environment SOUTHLAND
Te Taiao Tonga

Regional Mapping of Groundwater Denitrification Potential and Aquifer Sensitivity

Technical Report

Clint Rissmann
Groundwater Scientist

November 2011

Publication No 2011-12

Contents

List of Figures and Table

1. Executive Summary

Groundwater is one of the Southland's region most important natural resources. It is used for domestic and stock drinking water, irrigation and community supply and is critical in sustaining stream flows, particularly during droughts and other low-flow periods (Wilson, 2010 - 2011). However, ongoing intensification of land use within the Southland region is driving the degradation of regional groundwater quality (Hughes, 2011). Any degradation in regional groundwater water quality threatens the utility of the groundwater resource and in particular the use of groundwater for human consumption and the water quality and ecological health of our rivers, lakes, estuaries and coastal marine environments.

This report synthesises regional geological data (geomorphology, hydrogeology and geochemistry) in an attempt to spatially model the natural capacity of regional aquifers to attenuate or remove nitrate through natural chemical reactions. The model is presented as a two dimensional map of aquifer denitrification potential, or by proxy aquifer sensitivity to nitrate accumulation, that provides an important spatial context for the management and understanding of regional groundwater quality. The spatial relationship between modelled aquifer sensitivity and measured nitrate concentrations demonstrates a strong spatial correlation supporting the generalised model of aquifer denitrification potential/sensitivity presented in this report.

The Southland region has a complex geological history. Consequently, the materials that comprise shallow groundwater aquifers exhibit a high degree of spatial variability (Figs. 1 and 2). However, the sensitivity of aquifers to nitrate accumulation shows less variability with approximately 85% of regional aquifers exhibiting a high to very high sensitivity to nitrate accumulation[1]. Regionally, the high proportion of sensitive aquifers reflects the predominance of alluvial (water deposited) sediments that contain little, if any, materials (organic carbon, iron pyrite or glauconite) that promote the removal of nitrate by bacterially mediated reactions.

Conversely, a much smaller percentage (~10%) of regional aquifers exhibit a high to very high ability to remove nitrate (i.e., a low to very low sensitivity to nitrate accumulation) that has infiltrated through the soil zone. Low sensitivity aquifers contain a high proportion of materials (organic carbon (peat), iron pyrite and/or glauconite) that favour the removal of nitrate by a bacterially mediated process known as denitrification. During denitrification, nitrate that infiltrates from the soil zone is converted to gaseous nitrogen (N_2) or nitrous oxides (N_xO) and ultimately escapes from the aquifer to the atmosphere. The remaining aquifers (~5%) exhibit an intermediate sensitivity to nitrate accumulation due to varying proportions of the above materials and variable denitrification potential.

Aquifers with a low or very low sensitivity to nitrate accumulation have a high or very high denitrification potential and actively attenuate nitrate concentrations infiltrating from the soil zone. These aquifers have a high capacity to remove leached nitrate and are

---

[1] This number does not include the contribution of major mountain ranges that host fractured rock aquifers. If these ranges were included the percentage of high to very high sensitive aquifers would increase to at least 95%.

unlikely to show elevated nitrate concentrations even if soil zone leaching rates are high. On the other hand, aquifers with a high to very high sensitivity to nitrate accumulation can accumulate nitrate to high levels. The latter can affect potability or contribute groundwater of high nitrate concentration to streams as base flow. In aquifers with intermediate sensitivity to nitrate accumulation, some fraction of the total volume of groundwater nitrate may undergo denitrification, and nitrate concentrations in discharging waters may be relatively low but may still exceed natural background levels (typically less than or equal to 1.0 mg/L for the Southland region; Rissmann et al., 2011).

Regionally, the Makarewa and Waihopai groundwater zones contain the greatest areas of low or very low sensitivity aquifers due to the prevalence of shallow lignite measures and large tracts of peat wetlands, respectively (Figs. 1 and 2). Nitrate entering these aquifer systems is removed via the process of denitrification. The lower half of the Waituna catchment is dominated by aquifers of low to very low sensitivity to nitrate accumulation (high denitrification potential) that may be of importance for the assessment of groundwater in the health of the Waituna Lagoon.

Coastal marine-deltaic (river delta) sediments of intermediate nitrate sensitivity occur as a thin margin around the majority of the southern coastline and likely play an important role in the removal of a proportion of groundwater nitrate before discharging offshore. However, rivers and streams convey nitrate rich waters across the surface of lowland coastal wetland and marine-deltaic aquifers limiting any potential nitrate removal. Historic (and ongoing) drainage of lowland wetlands has greatly enhanced bypass volumes and restricted the natural ability coastal aquifers to attenuate nitrate concentrations.

Those areas most susceptible to the development of nitrate "hot-spots" coincide with basins, river headwaters (where they debouch from gorges) and elevated terraces where thick deposits of gravel accumulate. Areas of greater gravel thickness and higher susceptibility to nitrate accumulation include the Waimea Plains, Five Rivers, Wendonside, Waiau, Te Anau, Whitestone, Edendale and Central Plains areas the more developed of which show elevated nitrate concentrations and the occurrence of nitrate "hot-spots"[2]. The spatial mapping process also identified the Waiau, Whitestone and Te Anau groundwater zones as being especially vulnerable to nitrate accumulation. The Waiau, Whitestone and Te Anau groundwater zones are considered as susceptible to nitrate accumulation as the Waimea Plains and Edendale groundwater zones given enough time and sufficient land use intensification.

A key finding of this report is that the vast majority of the Southland aquifers exhibit a high to very high sensitivity to nitrate accumulation. Although the sensitivity of the majority of Southland's aquifers to nitrate accumulation has been known for some time, this report provides an important spatial context by quantifying the extent, spatial relationships and composition of sensitive aquifers regionally. This observation highlights the obvious risk of the current level of land use activities and forecast intensification on regional groundwater quality.

---

[2] Nitrate hotspots are defined as areas (≥ 2 km^2) where more than one bore regularly exceeds the maximum acceptable value of 11.2 mg/L.

It is intended that the spatial model presented in this report will inform a number of council projects including:

- assessment of groundwater nutrient loading to Waituna Lagoon;
- limit setting for surface and groundwater systems under the National Policy Statement;
- development of land use management strategies for nitrate vulnerable aquifers;
- technical reporting on the role of redox status on groundwater quality; and
- development of regional groundwater quality zones.

2. Introduction

Statistically significant declining trends in ground and surface water quality throughout Southland and new national requirements for setting limits on nutrient inputs highlights the need for better nutrient management tools (Hughes, 2011; Environment Southland, 2011). However, many management tools designed to reduce nitrate inputs from nonpoint sources are often applied uniformly without consideration of differences in natural setting that may mitigate or exacerbate contamination problems (Powars and Krantz, 2002). For example, some hydrogeological settings may enhance the removal, or natural attenuation, of nitrate from shallow groundwater. Natural attenuation is the reduction in concentration of a contaminant by natural processes.

The natural attenuation of groundwater nitrate may occur by plant uptake, mixing and dilution with low-nitrate water, bacterial activity, or consumption in chemical oxidation-reduction reactions (known as "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 the nitrate (NO_3^-) are removed by chemical reduction to produce nitrogen gas (N_2), which is effectively non-reactive and commonly lost from an aquifer by degassing to the atmosphere (Fig. 3). Therefore, denitrification is a process by which leached nitrate may be partially or wholly removed from groundwater.

The accumulation of nitrate or its removal by denitrification is strongly dependent upon the materials that comprise an aquifer. In Southland, as with other regions, the type and spatial distribution of different aquifer materials (i.e. gravels, lignite measures, peats, fractured rock aquifers (including limestone), marine sediments) is highly variable. As such, nitrates may be removed through denitrification in one area but accumulate in another. Therefore, identifying and delineating aquifers that are susceptible to nitrate accumulation, or capable of attenuating nitrate inputs, is important for groundwater quality and nutrient management regionally.

2.1. Objectives

The purpose of this report is to assess and map the spatial variability in denitrification potential, and by proxy the relative sensitivity, of Southland's aquifers to nitrate accumulation. It is intended that this regional scale assessment will inform a number of council projects including:

- assessment of groundwater nutrient loading to Waituna Lagoon;
- limit setting for surface and groundwater systems;
- development of land use management strategies for nitrate vulnerable aquifers;
- technical reporting on the role of redox status on groundwater quality; and
- the development of regional groundwater quality zones.

2.2. Location and Composition of Primary Aquifers

2.2.1 General Location

The Southland plains extend from the Waiau River in the west to the Mataura River which forms the border with Otago to the east. It can be divided into three broad areas - the lowland eastern and central Southland plains, the northern Southland plains (Waimea Plains) and the lower Waiau plain to the west near the Waiau River (Fig. 1).

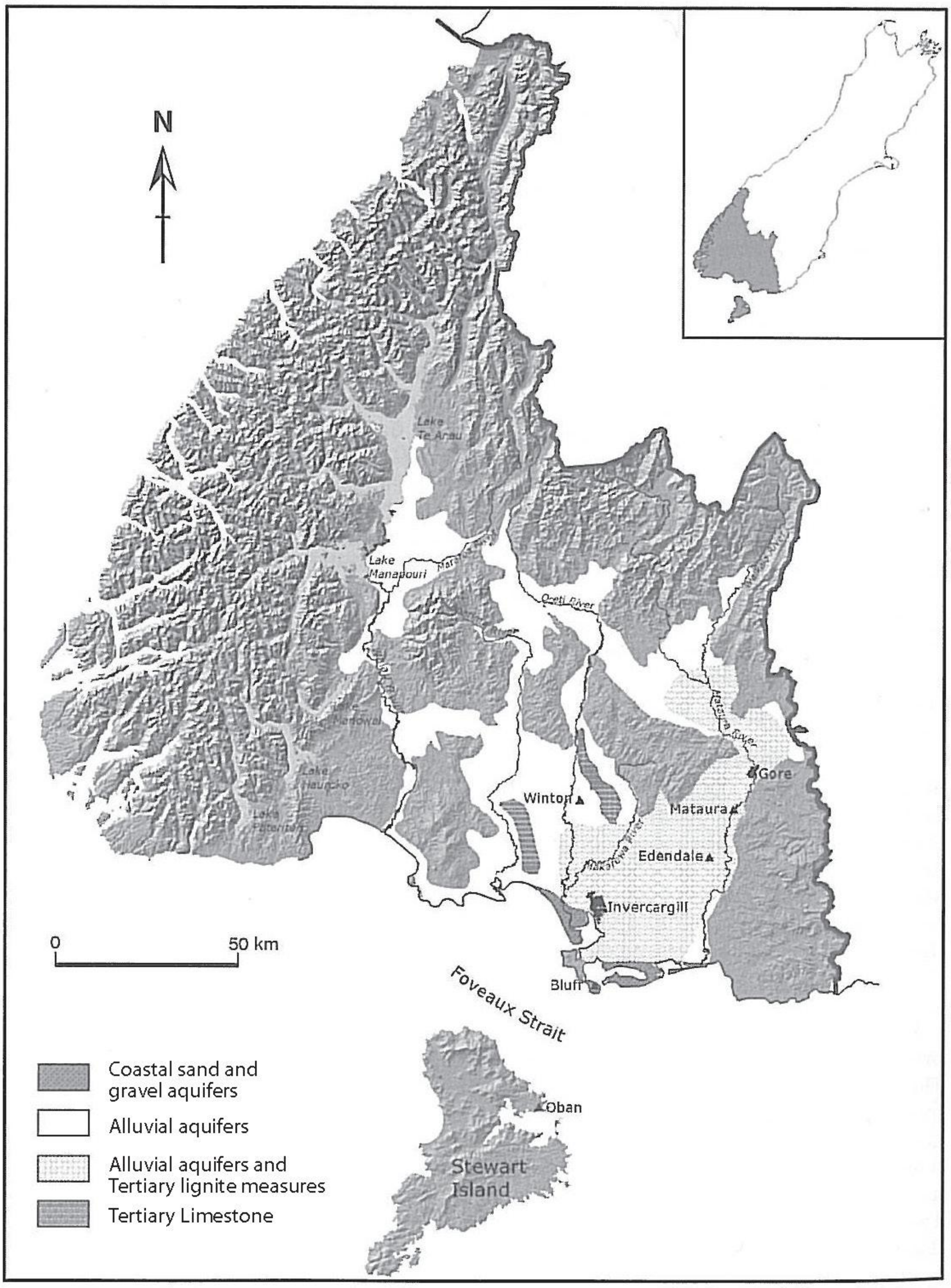


Figure 1: Location and simplified regional geology of the Southland region, including major rivers (Hughes, 2001).

The Southland and Waimea plains are separated by the uplands of the Hokonui Hills, which lie to the west of Gore. The Southland plain lies to the north of the city of Invercargill, and is formed by several large rivers, the Aparima, the Oreti and the Makarewa. They stretch inland for over 45 km from the coast of the Foveaux Strait, and cover an area of close to 1,500 km^2.

To the northeast of Invercargill, the Waimea plains of the Mataura River and its tributary the Waimea River stretch inland as far as the town of Gore. At their southern extreme they become the Awarua plain, a large area of marshy land which stretches from near Bluff to the foot of the Catlins in the far east. Between them, the lowlands around the Awarua plain and Mataura River cover a further 2,000 km^2.

To the west lies the lower Waiau plain, which is situated around the mouth of the Waiau River. This smaller region is wedged between the Longwood Range to the east and Fiordland to the west.

2.2.2 Composition of Primary Aquifers

The Southland region lies between the Fordland massif and the Campbell Plateau, while the Alpine Fault runs to the northwest. Southland is dominated by actively rising mountain ranges (typically 1,500–1,800 m), especially around its western and northern margins (Figs. 1 and 2). The Southland mountains are constructed of uplifted blocks of Paleozoic and Mesozoic low-grade sedimentary and igneous rocks, including the Dun Mountain Ophiolite Belt.

The younger geological sequences (Tertiary and Quaternary aged) form the dominant aquifers of the region. The materials these aquifers are comprised of provide an important context for assessing the sensitivity of aquifers to nitrate accumulation and are therefore summarised below. A more detailed description of the regional geology and aquifer hydrogeology is provided by Turnball and Allibone, (2003) and Wilson, (2010-2011).

The geomorphic setting of the Southland lowlands is dramatic reflecting multiple outwash deposits from separate ice advances and interactions between fluctuating river courses (Fitzharris et al., 1992; Turnball and Allibone, 2003; McCraw et al., 2007). Glacial outwash gravels from the major glaciers of Fiordland and Wakatipu spread out as a great series of overlapping alluvial aprons. Different suites of terraces have been broadly described over the Southland lowlands, the Waiau and Monowai Valleys (Fitzharris et al., 1992).

Suites of outwash terraces appear to be related to climatic deterioration and glacial advance in the mountains, with meltwater redistributing material into the lowland depressions (basins and lowlands); changes in climate and ice mass brought changes in river discharge and bed load (Fitzharris et al., 1992). The alteration in hydrological regime led to incision of the lowlands and formation of long terraces (e.g. Edendale Terrace). Older, high fan and terrace surfaces possess more local relief because of faulting and development of drainage patterns (Fitzharris et al., 1992). Lower, younger surfaces become progressively less dissected towards the coast. Downstream, the outwash aprons graded to the existing coast, which would have been beyond the present-day Foveaux Strait during cold periods (Fitzharris et al., 1992; McCraw et al., 2007).

Alluvial gravel aquifers tend to be organic carbon poor, containing little, if any, residual organic matter (decomposed plant materials) (Krantz and Powars, 2002). This is especially true for older highly weathered gravel aquifers.

Across northern Southland, the Waimea plains, surficial aquifers are formed in thick (greater than 70 m) gravel deposits that extend into the Five Rivers, upper Oreti and Waikaia Valleys (Figs. 1 and 2; Fitzharris et al., 1997; Turnball and Allibone, 2003). Here the alluvial gravel deposits are comprised of chemically inert (poorly-reactive), organic matter poor, quartz-greywacke gravels in a highly weather matrix of sand and clay. Due to low matrix permeability, these gravel deposits form relatively low-yielding aquifers (Hughes, 2001). Aquifer permeability increases in the lower terraces and recent floodplain deposits, reflecting the greater degree of reworking of these materials (e.g. the Edendale Terrace, adjacent to the Mataura River) (Hughes, 2001).

The lowland aquifers of eastern and central Southland are remnants of the original Quaternary gravel outwash surface, which have been locally dissected by first and second-order streams to form a highly weathered and gently undulating topography (Fitzharris et al., 1992). Here the aquifers are comprised of relatively thin (less than 20 metres) chemically inert deposits of poorly sorted, weathered gravels overlying Tertiary lignite, mudstone and limestone sediments.

The terrestrial Gore Lignite Measures were laid down during the Tertiary period (65 million to 2.6 million years ago). The Gore Lignite Measures are especially thick within the Mataura Valley, outcrop close to the surface in the north-western sector of the Makarewa groundwater zone, and extent beneath the gravels and peat wetlands of the southern Waihopai groundwater zone (Figs. 1 and 2). Other thick outcrops occur in the Chatton and Otikerama areas of north-eastern Southland. The Gore Lignite Measures are of low rank and consequently are comprised of abundant oxidisable carbon (formerly peat) and inclusions of iron pyrite (FeS_2), both of which are important materials when considering the role of aquifer materials in nitrate accumulation.

Deposits of limestone flank many of the mountain blocks about the Southland lowlands and form isolated hills and shallow fractured rock aquifers within the central plains – for example, near Browns and at Limehills (Fig. 1). Due to their marine origin, these limestone contain variable quantities of glauconitic iron clays, which are important when considering the role of aquifer materials in nitrate accumulation.

To the west, the Waiau River catchment covers a large portion of western Southland (Fig. 1). Significant aquifers are developed in the thick alluvial (greater than 30 m) gravel sequences filling the Manapouri and Te Anau basins. In the lower Waiau River, an unconfined alluvial aquifer overlies thick deposits of tertiary mudstone and siltstone (Hughes, 2001).

Along the southern coast, shallow aquifers of mixed marine-terrestrial sediments reflect the complex interaction between fluctuating sea levels, changing hydrological regime, sediment supply, and vegetation which accompanied the climatic changes of the Quaternary (Fitzharris et al., 1992). Coastal marine sediments commonly contain glauconite, iron pyrite and abundant oxidisable organic carbon.

Reworking of unconfined lowland gravel aquifers by the Mataura, Oreti, and Makarewa rivers has resulted in the exposure and intercalation of lignite measures within the thin unconfined gravel aquifers. Similarly, river channel migration and reworking of alluvial gravels favoured development of wetland deposits (peat swamps) within floodplain and overbank areas. South and southeast of Invercargill city the actively forming peat wetlands of the Awarua plains host shallow groundwater within massive fibrous peat deposits (Figs. 1 and 2). Numerous small pockets of peat wetlands occur throughout the Southland area and form important aquifers containing abundant organic carbon.

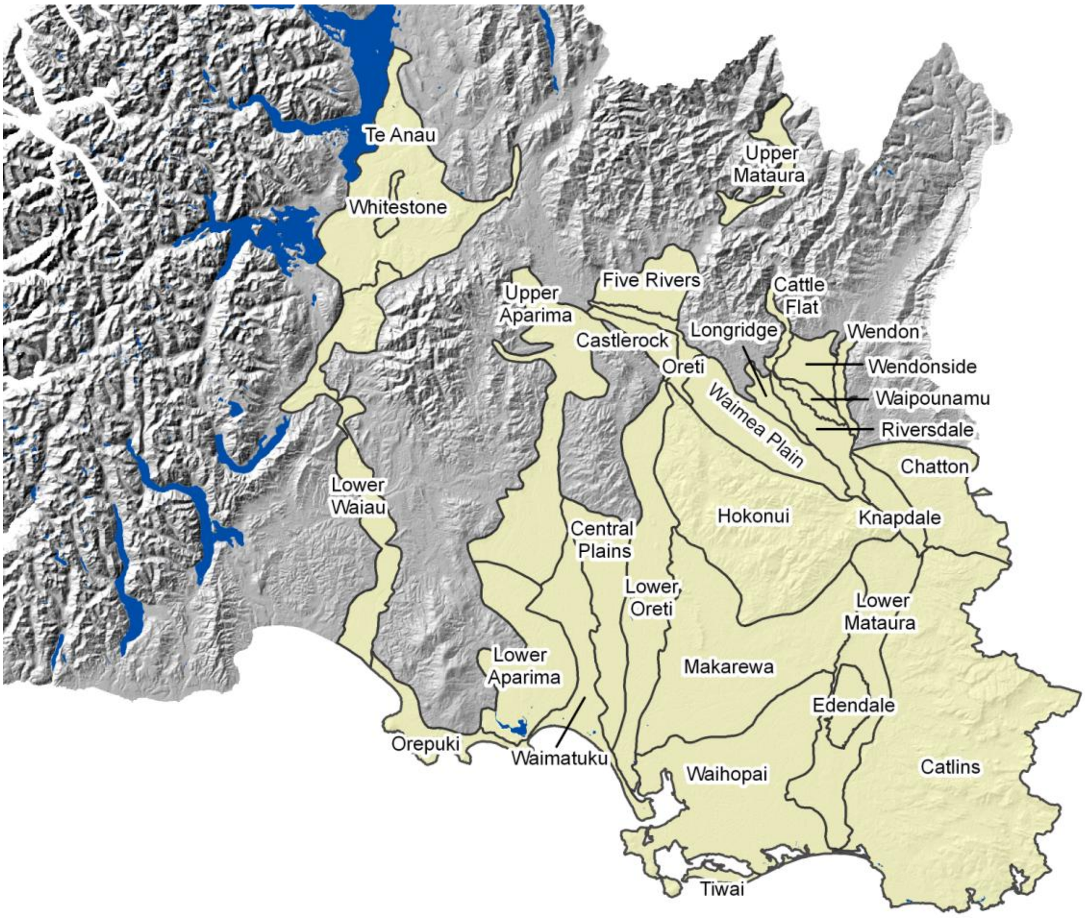


Figure 2: Location of regional groundwater zones (Regional Water Plan for Southland, 2010).

3. Redox Chemistry of Groundwater

3.1 Background

The amount of oxygen dissolved in groundwater is very important to the overall water quality of a given aquifer or groundwater zone. For this reason, scientists classify groundwater according to oxygen status or more correctly "redox status" (reduction-oxidation status). A redox reaction is defined by the transfer of electrons from one chemical species to another. Therefore, for a redox reaction to proceed there must be an electron donor and an electron acceptor. The most common electron donor in groundwater systems is dissolved and particulate organic carbon (organic matter from plant material and low rank coal measures (i.e. lignite and brown coal)) although in some instances minerals such as pyrite (FeS_2) and/or glauconite (iron rich clays) may act as electron donors. The most common electron acceptors include dissolved oxygen (O_2), nitrate (NO_3^-), manganese (Mn^{4+}) and ferric iron (Fe^{3+}), although in some extreme settings sulphate (SO_4^{2-}) and carbon dioxide (CO_2) may predominate (Fig. 3).

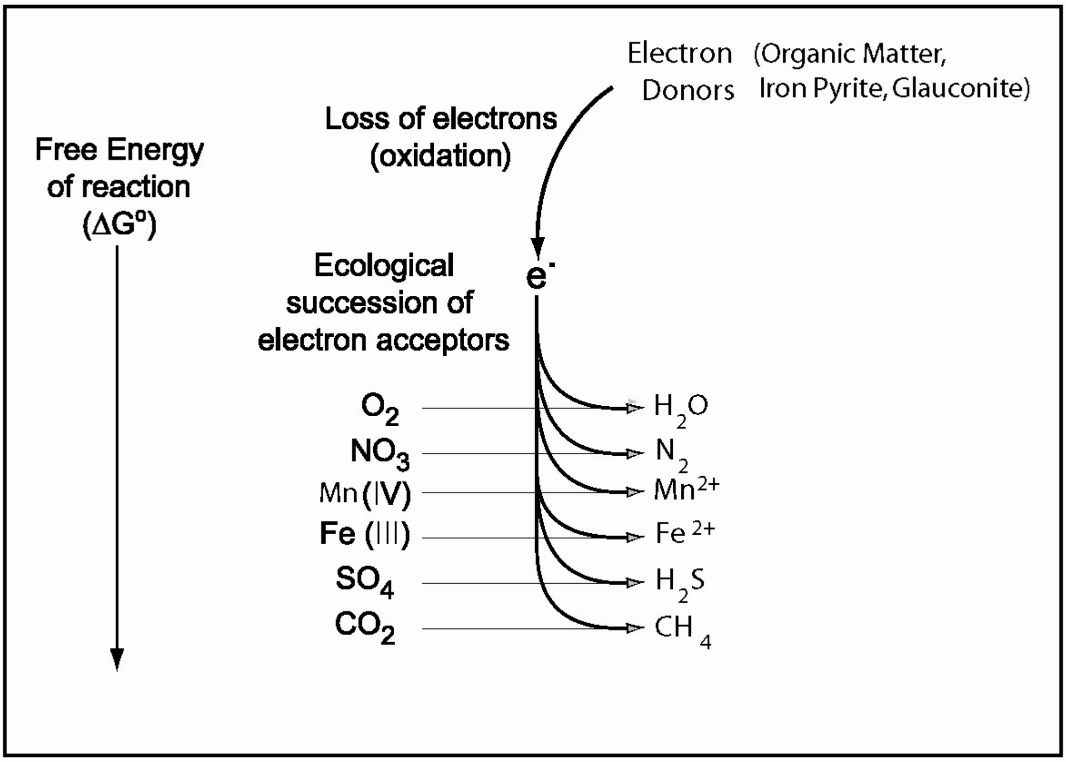


Figure 3: Ecological succession of electron-accepting processes and sequential production of final products in groundwater. ***A decrease in free energy available to microbes occurs as each successive electron acceptor is consumed. Typically organic matter (organic carbon) is by far the most common electron donor in groundwater but iron pyrite and glauconite may be locally significant (modified from McMahon and Chappelle, 2008)***

In groundwater, redox reactions are largely driven (catalysed) by bacteria, which gain energy by facilitating the transfer of electrons from organic matter to an electron acceptor. 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.

Because micro-organism gain energy by catalysing the transfer of electrons from donor (almost always organic matter) to an electron acceptor they tend to favour the acceptor that supplies them with the most amount of energy (Fig. 3). 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 groundwater can be isolated from the atmosphere oxygen tends to be consumed as groundwater moves through an aquifer. Once oxygen has been consumed bacteria move onto the next most energetically favourable electron acceptor, nitrate (NO_3^-), followed by manganese (Mn^{4+}), ferric iron (Fe^{3+}), sulfate (SO_4^{2-}) and eventually carbon dioxide (CO_2). This order of preferential electron acceptor utilisation - $O_2 > NO_3 > Mn > Fe > SO_4 > CO_2$ – is referred to as the ecological succession of terminal electron-accepting processes (Fig. 3).

Therefore, once oxygen has been depleted from groundwater the decay of organic matter continues through a succession of reactions that represent a progressively lower tendency of the groundwater to remove electrons from organic matter (Fig. 3). All electron acceptors (oxidising agents) are themselves reduced when they gain electrons. Therefore, during the ecological succession of terminal electron accepting reactions groundwater becomes 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 3. The rate of progression through each of the terminal electron accepting reactions is dependent on a number of factors including the material makeup of an aquifer, aquifer sediment size and groundwater temperature.

3.2 The Importance of Groundwater Redox State on Nitrate Concentration

If an energetically more favourable electron acceptor is introduced to a chemically reducing groundwater, bacteria will quickly switch to using this compound to breakdown organic matter. An important example is the leaching of nitrate, a relatively high energy electron acceptor, into reduced groundwater. In these circumstances, microbes will quickly utilise the introduced nitrate converting it to nitrogen gas or gaseous nitrous oxides. Nitrogen gas or nitrous oxides are poorly soluble in water and will tend to migrate as bubbles towards the atmosphere resulting in a net loss of nitrogen from the groundwater. This process, called denitrification, effectively removes nitrate from groundwater and may prevent the accumulation of nitrate and the degradation of water quality. However, if the groundwater is not reducing (i.e. containing abundant oxygen) nitrate will accumulate.

Groundwater dissolved oxygen concentrations typically vary between 0–10 mg/L. Groundwater with dissolved oxygen concentrations of 7-10 mg/L is said to be fully saturated and strongly oxidised whereas those with 0 mg/L dissolved oxygen are fully reduced. The accumulation of nitrate to high levels necessitates the presence of dissolved oxygen at concentrations in excess of 2 mg/L and it is only when dissolved oxygen falls below this threshold that nitrate is removed via denitrification.

3.3 Controls over the Redox Status of Groundwater

Understanding the redox status of a shallow groundwater aquifer is critical to issues of groundwater quality. In particular, the redox status determines such factors as:

- whether nitrate will accumulate or be attenuated by denitrification;
- the solubility of toxic metals such as arsenic;
- the presence of nuisance chemicals that degrade water quality such as dissolved iron (Fe^{3+}), manganese (Mn^{4+}) and hydrogen sulphide (H_2S) with its distinctive rotten-egg smell.

The controls over the redox status of groundwater are determined by the materials that comprise an aquifer, the relative rates of introduction of oxidants (i.e. oxygen and nitrate) and the consumption of these oxidants by bacterially catalysed decomposition of organic matter. The most important variables governing the redox status of groundwater include (Drever, 2002; McMahon and Chappelle, 2008):

1. *Distribution and reactivity of organic matter and other potential reductants in the aquifer*

   Aquifers vary greatly in the amount of organic matter present, and more importantly, the reactivity of that organic matter. Organic material locked up in sedimentary rocks (mud-, silt- and sandstone etc.) tends to be both poorly available and indigestible to microbes as a food source. Conversely, peats and weakly metamorphosed coal measures (lignite and brown coal) along with marine and estuarine sediments have an abundance of freely available and readily oxidisable organic matter. 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. Aquifers with an abundant supply of electron donators tend to rapidly consume oxygen and progress quickly through the ecological succession of terminal electron accepting species (Fig. 3) (occasionally, electron donors other than organic matter play an important role as electron donors and include iron pyrite and glauconite (an iron clay)).

2. *Distribution of inorganic terminal electron acceptors in an aquifer*

   The mass of the inorganic terminal electron acceptors, specifically the oxides of iron and manganese, within groundwater aquifers is often large. Consequently, these oxides provide a large reservoir of oxidising materials. Due to the large mass of manganese and iron oxides, often groundwater does not evolve beyond sulfate or even methane reducing conditions.

3. *Oxygen content of recharge water*

   Recharge water may enter an aquifer through fractures in bare rock, or it may percolate through a soil rich in organic matter. In the first case, the recharge water will be high in oxygen so microbes within the groundwater 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 infiltrating to the aquifer. In this instance, the infiltrating water will be reducing before reaching the groundwater zone and bring with it a low capacity to oxidise organic matter.

4. *Circulation rate of groundwater*

   Because the bacterial catalysis of organic matter is typically slow, the redox status of a particular groundwater system depends very much on the residence time of the water in the aquifer. The residence time depends on both the velocity of the water and the "length" of the aquifer system from recharge to discharge points. In general, the longer the residence time the more advanced groundwater is along the ecological succession of terminal electron accepting processes.

4. Aquifer Denitrification Potential or Sensitivity to Nitrate Accumulation

The removal or accumulation of nitrate within groundwater is determined by the redox status. Put simply, groundwater with high dissolved oxygen concentrations (>2 mg/L) receiving nitrate rich leachate will favour the accumulation of nitrate to high levels. Whereas groundwater with low dissolved oxygen concentrations (<2 mg/L) will tend to consume nitrate and remove it from the aquifer. One of the most significant controls over whether nitrate will accumulate or be removed from groundwater via denitrification is the composition of aquifer materials.

4.1 Role of Aquifer Materials in Denitrification

Aquifers containing high concentrations of reducing materials (organic carbon, pyrite, and glauconite) are more likely to contain low oxygen groundwater and therefore convert infiltrating nitrate to gaseous nitrogen or nitrous oxide, resulting in a net loss of nitrate from the aquifer. Such aquifers are said to have a high denitrification potential and consequently are less likely to display elevated nitrate concentrations.

In contrast, alluvial (water deposited sediments) gravels, sands and silt aquifers typically contain little or no organic carbon and are comprised of relatively inert lithologies (rock types) that do not react with nitrate. The lack of reducing species in these aquifers results in little or no denitrification allowing nitrate leached from the soil zone to accumulate within the aquifer. Aquifers comprised of materials of low denitrification potential are the most sensitive/susceptible to nitrate contamination. Similarly, most consolidated sedimentary, metamorphic and igneous rocks contain very low organic carbon concentrations and/or contain carbon that is recalcitrant (i.e. not able to be metabolised by microbes) or inaccessibly locked up within the rock matrix. Accordingly, fractured rock aquifers typically have a low denitrification potential (McMahon and Chappelle, 2008).

The relative thickness of aquifer materials also influences the denitrification potential of an aquifer. Commonly, groundwater becomes more reducing (i.e. greater denitrification potential) with increasing proximity to an aquitard or aquifer of high denitrification potential (McMahon, 2002; McMahon and Chappelle, 2008). Therefore, the thickness of low denitrification potential materials, such as alluvial gravels, overlying materials of high denitrification potential (i.e. lignite measures) play an important role in the denitrification potential of a shallow aquifer. For example, groundwater hosted by a thick layer of alluvial gravels is more likely to show elevated nitrate concentrations than an equivalent layer of thinner gravels also overlying the same high denitrification potential aquifer. The so called “proximity effect” of the sub-unit layer plays an important role in the denitrification potential of shallow aquifers (McMahon, 2002).

4.2 Assigning Denitrification Potential to Southland Aquifers

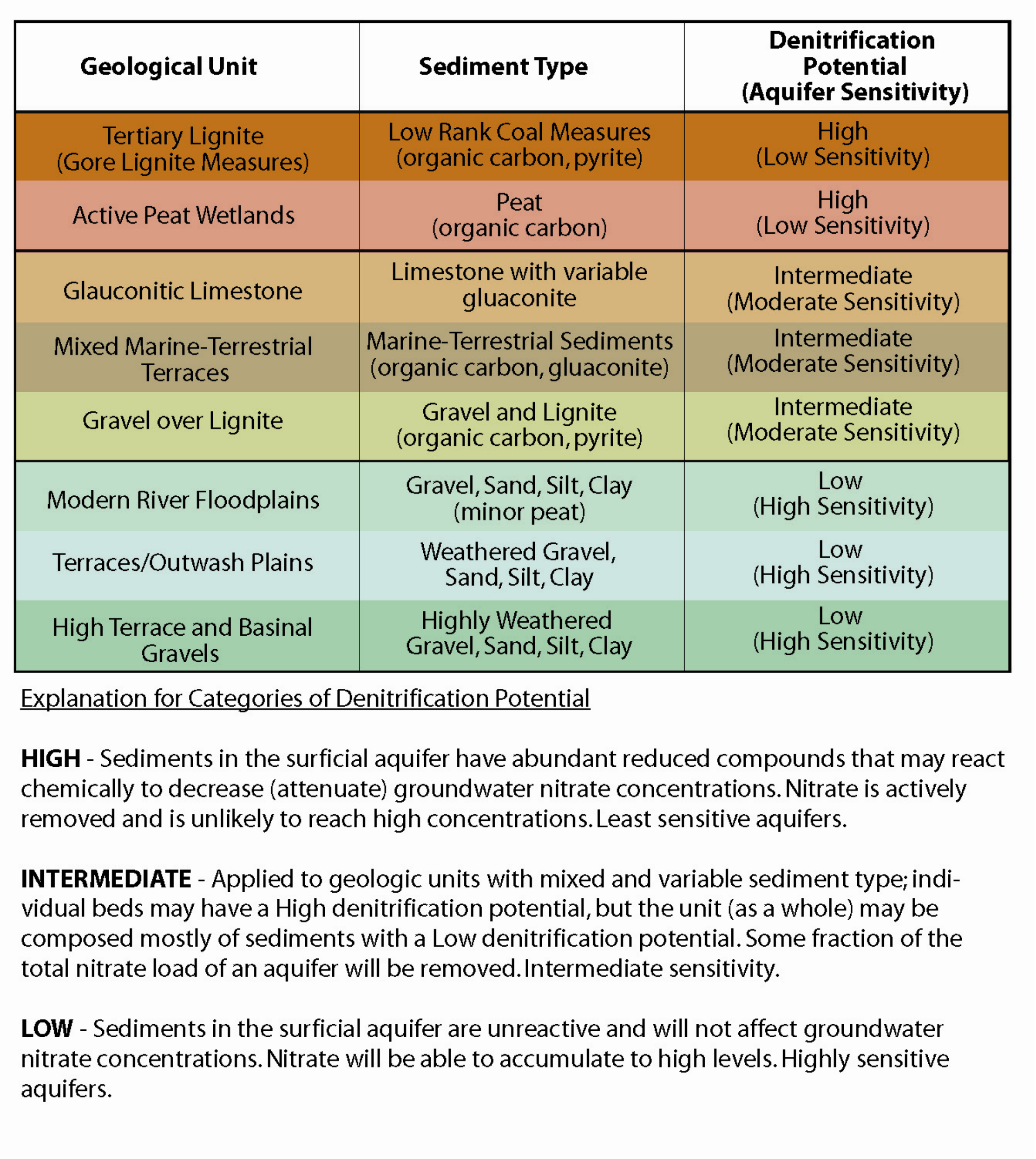
In this report we synthesise the geomorphology (sediment type, thickness, texture and depositional environment), lithology and chemical composition of the geologic units that comprise the shallow aquifer units of Southland using the digitised QMAP (map scale 1:250,000) series of geological maps generated for New Zealand (GNS Science, 1996–2003). The three QMAP areas used in this study include the Murihiku, Wakatipu, and Dunedin tiles. Each of these map tiles are built on existing geological data sources (several hundred sources for the regional map layers) and substantial fieldwork where geological data was lacking.

The three QMAP tiles were imported into the ESRI ArcGIS software suite. Each of the 1,000 or so surface and shallow subsurface units were assessed in terms of the presence of reduced chemical species (oxidisable organic carbon, iron sulfides and glauconite minerals) thereby translating the surficial geology into a map of the potential for denitrification in Southland's shallow aquifers. Assignment of the denitrification potential to individual units was guided by knowledge of sediment, rock and groundwater biogeochemistry and the geomorphology of fluvial and marine sediments. The methods of Krantz and Powars, (2002) provided important guidance on assignment of denitrification potential. Krantz and Powars, (2002) undertook similar work assessing the denitrification potential of shallow aquifers on groundwater nitrate for the coastal plains of Southern Maryland, USA.

Each QMAP tile provides a "main rock" and an underlying or "sub-rock" unit (referred to as surficial aquifer and sub-aquifer units, respectively). The denitrification potential of the sub aquifer was also assessed because such units play an important role, when in direct contact, in the denitrification potential of overlying surficial aquifers (McMahon, 2002). Three levels of denitrification potential were assigned to each of the surficial and sub-aquifer units – **high**, **intermediate** and **low** (Table 1).

For young sedimentary deposits that comprise the bulk of Southland aquifers the geomorphology (sediment type, texture and depositional environment) was also considered.

Table 1: Denitrification Potential of Southland Aquifers



Geological Unit	Sediment Type	Denitrification Potential (Aquifer Sensitivity)
Tertiary Lignite (Gore Lignite Measures)	Low Rank Coal Measures (organic carbon, pyrite)	High (Low Sensitivity)
Active Peat Wetlands	Peat (organic carbon)	High (Low Sensitivity)
Glauconitic Limestone	Limestone with variable gluaconite	Intermediate (Moderate Sensitivity)
Mixed Marine-Terrestrial Terraces	Marine-Terrestrial Sediments (organic carbon, gluaconite)	Intermediate (Moderate Sensitivity)
Gravel over Lignite	Gravel and Lignite (organic carbon, pyrite)	Intermediate (Moderate Sensitivity)
Modern River Floodplains	Gravel, Sand, Silt, Clay (minor peat)	Low (High Sensitivity)
Terraces/Outwash Plains	Weathered Gravel, Sand, Silt, Clay	Low (High Sensitivity)
High Terrace and Basinal Gravels	Highly Weathered Gravel, Sand, Silt, Clay	Low (High Sensitivity)

Explanation for Categories of Denitrification Potential

HIGH - Sediments in the surficial aquifer have abundant reduced compounds that may react chemically to decrease (attenuate) groundwater nitrate concentrations. Nitrate is actively removed and is unlikely to reach high concentrations. Least sensitive aquifers.

INTERMEDIATE - Applied to geologic units with mixed and variable sediment type; individual beds may have a High denitrification potential, but the unit (as a whole) may be composed mostly of sediments with a Low denitrification potential. Some fraction of the total nitrate load of an aquifer will be removed. Intermediate sensitivity.

LOW - Sediments in the surficial aquifer are unreactive and will not affect groundwater nitrate concentrations. Nitrate will be able to accumulate to high levels. Highly sensitive aquifers.

After assignment of the denitrification potential to surficial and sub-aquifer units the two layers were overlaid. Before the combined denitrification potential (CDNP) of both layers were assessed, the thickness of the surficial aquifer was generalised according to regional bore log data, hydrogeology and geomorphology (Fitzharris et al., 1992; Turnball and Allibone, 2003; Craw et al., 2007). Due to the scarcity of high quality bore log data, interpretation of the thickness of surficial aquifers is highly generalised, albeit supported by regional geological and geomorphic interpretations[3]. Therefore, by combining thickness and denitrification potential of surficial aquifers with the denitrification of sub-aquifer units five CDNP categories were defined - **very high**, **high**, **intermediate**, **low**, and **very low**. Each of these five CDNP categories function as a proxy for aquifer sensitivity to nitrate accumulation. These assignments were made on the basis of a subjective knowledge of gravel thickness, geomorphology and sediment geochemistry by the author.

---

[3] A regional map of surficial aquifer thickness has yet to be developed for the Southland region.

In general, a greater weighting in terms of the CDNP was given to the surficial unconfined aquifer than the sub-unit with the relative weighting dependent on the thickness of the surficial aquifer. For example, whenever surficial aquifers are relatively thin (<10 m) and directly overlay a high denitrification potential sub-unit, the surficial aquifer may still be assigned a high CDNP. Conversely, a thick (>20-30 m) surficial aquifer of low denitrification potential will be assigned a low or very low CDNP even if it directly overlies a sub unit of high denitrification potential.

For areas where surficial and sub-rock units are of differing denitrification potential, one high and the other low for example, they are assigned either a **high**, **intermediate** or **low** CDNP depending on the relative denitrification potential, the thickness of the surficial aquifer and the stratigraphic relationship. Again, these assignments were made on the basis of a subjective knowledge of gravel thickness, geomorphology and sediment geochemistry by the author.

Although major mountain ranges comprising fractured rock aquifers were assessed for their denitrification potential, they were excluded from the resultant map due to the scarcity of groundwater wells within these aquifers and the lower intensity land use in these high relief areas and lower impact on groundwater quality.

4.3 Description of Combined Denitrification Potential

In this classification, a high or very high CDNP means that groundwater passing through an aquifer will discharge with low nitrate concentrations regardless of the nitrate concentrations from the source. This indicates that nitrate has been removed from the groundwater. A low or very low CDNP means that nitrate can accumulate to high levels within these aquifers (or that groundwater with a high concentration will have a high nitrate concentration when it discharges as stream base flow). For settings with intermediate denitrification potential, some fraction of the total volume of groundwater nitrate may undergo denitrification, and nitrate concentrations in discharging waters may be relatively low but may still exceed the natural background level of ≤1.0 mg/L for Southland (Rissmann et al., 2011). Commonly, a continuum between very high and very low CDNP exists within natural groundwater systems.

5. Regional Map and Spatial Relationships

5.1 Aquifer Sensitivity to Nitrate Leaching

The CDNP of regional aquifers is a measure of the sensitivity of aquifers to nitrate contamination. Accordingly, the regional map of CDNP generated in this report also serves as a measure of aquifer sensitivity to nitrate accumulation. By definition, a low or very low CDNP aquifer will have a high to very high sensitivity to nitrate accumulation. Conversely, a high or very high CDNP aquifer will have a low or very low sensitivity to nitrate accumulation due to the prevalence of denitrifying conditions.

5.2 Regional Map of Denitrification Potential

The generalised relations between geomorphology (including a generalised thickness of surficial aquifer units), lithology and the presence of organic carbon, iron sulfides and glauconite within the geologic units that comprise the shallow aquifer units of Southland are displayed in maps of regional CDNP (Figs. 4-6). It is immediately evident that the majority of aquifers across the Southland region have low to very low potential for denitrification due to the prevalence of alluvial aquifers. The alluvial terrace aquifers of the Kamahi, Waikiwi Terrace and Gore Piedmont Formations are examples of this type of aquifer and in conjunction with unconsolidated gravel and sand in modern stream beds and floodplains constitute approximately 85% of the mapped Southland groundwater zones. Where intensive land use occurs above these aquifers, nitrate concentrations are expected to be significantly elevated above the regional background of 1 mg/L.

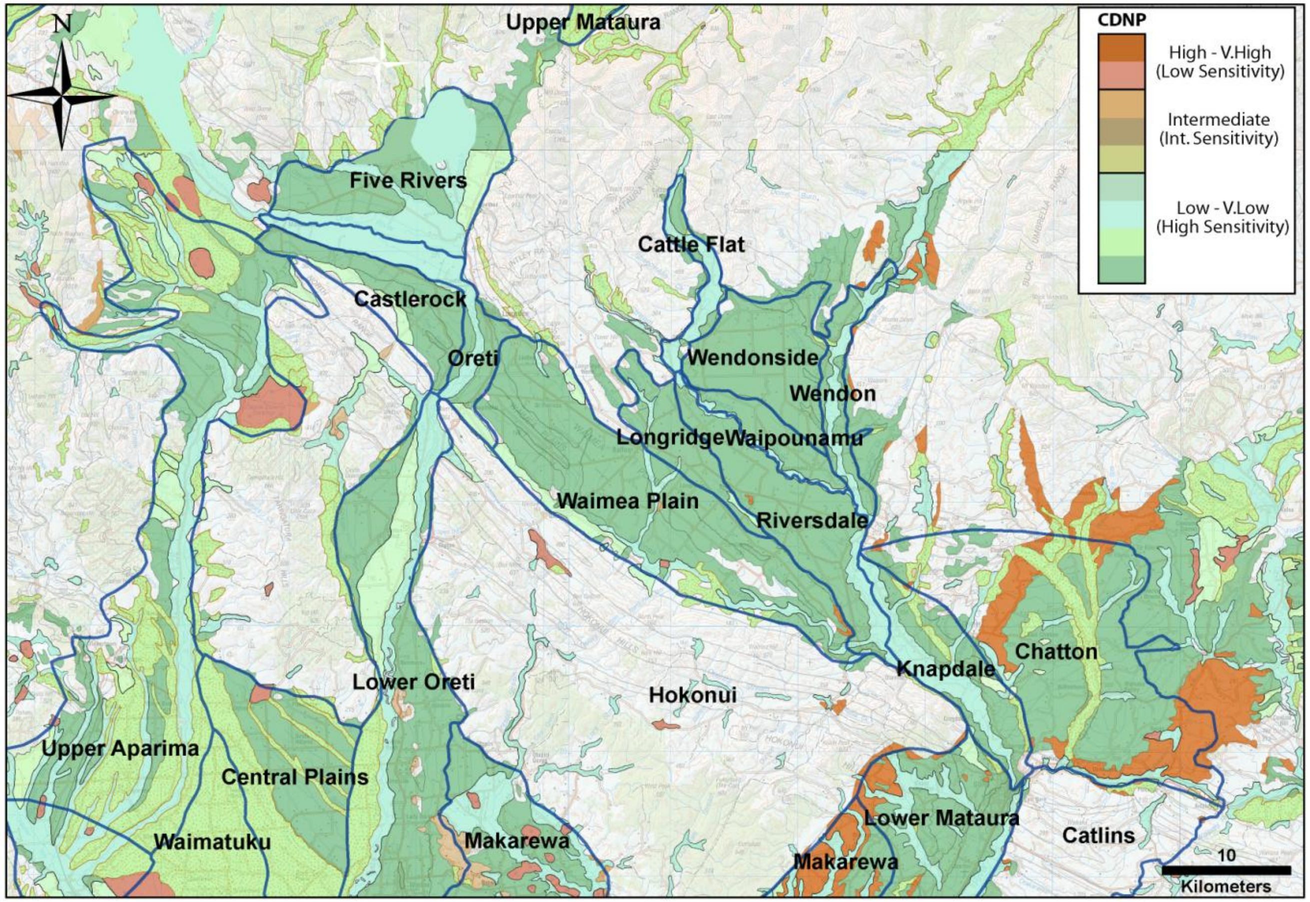


Figure 4: Spatial distribution of Combined Denitrification Potential (Aquifer Sensitivity) for the *Northern Southland* Region. *Where blue lines delimit regional groundwater zones. Note the predominance of low to very low Combined Denitrification Potential aquifers across the major groundwater zones.*

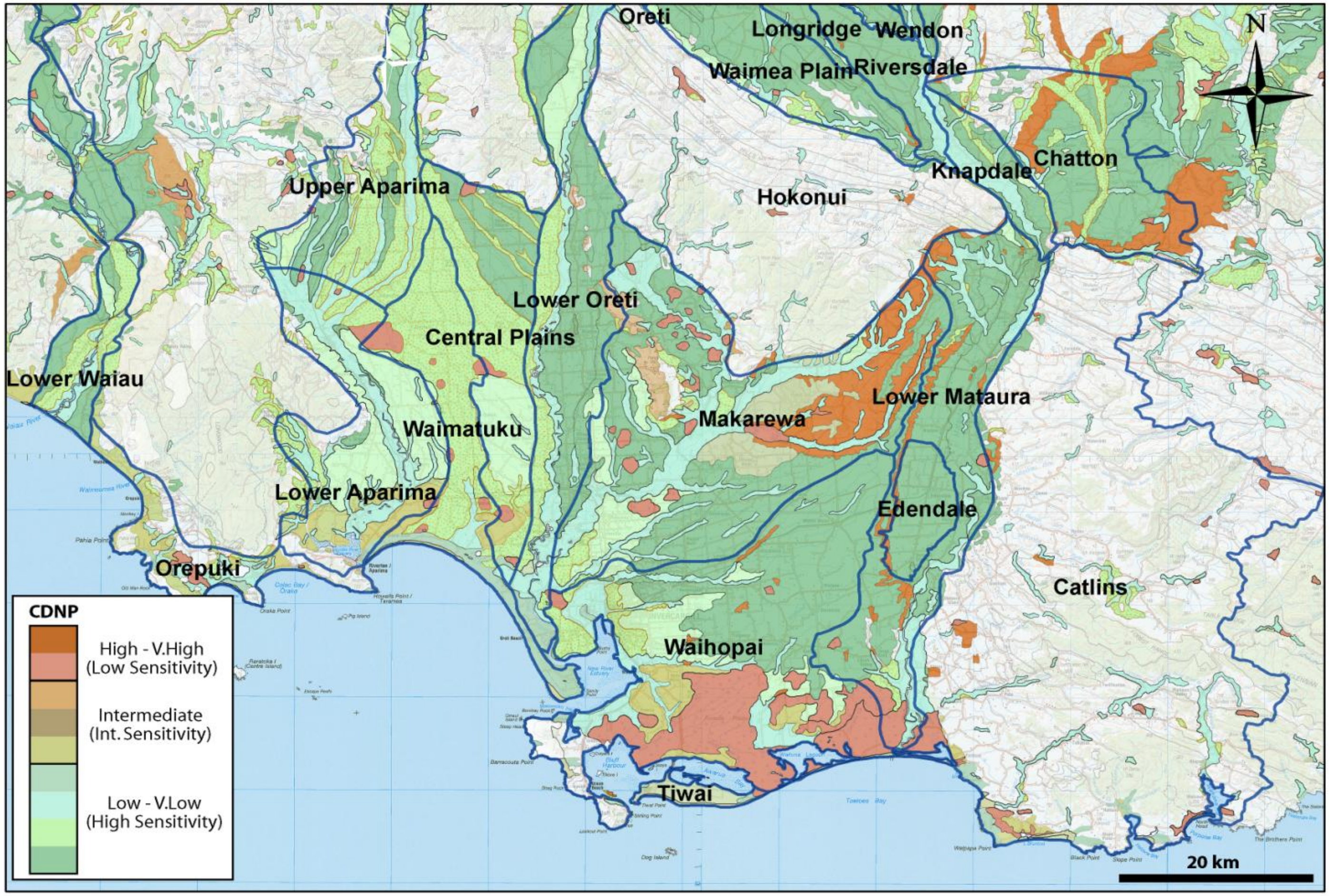


Figure 5: Spatial distribution of Combined Denitrification Potential (CDNP)(Aquifer Sensitivity) for the *Southern Southland* Region. ***Where, blue lines delimit regional groundwater zones. Note the: (i) predominance of low to very low Combined Denitrification Potential aquifers across the major groundwater zones; (ii) occurrence of high to very high CDNP values associated with sections of the Makarewa, Waihopai and Chatton groundwater zones, and; (iii) thin margins of marine-terrestrial aquifers of intermediate CDNP along the Southland coast.***

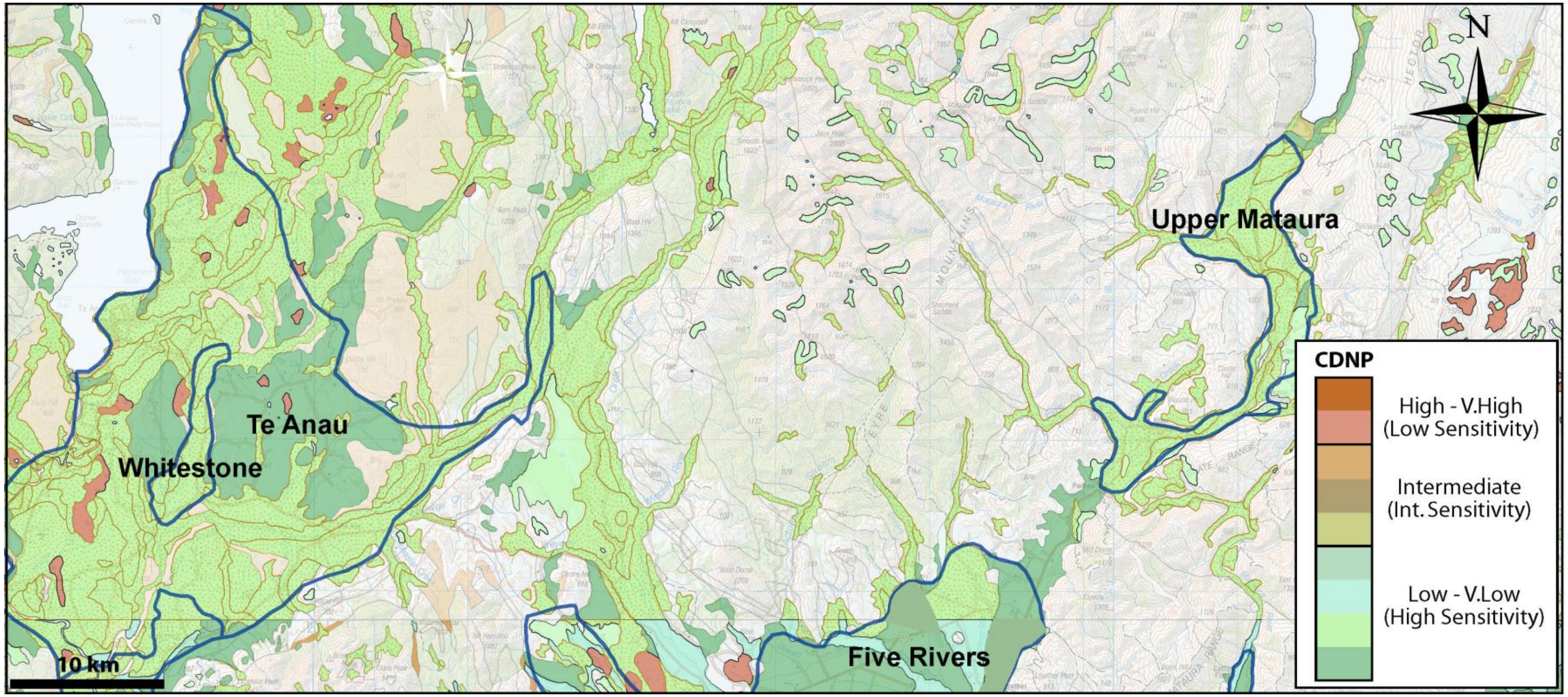


Figure 6: **Spatial distribution of Combined Denitrification Potential (Aquifer Sensitivity) for the *Te Anau, Whitestone and Upper Mataura* groundwater zones, northern Southland.** ***Where blue lines delimit regional groundwater zones. Note, the high sensitivity of these relatively undeveloped groundwater zones to groundwater nitrate accumulation.***

Of particular importance is the greater prevalence of very low CDNP aquifers associated with the thick gravel aquifers of the Edendale, Waimea Plains, Five Rivers, Waiau, Whitestone and Te Anau groundwater zones (Figs. 4-6). Across the Waimea plains the Kamahi Formation is underlain by weathered greywacke-quartz sandy gravels up to 70 m thick which extend into the Five Rivers, upper Oreti and Waikaia Valleys (Turnball and Allibone, 2003). At Edendale, 2–5 m of windblown loess overlies 20-50 m of highly weathered gravel.

From the generalised model gravel thickness and associated CDNP is greater within the upper reaches of the Aparima, Oreti, and Mataura catchments upstream of where they flow into the lowland plains (i.e. Gore, Ram Hill and Wreys Bush). The lower reaches of the same catchments are characterised by thinner gravel thicknesses (outwash and floodplain deposit) and display both a higher CDNP rank (less sensitive) and enhanced spatial heterogeneity in CDNP (Fig. 5), due primarily to:

(i) incorporation of underlying high CDNP materials within surficial gravel aquifer units by riverine processes; and
(ii) a greater proportion of minor peat wetlands associated with modern day stream and floodplain (over bank deposits) processes.

Aquifers of high to very high CDNP cover approximately 10% of the mapped Southland groundwater zones and occur primarily as large tracts of wetlands or areas where the Gore Lignite Measures crop out at or near the surface (Fig. 5). Examples include the large area of peat wetlands that form the Awarua plains, the lower portion of the Waituna Lagoon catchment and outcrops of Gore Lignite Measures, at the surface or in direct contact with thin unconfined aquifers, in the vicinity of Hedgehope, Chatton North, Pukerau and Waimumu. Nitrate concentrations in these aquifers are expected to be low. Other high denitrifying aquifers include the numerous small peat wetlands that occur as isolated pockets of high denitrification potential within the regionally more extensive, and low CDNP, alluvial sediment aquifers (gravels, sands and silts).

Geologic units with variable textures and organic carbon contents may have denitrification occurring in one part of the formation but not elsewhere. These units are classified as having an intermediate denitrification potential (Krantz and Powars, 2002). Examples of aquifers with intermediate CDNP potential include the mixed marginal marine – terrestrial deltaic deposits, that occur along the southern coast of Southland and form important aquifers of the lower reaches of the Orepuki, lower Aparima, Waimatuku, Central Plains, Waihopai and Catlins groundwater zones (Fig. 5). Marine sediments commonly contain glauconite, pyrite and oxidisable organic carbon providing abundant material for denitrification (Krantz and Powars, 2002). Interbedding of alluvial gravels and sands with marine sediments along the Southland coast reflects the complex interaction between fluctuating sea levels, changing hydrological regime, sediment supply, and vegetation which accompanied the climatic changes of the Pleistocene (Fitzharris et al., 1992).

Other rock units of intermediate denitrification potential include regional deposits of variably interbedded Tertiary lignite and lithified sedimentary rock (sand, silt and mudstones) and more localised deposits of variably glauconitic limestone of the Forest Hill/Castle Hill/Winton Hill Formations that outcrop across the upper northwest arm of the Makarewa groundwater zone (i.e. Browns, Forest Hill and Springhills area - Fig. 5). For aquifers of intermediate CDNP, it is assumed that some fraction of the total volume of groundwater nitrate may undergo denitrification, and that nitrate concentrations may be relatively low but may still be able to accumulate to concentrations in excess of natural background levels for Southland.

5.3 Spatial Relationships, CDNP and Groundwater Nitrate Concentrations

Overlays of median groundwater nitrate concentrations, contoured from 1,352 individual shallow (≤ 35 m) bores[4], across the Southland plains exhibits a strong spatial correlation with the spatial distribution of aquifer CDNP (Figs 7 and 8). Importantly, all recognised nitrate hotspots within the Southland region coincides spatially with aquifer systems of very low CDNP. Specifically, portions of the Five Rivers, Edendale, Waimea Plains, Knapdale, Lower Mataura, Wendonside, Central Plains, Lower Oreti, Waimatuku and Makarewa groundwater zones.

---

[4] The nitrate concentration map is modelled from water quality data held within the Environment Southland groundwater quality database. Median nitrate is modelled between thresholds of 0.01 mg/L and 8.4 mg/L nitrate as nitrogen, which denote the nitrate nitrogen detection limit and 75% of the Maximum Allowable Value of 11.2 mg/L for nitrate in drinking water, respectively.

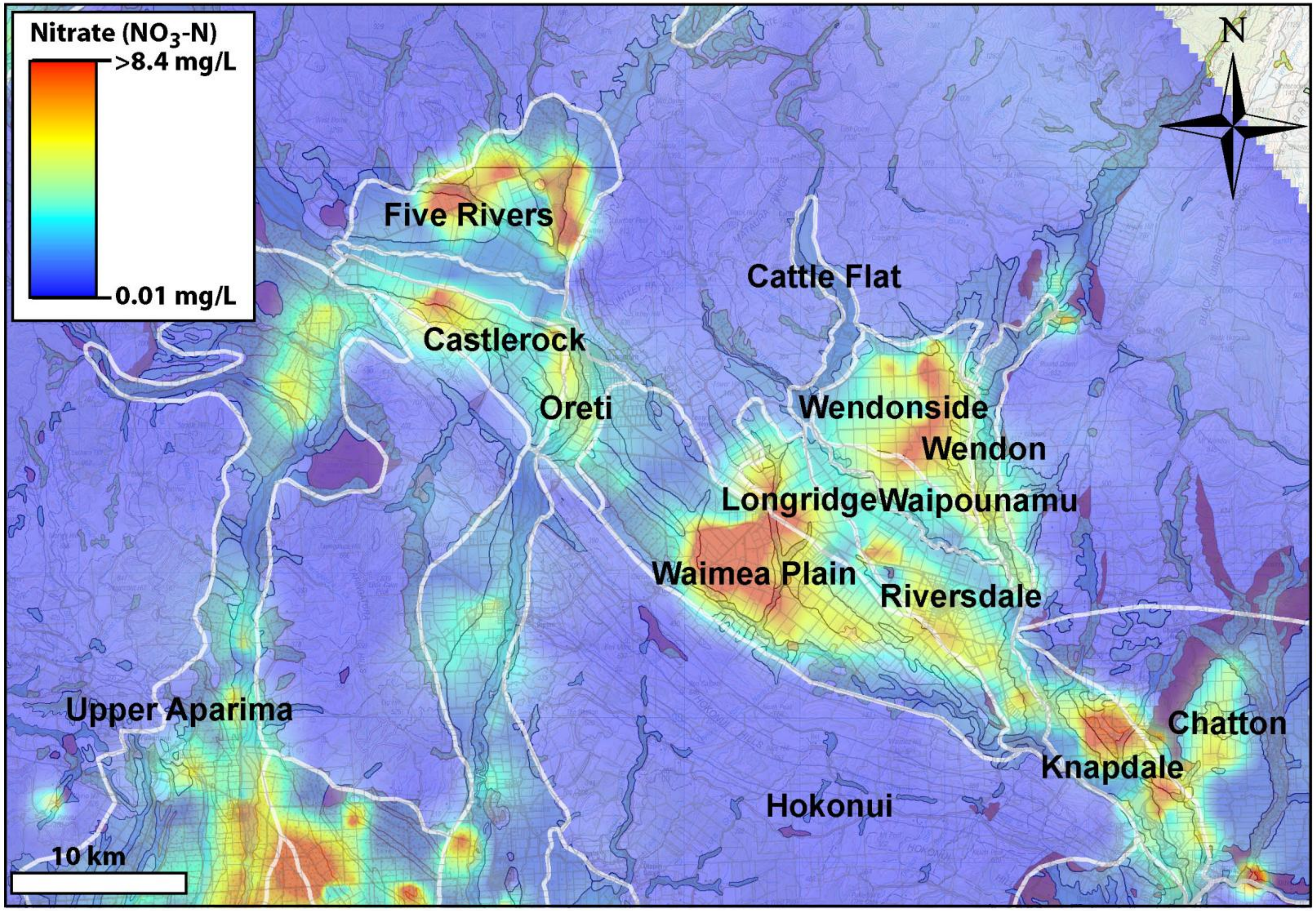


Figure 7: Overlay of contoured median NO_3 concentrations for northern Southland onto spatial distribution of Combined Denitrification Potential. ***Maximum threshold set at 8.4 mg/L or 75% of the Maximum Allowable Value (MAV) of 11.2 mg/L nitrate. Note, the spatial correlation between elevated median nitrate and low to very low Combined Denitrification Potential Aquifers (CDNP) of the broader Waimea Plains.***

Of the nitrate "hot-spot" areas, the Central Plains, Edendale, Waimea plains and Five Rivers aquifers display the greatest homogeneity in elevated nitrate concentrations (Figs. 7 and 8). The homogeneity of elevated nitrate across these areas coincides with the generally greater thickness of alluvial gravels and lesser spatial variability in aquifer CDNP. Water quality data from these aquifer systems supports a strongly oxidising groundwater regime with little evidence for reducing conditions.

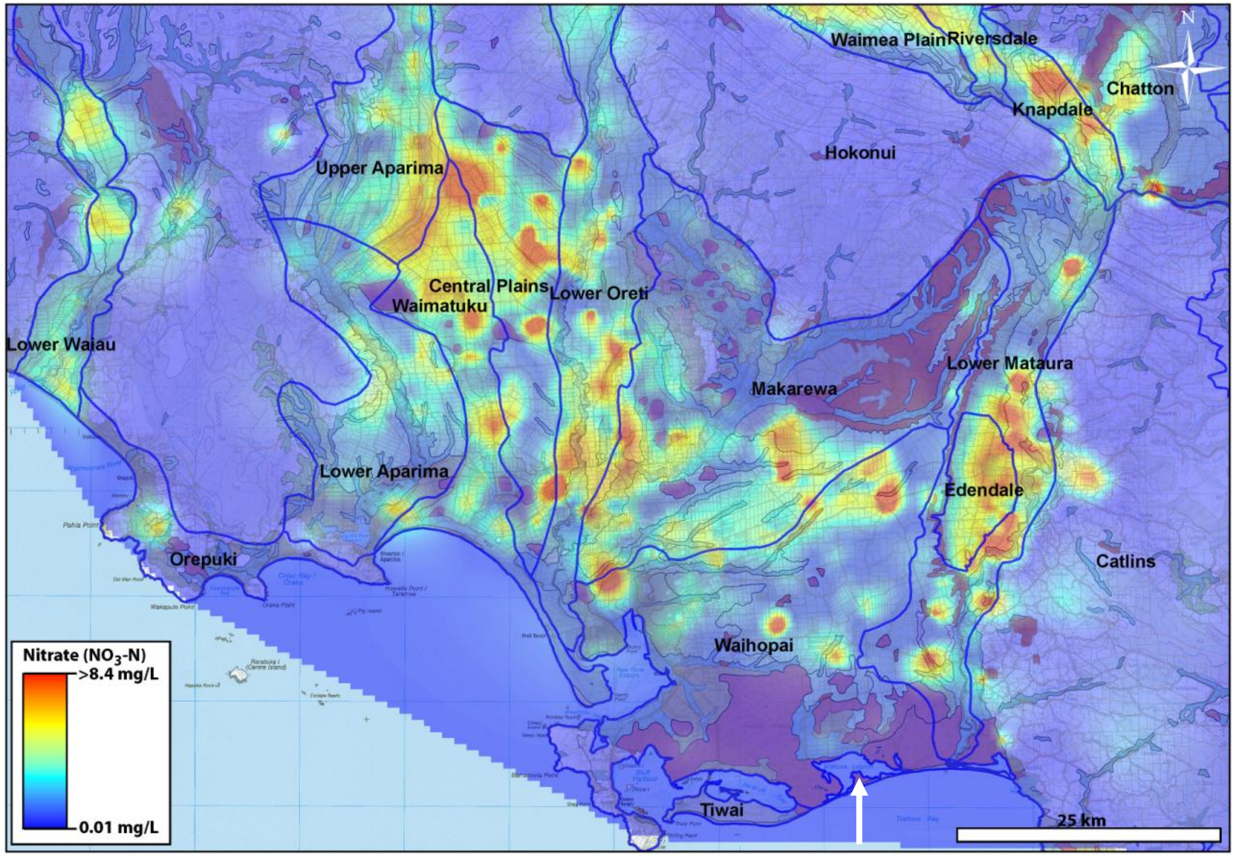


Figure 8: Overlay of contoured median nitrate concentrations for Southern-Central Southland Spatial distribution of Combined Denitrification Potential. ***Where the white arrow denotes the Waituna Lagoon. Note the low nitrate concentrations associated with the: (i) peat wetlands (Awarua Plains) of the lower Waihopai Groundwater Zone; (ii) Tertiary Lignite Measures of the NE arm of the Makarewa Groundwater Zone, and; (iii) variably glauconitic limestone and minor peat wetlands of the NW Makarewa Groundwater Zone. Also evident is a high degree of heterogeneity in spatial nitrate concentrations within the lower reaches of groundwater zones associated with floodplain processes (see text).***

Several large areas of low nitrate groundwater coincide with aquifer materials designated as high CDNP (Figs. 8-10). The regionally most extensive zones of low nitrate groundwater coincides with the very high CDNP aquifers of the Makarewa and Waihopai groundwater zones (Fig. 8 -10). Low nitrate groundwater associated with the northeast arm of the Makarewa groundwater zone is hosted by Gore Lignite Measures. Water quality data from shallow wells within this area exhibit elevated concentrations of ammoniacal-N (greater than 0.1 mg/L), iron and manganese supporting the existence of reducing conditions and a high denitrification potential. To the south, the Awarua plains and the lower quarter of the Waituna Lagoon catchment occur within the Waihopai groundwater zone (Figs. 8 and 9). Like the chemical signatures of groundwater in Gore Lignite Measures, elevated concentrations of ammoniacal-N, iron and manganese within these aquifers support the existence of reducing conditions and a high denitrification potential associated with peat wetlands. North of the Awarua plains, around Mokotua/Kapuka, nitrate concentrations increase in conjunction with a transition to terrace gravels and sands of low CDNP (Fig. 9).

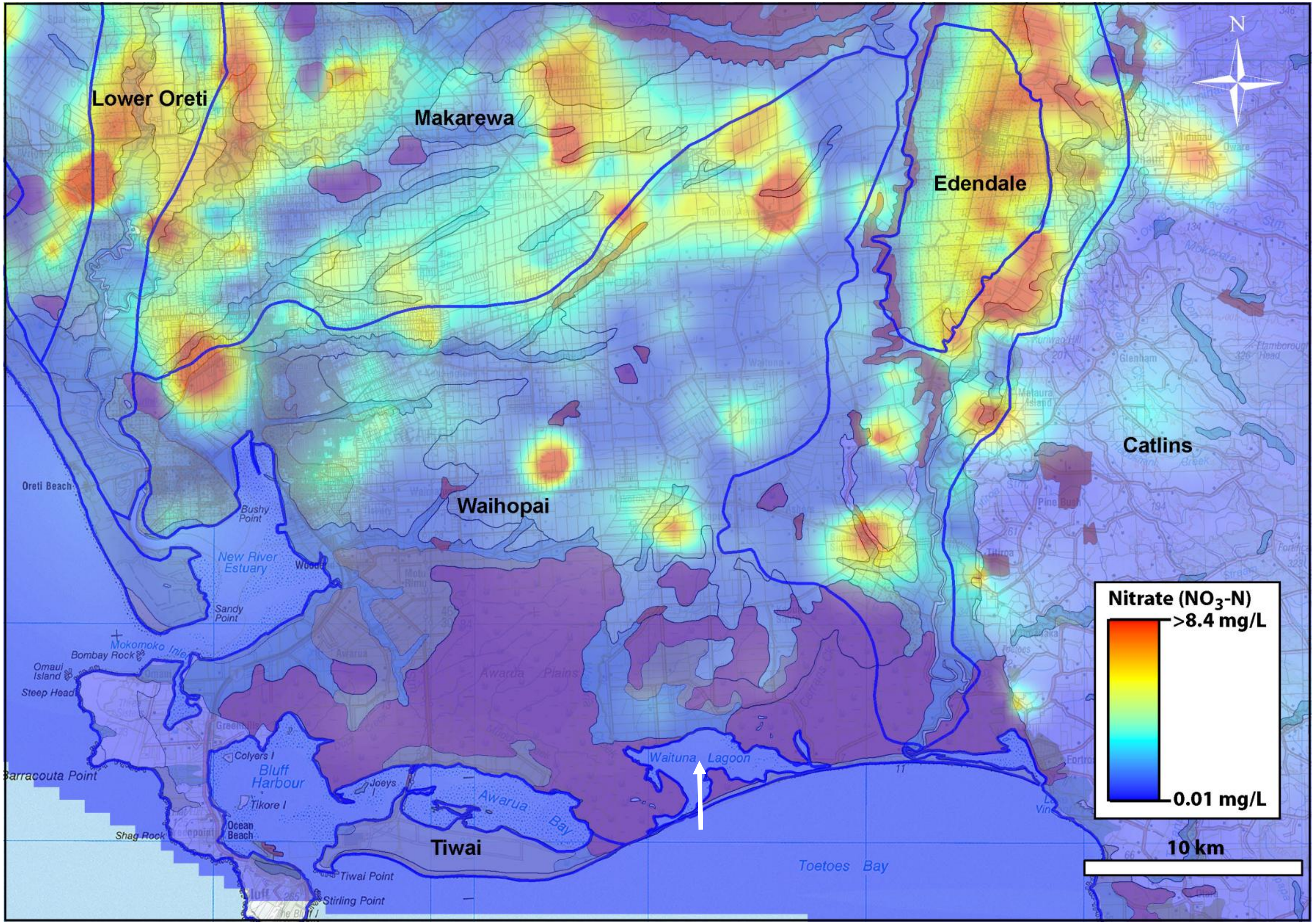


Figure 9: Close up of the spatial relationship between low nitrate concentrations and the high denitrification potential of the peat wetlands of the Awarua Plains – lower half of the Waihopai Groundwater Zone including the Waituna Lagoon (white arrow).

Aquifer units of intermediate denitrification potential include marine terraces underlain by terrestrial peat deposits that occur along coastal margins of Southland (Figs. 5 and 8). Groundwater chemistry from within these mixed aquifers display spatially variable redox states, predominantly mildly reducing but oxidising in places. The mildly reducing redox state is sufficient to promote denitrification but to a lesser degree than aquifers of high to very high CDNP that occur within Gore Lignite Measures and peat wetlands.

A localised intermediate CDNP aquifer coincides with the northwest arm of the Makarewa groundwater zone where variably glauconitic limestone (Forest Hill/ Castle Hill/Winton Hill Formations) outcrops and/or underlies terrace and floodplain gravels (Figs. 5 and 10). A high proportion of minor peat wetlands (high CDNP) within the NW arm of the Makarewa may also contribute to the moderately reducing conditions and minor nitrate. The sparse groundwater chemistry data from wells within this area exhibits variably elevated ammoniacal-N, iron and manganese concentrations supporting the existence of intermediate to high denitrification potential within these shallow aquifers.

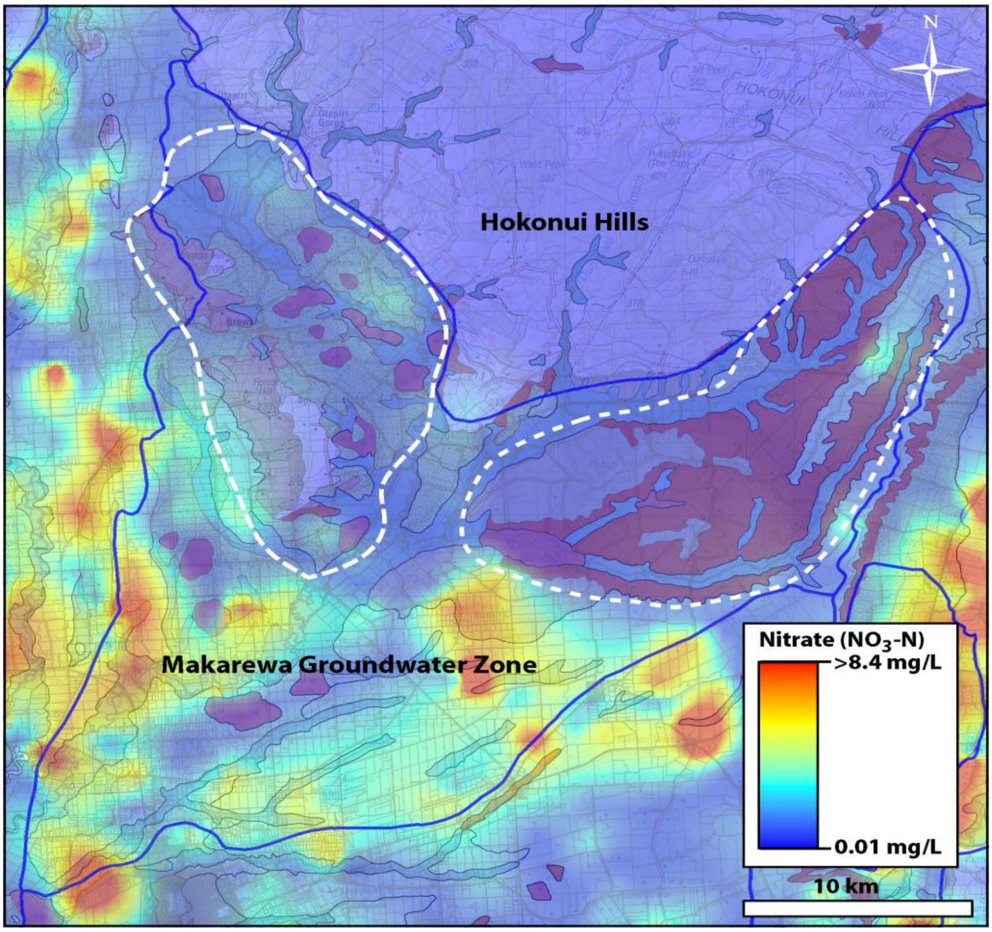


Figure 10: Overlay of median nitrate concentrations on to aquifer Combined Denitrification Potential - Makarewa Groundwater Zone. ***Note, the low median nitrate concentrations associated with the NE (large white dashed) and NW (small white dash) arms of the Makarewa groundwater zone associated with the outcropping of the Gore Lignite Measures (very high CDNP) and variably glauconitic limestone (intermediate CDNP), respectively. A high proportion of minor peat wetlands (high CDNP) within the NW arm of the Makarewa may also contribute to the moderately reducing conditions and minor nitrate.***

A feature of the Central Plains, Waimatuku, Lower Oreti, Waihopai, and southern portion of the Makarewa groundwater zones is the high degree of heterogeneity in nitrate concentrations when contrast with the Edendale, Five Rivers and Waimea Plains groundwater zones (Figs. 7 – 9). Bearing in mind the limitations in the spatial coverage of nitrate data, the patchy nature of groundwater nitrate concentrations in these more southern groundwater zones likely reflect the:

(i) generally thinner layer of alluvial gravels (less than equal to 20 m) when contrast with northern groundwater zones (gravel thicknesses of 30–80 m);
(ii) reworking and incorporation of underlying high CDNP units with alluvial gravels by major rivers; and
(iii) a greater proportion of minor peat wetlands associated with modern day stream and floodplain (over bank deposits) processes.

Therefore, the heterogeneity of groundwater nitrate concentrations in southern groundwater zones likely reflects the greater heterogeneity in CDNP due to the thinner gravels and intercalation of high CDNP materials by riverine processes. A high degree of spatial variance in redox status (CDNP) is a common feature of lowland plain alluvial aquifers globally (Du Laing et al., 2008).

Another example of the influence of spatial changes in aquifer CDNP on nitrate concentration is demonstrated by the Edendale groundwater zone (Fig. 11). The western extent of the elevated nitrate "hot-spot", associated with the Edendale aquifer, peters out in conjunction with the out cropping of high denitrifying potential Gore Lignite Measures. The influence of the Gore Lignite Measures extends westward into the Edendale groundwater zone before waning, likely in response to the deepening of the unit beneath the low denitrification potential terrace gravels that host the main Edendale aquifer. The transition from high to low CDNP forms a boundary that runs NNE along the eastern margin of the Edendale groundwater zone, tracing the outcrop of Gore Lignite Measures, and extending northwards into the lower Mataura groundwater zone.

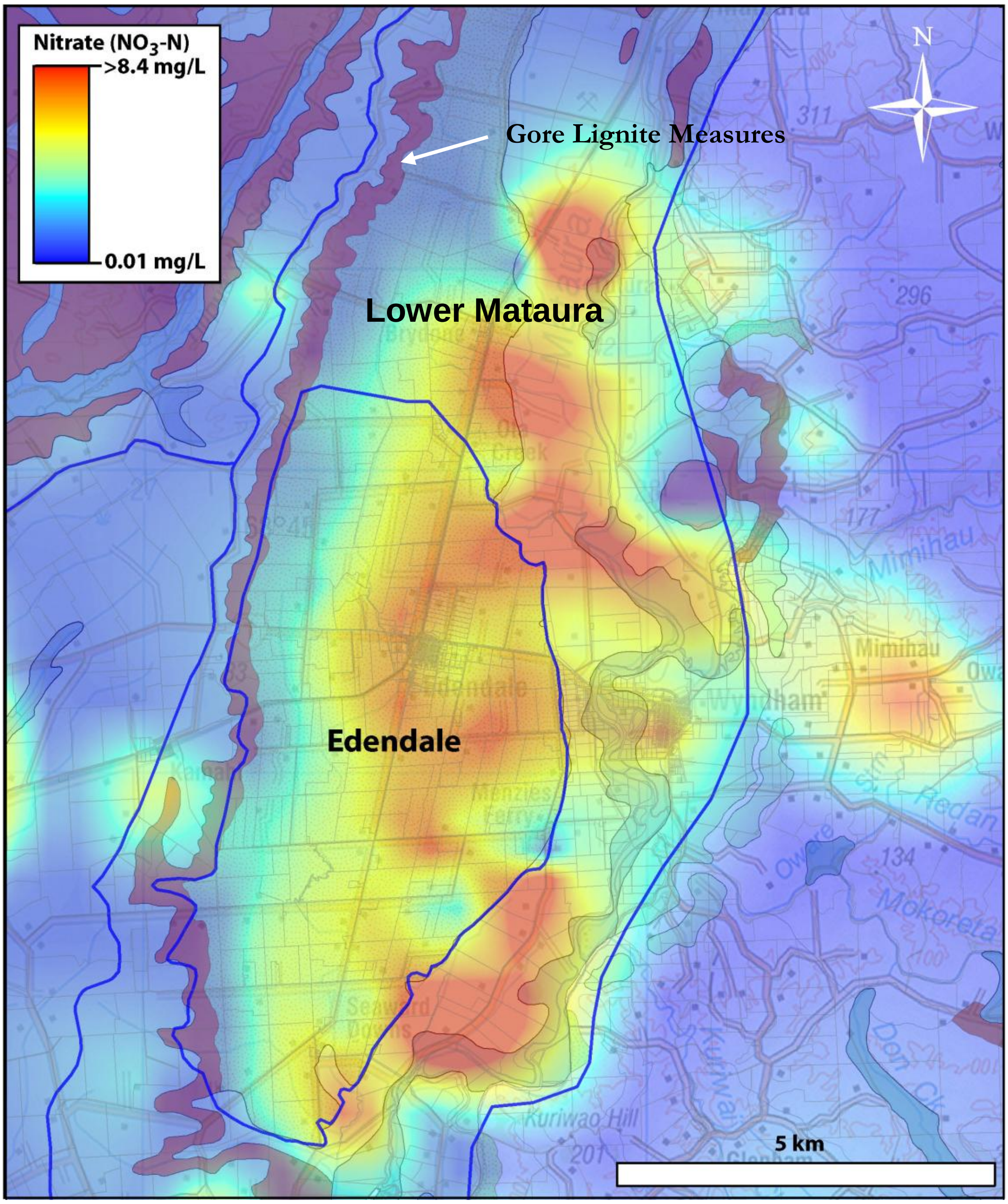


Figure 11: Overlay of median nitrate concentrations on to aquifer Combined Denitrification Potential – Edendale/Lower Mataura groundwater zones. ***Note; (i) the western outcropping of the very high Combined Denitrification potential (CDNP) of the Gore Lignite Measures (GLM) governs the western most extent of the Edendale nitrate 'hot-spot', and; the diffuse nature of the western boundary to the 'hot-spot.'***

5.4 Limitations of the Spatial Denitrification Model

The current model of the spatial variability in denitrification potential/aquifer sensitivity is preliminary and has not been verified by detail field based studies. The regional scale of the CDNP map limits interpretations to a regional or groundwater zone level. However, it does provide valuable context for finer scale investigations of groundwater zones and for placing property scale investigation within a wider regional context.

Other limitations over the accuracy of this model include:

(i) No consideration of how age and residence time of groundwater influences the denitrification status and potential of an aquifer;
(ii) Large gaps in the spatial coverage of regional groundwater chemistry that limits validation of the spatial controls of aquifer CDNP on nitrate concentrations; and
(iii) A critical lack of high quality bore log or other data defining the thickness of shallow aquifers and/or the proximity of underlying sub aquifer units.

Nonetheless, the strong spatial relationship between mapped denitrification potential/aquifer sensitivity and groundwater chemical data supports the generalised model.

6. Summary and Recommendations

6.1 Summary of Key Points

The assignment of CDNP to regional aquifers and a preliminary assessment against groundwater chemistry provides some important outcomes for groundwater quality management in Southland. Bearing in mind the limitations of the reported model, the key findings are summarised below:

- the majority (~85%) of Southland aquifers exhibit a high or very high sensitivity to nitrate accumulation. This observation highlights the obvious risk of the current level of land use activities and forecast intensification on regional groundwater quality. Those aquifers of especially high sensitivity to nitrate accumulation are characterised by thick (greater than or equal to 20 m) sequences of alluvial gravels. These thick gravel aquifers already show elevated nitrate levels and include the known "hot-spot" areas of the Waimea Plains, Knapdale, Five Rivers, Castlerock, Wendonside, Edendale, and upper Central Plains groundwater zones;

- upland plains groundwater zones exhibit higher total nitrate levels and greater homogeneity in nitrate concentration when contrasted with the lower reaches of the lowland plains groundwater zones. This difference is attributed to the generally greater thickness of alluvial gravels hosting the upland plains aquifers and consequently the:
  (i) reworking and incorporation of underlying high CDNP units with alluvial gravels by major rivers, and;
  (ii) a greater proportion of minor peat wetlands associated with modern day stream and floodplain (over bank deposits) processes;

- on the basis of gravel thickness and aquifer material, this report raises the high potential risk of ongoing land use intensification within the upper and lower Waiau, Te Anau and Whitestone groundwater zones. These relatively undeveloped groundwater zones are characterised as being very sensitive to nitrate accumulation and should be managed with care. Similarly, the upper Mataura, upper Aparima and upper portion of the lower Oreti are also areas of high sensitivity to groundwater nitrate accumulation;

- approximately 10% of Southland's aquifers exhibit low or very low sensitivity to groundwater nitrate accumulation and exhibit a natural ability to attenuate the build-up of nitrate through the process of denitrification. Areas of high to very high denitrification potential are proportionally greatest across the Makarewa and Waihopai groundwater zones. Of significance are the high CDNP aquifers that make up the lower half of the Waituna catchment. The highly reduced groundwater within these aquifers may play an important role in removing nitrate inputs to groundwater from soil leaching or attenuate high nitrate concentrations as groundwater flows through these units;

- coastal areas with lowland peat wetlands and marine sediments of high CDNP may buffer high nitrate loads prior to the groundwater discharging to lowland surface water bodies (lakes, rivers, estuaries) or the marine environment. The Awarua Plains and lower part of the Waituna catchment are such examples;

- rivers and streams convey nitrate rich waters across the surface of lowland coastal wetland and marine-deltaic aquifers limiting any potential nitrate removal. Historic (and ongoing) drainage of lowland wetlands has greatly enhanced bypass volumes and restricted the natural ability coastal aquifers to attenuate nitrate concentrations. The ongoing drainage of wetlands (Waituna catchment) reduces the capacity of these aquifers to remove nitrate and increase the risk of eutrophication of lowland lakes, estuaries and the coastal marine environment. Increased bypass flow highlights the importance of up catchment nutrient management in areas of high sensitivity to nitrate accumulation;

- aquifers of intermediate denitrification potential fringe the coastal margins of the Southland region and may play a minor albeit important role in attenuating nitrate loads to the coastal marine environment.

6.2 Conclusion and Recommendations

The surficial aquifers of the Southland region are not a homogeneous layer of gravel and sand, they are a mix of sediments and rock units deposited in different environments that have dramatically different chemical properties. Lignite and wetland peats commonly contain abundant organic carbon and other reduced compounds that may react to remove nitrate from groundwater. However, the majority (~85%) of the shallow aquifers of the Southland region are hosted by alluvial gravels and sand, which are inherently more sensitive/susceptible to nitrate contamination. The distribution of these reactive and non-reactive sediments have been mapped and validated against groundwater chemical data.

The spatial model (map) of aquifer denitrification potential/sensitivity shows the importance of the natural spatial variability in aquifer materials over the potential accumulation of nitrate in regional groundwater. The denitrification and aquifer sensitivity map presented here is a step toward a spatial assessment of those parts of the region where aquifer systems are most sensitive to nitrate contamination. This information, although at a regional scale, may be used by resource managers to evaluate alternative strategies for decreasing nitrogen loads to shallow aquifers, rivers, estuaries and the coastal marine environments of Southland. However, due to the regional scale of this work the spatial model should not be applied at the property scale.

Recommendations:

- It is intended that this work provide guidance, at a regional scale, over the implementation of land use management techniques for areas that are susceptible to nitrate accumulation and guide limit setting for surface and groundwater systems under the National Policy Statement. The identification of aquifers vulnerable to nitrate accumulation is a fundamental step in managing land use activities (see http://defranvz.adas.co.uk/). Pending the availability of finer scale geological data the refinement of the aquifer sensitivity model to the property scale may be possible.

- Use the spatial model of denitrification potential to help define individual groundwater quality zones. Southland's groundwater resources have been delineated into 29 groundwater zones based primarily on geophysical characteristics i.e. aquifer geology, the presence of structural and hydrological boundaries, aquifer hydrological properties and response to groundwater abstraction. The potential need for separate groundwater quality zones based on regional geochemistry been raised on a number of occasions by Environment Southland's groundwater scientists (pers. comm. Wilson, 2011) as a means of improving the efficiency and effectiveness of groundwater quality monitoring and reporting programmes. Delineation of groundwater quality zones would require an assessment based on the chemical characteristics of aquifer systems, including aquifer materials, which may have more of an influence on water quality issues than physical hydrology.

- Assess and assign groundwater oxygen status, redox status and key terminal electron accepting processes operating in the various aquifer systems of Southland. The assignment of the redox status and dominant redox process is fundamental to understanding the variability in groundwater quality regionally. Redox status governs the solubility of toxic metals, the accumulation/attenuation and transport of contaminants such as nitrate and phosphorus, and the presence of nuisance chemicals such as iron, manganese and hydrogen sulphide. A better understanding of redox process operating in regional aquifers underpins the future development and protection of the groundwater resource.

- This work should be used in the assessment of groundwater nutrient loading to the Waituna Lagoon.

- Of the regional groundwater zones, it is recommended that at least one groundwater zone be assessed for fine scale spatial variability in aquifer architecture/composition within the next five years (see http://cgiss.boisestate.edu/~billc/BHRS/).

7.0 References

Drever, J.I., (2002). *The Geochemistry of Natural Waters: Surface and Groundwater Environments* (3rd Edition), (ISBN: 0132727900 / 0-13-272790-0).

Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., Tack, F.M.G., (2009). *Trace metal behaviour in estuarine and riverine floodplain soils and sediments: A review*. Science of the Total Environment, 407 (13), pp. 3972-3985.

Environment Southland, (2010). Regional Water Plan for Southland. Publication No 2011-04.

Fitzharris, B.B., Mansergh, G.D., Soons, J.M., (1992). *Basins and Lowlands of the South Island. In Landforms of New Zealand*, 2nd Edition, Ed. Soons, J.M., and Selby, J.M. Longman Paul Publishers, Auckland, New Zealand.

GNS Science, (1996 – 2003). QMAP (map scale 1:250,000) series of geological maps generated for New Zealand; Murihiku, Wakatipu, and Dunedin tiles.

Hughes, B., (2011). *Environment Southland State of the Environment: Groundwater Quality Technical Report*. A report for Environment Southland by Liquid Earth Consulting Ltd.

Krantz, D.E., and Powars, D.S., (2002). *Hydrogeologic setting and potential for denitrification in groundwater, Coastal Plain of Southern Maryland: U.S. Geological Survey Water-Resources Investigations Report* 00-4051.

McMahon, P., (2002). *Aquifer/aquitard interfaces: Mixing zones that enhance biogeochemical reactions*. Hydrogeology Journal 9, no. 1: 34–43.

McMahon, P. and Chapelle, F. (2008), *Redox Processes and Water Quality of Selected Principal Aquifer Systems*. Groundwater, 46: 259–271.

Turnbull, I.M., Allibone, A.H., (2003). *Geology of the Murihiku area*. Institute of Geological and Nuclear Sciences 1:250 000 geological map 20. 1 sheet + 74 pp. Lower Hutt, New Zealand Institute of Geological and Nuclear Sciences Ltd.

Rissmann, C.F., Panno, S.V., Wilson, K.L., Elliotte, D.M., (2011). *Estimating Background and Threshold Nitrate Concentrations in Southland groundwaters – A Graphical Statistical Approach*. Accepted abstract submitted to the New Zealand Hydrological Society Conference, Wellington, 2011.

Wilson, K. L., (2010a). *Groundwater Report on the Balfour Groundwater Quality Study*. Environment Southland, Invercargill. 52p.

Wilson, K. L., (2010b). *Edendale Groundwater Management Zone Technical Report*. Environment Southland, Invercargill. 55p.

Wilson, K. L., (2011). *Riversdale Groundwater Management Zone Technical Report*. Environment Southland, Invercargill.

8. Glossary

Attenuation: Is the reduction in concentration of a contaminant by natural processes.

Denitrification: Is a chemical process in which nitrate is convert to gaseous nitrogen or nitrous oxides. During denitrification nitrate is essentially removed from the aquifer.

Dissolved Oxygen: That fraction of oxygen dissolved within groundwater.

Glauconite: A reduce iron clay mineral which commonly forms in marine environments. Glauconite may act as an electron donor for denitrification.

Iron Pyrite: A reduced iron mineral that may act as an electron donor for denitrification.

Organic Matter/Organic Carbon: An organic material derived from living organisms, generally decomposed plant remains.

Oxidising: Having abundant oxygen or capability to donate electrons.

Reducing: Having little or no oxygen and limited capability to donate electrons.