

# NITRATE IN GROUND WATER IN THE WAIKATO REGION

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## Abstract

There is wide concern that intensive farming practices are likely to provide non-point sources of ground water NO<sub>3</sub>-N pollution. Similarly, land based disposal of industrial effluent provides numerous point sources of ground water NO<sub>3</sub>-N. This study uses ground water NO<sub>3</sub>-N data (including consents monitoring data) collected by Environment Waikato to investigate both non-point and point sources of NO<sub>3</sub>-N pollution in the Waikato region. Elevated ground water NO<sub>3</sub>-N levels are found in the north Waikato (south of Pukekohe), Coromandel coastal settlements, Tokoroa, Upper Piako catchment (Hauraki District), and Hamilton Basin. The full extent of ground water NO<sub>3</sub>-N pollution in the Waikato region will not be known until extensive ground water monitoring is completed.

Monitoring wells in an intensively farmed area between Hamilton and Cambridge reveal NO<sub>3</sub>-N concentrations above 10 mg L<sup>-1</sup>. The effects of non-point sources of NO<sub>3</sub>-N are found predominantly in shallow bores (<30 metres) with water levels within several metres of ground surface. The major mechanisms that control NO<sub>3</sub>-N fluctuation in shallow aquifers are water recharge and ground water outflow to adjacent streams. Rapid increases in NO<sub>3</sub>-N levels are attributed to accumulation of soil NO<sub>3</sub>-N during dry periods, combined with the NO<sub>3</sub>-N flushing effect of infiltrating rainwater. It has been estimated that NO<sub>3</sub>-N leaching from intensively farmed areas contributes at least 60 kg NO<sub>3</sub>-N ha<sup>-1</sup> y<sup>-1</sup> to shallow aquifers in the Hamilton Basin. During a period of declining ground water levels, the apparent NO<sub>3</sub>-N decrease from these shallow aquifers equals 280 g NO<sub>3</sub>-N d<sup>-1</sup>.

Regardless of intensive land use, certain shallow aquifers contain little or no NO<sub>3</sub>-N. This may be attributed to reducing soil and water conditions prevailing in these areas (e.g. Lower Piako catchment). Under these conditions there is little or no dissolved oxygen present, and NO<sub>3</sub>-N is reduced by Fe<sup>2+</sup>. Consequently, ground water containing elevated levels of Fe<sup>2+</sup> (>0.2 mg L<sup>-1</sup>) has very low NO<sub>3</sub>-N levels. A significant part of the intensively farmed area in the Waikato region falls into this category.

Nitrogen loading rates at industrial waste disposal sites are several fold greater than N loading due to non-point sources. A case study of one such industrial disposal site is presented, where dairy factory waste water disposal onto land has markedly increased ground water NO<sub>3</sub>-N pollution. At individual bores, NO<sub>3</sub>-N levels have increased over the last decade from background levels (e.g. <1 mg L<sup>-1</sup>) to more than 70 mg L<sup>-1</sup>. The high N and hydraulic loading from this point source contribute at least 13 t NO<sub>3</sub>-N y<sup>-1</sup> to the adjacent Mangaone Stream. Proposals for the disposal of industrial waste water onto land will require an appropriate N management strategy. These N management strategies must demonstrate that applied-N is unlikely to adversely affect ground water quality in the region.

## Introduction

New Zealand has an abundance of good quality surface and ground water resources. In the Waikato region (Figure 1) approximately 50% of the population depend on ground water supplies. Dependency on ground water is steadily increasing due to increasing farming activity and population growth. For the last three years, on average about 400 ground water bores have been drilled in the Waikato region. Moreover, there is also a growing domestic and overseas interest in using ground water for commercial bottling as drinking water (e.g. bore water at Raglan). Industrial and agricultural uses place considerable demands on water resources in the Waikato region, and the dairy farming, horticulture and market gardening industries are particularly dependent on ground water supplies.

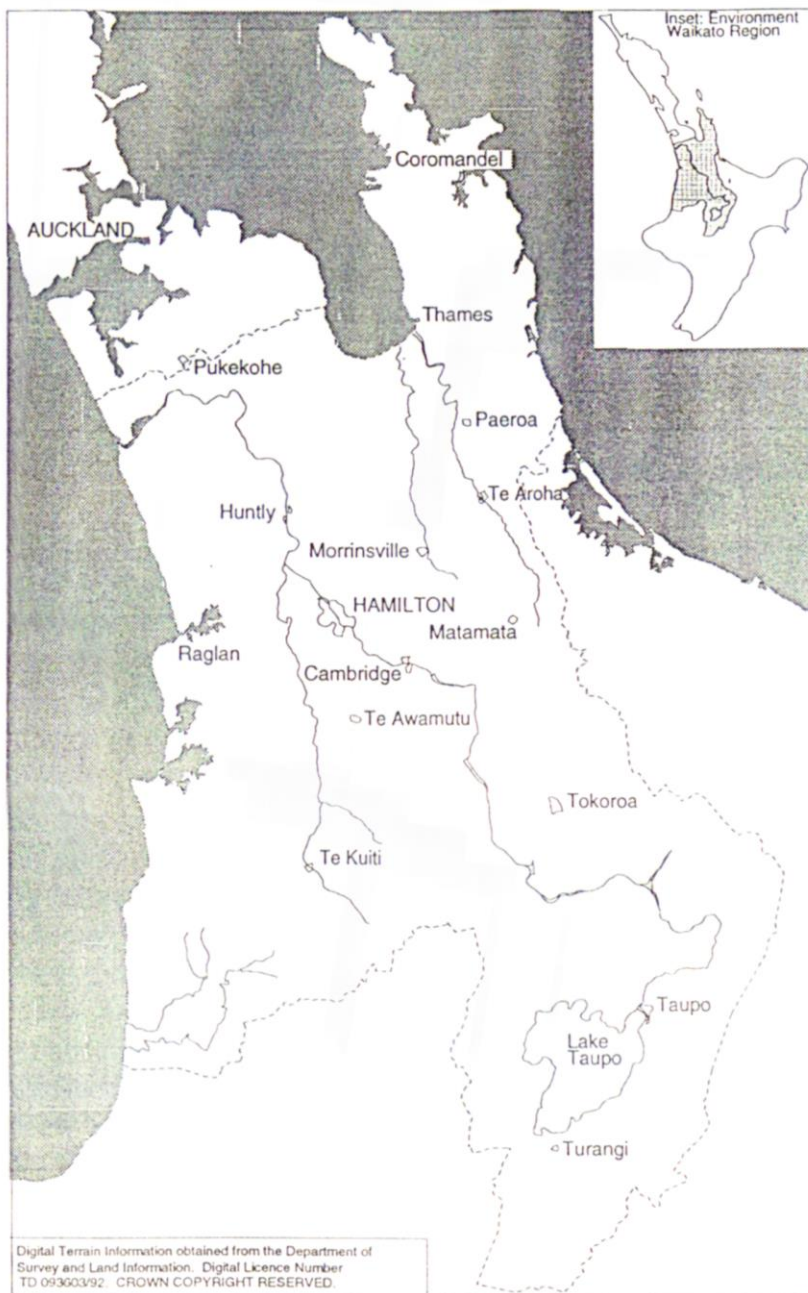


Figure 1. Location of the Waikato region.

Selvarajah, N., Maggs, G.R., Crush, J.R. and Ledgard, S.F. 1994. Nitrate in ground water in the Waikato region. *In The Efficient Use of Fertilizers in a Changing Environment: Reconciling productivity with sustainability.* (Eds. L D Currie and P Loganathan). Occasional Report No. 7. Fertilizer and Lime Research Centre, Massey University, Palmerston North, pp 160-185.

According to the New Zealand drinking water standards, the maximum acceptable level for NO<sub>3</sub>-N is 10 mg L<sup>-1</sup> (Board of Health, 1989; Australian and New Zealand Environment and Conservation Council (ANZECC), 1992). The significance of this level and health hazard due to the presence of NO<sub>3</sub>-N in drinking water have been explained elsewhere (e.g. Johnson *et al.*, 1987; Weisenburger, 1991; Burden, 1992). High levels of NO<sub>3</sub>-N in drinking water can also affect livestock (Driscoll, 1987). The ANZECC guideline for NO<sub>3</sub>-N for livestock drinking water is 30 mg L<sup>-1</sup> (ANZECC, 1992). Moreover, in the Waikato region, ground water often contributes directly to surface water bodies such as streams, rivers and wetlands. Consequently, water polluted with NO<sub>3</sub>-N can pollute waterways causing algal blooms and may subsequently affect aquatic life such as fish. Many waterways in the region are used for recreation, and unwanted algal growths can be a nuisance and may affect the revenue gained by tourism.

The dairy export market is becoming increasingly competitive, and meeting stringent quality standards is very important for assuring successful participation in international trade, especially in the European market. Consequently, heavy emphasis is placed on the quality of water used in the dairy farming industry. Thus dairy farming requires good quality water (Class 1 - used for human consumption) for stock consumption, milking sheds, and washing requirements. New Zealand's economy depends heavily on the dairy industry and about 50% of milk production is generated in the Waikato region. Every effort must be made to prevent ground water contamination in the region so that such a valuable industry remains viable.

In the past the task of ground water quality monitoring has been undertaken either by the Department of Health or regional authorities. Department of Health monitoring programmes are used to assess the quality of potable ground water supplies. Most of the regional authority monitoring programmes have been carried out to investigate the hydrogeochemistry of ground water. The objective of these programmes is usually to understand the formation from which ground water is derived, and to assess the general quality of ground water (e.g. mineral composition and contaminants such as NO<sub>3</sub>-N) for different uses. Such studies generally require one-off sampling and hence the majority of bores monitored during these ground water studies have been sampled only once. Excluding consent monitoring programmes, the only systematic ground water NO<sub>3</sub>-N studies conducted in the Waikato region have been that of Baber (1978) and Marshall (1986).

Nitrate-N contamination of ground water is identified as a major threat to ground water quality in the region. The first part of this paper identifies sources of non-point NO<sub>3</sub> pollution in the Waikato region, and presents a case study of ground water NO<sub>3</sub> levels in the Hamilton to Cambridge area. The second part discusses NO<sub>3</sub>-N contamination from point sources and presents a case study of NO<sub>3</sub> pollution adjacent to a dairy factory waste water irrigation site in the Hamilton Basin.

## **(1) Ground water NO<sub>3</sub>-N contamination caused by non-point sources in the Waikato region**

The potential non-point sources for NO<sub>3</sub>-N are soil organic-N, N fertilisers, grazed pasture, cultivated soils and on-site sewage treatment. The literature on non-point sources of ground water NO<sub>3</sub>-N in New Zealand is abundant (e.g. Baber, 1978; Burden, 1982; Sinton, 1984; Hoare, 1986; Cameron, 1993; Smith *et al.*, 1993). Thus the following discussion emphasises processes that generate non-point sources of ground water NO<sub>3</sub>-N, which have previously received little or no attention in the literature.

## Soil organic-N

Surface soils in the Waikato region (up to 20 cm depth) contain about 0.3-0.6% N, mainly in the form of organic-N. During mineralisation, heterotrophic microbes (ammonifiers) breakdown soil organic-N into ammoniacal-N ( $\text{NH}_4\text{-N}$ ) when moisture and warm conditions are available. Depending on the labile organic-C availability in soil the released ammoniacal-N can be assimilated by microbes, a process referred to as immobilisation (Okereke and Meints, 1985). Both mineralisation and immobilisation are dynamic processes, and depending on the rate of these processes, there will be a net mineralisation or net immobilisation. Net mineralisation can also depend on the quality and quantity of organic-N substrates available in soil, soil type, soil management and climatic conditions. Often net mineralisation is estimated using the amount of N removed by herbage from unfertilised soils (Ryden, 1984). Using this approach, it has been reported that the annual rates of net mineralisation are between 100 and 900 kg N ha<sup>-1</sup> for 38 different sites in the U.K. (Brockman, 1969). Such an estimate does not indicate any excess mineral-N remaining in soil following plant uptake and other N loss pathways, which is important from the point of view of  $\text{NO}_3\text{-N}$  leaching.

When surplus  $\text{NH}_4\text{-N}$  is present in soils, under aerobic conditions, nitrifiers can oxidise  $\text{NH}_4\text{-N}$  into  $\text{NO}_3\text{-N}$ . Once  $\text{NO}_3\text{-N}$  is produced in soil, unlike  $\text{NH}_4\text{-N}$  little is incorporated into biomass by heterotrophs, and a build-up of  $\text{NO}_3\text{-N}$  occurs in soil provided plant uptake and denitrification are low. There is evidence for the preference for  $\text{NH}_4\text{-N}$  over  $\text{NO}_3\text{-N}$  by heterotrophs during immobilisation (Hauck, 1984; Wickramasinghe *et al.*, 1985; Recous *et al.*, 1988). Thus the low nitrifying potential of a soil can lead to high immobilisation (Nannipieri *et al.*, 1990). Most Waikato soils have a high nitrification potential due to the presence of allophanic minerals (Baber, 1978; Sarathchandra, 1978). These soils are expected to have low immobilisation potential and hence a high  $\text{NO}_3\text{-N}$  build-up in soil. Nevertheless,  $\text{NO}_3\text{-N}$  build-up in soil also depends on season and is substantially reduced during cold (autumn and winter) and dry (summer) weather conditions due to lower nitrification rates.

Intensively grazed land in the Waikato region typically comprises a well established clover-based pasture. Under Waikato conditions, a well established clover-based pasture could contribute approximately 200 kg N ha<sup>-1</sup> y<sup>-1</sup> to soil-N, although certain cultivars are capable of fixing up to 280 kg N ha<sup>-1</sup> y<sup>-1</sup> (Ledgard *et al.*, 1990). In the absence of livestock, N fixed by clover is in the form of organic-N and is unlikely to cause  $\text{NO}_3\text{-N}$  build-up in soil.

## Animal excreta

Urine deposition has been identified as the major source of  $\text{NO}_3\text{-N}$  loss by leaching from pasture (Walker, 1956; Quin, 1982). Such major losses by leaching do not occur from ungrazed grassland (Foster *et al.*, 1982). Ryden *et al.* (1984) demonstrated that the amount of  $\text{NO}_3\text{-N}$  leached below a grass sward grazed by cattle was 5.6 times greater than that leached below a comparable cut sward. Under grazing the source of N is unimportant - when inputs of N from fertiliser and clover are similar there is little difference in  $\text{NO}_3\text{-N}$  leached (Jarvis, 1990; Cuttle, 1992).

The typically large volume of urine voided per urination by dairy and beef cows applies N at rates of up to 970 kg N ha<sup>-1</sup> under New Zealand conditions (Steele 1982). Sheep return N at lower rates (480 kg N ha<sup>-1</sup>) (Doak, 1952). Most N in urine is urea, and this urea is rapidly hydrolysed to  $\text{NH}_3$  in soil. Some of the  $\text{NH}_3$  may be volatilised (Ball *et al.*, 1979), with the

remainder being nitrified to  $\text{NO}_3\text{-N}$ . Since the amount of  $\text{NO}_3\text{-N}$  in these urine patches is much greater than  $\text{NO}_3\text{-N}$  used by pasture, the excess  $\text{NO}_3\text{-N}$  is at risk of being leached.

Intensive dairying has greater potential to leach  $\text{NO}_3\text{-N}$  than intensive sheep farming. Leaching occurs whenever water drains down the soil profile, but rates tend to be highest in winter because of wet soils and low  $\text{NO}_3\text{-N}$  uptake rates by pastures. Soil factors such as friable texture and earthworms that promote pasture growth may also exacerbate  $\text{NO}_3\text{-N}$  leaching down channels in the soil.

During milking periods about 8% of the excreta is deposited in milking sheds. Most dairy shed 'waste' is water (more than 95%) that has been used for washing. Liquid 'wastes' are either applied onto land or treated and disposed into surface water bodies. Disposal of liquid 'waste' may be a problem due to the large volumes generated. When managed poorly, land application of 'waste' can cause leaching of  $\text{NO}_3\text{-N}$  into ground water.

### Nitrogen fertiliser

The use of nitrogenous fertilisers is steadily increasing in New Zealand. When used in excess,  $\text{NO}_3\text{-N}$  accumulates in soil and causes substantial leaching loss of applied-N. Dairy farming in New Zealand often relies on nitrogenous fertilisers to increase soil  $\text{NO}_3\text{-N}$  levels and to compensate a natural reduction in soil  $\text{NO}_3\text{-N}$  during autumn and winter. During wet conditions residual  $\text{NO}_3\text{-N}$  may be washed down below the root zone to reach the water table. However, heavy rainfall immediately following the application of fertiliser N may contribute directly to  $\text{NO}_3\text{-N}$  pollution of ground water and surface water, because leaching and surface runoff remove applied-N before it can be absorbed.

Three New Zealand studies have examined leaching losses in grazed pastures with or without N fertiliser addition (Appendix I). In all cases, the application of N fertiliser enhanced pasture and animal production, and increased  $\text{NO}_3\text{-N}$  leaching. Associated analyses indicated that much of this extra  $\text{NO}_3\text{-N}$  in leachate was not from direct leaching of fertiliser N, but was from urine-N after uptake into pasture and consumption by grazing animals. Increased N fertiliser input simply increases N flow in a dairy pasture system, which in turn increases  $\text{NO}_3\text{-N}$  leaching potential (Jarvis *et al.*, 1989). The leaching losses from N fertilised pastures in Appendix I are similar to those measured under grazing in the U.K. (Garwood and Ryden, 1986; Jarvis *et al.*, 1989).

There is an important role for strategic use of N fertiliser in intensive farming systems in New Zealand. However, regular application of N fertiliser at rates similar to those used on European grassland seems inappropriate in view of our favourable climate for clover growth and  $\text{N}_2$  fixation. Various studies on flat land (e.g. Field *et al.*, 1985; Crush *et al.*, 1982) have shown that increasing N fertiliser inputs lead to decreasing  $\text{N}_2$  fixation by legumes due to partial replacement of N fixation by fertiliser N and to increased competition by grasses.

### Septic tanks or sewage outflows

After the introduction of reticulated sewage systems in many parts of the region, the threats to ground water from sewage systems are relatively small. However, some coastal settlements on the Coromandel Peninsula have elevated ground water  $\text{NO}_3\text{-N}$  levels that may be attributable to the number and spacing of septic tanks.

### (a) Extent of ground water NO<sub>3</sub>-N pollution

Except for hill country areas such as Te Kuiti, western coastal catchments, and the Taupo Basin, most of the Waikato region has been studied for ground water quality. Nitrate-N data are available for the north Waikato (Ringham *et al.*, 1990), Hamilton Basin (Hoare, 1986; Marshall, 1986), Tokoroa (Bird, 1987), Piako catchment (Hadfield, 1993), and Coromandel Peninsula (Selvarajah, 1993a). Except for the Coromandel study all the others have been terminated. The Coromandel investigation is currently performed on a quarterly basis at 30 different locations.

Approximately half of the bores sampled in the Hamilton Basin have NO<sub>3</sub>-N levels > 10 mg L<sup>-1</sup> (Appendix II). In contrast, most bores in the Piako catchment, north Waikato (south of Pukekohe), and Coromandel areas have little or no NO<sub>3</sub>-N. This is surprising because some of these areas are used for intensive farming and receive relatively high N input. Low NO<sub>3</sub>-N levels in these areas can be attributed to greater use of deeper aquifers, and to soil and/or water reducing conditions.

It has been well established that NO<sub>3</sub>-N levels generally decline with increasing depth (Trudell *et al.*, 1986; Hallberg, 1989; Postma and Boesen, 1991). Our data indicate a similar trend (Figure 2). Various hypotheses have been proposed to explain the vertical distribution of NO<sub>3</sub>-N in ground water. High NO<sub>3</sub>-N levels in shallow unconfined aquifers may be attributed to greater dissolved oxygen levels and the proximity of the NO<sub>3</sub>-N source. The absence of NO<sub>3</sub>-N at greater depth has been attributed previously to the presence of denitrifying bacteria (Behnke and Haskell, 1968). Recent papers emphasise that in addition to anaerobic conditions and the presence of heterotrophic bacteria, the denitrification process requires an electron donor such as dissolved organic-C (DOC) (Postma and Boesen, 1991; Korom, 1992). Consequently, DOC is the main factor limiting denitrification of NO<sub>3</sub>-N in ground water. However, in the absence of DOC other electron donors such as Fe<sup>2+</sup> and Mn<sup>2+</sup> can enhance the denitrification process through autotrophic bacteria (Korom, 1992).

Ground water scientists have frequently observed that ground water containing Fe<sup>2+</sup> has little or no NO<sub>3</sub>-N (Postma and Boesen, 1992). Regardless of the depth of ground water, many ground waters in the Waikato region contain high Fe<sup>2+</sup> levels. Of the known bores in the Waikato region with Fe<sup>2+</sup> > 0.2 mg L<sup>-1</sup>, over 90% have less than 1 mg NO<sub>3</sub>-N L<sup>-1</sup> (Appendix III). However, the absence of NO<sub>3</sub>-N in ground water cannot be attributed entirely to autotrophic denitrification in ground water. Many areas in the Waikato region have reduced soil conditions (e.g. peat and gley soils in the Lower Piako catchment; Appendix II). Soils with a moisture content near saturation or a high water table are able to reduce NO<sub>3</sub>-N due to prevailing anaerobic conditions (Barkle *et al.*, 1993).

Ground water NO<sub>3</sub>-N levels decrease from the southern Piako towards the north (Firth of Thames) (Figure 3). In the south, greater NO<sub>3</sub>-N levels are detected in the shallow sand and gravel aquifers, whereas fine-grained silt and clay sediments in the north provide reduced conditions conducive for NO<sub>3</sub>-N reduction. Higher NH<sub>4</sub>-N concentrations found in the northern part of this catchment suggest a possible mechanism of dissimilatory NO<sub>3</sub>-N reduction to NH<sub>4</sub>-N in ground water or low nitrification rates in soil.

Figure 2 clearly indicates that except for the Hamilton Basin, other areas may have NO<sub>3</sub>-N contamination at greater depths. In the case of north Waikato bores, NO<sub>3</sub>-N contamination occurs at considerable depths (e.g. >100 m). High use of fertiliser-N and intensive cultivation

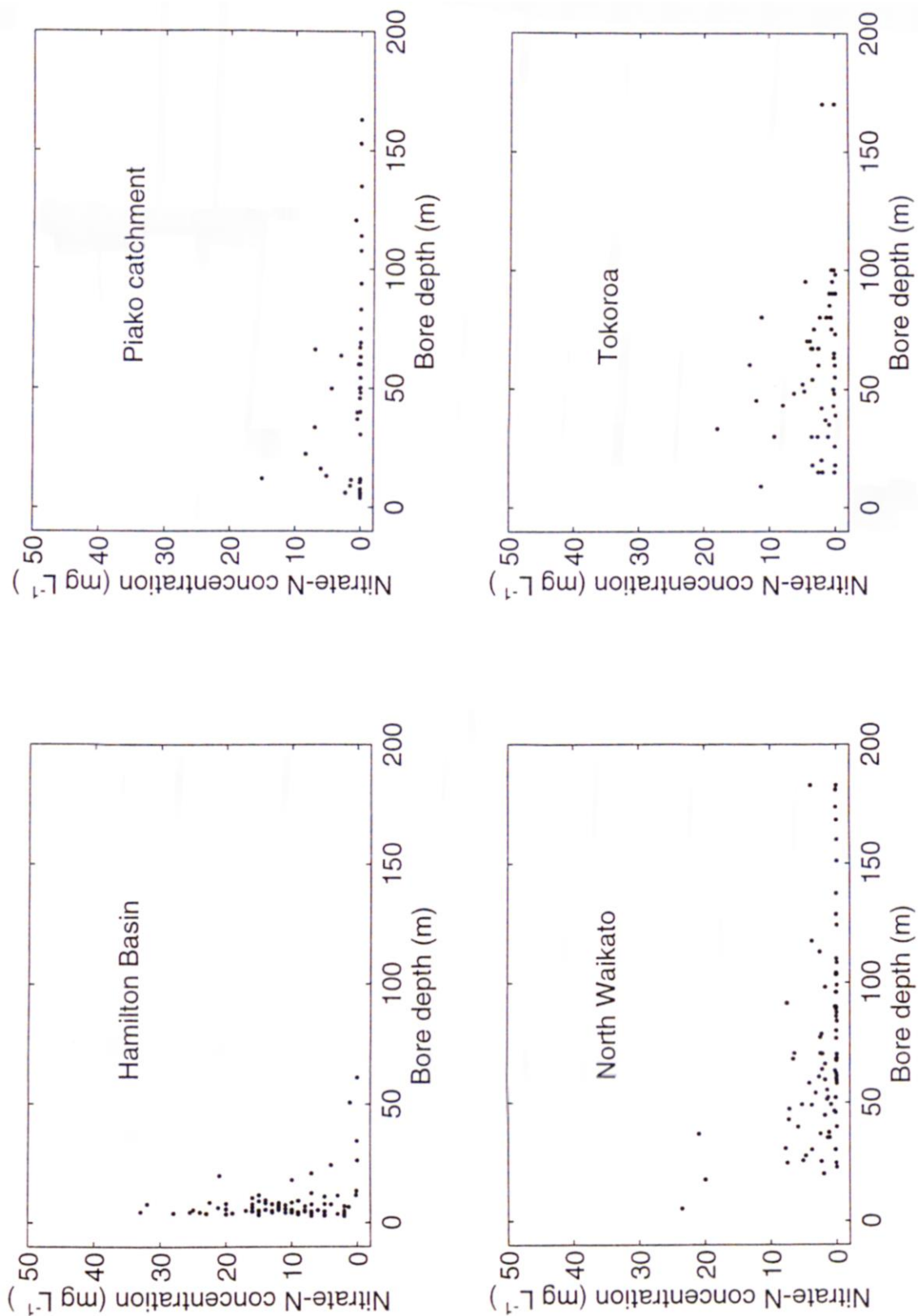


Figure 2. Nitrate-N concentration versus bore depth for selected areas in the Waikato region.

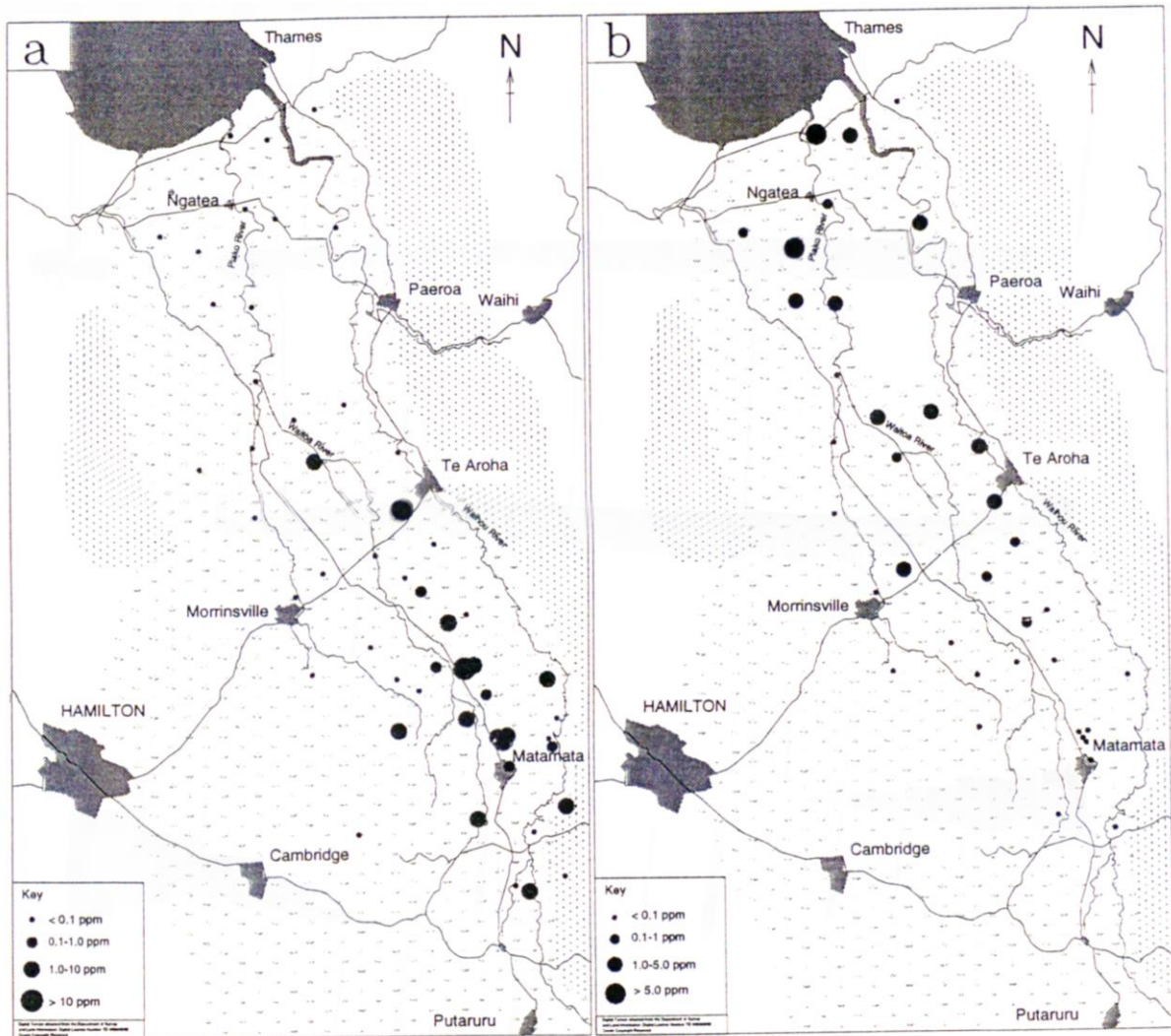


Figure 3. Distribution of (a) nitrate-N concentrations and (b) ammoniacal-N concentrations in the Piako catchment (after Hadfield, 1993).

practices are considered to be the main source of  $\text{NO}_3\text{-N}$  pollution in the market gardening and intensive horticultural areas of the north Waikato (south of Pukekohe) (where most bores are  $>50$  m deep). However, it should be emphasised that the presence of  $\text{NO}_3\text{-N}$  in deeper bores may not always indicate that deeper aquifers are polluted. The casing of some deep bores can allow mixing of shallow and deep ground water.

Even if bores are cased appropriately to exclude shallow aquifer sources, large abstraction volumes taken from deep bores may induce leakage from overlying shallow aquifers, and hence allow mixing of  $\text{NO}_3\text{-N}$  contaminated shallow ground water with deeper uncontaminated aquifers. Consequently, the construction and use of deeper bores may not provide a satisfactory alternative to the use of  $\text{NO}_3\text{-N}$  contaminated shallow aquifers.

### (b) Case study - Non-point source

Ground water  $\text{NO}_3\text{-N}$  data have been collected from Environment Waikato's electronic data base, technical reports, and resource monitoring data sets. Apart from the resource consent

monitoring programmes, most data have been collected for catchment based ground water studies rather than for state of the environment (SOE) monitoring. The only SOE monitoring

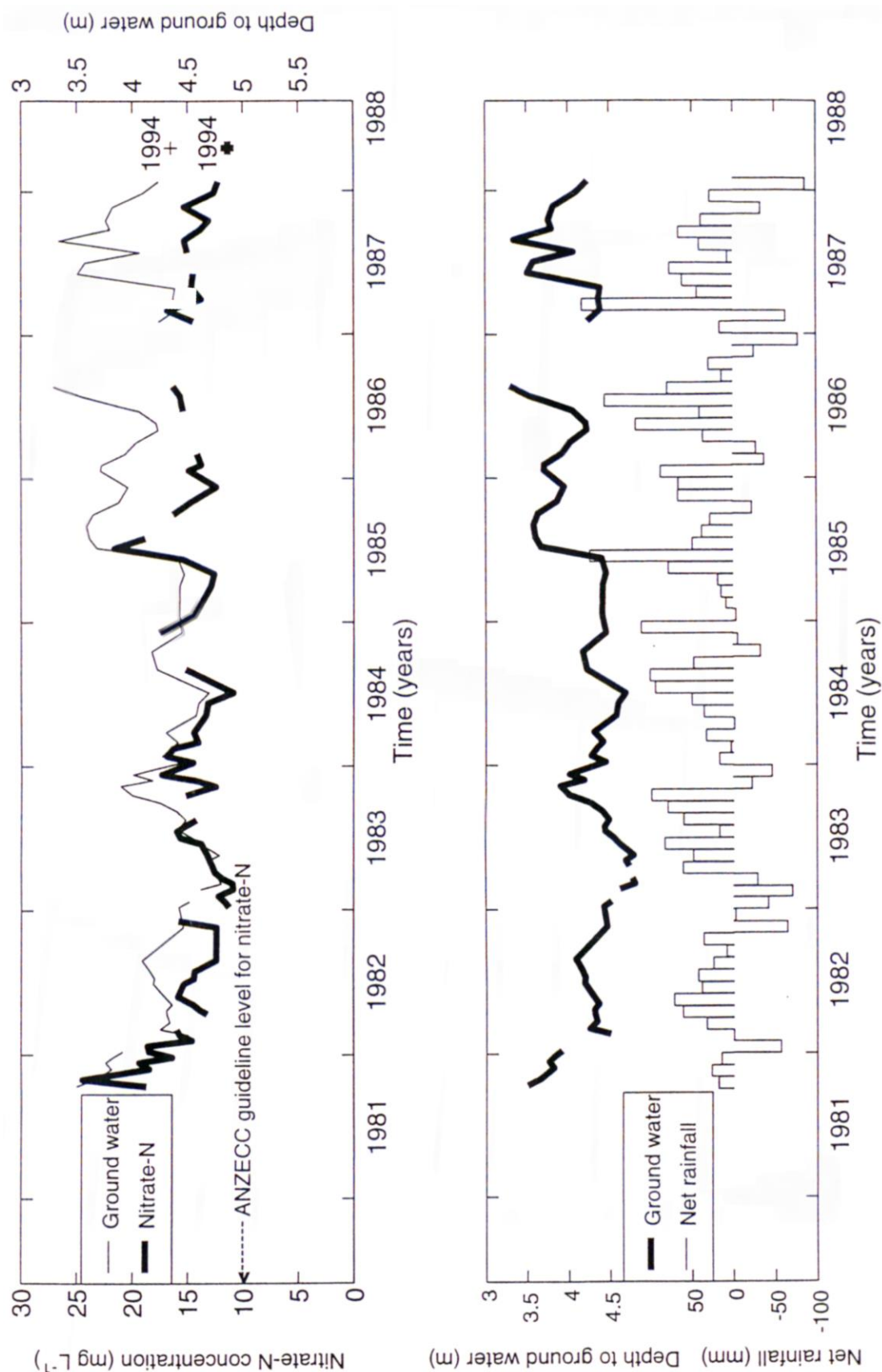


Figure 4. Average nitrate-N concentration and ground water level for 8 selected wells in the Hamilton Basin.

performed on a regular basis was a monthly ground water NO<sub>3</sub>-N data collection programme which monitored 12 different wells and 2 bores in the Hamilton to Cambridge area (Figure 1) from October 1981 to February 1988. Data from 6 sites were omitted from the analysis of non-point sources of NO<sub>3</sub>-N, because these sites were either (a) located near a known point source of NO<sub>3</sub>-N contamination or (b) a deep bore with NO<sub>3</sub>-N levels typically below detection limits. The remaining 8 sites were originally chosen on the basis of higher than average NO<sub>3</sub>-N levels, and therefore, may provide a slight overestimate of spatially averaged NO<sub>3</sub>-N levels in the sampling area. The sampling area is representative of the Hamilton Basin, which covers an area of 2040 km<sup>2</sup> centred around Hamilton City. Land use in the Hamilton to Cambridge sampling area comprises dairying; small drystock farms; horticulture; cropping (especially maize); and rural residential blocks.

Figure 4 illustrates the fluctuation of ground water and NO<sub>3</sub>-N levels for the sampling period. Changes in NO<sub>3</sub>-N in shallow (< 10 m depth) aquifers in the Hamilton Basin correspond generally with ground water levels ( $r = 0.53$ ;  $P < 0.01$ ). Ground water NO<sub>3</sub>-N levels are consistently greater than 10 mg L<sup>-1</sup> but less than 25 mg L<sup>-1</sup>. Ground water level increases following winter rainfall (June/July) to reach a typical peak value in August/September. Net rainfall provides the driving force for NO<sub>3</sub>-N contamination in these shallow aquifers (Hall, 1992). However, a rapid decline of ground water NO<sub>3</sub>-N appears to correspond with relatively stable ground water levels - indicating a reduction in the rate of NO<sub>3</sub>-N leaching.

Nitrate-N levels and ground water levels (Figure 4) in February 1994 (one-off sampling run) are very similar to those measured in February 1988. Consequently, it may be assumed that non-point sources of NO<sub>3</sub>-N in the Hamilton Basin sampling area remain unchanged since monitoring began in October 1981.

Figure 5 shows a schematic representation of changing ground water NO<sub>3</sub>-N concentration and ground water level for a shallow, idealised aquifer in the Hamilton Basin. Nitrate-N leaching to the aquifer is estimated from the difference in NO<sub>3</sub>-N concentration, water level change and aquifer storage, and NO<sub>3</sub>-N outflow as a component of ground water outflow to surface waters. Consequently, NO<sub>3</sub>-N leaching to shallow aquifers in the Hamilton Basin is as follows:

$$(\text{NO}_3\text{-N})_l = 10000 ((\text{NO}_3\text{-N})_{\text{final}} \times W_{\text{final}} \times S) - 10000 ((\text{NO}_3\text{-N})_{\text{initial}} \times W_{\text{initial}} \times S) + 10000 \frac{((\text{NO}_3\text{-N})_{\text{initial}} + \text{NO}_3\text{-N}_{\text{final}})/2 \times q_t}{[1]};$$

where (NO<sub>3</sub>-N)<sub>l</sub> is mass nitrate-N per hectare leaching to the aquifer (g ha<sup>-1</sup>);

(NO<sub>3</sub>-N)<sub>initial</sub> is nitrate concentration at time zero (g m<sup>-3</sup>);

(NO<sub>3</sub>-N)<sub>final</sub> is nitrate concentration at some later time (g m<sup>-3</sup>);

W<sub>initial</sub> and W<sub>final</sub> are initial and final ground water level (m);

S is aquifer storativity; and

q<sub>t</sub> is ground water outflow (m) during time,  $t = t_{\text{final}} - t_{\text{initial}}$ .

Assuming an average storativity of 0.1 for the generally poorly sorted sediments (Sherwood, 1972) of these shallow alluvial aquifers, and using an average ( $n = 150$ ) aquifer thickness of approximately 7 m (Figure 5) gives an estimate of NO<sub>3</sub>-N leaching for the period 3 May to 8 July 1985:

$$(\text{NO}_3\text{-N})_l = 10000 (21.7 \times 4.325 \times 0.1) - 10000 (12.7 \times 3.538 \times 0.1) + 10000 \frac{((12.7 + 21.7)/2) \times 0.053}{[1]}$$

$$\begin{aligned}
 &= 93852.5 - 44932.6 + 9116 \\
 &= 58035.9 \text{ g ha}^{-1}
 \end{aligned}$$

Annual  $\text{NO}_3\text{-N}$  leaching may be greater than  $58 \text{ kg NO}_3\text{-N ha}^{-1}$  if allowance is made for  $\text{NO}_3\text{-N}$  influx during periods of apparent  $\text{NO}_3\text{-N}$  reduction. This conservatism allows for error in the estimate of aquifer storativity, which because of the mixture of grain sizes present in the various strata (Table 1), is likely to vary between 0.05 and 0.15. Furthermore, as the sampling area is used only partially for intensive farming,  $\text{NO}_3\text{-N}$  leaching from grazed pasture in the Hamilton Basin is likely to be greater than  $58 \text{ kg NO}_3\text{-N ha}^{-1} \text{ y}^{-1}$ . This estimate is in close agreement with an estimate of annual  $\text{NO}_3\text{-N}$  leaching ( $59 \text{ kg NO}_3\text{-N ha}^{-1} \text{ y}^{-1}$ ) obtained using all periods (1981 to 1988) of apparent  $\text{NO}_3\text{-N}$  increase (Figure 4).

Using a similar approach to Equation [1], a decrease in ground water  $\text{NO}_3\text{-N}$  levels of  $280 \text{ g d}^{-1}$  is apparent during a 5 month period of declining  $\text{NO}_3\text{-N}$  levels. It is suspected that dilution is the main mechanism for decreases in  $\text{NO}_3\text{-N}$  levels. Ground water outflow contributes most of the flow of rivers and streams in the Waikato region, and therefore, most of the  $\text{NO}_3\text{-N}$  entering shallow aquifers in the region eventually reaches surface waterways.

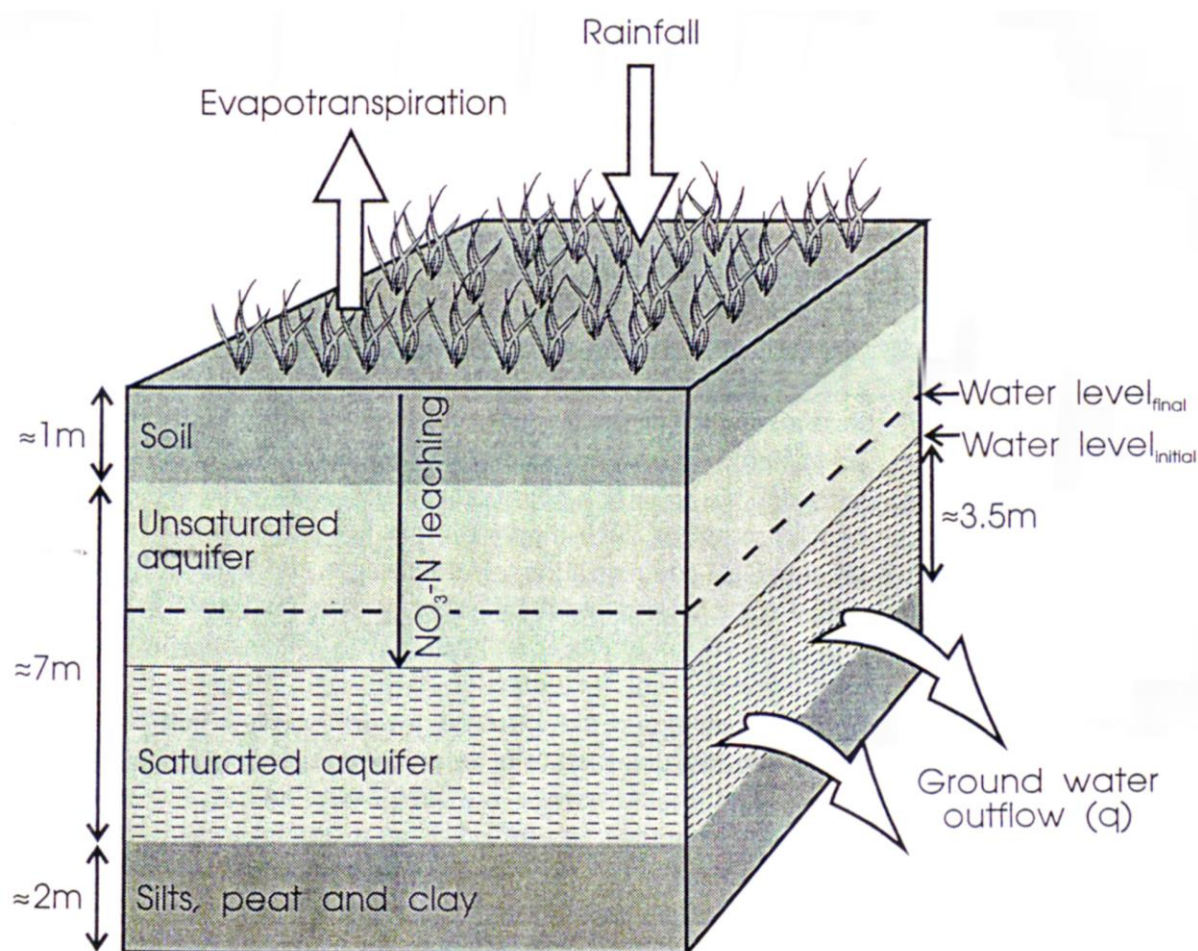


Figure 5. Schematic representation of nitrate leaching in an idealised aquifer.

Table 1. Typical stratigraphic sequence for shallow sediments in the Hamilton Basin.

Depth from ground surface (m)	Lithology
1	soil
8	rhyolitic and pumiceous sands and gravels
10	Silt, clay, peat
15	pumiceous sands and gravels
>15	Pumiceous sands and gravels with layers of silt, clay and peat

## (2) Ground water NO<sub>3</sub>-N contamination caused by point sources in the Waikato region

It was common practice a decade ago for many industries to discharge their effluent into waterways. Dairy factories, tanneries, rendering plants, meat processing plants, sewage treatment plants, wood treatment plants, dairy sheds and piggeries are some examples. Former catchment authorities placed pressure on many of these waste generators, and consequently, land application of waste became popular. Currently, Environment Waikato strongly encourages waste water disposal onto land.

### (a) Discharge to waterways

Despite the increasing number of resource users who discharge waste water to land, many waste generators are still using surface water as a receiving environment for waste disposal. There are about 30 major permanent discharges to the Waikato River from various industries. Many of these discharges are sewage outfalls. For example, the Hamilton City sewage outflow carries on average 1.3 t N d<sup>-1</sup>. Apart from these direct discharges, the Waikato River receives N from other rivers and streams and subsurface flow of ground water. Another source of N for the Waikato River is surface runoff and storm water produced from paved areas. It is estimated that on average the Waikato River discharges about 10.5 t dissolved inorganic N (DIN) d<sup>-1</sup> into the Tasman Sea at Port Waikato. The amount of total-N transported would be many fold higher than the estimated daily DIN amount. Since the volume of water flow is large in Waikato River, the concentration of DIN is only 0.3 mg L<sup>-1</sup>. Small rivers or streams in the Waikato region have greater DIN concentrations. For example, the Waitoa River DIN level is 4.0 mg L<sup>-1</sup>. An estimated 0.4 t DIN d<sup>-1</sup> is discharged by the Waitoa River into the Piako River.

Although high treatment standards are required for treating waste prior to surface water disposal, the large volume of waste generated results in a large mass loading in waterways. For example, the concentration of a major sewage outflow described in the preceding paragraph is only 33 mg total-N L<sup>-1</sup>. In contrast an outflow from a typical treated dairy shed effluent pond system contains 200 mg total-N L<sup>-1</sup>. Nevertheless, considering the small volume of 'waste' (10 m<sup>3</sup> d<sup>-1</sup>) discharged, the daily N loading to surface water from a dairy farm will be 0.002 t d<sup>-1</sup>. Consequently, on a daily basis, the waste-N from a major sewage outfall is equivalent to the 'waste-N' from 650 dairy farms.

### *(b) Discharge to land*

#### Dairy shed effluent

Currently, many industries in the Waikato region are using land for waste water disposal. Most of these industries still use surface water for waste discharge during part of the year. One of the major waste water generators in the Waikato region is the dairy industry. There are more than 6000 dairy farms with an average herd size of 185 cows and 10 dairy factories in the Waikato region. More than 4000 of these farms had been disposing treated effluent into waterways until the 1990s. The treatment systems comprise either a barrier ditch or oxidation pond system. Approximately two-thirds of the 4000 farms described previously have oxidation pond systems. These systems have been constructed and maintained according to Ministry of Agriculture and Fisheries specifications (Ministry of Agriculture and Fisheries, 1991). Although these systems are capable of reducing total-N in dairy shed effluent by 75%, the discharge from these systems is generally of poor quality (Taranaki Regional Council, 1990). More than 50% of the N in the raw dairy shed effluent is urea-N. Removal of urea-N does not require any treatment system since it can be hydrolysed and volatilised rapidly as ammonia gas within 1-2 days. Thus the 75% removal of total-N attained by oxidation ponds is mainly due to  $\text{NH}_3$  volatilisation. The N treatment efficiency of the ponds is only 50% of the residual N after  $\text{NH}_3$  volatilisation loss of N.

Recently, there has been a substantial move towards land application of dairy shed effluent by dairy farmers. Environment Waikato's transitional regional plan for dairy shed effluent management has proposed land disposal of dairy shed effluent as a permitted activity (i.e. does not require a resource consent). The proposal is currently being reviewed by Environment Waikato after a hearing to consider submissions from the public and other organisations. The current statistics indicate that many dairy farmers are changing from pond systems to dairy shed effluent irrigation systems. Among the 5571 dairy farms surveyed in the 1992-1993 season in the Waikato region, 33.2% of the farms were disposing dairy shed effluent onto land. This was a 16.3% increase from the 1991-1992 survey conducted on 5427 dairy farms where 29.3% of the farms used land based disposal. The 1993-1994 season survey currently in progress shows that among the 2474 farms surveyed to date, 37.5% are using a land based disposal system. Future projected dairy shed effluent disposal to land is much higher and within the next 3 seasons it is anticipated that more than 50% of dairy farms in the Waikato region will use a land based disposal system.

Although the land application of dairy shed effluent will be a permitted activity, careful consideration has been given to hydraulic and N loading of the effluent applied onto land. A recommendation for N loading ( $100 \text{ kg ha y}^{-1}$ ) for a well established clover based pasture has been determined using a rigorous N budget for a typical dairy farm in the Waikato region (Selvarajah, 1993b). The N loading is currently under review by Environment Waikato's Hearings Committee. Once the decision is made, a specific N loading rate will be approved as part of the condition for land application of dairy shed effluent. However, considering the relatively small volume of 'waste' water generated, coupled with the large land area available at most dairy farms, the N loading due to dairy shed effluent land application will be minor compared to most industrial waste loading onto land.

#### Industrial waste

In an attempt to save waterways from excessive nutrient loading and depleted dissolved oxygen levels caused former catchment authorities to grant very lenient hydraulic and nutrient loading rates for land application of waste. Industrial wastes can vary substantially in the composition and concentration of N. Characteristics of these wastes have been well documented (Hart and

Selvarajah, N., Maggs, G.R., Crush, J.R. and Ledgard, S.F. 1994. Nitrate in ground water in the Waikato region. *In The Efficient Use of Fertilizers in a Changing Environment: Reconciling productivity with sustainability.* (Eds. L D Currie and P Loganathan). Occasional Report No. 7. Fertilizer and Lime Research Centre, Massey University, Palmerston North, pp 160-185.

Speir, 1992). The rationale for land application of a waste was often based on engineering principles, hence the main objective was to avoid surface runoff of irrigated waste water into drains or streams. Well drained soils have often been preferred over poorly drained counterparts to achieve rapid infiltration of waste water. Waste water irrigation is often performed regardless of wet weather conditions. Most of these waste waters contain a high level of N. Consequently, the nutrient loading problem has been gradually shifted from surface water to ground water resources.

### Case study - Point source

Land application of dairy factory waste water in the Hamilton Basin has been taken here as an example of the effect of high N waste loading (and high volume) on the receiving environment. The dairy factory waste water disposal operation involves several dairy farms. Only one farm has been considered for the current discussion. The farm size is 140 ha with a herd of 300. The soil is predominantly Horotiu sandy loam, although some parts of the farm have Te Kowhai silt loam. Pasture comprises ryegrass with little or no clover. A fixed sprinkler irrigation system was installed in 1968, with an initial disposal area of 56 ha. This irrigation area has been used extensively since 1969. The irrigation system was replaced in the early 1980s and 110 ha of the 140 ha area is now used for irrigation. Irrigation is carried out soon after the grazing is completed.

The waste water characteristics are given in Table 2. Average annual loading of N applied is 1200 kg ha<sup>-1</sup>. The waste water disposal operation holds a current consent, first issued by the Waikato Valley Authority in 1978 which has been reviewed twice and will expire in 1997. The consent holder is authorised to discharge waste water up to 2700 m<sup>3</sup> d<sup>-1</sup> over any 20 day period. Special conditions attached to this consent require the system to be operated in accordance with a waste management plan. The consent holder is required to provide Environment Waikato with irrigation records (including whey equivalents and total-N data) and NO<sub>3</sub>-N and NH<sub>4</sub>-N levels for a network of shallow piezometers located beneath and adjacent to the disposal area. Nitrate-N data are available for the Mangaone Stream adjacent to the farm at sites upstream and downstream of the disposal area.

Table 2. Waste water characteristics for a selected 2 ha paddock at the effluent disposal site (1985-1993).

Irrigation Season	Hydraulic loading (mm)	NO <sub>3</sub> -N (mg L <sup>-1</sup> )	Total-N (mg L <sup>-1</sup> )
1985/86	582	*	*
1986/87	565	*	*
1987/88	434	16	261
1988/89	453	42	300
1989/90	550	51	267
1990/91	459	52	247
1991/92	502	49	222
1992/93	522	67	215

\* missing value

Ground water NO<sub>3</sub>-N and ground water levels have been monitored on an approximate monthly basis at 18 piezometers. Continuous data are available for only 4 piezometers for the period June 1982 to January 1994. However, a continuous record has been synthesised at a further 4 piezometers using simple linear regression to estimate values for the missing record (about 10% of the complete record). Figure 6 shows mean water levels and ground water NO<sub>3</sub>-N levels for the 8 piezometers. The total-N data include 64 values estimated from the very strong relationship ( $r = 0.97$ ;  $P < 0.01$ ) between whey equivalents and total-N. Monthly net recharge of ground water has been estimated as in equation [2].

$$R = (I + P) - E_T \quad [2];$$

where R is net recharge of ground water (or net hydraulic loading) (mm);

I is waste water irrigation (mm);

P is precipitation (mm); and

E<sub>T</sub> is potential evapotranspiration<sup>1</sup> for the Hamilton Basin (mm).

<sup>1</sup> As site specific evapotranspiration data are not readily available and because annual variations in monthly evapotranspiration data have a negligible effect on the recharge estimate, long-term (normal) evapotranspiration data were estimated using raised pan evaporation estimates at Ruakura, Hamilton. Pan evaporation data have been reduced by a factor of 0.73 (Finkelstein, 1973).

The N in the waste water comprises mainly organic-N and NO<sub>3</sub>-N (Table 2). Nitrate-N is derived from nitric acid (HNO<sub>3</sub>) used in the cleaning process. Approximately 40 t y<sup>-1</sup> of elemental-N is contributed by the use of HNO<sub>3</sub>. The amount of NO<sub>3</sub>-N present in the waste water reached a peak in the 1992/93 season.

#### *Effect on ground water quality*

Ground water NO<sub>3</sub>-N levels have increased markedly during the last decade under grazed pasture applied with dairy factory waste water. There has been a steady increase in ground water NO<sub>3</sub>-N levels since detailed monitoring commenced. Within 3 seasons of waste water application, NO<sub>3</sub>-N increased 4 fold, from approximately 10 to 40 mg L<sup>-1</sup>. The ground water NO<sub>3</sub>-N levels attained a peak of approximately 70 mg L<sup>-1</sup> following the 1990/91 season (Figure 6).

There is no obvious seasonal pattern during the steady increase of ground water NO<sub>3</sub>-N until the 1987/88 season. Since the 1987/88 season, ground water NO<sub>3</sub>-N has followed a seasonal cycle of NO<sub>3</sub>-N build-up and decrease. Peak NO<sub>3</sub>-N levels are usually attained early (February-March) in a calendar year. The annual N loading does not appear to have a direct influence on either the peak NO<sub>3</sub>-N levels ( $r = 0.09$ ; not significant) in ground water or average NO<sub>3</sub>-N levels during an irrigation season ( $r = 0.18$ ; not significant). For example, a high total-N loading (155.1 t y<sup>-1</sup>) during the 1988/89 season corresponds with a NO<sub>3</sub>-N peak of 58 mg NO<sub>3</sub>-N L<sup>-1</sup>. In contrast, the 1990/91 season had a loading of 127.3 t total-N y<sup>-1</sup> and attained a peak of 68 mg NO<sub>3</sub>-N L<sup>-1</sup>.

There is an approximate 5 month lag between ground water NO<sub>3</sub>-N concentration and ground water levels beneath the effluent disposal site. It may be inferred that large increases in NO<sub>3</sub>-N levels are related to peak hydraulic loading rates (e.g. 218 mm net rainfall and 29 mm irrigation during August 1990) and supply of total-N. For example, at this site, Barnett and

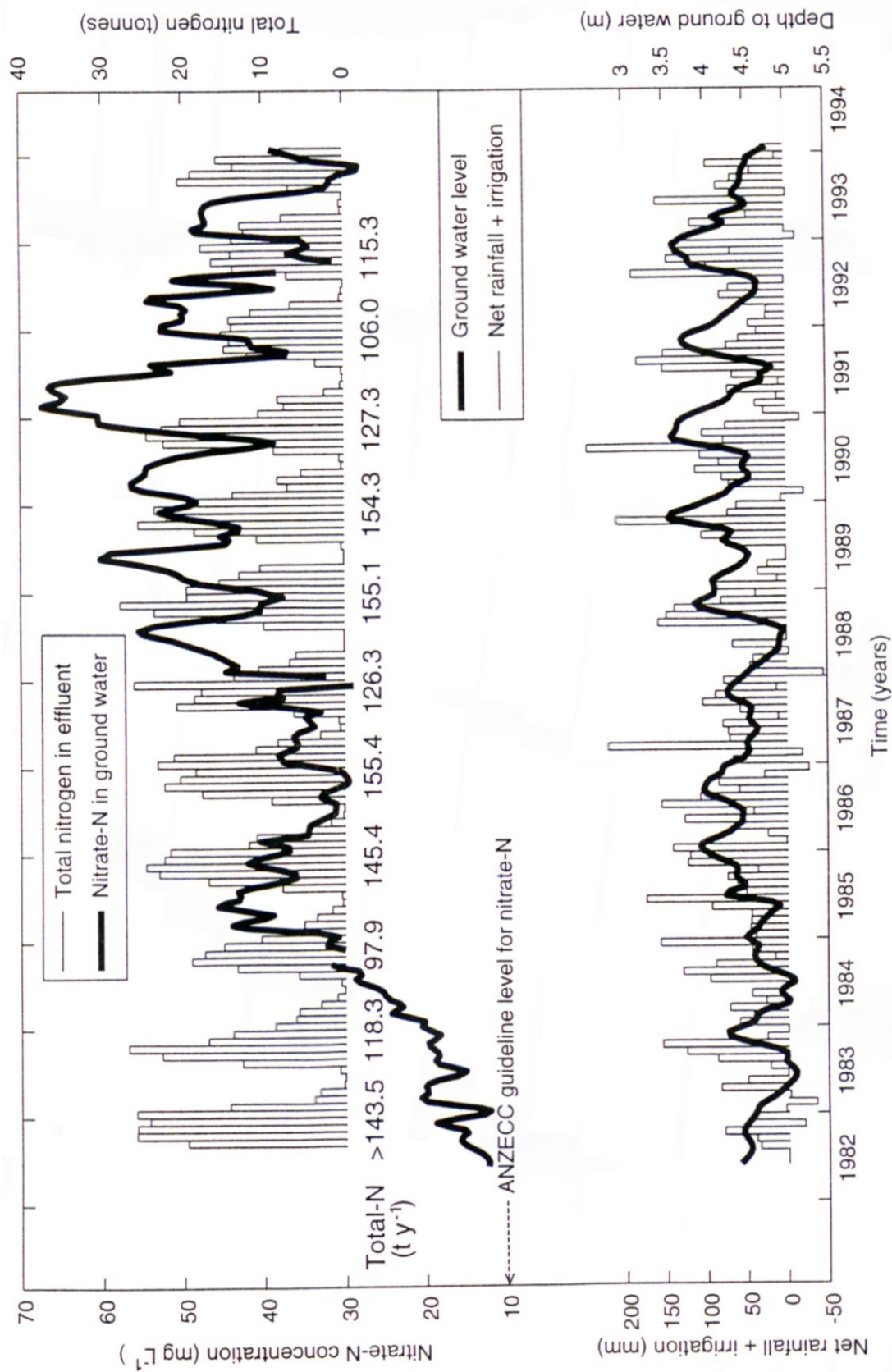


Figure 6. Effect of dairy factory waste water and rainfall on ground water beneath grazed pasture in the Hamilton Basin.

Parkin (1985) report  $\text{NO}_3\text{-N}$  levels above  $400 \text{ mg L}^{-1}$  in soil water at 30 cm depth in the Horotiu sandy loam. At this depth in the soil profile, peak  $\text{NO}_3\text{-N}$  levels typically occur from February to April. Nitrate-N levels in ground water decline very rapidly corresponding with the end of each irrigation season (June/July) because of moderate to large net rainfall occurring during this period. Sharp reductions in ground water  $\text{NO}_3\text{-N}$  may be due principally to dilution, corresponding with rising ground water levels and increasing  $\text{NO}_3\text{-N}$  in the adjacent stream. Ground water denitrification may also contribute towards  $\text{NO}_3\text{-N}$  loss from the system.

Beyond the boundaries of the effluent disposal site several monitoring sites (including water supply wells) have increased from background levels (e.g.  $< 0.5 \text{ mg NO}_3\text{-N L}^{-1}$  in 1982) to  $> 40 \text{ mg NO}_3\text{-N L}^{-1}$  in 1994. Furthermore, at the boundary of the disposal site, 3 piezometers not used in Figure 6 had  $\text{NO}_3\text{-N}$  concentrations of 63, 68, and  $77 \text{ mg L}^{-1}$  respectively in December 1993.

#### *Effect on water quality of the Mangaone Stream*

In most cases ground water provides base flow for rivers and streams in the Waikato region (approximately  $3000 \text{ m}^3 \text{ ha}^{-1} \text{ y}^{-1}$  in the Hamilton Basin). Dairy factory waste water applied onto pasture has significantly increased  $\text{NO}_3\text{-N}$  levels in the adjacent stream through ground water outflow (Figure 7). On average, downstream  $\text{NO}_3\text{-N}$  levels increased to  $> 20 \text{ mg L}^{-1}$  from an already polluted level upstream of  $> 7 \text{ mg L}^{-1}$  (an increase of 185%). An estimated 13 tonnes ground water  $\text{NO}_3\text{-N}$  enters the stream adjacent to the waste water disposal farm every year. This is a conservative estimate based on stream flow upstream of the disposal site and the estimate does not consider ground water outflow from the disposal site. The increase of  $\text{NO}_3\text{-N}$  downstream generally follows an annual bimodal pattern. Peaks during summer/autumn correspond with periods where ground water contributes a large proportion of stream flow, and peaks during winter correspond with peak ground water  $\text{NO}_3\text{-N}$  levels.

#### *Nitrogen management*

The consent holder has been making efforts to reduce N loading through better N recovery and reduction of  $\text{HNO}_3$  use in the factory. Consequently, total-N in the waste water has been reduced over recent years (e.g. Table 2; Figure 6). Ideally, the use of  $\text{HNO}_3$  should be avoided completely. Alternative chemicals such as phosphoric or sulphuric acid should be considered. However, the environmental impact of these alternative chemicals should not be overlooked (e.g. P accumulation and  $\text{SO}_4$  leaching).

It must be emphasised that a high N loading onto grazed pasture requires careful N balancing. The amount of N removed through milk production is small compared to the large total-N flow in the system (e.g. at a stocking rate of  $2.7 \text{ cows ha}^{-1}$  and milk protein production of  $350 \text{ kg ha}^{-1}$  the approximate annual N removal will be  $60 \text{ kg N ha}^{-1}$ ). With an average N application rate of  $1200 \text{ kg N ha}^{-1} \text{ y}^{-1}$ , this will be only 5% of the N applied onto land. A considerable amount of applied-N can be lost through denitrification, due to high hydraulic loading combined with waste water enriched with carbonaceous materials. Under these conditions, maximum denitrification loss is unlikely to exceed 50% of applied-N. Denitrification losses of up to 30% of applied-N have been recorded from meat processing effluent irrigation with a N loading of about  $1000 \text{ kg ha}^{-1} \text{ y}^{-1}$  (Russell and Cooper, 1992). Using a conservative denitrification loss of up to 50% of applied-N, there will be at least  $570 \text{ kg}$  left as residual-N in the soil annually. Thus it is not surprising that large amounts of  $\text{NO}_3\text{-N}$  leach every year. It becomes clear that the system is overloaded with applied-N, and N loading should be reduced substantially if  $\text{NO}_3\text{-N}$  leaching and ground water contamination are to be reduced.

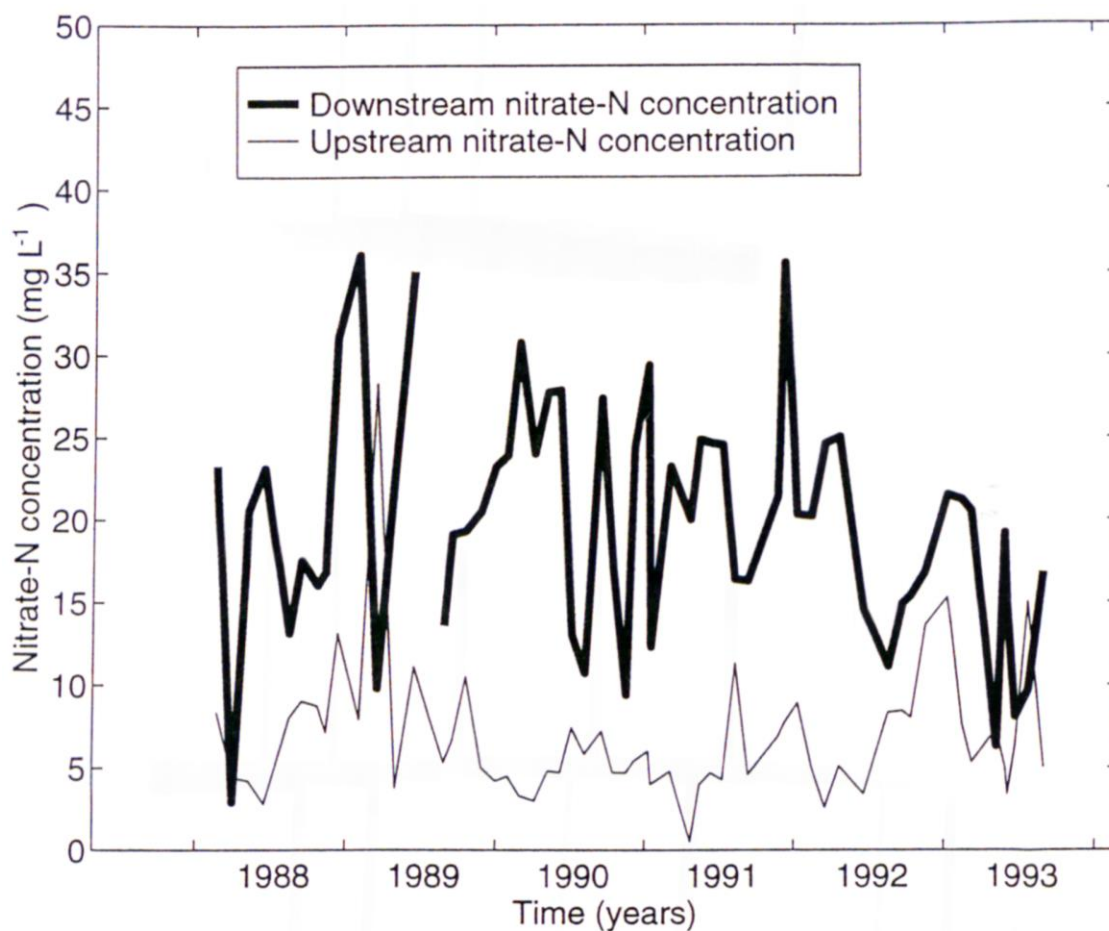


Figure 7. Surface water nitrate-N levels adjacent to a dairy factory waste water disposal area in the Hamilton Basin.

## Conclusions

A substantial amount of N (at least 60 kg N ha<sup>-1</sup> y<sup>-1</sup> as NO<sub>3</sub>-N) is lost through leaching from intensively farmed land in the Waikato region. This occurs during autumn and winter after shallow aquifers are recharged by infiltrating rainfall. Decreases in NO<sub>3</sub>-N levels in shallow aquifers occur mainly through dilution due to ground water recharge and subsurface flow of ground water into streams.

Ground water is polluted with NO<sub>3</sub>-N in many areas of the region. The extent of pollution depends on aquifer characteristics (e.g. aquifer thickness and the presence of confining units) and the occurrence of reducing soil and water conditions. Despite intensive farming, little or no NO<sub>3</sub>-N is found in ground water under reducing conditions (i.e. waters containing >0.2 mg Fe<sup>2+</sup> L<sup>-1</sup>). The full extent of ground water NO<sub>3</sub>-N pollution in the Waikato region will not be known until an extensive ground water monitoring programme is completed. Sampling should be conducted on a regular basis for this monitoring programme. One-off ground water samples obtained for ground water NO<sub>3</sub>-N investigations will be misleading, because ground water

NO<sub>3</sub>-N levels demonstrate significant temporal and spatial fluctuations. It is also recommended that future work be directed at investigating the effects of soil and water reducing conditions on ground water NO<sub>3</sub>-N levels.

Point sources can affect ground water quality adversely when applied-N is managed poorly (e.g. from background levels of 0.5 mg L<sup>-1</sup> (1982) to current levels of 30-70 mg L<sup>-1</sup> (1994)). In such cases ground water monitoring for NO<sub>3</sub>-N in shallow aquifers will not indicate the full extent of NO<sub>3</sub>-N leaching and ground water contamination, because a substantial quantity of leached NO<sub>3</sub>-N is continuously drained into streams (e.g. >13 t NO<sub>3</sub>-N y<sup>-1</sup> are lost from one waste water disposal site through subsurface flow of ground water into the Mangaone stream in the Hamilton Basin). Any proposal to apply waste onto land requires careful consideration, including the development of an appropriate N management strategy. This requirement is necessary especially when nitrogenous waste is applied onto grazed pasture, where most applied-N is recycled in the system and hence is available for NO<sub>3</sub>-N leaching.

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**Appendix I** Leaching losses of  $\text{NO}_3\text{-N}$  from grazed pastures receiving various inputs of N fertiliser. All sites were intensively grazed and on flat land in New Zealand (Ledgard, 1993).

Grazing animal	Pasture	Fertiliser N (kg N ha <sup>-1</sup> y <sup>-1</sup> )	N <sub>2</sub> Fixation (kg N ha <sup>-1</sup> y <sup>-1</sup> )	Leaching Losses		Reference
				Av. conc. (mg $\text{NO}_3\text{-N L}^{-1}$ )	Amount (kg N ha <sup>-1</sup> y <sup>-1</sup> )	
Sheep	Grass-only	0	0	NA	42	Field <i>et al.</i> , 1985
	Grass+clover	0	320	NA	73	
	Grass+clover	110	220	NA	101	
	Grass+clover	450	90	NA	222	
Sheep	Grass+clover	0	140	2.9	7	Ruz-Jerez, 1991
	Grass only	410	0	10.1	26	
Cattle	Grass+clover	0	NA	7.3	88	Steele <i>et al.</i> , 1984
	Grass+clover	172	NA	21.2	193	

NA - Not available

**Appendix II** Factors influencing ground water NO<sub>3</sub>-N levels in the Waikato region for selected areas.

Area	Major land use	Possible source	No. of bores sampled	Bore depth (m)		NO <sub>3</sub> -N (mg L <sup>-1</sup> )			Extent of NO <sub>3</sub> -N reducing conditions	
				Min.	Max.	Min.	Max.	Number of bores with >10 mg L <sup>-1</sup>	Soil	Water
Hamilton Basin	Dairying and drystock	Animal excreta/ N Fertiliser	92	2.9	61	0	33	50	Medium	Medium
Piako	Dairying	Animal excreta/ N fertiliser	41	4.0	163	0	15	1	High	High
North Waikato	Drystock, market gardening and dairying	Animal excreta/ N fertiliser	91	5.2	280	0	24	3	Medium	Medium
Tokoroa	Dairying	Animal excreta/ N fertiliser	55	9.0	170	0	18	5	Low	Medium
Coromandel (Coasts)	Lifestyle blocks and horticulture	N fertiliser/on-site sewage disposal	30	4.0	146	0	25	2	Low	Medium

**Appendix III** Concentration of total iron, acid soluble iron and NO<sub>3</sub>-N in the north Waikato and Piako catchment.

North Waikato			Piako catchment		
Total Iron (mg L <sup>-1</sup> )	Acid Soluble Iron (mg L <sup>-1</sup> )	Nitrate-N (mg L <sup>-1</sup> )	Total Iron (mg L <sup>-1</sup> )	Acid Soluble Iron (mg L <sup>-1</sup> )	Nitrate-N (mg L <sup>-1</sup> )
2.40	2.40	<0.002	47.00	18.70	0.837
2.73	0.24	2.300	4.60	4.30	1.420
0.54	0.41	<0.002	1.19	1.11	0.077
7.10	6.80	0.015	17.20	14.20	0.003
7.13	0.70	0.113	2.90	2.90	2.300
0.60	0.39	0.061	26.00	20.00	0.002
2.10	0.28	0.004	1.55	1.47	0.102
1.30	1.30	0.005	2.80	2.70	0.141
0.49	0.47	0.001	9.40	8.90	0.026
5.60	1.09	5.300	38.00	29.00	0.005
1.62	0.45	0.206	4.30	4.20	0.002
1.80	1.25	0.013	10.10	10.10	0.025
2.52	2.34	0.008	60.00	46.00	0.006
0.72	0.26	0.011	18.30	6.90	0.009
1.82	1.77	0.024	10.00	8.80	0.004
2.50	2.50	0.004	5.90	4.20	0.010
1.08	1.03	<0.001	30.00	22.00	0.002
0.90	0.24	1.100	2.70	0.67	0.031
0.44	0.22	2.000	8.00	8.00	0.004
0.60	0.60	<0.002	22.00	7.90	0.043
1.18	1.04	<0.100	100.00	47.00	0.042
1.14	0.99	<0.100	34.00	14.80	0.016
2.90	2.80	0.140	1.75	1.71	0.016
1.78	1.77	0.170	0.93	0.40	0.004
9.70	7.70	0.300			
3.60	3.50	0.220			
10.20	0.63	0.019			
0.24	0.24	0.075			
1.23	0.26	0.100			
0.94	0.93	0.100			
0.35	0.31	<0.100			
0.89	0.63	<0.100			
0.31	0.27	<0.100			
1.18	1.04	<0.100			
1.56	1.26	0.270			
0.55	0.25	<0.100			
0.31	0.27	0.012			
1.14	0.91	<0.100			
0.60	0.60	<0.002			