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Predicting groundwater nitrate concentrations in a region of mixed agricultural land use: a comparison of three approaches

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"Capsule": *Non-point source groundwater nitrate nitrogen contamination in the region reflects intensive agricultural practices in the area.*

Abstract

We investigated whether nitrate-N (NO_3^--N) concentrations of shallow groundwater (< 30 m from the land surface) in a region of intensive agriculture could be predicted on the basis of land use information, topsoil properties that affect the ability of topsoil to generate nitrate at a site, or the 'leaching risk' at different sites. Groundwater NO_3^--N concentrations were collected biannually for 3 years at 88 sites within the Waikato Region of New Zealand. The land use was classed as either the predominant land use of the farm where the well or bore was located, or the dominant land use within a 500 m radius of the well or bore. Topsoil properties that affect the ability of soil to generate nitrate were also measured at all the sites, and a leaching risk assessment model 'DRASTIC' was used to assess the risk of NO_3^--N leaching to groundwater at each site. The concentration of NO_3^--N in shallow groundwater in the Waikato Region varied considerably, both temporally and spatially. Nine percent of sites surveyed had groundwater NO_3^--N concentrations exceeding maximum allowable concentrations of 11.3 ppm recommended by the World Health Organisation for potable drinking water which is accepted as a public health standard in New Zealand. Over half (56%) of the sites had concentrations that exceeded 3 ppm, indicating effects of human activities (commonly referred to as a human activity value). Very few trends in NO_3^--N concentration that could be attributed to land use were identified, although market garden sites had higher concentrations of NO_3^--N in underlying groundwater than drystock/sheep sites when the land use within 500 m radius of a sampling site was used to define the land use. There was also some evidence that within a district, NO_3^--N concentrations in groundwater increased as the proportion of area used for dairy farming increased. Compared to pastoral land, market gardens had lower total C and N, potentially mineralisable N and denitrifying enzyme assay. However, none of these soil properties were directly related to groundwater NO_3^--N concentrations. Instead, the DRASTIC index (which ranks sites according to their risk of solute leaching) gave the best correlation with groundwater NO_3^--N concentrations. The permeability of the vadose zone was the most important parameter. The three approaches used were all considered unsuitable for assessing nitrate concentrations of groundwater, although a best-fit combination of parameters measured was able to account for nearly half the variance in groundwater NO_3^--N concentrations. We suggest that non-point source groundwater NO_3^--N contamination in the region reflects the intensive agricultural practices, and that localised, site-specific, factors may affect NO_3^--N concentrations in shallow groundwaters as much as the general land use in the surrounding area.

Keywords: Contamination; Groundwater; Land use; Nitrate; Soil; Leaching

1. Introduction

Contamination of groundwater with nitrate is a global problem (Spalding and Exner, 1993) and is commonly associated with diffuse sources such as intensive agriculture, high density housing with unsewered sanitation, and point sources such as irrigation of sewage effluent onto land (Keeney, 1986; Eckhardt and Stackelburg,

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1995). Increased NO_3^--N concentrations in groundwater can be a concern as it may represent a loss of fertility from overlying soil, cause eutrophication when the groundwater discharges into surface water, and can potentially cause health problems to animals and humans.

In New Zealand, the Resource Management Act (1991) requires the natural environment to be managed in a sustainable manner. The Waikato Region of New Zealand has varied land uses, ranging from intensive grazing, market gardening and horticulture, to extensive sheep and beef grazing. Pastoral land uses account for over half the area in the region, whilst market gardens and intensive horticulture represents less than 1% of the area. Nitrogen fertiliser rates are considerably higher in market gardens than pastoral agriculture (Table 1), and waste effluent from milking sheds is commonly applied to pastures on dairy farms at rates up to 150 kg N/ha/year. There has been anecdotal evidence that market garden and dairy land uses may be causes of localised groundwater contamination (Ledgard et al., 1996; Selvarajah, 1996), although no direct evidence has been reported to prove this.

The maximum allowable concentration of NO_3^--N used for potable water varies considerably worldwide, although the two most commonly used values are 10 μg ml^{-1} used in the USA (MAV_{US}) and 11.3 μg ml^{-1} recommended by the World Health Organisation (MAV_{WHO}). The MAV_{WHO} is used in New Zealand as a public health standard. Groundwater concentrations exceeding an arbitrary threshold of 3 μg ml^{-1} may be indicative of contamination of natural groundwaters as a result of human activities (referred to as the human affected value; HAV; Burkart and Kolpin, 1993; Echardt and Stackelberg, 1995).

Predicting where contamination will occur is very difficult, especially in areas with a mixture of land uses. Numerous studies of 'potential' groundwater contamination with NO_3^--N have been reported from solute leaching studies, whereby NO_3^--N concentrations are measured in drainage water moving beyond the effective rooting zone of plants. Commonly, if the concentration of NO_3^--N in drainage water has exceeded a MAV, the groundwater is suggested to be at risk of contamination due to the overlying land use or management activity (e.g. Ledgard et al., 1996). Many solute leaching models exist in the literature (for a review, see Addiscott and Wagenet, 1985). However, many leaching models are constrained by the need for stringent boundary conditions to be satisfied, which is not possible in areas of mixed land use. Further, many models need intensive on-site calibration, and do not cope well with non-uniform strata and the numerous biological and chemical processes can affect the fate of nitrate in the vadose zone between the soil and an underlying aquifer.

Table 1
Fertiliser rates for agricultural land uses in the Waikato

Land use	Fertiliser rates (kg N ha^{-1} $year^{-1}$)	Reference
Drystock/Sheep (average)	2	BOP Fert, 1997[a]
Drystock (average)	8.5	BOP Fert, 1997
Dairy (average)	62	BOP Fert, 1997
Orchards	150–250	Crush et al., 1996
Market Gardens (summer crops)	250–350	Crush et al., 1996
Market Garden (winter crops)	350–600	Crush et al., 1996

[a] Unpublished report on fertiliser sales for the Waikato Region between 1996 and 1997. B.O.P. Fertiliser Ltd, Mt Maunganui, NZ.

An alternative approach for predicting groundwater NO_3^--N contamination has been at a broader scale by correlating the dominant land use in an area with nitrate concentrations actually measured in underlying aquifers (e.g. Pionke et al., 1988; Barringer et al., 1990; Issensee et al., 1990; Burkart and Kolpin, 1993; Koterba et al., 1993; Eckhardt and Stackelburg, 1995). Land use is suggested to influence groundwater quality because the land use commonly influences the nitrogen flow in the surface soil. Many of the larger-scale studies of NO_3^--N groundwater contamination have been conducted in North America, and generally it has been found that a fairly small proportion of sites exceed public health guidelines (Table 2). However, contamination of shallow groundwater with NO_3^--N has been reported in all states of the USA (Hallberg and Follett, 1989) and within all land uses (Harris et al., 1996). The proportion of sites in large scale surveys that have been reported to exceed HAVs (10–70%) are much higher than the proportion exceeding MAVs (e.g. Burkhart and Kolpin, 1993; Spalding and Exner, 1993; Eckhardt and Stackelberg, 1995; Richards et al., 1996; Lichtenberg and Shapiro, 1997). The most severely contaminated groundwaters that are reported in agricultural areas are often associated with vegetable production, orchards and floriculture land uses due to the greater amount of N fertiliser used than other agricultural land uses, and also with land uses where wastes are frequently applied to soils.

The aim of the study was to use an existing groundwater nitrate monitoring database to establish the variation in NO_3^--N concentrations in shallow groundwater (< 30 m depth from surface) in a region of mixed agricultural land uses, which is not influenced by high density housing, and to investigate whether the variation could be explained by:

1. the dominant land use where groundwater was sampled;
2. easily measurable topsoil properties that affect N cycling in the soil; or

Table 2
Examples of large scale groundwater nitrate surveys conducted in North America

Reference	No. sites	Location	Well type	% of sites exceeding the MAV_{US} [a]
Spalding and Exner, 1993	566	50 states of USA	Community Supply	1.2
	783	38 states of USA	Rural Domestic	2.4
	1430	26 states of USA	Agricultural	4.9
Richards et al., 1996	34 579	5 states of USA	Rural domestic	3.4
Stuart et al., 1995	2588	Georgia, USA	Rural	2
Lichtenberg and Shapiro, 1997	213	Maryland, USA	Community supply	<2
Goss and Goorahoo, 1995	1300	Ontario, Canada	Rural domestic	14
Hamilton and Helsel, 1995	937	5 Eastern and Central states, USA	Observation, irrigation, domestic, agricultural	12–46

[a] $MAV_{US} = 10$ μg NO_3^--N ml^{-1}.

3. risk of solute leaching at a site (as predicted by a site 'leaching risk' assessment model).

2. Materials and methods

2.1. Groundwater data

Groundwater nitrate data were obtained from the Groundwater Nitrate Monitoring Project (GWNMP), conducted by the Waikato Regional Council to monitor groundwater nitrate concentrations in shallow aquifers (<30 m depth) across the Waikato Region. The GWNMP data collected between 1995 and 1998 (the first three years of data collection) were used for the study. All sites were away from the influence of high density housing. The Waikato Region is 25 000 km^2 and is the most intensively farmed region of New Zealand (with 17.5% of New Zealand farms in only 10% of the nationally farmed area. Over half the Region is used for pastoral farming, with a large area of indigenous forest (28%) and production forestry (12%), and small areas of horticulture and urban uses (<5%). The Waikato Region is divided into 11 districts.

Water samples were taken twice annually, in March and September, to measure nitrate concentrations in early autumn and spring, respectively. To ensure adequate replication, only those land uses represented at more than five sampling sites in the GWNMP were included in the present study. The selection of five sites as the minimum was arbitrary, but enabled most of the major agricultural land uses of the Waikato Region to be included. As a result, 88 sites were studied, covering five major land uses: Dairy ($n=50$), Drystock ($n=19$), Drystock/sheep ($n=5$), Orchards ($n=7$), and Market Gardens ($n=7$). The differentiation between drystock and drystock/sheep land uses was made on the basis that farms which included sheep as well as beef (i.e. drystock/sheep), were likely to have different management systems and patterns of N excretion from the animals than on the beef-only drystock farms, which could potentially affect groundwater NO_3^--N concentrations. It is assumed that all current land uses at a site were representative for site since developed for agriculture. This would appear reasonable for the sites, especially for the pastoral land uses. Annual rainfall over the district varies from about 1000 to over 2000 mm and is fairly evenly distributed throughout the year, and annual groundwater recharge varies from 400 to 1600 mm. Water deficits occur in all districts in summer months.

Land use category for each groundwater-sampling site was determined in two ways: as the dominant land use on the property where the well or bore was located (determined by visual examination of the site at the time of groundwater sampling and discussion with the landowner), or by the dominant land use in a 'buffer area'. A buffer area approach works on the principle that the effect of land use on groundwater nitrate concentrations may be better reflected by the distribution of land use in a greater catchment area that contributes to recharge at the groundwater sampling point (Kolpin, 1997) rather than the land use of the farm where the well was located.

2.2. Determining buffer areas

It has been suggested that buffer areas are best calculated as circular entities, allowing ease of generation in a geographic information system (GIS), and avoiding problems of orientation when groundwater flow direction is unknown (Barringer et al., 1990). The radius defining the buffer area that past researchers have used varies, but is an important consideration. If the radius is too large, the land in the perimeter of that buffer contributes proportionally less water to the bore, and correlations between groundwater quality and land use may be decreased. However, in smaller buffer areas, if the size of the buffer area radius is similar to the size of the minimum mapping unit (used in defining the land use), then the risk of misclassification of land use is high. This in turn also makes correlations between groundwater quality and land use poorer (Barringer et al., 1990). The selection of an appropriate buffer area radius is therefore important to maximising the accuracy of an association between groundwater quality and land use. Eckhardt and Stackelburg (1995) used a radius of approximately 800 m to define their buffer areas on Long Island, New York, whereas Kolpin (1997) used a range of buffer radii from 200 to 2000 m. Kolpin (1997) showed that a 500 m radius gave the best correlation with NO_3^--N in groundwater across a wide range of soil types and land uses in the USA. Barringer et al. (1990) suggested that a buffer radius between 250 and 1000 m was most appropriate. A radius of 500 m was therefore arbitrarily chosen as the buffer area radius for this study, which provided buffer areas of 0.785 km^2 or 78.5 ha.

Land uses within buffer areas were obtained using GIS technology held at Waikato Regional Council. Land use information was derived using AGRIBASE, an agricultural database compiled and maintained by the Ministry of Agriculture and Forestry, New Zea land. The AGRIBASE database contains some detailed information on parameters such as farm boundaries, primary land uses, stocking rates, and land application of dairy shed effluent. However, the stocking rate data held in the data base did not always agree with either the information gathered from farmers, or with visual observations, so was not used in the study. Data on effluent irrigation was not available on many of the sites and could not be used. Farms that fell within the buffer area of a sampling well were assumed to have the same land use over the entire farm. If land use was not listed in AGRIBASE, the land use was estimated using a Land Cover Data Base (LCDB; e.g. Fig. 1). The LCDB contains classifications of land cover types in 16 classes, derived from SPOT satellite imagery (Terralink NZ Ltd.). If the land use was still undefined, it was assumed to be the same as a known land use on a neighbouring property with the same land cover classification.

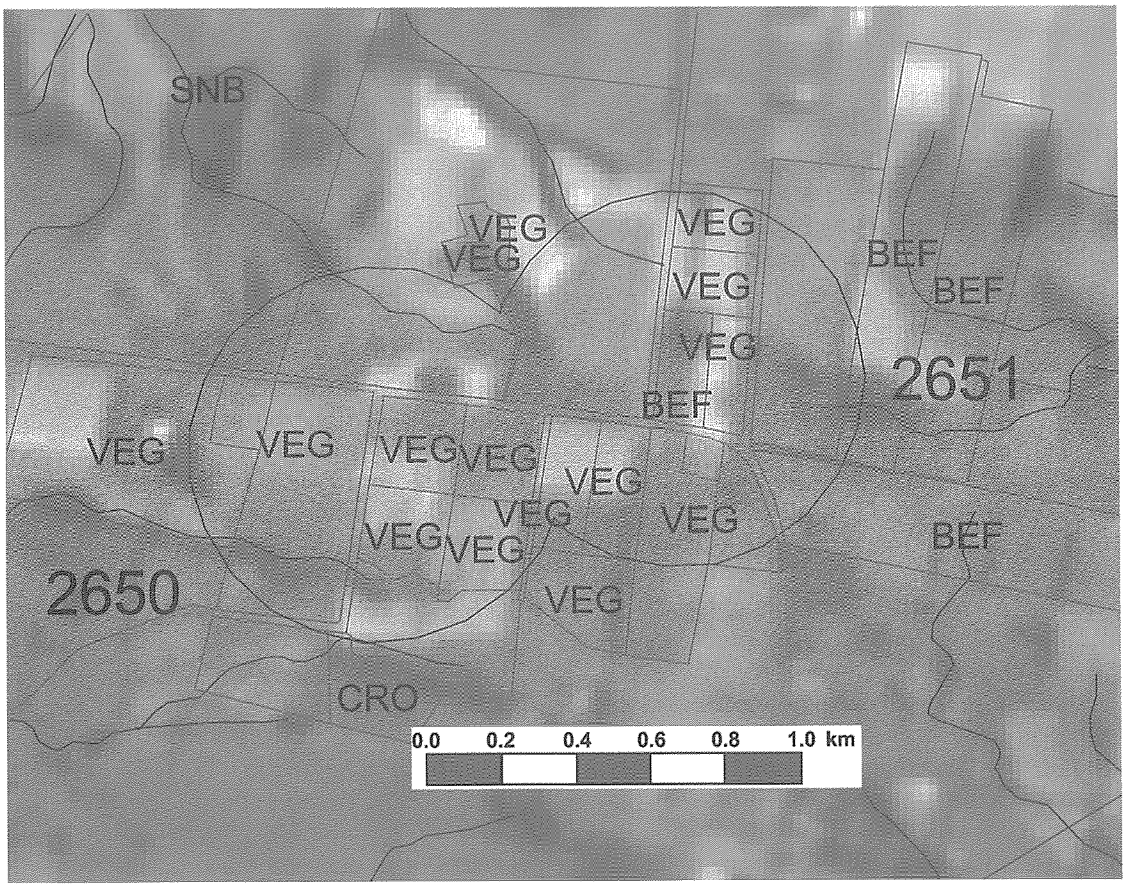

Fig. 1. An example of the images used to define 500 m radius buffer areas, and land use data. Property boundaries were derived from AGRIBASE, and the colours represent different wavelengths from spot satellite imagery, making up the Land Cover Data Base (with permission from Waikato Regional Council). The circles represent the 500 m radius around two bores. BEF, Beef farming; VEG, vegetable growing; CRO, cropping; SNB, sheep and beef.

2.3. Water sampling and analysis

Bores were flushed by turning on the bore pump and allowing it to run for approximately 5–30 min, until it was freshly drawn from the aquifer. Groundwater samples were collected from wells by descending a bunged, lead-weighted bottle by rope into the well. The bottle was lowered to a depth of at least 1 m below the water surface to prevent sampling the surface residue. The bung was removed from the bottle with a second rope when at the appropriate depth, and the bottle was allowed to fill with water. Plastic 150-ml bottles were filled with the groundwater sample. Samples for NO_3^--N analysis were filtered through a Sartorius cellulose acetate filter paper (0.45 μm), and stored in an insulated cooler until frozen later in the day. Samples were analysed for NO_3^--N by automated cadmium reduction, using an auto analyser. The lower detection limit for the analysis was 0.002 μg N ml^{-1}. The cadmium reduction technique cannot distinguish between NO_2^- and NO_3^-, but NO_2^- is usually insignificant in groundwater so the reported NO_3^--N concentrations represent the sum total of NO_3^--N and NO_2^--N nitrogen in the water sample.

2.4. Statistical analysis of groundwater data

There was considerable temporal variability in NO_3^--N concentration at some sites (Fig. 2). We assumed that the temporal distribution of groundwater NO_3^--N concentrations in a single bore would be approximately normal through time and the average groundwater nitrate concentration over time was calculated to represent the groundwater nitrate concentration for each site. Within each land use, the average groundwater NO_3^--N concentrations were not normally distributed and required logarithmic transformation. Two-way analysis of variance, correlation and regression analysis of log transformed data was performed using SYSTAT 7.01 (SPSS Inc, USA). All statistical tests were performed at the 95% level of significance.

The buffer area data were considered in two ways. Firstly, the land use where the bore was located was defined according to the dominant land use of the buffer area rather than that of the farm where the well was located. Two-way analysis of variance was used to assess if the buffer area land use affected average groundwater NO_3^--N concentration. Secondly, the areas of each type of land use within the buffer area were expressed as a proportion of the total area of the buffer area. The proportion of the buffer areas under each of the five land uses was then examined for correlations between land use and the groundwater NO_3^--N concentration.

2.5. Soil collection

Soil samples were collected between January and May 1998, at the 88 sites where groundwater was sampled. Soils were sampled using a 2.5-cm diameter tube auger. Thirty cores (0–10 cm depth) were taken at each site, along three transects radiating away from the bore or well, with each transect starting as close as possible to the bore or well. If a bore or well was located in an area not representative of the general farm activities (e.g. roads, tracks and access areas), then the nearest representative field to the bore or well was sampled. Soil

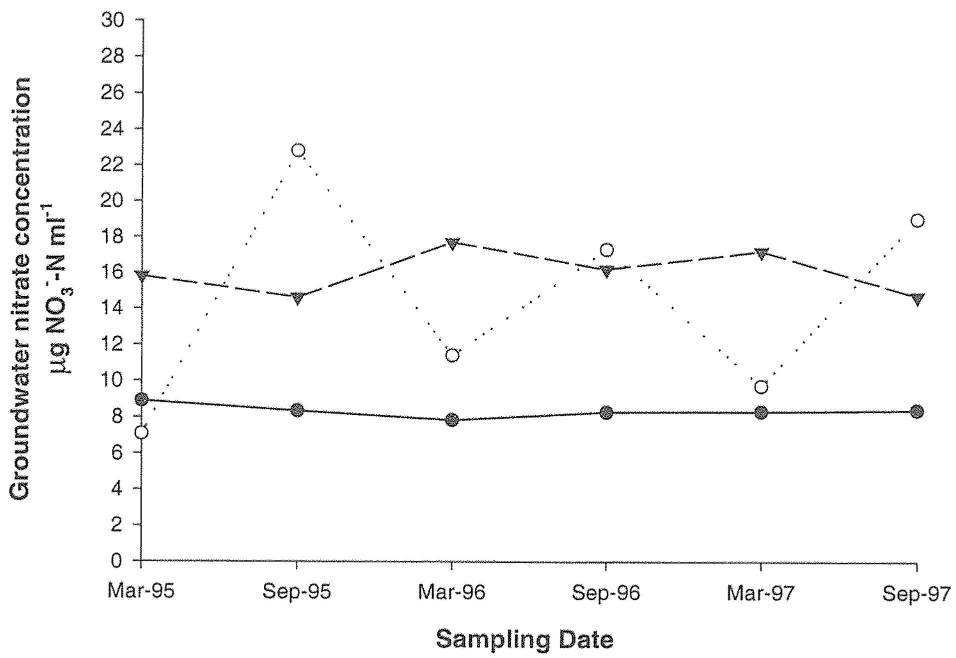

Fig. 2. Examples of types of temporal variation in groundwater nitrate concentrations at different sites.

cores were bulked and stored in large polyethylene bags in an insulated box on the day of sampling. Upon returning to the laboratory, samples were refrigerated at 4°C. The next day, soils were sieved (<4.5 mm), and gravel or vegetation removed.

Soil bulk density was determined on 10 undisturbed soil cores (0–10 cm) collected at each site.

2.6. *Soil properties that reflect the ability of a site to generate nitrate*

As most NO_3^--N in soil is formed in the topsoil following mineralisation of organic matter or conversion from other forms of N added to the soil (such as fertiliser and urine N), the amount of NO_3^--N present to be leached is affected by the ability of the soil to transform N into a NO_3^--N form. At all the sites, we assessed three topsoil properties that reflect the ability of soil to generate NO_3^--N (mineralisation and nitrification) and deplete NO_3^--N (denitrification), as well as inorganic nitrogen and total carbon and N. The biochemical assays that we measured have been shown to be stable over time (e.g. Groffman and Tiedje, 1989; Patra et al., 1990) and probably reflect the history of the site to undertake the processes rather than measuring spot rates per se. The assays were therefore used to rank sites on their longer term potential to generate NO_3^--N which is available to be leached.

2.6.1. *Potentially mineralisable nitrogen*

The potentially mineralisable nitrogen assay (PMN) was used to rank soils according to the size of the pool of mineralisable N, as the PMN assay has been commonly supported as an appropriate measure of soil N availability (e.g. Gianello and Bremner, 1986; Hart et al., 1986). Potentially mineralisable nitrogen was measured under anaerobic conditions following the method of Keeney and Bremner (1966). The PMN was calculated as the flush of NH_4^+-N after seven days incubation at 40°C.

2.6.2. *Net nitrifying activity*

An assay of nitrification activity was used to indicate the relative potential of sites to transform immobile NH_4^+-N to NO_3^--N. Net nitrifying activity (NNA) was measured by incubating soil under aerobic and high humidity conditions at 25°C, for 7 days. Two replicates of soil (10 g) were prepared. The first replicate was extracted immediately to quantify initial soil inorganic N concentrations. To the second replicate, a 1 ml aliquot of 0.11 M NH_4-N was added, resulting in a final moisture content of approximately 60% of WHC (water holding capacity). The sample was incubated at 25°C for seven days under aerobic and high humidity conditions. Soils were extracted by end-over-end shaking with 50 ml of 2.0 M KCl, for 1 h. The extraction slurries were filtered overnight through Whatman filter papers (No. 42) at 4°C, and the samples were analysed for NO_3^--N + NO_2^--N colorimetrically using an auto analyser. Net nitrification activity was determined as the flush of NO_2^--N and NO_3^--N (i.e. the difference between the two replicates) that occurred over the period of incubation. The NNA was reported as an hourly rate to allow comparison with the literature, and is therefore a linear interpolation of nitrification activity over the 7-day period.

2.6.3. *Denitrifying enzyme activity*

The denitrification enzyme assay (DEA) was measured using the method proposed by Smith and Tiedje (1979) and conducted in triplicate. Soil (10 g) was added to a 130-ml Schott bottle containing 10 ml of 1 mM glucose/nitrate solution and 0.125 g l^{-1} chloramphenicol. The bottle was sealed tightly and the headspace flushed with 100% N_2 gas by inserting two hypodermic needles through the gas sampling septum. After 2 min, the two syringe needles were removed and 10 ml of purified acetylene (bubbled sequentially through $CuCl_2$ then de-ionised water; Hyman and Arp, 1986) was added and the pressure in the bottle equalised. The bottles were placed on a reciprocating shaker (200 rpm) in a darkroom incubator at 25–27°C, and gas samples (5 ml) withdrawn after 15 and 75 min for measurement of N_2O using a Phillips PU4410 gas chromatograph fitted with an electron capture detector, and an Alltech poropak Q 80/100 column.

2.6.4. *Inorganic N*

The inorganic N represents the sum of the NO_3^--N and NH_4^+-N measured in the soil extracts.

2.6.5. *Total carbon and nitrogen*

Total carbon and nitrogen percentages were measured on air-dry, finely-ground soil samples using a LECO FP-2000 analyser.

2.7. *Data analysis for soil properties*

The data from the biochemical assays, inorganic N extractions, total N and total C determinations were not normally distributed and required logarithmic transformation for statistical analysis. Two-way analysis of variance, correlation and regression analysis of log-transformed data were performed using SYSTAT 7.01 (SPSS Inc, USA). Spearman rank-order correlations were used to determine the non-parametric correlations, as it could not necessarily be expected that correlations would be linear, and the rank-order correlation is applicable to both linear and non-linear relationships. Furthermore, the assays being used were designed to rank sites according to potential activity rather than give absolute values. All statistical tests were performed at the 95% level of significance.

2.8. Farm management surveys

A survey of farm managers at each site was conducted to ascertain land management practices, including stocking rate (for animal production farms), effluent irrigation (for dairy farms), types and quantities of fertilisers used, timing of fertiliser applications, and use of water irrigation. Due to considerable variation in management practices within a land use, and irregular recording by farmers, only fertiliser application rates were considered sufficiently reliable and replicable amongst the management strategies.

2.9. Site leaching risk assessment

The leaching risk at each site was assessed using the hydrogeological setting categories of the leaching risk assessment model 'DRASTIC' (Aller et al., 1987). The properties used in DRASTIC are site properties that affect the movement of nutrients from the surface soil to groundwater: **D**epth to groundwater, **R**echarge, **A**quifer media (aquifer porosity), **S**oil media (soil texture), **T**opography (slope angle), **I**nfluence of the vadose zone (effectively vadose zone permeability), and aquifer hydraulic **C**onductivity. The letter denoted in bold make up the acronym DRASTIC.

In the DRASTIC model, each factor has a weighting according to its relative importance in controlling groundwater contamination (Table 3), as defined by Aller et al. (1987). Each site factor in DRASTIC must be assigned a rating (between 1 and 10), according to local hydrogeology. For example, in the case of depth to groundwater, a site may be given a rating of 10 (high risk of contamination) if groundwater is very shallow, but a rating of 1 (low risk of contamination) if groundwater is very deep. The DRASTIC handbook provides guidelines for assigning the ratings, but the researcher can depart from these guidelines if the local circumstances differ from those suggested in the handbook. The final DRASTIC value is the weighted sum of the ratings for each factor (Eq. (1)). The DRASTIC value can range from a minimum of 23 to a maximum of 230, and can be used to rank a site's vulnerability to groundwater contamination.

Table 3
Weightings for DRASTIC factors

DRASTIC factors	Weighting
Depth to groundwater	5
Recharge	4
Aquifer media	3
Soil media	2
Topography	1
Influence of the vadose zone	5
Hydraulic conductivity of the aquifer	3

$$\text{DRASTIC value} = DrDw + RrRw + ArAw \ldots \quad (1)$$

where r represents the rating for each factor at each site, and w the weighting for that factor.

For the current project, depth to groundwater data was defined as the depth of the well, as shallow groundwater can vary seasonally and suitable data for all the sites was unavailable.

Annual recharge at each site was calculated as the sum of the differences between monthly rainfall and evaporation, with runoff assumed to be negligible. Rainfall and evaporation data were obtained using climate surfaces generated from a spline model for New Zealand (Leathwick and Stephens, 1997). All sites in this study had recharge exceeding 250 mm year^{-1}, thus all sites were assigned the maximum recommended rating of nine. Recharge, therefore, did not influence the final ranking of sites by the DRASTIC index.

Ratings for Aquifer media, Soil media, Influence of the vadose zone and Topography were all defined using the New Zealand Land Resource Inventory database, which holds geological, topographic, vegetation and soil information for New Zealand.

It was not possible to obtain aquifer hydraulic conductivity at the study sites and the DRASTIC index calculated in this study does not include this factor.

3. Results

3.1. Groundwater nitrate concentrations

The groundwater nitrate concentrations, averaged over the three years of data collection, ranged from 0.02 μg NO_3^--N ml^{-1} to nearly 25 μg NO_3^--N ml^{-1}. The average and median groundwater nitrate concentrations for all sites and years of data collection were 4.8 and 3.7 μg NO_3^--N ml^{-1}, respectively. However, considerable variation in average groundwater concentrations (up to approximately 13-fold) was recorded between districts (data not presented).

The recommended maximum allowable value for NO_3^--N in drinking water in New Zealand (MAV_{WHO}) of 11.3 μg ml^{-1} was exceeded in approximately 9% of the bores sampled. In two districts (Franklin and Rotorua), approximately 25% of bores sampled had NO_3^--N concentrations in excess of the MAV_{WHO} while in three other districts (Matamata-Piako, Waikato and Waipa), between 7 and 8% of bores exceeded the MAV_{WHO} (Fig. 3). In the remaining districts, groundwater NO_3^-concentrations did not exceed the MAV_{WHO}. More than half (56%) of the sites monitored had groundwaters that were in excess of HAV, and were located in seven of the 11 districts in the Waikato Region. Within these districts, the proportion of sites with groundwater nitrate concentrations exceeding the

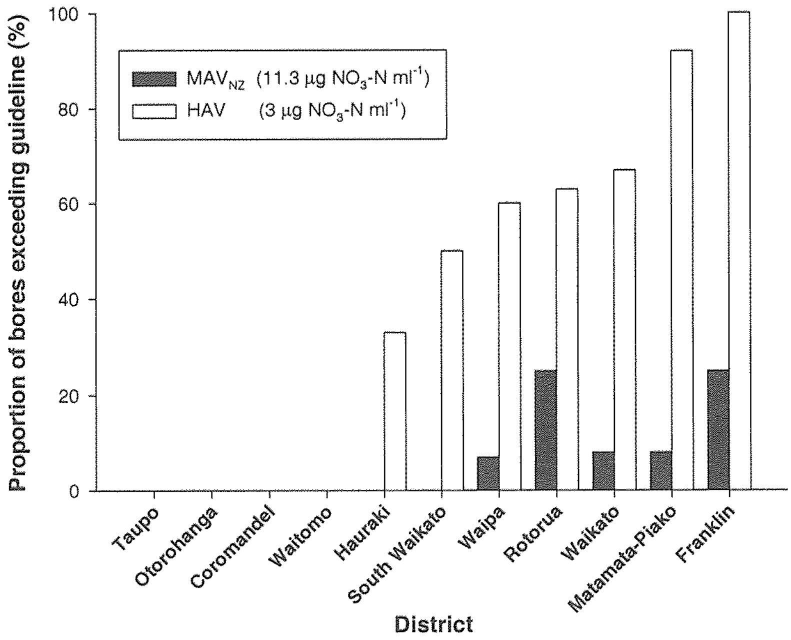

Fig. 3. The percentage of bores sampled in each district that either exceeded either the MAV_{WHO} or the HAV.

HAV varied from 100 (Franklin District) to 33% (Hauraki District). In four districts (Coromandel, Otorahanga, Taupo and Waitomo), average nitrate concentrations in groundwater were not significantly ($P>0.05$) different to zero.

3.2. *Effect of land use on groundwater nitrate concentrations*

Groundwater NO_3^--N concentrations were not related to land use, when defined as the dominant land use on the farm where samples were collected (Fig. 4). When land use was defined according to the dominant land use of a buffer area, the only significant difference ($P<0.05$) in groundwater NO_3^--N concentration attributable to land use was that the NO_3^--N concentration was greater under market gardens than under mixed drystock and sheep farms (Fig. 4).

The groundwater nitrate concentration was generally poorly correlated with the proportion of a land use class within a buffer area (Table 4). Although the relationship between land use and groundwater NO_3^--N concentration was positive and significant ($P<0.001$) for market gardening, the correlation was relatively poor, and accounted for only 16% of the variance.

3.3. *Effect of land use on soil properties*

Market gardens had smaller ($P<0.05$) concentrations of PMN than all the other land uses. Market gardens also had smaller ($P<0.05$) DEA than the dairy pasture sites (Table 5). However, no differences ($P<0.05$) in PMN, or DEA were detected between any of the pastoral land uses, and no differences in either NNA, soil NO_3^--N, NH_4^+-N, or inorganic N concentrations between any of the land uses. The total C and total N content in the market gardens was less ($P<0.05$) than the total C and total N content of all pastoral land uses, while the total C and N content of the orchards was less than that in the dairy sites. However, no differences were observed within the pastoral land uses or between market gardens and orchards. There were significant ($P<0.05$), but weak correlations recorded between total C and PMN ($r=0.37$), and total C and DEA ($r=0.31$).

3.4. *Correlation of soil properties with groundwater concentrations*

The PMN, soil NO_3^--N and soil inorganic N were significantly ($P<0.05$) correlated with groundwater nitrate concentration on a rank-order basis, although the correlation coefficients were fairly weak (Table 6). Stepwise, backward, multiple linear regression of soil properties against groundwater nitrate concentration showed that PMN plus soil inorganic N were linearly related to groundwater nitrate concentration ($P<0.01$), although the goodness of fit was poor ($r^2=0.20$).

3.5. *Leaching risk assessment*

The DRASTIC indices ranged from a minimum of 73 to a maximum of 170 across sites. The individual DRASTIC components depth to groundwater, influence of the vadose zone, aquifer media and topography data were all significantly ($P<0.05$) and positively

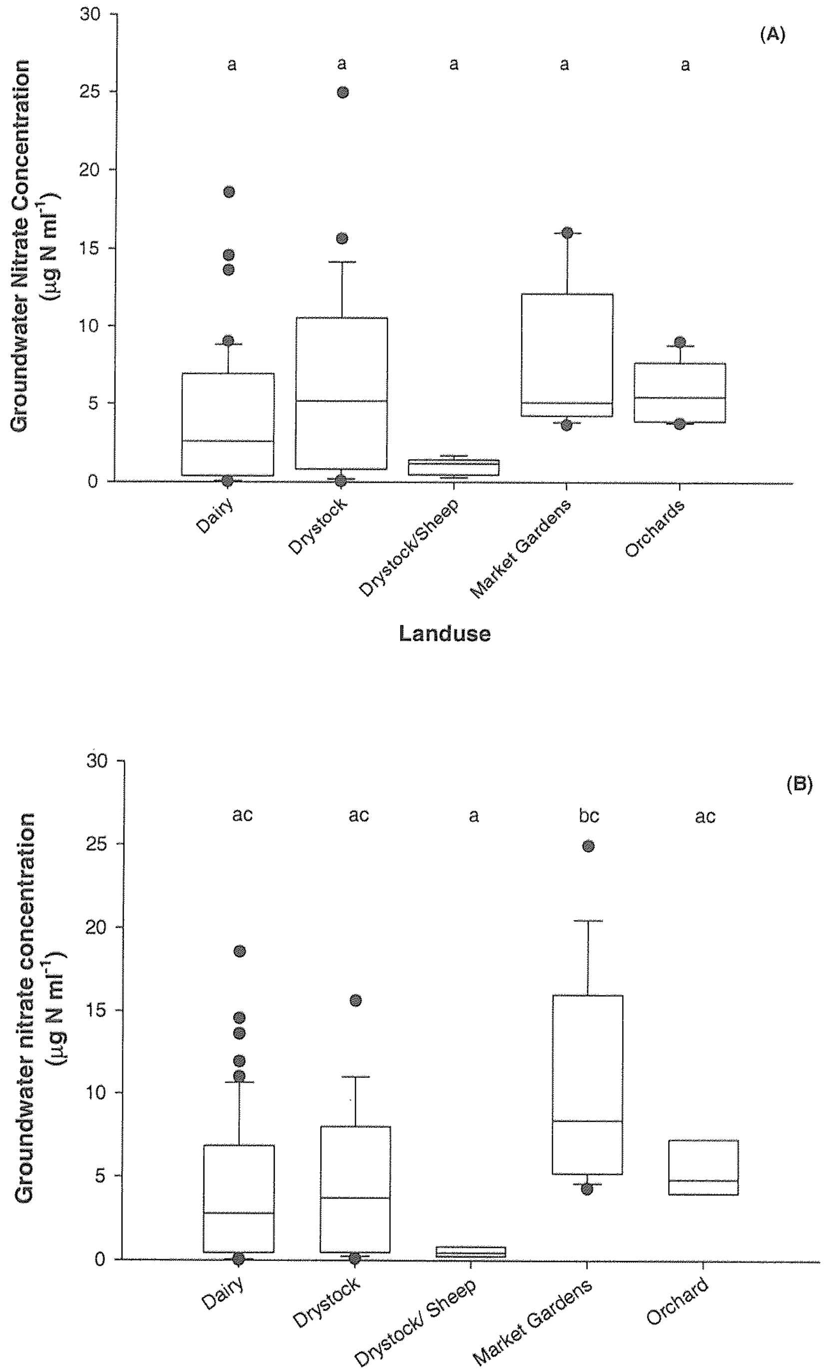

Fig. 4. Boxplots showing the distribution of groundwater nitrate concentrations for different land uses where land use is defined by the dominant land use on a farm where groundwater was sampled (A) or the dominant land use within a buffer area (B). Land uses with the same letter within each graph are not significantly different ($P<0.05$).

correlated with groundwater nitrate concentration on a rank-order basis, and recharge was significantly ($P<0.05$) but negatively correlated with groundwater nitrate concentration (Table 7). It should be noted that the positive relationship between depth and groundwater nitrate concentration is because the depth variable used was the DRASTIC depth index, which assigns a larger rating (i.e. greater risk) to shallower groundwater. Therefore the positive relationship shown is between the groundwater nitrate concentration and the 'riskiness' of the depth, and shows that generally NO_3^--N concentrations are less in the deeper wells. Although the combined DRASTIC index showed the strongest rank-ordered correlation with groundwater nitrate concentration, the influence of the vadose zone accounted for most of the correlation. The general trend was that groundwater nitrate concentration increased as the DRASTIC index also increased (Fig. 5).

Table 4
Correlations between the proportion of the buffer area (500 m radius around each well) used for each land use and groundwater nitrate concentration

Land use	Spearman rank correlation coefficient
Dairy	−0.139
Drystock	0.134
Drystock/sheep	−0.103
Orchards	0.225
Market Gardens	0.349***

***$P<0.001$.

3.6. *Farm fertiliser use*

Nitrogen fertiliser applications ranged from zero to 325 kg N ha^{-1} $year^{-1}$, with a mean rate of 54 kg N ha^{-1} $year^{-1}$. Fertiliser N applications were largest in the market gardens with mean annual applications of 168 kg N ha^{-1} $year^{-1}$, followed by dairy farms (60 kg N ha^{-1} $year^{-1}$), orchards (28 kg N ha^{-1} $year^{-1}$), and mixed drystock and sheep farms (16 kg N ha^{-1} $year^{-1}$). Fertiliser usage was not significantly correlated with groundwater nitrate concentrations (data not presented).

3.7. *Combined effects of all factors on groundwater nitrate concentration*

A backward, stepwise, multiple linear regression was used to determine which factors were best able to predict groundwater nitrate concentration (predicted as log GWN). The equation that gave the best fit is shown in Eq. (2). All factors were significant ($P<0.05$), although the equation explained less than half of the total variance in groundwater nitrate concentrations ($r^2=0.46$).

$$\mathrm{LogGWN} = -0.429 \times \mathrm{LogDEA} + 0.549 \times \mathrm{LogInorgN} + 0.092 \times \mathrm{Depth} + 0.122 \times \mathrm{Vadose} \quad (2)$$

where LogGWN is the log of the groundwater nitrate concentration, LogDEA is the log of the denitrifying enzyme activity, LogInorgN is the log of the inorganic N content of the soil (i.e. the sum of the soil NO_3^--N and soil NH_4^+-N contents), Depth is the DRASTIC parameter rating the depth of the well, and Vadose is the DRASTIC parameter rating the influence of the vadose zone.

Table 6
Spearman rank-order correlation coefficients for linear relationships between groundwater nitrate concentration and individual soil properties

Soil properties	Spearman correlation coefficient
PMN	−0.279*
NNA	−0.130
DEA	−0.160
Soil NO_3^--N	0.254*
Soil NH_4^+-N	0.081
Soil Inorganic N	0.253*
Total Carbon	−0.194
Total Nitrogen	−0.195

*$P<0.05$.

4. Discussion

This study has highlighted some important observations about the NO_3^--N status of shallow groundwaters (< 30 m depth from land surface) in a region of mixed agricultural land uses. The proportion of sites that exceeded MAV_{WHO} (9%) and HAV (56%) is greater than commonly reported in many overseas studies (Table 2), although overseas studies are not always confined to shallow groundwater as used in the current study. The Waikato Region is an important agricultural area of New Zealand, and it is apparent that agricultural activities over the past 100 years have affected groundwater nitrate concentrations in some districts. It is worth noting that the districts where the contamination is most evident are also those districts associated with intensive dairying and market gardening. The districts with less evidence of contamination are those where the land use is predominantly mixed sheep and beef (e.g. Otorohanga, Waitomo) and/or where a large proportion of the area is non-agricultural land (e.g.

Table 5
Effect of land use on soil properties[a]

Land use	n[b]	PMN (μg N cm^{-3})	NNA (μg N cm^{-3} h^{-1})	DEA (μg N_2O-N cm^{-3} h^{-1})	Soil NO_3^- (μg N cm^{-3})	Soil NH_4^+ (μg N cm^{-3})	Inorganic N (μg N cm^{-3})	Total C (%)	Total N (%)
Drystock/sheep	5	146.2a	0.76a	0.61a	6.01a	8.78a	14.78a	8.68ac	0.77ac
Drystock	18	137.6a	0.78a	0.50a	24.67a	6.86a	31.52a	6.44ac	0.57ac
Dairy	50	148.8a	1.10a	0.73a	27.37a	6.17a	33.54a	7.53a	0.69a
Orchard	8	104.2ab	0.58a	0.54a	33.42a	0.94a	34.37a	5.26bc	0.46bc
Market Gardens	7	59.0b	1.02a	0.21b	57.80a	5.75a	63.55a	3.91b	0.34b

[a] Mean values followed by the same letter within a soil property are not significantly ($P<0.05$) different.
[b] n = Number of sites.

Table 7
Correlations between DRASTIC index parameters and groundwater nitrate concentration

DRASTIC parameter	Spearman rank-order correlation coefficient
DRASTIC (Combined)	0.631***
Depth	0.447***
Recharge	−0.307***
Aquifer media	0.371**
Soil media	0.190
Topography	0.270*
Influence of the vadose zone	0.607***

*$P<0.05$.
**$P<0.01$.
***$P<0.001$.

Coromandel). Therefore, a relationship between land use and groundwater NO_3^--N concentration could be expected. However, the only significant effect of land use on groundwater NO_3^--N concentrations that was observed was that market gardening had larger NO_3^--N concentrations in underlying groundwater than drystock/sheep grazing. The latter land use represents mainly small 'hobby farms', in which the farmers are likely to have less intensive farming practices than the other land uses studied.

The greater proportion of contaminated sites in the Franklin District than other districts is attributed to the larger proportion of market gardening in that area. Inorganic fertiliser N usage is much greater in vegetable production than in any other land uses in the Waikato Region. The fertiliser survey showed that N application rates up to 325 kg N/ha were used in market garden sites used for this study, which was substantially higher than any other land use. It has previously been reported that fertiliser N is applied at rates up to approximately 600 kg N/ha in the Franklin District (Crush et al., 1996). It has also been shown that N recovery in crops at sites receiving large N application rates in the Franklin District are fairly low (16–20%), and that NO_3^--N concentrations in leachate below heavily fertilised crops are fairly high (28–42 μg NO_3^--N ml^{-1}; Crush et al., 1996).

The finding that market gardening had lower total C, total N, DEA and PMN than pastoral sites is consistent with the higher groundwater NO_3^--N concentrations in the market garden sites. The smaller amount of organic matter results in less soil microbial cycling of applied N in topsoil at market garden sites, and fertiliser N unused by plants would be present in a leachable form in the soil. Long-term cultivation of soils for arable agriculture has commonly been reported to decrease soil organic matter levels in soils around the world (Rosswall and Paustian, 1984; Francis et al., 1992; Crush et al., 1996) and it is not surprising, therefore, that lower PMN and DEA were reported under market gardening than the pastoral land uses in this study.

Dairy farming has been associated with large N leaching losses in the Waikato Region (e.g. Ledgard et al., 1996; Selvarajah, 1996) but it was not possible to show a difference between groundwater NO_3^--N concentrations under dairy, drystock, or mixed drystock and sheep farming in the current study. In general, dairy farmers maintain higher animal stocking rates, and apply greater amounts of inorganic fertilisers than

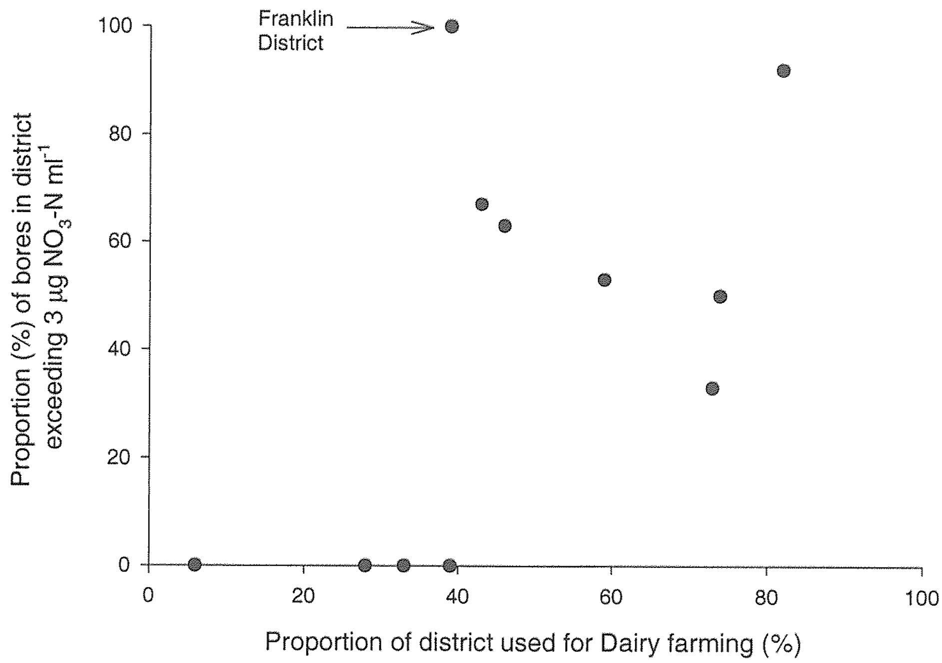

Fig. 5. Relationship between the percentage of the district used for dairy farming and the percentage of the wells sampled that HAV. It should be noted that market gardening rather than dairy farming is probably the major source of NO_3^--N in the Franklin district.

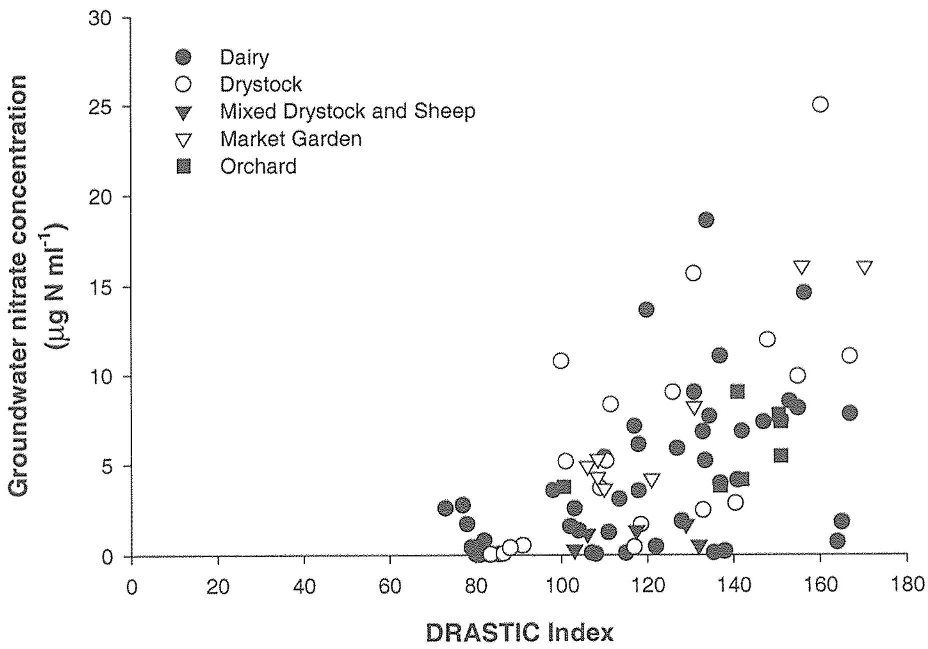

Fig. 6. Relationship between the DRASTIC index and groundwater nitrate concentration for different land uses in the Waikato region. Land use is defined as the land use of the farm where the sampling bore was located.

either drystock or mixed drystock and sheep farmers. The preferred treatment method of farm dairy effluent by irrigation onto pastures has further increased the amount of N applied (Di et al., 1999). Consequently, soil N surpluses have been calculated to be much higher for dairy farms than other pastoral land uses (Crush et al., 1996). This would lead to higher groundwater nitrate concentrations. The NO_3^--N concentration in groundwater for the dairy farm land use ranged from below the detection limit to 18 µg NO_3^--N ml^{-1}. Further, no differences were detected between the pastoral land uses, which suggests that site specific management or hydrogeological factors may override the more general effect of land use on NO_3^--N contamination of groundwater. If the effect of dairy farming on groundwater data is considered on a regional scale (Fig. 6), when the proportion of a district used for dairy farming is greater than 40%, then more of the groundwater sites tend to have NO_3^--N concentrations above the HAV.

The poor predictive value of any of the measured soil properties to account for groundwater nitrate concentrations (<20%), suggests that easily measurable properties of the topsoil have limited use on their own as tools for predicting groundwater quality. The stronger association between the permeability of vadose zone strata and groundwater nitrate concentrations implies that local hydrogeology may play an important role in determining whether shallow groundwater is at risk of contamination from NO_3^-. The importance of accounting for the effect of the vadose zone on nitrate contamination of aquifers has been previously recognised (Timmons and Dylla, 1981; Richards et al., 1996; Johnson et al., 1997). Of less importance in terms of explaining variance in groundwater nitrate concentration, but still a significant factor, was the depth to the groundwater. The depth to groundwater has been shown to be important in many other studies of groundwater nitrate contamination (e.g. Kolpin, 1997; Richards et al., 1996; Spalding and Exner, 1993), with NO_3^--N concentrations decreasing with depth. Since components of the DRASTIC index had the best correlations with groundwater nitrate concentration, it is suggested that the transport of NO_3^--N to groundwater may control groundwater nitrate contamination in the Waikato Region more than NO_3^--N production. Other studies have also suggested that subsoil and vadose zone factors are important in determining the likelihood of NO_3^--N being transported to groundwater. For example, Vellidis et al. (1996) reported that the leaching of liquid dairy manure to pasture was inhibited by very low subsoil permeability, and other studies have reported rapid leaching due to high subsoil permeabilities (e.g. Hansen and Djurhuus, 1996). On a larger scale, wells located in a karst region in Ohio had greater NO_3^--N concentrations than the rest of the district (Richards et al., 1996) as karst geology is associated with shallow soils and rapid preferential flow down sink holes and cracks.

5. Conclusions

Concentrations of NO_3^--N in groundwater at 88 sites in the Waikato region of New Zealand ranged from 0.02 to 25 µg ml^{-1}, and exceeded maximum recommended concentrations for potable water (MAV_{WHO}) in 9% of sites. Nearly half of the sites in the region had NO_3^--N concentrations exceeding 3 μg ml^{-1} (HAV), suggesting effects of human activities on the groundwater.

None of the three approaches used (dominant land use at or surrounding the sites where ground water was sampled, topsoil properties which reflect N cycling or the risk assessment model) was highly suitable for predicting ground water nitrate concentrations. Site-specific factors (e.g. local climate, hydrogeology, soils, management) may over-ride general land use effects. Consequently, it is suggested that models such as DRASTIC that assess the risk of solute leaching to ground water at a site, perhaps with a land management index included, may be useful for predicting areas for more intensive monitoring of ground water. The results also emphasise that there is a greater need to test the link between measurements of nitrate leaching from a variety of land use activities with measurements of ground water nitrate concentrations below these activities.

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