

Distribution of nitrogen species in groundwater in the Taieri Plain aquifer, New Zealand

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Abstract

In New Zealand, up to 51% of people use at least some groundwater for drinking, and there is growing concern that intensification of agriculture may lead to nitrate contamination of aquifers. Nitrogen contamination of drinking water has been linked to health risks, including 'blue baby syndrome'. This study focuses on identifying and accounting for the distribution of nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+) in the groundwater throughout the Taieri Plain aquifer, New Zealand, during March-November 2002. Electrical conductivity and pH were also measured on site, while a smaller number of samples were also analysed for organic nitrogen, total dissolved iron, and total dissolved manganese.

Nitrate and ammonium concentrations showed significant variation across the Taieri Plain aquifer. Nitrate was present in low concentrations in the confined region of West Taieri ($<0.6 \text{ g m}^{-3} \text{ NO}_3\text{-N}$), while it was present in elevated concentrations (up to $11.36 \text{ g m}^{-3} \text{ NO}_3\text{-N}$) in distinct unconfined regions in East Taieri, and in bores tapping groundwater from alluvial fans. Ammonium was present in elevated concentrations (up to $2.36 \text{ g m}^{-3} \text{ NH}_4\text{-N}$) along the Titri Fault side of West Taieri and commonly toward the

southwest extent of the plain, while concentrations were generally low or undetectable throughout the remainder of West Taieri and all of East Taieri ($<0.2 \text{ g m}^{-3} \text{ NH}_4\text{-N}$). Both species showed no significant variation over time. Nitrite concentrations were universally low ($<0.03 \text{ g m}^{-3} \text{ NO}_2\text{-N}$), with only twenty bores yielding values above the detection limit ($0.002 \text{ g m}^{-3} \text{ NO}_2\text{-N}$). Mean nitrate concentrations for bores tapping confined and unconfined zones were well below the maximum limit for drinking water in New Zealand ($11.3 \text{ g m}^{-3} \text{ NO}_3\text{-N}$), although in the unconfined zone of East Taieri some individual measurements approached or slightly exceeded this limit. Some individual measurements for ammonium exceeded the New Zealand aesthetic guideline for drinking water ($1.2 \text{ g m}^{-3} \text{ NH}_4\text{-N}$).

The Waihola silt/sand unit, deposited by a Holocene marine transgression, is confining the aquifer in West Taieri. The unit effectively protects the aquifer from any potential surface contamination that may arise from intensive dairying operations in this region. In contrast, nitrate is able to directly enter the alluvial fans along the northern and western margins of the basin, and the main aquifer in parts of East Taieri. Strategic groundwater monitoring and regulation of land-use practices in these areas is recommended.

Keywords

nitrogen, nitrate, nitrite, ammonium, GIS mapping, Taieri Plain aquifer.

Introduction

Throughout the world there is increasing concern over the pollution of the environment with inorganic nitrogen species, especially nitrate, nitrite, and ammonium. Of particular concern is the contamination of current and future drinking water supplies from groundwater, which is being increasingly relied upon as a source of potable water. In New Zealand, 26% of the population are totally dependent on groundwater for drinking, including the residents of Christchurch, Lower Hutt, Napier, Hastings, and Wanganui, and many rural households (White and Rosen, 2001). A further 25% of the population drink water from a combination of groundwater and surface water sources.

The various inorganic forms of nitrogen involve a range of oxidation states from +5 (nitrate, NO_3^-), +3 (nitrite, NO_2^-), 0 (elemental N_2) to -3 (ammonia/ammonium, $\text{NH}_3/\text{NH}_4^+$ and organic forms of N such as amino acids). Under *oxic* conditions, NO_3^- -N dominates, while under *reducing/anoxic* conditions or in organic matter, nitrogen is present in a range of organic compounds or demineralised to form ammonium (NH_3 , NH_4^+) (McLaren and Cameron, 1996). *Denitrification* of NO_3^- -N to form either N_2 or N_2O can occur in reducing (anaerobic) environments with the assistance of facultative anaerobic bacteria (McLaren and Cameron, 1996). Organisms can also undertake *assimilatory nitrate reduction*, in which NO_3^- -N is reduced NH_4^+ , which is then converted into organic nitrogen (Kendall and McDonnell, 1998). Conversely $\text{NH}_3/\text{NH}_4^+$ -N can be oxidised to NO_3^- -N in oxidising environments by nitrifying bacteria in the

nitrification process (Kendall and McDonnell, 1998). In both nitrification and denitrification, NO_2^- -N is formed in variable amounts as an intermediate species and can be involved in the rate-determining step (Ardacani *et al.*, 1974; McLaren and Cameron, 1996).

Nitrogen is an essential component of the amino acids and proteins composing all forms of life. However, if present in high concentrations in drinking water, nitrate and nitrite become a risk to human health. The most well documented health effect is the potentially fatal condition methaemoglobinaemia or 'blue baby syndrome'. Haemoglobin reacts with nitrite to form methaemoglobin, which cannot bind oxygen (Hunter, 1969). Tentative links have also been found to certain cancers, the development of abnormalities in offspring, hypertension, and diabetes (Ministry of Health, 1995; Canter, 1997; Close *et al.*, 2001). As growth limits are determined by the levels of nitrate available in many aquatic systems (Hessen, 1997), increased nitrate concentrations can also result in algal blooms and eutrophication of waterways, which leads to a loss of organisms due to the removal of dissolved oxygen.

Historically, New Zealand has had no real problem with nitrate pollution, due to the predominance of low-intensity sheep farming (Burden, 1982). Economic pressures have now seen landowners intensify operations to remain profitable, with an increase in the intensity of sheep farming and, more significantly, the conversion of many lowland properties to dairying. Dairying greatly increases the potential for nitrate pollution, due to the widespread application of nitrogen-based fertilizers to increase feed production, and the increases in cow urine and manure highly enriched in nitrogen species. Since 1982 the number of dairy cattle in New Zealand has gone from 3 million to 4.73 million, with milk production doubling

in this time (Statistics New Zealand, 2002), and this has caused a significant increase in nitrate concentration in some aquifers (Selvarajah *et al.*, 1994; Close *et al.*, 2001; Rosen, 2001).

In this study we examine nitrogen in the groundwater of the Taieri Plain aquifer, Otago, New Zealand. The goal of the study is to understand the cycling of nitrogen through the aquifer system, including the relationship between the physical structure of the aquifer and the chemical processes affecting nitrogen in the groundwater. The aims of the study are to: (1) identify and account for the spatial distribution of nitrate, nitrite, and ammonium in the Taieri Plain aquifer; (2) assess temporal variation of these species in the aquifer; and (3) use the chemical findings of the study to help

understand the physical makeup of the groundwater system, especially the pattern of groundwater flow.

Concern for the quality of the groundwater beneath the Taieri Plain has already resulted in a small number of reports (Irricon, 1994, 1997; Otago Regional Council, 1999). These reports have crudely identified some patterns in the concentrations of inorganic nitrogen species, but the sources and chemical reactions occurring in the aquifer influencing these patterns are still not well understood (Otago Regional Council, 1999).

Physical setting

The Taieri Plain is the surface expression of the northeast-trending tectonic depression known as the Taieri Basin (Fig. 1). The basin, which is 35 km long and 5-10 km wide, has

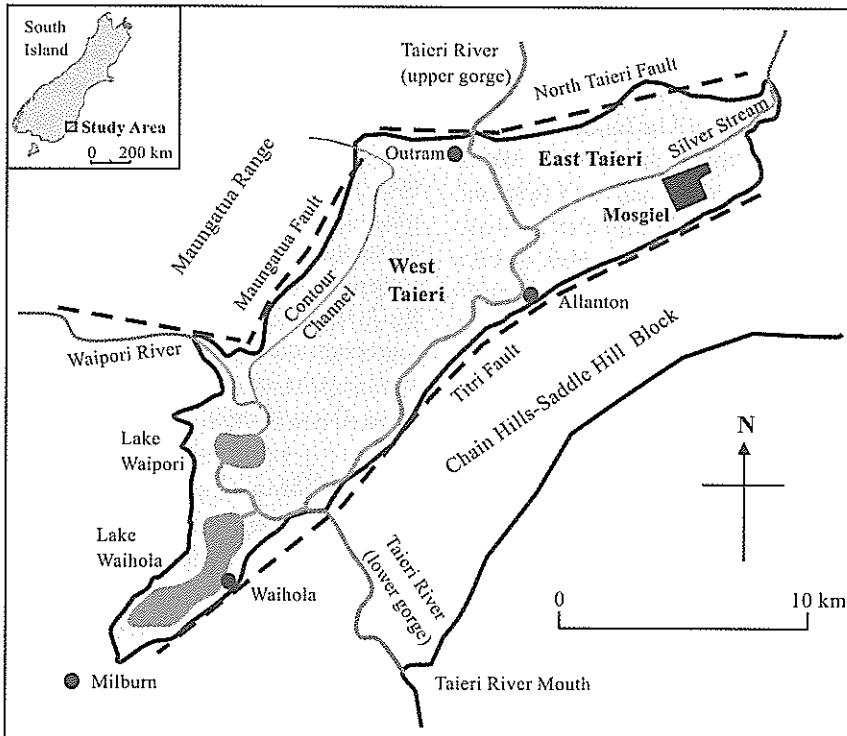


Figure 1 The extent of the Taieri Plain aquifer, showing geological and surface hydrological features, and the location of settlements and regions.

formed as a result of subsidence relative to the uplift of the adjacent Chain Hills and Maungatua Range. The basin deepens to the southeast. It narrows and 'pinches out' at a low bedrock divide centred near the town of Milburn (Litchfield *et al.*, 2002). Three rivers of significance enter the basin—the Taieri River, the Waipori River, and Silver Stream. The Taieri River forms the boundary between two regions, East and West Taieri. Silver Stream is the smallest of the three rivers, and joins the Taieri River west of Mosgiel.

The Taieri Plain aquifer is located 6 km southwest of Dunedin. Irricon (1994) estimates the total groundwater usage here to be approximately 2,335,000 m³ yr⁻¹, of which approximately 80% is drawn for the Mosgiel township water supply. Groundwater usage in 2002–2003 is likely to have increased significantly with intensification of farming practices, especially dairying, and movement of people to lifestyle blocks on the Taieri Plain (Irricon, 1997).

Otago Schist is the basement rock beneath the fault-bounded basin. The basin is infilled predominately by Quaternary gravels, sands and silts from coalescing fan and alluvial overbank deposits, which may be at least 150 m thick in places (Litchfield *et al.*, 2002). Alluvial fan material lies at the surface in some areas of the basin, including immediately beneath the Maungatua Range at the northwest edge of the basin (Fig. 1). Of hydrogeological interest is the fine-grained, Holocene marine layer named the Waiholo silt/sand unit. This wedge-shaped layer is dominated by silt horizons up to 15 m thick, with sand beds of 1–8 m thickness. It is ~25 m thick around the Lower Taieri Gorge and 'pinches out' near Outram and southwest of Mosgiel. It covers approximately two-thirds of the basin—essentially West Taieri—and acts as a confining layer to the groundwater contained in the gravels of the underlying aquifer

(Irricon, 1994; Litchfield *et al.*, 2002). Virtually all bores within the region underlain by the Waiholo silt/sand unit extend through the unit to the underlying gravels.

In East Taieri, discontinuous and thin (<1 m) layers of silts and sometimes clays act as local aquitards to groundwater in the gravel and sand layers between them (Irricon, 1997; Litchfield *et al.*, 2002). The result is a series of semi-confined water-bearing layers at varying depths, e.g., Irricon (1997) identified 5 to 6 water-bearing layers between ground level and 50 m depth at a site in East Taieri. Flow and chemical conditions within these units are highly localised, and bore depths vary widely (Irricon, 1997; Litchfield *et al.*, 2002).

The east and west areas are connected hydrologically *via* the fluviially derived sequences which underlie East Taieri and West Taieri, to make a single aquifer system. A potentiometric survey by Irricon (1994) indicates that groundwater flow through the basin is generally to the southwest. Any contaminants entering the basin in East Taieri will thus eventually migrate down-gradient to the confined aquifer in West Taieri. Further, while both the elevation of the plain and the piezometric surface of the main aquifer generally decrease in a southwesterly direction, the decrease in elevation of the piezometric surface is at a slightly lower rate, resulting in extensive artesian conditions in West Taieri (Edge, 2000).

Methods

Data collection

Over five sampling periods, in March, April, May, August, and November 2002, 103 suitable groundwater bores from the Taieri Plain were sampled. Bores were selected if they: were of suitable depth, had a working pump that allowed groundwater to be drawn to the surface for sampling and flushing, were properly capped to prevent well-head

contamination, and permission had been obtained to carry out sampling. Many bores in the study area failed to meet at least one of these criteria, with the vast majority unsuitable because they lacked a working pump. A few bores were not selected as their casings were poorly finished, and thus provided a direct path for surface runoff to enter the aquifer. Wells, i.e., large bores around 1 m in diameter, were not sampled due to their propensity for contamination, and the difficulty of obtaining representative samples from them. Not every bore could be sampled in each sampling period.

The Taieri Plain aquifer system can be divided into confined and unconfined zones. The bores located in West Taieri are considered to be in the confined aquifer, while those in East Taieri are considered to be in the unconfined aquifer. There are undoubtedly localised semi-confining units present within the aquifer in East Taieri. However, the level of confinement provided by these units is likely to be insignificant compared to the extensive Waiholo silt/sand confining unit. The exceptions are four bores located immediately beneath the Maungatua Range (Fig. 1), which are almost certainly drawing groundwater from within the permeable alluvial fans located there. The four bores are located on or above the 20 m asl contour and are all less than 21 m. These bores are too shallow to extend below the Waiholo silt/sand unit into the confined aquifer. They are thus considered to be in an unconfined aquifer, and are therefore included in the unconfined population for analysis, even though they are located in West Taieri. This interpretation is supported by the results, which indicate these bores yield

groundwater with nitrate concentrations typical of bores in the eastern, unconfined aquifer, i.e. at least an order of magnitude higher than values from any of the bores in the western, confined aquifer.

Sampling methods

On-site measurements and grab samples for laboratory analyses were taken at each selected bore. The on-site measurements consisted of pH and electrical conductivity of the groundwater, while the grab samples were taken back to the laboratory and analysed for their nitrate, nitrite, and ammonium¹ concentrations. After preliminary assessment of the results from the first three sampling periods, it was decided it would be beneficial to analyse samples for organic nitrogen, iron and manganese. Groundwater from twelve bores was analysed for organic nitrogen. The twelve bores chosen covered approximately the whole of the plain, and the various aquifer zones with unique chemistry, as determined from the results from the first three sampling periods. Six of the chosen bores were sampled at the end of sampling period 3, and six were sampled at the end of sampling period 5.

Prior to sampling, each bore was purged to obtain a 'fresh' groundwater (representative) sample. Purging consisted of pumping the bore for a minimum of 10 minutes, after which the groundwater was then run into an overflowing bucket containing the pH and electrical conductivity electrodes. In accordance with Rosen *et al.* (1999), if the readings from these meters were stable for a period of five minutes, then the bore was assumed to be fully purged and the groundwater was considered to be a representative sample. If not, purging of the bore continued until the

¹ At the pH values observed in this study (~5-7.5) use of the formula $[\text{NH}_3] = [\text{NH}_3]_{\text{Total}} / (1 + 10^{(\text{pK}_a - \text{pH})})$ (pK_a = 9.24; Aylward and Findlay, 1972) indicates that all ammonium species are present as the ammonium ion (NH₄⁺).

readings from the discharge water were stable for five minutes. Each bore was sampled as close as possible to the outlet of the pump. In practice, this meant samples often had to be taken at the outlet of a pressure tank. In such cases, the 10 minutes flushing was timed from when the pump engaged. Sampling commenced once the pH and electrical conductivity readings were stable. The on-site measurements were taken first, followed by collection of the grab samples for laboratory analysis.

pH was measured with a portable pH meter (*YSI Model 60*), which had an accuracy of ± 0.1 pH and was automatically referenced to a standard temperature of 25°C, to allow pH values to be compared despite fluctuations in the temperature of the groundwater.

Electrical conductivity was measured with a portable conductivity-temperature meter (*YSI Model 30*). The conductivity was also referenced to a standard temperature of 25°C, again to allow comparisons despite fluctuations in the temperature of the groundwater. Conductivity values are expressed as micro-siemens per centimetre ($\mu\text{S cm}^{-1}$), and have an accuracy of $\pm 0.5\%$.

Laboratory analysis of nitrite was carried out on the day of collection to prevent bacterial conversion of nitrite to nitrate, within the 48 hours specified by the American Public Health Association (APHA, 1998). Acid was not added for preservation because workers such as Roman *et al.* (1991) have found nitrite can become unstable and be oxidised to nitrate under acidic conditions. Initially, ion chromatography was used to analyse the samples for nitrite, but other unknown ions in the samples interfered with the nitrite peak, making the method inaccurate. Consequently, nitrite concentrations were measured using the APHA (1998) standard colorimetric method 4500-NO₂ B. Concentrations of nitrite were calculated as the weight of nitrogen in this

species (i.e. NO₂-N), rather than the weight of the nitrite ions in each sample, and were expressed as grams per cubic meter (g m^{-3}). Concentrations of nitrate and ammonium were calculated in the same manner (i.e., NO₃-N, and NH₄-N).

Analysis of ammonium was carried out the day after collection. This is well within the seven days specified by the American Public Health Association (APHA, 1998). The ammonium concentrations were measured using the ISO (1997) standard method 11732, for determination of ammonium nitrogen in water by flow injection analysis and spectrometric detection, using a *FIA Star 5012* system, under specifications documented in the Foss Tecator Application Note AN 65/83, AN 50/84, ASN 50-01/84.

Nitrate analysis was carried out as soon as possible at the end of each sampling period (always within one week), with samples awaiting analysis stored at -20°C. Ideally, the samples should be analysed within 48 hours to prevent the possibility of nitrite being oxidised to nitrate (APHA, 1998). Analysis of groundwater samples from the first two runs showed that the vast majority of samples had no nitrite present, or concentrations of nitrite many orders of magnitude lower than the nitrate concentration, so any distortion that may have occurred was not considered significant. Nitrate concentration was measured by ion chromatography, using the APHA (1998) standard method 4110 B - Ion Chromatography with Chemical Suppression of Eluent Conductivity.

Samples for organic nitrogen were suitably treated (Table 1) and sent to Hill Laboratories, Hamilton, which carried out the analysis.

Analysis for iron was performed on the samples collected for ammonium analysis from sampling periods 3 and 5. Total acid-soluble iron was measured, as the samples had been acidified. Analysis of the Fe²⁺

Table 1 Summary of the methods used for the analyses, and their detection limits and precision.

Parameter	Method Used	Method Detection Limit	Method Precision	Treatment
Nitrite	APHA (1998) standard colorimetric method 4500-NO ₂ B	0.002 g m ⁻³ NO ₂ -N	5 %	None
Ammonium	ISO (1997) standard method 117322 for flow injection analysis	0.02 g m ⁻³ NH ₄ -N	5 %	Sulphuric acid to pH<2. Stored in dark at 4°C.
Nitrate	APHA (1998) standard method 4110 B	0.01 g m ⁻³ NO ₃ -N	8 %	Frozen prior to analysis
Organic nitrogen	Kjeldahl Digestion	0.1 g m ⁻³ org-N	5 %	Sulphuric acid to pH<2
Acid-soluble iron	ISO (1997) standard method 11885	0.01 g m ⁻³ Total Fe	5 %	Sulphuric acid to pH<2. Stored in dark at 4°C.
Acid-soluble manganese	ISO (1997) standard method 11885	0.01 g m ⁻³ Total Manganese	5 %	Sulphuric acid to pH<2. Stored in dark at 4°C.

concentration would have been desirable, however, the method used was sufficient to give a relative indication of total iron concentrations in the groundwater derived from each bore. Analysis was carried out using the ISO (1997) standard method 11885, on acidified (pH < 2) samples that had been frozen for two weeks after collection, using a *Varian 220 FS* Atomic Absorption Spectrometer.

Total acid-soluble manganese was measured from sampling period 5 using the water from the acidified, chilled (ammonium) water sample. As with the iron measurements, the total acid-soluble manganese was sufficient to give an indication of the relative total manganese concentrations in the groundwater. Analysis was performed in the same manner as described above for iron (ISO 1997 standard method 11885), with only the wavelength of the atomic absorption spectrometer changed.

Table 1 summarises the methods used to

analyse the various chemical species, the detection limits of the methods, and their precisions. Excluding the organic nitrogen analysis, all the methods have detection limits of 0.02 g m⁻³ or lower, with the detection limit for nitrite being very low at 0.002 g m⁻³. All the methods have a precision of 5%, except for the method used for nitrate analysis (APHA 1998 - 4110 B), which has a precision of 8%. As with all the precision values, the 8% value reflects a minimum level of accuracy over a significant period, using the particular method; in reality the precision was much better than 8% for the samples analysed for nitrate in this study.

Statistical analysis was undertaken using the *Minitab*TM statistical software package. A Geographic Information System (GIS) was used for presenting the spatial data, using the *ArcCatalog* package within the program *ArcGIS*, with inverse distance weighting as the method of interpolation used to construct the GIS contour maps.

Results

Electrical conductivity and pH

Electrical conductivity varied substantially throughout the aquifer, with values ranging from 70 to 2660 $\mu\text{S cm}^{-1}$. There is a clear difference between the mean conductivities of the confined and unconfined populations. A two-sample t test indicates that the mean electrical conductivity in the confined aquifer (505 $\mu\text{S cm}^{-1}$; standard deviation (SD) = 401 $\mu\text{S cm}^{-1}$) is significantly higher at the 95% level of confidence ($p = 0.000$) than the mean electrical conductivity for the unconfined zones (223 $\mu\text{S cm}^{-1}$; SD = 105 $\mu\text{S cm}^{-1}$).

pH values ranged from 5.28 to 7.66. The mean pH of the confined aquifer is close to neutral at 6.87 (SD = 0.25), while the unconfined sections of the aquifer are more acidic, with a mean of 6.27 (SD = 0.43). A two-sample t test confirms this variation in pH is statistically significant ($p = 0.000$, 95% level of confidence). The mean of the unconfined zones is therefore outside the New Zealand drinking water standard of 6.5–8.5, although this standard is based primarily on the need to reduce corrosion and encrustation of pipes rather than on health concerns (Ministry of Health, 1995).

Nitrate

The bores in the unconfined aquifer show a wider range of nitrate concentrations (<0.01–11.36 $\text{g m}^{-3} \text{NO}_3\text{-N}$) than bores in the confined aquifer (<0.01–0.32 $\text{g m}^{-3} \text{NO}_3\text{-N}$), with mean nitrate concentrations for the populations of 1.93 and 0.04 $\text{g m}^{-3} \text{NO}_3\text{-N}$, respectively. Figure 2 highlights the difference between the means of the two aquifer zones, with nitrate means in the unconfined aquifer roughly two orders of magnitude higher. The difference between the aquifer zones is statistically significant: two sample t tests give $p = 0.000$ (95% level of confidence) for each sampling period. Both aquifer zones are generally below the Maximum Acceptable Value (MAV) for drinking water in New Zealand of 11.3 $\text{g m}^{-3} \text{NO}_3\text{-N}$ (Ministry of Health, 1995). However, a small number of individual measurements in the unconfined aquifer population approach or slightly exceed this limit.

Figure 3 shows the spatial distribution of average nitrate concentration in the aquifer. The pattern in West Taieri (see Figure 1 for location of place names) is relatively uncomplicated, with uniformly low concentrations (<0.6 $\text{g m}^{-3} \text{NO}_3\text{-N}$), well below the 1 g m^{-3} level of $\text{NO}_3\text{-N}$ generally

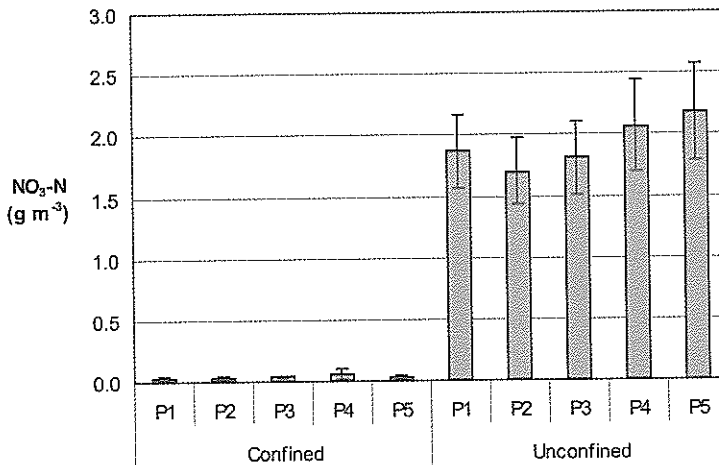


Figure 2 Mean nitrate concentrations (with standard error) for sampling periods P1 to P5 from the confined and unconfined zones.

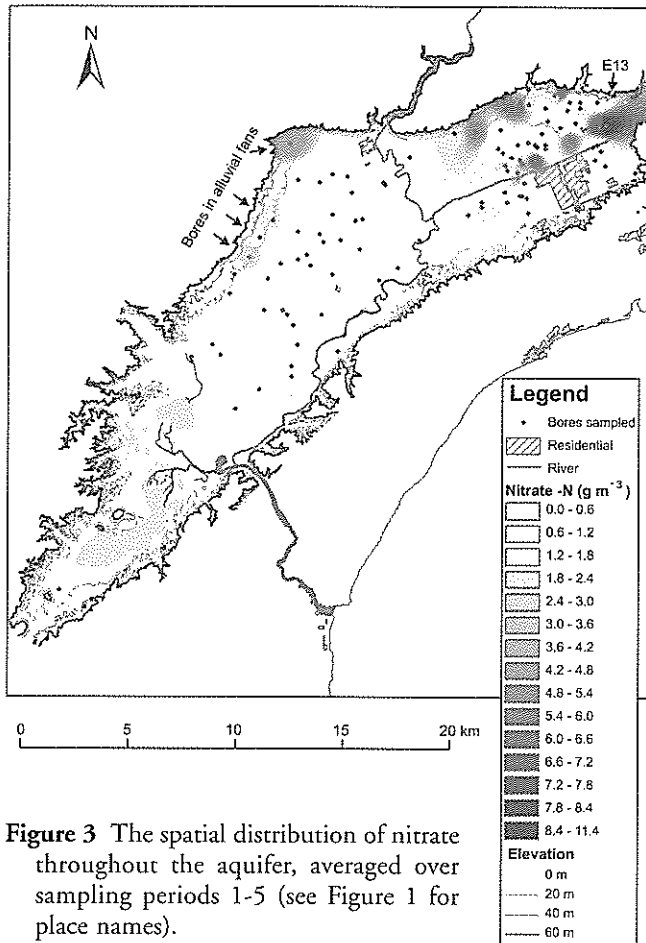


Figure 3 The spatial distribution of nitrate throughout the aquifer, averaged over sampling periods 1-5 (see Figure 1 for place names).

considered to be the boundary between naturally derived nitrate and those concentrations elevated by human influence (Close *et al.*, 2001). The four bores in the unconfined alluvial fan aquifer at the base of the Maungatua Range (shown by arrows) are the only bores in West Taieri yielding groundwater with nitrate above this background level.

More spatial variability is seen in East Taieri. A band of elevated nitrate groundwater bounds the northern margin of the plain. A significant northeast-southwest-trending corridor of low concentration groundwater (approximately 2 km wide) occupies the

centre of the plain (mostly $<0.6 \text{ g m}^{-3} \text{ NO}_3\text{-N}$). To the north of Silver Stream (Fig. 1) a narrow band of elevated nitrate groundwater extends from the head of the plain in a southwest direction down the centre of East Taieri. The highest concentration in each sampling period comes from bore E13 within this band (mean = $9.59 \text{ g m}^{-3} \text{ NO}_3\text{-N}$). Slightly elevated nitrate concentrations exist to the west of Mosgiel, while to the south, in the region around the margin of the plain, nitrate levels are low.

The particular method of spatial interpolation used in this study (inverse distance weighting) tends to produce a 'bulls-eye' pattern around individual points with high value, when these are far apart. This means bores with elevated nitrate tend to appear as isolated 'hot spots' in Figure 3. More field data would be needed to test whether these

sites are physically linked, e.g., in a southwest direction, in accord with the general southwest flow through the basin.

The boundary shown in Figure 3 between the elevated concentrations in East Taieri ($0.6\text{-}1.2 \text{ g m}^{-3} \text{ NO}_3\text{-N}$) and the universally low concentrations in West Taieri ($0.0\text{-}0.6 \text{ g m}^{-3} \text{ NO}_3\text{-N}$) approximately matches where the confining layer is thought to 'pinch out', i.e., immediately to the east of the Taieri River (Litchfield *et al.*, 2002). However, because of the lack of bores in this region, it is difficult to define this northern limit with precision.

The five sampling periods produce

extremely similar distributions to that shown in Figure 3, with little statistically significant variation over time in mean data over the course of the study (Pearson correlation tests give p values of 0.000-0.028, 95% level of confidence, between the sampling periods). Only a single bore located near the base of the Maungatua Range showed a noticeable fluctuation in nitrate concentration, and this involved only one sampling period. There is no significant correlation between bore depth and mean nitrate concentration for those bores with accurately known depths from East Taieri (a Pearson correlation test gives $p = 0.447$, 95% level of confidence, for bores 3-50 m in depth).

Ammonium

Ammonium concentrations show a general increase from east (unconfined aquifer) to west (confined aquifer). Water samples from the unconfined and confined aquifers yield a range of values, i.e., <0.02 - $1.48 \text{ g m}^{-3} \text{ NH}_4\text{-N}$ for the unconfined aquifer, and <0.02 - $2.39 \text{ g m}^{-3} \text{ NH}_4\text{-N}$ for the confined aquifer. More of the latter yield high concentrations, e.g., 55% of bores in the confined aquifer yielded concentrations $\geq 0.2 \text{ g m}^{-3} \text{ NH}_4\text{-N}$, while only 7% of bores in the unconfined aquifer exceeded this value.

The mean ammonium concentration from the bores in the confined aquifer are more than four times larger than the means from the bores in the unconfined aquifer (Fig. 4), with two-sample t tests proving the differences are significant (all tests $p = 0.000$, 95% level of confidence). Some individual measurements in the confined zone exceed the aesthetic guideline value for drinking water of $1.2 \text{ g m}^{-3} \text{ NH}_4\text{-N}$ (Ministry of Health, 1995), which is based primarily on odour. In New Zealand, drinking waters range up to approximately $1.5 \text{ g m}^{-3} \text{ NH}_4\text{-N}$, although most waters contain less than $0.04 \text{ g m}^{-3} \text{ NH}_4\text{-N}$ (Ministry of Health, 1995).

The highest ammonium concentrations occur around Lake Waipori (see Figure 1 for location) and in a band extending up the Titri Fault (southeast) side of the basin (Fig. 5). The remaining area of West Taieri, including the bores in the unconfined alluvial fan aquifer beneath the Maungatua Range, has low ammonium concentrations. The exception is a single bore immediately southwest of Outram (arrow), which yields high levels in each sampling period. East Taieri has uniformly low or undetectable ammonium levels, except for two bores with relatively high concentrations in each

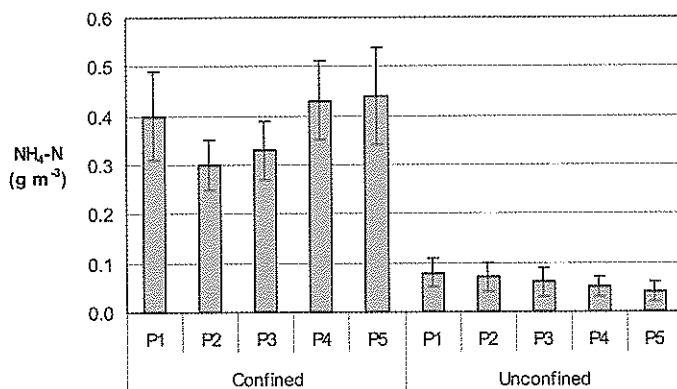


Figure 4 Mean ammonium concentrations (with standard error) for sampling periods P1 to P5 from the confined and unconfined zones.

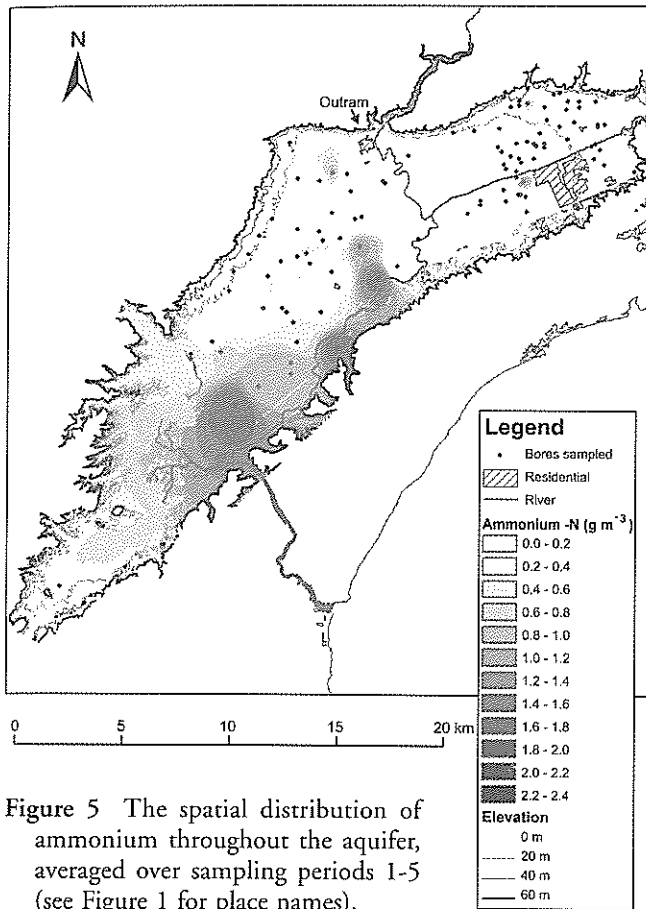


Figure 5 The spatial distribution of ammonium throughout the aquifer, averaged over sampling periods 1-5 (see Figure 1 for place names).

sampling period. These two bores are not in the same vicinity, and their neighbouring bores showed no significant ammonium concentrations.

Once again the five sampling periods have extremely similar distributions to that shown in Figure 5, with a lack of statistically significant temporal variation over the course of the study (Pearson correlation tests give $p = 0.000$, 95% level of confidence). A few individual bores do fluctuate in value, but only by the equivalent of one or two of the concentration classes shown in Figure 5. There is no correlation between bore depth and ammonium in the confined aquifer (a

Pearson correlation test gives $p = 0.547$, 95% level of confidence, for bores 12-85 m in depth).

A statistically significant, mutual exclusivity exists between nitrate and ammonium concentrations in the aquifer (a Pearson correlation test gives $p = 0.008$, 95% level of confidence, for a negative correlation of -0.260). Bores in the confined aquifer had nitrogen present as ammonium, while bores from the unconfined zones generally had any nitrogen present as nitrate. The few exceptions are all bores in the unconfined aquifer, either with nitrogen present in the form of ammonium and no nitrate, or with both nitrate and ammonium present.

Nitrite and organic nitrogen

Nitrite concentrations are universally low in all parts of the aquifer. Only 20 bores yielded groundwater with concentrations above the detection limit of $0.002 \text{ g m}^{-3} \text{ NO}_2\text{-N}$: five from the confined and fifteen from unconfined parts of the aquifer (Fig. 6). Mean and median values for both zones are below the detection limit of $0.002 \text{ g m}^{-3} \text{ NO}_2\text{-N}$, while the highest concentration detected is $0.022 \text{ g m}^{-3} \text{ NO}_2\text{-N}$. This is well below the Maximum Acceptable Value for drinking water in New Zealand of $0.91 \text{ g m}^{-3} \text{ NO}_2\text{-N}$ (Ministry of Health, 1995). Organic nitrogen was sampled in twelve bores, and is present in detectable concentrations in ten of these. It was the dominant form of nitrogen in two bores where levels of inorganic nitrogen were low.

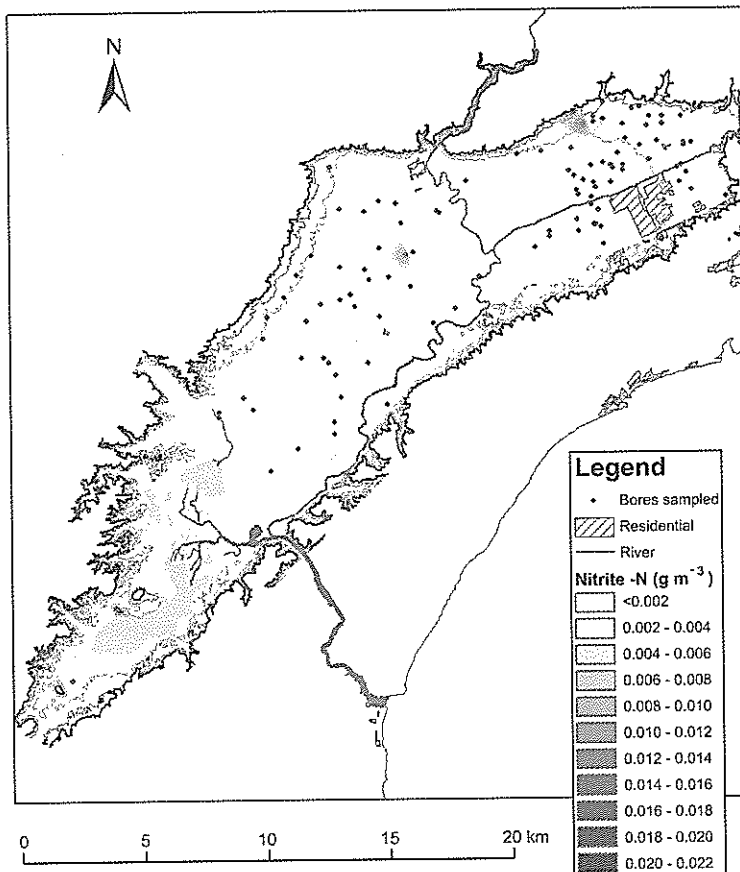


Figure 6 The spatial distribution of nitrite throughout the aquifer, averaged over sampling periods 1-5 (see Figure 1 for place names).

Acid-soluble iron and acid-soluble manganese

The mean concentrations of total acid-soluble iron showed no significant difference between the unconfined and confined zones (2.6 and 3.7 g m⁻³ total Fe respectively, with a two-sample t test giving p = 0.25, 95% level of confidence). Figure 7 shows the majority of East Taieri (unconfined) has low iron (<3.2 g m⁻³ total Fe), except for a distinct region of

high concentration north of Mosgiel (see Figure 1 for locations). In West Taieri iron concentrations are high in a band extending down the Titri Fault side of the basin. This band extends approximately a third of the way across the plain.

The unconfined and confined aquifers have mean concentrations of acid-soluble manganese of 0.2 and 0.7 g m⁻³ respectively, which a two-sample t test indicates are significantly different (p = 0.0046, 95% level of confidence). East Taieri is dominated by low-manganese groundwater (<0.5 g m⁻³ total Mn), except for a small group of bores north of Mosgiel with moderate concentrations. The highest concentrations in the system are generally present in the southern half of the confined aquifer.

In the unconfined aquifer of East Taieri a mutually exclusive relationship exists between nitrate and acid-soluble iron (a Pearson correlation test gives p = 0.008, 95% level of confidence, for a correlation of -0.245), and nitrate and acid-soluble manganese (a Pearson correlation test gives p = 0.036, 95% level of confidence, for a negative correlation of -0.307). That is, where one is present in a high concentration, the other tends to be of low concentration.

Discussion

Electrical conductivity and pH

The electrical conductivity of groundwater in East Taieri is low because this part of the aquifer is relatively unconfined, which enables water with low electrical conductivity from several recharge sources (especially rainfall and Silver Stream recharge) to enter the aquifer. Because of the higher groundwater velocities and shorter flow paths in East Taieri, the groundwater here has a shorter residence time. The higher electrical conductivity of much of West Taieri groundwater reflects the lack of direct infiltration of surface waters due to confinement by the Waihola silt/sand unit. The very low hydraulic gradient, and thus very slow flow rate, further increases the age of the groundwater in the confined aquifer.

The body of acidic groundwater north of Mosgiel most likely reflects the breakdown of organic matter in soils by biochemical and hydrochemical reactions, which consumes dissolved oxygen, yielding CO_2 and H^+ ions. This inference is consistent with the plots of free CO_2 and pH, from bores in East Taieri, generated by Irricon (1994), which exhibited an almost exactly inverse relationship. This may be a function of higher dissolved oxygen concentrations and/or organic matter concentrations, and therefore oxidation reactions generating hydrogen ions in this part of the aquifer. The approximately neutral to slightly basic values obtained from the majority of West Taieri is likely to be a function of greater concentrations of HCO_3^- (i.e., alkalinity) from interactions with the aquifer materials over time. This may also be influenced by oxygen depletion and reducing conditions in the confined aquifer, which often are associated with higher pH values. The low pH values of water from bores in the alluvial fan aquifer reflect the replenishment of dissolved oxygen by infiltration of surface waters into the alluvial fans, allowing oxidation reactions to proceed, leading to

increased hydrogen ion levels and hence decreased pH values.

Nitrate

The variation in nitrate concentrations across East Taieri is probably a function of differences in the structure of the aquifer, and/or differences in the chemistry of the groundwater in the aquifer. That is, the variation in nitrate concentration is attributed to differences in the ease of entry of nitrate into the aquifer, and/or differences in the chemical conditions that can affect the stability of nitrate in the aquifer. Comparison of stock densities across East Taieri with nitrate concentration indicates there is no correlation with the spatial variation in nitrate concentrations seen in Figure 3. There is also no apparent spatial correlation between soil types and nitrate concentration across East Taieri (Kensington, 2003).

The high nitrate concentrations in the bores that tap the alluvial fan aquifer indicate that the alluvial fans are sufficiently permeable to allow infiltration of surface water and associated leaching of nitrate from the ground surface to groundwater. This is not unexpected, as alluvial fans are commonly dominated by coarse-grained materials deposited under the high-energy conditions associated with their steep gradients. The major source of the nitrate derived from these fans is likely to be the intensive farming operations at the edge of the basin, immediately up-gradient of the bores sampled.

The corridor of low nitrate groundwater (mostly $<0.6 \text{ g m}^{-3} \text{ NO}_3\text{-N}$) encountered between the northern margin of the basin and Silver Stream has two possible causes. First, there may be sufficient confinement by lenses of fine-grained materials to prevent infiltration and subsequent leaching of nitrate. Second, reducing conditions may be present in the groundwater in this region, causing denitrification of any nitrate that may

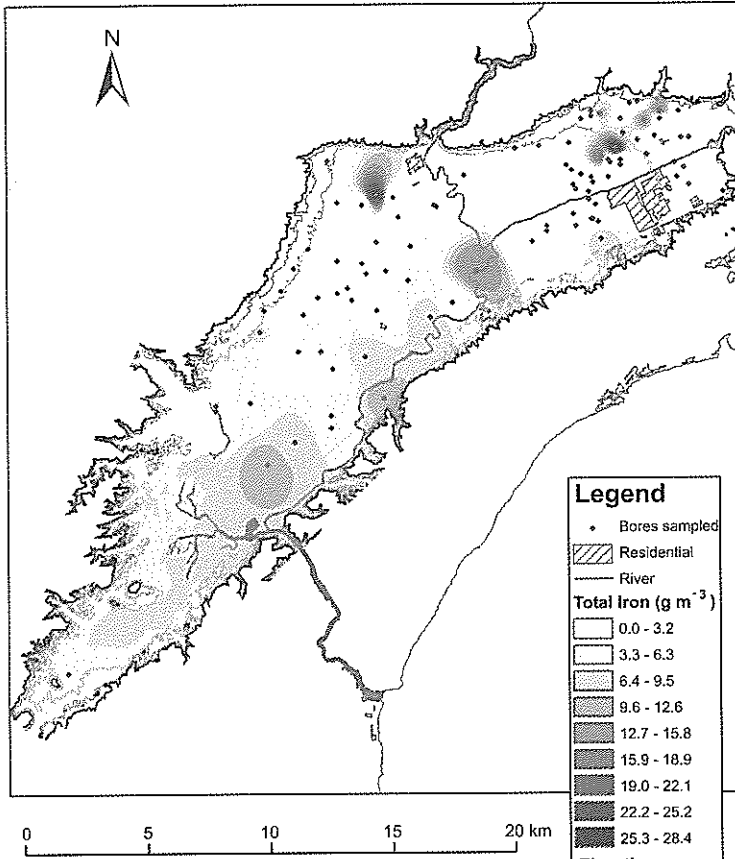


Figure 7 The spatial distribution of acid soluble iron throughout the aquifer, averaged over sampling periods 3 and 5 (see Figure 1 for place names).

be entering the aquifer. This is supported by the discrete zones of water with high iron and manganese concentrations (Fig. 7) found in this part of the aquifer. Under reducing conditions iron and manganese concentrations increase in the groundwater, as insoluble Fe^{3+} and Mn^{5+} ions are reduced to soluble Fe^{2+} and Mn^{2+} ions. Reduction of nitrate occurs prior to the reduction of Fe^{3+} and Mn^{5+} , so if the high iron and manganese concentrations reflect Fe^{2+} and Mn^{2+} in solution, then denitrification will have

reduced any nitrate entering this part of the aquifer. The significant mutual exclusivity between nitrate and iron, and nitrate and manganese in the groundwater throughout East Taieri further supports the presence of distinct oxidising and reducing conditions. Mariotti *et al.* (1988) identified strong mutual exclusivity between nitrate and iron, and nitrate and manganese levels in an aquifer in northern France, where subsequent isotopic analysis proved nitrate was being reduced by denitrification. Likewise, McLarin *et al.* (1999) found mutual exclusivity between high iron and nitrate levels in an unconfined aquifer in Horowhenua, New Zealand; here isotopic analysis also indicated nitrate had been reduced. Further investigation is required before either theory can be tested for the Taieri Plain.

There is some evidence that the elevated nitrate concentrations in a narrow band down the centre of East Taieri are associated with a local absence or coarsening of otherwise fine-grained (and, thus, impermeable) sediment lenses that inhibit infiltration in other parts of East Taieri. This may reflect the tendency toward larger particle sizes, and therefore greater permeability, toward the main channel of a river or stream (i.e., Silver Stream).

Alternatively, the breakdown and subsequent nitrification of organic matter within the sedimentary profile in this area may be the cause. Peat recorded in drill logs made in this area (Irricon, 1997) adds weight to this view, but a detailed isotopic analysis is required to confirm or refute this theory. The highest nitrate concentration from each sampling period comes from a bore in this band (E13). Previous reports (e.g., Irricon, 1997) also identify high concentrations of nitrate from this bore ($\sim 10 \text{ g m}^{-3} \text{ NO}_3\text{-N}$). Irricon (1997) conclude that the source may be offal known to be buried at depth $\sim 325 \text{ m}$ as hydrologically up-gradient. A local dairy farm is also a potential source of nitrogen input.

Much of the groundwater around Mosgiel is characterised by low nitrate concentrations (generally $< 0.6 \text{ g m}^{-3} \text{ NO}_3\text{-N}$). This suggests that fine-grained units are more common in this region, and are preventing significant quantities of nitrate from reaching the aquifer. Low iron and manganese concentrations around Mosgiel would seem to exclude this low nitrate concentration from being a function of reducing conditions and denitrification. It seems probable that the municipal area contributes nitrogen to the groundwater (e.g., from the sewage leakage inevitable with any reticulation system; Spalding and Exner, 1993), and this may therefore be flowing away from Mosgiel and contributing to some elevated concentrations measured near Silver Stream. This theory could be tested by further investigation of the flow paths in the vicinity of Mosgiel, and by isotopic analysis of the nitrate derived from the bores in the vicinity of Silver Stream.

Several studies report significant decreases in nitrate concentration with depth (e.g., Mariotti *et al.*, 1988; Hallberg, 1989; Selvarajah *et al.*, 1994). However, as in this study, many report no correlation (e.g., Wassenaar, 1995; McLarin *et al.*, 1999). This is likely a function of several factors. Because

of the shallow depth of the aquifer in East Taieri, the groundwater does not have a long enough residence time for reducing conditions to develop and denitrification to proceed. The differences in the structure of the aquifer and the resulting chemical conditions may cause large variations in nitrate concentration, independent of depth.

Dairying is the dominant land use in West Taieri, with 80% of bores sampled in this region located on dairy farms and the remainder surrounded by land used for dairying (Irricon, 1997). Despite the high nitrogen flux in the area overlying this part of the aquifer, the negligible nitrate concentrations in the groundwater indicate that the confining layer is preventing the infiltration of surface water to the groundwater. The presence of artesian conditions within the confined aquifer will further inhibit the entry of contaminants. In contrast, high nitrate concentrations (e.g., $> 10 \text{ g m}^{-3} \text{ NO}_3\text{-N}$) are associated with a number of areas of intensive dairying in the Waikato, where the aquifer is unconfined (Burden, 1982; Selvarajah *et al.*, 1994). The few bores in West Taieri with nitrate concentrations greater than $0.6 \text{ g m}^{-3} \text{ NO}_3\text{-N}$ are all located beneath the Maungatua Range and are tapping groundwater from the alluvial fans in this region. Elevated nitrate concentrations near the Maungatua Range indicate these fans are sufficiently permeable to allow infiltration of surface water and nitrate in this area.

Over the time scale of this study, little temporal variation was expected within the confined aquifer, because the confining unit and slow groundwater velocity result in an absence of pathways for the exchange of nitrate. Seasonal-scale variation in unconfined aquifers has been observed (Selvarajah *et al.*, 1994; Wassenaar, 1995; Close *et al.*, 2001), although seasonal variations were not observed in this study. This may have been expected for the shallower bores, but at

greater depth variations in nitrate leaching to groundwater are more subtle (Freeze and Cheery, 1979). The lack of temporal variation in the shallow bores (8-15 m depth) suggests fine-grained units are significant from very shallow depths. Alternatively, there may be little difference in the volume of nitrogen being leached into the aquifer over time, and/or limited variation in the rates of any nitrification or denitrification processes affecting nitrate concentrations. Whatever the reason for the lack of temporal variation, it seems any variation in nitrate leaching rates throughout the year do not appear to have a short-term/seasonal effect.

Ammonium

High ammonium concentrations near Lake Waipori and extending up the Titri Fault side of the confined aquifer are probably due to the degradation of organic matter trapped in the overlying Waihola silt/sand unit or in peaty deposits in the aquifer itself (Downes, 1980; Close *et al.*, 2001). Concentrations are highest in this area, as this is the oldest groundwater in the system and therefore has had significant time for slow degradation to occur. This is likely to have been accentuated by the low dilution and dispersion capacity in this part of the aquifer, reflecting its location furthest from recharge sources and low flow rates. Litchfield *et al.* (2002) identifies a few locations with high ammonium concentrations in the lower West Taieri, and suggests that these may indicate a degree of surface connectivity in this area of intensive dairying. However, this seems unlikely, due to the 20-25 m thickness of the intervening Waihola silt/sand unit in the lower West Taieri and upward hydraulic gradient due to artesian conditions in the aquifer. The high concentrations measured in the present study in one bore near Outram and two in East Taieri may be associated with localised surface sources of contamination, e.g., septic tanks (Gallegos *et al.*, 1999).

As with nitrate, ammonium concentrations varied little over the period of the study. Again, this was expected, because of the confinement provided by the Waihola silt/sand and the slow groundwater velocity in this part of the aquifer. The mutually exclusive relationship between nitrate and ammonium suggests that zones of distinct oxidising and reducing conditions are present in the groundwater of the aquifer. Nitrate is the first species reduced after oxygen, and so its presence in elevated concentrations indicates that the groundwater is oxidising in nature (Mariotti *et al.*, 1988). This result supports the interpretation of the aquifer in East Taieri as relatively unconfined. As well as allowing the initial entry of nitrate, it also allows sufficient surface water to infiltrate to maintain the dissolved oxygen content of the groundwater, and hence the stability of nitrate. In the confined aquifer, ammonium concentrations were often high, while nitrate concentrations were universally low. As ammonium is a reduced form of nitrogen, it is generally present in significant concentrations only under reducing conditions (Rosen, 2001). That nitrogen has remained stable as ammonium, rather than being nitrified to nitrate, strongly suggests reducing conditions in at least the region of the confined aquifer with high ammonium concentrations.

Nitrite

Nitrite concentrations are extremely low in the groundwater across the entire aquifer, with only 20 bores yielding a detectable concentration ($>0.002 \text{ g m}^{-3} \text{ NO}_2\text{-N}$) in any sampling period. Nitrite is a relatively unstable species, so its presence suggests either nitrification or denitrification is actively occurring at the sites where it is detected. The presence of relatively high nitrite concentrations in the oxygenated alluvial fan aquifer may reflect the active occurrence of nitrification.

fication, whereas the less well defined zone of nitrite to the north of Mosgiel is more likely a function of denitrification. However, concentrations are so low it is difficult to make definite statements about its sources.

Conclusion

There was significant spatial variation in the concentrations of dissolved nitrogen species in the groundwater of the Taieri Plain aquifer system during the study period, March-November 2002. The primary control on groundwater nitrogen species concentrations is the level of confinement of the aquifer, which governs hydrological and chemical conditions in the aquifer. Concentrations of nitrate are generally moderate to high in East Taieri, in some instances reaching the Maximum Acceptable Value for drinking water in New Zealand. The presence of zones of low concentration suggests localised confinement in places. Nitrate concentrations are low or undetectable in the confined aquifer in West Taieri, but high in bores in the alluvial fan aquifer where infiltration of surface runoff to groundwater appears to occur. Most of the observed nitrate is likely to be derived from land-use practices, with a component probably derived from mineralisation of organic matter in the aquifer. Ammonium concentrations are generally negligible in the unconfined parts of the aquifer, but reached concentrations up to $2.39 \text{ g m}^{-3} \text{ NH}_4\text{-N}$ along the Titri Fault side of the confined aquifer. The latter are probably due to mineralisation of organic matter trapped in the aquifer, and the stability of this nitrogen in the form of ammonium suggests that at least the Titri Fault side of the confined aquifer is reducing in nature. Nitrite concentrations were universally low, with only 20 bores yielding a nitrite concentration above the detection limit of $0.002 \text{ g m}^{-3} \text{ NO}_2\text{-N}$ over the five sampling periods. Very

few samples were analysed for organic nitrogen, but results suggest this is relatively ubiquitous, albeit in low concentrations, and is derived from degradation of organic matter in the aquifer. Little temporal variation is seen in the concentrations of the nitrogen species over the relatively short timescale of the study, and little correlation is seen between levels of concentration and depth.

The study provides no evidence to suggest that surface water, and thus nitrogen species, is able to enter the confined aquifer through the confining layer. The Waihola silt/sand unit provides excellent natural protection to the underlying aquifer, and therefore mitigates the many potential contamination problems associated with intensive dairying. However, the precise boundary where confinement begins remains unclear because of the lack of bores that could be sampled in the particular area. The unconfined/semi-confined aquifer in East Taieri and the alluvial fan areas at the edges of the plain are far more vulnerable to contamination from nitrogen species. Ideally, land-use practices should be closely monitored or regulated in these areas by local authorities, while rates of abstraction from the confined aquifer should be monitored to ensure artesian conditions persist.

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