Nitrate concentrations in Canterbury groundwater

- a review of existing data

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Executive summary

A review of nitrate nitrogen concentrations in Canterbury groundwater was undertaken using existing data held in Environment Canterbury's water quality database. As of 31 December 2001, the database contained nitrate nitrogen concentrations for 14,015 samples (excluding duplicates) collected from 2,350 wells. The concentrations in 942 of the samples exceeded the MAV of 11.3 mg/L, while almost two-thirds of the samples had concentrations less than 5.65 (one half MAV). Concentrations ranged from below detection limits to a maximum of 89 mg/L. The earliest samples in the database date from 1954, but data from regional groundwater quality surveys were not collected until the late 1970s.

Nitrate nitrogen concentrations in Canterbury groundwater vary considerably both with time and location, but some patterns can be identified based on the existing data. Concentrations are less than 1 mg/L over fairly well defined areas, especially in the coastal confined aquifers and in areas dominated by recharge from rivers. Outside of these areas, where groundwater is recharged primarily by soil drainage, concentrations are generally higher than 3 mg/L, indicating influence from agriculture and waste disposal activities.

There is no correlation between nitrate concentration and well depth in wells up to 50 metres deep. Concentrations are generally less than MAV in wells deeper than 50 metres, but they are near or greater than one half MAV even in some wells that are deeper than 100 metres. In shallow, unconfined groundwater that is not diluted by recharge from surface water, nitrate nitrogen concentrations commonly fluctuate on a seasonal cycle, with higher concentrations in winter and spring and lower concentrations in autumn. The magnitude of these fluctuations is typically on the order of 2-6 mg/L over a single year, but there is substantial variation in both the magnitude and the timing of the fluctuations, largely owing to variations in rainfall and groundwater recharge.

Mann-Kendall trend analysis tests were conducted on nitrate nitrogen concentrations from 255 wells. Long-term increasing trends were identified in 43 wells, while 21 wells showed trends toward decreasing concentrations. Most of the increasing trends had slopes between .01 and 1 mg/L per year, with a median slope of about 0.2 mg/L per year, at which rate it would take approximately 30 years for the nitrate nitrogen concentration at a given location to increase from 5.6 to 11.3 mg/L.

The data clearly demonstrate the effects of land surface activities on groundwater nitrate concentrations, and they indicate that without proper management, the intensification of agricultural land uses in Canterbury could pose a significant threat to groundwater quality.

Table of Contents

Exec	utive summary1								
1	Introduction5								
2	Objective								
3	Description of Environment Canterbury data								
4	Spatial patterns in nitrate nitrogen concentrations104.1Method of illustration10								
	4.2 Discussion of spatial patterns10								
5	Variations in nitrate concentrations with depth17								
6	Seasonal fluctuations in nitrate concentrations								
7	Analysis of long-term trends in nitrate concentrations227.1Methods227.2Results23								
8	Regional summaries29								
	8.1 Northern Canterbury Plains								
	8.2 Central Canterbury Plains								
	8.3 Southern Canterbury Plains								
	8.4 South of Timaru								
	8.5 Other areas								
9	Conclusions								
10	Further investigations and monitoring35								
11	Acknowledgements								
12	References cited								
Арре	Appendix 1 - Extraction of data from Environment Canterbury water quality database40								
Арре	Appendix 2: Nitrate nitrogen concentrations in wells that are in Environment Canterbury's current monthly monitoring programme45								
Appe	ndix 3 – Trend analysis methods49								

List of Figures

Figure 3.1	Nitrate-nitrogen concentrations in Environment Canterbury's water quality database	7
Figure 3.2	Numbers of samples and sampling sites per year for nitrate nitrogen in groundwater	8
Figure 3.3	History of groundwater sampling in Canterbury, based on nitrate nitrogen data in Environment Canterbury's water quality database	8
Figure 3.4	Locations of wells in Environment Canterbury's 2001 groundwater quality monitoring programme that were sampled for nitrate-nitrogen	9
Figure 4.1	Median nitrate nitrogen concentrations in the northern and central Canterbury Plains	2
Figure 4.2	Median nitrate nitrogen concentrations in the southern Canterbury Plains \dots 1	3
Figure 4.3	Median nitrate nitrogen concentrations between Timaru and the Waitaki River	4
Figure 4.4	Median nitrate nitrogen concentrations in northern Canterbury 1	5
Figure 4.5	Comparison of ammonia nitrogen and nitrate nitrogen concentrations 1	6
Figure 5.1	Nitrate-nitrogen concentration versus well depth below ground surface 1	8
Figure 5.2	Median nitrate nitrogen concentration versus depth below piezometric surface	9
Figure 5.3	Median nitrate nitrogen concentrations in wells that are more than 100 metres deep	9
Figure 6.1	Monthly nitrate nitrogen concentrations in well M35/1003, West Melton (39.6 metres deep)	1
Figure 6.2	Quarterly nitrate nitrogen concentrations in well L37/0914, near Ashburton (6 metres deep)	1
Figure 7.1	Results of Mann-Kendall trend analysis using wells that have data from at least 10 separate years over the period 1977 - 2001. Only samples collected during the spring months of September to December were used in the analysis. 2	4
Figure 7.2	Results of Mann-Kendall trend analysis using wells that have data from at least 5 separate years over the period 1995 - 2001. Only samples collected during the spring months of September to December were used in the analysis. 2	5

List of Tables

Table 7.1	Summay of wells displaying increasing nitrate-nitrogen trends	26
Table 7.2	Summay of wells displaying decreasing nitrate-nitrogen trends	28
Table A3-1.	Critical values used in Mann-Kendall trend analysis	52
Table A3-2.	Data points considered to be outliers and not used in the Mann-Kendall trend analysis	53
Table A3-3.	Data points outside two standard deviations of the median but not conside to be outlers based on visual inspection of the data	red 54

1 Introduction

In recent years, the growth of the dairy industry in Canterbury and proposals for new, largescale irrigation schemes have led to renewed questions about the effects of agriculture on groundwater quality. Concern over nitrate concentrations in Canterbury groundwater dates back at least to the 1970s, when high nitrate concentrations were reported in the Lincoln area (Adams *et al.*, 1979; Saffigna, 1977). In the 1980s, Bowden *et al.* (1983) and Burden (1982, 1984) reported that new irrigation schemes and more intensive land use in the central Canterbury plains could lead to higher nitrate concentrations in the groundwater, threatening its suitability as a source of drinking water.

Nitrates occur naturally in groundwater, but generally at concentrations less than about 1 to 3 mg/L nitrate nitrogen¹ (Close and Smith, 2001; Chapelle, 1993; Madison and Brunett, 1985). Concentrations greater than 3 mg/L probably indicate contamination from human activities such as waste disposal or fertiliser application.

In its *Drinking-Water Standards for New Zealand 2000* (MoH, 2000), the Ministry of Health has set a Maximum Acceptable Value (MAV) for drinking water at 11.3 mg/L nitrate nitrogen², based on a health risk for bottle-fed babies. The standards advocate increased monitoring and preventive measures if the nitrate nitrogen concentration in a water supply reaches half this value (5.6 mg/L).

High nitrate concentrations in groundwater can also threaten streams and lakes that are fed by groundwater, increasing the risk of eutrophication from excessive growths of plants and algae. Published guideline values for nitrate nitrogen concentrations in surface water bodies are generally less then 1 mg/L (Biggs, 2000; ANZECC, 2000).

2 Objective

The objective of this report is to address the following questions based on a review of existing groundwater nitrate data held by Environment Canterbury:

- What is the range of nitrate concentrations found in Canterbury groundwater?
- Are there any spatial patterns to the concentrations, and if so, how can these patterns be interpreted?
- How do concentrations vary with well depth?
- What seasonal variations in nitrate concentrations are observed?
- Are there any discernible long-term trends in the data?

The report is organised with a section addressing each of these objectives in terms of the entire region, followed by notes on the nitrate concentrations found in different areas within Canterbury.

¹ Nitrate concentrations in this paper are expressed as milligrams of nitrogen per litre, abbreviated as mg/L nitrate nitrogen.

² The MAV is actually expressed as 50 mg/L of nitrate ion (Ministry of Health, 2000), which is equivalent to approximately 11.3 mg/L nitrate nitrogen.

3 Description of Environment Canterbury data

3.1 Nitrate nitrogen data

Environment Canterbury's water quality database holds analytical data from over 17,000 groundwater samples collected from over 2,600 wells. The samples date back as far as 1954, and they have been collected for a variety of purposes, including regional monitoring programmes, specific investigations, public water supply testing, resource consent monitoring, and one-off sampling of individual wells.

As of 31 December 2001, the database contained nitrate nitrogen data from 14,014 groundwater samples (excluding duplicates), collected from 2,350 wells. The methods for extracting these data from the database are detailed in Appendix A. Groundwater nitrate nitrogen concentrations in the database range from below detection limits (generally 0.05 to 0.1 mg/L) to a maximum of 89 mg/L³. Out of the 14,014 samples in the database, 942 samples (6.7% of the total) had nitrate nitrogen concentrations greater than the MAV of 11.3 mg/L (Figure 3.1). Over one quarter of the samples had nitrate nitrogen concentrations less than 1 mg/L, reflecting the number of samples from the confined aquifers beneath Christchurch and from areas where groundwater recharge comes predominantly from major rivers (see Section 4). Almost two-thirds of the samples had nitrate nitrogen concentrations less than 5.65 (one half MAV).

The water quality database has evolved from numerous monitoring and investigation programmes, many of which were targeted specifically at areas with higher population, more intensive land use, and higher nitrate concentrations. The database therefore provides neither a truly random nor a completely representative picture of groundwater quality in Canterbury. However, no attempt has been made to remove sites that may be biased toward higher nitrate concentrations because the identification of such sites would inevitably become a subjective exercise, and the resulting subset of data would have no less bias than the complete database. All of the sites have been retained for this review, and areas where the results are skewed by the locations of the sampling sites will be discussed later in the report.

3.2 Sampling history

The database contains data from relatively few samples collected prior to 1977 (Figure 3.2). These early samples were restricted to northern Canterbury (Figure 3.3), and most of them were collected for public water supply testing or one-off sampling of individual wells. Between 1977 and 1983, the North Canterbury Catchment Board conducted the first regional groundwater quality surveys in Canterbury. Groundwater samples were collected from approximately 600 wells, with many wells being sampled more than once. A number of site-specific groundwater contamination investigations were also conducted during this period (Burden, 1984).

In 1986, the North Canterbury Catchment Board established regular groundwater quality surveys. Most of the wells in these surveys were sampled once annually, but some were sampled bi-annually, quarterly, or monthly. The surveys of the late 1980s were confined primarily to the northern and central Canterbury Plains, between the Ashley and Rakaia rivers. In 1991, the surveys expanded into the southern plains. The surveys further expanded into the Waitaki-Timaru area in 1993, the Culverden, Cheviot, and Kaikoura areas in 1994, and the Ashwick Flat area in 1995. The annual surveys are conducted in the spring

³ Detected in a sample from well number L37/0915 that was collected on 17 July 1996 as part of a resource consent monitoring programme. The well is located in a paddock used for land disposal of effluent from a meat processing plant.

months of September to December to correspond with annual high water tables, and the 2001 survey included 268 wells (Figure 3.4).

Monthly sampling of seven wells around the perimeter of Christchurch began in the early 1990s to monitor the source of the city's drinking water supply. The sampling expanded farther from the city in the late 1990s, and by 2000 it included 12 wells (Figure 3.4). Also in the late 1990s, quarterly and monthly sampling began in southern Canterbury to monitor long term trends that might result from land use changes in the area, especially conversions from sheep to dairy farming. In 2001, there were 30 wells in the southern Canterbury quarterly sampling programme, and 10 of these were also in the monthly programme (Figure 3.4).

3.3 Analytical methods

Until 1996, nitrate nitrogen was analysed primarily by ultraviolet spectrophotometry, with a detection limit generally around 0.1 mg/L. Since 1997, analysis has been done by ion chromatography, with a detection limit generally about 0.025 mg/L. There should be essentially no difference in the overall results between the two methods, so analysis of long term trends should not be affected by the different analytical techniques. However, the ultraviolet methods were less reliable that ion chromatography, so errors were more likely in the older samples.



Figure 3.1 Nitrate-nitrogen concentrations in Environment Canterbury's water quality database



Figure 3.2 Numbers of samples and sampling sites per year for nitrate nitrogen in groundwater



Figure 3.3 History of groundwater sampling in Canterbury, based on nitrate nitrogen data in Environment Canterbury's water quality database.



Figure 3.4 Locations of wells in Environment Canterbury's 2001 groundwater quality monitoring programme that were sampled for nitrate-nitrogen

4 Spatial patterns in nitrate nitrogen concentrations

4.1 Method of illustration

The spatial distribution of nitrate nitrogen concentrations in Canterbury groundwater is illustrated on the maps in Figures 4.1 to 4.4. The maps were created by calculating a single, median nitrate nitrogen concentration for each well in the database, then plotting these median values on the maps as colour-coded dots. The median of a data set is less affected by skewed data and outlier values than the mean, and it is therefore a better indicator of the central tendency of the data (Gilbert, 1987).

The median concentration for each well was calculated using all available data, regardless of whether the well was sampled once in 1978, twice in 1995, or 87 times between 1954 and 2001. As a result, the maps do not account for any seasonal variations or long-term temporal trends in the data, even though seasonal variations in nitrate nitrogen concentrations are common and at least some wells in the database do show long-term increasing or decreasing trends. Therefore, differences in concentrations between some of the wells shown on the maps may be an artifact of the time of sampling rather than a true spatial variation, which could mask some local spatial patterns. Temporal variations in the data will be discussed in Sections 6 and 7.

The maps also do not account for well depth - all wells with nitrate nitrogen data are plotted on the maps regardless of depth. Again, though this may distort local spatial patterns to a degree, the number of deep wells represented in the database is relatively small, and the overall regional picture shown by the maps is still valid. The relationship between well depth and nitrate nitrogen concentrations will be examined in Section 4.

4.2 Discussion of spatial patterns

The maps in Figures 4.1 to 4.4 show that of nitrate nitrogen concentrations are generally less than 1 mg/L in groundwater along rivers and streams and in groundwater from the coastal Canterbury Plains between the Rakaia and Ashley rivers. Outside of these areas, the concentrations vary considerably but are generally greater than 3 mg/L. Burden (1984) noted a similar pattern in his review of the 1977-83 groundwater quality surveys in the central Canterbury Plains.

Low concentrations adjacent to rivers

Concentrations are low in groundwater adjacent to rivers because the rivers, which typically have nitrate nitrogen concentrations much less than 1 mg/L (A. Meredith, Environment Canterbury, personal communication), are the dominant source of recharge in these areas. Examples include the area along the south side of the Waimakariri River near Christchurch (Figure 4.1), area along the Rangitata, Opihi, and Orari rivers (Figure 4.2), and areas along some smaller rivers like the Pareora and the Otaio, south of Timaru (Figure 4.3), and the streams in the Kaikoura area (Figure 4.4).

In some areas, nitrate concentrations can be observed to increase with distance from a river. For example, concentrations decrease in a north-eastward direction from the lower Rakaia River, and they decrease in a southward direction from the Waimakariri River (Figure 4.1).

Low concentrations in the coastal Canterbury Plains

There are several reasons for the low nitrate nitrogen concentrations that occur in the coastal aquifers between the Rakaia and Ashley rivers (Figure 4.1). First, parts of these aquifers are recharged directly by rivers, and the concentrations are kept low by dilution, as

discussed above. Second, large parts of these aquifers are confined, so the groundwater is protected from direct contamination from the ground surface. In addition, groundwater in the deeper aquifers may pre-date human activity, so that nitrate contamination has not yet reached these aquifers.

In parts of the coastal aquifers, the low nitrates are a result of low oxidation potential. Under reducing conditions, nitrate can be converted to nitrogen gas or ammonia in processes that are also driven by microbiological activity (Chapelle, 1993; Freeze and Cherry, 1979). Oxidation potentials in Canterbury groundwater have not been studied in detail, but a simple test for reducing conditions can be made by identifying wells where the ammonia nitrogen concentration exceeds that of nitrate nitrogen (Rosen, 2001). A preliminary analysis of available Canterbury data (Figure 4.5) indicates that reducing conditions do exist in the groundwater in coastal Canterbury, as well as in some areas near Timaru and Kaikoura.

Reduced groundwater in parts of the coastal Canterbury Plains, as well as in parts of the Kaikoura and Waipara areas, is associated with the presence of peat layers in the aquifer. The decomposition of the organic material in the peat quickly consumes the available oxygen, and the groundwater becomes strongly reduced. In addition to the dominance of ammonia nitrogen over nitrate nitrogen, groundwater in these areas is characterised by high concentrations of dissolved metals such as iron, manganese, and in some cases arsenic, because the solubility of these metals is increased under reducing conditions. In addition, the groundwater commonly has a strong hydrogen sulphide odour due to the reduction of sulphate ions.

Oxidation potential is commonly low in confined aquifers because the groundwater has no direct contact with the atmosphere and therefore no way to replenish oxygen that is consumed through microbiological activity. However, there are indications that oxidation potentials in much of the groundwater in the confined aquifers below Christchurch are not particularly low (Hayward, 2002). Though ammonia nitrogen concentrations exceed nitrate nitrogen in many of the wells tapping these aquifers, nitrate is the dominant form of nitrogen in many others (Figure 4.5). However, neither nitrate nitrogen nor ammonia nitrogen concentrations exceed 0.5 mg/L in most of these wells, and the low concentrations probably reflect both the age of the groundwater and the dilution by water from the Waimakariri River, consistent with piezometric contours (Bowden *et al.*, 1986; J. Weeber, Environment Canterbury, personal communication).

Ammonia nitrogen concentrations exceed those of nitrate nitrogen at a few individual well locations in other parts of Canterbury, in many cases owing to septic tank discharges or land disposal of effluent. In such cases, the groundwater may not actually be reduced; it may be instead that the discharge from a waste disposal system simply had not yet been oxidised at the time and location of sample collection.

Elevated concentrations in other areas

Outside of the confined aquifers, areas with low oxidation potential, and areas dominated by river recharge, nitrate nitrogen concentrations in groundwater are generally higher than 3 mg/L (Figures 4.1 to 4.4), suggesting influence from human activities. The concentrations are highly variable with no clear spatial pattern, although specific sources can be identified for many of the highest concentrations. For example, many of the high concentrations in the area north and east of Ashburton (Figure 4.2) are associated with the land disposal of effluent from the four meat processing plants in the area, and the Burwood landfill contributes to high nitrate nitrogen concentrations in north-east Christchurch (Figure 4.1).

Some of the samples with concentrations above the MAV of 11.3 mg/L do not have a clear source, such as some wells near Waimate (Figure 4.3) and Tinwald (Figure 4.4). However, localised sources cannot be ruled out. Septic tanks and offal pits can cause localised nitrate contamination in groundwater, and some wells may be contaminated by surface runoff that enters the well through a poorly protected well head.



Figure 4.1 Median nitrate nitrogen concentrations in the northern and central Canterbury Plains



Figure 4.2 Median nitrate nitrogen concentrations in the southern Canterbury Plains



Figure 4.3 Median nitrate nitrogen concentrations between Timaru and the Waitaki River



Figure 4.4 Median nitrate nitrogen concentrations in northern Canterbury

These isolated areas of the highest concentrations are found in areas where the general concentrations are below MAV but above concentrations that would be considered natural. In fact, there are several areas, especially south-west of Christchurch and on either side of the Eyre River (Figure 4.1), where numerous wells have median concentrations above 5.6 mg/L (half the MAV). The concentrations in these areas probably reflect the land uses, which include agriculture, lifestyle blocks, and small communities. A recent review of nitrate nitrogen in soil drainage beneath agricultural land (Cameron and Di, 2001) indicates average annual concentrations ranging from approximately 2 to 50 mg/L, depending on factors such as land use, irrigation, fertiliser application, and cultivation practices.



Figure 4.5 Comparison of ammonia nitrogen and nitrate nitrogen concentrations

5 Variations in nitrate concentrations with depth

Numerous studies worldwide have shown that groundwater nitrate concentrations decrease with depth (Freeze and Cherry, 1979; Hallberg, 1989; Close *et al.*, 2001). In many cases, this occurs because oxidation potential decreases with depth and distance from the groundwater recharge source (Fetter, 1988), and nitrate is reduced to nitrogen gas or ammonia. In other cases, it may be that nitrates from human activities have not yet penetrated to the deeper water. In his review of the central Canterbury Plains groundwater, Burden (1984) suggested that deep water in Canterbury flows in a separate flow regime to the shallow groundwater and is recharged primarily by runoff from the Canterbury foothills.

Depth may be considered in three ways: the depth of the water table below the ground surface, the depth of a well screen below the water table, and the total depth of a well below ground surface.

The depth of the water table below the ground surface may influence the attenuation of the nitrate concentrations in the soil drainage that reaches the water table. Nitrate is a conservative contaminant that does not decay in the unsaturated zone and is not adsorbed to the sediment (Close *et al.*, 2001; Freeze and Cherry, 1979), so the primary effect of a deeper water table would be to reduce peak concentrations and the magnitude of seasonal variations in concentration, rather than reducing the overall nitrate loading to the groundwater.

The depth of a well screen below the water table is also likely to influence the nitrate nitrogen concentrations observed in a well because of the dilution that occurs as the soil drainage water mixes with the groundwater. The depth to which nitrates penetrate the saturated zone is not well understood.

The total depth of the well below ground surface is a combination of the first two depth values, and it does not itself directly affect the nitrate concentration in the groundwater. However, it is the most commonly available value of the three. Accurate water level measurements are often not made at the time of sample collection, and in the case of deep or artesian wells, the water level measurements that are made may not reflect a true water table.

Median nitrate nitrogen concentrations are plotted against total well depth in Figure 5.1. The data show no correlation in wells up to about 50 metres deep. Many shallow wells have low concentrations, and several wells close to 50 metres deep have median concentrations greater than 25 mg/L. In wells deeper than 50 metres, concentrations fall off rapidly and there are no median concentrations greater than the MAV of 11.3 mg/L. However, only in wells deeper than 150 metres are concentrations consistently less than 5 mg/L (Figure 5.1).

For comparison, median nitrate nitrogen concentrations are plotted against the depth of the bottom of the well below water level in Figure 5.2. The graph has several limitations. It does not take into account the depth interval of the well screen nor the possibility of multiple screens; the implicit assumption is that the screen is at the bottom of the well. Also, the water level measurements used may not have been made at the time of sample collection, and where more than one measurement was available for a well, the highest value (i.e., closest to the ground surface) was used.

The shape of the plot is similar to the plot of total well depth, except that nitrate nitrogen concentrations begin to decrease at around 30 meters below the water level, and concentrations are consistently less than 5 mg/L in wells deeper than 100 metres below the water level. Note that total well depth values were available for 2,125 of the wells with nitrate nitrogen data, but only 768 of these wells had water level data.

Burden (1984) reported that nitrate nitrogen concentrations in the central Canterbury Plains were less than 1 mg/L in wells deeper than 50-60 metres below water level. Current observations are not consistent with that conclusion. Though concentrations are lower in wells deeper than 50 metres, they are greater than 3 mg/L in some of the deepest wells represented in the database. Figure 5.3 shows the locations of all wells deeper than 100 metres below ground surface for which nitrate nitrogen data are available. Median concentrations are greater than 1 mg/L in most of the deep wells in the Canterbury Plains outside the coastal confined aquifer zone. Many of these median values are based on a single sample from a well, but some of the wells have been sampled more than once. A 115-metre deep well (L35/0191) at Kirwee has been sampled annually since 1985 and has a median concentration of 3.9 mg/L; the concentrations in this well also show a long-term increasing trend, as discussed in Section 7.



Figure 5.1 Nitrate-nitrogen concentration versus well depth below ground surface



Figure 5.2 Median nitrate nitrogen concentration versus depth below piezometric surface



Figure 5.3 Median nitrate nitrogen concentrations in wells that are more than 100 metres deep

6 Seasonal fluctuations in nitrate concentrations

Nitrate concentrations at a given location are variable over time, and they commonly display a seasonal cycle, with higher concentrations in the winter or spring and lower concentrations in the autumn. Environment Canterbury currently samples 22 wells for nitrate nitrogen on a monthly basis (Figure 3.4), and half of these wells show a clear seasonal pattern (Appendix 2).

The reason for the seasonal fluctuations is interpreted to be that during the winter, when rainfall is greater and evaporation rates and plant activity are lower, there is available soil moisture to percolate downward through the soil profile and carry nitrates to the groundwater. Nitrate concentrations then decline over the summer when there is little available soil moisture, so they are generally lowest in the autumn. An early winter flush of nitrates past the root zone has also been noted in an Auckland study (Rosen *et al.*, 1999).

In well M35/1003, a 39.4-metre deep well near West Melton, the highest nitrate nitrogen concentrations are consistently detected in the spring or early summer (Figure 6.1). In contrast, in well L35/0915, a 6-metre deep well near Ashburton that is sampled quarterly, the highest concentrations are detected in the winter, and by summer the concentrations are approaching the lowest values of the year (Figure 6.2). The difference in timing is a reflection of the depths of the wells. The nitrate recharge reaches the shallower well first, and it takes the soil drainage water longer to percolate to the depth of the deeper well. The low summer concentrations in the Ashburton well may also reflect dilution due to excessive irrigation from the Ashburton-Lyndhurst irrigation scheme, directly upgradient of the site.

Eleven of the 22 monthly monitoring sites do not show clear seasonal trends. For some, the reason is quite clear. For example, well J39/0259 is 54 metres deep and derives its water from a confined, basalt aquifer near Timaru; it has never had a clear detection of nitrate nitrogen. For other wells, the lack of any pattern is not clear. Nitrate nitrogen concentrations in well J40/0080 near Waimate (21m deep) have consistently been around $12 \pm 1 \text{ mg/L}$ since sampling began there in 1997. The concentration has dipped to below 10 mg/L on two occasions, but there is no pattern to the fluctuations. The source of the nitrate in this well is not clear.

The magnitude of seasonal fluctuations in the nitrate nitrogen concentrations from the monthly monitoring sites ranges from less than 1 mg/L to over 10 mg/L, but it is typically on the order of 2 to 6 mg/L. There is no clear correlation between the magnitude of seasonal fluctuations and the depth of the well.

In addition to the annual seasonal cycles, nitrate nitrogen concentrations in a single well can respond dramatically to heavy rainfall events. For example, the concentrations in well M35/1003 (Figure 6.1) were generally decreasing between 1995 and 1999, but the concentration rose dramatically after heavy rain in July 1999. A similar increase, though somewhat smaller in magnitude, was observed a year later after heavy rain in August 2000.



Figure 6.1 Monthly nitrate nitrogen concentrations in well M35/1003, West Melton (39.6 metres deep)



Figure 6.2 Quarterly nitrate nitrogen concentrations in well L37/0914, near Ashburton (6 metres deep)

7 Analysis of long-term trends in nitrate concentrations

7.1 Methods

In addition to the seasonal fluctuations discussed in the previous section, nitrate concentrations in groundwater may display long-term trends. Increasing trends may be caused either by the accumulation of nitrates in the groundwater from continued land use practices or by changes in land use, such as changes to more intensive agricultural activities or increased rates of wastewater effluent application. Decreasing trends may also be caused by changes in land use, such as changes to less intensive agriculture or reduced waste disposal rates. Decreasing trends could also be caused by increased abstraction rates, which would increase the hydraulic gradients around the well and could cause more water to be drawn from areas with lower nitrate concentrations, such as deeper groundwater or nearby rivers.

Long term trends in the data from individual wells were investigated using a Mann-Kendall trend analysis, a non-parametric test that does not depend on the data being drawn at random from a normally-distributed population (IDT, 1998: Gilbert, 1987). This is appropriate for the available groundwater quality data, where the number of samples is generally small and the actual distribution of concentrations in the groundwater is not known. The Mann-Kendall test does not calculate the magnitude of a trend. It simply determines whether or not a trend is present, based on the frequency with which the concentrations observed in later samples are greater or less than those observed in earlier samples.

For wells where a long-term trend was identified, the magnitude of the trend was estimated using Sen's slope estimator, a non-parametric test that is less affected by data errors, outliers, or missing data than a simple linear regression (IDT, 1998: Gilbert, 1987). Linear regressions were calculated as well for comparison. The details of the Mann-Kendall, Sen's slope estimator, and linear regression tests are given in Appendix 3.

To minimise the effects of seasonal variations in nitrate nitrogen concentrations, the trend analyses were done using only data from a single season. The spring season, namely the months of September through December, was chosen because this is the time of year when Environment Canterbury conducts its annual groundwater quality survey. It is also the season in which nitrate concentrations tend to be at their highest.

Two sets of tests were conducted. For the first set, 129 wells were identified for analysis based on the criteria that *a*) the well had data from at least 10 separate years over the period 1977 to 2001, and *b*) the well was sampled in 2000 and/or 2001. For the second set, 252 wells were identified for analysis based on the criteria that *a*) the well had data from at least 5 separate years over the period 1995 to 2001, and *b*) the well was sampled in 2000 and/or 2001. There were 126 wells that met the criteria for both sets of tests, so the total number of wells tested was 255.

The first set of tests was intended as a means of investigating the wells with the longest periods of record, including wells in the central and northern Canterbury Plains that have monitoring data from as far back as the 1977-1983 surveys, and wells from the southern Canterbury Plains that have been sampled since 1991-1992. The second set of tests allowed analysis of data from outside the Canterbury Plains, where wells have only been sampled since the mid-1990s, but it also included most of the wells from the first set of tests so that the results of the two sets could be compared.

7.2 Results

In the first set of tests, based on a minimum of 10 years of data from the period 1977 - 2001, increasing trends were identified in 20 (16%) of the 129 wells tested and decreasing trends were identified in 15 (12%) of the wells (Figure 7.1). In the second set of tests, based on a minimum of 5 years of data from the period 1995 - 2001, increasing trends were identified in 33 (13%) of the 252 wells tested and decreasing trends were identified in 7 (3%) of the wells (Figure 7.2). The confidence level of the tests was 95% (alpha = 0.05).

There was generally very good agreement between the Sen's slope estimator and the linear regression slope (Appendix 3). The magnitudes of most slopes were less than 1 mg/L per year, with the exception of four resource consent monitoring wells located in effluent disposal areas, and one well that is part of Environment Canterbury's regular monitoring programme. Slopes calculated in the first set of tests ranged from near zero to positive or negative 0.4 mg/L per year. Slopes calculated in the second set of tests had a wider range, with the magnitudes of the slopes in several tests close to 1 mg/L per year.

Increasing trends

Increasing trends were identified in a total of 43 wells between the two sets of tests, but only 11 wells showed increasing trends in both sets of tests (Table 7.1). Seven of the 43 wells were resource consent monitoring wells associated with land disposal of effluent from meat processing plants or a dairy factory, and all of these had trends with slopes of 0.5 mg/L or greater Of the 36 regular monitoring wells with increasing trends, seven had slopes of 0.5 or greater and nine had slopes of 0.1 or less. To put these slope values in perspective, if the concentration starts at half the MAV (5.65 mg/L) and increases at 0.1 mg/L per year, it will reach MAV (11.3 mg/L) in 56.5 years. If the slope is 0.5 mg/L per year, the concentration will reach MAV in 11.3 years.

The wells with increasing trends are distributed across the Canterbury Plains but are primarily on the lower (seaward) half of the plain. There are also wells with increasing trends in the Waitaki, Ashwick Flat, Culverden, and Kaikoura areas. Though all of the tests using data from areas outside the Canterbury Plains are based on only 5-7 years of data, it is notable that none of the wells in these areas show decreasing nitrate nitrogen trends (Figure 7.2).

The land use activities in the area surrounding each well are summarised in Table 7.1. While there is not a clear pattern, the land uses associated with these wells tend to include intensive agricultural activities like effluent spreading, dairy farming, and horticulture. In contrast, land uses around wells with decreasing trends (Table 7.2) include a higher proportion of grazing and residential land.

Decreasing trends

Decreasing trends were identified in a total of 21 wells between the two sets of tests, but only one well showed a decreasing trend in both sets (Table 7.2). The well, M35/1860, is a 78.5-metre deep well located in south-western Christchurch, and based on a comparison of its bore log with the stratigraphy described by Bowden *et al.* (1986), the well is probably screened in the second confined aquifer. Its median nitrate nitrogen concentration is 0.7 mg/L. The concentrations fluctuated considerably between 0 and 2 mg/L through the 1980s and early 1990s, but they have been consistently less than 1 mg/L since1994 (Appendix 3). The significance of a trend at such low concentrations is difficult to interpret.

Fourteen wells showed decreasing trends in the first set of tests but showed no trend in the second set, when only the later data were analysed. Inspection of the data for these wells (Appendix 3) shows that in most, the concentrations were decreasing during the late 1980s to early 1990s, but the trends levelled off in the late 1990s.



Figure 7.1 Results of Mann-Kendall trend analysis using wells that have data from at least 10 separate years over the period 1977 - 2001. Only samples collected during the spring months of September to December were used in the analysis.



Figure 7.2 Results of Mann-Kendall trend analysis using wells that have data from at least 5 separate years over the period 1995 - 2001. Only samples collected during the spring months of September to December were used in the analysis.

	First set of tests		Second se	et of tests	_	Well				
Well Number	Trend	Sen's slope	Trend	Sen's slope	Project	Depth (m)	Median NO3-N	Land use on the well property	Land use up-gradient of the well	Septic tank
J37/0013	х	х	increase	0.40	EMQ	6	3.0	Farm house-sheep	Dairy/Grazing-sheep	Ν
J38/0045	increase	0.07	increase	0.10	EMQ	24	5.6	Lifestyle block-grazing	Grazing-cattle	Ν
J38/0242	х	х	increase	1.05	EMQ	3.3	3.8	Orchard house	Orchard/Golf course	Ν
J40/0053	х	х	increase	0.63	EMQ	22.86	4.5	Farm house/yard-dairy	Dairy/Grazing-sheep	Ν
J40/0106	х	х	increase	0.17	EMQ	18.2	2.6	Farm house-dairy	Dairy	Ν
J40/0118	х	х	increase	0.32	EMQ	10	2.9	Dairy Shed	Dairy	Ν
K37/0234	increase	0.16	none	х	EMQ	17.06	5.3	Farm house-sheep	Dairy	Ν
K37/0243	none	х	increase	0.13	EMQ	21.33	5.7	Farm yard-dairy	Dairy	Ν
K37/0245	increase	0.07	none	х	EMQ	24.5	5.4	Farm yard-dairy	Dairy	Ν
K37/0493	increase	0.31	none	х	EMQ	29	2.8	Farm house-sheep	Grazing-sheep	Ν
K38/0408	х	х	increase	0.11	EMQ	9	0.2	Farm house-sheep	Grazing-sheep	Ν
K38/0412	increase	0.30	increase	0.50	EMQ	4.9	5.3	Farm house/yard-grazing	Grazing-cattle	Ν
K38/0957	х	х	increase	1.07	CON	8	6.6	Dairying	effluent disposal - dairy factory	N/R
K38/1077	х	х	increase	1.11	CON	8	7.5	Sheep	effluent disposal - dairy factory	Y
K39/0006	х	х	increase	0.17	EMQ	16	2.8	Lifestyle block-grazing	Grazing	Ν
L35/0086	none	х	increase	0.67	EMQ	39.6	2.7	Farm yard-sheep	Grazing/Forestry	Ν
L35/0171	none	х	increase	0.20	EMQ	53.8	2.5	Farm yard-sheep/deer	Grazing	N/R
L35/0191	increase	0.07	none	х	EMQ	115.2	3.9	Domain-rugby field	Grazing	Ν
L36/0109	increase	0.11	none	х	EMQ	48.8	3.1	Farm yard-sheep	Grazing/Dairy	Ν
L36/0200	increase	0.18	increase	0.33	EMQ	30.8	4.8	Farm yard-dairy	Dairy	Y
L36/0647	none	х	increase	0.72	EMQ	7.6	3.4	Farm yard-sheep	Grazing-sheep	Ν
L37/0020	increase	0.17	increase	0.20	EMQ	67.66	6.6	Farm yard-dairy	Dairy	Ν

First set of tests based on data from at least 10 separate years between 1977 and 2001

Second set of tests based on data from at least 5 separate years between 1995 and 2001

Project: EMQ - well sampled for groundwater quality survey purposes; CON - well sampled for resource consent monitoring purposes

Septic tank: "Y" - septic tank less than 50m up-gradient of well head; "N" - no septic tank within 50 m up-gradient of well head; "N/R - septic tank location not recorded

Table 7.1 Summay of wells displaying increasing nitrate-nitrogen trends (page 1)

of 2)

Nitrate concentrations

in Canterbury groundwater –

a review of existing data

Environment Canterbury Technical Report

First set of tests		Second se	et of tests	_	vveii					
Well Number	Trend	Sen's slope	Trend	Sen's slope	Project	Depth (m)	Median NO3-N	Land use on the well property	Land use up-gradient of the well	Septic tank
L37/0157	х	х	increase	0.67	CON	33.53	15.0	Lifestyle block	Meat works/effluent disposal	N/R
L37/0197	none	х	increase	0.50	CON	41.28	9.5	Lifestyle block	Meat works/effluent disposal	N/R
L37/0254	increase	0.25	increase	0.30	EMQ	70.7	6.6	Farm yard-dairy	Dairy/Cropping	Ν
L37/0397	increase	0.31	increase	0.45	CON	45.4	7.8	Meat works/effluent disposal	Meat works/effluent disposal	Ν
L37/0403	х	х	increase	0.05	EMQ	37.79	5.0	Golf club	Grazing	Ν
L37/0415	increase	0.25	none	х	EMQ	30	11.0	Farm yard-crop	Cropping/Dairy	Ν
L37/0896	increase	0.86	none	х	CON	41.5	18.0	Meat works/effluent disposal	Meat works/effluent disposal	Ν
L37/0915	х	х	increase	4.83	CON	9.3	16.0	Meat works/effluent disposal	Meat works/effluent disposal	Ν
M35/4795	none	х	increase	0.24	EMQ	13.8	7.8	Industry	Dairy/Grazing	Ν
M36/0456	increase	0.15	increase	0.18	EMQ	9	6.3	Farm yard-horses	Dairy	N/R
M36/0473	increase	0.00	none	х	EMQ	45.7	0.3	Farm yard-cattle	Dairy	Ν
M36/0698	increase	0.03	increase	0.08	EMQ	25	1.7	Public Supply	Residential/Crop	Ν
M36/3588	increase	0.11	increase	0.22	EMQ	12.2	5.2	Farm yard-dairy	Dairy	Y
M36/3596	increase	0.07	increase	0.10	EMQ	9.1	2.8	Farm yard-dairy	Dairy	N/R
M36/3683	increase	0.03	none	х	EMQ	10	1.8	Farm house	Grazing/Cropping	Y
M37/0065	increase	0.06	increase	0.23	EMQ	18.3	2.0	Farm yard- grazing/crop	Cropping	Ν
N32/0140	х	х	increase	0.30	EMQ	5.4	2.6	Residential	Residential/Dairy	Ν
N33/0200	х	х	increase	0.25	EMQ	18	6.7	not recorded	not recorded	N/R
N33/0205	х	х	increase	0.19	EMQ	27.5	4.6	Dairy Shed	Dairy	Ν
O31/0096	х	х	increase	0.53	EMQ	8.22	3.0	Farm yard-dairy	Dairy	Y
O33/0049	х	х	increase	0.57	EMQ	8	11.6	not recorded	not recorded	N/R

First set of tests based on data from at least 10 separate years between 1977 and 2001

Second set of tests based on data from at least 5 separate years between 1995 and 2001

Project: EMQ - well sampled for groundwater quality survey purposes; CON - well sampled for resource consent monitoring purposes

Septic tank: "Y" - septic tank less than 50m up-gradient of well head; "N" - no septic tank within 50 m up-gradient of well head; "N/R - septic tank location not recorded

 Table 7.1
 Summay of wells displaying increasing nitrate-nitrogen trends (page 2)

of 2)

27

	First set of tests		Second se	t of tests		Well				
Well Number	Trend	Sen's slope	Trend	Sen's slope	Project	Depth (m)	Median NO3-N	Land use on the well property	Land use up-gradient of the well	Septic tank
J37/0012	decrease	-0.32	none	х	EMQ	6.7	4.6	Farm yard-sheep	Grazing-sheep	Ν
J38/0055	decrease	-0.33	none	х	EMQ	5.5	5.6	Lifestyle block-sheep	Grazing-sheep	Y
J38/0125	decrease	-0.12	none	х	EMQ	47	1.1	Lifestyle block-sheep	Grazing-sheep	Ν
K36/0118	none	х	decrease	-0.70	EMQ	11.3	5.2	Farm house-sheep	Grazing-sheep	Ν
L36/0323	none	х	decrease	-0.03	EMQ	8.6	0.1	Farm yard-sheep/cattle	Grazing	Ν
L36/0477	decrease	-0.11	none	х	EMQ	48	1.7	Farm yard-sheep	Dairy	Ν
L36/0948	decrease	-0.09	none	х	EMQ	66.45	5.1	Farm yard-sheep	Grazing-sheep	Ν
L37/0405	decrease	-0.07	none	х	EMQ	115.8	4.3	Farm yard-sheep	Dairy/Grazing	N/R
L37/0422	none	х	decrease	-5.50	CON	45	23.0	Meat works/effluent disposal	Meat works/effluent disposal	Ν
M35/0925	х	х	decrease	-0.02	EMQ	53.8	0.5	Farm yard-sheep	Grazing	N/R
M35/1860	decrease	-0.04	decrease	-0.06	EMQ	78.5	0.7	Public Supply	Industry/Residential	Ν
M35/1883	decrease	-0.27	none	х	EMQ	28.9	7.8	Yard- meat processing	Industry/Residential	Ν
M35/4682	decrease	-0.16	none	х	EMQ	15.8	4.6	Residential	Grazing/Olives	N/R
M35/5440	decrease	-0.08	none	х	EMQ	20.9	6.6	Farm yard-crop	Dairy/Cropping	Ν
M35/5918	decrease	-0.17	none	х	EMQ	36	3.2	Farm yard-horses	Grazing/Cropping	Ν
M35/6385	х	х	decrease	-0.49	EMQ	40.2	5.6	Farm yard-grazing	Grazing/Forestry	N/R
M36/0974	decrease	-0.11	none	х	EMQ	40.5	6.8	Public Supply	Residential	Ν
M36/1016	decrease	-0.13	none	х	EMQ	31.4	6.5	Industry	Industry/Residential	Ν
M36/1059	decrease	-0.12	none	х	EMQ	31.6	6.2	Public Supply	Industry/Residential	Ν
M36/2528	decrease	-0.21	none	х	EMQ	33.8	7.7	Public Supply	Industry/Residential	Ν
M36/5128	х	х	decrease	-0.02	EMQ	12	0.3	Residential	Residential/Grazing	Ν

First set of tests based on data from at least 10 separate years between 1977 and 2001

Second set of tests based on data from at least 5 separate years between 1995 and 2001

Project: EMQ - well sampled for groundwater quality survey purposes; CON - well sampled for resource consent monitoring purposes

Septic tank: "Y" - septic tank less than 50m up-gradient of well head; "N" - no septic tank within 50 m up-gradient of well head; "NR - septic tank location not recorded

Table 7.2 Summay of wells displaying decreasing nitrate-nitrogen trends

Six wells showed decreasing trends in the second set of tests but not in the first set. In three of the wells, L37/0422, K36/0118 and M35/0925, the nitrate nitrogen concentrations increased in the early to mid-1990s, then decreased. A fourth well, L36/0323, is only 200 metres from the Rakaia River and has a median nitrate nitrogen concentration of only 0.12 mg/L; visual inspection of the data (Appendix 3) suggests that the short-term trend has little significance compared to concentrations in previous samples. M36/5128, located near the lower Selwyn River (Figure 7.2) has shown a fairly steady decrease since 1995, but the concentrations are only 0.3 to 0.4 mg/L, so the Sen's slope is quite low (-0.02 mg/L per year).

M35/6385, located north of the Waimakariri River in an agricultural and forestry area, has shown a fairly steady decreasing trend since 1997, with a Sen's slope = -0.49. The reason for the trend is not clear at this point.

There is a group of five wells in south-western Christchurch (M35/1883, M36/0974, M36/1016, M36/1059, and M36/2528), all approximately 30-40 metres deep, that show decreasing trends based on the first set of tests (Figure 7.1) but no trends based on the second set of tests (Figure 7.2). The wells all show a decrease in nitrate nitrogen concentrations of 1-2 mg/L during the early 1990s, after which the concentrations stabilised around 6 mg/L. The pattern may be a result of a local meat processing plant stopping its effluent spreading operations in the area in the early 1990s.

8 Regional summaries

8.1 Northern Canterbury Plains

The northern Canterbury Plains, between the Waimakariri and Ashley rivers, are characterised by low nitrate nitrogen concentrations (less than 0.25 MAV) near the coast and along the Eyre River, with higher concentrations elsewhere (Figure 4.1). The low concentrations near the coast, generally seaward of the Rangiora and Kaiapoi townships, correspond with areas of confined aquifers and chemically reduced groundwater conditions. The low concentrations along the Eyre River probably indicate groundwater recharge from the river. The concentrations increase in a downstream direction, consistent with a decrease in surface water influence (since the river is often dry downstream of the Oxford area) and an increase in the effects of surrounding land use.

On either side of the Eyre River, concentrations are generally above 3 mg/L and commonly above half the MAV, which has led to concern for public drinking water supplies in the area (Nokes, 1997). Some lower concentrations are observed in the Cust River area, possibly reflecting recharge from surface water there, but the trend is not as clear as it is along the Eyre River.

Some of the highest concentrations recorded, for example in the Bennets and Cust areas, may be related to septic tank discharge or other localised sources rather than regional land use.

8.2 Central Canterbury Plains

In the Central Plains, between the Rakaia and Waimakariri rivers, nitrate nitrogen concentrations are lowest in the coastal confined aquifer zone and along the Waimakariri and Rakaia rivers (Figure 4.1). An area of low concentrations fans southward from the Waimakariri River and underlies most of Christchurch. This is probably a combination of dilution by river recharge from the Waimakariri River and chemical reduction in the confined aquifers that underlie Christchurch.

Low nitrate nitrogen concentrations around the base of the Port Hills and the edges of Lake Ellesmere also coincide with areas of confined or reduced groundwater. Nitrate nitrogen concentrations are also low along the Rakaia River and much of the Selwyn River, probably again reflecting recharge from the rivers.

Most wells in the upper plains have fairly low (less than 0.5 MAV) concentrations. The water table over much of this area is deep (>30-50m), so the groundwater is buffered from surface activities. Closer to the Selwyn River tributaries, wells are shallower, but river recharge keeps concentrations low. Higher concentrations observed in Hororata are associated with shallow wells and are likely to be related to local septic tanks or gardening practices. A monthly monitoring site in Greendale (L36/317) with consistently high nitrate nitrogen and frequent bacteria detections, is probably affected by a septic tank boulder hole located 30 metres up-gradient.

High nitrate nitrogen concentrations have been observed in the area south and west of Christchurch since the 1970s, when surveys detected high nitrate nitrogen concentrations in the Lincoln area (Adams *et al.*, 1979; Saffigna, 1979; Campbell, 1978). High nitrate concentrations were also recorded in the Lincoln / Burnam / West Melton area during the 1977-83 surveys (Bowden *et al.*, 1983), when intensive sampling was carried out in the area. Though most of the wells from that survey have not been re-sampled recently, many of those that have been re-sampled continue to show concentrations above 0.5 MAV, and a number of samples have had concentrations above MAV. The reason for the high concentrations in these areas is probably a combination of agricultural land uses and a relatively shallow water table, with local contributions from septic systems and sewage effluent disposal.

Figure 4.1 also shows an area of elevated nitrate nitrogen concentrations extending into the Spreydon / Sydenham area of southern Christchurch. The elevated concentrations are observed in wells about 25-35 metres deep, corresponding to the first aquifer (Brown and Weeber, 1992; Bowden *et al.*, 1986). The nitrate data indicate that the overlying sediments in this area do not protect the groundwater from contamination from the ground surface; excavations may have increased groundwater vulnerability in the area.

8.3 Southern Canterbury Plains

In shallow wells of the Southern Plains area, between Timaru and the Rakaia River, average nitrate nitrogen concentrations are generally in the range of 2 to 8 mg/L (Figure 4.2). Higher concentrations are found in localised areas, especially in areas where dairy and meat packing industries discharge waste effluent to land. Lower concentrations are found along rivers, in deep wells, and in a few shallow wells that are not close to rivers, especially in the Hinds-Ashburton area.

High nitrate nitrogen concentrations are found in effluent disposal areas associated with four meat processing plants near Ashburton and a dairy factory at Clandeboye (Figure 4.2). Most of the data from these areas come from wells that are sampled to fulfil resource consent monitoring conditions. Since these wells are located at points where high nitrate nitrogen concentrations are anticipated, they do not necessarily give a representative picture of the local groundwater, but it is clear that the nitrate nitrogen concentrations are elevated in these localised areas. As discussed in Section 7, the concentrations in a number of the consent monitoring wells in this area show long-term increasing trends of 0.5 mg/L per year or greater.

There is also an area just west of Tinwald that has elevated nitrate nitrogen concentrations. Well K37/0358 has been sampled every spring since 1995 and has consistently had nitrate nitrogen concentrations in the range of 11 to 13 mg/L, and four other wells nearby have had nitrate nitrogen concentrations over 10 mg/L. The source of the elevated nitrate nitrogen concentrations in this area is not known.

High nitrate nitrogen concentrations are also found in the vicinity of a fertiliser plant at Seadown that was the subject of a 1993 investigation (Smith, 1993) that found elevated concentrations of fluoride, sulphate, and chloride as well as nitrate.

Nitrate nitrogen concentrations in the coastal Ashburton-Rakaia plains (south-east of State Highway 1) are commonly above 5 mg/L (Figure 4.2). This includes not only the data associated with the four Ashburton area meat processing discharges, but also wells further east in the Pendarves area. Groundwater levels are fairly deep there (20 metres to >50 metres), and the groundwater is thought to be largely confined with upward hydraulic gradients (Sanders, 1999). It is possible that the nitrates are being transported from further up the plains, but the few data points available do not indicate any high concentrations upgradient, so it seems likely that the groundwater in the area is influenced by surface activities.

8.4 South of Timaru

Wells south of Timaru were first sampled for groundwater quality tests in 1993. In the area between Timaru and the Waitaki River (Figure 4.3), the lowest nitrate nitrogen concentrations are found along the numerous small rivers, such as the Pareora, the Otaiao, and the Waihao, that flow to the coast from the Hunters Hills. The low concentrations probably reflect dilution by recharge from the rivers. Most of the wells with concentrations greater than 3 mg/L are located in areas between these rivers, where soil drainage probably accounts for a large portion of the groundwater recharge.

Groundwater in the confined basalt aquifer on the south side of Timaru also has concentrations less than 1 mg/L. The groundwater in this aquifer appears to be reduced, based on the dominance of ammonia nitrogen over nitrate nitrogen (Figure 4.3).

Nitrate nitrogen concentrations are low on the alluvial plain north of the Waitaki River, consistent with a large component of groundwater recharge being derived from the river. The fact that many median concentrations are in the 1-3 mg/L range rather than being less than 1 mg/L is probably a result of the heavy border strip irrigation that occurs in the area. Two wells in the area (J40/0106 and J40/0163, Figure 3.4) have been sampled monthly since 1996, but the nitrate nitrogen concentrations do not show strong seasonal trends. In contrast to spray irrigation, which uses less water and probably results in little percolation of water beyond the root zone, border strip irrigation uses large quantities of water, and as a result nitrates from the upper soil layers can be washed through to the groundwater in the summer irrigation system as well as in the winter.

There are nine wells south of Timaru that have median nitrate nitrogen concentrations greater than the MAV of 11.3 mg/L. Five of these have only been sampled once, two have been sampled twice, and two have been sampled more than two times. Three of the sites are near Waimate. The sources of the high nitrates are unknown, but localised sources such as septic tanks or gardens cannot be ruled out.

8.5 Other areas

Kaikoura

Of the 18 wells on the Kaikoura plain that have been sampled, only 3 have median concentrations > 1 mg/L (Figure 4.4). The plain is crossed by many small streams that drain the Kaikoura ranges, and these streams are probably the dominant source of groundwater recharge.

In some parts of the plain near the coast, the oxidation potential of the groundwater is low, demonstrated by the dominance of ammonia nitrogen over nitrate nitrogen as well as by elevated iron, manganese, and arsenic concentrations. Layers of peat are indicated on the geologic logs from all of the wells with reduced groundwater.

Amuri Plain (Culverden area)

The Amuri Plain around Culverden (Figure 4.4) was one of the first parts of Canterbury to undergo extensive conversion from sheep and cattle grazing to dairy farms. Border strip irrigation from the Waiau irrigation scheme covers most of the plain. Environment Canterbury began regular groundwater quality sampling began on the plain in 1993. One well has been sampled quarterly since 1994, and 10 wells have been sampled annually since 1994 or 1995.

The soils on the plain are recent alluvial gravels with high permeabilities, covered by 10 to 60 centimetres of soil (Close and Woods, 1983), and the water table is shallow, especially in the north-east part of the plain where most wells are less than 10 metres deep. These conditions make groundwater vulnerable to contamination from surface activities. On the other hand, much of the groundwater beneath the plain is recharged by seepage from the Waiau and Hurunui rivers, providing a large degree of contaminant dilution.

Nitrate nitrogen concentrations on the plain are commonly in the range of 3 - 8 mg/L, but toward the north-east end of the plain they are less than 1 mg/L. This may indicate that seepage from the Waiau River is the main source of groundwater recharge in that part of the basin.

In the southern part of plain, most wells are less than 30 metres deep and have median nitrate nitrogen concentrations in the range of 3 to 8 mg/L, except for one well 54 metres deep that has nitrate nitrogen concentrations much less than 1 mg/L.

Close and Woods (1986) suggested that the irrigation could reduce groundwater nitrate concentrations on the plain, which they reported to average 6.8 mg/L between 1976 and 1980. However, increasing trends were noted in two of ten wells tested, using data from 1995 to 2001 (see Section 7 for discussion).

Spotswood-Cheviot area

Nitrate nitrogen concentrations are low in the Spotswood area (Figure 4.4), probably reflecting a large component of recharge from the Waiau River to the groundwater. In the area around Cheviot, eight kilometres to the south, concentrations are higher, and three wells have median concentrations above 5.6 mg/L (half the MAV). Groundwater recharge in the Cheviot area (Figure 4.4) is probably dominated by soil drainage, so nitrate nitrogen concentrations are not diluted, and groundwater movement may be slower than in the Spotswood area, allowing nitrates to accumulate to higher concentrations in the groundwater. It is uncertain whether the high concentrations are due to agricultural land uses in the area or to septic tanks or other localised sources.

Waipara area

Most of the available data from the Waipara area (Figure 4.4) were collected for a masters degree thesis on groundwater in the area (Loris, 2000), and only a few of the wells with data have been sampled more than once. Nitrate nitrogen concentrations are low in groundwater samples from wells located along the Waipara River and Omihi Stream, including wells deeper than 50 metres as well as some shallower wells.

Concentrations are higher in the south-western part of the basin, where groundwater is not diluted by recharge from the Waipara (or its tributaries) and soil drainage has more influence on the groundwater quality. As in the Cheviot area, slow flow rates in this area may also allow nitrates to accumulate in the groundwater.

In the southernmost part of the basin, nitrate nitrogen concentrations less than 1 mg/L are probably associated with reducing conditions in the groundwater. Some bore logs from the area indicate layers of peat in the sediments, and arsenic has been detected in two wells in

the area (B. Ingram, Food and Health Standards New Zealand Ltd., personal communication; R. Rait, Pattle Delamore Partners Ltd., personal communication).

Ashwick Flat

The Ashwick Flat area (Figure 4.2) is a shallow alluvial basin of approximately 120 square kilometres. The water table is generally less than 5 metres below ground surface. The area has traditionally been dryland sheep pasture, but an increase in irrigation in recent years has allowed more intensive grazing and dairy farming to develop.

Groundwater quality monitoring in the Ashwick Flat area near Fairlie began in 1995, and the current programmes include 11 wells that are sampled annually and 4 wells that are sampled quarterly. Of the 16 wells in the area from which nitrate nitrogen concentrations are available, all but two have median concentrations less than 5.6 mg/L (one half MAV). However, an increasing trend was identified in the one well for which a Mann-Kendall trend analysis was done.

9 Conclusions

Existing data demonstrate a clear connection between land use and nitrate nitrogen concentrations. Where groundwater recharge is dominated by rainfall and soil drainage rather than by seepage from rivers, nitrate concentrations are generally greater than 3 mg/L, which has been reported to be the upper limit of concentrations that would typically occur in groundwater under natural conditions. Over substantial areas of the Canterbury Plains, especially the Ashburton-Pendarves area, the area south and west of Christchurch, and the area between the Waimakariri and Ashley rivers, concentrations above 5.6 mg/L, or one half the MAV, are widespread.

Groundwater depth does provide some protection from nitrate contamination, but concentrations above 1-2 mg/L have been recorded in a number of wells deeper than 100 metres. There is no correlation between well depth and nitrate concentrations in wells up to 50 metres deep. A full analysis of nitrate concentrations versus depth below the water table was beyond the scope of this report but would provide valuable information.

Nitrate nitrogen concentrations commonly fluctuate on a seasonal cycle, especially in shallow, unconfined groundwater that is not diluted by recharge from major rivers. Higher concentrations occur in winter and spring and lower concentrations occur in autumn. The magnitude of these fluctuations is typically on the order of 2-6 mg/L over a single year, but there is substantial variation from well to well, and even in the same well the magnitude and timing of the fluctuations are not consistent from one year to the next, probably dependent largely on the magnitude and timing of rainfall recharge.

There is evidence that nitrate concentrations in Canterbury groundwater are increasing on a long-term trend. Out of 255 wells tested, 43 (17%) showed long-term trends toward increasing nitrate nitrogen concentrations, while only 21 (8%) showed trends toward decreasing concentrations. Wells with increasing trends were distributed across the Canterbury Plains and in most other areas of Canterbury where groundwater quality is monitored. In contrast, wells with decreasing trends were identified only on the Canterbury Plains, and many of them were located in the Christchurch area where changes in industrial practices have probably contributed to the decline in nitrate nitrogen concentrations.

Most of the increasing trends had slopes between .01 and 1 mg/L per year, and the median slope was about 0.2 mg/L per year. At this median rate, it would take approximately 30 years for the nitrate nitrogen concentration at a given location to increase from 5.6 to 11.3 mg/L.
It must be kept in mind that many of these trends are based on only five years of data, and it is debatable whether five years, or even ten years, is a sufficient time period to establish a long term trend. However, the dominance of increasing trends over decreasing trends, especially in rural areas of Canterbury, is notable, and the correlation of the increasing trends with intensive agricultural activities like dairy farming and wastewater disposal, rather than grazing and residential land, indicates that agricultural activities and associated industries can pose a significant threat to groundwater quality if they are not managed properly.

10 Further investigations and monitoring

- There is room for refinement of the analysis presented in this report. The presentation of median concentrations from the entire database was a crude means of illustrating the main spatial trends that can be gleaned from the database. More careful analysis of the data may provide further insight into the extent of areas that are most at risk from land use development, or it may provide more information on the sources of the high nitrate nitrogen concentrations that are observed in the region.
- The analysis of nitrate versus groundwater depth should also be refined, with more effort put into establishing water table levels to accompany the nitrate nitrogen concentrations. Wells tapping confined aquifers should also be separated from those tapping unconfined aquifers. A better understanding of the relationship between nitrates and groundwater depth would be useful toward understanding the fate and attenuation of nitrates within groundwater.
- A careful analysis well depths, confining layers, water table levels, and nitrate concentrations could provide additional information on natural (*i.e.* before human settlement) background nitrate concentrations in areas dominated by rainfall recharge. Such an analysis would identify shallow wells that tap groundwater near the water table, with no low-permeability soils between the well screen and the ground surface. Though the concentrations in these wells may still reflect contamination from human activities, they would at least put a firm ceiling on "natural background" nitrate concentrations in Canterbury groundwater.
- Oxidation potential in Canterbury groundwater and its effects on nitrate concentrations could be better understood.
- More research should be done to investigate the effects of major irrigation schemes on groundwater quality. A full comparison of existing nitrate data with known irrigation schemes was beyond the scope of this report but may provide important insight into such questions as whether increased irrigation leads to increased nitrate concentrations in groundwater, or whether nitrate concentrations are diluted by high rates of border strip irrigation.
- The existing nitrate nitrogen data provide clear evidence that human activities such as agriculture and waste disposal have a marked effect on groundwater quality, especially in areas where groundwater recharge is dominated by soil drainage rather than seepage from rivers. However, there is a need to quantify the relationship between land use and groundwater quality so that the effects of future activities and development can be predicted and managed.
- Substantial research has been done to investigate soil nitrogen budgets and leaching losses to soil drainage water, but the next step is to investigate the fate of the nitrogen compounds as they travel through the unsaturated zone and when they mix with groundwater in the saturated zone. Investigations could include field studies at facilities like the dairy research farm at Lincoln University or the linear lysimeter at Te Parita, or they could focus on developing computer models that would link the results of the soil nitrogen research to groundwater flow and contaminant transport models.

- The existing data highlight a number of locations in Canterbury where nitrate nitrogen concentrations are greater than the MAV, and in many of these locations, the sources of contamination are not known. More research is needed to find and understand these sources so that they can be managed and so that contamination from similar sources elsewhere can be prevented.
- Environment Canterbury's current monitoring programme needs to be reviewed to make sure that it is addressing the nitrate question in the best possible manner. The trend analysis presented in this report highlights the need to maintain a network of long-term monitoring sites to provide more data for future analyses. Monthly and quarterly monitoring wells are limited to southern Canterbury and the Central Plains; this scheme may need to be modified to provide more complete regional monitoring coverage. There are also still areas where little or no groundwater quality exploration has been done, especially in the MacKenzie Basin and the southern part of the Culverden basin, south of the Hurunui River toward Hawarden.

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Appendix 1 - Extraction of data from Environment Canterbury water quality database

1. SUMMARY OF DATABASE STRUCTURE

Environment Canterbury's water quality database is stored as a series of tables on a SQL server, accessed through Microsoft Access 97. There are four main tables:

dbo_SITES	
<u>Field name</u>	<u>Description</u>
* SITE_ID	CRC / SCY / WTK number
SOURCE	river name or well number
SITE_NAME	descriptive name of site
MAP_REF	grid reference
SITE TYDE	seems incomplete - code that should link to SiteTypeID in
SHL_HFL	dbo_SQLSiteType table
RIVER_ID	8-digit ID code for river
APPNO	some sort of 8-9 digit code
WELARC_ID	mostly blank; a few with a number followed by "M"
MGRIDE	map grid easting
MGRIDN	map grid northing
REGISTER_BY	name of person entering data
LAST_MODIFY	name of person that last modified the data
COMMENT_COUNT	number of comments
COMMENTS	comments
WELL_NO	Well number (for wells only)
First_Registerd_Date	date first entered
Last_Modified_Date	date last modified
SiteType	code that links to SiteTypeID in dbo_SQLSiteType table

* indicates primary key

dbo_SQL_Samples					
Field name	<u>Description</u>				
* SAMPLE_NO	sample number				
ENT_ON	date entered				
APP_ON	date approved				
APP_BY	approved by (lab person)				
TEXT1	sampler				
TEXT2	project code				
TEXT6	sample collection time				
DATE1	sample date				
REMARKS	remarks				
PROJECT_NO	project name or code				
Site_ID	CRC / SCY / WTK number				
LOT	laboratory lot				

* indicates primary key

dbo_SQL_Sample	MethodsID
Field name	<u>Description</u>
SAMPLE_NO	sample number
ME_N	method number
ME_VERS	method version number
PA_N	parameter number
PA_VERS	parameter version number
SRESULT	analytical result
MODIFIED_ON	date modified
MODIFIED_BY	person who modified it
MOD_REASON	reason for modification
LAB	analytical laboratory (or "Field")

dbo_SQL_PARAMETERS_METHODS						
Field name	Description					
* ME_N	method number					
* ME_VERS	method version number					
ME_TYP	"Field", "Micro", "Pesticide", "Hydroc", "Pesticide", "Chem",					
	"Invoicing",or blank					
* PA_N	parameter number					
* PA_VERS	parameter version number					
PA_NAME	parameter name					
Description	method description					
Units	parameter units					
PARAMETER_ID	acronym or abbreviation for parameter					
UDL	upper detection limit					
LDL	lower detection limit					

* indicates primary key

Effectively, the database is a record of the individual analytical results (*i.e.*, the individual records in *dbo_SQL_Sample_MethodsID*), and each result is linked to its associated sample number, analytical method details, sampling site ID, well number, collection date, parameter name, etc.

2. PROCEDURE FOR EXTRACTING NITRATE NITROGEN DATA

2.1 Data extraction

To extract the nitrate nitrogen data, the database was queried for all results (stored under the field name "SRESULT") that met the following criteria:

SiteType = "00": this designates the sample as a groundwater sample as opposed to surface water

WELL_NO = *"IS NOT NULL"*: Some groundwater sampling sites have no well number, possibly indicating an uncertain groundwater source such as a mixing tank, a tap with unknown reticulation, or a spring. This criterion eliminated 77 samples. It did not eliminate "well" number L35/0155, which is in the water quality database but not the Environment Canterbury "Wells" database (the well had two samples, one from 1979 and one from 1982), nor did it eliminate "well" number N32/0105, which is actually a thermal spring at Hanmer Springs, with one sample from 1987. *DATE1* = "<#01/01/02#": only samples collected through 2001 were considered in this review

PA_NAME = *"nitrate nitrogen"*: this criterion eliminated 18 results for "Nitrate" and 689 results for "Nitrate + Nitrite Nitrogen"

The query extracted data from the fields WELL_NO, SITE_ID, MGRIDE, MGRIDN, DATE1, SAMPLE_NO, SRESULT, and UNITS. It yielded nitrate nitrogen results for 14,412 samples.

2.2 Data edits

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2.2.1 Remove errors and non-results:

The results were copied from Access and pasted into and Excel spreadsheet, where they were edited by removing the following records:

- 20 results where SRESULT = N/R
- 2 results where SRESULT = N/A
- 1 result where "*"
- 1 result where "?12"
- 4 samples from Urral well (SCY006128, K36/0439) from Sep/Oct00,

because the results are questionable (Weeber, pers comm)

This left 14,384 samples, including 369 non-detects ("<xx", detection limits range from 0.002 to 0.5 mg/L) and 215 "0"s (all date from 1989 or earlier, as early as 1954).

2.2.2 Convert text values and non-detections:

Some of the values in the database are stored as text, and others are stored as numeric values. In Excel, all text values in the SRESULT field were converted to numeric values in a new field (" $NO3_N$ ").

All non-detects ("<xx") were converted to 0.001, equal to one half the lowest detection limit in the database.

The resulting table of 14,383 records was **then exported back into an Access database** (*nitrate.mdb*) as a new table called "edited nitrate results w dups", indicating that the data had been edited but that duplicate samples had not yet been dealt with.

2.2.3 Edit results for duplicate samples:

The edited nitrate results contained 356 cases where more than one sample was collected from a single site on the same date, including:

- 349 site/dates with two samples
- 7 site/dates with more than two samples; avg and med all within 0.5 mg/L
 - CRC301946, M36/0017, 12/11/86, 5 samples, avg 18.5, med 18.0
 - CRC302327, M36/1817, 9/05/84, 5 samples, avg 1.0, med 1.0
 - CRC301365, M35/0470, 19/07/79, 4 samples, avg 0.2, med 0.2
 - CRC301951, M36/0028, 20/07/82, 4 samples, avg 4.4, med 4.4
 - CRC301827, M35/4722, 6/12/85, 3 samples, avg 7.4, med 7.4
 - CRC302322, M36/1545, 9/06/82, 3 samples, avg 1.8, med 1.9
 - CRC303853, M36/5325, 3/11/97, 3 samples, all non-detects (<0.25 mg/L)

In all of these cases, the duplicate values were converted to a single, average value. For two values, the average and the median are equal, but this may not hold where there are more than two values. However, averages were used instead of medians because the operation was done in Access, which does not have a data summary function for calculating medians. The operation was considered acceptable because there were only seven cases where more than 2 samples were collected for a given site/date, and the mean and median for each of these cases were either equal or not very different.

The operation was performed as an Access query called "edited nitrate data no dups", based on the imported table "edited nitrate results w dups". The query calculated a single, average NO3_N concentration for each site and date. The result was a table of 14,015 records.

3. PROCEDURE FOR EXTRACTING AMMONIUM NITROGEN DATA

Ammonium nitrogen data was compared with nitrate nitrogen data in Section 4.2 of the report to identify wells with reducing groundwater conditions. The ammonium nitrogen data was extracted and edited following a similar procedure to that followed for the nitrate nitrogen data.

The data extraction query was linked to the "edited nitrate results w dups" query to consider only wells for which nitrate nitrogen data was also available. The criteron for PA_NAME was set to 'Like "ammonia*", to include values for "Ammonia Nitrogen" and "Ammoniacal Nitrogen". The result was 6,563 records from 1,634 wells, representing all of the ammonium nitrogen data in the database (up to 31/12/2001) from sites that also have nitrate nitrogen data.

The data was copied and pasted into an Excel spreadsheet, and one record with an ammonium nitrogen result of "N/A" was deleted, leaving 6,562 records (still 1,634 wells). The data included 1,881 non-detects ("<xx", detection limits range from 0.001 to 0.06 mg/L) and 1,121 "0"s (all date from 1994 or earlier, as early as 1954).

In Excel all text values in the SRESULT field to numeric values in a new field ("NH3-N"). Non-detects ("<xx") were converted to 0.0025, equal to one half the lowest detection limit. The results were then imported back into the Access database (*nitrate.mdb*) as a new table called "edited ammonia N results w dups".

Duplicate values were averaged to single values for each well/date. There were 2 wells with more than 2 samples per date

- M36/0017, 12/11/86, 5 samples; median 0.01, average 0.009
- M36/5325, 3/11/97, 3 samples; median 1.8, average 2.1

As with the nitrate nitrogen data, averages were used instead of medians because Access does not have a data summary function for calculating medians, but in the 2 cases above with more than two samples per well/date, the mean and median values were not very different.

The result, calculated using an Access query "ammonia N no dups", was 6,337 records. These records were copied and pasted back into Excel, and the median and max ammonium nitrogen values were calcuated for each well as described below.

4. CALCULATING MEDIAN VALUES FOR INDIVIDUAL WELLS

Median nitrate nitrogen values for individual wells were used in the maps in Figures 4-8 and Figure 11 and in the plots of nitrate nitrogen versus depth in Figures 9 and 10. Median ammonium nitrogen values were used to create the map in Figure 8. The values were calculated in Excel by copying and pasting the data from the Access queries "edited nitrate data no dups" and "ammonia N no dups" described above. Medians were calculated using the Excel "MEDIAN" worksheet function.

The data was exported to tab-delimited text file "site nitrate data.txt" for plotting the maps in ArcView. The well coordinates used were the MGRIDE and MGRIDN values from the water quality database.

5. WELL DEPTH DATA

Well depths were obtained from Environment Canterbury "Wells" database, another SQL database accessed using Microsoft Access. Values were obtained in January 2002, which may be important to note in case well details are changed in the future. For example, for well M35/0069, a note was added to the Wells database on 6 March 2002 indicating that the well has been deepened to 40 m. However, the well was 15.2 metres deep when sample collected, so the shallower depth was kept in this report.

Appendix 2: Nitrate nitrogen concentrations in wells that are in Environment Canterbury's current monthly monitoring programme

Page 1: wells in central Canterbury



Graphs labelled by Environment Canterbury well number. Well depths shown in parentheses.

Vertical axis: nitrate nitrogen concentration in mg/L nitrogen. *Horizontal axis*: sample date (labels mark January 1 of each year).

J40/0080 (21m) J40/0163 (4.6m) J40/0106 (18.2m) J40/0333 (8m) M J40/0343 (8.5m) J40/0042 (6.78m) J39/0232 (9m) J39/0135 (10.5m) 4.0 3.0 2.0 1.0 0.0 Jan-99 Jan-00 Jan-99 Jan-01 Jan-00 Jan-01 J39/0259 (54m) J39/0261 (8.3m) 0.020 0.015 0.010 0.005 0.000 Oct-00 Jan-01 Apr-01 Jul-01 Oct-01 Jan-00 Jul-00 Jan-01 Jul-01

Page 2: wells in southern Canterbury

Graphs labelled by Environment Canterbury well number. Well depths shown in parentheses.

Vertical axis: nitrate nitrogen concentration in mg/L nitrogen. *Horizontal axis*: sample date (labels mark January 1 of each year unless otherwise marked).

Appendix 3 – Trend analysis methods

1. STATISTICAL METHODS

1.1 Mann-Kendall trend analysis

For a time-ordered series of observations, the Mann-Kendall statistic is calculated using the following equation:

$$\sum_{k=1}^{n-1}\sum_{j=k+1}^n sign(x_j-x_k)$$

where *n* is the total number of samples, x_j is the concentration in sample number *j*, x_k is the concentration in sample number *k*, and *j* and *k* are ordinal numbers where *j* is greater than *k*, indicating a sample collected at a later date. The sign function determines whether the concentration in sample *j* is greater or less than the concentration in sample *k*. If x_j is greater, the function returns a positive 1, if x_k is greater it returns a negative 1, and if they're equal it returns a zero. The greater the magnitude of the Mann-Kendall statistic, the greater the number of instances in which a later concentration is higher (or, in the case of a decreasing trend, lower) than earlier concentrations, and the greater the probability that the values represent a real trend rather than random chance.

The Mann-Kendall statistic for each well was compared to a "critical value" corresponding to the number of years of data for that well (Table A3-1). The critical values were taken from IDT(1998), using an "alpha" confidence level of 0.05. If the absolute value of the Mann-Kendall statistic was greater than the critical value, then the trend was considered significant. The sign of the statistic indicated whether the trend was increasing or decreasing.

1.2 Sen's nonparametric estimator of slope

For each site where a trend was identified, Sen's slope estimator (Gilbert, 1987) was used to estimate the slope of the trend. Only springtime data were used in the calculation, and outlier values were removed as discussed in Section 3 below. Sen's estimator is less affected by gross data errors or outliers than a standard linear regression. It is a nonparametric calculation closely related to the Mann-Kendall analysis. First, a slope *Q* is calculated for between each pair of concentration values, similar to the way in which the sign of each pair of values is calculated in the Mann-Kendall analysis:

$$Q = \frac{y_j - y_k}{x_j - x_k}$$

where x represents a sample year, y is the corresponding median nitrate nitrogen concentration value for that year, and j is greater than k. Then, Sen's slope estimator is simply the median of all of the Q values.

1.3 Linear regression

For each site where a trend was identified, a standard linear regression slope was calculated for comparison with the Sen's slope estimator. Only springtime data were used in the calculation, and outlier values were removed as discussed in Section 3 below. Linear regression slopes were calculated using Microsoft Excel's "SLOPE" function, which uses the equation

$$b = \frac{n \sum xy - (\sum x)(\sum y)}{n \sum x^2 - (\sum x)^2}$$

where *b* is the linear regression slope in mg/L per day of nitrate nitrogen; *n* is the number of years of data; *x* represents each sample year, and *y* is the median nitrate nitrogen concentration value for that year.

2. DATA COMPILATION

Long-term trend analyses were done on two sets of data. The criteria for the data used in the tests were:

- the well was sampled in 2000 and/or 2001
- the sample was collected in the spring months of September to December
- For the first set of tests:
 - the well had data (collected during September to December) from at least 10 calendar years between 1977 and 2001
- For the second set of tests:
 - the well had data (collected during September to December) from at least 5 calendar years between 1995 and 2001

The wells to be used for each set of tests were identified through a series of queries using Microsoft Access, based on the query "edited nitrate data no dups" that is discussed in Appendix 1, Section 2. The queries identified 129 sites that met the criteria for the first set of test and 252 sites that met the criteria for the second set of tests. There were 126 sites that met the criteria for both sets of tests, so the total number of sites identified for both tests was 255.

All post-1976 data from these 255 sites were extracted from the "edited nitrate data no dups" query and copied into a Microsoft Excel spreadsheet.

3. OUTLIER VALUES and CREATION OF GRAPHS

Outlier values were identified and removed from the trend analyses through the following procedure in the Excel spreadsheet:

- For each site, identify all values collected outside the springtime (Sep-Dec) and move them to a separate column
- For each site, using only the spring data, identify all values that are outside two standard deviations from the median and move them to a third column
- Create graphs of the data for each, with Date on the x-axis and three series on the yaxis, using the three separate columns of data (1: spring data; 2: non-spring data; 3: data outside two standard deviations of the median).
- Visually examine each graph with outlier data; based on the range and variations in the data, make a subjective decision as to whether the points that fall outside two standard deviations of the median are actually outliers; where there is reasonable doubt that a point is not an outlier, go back to the data worksheet page and move the value back to the "spring" data column so that it is included in the trend analyses.
- The resulting graphs are included in this appendix. Black squares on the graphs represent data used in the trend analyses. White squares represent data collected outside the spring months of September to December. "X"s represent data points that are considered to be outliers and were therefore not used in the trend analyses.

4. SUMMARY OF DATA

- 252 wells identified for trend analyses
 - 129 wells in first set of tests (springtime data from at least 10 separate years between 1977 and 2001)
 - 252 wells in second set of tests (springtime data from at least 5 separate years between 1995 and 2001)
 - 126 wells in both sets of tests
- 5,367 data points (sample concentrations, excluding duplicates) from the 252 wells
- 3,042 data points from the springtime months of September to December
 - 186 of the springtime data points were outside two standard deviations of the well's median concentration, based only on springtime data (Table A3-2)

- 48 data points were considered to be outlier values, including 47 that were outside two standard deviations of the median, plus one other point inspection (well K37/0234, 14 Sep 88) that was identified on visual inspection (Table A3-2)
- after removing the outlier values, a total of 2,994 data points were used in the trend analyses

5. CALCULATION OF TRENDS AND SLOPES

All springtime data for the 129 sites identified for the first set of tests were copied and pasted onto a new Excel worksheet. Similarly, all springtime data for the 252 sites identified for the second set of tests were copied and pasted onto a separate worksheet.

For each well in each set of tests, a median nitrate nitrogen concentration was calculated for each year of data. A Mann-Kendall statistic was calculated then calculated, the statistic was compared with the critical value (Table A3-1) corresponding to the number of years of data for the well. If the absolute value of the statistic is greater than the critical value, then the trend was considered significant. The sign of the statistic indicated whether the trend was increasing or decreasing.

For each well where a trend was identified, Sen's slope estimator was calculated using the procedure in Section 1.2 above, and a linear regression slope was calculated as discussed in Section 1.3 above. As for the Mann-Kendall statistic, the slopes were calculated using median nitrate nitrogen concentrations for each year of data.

TABLES

Years of	Years of Critical		Critical	Years of	Critical	
data	value	data	value	data	value	
4	6	9	17	14	32	
5	8	10	20	15	35	
6	10	11	23	16	38	
7	13	12	26	17	42	
8	15	13	29	18	45	

Table A3-1. Critical values used in Mann-Kendall trend analysis

Confidence interval of 95% (alpha = 0.05)

Well Number	Sample Date	Nitrate nitrogen concentration (mg/L N)	Well Number	Sample Date	Nitrate nitrogen concentration (mg/L N)
J38/0171	27/09/00	14.95	L37/0893	23/10/01	15
J40/0022	20/09/00	0.2	L37/0896	4/11/99	35.7
J40/0077	1/11/00	13.8	L37/0898	28/11/95	3.5
J40/0163	18/09/00	11.55	M34/0154	30/10/67	0
J40/0217	1/11/00	5	M35/0174	25/09/89	1.2
K37/0083	28/11/88	1.11	M35/0925	31/10/77	0.3
K37/0234	14/09/88	8.33 *	M35/1424	14/11/78	1.5
K37/0234	28/11/88	1.07	M35/1737	28/09/95	0.5
K37/0245	28/11/88	0.94	M35/2242	19/10/94	0.56
K37/0260	28/11/88	1.15	M35/2379	18/11/93	2.8
K37/0468	15/10/97	1.6	M35/2557	7/12/92	5.7
K38/0105	10/09/98	0.83	M35/4264	25/10/88	0.022
K38/0231	25/09/96	8	M35/5086	2/11/87	1.5
K38/0287	27/09/00	5.9	M35/5251	20/10/98	0.05
K38/0356	21/11/01	0.1	M35/5251	13/12/00	0.1
K38/0637	1/09/99	29	M35/6662	22/09/93	0.1
L35/0205	27/10/88	2.4	M35/6670	26/10/99	0.5
L37/0157	28/11/95	5.9	M36/0974	22/10/98	0.48
L37/0392	12/10/99	30	M36/1045	17/11/94	1.4
L37/0397	4/11/99	34.7	M36/1057	22/12/58	1.1
L37/0555	12/10/92	2.7	M36/1225	1/12/92	0.3
L37/0659	13/12/00	4.4	M36/1504	18/10/99	0.1
L37/0661	5/10/98	9.8	O31/0156	3/12/01	6.6
L37/0893	4/11/99	16.1	O33/0049	9/09/99	0.3

Table A3-2. Data points considered to be outliers and not used in the Mann-Kendall trend analysis

* value within two standard deviations of the median but considered to be an outler based on visual inspection of the data

		Nitrate			Nitrate			Nitrate			Nitrate
Well	Sample	nitrogen	Well	Sample	nitrogen	Well	Sample	nitrogen	Well	Sample	nitrogen
137/0012	8/10/02		K39/1075	1/00/00	(mg/L N) 12.5	M35/1051	1/00/00	(mg/L N) 10	M36/0608	0/10/01	(mg/L N)
138/0125	7/11/01	4 1	K38/1075	6/00/00	12.5	M35/1051	1/09/99	37	M36/0712	20/00/05	2.2
120/0120	7/11/91	7 15	K20/0012	0/09/00	10.1	M25/1051	1/12/00	3.7	M26/0712	20/09/95	0.5
140/0011	1/11/00	7.15	K39/0013	0/11/00 25/10/00	12.2	M25/1001	26/00/90	3.0	M26/0017	9/10/01 7/11/79	0.5
J40/0011	1/11/99	0.5	K39/0033	25/10/00	15.2	M25/1093	20/09/09	2.2	M26/1050	7/11/70	05
J40/0080	20/00/00	9.9	L35/0171	10/09/93	1.0	N25/1093	1/10/91	2.2	M36/1059	1/12/07	9.5
J40/0001	20/09/00	0.0	L35/0191	29/09/00	2.0	M25/1093	20/09/90	2.1	M26/1059	6/10/05	9.2
J40/0100	3/12/01	4.05	L30/0059	24/09/92	3.0 7.7	N35/1093	3/10/01	10	M36/1039	7/11/90	3.1
J40/0103	2/10/00	9.9	L30/0200	5/11/00	1.1	IVIS5/1095	0/11/00	1.9	N36/1099	7/11/09	0.012
J40/0200	19/09/00	7.0	L30/0317	5/10/99	0.29	IVISO/ 1302	0/12/92	1.1	IVI30/1440	20/10/05	0.013
K30/0033	12/12/00	1	L30/0323	9/10/90	0.20	N25/1000	9/12/92	1.0	M36/1009	20/10/95	2.0
K30/0000	10/12/92	4.4	L30/04/7	10/11/07	4.1	IVISS/ 1000	19/12/91	2.3	N36/2050	0/09/07	7
K30/0104	12/12/00	10.1	L30/000Z	20/09/92	12	IVI35/1000	10/11/93	2.3	N130/2030	22/09/97	5 10
K36/0119	18/10/94	10.2	L30/08/1	6/12/00	0.3	IVI35/1860	1/12/8/	1.9	N136/2232	2/12/92	13
K37/0210	19/10/99	10.3	L37/0197	9/10/95	1.2	IVI35/1864	7/12/81	0.2	NI30/2079	8/10/01	0.4
K37/0243	13/10/92	8.1	L37/0391	12/10/99	37	IVI35/1883	7/12/92	13	IVI36/2961	2/12/92	10
K37/0266	16/10/01	2.2	L37/0393	9/10/01	38	M35/2249	9/12/92	3.9	M36/3071	10/10/01	0.7
K37/0465	8/10/92	4.7	L37/0393	15/10/98	37	IVI35/3653	17/10/01	0.3	M36/3085	27/11/00	0.2
K37/0473	25/10/01	2.7	L37/0396	28/11/95	3.8	M35/4682	28/09/92	13	M36/3467	28/09/93	0.4
K37/0562	17/10/00	8.1	L37/0415	4/11/91	8.2	M35/4757	24/09/90	8.7	M36/3467	29/09/97	0.39
K38/0106	6/09/00	14.7	L37/0660	5/10/98	13	M35/5353	8/09/87	0.52	M36/3588	27/09/01	6.75
K38/0106	9/11/92	14	L37/0660	22/11/94	12	M35/5440	23/09/99	5	M36/3588	14/11/00	6.55
K38/0106	28/09/94	14	L37/0894	6/09/99	48	M35/5918	26/09/01	1.8	M36/3712	9/11/88	0.2
K38/0148	16/10/00	4.6	L37/0897	13/10/93	5.5	M35/6791	12/09/00	0.4	M36/3712	18/10/99	0.2
K38/0172	8/11/00	35.9	L37/0905	28/11/95	9.7	M35/7644	26/10/99	1.2	M36/4151	2/09/99	10
K38/0240	5/10/00	8.4	M35/0132	4/12/00	6.7	M36/0271	5/10/92	11.6	M36/4151	5/09/00	9.45
K38/0404	12/10/99	10	M35/0132	18/09/89	6.6	M36/0271	4/09/95	4.1	M36/4151	5/10/00	8.5
K38/0407	3/10/01	2.9	M35/0217	28/09/92	1.8	M36/0271	30/09/86	4	M36/4227	2/09/99	11.6
K38/0408	4/10/01	0.7	M35/0225	11/11/87	0.026	M36/0271	28/09/95	3.9	M36/5248	10/11/97	7.5
K38/0410	5/10/00	7.5	M35/0225	2/10/89	0.022	M36/0271	26/10/95	3.9	M37/0065	9/10/01	5.6
K38/0430	8/11/00	25.9	M35/0698	15/11/93	7	M36/0297	31/10/89	7.2	N33/0194	12/09/95	4
K38/0473	9/11/92	14	M35/0698	14/12/92	6.7	M36/0456	27/10/77	3.9	N33/0200	29/11/94	3.8
K38/0473	8/12/93	8	M35/0834	8/11/95	0.8	M36/0473	18/09/95	0.4	N33/0205	3/12/01	6.6
K38/0957	5/09/01	12.5	M35/1003	5/10/92	10.8	M36/0473	14/11/00	0.4	N33/0219	7/10/96	2.71
K38/0957	6/09/00	12.3	M35/1003	7/12/88	2.8	M36/0473	11/10/01	0.4	O31/0096	12/09/00	6
K38/0957	1/09/99	12	M35/1051	4/09/95	10.8	M36/0698	15/11/00	2.2			

Table A3-3. Data points outside two standard deviations of the median but not considered to be outlers based on visual inspection of the data

Nitrate concentrations in Canterbury groundwater – a review of existing data



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 1 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 2 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 3 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 4 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 5 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 6 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 7 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 8 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 9 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 10 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 11 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 12 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 13 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 14 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 15 of 32)


Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 16 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 17 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 18 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 19 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 20 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 21 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 22 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 23 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 24 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 25 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 26 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 27 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 28 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 29 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 30 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 31 of 32)



Appendix 3: Graphs of nitrate nitrogen concentrations and results of trend analysis (page 32 of 32)