The Extent of Nitrate in Southland Groundwaters

Regional 5 Year Median (2007–2012 (June))

Technical Report

July 2012

Dr Clint Rissmann
Groundwater Scientist, Environment Southland

Publication No 2012-09

Environment Southland is the brand name
of Southland Regional Council

Document Quality Control

Environment Southland Division:	Environmental Information		
Report reference:	Title: The Extent of Nitrate in Southland Groundwaters Regional 5 Year Median (2007–2012 (June))		No: 2012-09
Prepared by:	Dr Clint Rissmann, Groundwater Scientist, Environment Southland		
Reviewed by:	Dr Chris Daughney, GNS Science	Approved for issue by:	Karen Wilson
Date issued:	July 2012	Project Code:	EMGRD1

Document History

Version:	**Status:** Final Draft
Date:	**Doc ID:**

Table of Contents

List of Figures

List of Tables

1. Introduction

Nitrate-nitrogen (NO_3-N) is a common contaminant of ground and surface water the world over. The New Zealand Drinking Water Standards (NZDWS, 2008) specify a limit of 11.3 mg/L NO_3-N for drinking water in order to protect human health. The primary criteria for this limit are associated with the elevated risk of a condition known as methemoglobanemia ("blue baby syndrome") in infants and pregnant women ingesting water with nitrate (NO_3) at elevated concentrations.

Much lower limits of 0.167 and 0.444 mg/L NO_3-N are recommended for protection of upland and lowland surface water bodies respectively, in the ANZECC, (2000) water quality guidelines. Compared to levels considered safe for potable supply, these much lower values reflect the greater sensitivity of surface fresh and saline water bodies to nitrogen loading. The relevance of surface water ecological NO_3-N limits to groundwater reflects the considerable contribution of groundwater as base flow to rivers, lakes, estuaries and the costal marine environment throughout Southland (Liquid Earth, 2011a,b; Rissmann et al., 2012).

The following document summarises the spatial variation of NO_3-N concentrations within Southland groundwater for the last five years (2007–2012 (June)). The spatial variability of NO_3-N is presented according to specific threshold values defined for NO_3-N concentrations in Southland and New Zealand groundwater (Daughney and Reeves, 2005; Daughney et al., 2012; Morgenstern and Daughney, 2012; Rissmann et al., 2011, 2012). These thresholds relate to specific sources of NO_3-N and/or human health effects and provide a relevant context for assessing the extent of NO_3-N contamination of Southland aquifers. Importantly, this map is not a predictive tool but is intended to reflect overall conditions of groundwater quality with regards to the New Zealand Drinking Water Standards. The methodology used to develop the maps is discussed in detail in **Appendix 1**.

2. NO_3-N Thresholds

Groundwater research in New Zealand and Southland indicates that prior to European colonisation NO_3-N concentrations in shallow oxidised groundwater was at or below 0.4 mg/L (Daughney and Reeves, 2005; Morgenstern and Daughney, 2012; Rissmann et al., 2011, 2012). NO_3-N concentrations of 0.4 mg/L are similar to pre-anthropogenic NO_3-N concentrations reported for groundwater throughout the world (see Riemann et al., 2005; Daughney and Reeves, 2005; Panno et al., 2006).

In Southland a "pre-European" NO_3-N concentration of 0.4 mg/L, is supported by a median NO_3-N concentration of 0.4 mg/L (n = 54) for shallow oxidising groundwater beneath old growth indigenous forests in Fiordland, Stewart Island and conservation estate areas throughout Southland (**Table 1**; Rissmann et al., 2011). These areas have little if any history of intensive land use. In addition to an absence of intensive land use, these areas tend to be remote and isolated from cities, agricultural activities and human industry.

Importantly, strongly reducing groundwater (low oxygen, high reduced Fe concentrations) typically contains low NO_3-N concentrations (<0.4 mg/L) irrespective of the land use intensity due to the process of denitrification. However, impacted reduced groundwaters typically show other signs of intensification, such as elevated phosphate and major ion concentrations with or without elevated *E.coli* counts (Rissmann et al., 2012).

Table 1. NO_3-N classes defined for oxidised groundwaters in Southland.

NO_3-N Class (mg/L)	**Description of Each Class**	**Characteristic Areas for each NO_3-N Class**
0.01 - 0.4	Pristine, pre-European groundwaters showing no impact from human activity	Fiordland National Park or large undeveloped areas remote from regions of high intensity land use.
0.4 to 1.0	Modern day background showing only diffuse inputs of NO_3-N from human activity	Undeveloped or low intensity land receiving indirect NO_3-N inputs from diffuse sources. Commonly, land areas surrounding regions of greater intensity land use both urban and agricultural.
1.0 to 3.5	Minor to moderate anthropogenic land use impacts from intensive land use	Developed land dominated by intensive agriculture.
3.5 to 8.5	Moderate to high anthropogenic land use impact	Developed land dominated by intensive agriculture.
8.5 to 11.3	Groundwaters with NO_3-N in excess of the 75 percent of Maximum Allowable Value for Drinking Water in New Zealand	Developed land dominated by intensive agriculture.
>11.3	Groundwater with NO_3-N concentrations in excess of the New Zealand Drinking Water Standards	Developed land dominated by intensive agriculture.

A threshold of 1.0 mg/L NO_3-N is considered the upper bound defining "modern day background" concentrations for Southland (Rissmann et al., 2011). Areas defined as "modern day background" can be described as young, oxidising groundwaters subject to diffuse anthropogenic inputs. Diffuse inputs define NO_3-N contributions from indirect sources such as wet and dry (dust) deposition of nitrogen compounds to the land surface from combustion of fossil fuels and/or volatilisation of ammonia from application of urea or animal wastes (see Panno et al., 2006; Rissmann et al., 2012). Therefore, oxidised groundwater with NO_3-N concentrations consistent with modern day background levels may include conservation estate land occurring within or adjacent to a region dominated by intensive agriculture or urban activity. Hence, modern day pristine groundwater may occur in or adjacent to more densely populated or intensively farmed areas.

At concentrations greater than 1.0 mg/L NO_3-N, the contribution from intensive land use becomes increasingly important (Daughney et al., 2005; 2010). Where NO_3-N concentrations are above 1.0 mg/L, the most important contributors to elevated NO_3-N include synthetic fertilisers, animal urine and manure, human effluent and industrial wastes. Groundwater research in New Zealand and Southland indicates that concentrations above 3.5 mg/L, NO_3-N, are almost certainly indicative of human impact (Daughney, 2004; Daughney and Reeves, 2005; Morgenstern and Daughney, 2012). At any one site the elevated NO_3-N concentrations may originate from multiple origins or be dominated by a single source[1].

2.1 Median NO_3-N Maps

The susceptibility to groundwater contamination by NO_3-N for Southland aquifers is presented in **Figure 1**. Areas of elevated risk to groundwater contamination were generated from an assessment of groundwater quality risk associated with land disposal of Farm Dairy Effluent (FDE) using a weighted overlay of soil and receiving environment risk factors (Wilson and Hughes, 2007).

---

[1] Threshold values for all NO_3-N classes, with the exception of the 3.5 mg/L NO_3-N threshold, are based on median values. The 3.5 mg/L threshold is based on the 95th percentile NO_3-N concentration for Southland and New Zealand groundwaters as defined by Daughney, (2004) and Daughney and Reeves, (2005).

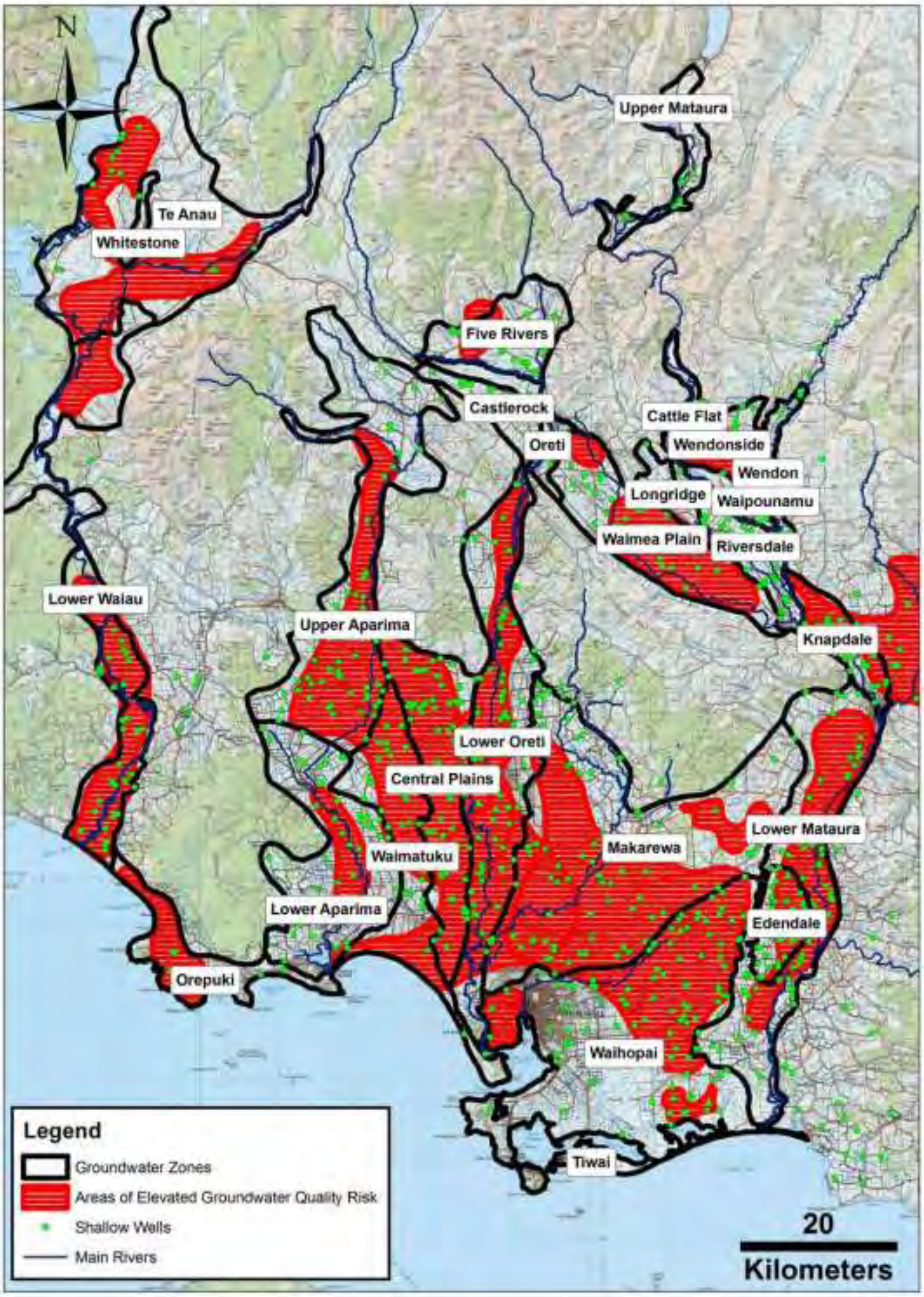

Figure 1: Map of elevated groundwater quality risk for the Southland region
(Note: Generated based on a regional risk assessment of water quality (Wilson and Hughes, 2007). Included are groundwater zones and the shallow wells used in NO_3*-N modelling.)*

In **Figure 2** the extent of NO_3-N concentrations at a threshold of 1.0 mg/L (modern day background) is overlaid onto a theoretical map of elevated groundwater quality risk for the Southland region (Wilson and Hughes, 2007). Comparing the extent of NO_3-N concentrations in excess of 1.0 mg/L with the extent of elevated groundwater quality risk shows a good correlation, corroborating the relationship between areas mapped as having an elevated groundwater risk and observed NO_3-N concentrations.

However, some notable exceptions occur, including the extent of elevated NO_3-N in northern Southland beyond the mapped area of elevated groundwater risk. Low NO_3-N also occurs across the northeast corner of the Makarewa groundwater zone and lower portions of the Waihopai groundwater zone. These discrepancies can be explained in terms of an updated assessment of aquifer sensitivity to NO_3-N loadings that predicts elevated NO_3-N across the Five Rivers, Castlerock, and Oreti groundwater zones (see Rissmann, 2011). A similar rationale is used to explain the elevated NO_3-N across the Lower Aparima groundwater zone observed in **Figure 2**. Aquifer sensitivity mapping also predicts low NO_3-N concentrations throughout the lower portions of the Waihopai groundwater zone due to the presence of peat and/or lignite measures which active remove NO_3-N that reaches the groundwater table via the process of denitrification (**Figure 2**).

The lack of an elevated NO_3-N across large portions of the Whitestone and Te Anau groundwater zones should be viewed with caution, primarily because this area is not well represented spatially in terms of sampling points (**Figure 2**). As both of these groundwater zones are mapped as being of high sensitivity to NO_3-N accumulation (Wilson and Hughes, 2007; Rissmann, 2011) it is not unreasonable to expect elevated NO_3-N in excess of modern day background which are not represented in subsequent figures. An example includes a recent NO_3-N investigation survey of the Lower Waiau groundwater zone, which revealed significantly elevated groundwater NO_3-N across an area for which levels were previously unknown (Rissmann, 2012). The discovery of elevated NO_3-N throughout the Lower Waiau may be relevant to the Whitestone and Te Anau groundwater zones given the potentially elevated NO_3-N risk of these areas. However, higher risk does not always mean higher NO_3-N concentrations, with elevated values expected only where elevated contaminant inputs occur to oxidising groundwaters that are young enough to show the impact of recent land use[2].

---

[2]

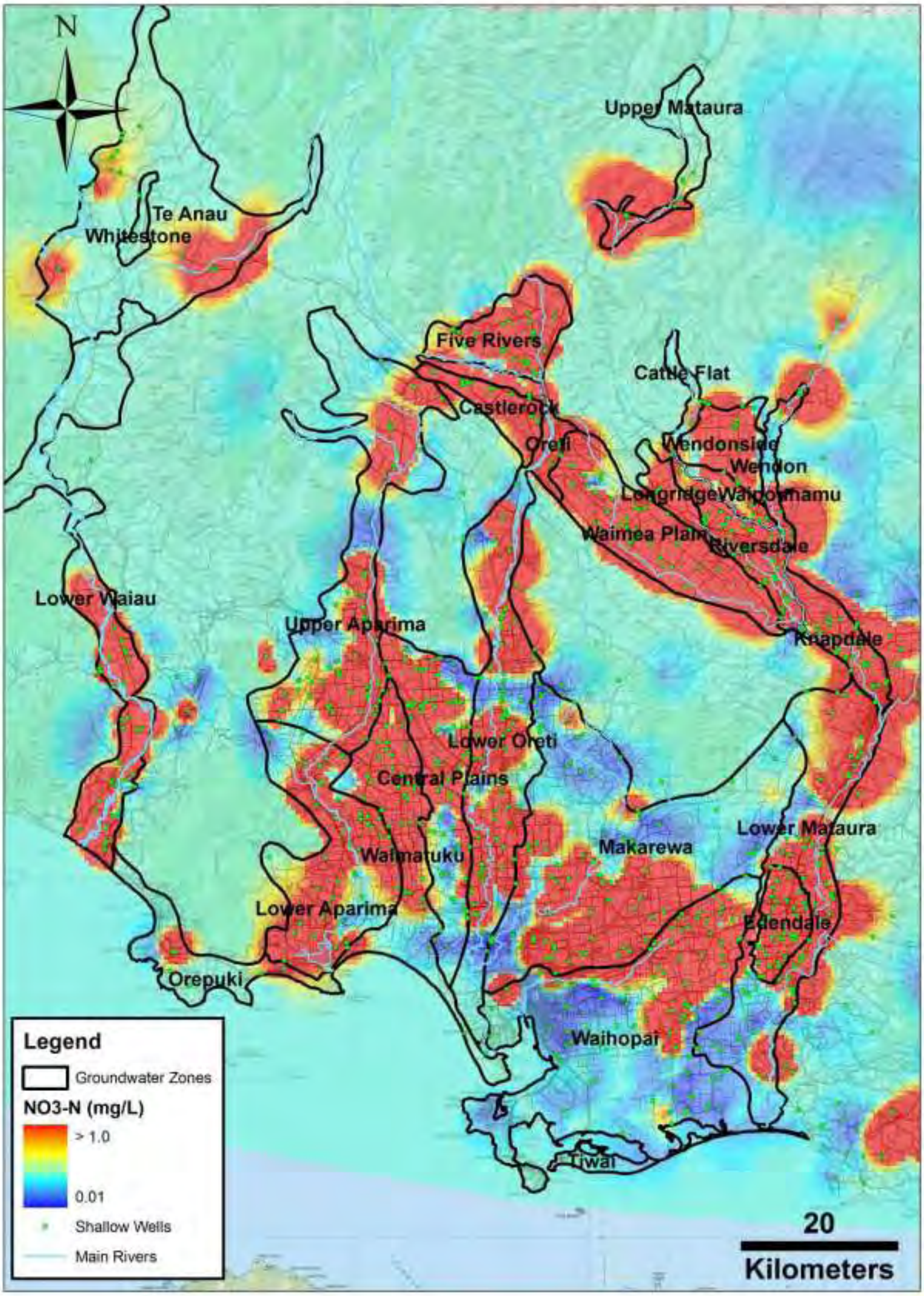

Figure 2: Extent of nitrate (NO_3-N) concentrations in excess of the modern day background threshold of 1.0 mg/L

(Note: Overlaid onto a theoretical map of Elevated Groundwater Quality Risk for the Southland Region (Wilson and Hughes, 2007). Concentrations in excess of 1.0 mg/L occur as red shaded areas.)

The interpolated extent of groundwater NO_3-N in excess of 3.5 mg/L is displayed in **Figure 3**. NO_3-N at concentrations at or above 3.5 mg/L are seldom the result of natural inputs, rather they reflect contamination of groundwater by intensive land use (Daughney et al., 2005, 2012; Morgenstern and Daughney, 2012; Rissmann et al., 2012). From **Figure 3** it is evident, that anthropogenically contaminated groundwater underlies a significant area of the Southland plains (see below for discussion on the extent/area of each NO_3-N class).

Comparison of the extent of NO_3-N concentrations in excess of 3.5 mg/L with the extent of elevated groundwater quality risk (Wilson and Hughes, 2007) shows a strong correlation - again corroborating the relationship between areas mapped as having an elevated groundwater risk and observed NO_3-N concentrations (**Figure 3**). The strong spatial relationships between mapped areas of elevated groundwater quality risk and observed NO_3-N is not surprising given the current intensity of land use, the youthfulness of Southland groundwaters, declining regional ground and surface water quality trends (ES and TAMI, 2010; Liquid Earth, 2011a,b) and the observation that 90 percent of Southland's aquifers are classified as highly sensitive to NO_3-N accumulation (Rissmann, 2011).

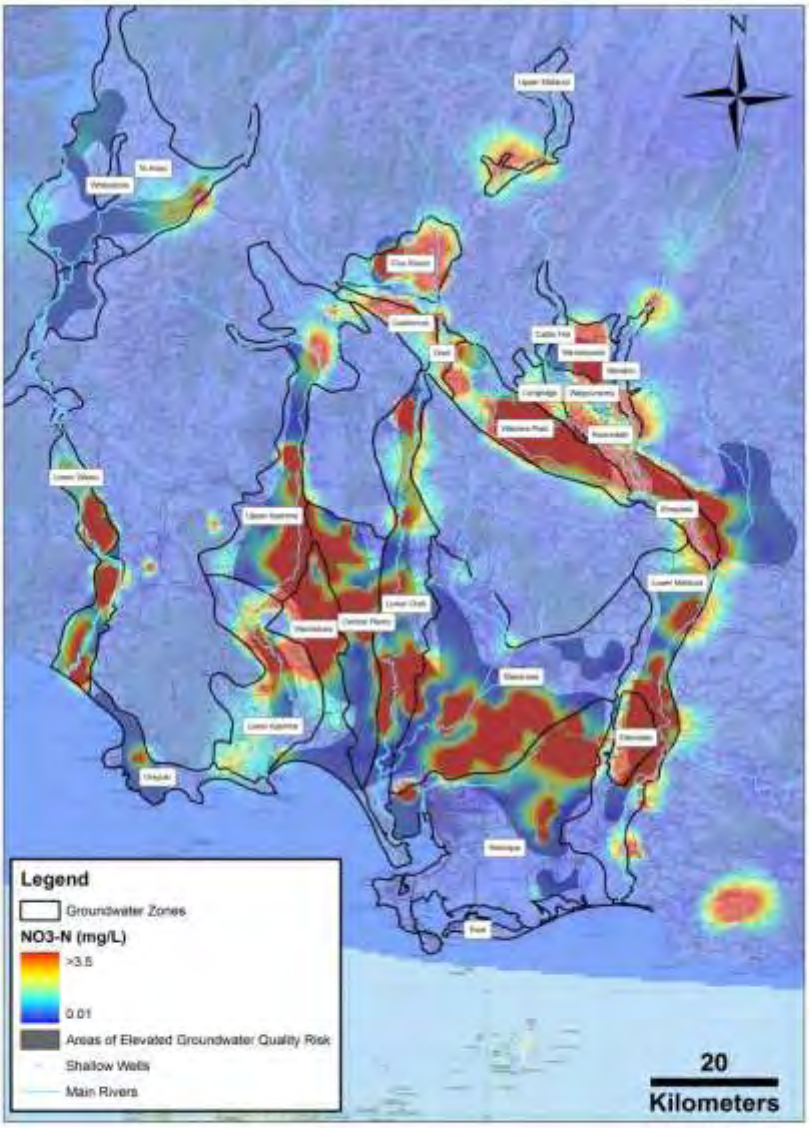

Figure 3: Extent of anthropogenic nitrate (NO_3-N) contamination in Southland groundwater

Note: Overlaid onto a map of Elevated Groundwater Quality Risk (Wilson and Hughes, 2007). Concentrations in excess of 3.5 mg/L occur as red shaded areas.

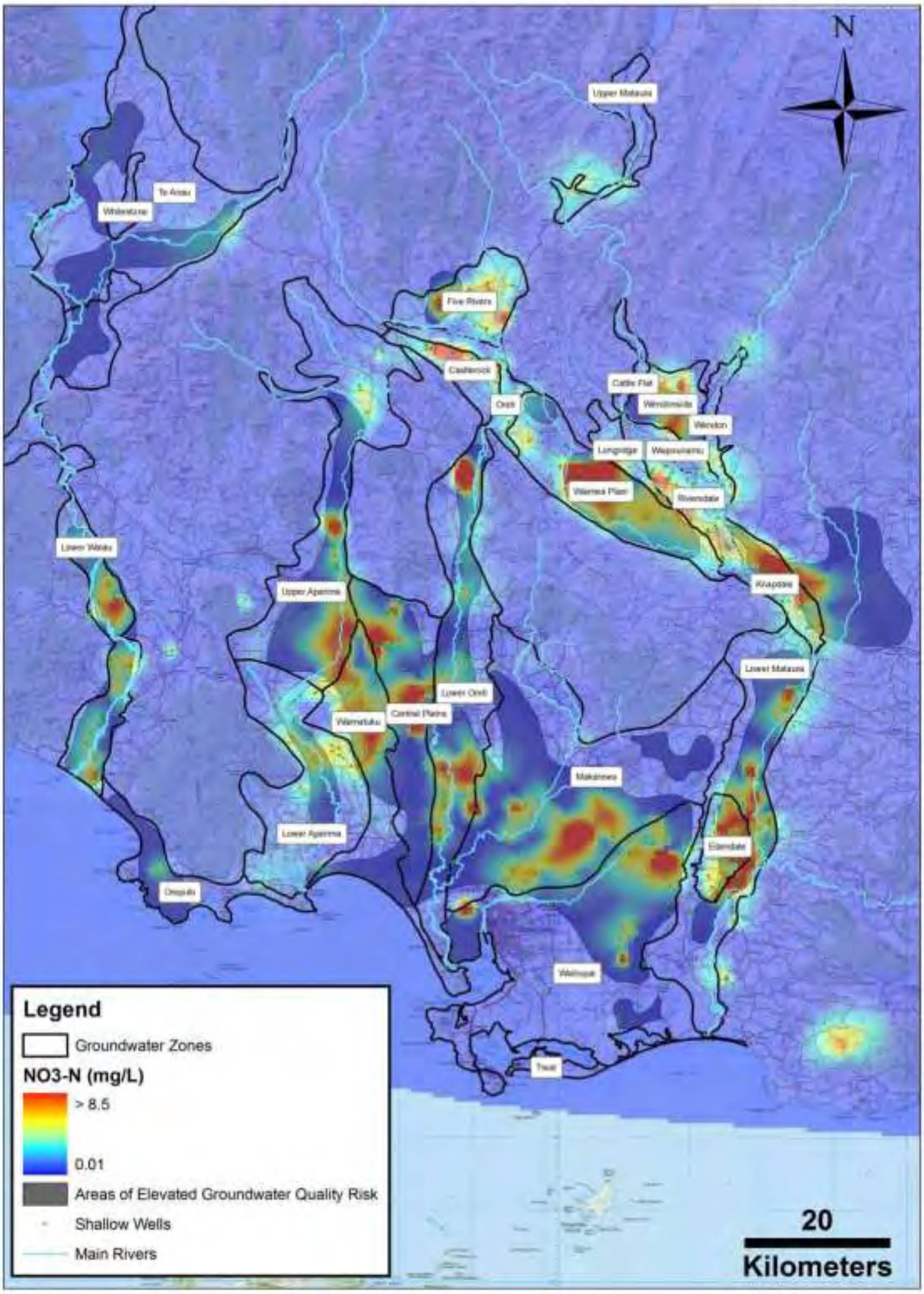

Figure 4: Extent of nitrate (NO_3-N) concentrations relative to 75 percent of the maximum allowable value for drinking water

(Note: Groundwater with NO_3-N concentrations in excess of 8.5 mg/L occur as red shaded areas.)

The interpolated extent of NO_3-N concentrations that currently exceed 75 percent of the Maximum Allowable Value (MAV) are shaded in red in **Figure 4**. NO_3-N concentrations in a number of these known "hotspots" show increasing temporal trends, as well as the expansion in the physical extent of hotspot areas defined by NO_3-N values in excess of 75 percent of MAV (Wilson, 2010; Liquid Earth, 2011a,b).

2.2 Summary of NO_3-N Classes

A summary of the extent of the various NO_3-N classes for Southland are presented in **Figures 5 and 6** along with a table (**Table 2**) quantifying the areal extent of each of the following generalised NO_3-N classes[3]:

1. ***0.01–0.4 mg/L = Pristine, pre-European groundwater NO_3-N concentrations***
   Where 0.01 mg/L is the NO_3-N detection limit and 0.4 the threshold for pre-European groundwater. These groundwaters either pre-date European colonisation and/or occur in remote, undeveloped catchments with little or no history of intensive land use. The NO_3-N trigger values for 95 percent protection of upland and lowland surface water bodies fall within this range (ANZECC, 2000). Strongly reduced groundwater (low oxygen and high iron) may also fall within this category, which causes the extent of this generalised class to be over represented in **Figures 5 and 6**. For this reason, the extent of high cumulative denitrification potential (CDNP) aquifers, after Rissmann (2011), has been included (black hatching) in the aforementioned figures. These aquifers are comprised of peat and/or lignite, which facilitate the removal of leached NO_3-N (see Rissmann, 2011 and Rissmann et al., 2012).

2. ***0.4–1.0 mg/L = Modern day background threshold for Southland groundwater that shows minimal impact of land use***
   This class defines pristine modern day groundwater that occurs in or adjacent to populated regions. Some of the NO_3-N in this groundwater is likely to have originated from diffuse inputs of nitrogen from combustion of fossil fuels or volatilisation of ammonia from fertilisers and/or animal wastes. The NO_3-N trigger values for protection of upland and lowland surface water bodies are lower than but close to this range (ANZECC, 2000). Moderately reduced groundwater may also fall within this category.

3. ***1.0–3.5 mg/L = Evidence of minor to moderate land use impacts, but generally of low magnitude***
   This NO_3-N class typically surrounds regions of highly elevated NO_3-N ("hotspots") or occur across areas that are less impacted by anthropogenic NO_3-N due to dilution, recharge by pristine waters and/or lower intensity land use. Some weakly reducing groundwater may fall within this threshold but overall reducing conditions are considered less important to this NO_3-N class.

4. ***Greater than 3.5 mg/L = moderate to high anthropogenically impacted groundwater where the majority of NO_3-N is derived from human activities at the land surface***
   As NO_3-N concentrations increase beyond 3.5 mg/L the magnitude of human sourced contamination becomes increasingly important. Beyond concentrations of 3.5 mg/L, the most important contributors to elevated NO_3-N include synthetic fertilisers, animal urine and manure, human effluent and industrial wastes. At any one site the elevated NO_3-N concentrations may originate from multiple origins or be dominated by a single source.

5. ***Greater than or equal to 8.5 mg/L = Defined as 75 percent of the MAV (11.3 mg/L) for drinking water in New Zealand***

---

[3] Note, reduced groundwaters (low oxygen and high iron) typically contain low NO_3-N concentrations that fall within categories 1–2 (less for category 3), which causes the extent of these generalised classes to be over represented in **Figures 2-6**. To rectify this issue areas of high cumulative denitrification potential (CDNP) as mapped by Rissmann (2011) are comprised of peat swamps and/or lignite measures and have been included within **Figures 5 and 6** for sake of clarity.

This limit is based on the risk to human health and is at a level where almost all the NO_3-N is derived from anthropogenic sources. This threshold is included within **Figure 5 and 6** to illustrate the extent of groundwater approaching or exceeding the New Zealand Drinking Water Standard (NZDWS).

6. **Greater than or equal to 11.3 mg/L = Groundwater that exceeds the NZDWS threshold for NO_3-N**
   Groundwater that exceeds the NZDWS for NO_3-N is potentially unsafe for human consumption. Again, almost all (greater than 85 precent) the NO_3-N in this class is derived from anthropogenic sources.

2.3 Regional Extent of NO_3-N Classes

The relative extent (area in hectares) of NO_3-N associated with the above categories is defined in **Table 2**. Also presented is the proportion of each category as it pertains to the entire Southland region (3,007,115 ha, including Fiordland National Park) and to the area of Southland's intensively managed groundwater zones (i.e. 592,588 ha). To account for the role of denitrification over low NO_3-N values, the extent of aquifers with a high combined denitrification potential (CDNP) were quantified for each NO_3-N class and subtracted from the total area of each respective class (after Rissmann, 2011) for the entire Southland region and for the managed groundwater zones (**Table 2**). The extent of reducing groundwater, aquifers classified as having a high CDNP is also included in **Figures 5 and 6**.

After taking into account the extent of high CDNP aquifers the extent of pristine, pre-European groundwater is estimated to cover approximately 73 percent (2,160,644 ha) of the Southland region, the majority of which (70 percent) occurs within Fiordland National Park (**Table 2** and **Figure 5)**[4]. Outside of Fiordland, it is likely that the areal extent of this class is over estimated due to the limited spatial extent of data coverage across a number of critical groundwater zones[5]. By subtracting the extent of high CDNP aquifers from the extent of 0.01 – 0.4 mg/L NO_3-N groundwaters returns an areal extent of approximately 25 percent for pristine, pre-European groundwater occurring within the managed groundwater zones.

The NO_3-N class for modern day background, 0.4–1.0 mg/L, defines pristine modern day groundwater that occurs close to, or within, areas of intensified land use (**Figures 5 and 6**). Some of the NO_3-N in this groundwater is likely to have originated from diffuse inputs of nitrogen from combustion of fossil fuels or volatilisation of ammonia from fertilisers and/or animal wastes. This NO_3-N class covers approximately 453,656 ha, or 15.4 percent of the entire Southland region (**Table 2**). Oxidised groundwaters with modern day background NO_3-N concentrations occur across approximately 26 percent (144,236 ha) of Southland's managed groundwater zones. Again, it is likely that the areal extent of this class is over estimated, primarily due to limited data coverage within a number of critical groundwater zones (Te Anau and Whitestone) and the possibility that the total extent of high CDNP aquifers have not been quantified.

The NO_3-N class defined for minor to moderate land use impact (i.e. 1.0–3.5 mg/L) covers 6.9 percent of the entire Southland region (**Table 2**). Within the managed groundwater zones this class accounts for 27 percent (147,081 ha) of the areal extent, which is consistent with the higher density of intensive land use occurring within these zones. From **Figures 5 and 6** it can be seen that the majority (90 percent or more) of this class occurs within the managed groundwater zones. Again, it is likely that the areal extent of this class is under estimated, primarily due to limited data

---

[4] It is important to note the majority of Fiordland has no groundwater data.

[5] Poor data coverage occurs across the Te Anau, Whitestone, Lower Waiau, Upper Mataura, Upper Aparima, Orepuki and Catlins groundwater zones.

coverage within a number of critical groundwater zones and the possibility that the extent of high CDNP aquifers have not been entirely quantified.

The 3.5 – 8.5 mg/L NO_3-N class defines groundwaters displaying NO_3-N values consistent with moderate to high land use impact. This class occurs across approximately 4 percent of the entire Southland region and a much larger 19 percent of the managed groundwater zones. Again, it is likely that the areal extent of this class is over estimated, primarily due to limited data coverage within a number of critical groundwater zones and the possibility that the extent of high CDNP aquifers have not been entirely quantified.

The NO_3-N class defined at greater than 75 percent of the MAV for the NZDWS (i.e. 8.5 mg/L NO_3-N) has an areal extent of 9,288 ha or 0.3 percent of the entire Southland region (**Table 2**). This class defines groundwater containing NO_3-N concentrations approaching the regulatory limit of 11.3 mg/L NO_3-N. The areal extent of this class, within the managed groundwater zones, is approximately five times larger but still only accounts for approximately 2 percent (9,288 ha). Importantly, this class defines 7 discrete "nitrate hotspots," all of which occur within the managed groundwater zones and were previously known to Environment Southland staff. Perhaps not surprisingly, hotspots occur in regions with no evidence for aquifers of high CDNP.

The largest of these "hotspots," the Balfour hotspot, occurs within the Waimea Plains groundwater zone. Other smaller but significant "hotspots" occur within the Edendale, Makarewa, Knapdale, Castlerock, Lower Oreti, Central Plains and Waihopai groundwater zones. Recent work on the Balfour "hotspot" indicates a significant increase in the spatial extent of the aquifer where groundwater NO_3-N exceeds 75 percent of the MAV as well as strong temporal trends of increasing NO_3-N (Wilson, 2010). Similar increasing temporal trends in NO_3-N concentration have been observed for a large number of Southland's groundwater zones (Liquid Earth, 2011a). The origin of NO_3-N within this class is likely a combination of fertiliser and animal derived NO_3-N associated with intensive land use.

The NO_3-N class that exceeds the NZDWS limit of 11.3 mg/L NO_3-N has an areal extent of 0.1 percent of the entire Southland region. The areal extent of this class within the managed groundwater zones is eight times larger, albeit only accounting for 0.8 percent or 4,284 ha of the managed groundwater zones. This limit denotes the NO_3-N threshold beyond which it is considered unsafe to drink groundwater. The origin of NO_3-N within this class is likely an amalgam of fertiliser and human derived NO_3-N associated with intensive land use.

Despite the relatively small area of groundwaters exceeding the 75 percent MAV the potential influence on human health, economic endeavour and ecosystem health extends far beyond the boundaries of these areas. Specifically, hotspots reflect major NO_3-N inputs to regional groundwater systems and are likely responsible for the expansion of the lower NO_3-N classes down gradient - as is supported by the observed increase in the extent of anthropogenic NO_3-N with time (Wilson, 2010; Liquid Earth, 2011a).

If the areas of impacted groundwater classes (i.e., NO_3-N $>$ 1.0 mg/L) are combined approximately 11 percent of the entire Southland region shows impact by human activities. However, within the managed groundwater zones approximately 50 percent or 265,600 ha show evidence of human impact. The large difference in proportional cover of impacted groundwaters is consistent with the majority of intensive land use occurring within managed groundwater zones. It is likely that the extent of groundwaters that show signs of impact by human activities are underestimated due to large spatial data gaps across a number of significant groundwater zones and the possibility that the extent of high CDNP aquifers have not been entirely quantified.

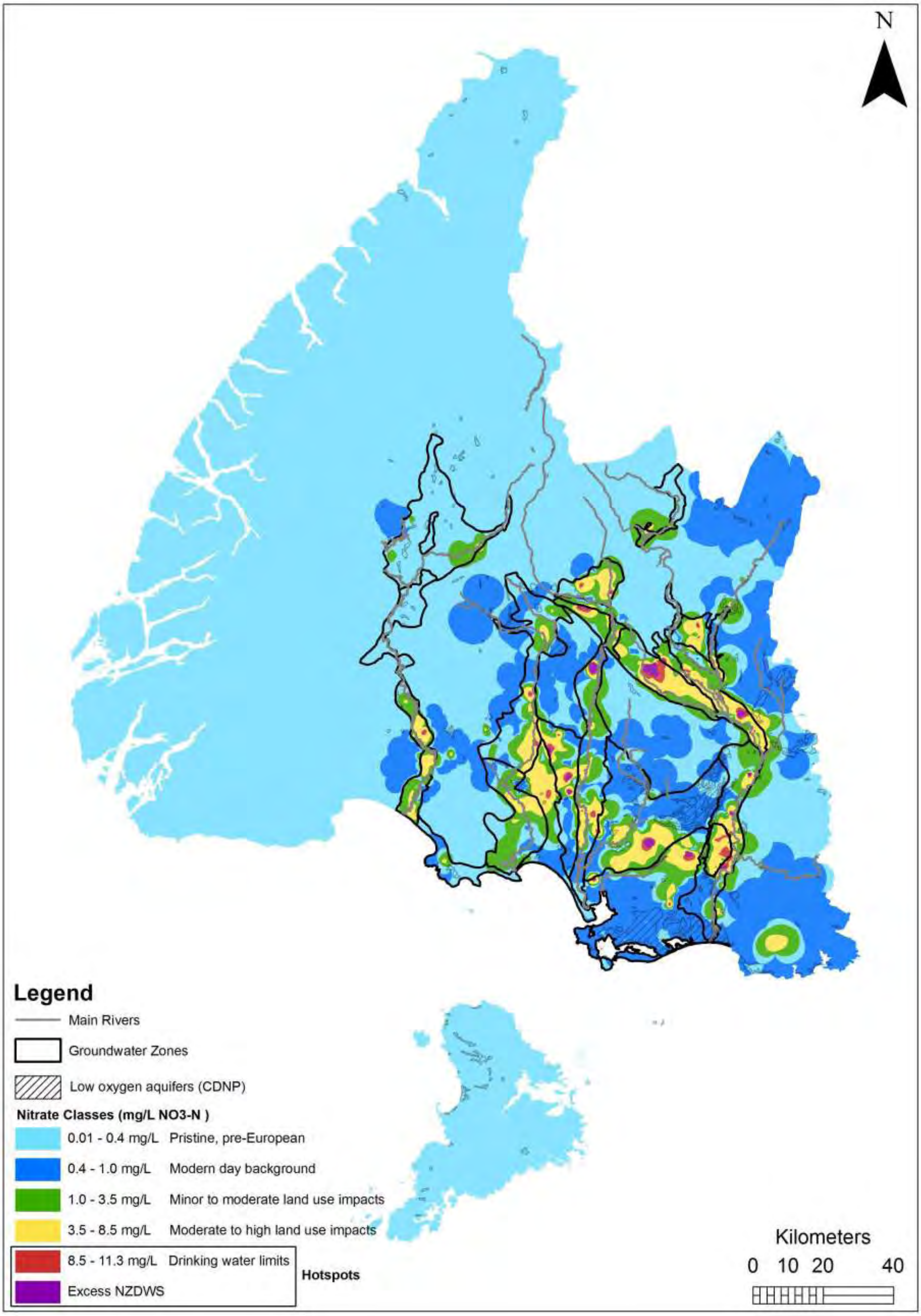

Figure 5: Classed NO$_3$-N map for regional Southland groundwater

(Note: Values in excess of 3.5 reflect human sourced contamination. Red areas define those zones occurring with areas of significant human contamination where NO$_3$-N values exceed the 75 percent MAV for drinking water. Reduced groundwater may also exhibit low NO$_3$-N values and be erroneously defined as pristine. For this reason, the extent of high cumulative denitrification potential (CDNP) aquifers has been included (black hatching).)

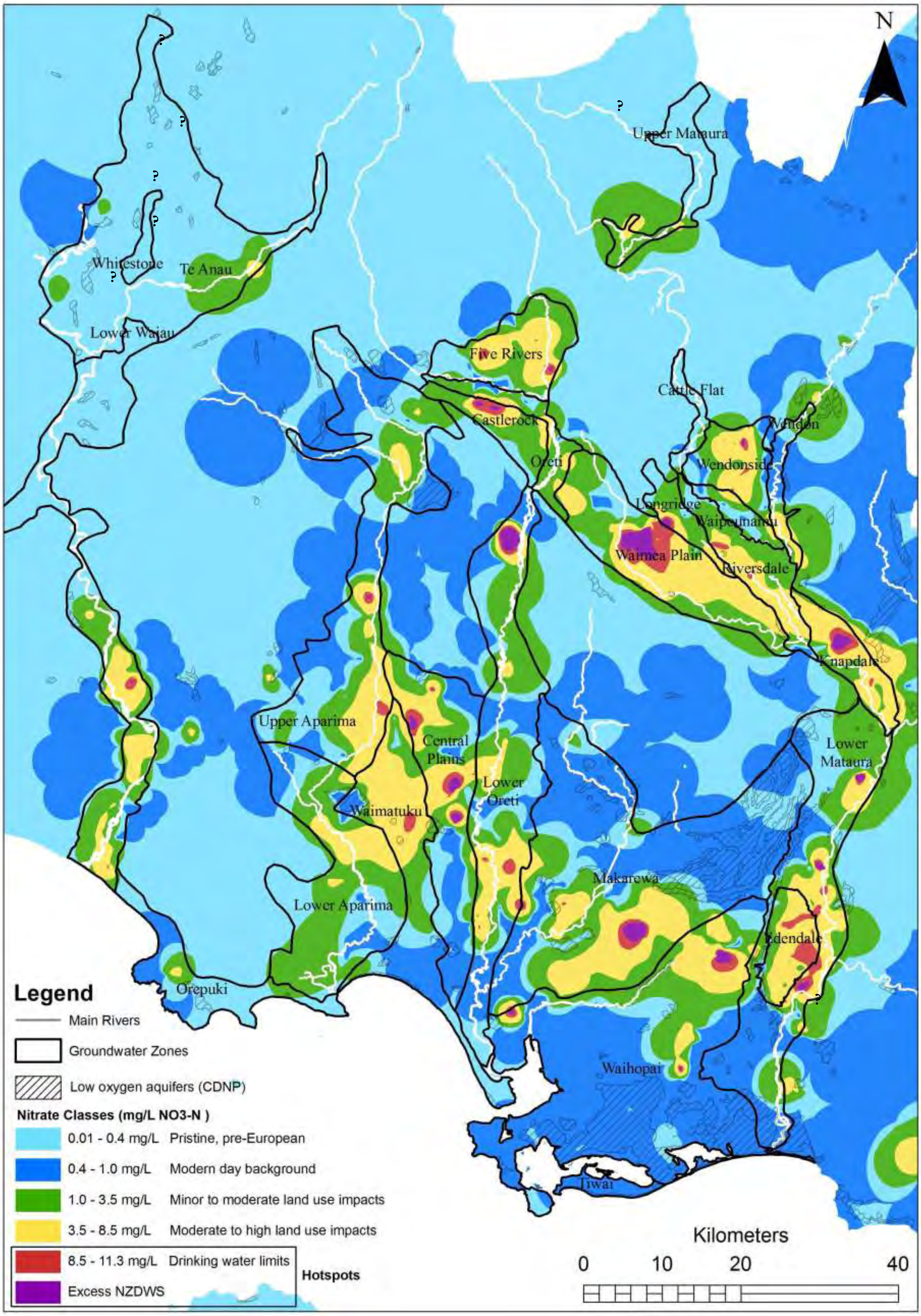

Figure 6: Classed NO$_3$-N map for Southland's managed groundwater zones

(Note: Values in excess of 3.5 reflect human sourced contamination. Red areas define those zones occurring with areas of significant human contamination where NO$_3$-N values exceed the 75 percent MAV for drinking water. Reduced groundwater may also exhibit low NO$_3$-N values and be erroneously defined as pristine. For this reason, the extent of high cumulative denitrification potential (CDNP) aquifers has been included (black hatching).)

Table 2: Breakdown of NO_3-N Classes by area for entire Southland region and managed groundwater zones

Classed NO_3-N	NO_3-N (mg/L)	Area (Ha) by NO_3-N Class for entire Southland Region*	Percentage cover of each class for entire Southland Region**	Area (Ha) by NO_3-N class for all Managed groundwater zones*	Percentage cover of each class for Managed groundwater zones**
Pristine, pre-European	0.01 - 0.4	2,160,644	73.4	137,666	25.1
Modern day background	0.4 - 1.0	453,656	15.4	144,236	26.3
Minor to moderate land use impacts	1.0 - 3.5	202,507	6.9	147,081	26.9
Significant land use impacts	3.5 - 8.5	111,667	3.8	104,944	19.2
75% Maximum Allowable Value (NZDWS)	> 8.5	9,288	0.3	9,288	1.7
Excess NZDWS (>11.3 mg/L)	>11.3	4,284	0.1	4,284	0.8
		2,942,046	100.0	547,498	100.0

*This data is derived from the median NO_3-N values for 2007 – 2012. Areas (ha) for pre-European and modern day background are likely over estimates (see text). Areas (ha) for groundwater impacted by land use are likely under estimates due to gaps in data coverage within specific groundwater zones and the occurrence of reducing groundwater (see text). Where: CDNP = Combined Denitrification Potential; *Area values calculated after subtracting the extent of high CDNP aquifers occurring within each NO_3-N class; **Percentage cover based on extent of each NO_3-N class after area of high CDNP aquifers subtracted.*

3. Summary

In summary, elevated NO_3-N concentrations indicative of contamination of shallow oxidised groundwater by human activities are associated with approximately 11 percent or 327,746 ha of the entire Southland region, including Fiordland National Park. By comparison, elevated NO_3-N concentrations indicative of contamination of groundwater by human activities accounts for approximately 50 percent or 265,600 ha of the managed groundwater zones. The greater percentage of NO_3-N contaminated groundwater occurring within the bounds of the managed groundwater zones is consistent with increased NO_3-N inputs and losses associated with high intensity land use, primarily agriculture, across the alluvial plains of northern and southern Southland.

The extensive nature of NO_3-N contamination of shallow oxidised groundwater within the managed groundwater zones reflects the high sensitivity of the majority of Southland aquifers to NO_3-N losses associated with intensive land use as defined by groundwater quality risk (Wilson and Hughes, 2007) and aquifer sensitivity mapping (Rissmann, 2011). Risk and aquifer sensitivity mapping in conjunction with significant increasing temporal trends in NO_3-N concentrations, across the managed groundwater zones, highlights the high degree of sensitivity of Southland aquifers to the current level of land use intensity. The latter, in conjunction with current temporal trends of increasing NO_3-N for many groundwater zones, suggest there will be ongoing expansion of each of the anthropogenic NO_3-N classes within the managed groundwater zones in the near future.

The occurrence of elevated NO_3-N concentrations in a large proportion of Southland's managed groundwater zones is important in terms of the down-gradient impacts on ecosystems and the future effects on the region's economy. Specifically, elevated groundwater NO_3-N is a significant contributor to the NO_3-N load of Southland's rivers, lakes and estuaries. This is because the majority of Southland's rivers and streams derive a significant component (between 40 – 60 percent) of their flow from groundwater. Therefore, for areas with elevated groundwater NO_3-N it is likely that a significant proportion of the NO_3-N entering a river has originated from groundwater. In this instance, riparian fencing or reduction of overland flow to surface waters cannot reduce that component of dissolved NO_3-N originating from groundwater.

Commonly, NO_3-N concentrations are higher in impacted groundwater than surface waters due to dilution of surface waters by rainfall. As a result, impacted groundwaters can act as a reservoir of high NO_3-N that is released to surfacewater bodies as base flow or direct groundwater seepage. Of our major waterways and coastal estuaries, most show signs of significant eutrophication and a decline in keystone species due to high nutrient inputs. Issues surrounding the degradation of the Waituna Lagoon have recently highlighted the contribution of groundwater to eutrophication of coastal waterways.

4. Acknowledgements

The author of this report gratefully acknowledges a technical review by Dr Chris Daughney, Head of Department: Hydrogeology of GNS Science. Environment Southland technical staffs, Chris Jenkins and Dean Petricevich are thanked for field data collection and processing, data extraction and GIS rendering, respectively. Finally, we thank Brydon Hughes of Liquid Earth Ltd for his review and important comments as to the regional context of this work.

5. References

ANZECC, (2000): *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*. NIWA Client Report: MfE002/22. May 2000.

Daughney, C (2004). *Institute of Geological & Nuclear Sciences. Review of the Environment Southland, baseline groundwater quality monitoring programme*. Client Report 2004/68. Job Number 520W2009.

Daughney, C.J. and Reeves, R. (2005). *Definition of hydrochemical facies for New Zealand's groundwaters using data from the National Groundwater Monitoring Programme*. Journal of Hydrology (NZ) 44: (2): 105 -130.

Daughney, C.J., Raiber, M., Moreau-Fournier, M., Morgenstern, U., van der Raaij, R., (2012). *Use of Hierarchical Cluster Analysis to assess the representativeness of a baseline groundwater quality monitoring network: comparison of New Zealand's national and regional groundwater monitoring programs*. Hydrogeology Journal: Vol. 20, Issue 1, pp 185-200.

ES and TAMI, (2010): *Our Health: Is our water safe to play in, drink and gather kai from?* Part 1 of Southland Water 2010: Report on the State of Southland's Freshwater Environment. Publication number 2010/6 ISBN 0-909043-41-8.

Hughes, B.N., (2011). *Groundwater Quality and Implications for Ecosystem Health*. Unpublished report prepared for Environment Southland by Liquid Earth Limited, January 2011. 19p.

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

Liquid Earth, (2011b): *Groundwater Quality and Implications for Ecosystem Health*. Unpublished report prepared for Environment Southland by Liquid Earth Limited, January 2011. 19p.

McMahon, P.B, Chapelle, F., (2008): *Redox Processes and Water Quality of Selected Principal Aquifer Systems*. Groundwater: doi: 10.1111/j.1745-6584.2007.00385.x.

Morgenstern, U., Daughney, C.J, (2012): *Groundwater age for identification of impacts of land-use intensification and natural hydrochemical evolution on groundwater quality - The National Groundwater Monitoring Programme of New Zealand*. (in review, Journal of Hydrology).

Nicol, S.E., Harvey, M.J., Boyd, I.S., (1997). *Ten years of rainfall chemistry in New Zealand*. Clean Air, vol. 31, No. 1.

NZDWS, (2008): *New Zealand Drinking-Water Standards*. Ministry of Health. Publication WA 675 NEW 2008. New Zealand 2005 (revised 2008).

Panno, S.V., Kelly, W.R., Martinsek, A.T., Hackley, K.C., (2006): *Estimating Background and Threshold Nitrate Concentrations Using Probability Graphs*. Journal of Groundwater: Vol. 44, No. 5.

Reimann, C., Filzmoser, P., Garrett, RG. (2005): *Background and threshold: critical comparison of methods of determination*. Science of the Total Environment. 15; 346(1-3):1-16.

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.

Rissmann, C.F., (2011): *Regional Mapping of Groundwater Denitrification Potential and Aquifer Sensitivity - Technical Report.* Environment Southland, Invercargill. Publication No. 2011-12.

Rissmann, C., Wilson, K L., and Hughes, B. N., (2012): *Waituna Catchment Groundwater Resource Technical Report.* Environment Southland publication number 2012-04, Invercargill. 103 p.

Rissmann, C., (2012): *Groundwater quality results for Lower Waiau nitrate survey.* Lower Waiau Groundwater Technical Report. Environment Southland, Invercargill.

Sanford RF, Pierson CT, Crovelli RA (1993): *An objective replacement method for censored geochemical data*. Math Geol 25:59–80.

UNEP, (2012). *Water Quality: The Impact of Eutrophication Lakes and Reservoirs vol. 3*. United Nations Environment Program.

Wilson, K (2010): *Groundwater Report on the Balfour Groundwater Quality Study*. Published by Environment Southland.

Appendix 1: Methodology

Groundwater nitrate nitrogen (NO_3-N) data for 710 wells in Environment Southland's groundwater database were extracted from 2007 to present (June 2012). For wells having more than one NO_3-N measurement, the median NO_3-N value was computed. Censored data, those median NO_3-N concentrations that fall below the NO_3-N detection limit of 0.01 mg/L, were transformed using the recommendations of Sanford et al., (1993). Specifically, where a small proportion of "less than" substitutions occur a simple-substitution replacement factor of 0.55 is recommended:

$$R_{CV} = DL * 0.55$$

where R_{cv} is the revaluated censored value and DL is the detection limit for the analytical method.

From **Figure A1** it is evident that the greatest range and highest maximum NO_3-N concentrations occur in shallow wells less than 10 m deep. With increasing depth, NO_3-N concentrations exhibit a general decline, which is a common observation of groundwater systems around the world (McMahon and Chapelle, 2008). The tendency for deep wells to have low NO_3-N concentrations is primarily related to low oxygen (reducing) conditions within deep water bearing layers (McMahon and Chapelle, 2008), although deeper groundwater also tends to have lower NO_3-N concentrations due to the presence of low permeability layers that limit vertical percolation of surficial contaminants to depth.

Therefore, due to the tendency for NO_3-N to be actively removed under low oxygen conditions the NO_3-N data set was further reduced to a subset of 584 wells of a depth of less than 40 m below ground level (m bgl) (**Figure A1**). A depth of 40 m was selected in an attempt to strike a balance between having a sufficient number of wells for mapping and the likelihood that the NO_3-N concentrations of deep wells are not representative of land use inputs. Inherent in the selection of a 40 m depth cut-off is a degree of conservatism due to the aforementioned tendency for deeper wells to remove NO_3-N under low oxygen conditions.

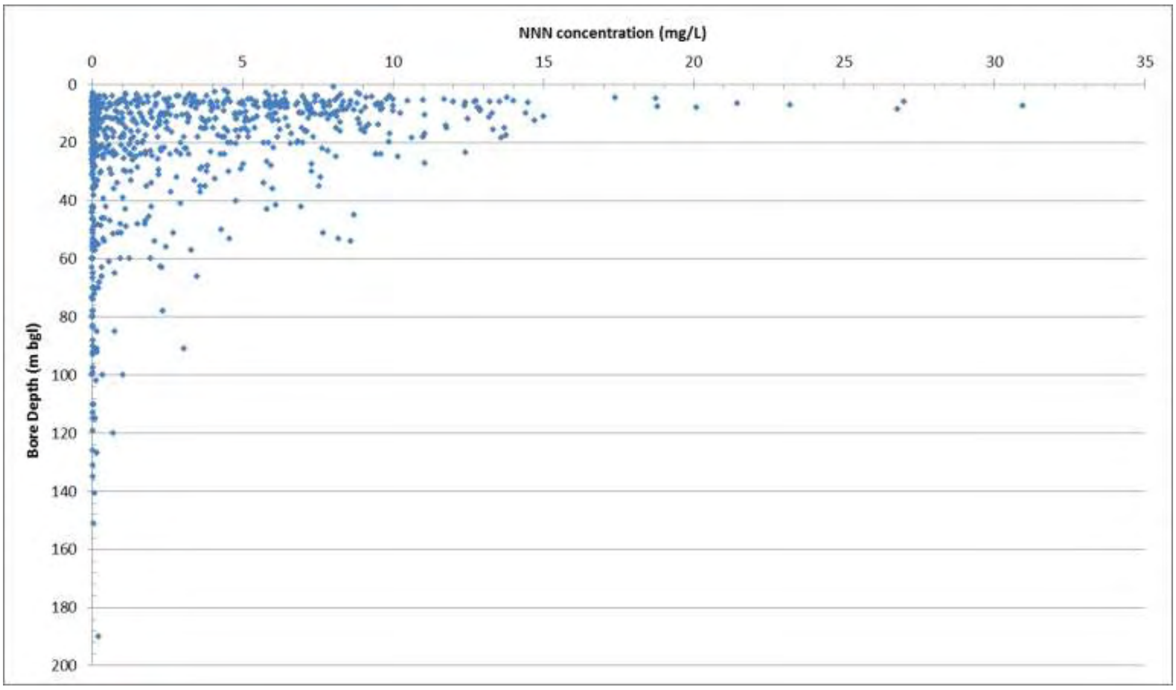

Figure A1: Relationship of well depth in meters below ground level and median NO_3-N concentration for Southland wells (2007–2012 data)

The remaining 584 median NO_3-N values computed for the last five years were then contoured using natural neighbour spatial analysis. Natural neighbour spatial analysis finds the closest subset of input samples to a query point and applies weights to them based on the increasing distance from the query point to interpolate new values where no sampling point has been measured. However, the limitation of any interpolation method is that it is only a representation (model) of the true natural spatial variance. How true a representation is of a natural phenomenon is largely dependent upon the quality of the input data, especially spatial coverage.

In Southland, as with other regions, there are large gaps in the spatial coverage of shallow groundwater wells due primarily to the presence of mountain ranges, specific rock or aquifer types[6] and limited population densities. In more intensively farmed regions, the converse is true with high densities of wells resulting in dense clusters of wells. Furthermore, many aquifer systems are highly heterogeneous in terms of permeability and relative recharge contribution, which can also strongly influence NO_3-N concentration.

Therefore, in order to constrain the spatial variability in NO_3-N concentrations across Southland, concentrations were assigned to specific locations based on known patterns and behaviour of oxidisable nitrogen (NO_3-N), specifically:

1. areas mapped as peat swamps or surficial lignite deposits were assigned a low (0.2 mg/L) NO_3-N groundwater concentration; and

2. mountainous and/or remote areas (National and World Heritage Parks) were assigned a NO_3-N concentration of 0.4 mg/L NO_3-N.

NO_3-N values were not assigned to any areas that fall outside of these criteria.

---

[6] Certain rock types or aquifer materials may hinder successful well drilling or contain groundwaters that are deemed unsuitable for use.

Assigning low NO_3-N values to wells terminating within peat deposits and/or lignite measures is justified by the outcomes of cross-referencing ("intersecting") aquifer composition (after Rissmann, 2011) with known NO_3-N and Total Ammoniacal Nitrogen (TAM) concentrations for Southland wells (**Table A1**)[7].

Table A1: Relationship between shallow (<40 m bgl) aquifer compsotion and NO_3-N and TAM concentrations for Southland

Aquifer CDNP	Species	Valid Cases	Mean	Median	Standard Deviation
High	NNN	86	1.36	0.20	2.10
	TAM	86	0.17	0.10	0.37
Low	NNN	466	3.95	2.92	4.47
	TAM	466	0.07	0.01	0.53

Where CDNP = Cumulative Denitrification Potential; NNN = Nitrate, Nitrite Nitrogen;
TAM = Total Ammoniacal Nitrogen; units in mg/L

The outcome of the intersection supports the general observation that:

(i) shallow (< 40 m bgl) wells terminating in materials classified as having a high combined denitrification potential (CDNP) typically exhibit low (median of 0.2 mg/L) NO_3-N concentrations; whereas

(ii) wells terminating in low CDNP aquifers contain elevated NO_3-N concentrations (a median NO_3-N value approximately 15 times greater than high CDNP aquifers)[8]. This general spatial relationship reflects the relative availability of organic carbon for microbially mediated redox reactions. Specifically, where organic carbon concentrations are low, NO_3-N is able to accumulate to higher concentrations and where organic carbon concentrations are high, NO_3-N is removed is removed via the process of denitrification (see Rissmann, 2011; Rissmann et al., 2012).

Justification for a NO_3-N concentration of 0.4 mg/L for mountainous areas throughout Southland is based on a number of sources. Firstly, the median NO_3-N concentration for shallow groundwater occurring within large forested catchments (n = 54) throughout Southland, including National and World Heritage Parks, is equal to 0.4 mg/L (Rissmann et al., 2011). A NO_3-N value of 0.4 mg/L has also been reported as the natural, "pre-European" background[9] concentration of NO_3-N for New Zealand groundwater (Morgenstern and Daughney, 2012). Secondly, natural snowmelt collected from across Southland has a median inorganic nitrogen concentration of 0.04 mg/L that is similar to median values reported for pristine rainfall throughout New Zealand (Nicol et al., 1997). Relevant here, is the large component of rainfall recharge in mountainous areas as well as the absence of intensive land use, or the generally low intensity of land use activities, in high country catchments under which NO_3-N values are not expected to reach high levels.

---

[7] Wells and aquifer composition (after Rissmann, 2011) were intersected using the Spatial Analyst tool in ArcGIS.

[8] The converse of NO_3-N was evident for TAM (i.e., higher TAM concentration in high CDNP aquifer materials and *vice versa*).

[9] Natural background refers to NO_3-N concentrations in groundwaters that existed prior to human intensification.

Following assignment of NO_3-N concentrations to the domains outlined above, both data sets were combined and NO_3-N concentrations for Southland were contoured (interpolated) using the natural neighbour spatial analysis tool in ArcGIS. The spatial distribution of NO_3-N was then modelled at different thresholds, as outlined above, and contrast with groundwater quality risk maps.