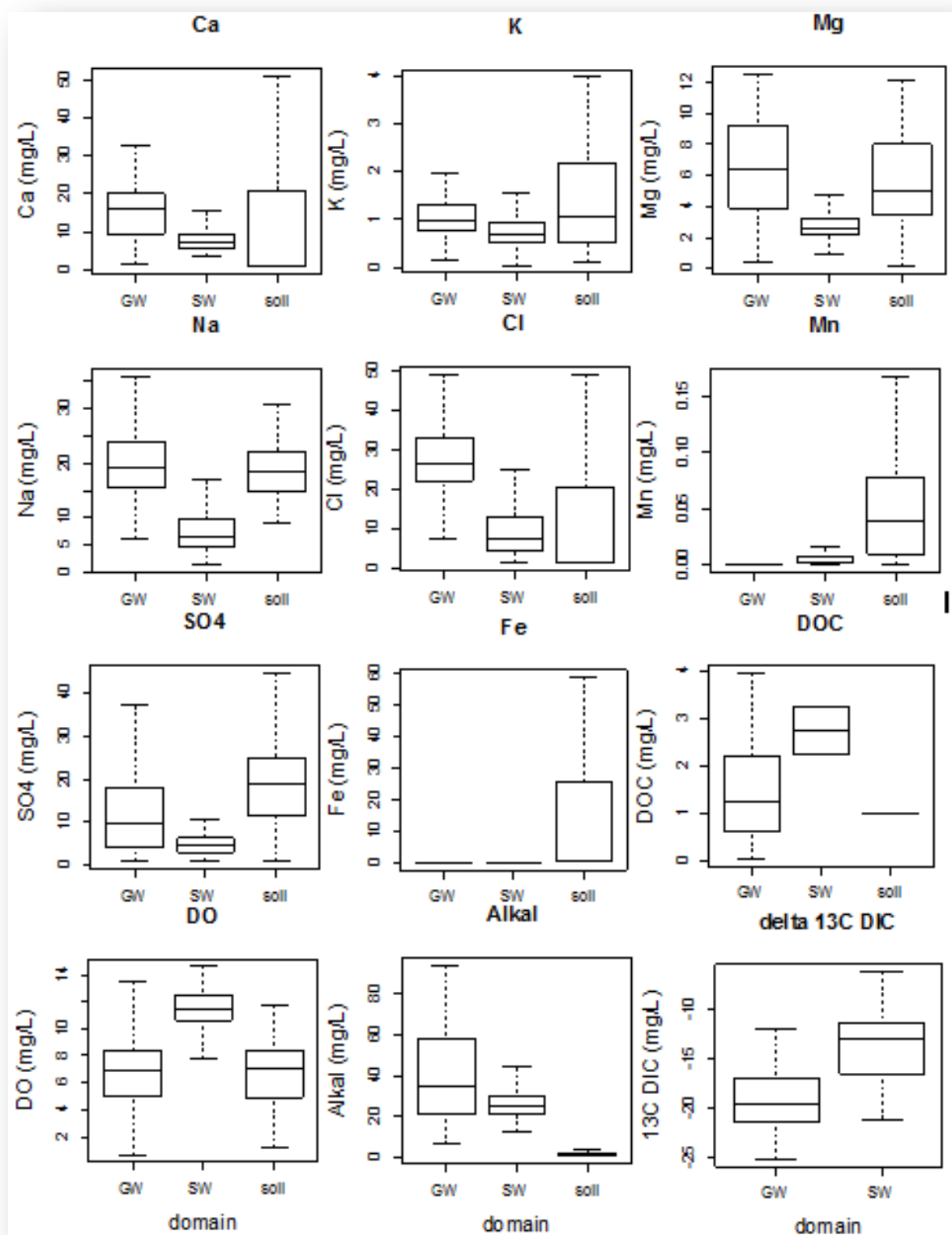


Figure 5-5: Selected parameter boxplots for soil waters and southern oxic groundwater.

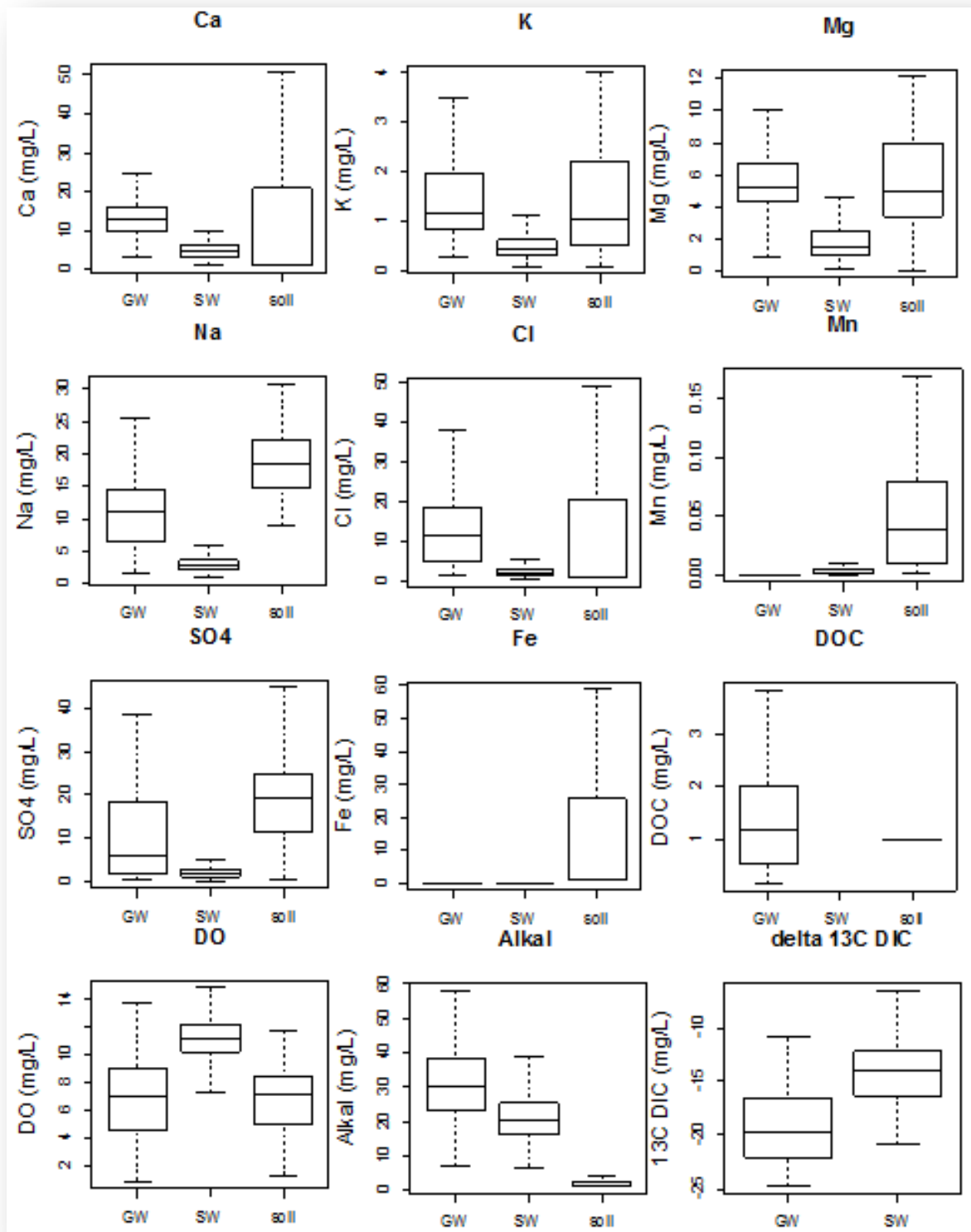


Figure 5-6: Selected parameter boxplots for soil waters and northern oxalic groundwater.

Overall, the similarity of soil water composition and groundwater composition indicates that post infiltration water-rock interaction is not an important source of Ca or alkalinity (also highlighted in TC 3 and TC 4). The differences that do exist between the composition of soil waters and groundwater are readily explained by filtration, redox reactions, and anion exchange within the soil zone and to a lesser extent, the unsaturated zone. Specifically, soil waters have higher median DOC,  $SO_4$ , Mn, and

Fe concentrations whereas the oxic groundwater subset has higher median Si (Wilcoxon p-value <0.05; Figure 5-5 and Table 5-1) as further detailed in the following.

### **Dissolved Organic Carbon (DOC)**

DOC in ground- and surface water is statistically significantly lower than in soil (Table 5-1). Generally, most soil zone DOC is filtered out during percolation to depth and does not reach the underlying aquifer (Clark and Fritz, 1997; McMahon and Chappelle, 2008; Tratnyek et al., 2011). The abundance of soil organic carbon within the soil zone favours redox progression and all soil waters show buffering with respect to Fe-oxides/oxy-hydroxides, whereas organic carbon within alluvial aquifers is low (McMahon and Chappelle, 2007; Rissmann, 2011; Tratnyek et al., 2011; Rissmann et al., 2012).

### **Sulphate (SO<sub>4</sub>)**

The concentration of SO<sub>4</sub> in groundwater and surface water is statistically significantly lower than that in soil (Table 5-1). Anion exchange selectively retains SO<sub>4</sub> within the subsoil and/or unsaturated zone with high to very high concentrations of subsoil SO<sub>4</sub>, a regular feature of some Southland soils (Topoclimate South, 1996; McBride, 1998; McLaren and Cameron, 2005). Due to Mn and Fe buffering, SO<sub>4</sub> reduction within the soil zone is not considered to be important in terms of SO<sub>4</sub> removal. In areas of old weathered soils or in the unsaturated zone, SO<sub>4</sub> retention by Al-oxides/oxy-hydroxides results in the infiltration of SO<sub>4</sub>-poor soil water recharge as exemplified by shallow groundwater hosted by the Luggate Shotover and Kamahi Formations.

### **Silicon (Si)**

Higher median Si concentration of groundwater relative to soil waters may reflect the greater mineral and lower organic carbon content of felsic or mafic aquifers and the eventual equilibration with the groundwater aquifers that have longer residence times (*c.* > 15 years; Daughney et al., 2015). Therefore, post infiltration water-rock interaction is not considered a significant source of solutes for oxidised, non-carbonate groundwater of southern Southland.

Limited post-infiltration water-rock interaction is also considered a key feature of waters across northern Southland. Here, lithologies are siliceous and mainly inert and the proportion of fine textured loess soils is much smaller, equating to less surface area and lower stores of exchangeable cations. Northern groundwaters are also more dilute and show higher recharge altitudes with more negative  $\delta^{18}\text{O-H}_2\text{O}$  and  $\delta^2\text{H-H}_2\text{O}$  signatures, larger Cl/Br ratios and significantly less positive  $\delta^{11}\text{B}$  signatures (Figure 5-5).

### **Calcium (Ca) and Magnesium (Mg)**

When compared with southern soil waters, the concentration of Ca and Mg are statistically significantly lower for northern groundwater, probably due to greater proportions of coarse textured gravel soils and a greater component of dilution by higher altitude river recharge sources (Wilcoxon p-value <0.05). The one tile drain site in northern Southland shows lower concentrations of Ca and Mg than equivalent tile drain waters in southern Southland. Although more soil water data is required, it would appear that other than being slightly more dilute, oxic northern groundwaters are broadly similar to southern soil waters in terms of relative proportions of major ions (*i.e.*, Ca > Mg > K), carbonates and alkalinity (Figure 5-5 and Figure 5-6).

### **$\delta^{13}\text{C-DIC}$**

The median  $\delta^{13}\text{C-DIC}$  signature of oxic northern groundwater of -18.8‰ is slightly more positive than that of soil water. This may be related to a greater proportion of high altitude river water recharge of

northern groundwater. However  $\delta^{13}\text{C}$ -DIC values of soil are still similar enough to those of southern groundwater and soil waters to suggest the soil zone is the major source of alkalinity with little post-infiltration evolution due to water-rock interaction.

River waters with high altitude (i.e. > 800 m RSL) headwaters across northern Southland have a median  $\delta^{13}\text{C}$ -DIC value of -14.6‰ (n = 86) whereas snowpack collected at altitudes > 1,000 m RSL has a median value of -21.7‰ (n = 9) suggesting head water degassing and/or lower  $\text{pCO}_2$  values and higher precipitation volumes within alpine soil zones equate to more positive  $\delta^{13}\text{C}$ -DIC values.

**Table 5-1: Median values for selected parameters for soil, oxalic groundwater and surface waters. Grey background indicates a statistically significant difference at the 95% level in the median value of southern or northern oxalic groundwater relative to soil water. The asterisk indicates where the Wilcoxon test could not be performed.**

Parameter	Southern Oxidic GW	Northern Oxidic GW	Soil
$\text{pCO}_2(\text{g})$	0.0051	0.0040	0.0046
$\delta^{11}\text{B}$ (ppt VSMOW)	17.6	12.2	24.8
$\delta^{13}\text{C}$ DIC (ppt VSMOW)	-19.1	-18.8	-19.8
$\delta^{18}\text{O}$ $\text{H}_2\text{O}$ (ppt VSMOW)	-7.22	-8.73	-6.64
$\delta^2\text{H}$ $\text{H}_2\text{O}$ (ppt VSMOW)	-48.6	-61.8	-43.3
Conductivity ( $\mu\text{S}/\text{cm}$ )	234	148	228
Bicarbonate alkalinity (mg/L)	37.4	31.7	24.9
Calcium (mg/L)	15.2	11.7	15.3
Chloride (mg/L)	25.6	7.0	30.6
Potassium (mg/L)	0.92	1.02	1.07
Magnesium (mg/L)	6.00	5.13	4.69
Sodium (mg/L)	18.4	7.6	18.4
Sulphate (mg/L)	9.9	3.9	18.5
Bromine (mg/L)	0.082	0.045	0.090
Chloride/Bromide ratio	271	177	336
DOC (mg/L)	0.93	0.88	6.40
Dissolved Inorganic Carbon (mmol/L)	1.65*	1.54*	N/A
Iron (mg/L)	0.010	0.010	0.250
Manganese (mg/L)	0.001	0.001	0.035
Silica (mg/L)	22.0	16.9	10.9

### Redox state of groundwater

Shallow groundwater appears to be the best indicator of the reduction capacity of the soil zone, because unsaturated zone lags of at least two to three years should not be kinetically limiting, assuming electron donors occur in concentrations that are also non-limiting (Vroblesky and Chappelle, 1994; McMahon and Chappelle, 2008).

The majority of groundwater samples show a mixed redox signature using the method of McMahon and Chappelle (2008) indicating that both oxidised and reduced species co-exist in groundwater. This may be related to the effect of soil zone processes on groundwater redox state. Southland's groundwater table is shallow (median depth of -2.75 m BGL; n = 1,750 wells) relative to the depth of pedogenic differentiation (which is at least 2 m under Southland's cool, humid, temperate climate) allowing for direct connection of soil zone to underlying aquifer systems. In addition, rapid changes in recharge rates, water table fluctuations and/or bypass flow, may result in differing amounts of nutrients and dissolved oxygen recharging to groundwater and mixing of water of differing redox state. Furthermore, groundwater residence times are short (i.e., MRT <10 years) so that processes

may not have had enough time to reach thermodynamic equilibrium (Lindberg and Runnels, 1984; Christensen et al., 2000). The effect of soil zone on redox state of freshwater is further discussed in TC 6 and TC 7.

#### **TC5.4 Summary**

In this chapter, comparison of soil water with surface water and groundwater chemistry indicated that, across the region as a whole, the populations of all soil samples, all groundwater samples and all surface water samples have similar median values for several chemical parameters. This suggests that the soil zone is highly influential in determining the hydrochemical composition of Southland's groundwater and surface waters. Most importantly, there is no statistical significant difference in Na, Ca, Mg, K, Cl, and Total Alkalinity between soil waters and southern groundwaters (and northern and southern groundwaters combined) indicating little if any significant post-infiltration water rock interaction.

Overall, comparison of soil water with surface water and groundwater chemistry indicates that the soil zone and not the aquifer is highly influential in determining the hydrochemical composition of Southland's groundwater and surface waters. A key conceptual output from this chapter is the awareness of the key role the soil zone plays over the hydrochemical evolution of Southland groundwater and surface water.