UNIVERSITY OF SOUTHERN QUEENSLAND

Exploring Changes in Nitrate Contamination in the Coastal and Hautere Zone Aquifers, Wellington, New Zealand

A Dissertation Submitted by

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Abstract

Fifteen years of groundwater quality monitoring in the Kapiti Coast by the local authority in Wellington, New Zealand, has identified an area of elevated nitrate concentrations in the Te Horo area, with some monitoring bores testing for concentrations above 5 mg/L. However, recent analysis seems to indicate that contaminant levels have decreased from what was previously recorded, although still remaining elevated.

The purpose of this study was to investigate if changes in nitrate concentrations over time were significant and, if so, determine which factors have contributed to these changes.

Initial temporal trend analysis indicated that nitrate concentrations since 1993 have decreased in the majority of monitoring bores. Tobit regression analysis was subsequently undertaken using several land use, land cover, soil type, climate and chemical explanatory variables. Results indicated that beef cattle farming, fruit growing, settlements and lifestyle blocks were associated with increased nitrate concentrations. Groundwaters higher in dissolved oxygen which underlie fine sandy loam soils (which are highly permeable soils) were also identified as been susceptible to higher nitrate concentrations.

Analysis of nitrate plume migration also indicated that, although concentrations appeared to have reduced during the fifteen year monitoring period, the plume could be spreading laterally in an east-west direction.

It was ultimately determined that the temporal decrease in concentrations is best explained by improved land use practices as physical characteristics and land cover overlying groundwater had not changed substantially and thereby explaining the decreasing trend in nitrate concentrations.

Certification of Dissertation

I certify that the ideas, experimental work, results, analyses, software and conclusions reported in this dissertation are entirely my own effort, except where otherwise acknowledged. I also certify that the work is original and has not been previously submitted for any other award, except where otherwise acknowledged.

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Deepthi Jayatha Dias-Wanigasekera

Endorsement

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Dr John M. Worden

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Dr Gregory De Costa

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As I type these acknowledgements, the last page of my thesis, I cannot help but feel that I could not have reached this point without my parents, Beatrice and Swithen. I would like to thank them for their undying support, patience, and much needed sternness. I would also like to thank my brother, Richard, for his playful support. I feel blessed to have such a wonderful family.

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1 Introduction

1.1 Background

The Resource Management Act (RMA) 1991 is the principal legislation governing the allocation and use of New Zealand's natural resources. Under the provisions of the RMA, regional councils are responsible for the management of groundwater resources. In Wellington, a baseline groundwater quality monitoring network in the regions of Hutt Valley and Kapiti Coast was first set up in 1993 by the Greater Wellington Regional Council (GWRC) (Hughes 1995). Since then, the network has expanded significantly and quarterly monitoring of what is now known as the Groundwater State of the Environment (GWSoE) Network is conducted in order to establish current and long term trends in water quality.

Continued State of The Environment (SoE) monitoring and has resulted in the identification of the Coastal and Hautere groundwater zones of the Kapiti Coast district in Wellington as areas of persistent nitrate contamination (Hughes 1995, 1996, 1997; Jones & Baker 2005). Sampling from a number of wells showed elevated NO_3-N (future reference to "nitrate" concentrations in this report will be in terms of NO_3-N in mgL^{-1}) levels close to or exceeding the Maximum Acceptable Value (MAV) for drinking water of $11.3mgL^{-1}$. The MAV is a standard of drinking water outlined in the Drinking Water Standards for New Zealand (Ministry of Health 2008).

Recent groundwater quality sampling of the area indicates reduced nitrate levels at some sampling sites (Tidswell 2009). However, no detailed investigation has been undertaken in order to identify reasons behind the changes in nitrate concentrations over time. This will require temporal trend analyses of groundwater chemical data, analyses of catchment changes (such as land use change, changes in rainfall, climate etc.) and an understanding of how the contaminant is transported within the aquifer system.

This study will collate datasets for the above variables from different sources, and in conjunction with current software tools (such as ArcGIS Desktop 10), provide a more holistic analysis of changes in nitrate concentrations over time.

1.2 Literature Review

The existence of high nitrate concentrations in groundwaters is a worldwide issue. Above background levels of nitrate concentrations in groundwater is an indicator of system alteration due to human influence (Ministry for the Environment 2007a). This phenomenon has largely been attributed to intensive land use practices such as agriculture, horticulture and excess fertilizer application (Behnke 1975; Gulis, Czompolyova & Cerhan 2002; Hudak 2000).

Consumption of drinking water containing excess nitrate has also been linked with a number of detrimental health effects such as methemoglobinaemia (commonly known as blue baby disease), non-Hodgkin's lymphoma and gastric cancer (Gelberg et al. 1999; Walton 1951; Ward et al. 1994). As a result of these findings and a growing demand for groundwater resources, a Maximum Acceptable Value (MAV) of 50mg/L (11.3mg/L in NO_3-N) for nitrate concentrations in drinking water was determined by the World Health Organisation 2002 (Benson et al. 2007). This standard is adopted for New Zealand's MAV for NO_3-N (Ministry of Health 2008).

Nitrate is one of the most reactive and mobile substances in water bodies and concentrations typically display seasonal, annual and longer term fluctuations within the aquifer. The amount of nitrate initially entering a groundwater system is dependent on the spatial (diffuse and point sources) and temporal variability of nitrate sources on the land surface (Chen et al. 2007; Molénat & Gascuel-Odoux 2002; Stewart et al. 2011)

Chen et al. (2007) used chemical isotope methods in order to attribute spatial distributions of nitrate contamination in groundwaters of the Yellow River Delta, China, to surface nitrate loading originating from land use and irrigation in combination with local geomorphology. Similarly, Stewart et al. (2011) used nitrate isotope dating and tritium dating to assess nitrate sources in groundwater and groundwater age of alluvium aquifers of the Waimea Plains in Nelson, New Zealand.

Their investigation revealed that diffuse nitrate contaminant plumes were related to widespread inorganic fertilizer application and nitrate input originating from animal wastes within a recharge area. These diffuse nitrate sources were attributed to market gardening land use practices which covered the surface areal extent of the contaminated site. They also discovered a narrow, spatially restricted band of nitrate contamination which varied in concentration over time. Using residence time data, nitrate isotope data, and historical land use records, the source of nitrate was determined as animal wastes resulting from a piggery. The temporal decrease of this narrow nitrate contamination plume was quite clearly related to the closure of the piggery. This is an example of a point source contaminating a very specific area of the aquifer.

The above studies clearly reflect the relationship between surface nitrate application and their spatial distribution in groundwater. In addition to these specific examples, internationally, similar patterns of diffuse nitrate contamination have been linked to agricultural nitrogen loading on the land (Aelion & Conte 2004; Gurdak & Qi 2012; Haslauer et al. 2004; Houben 2001; Howden et al. 2011) . These land use and land cover factors are generally termed source factors (Gurdak & Qi 2012). According to Daughney and Reeves (2005), concentrations exceeding 1.6 mg/L of NO_3-N in New Zealand aquifers are reflective of human interference.

Natural sources of nitrates in groundwater include organic nitrogen in plant and decomposing material, nitrification of atmospheric nitrogen and soil mineralization (Stewart et al. 2011). The baseline concentration of nitrate in New Zealand groundwater sources is around 0.7 mg/L of NO_3-N (Daughney & Reeves 2005). Figure 1.1 shows the potential transformation paths of nitrogen once it enters the vadoze zone.

In addition to the availability of excess nitrogen input to land surfaces, there are many physical and chemical properties of aquifers and surrounding catchments which influence nitrate transport and attenuation in groundwater. A recent, nationwide analysis of principle aquifers in the United States revealed that the presence or absence of dissolved oxygen was the most important control on the concentrations of nitrate in groundwater. This was classified as an attenuation factor. The study also revealed that nitrate sources (i.e. land use types) were the second most important factors controlling nitrate concentrations in aquifers (Gurdak & Qi 2012).

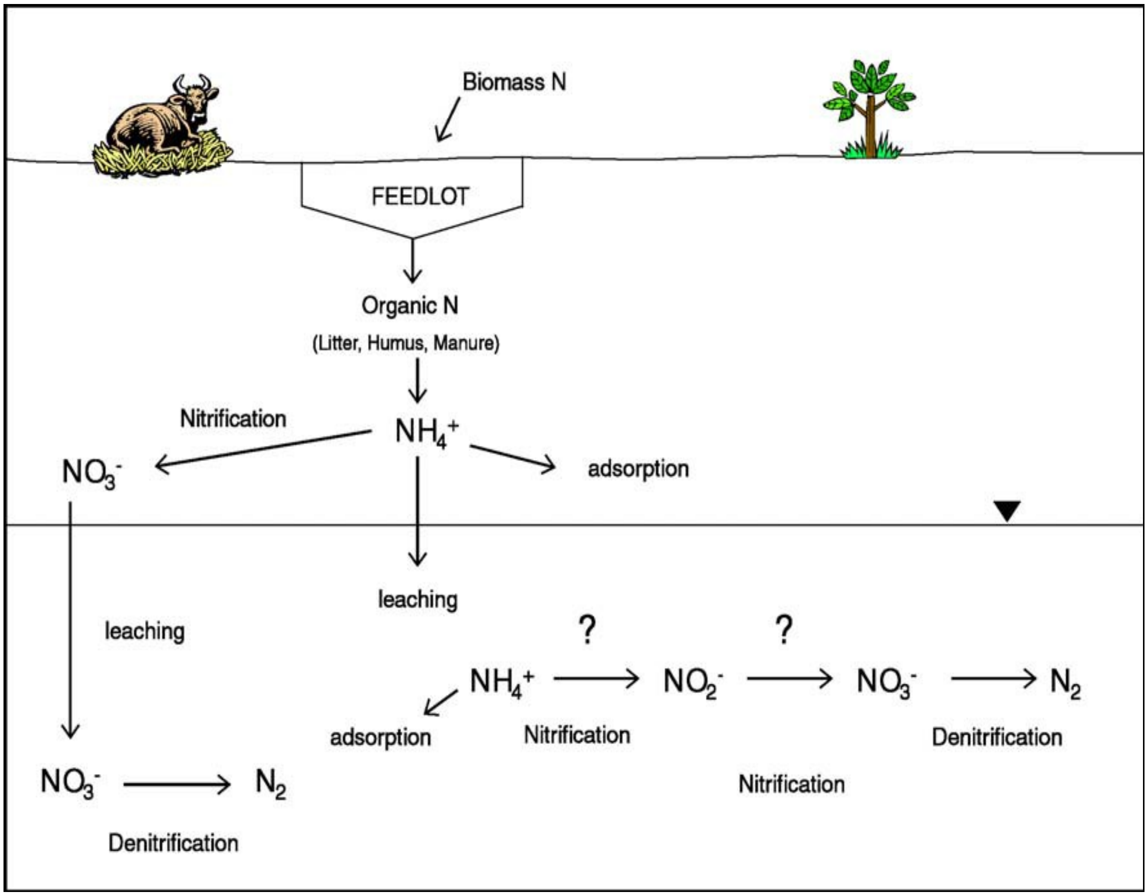

Figure 1.1: Diagram illustrating possible transformation paths of organic nitrogen as it enters the subsurface (Lee et al. 2006)

The presence of dissolved oxygen dictates nitrogen chemistry in aquifers. For example, when aqueous ammonium first enters the groundwater system, it can be immobilized and adsorbed to negatively charged soil sediments (Lee et al. 2006). Alternatively, in the presence of ample concentrations of dissolved oxygen, ammonia is rapidly chemically oxidized to nitrite by autotrophic ammonia oxidizing bacteria as shown in figure 1.1 (Lee et al. 2006; Ministry for the Environment 2007a; Reay, Gallagher & Simmons

1992; Speiran 1996). This is the first step in the nitrification process. As Nitrite travels to the saturated zone below the water table, it is further oxidized to nitrate by nitrite-oxidizing bacteria (Lee et al. 2006). Nitrate is usually the end product of the nitrification process (Behnke 1975).

When water initially percolates down through the soil vadoze zone, it contains high percentages of dissolved oxygen (Chen & Liu 2003), however, as the water enters the subsurface, and travels through the unsaturated zone into the saturated zone, dissolved oxygen is gradually depleted by microbial consumption, chemical reduction and reactions with organic matter (Chen & Liu 2003). Chen & Liu (2003) noted that dissolved oxygen concentrations decrease further along flow paths. Groundwater in the study site flowed in an East to West direction, and groundwater displayed an oxic-anoxic gradient in the East-West direction.

When dissolved oxygen is limited, nitrate already present in the aquifer is chemically reduced, or denitrified, to ammonia or nitrogen gas. For example, total dissolved solids (TDS) can react with dissolved oxygen, depleting the oxygen available for nitrification (Chen & Liu 2003). Fine grained soils and aquifer material contain more TDS. Therefore aquifers with fine grained material tend to have low nitrate concentrations (Lindsey, Chesapeake Bay Program & Geological Survey 2003). Denitrification is a process which is used in the energy production of aerobic bacteria. Aerobic bacteria obtain energy from oxidizing dissolved organic carbon (electron donor) with the electron acceptor which provides the most energy. This tends to be oxygen. The electron acceptor which provides most energy is consumed preferentially until depletion, and in the presence of more dissolved carbon, other electron acceptors are subsequently consumed in this process. In the absence of dissolved oxygen facultative anaerobes (bacteria which can exist with or without oxygen) use the second most energetically favourable electron acceptor, nitrate, in this reaction (Rivett et al. 2008).

Some studies have found that lithology and groundwater residence times also play a large role in the rate of denitrification. Rates of denitrification tend to be greater in watersheds underlain by unconsolidated rock types such as sandstone and shale (Lindsey, Chesapeake Bay Program & Geological Survey 2003) and denitrification is more significant in aquifers with residence times greater than 20 years (Lindsey, Chesapeake Bay Program & Geological Survey 2003; McMahon et al. 2008).

A study conducted in a small agricultural area in Korea (Kaown, Koh & Lee 2009) found that shallow groundwaters underlying the western and eastern parts of the study area displayed different concentrations in nitrate. The western side of the study site was a recharge zone which received more precipitation than the eastern side. In addition to this, agricultural land use (and subsequently a larger source of nitrates) was more predominant on the western side. The researchers also conducted isotope analysis to determine groundwater age in the region, and it was determined that residence times in the western low lands were lower (around 15 years) than those of the eastern slopes (around 30 years). They were therefore able to determine that land use, recharge rate and groundwater residence times were important factors in nitrate distribution within shallow aquifers. Similar controls on nitrate distribution in shallow groundwater have been found in other studies (Böhlke & Denver 1995; Puckett & Cowdery 2002).

Reporting of groundwater quality is routinely conducted in New Zealand as a national requirement, and regional groundwater quality studies have found similar patterns of nitrate contamination throughout New Zealand. Morgenstern and Daughney (2012) combined the national groundwater dataset in order to undertake a combined groundwater dating and chemical parameter analysis. Their results show a clear demarcation of nitrate concentrations associated with pre-colonial, colonial low intensity agriculture, and intense agriculture land use eras.

Their study found that very low nitrate concentrations (below 1.6 mg/L) were correlated with groundwaters older than 133 years, which is indicative of pristine, pre agricultural New Zealand groundwater. There was also a clear transition from pristine, old groundwater to younger (<133 years) groundwater with elevated nitrate concentrations (1.6 mg/L to 2.5 mg/L). This groundwater age group reflected the rise of agriculture in

New Zealand due to increased export of meat products resulting from the invention of refrigeration in the 1880's (Morgenstern & Daughney 2012).

A further demarcation of groundwater age and nitrate contamination occurs for groundwater less than 55 years old. The majority of samples from this category displayed nitrate concentrations greater than 2.5 mg/L, which, in the context of this particular study, was considered to be elevated and indicative of significant anthropogenic impact (Morgenstern & Daughney 2012). This reflects the post World War Two growth of agriculture and market gardening in New Zealand.

Many regional New Zealand groundwater quality studies, especially in catchments where agricultural and horticultural activities have been the predominant land use activity, display elevated nitrate concentrations indicative of this post World War Two era. Widespread nitrate contamination of shallow unconfined and semi-confined aquifers in the Canterbury plains has been documented (Adams & Pattinson 1985; Burden 1984; Haynes & Francis 1990). Sources of nitrate contamination have been attributed to pastoral and arable agricultural activities, especially in combination with irrigation (Burden 1984). Point source contaminants from septic tanks and poultry farms have also been documented in the region (Burden 1984).

In the Waimea Plains of Nelson, nitrate contamination of shallow groundwater became evident in the 1960's (Stanton & Martin 1975). The contamination appeared to be restricted to a narrow North-South band, but further study identified a broader zone of contamination surrounding the narrow area, which reflected the widespread market gardening in the area (Stevens 2005). Groundwater age and isotope analyses undertaken in more recent studies have attributed these patterns to point source and diffuse land use activities, specifically the opening of a piggery and the onset of market gardening from the 1940's (Stewart et al. 2011).

Table 1.1 below provides a list of some of the main New Zealand groundwater studies referred to in this chapter.

Table 1.1: List of main groundwater studies by region

Region	Title/Author/Year
Canterbury	• Chemical zonation in groundwater of the Central Plains, Canterbury (Burden 1984) • Nitrate losses under a legume-based crop rotation in central Canterbury, New Zealand (Adams & Pattinson 1985) • Effects of mixed cropping farming systems on changes in soil properties on the Canterbury Plains (Haynes & Francis 1990)
Nelson	• Nitrate levels in subsurface waters of the Waimea Plains, Nelson (Stanton & Martin 1975) • 2005 Waimea plains groundwater nitrate survey (Stevens 2005) • Nitrate sources and residence times of groundwater in the Waimea Plains, Nelson (Stewart et al. 2011)
Wellington	• Groundwater resources of the Waitohu, Otaki and Mangaone. Wellington, Manawatu Catchment Board and Regional Water Group (Kampman & Caldwell 1985) • Hydrology of the Kapiti Coast. Wellington, New Zealand (Hydrological Services Group 1994) • The Hydrology and Hydraulic Characteristics of the Unconfined Aquifers of the Otaki-Te Horo Area (Cussins 1994) • Baseline groundwater quality monitoring, Hutt Valley and Kapiti Coast (Hughes 1995, 1996) • Nitrate contamination of groundwater on the Kapiti Coast, December 1996 (Hughes 1997) • Groundwater monitoring technical report (Jones & Baker 2005) • Kapiti Coast groundwater quality investigation, 2008 (Tidswell 2009)
National	• Definition of Hydrochemical Facies in the New Zealand National Groundwater Monitoring Programme (Daughney & Reeves 2005) • Groundwater Quality in New Zealand : State and Trends 1995-2006 (Ministry for the Environment 2007a) • Environment New Zealand 2007 (Ministry for the Environment 2007b) • Groundwater age for identification of baseline

	groundwater quality and impacts of land-use intensification – The National Groundwater Monitoring Programme of New Zealand (Morgenstern & Daughney 2012)

Site specific studies of the Kapiti Coast groundwater system have been conducted in the past. The first detailed investigations occurred in the 1980's when scientists were commissioned to provide detailed hydrogeological data on behalf of Kapiti Coast landowners. Kampman and Caldwell (1985) summarized these findings. In the context of the study area, they were able to identify three aquifer systems. The presence of high nitrate concentrations in the shallowest aquifer became apparent during this time. However, their only interest in nitrate concentrations was to aid in identification and classification of aquifer layers. Detailed logs of the investigation bores and hydrogeological calculations have since been published (Greater Wellington Regional Council 2003).

Brydon Hughes (1996) investigated the potential reasons behind high nitrate levels in the Kapiti Coast based on the annual baseline groundwater monitoring results. This also coincided with the adoption of drinking water standards by New Zealand authorities. Excess nitrate levels were linked to land use variables such as agricultural effluent disposal, fertilizer application and septic tank effluent discharge based on the spatial distribution of the sample wells.

When assessing international and national literature above, it becomes clear that land use is a primary control on nitrate concentrations. Wider literature suggests that nitrate concentrations are also controlled by aquifer processes as well as external factors such as recharge, land use change, climate and aquifer lithology (Overgaard 1984; Spalding & Exner 1993; Trojan et al. 2003). For this reason, a comprehensive analysis of temporal nitrate concentration has to include a consideration of some of these variables. This study seeks to analyse the main reasons behind changes in nitrate concentrations in the Hautere and Coastal aquifers by incorporating some of these variables.

1.3 Aim

The aim of this investigation is to identify long term temporal trends in ground water nitrate levels from 1993 to December 2009 and link these patterns to land use changes and aquifer properties by using available datasets. It will also explore the nature of nitrate movement within the aquifer through time in order to estimate the possible down-gradient spread of the original contamination plume.

1.3.1. Objectives

- *Temporal trend analysis of nitrate data and other chemical data associated with nitrate pollution in order to establish significant changes in concentrations over time.*
- *Analyse relevant catchment data and correlate changes in catchment data to trends in nitrate concentrations.*
- *Interpolate nitrate contamination contour plots in order to undertake a rudimentary analysis of possible plume migration over time.*

1.4 Groundwater Hydrology Concepts

This subsection provides a quick overview of the basic hydrogelogical principles in order to provide the reader with a greater understanding of some of the terminology used to describe the hydrogeology of the study site.

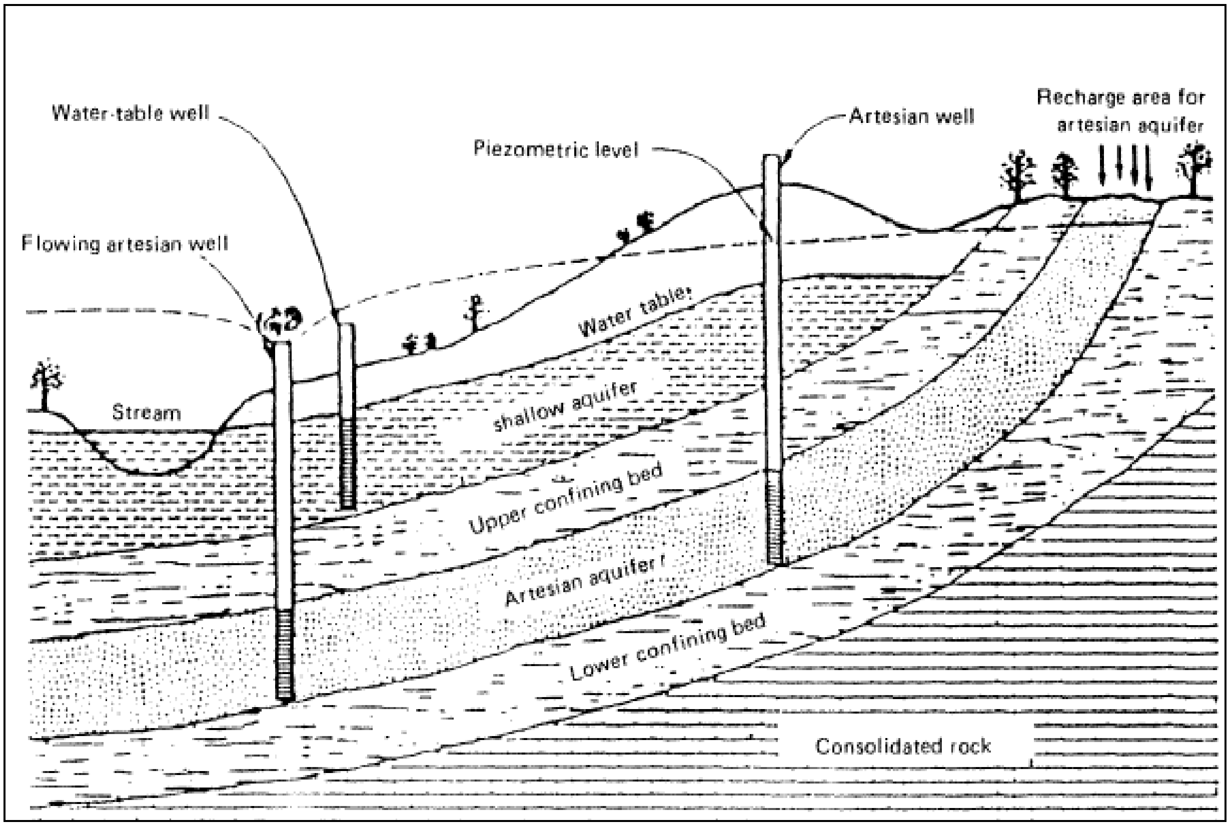

Figure 1.2: Simplified diagram of a stratified aquifer system (Cussins 1994).

Figure 1.2 above shows a generalized cross section of a series of water bearing layers and confining beds. An *aquifer* is a rock layer that has the ability to yield economically useful quantities of water to a well or spring (Cussins 1994). In geologic terms, a layer of rock includes unconsolidated material (Heath 1983).

There are two types of aquifers, *unconfined* (water table) and *confined* (artesian) aquifers. In unconfined aquifers, the free surface of the saturated zone is free to rise and fall, whereas in confined aquifers, the water saturated layer is bounded by one or more confining beds (Heath 1983). Confining beds transmit small quantities of water, but not enough for a supply well. They play and important part in regulating the vertical movement between beds (Cussins 1994).

For a rock layer to be able to hold adequate amounts of water, these formations must be *porous* (Cussins 1994). Porosity is the ratio of void space to volume of soil or rock, and it is expressed as a percentage or decimal. In unconsolidated rock formations, the volume of pore space depends the degree of sorting (porosity increases with greater sorting) of grains and the shape of grains within an aquifer (Heath 1983).

Wells screened in confined aquifers are called artesian wells. The water level inside an artesian well will stand at a certain height inside the well, this level is called the *pieziometric head* (Heath 1983). This level is an indication of the pressure inside the artesian aquifer. The higher the water level inside a well, the higher the pressure. For an unconfined aquifer, the piezometric head is the same as the water table height (Heath 1983). When water moves within an aquifer, it moves from areas of high pressure to areas of low pressure. When piezometric head is measured relative to a common datum and mapped, it can provide an indication of the direction of flow within an aquifer (Heath 1983). The *hydraulic gradient* provides a measure of the rate of groundwater movement. It is formally defined as the rate of change in head per unit of distance in a particular direction (Heath 1983).

In broad terms, groundwater moves from areas of recharge to areas of discharge. The rate of this movement is determined by the hydraulic conductivity of the aquifer and the hydraulic gradient. *Hydraulic conductivity* is the volume of water (Q) moving in a unit of time, under a unit of hydraulic gradient, in a unit area. It is a good measure of the water transmitting capability of an aquifer (Heath 1983). *Transmissivity* is the product of hydraulic conductivity and saturated thickness (Cussins 1994).

2 Study Area

2.1 Groundwater Zones

Located on the South-Western coast of the North Island, New Zealand (figure 2.1), the Kapiti Coast groundwater reserve has been classed into six different groundwater zones based on similar hydrogeological characteristics. These are the Raumati Paekakariki Zone, Waikanae Zone, Coastal Zone, Hautere Zone, Otaki Zone and Waitohu Zone.

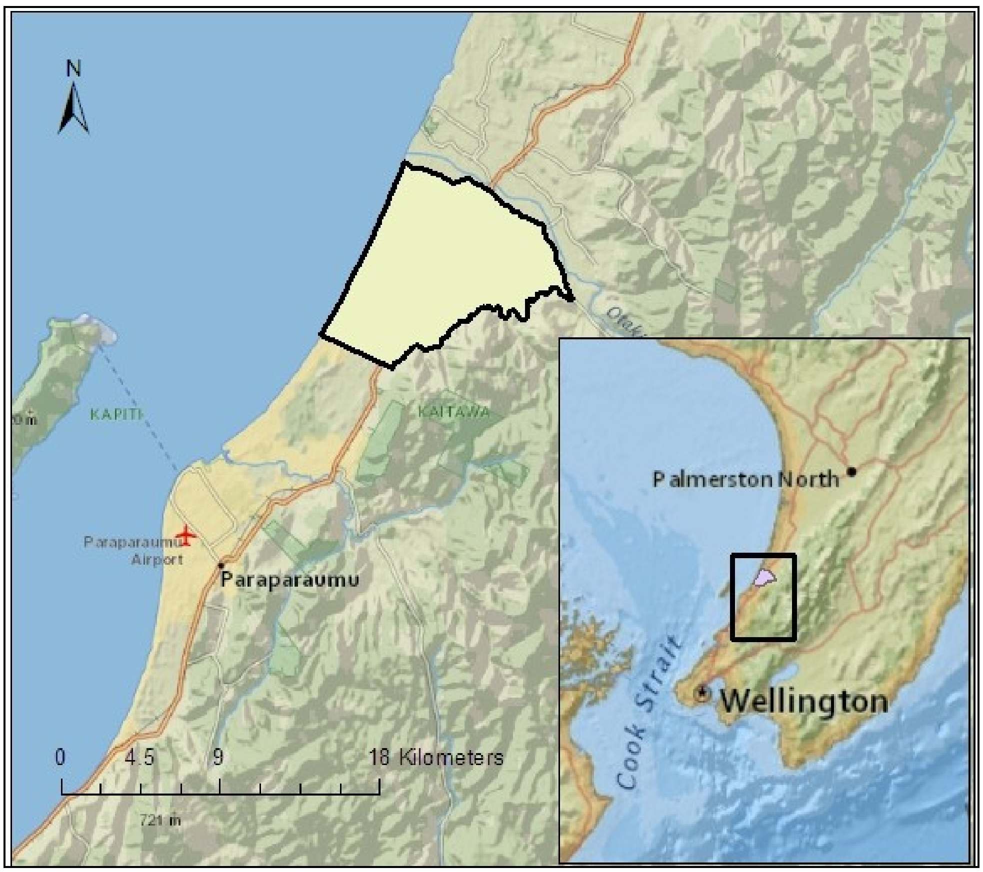

Figure 2.1: Focused diagram of the study site relative to its location in Wellington, New Zealand. The Kapiti Coast is located on the West Coast.

The area is a plain of river gravels and undulating sand dunes along the coast, bounded on the East by the foothills of the Tararua Ranges.

This study focuses on a roughly $60km^2$ zone which comprises of the Hautere and Coastal groundwater zones (figure 2.2).

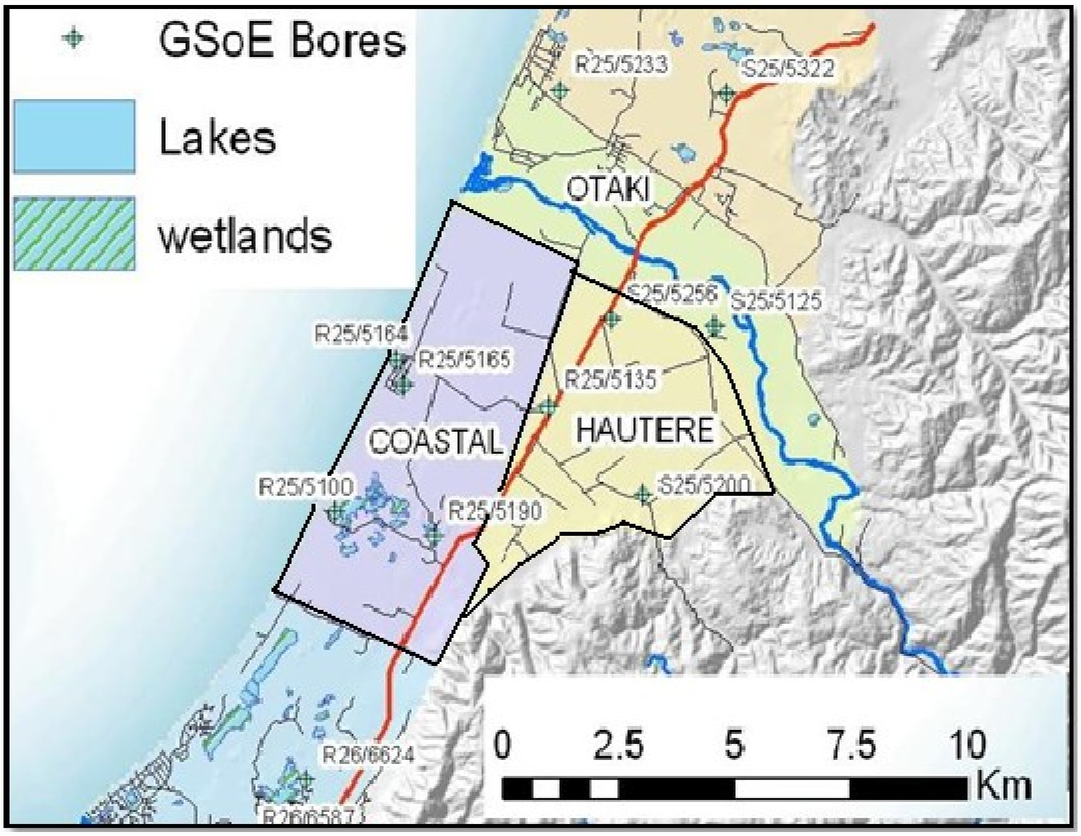

Figure 2.2: Showing the study site by aquifer zone. The Hautere and Coastal Zones are delineated by the black outlines.

2.2 Geology

The geology of the Kapiti coast is characterized by alternating layers of strata deposited during glacial and interglacial cycles, particularly in the last 250,000 years (Tidswell 2009).

2.2.1 Glacial deposits

The expansion of ice caps during glacial periods resulted in lowered sea levels. The present day coastline along the Kapiti coast would have been approximately 10 kilometers offshore during these periods. Steeper flow gradients of rivers sourced from the Tararua Ranges meant that rivers had more down cutting erosional power. Freeze thaw processes and accelerated erosion of the Ranges would have also added to increased amounts of sediment and rock being transported by rivers.

These large loads of rock and sediments were deposited as alluvial fans of poorly sorted gravel further down in the river valleys (Hydrological Services Group 1994; Tidswell 2009).

The Hautere Groundwater Zone is comprised of outwash fan material deposited during the Otiran glaciation interspersed with silt and silt and clay layers. The lower confined, water bearing layers of the Coastal zone are also comprised of gravel material deposited during the Otiran glaciation. These deeper gravel deposits are said to be a continuation of the outwash deposits forming the Hautere Groundwater Zone.

2.2.2 Postglacial and Interglacial Deposits

During warmer interglacial cycles, increased vegetation cover at higher altitudes and milder climatic conditions resulted in less erosion of the ranges. Significant volumes of water were released from ice caps due to warmer global temperatures, causing sea level rise. Coasts gradually migrated inland, which also decreased river flow gradients. This enabled a period where rivers could entrench into glacial period deposits which were poorly sorted and poorly rounded. This material was reworked during fluvial transport and re-deposited as gravel, sand, and silt further downstream within the confines of the river channels. The reworked deposits were usually better sorted and contained less silt and clay in the matrix.

The rise in sea level also resulted in transgression deposits of fluvial gravel, sand, silt and clay along the coast. These transgression deposits are overlaid by marine and estuarine sand, as well as lagoon clay and peat. The upper 40 meters of the Coastal Groundwater Zone is comprised of postglacial and interglacial sand, silt, and swamp material. Figures 2.3 and 2.4 below provide an indication of how the area is structured from a cross sectional view.

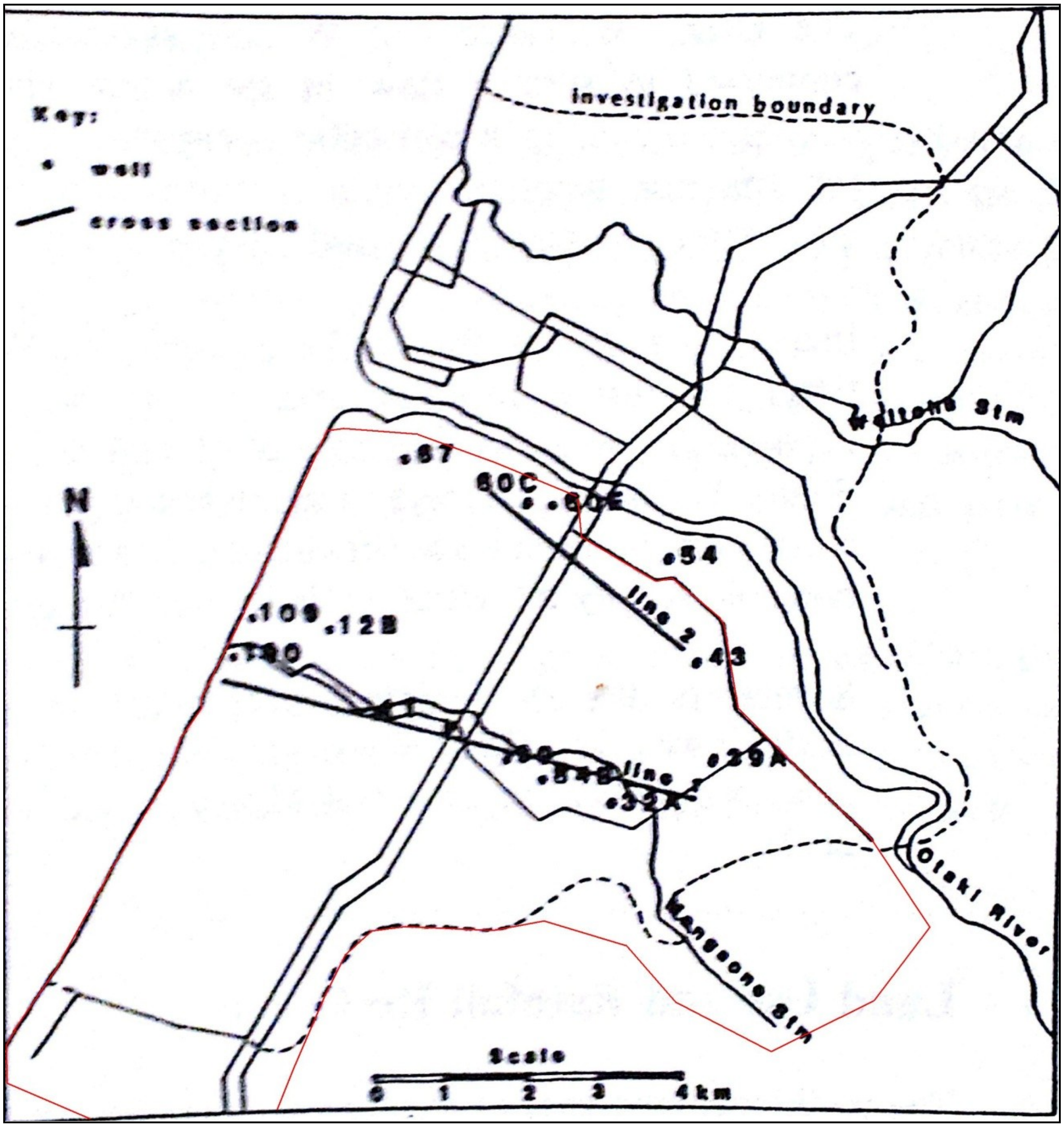

Figure 2.3: Showing two cross section transects – Line 1 (bottom) and Line 2 (top) along with bore log sites. Study site is outlined in red.

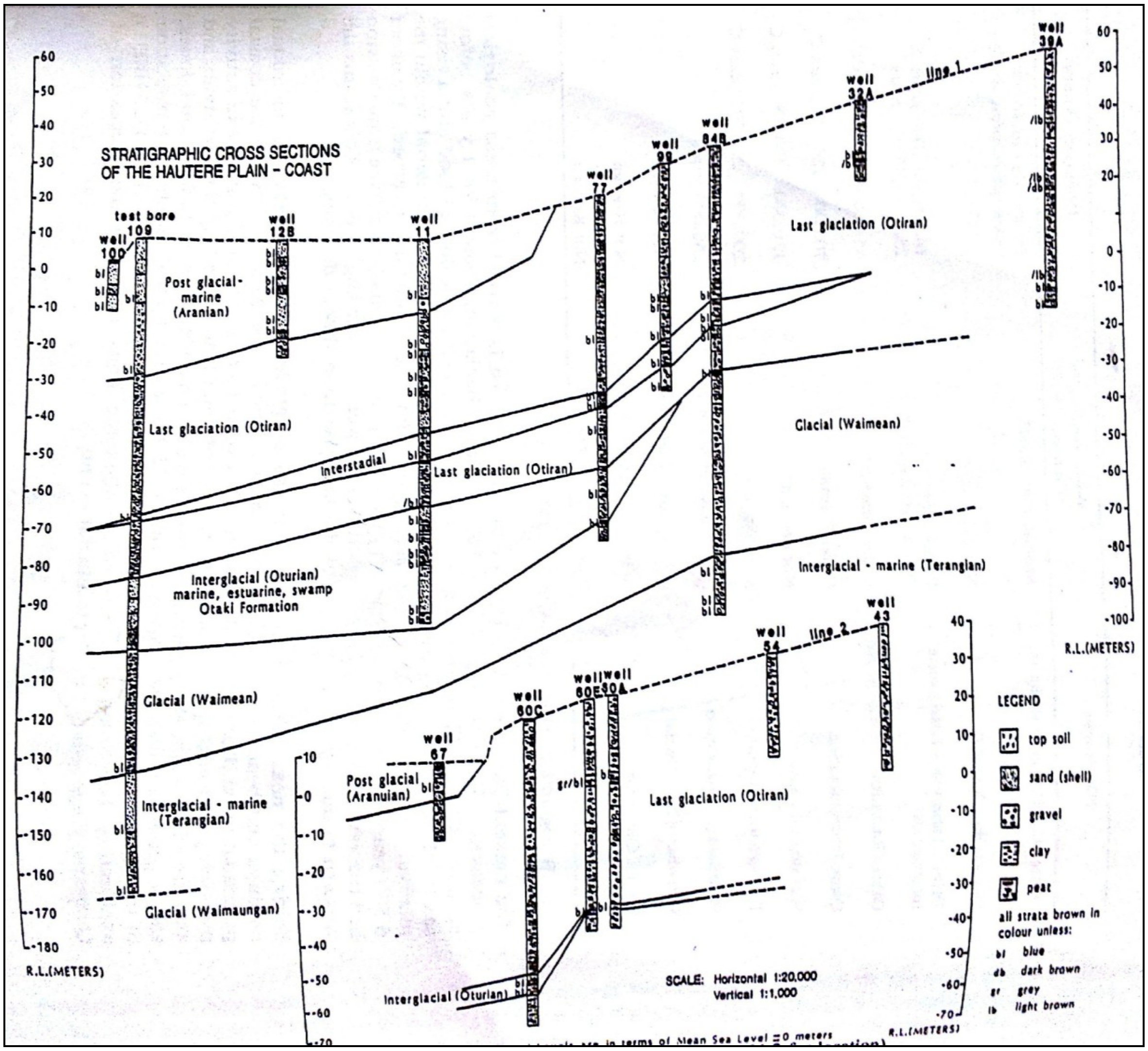

Figure 2.4: Showing cross sections along line 1 and line 2 (refer to figure 2.4). The top cross section corresponds to line 1 and the bottom cross section corresponds to line 2 (Hydrological Services Group 1994)

2.3 Hydrogeology

2.3.1 Hautere Groundwater Zone

This groundwater zone covers an area of approximately 25km^2 and underlies what is presently known as the Hautere Plain. It is composed of fluvial outwash fans deposited during the last glacial (Otira glaciation) period.

The plain forms a high terrace along the Otaki River which defines the Northern border of this zone. To the West, The alluvial fans are truncated by a sea cliff. This marks the marine transgression event which took place 6,000 years before present (BP) during the Aranuian interglaciation when sea level rose above the present day level (Hydrological Services Group 1994). This sea cliff signifies the Western limit of the groundwater zone. The Eastern and Southern borders are formed by the foothills of the Tararua Ranges.

The Hautere zone is conceptualized as consisting of three aquifers (Kampman & Caldwell 1985). This distinction was largely based on water quality results. Similar water levels in all three aquifers indicate that there is vertical leakage between the layers (table 2.1).

Table 2.1: Depth of aquifers in the Hautere Zone and their dominant chemical characteristics.

Aquifer Depth (m)	Characteristics
10-30	High nitrate-nitrogen levels
40-70	High iron levels
90-150	High boron levels

2.3.2 Coastal Groundwater Zone

This is an area of roughly $33km^2$ bounded by a high terrace running along the Otaki River to the North and Peka Peka and Hadfield Roads in the South (refer to figure 2.2). The Eastern boundary is roughly defined by the 6,000 BP sea cliff. Kampman and Caldwell (1985) identified four aquifers at various depths. These are shown in the generalized bore log for the Coastal area (figure 2.5).

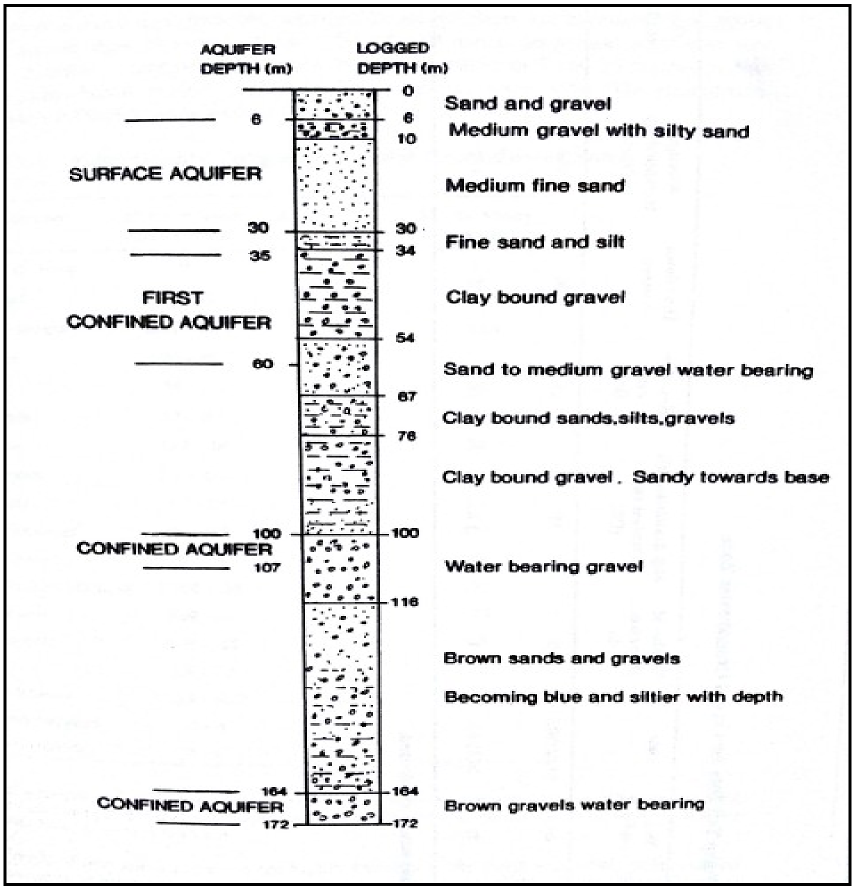

Figure 2.5: Generalised bore log for the Coastal Zone showing depth and thickness of aquifers (Hydrological Services Group 1994)

2.3.3 Groundwater Flow and Storage

Piezometric surveying was conducted in 1993 and contours of groundwater head were plotted (figure 2.6). The pressure head decreases in an east to west direction, showing that groundwater flows from the Tararua ranges towards the coast. The Piezometric contours are illustrated in figure 2.6. A gradual widening in contour lines towards the west shows a decline in hydraulic gradient. This represents a decrease in the rate of flow towards the coast (Allen 2010; Cussins 1994; Tidswell 2009).

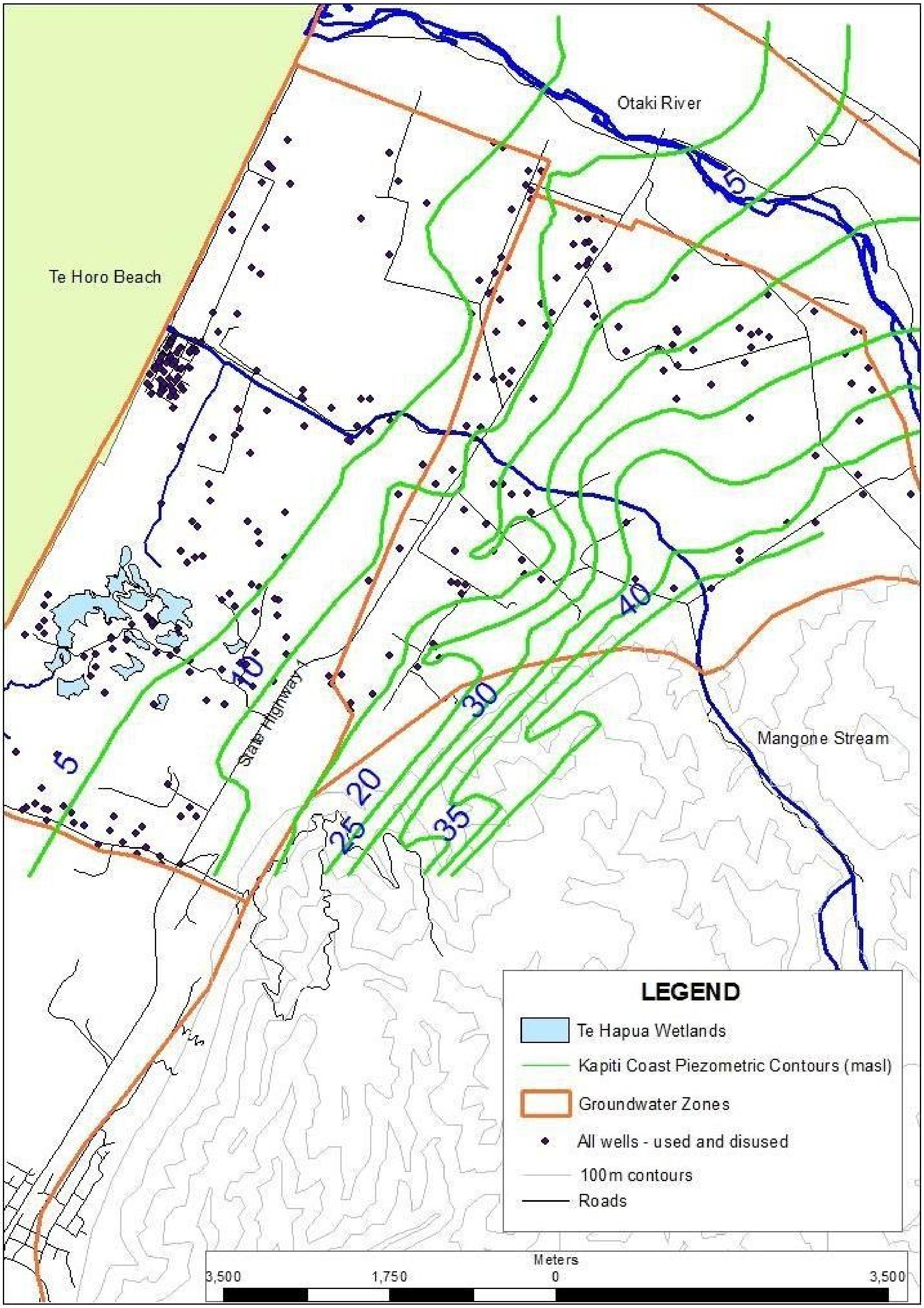

Figure 2.6: Piezometric contours for study area (Allen 2010)

Bores penetrating deeper aquifers in the Coastal zone have piezometric heads closer to the ground surface than the surface aquifer, indicating that there is an upward pressure gradient at depth. Bores located in the deeper Hautere groundwater zone have a downward pressure gradient (Tidswell 2009).

Hydraulic conductivity is highly variable due to the lateral and cross sectional variation in aquifer material. This is typical of the complex environment during which these sediments were deposited. In general, hydraulic conductivity is thought to decrease towards the coast. Cussins (1994) estimated representative hydraulic conductivities of 10 m/day for the Hautere zone unconfined aquifer and 5 m/day for the Coastal unconfined aquifer.

Previous investigations have found that seepage velocity in the Coastal, unconfined aquifer is as low as 0.1m/day (Allen 2010; Cussins 1994) whereas seepage velocities in the Hautere unconfined aquifer was estimated to be around 1m/day (Cussins 1994). Calculated seepage velocities for confined aquifers in the Coastal zone are similar to those in Hautere zone, reflecting the connectivity between aquifers at depth. The observed springs and seepage channels along the 6000 BP sea cliff are due to the sharp change in aquifer hydraulic conductivities at the boundary between the two unconfined aquifers (Cussins 1994).

Trasmissivities are locally variable, but generally low (30 – 150 m^2/day). However, average transmissivities were similar for all aquifers within the Hautere zone (Cussins 1994; Kampman & Caldwell 1985). Transmissivities for the unconfined sandy aquifer in the Coastal zone were about 15 – 100 m^2/day. Deeper Coastal zone aquifers show similar transmissivities as the Hautere zone water bearing layers. The Wellington Regional Council calculated representative values for transmissivity and storage coefficients for the different aquifers within the study site (Hydrological Services Group 1994). Table 2.2 below summarizes their findings.

Table 2.2: Representative transmissivities and storage coefficients of aquifers within the Hautere and Coastal groundwater zones

Aquifer Depth (m)	Transmissivity (m^2/day)	Storage Coefficient
10-30 (Hautere)	124	5×10^{-4}
40-70 (Hautere)	54	3×10^{-4}
90-150 (Hautere)	68	1×10^{-4}
5-30 (Coastal)	10	0.3
35-56 (Coastal)	120	5×10^{-4}
65-110 (Coastal)	170	3×10^{-4}
164-172 (Coastal)	150	1×10^{-4}

The calculated storage coefficient for the Hautere surface aquifer is more reflective of a confined aquifer. Pump tests undertaken by Cussins (1994) yielded similar results. This indicates that the surface aquifer shows a degree of confinement, most likely due to the presence of discontinuous silt lenses throughout this layer which act as localized aquitards. However, due to the rapid response of groundwater levels to rainfall events, the aquifer is considered to be largely unconfined (Cussins 1994).

2.3.4 Groundwater Recharge and Discharge

The aquifers are primarily recharged by rainfall infiltration (Cussins 1994). Previous studies indicate that the volume of rainfall increases from a West to East gradient. This is primarily due to orographic lift. Higher volumes of rainfall at the foot of the Tararua ranges (at the eastern boundary of the study site) is thought to be a source of recharge for both the unconfined aquifer and the deeper confined aquifers in the Hautere zone. Mean annual rainfall at the coast is about 1000mm and increases to about 1400mm around the base of the Tararua ranges (Tidswell 2009).

Cussins (1994) estimated that 27% of incident rainfall recharges to groundwater and about ¼ of this amount recharges the upper unconfined aquifer (Allen 2010).

Nine springs roughly located along the 6000 BP sea cliff discharge water from the Hautere to the Coastal zone. This may also provide and intermittent source of groundwater recharge to the Coastal unconfined aquifer (Cussins 1994). The amount of recharge has not yet been quantified.

Kampan and Caldwell (1985) observed that the lithological layers of the Hautere zone are connected to the deeper aquifers of the Coastal zone. Groundwater flows through these layers and in an east to west direction and discharges into the sea.

2.4 Soils

It is important to consider the overlying soil profile in the region. Soil properties play an important part in controlling infiltration rates and amount of rainfall infiltration, thus affecting aquifer recharge rates as well as the ease by which contaminants move through the soil profile and into the water table (Cussins 1994).

2.4.1. Soils in the Hautere Zone

There are several recognized soil profiles in the area. A quick data analysis using ArcGIS 10 indicates that the four main soil series present in the Hautere zone are Ashhurst stony silt loam (29% of area), Kawhatau stony silt loam (17% of area), Hautere silt loam (19% of area) and Paraha silt loam (19% of area).

Soils overlying the northern part of the Hautere zone (the stony silt loams) appear to be highly permeable, whereas soils located towards the south of the zone are of moderate permeability. Deeper soil horizons in the Paraha series tend to have low permeability at depth and drain poorly due to the high density of the subsoil (Cussins 1994). With the exception of the above, soils of the Hautere zone tend to drain well.

2.4.2. Soils in the Coastal Zone

The Coastal zone is dominated by the Omanuka peat (25%), the Foxton sand (28%), Motuiti sand (10%) and the Waitarere sand (13%).

These soils are highly permeable and drain well with the exception of the Omanuka series which drains very poorly. This is because peat has a very high soil moisture capacity. The peat lands in the Coastal zone were once covered by extensive wetlands due to this reason (Allen 2010).

For the analytical purposed of this study, soil series were simplified into broader soil categories. These are represented in figure 2.7 below.

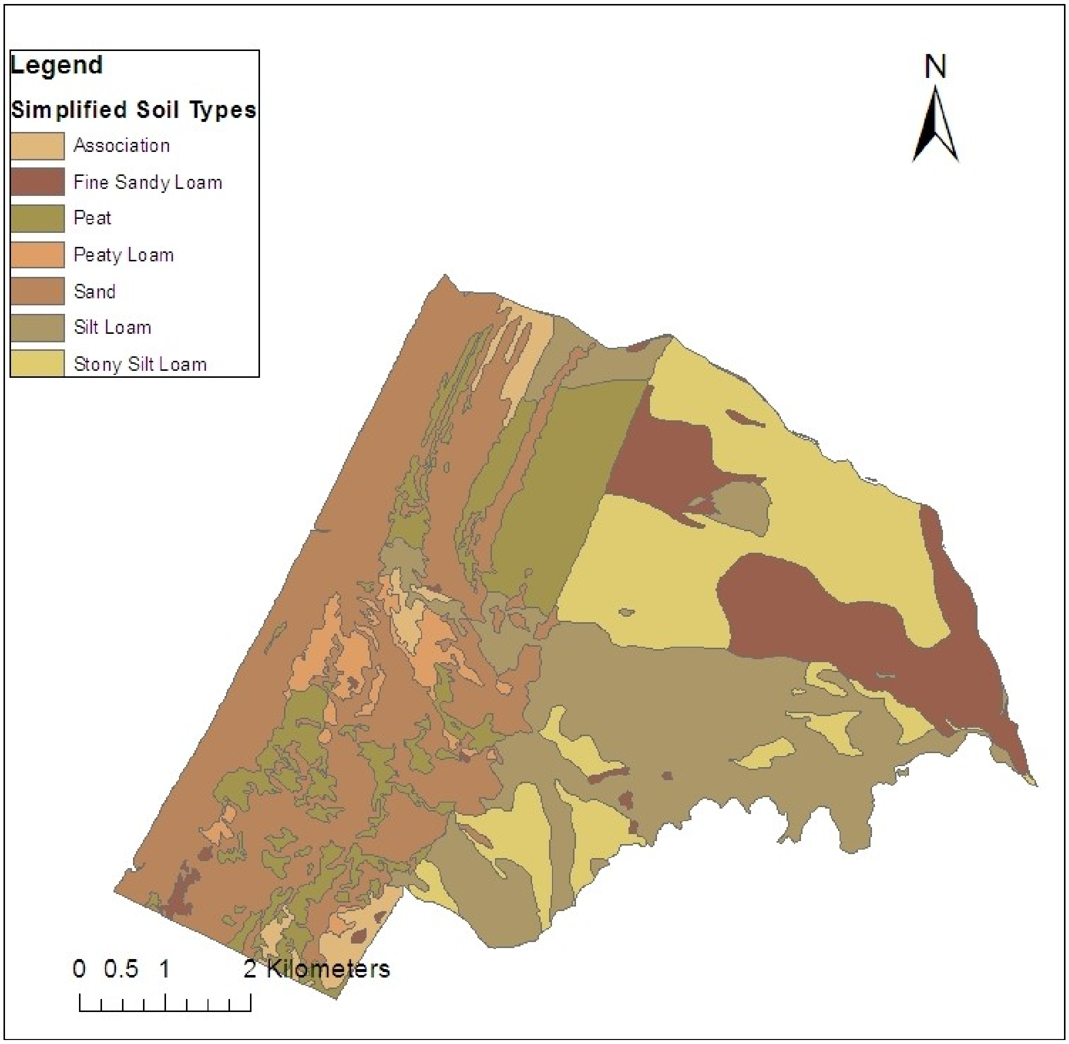

Figure 2.7: Distribution of soil types in the study site. Identified by dominant soil series (Landcare Research NZ Ltd 2005)

2.5 Land Cover and Land Use

The Hautere and Coastal areas have historically been used for dairy farming and market gardening (figure 2.8). The area is still extensively covered by pasture lands. This was expanded to include horticulture in the 1970's and 1980's. This period saw a steep rise in kiwifruit production in the area. However, in recent years, some of the kiwifruit orchards have been replaced by apple orchards or converted back into pasture lands (Cussins 1994; Kampman & Caldwell 1985).

The growth of horticulture in the area required much larger volumes of water for irrigation purposes. This water was sourced from the Otaki river and aquifers within the Otaki groundwater zone (Kampman & Caldwell 1985). The unconfined aquifers within the Hautere and Coastal groundwater zones have been utilized for low to medium volumes of water due to higher demand for irrigation in the last 20 years (Tidswell 2009).

In recent years, a shift in groundwater management practices has also seen an increase in discharges of agricultural waste products to land instead of surface water bodies. Many of the consented discharges to land within the study site are for animal waste discharge and treated sewage discharges to land (Tidswell 2009).

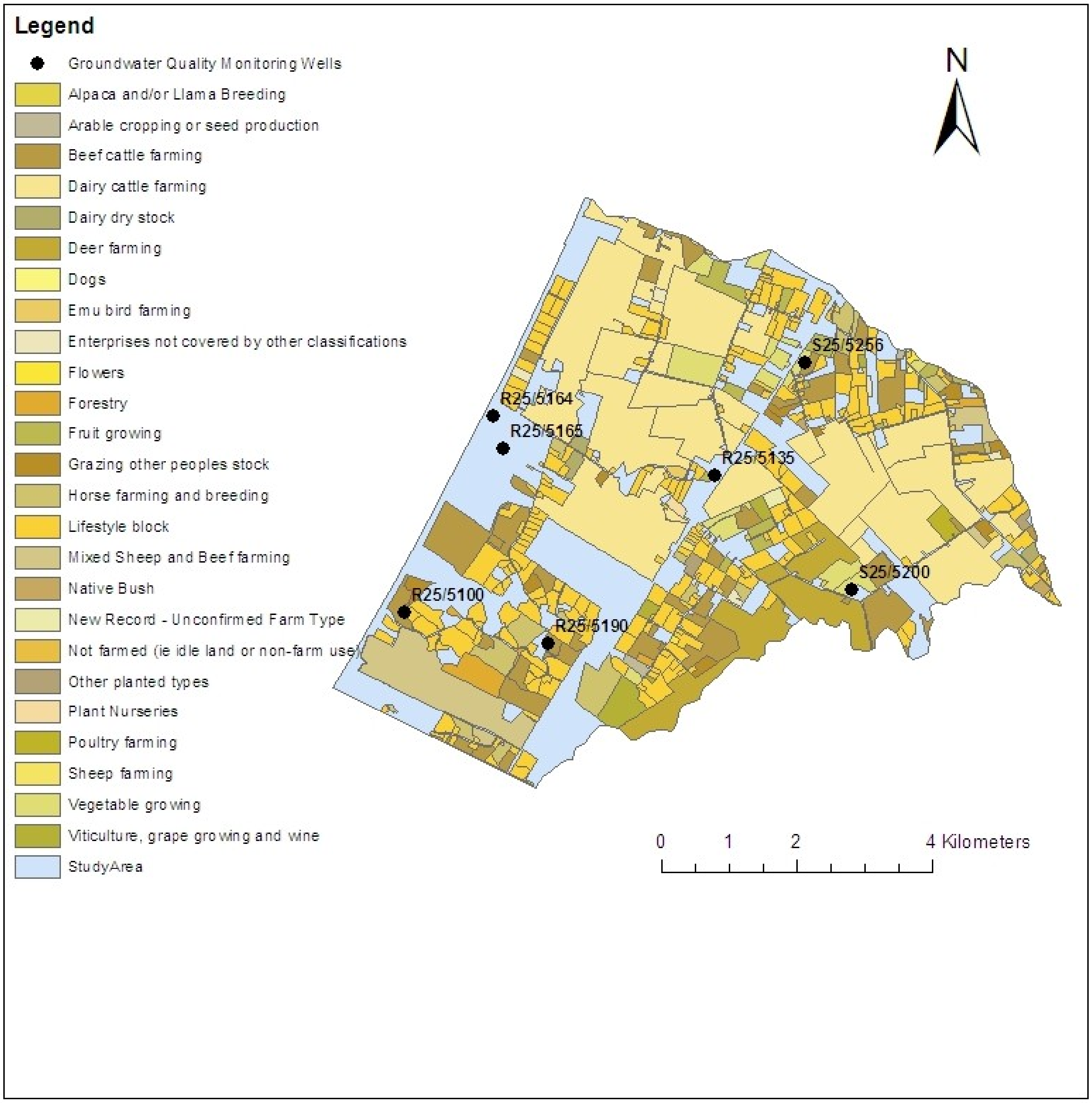

Figure 2.8: Distribution of main land use types relative to SoE groundwater monitoring bores

3 Methodology

3.1 Temporal Analysis of Chemical Data

3.1.1 Data Collection

All chemical data was provided by the GRWC as part of the regional groundwater monitoring programe. This data was used as it is subject to strict national quality controls. Regional monitoring networks are also reviewed by professionals in state authorities to ensure the most representative monitoring wells are selected. Data was collected on a quarterly basis from 1993 to December 2009. Samples were gathered, transported and stored according to guidelines outlined in the National protocol for State of the Environment groundwater sampling (Ministry for the Environment). Chemical analysis was subsequently undertaken by GRWC's contracted laboratory in Hamilton; Hill Laboratories where concentrations of all major cations, anions, and organic matter were determined (Tidswell 2009). Appendix 1 contains details of analytical methods and equipment used by the laboratory as well as detection limits and analysis precision.

3.1.2 Calculation of Summary Statistics

Minitab v 16.1.0 (2010) was used to calculate summary statistics for the chemical data. Summary statistics were calculated for each dissolved oxygen, total dissolved solids and nitrate-nitrogen concentration time series per monitoring site.

Time series of some of the nitrate concentration time series' analysed had a large number of left censored data points. Left censored data, in the context of this study, are chemical concentrations that are *below* a certain detection limit. These data values are often defined as less than the detection limit and above zero, but have no distinct value. The detection limit is often determined by the ability of a particular analytical method or instrument to detect the smallest possible concentration with reliable precision.

Dennis R. Helsel (2011) developed a Minitab Macro package to accompany his publication on how to deal with censored data. This package is called NADA for Minitab Macro Collection version 3.0.3. Diagnostic graphs such as censored probability plots were drawn using the relevant Macros (see Appendix 2 for probability plots). Regression on Order (ROS) statistics were used to calculate summary statistics for time series containing censored data as explained by Helsel (2011).

ROS involves regressing data points against their normal scores. For nitrate time series which include censored data, the regression slope and intercept are calculated using uncensored (detected) data points only. The regression equation describes the normal distribution specific to the dataset. Groundwater chemical data usually tends to follow a log-normal distribution. If the diagnostic probability plots indicate an approximate log-normal distribution, the macro uses log transformed data values in ROS calculations (Helsel 2011).

The regression line based on the normal scores of uncensored values is then used to impute values for censored observations based on their normal scores. The modelled values for censored and uncensored values are then combined and used to compute summary statistics using standard statistical methods.

Summary statistics for time series without any censored data points were calculated using standard statistical methods.

3.1.3 Time Series Analysis

Temporal trends for chemical data were analysed using the Seasonal Mann-Kendall test. This is a modification of the non parametric Mann-Kendall which accounts for seasonal dependence of data and tests for the presence of a monotonic trend (Hirsch & Slack 1984). This method has been used in previous studies to analyse chemical groundwater data (Ministry for the Environment 2007a; Tidswell 2009).

The null hypothesis is that there is no significant monotonic trend in either a positive, or negative direction. This test was chosen due to its robustness against highly skewed, non-normal data, censored data points, outliers and multiple detection limits (Helsel 2011).

For the purpose of running the test, time series data were first ordered according to sampling date and categorised into one of four New Zealand seasons: Summer (December, January, February), Autumn (March, April, May), Winter (June, July August) and Spring (September, October, November). This was in order to calculate the seasonal Mann Kendall test, which accounts for any possible seasonal correlation in the data (Hirsch & Slack 1984).

The Mann Kendall test statistic is first calculated for each season (ω) as follows:

$$T_j = \sum_{k<l} sgn\left(Z_{lj} - Z_{kj}\right) \qquad j = 1 \ldots\ldots \omega \qquad (1)$$

Where

$$sgn\left(Z_{lj} - Z_{kj}\right) = \begin{cases} 1, & \text{if } (Z_{lj} - Z_{kj}) > 0 \\ 0, & \text{if } (Z_{lj} - Z_{kj}) = 0 \\ -1, & \text{if } (Z_{lj} - Z_{kj}) < 0 \end{cases} \qquad (2)$$

Z_{lj} is the data point at time l and series j, and Z_{kj} is the data point at time k and series j. The seasonal test statistic is summed over all seasons in order to obtain the overall Mann Kendall test statistic, S:

$$S = \sum_{j=1}^{\omega} T_j \qquad (3)$$

Data values below a detection limit were substituted by one half of the highest detection limit. As defined above, the Mann Kendall test statistic does not depend on the actual value of a data point, instead, it is based on the position of a data point relative to the data value preceeding it in the time series. Substitution of a value for censored data points does not bias the test statistic.

Where more than ten data points are present in each series, a normal approximation can be applied to the data in order to calculate the probability associated with the Mann Kendall statistic (Kendall 1975). However, the test statistic has to be adjusted for the presence of tied values, especially in the context of this study where censored data values were substituted as described above. The adjustment for ties is built into the variance calculation of S:

$$VAR(S) = \frac{1}{18}\left[n(n-1)(2n+5) - \sum_{p=1}^{g} t_p\left(t_p - 1\right)\left(2t_p + 5\right)\right] \qquad (4)$$

Where n is the number of data points, g is the number of tied groups and t_p is the number of data points in the p^{th} tied group. Once the variance has been calculated, a normalised Z score can also be calculated. This figure will differ depending on whether S is below zero, equal to zero, or greater than zero:

$$Z = \frac{S-1}{\sqrt{VAR(S)}} \quad \text{if } S > 0,$$

$$Z = 0 \quad \text{if } S = 0,$$

$$Z = \frac{S+1}{\sqrt{VAR(S)}} \quad \text{if } S < 0 \qquad (5)$$

The United States Geological Survey (USGS) computer program Kendall.exe (2006) was used to calculate the seasonal Mann Kendall test for each well. Helsel & Hirsch (2002) contains the program documentation. The main software details are summarised below.

The only assumption of the test is independence of data. It is therefore important that serial correlation of data was accounted for if present. The program has a code for calculating an adjusted p-value in the presence of serial correlation (Helsel & Hirsch 2002; Hirsch, Alexander & Smith 1991). This adjusted p-value was calculated in addition to the normal p-value if more than ten years of data was present for each time series.

The program automatically calculated a normalised Z statistic if the datasets contained more than 10 data values. An adjusted Z statistic was calculated if tied values are present, and a two tailed test for significance of trend was calculated at a significance level of $\alpha = 0.05$.

The sign which preceded the Z statistic indicated the direction of the monotonic trend. A negative Z statistic signifies a decreasing trend and a positive Z statistic signifies an increasing trend. The program also calculated an equation for the trend. The slope of the equation is an estimate of the rate of change per year.

3.2 Regression Analysis

3.2.1 Tobit Regression Theory

Tobit regression analysis was conducted on available land surface data, climate data and chemical data (from section 3.1) variables in order to determine if they significantly influenced observed nitrate concentrations.

Several studies have incorporated Tobit regression models in order to predict or investigate contaminant concentrations with respect to chosen explanatory variables (Barringer et al. 1990; Gardner & Vogel 2005; Liu et al. 1997; Stackelberg et al. 2012; Tesoriero & Voss 1997). The advantage of Tobit regression over ordinary least squares regression is its ability to incorporate values below a reporting limit in the dependent variable (Helsel 2011) and produce unbiased multivariate regression models.

The Tobit regression model is expressed in terms of the latent dependent variable:

$$y_i^* = \alpha + \bar{\beta}\bar{x}_i + \varepsilon_i \qquad (6)$$

Where, in the context of this study, y_i* is the latent variable, α is a constant, β is a vector of parameter slope estimates, x_i represents the explanatory variables, and ε_i are normally and independently distributed residual errors with mean zero and variance σ^2.

Observed nitrate concentrations can be described in terms of the latent variable if concentrations are above the detection limit, c. Alternatively, if nitrate concentrations are below the detection limit (0.01mg/L), then the latent variable becomes c:

$$y_i = y_i^* \quad if\ N_i > c$$

$$y_i = c\ otherwise \qquad (7)$$

Assuming the errors are independent and homoscedastic, the vector parameters in the linear equation can be estimated using Maximum Likelihood Estimation (MLE) (Gardner & Vogel 2005; Helsel 2011; Liu et al. 1997). Statistical software (Minitab 2010) was used to perform interval censored likelihood estimation on selected explanatory variables.

3.2.2 Data Sources

The dependent variable in this study was nitrate concentration values (mg/L) measured as part of the GWRC quarterly monitoring network. Dissolved oxygen and TDS data was also obtained from the groundwater quality sampling results. This was the same data as used in section 3.1.

Explanatory variables were land use, land cover, soil type, rainfall, temperature, dissolved oxygen and TDS. The choice of explanatory variable was dictated by studies found in previous literature (further explained in Chapter 1 and Chapter 2) as well as the availability of data.

Land use data was originally sourced by the AsureQuality's Agribase™ (AsureQuality 2008) database. GWRC could only provide 2008 data for this study. Agribase collates voluntary rural land use data and stores this information in a high quality GIS database. Land use data was provided as a GIS shapefile.

Land cover data was extracted from New Zealand's Ministry for the Environment (MFE) (Ministry for the Environment 2009), who survey land cover as part of their Land Use Carbon Analysis System (LUCAS). Although termed "land use" on the MFE website, the data only provides an idea of the immediate land cover. For example, GIS parcels would be grouped as "Grassland type A" or "Grassland type B", but not grouped according to the type of activity that occurred on that particular grassland (such as beef farming or sheep farming). It was therefore more appropriate to use the data as land cover information rather than land use data. Land cover was available for 1990, 2008 and 2012 and was provided in shapefile format.

Soil type data for the study site was extracted from the "Soil Map of Otaki District" GIS shapefile published by Landcare Research NZ (Landcare Research NZ Ltd 2005). The data represents information obtained from a national soil survey undertaken by the Soil Bureau prior to 1992. Due to the high variability of soil classifications across the study site, soil types were reclassified into their broader soil types. That is, high order soil type classification polygon parcels were merged to represent their lower order general soil type using ArcGIS software. This was decided with the intent of making regression results easier to interpret by having fewer variables.

Rainfall and air temperature data from 1993 to 2009 were obtained from the National Institute of Water and Atmospheric Research (NIWA). NIWA's virtual climate station database is a set of modelled climate data interpolated from measured climate stations. The method of interpolation used is a thin plate smoothing spline interpolation. More information about the interpolation method can be obtained from the NIWA website (NIWA 2012).

3.2.3 Data Preparation and Regression Procedure

Nitrate data was only regressed against land use, land cover and soil type from 2007 to 2008. This was due to the fact that land use was only available for 2008 (which restricted the scope of the analysis), and land cover from 1990 to 2008 showed no change. Soil type was assumed to be constant over the time period of the study.

The variables were not combined into one equation as is often found in prediction-type regression models. The inclusion of all variables in one model equation showed a high level of multicollinearity and caused non-convergence of iterations. This was tested using the Minitab software and including over six random variables caused the system to abort calculations due to the appearance of multicollinearity between variables land use, soil type and land cover. Individual regression models for the variables were therefore conducted in order to provide an idea of which variables had a significant effect on nitrate concentrations. The issue of multicollinearity will be investigated further in the discussion.

A circular buffer of radius 500m was constructed around each of the seven monitoring bores in the study site using ArcMap 10. 1km and 2km circular buffer zones were also tested against land use initially, however a 500m buffer radius was chosen as it provided the best fit for the data (Gardner & Vogel 2005; Tesoriero & Voss 1997). Circular buffer zones were overlain separately on land use, land cover and soil type GIS layers in order to calculate the amount of each variable within each buffer zone. The amount of land use and land cover was recorded in hectares and soil type was recorded in percentages.

Three virtual climate stations were available for regression analysis of climate variables. For the preparation of rainfall data, the study site was divided into three “strips” arranged West – East in order to reflect the change in rainfall from the coast to the mountain ranges (figure 3.1). Each strip contained a certain number of groundwater quality bores and a virtual climate station. Interpolated daily rainfall from each climate station was taken as representative daily rainfall for any bore within that particular strip.

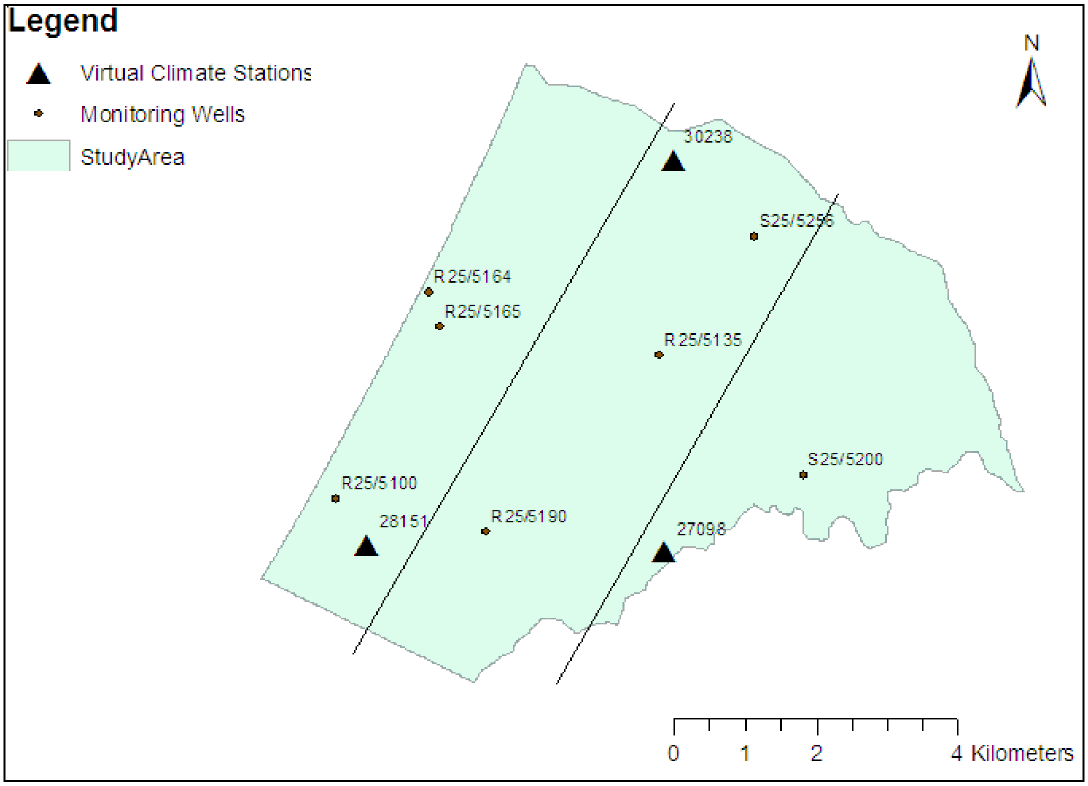

Figure 3.1: Separation of bores within the study site into rainfall zones.

A regional average daily temperature was calculated by averaging the mean daily temperatures from all three climate stations.

Table 3.1: Number and types of variables tested within each regression group.

Land Use Variables (Ha)	Land Cover Variables (Ha)	Soil Type Variables (%)	Chemical Variables (mg/L)	Climate Variables
Beef Cattle Farming	High Producing Grasslands	Peat	Dissolved Oxygen	Rainfall (mm)
Dairy Cattle Farming	Low Producing Grasslands	Sand	TDS	Mean Air Temperature (^{o}C)
Settlement	Vegetated Wetlands	Peaty Loam		
Lifestyle Block	Township	Silt Loam		
Mixed Sheep & Beef Farming	Annual Cropland	Fine Sandy Loam		
Fruit Growing	Perennial Cropland	Stony Silt		
Emu Farming				
Horse Rearing and Breeding				
Deer Farming				
Vegetable Growing				
Forest				

Regression models were subsequently calculated for the main types of different land use, land cover, soil type, climatic factors and chemical influences in a step wise regression processes (table 3.1). Variables were added step by step and excluded from the model if they did not make a significant improvement to the model equation. Partial likelihood tests were conducted in order to determine this significant improvement (or lack of). The partial likelihood statistic is defined as:

$$G^2_{partial} = [-2L(\beta_{without})] - [-2L(\beta_{with})] \qquad (8)$$

Where $L(\beta_{without})$ was the model log likelihood of the regression equation without the variable of interest and $L(\beta_{with})$ was the model log likelihood of the regression equation with the variable of interest. The resulting partial likelihood statistic was compared to a chi squared table of critical values with degrees of freedom 1 (as only one variable was being added with every step). If the p-value was less than or equal to 0.05, the variable was seen to provide a significant improvement to the model fit, and left in the regression equation (Helsel 2011).

After the best model for each group was determined, the regression models were tested against the null model (all β's = 0) in order to determine if having a regression model provided a better explanation of the data than having no model at all. The overall log likelihood test was used to determine the test statistic:

$$G_o^2 = [-2L(o)] - [-2L(\beta)] \qquad (9)$$

Where L(o) was the log likelihood of the null model and L(β) was the log likelihood of the final regression model. The test statistic was referenced to a chi squared distribution table of critical values with *k* degrees of freedom, where *k* was the number of explanatory variables in the final model. If the p-value was less than or equal to 0.05, the final model was considered to be a good fit for the data (Helsel 2011).

3.3 Nitrate plume delineation

Nitrate concentrations from two site specific studies (Hughes 1997; Tidswell 2009) were used to perform a rudimentary analysis of plume migration from 1996 to 2008. The method of quadratic kriging was used to interpolate the nitrate plume. This is a nonparametric version of ordinary kriging which has shown to produce better results with groundwater quality data which is highly skewed and does not conform to assumptions of normality (Juang, Lee & Ellsworth 2001; Reed, Ellsworth & Minsker 2004).

Geostatistical interpolation methods use known data values in order to predict unknown values at neighbouring sites. The number of measured data points markedly improves the estimation of unknown values (Reed, Ellsworth & Minsker 2004). Unavailability of an adequate number of measured data points restricted plume delineation to December 1996 and December 2008.

The kriging procedure used in Juang et. al. (2001) was replicated in this study.

3.3.1 Rank Order Data Transformation

Assume that the cumulative distribution function (CDF), F(Z), which is uniformly distributed from 0 to 1, described nitrate concentrations (Z) in the Hautere and Coastal groundwater zone. The empirical distribution function (EDF) of a random sample z_i where i=1,2,3,….n can be used to estimate F(Z). The EDF of a sample is calculated by finding the order statistic of each data point, r_1, r_2……r_i, and relating it to the equation:

$$F(z_r) = \frac{r}{n} \qquad (10)$$

The standardised rank transformation, U, is:

$$U = F(Z) \qquad (11)$$

The CDF of U is defined as $U = u$

The measured nitrate value $z_{(x)}$ from a random sample described the concentration at location x. For the nitrate data set z_i where i = 1,2,3….n, the rank order statistics of all data points, r (x_i), were first calculated. Ties were assigned an average rank such that, if $z(x_{1)} = z(x_{2)} = z(x_{3)}$, then their tied rank was $(r_1 + r_2 + r_3)/3$.

By virtue of equations 10 and 11, the standardised ranks for the data set were calculated as follows:

$$u(x_i) = \frac{r(x_i)}{n} \qquad (12)$$

The method was repeated separately for the 1996 and 2008 data sets.

3.3.2 Ordinary Kriging

Ordinary kriging on the standardised ranks was performed using the Geostatistical Analyst tool in ArcGIS Desktop 10.

For Kriging, the spatial correlation between all pairs of points located at coordinates (x_i,y_i) and (x_j,y_j) was determined by calculating the semivariogram. The semivariogram was characterised by plotting semivariance over distance:

$$distance\ (d_{ij}) = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2} \qquad (13)$$

and semivariance is:

$$\gamma_u(d) = \frac{\sum_{i=1}^{N(d)}(u_i[x_i,y_i] - u_i[x_j,y_j])^2}{2N(d)} \qquad (14)$$

where γ_u(d) is the semivariance, $u_i[x_i,y_i]$ and $u_i[x_j,y_j]$ are the standardised ranks at locations ($x_{,i}$,y_i) and (x_j,y_j) respectively, *d* is the distance between the two locations and N(d) are the number of pairs at the two different locations.

The process is automated in ArcGIS, which fits a semivariogram least squares regression model to averaged values of semivariance and distance. The regression model is forced to have an intercept of zero and positive slope (Johnston et al. 2003).

A value for an unknown standardised rank value (u) at a location x_o was determined by the ordinary kriging equation:

$$u'(x_o) = \sum_{i=1}^{m} \lambda_i u(x_i) \qquad (15)$$

Where λ_i is the unknown weight value, and *m* is the number of known surrounding observations used in the estimate. By setting limiting conditions which ensure unbiased estimates, such as kriging variance is equal to zero and the sum of weights are equal to 1, the unknown weight values can be solved by a system of linear matrix equations:

$$\lambda = \Gamma^{-1} \times \boldsymbol{g} \qquad (16)$$

Γ^{-1} is the inverse matrix of the semivariance matrix between all known pairs and ***g*** is the semivariance between the unknown location and each of the surrounding points used to predict $u'(x_o)$ (Johnston et al. 2003).

This process was repeated for the 1996 dataset and 2008 dataset separately. Interpolated raster maps of predicted standardised rank values were created using ArcGIS 10 as well as the corresponding standard error map.

The values for each grid square were subsequently extracted so that the standardised rank values could be re-transformed back into the 'concentration space' (Juang, Lee & Ellsworth 2001).

3.3.3 Re-transformation of Standardised Ranks to Nitrate Concentrations

The estimated standardised rank value, $u'(x_o)$ is between two known adjacent values of $u(x_i)$ and $u(x_j)$. According to equation 2, the relationship between $u(x)$ and $z(x)$ is monotonically increasing, which means that the unknown concentration value $z'(x_o)$ lies between two adjacent known concentrations of $z(x_i)$ and $z(x_j)$, which are related to the standardised values of $u(x_i)$ and $u(x_j)$.

With consideration to the above relationships, the standardised ranks can be back-transformed into the concentration space by interpolating the EDF for measured nitrate data (Juang, Lee & Ellsworth 2001).

Juang et. al. (2001) employed a simple mid-point linear interpolation method. A similar method was used in this study.

The EDF distribution functions for the 1996 and 2008 nitrate concentration datasets were produced by plotting $u(x_i)$ vs $z(x_i)$ of the measured data. The standardised $u(x_o)$ values were back-transformed into nitrate concentrations using linear spline interpolation. This entailed drawing straight lines connecting adjacent data points on the EDF and calculating the set of linear equations of the form $z(x_o) = m * u(x_o)+b$ to describe each line segment (spline). The estimated $u(x_o)$ values were substituted into a particular linear equation depending on which known values of $u(x_i)$ the estimate fell between.

Back-transformed values were subsequently exported into ArcGIS 10 and raster maps of interpolated nitrate concentrations created. The procedure was repeated for the kriging standard error measurements.

4 Results

4.1 Analysis of Chemical data

4.1.1 Nitrate Data

The nitrate chemical data for many of the bores show a high percentage of censored data. The censored box plots below (figure 4.1) shows the distribution of nitrate data for each site and the percentage of censored observations at each well.

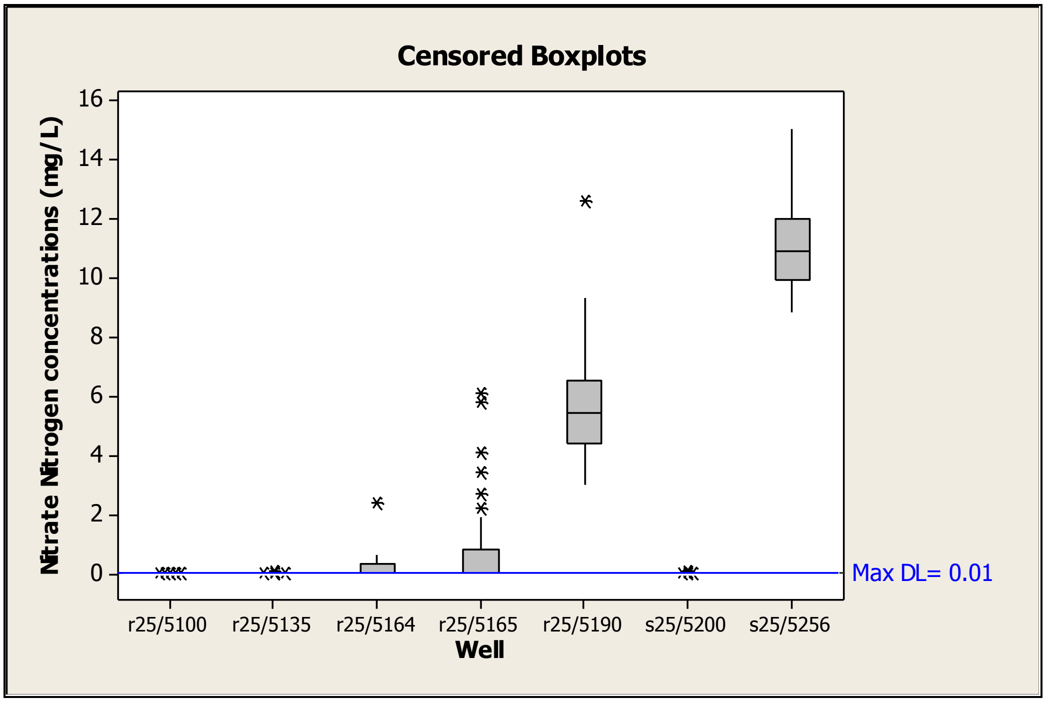

Figure 4.1: Censored box plot of nitrate concentrations of monitoring wells in the Hautere and Coastal groundwater zones. Maximum detection limit is 0.01 mg/L.

It is clear that bores r25/5100, r25/5135 and s25/5200 have a high percentage of censored data and consequently have much lower nitrate concentrations than the other wells. Conversely, bores r25/5190 and s25/5256 have the highest observed nitrate concentrations.

The estimated and observed quartiles are presented in the table 4.1 below.

Table 4.1: Summary statistics for nitrate concentrations in the Hautere and Te Horo groundwater zone monitoring bores. Lower Quartile = 25% quartile, Upper Quartile = 75% quartile

Bore number	Depth	N	Minimum	Lower Quartile	Median	Upper Quartile	Maximum
r25/5100	48.2	46	0.00041	0.00159	0.00329	0.01000	0.03000
r25/5135	93.27	37	0.00011	0.00072	0.00250	0.00769	0.08600
r25/5164	Unknown	45	0.0004	0.0055	0.0300	0.3210	2.4000
r25/5165	8	44	0.002	0.017	0.042	0.782	6.090
r25/5190	Unknown	24	3.000	4.360	5.395	6.533	12.600
s25/5200	45.8	41	0.00033	0.00134	0.00354	0.01000	0.08000
s25/5256	30.78	51	8.800	9.930	10.900	12.000	15.000

4.1.2 Total Dissolved Solids (TDS) Data

Observed TDS concentrations in well r25/5164 show quite a large spread about the median compared to all other wells (figure 4.2 & table 4.2). TDS concentrations in well r25/5135 are generally higher than concentrations measured in the other observation wells.

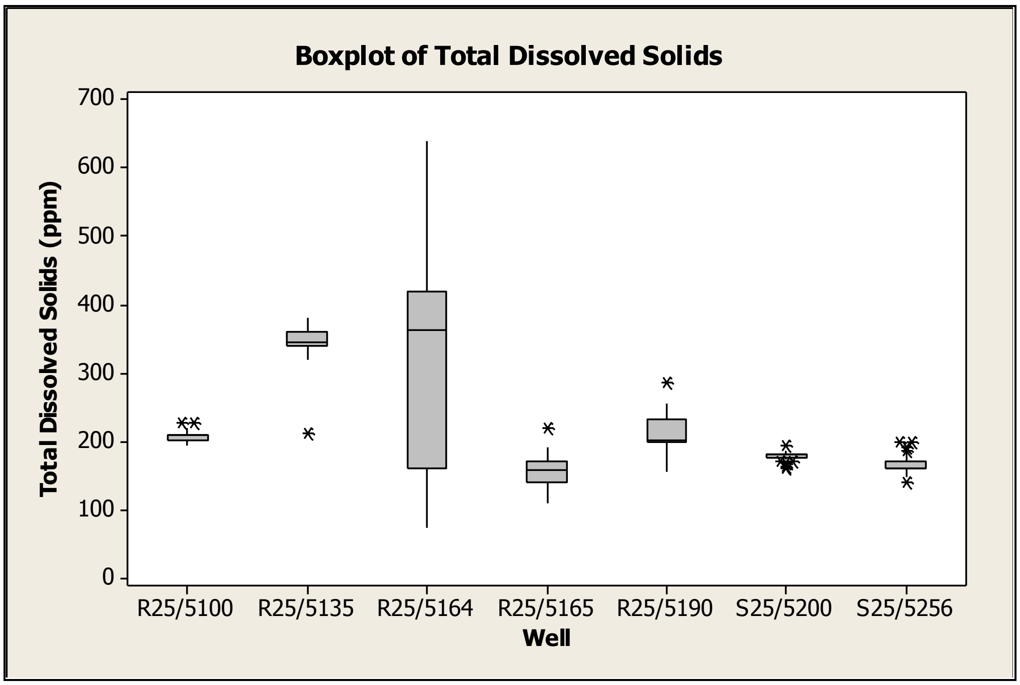

Figure 4.2: Box plot of Total Dissolved Solid concentrations of monitoring wells in the Hautere and Coastal groundwater zones.

Table 4.2: Summary statistics for TDS concentrations in the Hautere and Te Horo groundwater zone monitoring bores. Lower Quartile = 25% quartile, Upper Quartile = 75% quartile.

Bore number	Depth	N	Minimum	Lower Quartile	Median	Upper Quartile	Maximum
r25/5100	48.2	46	193.00	200.50	210.00	210.00	228.00
r25/5135	93.27	37	212.00	337.75	344.00	360.75	380.00
r25/5164	Unknown	45	73.0	160.0	363.0	420.0	640.0
r25/5165	8	44	110.00	140.00	157.00	170.00	219.00
r25/5190	Unknown	24	156.00	197.75	201.50	232.25	286.00
s25/5200	45.8	41	160.00	176.25	180.00	180.00	193.00
s25/5256	30.78	51	140.00	160.00	160.00	170.00	200.00

4.1.3 Dissolved Oxygen Data

The box plots exhibit a marked difference in percent to dissolved oxygen in groundwater between sites (figure 4.3). Four of the sites show much lower dissolved oxygen percentages with relatively constricted spread of values, whereas three of the sites have much higher dissolved oxygen values with a larger spread of data. The values of the various box plot data points are represented in table 4.3.

Wells r25/5164 and r25/5190 are located in the Coastal groundwater zone and are both very shallow wells. These two bores show higher dissolved oxygen content. However, bore r25/5165 is also located in the Coastal zone and is closer to bore r25/5164, yet does not have a similar pattern in dissolved oxygen concentrations.

It is interesting to note the different patterns exhibited by chemical data in bores r25/5165 and r25/5164 despite the similar depths of the bores and their close proximity.

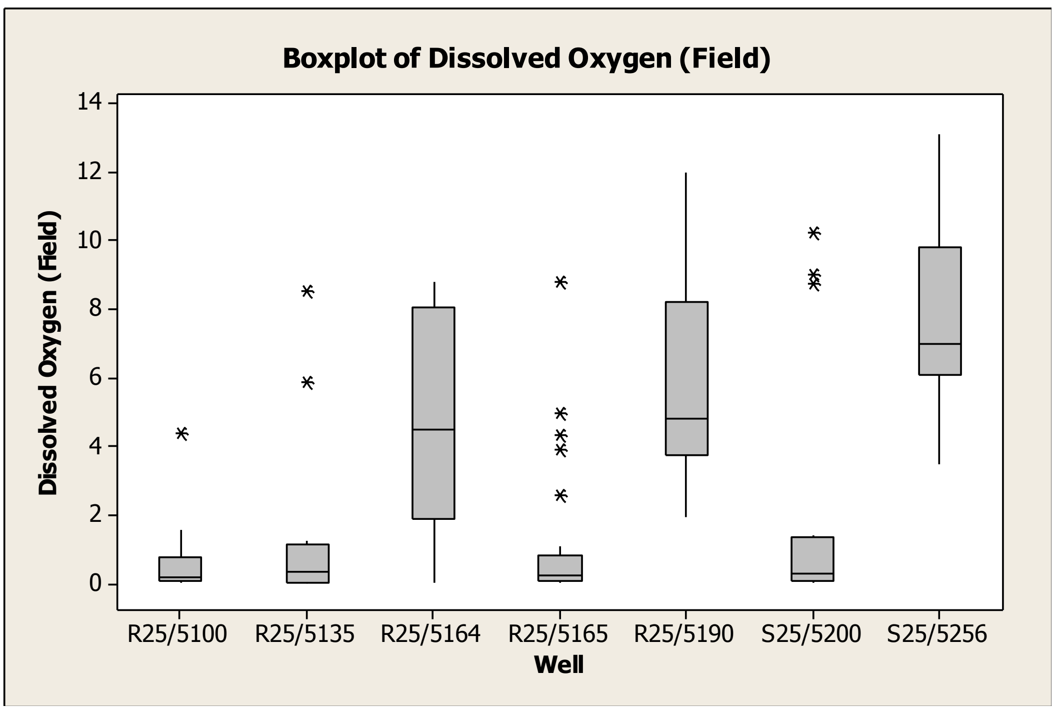

Figure 4.3: Box plot of dissolved oxygen concentrations of monitoring wells in the Hautere and Coastal groundwater zones.

Table 4.3: Summary statistics for dissolved oxygen in the Hautere and Te Horo groundwater zone monitoring bores. Lower Quartile = 25% quartile, Upper Quartile = 75% quartile.

Bore number	Depth	N	Minimum	Lower Quartile	Median	Upper Quartile	Maximum
r25/5100	48.2	46	0.000	0.045	0.150	0.730	4.380
r25/5135	93.27	37	0.000	0.033	0.310	1.105	8.510
r25/5164	Unknown	45	0.000	1.890	4.470	8.015	8.800
r25/5165	8	44	0.000	0.048	0.235	0.828	8.770
r25/5190	Unknown	24	1.950	3.720	4.820	8.175	12.000
s25/5200	45.8	41	0.000	0.090	0.300	1.330	10.200
s25/5256	30.78	51	3.450	6.060	6.985	9.770	9.770

4.1.4 Mann Kendall Results

Table 4.4: Seasonal Mann Kendal results for the presence of monotonic trend (U=up, D=down). Significance was tested at p=0.05. Slope gives an idea of magnitude of trend. Significant trends are highlighted.

		Total Dissolved Solids (ppm)			N-NO3 (mg/L)			Dissolved Oxygen (mg/L)		
Bore number	Depth (m)	Trend	P-value	Slope	Trend	P-value	Slope	Trend	P-value	Slope
s25/5256	30.78	U	0.075	0.6	D	<0.001	-0.2717	D	<0.001	-0.645
r25/5165	8	D	<0.001	-3.333	D	0.056	-9.83E-03	D	0.089	-7.67E-02
r25/5164	N/A	D	<0.001	-34.25	U	<0.001	4.17E-02	U	0.011	0.6214
s25/5200	45.8	U	0.86	0	D	0.662	0	D	<0.001	-0.7957
r25/5190	N/A	U	0.82	1.5	D	0.065	-0.3437	D	0.024	-0.1458
r25/5135	93.27	D	0.06	-1.896	D	0.025	-1.43E-04	D	0.396	-0.1357
r25/5100	48.2	U	0.02	0.222	U	0.187	0	D	0.169	-3.67E-02

Nitrate concentrations at majority of wells appear to have a downward trend (regardless of significance). Concentrations in bores s25/5256 and r25/5135 appear to be significantly decreasing, whereas nitrate concentrations in bore r25/5164 show a significant increase over time (table 4.4).

The significant increase or decrease of one chemical component does not appear to indicate a significant increase or decrease of the other components. However, there appears to be a positive relationship between the direction of trend in Nitrate concentrations and the direction of trend in dissolved oxygen with the exception of bore R25/5100.

The pattern is not so clear with TDS concentrations relative to the other two chemical components.

Significant changes for all three chemical components occur at bore r25/5164. The direction of monotonic trend in this bore is consistent with the chemical relationship identified in previous literature between dissolved oxygen, Nitrate, and TDS. That is, one would expect to see a significant increase in nitrate concentrations if there is a significant increase in percentage of dissolved oxygen, and an increase in percent oxygen should indicate a decrease in TDS.

Bores r25/5100, r25/5164, r25/5165, r25/5190 are located in the Coastal groundwater zone, the other three bores are located in the Hautere zone.

4.2 Regression Results

4.2.1 Effect of Land Use on Nitrate Concentrations

Land use does seem to have a significant effect on current nitrate concentrations in the area. According to the regression model for land use, the area (in hectares) of beef cattle farming, fruit growing, lifestyle blocks, and settlements within a 500m radius of a bore can potentially contribute to elevated nitrate concentrations within the wells. Minitab results include a Wald test statistic for each coefficient estimate. The absolute magnitude of the Wald's statistic determines the importance of that variable on nitrate concentrations. A summary of results is presented in the table below (table 4.5).

Table 4.5: Summary of Tobit regression results for significant land use variables.

Variable Name	Coefficient (	Standard Error	Wald's Stat	p-value
Beef Cattle Farming	0.0509	0.003	19.00	<0.001
Lifestyle Block	0.0956	0.004	24.35	<0.001
Settlement	0.0429	0.003	17.10	<0.001
Fruit Growing	0.4921	0.012	45.33	<0.001
Intercept	-2.825	0.141	-20.07	<0.001

Each of the final land use variables in the model have a positive relationship with nitrate concentrations. A unit increase in one of the above land use variables is modelled to have an increase in nitrate concentrations by the amount stipulated in the coefficient estimate. For example, an increase of one hectare in lifestyle block will increase the latent variable (observed nitrate concentration) by 0.0956 units.

The Wald statistics for each variable also suggests that the amount of land used for fruit growing within the 500m buffer zone has the greatest influence on nitrate concentrations whereas the area of settlement zone has the least additive effect on nitrate concentrations. Figures 4.4 and 4.5 provide a visual representation of the relative amounts of land use types within the buffer zones. The distribution of indentified land use parcels around each well is shown in magnified view in figure 4.5, whereas figure 4.4 shows the location of each well within the study site.

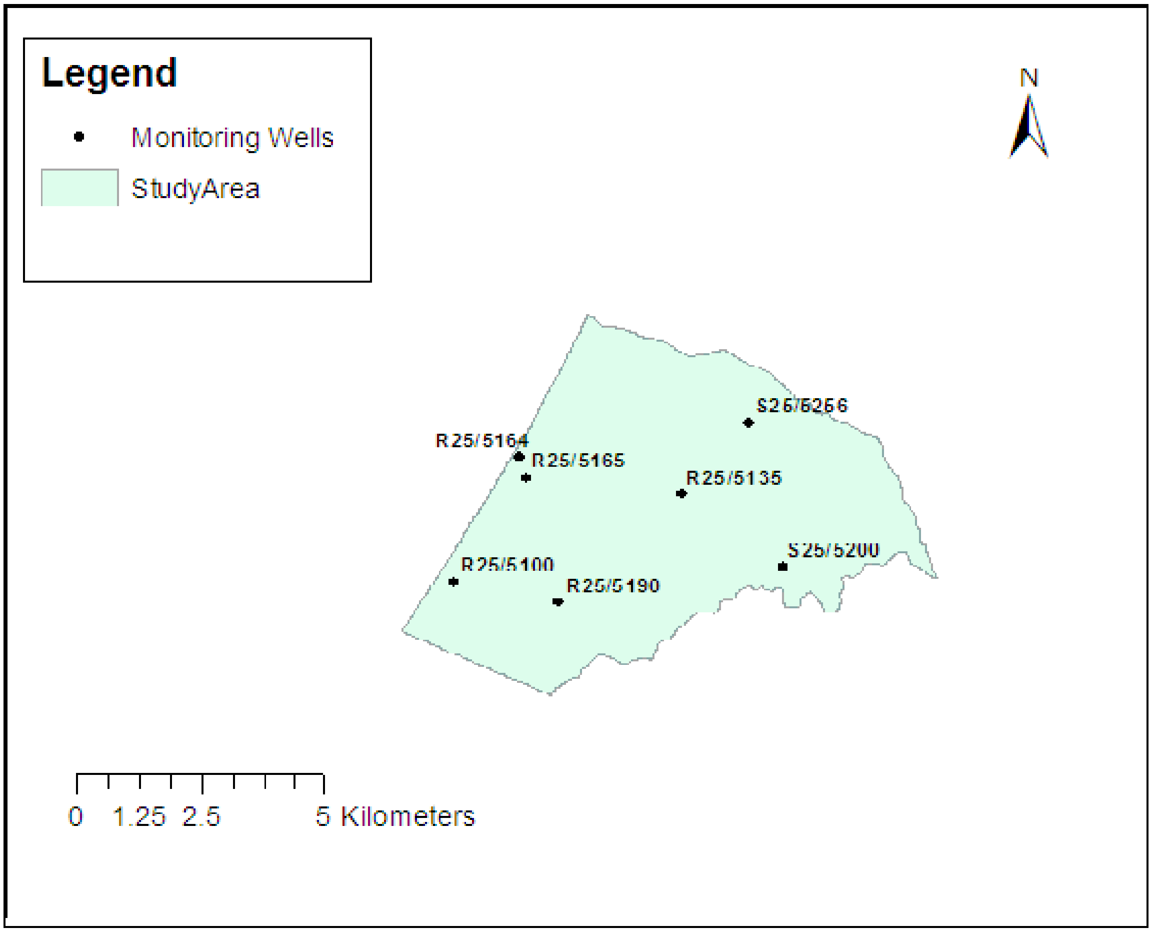

Figure 4.4: Location of sample wells within the study site.

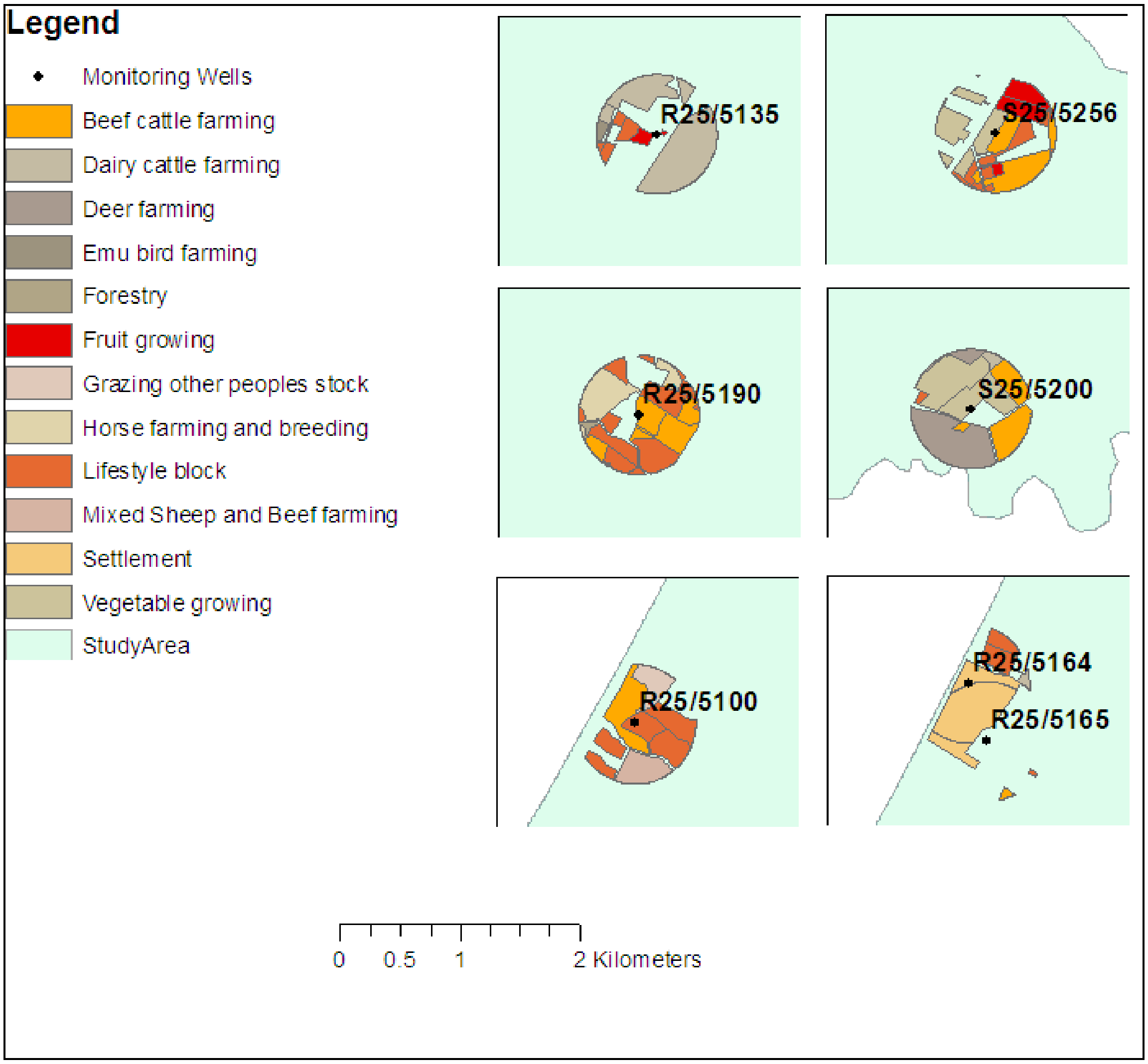

Figure 4.5: Showing distribution of land use variables around buffer zones. Land use types found to significantly influence nitrate concentrations according to Tobit regression analysis are displayed in colours. Other land use types are displayed in grey scale.

It is interesting to note that fruit growing land use type appears to be only present around bores S25/5256 and R25/5135, even though it is the most influential land use variable on nitrate concentrations.

Results from section 4.1.1 seem to corroborate the regression model as nitrate concentrations in bore S25/5256 are the highest and the bore is surrounded by three of the four major influential land use types. Bore R25/5190 has the second highest nitrate concentrations out of the set of seven bores. There are no fruit growing areas within the buffer zone, yet there are large areas of lifestyle blocks and beef cattle farms.

When observed nitrate concentrations above the censoring limit are plotted against predicted model nitrate concentrations, the resulting trend line appears to fit the data quite well (figure 4.6). The overall log likelihood test statistic is 257.25, which corresponds to a p-value of <0.005 with 4 degrees of freedom. The null model can therefore be rejected.

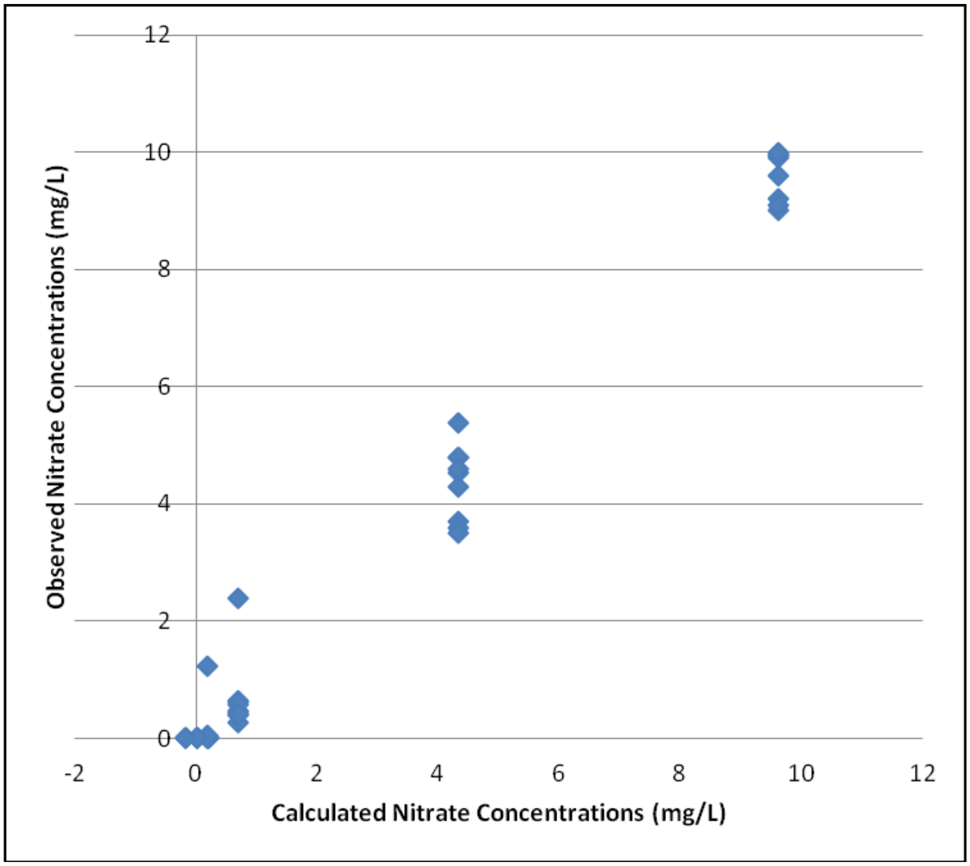

Figure 4.6: Observed nitrate concentrations from 2007 to 2009 versus calculated nitrate concentrations using Tobit land use model.

The vertical distribution of points is caused by differences in observed nitrate concentrations during repeated quarterly sampling, whereas calculated nitrate concentrations do not vary as land use distribution is assumed to have remained the same from 2007 to 2009.

4.2.2 Effect of Land Cover on Nitrate Concentrations

The land cover variables found to significantly influence nitrate concentrations within a 500m radius buffer zone are the areas of high producing grassland, vegetated wetlands, towns, natural forests, annual crops and perennial crops (table 4.6).

Table 4.6: Summary of Tobit regression results for significant land cover variables

Variable Name	Coefficient	Standard Error	Wald's stat	p-value
High Producing Grassland	-0.196	0.004	-44.50	<0.001
Vegetated Wetland	-0.431	0.017	-24.89	<0.001
Towns	-0.163	0.008	-19.42	<0.001
Natural Forests	0.078	0.014	5.60	<0.001
Annual Cropland	0.087	0.010	8.91	<0.001
Perennial Cropland	0.115	0.008	13.94	<0.001
Intercept	10.029	0.285	35.16	<0.001

Three of the variables, high producing grasslands, vegetated wetlands and towns, appear to have negative effects on nitrate concentrations whereas natural forests, and both types of croplands have a positive effect. The variable with the highest influence on nitrate concentrations is high producing grasslands. In fact, in terms of influence, the variables which show a negative correlation to the latent variable appear to have the biggest Wald's statistics (in terms of greatest deviation from zero). Natural forests seem to have the smallest influence.

Looking at the spatial distribution of land cover variables (figure 4.7), one would expect to see low nitrate levels in bores such as R25/5200, R25/5135, R25/5164 and R25/5165 as these bores appear to be surrounded by significant areas of high producing grasslands and towns. Comparing these predictions to the results in section 4.1.1, nitrate concentrations in these bores do appear to be quite low. R25/5135 is immediately surrounded by an area of perennial cropland. However, since the regression model attributes a higher influence to high producing grasslands and towns, it is expected that these land cover variables will outweigh the positive influence of perennial crops on nitrate concentrations.

Bore S25/5256 is surrounded by quite a large area of perennial and annual crops, which have a positive correlation with nitrate concentrations. Indeed, observed nitrate concentrations in this bore are quite high.

However, the same pattern should be present in bore R25/5190 as it has the second highest recorded nitrate concentrations in the study area. This bore is not surrounded by large areas of natural forests or croplands. There are larger areas of vegetated wetlands and high producing grasslands, and these variables are negatively correlated with nitrate concentrations according to the model. The expected pattern does not appear to fit the observed nitrate concentrations in this particular bore.

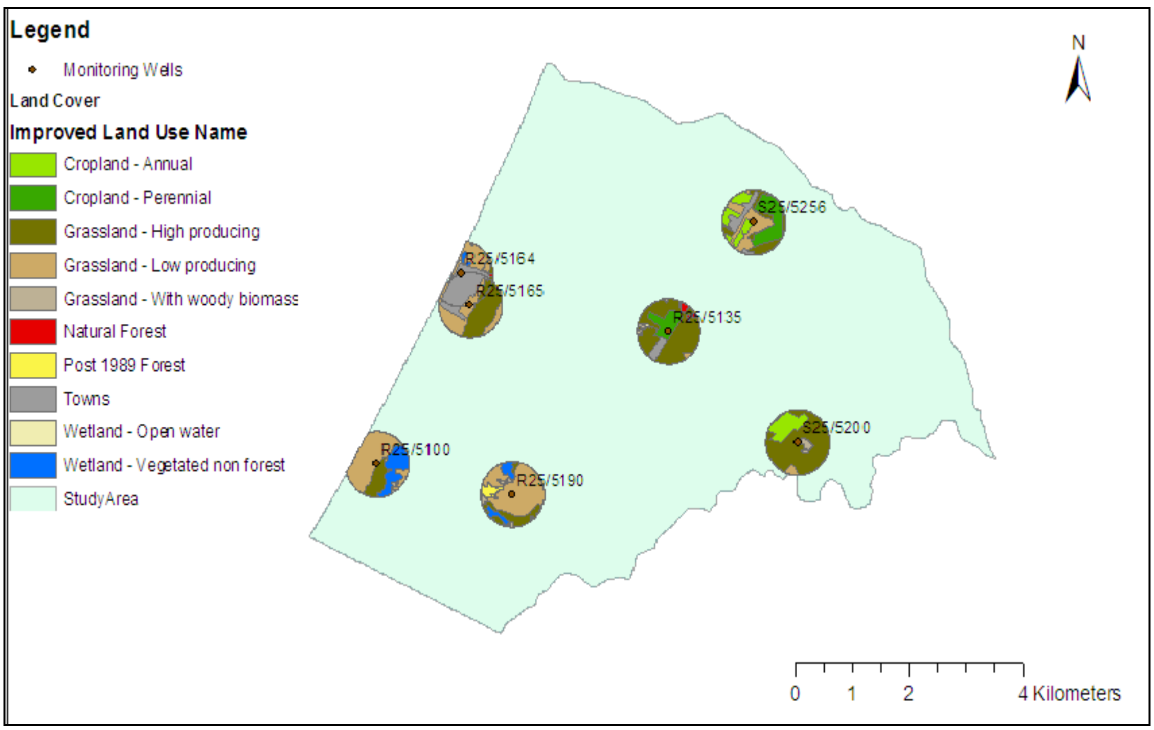

Figure 4.7: Distribution of land cover variables around buffer zones. Land use variables found to be significant predictive variables in the regression model are shown in brighter colours.

The overall log likelihood statistic for the land cover model is 261.576. The result is a significance value of $p < 0.005$ with 6 degrees of freedom. This suggests that the land cover Tobit model is a better fit than not having a model. A graph of observed nitrate values versus calculated values (figure 4.8) are shown below.

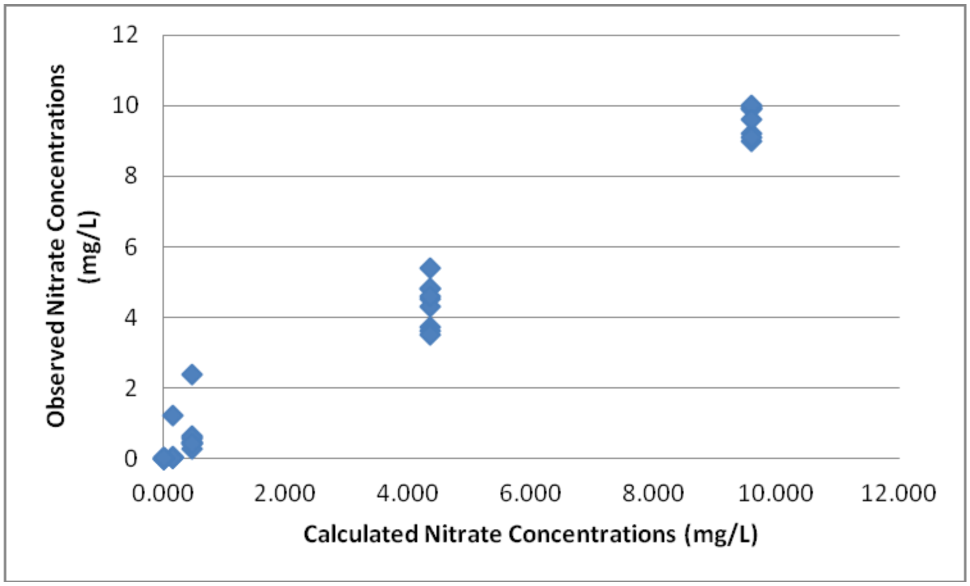

Figure 4.8: Observed nitrate concentrations from 2007 to 2009 versus calculated nitrate concentrations using Tobit land cover model.

4.2.3 Effect of Soil Type on Nitrate Concentrations

The soil types which appear to have a significant influence on nitrate concentrations are the loamy soils (table 4.7).

Table 4.7: Summary of Tobit regression results for significant soil types

Variable Name	Coefficient	Standard Error	Wald's Stat	p-value
Silt Loam	-3.168	0.576	-5.50	<0.001
Peaty Loam	-23.837	4.231	-5.63	<0.001
Fine Sandy Loam	14.922	0.851	17.54	<0.001
Intercept	2.216	0.259	8.56	<0.001

The silt loams and peaty loams have a negative correlation with observed nitrate concentrations whereas fine sandy loam shows a positive correlation. The Wald's statistic is much larger for fine sandy loam, indicating that the presence of this soil type might contribute to higher concentrations of nitrate concentrations at a particular site.

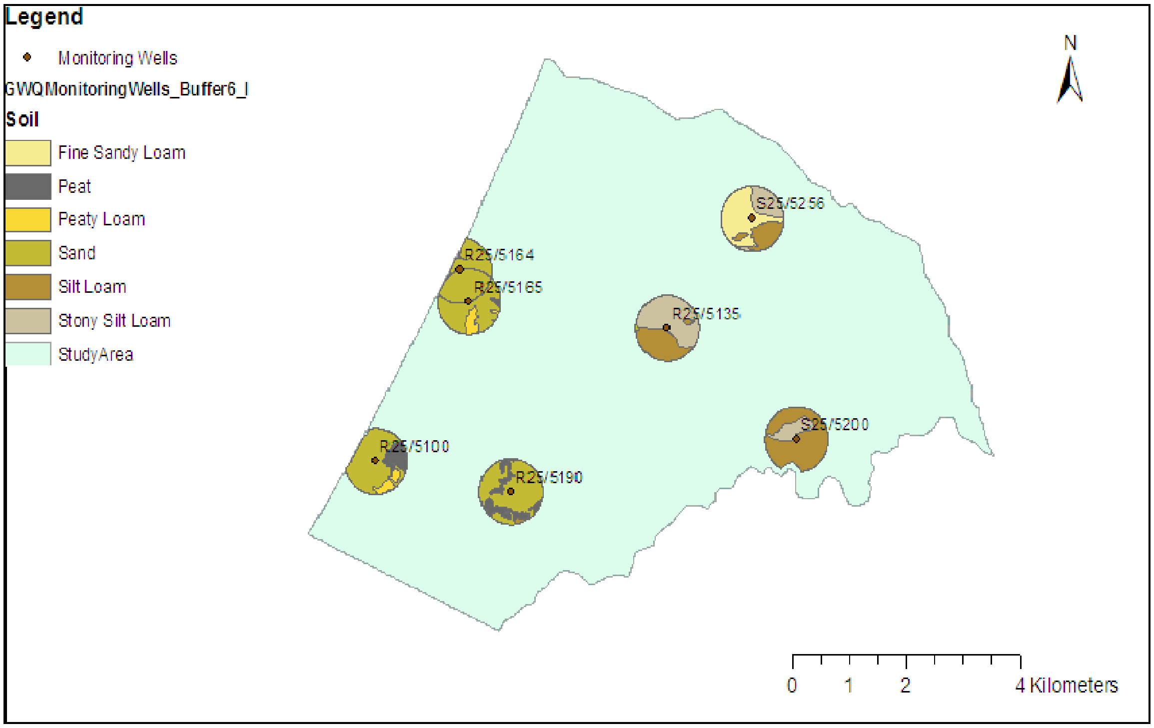

Figure 4.9: Distribution of soil type variables around buffer zones.

Similar to the other regression variables, bore number S25/5256 buffer zone contains the highest area of fine sandy loam soil, which fits in with the bore having high nitrate concentrations. Bores S25/5200 and R25/5135 include large areas of silt loam, therefore having lower nitrate concentrations. Again, the exception is bore R25/5190 which has exhibits high nitrate concentrations, but does not contain any of the soil variables which are indicative of high nitrate concentrations (figure 4.9).

So far, land use has been the best indicator of nitrate concentrations for bore R25/5190.

The overall log likelihood test statistic for the soil type model is 126.67, which corresponds to a p-level of less than 0.005 with 3 degrees of freedom. The null model is therefore rejected. A graph of observed concentrations versus calculated concentration is shown below (figure 4.10).

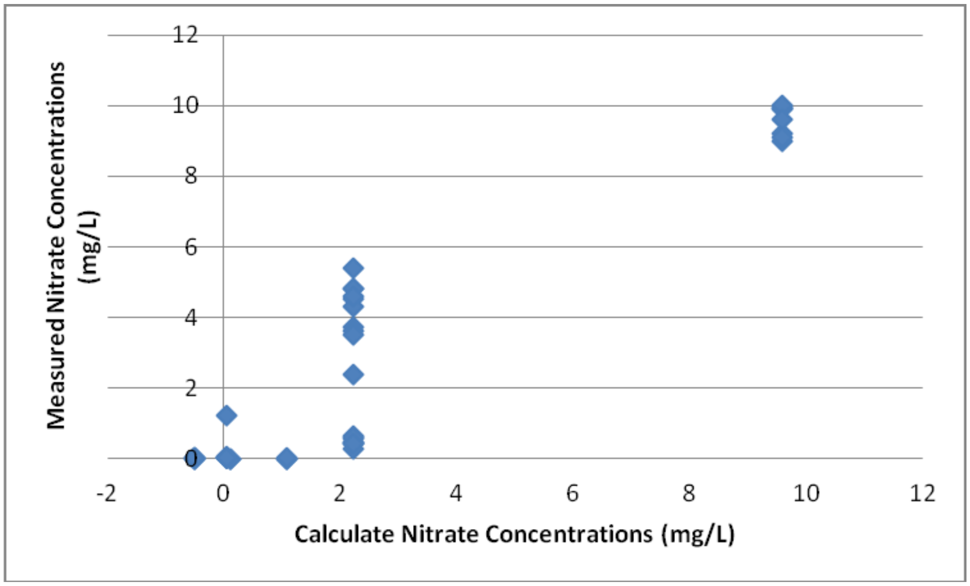

Figure 4.10: Observed nitrate concentrations from 2007 to 2009 versus calculated nitrate concentrations using Tobit soil type model.

4.2.4 Effect of TDS and Dissolved Oxygen on Nitrate Concentrations

Out of these two chemical variables, dissolved oxygen was the only significant predictor of nitrate concentrations. This confirms that the apparent relationship seen in section 4.1 between nitrate concentrations and dissolved oxygen is a significant relationship.

Both wells with the highest nitrate concentrations also display the highest dissolved oxygen content. The summary Tobit statistics for this variable are shown in table 4.8 below.

Table 4.8: Summary of Tobit regression results for significant chemical variables.

Variable Name	Coefficient	Standard Error	Wald's Statistic	p-value
Dissolved Oxygen	0.696	0.064	10.93	<0.001
Intercept	0.128	0.291	0.44	0.661

The corresponding graph of observed nitrate concentrations versus calculated nitrate concentrations has also been plotted below (figure 4.11). The intercept was left out of the model equation due to the lack of significance of the intercept coefficient estimate.

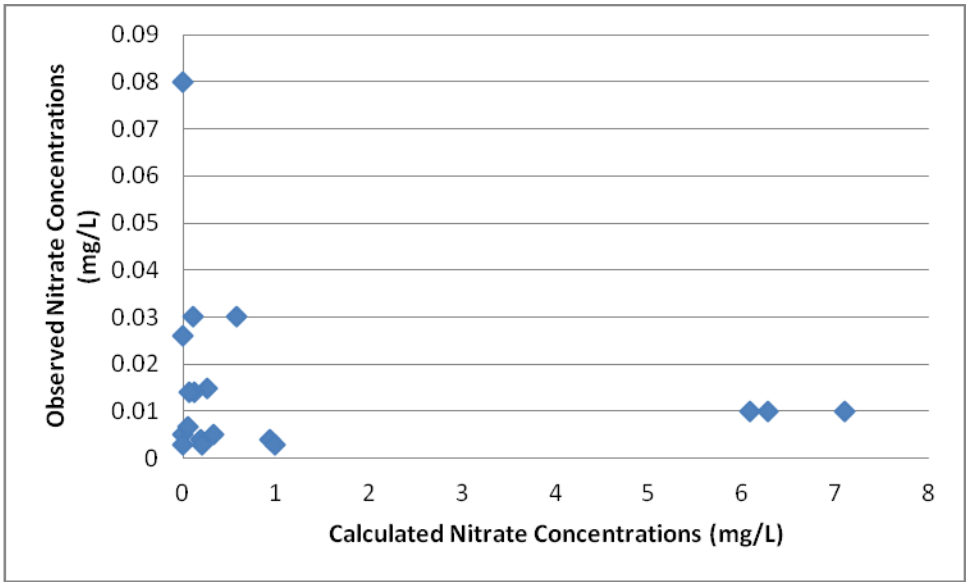

Figure 4.11: Observed nitrate concentrations from 1993 to 2009 versus calculated nitrate concentrations using tobit chemical component type model.

The modelled nitrate concentrations do not appear to fit the observed values very well. The overall log likelihood for this Tobit model was 1376.15, which is significant ($p<0.05$) with 1 degree of freedom, so the model will be accepted.

Neither of the two climate variables, regional temperature or rainfall, was a significant explanatory variable.

4.3 Nitrate Plume Migration

Both contour maps show a clear spike in nitrate concentrations in the northern area of the study site which seems to have remained for the last 20 years. Figures 4.12 and 4.13 represent the kriged nitrate plume data for the 1996 sampling year. Figure 4.13 is a visual representation of the kriging error associated with each data point. Similarly, figures 4.14 and 4.15 represent the kringing results and associated standard errors for the 2008 dataset.

The highest concentrations in 2008 are lower than 1996, indicating that concentrations have possibly declined over the study period. The plume appears to have migrated further north and increased its lateral spread.

There is a clear difference in distribution of sample points. In 1996, sampling points are clustered around the northern half of the study site, whereas sampling points are more evenly distributed for the study conducted in 2008. This obviously has an effect on the distribution of standard error. In both maps, the standard error increases sharply the further away predictions are from a measured data point. Prediction error also seems to be higher for the 1996 map. The tables provide an indication of the distribution of nitrate concentrations with depth.

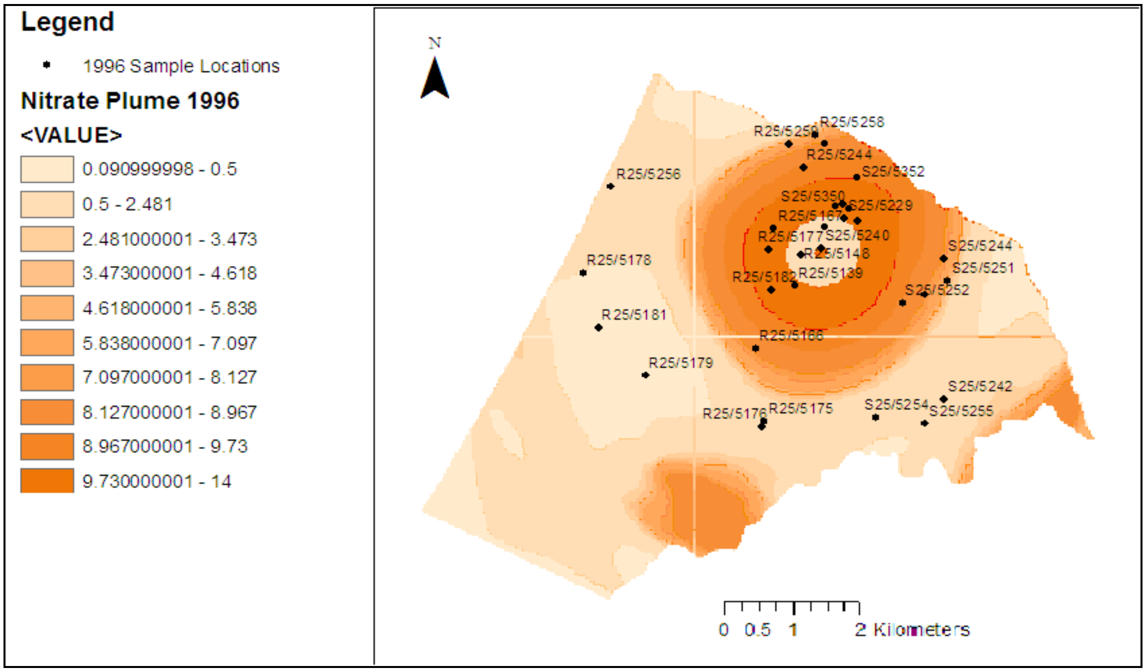

Figure 4.12: Kriged contours of nitrate concentrations (mg/L) based on 1996 sample results. Location of measured data points are also shown.

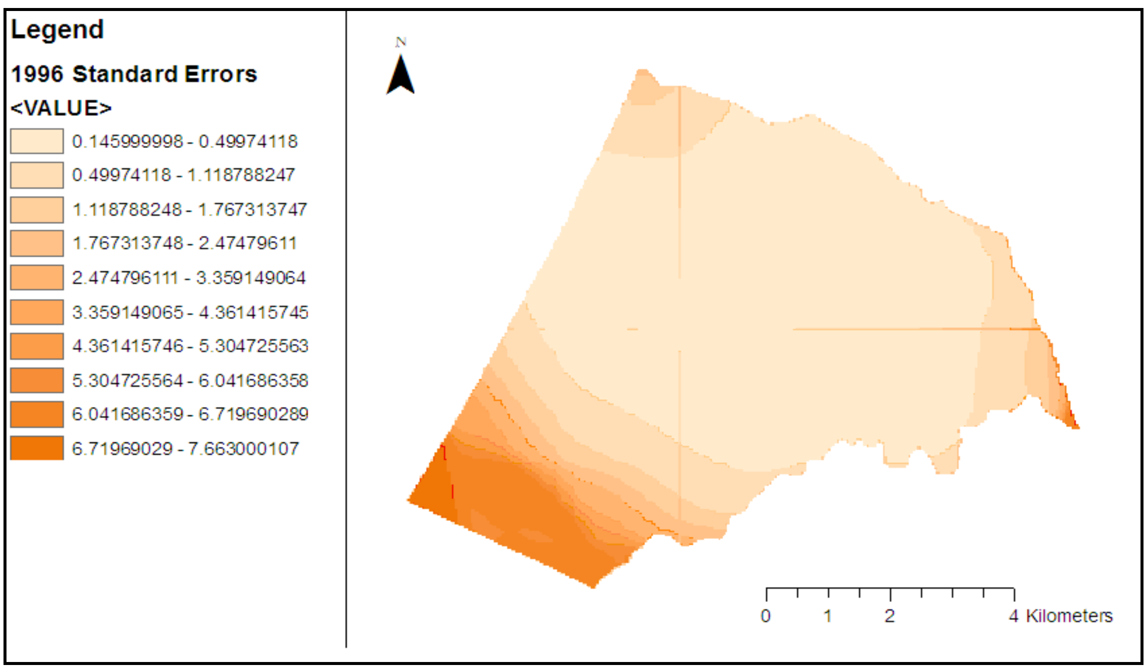

Figure 4.13: Standard error of estimation for kriged 1996 nitrate concentrations (mg/L).

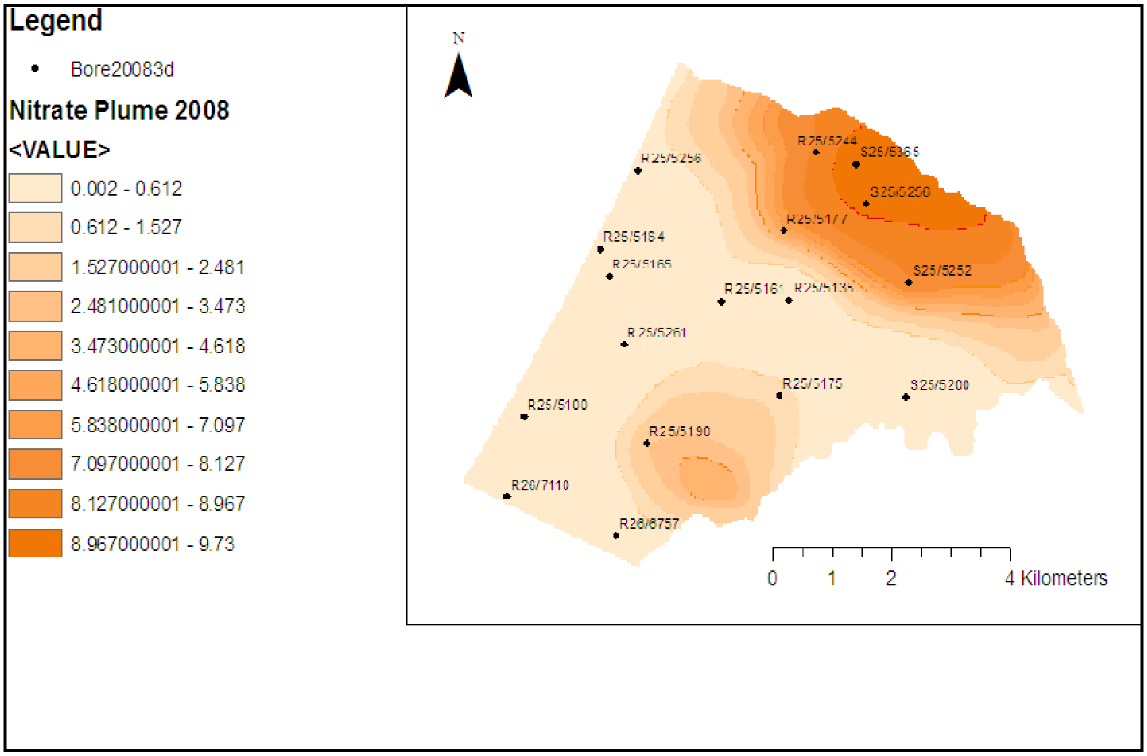

Figure 4.14: Kriged contours of nitrate concentrations (mg/L) based on 2008 sample results. Location of measured data points are also shown.

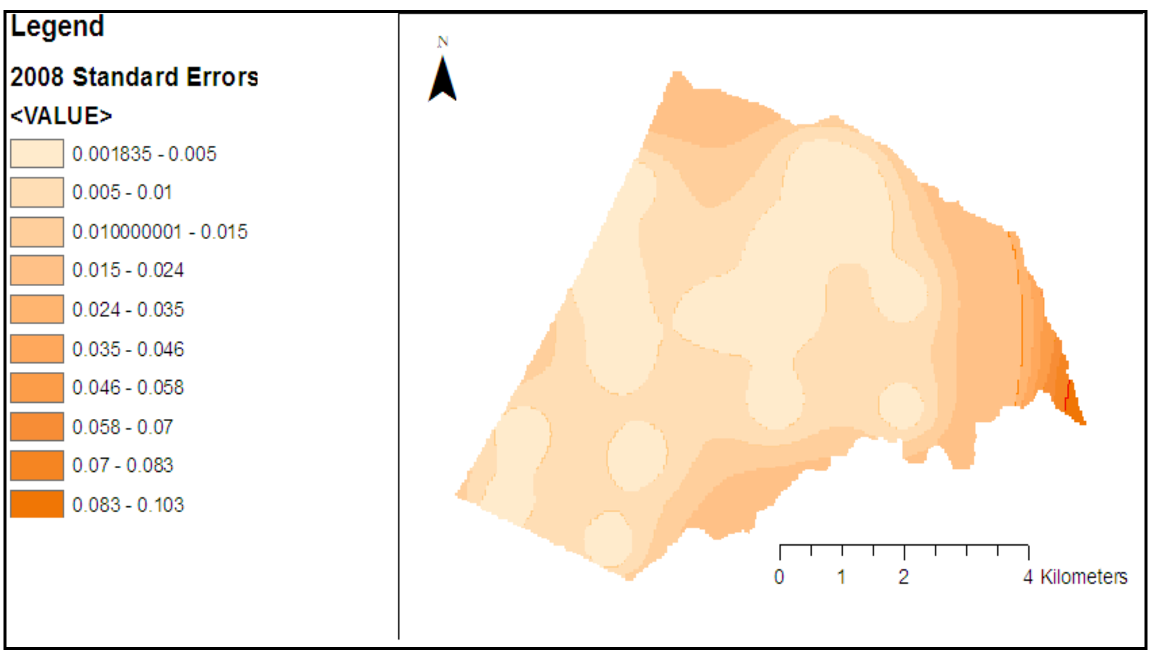

Figure 4.15: Standard error of estimation for kriged 1996 nitrate concentrations (mg/L).

The tables below outline the bore sites and associated nitrate and depth data used in the kriging analysis above. Table 4.9 outlines the 1996 data and table 4.10 displays the 2008 data.

Table 4.9: Showing 1996 sample data categorised by groundwater zone. Bore screen depths are also shown where available.

Well ID	Nitrate Nitrogen (mg/L)	Depth	Zone
R25/5181	0.05	24.2	Coastal
R25/5259	0.05	Unknown	Coastal
R25/5179	0.05	Unknown	Coastal
S25/5251	0.14	Unknown	Hautere
S25/5254	0.14	25	Hautere
S25/5255	0.15	Unknown	Hautere
S25/5250	0.18	Unknown	Hautere
R25/5178	0.90	7.3	Hautere
R25/5256	0.96	9	Coastal
R25/5176	1.70	4	Hautere
R25/5175	3.00	12.5	Hautere
R25/5257	6.20	30	Hautere
S25/5242	7.10	20.3	Hautere
R25/5166	8.50	9	Hautere
R25/5180	8.60	30	Hautere
S25/5352	8.70	Unknown	Hautere
S25/5244	8.70	48.5	Hautere
R25/5258	9.20	15.3	Hautere
R25/5182	9.40	Unknown	Hautere
R25/5148	10.00	30	Coastal
R25/5244	10.00	19.82	Coastal
S25/5359	11.00	20.1	Hautere
R25/5177	11.00	4	Hautere
S25/5366	12.00	22.8	Hautere
S25/5252	12.00	20.3	Hautere
S25/5256	13.20	30.78	Hautere
S25/5350	15.00	18.2	Hautere
R25/5139	15.00	51	Hautere
S25/5229	16.00	18	Hautere
S25/5240	16.00	18.2	Hautere
R25/5167	17.00	Unknown	Coastal

Concentrations in bores S25/5244 and bore R25/5139 are located in the deeper, confined aquifer in the Hautere Zone. This is according to the aquifer classification specified in Kampman & Caldwell (1985). These bores show highly elevated nitrate concentrations and could indicate the presence of a plume at depth (table 4.9). Both bores are located to the North of the study site. Note that bores with unknown depths are thought to be derived from surface, unconfined aquifers.

Table 4.10: Showing 2008 sample data categorised by groundwater zone. Bore screen depths are also shown where available.

Well ID	Zone	Nitrate Nitrogen (mg/L)	Depth
R25/5261	Coastal	0.023	5.9
R25/5256	Coastal	0.100	9
R26/6757	Coastal	0.210	7
R25/5161	Coastal	1.500	37
R25/5175	Hautere	2.500	12.5
R25/5177	Coastal	7.500	4
R25/5244	Coastal	8.200	19.82
S25/5252	Hautere	8.800	20.8
S25/5365	Hautere	10.000	7
R26/7110	Coastal	0.001	5
R25/5100	Coastal	0.003	48.2
R25/5135	Hautere	0.001	93.27
R25/5164	Coastal	0.410	Unknown
R25/5165	Coastal	0.016	8
R25/5190	Coastal	4.800	Unknown
S25/5200	Hautere	0.001	45.9
S25/5256	Hautere	9.600	30.78

The sample data is much smaller for the 2008 study and all except one bore (R25/5135) draw water from the surface aquifer, indicating that the estimated nitrate plume is representative of surface aquifers.

5 Discussion

5.1 Temporal Trends and Comparison to Previous Work

For the purpose of interpreting results, nitrate levels will generally be categorised into three groups: Low, elevated, high. The grouping of these levels are indicated in appendix 4.

Initial summary statistics and temporal analysis of available monitoring data indicate that nitrate contamination is restricted to surface aquifers. Bore S25/5256 has historically displayed the highest concentrations, and according to previous site specific studies conducted in the same area, it becomes clear that the bore is representative of a cluster of bores located in the northern part of the Hautere zone which have consistently displayed high nitrate concentrations, with some bores exceeding the drinking standard MAV (Hughes 1997; Tidswell 2009). Hughes (1997) compared results of his study with an earlier study undertaken in 1982 and stated that nitrate concentrations between 1982 and 1996 had increased from 20 to 40 percent.

Tidswell (2009) undertook sampling of bores in the Te Horo area in November/December 2008 in order to compare recent contaminant values from Hughes' December/November 1996 study. The subsequent report published in 2009 showed nitrate concentrations to be significantly reducing (using a significance level of 0.05 and 0.1) in two of the sampling bores within the study site (S25/5256, R25/5190), and concentrations in one bore (R25/5164) appeared to be increasing. These results were comparable with trends found in this study. Bore S25/5256 showed a decreasing, monotonic trend in nitrate at a significance level of 0.05, and bore R25/5190 showed a decreasing trend at a significance level of 0.1, but not 0.05. Bore R25/5164, located in the Te Horo township, displays a significantly increasing trend at a significance level of 0.05.

The estimates of rate of change (slope) in section 4.1 for nitrate concentrations indicate that concentrations in bore S25/5256 are decreasing rapidly by around -0.27 mg/L/year. The same rapidly decreasing trend is found for bore R25/5190 (-0.34 mg/L/year). These rates of decrease are very similar to those that have been calculated previously (Tidswell 2009). Conversely, the rate of increase for bore R25/5164 is low (0.042 mg/L/year).

Temporal trend analysis conducted for this study also detected a significant decrease in nitrate concentrations in bore R25/5135. Nitrate concentrations in this bore were very low (median value of 0.0025mg/L). This trend was not detected in Tidwell's study (2009) although the same data and the same trend analysis were used in the Tidswell study. This discrepancy in results is likely due to the software used and how this software deals with certain data inadequacies. For example, NIWA's Time Trends (used in the Tidswell study) ignores tied values in its Seasonal Mann-Kendall analysis (Ian Jowett 2011), whereas the USGS Mann-Kendall programme used to test this data accounts for tied values and calculates the Seasonal Mann Kendall test statistic after adjusting for ties. As there are a large proportion of tied values in the temporal dataset, this difference in calculation methods is likely to yield different results.

It is likely that nitrate concentrations up to mid 1990's were increasing quite dramatically. This was followed by a period of decreasing concentrations from the mid 1990's to the present (with the exception of bore R25/5165). Trend analysis undertaken in this study matches well with previous investigations.

5.2 Exploring Site Differences in Chemical Data

5.2.1 Differences in Nitrate Concentrations

Based on the classification of "above background" nitrate concentrations used in previous work (Daughney & Reeves 2005; Ministry for the Environment 2007a), concentrations >1.6 mg/L are indicative of anthropogenic impact. Bores S25/5200, R25/5135 and R25/5100 display concentrations well below this threshold (0.08 mg/L, 0.086 mg/L and 0.03 mg/L maximum concentrations respectively), for a monitoring period of 15 years. Therefore, it is assumed that these bores are not affected by anthropogenic activities on the surface.

All three bores are screened in deeper, confined aquifers away from the main contaminant plume located in the northern Hautere zone. The negative correlation between depth and nitrate concentrations has been observed in previous literature specific to this study area (Kampman & Caldwell 1985; Tidswell 2009) as well as studies exploring patterns of nitrate contamination in aquifers nationwide (Ministry for the Environment 2007a). This relationship between bore depth and contaminant concentrations could explain why these bores show low nitrate concentrations at these specific locations.

Bores R25/5164 and R25/5165 are located in or very near the Te Horo township. Both bores are screened in the shallow coastal aquifers and both bores are pumped for domestic use (Tidswell 2009). However, they display very different patterns in long term behaviour of nitrate. Bore R25/5164 has consistently tested for lower nitrate concentrations when compared with bore R25/5165 over the 15 year monitoring period, but concentrations have started to increase significantly since September/December 2004 (please see appendix 3 for relevant time series plots).

With reference to time series plots, where fluctuations in TDS and dissolved oxygen are also plotted for bore R25/5164, one can clearly see an inverse relationship between increasing nitrate concentrations and dissolved oxygen versus decreasing TDS concentrations. It has been observed in previous literature that even slightly elevated concentrations of dissolved oxygen make a big difference to the amount of nitrate formed (Gurdak & Qi 2012; McMahon et al. 2011; Ministry for the Environment 2007a). It is likely that the temporal increase in nitrate concentrations corresponds to the higher availability of dissolved oxygen at this bore and not due to increased nitrogen loading into the aquifer due to land use practises.

Bore R25/5165 has been monitored for groundwater quality since 1998 and is the only bore which displays a very obvious seasonal pattern of nitrate fluctuation until July 2007. This seasonal variation (peak nitrate concentrations around March of every year) has been tested in previous studies and shown to be significant (Tidswell 2009). Some studies have shown that seasonal fluctuation in nitrate concentrations can occur when land use and irrigation practices are combined with soil properties (Lorite-Herrera & Jiménez-Espinosa 2008; Mutti 2006). For instance, fertilizer application rates applied during the growth of summer crops could increase nitrogen loading into the soil profile. Increased application of irrigation during this period could provide irrigation recharge to the aquifer during the crop growing season. If the bore is located in an area overlying high permeability soils, this combination of fertilizer application and irrigation during summer could substantially increase nitrate concentrations in unconfined groundwater during the summer season. The applicability of this land use scenario to this particular bore will be discussed subsequently when investigating regression results.

Bore S25/5256 and bore R25/5190 have consistently measured for elevated nitrate concentrations. Predictably, these two bores also display the highest concentrations of dissolved oxygen which further confirms the relationship between nitrate-nitrogen concentrations in the presence of oxidised groundwater. It is unlikely that such high concentrations in nitrate concentrations can be explained in terms of the oxidation of ammonium and ammonia exclusively, as concentrations higher than 1.6 mg/L in New Zealand groundwaters is probably due anthropogenic factors.

The seasonally high nitrate concentrations of bore R25/5165, and elevated concentrations in bores R25/5190 and S25/5256 will have to be discussed within the context of land use.

5.2.2 Differences in Dissolved Oxygen

Dissolved oxygen concentrations in deeper aquifers appear to be lower. This is expected as dissolved oxygen is naturally sourced to aquifers from the atmosphere by diffusion or percolation of oxygenated precipitation (Newman & Kimball 1991). Therefore, one would expect to see lower concentrations of dissolved oxygen in aquifers which are further away from the land surface. Bores R25/5135, R25/5100 and S25/5200 display the expected pattern of low dissolved oxygen concentrations.

An exception to the above is bore R25/5165 which is screened in the unconfined Te Horo groundwater zone aquifer, where low concentrations of dissolved oxygen have been observed. Referring to the time series plots in appendix 3, it is possible that concentrations were higher earlier in the monitoring period. However, a gap in data collection makes it difficult to determine the long term trend in dissolved oxygen.

It was noted in section 5.2.1 that dissolved oxygen concentrations in bore R25/5164 showed a dramatic increase from September 2004. Some studies have linked increases in dissolved oxygen to increased pumping rates and large pump diameters (Liu, Lin & Kuo 2003; Rose & Long 1988). Large pump diameters could introduce significant amounts of oxygen into the cone of depression during pumping, and rapid pumping is also known to introduce atmospheric oxygen into aquifers. Although bore construction details and pumping rate information is not available for bore R25/5164, it is possible that the increase in dissolved oxygen in a short space of time might be due to higher pumping rates from September 2004 or greater utilization of bore R25/5164 from this date.

5.2.3 Differences in Total Dissolved Solids

Variability in TDS is quite limited for most of the bores, this is illustrated by the box plots in section 4.1 with most bores testing for low to moderate concentrations of TDS.

TDS concentrations are noticeably higher in bore R25/5135. Changes in total dissolved solids primarily reflect natural changes in groundwater processes and can be used to determine groundwater source and age in some instances (Ministry for the Environment 2007a). As recharge waters move through rock, rock-water interactions take place and salt concentrations accumulate in groundwater as it flows through an aquifer. Therefore, water that has travelled longer is likely to have higher TDS concentrations. Bore R25/5135 is a deeper aquifer. It is likely that water sourced from this aquifer is older and has travelled further than shallower aquifers, which might explain elevated TDS concentrations at this site.

5.2.4 Comparison with National Standards

At present, none of the bores display levels of nitrate exceeding the national drinking water standards (11.3 mg/L of nitrate-nitrogen). However, it is important to note that these values are measured against continued ingestion of contaminated water over 70 years, for an individual weighing 60 kilograms (Ministry of Health 2008). During the last four years, New Zealand has redirected the measure of fresh water quality to encompass wider considerations such as the ecological impact of lower water quality and the interconnectedness of freshwater bodies.

Recent national policies in freshwater management (New Zealand Government 2011) require regional authorities to safeguard the quality of fresh water bodies, their life supporting capacity and the health of the unique ecological communities sustained by that water body when considering discharge applications and water allocations. This would involve tighter regulation of land use activities. Although results indicate that groundwater quality is improving in the area, nitrate levels in bores such as r25/5190 and r25/5256 remain elevated and could potentially have additive detrimental effects on other surface water bodies (such as discharging springs and wetlands) as well as infants if ingested.

At present, new limits on water quality and quantity are not yet defined. These limits are likely to based on a catchment level, as determined by regional councils according to a national framework. Consideration will have to be given to improving the state of nitrate contamination in the study region if national policy guidelines are to be met by 2050.

The MAV for TDS is 1000mg/L, which is well over the concentrations found in any of the monitoring wells. However, it is noted that concentrations above 600mg/L could affect the taste of water. Bore R25/5164 has had TDS levels exceeding 600mg/L.

5.3 Differences in Physical Catchment Properties

5.3.1 Land Cover, Land Use and Nitrate Distribution

Results from section 4.2 indicate that bores located near lifestyle blocks, settlements, beef cattle farms and fruit growing activities and annual croplands are at a higher risk of being contaminated with nitrate.

The land use type with highest influence on elevated nitrate concentrations was fruit growing, which is a horticultural land use activity. Although land use data was limited to 2008, the land cover map can be used to determine that from 1990 to 2008, the area of high contamination in the northern Hautere and Coastal groundwater zone were covered by croplands, some of which intersect with lifestyle blocks which grow perennial and annual crops. Therefore, it is likely that, for the last 15 years, the highest nitrate concentrations in groundwater were caused largely by horticultural activities.

Well locations and nitrate concentrations measured by Tidwell (2009) and Hughes (1997) are shown in Appendix 4. When nitrate concentration measurements from 1996 (Hughes 1997) are overlain on land use and land cover data, it becomes clear that the majority of wells with highly elevated nitrate concentrations are found in crop lands, beef farming and lifestyle block areas. This provides a better visualization of the impacts of land use on nitrate concentrations as a larger number of bores were used in the 1996 and 2008 studies.

As noted in section 5.1 nitrate concentrations increased by 20 to 40 percent from the early 1980's to the early 1990's. According to Kampman and Caldwell (1985), large quantities of land were converted from dairy farming areas to horticultural areas, and lifestyle blocks were being established in the 1980's. This description of land use change conforms well to the results of this study and indicates that the original rise in nitrate contaminants in the area was probably due to an increase in market gardening and development of lifestyle blocks. Bores R25/5190 and S25/5256 are located in areas with dense distributions of croplands, lifestyle blocks and beef farming land use activities and therefore have the highest nitrate concentrations.

This pattern is possibly caused by the application of nitrate and ammonium based chemical fertilizers in croplands (Spalding & Exner 1993) which tend to be located over areas with well drained soils. In combination with ample dissolved oxygen in aquifers, leached ammonium from chemical fertilizers can also be oxidized to nitrate (Ministry for the Environment 2007a) . This would explain the pattern observed in the previous section where bores with high nitrate concentrations also have high dissolved oxygen concentrations. The regression analysis found dissolved oxygen to be a significant indicator of elevated nitrate concentrations in this study area.

Settlements were also attributed with higher nitrate concentrations. According to previous literature, septic tanks can be a major point source of nitrate contamination into groundwater (Burden 1984; Tidswell 2009). A greater number of septic tanks are likely to be located in settlements, and is likely to be the main cause of nitrate contamination into the soil.

5.3.2 Soil types and Nitrate Distribution

The permeability of vadose zone soils were found to be one of the most important factors determining nitrate leaching to aquifers in other studies (McLay et al. 2001; Spalding & Exner 1993). Soils of high permeability allow the percolation of irrigation water and rainfall into ground water at a faster rate, thereby contributing to high nitrate leaching into soils overlain by crop agriculture (Spalding & Exner 1993). Appendix 5 shows a soil permeability map created by Landcare Research. This is followed by the distribution of simplified soil types used in the regression analysis for this study. From the comparison of two maps, it is clear that the high permeability soils are sands, sandy loams and stony silt loams.

The results of the regression analysis only found fine sandy loam soils to have a significant effect on nitrate concentrations. Bore S25/5256 was located in an area of fine sandy loams, therefore the regression analysis fit the area of high concentrations quite well. However, bore R25/5190 also displayed elevated nitrate concentrations, but was overlain by sandy soils which did not appear to be significant as an explanation for high concentrations. Different results might be yielded if soil permeability had been used as one of the factors in this study.

As briefly mentioned in section 3.2.3, a high degree of multicollinearity exists between the variables of interest. That is, areas of land cover, land use and soil types are highly correlated to each other. The classification of land cover greatly depends on the type of land use activity in the area. For example, an area is classified as a perennial cropland or an annual cropland only if either vegetable growing or fruit growing land use activities are present on that location.

Similarly, land use activities such as beef and deer farming, mixed farming, emu farming etc. will only occur on land cover areas classified as high producing grasslands and low producing grasslands. Land use activities designated as either townships or lifestyle blocks will only occur on land cover parcels that are classified as settlements.

Spalding & Exner (1993) conducted a national summary of the occurrence of nitrate in groundwaters of the USA. One of their observations was that the majority of crop agriculture was underlain by well drained soils. It is likely that, for economically viable reasons, agricultural croplands and pasturelands are established on well drained, permeable soils. This could explain why croplands in the study area overlie a particular type of soil type, thus explaining the high degree of multicollinearity between land use, land cover and soil type.

The reader should be aware of the relationship between these groups of variables when interpreting regression results.

5.3.3 Changes in Physical Characteristics

Land cover and soil type have not changed since the beginning of the study period, therefore, although the initial distribution in elevated nitrate concentrations may be explained by a combination of land cover and soil type, it does not explain why concentrations have reduced over the last 15 years. It is also important to note that the original cause of nitrate contamination cannot definitively been confirmed in this study as it extends beyond the time period relevant to this study.

Land use was only available for 2008 thus making it difficult to quantify changes in land use over the study period. However, as discussed in the previous section, when descriptions of previous land use are provided in earlier studies, and are combined with land cover data, one can assume land use has not changed too significantly over the last 15 years.

Tidswell (2009) indicates a number of possible reasons for decreasing trends, such as a change from intensive to less intensive croplands, improved land use local authorities have implemented improved land use management processes and local farmers are more informed about timing of fertilizer application and optimal irrigation scheduling in order to reduce impacts to groundwater. Additionally, fertilizer technology has improved to incorporate organic compounds which release nitrates into the land slowly over a long period of time. These improvements in land management practices could explain the reduction of nitrate concentrations over the last decade.

A study in the Netherlands (Boumans, Fraters & Van Drecht 2001) compared the nitrate concentrations of groundwater in an upper, sandy aquifer underlying an experimental farm with best practise nitrogen management techniques verses 94 representative farms from the same region. The monitoring period extended for eight years. The study concluded that mean nitrate concentrations in the upper aquifer underlying the experimental farm decreased from 193mg/L to 30mg/L. The decrease of mean nitrate concentrations during the first year of monitoring were attributed purely to good management practises. In contrast, the mean nitrate concentrations of upper aquifers underlying the representative farms were 81% higher. Therefore, it is quite possible that better land use management practises implemented in the Te Horo district could account for the overall trend of decrease nitrate concentrations in groundwater.

It is important to note that there could be a lag time when detecting responses in water quality to land use management practices and land use impacts (Hughes 1997; Meals, Dressing & Davenport 2010). However, Cussins (1994) has observed rapid response water levels to rainfall events, suggesting that percolation occurs quite rapidly, and dissolved substances are likely to leach into groundwater rapidly within the area.

5.3.4 Nitrate Plume Migration

A further objective of this study was to determine if the decrease in nitrate concentrations were only apparent, and whether the real reason behind this apparent decrease was due to nitrate plume migration.

The plume delineation results indicate that concentrations have decreased in the area, and that the nitrate plume from 1996 has moved further to the north and spread laterally in a east-west direction. Piezometric contours (refer to figure 2.7) indicate that, in the northern part of the study site (North of the Mangaone Stream), groundwater flows in a north-easterly direction (Cussins 1994). This could be a reason behind northerly movement of the main contaminant plume in 1996, as well as the east-west spread of the plume fringes.

Studies have shown that kriging results are affected by the distribution of observed data points (Jones, Davis & Sabbah 2003). Observation points from Tidswell's (2009) study are likely to provide a more unbiased estimate of plume distribution as sample points are distributed more evenly throughout the study area. Sample points for Hughes' (1996) study were concentrated in the zone of high nitrate contamination.

A better result could be obtained if more data points were sampled across the areal extent of the site. A depth profile for the contaminant plume is also lacking due to unavailability of groundwater quality data from deeper aquifers.

6 Conclusions

6.1 Conclusions

Results of Tobit regression analysis provide a good regional explanation of bores displaying historically high nitrate concentrations.

Elevated nitrate concentrations in the Te Horo area are likely to be found in bores screened in unconfined surface aquifers which are overlain by crop agriculture, beef farming and lifestyle blocks, and which overlie soils of high permeability such as sandy loams. The above land use types provide the highest loads of nitrate and ammonium to highly permeable soils, which facilitate percolation of nitrate and ammonium enriched rainfall and irrigation water down to the water table.

High concentrations of dissolved oxygen are found in bores screened in the unconfined aquifers in the study area, with the highest concentrations of dissolved oxygen found in bores overlain by croplands or lifestyle blocks and permeable soils. This allows for additional nitrate production in affected ground waters as available ammonium is readily oxidised to nitrate.

Monitoring bores which do not show any response to land use or soil properties are generally screened in confined aquifers at greater depth.

Better land management practices, such as increased efficiency in irrigation scheduling and fertilizer application, tighter government controls on fertilizer application, and production of advanced fertilizers are likely to be the main reason behind improvements to groundwater quality observed over the last decade, particularly as land use and land cover characteristics have not changed significantly over the last 15 years.

It was not possible to delineate a depth profile of nitrate concentrations due to the lack of monitoring bores screened in deeper aquifers. Rudimentary analysis of plume migration does, however indicate that, although nitrate concentrations in the area are decreasing, a lateral spread of the existing contaminant plume in the East-West direction might be occurring over time, mainly in the North-East direction of groundwater movement.

Table 6.1: summarizing the findings of this studies and previous studies

Previous Studies	This Study
Kampman and Caldwell, 1985: • Aquifers in the Coastal Zone were of low transmissivity and unlikely to produce substantial yields. • There are three water bearing layers in the Hautere aquifer, but they are unlikely to provide suitable irrigation water supplies due to detrimental water quality. • Elevated nitrate-nitrogen concentrations are most likely present due to land use practices. Hughes, 1997 • Nitrate concentrations in the area have increased 20 – 40%. • Area of high nitrate was concentrated in the central Hautere Plain. • Elevated Nitrate concentrations are likely to result from surface land use practices.	• Nitrate concentrations in 3 bores appear to be significantly decreasing, whereas nitrate concentrations in one bore appear to be significantly increasing. • Better land management practices are likely to be the reason behind improving water quality. • The bore with increasing concentrations is likely to be linked with an increase in dissolved oxygen at that site. • The proportion of beef cattle farming, fruit growing, settlements and lifestyle blocks within a 500m radius of a bore seem to have a positive effect on nitrate concentrations. • The proportion of croplands (annual and perennial) within a 500m radius of a bore have a positive effect on nitrate concentrations present and vegetated wetlands seem to be negatively correlated with nitrate concentrations.

Tidswell, 2009 • Nitrate concentrations appear to be decreasing, with Mann Kendall analysis showing significant decreases. • A significant decrease in nitrate concentration was found in two bores, and a significant increase was found one bore. • Areas of highest contamination are located in the shallow bores screened in the Hautere Zone. • Nitrate in bores where concentrations were historically high nitrate remain elevated.	• The central Hautere Plain remains a nitrate hot spot. However, the original nitrate plue appears to have moved slightly north and spread in the East-West direction.

With reference to table 6.1, this study adds to previous literature by regressing nitrate pollution seen in the monitoring bores to the land surface properties, thereby attributing a cause to the changes in nitrate concentrations over the last 15 years.

The analyses used in this study have proven to be useful tools in assessing surface impacts on groundwater quality. Mann Kendall time series analysis is a great tool for datasets containing censored values which also do not conform to a particular distribution. It is also robust to outliers, and when coupled with the Sen Slope estimator, can provide a direction and magnitude of trend. However, like most non parametric tests, it is not as powerful as a parametric analysis.

Tobit regression is another popular form of regression analysis in the environmental field, especially in groundwater quality studies where uncensored data points are likely to be present. It has the added benefit of including a spatial component to the analysis with the inclusion of buffer zones. The test is parametric, so it is essential that explanatory variables conform to a chosen distribution and meet the assumptions of the test. If they do not, data transformations become necessary, and re-transformation bias can occur. One also has to be careful to limit co linearity. This could potentially hamper the number of explanatory variables investigated.

Quadratic kriging is a great, non parametric alternative to normal kriging which has provided superior results in other groundwater studies. However, it is important to note that results are influenced by the spread and density of data points within the study area. It is best to involve as many data points as possible, which are distributed as evenly as possible throughout the study site. Combining Kriging variances with some form of vulnerability index can also be a cost effective way of determining if monitoring networks should be expanded. For instance, if an area is classified as a moderate to high vulnerability zone, and displays a high kriging variance due to its distance from a measured bore, it could signal the necessity for a monitoring bore at that site.

These techniques are also particularly useful when faced with very limited research budgets as they are low cost forms of analyses. This is particularly useful in countries such as New Zealand, where funding for research and resources are relatively limited.

6.2 Recommendations

The most important recommendation for future studies is the development of a calibrated flow model for the Te Horo area. Flow models are extremely useful in groundwater analysis and groundwater management. A calibrated flow model can be used to delineate capture zones and recharge areas of monitoring bores. This can be combined with Tobit regression to provide highly useful predictive regression models and a groundwater vulnerability model for the study site instead of using the standard circular buffer zone and generic, DRASTIC type vulnerability models.

Monitoring of pumping rates is currently not a requirement. However, it is recommended that such a system be put in place if a flow model is to be developed. This is because a groundwater flow model requires a consideration of all inputs and outputs of flow.

As noted in the discussion, there can be a time lag between observed groundwater quality and contributing land use sources. It is often difficult to assure that the groundwater sampled at a particular bore is indicative of the area surrounding the bore. It is therefore recommended that isotope analysis is used to determine groundwater age and contaminant source.

In line with the latest freshwater policy statements, a calibrated nitrate contaminant transport model with a surface water body interaction would provide the best indication of nitrate migration through the groundwater zones and potential effects on water quality of discharge springs and surrounding wetlands.

The combination of isotope analysis with a groundwater flow and contaminant transport model (including a surface water body interaction component), will enable a more effective regional management plan specific to the catchment. This would allow for better groundwater allocation decisions based on clearer idea of the consequences of a decision.

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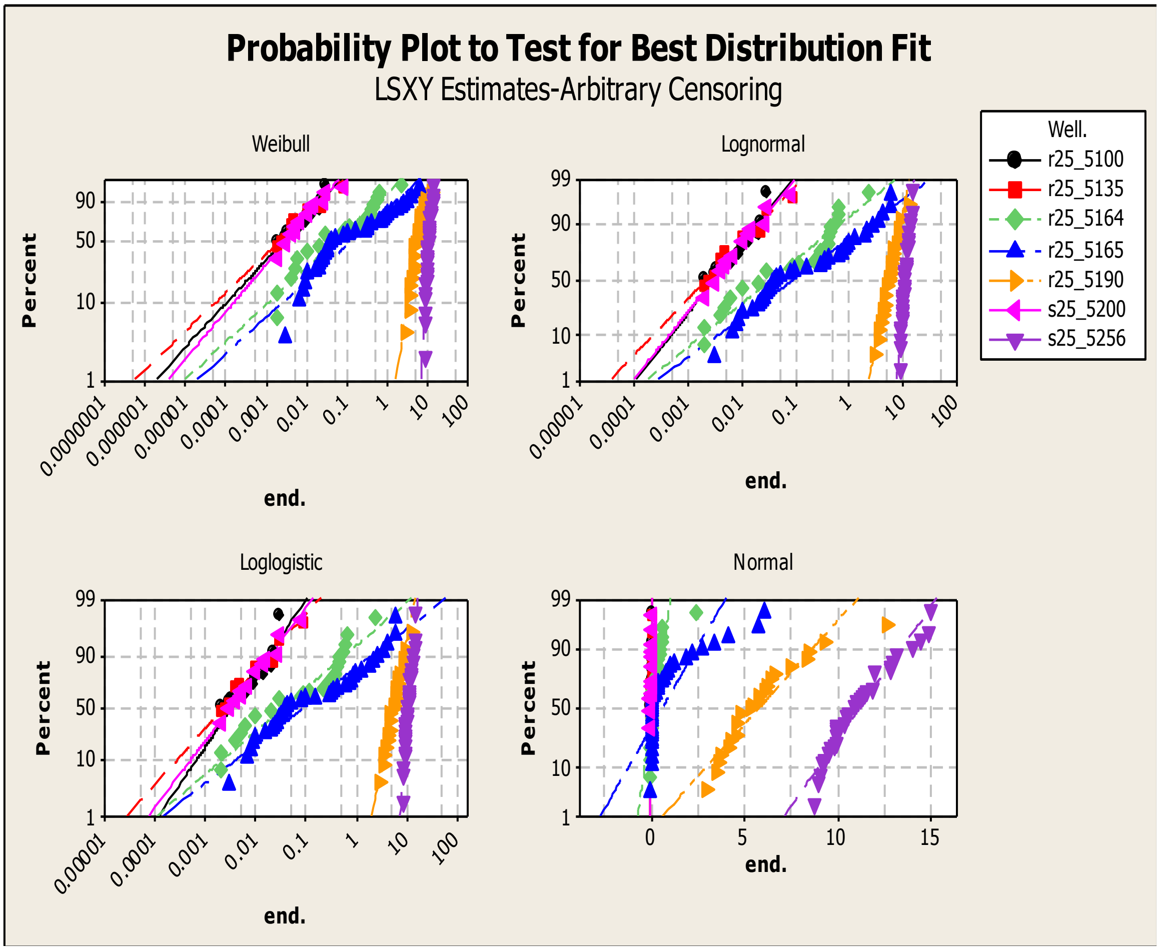
Appendix 1: Analytical Methods, Equipment and Detection Limits of Chemical Parameters

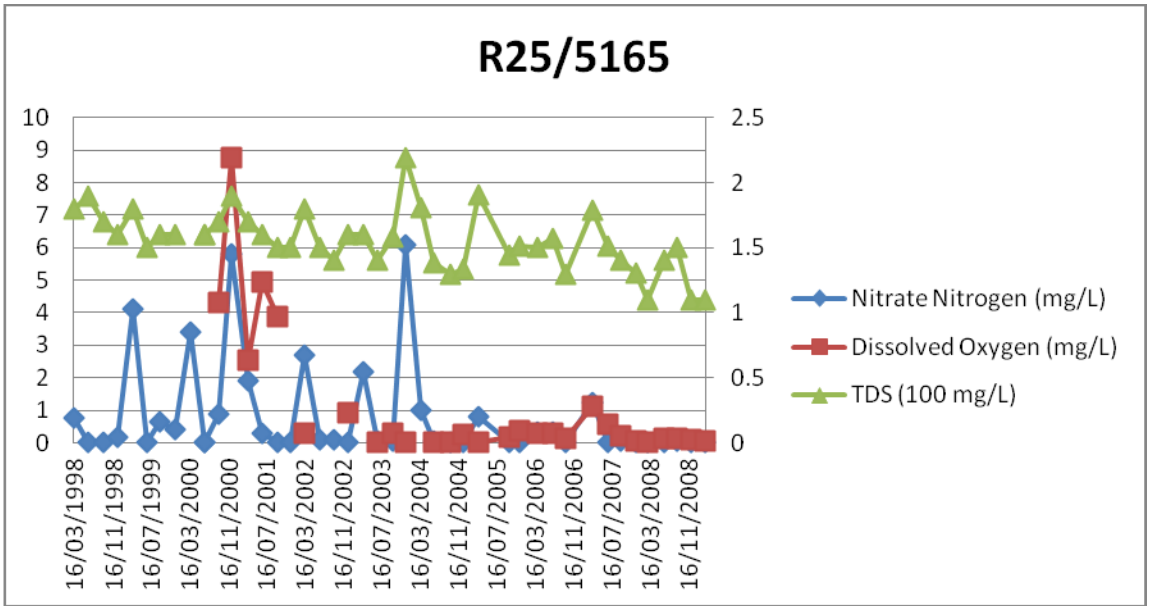
Laboratory	Variable	Method Used	Detection Limit
N/A	Temperature	Field meter – ExStik DO600 (Extech Imstruments), YSI 550A Meters and WTW350i Meters	0.01 °C
N/A	Dissolved Oxygen	Field meter – ExStik DO600 (Extech Imstruments), YSI 550A Meters and WTW350i Meters	0.01 mg/L
N/A	Conductivity	Field meter – ExStik DO600 (Extech Imstruments), YSI 550A Meters and WTW350i Meters	0.1 µS/cm
N/A	pH	Field meter – ExStik DO600 (Extech Imstruments), YSI 550A Meters and WTW350i Meters	0.01 units
Hills	pH	pH meter APHA 4500-H+ B 21st ed. 2005.	0.1 pH units
Hills	Electrical Conductivity	Conductivity meter, 25°C APHA 2510 B 21st ed. 2005.	0.1 mS/m, 1 µS/cm
Hills	Total Kjeldahl Nitrogen (TKN)	Total Kjeldahl digestion, phenol/hypochlorite colorimetry. Discrete Analyser. APHA 4500-N_{org} C (modified) 4500 NH3 F (modified) 21st ed. 2005.	0.10 mg/L
Hills	Total Nitrogen	Calculation: TKN + Nitrate-N + Nitrite-N	0.050 mg/L
Hills	Total Ammoniacal-N	Filtered sample. Phenol/hypochlorite colorimetry. Discrete Analyser. (NH_4-N = NH_4+-N + NH_3-N) APHA 4500-NH_3 F (modified from manual analysis) 21st ed. 2005.	0.01 mg/L
Hills	Nitrate-N + Nitrite-N (TON)	Total oxidised nitrogen. Automated cadmium reduction, Flow injection analyser. APHA 4500-NO_3 - I (modified) 21st ed. 2005.	0.002 mg/L
Hills	Nitrate-N	Calculation: (Nitrate-N + Nitrite-N) - Nitrite-N.	0.002 mg/L
Hills	Nitrite-N	Automated Azo dye colorimetry, Flow injection analyser. APHA 4500-NO_3 - I (modified) 21st ed. 2005.	0.002 mg/L
Hills	Dissolved Reactive Phosphorus	Filtered sample. Molybdenum blue colorimetry. Discrete Analyser. APHA 4500-P E (modified from manual analysis) 21st ed. 2005.	0.004 mg/L
Hills/ELS	*E. coli*	APHA 21st ed. Method 9222 G	1 cfu/100 mL

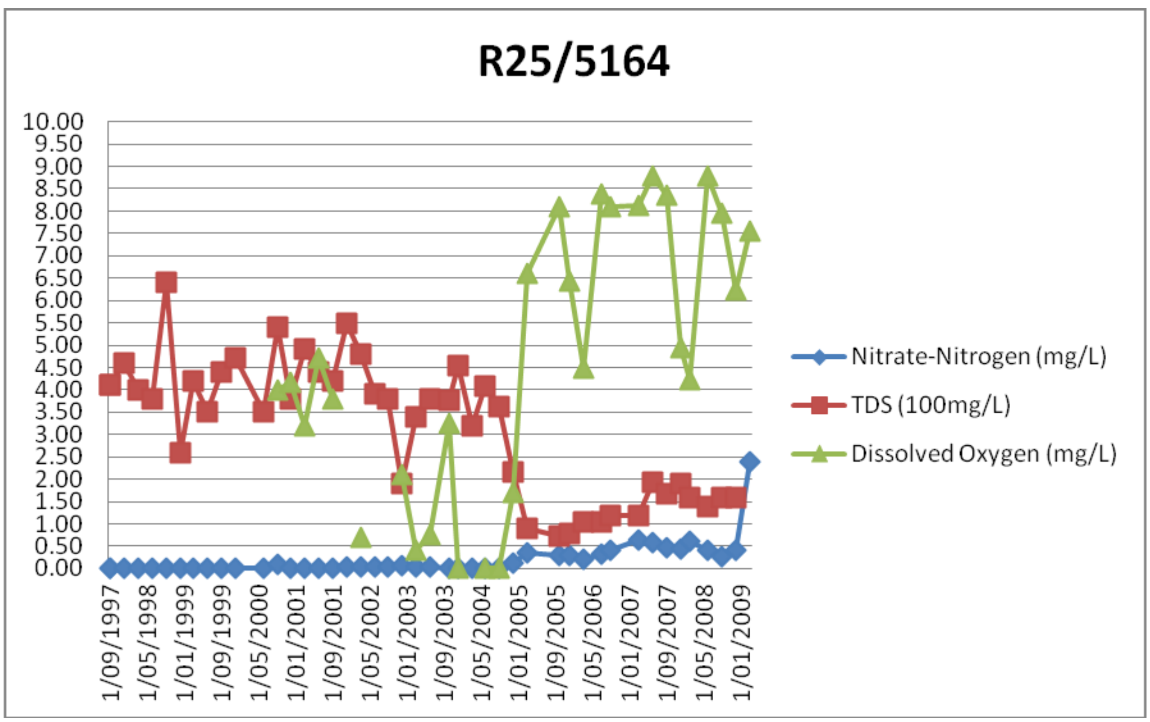
Appendix 2: Diagnostic Probability Plots to Test for Assumed Log-Normal distribution of Censored Nitrate datasets for Regression on Order Summary Statistics

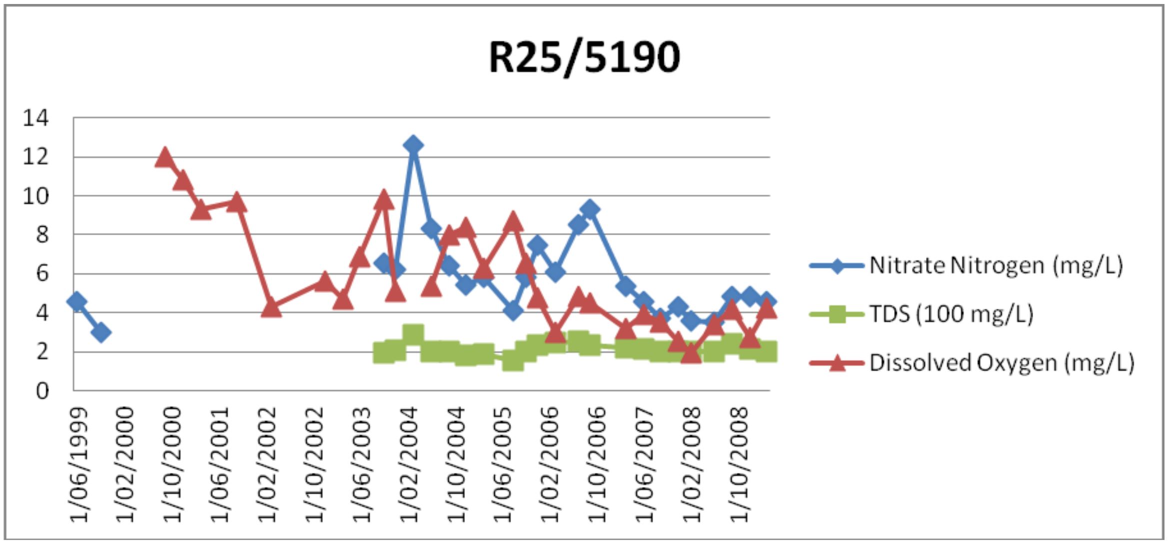


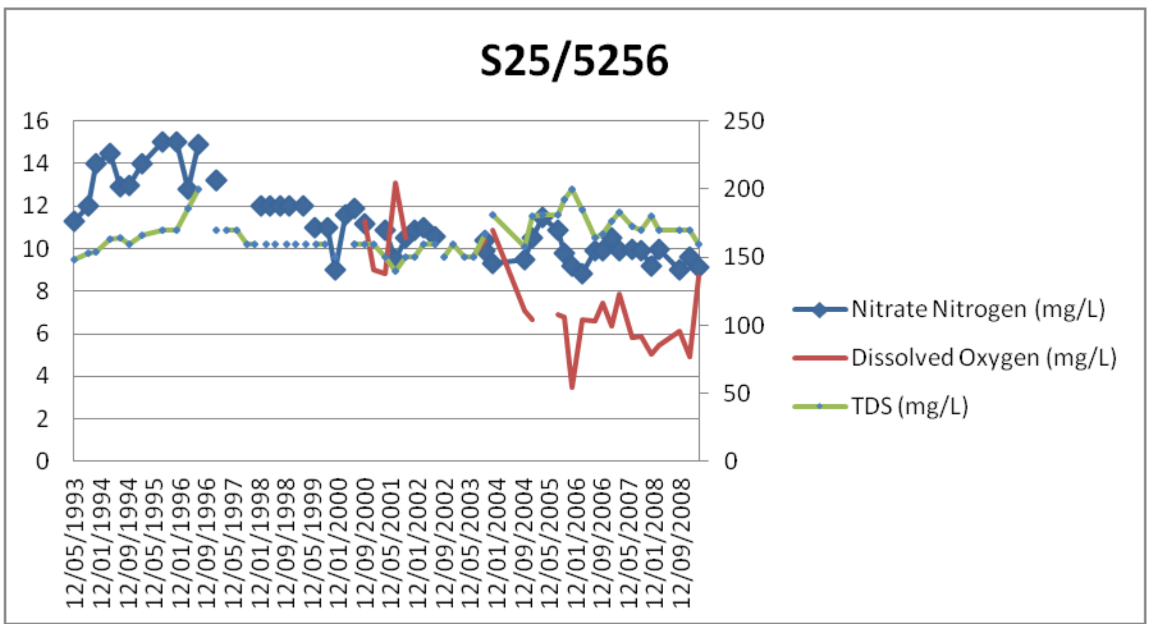
Appendix 3: Time Series Plots showing changes in Dissolved Oxygen, Nitrate-Nitrogen and TDS for Relevant Monitoring Wells

Some of the graphs below have two y-axes in order to better display data. For these graphs, the left hand y-axis reads nitrate-nitrogen and dissolved oxygen levels, while the right hand y-axis displays total dissolved solids.






R25/5190
14
12
10
8
6
4
2
0
1/06/1999
1/02/2000
1/10/2000
1/06/2001
1/02/2002
1/10/2002
1/06/2003
1/02/2004
1/10/2004
1/06/2005
1/02/2006
1/10/2006
1/06/2007
1/02/2008
1/10/2008
Nitrate Nitrogen (mg/L)
TDS (100 mg/L)
Dissolved Oxygen (mg/L)


S25/5256
16
14
12
10
8
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4
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250
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12/05/1993
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12/09/2008
Nitrate Nitrogen (mg/L)
Dissolved Oxygen (mg/L)
TDS (mg/L)

Appendix 4: GIS Layers Showing Distribution of Monitoring Sites relative to Land Cover and Land Use

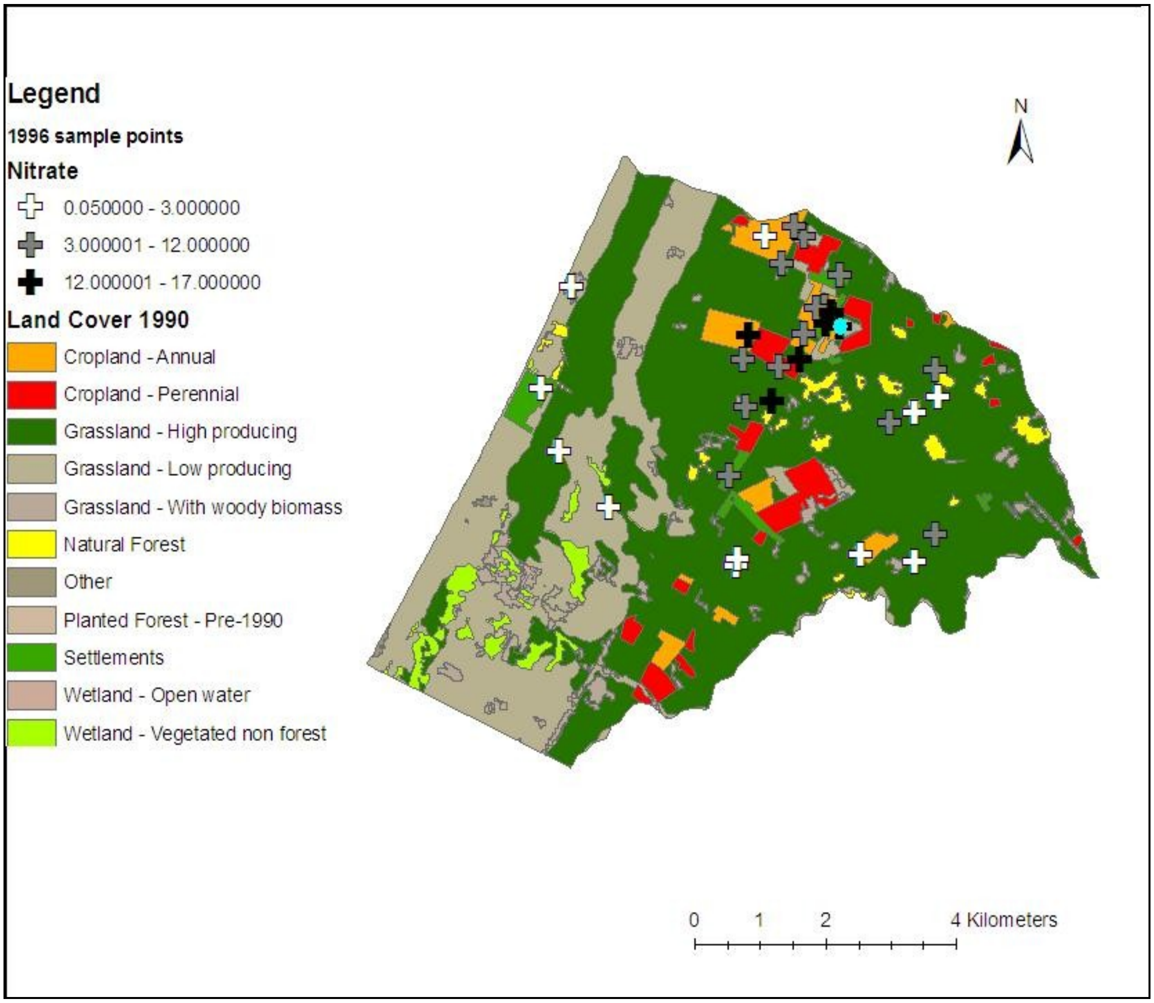

Fig 1: 1996 data relative to land cover. Brightly coloured parcels indicate land cover variables which were found to be significant in Tobit regression analysis.

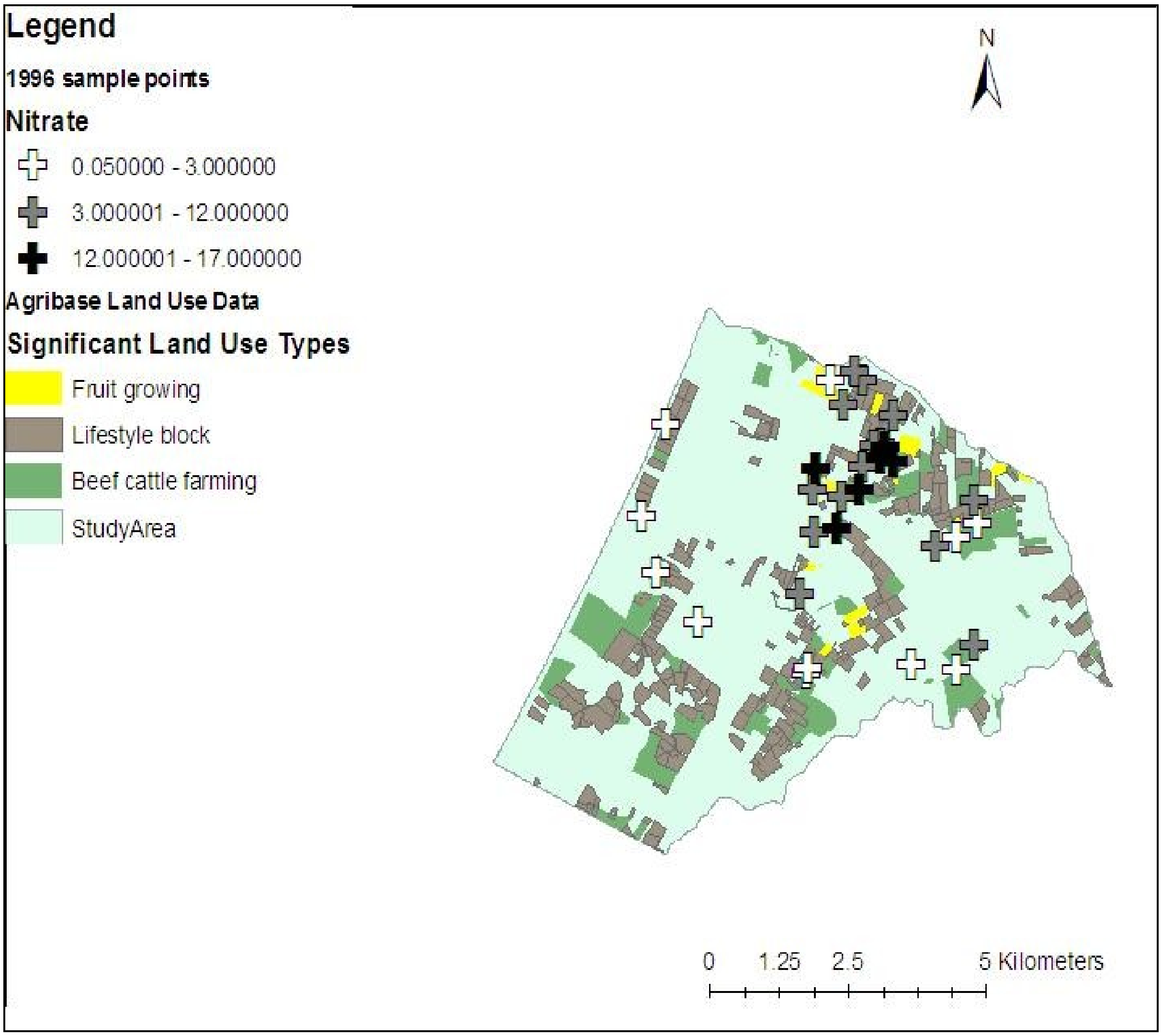

Fig 2: 1996 data relative to land use

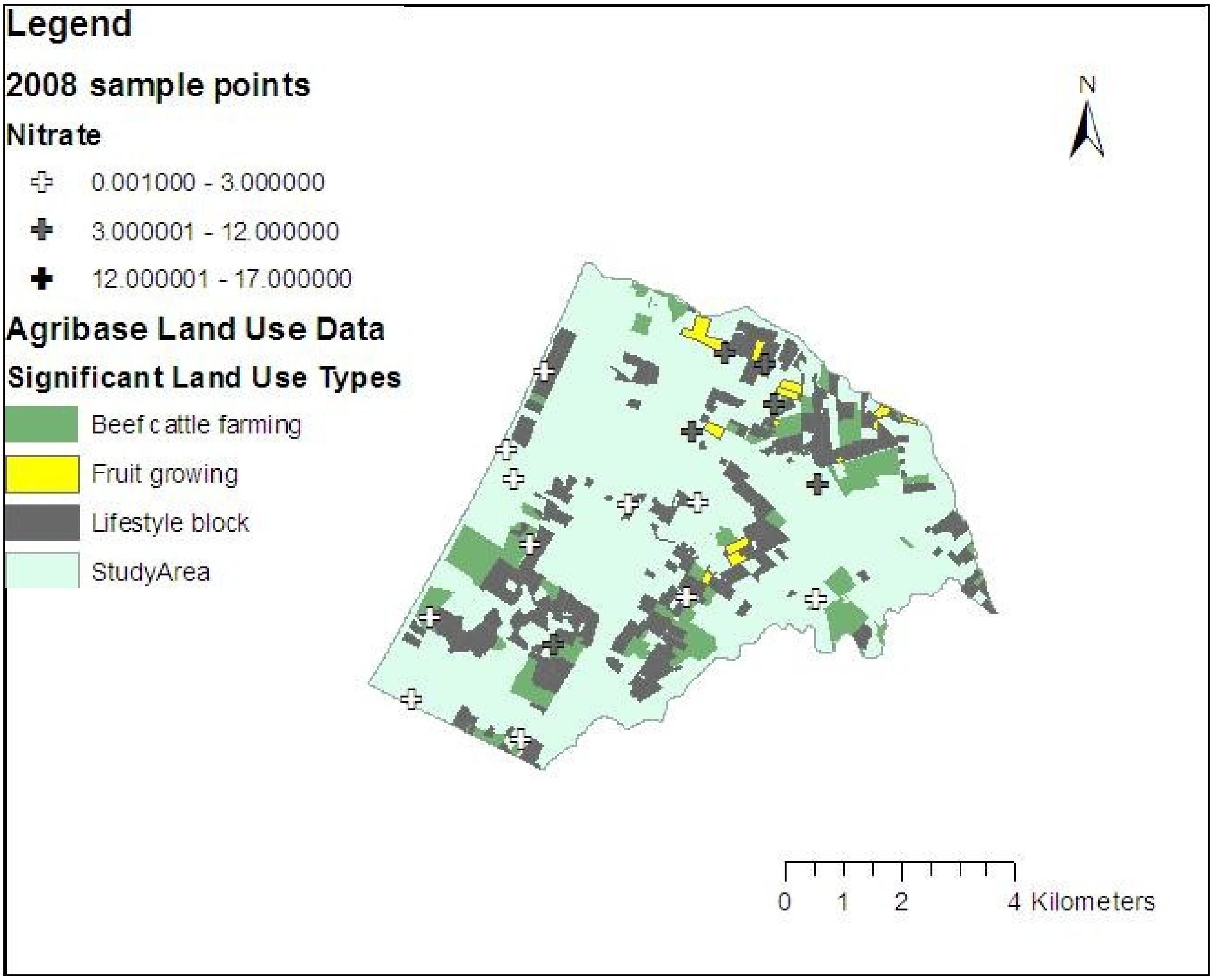

Fig 3: 2008 data relative to land use

Appendix 5: Soil Type, Permeability and Drainage

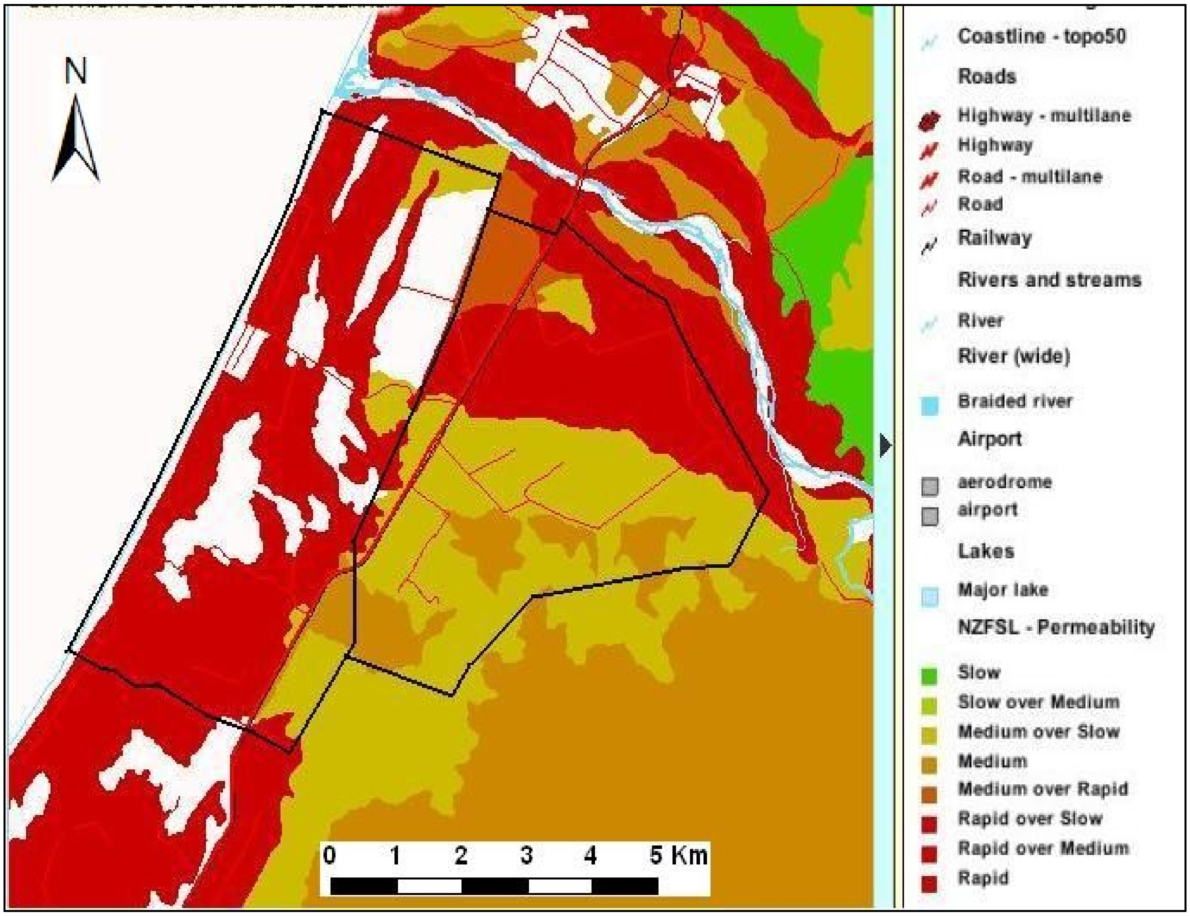

Fig 1: Soil Permeability map from Landcare Research.

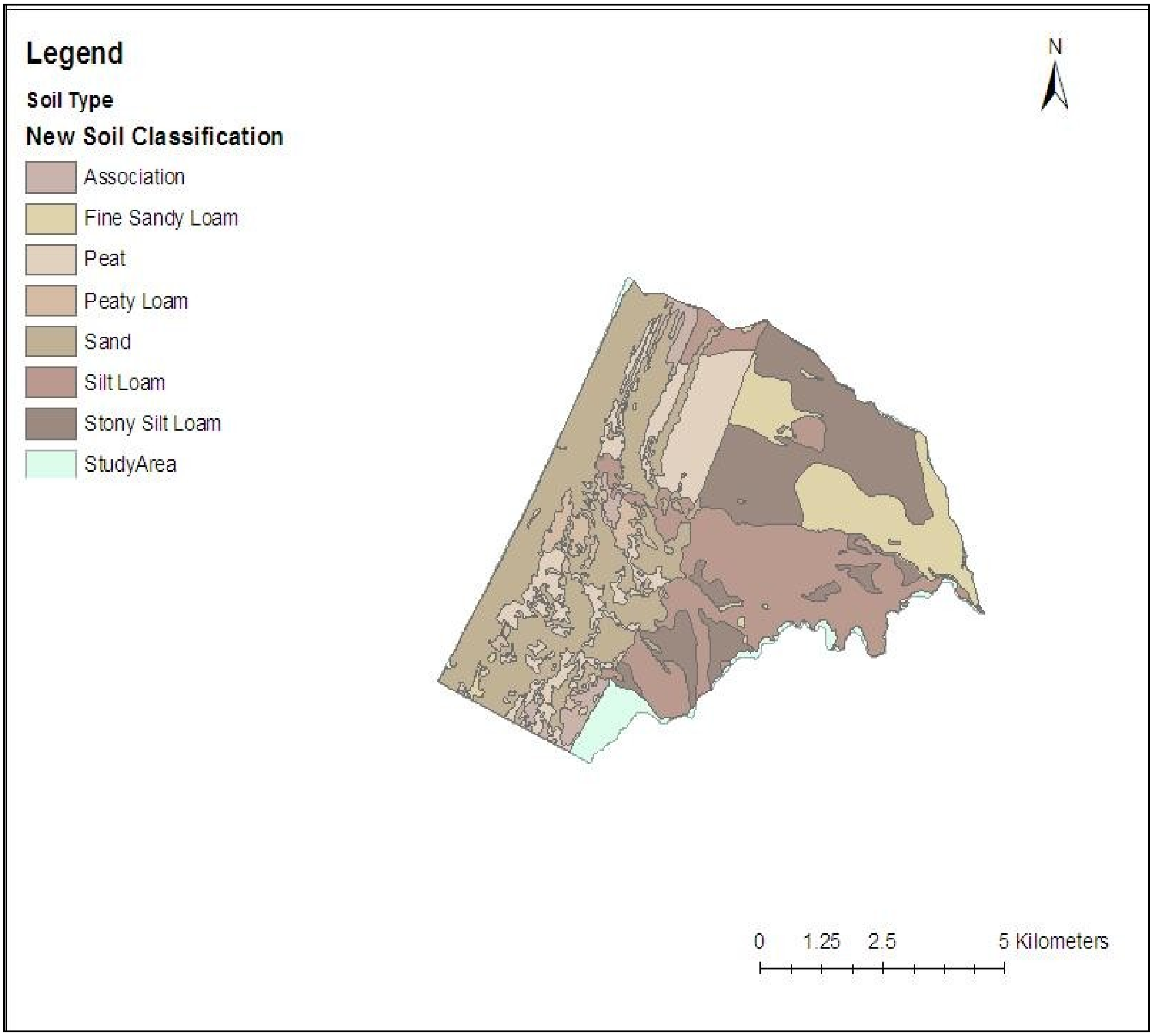

Fig 2: Simplified Soil Types

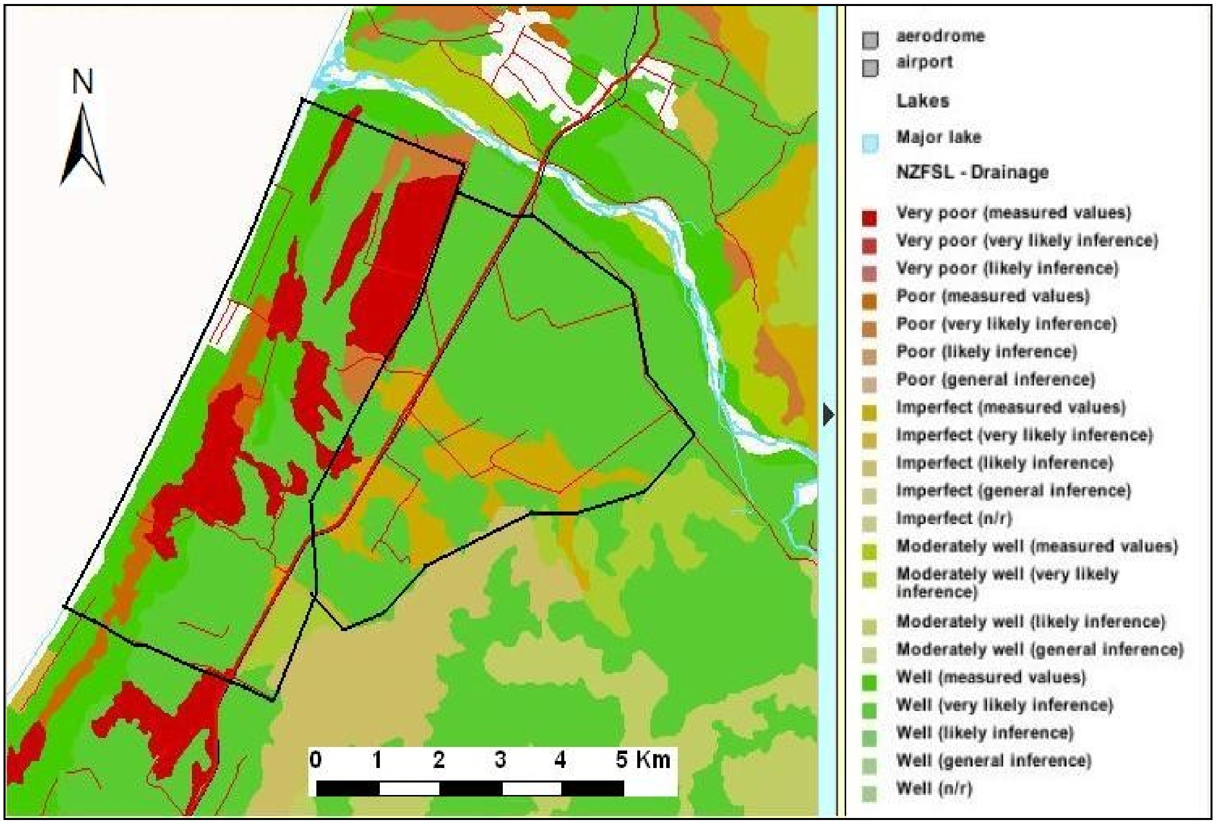

Fig 3: Soil drainage Map from Landcare Research.