

Physiographic Controls Over pH and Alkalinity in Southland's Freshwaters

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Overview

This poster explores some of the findings from the Physiographics of Southland work (Rissmann et al., 2016). One of the key aspects of this was identifying the control the soil zone has over freshwater chemistry in Southland. The particular focus of this poster is the role the soil zone plays in determining pH and Alkalinity in surface waters.

A biogeochemical and stable isotopic ($\delta^{13}\text{C-DIC}$) assessment of the relationship between soils, soil gases, soil waters, ground- and surface waters was performed in order to help understand the role of the soil zone in chemical variation in Southland freshwaters.

Alkalinity matters...

Various anthropogenic activities and physical and biogeochemical processes occurring within soils, aquifers and streams can alter pH. Without sufficient alkalinity to buffer these changes, pH can fluctuate in a manner that negatively impacts aquatic life (Figures 1 and 2). For example, macroinvertebrate abundance and community diversity is sensitive to pH.

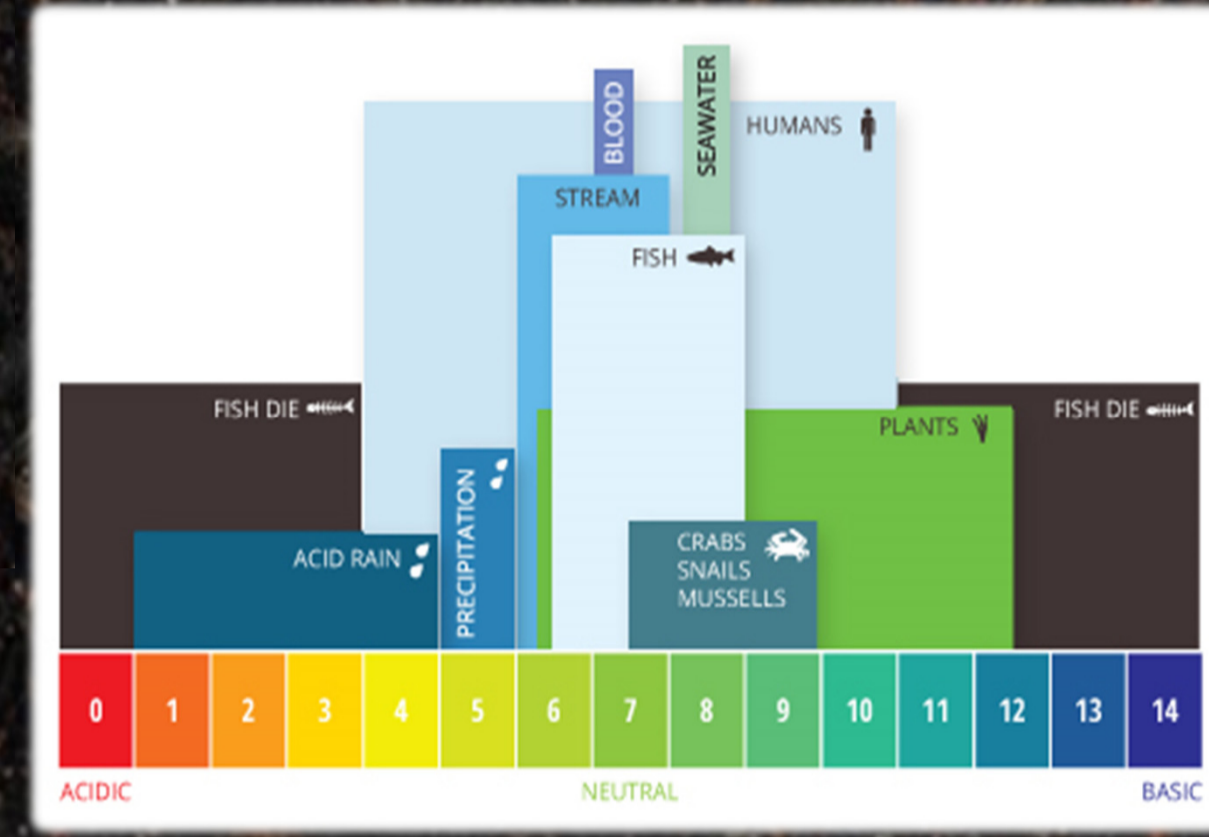


Figure 1: Diagram depicting the generalised pH ranges for a variety of animals, plants and environments.

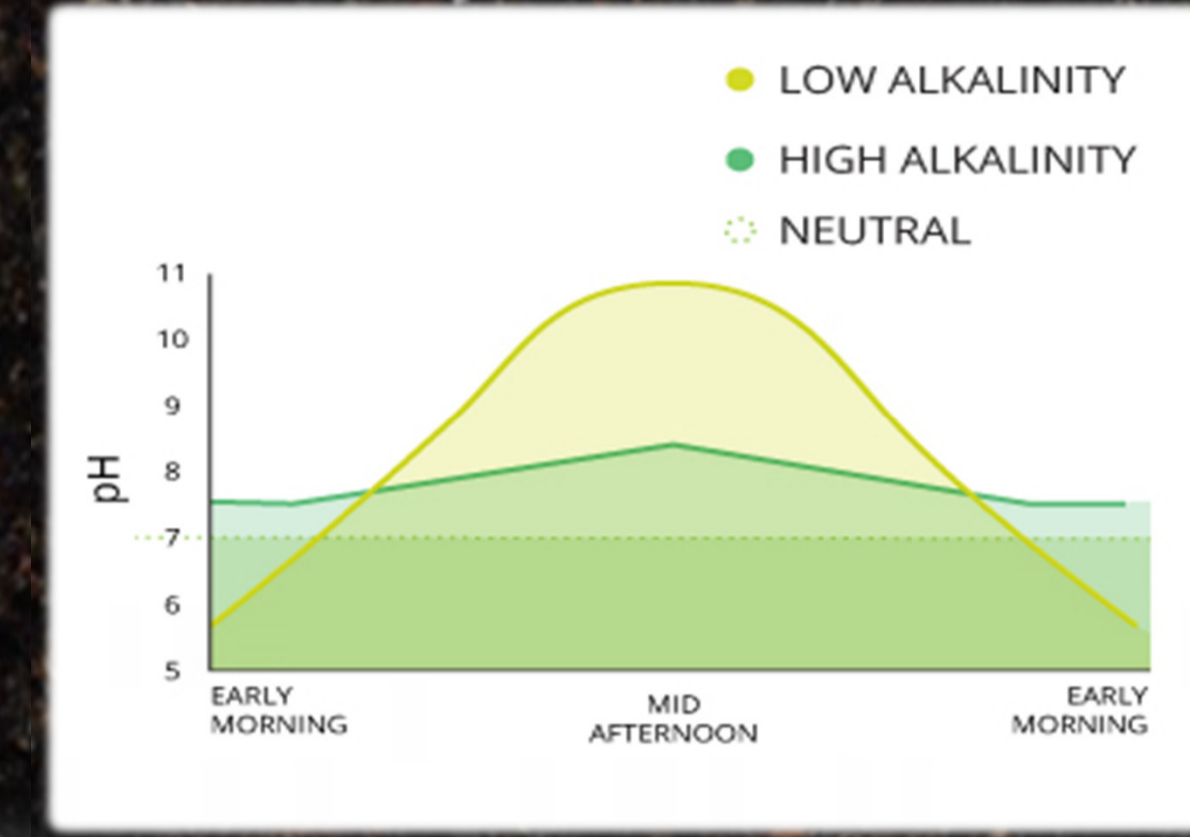


Figure 2: Generalised effect of alkalinity in a stream environment that is subject to diurnal photosynthesis and respiration fluctuation.

Then what controls Alkalinity?

The initial or primary alkalinity concentration in freshwater is dependent upon the pH (Figure 3) and the partial pressure of CO_2 within the recharge environment. For many parts of Southland, the soil zone is the dominant recharge environment, so soil pH becomes very important for alkalinity generation in Southland surface and groundwaters.

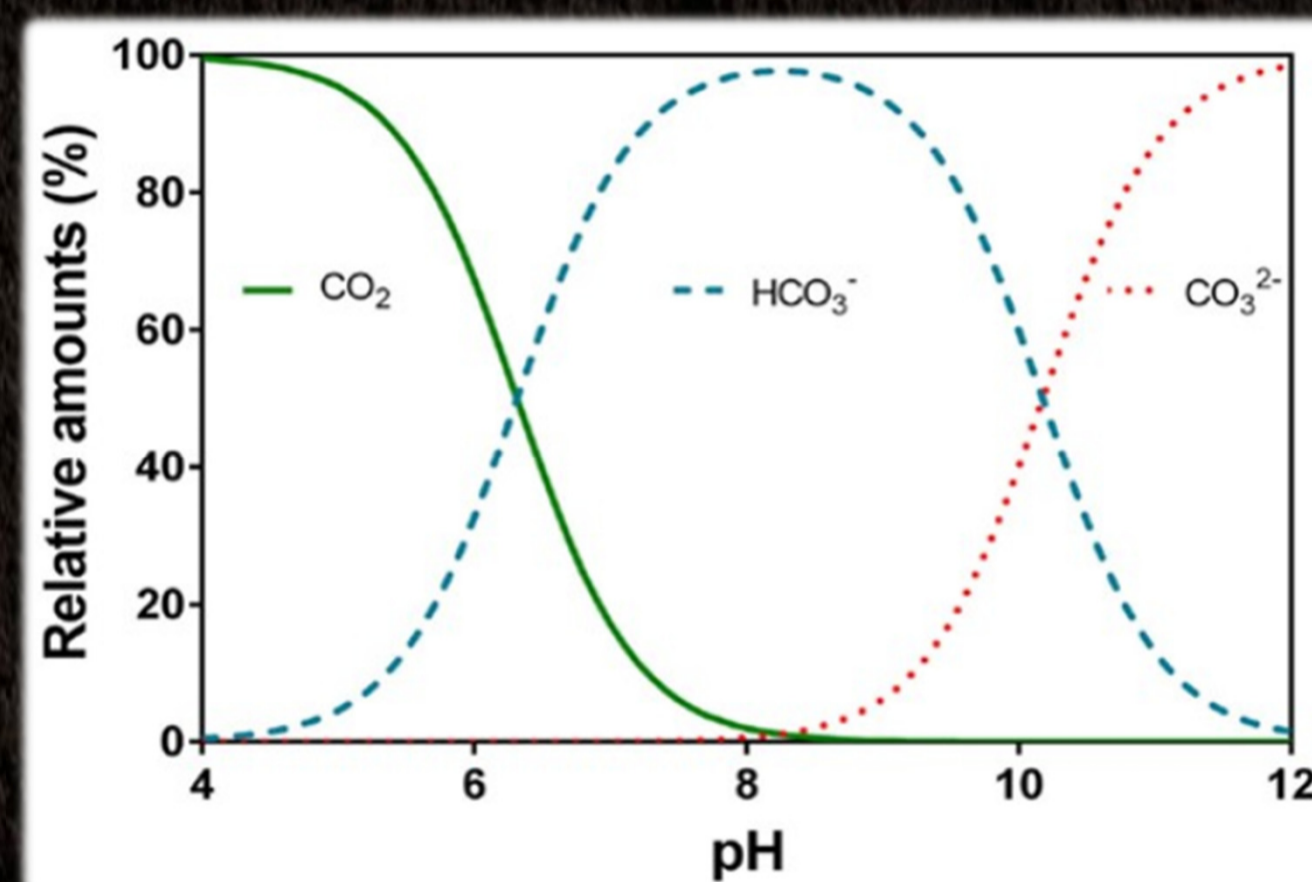


Figure 3: Carbonate equilibria depicting the control pH has over abundance of carbonate species after Plummer and Busenberg, 1982.

So what determines the pH in the soil?

Principal component analysis (PCA) performed on regional soil chemical data demonstrated that soil pH and base saturation are controlled primarily by the soil age (degree of weathering) and soil substrate composition (mineralogical and chemical makeup).

The soil composition is primarily a product of its parent material. For example soils with ultramafic or limestone parent material that contain a high proportion of Lewis bases produce soils with a high base saturation (BS) and in turn pH buffering capacity.

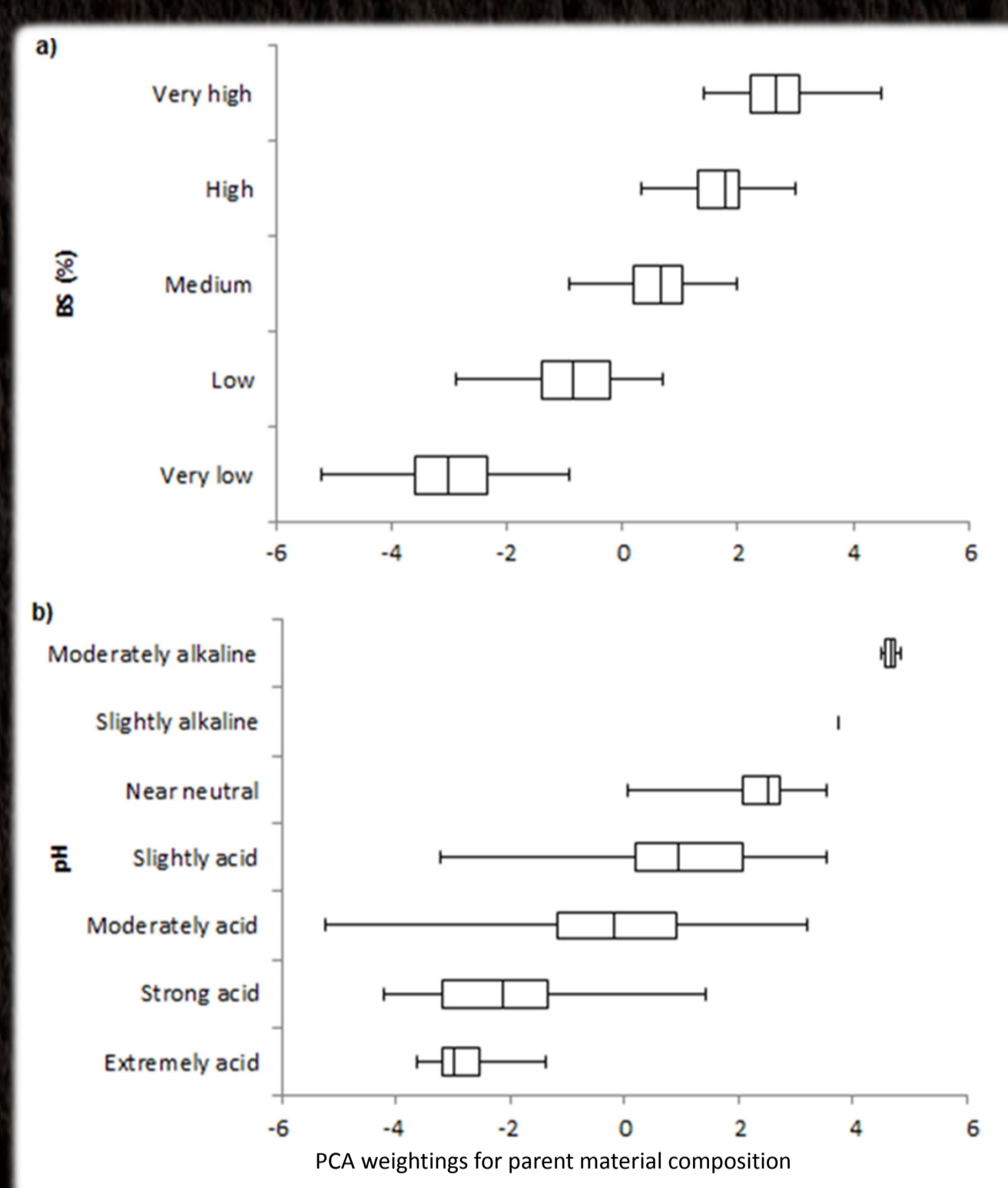


Figure 4: PCA output indicating the control of parent material composition over pH and BS.

How is this linked to Southland's fresh waters?

A leaching trial was carried out using Southland soils to determine the relationships between soil chemistry and leached soil water. The intent of this was to simulate recharge to groundwater and surface water via the soil zone. Some of the main findings from this were:

- Soil pH and BS were highly correlated as expected (Figure 5) reinforcing the importance of soil composition in controlling pH.
- Ca and Mg in leachate were highly correlated with soil BS (Figure 6)
- Dissolved organic carbon (DOC) in leachate is correlated with soil carbon (Figure 7).

These last two correlations help to support the idea that soil chemistry plays an important role in recharge water chemistry. Further work could be done to increase the sample size and explore these relationships further.

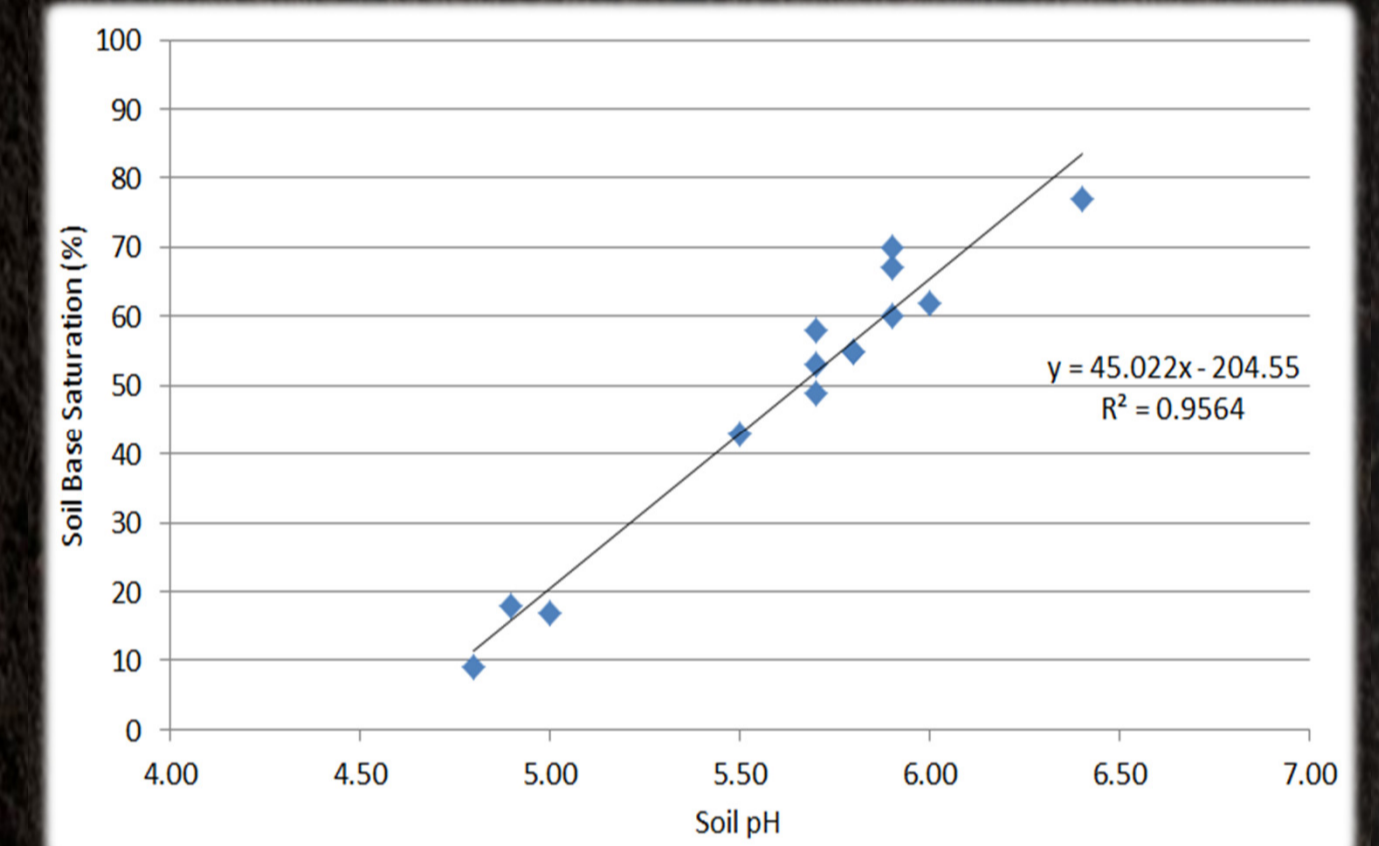


Figure 5: Soil pH vs. soil BS for soils used in the leaching experiment.

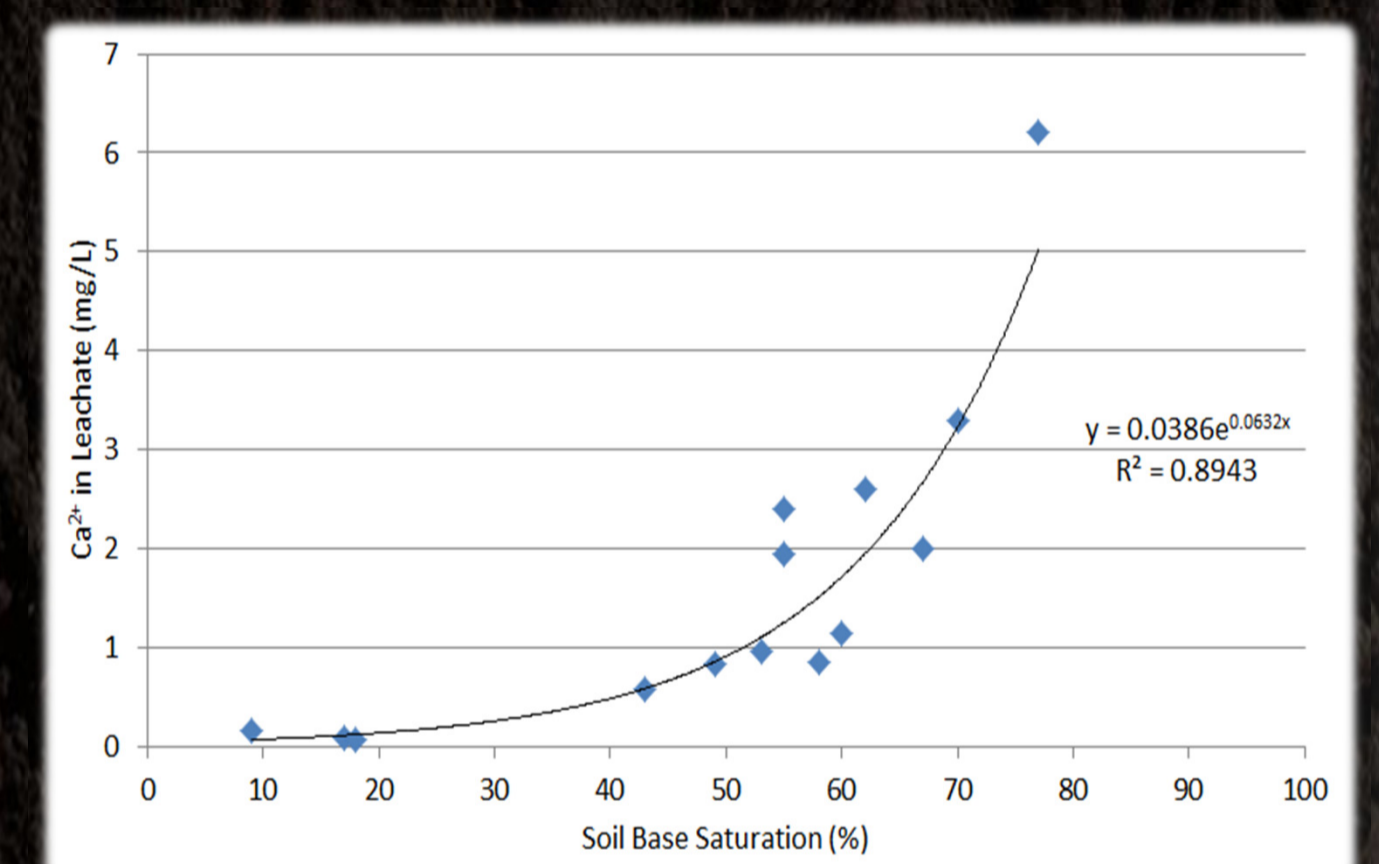


Figure 6: Soil BS vs. Ca^{2+} measured in leachate.

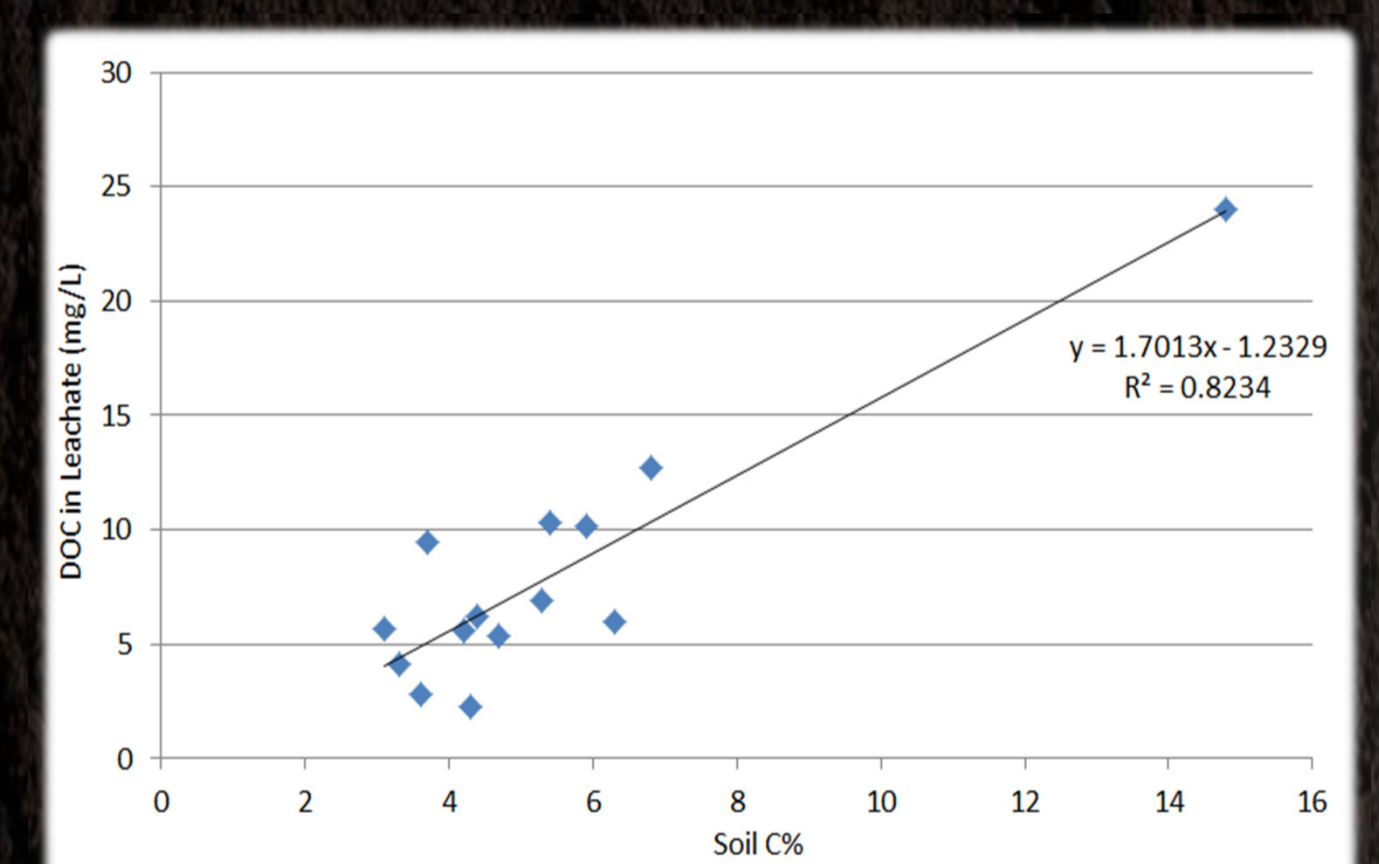


Figure 7: Soil carbon % vs. DOC measured in leachate.

Isotope links...

$\delta^{13}\text{C-DIC}$ signatures for surface waters (SW), tile drain waters (TD) and groundwaters (GW) are similar and cluster toward a soil organic carbon signature (c. -24 - -34%) (Figure 8). This is opposed to precipitation (PPT) which is more enriched in ^{13}C . This indicates a soil organic carbon source and supports the hypothesis that alkalinity is predominantly derived from the soil zone. Inevitably some degassing occurs, especially in TD and SW causing ^{13}C enrichment.

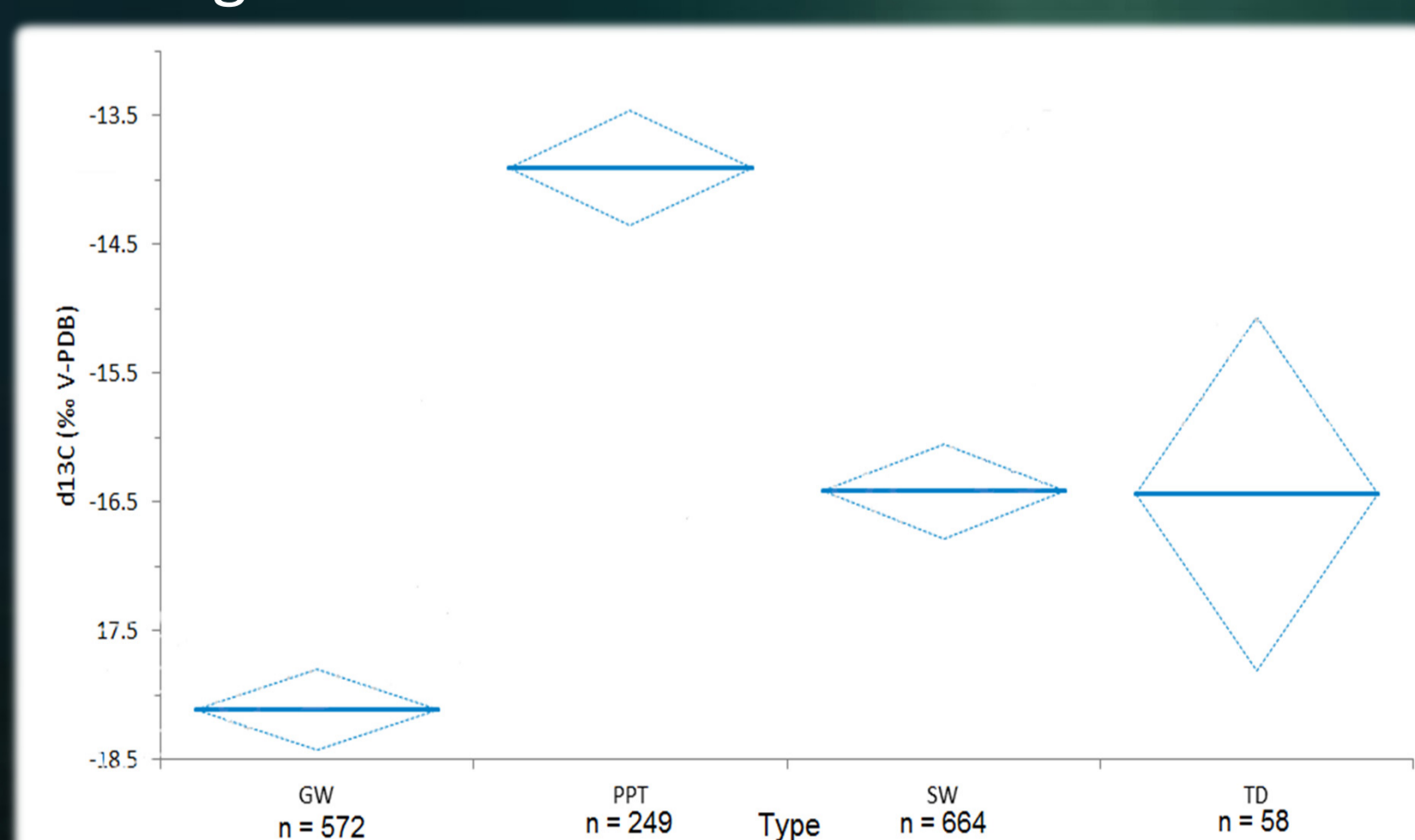


Figure 8: Mean plot for $\delta^{13}\text{C-DIC}$ of Southland waters. Grouped by water type. The solid line depicts the mean, the extent of the diamond encompasses the 95th percentile.

How can we use this?

The understanding of the controls over pH and alkalinity have been used to estimate surface water pH, alkalinity (Figure 9) and $\delta^{13}\text{C-DIC}$ for all state of environment monitoring sites across Southland. While pH and alkalinity impact on freshwater ecosystems directly, having a sound understanding of how and why these vary naturally is important for providing context and making interpretations of ecosystem health assessments.

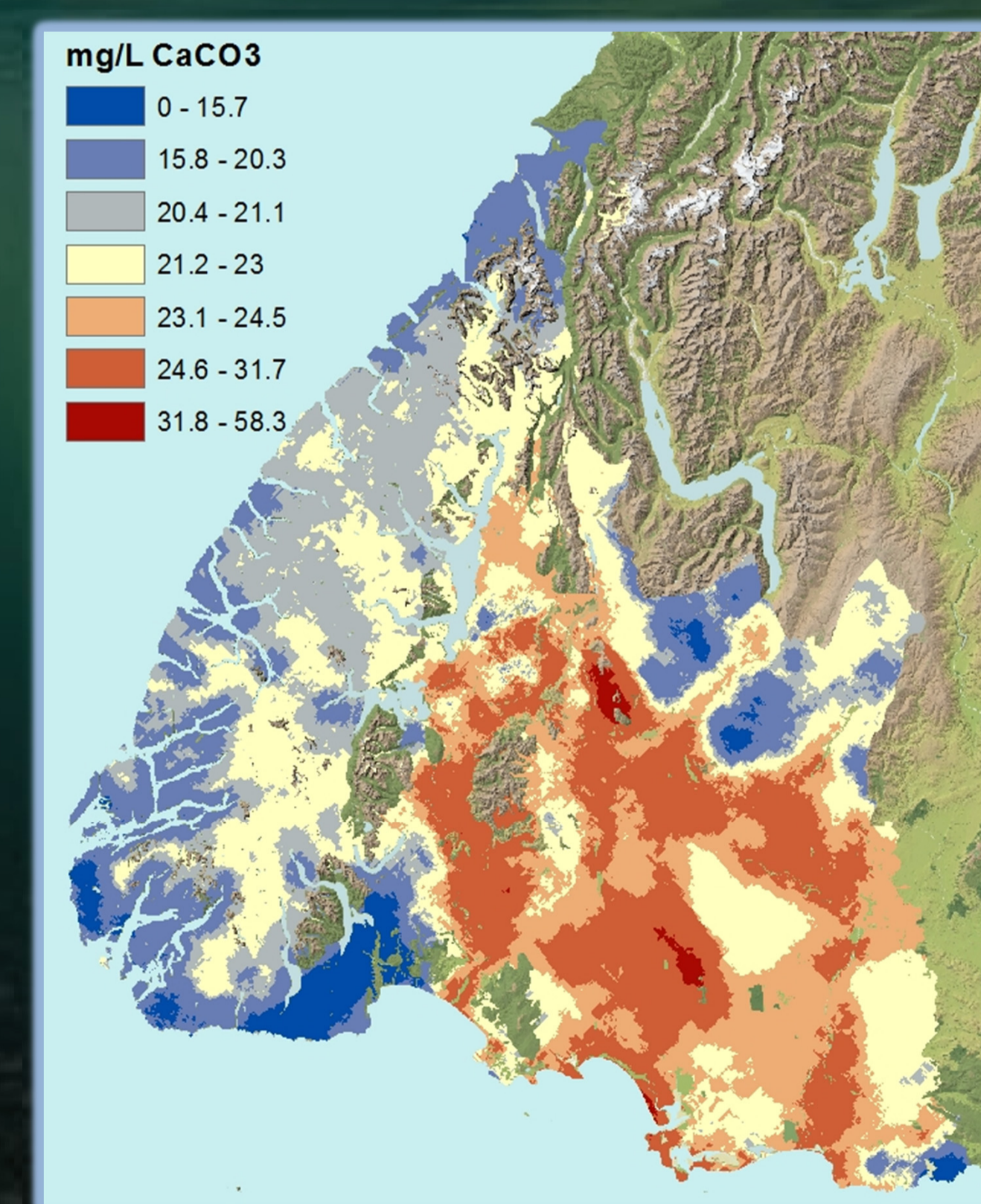


Figure 9: Predicted alkalinities for Southland using carbonate equilibrium relationships, a pCO_2 range of 0.001 – 0.0047 atm., horizon weighted mean soil pH (specific for each site), and the mean winter (May – August) recharge temperature of $7.0 \pm 0.5^\circ\text{C}$.

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References
Rissmann, C., Rodway, E., Beyer, M., Hodgetts, J., Snelder, T., Pearson, L., Killick, M., Marapara, T.R., Akbaripasand, A., Hodson, R., Dare, J., Millar, R., Ellis, T., Lawton, M., Ward, N., Hughes, B., Wilson, K., McMeeking, J., Horton, T., May, D., Kees, L. (2016). Physiographics of Southland, Part 1: Delineation of key drivers of regional hydrochemistry and water quality. *Environment Southland Technical Report*.

Plummer, L. and N. E. Busenberg. (1982). The Solubilities of calcite, aragonite and vaterite in CO_2 - H_2O solutions between 0 and 90°C , and an evaluation of the aqueous model for the system CaCO_3 - CO_2 - H_2O . *Geochimica et Geochimica Acta* 46.