Nitrogen Species Distribution in the Taieri Plain Aquifer, New Zealand.

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Presented at SIRC 2003 – The 15th Annual Colloquium of the Spatial Information Research Centre
University of Otago, Dunedin, New Zealand
December 1st-3rd 2003

ABSTRACT

Nitrogen contamination of drinking water has been linked to health risks including 'blue baby syndrome'. In New Zealand, up to 51% of people use at least some groundwater for drinking, and there is growing concern that the rapid growth of intensive dairying may lead to aquifer contamination. The distribution of nitrogen species nitrate (NO_3^-), ammonium (NH_4^+), nitrite (NO_2^-) and organic nitrogen were measured in groundwater bores in the Taieri Plain aquifer, New Zealand, during March-November 2002. There was significant spatial variation in the concentration of nitrate and ammonium across the aquifer. Concentrations of nitrate were low in the confined aquifer in West Taieri, but high in unconfined bores in East Taieri and in bores in alluvial fans, i.e. where infiltration of surface runoff can occur. Ammonium showed the reverse pattern, i.e. low concentrations in the unconfined aquifer, and high concentrations in parts of the confined aquifer. Nitrite concentrations were low everywhere. Mean nitrate concentrations for confined and unconfined bores were well below the maximum limit for drinking water in New Zealand (11.3 ppm NO_3-N), but in the unconfined zone some individual measurements approached or slightly exceeded this limit. Some individual measurements for ammonium species exceeded the aesthetic guideline for drinking water (1.2 ppm NH_4-N). No temporal variations were seen in species concentrations over the relatively short time scale of the study, and there was little correlation between concentrations and bore depth. Fortuitously, the Waihola silt-sand unit protects the underlying aquifer and mitigates the potential for contamination in the areas where intensive dairying occurs on the Taieri Plain. The unconfined/semi-confined aquifer in East Taieri, and alluvial fan areas, are far more vulnerable to contamination from nitrogen species. Ideally, conditions and land use practices in these areas should be closely monitored and, perhaps, regulated.

***Keywords and phrases*:** nitrogen, nitrate, nitrite, ammonium, mapping, Taieri Plain aquifer

1.0 INTRODUCTION

Nitrogen occurs in groundwater naturally and from anthropogenic sources. It exists in several oxidation states, including nitrate (NO_3^-, the most common), ammonium (NH_4^+), nitrite (NO_2^-) and organic nitrogen. In New Zealand 26% of the population rely solely on groundwater for drinking (White and Rosen, 2001). Up to 51% use groundwater for drinking exclusively, or in combination with surface water sources. High concentrations of nitrogen in drinking water has been linked to 'blue baby syndrome' (methaemoglobinaemia; Canter, 1997; Avery, 1999) and links have been suggested between inorganic nitrogen species and certain cancers (Ministry of

Health, 1995), birth abnormalities, hypertension and diabetes (Canter, 1997). Nitrate pollution can also lead to algal blooms and eutrophication of lakes. In New Zealand, there is growing concern that the rapid growth of intensive dairying may lead to contamination of aquifers, i.e. because nitrogen-rich fertilizers, cow urine and manure may infiltrate and pollute the aquifer.

The reactions of nitrogen species in groundwater are often governed by chemical conditions (e.g. whether oxidising or reducing conditions dominate) and physical factors, such as whether an aquifer is confined (i.e. capped by an impermeable geologic unit) or unconfined (open to infiltration by surface water). Nitrogen species in groundwater can arise from anthropogenic sources (e.g. fertiliser, animal wastes or human sewage), or natural sources such as precipitation and sedimentary rocks that contain organic matter.

The present study was undertaken on the Taieri Plain, near Dunedin, New Zealand. This area supplies about 2.3 million m^3 of water per year to local users (Irricon, 1994), with ~80% of this drawn for drinking water for Mosgiel. Several research reports document aspects of the quality of the groundwater on the Taieri Plain (e.g. Irricon, 1994, 1997; ORC, 1999), but local sources of nitrogen species, and the chemical reactions occurring in the aquifer are not well understood. The aims of the present study were to: 1) map nitrogen species for the Taieri Plain aquifer system, 2) assess any temporal variation in these species, and 3) use the resulting chemical data to increase the understanding of the physical makeup of this groundwater system.

2.0 METHODS

2.1 Physical Setting

The Taieri Plain occupies a tectonic (i.e. fault-bounded) depression near Dunedin, New Zealand (Figure 1). It is 40 km long, 5-10 km wide and bounded on all sides by minor hills and ranges. The basement rock is impermeable Otago Schist that is overlain predominately by Quaternary sediments, to depths of up to 150 m (Litchfield *et al*., 2002). The Taieri Plain aquifer is hosted in gravel and sand layers. A fine-grained sand-silt layer (the Waihola silt-sand unit; Barrell *et al*., 1999) covers approximately two-thirds of the basin. This is up to 25 m thick at its thickest point and forms an impermeable 'cap' for the aquifer in West Taieri. In East Taieri this continuous cap is absent, the sediments are spatially more diverse, and there are localised semi-confined units (lenses). Groundwater flow through the basin is generally to the south-west, so any contaminants entering the basin in East Taieri are thought to eventually migrate down-gradient to the confined aquifer in West Taieri.

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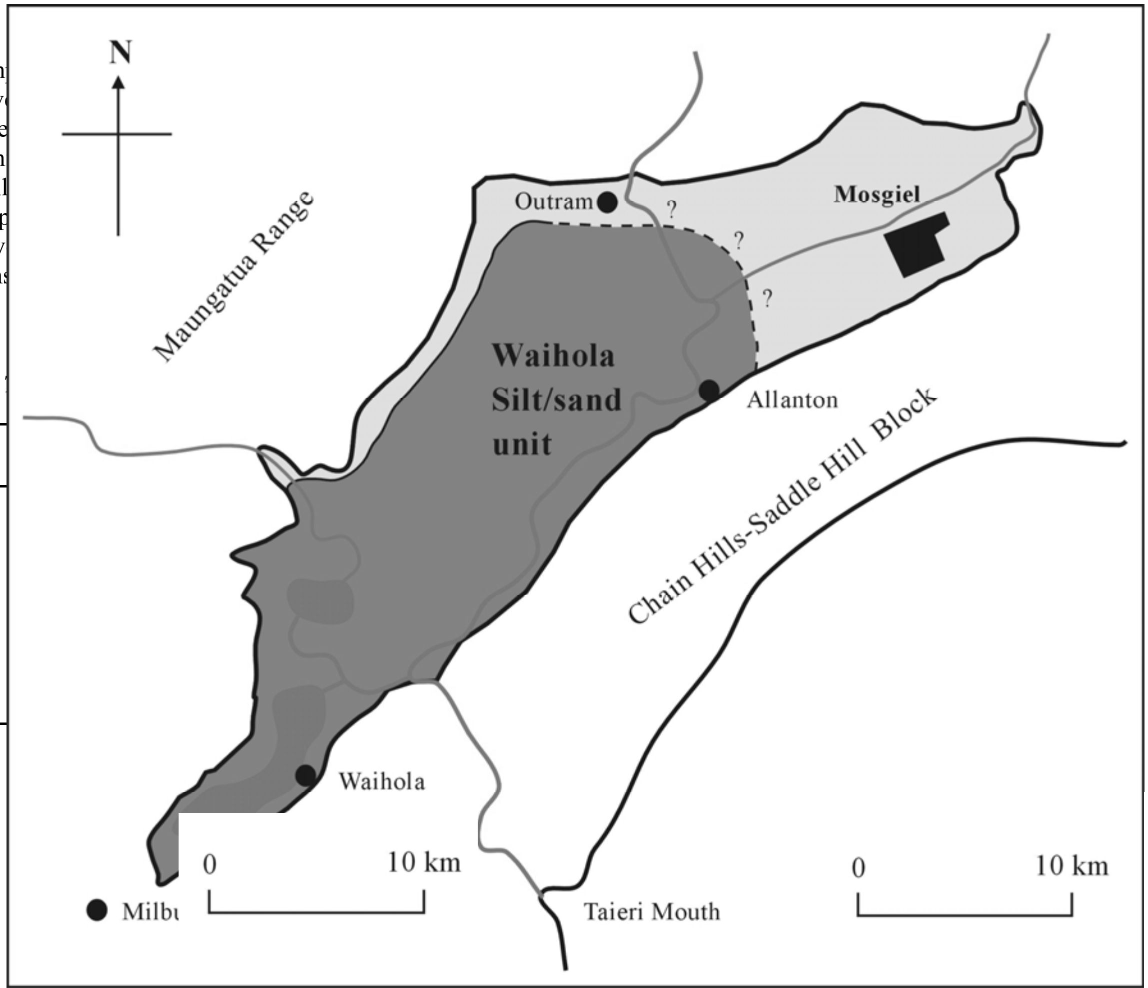

Figure 1: The study area on the Taieri Plain, showing the major topographic features, rivers and lakes, and extent of the Waihola sand-silt unit that confines the Taieri Plain aquifer in West Taieri. Insert: Location of study area in South Island, New Zealand

Statistical analysis was undertaken using *Minitab*, two-sample t-tests and Pearson correlation tests. *ArcGIS* and Inverse Distance Weighting (IDW) were used to create maps of the data. IDW was chosen because the highly variable sedimentary structure of the aquifer means that data from a bore is representative of groundwater from only a relatively small distance around the bore. A relatively small cell size (100 × 100 m), a power of 4 and a fixed search radius of 2000 m was set to limit the number of input points that were used in the interpolation. The minimum number of measured points needed to predict each cell was set at six. If there were not 6 points in the 2000 m radius, then it was expanded. This step was particularly useful for areas with few bores. The relatively high power setting meant that nearby bores retained the greatest influence on the value assigned to each cell. Maps were constructed in two dimensions with no regard for variations in ground surface elevation, the vertical thickness of the aquifer, bore depth or the acknowledged southwest flow direction of the groundwater within the aquifer. Finally, it must be noted that spuriously values were assigned by the mapping programme at the map boundaries, i.e. beyond the known data points. Any apparent patterns in these areas need to be ignored.

3.0 RESULTS

3.1 Nitrate

The unconfined bores showed a wider range of individual nitrate concentrations (<0.01-11.36 ppm NO_3-N), compared to the confined bores (<0.01–0.32 ppm NO_3-N), and much higher mean nitrate concentrations—roughly two orders of magnitude higher. The difference between the zones was statistically significant: two-sample t-tests give p = 0.000 at a 95% level of confidence (LOC) for each sampling period. The mean nitrate concentrations for both the confined and unconfined bores were well below the maximum allowable level for drinking water in New Zealand of 11.3 ppm NO_3-N (Ministry of Health, 1995). However, in the unconfined zone some individual measurements approached or slightly exceeded this limit.

When data for each bore were plotted against distance across the plain (Figure 2), expressed as distance along a transect line (see Figure 3), an increase in nitrate concentration was noted from the confined bores in West Taieri to the unconfined bores in East Taieri. The four unconfined 'fan' bores in West Taieri plotted as outliers (i.e. at ~16-22 km distance), with nitrate concentrations of >0.6 ppm NO_3-N. This is at least an order of magnitude greater than values for nearby, confined bores.

Spatial patterns in West Taieri were relatively uncomplicated (Figure 3). All values were low (<0.6 ppm NO_3-N) and well below the 1 ppm NO_3-N generally considered as the boundary between naturally derived nitrate and concentrations elevated by human influence (Close *et al*., 2001). Only the four 'fan' bores at the northwest corner of the plain yielded nitrate concentrations above this background level. More spatial variability was seen in East Taieri and there was a zone with elevated nitrate near the northern margin of the plain. A northeast-southwest trending corridor of low concentrations (about 2 km wide) occupied the centre of the plain (mostly <0.6 ppm NO_3-N). A narrow zone of elevated levels extended from the head of the plain in a southwest direction down the centre of East Taieri, with all the highest concentrations coming from one particular bore (E13; mean = 9.59 ppm NO_3-N). Slightly elevated nitrate concentrations existed to the west of Mosgiel, while to the south near the margin of the plain, low nitrate levels were present.

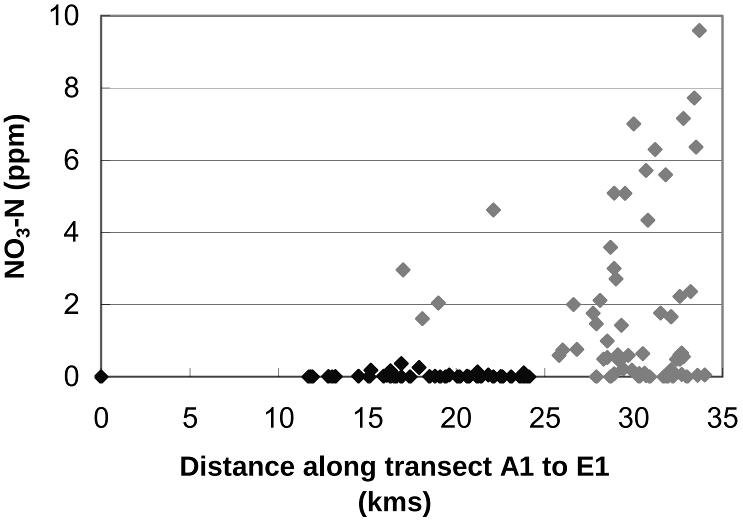

Figure 2: Variation in concentration (in parts per million (ppm)) of nitrate in bores on the Taieri Plain. The transect is from bore A1 (south) to bore E1 (north)(see Figure 3 for locations). Distance was determined using the intersect of a perpendicular line drawn from each bore to the transect line. Symbols are grey for confined, and black for unconfined bores (the latter including four 'fan' bores)

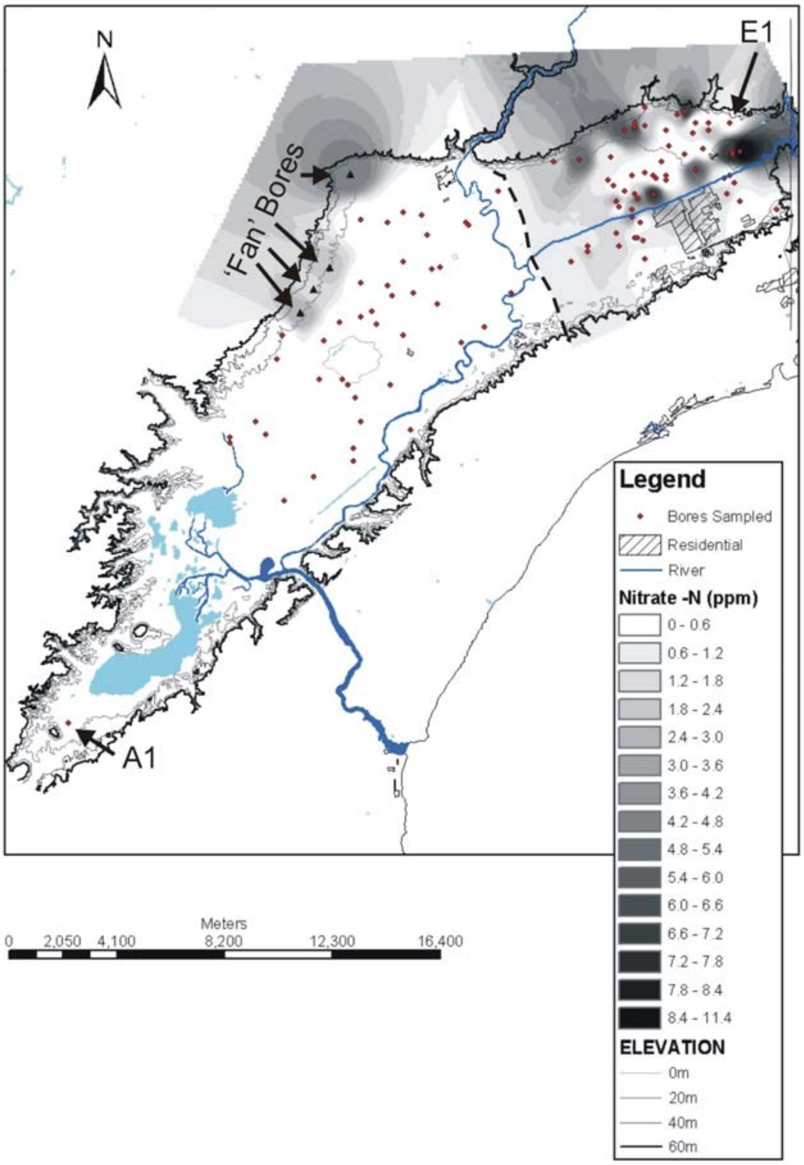

Figure 3: Mean nitrate concentrations in the Taieri Plain aquifer, where bores are shown as dots— except for the four 'fan' bores (arrowed) which are triangles—the dashed line is the 0.6 ppm boundary, and the bores at A1 and E1 (arrowed) are the end points of the transect (see Figures 2 and 4)

The boundary shown in Figure 3 between the concentration classes 0.0-0.6 ppm and 0.6-1.2 ppm approximately matches where the confining layer is thought to 'pinch out', i.e. immediately to the east of the Taieri River. However, because of the lack of bores in this region, it is difficult to define this northern limit with precision.

The five sampling periods produced very similar maps to that shown in Figure 3 and there was no significant temporal variation in mean data over the course of the study (Pearson correlation tests give p values of 0.000-0.028, LOC = 95%, between the sampling periods). Only one bore (A9) near the base of the Maungatua Range showed a noticeable fluctuation in nitrate concentration, and this involved only one sampling period. There was no correlation between bore depth and mean nitrate concentration for bores sampled in East Taieri and of known depth (a Pearson correlation test gives p = 0.447, LOC = 95%).

3.2 Ammonium Species

There was a general decrease in mean ammonium concentration with distance across the plain from east (unconfined) to west (confined)(Figure 4). Both unconfined and confined bores yielded a range of values, but more of the latter yield high concentrations, e.g. 55% of confined bores yield concentrations ≥ 0.2 ppm NH_4-N, whereas only 7% of unconfined bores exceeded this value. There was a significant difference between the mean ammonium concentrations in the confined (0.38 ppm NH_4-N) and confined (0.07 ppm NH_4-N) zones (two sample t-tests give p = 0.000, LOC = 95%). Some individual measurements in the unconfined zone exceeded the aesthetic guideline value for drinking water (1.2 ppm NH_4-N), which is based primarily on odour. In New Zealand, drinking water mostly contains <0.04 ppm, but may range up to ~1.5 ppm NH_4-N (Ministry of Health, 1995).

The highest mean ammonium concentrations occurred in West Taieri, particularly around Lake Waipori and along the side of the plain (Figure 5). This area includes about half of the confined aquifer. The remainder of West Taieri, including the unconfined 'fan' bores, exhibited low ammonium concentrations. The exception was a single bore near Outram, which yielded high levels in each sampling period. East Taieri had uniformly low or undetectable ammonium levels, except for two bores with relatively high concentrations. Their nearest neighbours showed no significant ammonium concentrations.

There was no correlation between bore depth and ammonium in the confined aquifer (a Pearson correlation test gave p = 0.547, LOC = 95%). There was however a significant correlation between sampling periods, i.e. sampling periods were statistically alike (Pearson correlation tests give p = 0.000, LOC = 95%). A few bores fluctuated in value temporally, but only by the equivalent of 1-2 of the concentration classes shown in Figure 5.

A statistically significant, mutual exclusivity was noted between nitrate and ammonium levels (Pearson correlation test: p = 0.008, LOC = 95%). Any nitrogen species in bores from the confined aquifer was present as ammonium ions, while for bores from the unconfined zones it was generally present as nitrate. The exceptions were a few unconfined bores with both nitrate and ammonium present.

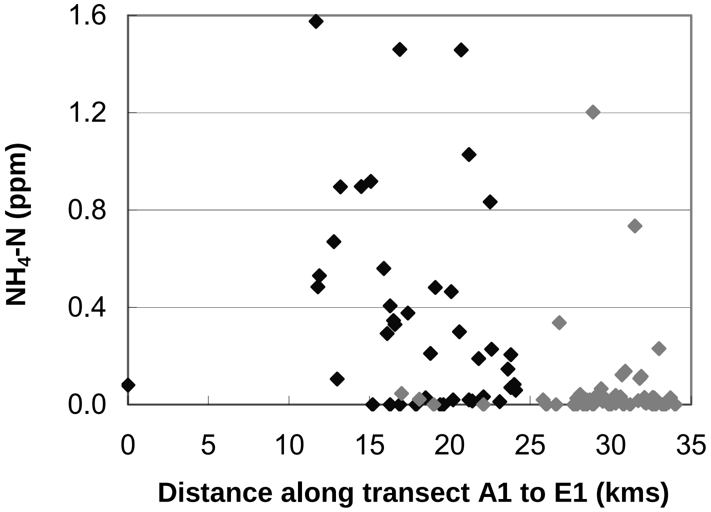

Figure 4: Variation in concentration (ppm) of ammonium species in bores on the Taieri Plain. The transect is from bore A1 (south) to bore E1 (north)(see Figure 3 for locations). Distance was determined using the intersect of a perpendicular line drawn from each bore to the transect line. Symbols are grey for confined, and black for unconfined bores (the latter including four 'fan' bores)

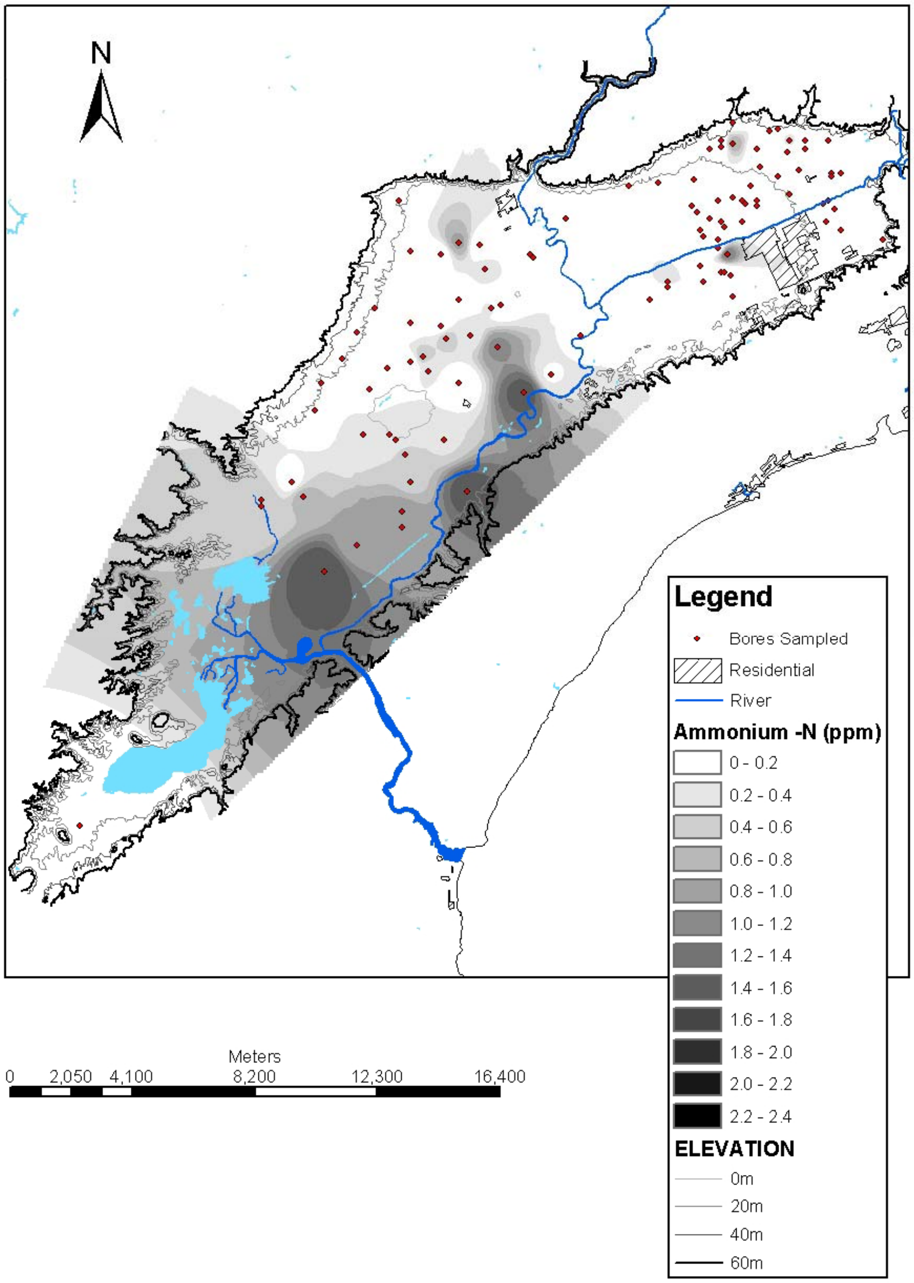

Figure 5: Mean ammonium concentrations in the Taieri Plain aquifer, where all bores sampled are shown as dots

3.3 Nitrite and Organic Nitrogen

Low nitrite levels were detected across the whole plain during all sampling periods. Only 20 bores yielded groundwater with levels above the detection limit of 0.002 ppm NO_2-N: five from the confined, and fifteen from the unconfined parts of the aquifer. Mean and median values were below the detection limit of 0.002 ppm NO_2-N with the highest detected concentration being only 0.022 ppm NO_2-N. This is value is well below the maximum limit for drinking water in New Zealand of 0.91 ppm NO_2-N (Ministry of Health, 1995). The groundwater from 12 bores were analysed for organic nitrogen. It was present in detectable concentrations in 10 of these and was the dominant form of nitrogen in two bores with low levels of inorganic nitrogen species.

4.0 DISCUSSION

4.1 Nitrate

It is proposed that the observed variation in groundwater nitrate concentrations in the Taieri Plain aquifer relates to differences in physical structure (i.e. how easily nitrogen enters the aquifer), and/or differences in the groundwater chemistry, i.e. in the chemical conditions which affect the stability of nitrate in the aquifer. The high nitrate concentrations in the 'fan' bores indicate that infiltration of surface water and leaching of nitrate is occurring at these locations. This is not unexpected because course-grained, highly permeable materials dominate in an alluvial fan. The corridor of low (<0.6 ppm NO_3-N) nitrate-containing groundwater to the north may have two causes. First, there may be sufficient confinement or semi-confinement to prevent the infiltration. Second, reducing conditions may be present, which causes denitrification of any nitrate that enters the aquifer in this region. Further investigation is needed before either of these two suggestions can be confirmed.

There is some evidence to suggest that certain areas of groundwater with elevated nitrate concentrations near Mosgiel are associated with local variations in sediment texture. That is, a local absence or coarsening of the otherwise fine-grained (and, thus, impermeable) sediment lenses which inhibit infiltration in parts of East Taieri. Alternatively, a breakdown of organic matter present in the sediments may be the cause. Peat has been recorded in drill logs made in this general area (McTavish, pers. comm.), but a detailed stable isotopic analysis involving measurement of $\delta^{13}C$ would be required to confirm or refute this theory. The highest nitrate concentrations were detected in groundwater from just one bore (E13). Previous reports (e.g. Irricon, 1997) have also reported high nitrate concentrations for this bore (~10 ppm NO_3-N). Irricon (1997) concluded that the source may be offal known to be buried ~325 m up the hydrologic gradient from this site. A local dairy farm is also a potential source of contamination.

Much of the groundwater near Mosgiel is characterised by low nitrate levels (<0.6 ppm NO_3-N), which suggests that sufficient semi-confining geologic units (lenses) are present in this area to prevent significant quantities of nitrate from reaching the aquifer. However, it is possible that this municipal area does contribute nitrogen species to the groundwater (e.g. from sewage leakage), but that this flows away from Mosgiel and contributes to the elevated concentrations measured near the Silverstream. This theory could be tested by further investigation into the groundwater flow-paths near Mosgiel, and by $\delta^{15}N$ isotopic analysis of the nitrate in the bores near the Silverstream.

Several studies have reported significant decreases in nitrate concentration with bore depth (e.g. Mariotti *et al*., 1988; Hallberg, 1989; Selvarajah *et al*., 1994). However, many (including the present study) have observed no correlation between nitrate levels and depth (Wassenaar, 1995; McLarin *et al*., 1999). The most likely reason why nitrate concentrations do not show a general decrease with depth in the present study, is because of the shallow depth of the aquifer in East Taieri. In the majority of New Zealand studies, shallow bores are considered to be less than 30 m in depth, whereas for the present study area even the deeper bores are often less than 30 m deep. This means the so-called 'deep' groundwater will often not have been away from atmospheric influence for long enough for reducing conditions to develop and denitrification to proceed. Another factor is the differences in the structure of the aquifer and/or chemical conditions in the aquifer across East Taieri, which could lead to large variations in nitrate concentration independent of depth.

Dairying is the dominant land use in West Taieri. In the present study, 80% of bores sampled in West Taieri are on dairy farms; the remainder are surrounded by this land use. Fortuitously, negligible nitrate concentrations are determined in groundwater from the underlying aquifer because the confining unit prevents the infiltration of surface water and nitrate. Artesian flow (i.e. water flow out of the aquifer, rather than into it) is present and this would appear to further inhibit the entry of contaminants. In contrast, high nitrate concentrations (e.g. ~10 ppm NO_3-N) have been associated with areas of intensive dairying in the Waikato region, where the aquifer is unconfined (Burden, 1982; Selvarajah *et al*., 1994).

Over the time scale of the present study, little temporal variation was expected in the confined aquifer because it was assumed that water flow and mixing was relatively slow, and that subsequent chemical changes were also slow. Seasonal-scale variation has been observed in nitrogen concentrations in studies of several other unconfined aquifers (Wassenaar, 1995; Selvarajah *et al*., 1994; Close *et al*., 2001) but was not observed in the present study. This may, perhaps, be due to a constant flux of nitrogen species being leached into the aquifer, lack of variation in the rates of any nitrification or denitrification, or because fine-grained units in the otherwise unconfined aquifer are inhibiting local flow.

4.2 Ammonium Species

High ammonium concentrations in groundwater sampled near Lake Waipori and at the side of plain are probably due to the degradation of sedimentary organic matter, i.e. in the overlying Waihola silt-sand unit or in peaty deposits in the aquifer itself (Downes, 1980; Close *et al*., 2001). This area contains the oldest groundwater in the system and so it has had time for the degradation process to occur. Litchfield *et al.* (2002) have identified several locations in the lower West Taieri exhibiting high ammonium concentrations, and suggests that these may indicate a degree of vertical connectivity to surface areas of intensive dairying. However, this would seem unlikely in view of the 20-25 m thickness of the intervening Waihola silt-sand unit, and the presence of artesian conditions. The high ammonium concentrations detected 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).

4.3 Nitrite

Only 20 bores yield a detectable nitrite concentration. Nitrite is a relatively unstable species and so its presence suggests that nitrification or denitrification is actively occurring at such sites. The relatively high nitrite concentrations in the groundwater from ‘fan’ bores may reflect the active occurrence of at least nitrification, whereas the less well defined zone of nitrite to the north of Mosgiel probably indicates denitrification.

5.0 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 nitrate concentrations was the level of confinement of the aquifer, which governs hydrological and chemical conditions in the aquifer. Concentrations of nitrate were low or undetectable in the confined aquifer in West Taieri, but high in the ‘fan’ bores where infiltration of surface runoff was likely. The source of the nitrate was probably farming and, perhaps, degradation of organic matter in the aquifer.

The study provided no evidence to suggest that surface water enters the confined aquifer through the overlying confining layer. However, the precise boundary where confinement begins remains unclear. Fortuitously, the Waihola silt-sand unit protects the aquifer and mitigates the potential for contamination in the areas where intensive dairying occurs. The unconfined/semi-confined aquifer in East Taieri, and the alluvial fan areas at the edges of the Taieri Plain, are far more vulnerable to contamination from nitrogen species. Ideally, conditions and land use practices in these areas should be closely monitored and/or regulated by appropriate local authorities.

ACKNOWLEDGEMENTS

This research was undertaken by Chris Kensington as part of a MSc degree in Geography, University of Otago. Thanks go to his co-supervisors Barry Peake, Katrina Richards and the late Dave Murray.

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