Journal of Hydrology (NZ) 38(2): 211-235, 1999

Nitrate contamination of the unconfined aquifer, Manakau, Horowhenua, New Zealand

Wendy McLarin[1], Gabor Bekesi[2], Len Brown[3], and Jack McConchie[4]

[1] *School of Earth Sciences, Victoria University of Wellington, now at Tonkin & Taylor Ltd, PO Box 12-152, Wellington, New Zealand.*
[2] *Manawatu-Wanganui Regional Council, Private Bag 11-025, Palmerston North, New Zealand.*
[3] *Institute of Geological and Nuclear Sciences, Lower Hutt, now Consultant, 61 Penrose Street, Lower Hutt 6009, New Zealand.*
[4] *School of Earth Sciences, Victoria University of Wellington, PO Box 600, Wellington, New Zealand.*

Abstract

Nitrate concentrations in bores studied in Manakau, Horowhenua, ranged from <0.5 mg/L NO_3-N to over three times the New Zealand drinking water standard of 11.3 mg/L NO_3-N. Bores with high nitrate concentrations appeared to be randomly distributed in the township. Expected correlations between nitrate and chloride concentrations and faecal coliform counts were not found. However, a mutually exclusive relationship between high iron and nitrate concentrations suggests a variability in redox conditions within the aquifer; this may influence high nitrate concentrations rather than simply the presence or absence of contamination.

The unconfined aquifer is composed of poorly sorted fluvial gravel of the postglacial and last glacial periods and relatively homogeneous last interglacial sand dune and beach deposits (Otaki Sandstone). Contrasting permeability of these strata affects the groundwater flow with more rapid flow through the gravel. The average hydraulic gradient is 0.018 and groundwater velocities were estimated at 7.3 m/day for the gravel and 0.15 m/day for the sandstone. The majority of bores with high nitrate concentrations were associated with the Otaki Sandstone. Sandstone aquifer bores with lower nitrate levels had either high iron or ammonium concentrations, indicating that contamination may still be present but not in the form of nitrate. The sandstone aquifer is contaminated because of its poor dilution capacity, resulting from its low permeability and slow groundwater velocity. Groundwater nitrate nitrogen and oxygen isotope analyses suggest that the

nitrate, formed from nitrification of ammonia, is being reduced and that the source of introduced ammonia is human or animal wastes rather than artificial fertilisers.

Introduction

In New Zealand in the 1960s, routine water quality monitoring of unconfined aquifers in several areas indicated high levels of nitrate contamination of groundwater used for domestic water supply. These occurred where there were high water table levels, intensive concentrations of stock on farms, and houses with individual septic tanks. This was of concern because overseas research (summarised by Shuval and Gruener, 1977), had established a link between drinking water with high nitrate concentrations and methaemoglobinaemia, a disease in infants in which blood becomes unable to carry oxygen around the body. In the late 1970s and early 1980s several groundwater research projects were begun in New Zealand to assess sources of the nitrates, the extent of the contamination and the reasons for the occurrences. The results are summarised in Burden (1982) and the knowledge acquired was applied to establishing groundwater quality monitoring networks in areas perceived to be vulnerable to contamination.

In 1994-1995 routine water quality analyses of groundwater at Manakau showed wells with nitrate concentrations exceeding the New Zealand drinking water standard of 11.3 mg/L NO_3-N (New Zealand Ministry of Health, 1995). Groundwater quality monitoring, begun in 1975, showed a gradual increase in nitrate concentrations to 1994. Elevated concentrations were noted particularly in 1988 (6.4 mg/L at bore 372074[1]) and 1979 (3.4 mg/L at bore 372052).

Between October 1994 and June 1995, Manawatu-Wanganui Regional Council (MWRC) collected water samples from a number of bores and streams in the Manakau area. Nitrate concentrations ranged from negligible amounts (<0.5 mg/L) to levels nearly three times the Ministry of Health standard. Streams had nitrate concentrations below 1.0 mg/L, and there appeared to be a random distribution of bores with high nitrate concentrations. Chloride concentrations were relatively uniform and faecal coliform counts were negligible. The results were presented in Bekesi (1996) and further studies were recommended to investigate the cause, magnitude and possible consequences of the contamination. These were begun in July 1995.

---

[1] Well number allocated by the MWRC

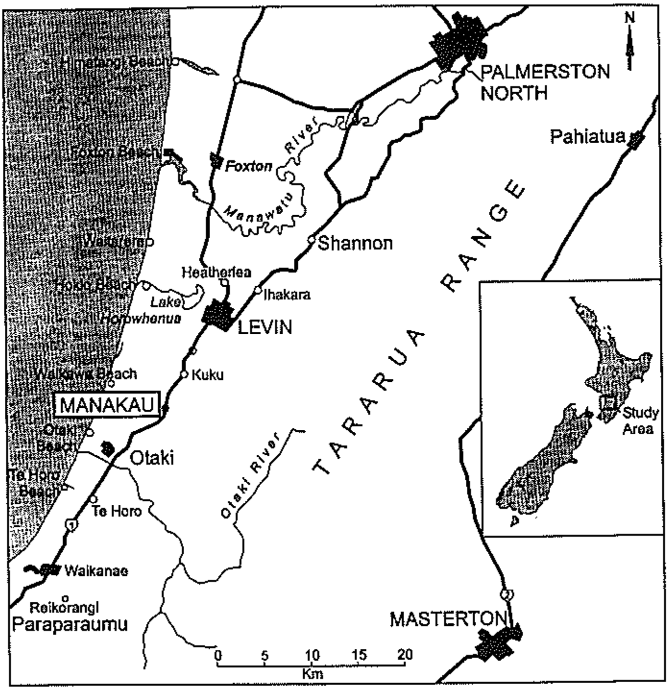

FIGURE 1 – Location of Manakau and surrounding area.

Study area

The village of Manakau is situated 80 km north of Wellington, on the coastal plain to the west of the Tararua Range (Fig.1). Manakau was first settled by Europeans in 1887 (Manakau School Centenary Board, 1988), with sheep, cattle and dairy farming, and market gardening on soils formed from alluvial silt, sand and swamps. Over the last 50 years, horticulture, including commercial nurseries and market gardens, has expanded, and dairy farms have amalgamated into larger units carrying more stock. Manakau village has also grown.

The majority of homes (approximately 120 within the study area) in Manakau use well water and all houses have septic tanks. MWRC has 60 bore records for the study area. The wells tap unconfined aquifers in alluvial gravel and sand deposits, and deeper confined aquifers in gravel.

Geology

East of Manakau are the Mesozoic greywacke Tararua Ranges; to the west dune sands have formed behind the post-6,500 yr BP prograding coast (Fig. 2). Remnants of older (penultimate glaciation) fluvial deposits have been uplifted at the margin of the mountain range to the south of Manakau. In the Manakau area two distinct lithological units crop out and underlie the plain. These are the last interglacial Otaki Sandstone and last glaciation and postglacial fluvial gravel, sand and silt.

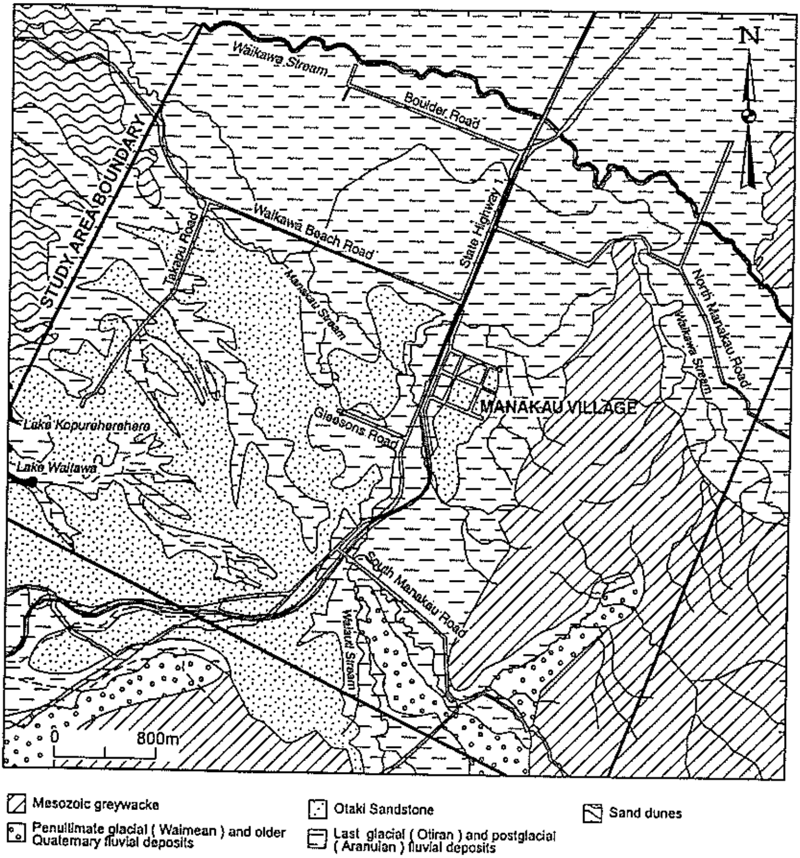

FIGURE 2 – Surface geology, Manakau.

Local streams (Waikawa, Manakau and Waiauti) and their tributaries, draining the western slopes of the Tararua Range, have downcut into the last glaciation floodplain to form entrenched postglacial floodplains occupied by meandering streams. To the west of Manakau, at the end of Gleesons Road, Manakau Stream has incised its course through Otaki Sandstone (Fig. 2). Sewell (1991) maps these glacio-fluvial surfaces at Manakau as the Ohakea Terrace, which has been dated at Otaki (8 km south of Manakau) as accumulating between 25,500 and 9,500 yrs BP (Barnett, 1984). Well logs record brown and grey gravel, silt and clay underlying the stream floodplains.

The Otaki Sandstone (Otaki Formation, Oliver, 1948) is composed predominantly of sand deposited during high sea level transgressions of the last interglacial. It has an undulating surface cut by past and present streams, underlain by a brown-weathered sandstone up to 45 m thick, with gravel and rare vegetation layers (Awatea Lignite, Fleming, 1972). In outcrop sections, beach sand and dune sand members can be distinguished (Sewell, 1991).

Otaki Sandstone unconformably overlies the informal Pukehou formation (Sewell, 1991), which consists of blue-grey gravel deposits commonly containing carbonaceous peat and wood debris. Well logs typically describe a range of lithologies including blue clay, blue fine sand, blue peaty sand, grey clayey silty sand, or fine grey sand. The blue and grey colours are a distinguishing feature of the Pukehou formation.

Three water bores (372009, 372031 and 371701) penetrate marine deposits (including blue clay, sand and shells) underlying Pukehou formation blue gravel. These marine deposits are penultimate (Karoro) interglacial high sea level deposits. Bore 372009 was drilled to a total depth of 90 m (Fig. 3), with blue gravel from 86 m to 89 m tentatively correlated with Waimaunga Glaciation.

Methods

Hydrogeology

There are over 60 bores in the study area, but only some have suitable access for water-level measurements. Static water levels were measured in 11 bores when water quality samples were collected (Fig. 4). Measurements were taken twice monthly in July, August and September 1995, and thereafter once a month until July 1996. These 16 measurements were used to map an average piezometric surface and determine the mean hydraulic gradient.

Falling head tests were carried out at five bores with suitable access and borelog information (Fig. 4). Two were screened in the fluvial gravels (372062 and 372100) and three in the Otaki Sandstone (372005, 372012 and 372013). An ISD pressure transducer was placed approximately two metres below static water level, and a slug volume equal to an approximate two metre rise in head was introduced to the bore. Water level readings were taken at one second intervals until water levels were back to their original levels. Hydraulic conductivities were calculated using Hvorslev's (1951) equations relating the fall of the slug water level with the hydraulic conductivity of the aquifer.

The lower and upper unconfined aquifer boundaries, and the sandstone/gravel boundary, were modelled in TECHBASE (1995). The algorithm used

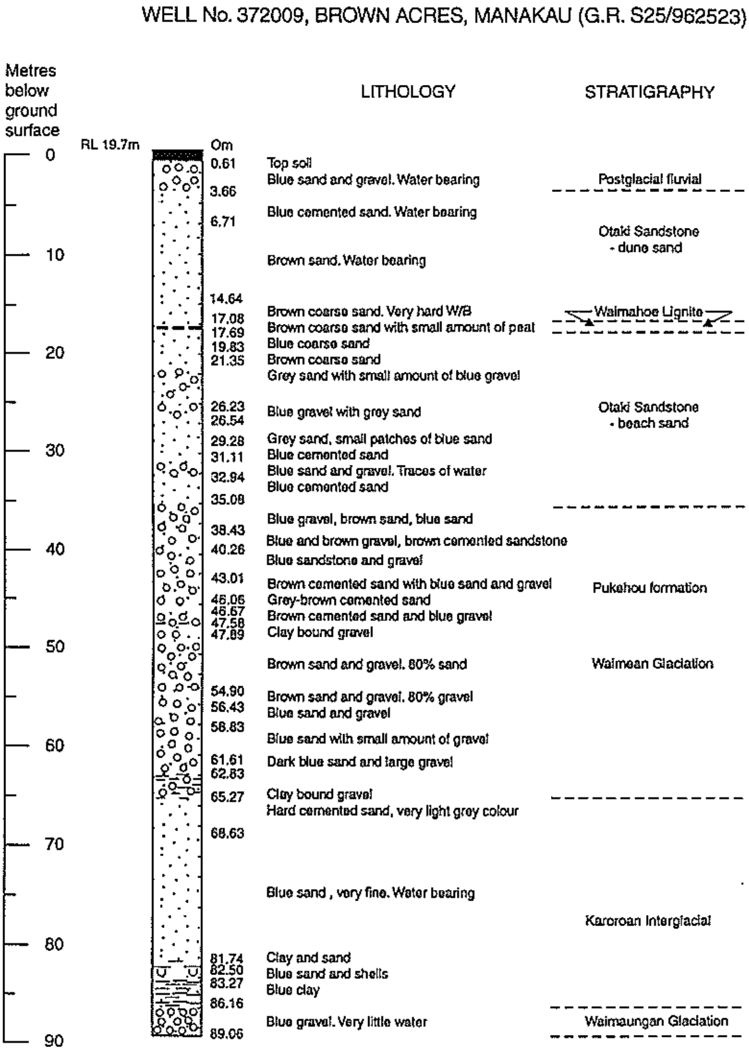

FIGURE 3 – Graphic bore log and regional stratigraphy correlation, Bore 372009, Manakau.

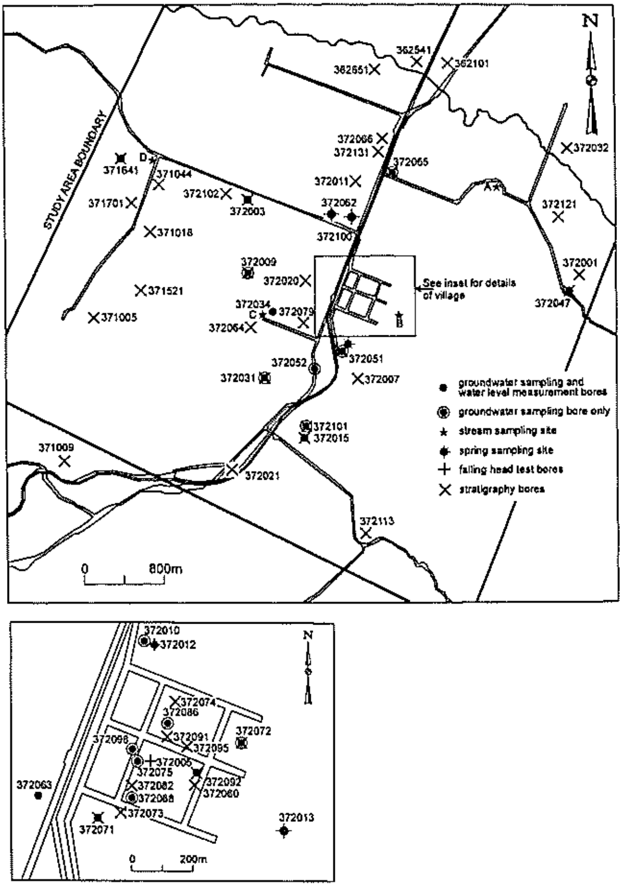

FIGURE 4 – Location of groundwater sampling bores and groundwater level measurements, Manakau.

was a 'smoothing' function that reduces any anomalies and highlights overall trends in the contoured surface. This method gives a smooth contoured fit to the data to determine an average aquifer thickness.

Groundwater quality

Groundwater samples for chemical analysis were collected from 23 bores considered to be representative of the study area (Fig. 4). These included deep (>30 m) and shallow bores (<30 m), bores with high and low nitrate concentrations, and a group of bores that provided good spatial coverage. One spring and four streams were also sampled.

Sampling was carried out twice a month from July to September 1995 and then monthly through to July 1996. Bores were purged for at least 15 minutes before sampling. Samples were taken as near to the bore outlet as possible, although in some cases it was necessary to collect samples from beyond the pressure tank. Usually the pressure tanks were small (20 litres), and bore purging ensured that 'fresh' groundwater was sampled. Samples were collected in polyethylene bottles that were chilled in the field and refrigerated on return to the laboratory. Analyses were carried out within 24 hours of collection, with the exception of analysis for faecal coliform bacteria, which was performed within six hours.

Temperature, pH, and conductivity were measured in the field. Nitrate-nitrogen (NO_3^--N), ammonium (NH_4-N), phosphate (PO_4^{3-}), chloride (Cl^-), and total iron (Fe) were measured using an HACH Spectrometer DR/2000 on unfiltered samples. The DR/2000 uses colourmetric methods based on those outlined in the Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 1989). Faecal coliform bacteria were measured using Millipore filtration equipment and incubator. A filtered 100 ml sample was incubated at 44.5°C for 24 hours with nutrient media. All chemical analyses were carried out on unfiltered samples.

Land use

A land use survey was sent to all Manakau residents in December 1995 to ascertain the location and extent of potential sources of nitrate contamination. The survey asked for information concerning the following:

- Land use (pasture, harvest crops, commercial orchards, commercial nurseries, market gardens, forestry, domestic houses and gardens);
- stock (type and stocking rate);
- location and age of potential point sources of contamination (septic tanks, dairy sheds, stockyards, and silage pits);
- fertilisers (type, quantity and application);
- spray irrigation of waste (quantity and application);
- irrigation (type of system, quantity and application).

Nitrate isotopes

Selected groundwater samples were analysed for nitrogen and oxygen isotopes in nitrate ions to help determine a nitrate source. Nitrogen has two naturally occurring stable isotopes, ^{14}N and ^{15}N; ^{14}N is the more abundant, at 99.63% of atmospheric nitrogen (Coplen, 1993). This atmospheric ratio is essentially constant and is used as the standard to which other $^{15}N/^{14}N$ ratios are compared. The delta notation for this comparison is as follows (Komor and Anderson, 1993):

$$\delta^{15}N = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{air}-1] \times 1000$$

Terrestrial nitrogen ratios differ because of the variation in oxidation states of nitrogen from –3 to +5. Generally the more oxidised a nitrogen compound is, the more positive the $\delta^{15}N$ value.

A complicating factor in the interpretation of $\delta^{15}N$ values is fractionation of nitrogen isotopes during transport from the nitrate source to the groundwater. The denitrification process is not uniform in the soil, vadose zone or aquifer, and a wide range of $\delta^{15}N$ values may be derived from the same nitrate source. The $\delta^{15}N$ values of the residual nitrate increase exponentially as the nitrate concentrations decrease because of denitrification (Coplen, 1993).

A recent study by Wassenaar (1995) suggests that use of the oxygen isotopes of nitrate in conjunction with the nitrogen isotopes can provide more reliable results, especially when denitrification is suspected. Nitrate derived from ammonia has only two possible sources of oxygen - atmospheric and meteoric. Artificial nitrate fertilisers are manufactured using atmospheric oxygen only and so their isotopic composition is similar to air (~+20‰). However, ammonia fertilisers also go through the nitrification process and show similar $\delta^{18}O$ values to natural ammonia, but the $\delta^{15}N$ values of these two sources differs. Therefore, use of both $\delta^{15}N$ and $\delta^{18}O$ can separate these influences.

Results

Hydrogeology of the Aquifer

Over 70% of the bores in the study area tap the last glacial fluvial gravels and the Otaki Sandstone, and analyses of borelog stratigraphy and drillers' notes indicate that they form a connected unconfined aquifer. The underlying Pukehou formation has a few discrete water-bearing layers and is assumed to act as a separate semi-confined aquifer.

The hydrogeological properties of the two strata forming the unconfined aquifer were tested separately. Strata thickness and hydraulic conductivities for each stratum were derived, yielding transmissivities differing by an order of magnitude.

The mean saturated aquifer thickness was 27.6 m. The mean saturated thickness of the fluvial gravels was 7.2 m and of the sandstone was 23.8 m. Table 1 shows results of the falling head tests as well as calculated transmissivities. Despite the narrower thickness of the saturated gravels, they still play a major role in the transport of water through the aquifer, with transmissivities up to 2412 m^2/day.

Regional groundwater flow is west-north-west, from the foothills towards the coast (Fig. 5). An average hydraulic gradient was calculated using the flowlines and equipotential lines. The mean hydraulic conductivity was 0.018, with a range of 0.004-0.033. Gradients were steeper to the east of State Highway 1, with an average of 0.023; west of the highway, gradients averaged 0.01.

TABLE 1 – Transmissivity – Manakau unconfined aquifer strata.[1]

	Hydraulic conductivity (m/day)	Saturated strata thickness (m)	Transmissivity (m²/day)
Gravels:			
mean (*number*)	122 (2)	7 (*847*)	854
range	109 - 134	0 - 18	0 - 2412
Sandstone:			
mean (*number*)	3 (3)	24 (*1553*)	72
range	2 - 6	0 - 36	0 - 216

[1] All values reported to the nearest whole number.

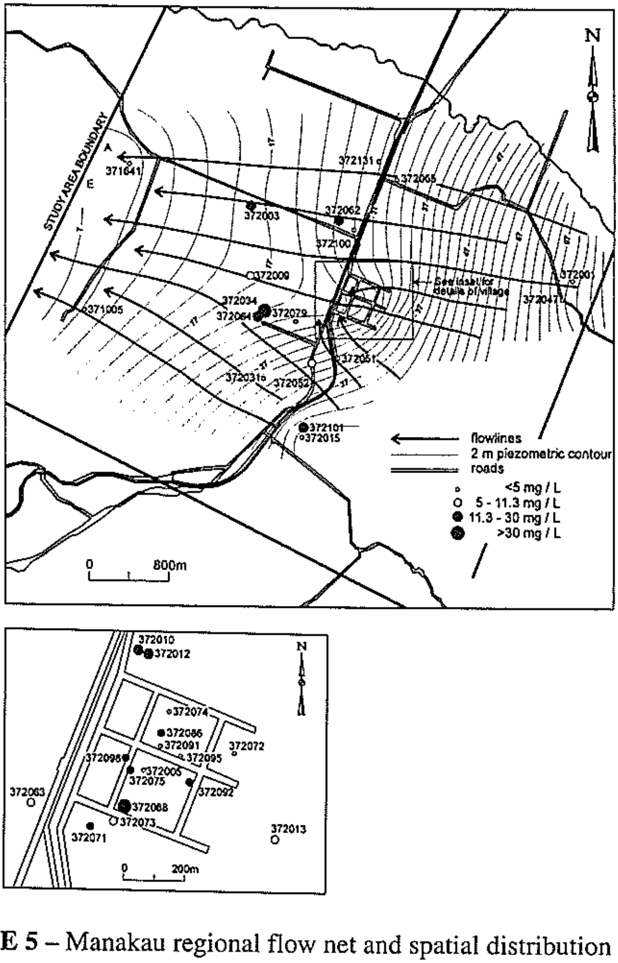

FIGURE 5 – Manakau regional flow net and spatial distribution of nitrate concentrations from bore samples, July 1996.

Groundwater quality

No significant patterns or trends emerged from the nitrate concentration results (Table 2). Of the 23 bores sampled and analysed for nitrate, 13 had concentrations above the drinking water standard (Table 3). The majority of these (62%) were shallow bores (<30 m in depth). Seven bores had low nitrate concentrations, and these were evenly divided between shallow and deep bores. In contrast, all four stream sites sampled consistently showed low nitrate concentrations.

At the end of the study period (July 1996), the spatial pattern of nitrate concentrations had changed little from that found by the MWRC study over the 1994/95 summer (Fig. 5). Four bores showed an increase in nitrate concentrations to above the drinking water standard.

Most bores had low concentrations of the other ions tested, except for some bores with very high concentrations of iron, ammonium and phosphate. Nitrate concentrations were low in all bores with high levels of ammonium, phosphate or iron and showed low correlation coefficients (Fig. 6). Relationships between iron and phosphate, iron and ammonium and phosphate and ammonium also had low correlation coefficients. It should be noted that, for analyses carried out on unfiltered samples, the phosphate may be bound to the iron particles. However, the results show a mutually exclusive relationship between the two suggesting that this is not the case.

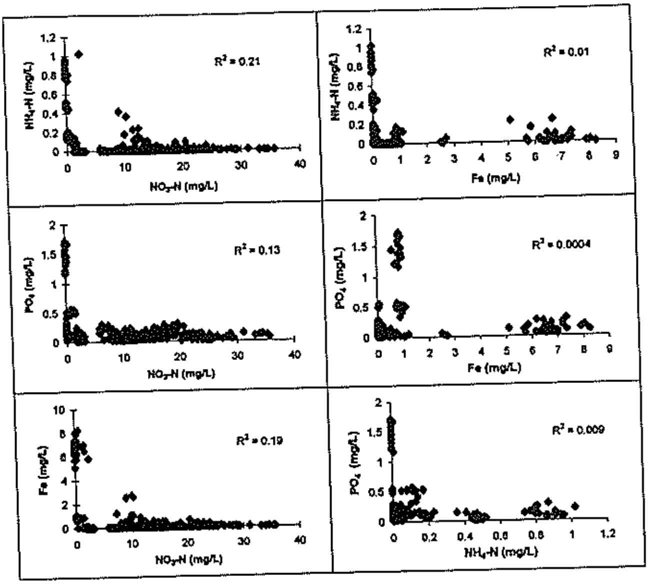

FIGURE 6 – Relationship between nitrate, ammonium, phosphate, and iron concentrations from bore samples, July 1995 to July 1996.

TABLE 2 – Summary of Manakau groundwater and stream quality, July 1995 to July 1996

Well No.	Phosphate mg/L		Total Iron mg/L		Chloride mg/L		Faecal Coliforms /100ml	
	Mean	SD*	Mean	SD*	Mean	SD*	Mean	SD*
371641	0.51	0.06	0.88	0.11	9.3	1.9	2.3	8.6
372003	0.001	0.003	0.02	0.02	13.5	3.0	0.0	0.0
372009	0.18	0.04	0.02	0.01	15.9	6.7	0.0	0.0
372010	0.11	0.02	0.05	0.02	17.9	4.3	0.0	0.0
372012	0.11	0.02	0.03	0.03	28.2	6.4	0.7	0.9
372013	0.04	0.02	0.66	0.60	18.3	4.6	0.0	0.0
372015	0.04	0.03	0.04	0.06	7.9	2.0	0.1	0.5
372034	0.10	0.03	0.01	0.01	14.1	3.3	0.0	0.0
372031	1.49	0.19	0.86	0.10	34.5	8.2	0.0	0.0
372047	0.18	0.11	0.08	0.04	10.5	2.5	0.0	0.0
372051	0.08	0.05	6.74	0.63	22.5	5.4	1.1	3.2
372052	0.05	0.02	0.08	0.08	10.8	3.5	0.0	0.0
372062	0.05	0.03	0.14	0.11	15.6	2.8	0.2	0.6
372063	0.22	0.04	0.02	0.01	19.2	4.4	1.3	2.9
372065	0.09	0.03	0.01	0.01	8.5	2.0	0.0	0.0
372071	0.15	0.04	0.04	0.07	16.4	4.2	0.9	1.9
372072	0.25	0.33	6.69	0.73	21.5	6.0	0.0	0.0
372075	0.22	0.06	0.03	0.03	16.4	3.6	0.0	0.0
372086	0.04	0.02	0.56	0.82	14.2	3.2	0.0	0.0
372088	0.08	0.02	0.28	0.17	21.6	9.4	0.0	0.0
372092	0.14	0.03	0.20	0.15	21.6	4.5	0.0	0.0
372098	0.04	0.02	0.10	0.04	10.0	1.7	0.2	0.6
372101	0.09	0.03	0.07	0.03	23.5	7.0	0.0	0.0
Stream A	0.05	0.02	0.04	0.03	6.4	1.9	87	99
Stream B	0.18	0.19	1.52	0.43	17.1	4.2	1990	1958
Stream C	0.06	0.04	0.33	0.20	10.3	4.8	1158	1313
Stream D	0.11	0.07	0.44	0.32	10.8	4.5	1506	2660
Spring	0.04	0.01	0.21	0.17	117.1	115.2	832	1764

Well No.	Temperature °C		pH		Conductivity mS/m		Nitrate-nitrogen mg/L		Ammounium mg/L	
	Mean	SD*	Mean	SD*	Mean	SD*	Mean	SD*	Mean	SD*
371641	13.9	1.6	7.56	0.15	21	1	0.5	0.4	0.11	0.03
372003	13.8	2.1	6.10	0.22	25	2	11.2	1.2	0.001	1.16
372009	14.8	1.2	7.32	0.10	32	1	9.4	1.6	0.01	0.01
372010	13.5	1.6	7.37	0.12	30	3	12.6	1.9	0.01	0.01
372012	13.6	1.5	6.67	0.08	47	1	21.2	1.3	0.002	0.004
372013	14.2	2.3	5.84	0.08	24	0.4	9.4	0.6	0.03	0.04
372015	14.7	2.3	5.77	0.13	12	1	2.2	0.4	0.01	0.02
372034	14.5	2.0	6.77	0.08	39	3	27.7	5.9	0.002	0.004
372031	14.5	1.6	7.26	0.07	48	1	0.1	0.1	0.47	0.02
372047	12.4	1.6	7.35	0.21	19	0.5	1.5	0.5	0.00	0.00
372051	14.8	1.1	6.63	0.07	38	3	0.4	0.6	0.18	0.09
372052	15.2	1.9	5.86	0.07	25	1	9.0	1.1	0.01	0.01
372062	12.8	2.3	5.58	0.13	26	2	14.3	1.8	0.01	0.01
372063	14.7	1.3	6.72	0.17	33	1	6.9	0.9	0.005	0.01
372065	13.1	2.1	6.69	0.13	15	1	2.7	0.3	0.00	0.00
372071	15.0	2.1	6.76	0.07	35	1	14.8	1.1	0.004	0.01
372072	14.3	1.7	6.90	0.06	31	1	0.2	0.6	0.86	0.08
372075	14.7	1.4	6.79	0.07	37	1	18.1	1.5	0.01	0.01
372086	14.4	2.3	6.23	0.10	28	1	12.4	1.7	0.12	0.14
372088	14.3	2.4	6.78	0.08	43	3	20.7	3.5	0.03	0.03
372092	14.2	1.6	6.89	0.08	41	1	16.6	2.0	0.03	0.04
372098	15.0	2.1	5.67	0.12	30	2	25.3	2.5	0.004	0.01
372101	14.6	2.0	6.39	0.07	37	3	13.9	1.8	0.001	0.004
Stream A	9.5	3.8	8.09	0.59	9	2	0.5	0.3	0.02	0.02
Stream B	14.6	5.5	7.06	0.15	19	2	0.6	0.8	0.93	0.36
Stream C	13.9	4.3	7.34	0.21	13	1	0.6	0.4	0.14	0.13
Stream D	12.7	4.7	7.34	0.28	14	2	0.9	0.5	0.27	0.33
Spring	15.7	2.9	7.17	0.21	79	50	2.1	1.6	0.14	0.18

* Standard Deviation

TABLE 3 – Summary of nitrate concencentrations and bore depth, July 1995 to July 1996.

Average nitrate concentration	Deep bores (>30 m)	Shallow bores (<30 m)	Unknown depth	TOTAL
High nitrate (>11.3 mg/L)	4	8	1	13
Elevated nitrate (5-11.3 mg/L)	1	2		3
Low nitrate (<5 mg/L)	4	3		7
TOTAL	9	13	1	23

Land use

The land-use survey identified areas of potential diffuse contamination and locations of potential point sources. Over 50% of the surveys were returned, but they covered only 20% of the study area. Many surveys were returned from house and garden owners within the village, whereas few were received from the larger land use areas surrounding the village. However, all farm types and land uses were represented in the survey returns, and field observation of land-use activities were used to provide full coverage of the study area.

Diffuse sources are associated with areas of stocked and/or fertilised land. Results showed that virtually all the pasture land is stocked and nearly 90% is fertilised. Although market gardens, nurseries and orchards represents a small area (4% of the study area), they are 100% fertilised and the majority are also irrigated.

Fertiliser application rates for Manakau are shown in Table 4. The high application rates of 800 kg/ha are based on two applications per year of 400 kg/ha. The pasture/market garden farm application of 1000 kg/ha is an annual total of several smaller applications through the year. Actual amounts of fertilisers used on market gardens and nurseries were not provided in any of the land use survey returns, however, one reply stated that "small amounts often" are applied. A wide variety of fertilisers are used on these areas.

Spatial distribution of potential point sources of nitrate contamination in Manakau is shown in Figure 7, including septic tanks, dairy sheds and stockyards. The high concentration of septic tanks in the village, where there are approximately 60 houses in an area of 43.5 hectares, is clearly shown. This results in a septic tank density of 1.4 per hectare. Septic tank density for the entire study area at Manakau is 0.05 tanks per hectare.

In addition to the 120 septic tanks in the area, there are six dairy sheds and seven stockyards. These are areas where stock and their waste are concentrated.

TABLE 4 – Summary of annual fertiliser application rates, Manakau (kg/hectare).

Farm type	Superphosphate	Cropmaster (NPK 15-10-10)	Urea
Pasture	150-800	300-800	30-50
Orchard	40	-	30
Pasture & Market garden	-	1000	-
Market gardens/Nurseries*			

*various fertilisers used, including potash, lime, dolomite, urea, ammophos, nitrophoska

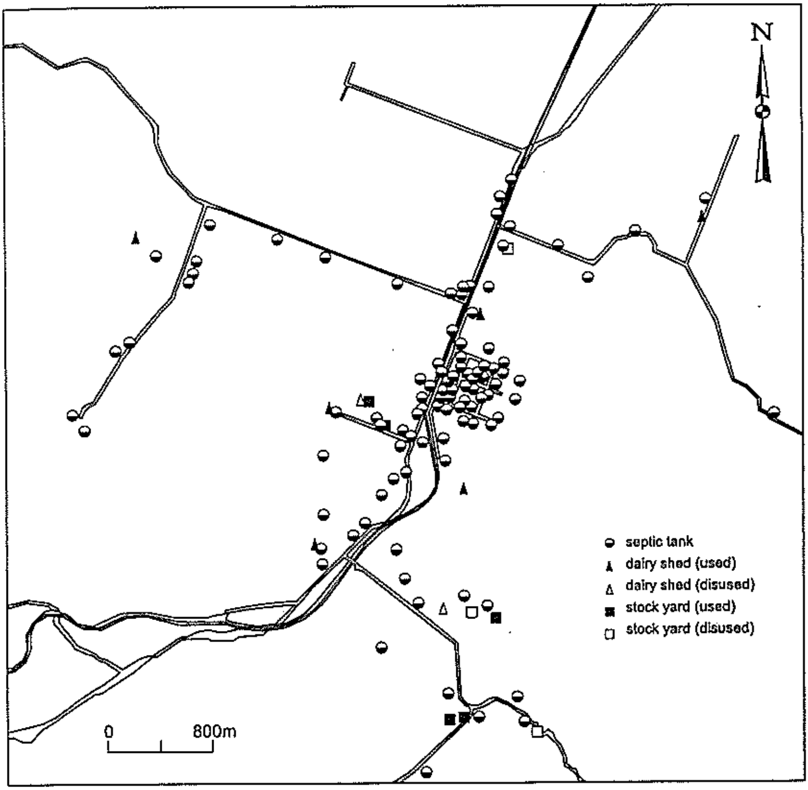

FIGURE 7 – Spatial distribution of contamination point sources, Manakau.

Nitrate isotopes

Figure 8 shows the results of the Manakau nitrate and oxygen isotope analyses in relation to the data from Wassenaar (1995) and Cathcart (1996). Oxygen isotope analyses were not carried out in the Cathcart study and so these results give an indication of the $\delta^{15}N$ range only. The $\delta^{15}N$ results from Manakau range from $+4^{\circ}/_{oo}$ to $+12^{\circ}/_{oo}$. This range overlaps with the reported range for fertilisers and animal/human wastes. However, when nitrate $\delta^{18}O$ results are included, fertiliser nitrate and nitrate from nitrification of ammonia are separated into two distinct zones. Manakau nitrate $\delta^{18}O$ values fall between $+6^{\circ}/_{oo}$ to $+10^{\circ}/_{oo}$. This narrow range is characteristic of oxygen from nitrate formed through nitrification of ammonia (Wassenaar, 1995). Ammonia available for nitrification can come from artificial (fertilisers) or natural (animal/human) sources, but, volatilisation of natural ammonia results in higher $\delta^{15}N$ values of the residual ammonia. The $\delta^{15}N$ results from Cathcart (1996) suggest that these two ammonia sources are easily distinguished in the New Zealand environment. Results from Manakau indicate that nitrate formed from the nitrification of ammonia is being reduced, and that the source of the ammonia is from human and animal wastes rather than artificial fertilisers.

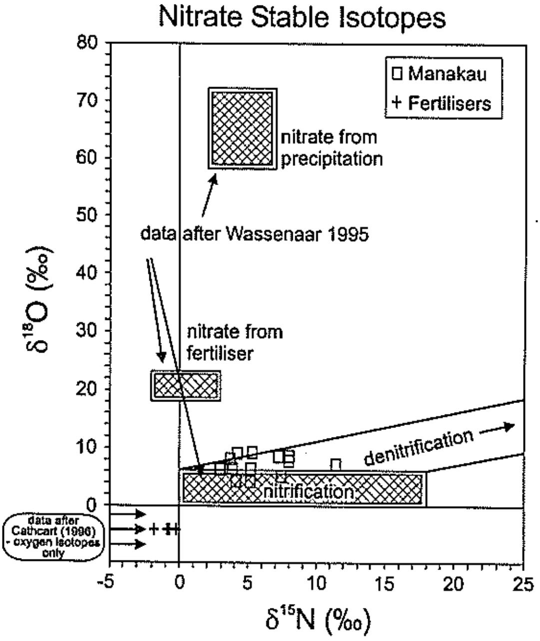

FIGURE 8 – Manakau nitrate and oxygen isotope results and data from Wassenaar (1995) and Cathcart (1996).

Discussion

Lithology and groundwater quality

The subsurface strata lithology and permeability vary. This affects local groundwater flow direction and contaminant transport. An irregularity in groundwater flow direction can be seen in the vicinity of the village (Fig. 9). It is most likely that the permeability differences between the strata influence flow paths around the village. Influences from well pumping in the village would be minor as rates are low and pumping is intermittent and generally for short periods of time. During the day, when the water level measurements were taken, water use is low and very little pumping occurs.

The 'finger' of 10-20 m deep sandstone, separating the near surface sandstone areas, represents a 'valley' cut into the Otaki Sandstone. Gravels filling this valley offer an easier path of travel for groundwater and so contours bend and flowlines converge towards it. To the west of the village the few well logs available suggest the Otaki Sandstone surface is almost flat and groundwater flow lines are directly towards the coast.

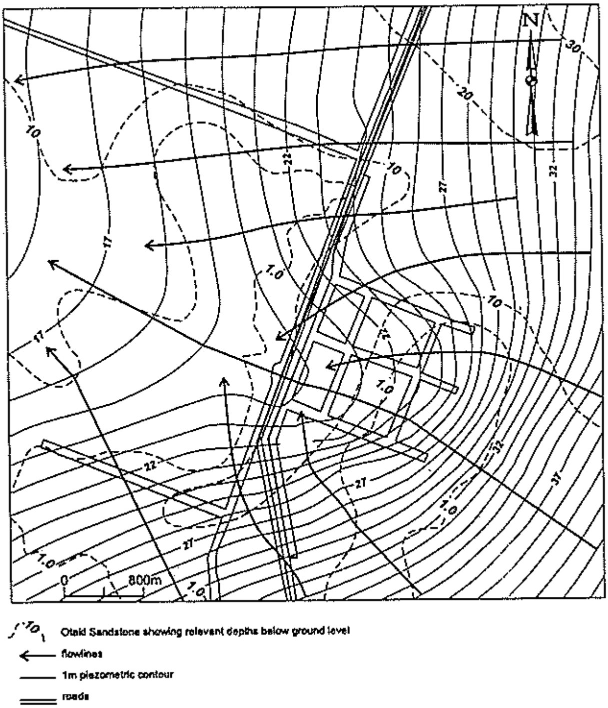

FIGURE 9 – Manakau Village flow net.

TABLE 5 – Bore screen stratigraphy and NO_3-N concentrations

a) numbers:

NO_3-N (mg/L)	LG Gravels	Otaki s/s	Pukehou	Greywacke	Other	TOTAL
over 11.3	2	11	0	0	0	13
between 5 and 11.3	3	6	2	0	0	11
under 5	7	10	6	2	4	29
TOTAL	12	27	8	2	4	53

b) percentages of each concentration class:

NO_3-N (mg/L)	LG Gravels	Otaki s/s	Pukehou	Greywacke	Other	TOTAL
over 11.3	15	85	0	0	0	100
between 5 and 11.3	27	55	18	0	0	100
under 5	24	34	21	7	14	100

c) percentages of each strata:

NO_3-N (mg/L)	LG Gravels	Otaki s/s	Pukehou	Greywacke	Other
over 11.3	17	41	0	0	0
between 5 and 11.3	25	22	25	0	0
under 5	58	37	75	100	100
TOTAL	100	100	100	100	100

LG - Last glacial
s/s - Sandstone

Table 5 compares the nitrate data with bore screen stratigraphy for 53 bores in the Manakau area. The nitrate concentration data are taken either as an average over the 1995/96 study period or from the latest data available (usually from the MWRC 1994/95 survey). Screen settings and aquifer stratigraphy correlations were made from borelogs for 42 of these bores and were inferred from the location and depth for the other eleven. Table 5b shows that the majority (85%) of bores with nitrate concentrations over the New Zealand drinking water standard (designated as "high"), are associated with the Otaki Sandstone; 55% of bores with elevated nitrate concentrations (between 5 and 11.3 mg/L) tap the Otaki Sandstone and 34% of bores with low nitrate concentrations (under 5 mg/L) are also associated with this stratum. These high percentages reflect the large number of bores tapping the sandstone. This influence can be minimised if percentages are taken for each stratum (Table 5c). However, the Otaki Sandstone still dominates, with high nitrate concentrations in 41% of its bores, compared to 17% for the gravels. Gravel, Otaki Sandstone and Pukehou formation bores have similar percentages of bores with elevated nitrate concentrations, but gravel and Pukehou formation bores have higher percentages of low nitrate bores compared to the Otaki Sandstone. Of the eight bores tapping the Pukehou formation, two have elevated nitrate concentrations. This suggests that the aquifer, aquiclude, aquitard system is 'leaky', and contamination is reaching the deeper confined strata. Bores tapping the deeper strata and greywacke all have low nitrate concentrations

Table 5 shows that nearly as many bores with low nitrate concentrations as high concentrations tap the Otaki Sandstone. The low nitrate concentrations are in bores with high levels of ammonium or iron, suggesting that the nitrogen was not in its oxidised NO_3 form. It is likely that two processes operate, one relating to the high ammonium concentrations and the other to the high iron levels.

High iron concentrations can indicate a reducing groundwater environment where oxygen is depleted and denitrification has taken place. A limited number of redox potential measurements of Manakau groundwater taken by MWRC in February and March 1995 confirms this relationship (Bekesi, 1996). Figure 10 shows the relationship between redox potential, and iron and nitrate concentrations in Manakau bore samples. The pattern suggests that iron and nitrate are mutually exclusive ions, dependent on the strength of the reducing environment of the groundwater.

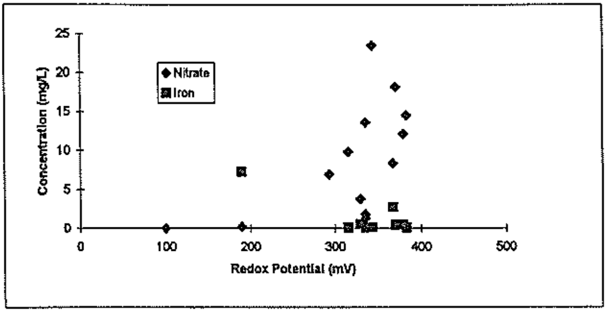

FIGURE 10 – Relationship between redox potential and nitrate and iron concentrations from Manakau bore samples.

The occurrence of high ammonium concentrations in samples with no nitrate suggests that nitrogen introduced into the groundwater system as NH_3 is not being nitrified to form NO_3. Nitrification requires oxygen as well as nitrifying bacteria, so conditions are generally more favourable in the unsaturated zone. However, nitrification can also take place in groundwater (Domenico and Schwartz, 1990). In the study area, the unsaturated zone and groundwater conditions are not favourable in some areas and nitrification is not taking place. Oxygen is probably the limiting factor in the groundwater, given the evidence for denitrification. In the unsaturated zone it is possible that clogging from septic tank effluent has reduced the rates of oxygen diffusion, thus limiting nitrification.

These processes could produce the seemingly random spatial distribution of bores with high nitrate concentrations seen at Manakau, from either diffuse contamination (e.g. fertiliser or stocked pasture) or many point sources (e.g. septic tank effluent). Therefore, the presence or absence of nitrate contamination in Manakau bores is a function not only of the location of a contamination source, but also of the chemical conditions of the groundwater.

Of the 23 bores surveyed in this study, 14 tap the Otaki Sandstone and three of these have low nitrate concentrations. These three bores have high concentrations of either ammonium or iron. Iron concentrations were over 6 mg/L in two of the bores. All bores associated with the Otaki Sandstone therefore show some level of nitrogen contamination, be it through high or elevated nitrate concentrations, high ammonium concentrations or high iron concentrations suggesting denitrification of nitrate. This is attributed to the distinct hydraulic properties of the Otaki Sandstone aquifer, with its low permeability and slow groundwater velocities relative to the postglacial and last glaciation gravels. Contamination probably occurs within the gravel aquifers, but their dilution and dispersion capacity is higher, so the contamination does not build up to the extreme levels found in the Otaki Sandstone.

Land use

The major land use in Manakau is pasture grazing, with fertiliser applied to boost pasture growth. With this type of land use diffuse contamination is possible. However, the intensity of these activities is also important. Table 6 compares stocking rates and spray irrigation amounts in Manakau with other regions in New Zealand and with the national average. Manakau is not an intensive dairying area, but has a relatively high stocking rate for sheep and beef farming. Spray irrigation of waste is also not as intensive as for larger dairy farms in Waikato.

TABLE 6 – Summary of stocking rates and spray irrigation amounts, Manakau and New Zealand

	Manakau	New Zealand average	Region
Stocking Rates			
Dairy (cows/ha)	1.5-2.8	2.5[1]	2.5-3.0[3] (S. Waikato)
Sheep & beef (su/ha)	9-11	6.4[2]	12[3] (Taranaki finishing farms)
Spray Irrigation			
(L/day)	100-15,000	-	>20,000[3] (Walkato)

[1] Livestock Improvement Corporation, 1994

[2] New Zealand Meat and Wool Boards Economic Service, 1996

[3] Enviroment Waikato, *pers. comm.*

Numerous overseas studies show a direct relationship between nitrate concentrations in groundwater and nitrate fertilisation rates and/or fertilisation history (Cathcart, 1996; Hallberg, 1986). Many variables affect the resultant concentrations of nitrate that reach groundwater. Studies indicate four primary controlling factors: 1) the amount of nitrogen source available, 2) the amount of infiltrating or percolating water, 3) the hydraulic conductivity of the unsaturated and saturated zones, and 4) the potential for nitrate reduction and/or denitrification in the unsaturated zone and the groundwater (Hallberg, 1986). Cathcart (1996) gives information on fertiliser usage in Pukekohe, South Auckland, an intensive market gardening area where fertilisers have been implicated as the source of nitrate contamination of groundwater. The main cash crops are onions and potatoes grown on a large scale. Nitrophoska (NPK 15-7-5) is applied to onion crops at planting time at rates of between 600-1300 kg/ha. This is similar to the 1000 kg/ha of Cropmaster(NPK 15-10-10) used on market gardens in Manakau. In addition, the onion crops in Pukekohe receive two to three applications of calcium-ammonia-nitrate fertilisers at rates of 150-200 kg/ha over their growing cycle. Potato crops receive between 125-374 kg of urea per hectare just prior to planting. After planting, a special fertiliser mix (NPK 8-9-8), used only for potato growing, is applied at rates between 2500-4400 kg/ha. These amounts are far in excess of those used at Manakau (Table 4).

Potential point sources of contamination have been identified in Manakau. The most concentrated sources are septic tanks in the village. Sinton (1982) considered the septic tank density in a study area at Yaldhurst on the Canterbury Plains, with alluvial soils on fluvial, gravel, sand and silt, high at 0.2 tanks per hectare. Septic tank effluent was estimated to contribute 20-30% of the nitrate loading in the area, the remainder being from grazed pasture land. Manakau village has a much higher septic tank density at 1.4 tanks per hectare.

There are many possible sources of the nitrate contamination in the Manakau area. However, agricultural and horticultural practises are less intensive than in other regions around New Zealand. Stocking rates and fertiliser application are generally low. In contrast, housing density in the village is high and septic tank point sources are concentrated in this area (1.4 tanks per hectare).

Nitrate sources in the village

Groundwater flow through the unconfined gravel aquifer is faster than through the less permeable unconfined Otaki Sandstone aquifer. Thus nitrate-contaminated groundwater is retained longer in the sandstone and is slowly dispersed and diluted. Septic tank systems in the village would appear to be the main contamination source, as there are few upgradient sources (Fig. 7). Usual indicators of septic tank effluent contamination (e.g. faecal coliform bacteria counts, high chloride concentrations and contamination plumes) however were not found in correlation with high nitrate concentrations. This study demonstrates that in the Manakau groundwater environment these contamination indicators are controlled by other factors and not just the presence of high nitrate concentrations. Depth to the water table will influence the likelihood of contaminants reaching the groundwater, and redox conditions of the unsaturated zone, as well as of the saturated zone, will dictate their oxidation state.

The variability in redox conditions found in Manakau affects nitrification and denitrification processes. This, rather than the presence or absence of a contamination source, causes the seemingly random spatial distribution of high nitrate concentrations. In addition, contamination plumes associated with point sources can become unrecognisable when they overlap and groundwaters mix. This is likely in the village, where many point sources are located in a small area. On this scale the point sources take on the characteristics of a diffuse source.

Nitrate sources outside the village

Areas of contamination outside the village are more diverse. Not all are associated with the Otaki Sandstone, nor are they necessarily in areas of intensive land use or near a nitrate point source. Nitrate nitrogen and oxygen isotope results can provide direction in identifying a source in these areas, as well as suggesting septic tank contamination in the village. Results from Manakau indicate that nitrate, formed from nitrification of ammonia, is being reduced and that the source of the ammonia is manure rather than artificial fertilisers. However, this classification does not differentiate between human and animal wastes. Therefore, for areas outside the village, identifying specific sources such as septic tanks, dairy sheds or diffuse nitrate leaching from stocked pasture areas is not possible. However, the nitrate isotope results do exclude the use of fertilisers as the dominant nitrate source for Manakau. This also supports the implication of septic tank effluent as the contamination source for the village.

Summary

Nitrate concentrations in groundwater beneath the Manukau area range from <0.05 mg/L to over 30 mg/L. The complexity of the interconnected unconfined fluvial gravel and Otaki Sandstone aquifer system is reflected in the seemingly random scatter of bores with high nitrate concentration groundwater.

Within this unconfined aquifer the lower permeability sandstone has slow groundwater velocities and the higher permeability gravels faster velocities. The majority of bores with high nitrate concentrations are associated with the Otaki Sandstone, which has a poor dilution capacity because of its low permeability and slow groundwater velocity. Those sandstone bores that do not show high nitrate levels have either high iron or ammonium concentrations, indicating that nitrogen contamination may have occurred, but the nitrates were denitrified or remain as ammonium.

Nitrate nitrogen and oxygen isotope analysis suggests that nitrate is formed from nitrification of ammonia from human or animal sources, and is not from use of fertilisers. Manakau village has a high septic tank density and lacks any well-defined up-gradient source of nitrates, suggesting that septic tank effluent is the main source of nitrate contamination of groundwater in the village.

Acknowledgements

This research was carried out as part of Wendy McLarin's MSc thesis at the School of Earth Sciences, Victoria University of Wellington. I would like to acknowledge the Manawatu-Wanganui Regional Council, who provided essential funding for the project and provided background information through access to the Council's groundwater database. Thanks to Doug Sheppard, Claude Taylor and Graeme Lyon of the Institute of Geological and Nuclear Sciences Ltd (GNS) in Lower Hutt for nitrate nitrogen and oxygen isotope analyses. Thanks again to Doug Sheppard for encouraging me to write this paper and for providing funding to do so through GNS, and to Margaret McDonald for drafting the figures. Thanks to James Goff, Catherine Chague-Goff, Murray Close and Mike Rosen for reviewing this paper. Lastly, I would like to thank the residents of Manakau for their cooperation and interest in the study.

References

American Public Health Association 1989: *Standard Methods for the Examination of Water and Wastewater, Seventeenth Edition.* Clesceri, L.S.; Greenberg, A.E.; Trussell, R.R. (*eds.*). American Public Health Association and Water Pollution Control Federation, USA.

Barnett, R. 1984: Upper Quaternary stratigraphy in the Otaki district. Unpublished BSc (Hons.) Thesis, Geology Department, Victoria University of Wellington, Wellington, New Zealand.

Bekesi, G. 1996: Nitrate-nitrogen in Horowhenua groundwater. *Manawatu-Wanganui Regional Council, Report 96/Ext/243*, Palmerston North, New Zealand.

Burden, R.J. 1980: Distribution of nitrate nitrogen concentrations in groundwater beneath intensively grazed pasture land in the Ngatarawa Valley, Hawkes Bay. *Journal of Hydrology (New Zealand) 19(2)*: 94-105.

Burden, R.J. 1982: Nitrate contamination of New Zealand aquifers: a review. *New Zealand Journal of Science 25*:205-220.

Cathcart, S.N. 1996: An investigation of the nitrate contamination of an unconfined, shallow, fractured basaltic aquifer at Pukekohe, South Auckland, New Zealand. Unpublished MSc thesis in Environmental Science, Auckland University, Auckland, New Zealand.

Coplen, T.B. 1993: Uses of environmental isotopes. In: Alley, W.M. (*ed.*), *Regional Groundwater Quality*. Van Nostrand Reinhold, New York.

Domenico, P.A.; Schwartz, F.W. 1990: *Physical and Chemical Hydrogeology*. John Wiley & Sons, Inc., Toronto.

Fleming, C.A. 1972: The contribution of C14 dates to the Quaternary geology of the "Golden Coast", Wellington. *Tuatara 19(2)*:61-69.

Hallberg, G.R. 1986: Overview of agricultural chemicals in groundwater. In: *Proceedings of the Conference on Agricultural Impacts on Groundwater*. National Water Well Association, Dublin, Ohio, August, 1986, pp.1-63.

Hvorslev, M.J. 1951: Time lag and soil permeability in groundwater observations. *Bulletin No.36*, Waterways Experiment Station, Corps of Engineers, U.S. Army, Vicksburg, Mississippi, USA.

Komor, S.C.; Anderson, H.W. Jr. 1993: Nitrogen isotopes as indicators of nitrate sources in Minnesota Sand-Plain aquifers. *Groundwater 31(2)*:260-270.

Livestock Improvement Corporation 1994: *Dairy Statistics, 1993-1994*. Livestock Improvement Corporation Ltd, Hamilton, New Zealand.

Manakau School Centenary Board 1988: *Manakau School Centenary, 1888-1988*.

New Zealand Meat and Wool Boards' Economic Service 1996: *The New Zealand Sheep and Beef Farm Survey, 1993-1994*. New Zealand Meat and Wool Boards' Economic Service, Wellington, New Zealand.

New Zealand Ministry of Health 1995: *Drinking water standards for New Zealand*. New Zealand Ministry of Health, Wellington, New Zealand.

Oliver, R.L. 1948: *The Otaki Sandstone and its geological history*. New Zealand Department of Scientific and Industrial Research, Geological Memoirs No. 7, 49 p.

Sewell, A. 1991: *Paleoenvironmental analysis of Quaternary strata in the Levin area*. Unpublished MSc thesis, Massey University, Palmerston North, New Zealand.

Shuval, H.I.; Gruener, N. 1977: Infant methaemoglobinaemia and other health effects of nitrate in drinking water. *Progress in Water Technology 8(4/5)*: 183-193.

Sinton, L.W. 1982: A groundwater quality survey of an unsewered semi-rural area. *New Zealand Journal of Marine and Freshwater Research 16*: 317-326.

TECHBASE 1995: *Introduction to TECHBASE: Training notes*. TECHBASE Australasia Pty Ltd.

Wassenaar, L.I. 1995: Evaluation of the origin and fate of nitrate in the Abbotsford aquifer using the isotopes of ^{15}N and 18O in NO_3^-. *Applied Geochemistry 10*: 391-405.