

Physiographics of Southland

Part 1:

Delineation of key drivers of regional hydrochemistry and water quality

Technical Report

June 2016

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

^aLWP Ltd; ^bLandpro Ltd; ^cGeological Sciences, University of Canterbury

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Prepared by:	Rissmann, C., Rodway, E., Beyer, M., Hodgetts, J., R., Snelder, T., Pearson, L., Killick, M., Marapara, T. R., Akbaripasand, A., Hodson, R., Dare, J., Millar, R., Ellis, T., Lawton, M., Ward, N., Hughes B., Wilson K., McMecking, J., Horton, T., May, D., Kees, L.		
Illustrations by:	Hodgetts, J.	Maps produced by:	Rodway, E., Beyer, M.
Reviewed by:	<p>Peter Almond¹, Troy Baisden², Vincent Bidwell³, Chris Daughney², Bill Dyck⁴, Allan Hewitt⁵, Clive Howard-Williams⁶, Scott Larned⁶, Matthew Leybourne⁷, Mike Scarsbrook⁸, Hanspeter Schreier⁹, Ranvir Singh¹⁰, Trevor Webb⁵, Jenny Webster-Brown¹¹; Southland Science Technical Advisory Group¹².</p> <ol style="list-style-type: none"> 1. Soils and Physical Sciences, Lincoln University 2. GNS Science 3. Vincent Bidwell Consulting 4. Bill Dyck Ltd 5. Landcare Research 6. NIWA 7. Department of Earth Sciences, Laurentian University 8. Dairy New Zealand 9. Professor Emeritus, Land and Water Systems, University of British Columbia 10. Massey University, Institute of Natural Resources 11. Waterways Centre for Freshwater Management, University of Canterbury and Lincoln University 12. Southland Science Technical Advisory Group comprised of National and International Experts advising on the Southland Science Programme. Members: Dr Clive Howard-Williams, NIWA; Dr Chris Daughney, GNS; Dr Murray Close, ESR; Dr Cath Moore, GNS/ESR; Dr Liz Wedderburn, AgResearch; Prof. Jenny Webster-Brown, University of Canterbury; Associate Prof. Peter Almond, Lincoln University; Dr Mike Scarsbrook, DairyNZ; Dr Vince Bidwell (independent consultant); Bill Dyck, Envirolink Coordinator. 		
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Physiographics of Southland

Part 1:

Delineation of key drivers of regional hydrochemistry and water quality


Technical Chapter 6:

Influence of Soil and Geological Composition over Redox conditions for Southland groundwater and surface waters

June 2016

Beyer, M., Rissmann, C., Rodway, E., Killick, M., Pearson, L.,
Marapara, T. R., Hodgetts, J.

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TC6 Influence of Soil and Geological Composition over Redox conditions for Southland groundwater and surface waters

TC6.1 Introduction

TC6.1.1 Scope of this work

Many studies of groundwater chemistry and water quality have shown that redox processes are the main determining factor for the variability in water chemistry and water quality outcomes (Winter et al., 1998; Daughney et al., 2005; 2010; 2015; McMahon and Chapelle, 2008; Guggenmos et al., 2011; Rissmann et al., 2012; Essington, 2015). For example, some hydrogeological settings may enhance the removal or natural attenuation¹ of nitrate from the soil zone or water bearing layers (Rissmann, 2011; Rissmann et al., 2012; Jahangir et al., 2012; Stenger et al., 2013; Rivas et al., 2014; Elwan et al., 2015). However, many management tools designed to reduce contaminants from non-point sources e.g. nitrate, are often applied uniformly without consideration of differences in the natural setting that may mitigate or exacerbate contamination problems (Krantz and Powars, 2002; Stenger et al., 2014; Singh et al., 2014).

Spatial variability in the redox processes responsible for nitrate removal are a factor of biogeochemical and physical processes which include electron donor abundance, mainly organic carbon, temperature control and hydrological factors such as natural macropore vertical bypass of the soil zone, intrinsic permeability of soil and geological materials as well as recharge mechanism.

The aim of this chapter is to classify Southland's soil and geological materials according to their varying potential to reduce terminal electron accepting species, such as DO, Mn(IV), Fe(III) and NO₃, also referred to as reduction potential and further described subsequently. Reduction potential is one of the four key drivers of hydrochemical variation of Southland's surface water and shallow, soil-influenced, groundwaters. The classification was used to create a regional scale map of combined soil and geological redox potential (CRP). The roles of water source and recharge mechanism (TC2) over redox signatures are not discussed in this chapter. The combination of CRP and hydrological (recharge mechanism) drivers over redox signatures is assessed in Chapter 3 (Conceptual Model).

The terms 'reduction potential' and 'denitrification potential' are used as appropriate within the text. The term oxidation refers to either a gain of oxygen or a loss of electrons. Because of mass conservation, oxidation can only happen alongside reductions that are either a loss of oxygen or gains of electrons (Drever, 2002). Here, reduction potential refers to the broader reduction-oxidation (redox) process associated with the ecological succession of terminal electron accepting processes. Denitrification potential refers exclusively to the removal of oxidised forms of nitrogen (TON) from nutrient cycling due to conversion either to nitrous oxides or N₂ gas. Consideration of the broader redox setting is a more robust approach to understanding the controls over redox state and process in surface and shallow ground waters across Southland.

In the following section, it is demonstrated that at a regional scale, ground and surface water redox signatures are to some extent predictable. Specifically, it is shown that redox reactions in the soil zone and/or underlying geology (aquifer, stream hyporeic zone, unsaturated zone) are the controlling factors on selected analyte concentrations in regional waters. It is demonstrated that only

¹ Natural attenuation is the reduction in concentration of a contaminant by natural processes.

through consideration of both the soil zone and geological reduction, can the spatial patterns of reduction be understood. Note that the soil zone exerts by far the greatest control over the redox signatures of regional surface water and shallow, soil influenced groundwater. However, it is also noted that only through the inclusion of hydrological factors are predictive efficiencies greatly improved (Chapter 4 – Conceptual Model Validation). Therefore, the main point of this chapter is to test to see if the underlying mechanistic controls over soil and geological reduction can be adequately described.

TC6.1.2 Redox background

Natural attenuation of nitrate concentrations may occur by plant or microbial uptake, mixing and dilution with low-nitrate water, or consumption in microbially mediated redox reactions (McMahon, 2002; Krantz and Powars, 2002; McMahon and Chappelle, 2008). An example of the latter case is denitrification, in which the oxygen atoms of nitrate (NO_3^-) are removed by chemical reduction to produce oxides of nitrogen or molecular nitrogen, which is commonly lost from a soil or aquifer by degassing to the atmosphere (Figure 6-1). Therefore, denitrification is the only natural process through which leached nitrate may be partially or wholly removed from soils, aquifers or streams (McMahon, 2002; Krantz and Powars, 2002; McMahon and Chappelle, 2008).

The nature of the materials that comprise regional soils, stream hyporheic zones and aquifers are critical to the accumulation or removal of nitrate. In Southland, as with other regions, the type and spatial distribution of different geological materials and soils is highly variable (TC3 and TC4). As such, nitrates may be removed through denitrification in one area, but accumulate in another. Therefore, identifying and delineating areas that are susceptible to nitrate accumulation, or capable of attenuating nitrate inputs, is important for nutrient management regionally. Apart from their importance for nitrate attenuation, redox reactions also play a critical role in the solubility and migration of redox sensitive species such as phosphorus, iron, manganese and arsenic (Rissmann et al., 2012 and references therein).

For a redox reaction to proceed there must be an electron donor and an electron acceptor. The most common electron donor in the natural environment is organic carbon most commonly derived from plant material (McMahon and Chappelle, 2008). Accordingly, the soil zone is a rich source of organic carbon for microbial metabolism. In Southland, low rank coal measures, i.e. lignite and brown coal, are an important source of organic carbon and in some rare instances iron sulphides (Fe_xS_x) and/or glauconite (iron rich clays) may act as electron donors. The most common electron acceptors include dissolved oxygen (DO), nitrate (NO_3^-), manganese (Mn(IV)) and ferric iron (Fe(III)), although in some extreme settings sulphate (SO_4) and carbon dioxide (CO_2) may predominate (Figure 6-1). The dominant Terminal Electron-Accepting Process (TEAP) is often determined to assess redox conditions of freshwater and predict whether contaminant reduction or attenuation is likely to occur.

In natural waters and soils, redox reactions are largely driven (catalysed) by bacteria, which gain energy by facilitating the transfer of electrons from organic matter to an electron acceptor (Figure 6-1). This process results in the breakdown of organic matter into its constituent elements (carbon, oxygen, nitrogen, phosphorus and some minor trace elements), the consumption of the electron acceptor, and a net energy release for the micro-organism (McMahon and Chappelle, 2008).

Of the possible terminal electron acceptors, oxygen provides the greatest amount of energy and for this reason it is preferentially used by microorganisms. However, because soil and groundwater can be isolated from the atmosphere, oxygen may be consumed. Once oxygen has been depleted from water, the decay of organic matter continues through a succession of reactions that represent a progressive decline in the free energy available to microbes as each successive electron acceptor is

consumed. For example once oxygen has been consumed, bacteria move onto the next most energetically favourable electron acceptor, nitrate (NO_3), followed by manganese (Mn(IV)), ferric iron (Fe(III)), sulphate (SO_4) and eventually carbon dioxide (CO_2). This order of preferential electron acceptor utilisation, $\text{O}_2 > \text{NO}_3 > \text{Mn(IV)} > \text{Fe(III)} > \text{SO}_4 > \text{CO}_2$ is referred to as the ecological succession of terminal electron-accepting processes (Figure 6-1) (McMahon and Chappelle, 2008).

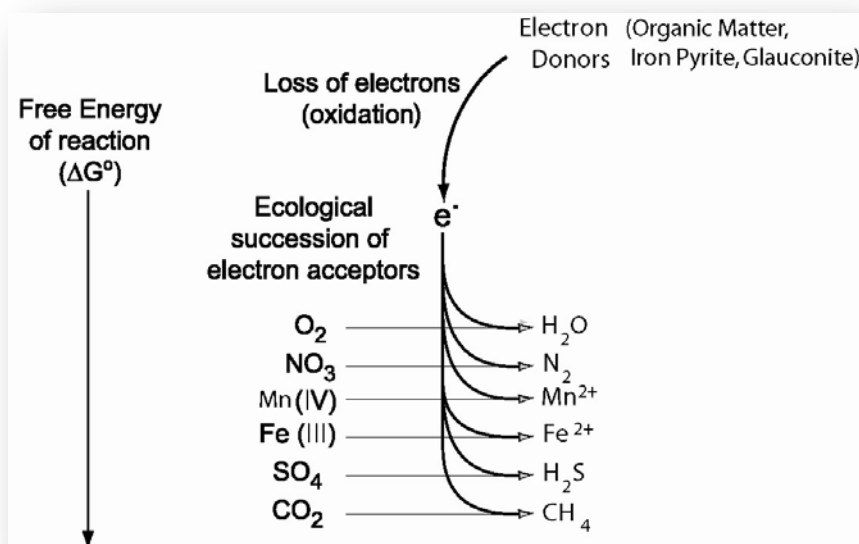


Figure 6-1: Ecological succession of electron-accepting processes and sequential production of final products in natural waters. A decrease in free energy available to microbes occurs as each successive electron acceptor is consumed. Typically organic matter (organic carbon) is by far the most common electron donor in groundwater but iron pyrite and glauconite may be locally significant (modified from McMahon and Chappelle, 2008).

All electron acceptors (oxidants) are themselves reduced when they gain electrons. Therefore, during the ecological succession of terminal electron accepting reactions, natural waters become increasingly reduced. Each step in the ecological succession of terminal electron accepting reactions causes the chemical reduction and subsequent removal of the oxidant as defined by the reactions in Figure 6-1. As described, in most instances one key terminal electron acceptor dominates – the TEAP (McMahon and Chappelle, 2008). However, other less dominant TEAP may occur simultaneously due to a natural overlap in ecological niches.

Understanding the redox state and TEAP of soils and shallow groundwater is critical to issues of e.g. nitrate loss from soils and whether or not nitrate will persist or be removed subsequent to oxygen removal. Other factors that redox status determines include:

- the solubility and mobility of P species;
- the solubility of toxic metals such as arsenic;
- the presence of nuisance chemicals that degrade water quality such as dissolved Mn(IV) and Fe(III) , and hydrogen sulphide (H_2S) with its distinctive rotten-egg smell.

The controls over the redox status of soils and geology are determined by the materials they are comprised of; the relative rates of introduction of oxidants i.e. oxygen and nitrate and the consumption of these oxidants by bacterially mediated decomposition of organic matter. The most important variables governing the redox status of groundwater include the following (Drever, 2002; McMahon and Chappelle, 2008; Rissmann, 2011; Tratnyek et al., 2011 and references therein; further detailed in Daughney et al., 2012):

1. Distribution and reactivity of organic matter and other potential reductants

The mass of easily oxidisable organic matter is one factor critical to the evolution of the redox status of a groundwater from oxidising through to reducing conditions. Soils and aquifers, with an abundant supply of electron donors, tend to rapidly consume oxygen and progress quickly through the ecological succession of terminal electron accepting species (Figure 6-1). Occasionally, electron donors other than organic matter play an important role as electron donors, they include iron pyrite and glauconite, an iron clay.

2. Distribution of inorganic terminal electron acceptors in a soil or water bearing layer

The mass of the inorganic terminal electron acceptors, specifically the oxides of iron and manganese, within soils, stream hyporeic zones and aquifers is often large. Accordingly, substrates containing a large store of Fe(III) oxides seldom evolve beyond iron reducing conditions. Large inputs of anthropogenic TON may also buffer the ecological progression towards more reducing conditions including the reduction of Fe(III).

3. Oxygen content of recharge water

Recharge water may enter an aquifer or stream bed through fractures in bare rock, or it may percolate through a poorly or imperfectly drained soil. In the first case, the recharge water will be high in oxygen, so microbes within the water reservoir will have an abundant supply of a powerful oxidant for organic matter decomposition. In the second case, oxygen, and perhaps nitrate, may be consumed within the soil profile before percolating to the aquifer or draining to a stream. In this instance, the infiltrating water will be reducing before reaching the stream or aquifer and bring with it a low capacity to oxidise organic matter.

4. Water residence time

Because the bacterial catalysis of organic matter is at times slow, the redox status of a soil, stream hyporeic zone or aquifer system depends highly on the residence time of the water in contact with reducing reactants. The residence time is a function of both the velocity of the water moving through the soil, aquifer or hyporeic zone and the “length” of flow path from recharge to discharge points. In general, the longer the residence time the more advanced water is along the ecological succession of terminal electron accepting processes. The latter of course assumes that there is an abundant supply of electron donors and some restriction in the supply of strong terminal electron acceptors such as O_2 and TON. In soils, seasonal variation in soil moisture, water logging and water table rise and fall, influence the timing and degree of denitrification.

5. Hydrology

Generally reducing conditions develop in water saturated environments, where the water filled pores are disconnected from the atmosphere and assuming a sufficient supply of electron donors (Figure 6-1). Consequently, the connectedness of a soil or water bearing layer, aquifer or aquitard, to the atmosphere is a critical hydrological determinant of redox evolution (e.g. Rupp et al., 2004; Shenker et al., 2005; Rissmann, 2011; Rissmann et al., 2012; Peralta et al., 2013). Soil drainage class is an important hydrological metric determining the degree of connectivity to the atmosphere. Specifically, poorly to imperfectly drained soils may become decoupled from the atmosphere during periods of saturation. Well drained soils with high infiltration rates are seldom decoupled from the atmosphere and/or meteoric recharge high with high DO content. Recharge mechanism is also an important factor with river recharge of aquifers playing an important role in the supply of DO rich recharge to riverine aquifer systems (TC2). Macropore cracking or artificial drainage may modify soil

hydrology and the degree of connectivity to the atmosphere. For example, soils with argillic horizons are usually poorly to imperfectly drained and yet are also prone to cracking during dry periods. Cracking of the soil provides a mechanism by which the poorly drained soil matrix is periodically bypassed, linking the atmosphere to the underlying aquifer. Less reducing/oxidising conditions often develop in dry soils that are connected to the atmosphere, where redox processes cannot proceed beyond oxygen depletion because oxygen is not limited.

In this study, it will be demonstrated that in Southland, as with other regions of New Zealand, the depth of a well or aquifer, as well as the depth to which soil waters percolate through a soil, play important roles over redox state and condition of natural waters. Specifically, nitrate-nitrogen ($\text{NO}_3\text{-N}$) and total nitrogen (TN) decline with depth for regional groundwaters (Figure 6-2), reflecting the relationship between decreasing hydrological connection to the atmosphere, increasing residence time and lower atmospheric and soil zone contributions of terminal electron acceptors such as O_2 , TON and SO_4 (Rissmann, 2012; Rissmann et al., 2012). The reduction in $\text{NO}_3\text{-N}$ (and TN) with depth in groundwater reflects both a greater incidence of reducing conditions with depth or older waters that are less impacted by recent (c. last 50 years) land use (Daughney et al., 2015).

In reducing soils, $\text{NO}_3\text{-N}$ and TN also tend to decrease with depth. In such soils the rate of O_2 consumption exceeds the rate of advection-diffusion of O_2 into the soil. For example, soil waters from within the Dunsdale Reserve (Hokonui Hills) exhibit a sharp pattern of $\text{NO}_3\text{-N}$ decline with depth from 2.5 mg/L at 0.1 m b.g.l. to below detection at 1.0 and 1.4 m b.g.l. (TC 5). Over the same depth interval dissolved Mn(II) and Fe(II) increase by 25x and 17x, respectively. A similar pattern of increased reduction with depth was observed within peat soils of the Waituna Reserve with dissolved Fe increasing from 0.17 to 1.6 mg/L over a depth interval of 0.6 m (i.e. from 0.05 m – 0.65 m bgl). Bearing in mind the limitation of applying redox assignments to tile drain waters, it is still apparent that 27 of the 42 of tile drain waters (64%) with complete redox assignments are categorised as mixed oxic-anoxic. The latter is consistent with greater than 64% of tile drain waters showing some sign of reduction associated with either elevated Mn(II) (>0.06 mg/l), Fe(II) (>0.2 mg/L), low DO <7.0 mg/L and/or low TON concentrations. Low TON concentrations are particularly relevant as all tile drain waters are associated with highly productive agricultural land where N is seldom limiting.

TC6.2 Reduction potential for soils and aquifers

In the following section, we assess the reduction potential for Southland soils and aquifers using different indicators. We then study the relationship between predicted and observed redox indicators for ground and surface waters. Note that previous work has shown that it is not possible to predict the redox status of Southland waters without consideration of the composition of both soil and geological zones (Rissmann, 2011). Specifically, the soil is pedogenically differentiated and overlies geological materials that show little sign of pedogenic evolution. Geological materials include peat, loess, alluvium in addition to a wide variety of rock types e.g., lignite, granite, greywacke.

As a basis for an integrated assessment of soil and geological reduction potential with an emphasis on TON accounting for NO_3 and nitrite (NO_2) nitrogen species, we used the qualitative soil and geological denitrification assessments of Killick et al. (2015) and Rissmann (2011), respectively. We consider both inferred denitrification potentials a reasonable proxy for the broader assessment of the reduction potential. However, there is currently a lack of direct and quantitative investigations of geological reduction potential in different hydrogeological settings across the Southland region. Similarly, direct and quantitative investigations of soil reduction potential are lacking at the regional scale.

Killick et al. (2015) assigned Soil Denitrification Potential (SDP) rankings to soils of the agricultural lands of Southland described in the Topoclimate South soil survey (Figure 6-3). These rankings, high, moderate-high, moderate, moderate-low or low², were based on organic matter content and indicators of oxygen depletion (redoximorphic features), found in soil profile descriptions and supplementary data from the Topoclimate survey.

Rissmann (2011) assessed the reduction potential of geological materials occurring across Southland to produce a map of geological denitrification potential (GDP) rankings (Figure 6-4). These rankings, high to very high, intermediate or very low to low², were based on the abundance and reactivity of electron donors associated with over 500 classes of rock and biological sediments i.e., peat and lignite occurring across Southland. Rissmann's work closely followed the studies of Krantz and Powars (2002).

Due to the abundance of shallow groundwater wells, Rissmann (2011) was able to qualitatively assess the relationship between predicted and observed NO₃-N and other redox sensitive species. It was apparent that the map of Geological Reduction Potential (GRP) worked well in areas of high reduction potential sediments but without the inclusion of the soil zone it was difficult to correctly predict the general pattern of observed groundwater NO₃-N in areas of low GRP. It was not possible to undertake a similar comparison with soil waters due to a lack of soil water samples.

Both Killick's et al. (2015) and Rissmann's (2011) predictors of soil and geological denitrification potentials are purely theoretical, being based on the knowledge of processes governing redox reactions. Neither of these studies quantified the influence of water source or residence time over reduction potential. Assuming electron donors are abundant and soil zone temperatures are favourable, the extent to which soil zone TON is denitrified will depend on the relationship between water residence time and the kinetics of microbial respiration.

Deep percolation of soil waters to underlying water bearing units is on the order of 2 - 5 years for the majority of Southland's lowland aquifers based on a loosely coupled model (Wilson et al., 2014; Chanut, 2014³). Areas with longer lag times include the Balfour region, Wendonside Terrace and the Te Anau Basin.

Unsaturated zone lags of at least 2 - 3 years should not be kinetically limiting, assuming electron donors occur in concentrations that are also non-limiting (McMahon and Chappelle, 2008; Vroblesky and Chappelle, 1994). For this reason, we consider shallow, soil-influenced groundwater to perhaps be the best indicator of the maximum potential reduction capacity of the soil zone. Conversely, the residence time of soil water in areas of artificial subsurface drainage may be highly variable. In such settings, rapid movement of high nitrate soil waters may overwhelm the capacity of the soil zone to denitrify as is demonstrated by the Wallacetown Demo farm real time nitrate trial (Cameron et al., 2014). Nitrate loss in these settings often corresponds to 'hot moments' during periods of peak soil drainage usually associated with heavy rainfall events.

² Where a 'high' SDP or a 'high to very high' GDP refers to a high denitrification potential, i.e. low nitrate accumulation rates. Specifically, soils or geology of high/high to very high SDP or GDP, respectively, have a high capacity to remove leached nitrate and are unlikely to show elevated nitrate concentrations even if nitrate inputs are high. In contrast, a 'low', 'very low to low', SDP/GDP refers to a low denitrification potential, i.e. high nitrate accumulation rates (depending on nitrate inputs).

³ Preliminary assessment of the model showed a good correlation of predicted lag-times and age of water at the top of the aquifer.

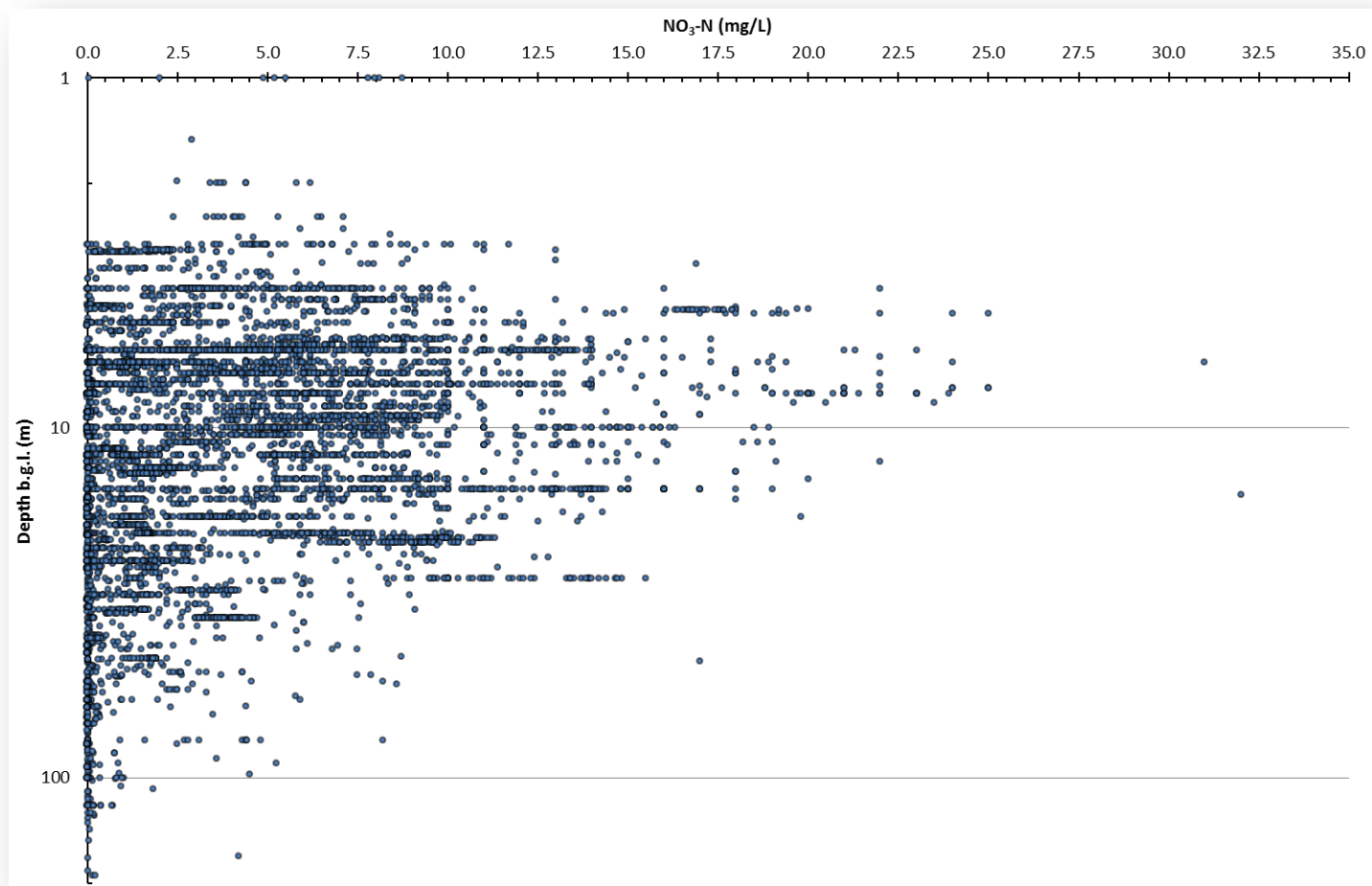


Figure 6-2: Southland groundwater NO₃-N concentrations (Rissmann, 2012).

As discussed in TC4, the median soil zone temperature at the very shallow depth of 0.1 m for Southland soil moisture sites is c. 7°C for May to August, which is above the often quoted threshold of 4°C below which microbial metabolism is limited (Tratnyek et al., 2011 and references therein). Therefore, temperature is not limiting denitrification/redox progression in Southland.

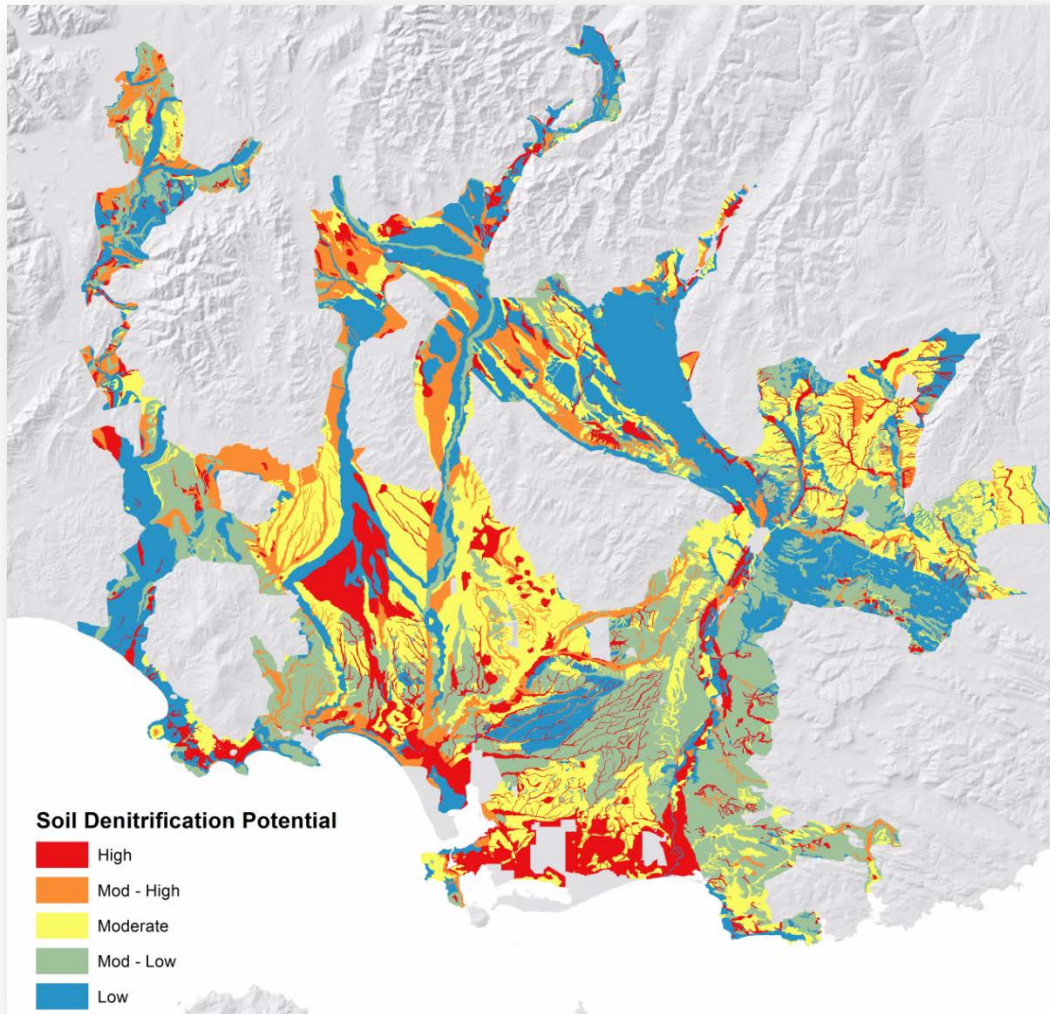


Figure 6-3: Soil denitrification potential (from Killick et al., 2015).

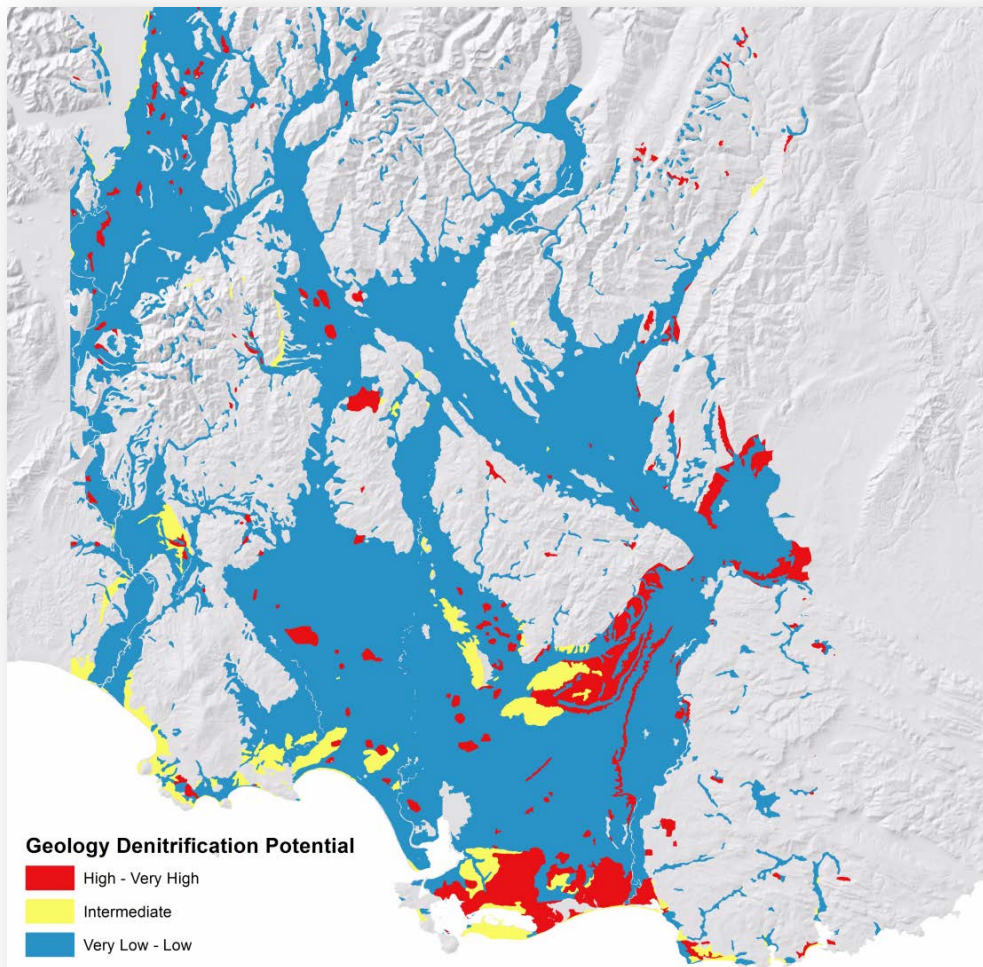


Figure 6-4: Geological reduction potential (from Rissmann, 2011).

TC6.3 Method and Materials

The following sections describe how the SDP and GRP (Killick et al., 2015; Rissmann, 2011) are combined into the CRP classes to depict Southland’s soil and geological reduction capacity. The resulting map must, however, be combined with regional hydrological drivers (recharge mechanism and water source, TC2) to robustly estimate reduction and general denitrification potential for regional surface waters and shallow, soil-influenced, groundwaters associated with specific soil and geological combinations across Southland.

TC6.3.1 Data QA/QC

At the time of writing, Environment Southland’s hydrochemical dataset consisted of 1,329 groundwater sites (6,964 samples) and 393 surface water sites (20,226 samples), for which at least one of the followings: DO, NO₃-N, TON, Total Ammonical Nitrogen (TAN), Mn(II), Fe(II) and SO₄ concentrations. Only 213 groundwater sites (657 samples) and 82 surface water sites (1,260 samples) had a full redox record, i.e. measured concentrations of DO, Fe(II), Mn(II), NO₃ and SO₄. Anomalous or outlier analytical results were identified using acceptance thresholds within normal probability plots, coinciding with discrete values for a given analyte. Specifically, the normal probability plot technique was applied to electrical conductivity (EC), TON, potassium (K), calcium

(Ca), magnesium (Mg) and SO_4 . The method is further described in Appendix C, see also Sinclair, 1974, 1991; Reimann, 2005. Anomalous data and outliers were removed from the dataset.

Identified outliers and anomalies were mainly associated with compliance investigations of contaminated bores or surface waters. These samples tend to show anomalous values for at least two analytes. Specifically, normal probability plots identified anomalous populations at threshold values of 2 mg/L TAN; 40 mg/L SO_4 , and 7 mg/L K. Samples with at least one analytical result greater than these threshold values were manually inspected prior to removal. None of the groundwater samples with only TAN outliers were excluded from the dataset, as in all cases, the corresponding samples were sourced from lignite or peat aquifers, where elevated TAN concentrations is a common occurrence owing to ammonification of organic matter within the aquifer.

Although the normal probability plot of EC identified a large outlier population, the majority of these samples were associated with carbonate catchments and therefore were not excluded from the analysis dataset. The remaining groundwater sites with anomalous EC population that did not exhibit saturation, or approach saturation (ca. $\log Q/K$ of > -1.0) with respects to calcite were associated with sites known for poor well positioning where direct contamination has periodically been a recognised issue. Total oxidisable nitrogen and Cl did not show anomalous populations.

Hydrochemical data collected at wells for which well depth is greater than the depth of a confining layer. This was done on the basis that these deep groundwaters are less hydrologically connected to the soil zone, tend to be more reducing irrespective of the shallow geological reduction capacity and that these waters are often much older than equivalent shallower waters (Rissmann, 2012; Daughney et al., 2015).

TC6.3.2 Assignment of Redox State and Dominant Redox Reaction

To assign redox state (i.e. general redox category) and dominant TEAP of ground and surface waters, we initially used the redox assignment workbook of Jürgen et al. (2009)⁴. However, as per the recommendations of Jürgen et al. (2009) the default threshold values used within the framework were reviewed in light of local dynamics. Applying the default thresholds defined in the workbook (Table 6-1), c. 80% of Southland's groundwaters were assigned an oxic status, as based on DO, Mn(II), Fe(II), TON and oxygen redox potential (ORP), where some evidence of reduction was actually observed (e.g. DO values as low as 0.7 mg/L and TAN as high as 0.7 mg/L). For these waters, data suggest that a mixing between reduced and oxidised waters may result in dilution of reduced species (e.g. Mn(II) and Fe(II)) below the default thresholds specified within the redox assignment workbook (Jürgen et al., 2009).

The need to develop regionally specific redox thresholds reflects the unique hydrogeological setting of Southland. Typically, Southland's groundwater table is shallow, median depth of 2.75 m bgl; $n = 1,750$ wells, relative to the depth of pedogenic differentiation and as such the soil zone is often in direct connection to underlying aquifer systems. Furthermore, groundwater residence times are short (i.e., MRT < 10 years, $n = 55$ measurements, Daughney et al., 2015) and unconfined

⁴ The workbook uses the redox assignment framework of McMahon and Chappelle (2008) to define redox state and TEAP based on set thresholds for redox sensitive species. The redox assignment framework of McMahon and Chappelle (2008) is designed specifically to assess the redox status of aquifer systems although can be applied to surface waters (pers. com. McMahon, 2015).

quaternary aquifers are thin, typically < 30 m and the soil zone is more often than not the dominant control over regional hydrochemistry (TC7). The latter characteristics differ markedly from those of the large scale aquifer systems of North America and other parts around the world for which the redox assignment workbook and current understanding around redox processes has been developed.

Consequently, Southland specific thresholds were developed for redox sensitive species (DO, NO₃-N, Mn(II), Fe(II) and SO₄) to assign redox state and TEAP of Southland freshwaters (Table 6-2; Appendix B for detail on the determination of Southland specific redox thresholds). In the following section 'regionally specific' redox thresholds are used to assess relationships between redox state, TEAP and the concentrations of redox sensitive species with the combined denitrification potential of soil and geology.

It is noted that the redox state and TEAP are only indicative of the redox progression. Often waters of different redox state mix during sampling, particularly for groundwaters, as reduction may be localised, e.g. on the surface of peat inclusions in the subsurface. In addition, redox progression is also often depth and seasonality dependent, whereas the water samples, whether groundwater or surface water presented here, represent a collection of waters from a wide zone, i.e. capture zone (McMahon and Chapelle, 1991, 2008; Vrobesky and Chapelle 1994; Champ et al. 1979) Therefore, low NO₃-N and/or high Mn(II) and Fe(II) are sometimes seen concurrently with high DO in same water sample.

TC6.3.3 Map Intersection and assignment of CRP to surface and groundwater sites

As previously mentioned the reduction potential of soil and geology defined in Killick et al. (2015) in Figure 6-3 and Rissmann (2011), respectively (Figure 6-4) were used as a basis for establishing the Southland regional CRP map of soil and geology.

Initially, the soil SDP rating was classified into five categories as per Killick et al. (2015). For this work, classification is simplified into three categories 'Low', 'Moderate' and 'High'. Specifically, natural "breaks"⁵ in the SDP rating (as identified by Killick et al., 2015) using ESRI ArcGIS were used in addition to information on soil hydraulic properties to simplify the SDP categories. The new rankings do not therefore necessarily bear any relationship with the Killick et al. (2015) rankings.

Soil drainage status, infiltration rate and the presence or otherwise of redoximorphic features (mottles and gleying) were used to guide partitioning of the numerical or continuous SDP ranking (Table 6-3, Table 6-4 and Table 6-5). Specifically, the 'Low' category is dominated by Brown and Recent soils with slight to nil waterlogging and aeration. The 'Moderate' category is dominated by Pallic and Brown soils with very severe to moderate aeration ratings and severe to slight waterlogging. The 'High' category is dominated by Gley, Organic and Pallic soils with extreme to very severe aeration ratings and severe waterlogging.

⁵ Based on breaks in cumulative probability plots.

Table 6-1: Criteria and threshold concentrations for identifying redox processes in ground water defined in Jürgen et al. (2009) after McMahon and Chapelle (2008).

Redox category	Redox process	Electron acceptor (reduction) half-reaction	Criteria for inferring process from water-quality data					
			DO (mg/L)	NO ₃ -N (mg/L)	Mn(II) (mg/L)	Fe(II) (mg/L)	SO ₄ ²⁻ (mg/L)	Fe(II)/T.S. (mass ratio)
Oxic	O ₂	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	≥0.5	—	<0.05	<0.1	—	
Suboxic	Suboxic	Low O ₂ ; additional data needed to define redox process	<0.5	<0.5	<0.05	<0.1	—	
Anoxic	NO ₃	$2NO_3^- + 12H^+ + 10e^- \rightarrow N_{2(g)} + 6H_2O$; $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$	<0.5	≥0.5	<0.05	<0.1	—	
Anoxic	Mn(IV)	$MnO_{2(s)} + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	<0.5	<0.5	≥0.05	<0.1	—	
Anoxic	Fe(III)/SO ₄	Fe(III) and (or) SO ₄ ²⁻ reactions as described in individual element half reactions	<0.5	<0.5	—	≥0.1	≥0.5	no data
Anoxic	Fe(III)	$Fe(OH)_{3(s)} + H^+ + e^- \rightarrow Fe^{2+} + H_2O$; $FeOOH_{(s)} + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$	<0.5	<0.5	—	≥0.1	≥0.5	>10
Mixed (anoxic)	Fe(III)-SO ₄	Fe(III) and SO ₄ ²⁻ reactions as described in individual element half reactions	<0.5	<0.5	—	≥0.1	≥0.5	≥0.3, ≤10
Anoxic	SO ₄	$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$	<0.5	<0.5	—	≥0.1	≥0.5	<0.3
Anoxic	CH ₄ gen	$CO_{2(g)} + 8H^+ + 8e^- \rightarrow CH_{4(g)} + 2H_2O$	<0.5	<0.5	—	≥0.1	<0.5	

Table 6-2: Southland specific criteria and threshold concentrations for identifying redox processes in surface (SW) and ground water (GW) defined in this study.

Redox category	Redox process	Electron acceptor (reduction) half-reaction	Criteria for inferring process from water-quality data in surface water (SW) and groundwater (GW)					
			DO in SW; GW (mg/L)	NO ₃ -N in SW; GW (mg/L)	Mn(II) in SW; GW (mg/L)	Fe(II) in SW; GW (mg/L)	SO ₄ ²⁻ in SW; GW (mg/L)	Fe(II)/T.S. in SW; GW (mass ratio)
Oxic	O ₂	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	≥3; ≥4	—	<0.003; <0.002	<0.02; <0.01	—	
Suboxic	Suboxic	Low O ₂ ; additional data needed to define redox process	<3; <4	<2; <3	<0.003; <0.002	<0.02; <0.01	—	
Anoxic	NO ₃	$2NO_3^- + 12H^+ + 10e^- \rightarrow N_{2(g)} + 6H_2O$; $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$	<3; <4	≥2; ≥3	<0.003; <0.002	<0.02; <0.01	—	
Anoxic	Mn(IV)	$MnO_{2(s)} + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	<3; <4	<2; <3	≥0.002; ≥0.003	<0.02; <0.01	—	
Anoxic	Fe(III)/SO ₄	Fe(III) and (or) SO ₄ ²⁻ reactions as described in individual element half reactions	<3; <4	<2; <3	—	≥0.02; ≥0.01	≥2; ≥3	no data
Anoxic	Fe(III)	$Fe(OH)_{3(s)} + H^+ + e^- \rightarrow Fe^{2+} + H_2O$; $FeOOH_{(s)} + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$	<3; <4	<2; <3	—	≥0.02; ≥0.01	≥2; ≥3	>10
Mixed (anoxic)	Fe(III)-SO ₄	Fe(III) and SO ₄ ²⁻ reactions as described in individual element half reactions	<3; <4	<2; <3	—	≥0.02; ≥0.01	≥2; ≥3	≥0.3, ≤10
Anoxic	SO ₄	$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$	<3; <4	<2; <3	—	≥0.02; ≥0.01	≥2; ≥3	<0.3
Anoxic	CH ₄ gen	$CO_{2(g)} + 8H^+ + 8e^- \rightarrow CH_{4(g)} + 2H_2O$	<3; <4	<2; <3	—	≥0.02; ≥0.01	<2; <3	

Table 6-3: Summary of new soil SDP classes with respect to waterlogging defined in S-map.

Soil SDP Class	Waterlogging					
	Severe	Moderate	Slight	Minimal	Nil	No rating
High	93.76%	0.75%	0.05%	0.00%	5.44%	0.00%
Moderate	48.09%	33.39%	13.34%	0.20%	4.99%	0.00%
Low	0.00%	5.19%	53.09%	1.35%	39.99%	0.38%

Table 6-4: Summary of new soil SDP classes with respect to aeration defined in S-map. Note the scale refers to the level of aeration impedance.

Soil SDP Class	Aeration						
	Extreme	Very Severe	Severe	Moderate	Slight	Minimal	No Rating
High	16.03%	77.85%	0.63%	0.00%	0.05%	5.44%	0.00%
Moderate	0.00%	48.61%	7.81%	25.90%	9.17%	8.52%	0.00%
Low	0.00%	0.00%	0.26%	7.59%	28.00%	63.78%	0.38%

Table 6-5: Summary of new soil SDP classes with respect to NZSC Order defined in S-map.

Soil SDP Class	NZSC Order						
	Gley	Pallic	Organic	Brown	Recent	Melanic	Other
High	65.76%	12.73%	16.03%	5.44%	0.00%	0.00%	0.05%
Moderate	6.82%	44.48%	0.00%	43.94%	0.49%	0.29%	3.98%
Low	0.00%	1.62%	0.00%	68.82%	16.27%	8.37%	4.93%

Since the SDP layer was limited to the extent of the Topoclimate soils layer, we used regional hydrochemical data on redox sensitive species and electron donor abundance (i.e., DOC) in conjunction with vegetative cover and some soil profile data to derive an understanding of the redox setting of the remaining area for which SDP rating was unavailable. This was important because many of Southland’s ground and surface waters, e.g. the region’s main stem rivers, have their sources in alpine or hill country, known hereafter as bedrock; areas for which SDP rating was not defined. Hence defining SDP of bedrock and alpine areas is important for understanding regional hydrochemistry and water quality.

Analysis of alpine streams and rivers showed that these waters are predominantly oxic and have the lowest concentration of reduced species, the highest ORP and the lowest DOC of regional surface waters, all of which indicate oxidising conditions within alpine recharge areas (Figure 6-5). This is consistent with little organic carbon biomass above the tree line and in particular the 0°C isotherm. Conversely, bedrock derived streams and rivers are predominantly mixed (oxic-anoxic) waters with elevated dissolved Mn(II), Fe(II) and NH₄-N and have high concentrations of DOC consistent with the measurement of strong reduction within the soil and thin saturated zone (Figure 6-5). A significant carbon store across the bedrock areas of Southland is consistent with a long history of forest or red tussock cover in these areas (Monaghan and Smith, 2004; McLeod et al., 2008). However, groundwaters associated with bedrock areas are generally low in Mn(II) and Fe(II) and high in DO and TON, probably due to recharge through outcropping fractured rocks (Figure 6-6). Significant groundwater resources in alpine areas do not exist. Accordingly, it is reasonable to infer oxidising conditions within thin Alpine soils and raw geomorphic surfaces and moderately to strongly reducing conditions in thin Bedrock ‘Hill Country’ soils and colluvium overlying fractured bedrock.

Accordingly, Alpine and Bedrock areas are defined as having low and high soil zone reduction potential, respectively. Due to the different controls over soil zone reduction potential Alpine and

Bedrock SDP categories are discriminated from lowland areas with similar CRP categories (i.e. Alpine Low vs. Lowland Low; Bedrock High vs. Lowland High). It may also be important to discriminate between streams that have an alpine source but receive drainage from bedrock areas (in the following referred to as Bedrock 1) and those streams derived solely from bedrock (i.e., no alpine headwaters; in the following referred to as Bedrock 2). It appears that oxidising Alpine drainage dominates volumetrically thereby diluting the reducing signature of bedrock drainage. As demonstrated in TC4, the discrimination between Bedrock 1 and Bedrock 2 derived streams is important for understanding variation in regional hydrochemistry.

Any further holes in the map due to lack of soil information, estimated as 5%, were filled using geological information or local knowledge. For example reducing areas of peat wetland outside the boundary of the soils map were defined using geological and topographical maps and significant outcrops of lignite, not identified in regional geological maps, were delineated and included.

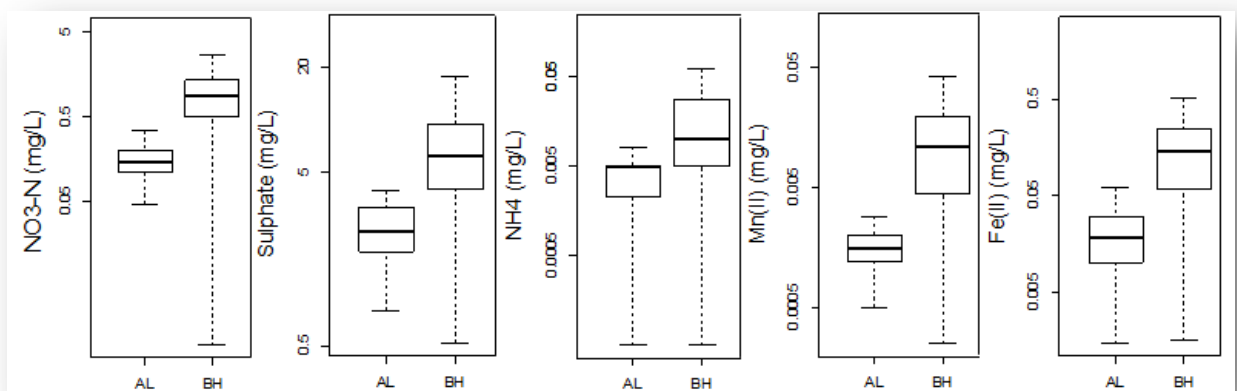


Figure 6-5: Concentrations of redox sensitive species in surface waters associated with alpine(AL) and Bedrock/Hill Country (BH) areas.

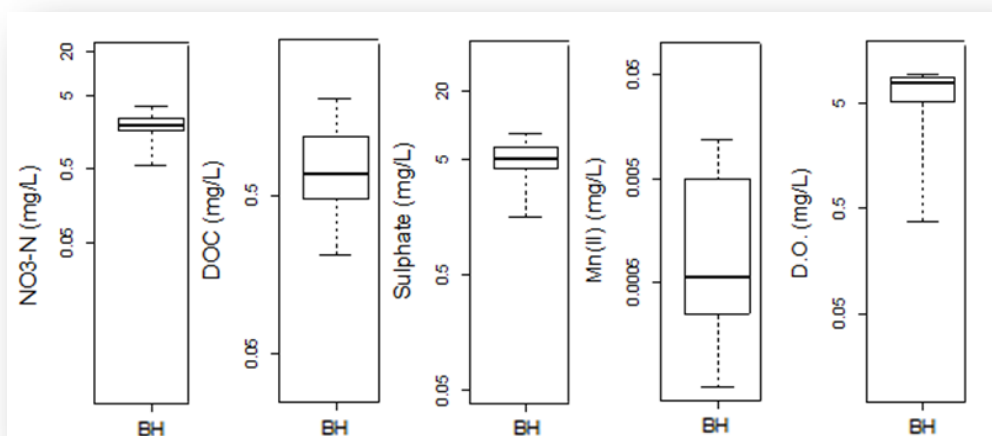


Figure 6-6: Concentrations of redox sensitive species associated with bedrock areas (BH) in Southland. Groundwaters in alpine areas do not exist.

TC6.3.4 Extent of Combined Reduction Potential Categories

The CRP map of Southland is presented below (Figure 6-7) along with a summary of the 9 CRP categories and associated areas (Table 6-6). The symbols denote soil over geology (i.e., High soil zone reduction over Low geological reduction = HL).

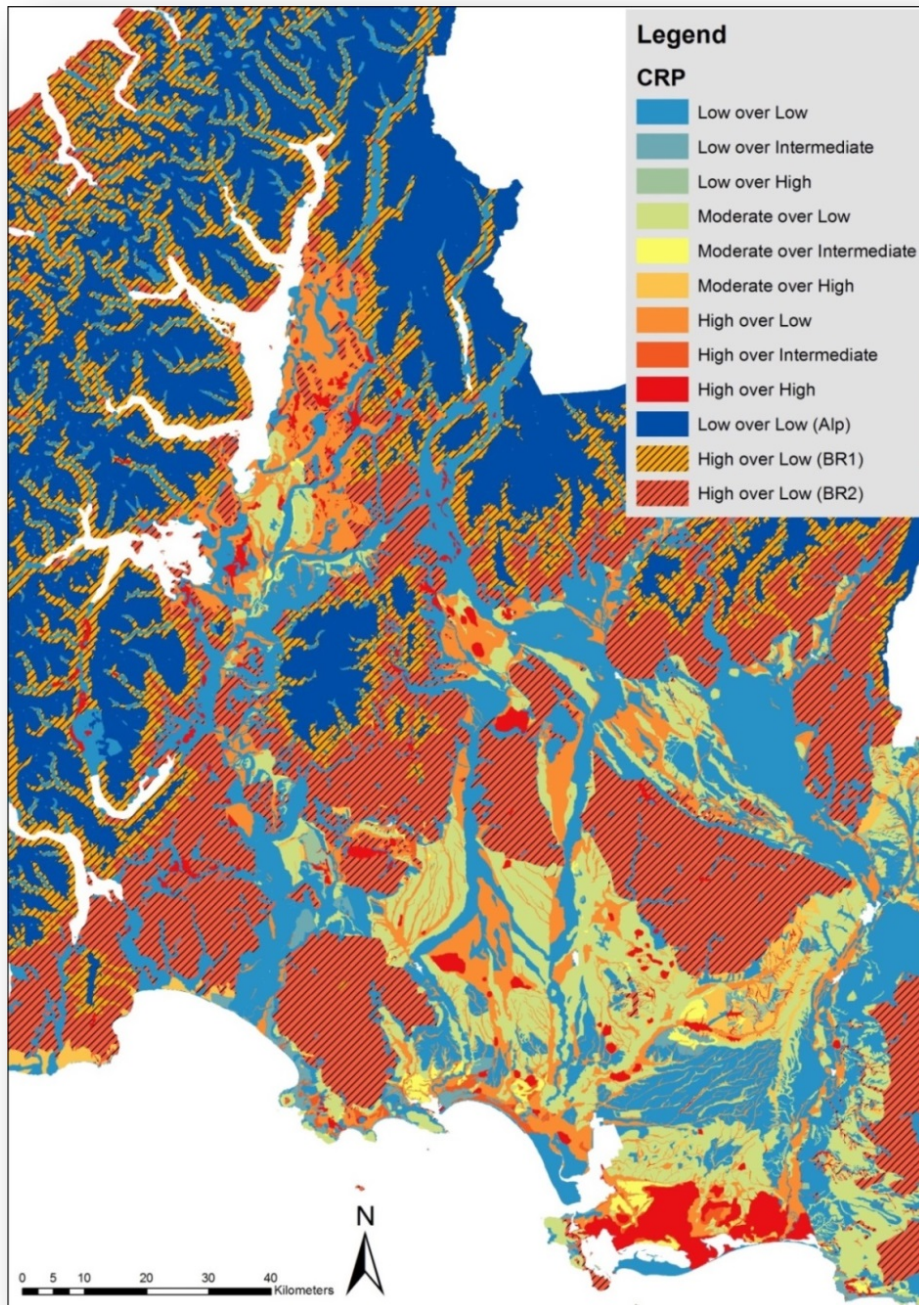


Figure 6-7: Combined reduction potential (CRP) map of soil and geology of Southland. The map also highlights bedrock 1 and 2 areas (cross hatched symbols) – Bedrock 1 (BR1) refers to bedrock areas that are adjacent to alpine areas and Bedrock 2 (BR2) are areas that are not connected to alpine areas.

Two of the nine CRP categories (HL and LL) cover 88.4% of the area, the remaining seven categories make up 9.2 percent of the area. The majority of LL (%) and HL (%) is associated with Alpine and Bedrock areas of Southland, including Fiordland National Park and Stewart Island. Assessing only the lowland areas of Southland characterised by intensive land use, the dominant CRP categories are ML

and LL (c. 89% of the lowland area of Southland). Lowland areas with reducing geology (H and I) or strongly reducing soils (H) making up only 9% and 2%, respectively. The extent of key CRP categories is important in the content of the following discussion.

TC6.3.5 Assessment of relationships between CRP and redox indicators

To assess whether relationships between the concentration of redox sensitive and CRP categories exists, we intersected the CRP map with the regional hydrochemical dataset for ground and surface waters. Specifically, groundwater and surface water sites and their associated capture zones (CZ) were intersected with the map. Capture zones are aerial projection of the land surface contributing water to a specific source (e.g. for Southland see Moreau et al. 2014). Surface water capture zones were based on REC classification polygons (see detail in Appendix D1). Surface water sites without previously characterised (REC) capture zones were not included in our analysis. Groundwater capture zones were defined according to a simple hydromorphic approach (Appendix D2).

Prior to assessing relationships between the concentration of redox sensitive and CRP categories, data for a number of repeat measurements, outliers, trends and seasonality, were evaluated. Specifically, some of the sites have as many as c. 50 replicates whereas many of the groundwater sites only have 1 or 2 repeat measurements. The lack of repeat measurements for a large number of the groundwater sites was not considered an issue given that the majority of Southland's SoE (State of the Environment) groundwater sites show minor seasonality with respect to TON (Moreau and Papanek, 2014) and little overall variation in TON concentration on a quarterly basis when contrast with regional surface waters.

Table 6-6: Categories for CRP and associated area; * no data = lakes, towns

SDP	Geology DNP	CRP	CRP code	Proportion of Southland [%]
High	High	High over High	HH	1.11
High	Intermediate	High over Intermediate	HI	0.11
High	Low	High over Low	HL	0.70
High (Bed)	Low (Bed)	High over Low (Bed)	BHL	43.33
Low	High	Low over High	LH	0.22
Low	Intermediate	Low over Intermediate	LI	0.23
Low	Low	Low over Low	LL	19.11
Low (Alp)	Low (Alp)	Low over Low (Alp)	ALL	25.33
Moderate	High	Moderate over High	MH	0.75
Moderate	Intermediate	Moderate over Intermediate	MI	0.18
Moderate	Low	Moderate over Low	MI	6.63
n/a	n/a	No Data	No data	2.30

TC6.3.6 Statistical tests of significant differences in redox sensitive species between CRP categories

Following the intersection of groundwater and surface water sites and their associated capture zones (CZ) with the map, CRP categories were assessed to determine if they were meaningful in terms of variation in redox sensitive species (i.e., DO, TON, Mn(II), Fe(II)). Where relevant, ancillary data such as the concentration of DOC were assessed as a proxy for solid state organic C and Total Ammonical Nitrogen (TAN).

A parametric one way ANOVA test was applied to log-transformed medians of the concentration of redox sensitive species to evaluate the degree of association between CRP categories. In addition, a non-parametric Kruskal-Wallis One-Way ANOVA test was used on redox state and redox process, TEAP, to evaluate the degree of association between CRP categories on the basis of redox state and TEAP. The null hypothesis of these tests is that all of the distribution functions are equal - ergo that there is no difference in assigned redox state, TEAP and measured DO, TON, Mn(II), Fe(II) and DOC concentrations between the various CRP categories. Where statistically significant differences occurred, multiple comparison testing were undertaken between the categories at the 95% level. To reduce bias caused by a small sample size associated with a CRP category, we removed all CRP categories that were associated with less than 5 samples.

Specifically, for multiple comparisons testing of redox state, TEAP, by CRP categories we used the t-distribution test within the Kruskal-Wallis One-Way ANOVA⁶. The Tukey's honest significant difference (HSD) test was used for multiple comparison testing of (log-transformed median) concentrations of redox sensitive species and CRP categories. This approach enables assessment of the existence, or otherwise, of homogenous subsets or 'groups' of CRP categories that are not significantly different from each other.

Non-parametric Kruskal-Wallis One-Way ANOVA and multi-comparison tests were run on the ground and surface water data sets separately. CRP categories, homogenous in terms of redox sensitive species, provide an objective method for assessing which of the CRP categories are truly meaningful in terms of redox indicators, in particular redox state, TEAP and TON.

Although TON is the most environmentally relevant factor for this study, multiple comparisons of DO, Mn(II), Fe(II) and DOC are considered a more rigorous approach than relying solely on TON. TAN was not included in the statistical testing due to a high proportion of less than detects in the samples analysed. However, TAN was used as an ancillary measure because it provides additional insight into process such as ammonification within regional aquifers.

TC6.4 Results and Discussion

TC6.4.1 Independent assessment of redox conditions as a function of soil and geological DNP for groundwater

Peer review of a draft of this report encouraged an assessment of the relationships between the concentrations of redox sensitive species and SDP and GDP independently. Therefore, before proceeding with an assessment of redox indicators against the CRP categories, it was assessed whether redox signatures vary according to the simplified geological and soil DNP categories outlined in Section TC6.2 (Figure 6-8 and Figure 6-9, respectively). This was done by assessing groundwater signatures on the basis that shallow, soil influenced groundwaters represent the maximum potential for soil zone reduction.

Groundwater Mn(II) and Fe(II) concentrations increase as NO₃-N and DO decrease with either increasing geological or soil reduction potential, although DO is quite variable, which can be linked to re-equilibration with atmospheric air and soil zone bypass (Figure 6-8 and Figure 6-9).

⁶ Since the numbers of hydrochemical samples associated with each CRP category were not equal; the presence of equal within-group variance across the groups (assumption of ANOVA test) was tested using the Bartlett test.

Considering the entire dataset, the relationships between redox sensitive species and soil reduction categories are less strong than the relationships between geological reduction categories and redox sensitive species. However, following the exclusion of the Central Plain samples (Figure 6-8 and Figure 6-9), which are subject to soil zone bypass (discussed in detail in TC2), a clearer picture of the relationship between soil reduction and redox sensitive species emerges⁷. Soil zone bypass to reducing aquifers also appears to influence the variability of redox sensitive species in reducing environments - specifically, reduced aquifers receiving oxidised recharge due to soil zone bypass show greater temporal variability in redox sensitive species (larger coefficient of variation) than oxidising aquifers receiving oxidised bypass.

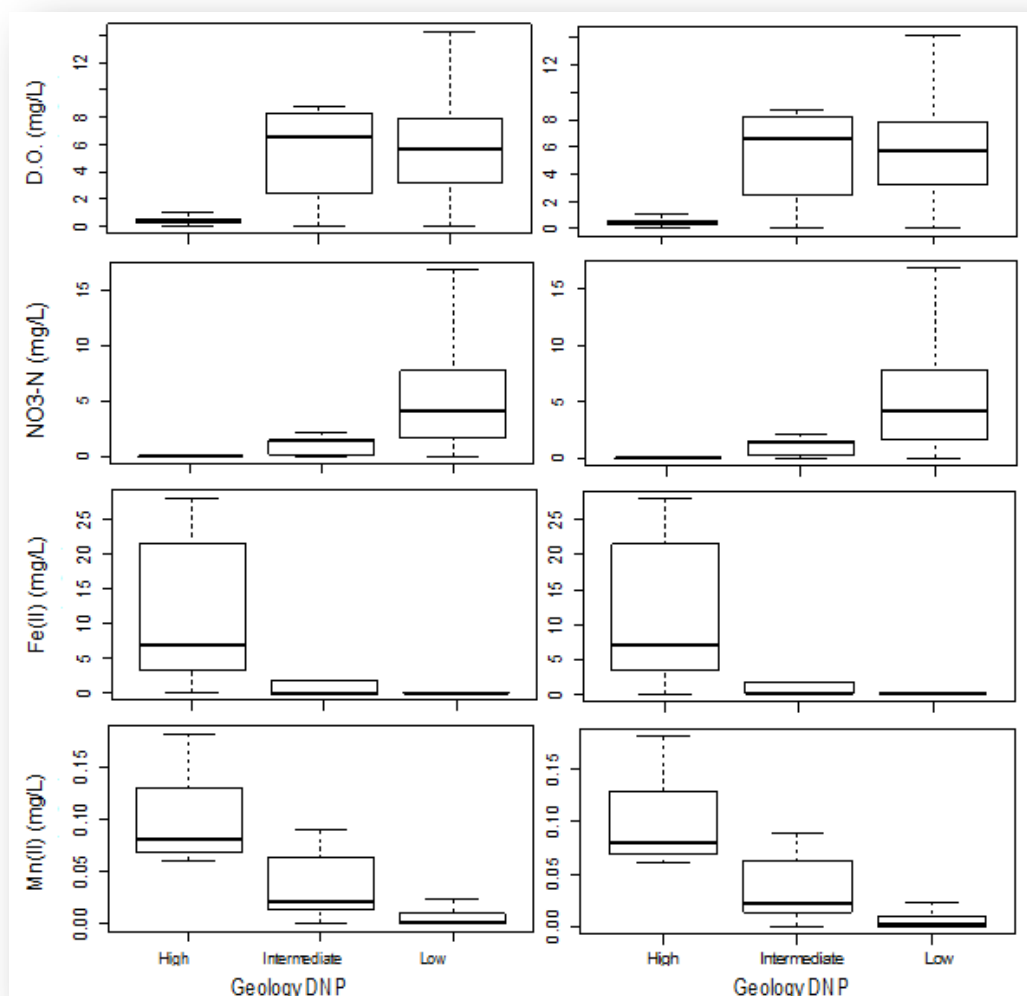


Figure 6-8: Geographical DNP and Groundwater. Concentration of redox sensitive species in groundwater using all data (LEFT) and excluding Central Plains data that are prone to bypass flow (RIGHT) suggests redox sensitive species vary in an anticipated manner with geological DNP defined in Rissmann (2011). Exclusion of Central Plains data (potential bypass data) did not significantly improve the relationships between redox sensitive species and geological DNP.

⁷ The Central Plains is one of the only areas in Southland for which large macropore cracks bypass the strongly reducing soil zone conducting nitrate rich soil waters into the underlying aquifer.

Overall, our assessment indicates that geological and soil reduction frameworks, as defined in Rissmann (2011) and Killick et al. (2015) can be used to predict the reduction signatures of groundwater. However, as further elaborated on in the following section, the domain, soil or geology, which is the locus of reduction varies significantly spatially across Southland. Specifically, in some areas only the soil zone or only the geology is reducing.

Overall, observing anticipated relationships between redox signatures and both soil and geological reduction categories supports the simplification through merging of the initial 5 soil DNP categories to 3 categories (described earlier). This is further supported by statistical analysis carried out in subsequent sections.

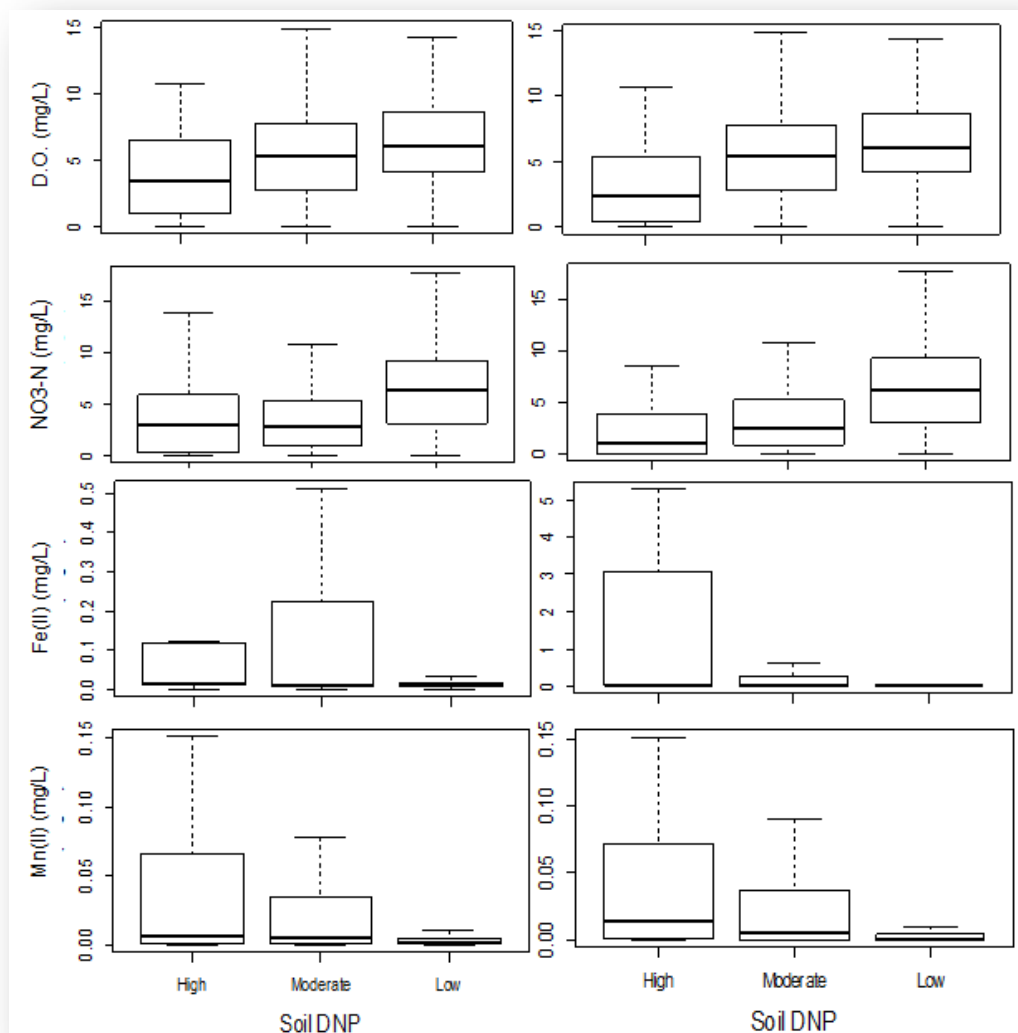


Figure 6-9: Soil DNP and Groundwater. Concentration of redox sensitive species in groundwater using all data (LEFT) and excluding Central Plains data that are prone to bypass flow (RIGHT) suggesting redox sensitive species vary in an anticipated manner with soil DNP, defined in Killick et al. (2015), particularly for the dataset not including Central Plains data where soil zone bypass is a key feature.

From this preliminary assessment of redox signatures in groundwater as a function of soil and geology reduction we conclude:

- 1) The observed relationships between redox signatures and both soil and geological reduction categories supports the simplification/merging of the initial five soil DNP categories to three categories (described earlier).
- 2) Due to spatial variance in the domain (soil or geology) where reduction is occurring, we need to consider both soil and geology reduction to predict the redox signatures of regional freshwaters.
- 3) Natural (soil cracking) bypass flow may also influence variability in redox conditions of both oxidising and reducing aquifers. Consideration of the role of bypass over ground and surface water redox is discussed in Chapter 3 and 4 (Conceptual Model and Validation of the Conceptual Model) where redox, recharge mechanism, geomorphic and compositional controls are combined in order to predict the spatial variability in hydrochemistry including redox sensitive species.

Two other aspects are considered fundamental to the work that follows. 1) Nitrogen loading is spatially variable and as demonstrated in Chapter 3 (Conceptual Model), 2) hydrology is a critical factor in accurately predicting the concentration of redox sensitive species, general redox state and TEAP for surface water sites.

Regarding the input or loading of nitrogen, we note that Alpine and large areas of Bedrock Hill Country across Southland have little to no anthropogenic nitrogen input. Extensively and intensively farmed areas also have variable nitrogen inputs or loading. Accordingly, nitrogen input is far less uniform than that of DO, Mn(II) and Fe(II) inputs which are controlled by atmospheric and mineral content, respectively. It is therefore important to consider the redox setting in its entirety when assessing the suite of redox sensitive species – DO, NO₃-N, Mn(II), Fe(II) and SO₄, in conjunction with ancillary indicators of redox processes such as DOC and/or TAN. In some instances, total sulphides (sum of H₂S dissolved, HS⁻ and S³⁻) and the stable isotopes of carbon also can, also be useful indicators of a redox setting in some cases. Furthermore, whether one or more redox indicator dominates is heavily dependent upon the natural thresholds in the ecological succession of terminal electron acceptors by bacteria, as discussed in the introduction of this TC. Therefore, reliance on one metric or variable is not considered robust.

All the same this work proceeds on the basis of a simple assessment of CRP over redox signatures.

TC6.4.2 Statistical Grouping (combination of redox indicator data with CRP categories) and supporting information

On the basis of our preliminary findings the relationships between redox conditions (i.e. the concentrations of redox sensitive species, redox state and TEAP) and the CRP of Soil and Geology are assessed using statistical analysis to support the assessment.

Due to the complexity of dealing with multiple CRP categories within a surface water capture zone we have restricted our initial assessment to the relationship between the dominant CRP category by area and redox sensitive species for all surface and groundwater sites. The assumption being that the CRP category with the largest representation area, within a capture zone will strongly influence redox signatures. However, given strong evidence for mixing of redox signatures, we also apply a second iteration whereby the subordinate or second largest CRP category by area is included within

the assessment⁸. For example, the two dominant CRP categories may differ significantly in their ability to denitrify and reduce (e.g. expected for categories HH and LL) or they may be relatively similar (e.g. expected for categories LL and ML).

Assessing surface water sites by the dominant CRP category resulted in association of six of the 10 CRP categories (Table 6-7). That surface water sites are not represented within all categories reflects the small area of some of the CRP categories (Table 6-6 and Figure 6-7).

For groundwater, six of the 10 CRP categories were associated with more than five samples. That groundwater sites are not represented within all categories reflects the small area of some of the CRP categories (Table 6-6 and Figure 6-7). Due to the smaller size of some of the geologically reducing CRP categories and fewer bores within these areas, three of the intersected categories (MH, BHL and HH) included less than five sites (Table 6-7 and Table 6-8). Since small sample sizes may introduce bias, the BHL, MH and HH categories were removed for further analysis, reducing the total number of dominant CRP categories for groundwaters from six to three. It was noted that groundwaters associated with these categories show signs of reduction. These waters are relatively low in TON, particularly for the waters associated with the BHL category (concentrations ranging from 3 to 6 mg/L), and relatively high in Fe(II) (for groundwaters associated with the MH and HH categories) suggesting a relationship between CRP and redox processes i.e. the concentrations of redox sensitive species exists.

Table 6-7: Summary of dominant CRP categories associated with surface water sites (left column) and CRP categories associated with groundwater sites (right column) in the region

CRP category	n	
	SW	GW
Moderate over Low (ML)	26	48
Low over Low (LL)	7	70
Low over Low (Alp) (ALL)	9	n/a
High over Low (HL)	10	47
Low over Intermediate (LI)	n/a	n/a
Moderate over Intermediate (MI)	n/a	n/a
High over Intermediate (HI)	n/a	n/a
Moderate over High (MH)	n/a	1
High over High (HH)	8	2
High over Low (Bed) (BHL)	46	1

Linking surface water sites with two dominant CRP categories resulted in the association of 18 and 14 CRP combinations with surface and groundwater sites, respectively (Table 6-8). Combinations with less than five samples were removed from subsequent analysis leaving 10 and 7 dominant two CRP category assemblages associated with surface and groundwater sites, respectively. Fewer ground and surface water sites within a number of the CRP categories reflect not only the smaller area of some of these categories but also the limited number of bores in areas of reducing geological units due to naturally high Fe (II) concentrations. In these localities high dissolved Mn (II) and Fe (II)

⁸ We also used the CRP at the site for further analysis but this resulted in less consistent relationships with redox sensitive species, redox state, TEAP and TON than the use of the dominant and two dominant CRP categories.

concentrations pose problems for stock drinking water, dairy filtration systems and potability for human consumption, consequently aquifer development has been limited in these areas⁹.

Table 6-8: Summary of dominant two CRP categories associated with surface water sites. Categories with less than four samples were excluded from further analysis (non-highlighted) to reduce bias.

Dominant CRP Categories	n	
	SW	GW
High over Low (Bed) -- Low over Low (BHL-LL)	26	n/a
High over Low (Bed) -- High over Low (BHL-HL)	10	n/a
Low over Low -- Moderate over Low (LL-ML)	10	1
High over Low -- Low over Low (HL-LL)	9	42
Low over Low - High over Low (LL-HL)	8	54
Moderate over Low -- High over Low (ML-HL)	8	13
High over Low (Bed) –Moderate over Low (BHL-ML)	6	n/a
Low over Low (Alp) High over Low (Bed) (ALL-BHL)	6	n/a
High over Low – High over High (HL-HH)	n/a	7
High over Low (Bed) –Moderate over High (BHL-MH)	1	7
High over High -- Low over Intermediate (HH – LI)	4	n/a
Moderate over Low -- Low over Low (ML – LL)	4	1
High over High --Moderate over High	2	0
Low over Low (Alp) -- Low over Low	2	0
High over High -- High over Low	1	0
High over Low (Bed) - Low over High	1	0
High over Low (Bed) -- High over Low (BHL-HL)	1	0
Low over Low --Low over High (LL-LH)	1	0
Low over Low (Alp) – Low over High (ALL-LH)	1	0
Low over Low – High over High (LL-HH)	1	0
Moderate over Low – High over High (ML-HH)	1	0
Moderate over Intermediate – High over Low (MI-HL)	0	1
High over Low - Moderate over Low (HL-ML)	0	2
Low over Low – High over Low (Bed) (LL-BHL)	0	4
High over Low – High over Low (Bed) (HL-BHL)	0	2
ML -none	0	2
LL -none	0	17
HL -none	0	9

6.4.2.1 Multi-comparisons test on one dominant CRP category and redox species

Surface water

Multi-comparison tests between redox sensitive species (log-transformed medians) and dominant CRP identified two to five homogenous subsets 'groupings' of dominant CRP categories for surface water sites at the 95% confidence level (Table 6-9). Boxplots of redox sensitive species (Figure 6-10) further supports the evidence that differences identified in the multi-comparisons test are meaningful. Redox state and TEAP also change in an anticipated manner with CRP category (Figure 6-11).

⁹ Areas of strongly reducing geology or biological sediments (peat) equate to c. 10% of the regions aquifers (Rissmann, 2011).

Specifically, the HL category is often grouped together with the ML category (for DO, NO₃-N, SO₄ and DOC). Boxplots confirm similar concentrations of redox sensitive species for surface waters associated with these categories. Furthermore HL and BHL as well as LL and ALL are always independent, not grouped together, although the concentration of redox sensitive species in waters associated with the BHL category is similar to those of LL category waters i.e. more oxidized (Figure 6-10). This suggests that it is important to distinguish between alpine LL and bedrock HL from lowland LL and HL, respectively.

Table 6-9: Homogeneous Subsets 'groupings' of dominant CRP categories for regional surface water.

Homogeneous Subsets 'groupings' of dominant CRP categories by DO	
Group 1	LL, HL, ML, BHL, ALL
Group 2	HH
Homogeneous Subsets 'groupings' of dominant CRP categories by Mn(II)	
Group 1	HL, HH
Group 2	BHL
Group 3	ML
Group 4	LL
Group 5	ALL
Homogeneous Subsets 'groupings' of dominant CRP categories by Fe(II)	
Group 1	HL,
Group 2	BHL
Group 3	LL
Group 4	ALL
Group 5	ML
Group 6	HH,
Homogeneous Subsets 'groupings' of dominant CRP categories by NO ₃ -N	
Group 1	HL, ML
Group 2	HH
Group 3	BHL
Group 4	LL
Group 5	ALL
Homogeneous Subsets 'groupings' of dominant CRP categories by DOC	
Group 1	ML, HL
Group 2	HH
Group 3	BHL
Group 4	LL
Group 5	ALL
Homogeneous Subsets 'groupings' of dominant CRP categories by SO ₄	
Group 1	HL, ML
Group 2	BHL
Group 3	ALL
Group 4	HH, LL

For LL and ALL associated surface waters there is little evidence for reduction so that there is little opportunity for TEAP variance other than perhaps NO₃-N due to landuse and SO₄ due to marine aerosols and landuse. Surface waters associated with the ALL category are most oxidizing of all surface waters (with lowest DO, NO₃-N and highest Mn(II) and Fe(II) concentrations, Figure 6-10). Overall, the composition of BHL and ALL associated waters is similar. This can be related to the

alpine source of most BHL associated surface waters. It appears that the volumetric contribution of alpine head waters dominates these waters. Hence these waters still carry an oxic (alpine) signature although they are associated with reducing soils and geology. As mentioned previously, it is noted that it may be important to distinguish between Bedrock type 1 (connected to alpine areas) and Bedrock type 2 waters (not connected to alpine areas) for the prediction of water chemistry. For this particular analysis, Bedrock 1 is not distinguished from Bedrock 2 waters, but it is in the conceptual model (Chapter 3).

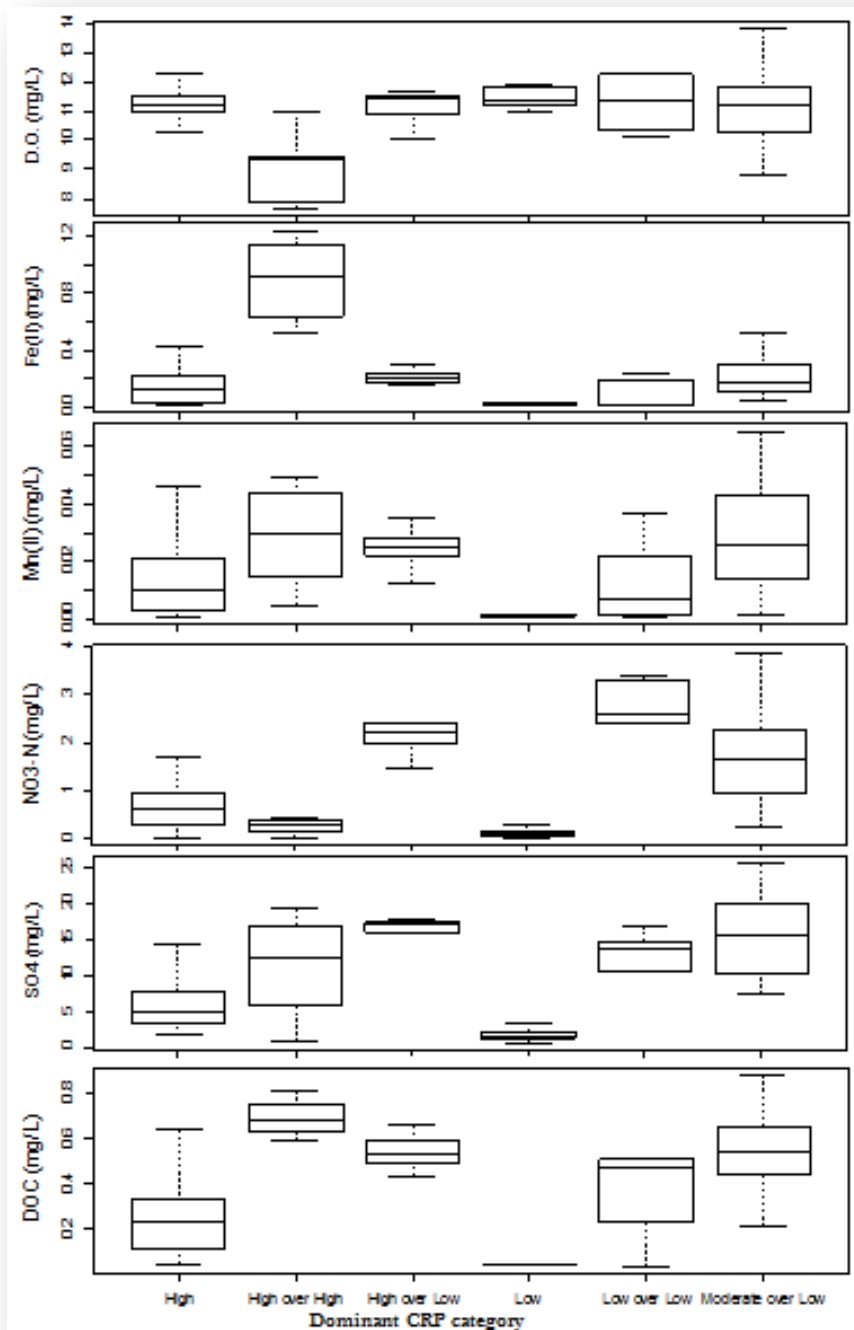


Figure 6-10: Box plots of redox sensitive species in surface water by dominant CRP category illustrating anticipated relationships between the concentrations of redox sensitive species and CRP. Low refers to Alpine Low over Low. High refers to Bedrock High over Low.

Assessment of redox state and TEAP by CRP category indicates that overall the redox state of surface waters is predominantly mixed (oxic-anoxic)(O₂-Fe(III)/SO₄ reducing) with an increasing proportion of oxic (O₂-reducing) waters for surface waters that are associated with the HL and LL category. Similarly, as the proportion of LL increases within a capture zone, O₂-reduction becomes a significant TEAP. As expected, alpine waters are the most oxidising surface waters followed by surface waters derived from bedrock and with peat wetlands being the most reducing. That Southland surface waters show a high number of mixed (oxic-anoxic) signatures is not surprising given the large area of reducing soils or reduced base flow.

As will subsequently be shown, mixed (oxic-anoxic) redox state is also a feature of aquifers for which the overlying soil zone is reducing and yet the aquifer is not (Figure 6-7), reflecting the significance of the soil zone over redox controls of surface water shallow groundwaters.

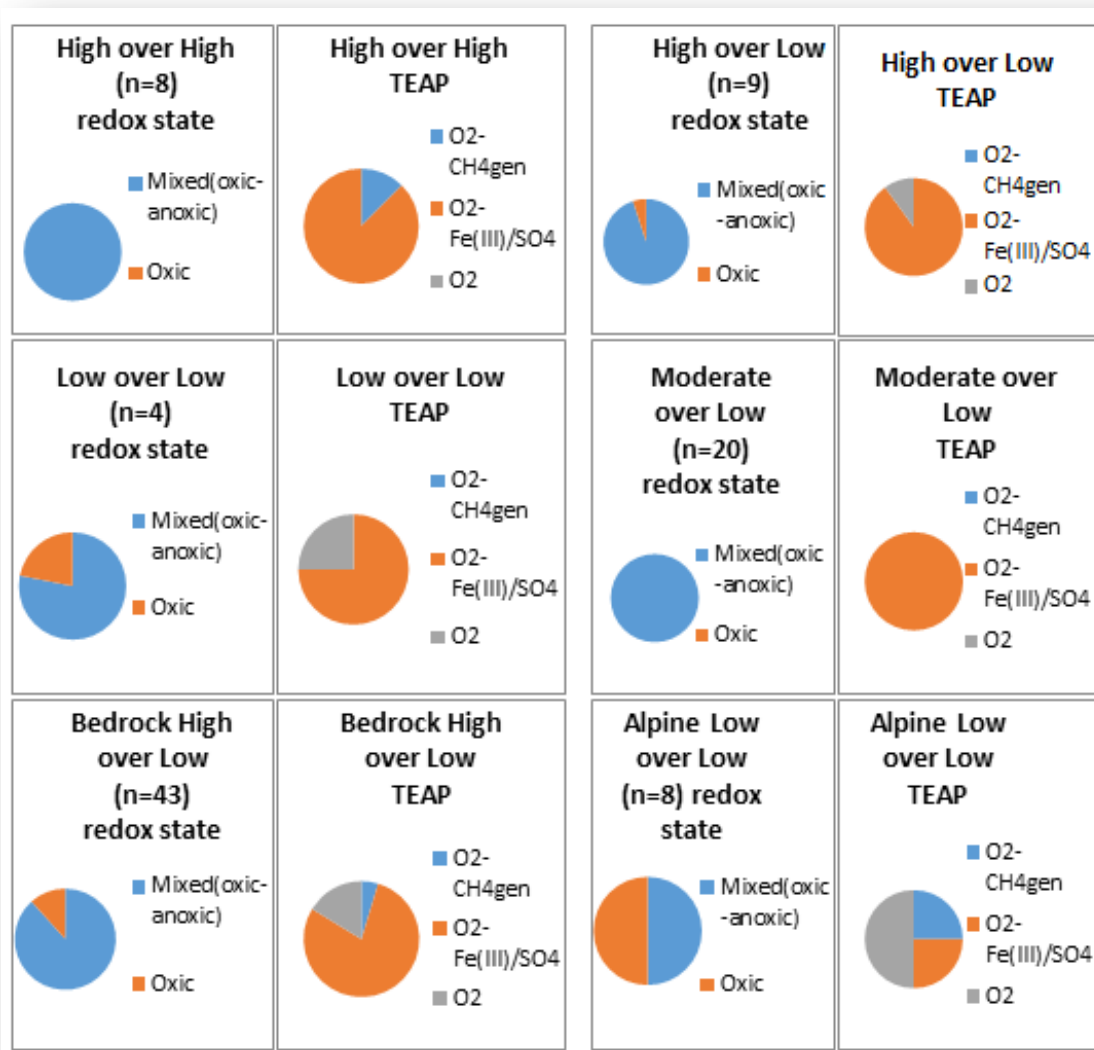


Figure 6-11: redox state and TEAP of surface water by CRP category illustrating redox conditions change in an anticipated manner with increasing CRP.

Groundwater

For groundwater, multi-comparison tests of individual terminal electron acceptors and CRP identified one to three homogenous subsets of CRP categories at the 95% confidence level (Table

6-10). Boxplots of redox sensitive species (Figure 6-12) further support that differences identified in the multi-comparisons test are meaningful. Redox state and TEAP also vary in an anticipated manner with CRP category (Figure 6-13).

Similar to surface waters, the moderately reducing CRP categories (HL and ML) are often grouped together. Importantly, the LL and HL categories are never grouped together, suggesting the assessed groundwaters do not receive significant proportions of alpine sourced waters or have longer exposure times in the subsurface for reduction to occur. Boxplots of redox sensitive species also suggest that the concentrations of redox sensitive species change in an anticipated manner e.g. DO decreases with increasing strength of CRP.

Table 6-10: Homogeneous Subsets ‘groupings’ of site CRP categories for regional groundwater.

Homogeneous Subsets ‘groupings’ of dominant CRP categories by DO	
Group 1	LL, ML, HL
Homogeneous Subsets ‘groupings’ of dominant CRP categories by Mn(II)	
Group 1	HL
Group 2	LL
Group 3	ML
Homogeneous Subsets ‘groupings’ of dominant CRP categories by Fe(II)	
Group 1	LL, ML, HL
Homogeneous Subsets ‘groupings’ of dominant CRP categories by NO ₃ -N	
Group 1	HL, ML
Group 2	LL
Homogeneous Subsets (‘groupings’) of dominant CRP categories by DOC	
Group 1	LL, ML, HL
Homogeneous Subsets (‘groupings’) of dominant CRP categories by SO ₄ ²⁻	
Group 1	LL, ML, HL

Assessment of redox state and TEAP by CRP category indicates that the proportion of oxic waters generally increases with decreasing CRP (i.e. the number of oxic waters is highest for LL category associated surface waters). Unexpectedly, the HL category has a greater number of oxic waters than the LL category. This may be explained by bypass flow or river influenced or mixed recharge associated with the HL category (in Chapter 4 it is shown that 20% of the HL categorised groundwaters are river influenced and 27% have potential bypass). Generally, mixed (oxic-anoxic) redox state are a feature of aquifers for which the overlying soil zone is reducing and yet the aquifer is not (Figure 6-7), reflecting the significance of the soil zone over redox controls of shallow groundwaters. In areas where the reducing soil zone is bypassed, i.e. the Central Plains area, or a significant amount of recharge is derived from a high altitude river source (e.g. Te Anau groundwater zone), groundwaters show oxic rather than mixed redox signatures. The Central Plains soils, for example, are categorised as having a high reduction potential and yet due to macropore bypass, recharge waters do not interact much with the reducing soil zone (further detailed in TC2)¹⁰. Due to

¹⁰ The existence of significant macropore bypass for the Central Plains area is based on anecdotal evidence from farmers who report large vertical cracks forming within the soil over the summer months. Empirical, anecdotal evidence from farmers reports that they are able to place their arms up to their shoulder down cracks. Research shows (i) oxic waters and elevated NO₃-N, despite strongly reducing soils, and; (ii) groundwater hydrographs for the area which show a rapid and sometimes instantaneous response in

bypass, the underlying groundwaters show little evidence of reduction with all groundwaters classified as oxic and containing highly elevated TON. This gives additional evidence, supporting a relationship between a reducing soil zone and the occurrence of reduction in shallow, soil zone connected groundwaters. The role of the soil in controlling groundwater the redox category is an important feature and places significant emphasis on the assimilative capacity of the soil zone for large areas of Southland.

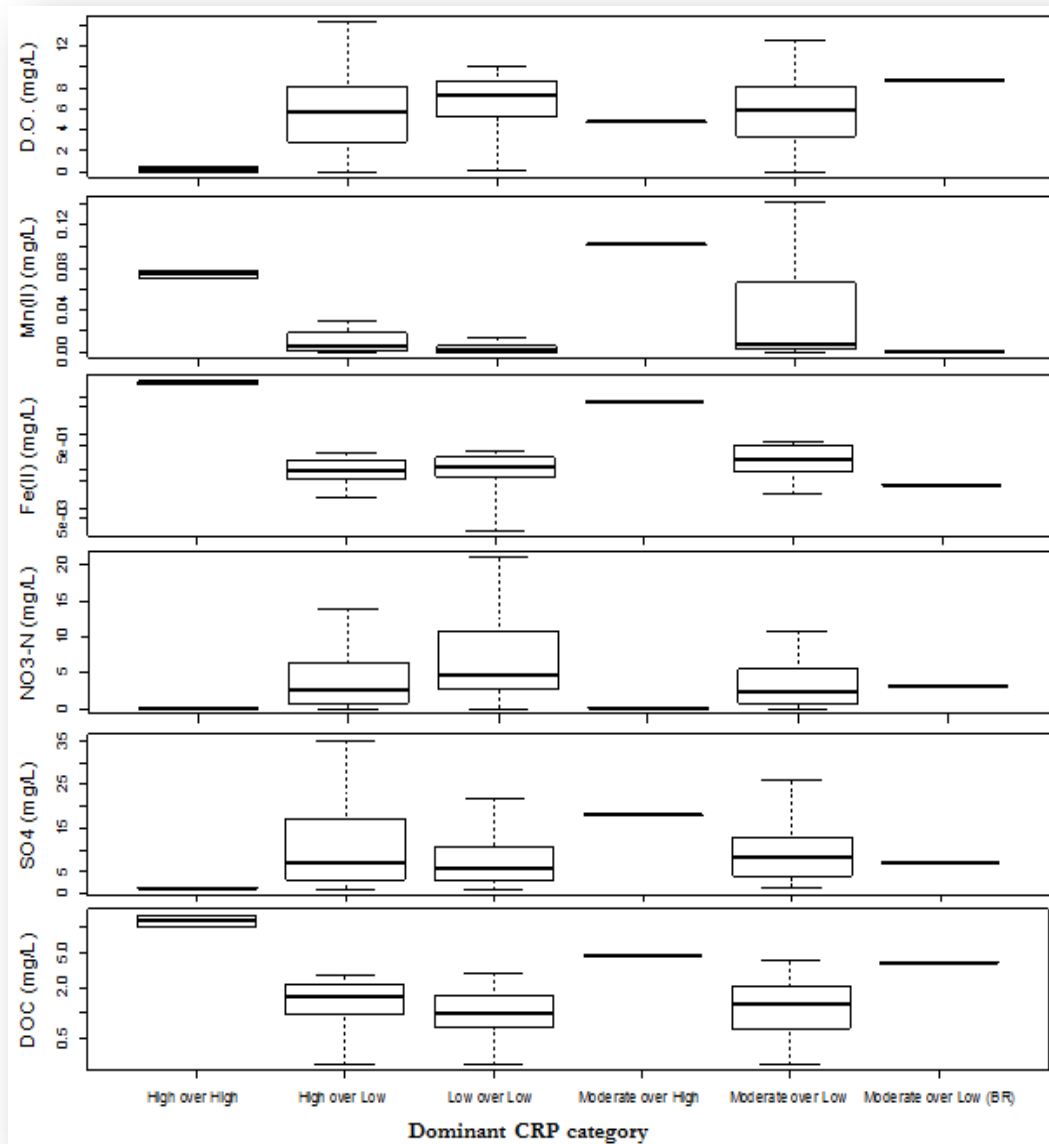


Figure 6-12: Box plots of redox sensitive species in groundwaters by dominant CRP category illustrating anticipated relationships between the concentrations of redox sensitive species.

groundwater levels under recharge conditions. Finally, the study of Greenwood (1994) identifies significant bypass flow for these soils using Br and other conservative ion tracer tests.

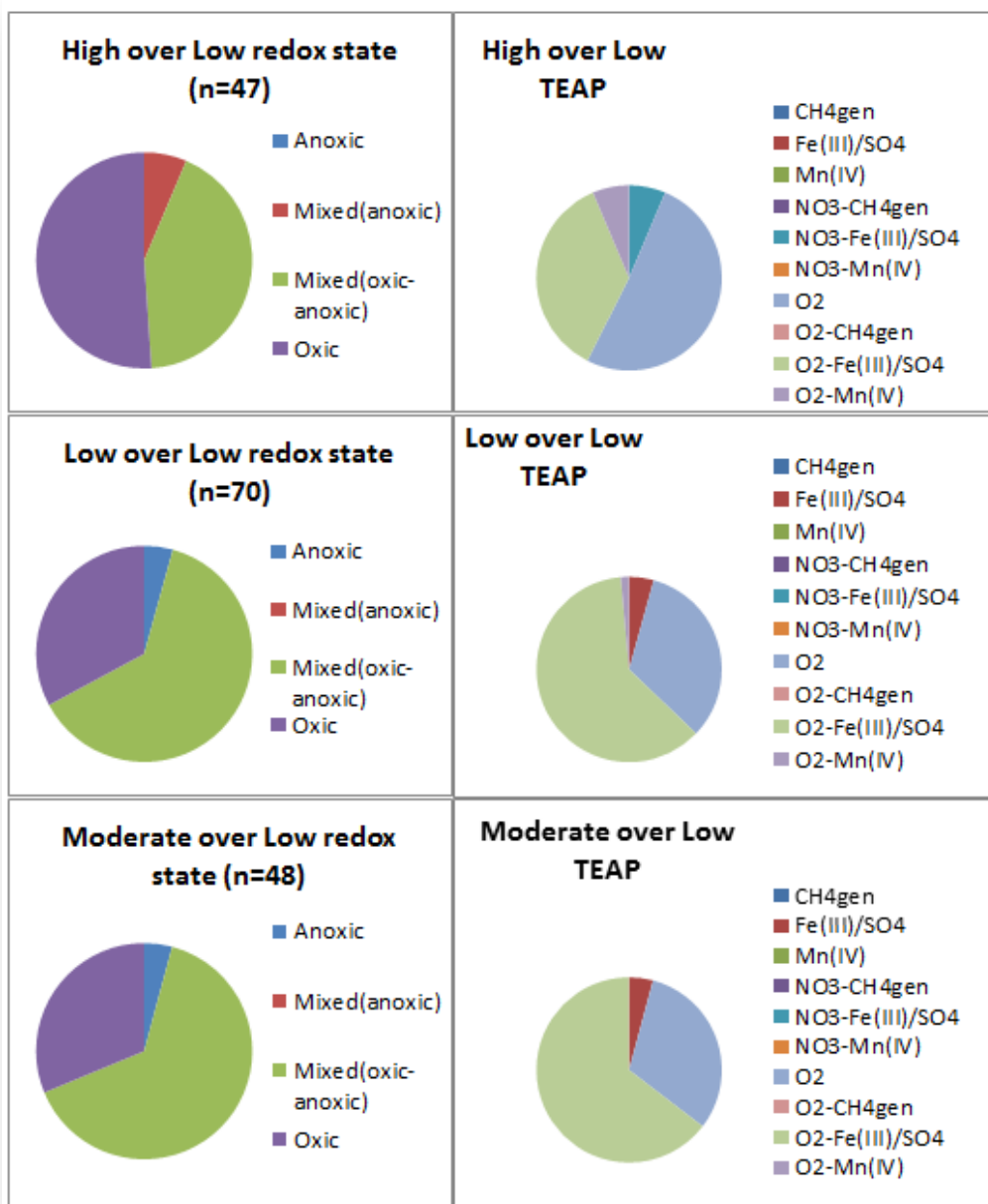


Figure 6-13: Redox state and TEAP of groundwater by dominant CRP category. General redox category and TEAP varies in a predictable manner with dominant CRP.

Summary

Multi-comparisons tests of the concentrations of redox sensitive species by CRP support the predictability of redox on the basis of CRP. The reasonable ability to predict surface water redox, despite limiting the assessment to the dominant CRP category within a capture zone is compelling. Irrespective of the domain, i.e., ground or surface water, CRP categories that were grouped together are associated with variance in soil reduction potential. Furthermore, these findings underline the importance of soil zone reduction when predicting redox processes in regional surface and groundwater.

Overall, we observed more variability in redox state and TEAP for groundwater associated with each CRP category than for surface waters. This may be linked to longer pathways and residence times of

groundwater than those of surface water but also the considerable uncertainty that is introduced by depth as a variable. However, relationships between redox conditions of groundwater and CRP are still clear and statistically significant, suggesting CRP is a reasonable predictor of groundwater redox conditions.

For both groundwater and surface water, Fe(II), Mn(II) and NO₃-N appear to be the best indicators for CRP. DO concentrations are variable and relationships to CRP are relatively poor. This can be linked to re-equilibration with atmospheric air and soil zone bypass. Similarly, SO₄ appears to be a relatively poor predictor of CRP, which is probably related to variable SO₄ inputs associated with different levels of land use intensity and SO₄ in rainout, specifically minor SO₄ loading in Alpine and Bedrock/Hill Country and high but variable SO₄ loading in areas of intensive land use, coastal precipitation and as noted above, hydrological factors¹¹.

Finally, the CRP categories with the highest and lowest reduction potential, i.e. HH and ALL, respectively, always occur independently - they are never grouped together irrespective of domain, groundwater or surface water, or redox sensitive species¹². As demonstrated below, these CRP categories may be viewed as end members in a redox continuum (i.e., ALL >>> HH) with much of the variance in redox analytes between these two end members, being associated with variance in soil zone reduction potential.

6.4.2.2 Multi-Comparisons Tests - Two Dominant CRP Categories

In the following, we assess the relationship between the two dominant CRP categories occurring within a capture zone and redox signatures of surface and groundwater. This assessment also allows us to study whether and to what extent differing proportions of CRP category influence freshwater redox processes.

Surface water

Multi-comparison tests of individual terminal electron acceptors and the two dominant CRPs identified one to five homogenous subsets of dominant CRP categories for surface water at the 95% confidence level (Table 6-11)¹³. Boxplots of redox sensitive species (Figure 8-14 and Figure 6-16) further support that differences identified in the multi-comparisons test are meaningful. Assessment of redox state by the two dominant CRP categories within a capture zone, also suggests redox state and TEAP vary in an anticipated manner (Figure 6-15).

¹¹ As mentioned previously, nitrogen input is spatially variable. Alpine and large areas of Bedrock/Hill Country have little to no anthropogenic N input. Extensively and intensive farmed areas also have variable N inputs or loading. Variable N input differs to that of oxygen, Mn(II) and Fe(II), which are controlled by atmospheric and mineral content and as such, are more uniform in space. It is therefore important to consider the redox setting in its entirety though assessing the suite of redox sensitive species – DO, NO₃-N, Mn(II), Fe(II) and SO₄ in conjunction with ancillary indicators of redox processes such as dissolved organic carbon (DOC) and ammonical nitrogen. Furthermore, whether one or more redox indicator dominates is heavily dependent upon the natural thresholds in the ecological succession of terminal electron acceptors by bacteria. Therefore, reliance on one metric or variable is not considered robust.

¹² We found the strongest and most meaningful relationships to CRP with DO and Mn(II), followed by NO₃-N and Fe(II). DOC, SO₄²⁻, redox state and TEAP show weaker relationships to CRP suggesting the best indicators for freshwater redox conditions in Southland are DO, Mn(II) and Fe(II).

¹³ Again, log transformed median data was used.

For surface waters, it appears that when similar CRP categories e.g. HL - LL vs. LL - HL occur in different proportions, that they are often not grouped together (specifically for Mn(II) and Fe(II)). This is especially true when there is a large contrast in CRP between the two dominant CRP categories (e.g. HL - LL). Furthermore, when contrasting capture zones that have the same CRP category but a different secondary or subordinate CRP category, e.g. HL - LL vs. HL - ML, or LL - HL vs. LL - ML, there is little grouping. This is also reflected in the hydrochemistry, specifically the concentrations of redox sensitive species. For example, although HL is the dominant CRP category for both HL - LL and HL - ML, the concentrations of redox sensitive species differs, i.e. DO is higher and Mn(II) and Fe(II) lower for HL - LL associated waters than for HL - ML associated water (Figure 6-14). Similarly, the number of oxic waters associated with HL - LL is higher than the ones associated with HL - ML (Figure 6-15). The latter patterns strongly support the mechanistic understanding we hold and indicates that CRP categories are able to predict redox signatures. Further, the variability in the data is reduced through the inclusion of the two dominant CRP categories of a surface water capture zone. Similar observations can be made for LL - HL and LL - ML.

Table 6-11: Homogeneous Subsets ‘groupings’ of dominant two CRP categories for regional surface water.

Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by DO	
Group 1	HL - LL, LL - HL, LL - ML, ML - HL, BHL - HL, BHL - LL, ALL - BHL, BHL - ML
Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by Mn(II)	
Group 1	LL - ML
Group 2	ML - HL
Group 3	BHL - ML, LL - HL
Group 4	HL - LL, BHL - HL
Group 5	BHL - LL, ALL - BHL
Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by Fe(II)	
Group 1	BHL - ML
Group 2	ML - HL
Group 3	LL - ML
Group 4	LL - HL, HL - LL
Group 5	BHL - HL, BHL - LL, ALL - BHL
Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by NO₃-N	
Group 1	ALL - BHL
Group 2	LL - HL, HL - LL
Group 3	LL - ML, ML - HL, BHL - HL, BHL - LL, BHL - ML
Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by SO₄²⁻	
Group 1	BHL - LL, ALL - BHL
Group 2	LL - ML, LL - HL, ML - HL
Group 3	HL - LL, BHL - HL, BHL - ML
Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by DOC	
Group 1	BHL - HL
Group 2	BHL - ML, HL - LL
Group 3	LL - HL, LL - ML, ML - HL, BHL - LL, ALL - BHL

In contrast to our previous findings, NO₃-N does not appear to be a good indicator for CRP categories, all two dominant CRP categories are grouped together, which is probably related to both variable N inputs associated with different levels of land use. In this assessment, for which hydrology is ignored, other redox species, in particular Mn(II) and Fe(II) appear better indicators of CRP than NO₃ as also demonstrated in the preceding sections. However, the more generalised metrics, redox

state and TEAP, still vary in an expected manner with CRP category, i.e. the number of oxic waters increases in association with oxidising CRP categories and vice versa for reducing CRP categories. As presented in Chapter 4 (Validation of the Conceptual model), the combination of hydrological factors with CRP proves a much better predictor of NO_3 , redox sensitive species, redox state and TEAP.

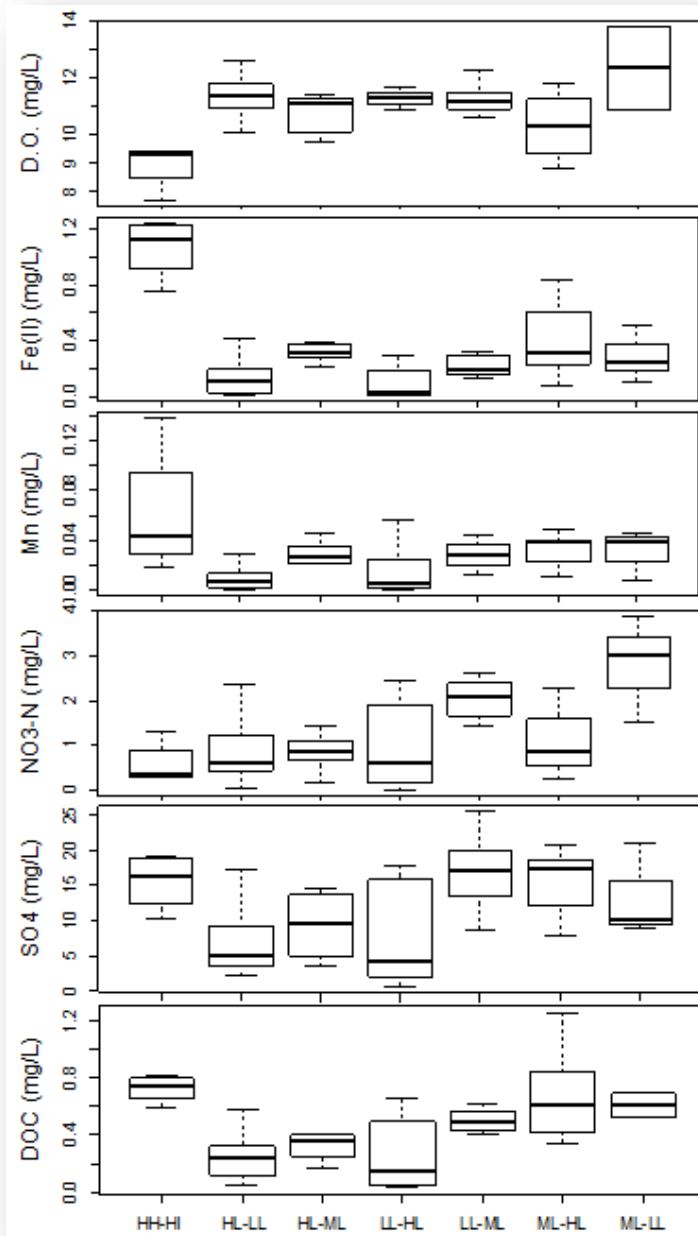


Figure 6-14: Box plots of redox sensitive species in surface water by two dominant CRP categories illustrating anticipated relationships between the concentration of redox sensitive species and CRP.

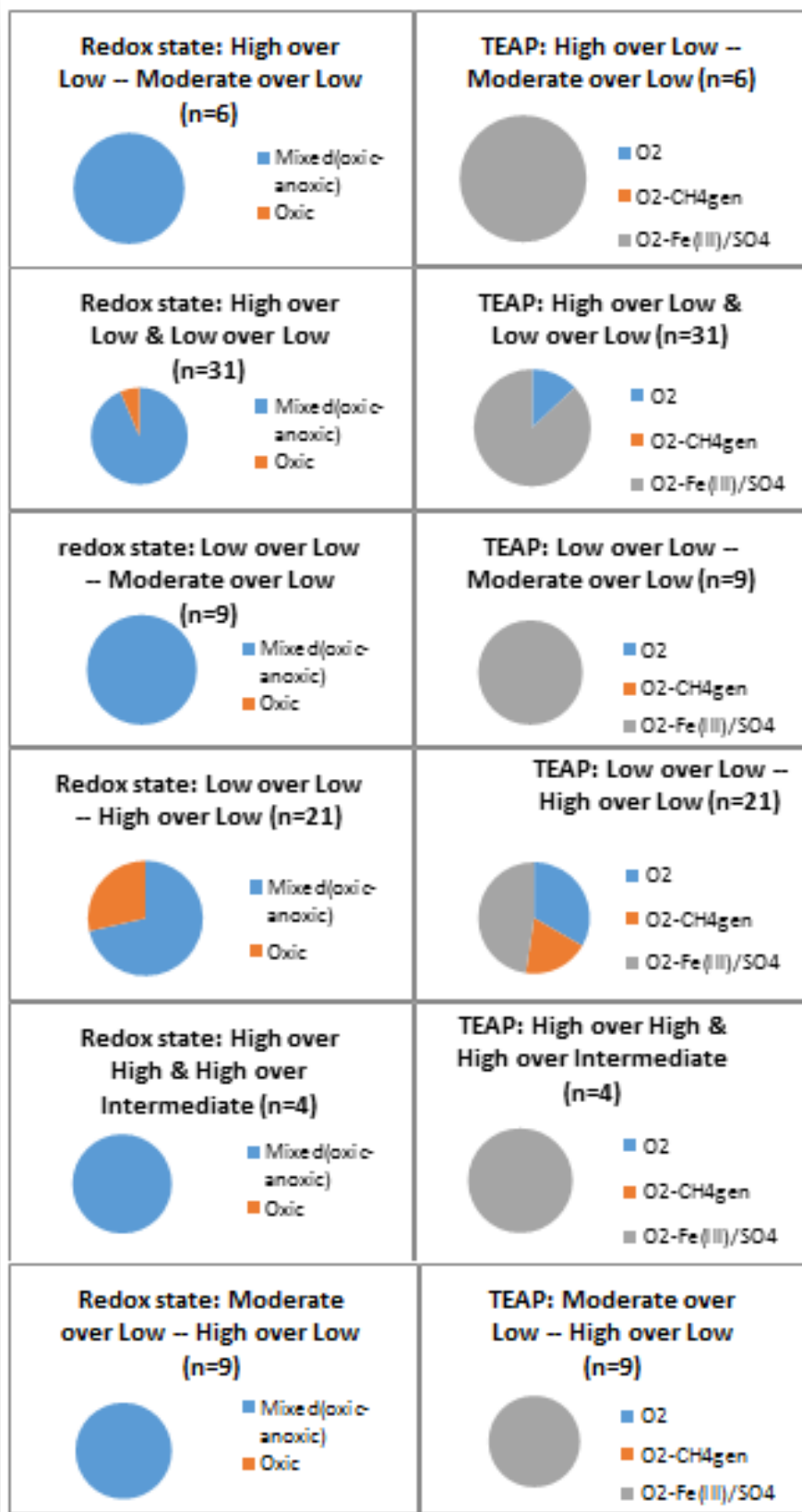


Figure 6-15: Redox state and TEAP by two dominant CRP categories for regional surface water.

Groundwater

Multi-comparison tests of individual terminal electron acceptors and the two dominant CRPs identified 1 to 3 homogenous subsets of dominant CRP categories for groundwater at the 95% confidence level (Table 6-11)¹⁴. Assessment of redox state by the two dominant CRP categories within a capture zone also suggests redox state and TEAP vary in an anticipated manner (Figure 6-15).

For groundwater, as opposed to surface water, data is limited and only allowed for assessment of 7 dominant 2 CRP combinations. For DO, NO₃-N, SO₄ and DOC all CRP combinations are grouped together, suggesting that these are poor predictors of 2 dominant CRPs. This can be related to limited data availability, poor definition of subsurface geology and therefore denitrification potential, and the use of simplified capture zones. However, Fe(II) and Mn(II) appear good indicators, as detailed in the following.

Table 6-12: Homogeneous Subsets ‘groupings’ of dominant two CRP categories for regional groundwater.

Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by DO	
Group 1	HL – LL, LL – HL, LL – ML, ML – HL, BHL-HL, BHL-LL, ALL-BHL, BHL-ML
Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by Mn(II)	
Group 1	LL – ML
Group 2	ML – HL
Group 3	BHL-ML, LL – HL
Group 4	HL – LL, BHL-HL
Group 5	BHL-LL, ALL-BHL
Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by Fe(II)	
Group 1	BHL-ML
Group 2	ML – HL
Group 3	LL – ML
Group 4	LL – HL, HL – LL
Group 5	BHL-HL, BHL-LL, ALL-BHL
Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by NO ₃ -N	
Group 1	ALL-BHL
Group 2	LL – HL, HL – LL
Group 3	LL – ML, ML – HL, BHL-HL, BHL-LL, BHL-ML
Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by SO ₄ ²⁻	
Group 1	BHL-LL, ALL-BHL
Group 2	LL – ML, LL – HL, ML – HL
Group 3	HL – LL, BHL-HL, , BHL-ML
Homogeneous Subsets ‘groupings’ of 2 dominant CRP categories by DOC	
Group 1	BHL-HL
Group 2	BHL-ML, HL – LL
Group 3	LL – HL, LL – ML, ML – HL, BHL-LL, ALL-BHL

As for surface waters, it appears that when similar CRP categories (specifically HL - LL vs. LL - HL) occur in different proportions, they are often not grouped together (specifically for Mn(II) and Fe(II)). Furthermore, when contrasting capture zones that have the same CRP category but a different

¹⁴ Again, log transformed median data was used.

secondary or subordinate CRP category (e.g. HL - LL vs. HL - HH, or LL - HL vs. LL - MH), there is minimal grouping for Mn(II) and Fe(II). This is also reflected in the hydrochemistry, specifically the concentrations of redox sensitive species.

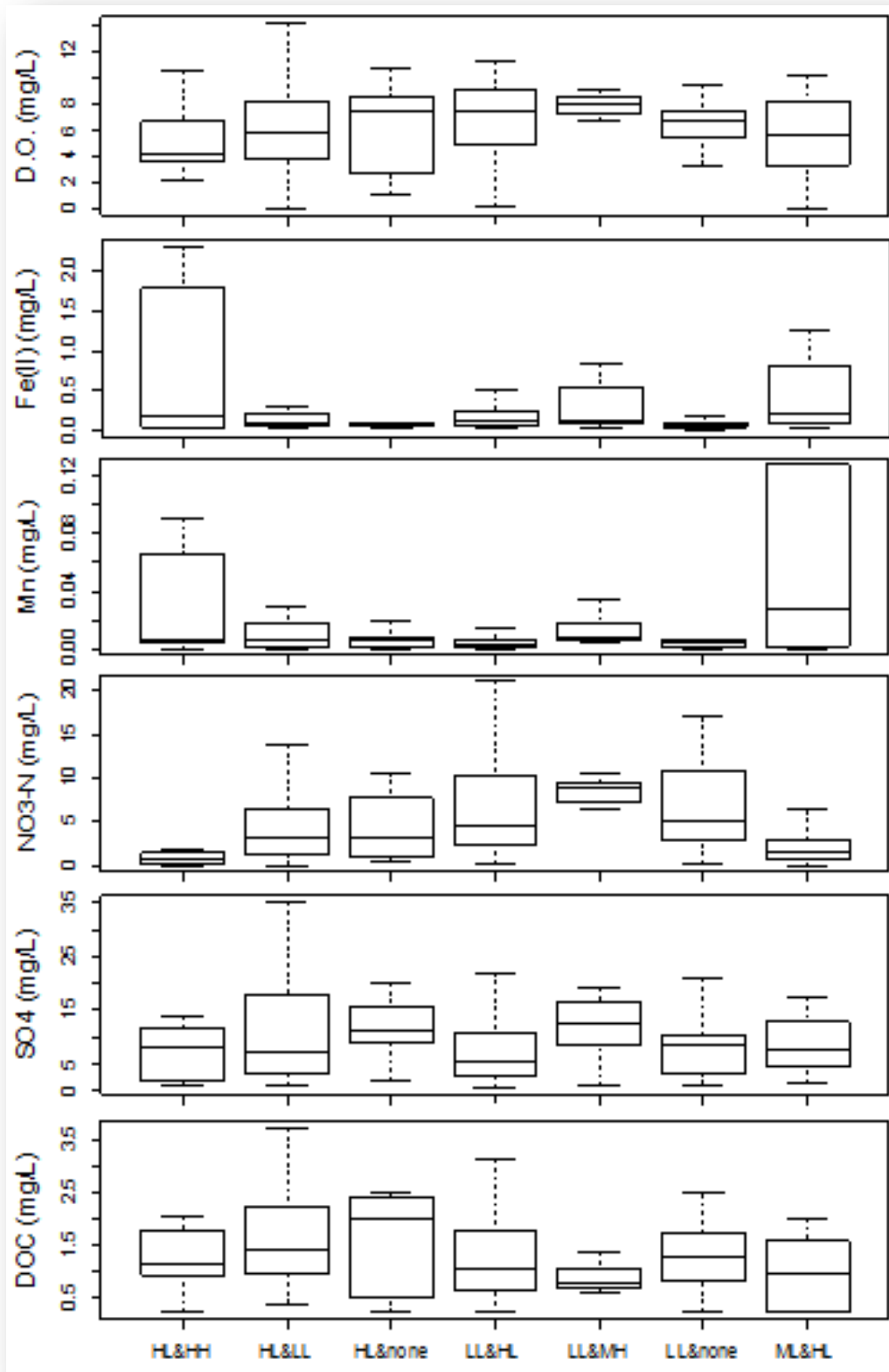


Figure 6-16: Box plots of redox sensitive species in groundwater by two dominant CRP categories illustrating anticipated relationships between the concentration of redox sensitive species and CRP.

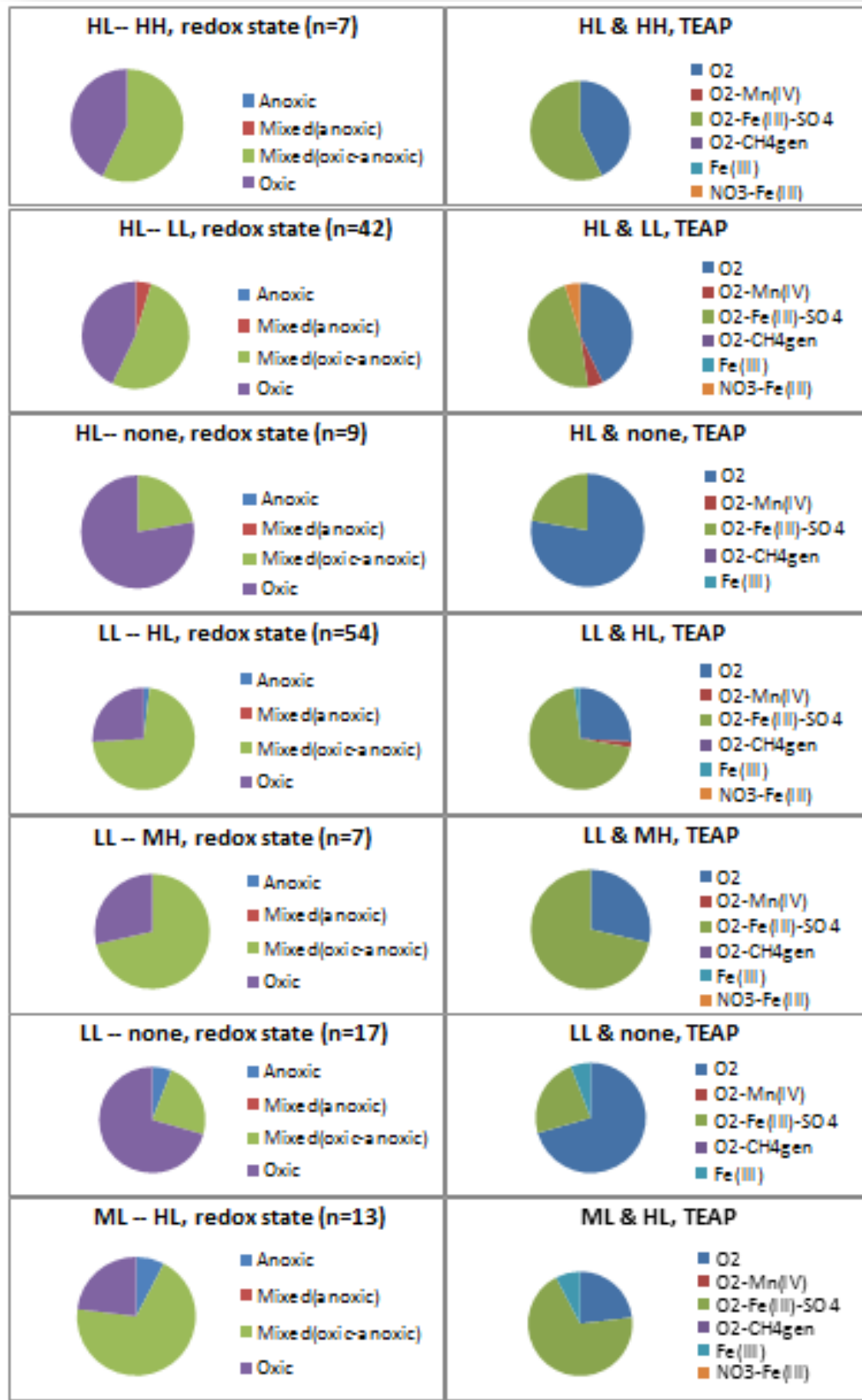


Figure 6-17: Redox state and TEAP by two dominant CRP categories for regional groundwater.

For example, although HL is the dominant CRP category for both HL - LL and HL - HH, the concentrations of redox sensitive species differs, i.e. DO is higher and Mn(II) and Fe(II) lower for HL - LL associated waters than for HL - HH associated water (Figure 6-16). Similarly, the number of oxic and mixed (oxic-anoxic) waters associated with HL - LL is higher than the ones associated with HL - HH (Figure 6-17). As for surface waters, the latter patterns strongly support the mechanistic understanding we hold.

Summary

Overall, the findings suggest that surface water redox conditions are affected by both the assemblage and the proportion of CRP categories within the capture zone, particularly if the CRP categories within the capture zone are very different e.g. a combination of highly oxidising and highly reducing soil and geology. Both the assemblage and proportion of CRP are therefore considered in Chapter 3 (Conceptual Model). Although, a clear relationship between CRP and redox conditions is demonstrated in this study it is enhanced in Chapter 4 (Conceptual Model Validation) due to the inclusion of hydrology, both river source and recharge mechanism, with the concentration of redox sensitive species (esp. NO_3 , Mn(II), Fe(II), SO_4^{2-} and DOC), redox state and TEAP).

The strong correlation of dominant and dominant 2 CRP categories within the catchment suggest that redox conditions of surface and groundwater can be estimated on the basis of CRP category assemblage within the capture zone. These findings suggest that ideally both the assemblage (i.e. types) and the proportions of all CRP categories within the capture zone need to be accounted for to better predict redox conditions in regional surface water. They also suggest that CRP categories should not be further simplified through consolidating further categories together because all information on CRP assemblage and proportion is required to predict redox conditions in regional surface and groundwater. This is also demonstrated in the conceptual model in Chapter 3.

TC6.5 Final CRP map

Overlay of the CRP map with a nitrate hotspot map¹⁵ of median and maximum nitrate concentrations in shallow groundwater (Figure 6-18) further supports the predictability of denitrification and reduction potential of Southland's soil and geology on the basis of mapping CRP. Specifically, all but one of the recognised groundwater nitrate hotspots are found in areas of LL CRP (e.g. Balfour, Edendale and Wendonside). The remaining hotspot occurs in the Central Plains area, where bypass of the reducing soil zone is an important feature in the high $\text{NO}_3\text{-N}$ concentrations. LL areas where nitrate hot spots do not occur include riparian areas, where groundwater receives significant amounts of low $\text{NO}_3\text{-N}$ inputs from alpine sourced rivers. This aspect is better resolved in a conceptual model through consideration of recharge mechanism. Overall, the findings are in line with the findings of Rissmann (2011), who showed that all of the 17 identified nitrate hotspot occurred within areas of low geological denitrification potential.

The established CRP map will be used as a key driver for prediction of water quality outcomes, in particular redox conditions of freshwater in the Southland region. It is observed that even stronger relationships are produced by including hydrology as a key driver of redox (see Chapter 3). Therefore

¹⁵ Interpolated using kriging in ArcGIS with aquifer management zone border as boundary (did not interpolate outside the boundary). Shallow groundwater included wells that tap into unconfined aquifers.

it is recommended that future work should consider the inclusion of bypass flow for groundwater. In addition, redox sensitive species should be included in all ground and surface water sampling. Further field measurements are required to measure and quantify denitrification rates in these settings.

TC6.6 Summary

In summary, the correlation of redox sensitive species and DOC supports the combination of soil and geological reduction potential as a good proxy for surface and groundwater denitrification or reduction potential at a regional scale. Most significantly, the fact that Mn(II) and Fe(II) and to some extent NO₃-N change in a predictable manner with CRP, further supports the use of this approach for predicting potential denitrification and accordingly TON accumulation risk to surface and ground water regionally. However, we note that when hydrological factors are included, the ability to predict the concentration of redox sensitive species, general redox state and TEAP is greatly improved (Conceptual Model, Chapter 3).

An important finding of this work is that the correlation of the same redox sensitive analytes with geology alone does not produce the same clear relationships in redox sensitive species and DOC (Rissmann, 2011). This is consistent with the observation that for the majority of Southland the soil zone is the dominant zone of reduction and for a much smaller area (ca. 10%) the underlying geology is important (Table 6-6). In fact, in terms of area, soil zone reduction as demonstrated by the data is inferred to be the main control over groundwater redox, general redox category and process across c. 52.8% of the total area mapped (Figure 6-7). If soil zone reduction is considered along with geological reduction (i.e. including the HH category) the area increases to 53.2%. Therefore, the assimilative capacity of the soil zone is the critical factor determining both ground and surface water quality outcomes across most of Southland.

The data also suggest it is possible to distinguish between soil zone and geological reduction by the CRP category of a given locality. Specifically, it was noted that the redox continuum represented by regional CRP categories is a good predictor of the site of reduction (i.e., soil, geology or both) as well as the strength of reduction for Southland's groundwaters.

This assessment determines more than just the vulnerability of groundwater to TON loading. It also indicates that there is clearly variability in the assimilative capacity of the soil zone to denitrify and that this variability is predictable and measurable. As such, lower yields of TON should be expected from reduced soils relative to oxidised soils, assuming sufficient mean residence time within the zone of reduction. This observation is especially relevant to the large area of artificially drained soils that discharge either directly to surface waters or via open drains, (76% of Southland's agricultural land; Pearson, 2015). To the authors knowledge there have been no specific assessments designed to assess how or if TON yields expressed through mole-pipe drainage vary between soils of differing reduction status, although there are a number of proxies (Overseer) or local studies (Monaghan and Smith, 2013; Cameron et al, 2014) that can be used to verify the relatively obvious hypothesis – “that soil zone TON yield, either to underlying aquifers or laterally via mole-pipe drainage, will vary according to the reduction capacity of the soil zone.” Clearly, in the instance of lateral soil zone drainage, especially that mediated by mole-pipe drainage, threshold relationships between soil reduction potential and drainage rate will be important. Slowing down the rate of soil water drainage is one way to increase assimilative capacity of the soil zone (Singh and Horne, 2014).

A key output of this chapter is the production of a regional CRP map based on the statistical assessment of homogenous, independent CRP categories (Figure 6-7), which in conjunction with other drivers, i.e., hydrology and biogeomorphic domain, can be used to predict denitrification or

reduction occurring in regional surface and groundwater. This assessment suggested that 1) CRP categories should not be further simplified, instead possibly consider bedrock 1 and 2 i.e. bedrock connected and not-connected to alpine areas, respectively as independent CRP categories and 2) consider assemblage and proportion of CDNPs for prediction of redox conditions and denitrification. Hydrology should also be considered to better predict redox conditions, which is demonstrated in Chapter 3. Specifically, the established CRP map is used in the Conceptual Model chapter in combination with the proportion of CRP assemblages and other driver maps (presented in preceding TCs) to predict regional freshwater chemistry.

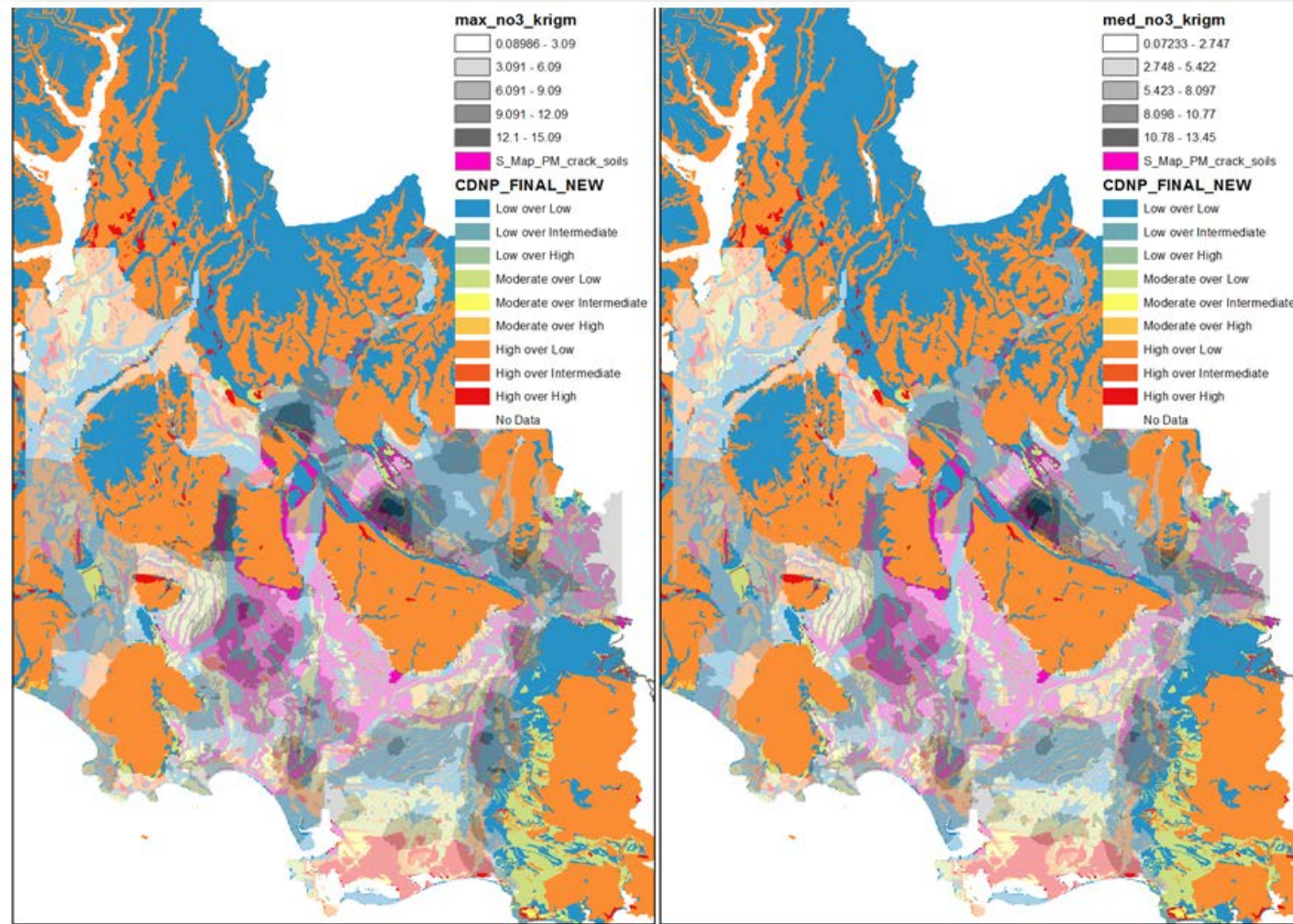


Figure 6-18: Maximum (UPPER) and median (LOWER) nitrate concentration overlaying the initial CRP map shown in Figure 6-7.